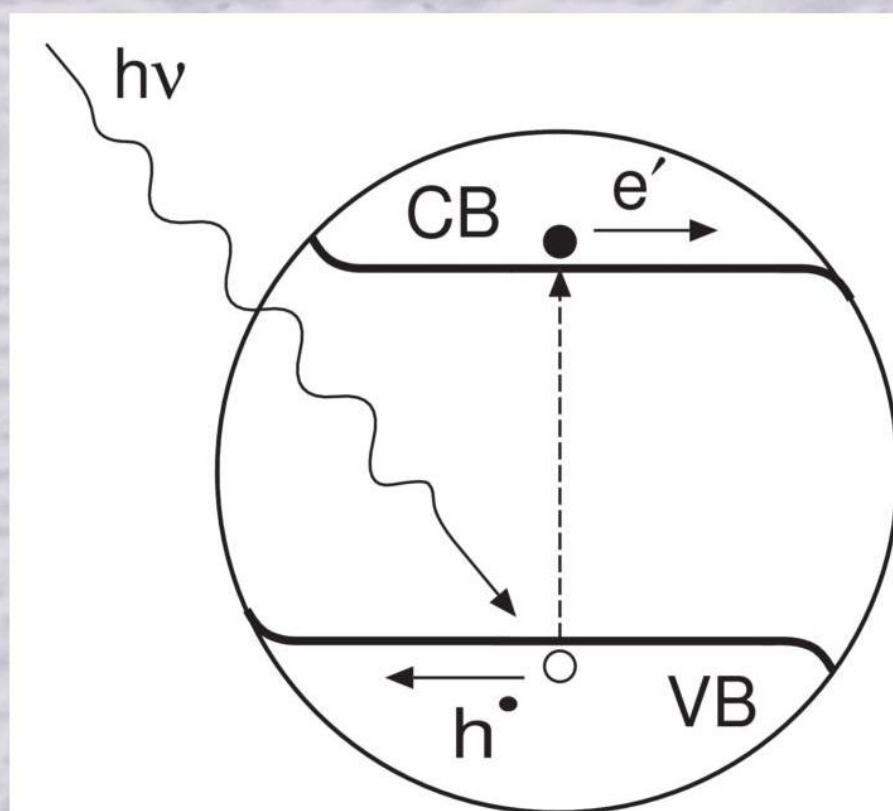


# Solid State Chemistry and Photocatalysis of Titanium Dioxide



Edited by  
Maria K. Nowotny and Janusz Nowotny

# **Solid State Chemistry and Photocatalysis**

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Maria K. Nowotny  
Janusz Nowotny

**THIS VOLUME IS DEDICATED TO  
AKIRA FUJISHIMA AND KENICHI HONDA  
THE PIONEERS OF TiO<sub>2</sub> PHOTOCATALYSIS**

# **Solid State Chemistry and Photocatalysis**

Special topic volume with invited peer reviewed papers only.

*Edited by*

**Maria K. Nowotny and Janusz Nowotny**



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## FOREWORD

Pollution of water resources, that affects access to drinking water, is a global problem. Therefore, there is an increasingly urgent need to address the problem through the development of efficient and cost effective means of water purification.

Current water treatment technologies require energy consumption. However, closely linked to the problem of water shortage is the impending energy crisis. Therefore, intensive research aims to develop water purification processes that are based on using renewable energy, such as solar energy, rather than the energy generated by fossil fuels.

There has been an accumulation of reports on the development of photocatalysts, which enable water purification using solar energy as the only driving force of the process. These photocatalysts, which are based on oxide semiconductors, allow conversion of solar energy into the chemical energy that is required for oxidation of toxic organic compounds in water.

Awareness is growing that the most promising photocatalyst for solar water treatment is titanium dioxide,  $\text{TiO}_2$ , and its solid solutions. Therefore, the research aims to develop  $\text{TiO}_2$ -based photosensitive oxide systems with high photocatalytic performance.

The research area of  $\text{TiO}_2$  photocatalysis is multidisciplinary. The progress of research in this area requires application of the concepts of catalysis and photocatalysis as well as the concepts of solid-state chemistry. The latter are

needed for the processing of well defined photocatalytic systems. Therefore, the aim of the present volume, collecting the papers in  $\text{TiO}_2$  photocatalysis as well as the chemistry and defect chemistry of  $\text{TiO}_2$ , is to form an interdisciplinary platform for a dialogue between the researchers working in these two research areas.

All papers reported in the present volume have been peer-reviewed. We would like to thank all the authors for their contributions.

Maria K. Nowotny & Janusz Nowotny

Sydney, January 2010

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## Molecular Mechanism of Water Oxidation Reaction at Photo-irradiated TiO<sub>2</sub> and Related Metal Oxide Surfaces

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**Keywords:** solar water splitting, photoelectrochemistry, photocatalysis, nanoparticles, atomically flat surfaces, FTIR, PL, in situ surface spectroscopy

**Abstract.** Recent studies on the molecular mechanism of water photooxidation (or oxygen photoevolution) reaction on TiO<sub>2</sub> and related metal oxides or oxynitrides are reviewed. It is shown that a lot of experimental and theoretical studies give definite support to our recently proposed new mechanism, called “nucleophilic attack of H<sub>2</sub>O” or “Lewis acid-base” mechanism. The new mechanism has the prominent features that it possesses energetic and kinetics different from the conventional electron-transfer mechanism and can explain water photooxidation reaction on *visible-light* responsive metal oxides or oxynitrides, contrary to the conventional one. The result indicates that the new mechanism is useful for searching for new efficient visible-light responsive materials for solar water splitting.

### Nomenclature

|                                         |                                                                                            |
|-----------------------------------------|--------------------------------------------------------------------------------------------|
| AFM                                     | Atomic Force Microscopy                                                                    |
| Ag/AgCl/sat.KCl                         | A silver/silver chloride/aq.saturated KCl electrode                                        |
| cm <sup>-1</sup>                        | The unit of wavenumbers (the number of waves per cm)                                       |
| $E^0$                                   | The standard redox (oxidation-reduction) potential                                         |
| $E^{\text{eq}}_{\text{redox}}$          | The equilibrium redox (oxidation-reduction) potential                                      |
| $E_v^s$                                 | The energy of the top of the valence band at the TiO <sub>2</sub> surface                  |
| ESR                                     | Electron Spin Resonance Spectroscopy                                                       |
| e <sup>-</sup>                          | An electron in the conduction band                                                         |
| Flat-band potential ( $U_{\text{fb}}$ ) | The electrode potential at which the electronic bands of asemiconductor electrode are flat |
| FTIR                                    | Fourier Transform Infrared Spectroscopy                                                    |
| h <sup>+</sup>                          | A photogenerated hole in the valence band                                                  |
| <sup>1</sup> H-NMR                      | Proton Nuclear Magnetic Resonance Spectroscopy                                             |

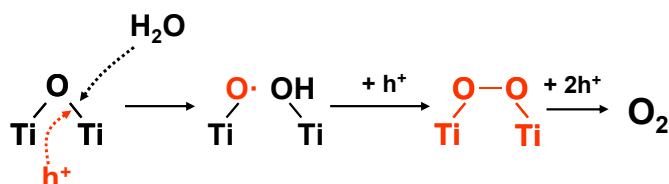
|          |                                                |
|----------|------------------------------------------------|
| IPCE     | Incident Photon to Current Efficiency          |
| $j$      | The photocurrent density                       |
| K        | The unit of the absolute temperature (Kelvin)  |
| LEED     | Low Energy Electron Diffraction                |
| MIR-IR   | Multiple internal reflection FTIR spectroscopy |
| NHE      | The normal hydrogen electrode                  |
| Nm       | nanometer ( $= 1 \times 10^{-9}$ m)            |
| PL       | Photoluminescence                              |
| STH      | Surface trapped hole                           |
| STM      | Scanning Tunnel Microscopy                     |
| $U$      | The electrode potential                        |
| $U_{fb}$ | The flat-band potential                        |
| $U_{on}$ | The onset potential of the photocurrent        |
| UHV      | Ultrahigh vacuum                               |
| UPS      | Ultraviolet-light photoelectron spectroscopy   |
| UV       | Ultraviolet light                              |

## Introduction

Oxygen photoevolution (or water photooxidation) reaction at the surface of  $\text{TiO}_2$  and related metal oxides or oxynitrides has been studied extensively from the point of view of solar water splitting [1,2]. The reaction has also attracted significant attention in relation with photocatalytic environmental cleaning [3-5] because primary active intermediates of oxygen photoevolution reaction play an important role in the mineralization of waste materials or the degradation of harmful compounds. For the purpose of increasing reaction efficiency, many efforts have been made to clarify the reaction mechanism on  $\text{TiO}_2$  by use of various photoelectrochemical [6-13] and spectroscopic techniques such as ESR [14-20], transient laser absorption [21-28], FTIR absorption [29-33], and  $^1\text{H}$ -NMR measurements [34].

Recently, mechanistic studies on water photooxidation reaction have shown new aspects in two respects. In the first place, a large number of metal oxides or oxynitrides, which can oxidize water under visible-light irradiation, have been discovered [2,35-49], though reported efficiencies are not high enough yet. The discovery has given rise to a new possibility to find efficient materials but simultaneously caused the new question of why photogenerated holes of an N-2p character in metal oxynitrides, for example, can oxidize water having only O-2p electrons.

Secondly, it has long been assumed [4] that water photooxidation reaction is initiated by electron-transfer type reaction, in which surface Ti-OH groups are oxidized to  $\bullet\text{OH}$  radicals by photogenerated holes, as depicted in Scheme 1(A).

**(A) Electron transfer mechanism****(B) Lewis acid-base mechanism**

**Scheme 1.** (A) conventional electron-transfer and (B) new “Lewis acid-base” mechanisms for oxygen photoevolution reaction at the TiO<sub>2</sub> rutile surface.

However, recently, we have reported [50-54] essentially a different mechanism, in which water photooxidation is initiated by the nucleophilic attack of an H<sub>2</sub>O molecule to a surface-trapped hole (STH) accompanied by bond breaking (Scheme 1(B)). A notable point is that the new mechanism can be regarded as a Lewis acid-base reaction and has energetics and kinetics quite different from those of the conventional electron-transfer mechanism. An important result is that the new mechanism has a possibility to explain water photooxidation on visible-light responsive metal oxides or oxynitrides in contrast to the conventional electron-transfer mechanism. The confirmation and the development of the new mechanism thus become of crucial importance for finding new active visible-light responsive materials.

In this article, we will survey the results of our studies on the new mechanism in comparison with those on the conventional mechanism. In Section 2, we give a brief overview of past mechanistic studies on water photooxidation reaction. It will be shown that there has been serious confusion on the interpretation of surface reaction intermediates detected by spectroscopic methods. In Section 3, the new mechanism will be explained in some detail. In subsequent sections, i.e. in Section 4 to 6, we will show results of a variety of experimental and theoretical studies on the new mechanism, which were made to obtain clear evidence for it. The direct in-situ spectroscopic detection of surface intermediates as well as the preparation of atomically flat and stable TiO<sub>2</sub> (rutile) surfaces has been very effective for mechanistic studies. Finally, in Section 7, we discuss the mechanism of water photooxidation reaction on visible-light responsive photocatalysts.

### Electron-transfer mechanism

In 1980, Wilson *et al.* first reported [6] the formation of a surface state as a possible intermediate of oxygen photoevolution reaction on an n-TiO<sub>2</sub> rutile electrode, as detected by a negative potential

sweep voltammetry after UV irradiation at a positive potential. Salvador *et al.* later studied the mechanism of this reaction in detail [7-10] and reported that Wilson's surface state was attributable to adsorbed hydrogen peroxide,  $\text{H}_2\text{O}_{2\text{ ad}}$ , produced by the coupling of surface  $\bullet\text{OH}$  radicals formed through the oxidation of surface hydroxyl ( $\text{Ti-OH}_s$ ) with photogenerated holes ( $h^+$ ).



Resultant  $\text{H}_2\text{O}_2$ , which is an easily oxidized compound, will be further oxidized by photogenerated holes, finally resulting in the formation of molecular oxygen.



Eq. 1 to 3 constitute Scheme 1(A).

In later studies, most of workers have either tacitly or intentionally assumed Scheme 1(A) as the molecular mechanism of oxygen photoevolution reaction on  $\text{TiO}_2$  probably under strong influences of the prominent progress of electron transfer theory by Marcus, Levich, Gerischer, and others [55]. However, spectroscopic studies, in particular, recent ones have not necessarily given clear support to Scheme 1(A). For example, Jaeger and Bard [14] and later Schwarz *et al.* [15] indeed reported that  $\bullet\text{OH}$  radicals were produced on UV irradiated  $\text{TiO}_2$  powder in aqueous solutions, using a spin-trapping method, and explained the result as due to Eq. 1. However, Nosaka *et al.* [16] recently pointed out that UV irradiation produced not free  $\bullet\text{OH}$  radicals but adsorbed  $\bullet\text{OH}$  radicals (called "surface-trapped holes" in their paper) and the latter radicals were able to give the same ESR signals as the former when reacted with spin-trapping agents. The ESR detection of  $\bullet\text{OH}$  radicals on irradiated  $\text{TiO}_2$  (anatase) particles at 77 K was also reported by Anpo *et al.* [17] though their ESR signal showed no spectral change by  $\text{H}_2\text{O} \rightarrow \text{D}_2\text{O}$  exchange in disagreement with their assignment. On the other hand, Howe and Grätzel [18] reported that photogenerated holes did not produce  $\bullet\text{OH}$  radicals but were trapped at lattice O atoms at a low temperature of 4.2 or 77 K. Micic *et al.* [19] showed that not  $\bullet\text{OH}$  radicals but  $\text{Ti-O}\bullet$  radicals were produced on  $\text{TiO}_2$ . Very recently, Tatsuma *et al.* reported [56] that  $\bullet\text{OH}$  radicals were produced not from photogenerated holes but from the photoexcitation of hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) formed via the photoreduction of molecular oxygen by electrons in the conduction band. The mechanism was supported by a direct measurement of an emission spectrum of  $\bullet\text{OH}$  radicals [57].

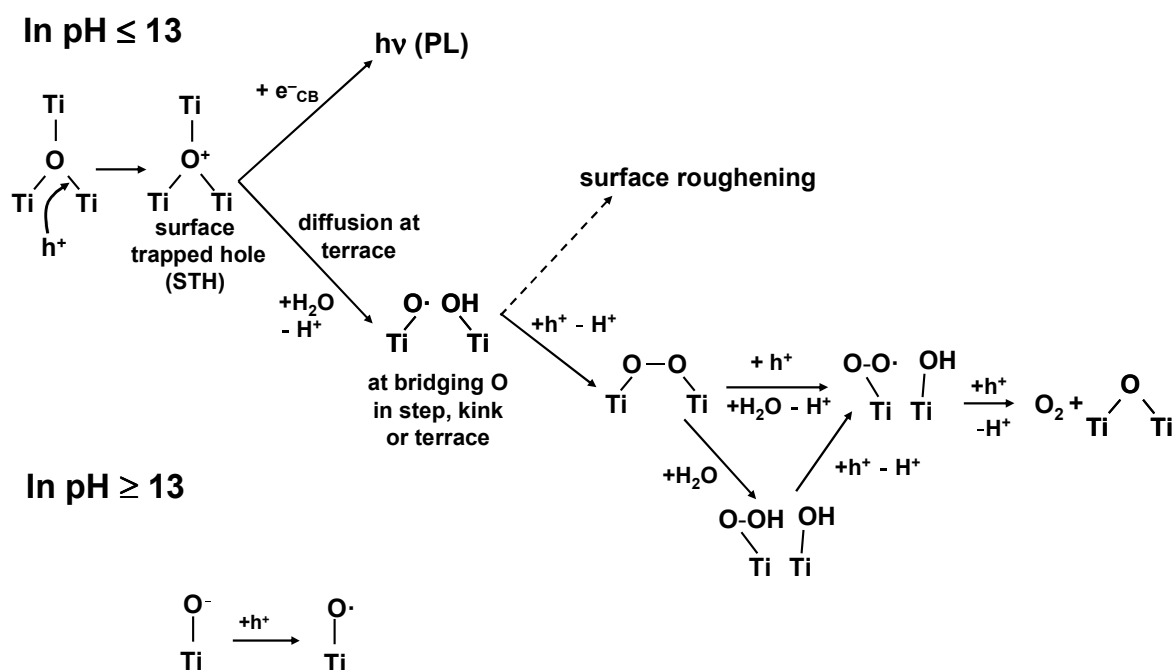
Surface intermediates on irradiated  $\text{TiO}_2$  were also studied by other spectroscopic methods. Szczepankiewicz *et al.* [31] reported by diffuse reflectance FTIR spectroscopy that a new band, assignable to surface  $\bullet\text{OH}$  radicals, was observed at  $3683\text{ cm}^{-1}$  for UV irradiated  $\text{TiO}_2$  powder in an oxygen atmosphere. Yates *et al.*, on the other hand, reported [29] that  $\bullet\text{OH}$  radicals did not play any role in the photoinduced oxidation of trichloroethylene on  $\text{TiO}_2$  in the gas phase. Hashimoto *et al.* also reported [58], by measuring the quantum yield of formation of  $\bullet\text{OH}$  radicals by means of a fluorescence probe method, that the formation of  $\bullet\text{OH}$  radicals was not the major process on irradiated  $\text{TiO}_2$  (anatase) in aqueous solutions.



Theoretically, the estimation of O-2p levels for surface O species by use of UPS data [59-62] has led to the conclusion that Eq. 1 is energetically implausible, as discussed later in detail. Recent ab-initio calculation has also shown [63] that surface Ti(OH) groups cannot act as hole traps by the formation of  $\text{Ti}^{4+}(\text{OH})\cdot$  radicals, the O-2p orbitals of surface Ti(OH) being entirely mixed with those of the valence band.

### Lewis acid-base mechanism

The new mechanism (“nucleophilic attack of  $\text{H}_2\text{O}$ ” or Lewis acid-base mechanism) was first proposed [50] to explain the experimental result that the photoelectrochemical etching of a single crystal n- $\text{TiO}_2$  (rutile) electrode produced regularly oriented nano-holes or grooves with the selective exposition of the (100) face at walls. The mechanism was later given definite support by a variety of experimental results [51-54]. The final version of the mechanism [54] is shown in Scheme 2.



**Scheme 2.** A plausible molecular mechanism expected for oxygen photoevolution reaction at the  $\text{TiO}_2$  (rutile) surface. (Reprinted with permission from [54] Copyright@The American Chemical Society)

In the new mechanism, photogenerated holes coming to the surface are first trapped at a triply coordinated O atom at the surface (terrace), forming a surface trapped hole (STH),  $[\text{Ti}_2=\text{O}\cdots\text{Ti}]^+_s$ , as a precursor of water photooxidation reaction.



Fig. 1 shows the location and the structure of an STH in surface lattice models for atomically flat  $\text{TiO}_2$  (rutile) (110) and (100) surfaces [53,54].

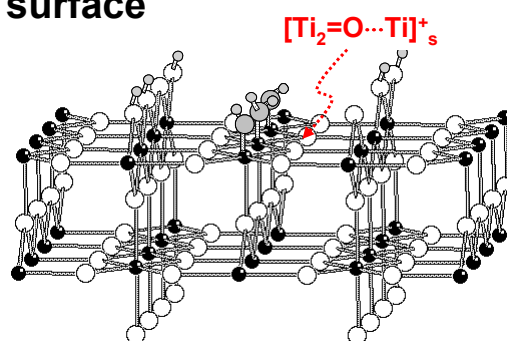
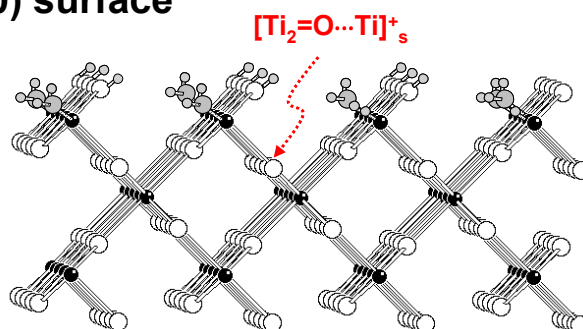
**(110) surface****(100) surface**

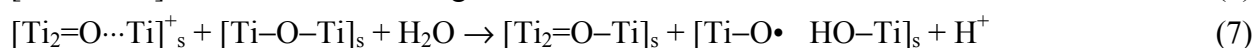
**Fig. 1.** Crystal lattice models for atomically flat (110) and (100)  $\text{TiO}_2$  (rutile) surfaces in contact with an aqueous electrolyte after the consideration of surface reconstruction, together with an expected model for a surface-trapped hole,  $[\text{Ti}_2=\text{O}\cdots\text{Ti}]_s^+$ .

The STH plays an important role in PL emission from an n- $\text{TiO}_2$  (rutile) electrode. Namely, the electrode shows a PL band peaked at around 840 nm [11-13,64-67], which is now assigned to a radiative recombination between a conduction-band electron ( $e^-_{\text{CB}}$ ) and an STH.



The STH can be regarded as a relaxed hole at the surface, accompanied with slight crystal lattice deformation due to bond lengthening caused by hole trapping (one-electron deficiency) as well as the atomic and orientation polarization of water molecules in an aqueous solution.

The direct nucleophilic attack of  $\text{H}_2\text{O}$  (or  $\text{OH}^-$ ) on an STH in a terrace may hardly occur because the insertion of OH-group to a rigid  $[\text{Ti}_2=\text{O}\cdots\text{Ti}]_s^+$  framework at a terrace needs a large distortion energy, i.e. a large activation energy. Thus, most of STH's will diffuse on a terrace and react at an easily distortable bridging O atom,  $[\text{Ti}-\text{O}-\text{Ti}]_s$ , located at a step or kink,



Eq. 7 implies that the O atom of  $\text{H}_2\text{O}$  (or  $\text{OH}^-$ ) attacks a Ti atom of a bridging O site, accompanied by the transfer of a hole (electron deficiency) from an STH to the O atom of the bridging O site in a concerted manner. Succeeding reactions in the new mechanism are shown in Scheme 2 and will be discussed later.

It is important to note that the rate of water photooxidation reaction in the new mechanism has no direct relation with redox potentials for one-electron transfer processes such as  $\text{Ti-OH} \rightarrow \text{Ti} \cdot \text{OH}^+ + \text{e}^-$ ,  $\text{H}_2\text{O} \rightarrow \cdot\text{OH} + \text{H}^+ + \text{e}^-$ , and  $\text{OH}^- \rightarrow \cdot\text{OH} + \text{e}^-$ , though these redox potentials play the key role in the conventional electron-transfer mechanism. The rate of water photooxidation reaction in the new mechanism is determined by the activation energy ( $\Delta G^\ddagger$ ) for Eq. 7, which will be governed by a distortion energy in surface lattice for inserting OH into Ti-O-Ti as well as changes in the atomic and orientation polarization energies of solvent water and adsorption energies for  $\text{O}^- \cdot$  and  $\text{HO}^-$ . Even in the Lewis acid-base mechanism, the redox level for the STH, which is expected to lie between the vacant O-2p level of STH and the top of the valence band (or the occupied O-2p level of lattice O), should be below the redox level for the total water oxidation reaction,  $2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^-$ . It is to be noted also that the  $\text{Ti-O} \cdot$  radical in  $[\text{Ti-O} \cdot \text{HO-Ti}]_s$  in Eq. 7 will have the ability to initiate the decomposition of organic compounds for photocatalytic organic degradation.

### ***In-situ* FTIR detection of surface intermediates of water photooxidation reaction**

Infrared (IR) spectroscopy is a powerful method to study adsorbed species on solid surfaces. This method can give fruitful information on the molecular structure, the molecular orientation, and the adsorption strength of surface species. However, IR spectroscopy has a serious difficulty in application to aqueous systems because of the strong IR absorption of water. The difficulty can be overcome to a large extent by using an internal reflection technique. We successfully adopted multiple internal reflection FTIR (MIR-IR) spectroscopy to detect surface intermediates of water photooxidation reaction on particulate  $\text{TiO}_2$  (rutile) films in contact with an aqueous solution [51,68]. Fig. 2 schematically illustrates a spectral cell for an MIR-IR experiment.

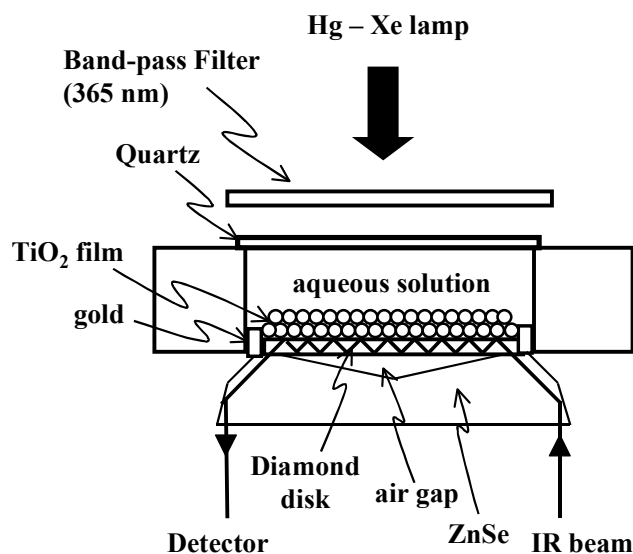


**Fig. 2.** Schematic illustration of a spectral cell used for in-situ MIR-IR absorption measurements. (Reprinted with permission from Ref. 51. Copyright©The American Chemical Society)

The use of a diamond single crystal as a multiple internal reflection element enabled us to obtain high-sensitivity spectra in a low-frequency region from 1500 to 650  $\text{cm}^{-1}$ , in which peroxy surface species as possible intermediates of water photooxidation reaction have characteristic IR absorption bands originating from O-O vibration (or  $\nu(\text{O-O})$ ) modes [69].

Fig. 3 shows an example of differential MIR-IR spectra obtained by taking a spectral difference before and after UV irradiation.

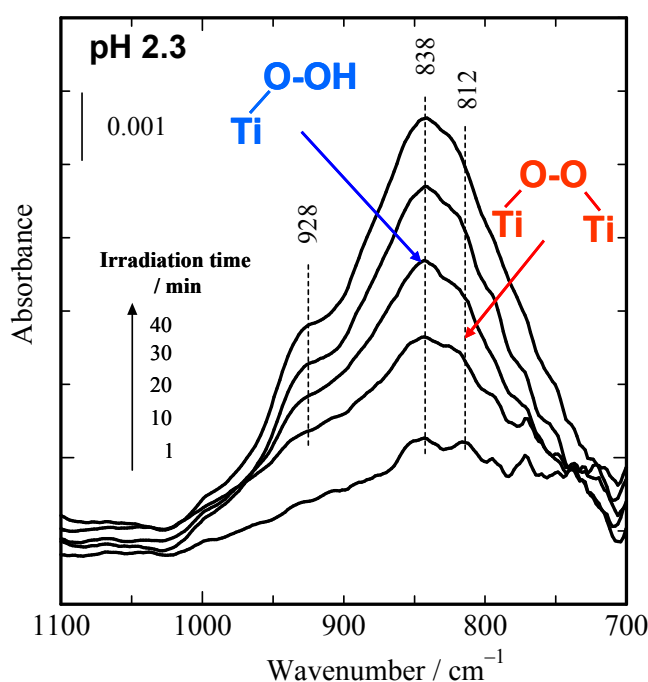


**Fig. 3.** Differential MIR-IR spectra for a particulate TiO<sub>2</sub> (rutile) film in contact with an aqueous solution of 10 mM Fe<sup>3+</sup> (pH 2.4), recorded in 1, 10, 20, 30, and 40 min after the start of UV irradiation.

Experiments were performed by irradiating a particulate TiO<sub>2</sub> (rutile) film in contact with an aqueous solution containing Fe<sup>3+</sup> as an electron acceptor. The UV irradiation was performed with a 365-nm band from a 200-W Hg-Xe lamp. Figure 3 indicates that spectral bands in the region of 700 to 1000 cm<sup>-1</sup> become stronger with UV-irradiation time, suggesting that they are due to reaction intermediates. Detailed analyses have shown that the spectral bands are assigned to surface peroxo species, as expected, the 837-cm<sup>-1</sup> and 812-cm<sup>-1</sup> bands being assigned to the  $\nu(\text{O-O})$  mode of TiOOH and that of TiOOTi, respectively.

The <sup>18</sup>O-isotopic labeling experiments by using H<sub>2</sub><sup>18</sup>O (99.9 atom% purity) as the solvent of an aqueous solution with Fe<sup>3+</sup> showed clear isotopic shifts in spectral bands to the lower frequency together with an increase in the number of spectral peaks, as shown in Figure 4. Based on the isotopic shift of 44 cm<sup>-1</sup> for the  $\nu(\text{O-O})$  band between Ti-<sup>16</sup>O<sup>16</sup>OH and Ti-<sup>18</sup>O<sup>18</sup>OH [70], the shoulder at 839 cm<sup>-1</sup> was assigned to Ti-<sup>16</sup>O-<sup>16</sup>OH, the peak at 820 cm<sup>-1</sup> assigned to Ti-<sup>16</sup>O-<sup>18</sup>OH and Ti-<sup>18</sup>O-<sup>16</sup>OH, and the shoulder at 798 cm<sup>-1</sup> assigned to Ti-<sup>18</sup>O-<sup>18</sup>OH.

A notable point is the formation of peroxy species containing both <sup>18</sup>O and <sup>16</sup>O such as Ti-<sup>16</sup>O-<sup>18</sup>OH or Ti-<sup>18</sup>O-<sup>16</sup>OH, which can only be explained by the new mechanism (i.e. Eq. 7) [51]. The conclusion is explained as follows. First note that it is reported by using H<sub>2</sub><sup>18</sup>O [71] that O atoms in surface Ti-OH in contact with an aqueous solution are rapidly and quantitatively exchanged with O atoms of H<sub>2</sub>O in the aqueous solution at room temperature, though surface lattice oxygen of TiO<sub>2</sub> showed no exchange with O atoms of H<sub>2</sub>O under the same conditions. This implies that in the experiment of Fig. 4 (in which TiO<sub>2</sub> particles were three times pre-washed with fresh H<sub>2</sub><sup>18</sup>O), all surface <sup>16</sup>OH groups were already substituted for <sup>18</sup>OH before UV irradiation, though surface lattice <sup>16</sup>O atoms remained to be <sup>16</sup>O.

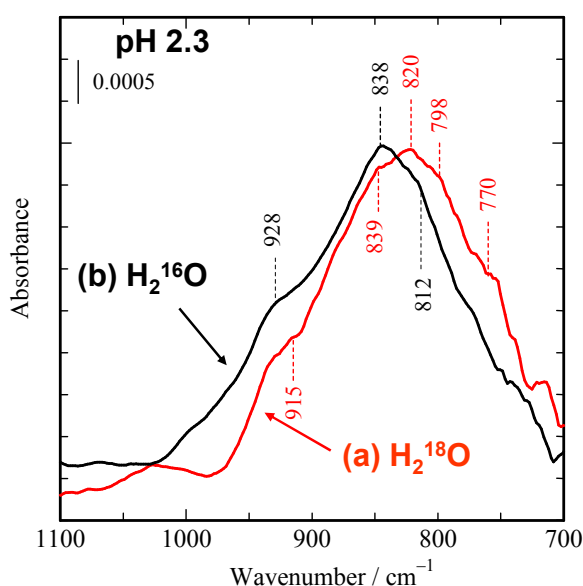
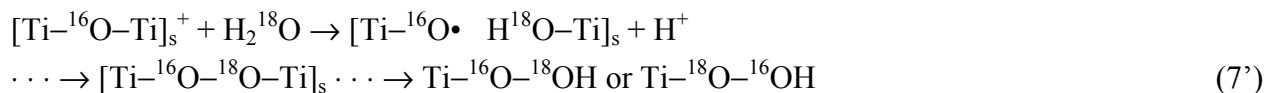
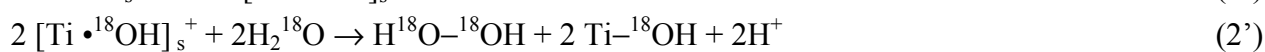


**Fig. 4.** Differential MIR-IR spectra for a particulate TiO<sub>2</sub> (rutile) film in contact with (a) H<sub>2</sub><sup>18</sup>O and (b) H<sub>2</sub><sup>16</sup>O, both containing 10 mM Fe<sup>3+</sup>, observed after 20-min UV irradiation.

Thus, the formation of peroxy species containing both  $^{18}\text{O}$  and  $^{16}\text{O}$  as reaction intermediates clearly demonstrates that water photooxidation reaction is initiated by the nucleophilic attack of  $\text{H}_2^{18}\text{O}$  to bridging (lattice)  $^{16}\text{O}$  sites.



If water photooxidation proceeded via the conventional electron transfer mechanism, only  $[\text{Ti}\cdot^{18}\text{OH}]_s^+$  and thus only  $\text{H}^{18}\text{O}-^{18}\text{OH}$  or  $\text{Ti}-^{18}\text{O}-^{18}\text{OH}$  should be formed.



It is important to note here [51] that in harmony with the above argument, differential MIR-IR spectra have shown no formation of free or adsorbed HO-OH, contrary to the expectation from the conventional electron transfer mechanism, though  $\text{TiO}_2$  powder dipped in a dilute aqueous  $\text{H}_2\text{O}_2$  solution shows strong IR bands assigned to HO-OH.

### Crystal-face dependence of water photooxidation reaction on n- $\text{TiO}_2$ (rutile)

The use of surfaces with atomic-level regulated structures as well as in-situ spectroscopic monitoring of reaction intermediates is of key importance in mechanistic studies. Eq. 5 and Eq. 7 indicate that water photooxidation and PL emission are competitive processes with each other (see also Scheme 2). This implies that the PL intensity becomes weaker as Eq. 7 gets faster, and thus the mechanism of water photooxidation reaction on atomic-level regulated  $\text{TiO}_2$  surfaces can be investigated by in situ PL measurements, though an in situ IR technique cannot be applied to such surfaces owing to insufficient detection sensitivity. It is to be noted that the assignment of the PL process (Eq. 5) is definitely proved by many experimental results, as argued in detail in a reported paper [54].

**Preparation of atomically-flat and stable  $\text{TiO}_2$  (rutile) surfaces.** The preparation of atomically-flat  $\text{TiO}_2$  surfaces have thus far been performed by the method of  $\text{Ar}^+$ -ion sputtering and thermal annealing under ultrahigh vacuum (UHV) conditions [72]. However,  $\text{TiO}_2$  surfaces prepared by this method are quite different in structures and properties from those of actual photocatalysts, which are in contact with aqueous solutions or wet air and are subjected to reconstruction by water adsorption and hydrolysis reactions. Moreover, a recent study has revealed [73] that atomically flat  $\text{TiO}_2$  (rutile) (110) surfaces prepared by the sputtering-annealing method become morphologically rough by immersion in neutral or alkaline aqueous solutions. This result indicates that the atomically flat  $\text{TiO}_2$  (rutile) surfaces prepared by the sputtering-annealing method are unstable in aqueous

solutions most probably because certain surface defects are produced by sputtering and remain even after annealing. Such surfaces can thus not be used for mechanistic studies of water photooxidation reaction.

Fortunately, we have recently found<sup>52</sup> another method to prepare atomically flat (110) and (100) n-TiO<sub>2</sub> (rutile) surfaces by collaboration with Koinuma et al. [74,75] The method is composed of chemical etching in 20% HF for 10 min, followed by thermal annealing at 600°C for 1 h. Fig. 5(a) and (b) show AFM images of commercially obtained (100)- and (110)-cut n-TiO<sub>2</sub> (rutile) surfaces, respectively, before the above HF-etching and annealing treatment is applied, while Fig. 5(c) and (d) depict those of (100)- and (110)-cut n-TiO<sub>2</sub> surfaces, respectively, after the above surface flattening treatment was applied.

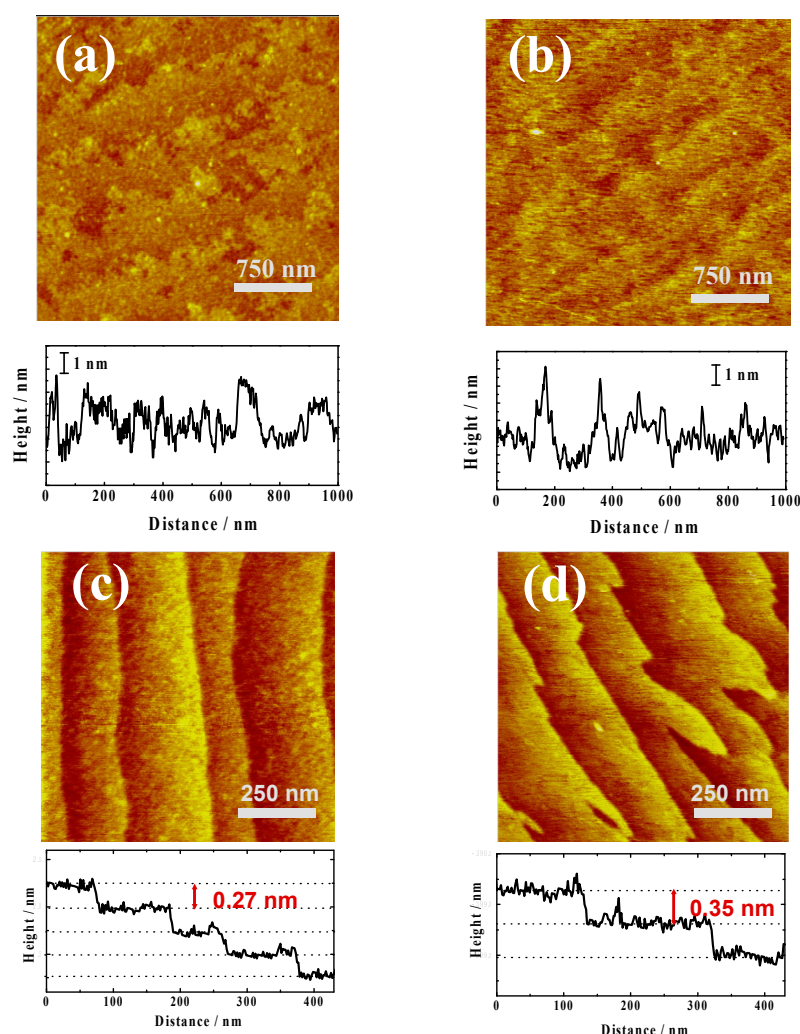


**Fig. 5.** (a) and (b): AFM images and cross-sectional height profiles for commercially available (100)- and (110)-cut surfaces of 0.05 wt% Nb-doped TiO<sub>2</sub> (rutile) single crystal wafers, respectively. (c) and (d): The same after a surface-smoothing treatment.

Contrary to the commercially obtained surfaces which are rough on a nm scale, both the (100) and (110) surfaces after the surface flattening treatment show clear step and terrace structures, indicating

that atomically flat (100) and (110) surfaces are really prepared. The observed step heights were 0.27 nm for the (100) surface and 0.35 nm for the (110) surface, in good agreement with unit-cell lengths of  $\text{TiO}_2$  (rutile). The conclusion is given further support by LEED experiments [52] and atomic-resolution noncontact atomic force microscopic (AFM) investigations [76].

Note also that we have confirmed [52,53] that atomically flat (100) and (110) surfaces prepared by the above HF-etching and annealing treatment are chemically stable, showing no change in surface morphology by exposition to aqueous solutions of pH from 1 to 13. The stability is most probably due to the fact that the surface flattening treatment does not include any extreme procedure, such as sputtering, which produces surface defects.

**Crystal-face dependence of surface band edges and  $j$ - $U$  curves.** The success in preparing atomically flat and stable n- $\text{TiO}_2$  rutile (110) and (100) surfaces has enabled us to carry out systematic investigations on the crystal-face dependence of water photooxidation reaction. First, measurements of Mott-Schottky plots have revealed [52] that the flat-band potential,  $U_{fb}$ , for the (100) surface,  $-0.34$  V vs.  $\text{Ag}/\text{AgCl}/\text{sat. KCl}$ , is about 0.09 V more negative than that for the (110) surface,  $-0.25$  V, though reasons for such a shift are unknown at present.

Fig. 6(A) compares the photocurrent density ( $j$ ) vs. potential ( $U$ ) for atomically flat (110) and (100) n- $\text{TiO}_2$  surfaces in 0.1 M  $\text{HClO}_4$  [52,53], where the anodic photocurrent is attributed to oxygen photoevolution reaction.

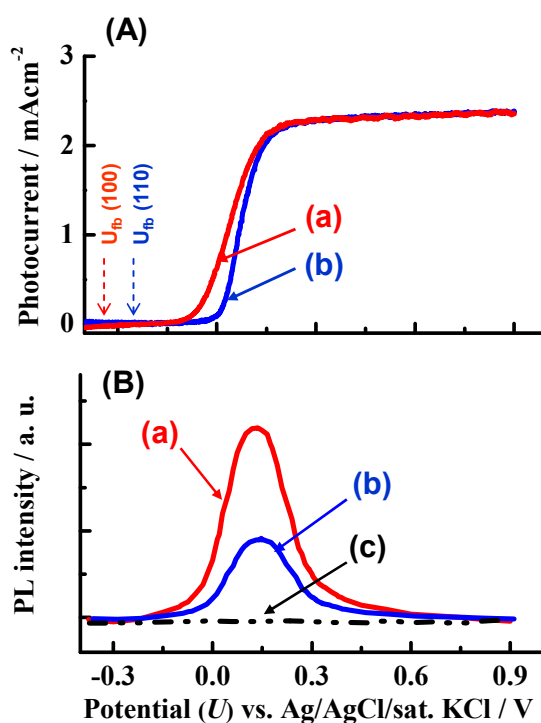


**Fig. 6.** (A) The photocurrent density vs. potential ( $U$ ), and (B) the PL intensity vs.  $U$  for  $\text{TiO}_2$  (rutile) electrodes. (a): an atomically flat (100) surface, (b) an atomically flat (110) surface, and (c) a commercially obtained (110)-cut surface with no surface-smoothing treatment. Electrolyte: 0.1 M  $\text{HClO}_4$ . The  $j$  vs  $U$  for n- $\text{TiO}_2$  electrodes with no surface-smoothing treatment was similar to that for the atomically flat (110) electrode.



The onset potential,  $U_{\text{on}}$ , of the anodic photocurrent for the (100) surface was about 0.1 V more negative than that for the (110) surface, in agreement with the shift in the  $U_{\text{fb}}$ . The  $U_{\text{on}}$  for commercially obtained (100)- and (110)-cut n-TiO<sub>2</sub> with no surface-flattening treatment was rather similar to that for an atomically flat (110) surface.

Another important feature of the  $j$  vs.  $U$  is that  $U_{\text{on}}$  is deviated considerably from  $U_{\text{fb}}$  to the positive for both the (110) and (100) surfaces (see Fig. 6(A)), indicating that efficient surface carrier recombination occurs under weak band bending near the  $U_{\text{fb}}$ . In harmony with this conclusion, the PL, which is assigned to radiative surface carrier recombination (Eq. 5), is observed under weak band bending near the  $U_{\text{fb}}$  (Fig. 6(B)).

**Differences in reaction rate between atomically flat and non-flat TiO<sub>2</sub> surfaces.** In the result of Fig. 6(B), we have to note also that PL is observed only for atomically flat TiO<sub>2</sub> (100) and (110) surfaces and not for non-flat surfaces with no surface-flattening treatment. This result was also confirmed by studies on the effect of photoelectrochemical etching on PL [64-67]. Namely, commercially obtained non-photoetched n-TiO<sub>2</sub> (rutile) with non-flat surfaces showed no PL while n-TiO<sub>2</sub> (rutile) photoetched in aqueous H<sub>2</sub>SO<sub>4</sub> emitted strong PL. Surface inspection indicated that the photoelectrochemical etching of n-TiO<sub>2</sub> (rutile) caused the production of regularly oriented nano-holes or grooves with the selective exposition of the atomically flat (100) face at walls, as already mentioned.

The result that PL is observed only for atomically flat TiO<sub>2</sub> surfaces is in harmony with the new mechanism, as explained below, and gives strong support to it. Note first that the PL-emitting process (Eq. 5) and the water photooxidation reaction (Eq. 7) are competitive with each other, as mentioned earlier (Scheme 2). For TiO<sub>2</sub> surfaces with no surface-flattening treatment, which have high densities of steps and kinks, surface-trapped holes (STH's) can easily undergo the nucleophilic attack of H<sub>2</sub>O at bridging O sites in steps or kinks. This leads to a very low density of STH's and hence to a very low PL intensity. On the other hand, for atomically flat TiO<sub>2</sub> (100) and (110) surfaces, which possess wide terraces (Fig. 5) and low densities of steps or kinks, STH's on terraces have a long lifetime because it takes time to diffuse to steps or kinks. This situation leads to a high density of STH's and hence to strong PL. A difference in the PL intensity between atomically flat (100) and (110) surfaces (Fig. 6(B)) can be explained by taking into account a difference in the mobility of STH in diffusion on a terrace [53].

On the other hand, the result that PL is observed only for atomically flat TiO<sub>2</sub> surfaces cannot be explained by the conventional electron-transfer mechanism (Scheme 1(A)). This is because surface Ti-OH exists at any TiO<sub>2</sub> face, irrespective of differences in atomic-level surface morphology, and thus resultant  $[\text{Ti} \cdot \text{OH}]^+$  radicals, which are expected to be the PL-emitting species in the conventional mechanism, should be formed at any TiO<sub>2</sub> face. Someone might assume the easier occurrence of Eq. 1 at atomically non-flat surfaces via certain active sites but this assumption leads to the conclusion that the PL intensity is higher at atomically non-flat surfaces, in disagreement with the experimental observation.

**Atomic-level surface roughening caused by water photooxidation reaction.** The use of atomically flat  $\text{TiO}_2$  surfaces has given another type of support to the new mechanism (Scheme 2). Fig. 7 shows how an AFM image of an atomically flat (110) surface was changed when it was UV-illuminated under strong band bending ( $U = 1.5$  V vs.  $\text{Ag/AgCl/sat.KCl}$ ) in 0.1 M  $\text{HClO}_4$  [53].

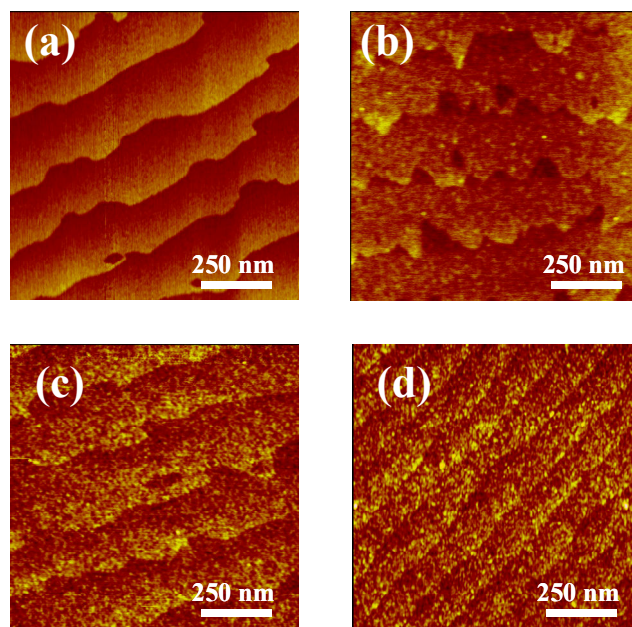


**Fig. 7.** AFM images for an atomically flat (110)  $\text{TiO}_2$  (rutile) surface, (a) before and (b)~(d) after the flow of a water-oxidation photocurrent by UV irradiation under anodic bias in 0.1 M  $\text{HClO}_4$ . The UV-irradiation intensity was (b) 0.04, (c) 1.3, and (d) 50  $\text{mW/cm}^2$ . The total electricity passing across the  $\text{TiO}_2$  surface ( $Q_p$ ) was kept constant at 0.5  $\text{C/cm}^2$  in all cases. (Reprinted with permission from [53]. Copyright@The American Chemical Society)

Compared with an atomically flat (110) surface before illumination (a), UV illumination caused atomic-level surface roughening ((b)-(d)). Moreover, the roughening became heavier with increasing illumination intensity, (b) 0.04, (c) 1.3, and (d) 50  $\text{mW/cm}^2$ , though the total electricity passing across the electrode surface ( $Q_p$ ) was kept constant at 0.5  $\text{C/cm}^2$  in all cases. With the progress of surface roughening, the PL intensity sharply decreased in agreement with the result of Figure 6(B). Essentially the same result was obtained for an atomically flat (100) surface.

The above result can be explained by the new mechanism as follows [53]. As mentioned earlier, most of STH's produced at terraces do not react with water there but diffuse on a terrace and reach easily distortable bridging O atoms at steps or kinks, at which they undergo the nucleophilic attack of  $\text{H}_2\text{O}$ . Now, the densities of steps or kinks are very low for an atomically flat (110) surface (Fig. 5). However, at a low illumination intensity, the flux of photogenerated holes to the  $\text{TiO}_2$  surface is also low and thus most of STH's produced will be able to undergo the nucleophilic attack of  $\text{H}_2\text{O}$  at bridging O sites at steps or kinks. This implies that almost no water photooxidation reaction occurs at

terraces, thus causing almost no roughening at terraces. On the other hand, at a high illumination intensity, the flux of photogenerated holes to the surface becomes high and may exceed the rate of water photooxidation reaction at bridging O sites at steps or kinks. In such a case, STH's are accumulated at terraces and finally undergo the nucleophilic attack of H<sub>2</sub>O at terraces, resulting in surface roughening in terraces. The argument is in harmony with the experimental result that the roughening became heavier with increasing illumination intensity (Fig. 7).

It is to be noted that the surface roughening can never be explained by the conventional electron-transfer mechanism because Eq. 1 or analogous processes cause no bond breaking at the surface lattice. This argument is also given definite support by studies on the pH dependence of surface roughening, as argued in the next sub-section.

**pH-dependence of water photooxidation reaction.** It is known that surface oxygen species cause protonation or deprotonation, depending on solution pH.



The reactions should strongly affect the mechanism of water photooxidation reaction. Fig. 8 shows the observed pH dependences of the PL intensity for atomically flat (110) and (100) TiO<sub>2</sub> surfaces [54], where the PL intensity is normalized at pH 1.1. In both surfaces, the PL intensity is the highest at pH 1.1 and decreases step-wise with increasing pH, namely, the PL intensity sharply decreases at around pH 4 and at about pH 13.

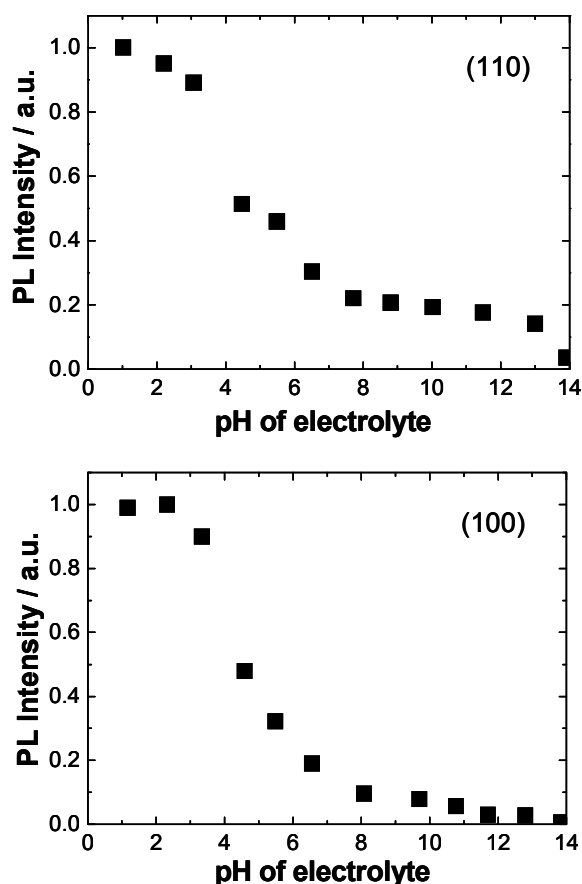


**Fig. 8.** The pH dependence of the PL intensity for atomically flat n-TiO<sub>2</sub> (rutile) (110) and (100) surfaces. (Reprinted with permission from [54]. Copyright@The American Chemical Society)

The results can be explained reasonably by the new mechanism [54]. Note first that a reported work by internal reflection FTIR spectroscopy in the pH range of 2.3 to 11.7 [77] has revealed that Ti-OH is present in the pH range from 4.3 to 10.7 (with the maximum at pH  $\approx$  8), Ti-OH<sub>2</sub><sup>+</sup> (protonated Ti-OH) exists in pH < 5, and Ti-OH<sup>+</sup>-Ti (protonated Ti-O-Ti) exists in pH < 4.3. A triply coordinated O atom, [Ti<sub>2</sub>=O...Ti]<sub>s</sub>, exists throughout the pH range with no protonation.

Based on the reported work, it is expected that in an acidic solution of pH 1.1, the TiO<sub>2</sub> surface is mainly covered with Ti-OH<sub>2</sub><sup>+</sup> and Ti-OH<sup>+</sup>-Ti as well as [Ti<sub>2</sub>=O...Ti]<sub>s</sub>. Under such a condition, the nucleophilic attack of a H<sub>2</sub>O molecule or Eq. 7 can hardly occur because positively charged STH's can hardly come near to positively charged, protonated bridging oxygen, Ti-OH<sup>+</sup>-Ti. As a result, STH's are accumulated at terraces and cause strong PL, in agreement with the experiment. The STH's will finally cause Eq. 7 under anodic bias by the downward shift of the surface band energies (or  $U_{fb}$ ) of n-TiO<sub>2</sub> due to the accumulation of STH's, for the downward shift accelerates the deprotonation of Ti-OH<sup>+</sup>-Ti and facilitates the nucleophilic attack of H<sub>2</sub>O.

With increasing pH, the surface density of deprotonated bridging oxygen (Ti-O-Ti) increases and thus the rate of Eq. 7 increases, which in turn leads to a decrease in the STH density and hence to a decrease in the PL intensity. The result of the above-mentioned reported work that Ti-OH<sup>+</sup>-Ti exists

in  $\text{pH} < 4.3$  [77] implies that the density of Ti-O-Ti increases around pH 4, namely, the density of STH's decreases around pH 4. This conclusion is in good agreement with the experimental result of Figure 8 that the PL intensity sharply decrease around pH 4.

The PL intensity shows the second sharp decrease near pH 13 (Figure 8). This can be attributed to the formation of readily oxidized surface species,  $\text{Ti-O}^-$ , by deprotonation of Ti-OH, which can cause an electron transfer reaction (see also Scheme 2) [54],



The formation of  $\text{Ti-O}^-$  in high pH was suggested previously [78] from an increased cathodic current due to increased adsorbed oxygen molecules in a form of  $\text{Ti-O}^- \cdots \text{O}_2$ . In relation with the argument, it is to be noted also that atomic-level surface roughening by UV irradiation, such as shown in Fig. 7, hardly occurs in pH 13 [54]. This result is in good agreement with the assumption of Eq. 12, which does not cause any bond breaking at surface lattice, contrary to Eq. 7.

### Studies on water photooxidation reaction by time-resolved laser spectroscopy

The pH dependence of surface reaction intermediates of water photooxidation has also been studied by time-resolved laser absorption spectroscopy, using an aqueous suspension of  $\text{TiO}_2$  particles as a sample. According to recent work [28], photogenerated holes produce two surface reaction intermediates, tentatively called Hole-1 and Hole-2. Their characteristics are summarized in Table 1.

**Table 1.** Absorption bands and their behavior for reaction intermediates produced from photogenerated holes at the  $\text{TiO}_2$  surface.

| Absorption Peak                   | Behavior of the Band |                                                                                          |
|-----------------------------------|----------------------|------------------------------------------------------------------------------------------|
| Hole-1                            | around 550 nm        | Observed throughout the pH range<br>Appears simultaneously with a laser pulse            |
| Hole-2                            | around 350 nm        | Observed only in $\text{pH} > 4$<br>Appears with a delay (i.e. with the decay of Hole-1) |
| Free $\cdot\text{OH}$ (reference) | ~250-nm              |                                                                                          |

It is interesting to note [54] that the behavior of the absorption bands for Hole-1 and Hole-2 in Table 1 can be reasonably explained if we assign Hole-1 to STH ( $[\text{Ti-O}=\text{Ti}_2]_s^+$ ) and Hole-2 to  $[\text{Ti-OH} \cdot \text{O-Ti}]_s$  formed by Eq. 7. In fact, the STH is produced in any pH and instantaneously with UV irradiation, as is seen from the argument made thus far. On the other hand,  $[\text{Ti-OH} \cdot \text{O-Ti}]_s$  is produced only in  $\text{pH} > 4$  (for  $\text{TiO}_2$  particles with no band bending, suspended in an aqueous solution) and with a delay, i.e. via the reaction of the STH with water. The red-shifts of the absorption bands from ~250-nm for free  $\cdot\text{OH}$  ( $\text{A}^2\Sigma^+ \leftarrow \text{X}^2\Pi$  transition) to ~350 nm for  $[\text{Ti-OH} \cdot \text{O-Ti}]_s$  and to ~550 nm for STH ( $[\text{Ti-O}=\text{Ti}_2]_s^+$ ) can be attributable to the incorporation of the  $\cdot\text{OH}$  radical into surface  $\text{TiO}_2$

lattice, namely, to the mixing of the O-2p orbitals of the  $\bullet\text{OH}$  radical with those of  $\text{O}^{2-}$  ions in  $\text{TiO}_2$  lattice. It is reasonable to assume that the stronger the mixing, the more red-shifted the absorption band. The above assignment is also given support by the experimental fact [28] that the reaction of free  $\bullet\text{OH}$  radicals with the  $\text{TiO}_2$ -particle surface gives a spectral band similar to  $\sim 350\text{-nm}$  band, because it is very likely that the addition of  $\bullet\text{OH}$  radicals to surface bridging O sites,  $[\text{Ti-O-Ti}]_s$ , leads to the formation of  $[\text{Ti-OH } \bullet\text{O-Ti}]_s$ .

### Energy levels of surface oxygen species relating with water photooxidation

In the conventional electron-transfer mechanism (Scheme 1(A)), redox potentials such as  $E^0(\text{Ti-OH/Ti } \bullet\text{OH}^+)$ ,  $E^0(\text{H}_2\text{O}/\bullet\text{OH}, \text{H}^+)$  and  $E^0(\text{OH}^-/\bullet\text{OH})$  or energies of occupied O-2p levels for surface oxygen species such as  $\text{Ti-OH}$ ,  $\text{H}_2\text{O}_{\text{aq}}$ , and  $\text{OH}^-_{\text{aq}}$  play the key role in determining the reaction rate, as mentioned earlier. Recent ultraviolet photoelectron spectroscopic (UPS) studies [59-62], combined with scanning tunnel microscopic (STM) inspection [59,79], have enabled us to estimate energies of the O-2p levels for surface oxygen species. Figure 9 shows the O-2p levels for  $\text{Ti-OH-Ti}$  at the (110)  $\text{TiO}_2$  (rutile) face and those for  $\text{Ti-OH}$  at the (100) face thus estimated [54], compared with the valence band energy of  $\text{TiO}_2$  (rutile), redox potentials such as  $E^0(\text{Ti-OH/Ti } \bullet\text{OH}^+)$ ,  $E^0(\text{H}_2\text{O}/\bullet\text{OH}, \text{H}^+)$  and  $E^0(\text{OH}^-/\bullet\text{OH})$  [80], and energies of the O-2p levels for solution species such as  $\text{OH}^-_{\text{aq}}$  and  $\text{H}_2\text{O}_{\text{aq}}$  estimated by photoelectron emission from aqueous solutions [81,82].

Here we have to note that UPS studies yield O-2p levels at the  $\text{TiO}_2$  (rutile)/vacuum interface. The O-2p levels at the  $\text{TiO}_2$  (rutile)/aqueous electrolyte interface will be slightly higher owing to stabilization by the electronic polarization of an aqueous electrolyte. The electronic polarization energy  $\Delta G_{\text{el}}$  of an aqueous electrolyte for a surface  $[\text{Ti } \bullet\text{OH}]^+$  species can be estimated [51] by the use of Born equation,  $\Delta G_{\text{el}} = (1/2) (e^2/8\pi\epsilon_0 r) (1-1/n^2)$ , where  $r$  is the van der Waals radius for OH group of  $\text{Ti-OH}$  and  $n$  the refractive index of water. The coefficient (1/2) is added because an aqueous electrolyte occupies only a half space. As there is no saturation effect for the electronic polarization, in contrast to orientation polarization, the estimation of  $\Delta G_{\text{el}}$  by Born equation should give a good approximation. A simple calculation gave a value of  $\Delta G_{\text{el}} = 1.1 \text{ eV}$  for  $r = 0.15 \text{ nm}$ . The top of the O-2p level for  $\text{Ti-OH-Ti}$  and  $\text{Ti-OH}$  at the  $\text{TiO}_2$ /aqueous electrolyte interface is thus estimated to be about 2.6 eV and 0.7 eV below the top of the valence band at the  $\text{TiO}_2$  surface,  $E_v^s$ , respectively (see Fig. 9). The result clearly indicates that Eq. 1 is energetically implausible.

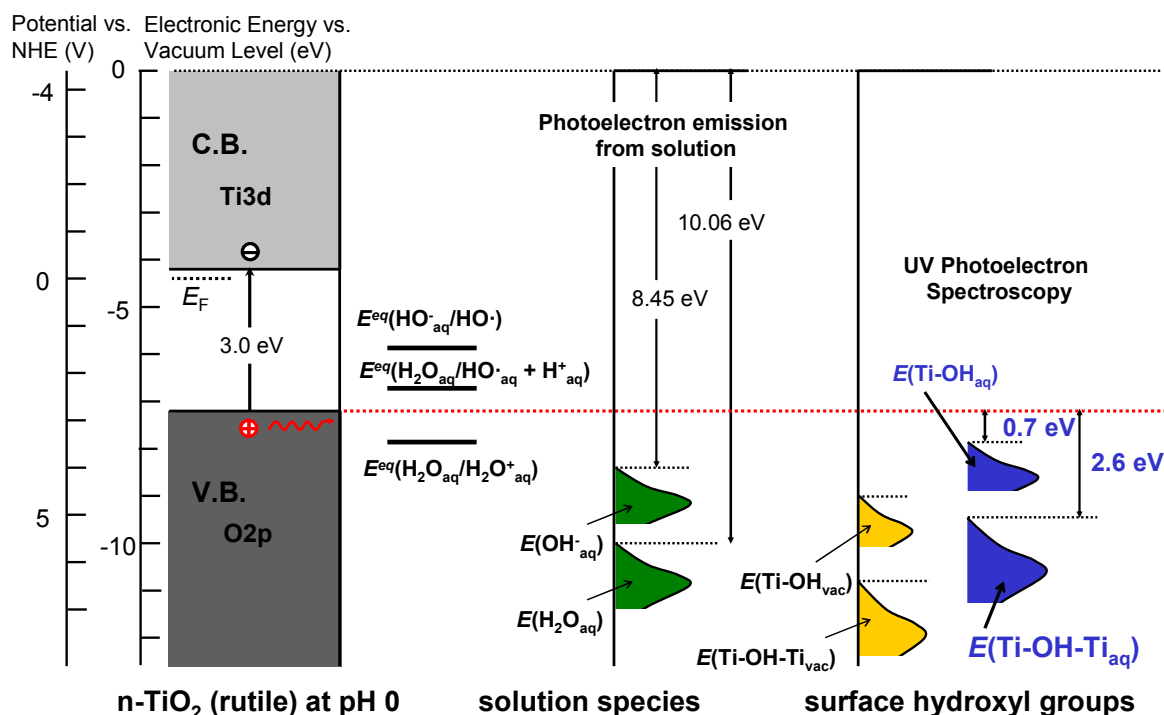


**Fig. 9.** O-2p levels for Ti-OH-Ti and Ti-OH at the TiO<sub>2</sub> (rutile) surface estimated from UPS data, compared with the valence band of TiO<sub>2</sub> (rutile) at pH 0, redox potentials  $E^0(\text{Ti-OH}/\text{Ti} \cdot \text{OH}^+)$ ,  $E^0(\text{H}_2\text{O}/\cdot\text{OH}, \text{H}^+)$ , and  $E^0(\text{OH}^-/\cdot\text{OH})$ , and O-2p levels for OH<sup>-</sup><sub>aq</sub> and H<sub>2</sub>O<sub>aq</sub> estimated by photoelectron emission from aqueous solutions.

Someone might point out that the following reaction, proposed by Micic et al. [19], is plausible energetically, in contrast to Eq. 1, owing to hydration energy for H<sup>+</sup>.



Indeed, Eq. 1'' looks energetically plausible but our experiments do not give any support to Eq. 1''. A possible reason may be that the rate constant for Eq. 1'' is much lower than that for Eq. 4.

### Water photooxidation on visible-light responsive photocatalysts

We have studied the mechanism of water photooxidation reaction on visible-light responsive materials such as N- [46] or C-doped [49] TiO<sub>2</sub>, tantalum oxynitride (TaON) [47], BiZn<sub>2</sub>VO<sub>6</sub> [48], etc. The studies have shown that water photooxidation on these materials does not proceed by the conventional electron-transfer mechanism.

Let us see the results of TaON as an example. Domen et al. reported [44] that an aqueous suspension of TaON powder in the presence of a sacrificial oxidizing reagent such as Ag<sup>+</sup> caused photocatalytic oxygen evolution at a high quantum efficiency of 34% under visible light irradiation.

A notable feature of this material is that it has the valence band composed of hybridized N-2p and O-2p orbitals and the top of the valence band is located at about 2.2 V vs. NHE (pH 0), considerably above the top of the valence band of  $\text{TiO}_2$ . Nevertheless, this material can cause photocatalytic oxygen evolution.

A particulate TaON film electrode shows an anodic photocurrent attributable to oxygen evolution in an aqueous electrolyte [47]. The action spectrum of the anodic photocurrent (Fig. 10A) agrees with the absorption spectrum of TaON. Fig. 10B shows the effect of the addition of a reducing agent to the aqueous electrolyte on the photocurrent action spectrum [47].

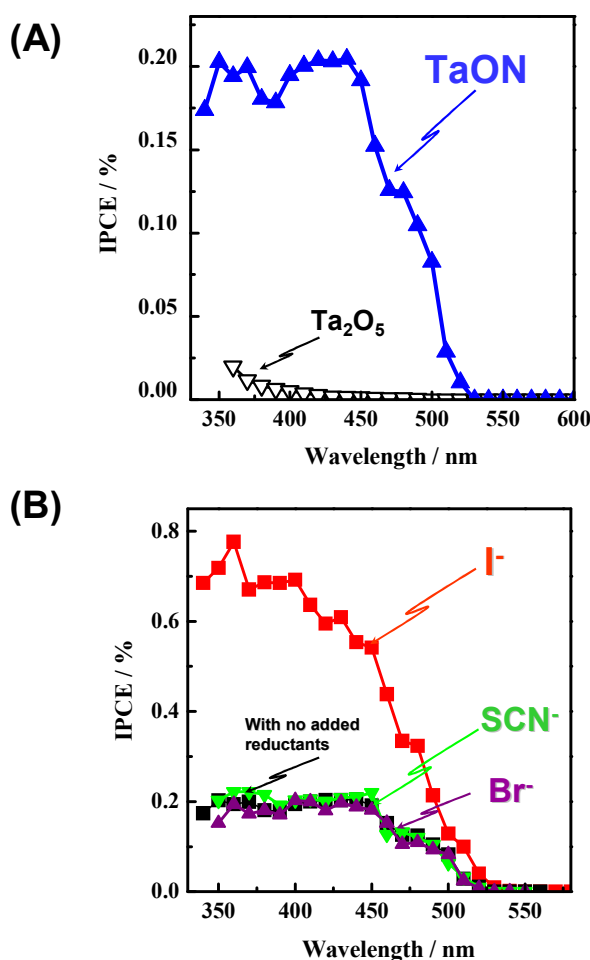


**Fig. 10.** (A) Photocurrent action spectra (IPCE vs. wavelength) for particulate TaON and Ta<sub>2</sub>O<sub>5</sub> film electrodes in 0.1 M HClO<sub>4</sub>. (B) Effect of the addition of 0.5 mM  $\text{I}^-$ ,  $\text{SCN}^-$ , and  $\text{Br}^-$  to the electrolyte (0.1 M HClO<sub>4</sub>) on the IPCE vs. wavelength for TaON. The electrode potential was 0.7 V vs. Ag/AgCl in both cases.

The addition of iodide ( $\text{I}^-$ ) caused a large increase in the photocurrent while the addition of  $\text{SCN}^-$  and  $\text{Br}^-$  induced no increase. The addition of methanol and ethanol also led to no increase.

The enhancement of the photocurrent by the addition of  $\text{I}^-$  can be explained as follows. In the presence of  $\text{I}^-$  in the electrolyte, photogenerated holes at the  $\text{TiO}_2$  surface react either with water or  $\text{I}^-$



competitively. In general, water oxidation reaction produces high densities of surface intermediates, which act as efficient carrier recombination centers. The competitive occurrence of  $\text{I}^-$  oxidation thus leads to decreases in densities of surface intermediates and hence to a decrease in surface carrier recombination and therefore to an increase in the photocurrent. No increase in the photocurrent by the addition of  $\text{SCN}^-$  and  $\text{Br}^-$  thus indicates that photogenerated holes only react with water, causing no oxidation of  $\text{SCN}^-$  and  $\text{Br}^-$ .

Fig. 11 shows equilibrium redox potentials ( $E_{\text{redox}}^{\text{eq}}$ ) [82,83] for the one-electron oxidation of  $\text{I}^-$ ,  $\text{SCN}^-$ ,  $\text{Br}^-$  and  $\text{H}_2\text{O}$  ( $\text{I}^-/\text{I}^\bullet$  1.35 V,  $\text{SCN}^-/\text{SCN}^\bullet$  1.64 V,  $\text{Br}^-/\text{Br}^\bullet$  2.00 V,  $\text{H}_2\text{O}/\text{HO}^\bullet, \text{H}^+$  2.38 V) compared with the energy bands for TaON [44]. Experimental results of Figure 10B show that only  $\text{I}^-$  and  $\text{H}_2\text{O}$  are oxidized by photogenerated holes in TaON.

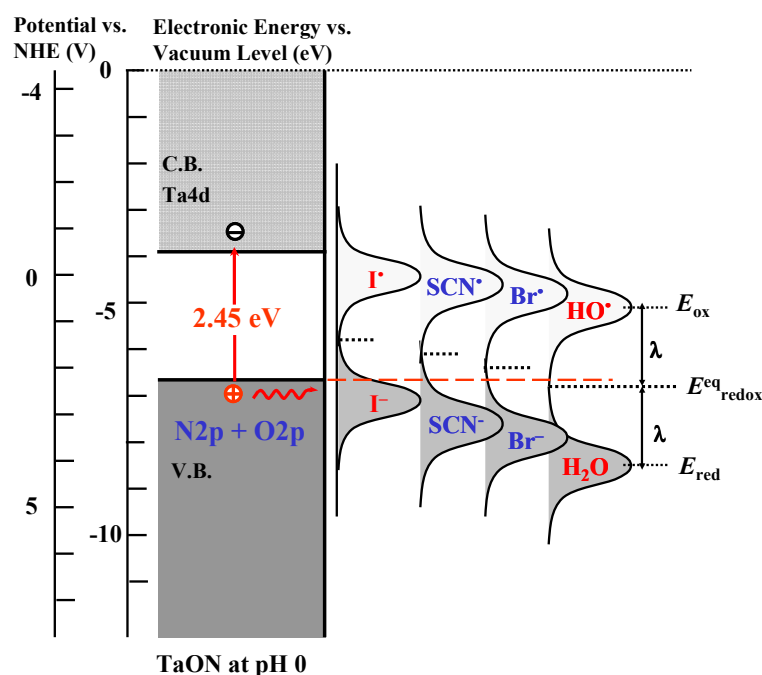


**Fig. 11.** Schematic illustration of energy bands for TaON at pH 0, together with state density distributions for  $\text{I}^-$ ,  $\text{SCN}^-$ ,  $\text{Br}^-$  and  $\text{H}_2\text{O}$  estimated from reported reorganization energies ( $\lambda$ ) [83].

The result is not in harmony with the order of  $E_{\text{redox}}^{\text{eq}}$  in Fig. 11. This indicates that water photooxidation reaction cannot be explained by the conventional electron-transfer mechanism, namely, it proceeds by a different mechanism from the conventional one. The water photooxidation on TaON (and N- or C-doped  $\text{TiO}_2$ ) can be explained by the new (Lewis acid-base) mechanism, as argued in detail elsewhere [47,49].

## Conclusion

Our recent studies on the molecular mechanism of water photooxidation reaction on TiO<sub>2</sub> (rutile) have shown that the reaction in  $\text{pH} \leq 12$  is initiated by the new “nucleophilic attack of H<sub>2</sub>O” or “Lewis acid-base” mechanism, not by the conventional electron transfer (ET) mechanism. The conclusion is supported by the following facts. (1) In situ MIR-IR experiments with <sup>18</sup>O isotope exchange have shown the incorporation of lattice oxygen into surface reaction intermediates (peroxides), which can only be explained by the new mechanism. (2) Water photooxidation reaction in  $\text{pH} \leq 12$  has caused atomic-level surface roughening, in harmony with the new mechanism. The result can never be explained by the conventional ET mechanism, which causes no bond breaking at the surface lattice. In fact, in  $\text{pH} \geq 13$ , in which water photooxidation is expected to proceed by the conventional ET mechanism owing to the formation of Ti-O<sup>-</sup>, no surface roughening is induced by UV irradiation. (3) In situ PL measurements have shown that water photooxidation reaction occurs more efficiently on atomically non-flat surfaces than on atomically flat ones. This result is in harmony with the new mechanism but cannot be explained by the conventional ET mechanism because surface Ti-OH is present at any face. (4) The pH dependence of the PL intensity has shown good correlations with the pH dependence of the protonated or deprotonated surface O species. (5) The experimental estimation of the O-2p energies of surface oxygen species has shown that the conventional ET mechanism is energetically implausible.

There, however, remain some issues to need further investigations. It is very likely that water photooxidation reaction on TiO<sub>2</sub> (anatase) occurs by the same mechanism as on rutile but this has not been verified enough yet. In relation to this problem, there is also a possibility that “hot” holes (holes generated deep in the valence band) participate in surface reactions, in particular, when the size of photocatalyst semiconductor particles becomes very small, 5-20 nm or less. As the size of TiO<sub>2</sub> (anatase) particles is in general small, in the range of 5-20 nm, this implies that photocatalytic experiments with TiO<sub>2</sub> (anatase) particles may include a contribution of Eq. 1 caused by hot holes, depending on experimental conditions. The participation of hot holes in surface reactions is experimentally suggested in N- or C-doped TiO<sub>2</sub> [46,49] by differences in photocurrent behavior between UV and visible-light irradiation. The contribution of hot holes is also reported by the irradiation-light wavelength dependence of the quantum yield of water photooxidation reaction [84].

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## Development of visible-light-driven TiO<sub>2</sub> and SrTiO<sub>3</sub> photocatalysts doped with metal cations for H<sub>2</sub> or O<sub>2</sub> evolution

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**Keywords:** Photocatalyst; water splitting; hydrogen evolution; oxygen evolution; visible-light response; doping; codoping.

**Abstract.** This review paper represents photocatalytic properties of metal cation-doped TiO<sub>2</sub> (rutile) and SrTiO<sub>3</sub> photocatalysts for O<sub>2</sub> evolution from an aqueous silver nitrate solution and H<sub>2</sub> evolution from an aqueous methanol solution under visible light irradiation. Photocatalytic activities for the O<sub>2</sub> evolution of Cr/Sb and Rh/Sb-codoped TiO<sub>2</sub> are strongly dependent on the codoping ratio and the amount of doped chromium and rhodium. The codopant controls the oxidation number of doped chromium and rhodium. Rh-doped SrTiO<sub>3</sub> in which the doped Rh species possesses a reversible redox property is active for the H<sub>2</sub> evolution reaction under visible light irradiation. Overall water splitting under visible light irradiation proceeds with Z-scheme photocatalyst systems consisting of the Rh-doped SrTiO<sub>3</sub> as a H<sub>2</sub> evolution photocatalyst combined with BiVO<sub>4</sub> as an O<sub>2</sub> evolution photocatalyst and an Fe<sup>3+</sup>/Fe<sup>2+</sup> electron mediator.

### Introduction

**Overall water splitting using UV-light-driven photocatalysts.** A research area in photocatalysis is classified into two categories, photon energy conversion as represented by water splitting and application of a TiO<sub>2</sub> photocatalyst to environmental purification. Photoelectrochemistry [1–7] and photocatalysis [8–39] using semiconductor materials for the photon energy conversion have extensively been studied since the Honda-Fujishima effect [40] was reported. Many metal oxide photocatalysts [22,24–26,33,34,39] and some metal nitrides Ge<sub>3</sub>N<sub>4</sub> [30,36] and GaN:Zn [35] can split water into H<sub>2</sub> and O<sub>2</sub> efficiently in a stoichiometric ratio under UV light irradiation. Table 1 shows representative TiO<sub>2</sub> and SrTiO<sub>3</sub> photocatalysts for water splitting into H<sub>2</sub> and O<sub>2</sub>. The TiO<sub>2</sub> photocatalyst has been studied for a long time. At the early stages of this research field, it was suspected if the TiO<sub>2</sub> photocatalyst could split water into H<sub>2</sub> and O<sub>2</sub> in a stoichiometric ratio by the band gap excitation. It is confirmed at present that the overall water splitting proceeds over the TiO<sub>2</sub> photocatalyst, if it is carried out under suitable reaction conditions and with modification by cocatalysts. On the other hand, a SrTiO<sub>3</sub> photoelectrode splits water into H<sub>2</sub> and O<sub>2</sub> by band gap excitation without an external bias being different from a TiO<sub>2</sub> photoelectrode [41]. Therefore, overall water splitting by SrTiO<sub>3</sub> powder has also been studied as shown in Table 1. These studies of TiO<sub>2</sub> and SrTiO<sub>3</sub> have confirmed the possibility of water splitting using powdered photocatalysts. A NiO/NaTaO<sub>3</sub>:La photocatalyst has recently proven that highly efficient water splitting is possible using a powdered photocatalyst under UV light irradiation [24].

**Overall water splitting using visible-light-driven photocatalysts.** The goal of this research field is to produce hydrogen by usage of solar energy, so-called "solar hydrogen production". In order to utilize solar energy efficiently, it is indispensable to develop visible-light-driven photocatalysts. There are several strategies to develop visible-light-driven photocatalysts [26,33,34,42]. Doping of metal cations is a well-known method of the design for the sensitization of wide band gap semiconductor photocatalysts such as TiO<sub>2</sub> and SrTiO<sub>3</sub> to visible light in photoelectrochemistry and



photocatalysis [43–51]. Sakata and coworkers have reported that Cu-doped  $\text{TiO}_2$  powder shows photocatalytic activity for  $\text{H}_2$  evolution from an aqueous methanol solution under visible light irradiation without Pt cocatalyst [43]. Ohno and coworkers have reported that Ru-doped  $\text{TiO}_2$  powder can evolve  $\text{O}_2$  from an aqueous solution containing  $\text{Fe}^{3+}$  ions under visible light irradiation [44]. Rh-doped  $\text{TiO}_2$  and  $\text{SrTiO}_3$  electrodes show visible-light response for photocurrents [48,49]. Recently, non-metal ion doping of nitrogen, sulfur, and carbon into  $\text{TiO}_2$  has also been investigated, especially for decomposition of organic compounds [52–55]. Moreover, many metal oxide, sulfide, and (oxy)nitride materials, besides the modified  $\text{TiO}_2$  and  $\text{SrTiO}_3$ , show photocatalytic activities for  $\text{H}_2$  or  $\text{O}_2$  evolution from aqueous solutions containing sacrificial reagents under visible light irradiation [22,26,33,34,42–44]. Some photocatalyst systems that can split water into  $\text{H}_2$  and  $\text{O}_2$  under visible light irradiation have recently been developed [23,26,28,31,33,34,37,38]. However, their photocatalytic activities are not satisfying the efficient solar hydrogen production.

In the present review paper, we focus on the development of visible-light-driven  $\text{TiO}_2$  (rutile) and  $\text{SrTiO}_3$  powdered photocatalysts by metal cation doping or codoping for  $\text{H}_2$  or  $\text{O}_2$  evolution in the presence of sacrificial reagents. The importance of the codoping for the  $\text{TiO}_2$  photocatalyst is discussed. Overall water splitting under visible light irradiation by Z-scheme photocatalyst systems consisting of metal cation-doped  $\text{SrTiO}_3$  is also introduced.

Table 1. Overall water splitting under UV light irradiation over  $\text{TiO}_2$  and  $\text{SrTiO}_3$  photocatalysts

| Catalyst                                                    | Reaction condition                                      |              |                  | Activity<br>[ $\mu\text{mol h}^{-1}$ ] |                | Ref. |
|-------------------------------------------------------------|---------------------------------------------------------|--------------|------------------|----------------------------------------|----------------|------|
|                                                             | Water condition                                         | Light source | Irradiation type | $\text{H}_2$                           | $\text{O}_2$   |      |
| Pt/ $\text{TiO}_2$                                          | Vapor                                                   | 200 W Hg     | Outer            | 0.4                                    | 0.2            | 8    |
| RuO <sub>2</sub> / $\text{TiO}_2$                           | Vapor                                                   | 500 W Hg     | Outer            | 0.6                                    | 0.2            | 11   |
| NaOH-coated Rh/ $\text{TiO}_2$                              | Vapor                                                   | 500 W Hg     | Outer            | 449                                    | Stoichiometric | 12   |
| NaOH-coated NiO <sub>x</sub> / $\text{TiO}_2$ <sup>a)</sup> | Vapor                                                   | 450 W Hg     | Outer            | 30                                     |                | 16   |
| NiO <sub>x</sub> / $\text{TiO}_2$ <sup>a)</sup>             | 3 mol L <sup>-1</sup> NaOH                              | 450 W Hg     | Inner            | 6                                      | 2              | 16   |
| CeO <sub>2</sub> / $\text{TiO}_2$                           | 10 mol L <sup>-1</sup> NaOH                             | 100 W Hg     | Outer            | 0.7                                    | 0.3            | 17   |
| Pt/ $\text{TiO}_2$                                          | Pure water                                              | 250 W Hg     | Outer            | 106                                    | 53             | 18   |
| Pt/ $\text{TiO}_2$                                          | 2.2 mol L <sup>-1</sup> Na <sub>2</sub> CO <sub>3</sub> | 400 W Hg     | Inner            | 568                                    | 287            | 19   |
| Pt/Ti-B binary oxide                                        | Pure water                                              | 400 W Hg     | Inner            | 22                                     | 11             | 20   |
| Rh/ $\text{SrTiO}_3$                                        | Pure water                                              | 1000 W Xe-Hg | –                | 9.3                                    | 4.7            | 10   |
| NaOH-coated Rh/ $\text{SrTiO}_3$                            | Vapor                                                   | 500 W Hg     | Outer            | 18                                     | 8.6            | 14   |
| NiO <sub>x</sub> / $\text{SrTiO}_3$ <sup>a)</sup>           | Pure water                                              | 450 W Hg     | Inner            | 24                                     | 11             | 15   |
| NiO <sub>x</sub> / $\text{SrTiO}_3$ <sup>a)</sup>           | 5 mol L <sup>-1</sup> NaOH                              | 450 W Hg     | Inner            | 40                                     | 19             | 15   |

<sup>a)</sup> NiO<sub>x</sub> represents a NiO cocatalyst that was reduced with  $\text{H}_2$  and reoxidized with  $\text{O}_2$  as an activation pretreatment.

## Development of visible-light-driven $\text{TiO}_2$ and $\text{SrTiO}_3$ photocatalysts for $\text{O}_2$ and $\text{H}_2$ evolution from aqueous solutions

**Strategy for development of metal cation-doped  $\text{TiO}_2$  and  $\text{SrTiO}_3$  photocatalysts with visible-light response [26,33,34].** The bottom of a conduction band level should be more negative than a redox potential of  $\text{H}^+/\text{H}_2$  (0 V vs. NHE) while the top of a valence band should be more positive than a redox potential of  $\text{O}_2/\text{H}_2\text{O}$  (1.23 V vs. NHE) for water splitting into  $\text{H}_2$  and  $\text{O}_2$  by using semiconductor photocatalysts as shown in Fig. 1-(a). Valence band levels of metal oxide photocatalysts with  $d^0$  or  $d^{10}$  configuration are usually too positive (ca. 3 V vs. NHE) compared with the redox potential of  $\text{O}_2/\text{H}_2\text{O}$  because the valence band consists of  $\text{O}2p$  orbitals. Therefore, the band gaps of photocatalysts for water splitting are inevitably wider than 3 eV. These photocatalysts respond to only UV light.  $\text{TiO}_2$  and  $\text{SrTiO}_3$  possess the narrowest band gaps among UV-light-responsive photocatalysts because the bottoms of their conduction band levels are close to the redox potential of  $\text{H}^+/\text{H}_2$ . Therefore, making new valence bands or electron donor levels above the valence band consisting of  $\text{O}2p$  orbitals (band engineering) is required for the sensitization of the  $\text{TiO}_2$  and  $\text{SrTiO}_3$  photocatalysts to visible light.  $\text{TiO}_2$  and  $\text{SrTiO}_3$  may show visible-light response if the dopant forms an electron donor level in the band gap as shown in Fig. 1-(b). For example, visible-light responses of nickel and either tantalum or niobium-codoped  $\text{TiO}_2$  and  $\text{SrTiO}_3$  are due to the electronic transition from the electron donor levels consisting of occupied  $\text{Ni}^{2+}3d$  orbitals to the conduction bands of host materials. The energy gaps of  $\text{TiO}_2:\text{Ni}/(\text{Ta}, \text{Nb})$  and  $\text{SrTiO}_3:\text{Ni}/\text{Ta}$  are 2.6 eV and 2.8 eV, indicating that the electron donor level consisting of the occupied  $\text{Ni}^{3+}$  orbitals is about 2.6 eV vs. NHE [56]. Some visible-light-driven  $\text{TiO}_2$  and  $\text{SrTiO}_3$  photocatalysts obtained by metal cation doping are introduced below.

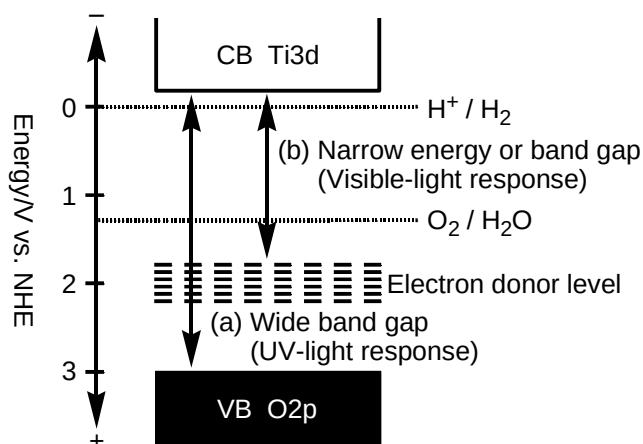


Fig. 1 Design of visible-light-driven photocatalysts by doping.

**Visible-light-driven  $\text{TiO}_2$  codoped with metal cations for  $\text{O}_2$  evolution [56,57,58].** Doping of transition metal cations usually results in a significant decrease in photocatalytic activity because the dopants work as recombination centers between photogenerated electrons and holes, even if it often gives visible light absorption band. In contrast to this common sense, the authors have succeeded in the development of visible-light-driven  $\text{TiO}_2$  (rutile) by a codoping technique as shown Table 2. The codoping of metal cations with high oxidation numbers such as  $\text{Sb}^{5+}$ ,  $\text{Nb}^{5+}$ , and  $\text{Ta}^{5+}$  improves photocatalytic activities of  $\text{TiO}_2$  doped with chromium, rhodium, and nickel for  $\text{O}_2$  evolution from an aqueous silver nitrate solution under visible light irradiation. Especially, drastic improvements are observed for the photocatalytic performance of  $\text{TiO}_2$  doped with chromium and rhodium.

Table 2. Photocatalytic O<sub>2</sub> evolution from an aqueous silver nitrate solution under visible light irradiation over TiO<sub>2</sub> doped or codoped with metal cations

| Dopant | Codopant | Energy gap [eV]   | Incident light <sup>a)</sup> [nm] | Rate of O <sub>2</sub> evolution [μmol h <sup>-1</sup> ] | Ref. |
|--------|----------|-------------------|-----------------------------------|----------------------------------------------------------|------|
| Cr     | –        | – <sup>b)</sup>   | ≥ 420                             | 0                                                        | 57   |
| Cr     | –        | 2.6 <sup>c)</sup> | ≥ 420                             | 0                                                        | 57   |
| Cr     | Sb       | 2.2               | ≥ 420                             | 45                                                       | 57   |
| Ni     | –        | 2.6               | ≥ 440                             | 3.8                                                      | 56   |
| Ni     | Nb       | 2.6               | ≥ 440                             | 7.6                                                      | 56   |
| Ni     | Ta       | 2.6               | ≥ 440                             | 7.4                                                      | 56   |
| Ni     | Sb       | 2.6               | ≥ 440                             | 12.8                                                     | 57   |
| Rh     | –        | – <sup>b)</sup>   | ≥ 440                             | 0                                                        | 58   |
| Rh     | –        | 2.0 <sup>c)</sup> | ≥ 440                             | 1.1                                                      | 58   |
| Rh     | Ta       | 2.2               | ≥ 440                             | 4.7                                                      | 58   |
| Rh     | Sb       | 2.1               | ≥ 440                             | 17                                                       | 58   |

Catalyst, 0.3–0.5 g; reactant solution, 150–320 mL of 0.05 mol L<sup>-1</sup> aqueous silver nitrate solution; light source, 300-W Xe lamp.

<sup>a)</sup> Cutoff filters (L42 and Y44) were employed.

<sup>b)</sup> Distinguishable absorption edges were not observed.

<sup>c)</sup> Treated with H<sub>2</sub> reduction.

Fig. 2 shows the dependence of photocatalytic O<sub>2</sub> evolution from an aqueous silver nitrate solution over TiO<sub>2</sub>:Cr/Sb and TiO<sub>2</sub>:Rh/Sb upon the ratio of codoped antimony to chromium and rhodium. This result clearly indicates that codoping of antimony plays an important role in visible-light response for the TiO<sub>2</sub> photocatalyst doped with chromium and rhodium. Visible-light responses of TiO<sub>2</sub>:Cr/Sb and TiO<sub>2</sub>:Rh/Sb are due to the electronic transition from the electron donor levels consisting of Cr<sup>3+</sup>3d and Rh<sup>3+</sup>4d occupied orbitals to the conduction band of the TiO<sub>2</sub> host. However, Cr<sup>6+</sup> and Rh<sup>4+</sup> ions form in TiO<sub>2</sub> due to self-charge compensation. These species predominantly work as recombination centers between photogenerated electrons and holes. No activities are observed for TiO<sub>2</sub>:Cr/Sb and TiO<sub>2</sub>:Rh/Sb with 0 and 0.5 of the codoping ratios (Sb/Cr, Sb/Rh) due to the formation of large amounts of Cr<sup>6+</sup> and Rh<sup>4+</sup> species. The formations of these species are confirmed by XPS and ESR analyses. In contrast, photocatalytic activities for the O<sub>2</sub> evolution are obtained when the codoping ratios are equal to or larger than the unity because codoped Sb<sup>5+</sup> ions suppress the formation of Cr<sup>6+</sup> and Rh<sup>4+</sup> ions by charge compensation. Ikeda, Onishi, and coworkers have confirmed by IR transient absorption by photogenerated electrons that the codoping of antimony to TiO<sub>2</sub>:Cr prolongs the lifetime of electrons photogenerated in a conduction band or a shallow trapping level [59]. This result indicates the suppression of the formation of recombination centers.

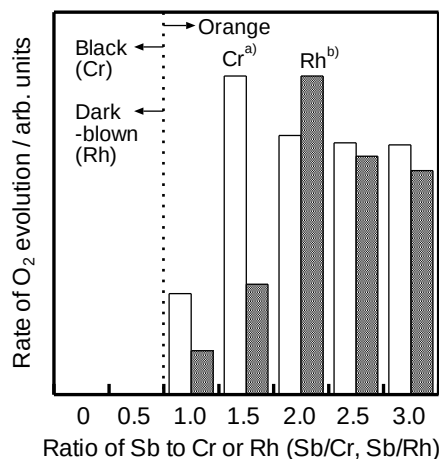


Fig. 2 Dependence of the codoping ratio of antimony to chromium and rhodium upon the photocatalytic activity of  $\text{TiO}_2\text{:Cr/Sb}$  and  $\text{TiO}_2\text{:Rh/Sb}$ . Catalyst, 0.3–0.5 g; reactant solution, 150–320 mL of  $0.05 \text{ mol L}^{-1}$  aqueous silver nitrate solution; light source, 300-W Xe lamp; incident light,  $\lambda \geq 420 \text{ nm}^{\text{a}}$  and  $440 \text{ nm}^{\text{b}}$  (L42 and Y44 cutoff filters).

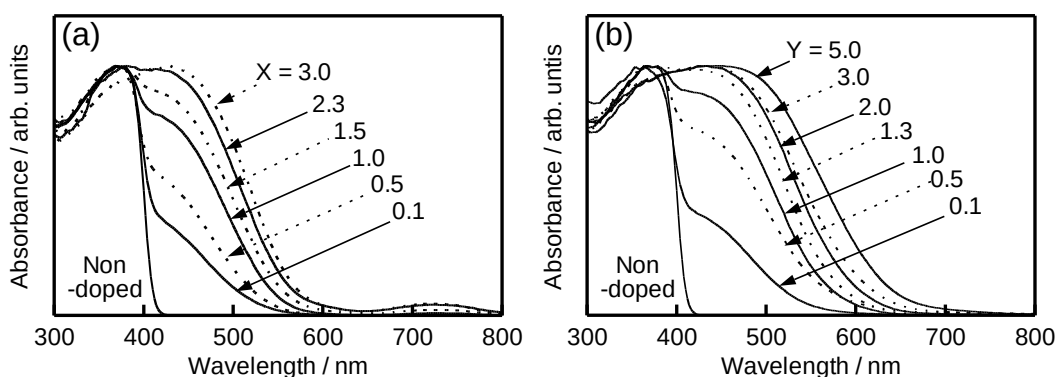


Fig. 3 Diffuse reflection spectra of (a)  $\text{TiO}_2\text{:Cr(X%)/Sb(1.5X%)}$  and (b)  $\text{TiO}_2\text{:Rh(Y%)/Sb(2Y%)}$ .

Fig. 3 shows the dependence of diffuse reflection spectra of  $\text{TiO}_2\text{:Cr(X%)/Sb(1.5X%)}$  and  $\text{TiO}_2\text{:Rh(Y%)/Sb(2Y%)}$  on the amounts of doped chromium and rhodium. When small amounts of chromium ( $X \leq 1.5$ ) and rhodium ( $Y \leq 1.0$ ) are doped, visible light absorption bands are observed as shoulders in addition to the intrinsic band gap absorption of the  $\text{TiO}_2$  host. These are typical profiles for doped materials. As the amounts of doped chromium and rhodium increase, the absorption bands in the visible light region become more intensive accompanied with red-shift of the absorption edges. In particular, the absorption profiles for  $\text{TiO}_2\text{:Cr(X%)/Sb(1.5X%)}$  ( $X \geq 2.3$ ) and  $\text{TiO}_2\text{:Rh(Y%)/Sb(2Y%)}$  ( $Y \geq 1.3$ ) with high doping levels become similar to those due to band gap transition, though they are not so steep. This result indicates that the doped  $\text{Cr}^{3+}$  and  $\text{Rh}^{3+}$  ions interact with each other at the high doping level, resulting in the formation of sub-bands with occupied  $\text{Cr}^{3+}3d$  and  $\text{Rh}^{3+}4d$  orbitals, respectively, as shown in Fig. 4. The electron donor levels of  $\text{Cr}^{3+}$  and  $\text{Rh}^{3+}$  are around 2.2 eV vs. NHE.

The increase in the doping amount gives several effects on the photocatalytic performance. One is a positive effect; that is an increase in a visible light absorption band as shown in Fig. 3. The other is a negative effect; that is an increase in the number of recombination centers. In addition, there is another positive effect that is the formation of the sub-band as shown in Fig. 4. The effects of the amounts of doped chromium and rhodium on the photocatalytic activities of  $\text{TiO}_2\text{:Cr/Sb}$  and

TiO<sub>2</sub>:Rh/Sb for the O<sub>2</sub> evolution are shown in Fig. 5. The codoping ratios are fixed at 1.5 and 2.0 for TiO<sub>2</sub>:Cr/Sb and TiO<sub>2</sub>:Rh/Sb, respectively. When 2.3% of chromium and 1.3 % of rhodium are doped, the highest activities are obtained. The donor levels formed by Cr<sup>3+</sup> and Rh<sup>3+</sup> ions become sub-bands with the optimum doping amounts of 2.3% and 1.3 % as shown in Fig. 4. Therefore, the formation of the sub-band is important to obtain good photocatalytic performance of transition metal cation-doped TiO<sub>2</sub> under visible light irradiation.

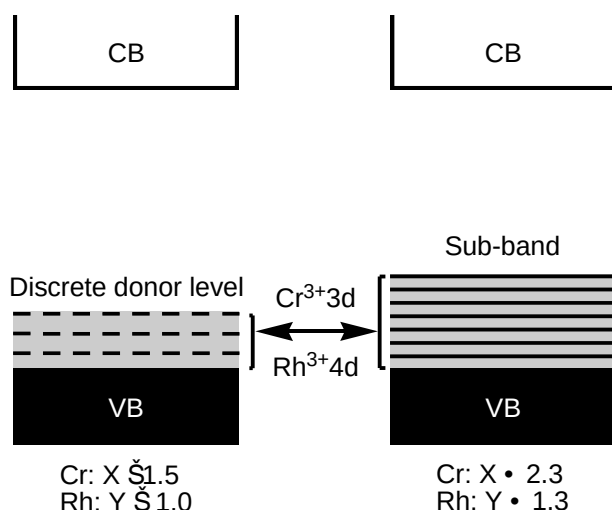


Fig. 4 Effect of the amounts of doped chromium and rhodium upon the energy structures of TiO<sub>2</sub>:Cr(X%)/Sb(1.5X%) and TiO<sub>2</sub>:Rh(Y%)/Sb(2Y%).

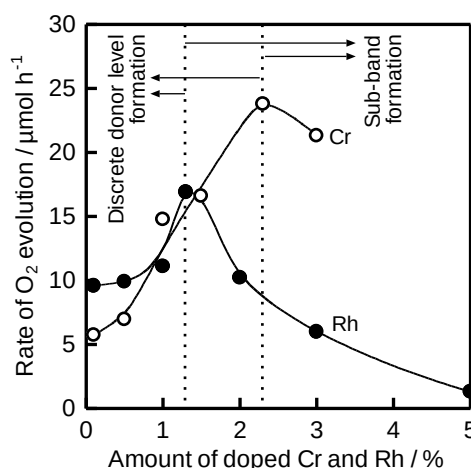


Fig. 5 Dependence of the amounts of chromium and rhodium upon the photocatalytic activities of TiO<sub>2</sub>:Cr(X%)/Sb(1.5X%) and TiO<sub>2</sub>:Rh(Y%)/Sb(2Y%). Catalyst, 0.3 g; reactant solution, 150 mL of 0.05 mol L<sup>-1</sup> aqueous silver nitrate solution; light source, 300-W Xe lamp; incident light,  $\lambda \geq 440$  nm (L42 and Y44 cutoff filters).

Although they show the photocatalytic activities for the O<sub>2</sub> evolution, they can not evolve H<sub>2</sub> under visible light irradiation. TiO<sub>2</sub> (rutile) does not possess a sufficient conduction band level for H<sub>2</sub> evolution. Moreover, the dopant may form a surface state below the conduction band level.

**Visible-light-driven SrTiO<sub>3</sub> doped with transition metal cations for H<sub>2</sub> evolution [56,57,60,61].**  
In contrast to the doped TiO<sub>2</sub> photocatalysts, some transition metal cation-doped SrTiO<sub>3</sub>

photocatalysts can evolve  $H_2$  from an aqueous methanol solution under visible light irradiation as shown in Table 3. Codoping of metal cations with high oxidation numbers is effective for improving photocatalytic performance of visible-light-driven  $SrTiO_3$  doped with chromium and nickel. This codoping effect is similar to those for  $TiO_2$  doped with chromium and nickel as shown in Table 2. Doping of rhodium, iridium, ruthenium and manganese gives absorption bands in a visible light region as shown in Fig. 6 and visible-light response of the  $SrTiO_3$  photocatalysts for  $H_2$  and  $O_2$  evolution without codoping as shown in Table 3.

Table 3. Photocatalytic  $H_2$  and  $O_2$  evolution from aqueous solutions containing sacrificial reagents under visible light irradiation over  $SrTiO_3$  doped or codoped with metal cations

| Dopant | Codopant | Energy gap [eV] | Incident light <sup>a)</sup> [nm] | Activity [ $\mu\text{mol h}^{-1}$ ] |                     | Ref. |
|--------|----------|-----------------|-----------------------------------|-------------------------------------|---------------------|------|
|        |          |                 |                                   | $H_2$ <sup>b)</sup>                 | $O_2$ <sup>c)</sup> |      |
| Cr     | –        | – <sup>d)</sup> | $\geq 440$                        | 16                                  | –                   | 60   |
| Cr     | Ta       | 2.3             | $\geq 440$                        | 70                                  | –                   | 60   |
| Cr     | Sb       | 2.4             | $\geq 420$                        | 78                                  | –                   | 57   |
| Ni     | –        | – <sup>d)</sup> | $\geq 420$                        | 0.7                                 | 0                   | 56   |
| Ni     | Ta       | – <sup>d)</sup> | $\geq 420$                        | 2.4                                 | 0.5                 | 56   |
| Rh     | –        | 2.4             | $\geq 440$                        | 117                                 | –                   | 61   |
| Ir     | –        | 1.9             | $\geq 440$                        | 8.6                                 | 0.4                 | 61   |
| Ru     | –        | 1.9             | $\geq 440$                        | 1.7                                 | 3.9                 | 61   |
| Mn     | –        | 1.7             | $\geq 440$                        | 0.2                                 | 2.7                 | 61   |

Catalyst, 0.3–1 g; reactant solution, 150–320 mL; light source, 300-W Xe lamp.

<sup>a)</sup> Cutoff filters (L42 and Y44) were employed.

<sup>b)</sup> 10 vol% aqueous methanol solution; Pt cocatalyst (0.1–1.0 wt%) was loaded.

<sup>c)</sup> 0.05 mol L<sup>-1</sup> aqueous silver nitrate solution.

<sup>d)</sup> Distinguishable absorption edges were not observed.

$SrTiO_3$ :Rh shows the highest activity among metal oxide photocatalysts for the  $H_2$  evolution under visible light irradiation, and the apparent quantum yield (AQY) at 420 nm is 5%. Its AQY value is determined by the following equation.

$$\text{AQY (\%)} = (\text{the number of } H_2 \text{ molecules} \times 2 / \text{the number of incident photons}) \times 100 \quad (1)$$

Fig. 7 shows an action spectrum of the  $SrTiO_3$ :Rh photocatalyst, and diffuse reflection spectra before and after the  $H_2$  evolution reaction. The color changes from dark purple to yellow during the photocatalytic reaction. At the same time, the intensities of absorption bands around 580 and 1000 nm decrease while that around 450 nm increases. These changes in the spectrum and color are observed during an induction period of the photocatalytic  $H_2$  evolution. These results indicate that doped rhodium species with high oxidation numbers such as  $Rh^{4+}$  is reduced to  $Rh^{3+}$  ions by photogenerated electrons at the beginning stage of the photocatalytic reaction. The  $Rh^{3+}$  ions generated by photoreduction in the photocatalytic reaction is reoxidized to the Rh species with the high oxidation numbers as soon as the  $SrTiO_3$ :Rh is exposed to the air. Thus, the rhodium species doped into  $SrTiO_3$

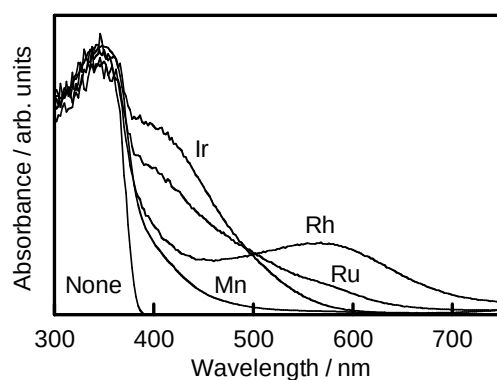


Fig. 6 Diffuse reflection spectra of transition metal cation-doped  $\text{SrTiO}_3$  photocatalysts.

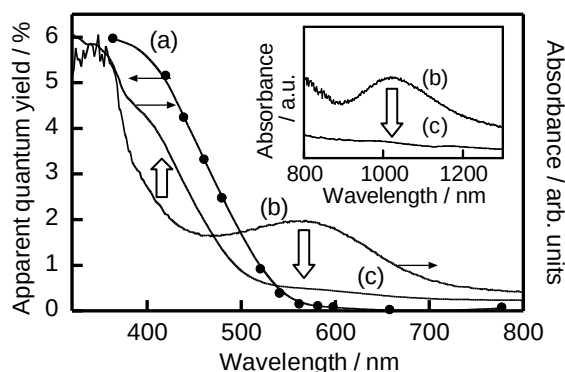


Fig. 7 (a) Action spectrum for  $\text{H}_2$  evolution from 10 vol% of an aqueous methanol solution and diffuse reflection spectra of (b) before and (c) after photocatalytic reaction. The inset shows diffuse reflection spectra in near-infrared region. Catalyst, 0.3 g of  $\text{Pt}(0.1 \text{ wt}\%)/\text{SrTiO}_3\text{:Rh}$ ; reactant solution, 150 mL; light source, 300-W Xe lamp with band pass filters.

host is reversibly reduced and oxidized. This property seems important for the  $\text{H}_2$  evolution on the  $\text{SrTiO}_3\text{:Rh}$  photocatalyst. The onset of the action spectrum agrees with that of diffuse reflection spectrum after the photocatalytic reaction, indicating that the photocatalytic  $\text{H}_2$  evolution proceeds with excitation from an electron donor level consisting of  $\text{Rh}^{3+}$  to the conduction band of the  $\text{SrTiO}_3$  host. The electron donor level consisting of  $\text{Rh}^{3+}$  is around 2.2 eV vs. NHE.

Thus, the sensitization of  $\text{TiO}_2$  and  $\text{SrTiO}_3$  photocatalysts to visible light is possible by transition metal cation doping if a suitable combination of dopant-codopant is chosen.

### Z-scheme photocatalyst systems involving transition metal cation-doped SrTiO<sub>3</sub> photocatalysts for overall water splitting under visible light irradiation [37,38]

The authors have developed many visible-light-driven TiO<sub>2</sub> and SrTiO<sub>3</sub> photocatalysts for H<sub>2</sub> or O<sub>2</sub> evolution from aqueous solutions containing sacrificial reagents by band engineering of metal cation doping as shown in Tables 2 and 3. Moreover, some valence band-controlled photocatalysts with visible-light response have also been found. However, their photocatalytic abilities do not satisfy overall water splitting by one-photon excitation under visible light irradiation, because they possess photocatalytic ability for only either H<sub>2</sub> or O<sub>2</sub> evolution. Although these photocatalysts can not split water into H<sub>2</sub> and O<sub>2</sub> by themselves, they can be employed for construction of two-photon excitation photocatalyst systems, so-called "Z-scheme", for overall water splitting under visible light irradiation as shown in Fig. 8 [37,38].

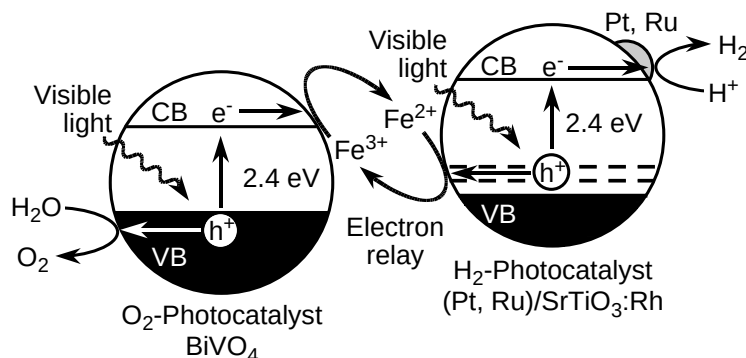


Fig. 8 Scheme of overall water splitting under visible light irradiation by Z-scheme photocatalyst system.

Sayama, Arakawa, and coworkers reported overall water splitting by the Z-scheme photocatalyst system consisting of a Pt-loaded SrTiO<sub>3</sub>:Cr/Ta photocatalyst for H<sub>2</sub> evolution [60], a WO<sub>3</sub> photocatalyst for O<sub>2</sub> evolution [62], and an IO<sub>3</sub><sup>-</sup>/I<sup>-</sup> redox couple [23]. We have also achieved overall water splitting under visible light irradiation by using a Pt or Ru-loaded SrTiO<sub>3</sub>:Rh photocatalyst for H<sub>2</sub> evolution, a BiVO<sub>4</sub> photocatalyst for O<sub>2</sub> evolution, and an Fe<sup>3+</sup>/Fe<sup>2+</sup> redox couple. Photogenerated electrons in (Pt, Ru)/SrTiO<sub>3</sub>:Rh reduces H<sup>+</sup> to H<sub>2</sub> while photogenerated holes in BiVO<sub>4</sub> oxidizes H<sub>2</sub>O to O<sub>2</sub> under visible light irradiation. An Fe<sup>3+</sup>/Fe<sup>2+</sup> redox couple mediates electrons from the conduction band of BiVO<sub>4</sub> to the electron donor levels of (Pt, Ru)/SrTiO<sub>3</sub>:Rh. In this system, undesirable back-reactions may proceed over Pt and Ru cocatalysts as described below.



These reactions decrease apparent rates of H<sub>2</sub> and O<sub>2</sub> evolution. However, water formation (Eq. 2) and the reduction of Fe<sup>3+</sup> by evolved H<sub>2</sub> (Eq. 3) are suppressed by shielding the Pt cocatalyst surface with [Fe(SO<sub>4</sub>)(H<sub>2</sub>O)]<sup>+</sup> and/or [Fe(OH)(H<sub>2</sub>O)]<sup>2+</sup> [37]. In the case of Ru/SrTiO<sub>3</sub>:Rh, XPS analysis revealed that the surface of the Ru cocatalyst is oxidized, resulting in the suppression of these reactions (Eq. 2–4) [38]. The ((Pt, Ru)/SrTiO<sub>3</sub>:Rh)–(BiVO<sub>4</sub>) systems respond up to 520 nm of visible light and are active for solar water splitting as shown in Fig. 9. In the Z-scheme photocatalyst system, the SrTiO<sub>3</sub>:Cr/Ta and SrTiO<sub>3</sub>:Rh photocatalysts developed by transition metal cation doping are key materials.



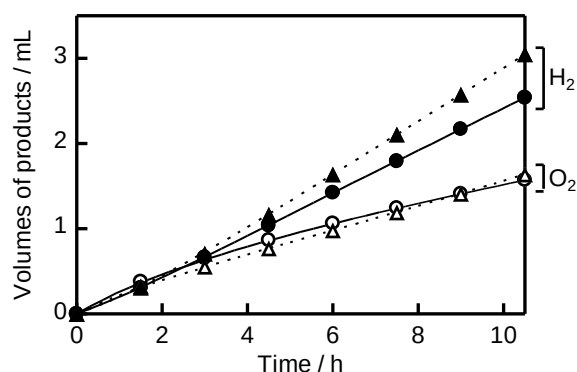


Fig. 9 Solar water splitting over (Pt/SrTiO<sub>3</sub>:Rh)-(BiVO<sub>4</sub>) system (triangle) and (Ru/SrTiO<sub>3</sub>:Rh)-(BiVO<sub>4</sub>) system (circle). Catalyst, 50 mg for each component; reactant solution, 120 mL of 2 mmol L<sup>-1</sup> aqueous FeCl<sub>3</sub> solution, pH 2.4; light source, Solar simulator AM-1.5; cell, top-irradiation type; irradiated area, 33 cm<sup>2</sup>. The water splitting was carried out using not a closed reaction cell but an Ar-flow reaction cell.

## Conclusions

Visible-light-driven TiO<sub>2</sub> and SrTiO<sub>3</sub> photocatalysts were developed by metal cation doping. Codoping of Sb<sup>5+</sup>, Ta<sup>5+</sup>, and Nb<sup>5+</sup> improves the photocatalytic performance of Cr, Rh, and Ni-doped TiO<sub>2</sub> for O<sub>2</sub> evolution from an aqueous silver nitrate solution under visible light irradiation. The codopants play an important role for charge compensation for doped Cr and Rh species, resulting in suppression for the formation of recombination centers. The amounts of doped chromium and rhodium affect the energy-structure of TiO<sub>2</sub>. When electron donor levels consisting of Cr<sup>3+</sup> 3d and Rh<sup>3+</sup> 4d orbitals get to form sub-bands above the valence band of TiO<sub>2</sub> with increases in the amounts of the dopants, the highest photocatalytic activities are obtained. On the other hand, Cr/(Sb, Ta) and Ni/Ta-codoped and Rh, Ru, Ir, and Mn-doped SrTiO<sub>3</sub> photocatalysts are active for H<sub>2</sub> evolution from an aqueous methanol solution under visible light irradiation. Among them, Rh-doped SrTiO<sub>3</sub> shows the highest photocatalytic activity. Rh-doped and Cr/Ta-codoped SrTiO<sub>3</sub> photocatalysts can be used to construct a Z-scheme photocatalyst system for solar water splitting. Thus, it was found that the selection of suitable dopant and codopant led to successful development of visible-light-driven TiO<sub>2</sub> and SrTiO<sub>3</sub> photocatalysts.

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## Investigations of Photo-Excited TiO<sub>2</sub> Based on Time Resolved Microwave Conductivity and Oxygen Isotopic Exchange

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**Abstract.** Charge recombination is the main drawback of heterogeneous photocatalysis; it considerably limits the applications. Consequently, it is of paramount importance to study this process. Time resolved microwave conductivity (TRMC) is an appropriate technique for that purpose since it allows measurements without electrical contacts. Here are presented and discussed results obtained by TRMC for TiO<sub>2</sub> powders. They indicate the importance of the TiO<sub>2</sub> particle diameter in determining the conductivity. The attraction of TiO<sub>2</sub> photoproduced electrons to deposited Pt particles was also shown by TRMC, as well as the very rapid charge recombination in TiO<sub>2</sub> homogeneously doped with 0.85 ion % of Cr<sup>3+</sup> cations. TRMC measurements for TiO<sub>2</sub> affixed on thin fiberglass tissues using SiO<sub>2</sub> as a binder demonstrated that TRMC is also adapted to composite materials; the type of SiO<sub>2</sub> had only a secondary influence on the conductivity. Additionally, the effects of alcohols were investigated by TRMC to illustrate the occurrence of interfacial charge transfer. On the other hand, oxygen isotope exchange (OIE) of gaseous <sup>18</sup>O<sub>2</sub> occurs over photo-excited Ti<sup>16</sup>O<sub>2</sub>. It is believed to be facilitated by surface irregularities which can thus be probed. OIE measurements in the presence of compounds whose photocatalytic oxidation primary step requires the incorporation of an O atom suggested that labile O atoms of TiO<sub>2</sub> do not play the dominant role. Contrasted effects on OIE and photocatalytic removal of methanol in air showed (i) the influence of thermal treatment on TiO<sub>2</sub> surface re-structuring (ii) the preferential adsorption and subsequent UV-induced reduction of Se salts at more labile surface O atoms.

### Introduction

Several properties govern the photocatalytic activity of semiconductors. Clearly, the recombination rate,  $k_r$ , of the charge carriers that are produced upon band-gap irradiation is one of the major factors. In the first part of this chapter, we present examples about the use of time-resolved microwave conductivity (TRMC) to assess  $k_r$ . These examples refer to TiO<sub>2</sub> because, until now, it is the only semiconductor employed in commercialized photocatalytic materials; however, TRMC can obviously be applied to other semiconductors. Although it is by far a less decisive factor, the lability of O atoms of semiconducting oxides can play a role in photocatalytic oxidations. The importance of this role depends on the conditions (air, aerated water, etc.) and the reacting compound. Examples of oxygen isotopic exchange (OIE) between UV-irradiated Ti<sup>16</sup>O<sub>2</sub> and gaseous <sup>18</sup>O<sub>2</sub> are reported in the second part of this chapter, showing that OIE is an appropriate method to evaluate the lability of O atoms and its potential roles. OIE can, of course, be utilized for photo-excited semiconducting oxides other than TiO<sub>2</sub>.

TRMC and OIE studies of photo-excited TiO<sub>2</sub> are complementary. TRMC provides a view from within the solid, whereas OIE probes the solid from the outside while presenting the advantage of giving information independently of another reactant whose properties can influence the data. Therefore, it is recommended to employ both characterizations whenever it is possible.

| Source | Elementary particle diameter [nm] | $\sigma$<br>[ $10^{-4} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$ ] |
|--------|-----------------------------------|---------------------------------------------------------------------|
| 1      | 10                                | 0.05                                                                |
| 1      | 38                                | 0.53                                                                |
| 1      | 62                                | 0.33                                                                |
| 1      | 94                                | 1.4                                                                 |
| 2      | 8                                 | 0.05                                                                |
| 3      | 15-25                             | 0.22                                                                |
| 4      | 30                                | 0.19                                                                |
| 4      | 30                                | 0.22                                                                |
| 4      | 30                                | 0.25                                                                |

Table 1. End-of-pulse conductivity value,  $\sigma$ , for  $\text{TiO}_2$  powders characterized by their source and particle diameter. Sources: 1.  $\text{TiCl}_4$ , laboratory flame reactor; 2.  $\text{TiOCl}_2$  hydrolysis, uncalcined, Rhodia; 3.  $\text{TiOSO}_4$  hydrolysis, calcined, Rhodia, precursor of PC105;  $\text{TiCl}_4$ , Degussa P-25, flame reactor, different lots

### Investigations of $\text{TiO}_2$ Based on Time Resolved Microwave Conductivity (TRMC)

**The Conductivity Depends Predominantly on the  $\text{TiO}_2$  Particle Size.** In these experiments, the  $\text{TiO}_2$  powder, which is manually compressed into a cavity of the TRMC cell, receives pulses (on a ns scale) of 3 MeV electrons issued from a Van de Graff accelerator [1-3]. The penetration depth is greater than the thickness of the powder layer, so that the energy deposition within  $\text{TiO}_2$  can be regarded as uniform. This energy is measured by a radiochromic film dosimeter. The TRMC cell and waveguide circuitries are purged with  $\text{SF}_6$  in order to efficiently scavenge free electrons formed in the gas phase which, because of their mobility higher than in  $\text{TiO}_2$ , would perturb the measurements.

After proper calibration, the microwave conductivity signal at the end of the pulse is considered to express the sum of the mobilities of the electrons and holes that have not recombined or have not been trapped during the pulse.

In an attempt to delineate the factors that determine the end-of-pulse conductivity value,  $\sigma$ , four  $\text{TiO}_2$  samples prepared in a laboratory flame-reactor were investigated (Table 1). The source of Ti was  $\text{TiCl}_4$ . Variations in  $\text{TiCl}_4$  concentration, as well as in the flame temperature and the  $\text{H}_2$  and  $\text{O}_2$  flow rates, allow one to change the size (usually with a narrow distribution) of the nonporous particles which are produced and are mainly anatase [4]. It was found that  $\sigma$  increased markedly with increasing elementary particle size [2]. However, the increase was not completely systematic (Table 1), suggesting that other factors can play a role even for these similarly prepared samples. One of these factors could be the shape of the particles, which were either spheres or polyhedra or a mixture of both. Another factor could be the presence of impurities (*vide infra* the case of purposely added Cr); however, it is surmised that they were the same since all these samples were prepared using the same lot of  $\text{TiCl}_4$ . Furthermore, a predominance of the elementary particle size in determining  $\sigma$  is illustrated by comparing two other anatase samples to those prepared in the flame reactor. For example (Table 1), a  $\sigma$  value of 0.05 was measured for an uncalcined sample, issued from the hydrolysis of  $\text{TiOCl}_2$ , whose average elementary particle diameter was 8 nm, while the  $\sigma$  value was 0.22 for a calcined sample issued from the hydrolysis of  $\text{TiOSO}_4$  whose average elementary particle diameter was in the 15-25 nm range (this latter sample prepared by Rhodia was a precursor of the PC105 brand now commercialized by Cristal-Millennium Chemicals). In spite of the fact that these anatase specimens are porous and presumably contain different impurities, these  $\sigma$  values fit relatively well within those found for the flame-reactor samples if the particle diameter is regarded as the dominant factor influencing the value of  $\sigma$  (Table 1). Also, the expected effect of

the presence of rutile is assumed to be secondary with respect to that of the particle diameter because the rutile content is at most 4 % in the flame-reactor prepared samples. Indeed, TiO<sub>2</sub> Degussa P-25, which is also produced in a flame reactor and is therefore nonporous, can roughly be incorporated in the series (Table 1), although it contains about 20 % of rutile. The slight, but significant, difference in  $\sigma$  between three Degussa P-25 lots illustrates both the sensitivity of TRMC and the influence of small changes (the lots slightly differed by the rutile content and the surface area, hence the particle size).

The importance of the particle diameter in determining  $\sigma$  can readily be related to an increase density of surface traps for electrons when the particles are smaller. It also suggests that recombination and/or trapping of photoproducted charge carriers occur predominantly at the surface. **TRMC Shows that Pt Particles Deposited on TiO<sub>2</sub> Attract Photoproducted Electrons.** To further demonstrate the capabilities of TRMC, measurements were carried out for Degussa P-25 samples supporting Pt particles. These samples were prepared by impregnating TiO<sub>2</sub> with a H<sub>2</sub>PtCl<sub>6</sub> solution and treating thermally in H<sub>2</sub>. The Pt particles obtained had a mean diameter of ca. 2 nm and a narrow size distribution whatever the Pt content in the range investigated [5]. For reference,  $\sigma$  was also measured for a sample treated as in the case of the Pt deposition procedure except that H<sub>2</sub>PtCl<sub>6</sub> was replaced by HCl. This acidic treatment markedly decreased  $\sigma$ , which can be interpreted as an increase in structural irregularities and hence in the density of surface traps for electrons. The decrease in  $\sigma$  was more pronounced for the samples treated with H<sub>2</sub>PtCl<sub>6</sub> and accordingly supporting Pt particles [2]. This is consistent with an attraction of the photoproducted electrons to the Pt particles.

**TRMC Shows that Cr Doping can Suppress TiO<sub>2</sub> Conductivity.** Also, to show the importance of trace foreign elements in the bulk lattice with respect to the sensitivity of TiO<sub>2</sub> to photo-excitation, a TRMC measurement was performed for a TiO<sub>2</sub> powder which was homogeneously doped with Cr<sup>3+</sup> cations using a laboratory flame-reactor into which CrCl<sub>3</sub> was added to TiCl<sub>4</sub> [6]. In fact,  $\sigma$  was not measurable [2]. This was suggested to be caused by very rapid (i.e., taking place within the excitation pulse) recombination of the photoproducted charge carriers. This recombination likely occurred at the Cr<sup>3+</sup> defect centers to which the charge carriers are supposed to easily diffuse because the average distance between these cations would only be a few nanometers at the concentration studied (0.85 ion % or 0.55 wt %).

**TRMC can be used with Affixed TiO<sub>2</sub>.** For environmental applications, TiO<sub>2</sub> is most often affixed on a solid support, in particular on thin fibrous materials which can be employed as filters. It was therefore deemed of interest to know whether TRMC measurements could be applied to this type of materials. For that purpose, a microwave cell into which a rectangular piece (2.5 cm x 1 cm) of the material can be inserted was used. The excitation was supplied by 7-ns laser pulses at 308 nm [7].

| Source | $\sigma$ , coated TiO <sub>2</sub><br>[10 <sup>-4</sup> m <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> ] |
|--------|----------------------------------------------------------------------------------------------------------|
| 2      | 0.016-0.028                                                                                              |
| 3      | 0.158-0.224                                                                                              |
| 4      | 0.183-0.235                                                                                              |
| 5      | 0.107-0.185                                                                                              |

Table 2. Ranges of the end-of-pulse conductivity values,  $\sigma$ , for TiO<sub>2</sub> coated with four different types of SiO<sub>2</sub>. Sources: as in Table 1; 5: TiOSO<sub>4</sub> hydrolysis, uncalcined, Rhodia, precursor of PC500

For a thin fiber glass tissue supporting 20 g m<sup>-2</sup> of TiO<sub>2</sub> and 20 g m<sup>-2</sup> of SiO<sub>2</sub> used as a binder,  $\sigma$  value fits very well with the value measured for powders in the case of Degussa P-25 and the sample denoted by source 3 in Tables 1 and 2. It was lower for the coating than for the powder in the case of the sample denoted by source 2, but the very low value is probably at the origin of the

apparent discrepancy. For these coated samples that were not thermally treated, but simply allowed to dry at room temperature, the adhesion of TiO<sub>2</sub> on the fibers resulting from the presence of SiO<sub>2</sub>, the type of SiO<sub>2</sub> had only a moderate effect on  $\sigma$  (Table 2). Nevertheless, this effect was significant, the repeatability of the TRMC measurements being *ca.* 2 % and their reproducibility *ca.* 3 %. The smaller the SiO<sub>2</sub> particle size was, the higher  $\sigma$ . One possible explanation for this phenomenon is that the TiO<sub>2</sub> grains are more isolated from one another when a smaller-size SiO<sub>2</sub> is used, so that interparticle recombination and/or trapping of photoproducted charge carriers is more restricted.

The decay in the conductivity was also studied for TiO<sub>2</sub> affixed on the fibrous material. As expected, it was observed that uncalcined TiO<sub>2</sub> with the lowest particle diameter and the lowest  $\sigma$  had also the fastest decay ( $t_{1/2} \sim 50$  ns compared with  $t_{1/2} > 250$  ns for calcined TiO<sub>2</sub> or flame-reactor prepared TiO<sub>2</sub>).

**TRMC Evidences Electron Transfers between TiO<sub>2</sub> and Alcohols.** The aforementioned experiments provided information on the electronic state of TiO<sub>2</sub> and on how this state is influenced by modifications of this semiconductor. Other experiments were undertaken to determine the effect of exposing TiO<sub>2</sub> to an organic compound. The purpose was to probe from within TiO<sub>2</sub> the changes caused by transfer of charge carriers at the interface. Alcohols were chosen as test molecules, since they are "good" electron-donors and, moreover, the organic radical produced by the removal of a labile H atom has been suggested to transfer an additional electron to TiO<sub>2</sub> [8].

About 10 vol. % of propan-2-ol was added to powder Degussa P-25 in the microwave cell. The irradiation using a Van de Graff accelerator was such that a 10 ns pulse was expected to produce one electron-hole pair per TiO<sub>2</sub> elementary particle on the average. For a single pulse, the conductivity decay was markedly elongated in the presence of propan-2-ol [2,3]. Furthermore, the decay was still slower when the sample was repetitively pulsed and  $\sigma$  was also increased very substantially, so that the sample changed from an absorber to a reflector of microwaves when it was continuously irradiated at 10 Hz, which corresponded to a "semiconductor-to-metal transition" [3]. These effects of repetitive pulsing were not observed in the absence of the alcohol. They are consistent with hole scavenging by propan-2-ol, which reduces  $k_t$ ; if the irradiation was pursued, the number of mobile electrons in each TiO<sub>2</sub> particle increased gradually. Also, a small growth in conductivity within the first tens of ns after the last pulse of a 100-pulse train at 5 Hz was tentatively suggested to be due to electron transfer from (CH<sub>3</sub>)<sub>2</sub>-C<sup>o</sup>-OH radicals formed as a result of the initial hole scavenging [3].

Similarly, the conductivity decay of TiO<sub>2</sub> affixed on a fibrous material was also slowed down when the material was impregnated with a "drop" of liquid methanol in the microwave cell. As was expected because of its interfacial origin, this phenomenon was particularly pronounced for small-size particles of TiO<sub>2</sub>. It also showed that TiO<sub>2</sub> was not completely encapsulated by SiO<sub>2</sub> used as a binder. For instance, no effect of propan-2-ol was observed for a TiO<sub>2</sub> pigment [2], viz. TiO<sub>2</sub> totally coated with alumina and/or silica to prevent the photocatalytic degradation of the other components of paints and polymers when TiO<sub>2</sub> is utilized as an absorber in these materials. In fact, if the sensitivity was judged to be sufficient, TRMC could even be used to test the effectiveness of the coatings for various batches of pigments.

### Investigations of TiO<sub>2</sub> Based on UV-induced Oxygen Isotopic Exchange (OIE)

**OIE Allows one to Probe the Lability of O atoms of TiO<sub>2</sub>.** UV-induced OIE obviously involves both the removal of <sup>16</sup>O atoms from the solid and the splitting of O<sub>2</sub> molecules. The first phenomenon should clearly be favored by highly coordinatively unsaturated O surface atoms found at surface irregularities, such as kinks and edges. Accordingly, OIE is a method that allows one to probe the presence of surface irregularities. These irregularities are also thought to increase the surface recombination of photoproducted charge carriers. Depending on several factors, such as the medium (e.g., air or aerated water) and the reactant, they can also intervene in the oxidation of molecules, although to a moderate extent as indicated in the following paragraph.

**OIE Shows that the Lability of O atoms of TiO<sub>2</sub> does not Play the Dominant Role in Photocatalytic Oxidations.** Pioneering studies have shown that UV-induced OIE over TiO<sub>2</sub> can be

completely suppressed in the presence of gaseous compounds, such as isobutane [9] and CO [10]. These results indicated that the species formed from gaseous  $O_2$  are incorporated by these compounds to produce acetone from isobutane or  $CO_2$  from CO rather than reacting with surface O atoms to effect OIE. It can also be inferred that labile O atoms of  $TiO_2$  do not play the major role in photocatalytic oxidations. Indeed, it has later been shown that the products whose volatility enabled detection in the gas phase, viz. CO and HCHO, generated during the photocatalytic oxidation of gaseous methyl chloride over  $Ti^{16}O_2$  using  $^{18}O_2$  contain very predominantly  $^{18}O$  atoms under the conditions used [11].

**Evaluation by OIE of the Sintering-Induced Changes in the Lability of O atoms of  $TiO_2$ .** To illustrate the effect of  $TiO_2$  sintering at increasing temperatures on the lability of O atoms of  $TiO_2$ , OIE rate was measured for the same mass of the PCs Cristal-Millennium Chemicals  $TiO_2$  prepared at increasing sintering temperatures in the order: PC500 (uncalcined gel), PC105, PC50, and PC10, the source being  $TiOSO_4$ . The  $TiO_2$  powder studied was uniformly sprayed onto a fused silica optical window constituting the lower end of the OIE cell. Under continuous UV irradiation, this cell was first evacuated; then,  $TiO_2$  was exposed to a  $^{16}O_2$  pressure of *ca.* 13.3 kPa overnight. The cell was again evacuated before introduction of the desired pressure of  $^{18}O_2$  (*ca.* 98.2 atom %  $^{18}O$ ) in the dark. After equilibration, the sample was UV-irradiated to start OIE. The oxygen isotopic composition in the cell was then periodically analyzed using a variable leak valve connecting the cell to the mass spectrometer and permitting one (i) to maintain a sufficiently low pressure in the spectrometer chamber and (ii) to not significantly change the pressure in the cell during the whole experiment [12,13].

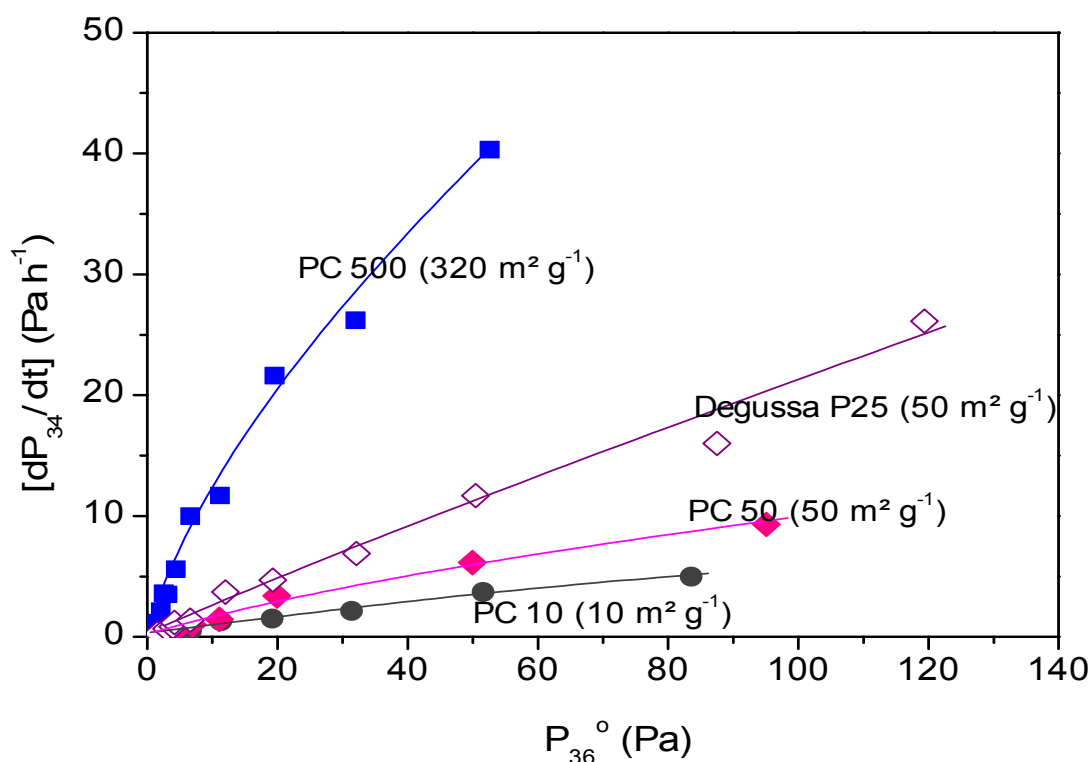
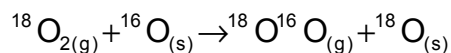


Figure 1. Initial rate of the increase in the  $^{16}O^{18}O$  pressure produced by the UV-irradiation against the  $^{18}O_2$  initial pressure for the  $TiO_2$  samples indicated.

First, it was found that OIE occurred according to the  $R_1$  mechanism meaning that one  $^{16}O$  atom from  $TiO_2$  replaced one  $^{18}O$  atom from the gas phase for each OIE act [14] according to the overall chemical equation:





If  $C_{34}$  and  $C_{36}$  are, respectively, the percentages of  $^{16}\text{O}^{18}\text{O}$  and  $^{18}\text{O}_2$ , their ratio for mechanism  $R_1$  is given by [9,14]:

$$C_{34}/C_{36} = (C_{34}^{\circ}/C_{36}^{\circ} + 2) \times (C_{36}^{\circ}/C_{36})^{1/2} - 2$$

where the superscript,  $^{\circ}$ , designates the initial value in darkness. Indeed, for the PCs samples the experimental points were exactly aligned on the line which represented this relationship in the plot of  $C_{34}/C_{36}$  as a function of  $(C_{36})^{-1/2}$ . Second, the initial OIE rate was observed to vary almost linearly with the starting  $^{18}\text{O}_2$  pressure in the range investigated as shown in Figure 1 for three of the PCs samples and Degussa P25. Consequently, the ranking of the OIE rates was nearly independent of the  $^{18}\text{O}_2$  pressure. This ranking was [13]: PC500 (317) > PC105 (85-95) > PC50 (54) > PC10 (10) where the numbers in parentheses indicate the surface area,  $S$ , in  $\text{m}^2 \text{g}^{-1}$ .

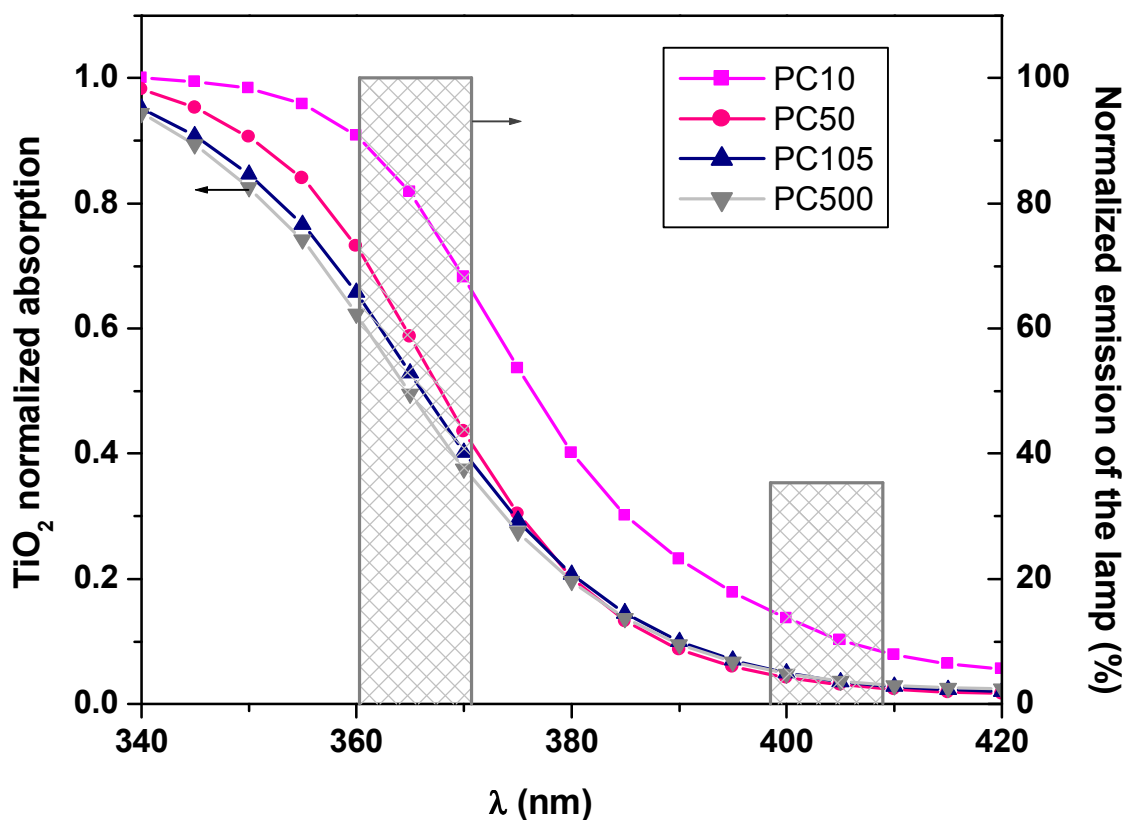


Figure 2. Absorption (normalized with respect to the maximum at wavelengths > 300 nm) of the  $\text{TiO}_2$  PCs samples indicated and emission (normalized with respect to the maximum at 365 nm) of the lamp used.

The absorption around 365 nm (the main emission wavelength of the mercury lamp employed) was almost equal for the three most active PCs, and significantly higher for the less active sample (Figure 2). Therefore, differences in absorption cannot be at the origin of the ranking. Clearly, the OIE rate decreased with decreasing  $S$ , which is explainable since the amount of

adsorbed  $O_2$  also decreased at equal  $TiO_2$  mass in the OIE cell. However, the relationship between the OIE rate and  $S$  was not at all linear; a jump in the OIE rate was observed between PC50 and PC105 although the ratio of  $S$  between these samples was the lowest in the PCs series. Consequently, the adsorption of  $O_2$ , and hence  $S$ , is not the only factor intervening in the ranking.

At least two other factors can affect the OIE rate, viz.  $k_r$  and the lability of the O atoms of  $TiO_2$ . To distinguish between them (even if the surface irregularities have an effect on  $k_r$ , they are not the only cause), the idea was to contrast OIE and the photocatalytic removal of methanol in air using the same  $TiO_2$  samples [13]. The experimental setting and procedure used for methanol removal in a mixture of 80 v/v % of  $N_2$  and  $O_2$  has been published elsewhere [12,13]. This removal is supposed to be roughly similarly affected as OIE by the change in  $k_r$ , whereas it should be less dependent on the lability of O atoms of  $TiO_2$  since the formation of the primary product, HCHO, does not need abstraction of surface O atoms to occur. Indeed, the plot of Figure 3 shows that the rates of the two reactions did not vary exactly in the same manner, even though they both decreased with  $S$ . In particular, the maximum change in activity was observed between PC10 and PC50 for methanol removal and between PC50 and PC105 for OIE. From that it can be deduced that the decrease in the density of surface structural defects (kinks, steps, etc.) corresponding to a thermal re-structuring of the surface would occur mainly in going from PC105 to PC50, and not so much in going from PC500 to PC105 as well as from PC50 to PC10. In this respect, OIE provides valuable, although qualitative, information.

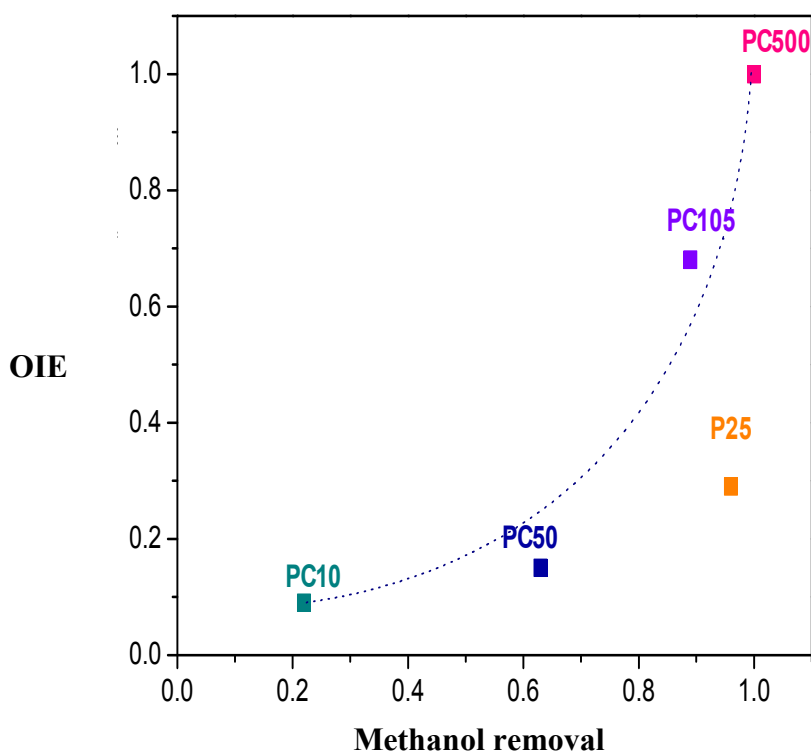


Figure 3. Plot of the OIE rate measured at the  $^{18}O_2$  initial pressure of 50 Pa against methanol removal (300 ppmv) at stationary state for the  $TiO_2$  samples indicated. Values were normalized to those measured for PC500.

The comparison between OIE and methanol removal was also carried out in the case of P25 (Figure 3). The activity of this sample was close to those of uncalcined PC500 and low-temperature calcined PC105 for methanol removal despite the lower  $S$  of P25, which was presumably compensated by a lower  $k_r$ . By contrast, it was close to that of PC50 for OIE. That was not unexpected since P25 is prepared in a flame reactor, which ensures a low density of surface

irregularities. Therefore, the results obtained with this other TiO<sub>2</sub> sample supports the interest of the comparison between OIE and methanol removal to evaluate the lability of the O atoms of TiO<sub>2</sub>.

#### **OIE Investigation of the Se Deposition Effect upon the Lability of Surface O Atoms of TiO<sub>2</sub>.**

This comparison was also found to provide information on the location of Se particles on TiO<sub>2</sub> P25. These Se particles had a size comprised between 60 and 200 nm depending on the Se content. They were obtained by UV-irradiation of a stirred aqueous TiO<sub>2</sub> P25 suspension containing Na<sub>2</sub>SeO<sub>4</sub> and HCOOH used as a hole scavenger. After filtration, the solid was dried in an oven at 313 K for one day and then ground to powder form [15,16]. The adsorption of methanol (about 300 ppmv) in the dark was not significantly changed by the presence of the Se deposits (2 or 8 wt %). The removal of methanol at stationary state was decreased for Se/TiO<sub>2</sub> P25 relative to bare TiO<sub>2</sub> P25, but considerably less than the OIE rate. For a 2 wt% Se deposit the decrease was of 36 % for methanol and of 84 % for OIE. For a deposit of 8 wt% Se, the decrease was of 77 % for methanol removal, whereas OIE was completely suppressed. This difference allows us to propose that the selenate ions were predominantly adsorbed, and subsequently reduced, on surface irregularities, thus markedly decreasing and even suppressing the availability of labile surface O atoms required for OIE [13].

#### **Nomenclature and Abbreviations**

$k_r$ : recombination rate of the charge carriers

OIE: oxygen isotopic exchange

S: surface area of TiO<sub>2</sub>

TRMC: time-resolved microwave conductivity

$\sigma$ : end-of-pulse conductivity value

#### **Acknowledgments**

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# Surface Modified Titania Visible Light Photocatalyst Powders

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**I) Introduction.** Titanium dioxide has received great attention both in fundamental and applied photocatalysis due to its low cost, non-toxicity, and stability against photocorrosion [1-6]. Unfortunately it can utilize only the very small UV part (about 3%) of solar light arriving at the earth surface. However, also the visible part ( $\lambda > 400$  nm) may induce photocatalysis if titania is modified by transition or main group elements. Accordingly, many publications appeared in the last 20 years dealing with the problem of sensitizing titania for visible light photooxidation reactions. This may be achieved by doping, which means substitution of lattice ions, and by surface modification. In many cases authors not clearly differentiate between these two possibilities and so called doped titania quite often is a surface modified material. The latter is easily prepared by heating titania or its precursor compounds like titanium hydroxide in the presence of a modifier at temperatures in the range of 100 – 500 °C. In the following we summarize our work in this field using inorganic and organic sensitizers.

### II) Modification by Inorganic Sensitizers

In general doping by transition metal ions is not connected with a shift of the photocatalytic activity into the visible but rather with promotion of photocorrosion and charge recombination. Exceptions are Cr<sup>3+</sup> [7], Fe<sup>3+</sup> [8, 9] and V<sup>4+</sup> [10] volume-doped materials prepared by rather sophisticated methods like ion implantation or chemical vapor deposition. The vanadium doped

titania was prepared as a monolayer and enabled the visible light photooxidation of gaseous ethanol as indicated by solid state NMR analysis [10].

## II.1 PtCl<sub>4</sub> Sensitization

In thermal catalysis it is well known that a soluble catalytically active metal complex catalyst can be supported onto an inorganic carrier without substantial loss of activity. In the following we report on the contrary case, in which an inactive transition metal complex becomes active upon supporting on an inorganic support. When the support is a semiconductor like e.g. titania, the carrier itself may exhibit also photocatalytic activity.

Recently we have found that simple inorganic compounds like Na<sub>2</sub>[PtCl<sub>6</sub>], AuCl<sub>3</sub>, and RhCl<sub>3</sub> introduced into the bulk of amorphous microporous titania [11-13] by sol-gel methods induce the photomineralization of the ubiquitous water pollutant 4-chlorophenol (4-CP) by visible light. In the platinum doped material isolated PtCl<sub>4</sub> units are present without any bonding interactions with the titania matrix. However, when these are introduced through an alternative synthetic method, a photocatalyst of the type {[TiO<sub>2</sub>]-O-PtCl<sub>4</sub>L}<sup>n-</sup>, L = H<sub>2</sub>O, OH<sup>-</sup>, n = 1,2, is obtained having a much higher activity [14-16]. In this heterogeneous transition metal complex titania plays the role of an unconventional ligand.

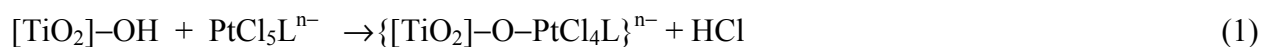
In this chapter we briefly summarize how the photoredox properties of titania are changed by the covalent attachment to chloroplatinate or chlororhodate and how the primary photoprocesses of charge separation and interfacial electron transfer can be described. Detailed information is available from recent original publications [14-17].

### Preparation and characterization of photocatalysts

Upon stirring a suspension of titania powders in an aqueous solution of H<sub>2</sub>[PtCl<sub>6</sub>] in the dark, different maximum amounts were adsorbed. For the anatase and anatase/rutile samples *TH* and *P25* there were taken up 4.0 and 1.1%, respectively, whereas only traces were adsorbed onto the rutile material *Ald*. The almost four times larger amount adsorbed by *TH* corresponds with the about four times larger surface area as compared to *P25* (vide infra). Subsequent heat treatment at 200 °C afforded the desired photocatalyst. Surface modification may be performed also by simple grinding with PtCl<sub>4</sub>, but the resulting powders are of lower photocatalytic activity and less stability [14, 16].

Analysis by transmission electron microscopy (TEM) and X-ray powder diffraction (XRD) of 4.0% H<sub>2</sub>[PtCl<sub>6</sub>]/*TH* revealed the presence of about 200 nm large aggregates composed of 2–4 nm sized anatase crystallites [18]. Specific surface areas of unmodified *P25* (50 m<sup>2</sup>/g) and *Ald* (3 m<sup>2</sup>/g) were not changed upon modification whereas a significant decrease from 334 m<sup>2</sup>/g to 260 m<sup>2</sup>/g was found for *TH*.

To find out if the chloroplatinate is physically or chemically adsorbed onto the titania surface, 4.0% H<sub>2</sub>[PtCl<sub>6</sub>]/*TH* was stirred in 0.01 M potassium fluoride at ambient conditions. It is known that fluoride irreversibly adsorbs through replacement of titania bound OH groups [19-23]. Surprisingly, no desorption of a chloroplatinate complex was observable under these experimental conditions. These observations strongly suggest that chloroplatinate is chemically bound to titania as summarized in Equation 1 (L = Cl, OH) and that desorption is an acid catalyzed process. From the amount of chloride released after stirring a NaOH suspension of 4.0% H<sub>2</sub>[PtCl<sub>6</sub>]/*TH* in the dark, the composition {[Ti]-O-PtCl<sub>4</sub>L}<sup>n-</sup>, L = H<sub>2</sub>O, OH<sup>-</sup>, n = 1,2, was proposed for the titania surface complex [24, 25].



In corresponding photochemical desorption experiments (λ ≥ 455 nm) with 4.0% H<sub>2</sub>[PtCl<sub>6</sub>]/*TH* suspended in water no desorption occurred within 24 h of irradiation time, whereas in the presence of 0.1 M HCl desorption of [PtCl<sub>6</sub>]<sup>2-</sup> was almost complete.

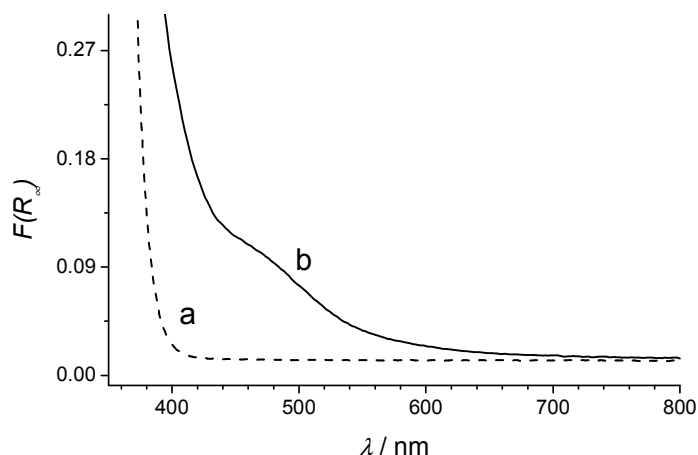


**Fig. 1.** Diffuse reflectance spectra of TH (a) and 4.0% $\text{H}_2[\text{PtCl}_6]/\text{TH}$  (b). The Kubelka-Munk function,  $F(R_\infty)$ , is equivalent to absorbance.

The diffuse reflectance spectra [26-30] of  $\text{TH}$  and 4.0% $\text{H}_2[\text{PtCl}_6]/\text{TH}$  are compared in **Fig. 1**. The pronounced absorption of the modified material in the visible region is tentatively assigned to a metal-centered transition of platinum(IV) chloride, by analogy with the solution spectrum of  $\text{Na}_2[\text{PtCl}_6]$  [14, 29, 30]. Below 400 nm the steep absorption increase of the modified sample originates from the bandgap transition of  $\text{TiO}_2$ . For an indirect crystalline semiconductor the bandgap energy is obtained by extrapolation of the linear part of the plot of  $(F(R_\infty)h\nu)^{1/2}$  vs.  $h\nu$  [31]. In the case of 4.0% $\text{H}_2[\text{PtCl}_6]/\text{TH}$  it amounts to 3.21 eV, what is slightly smaller than the value of unmodified  $\text{TH}$  (3.27 eV). The absorption of these materials extends down to 620-650 nm corresponding to about 2.0 eV.

The flatband potential of a semiconductor photocatalyst is a basic property for understanding the thermodynamics of interfacial electron transfer. It is easily obtained for semiconducting powders using the “suspension method” developed by Bard et al. [32, 33] and modified by Roy et al. [34]. The method is based on the pH-dependence of the flatband potential of  $\text{TiO}_2$  according to Equation 2 wherein  $E_{\text{fb}}(\text{pH})$  is the flatband potential at given pH and  $k$  is usually equal to 59 mV [35].

$$E_{\text{fb}}(\text{pH}) = E_{\text{fb}}(\text{pH}=0) - k \text{ pH} \quad (2)$$

Since the procedure requires irradiation, different to the classical Mott-Schottky method, it is more correct to replace  $E_{\text{fb}}$  by the quasi-Fermi energy of electrons ( ${}_nE_f^*$ ). Bard et al. [32] measured the photocurrent generated in the presence of methylviologen ( $\text{MV}^{2+}$ ) and a reducing agent as function of the pH value, whereas Roy recorded the photovoltage in the absence of a reducing agent. In the latter method the shape of the sigmoidal voltage/pH curve depends on the potential of the reference electrode, the  $[\text{MV}^{2+}]/[\text{MV}^{+}]$  ratio, the pH value,  $k$ , and on  ${}_nE_f^*$ . At the pH value of the inflection point ( $\text{pH}_0$ ) the quasi-Fermi level is equal to the one electron reduction potential of the methylviologen cation. From this the quasi-Fermi potential at any pH can be calculated according to Eq. 3 [34] if the factor  $k$  is known. Roy et al. obtained it from the slope of the voltage/current plot above the inflection point whereas Bard et al. calculated it from the slope of the onset of photocurrent vs. pH [33].

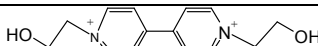
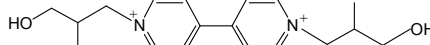
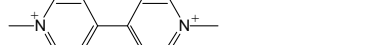
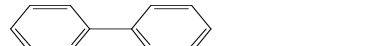
$${}_nE_f^*(\text{pH}) = E_{\text{MV}^{2+}/+}^\circ + k (\text{pH}_0 - \text{pH}) \quad (3)$$

However, in our hands only poorly reproducible values were obtained by the former and latter method due to considerable voltage fluctuations and too low photocurrents, respectively. We have determined the  $k$  value by an alternative method through measurement of the  $\text{pH}_0$  value not only for one but for a series of redox couples ( $\text{A}_i^{2+}/\text{A}_i^{+\bullet}$ ) [17]. In this case a linear relation between the  $\text{pH}_0$  and the redox potential of the pH-independent redox couple is expected (Eq. 4).

$$k = (E^\circ_{\text{Ai}^{2+}/\text{A}_i^{+\bullet}} - E^\circ_{\text{Aj}^{2+}/\text{A}_j^{+\bullet}}) / (\text{pH}_{0j} - \text{pH}_{0i}) \quad (4)$$

Table 1 summarizes structures and potentials of the bipyridinium redox couples. A plot of the  $\text{pH}_0$  values, as measured for *P25* as a reference material and for 4.0% $\text{H}_2[\text{PtCl}_6]/\text{TH}$  in the presence of appropriate redox systems, vs. the redox potential affords straight lines (**Fig. 2**). From the corresponding slope the  $k$  values of 50 and 60 mV for *P25* and 4.0% $\text{H}_2[\text{PtCl}_6]/\text{TH}$  are obtained, respectively. They are in good agreement with the value of 59 mV known for  $\text{TiO}_2$ ,  $\text{SnO}_2$ , and  $\text{SrTiO}_3$  electrodes [35].

**Table 1.** Potentials of reversible redox couples in water.

| Compound                             | Structure of redox couple                                                           | $E_{\text{A}^{2+}/\text{A}^{+\bullet}}^{\text{V vs. NHE}^{\text{a)}}$ |
|--------------------------------------|-------------------------------------------------------------------------------------|-----------------------------------------------------------------------|
| (HEV)(PF <sub>6</sub> ) <sub>2</sub> |    | −0.34                                                                 |
| (HiBV)Br <sub>2</sub>                |  | −0.41                                                                 |
| (MV)Cl <sub>2</sub>                  |  | −0.45                                                                 |
| (BQ)Br <sub>2</sub>                  |  | −0.64 <sup>b)</sup>                                                   |
| (DP)Br <sub>2</sub>                  |  | −0.27 <sup>b)</sup>                                                   |

<sup>a)</sup>  $\pm 0.01$  V; <sup>b)</sup> irreversible

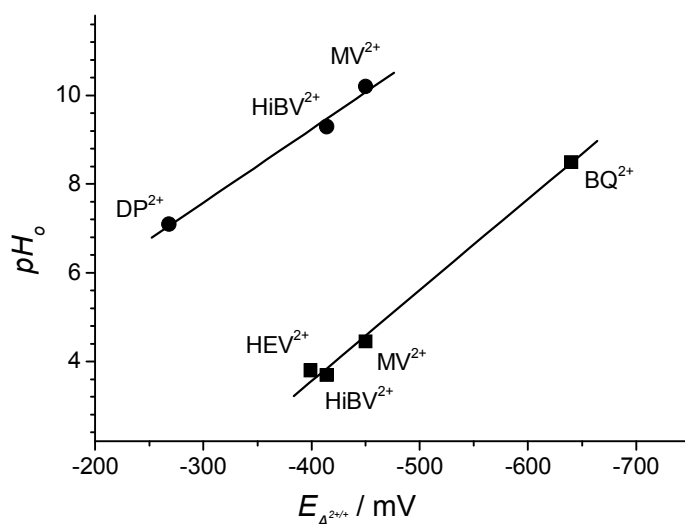


**Fig. 2**  $E_{A^{2+/+}}$  vs.  $pH_0$  for P25 (squares) and 4.0% $H_2[PtCl_6]/TH$  (circles) suspensions.

The plots of photovoltage vs. pH for *TH* and a series of  $H_2[PtCl_6]/TH$  materials are summarized in **Fig. 3**. From the inflection point ( $pH_0$ ) the corresponding quasi-Fermi potentials at  $pH = 7$ , as obtained via Eq. 3 assuming  $k = 0.059$  V, are  $-0.58$  V (P25) and  $-0.54$  V (TH).

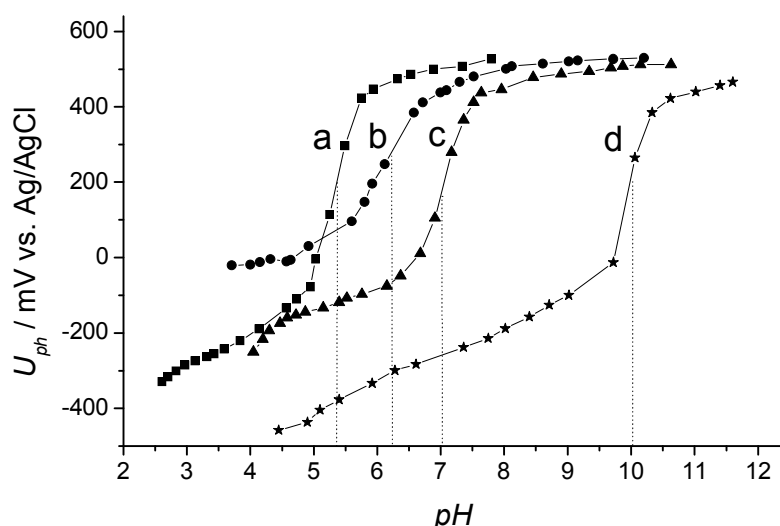


**Fig. 3**. Photovoltage recorded for TH (a), 1.0% (b), 2.0% (c) and 4.0% $H_2[PtCl_6]/TH$  (d) suspensions in 0.1 M  $KNO_3$  in the presence of  $(MV)Cl_2$  irradiated with the full light of an XBO-lamp. The position of the inflection point  $pH_0$  is marked with a dotted line.

The flatband potential of a single crystal of anatase was reported to be  $-0.59$  V ( $pH = 7$ ) [36]. Relative to the value of *TH* the quasi-Fermi level is shifted anodically by 0.05, 0.09, and 0.26 V in the case of 1%, 2%, and 4.0% $H_2[PtCl_6]/TH$ , respectively. Since the onset of the  $TiO_2$  part in the 4.0% $H_2[PtCl_6]/TH$  reflectance spectrum remains nearly unchanged (compare **Fig. 1** and **Table 1**), the anodic shift of the conduction band edge is accompanied by an anodic shift of the valence band edge. Although the resulting higher oxidation potential of the UV-light generated hole may be one of the reasons that the photocatalytic activity of 4.0% $H_2[PtCl_6]/TH$  upon excitation at  $\lambda \geq 320$  nm is higher than that of *TH* and P25 (**Fig. 4**), this may be due to the fact that the modified titania utilizes also the visible part of the exciting light [15-17]. Reproducibilities of quasi-Fermi potential and photocatalytic activity measurements reported in this paper are  $\pm 0.02$  V and  $\pm 10$  %, respectively.



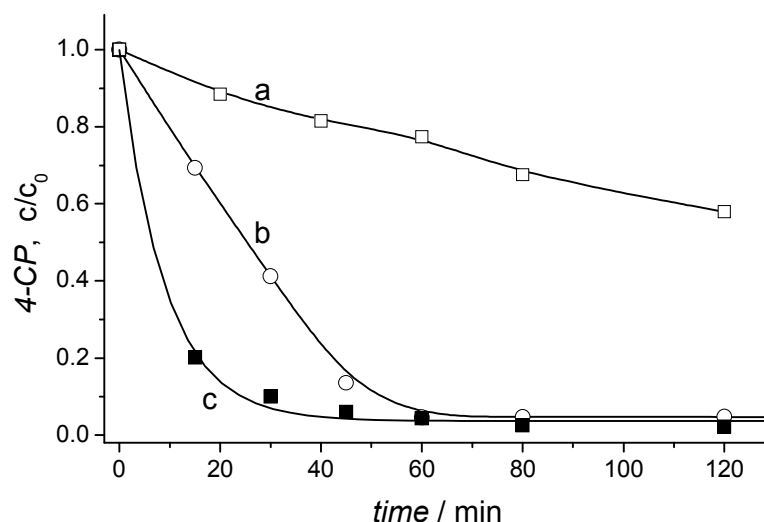


**Fig. 4.** UV light ( $\lambda \geq 320$  nm) induced degradation of 4-CP in the presence of TH (a) P25 (b), and 4.0% H<sub>2</sub>[PtCl<sub>6</sub>]/TH (c).

#### Photocatalytic degradation with artificial visible light ( $\lambda \geq 455$ nm)

**Fig. 5** illustrates the photodegradation of 4-CP [37] with visible light. Since reaction rates increased with increasing photocatalyst concentration, reaching a constant value at 0.5 g/L, all experiments were conducted at this value [38]. Whereas the rutile based H<sub>2</sub>[PtCl<sub>6</sub>]/Ald was inactive (**Fig. 5**, curve a), in accord with the very small surface area and the trace amounts of chemisorbed chloroplatinate, 1.1.% H<sub>2</sub>[PtCl<sub>6</sub>]/P25 and 4.0.% H<sub>2</sub>[PtCl<sub>6</sub>]/TH were active, inducing 50% degradation after 95 min and 15 min, respectively (**Fig. 5**, curves b, c). 4.0.% H<sub>2</sub>[PtCl<sub>6</sub>]/TH also initiated a fast mineralization as indicated by curve d in **Fig. 5**.

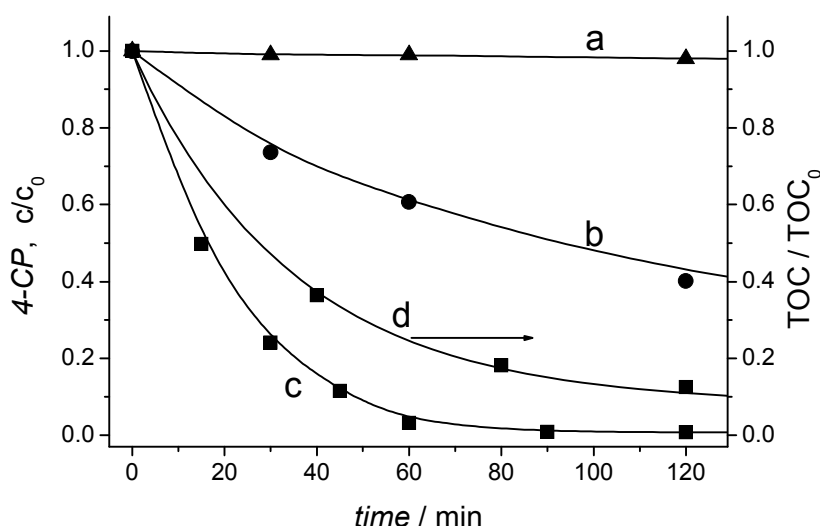


**Fig. 5.** 4-CP degradation upon visible light irradiation; H<sub>2</sub>[PtCl<sub>6</sub>]/Ald (a), 1.1.% H<sub>2</sub>[PtCl<sub>6</sub>]/P25 (b), 4.0.% H<sub>2</sub>[PtCl<sub>6</sub>]/TH (c), 4-CP mineralization as catalyzed by 4.0.% H<sub>2</sub>[PtCl<sub>6</sub>]/TH (d) [15].

Since the mineralization process produces CO<sub>2</sub>, H<sub>2</sub>O, and HCl, the initial pH value of 3.4 decreased to 3.0 at 120 min irradiation time. These conditions favor a proton catalyzed photodesorption (vide supra) and therefore a long-term irradiation was conducted in the presence of NaHCO<sub>3</sub> to neutralize the acid generated [15]. In this experiment the concentration of 4-CP was readjusted to its original value when the c/c<sub>0</sub> values approached zero (**Fig. 6**). Whereas in the absence of bicarbonate the activity decreased to 50% of its original value already at the third cycle,

it changed only little even after 19 cycles when bicarbonate was present. This clearly proves the catalytic nature of the photodegradation reaction.

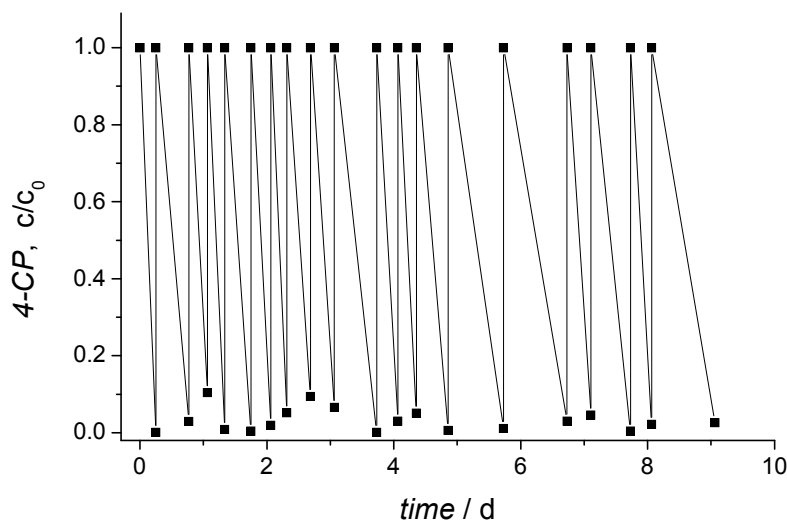


**Fig. 6** Long term visible light degradation of 4-CP in the presence of 4.0% $\text{H}_2[\text{PtCl}_6]/\text{TH}$  and 0.01 M  $\text{NaHCO}_3$ ;  $\lambda \geq 400$  nm [15].

Also other pollutants like atrazine, dichloroacetic acid, lindane, and trichloroethylene were almost completely mineralized ( $\lambda \geq 455$  nm). The degradation of atrazine in general affords cyanuric acid as the final product when unmodified titania were employed as photocatalysts [39]. However, when 4.0% $\text{H}_2[\text{PtCl}_6]/\text{TH}$  was used, even cyanuric acid was mineralized as indicated by TOC and nitrate determinations.

### Photodegradation with natural indoor daylight

The excellent photocatalytic activity of 4.0% $\text{H}_2[\text{PtCl}_6]/\text{TH}$  became even more evident, when the reaction was conducted in diffuse indoor laboratory daylight (4-10  $\text{Wm}^{-2}$  at 400-1200 nm). Under these conditions both unmodified *P25* and *TH* were inactive whereas the 1.1% and 4.0% surface modified counterparts after 420 min exhibited 10% and 50% degradation, respectively (**Fig. 7**).

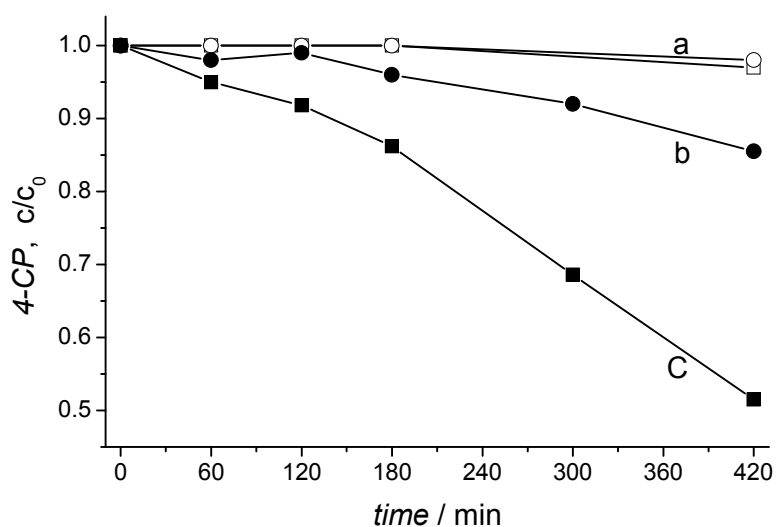


**Fig. 7.** Diffuse indoor daylight induced degradation of 4-CP in the presence of TH and P25 (a), 1.1% $\text{H}_2[\text{PtCl}_6]/\text{P25}$  (b), 4.0% $\text{H}_2[\text{PtCl}_6]/\text{TH}$  (c).

### Photodegradation with outdoor sunlight

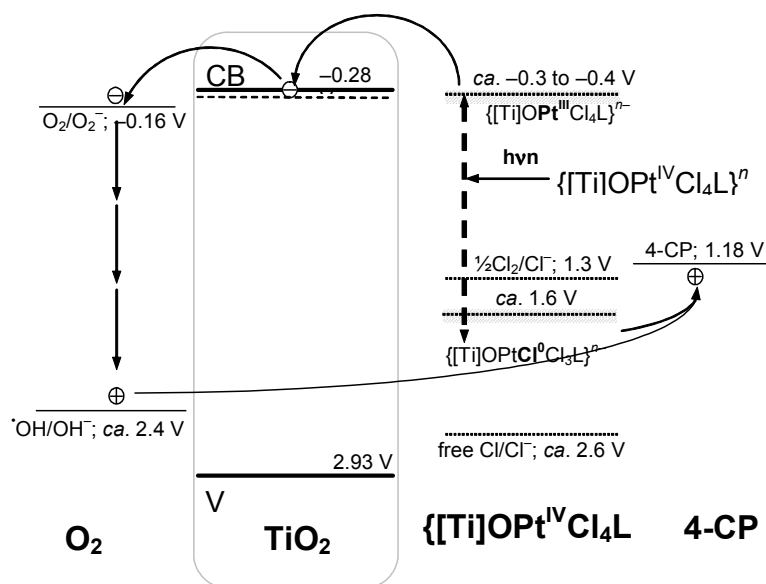
The superior activity of modified titania was demonstrated also, when the degradation of 4-CP was conducted with outdoor sunlight. Surprisingly, the  $\text{H}_2[\text{PtCl}_6]/\text{TH}$  materials were more active than *P25*. This higher reactivity was even more pronounced when the solar irradiation was replaced by artificial UV light. 2.0% $\text{H}_2[\text{PtCl}_6]/\text{TH}$  for instance induced 90% degradation already after 12 minutes, the time by which only 50% were degraded by *P25*. In the case of 4.0% $\text{H}_2[\text{PtCl}_6]/\text{TH}$  only traces of unreacted 4-CP could be detected after this irradiation time.

### Mechanism

Since the chloroplatinate component is the light absorbing species, it was proposed the primary photoprocess to be a homolytic Pt-Cl cleavage affording a  $\text{Pt}^{\text{III}}$  intermediate and an adsorbed chlorine atom, by analogy with the known photochemistry of hexachloroplatinate in solution [30, 40]. Electron injection from the platinum(III) complex into the titania conduction band reforms  $\text{Pt}^{\text{IV}}$ . Thus, the reductive and oxidative centers become spatially separated rendering charge recombination less probable. The trapped conduction band electron reduces oxygen to superoxide and finally hydroxyl radicals as evidenced by scavenging experiments with benzoic acid and tetranitromethane, an alternative electron acceptor. The adsorbed chlorine atom is assumed to oxidize 4-CP under deprotonation to the corresponding oxyl radical which is eventually converted to  $\text{CO}_2$  and HCl, by analogy with the photomineralization catalyzed by unmodified titania [41, 42]. Adsorbed chlorine atoms were also proposed as intermediates in the UV-induced photodegradation of trichloroethylene by titania [42]. It is noted, that the alternative mechanism, i.e. electron injection from the excited chloroplatinate resulting in a platinum(V) intermediate cannot be completely ruled out.

As summarized above, the primary photoprocess generates two surface redox centers. The oxidative one can be described as a kind of  $\text{Cl}/\text{Cl}^-$  redox pair weakly coordinated to a metal center. It is reasonable to assume that this oxidant is weaker than the free  $\text{Cl}/\text{Cl}^-$  pair ( $E^\circ_{\text{Cl}/\text{Cl}^-} = 2.6 \text{ V}$ , value for aqueous solution [43]), but stronger than the couple  $\frac{1}{2}\text{Cl}_2/\text{Cl}^-$  ( $E^\circ = 1.3 \text{ V}$  [44]) and the oxidation potential of 4-CP (1.18 V). Furthermore, the potential has to be lower than 2.4 V, the estimated redox potential of the  $\cdot\text{OH}/\text{OH}^-$  couple, because no hydroxyl radical formation could be observed in the presence of benzoic acid and tetranitromethane as OH and electron acceptor, respectively [14]. Thus, the potential of the oxidative center should be in the range of 1.3-2.4 V.

Unfortunately, the redox potential of the  $\text{Pt}^{4+/3+}$  couple is not known in the literature. Although some stable  $\text{Pt}^{\text{III}}$  compounds have been isolated and characterized [45], the oxidation state III is reached usually only in unstable intermediates of photoaquation reactions [46, 47, 48, 49, 50] and on titania surfaces as detected by time resolved diffuse reflectance spectroscopy [49]. The redox potential of the surface  $\text{Pt}^{4+/3+}$  couple should be equal or more negative than  $-0.28 \text{ V}$ , i.e. the flatband potential of 4.0% $\text{H}_2[\text{PtCl}_6]/\text{TH}$  at pH 7. Assuming a value of  $-0.40 \text{ V}$  and recalling that the difference between the redox potentials of reductive and oxidative centers can not be higher than the absorbed light energy divided by the elemental charge, which is about 2.00 V upon excitation at the absorption onset (620-650 nm), the potential of  $E_{\text{Pt}(\text{Cl}/\text{Cl}^-)}$  is obtained as 1.6 V (Scheme 1).



**Scheme 1.** Potential diagram for 4.0% $\text{H}_2[\text{PtCl}_6]/\text{TH}$  at  $\text{pH} = 7$ . All potentials are given versus NHE.

## II.2 $\text{RhX}_3$ Sensitization ( $\text{X} = \text{Cl}, \text{Br}$ )

To find out whether or not sensitization of titania as described above is feasible also with halides of other  $d^6$  metals, surface modification was also attempted with  $\text{RhX}_3$  ( $\text{X} = \text{Cl}, \text{Br}$ ) [50]. The novel hybrid photocatalysts  $x\%\text{RhCl}_3/\text{TH}$  containing 0.5, 1.0, 2.0, and 5.0 wt% of rhodium and  $2\%\text{RhBr}_3/\text{TH}$  were prepared as described above for chloroplatinate modification. Again the titania hydrate *TH* afforded photocatalysts which were very active in the photodegradation of 4-CP, whereas *Hombikat* 100 (Sachtleben) and *P25* based materials were less efficient. Maximum loading was observed at 5.0wt% of rhodium since the use of higher metal halide concentrations afforded powders from which excess rhodium is completely removed during washing.

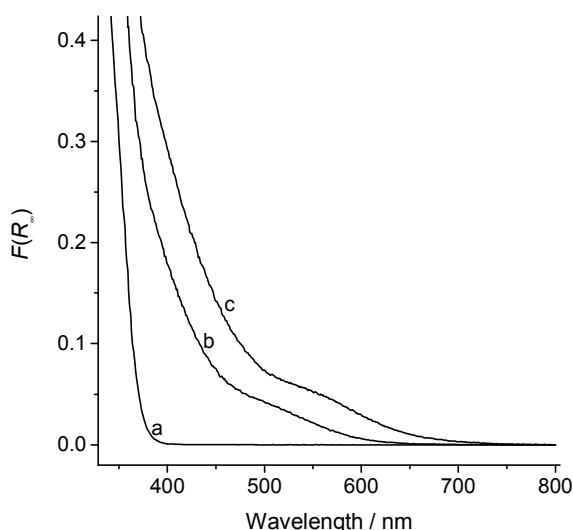


**Fig. 8.** Diffuse reflectance spectra of TH (a), 2.0% $\text{RhCl}_3/\text{TH}$  (b) and 2.0% $\text{RhBr}_3/\text{TH}$  (c). The Kubelka-Munk function,  $F(R_\infty)$ , is equivalent to absorbance.

$\text{RhCl}_3/\text{TH}$  and  $\text{RhBr}_3/\text{TH}$  have a pink and a dark yellow color, respectively, and are surprisingly stable to desorption of the rhodium component as compared to chloroplatinate modified *TH* [15-17]. In aqueous suspension upon stirring either in the dark or under irradiation with visible light, no dissolved rhodium complex was detectable by UV-Vis absorption spectroscopy. Both 4.0% $\text{RhCl}_3/\text{TH}$  and 4.0% $\text{RhBr}_3/\text{TH}$  did not undergo desorption of the rhodium surface-complex

even after stirring for five days in the dark in 0.5 M KF. Thus, one can conclude that Rh(III) is covalently bound to titania through a bridging oxygen ligand [50]. Whereas 4.0% $\text{H}_2\text{PtCl}_6/\text{TH}$  in 0.1 M HCl upon UV irradiation [15] for 24 h suffered almost complete desorption to  $[\text{PtCl}_6]^{2-}$ , only 40% of  $[\text{RhCl}_6]^{3-}$  were detectable in the case of 4.0% $\text{RhCl}_3/\text{TH}$ . This difference may reflect the fact that the metal-oxygen bond is about 40  $\text{kJ mol}^{-1}$  stronger in the case of rhodium [51]. In strongly alkaline suspension the chloride ligands are completely displaced, as also observed for 4.0% $\text{H}_2\text{PtCl}_6/\text{TH}$  [9]. Since from the amount of chloride produced in this experiment one can conclude that three chloride ligands are present in the surface rhodium complex, a composition of  $\{[\text{TiO}_2]\text{-O-RhCl}_3(\text{H}_2\text{O})_2\}^-$  is suggested.

Comparison of the diffuse reflectance spectra of TH and 2.0%Rh(III)/TH clearly indicates novel absorptions at 400 - 500 nm and 500 - 700 nm (**Fig. 8**). The shoulder at about 500 nm compares well with the lowest metal-centered transition of  $[\text{RhCl}_6]^{3-}$  observed in hydrochloric acid at 518 nm [52]. At wavelengths shorter than about 550 nm a strong absorption increase suggests that it does not originate exclusively from the second metal-centered transition occurring in  $[\text{RhCl}_6]^{3-}$  at 410 nm with about the same intensity as the 510 nm band. It rather may originate from a rhodium-to-titanium charge transfer transition as also reported for other titania-metal-complex systems like  $[\text{Fe}(\text{CN})_6]^{3-}/\text{TiO}_2$  [53]. This is corroborated by the fact that the silica analogue 2.0% $\text{RhCl}_3/\text{SiO}_2$  does not exhibit a strong absorption increase at  $\lambda \leq 550$  nm, most likely because, different from titania, silica does not have a low lying conduction band (**Fig. 9**, curve b). In the corresponding difference spectrum an unsymmetrical absorption band is observed at a maximum at 380 nm. In the case of 2.0% $\text{RhBr}_3/\text{TH}$  a similar comparison with 2.0% $\text{RhBr}_3/\text{SiO}_2$  afforded the MMCT maximum at 390 nm.

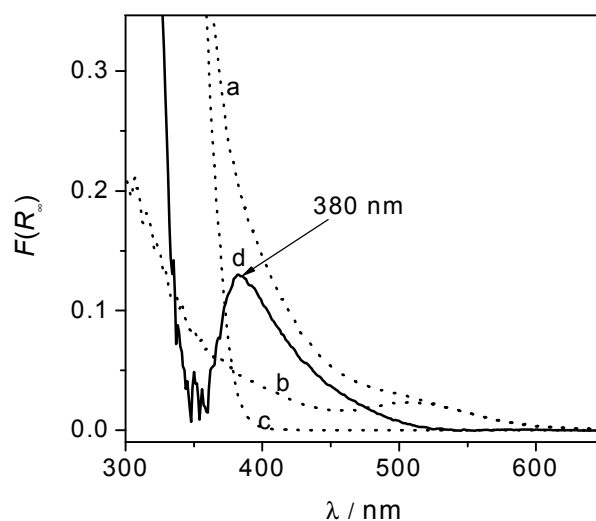


**Fig. 9.** Diffuse reflectance spectra of 2.0% $\text{RhCl}_3/\text{TH}$  (a), 2.0% $\text{RhCl}_3/\text{SiO}_2$  (b), TH (c). Spectrum d = a - (b + c).

Assuming that all samples are indirect crystalline semiconductors, as is anatase, the bandgap energy can be obtained by extrapolation of the linear part of a plot of  $[F(R_\infty)h\nu]^{1/2}$  vs. the energy of exciting light [31]. From this the bandgap of TH, 0.5, 1.0, 2.0, and 5.0% $\text{RhCl}_3/\text{TH}$  and of 2.0% $\text{RhBr}_3/\text{TH}$ , can be calculated as 3.29, 3.26, 3.25, 3.22, 3.21 and 3.10 eV, respectively (Tab. 2).

**Table 2** Bandgap energies and quasi-Fermi potentials of electrons.

| Photocatalyst              | $E_{bg} / \text{eV}^{\text{a}}$ | ${}_nE_F^*(\text{pH}=7, \text{NHE}) / \text{V}^{\text{b}}$ |
|----------------------------|---------------------------------|------------------------------------------------------------|
| TH                         | 3.29                            | -0.54                                                      |
| 0.5% RhCl <sub>3</sub> /TH | 3.26                            | -0.53                                                      |
| 1.0% RhCl <sub>3</sub> /TH | 3.25                            | -0.48                                                      |
| 2.0% RhCl <sub>3</sub> /TH | 3.22                            | -0.46                                                      |
| 5.0% RhCl <sub>3</sub> /TH | 3.21                            | -0.34                                                      |
| 2.0% RhBr <sub>3</sub> /TH | 3.10                            | -0.32                                                      |

a, b) Reproducibility was better than  $\pm 0.05 \text{ eV}$  and  $\pm 0.02 \text{ V}$ , respectively.

To investigate the photocatalytic activity, the disappearance and mineralization of 4-CP was performed in the presence of air. The activity of 5.0%RhCl<sub>3</sub>/TH was very high and after 60 min of visible light irradiation ( $\lambda \geq 455 \text{ nm}$ ) 95% of 4-CP had disappeared whereas 75% mineralized. 2.0%RhBr<sub>3</sub>/TH exhibited a photoactivity comparable to that of 2.0%RhCl<sub>3</sub>/TH. The unmodified powders *TH* and *P25* were inactive under these experimental conditions.

The photocatalytic activity increases with increasing rhodium loading, exhibiting the highest value for 5.0%RhCl<sub>3</sub>/TH (**Fig. 10**). This resembles the findings on the surface-loading of *TH* with [PtCl<sub>6</sub>] [6-15].

Photoelectrochemical measurements of the photovoltage as function of pH value [34] indicate that the quasi-Fermi level of electrons is shifted gradually more anodic upon increasing the rhodium loading. Thus, the value of  $-0.55 \text{ V}$  (vs. NHE, at  $\text{pH} = 7$ ) as observed for unloaded TH is shifted to  $-0.53$ ,  $-0.48$ ,  $-0.46$ , and  $-0.34 \text{ V}$  upon loading with 0.5, 1.0, 2.0, and 5.0%RhCl<sub>3</sub>/TH, respectively (Tab. 2). In the case of 2.0%RhBr<sub>3</sub>/TH the quasi Fermi level was found at  $-0.32 \text{ V}$ .

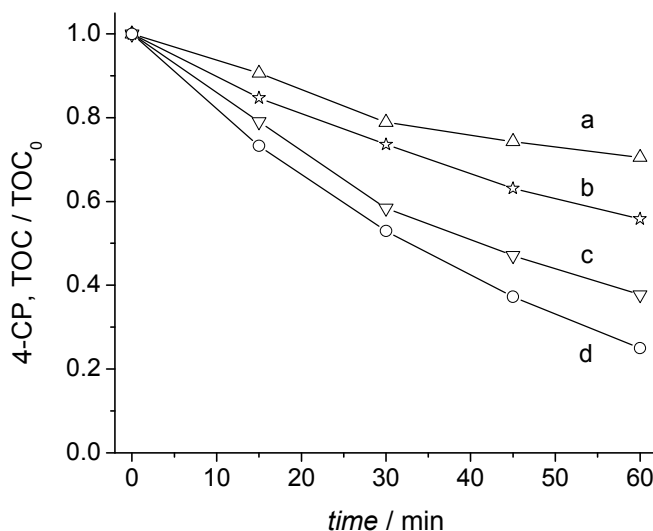


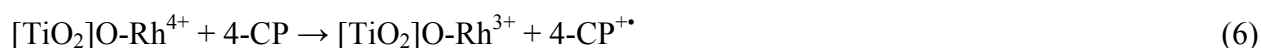
**Fig. 10** Mineralization of 4-CP as function of rhodium content; photocatalyst concentration:  $0.5 \text{ gL}^{-1}$ ; (a) 0.5%RhCl<sub>3</sub>/TH, (b) 1.0%RhCl<sub>3</sub>/TH, (c) 2.0%RhCl<sub>3</sub>/TH, (d) 5.0%RhCl<sub>3</sub>/TH.

To obtain experimental evidence for a mutual formation of OH radicals under visible light irradiation ( $\lambda \geq 400 \text{ nm}$ ), the photodegradation of benzoic acid in the presence of 4.0%RhCl<sub>3</sub>/TH and oxygen was investigated by monitoring the production of salicylic acid [14, 54, 55]. Surprisingly, no salicylic acid was detectable in solution. A likely reason for this could be a fast photodegradation of small amounts of initially produced salicylic acid. To test this hypothesis, photodegradation of salicylic acid was carried out under identical experimental conditions. It turned out that salicylic acid is efficiently adsorbed onto 4.0%RhCl<sub>3</sub>/TH and that its photodegradation is very fast. About 96% of salicylic acid had disappeared after 10 min of irradiation. These results

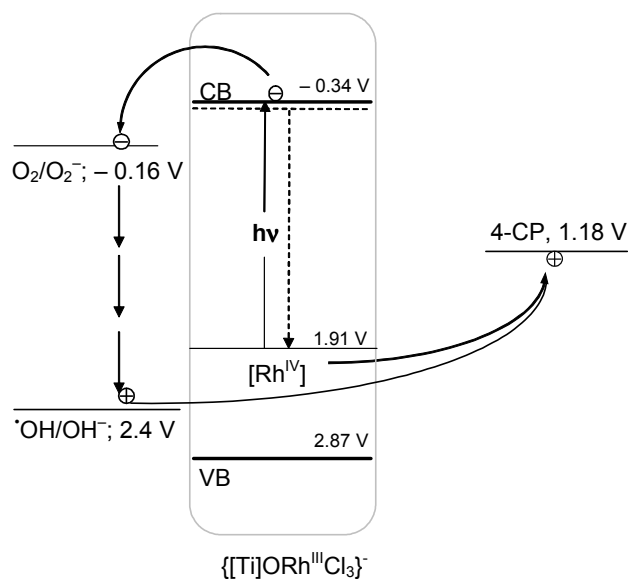
suggest that salicylic acid formed from benzoic acid largely remains adsorbed and is efficiently decomposed before being desorbed into solution.

### Mechanism

To test if the photocatalytic activity of RhCl<sub>3</sub>/TH is also initiated by a homolytic M-Cl bond cleavage, as proposed previously for platinum(IV) chloride modified TH, the photodegradation of phenol under visible light irradiation ( $\lambda \geq 455$  nm) was carried out. Formation of chlorophenol would evidence the presence of intermediate chlorine atoms. However, no significant amount of chlorophenol was detectable [56]. This differs from Pt(IV)/TH, in which case chlorophenol formation was observable [14]. Furthermore, cyanuric acid, a molecule which is mineralized in the presence of platinum(IV) modified TH [16], is not decomposed by 4.0%RhCl<sub>3</sub>/TH. These significant differences indicate that in the case of rhodium(III) modification visible light induced cleavage of the metal-halogen bond is not a major primary photoprocess. More likely seems a mechanism as proposed for UV light induced oxidation reactions in the presence of Rh(III) doped titania colloids [57].



Visible light excitation within the rhodium-to-titanium charge-transfer band of RhCl<sub>3</sub>/TH affords as primary products an electron in the titania conduction band and a Rh(IV) center (Eq. 5). The energetic position of the latter can be estimated by adding the energy of the Vis absorption onset (2.25 eV) to the quasi-Fermi level as depicted in Scheme 2 [58].



**Scheme 2.** Mechanistic scheme of titania sensitization by rhodium(III) complexes. Depicted values apply for 5.0%RhCl<sub>3</sub>/TH at pH = 7.

The resulting potential of 1.91 V is positive enough to oxidize water or more likely 4-chlorophenol to the radical cation (Eq. 6), which finally breaks down to CO<sub>2</sub>, HCl, and H<sub>2</sub>O, as well known from the UV photodegradation in the presence of unmodified TiO<sub>2</sub> [59]. The electron generated in the conduction band reduces oxygen to superoxide (Eq. 7) which through the reaction sequence according to Eq. 8-11 [60, 61, 62] is converted to an OH radical. The latter subsequently induces oxidation of 4-CP.

Recently it was reported that also the halogenides of Ru(III), Ir(IV), and Au(III) are able to form visible light active titania photocatalysts [63].

### III) Modification by Organic Sensitizers

In addition to metal compounds also non-metals like carbon, nitrogen, and sulfur were employed for visible light sensitization of titania. In many cases the nature of the dopant or modifier is unknown. For instance modification with thiourea was reported to afford a sulfur doped titania, having the dopant in the oxidation state +VI [64]. However, it was shown that the presence of sulfur is not responsible for visible light activity since after washing off sulfate the remaining material was more active than before [65]. In the following we address the nature of such dopants or modifiers species for nitrogen- and carbon-modified visible light active titania photocatalysts.

#### III.1 Nitrogen/carbon modified Titania

“N-doped” [66] titania has received great attention [67, 68]. It was prepared by essentially three methods consisting of (i) sputtering and implantation techniques, (ii) calcination of TiO<sub>2</sub> under N-containing atmospheres generated by nitrogen compounds like ammonia and urea, and (iii) by sol-gel methods [68]. Irrespective of many suggestions based more on theoretical than experimental results, the nature of nitrogen species in the resulting TiO<sub>2</sub>-N materials, however, is still an open question. NO<sub>x</sub> and various other nitrogen oxide species were proposed by Sato [69], our group [55, 65, 70], and others [71, 72]. But also nitridic and amidic (NH<sub>x</sub>) species were suggested; [73] in some cases even the presence of several oxidation states of nitrogen was postulated [74]. Depending on the preparation methods, the various TiO<sub>2</sub>-N samples most likely contain diverse nitrogen species and may have different photocatalytic activities. A significant example is the unique difference between TiO<sub>2</sub>-N prepared from ammonia [75] or urea [73] as nitrogen source. Only the material



obtained from the latter photocatalyzes the visible light mineralization of formic acid to carbon dioxide and water, whereas ammonia-derived  $\text{TiO}_2\text{-N}$  is inactive. Contrary to the generally made assumption that the nitrogen species is the origin of visible light photocatalysis, it was proposed that the nitrogen precursor during the modification procedure just induces formation of oxygen vacancies and color centers, which themselves are responsible for the visible light activity [76, 77, 78]. In an attempt to experimentally decide between the two proposals, we investigated the nature of the photoactive species in a  $\text{TiO}_2\text{-N}$  sample obtained from urea [71-74, 79-90].

Slightly yellow nitrogen modified titania was prepared by calcining a 1:2 (wt/wt) mixture of titania and urea at 400 °C. Elemental analysis revealed the presence of nitrogen and carbon and therefore these powders are abbreviated in the following as  $\text{TiO}_2\text{-N,C}$ . As obtained  $\text{TiO}_2\text{-N,C}$  has anatase structure and induced about 80% mineralization of formic acid and almost 60% degradation of 4-chlorophenol upon irradiating 3 h with visible light ( $\lambda \geq 455$  nm) [91]. Since it is known that at 300-420 °C urea is converted to ammonia and isocyanic acid [92, 93], this gas mixture was simulated by heating the isocyanic acid precursor cyanuric acid (CA) in the presence of ammonia and titania at 400 °C. The resulting material  $\text{TiO}_2\text{-N,C/CA,NH}_3$  was very active and induced 92% degradation within 3 h (**Fig. 11**). To check if ammonia is essential in this modification process,  $\text{TiO}_2$  was calcined at the same temperature in the presence of only cyanuric acid. The obtained  $\text{TiO}_2\text{-N,C/CA}$  after 3 h of irradiation degraded 80% of formic acid. Since it is known that in the same temperature range isocyanic acid in the presence of an OH groups containing heterogeneous catalyst

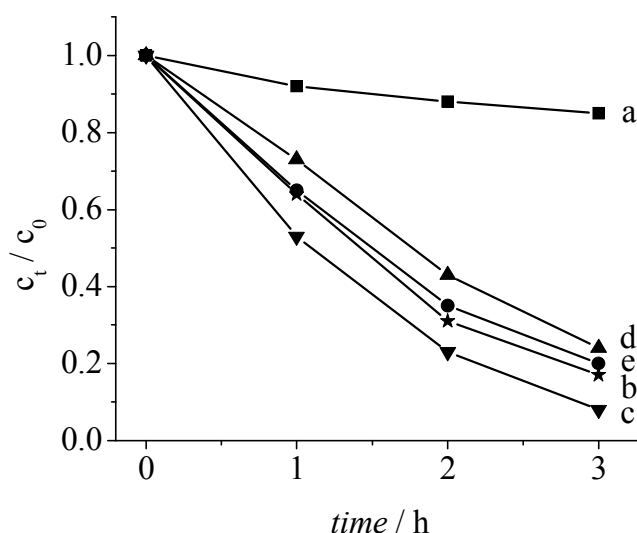
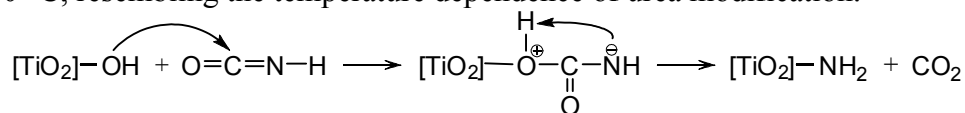


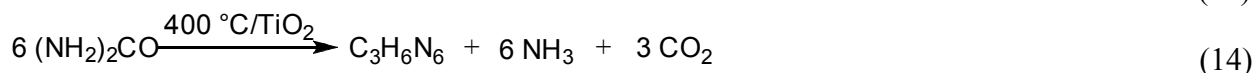
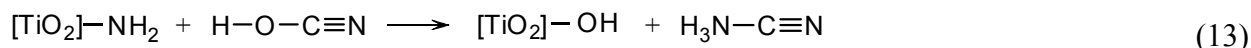
**Fig. 11** Photomineralization of formic acid ( $c = 1 \times 10^{-3}$  M);  $c_0$ ,  $c_t$  are concentrations at times 0 and  $t$ ; (a)  $\text{TiO}_2$ , (b)  $\text{TiO}_2\text{-N,C}$ , (c)  $\text{TiO}_2\text{-N,C/CA,NH}_3$ , (d)  $\text{TiO}_2\text{-N,C/melamine}$ , (e)  $\text{TiO}_2\text{-N,C/melem,melon}$ .

is converted via cyanamide to melamine, the latter could be produced also during the urea modification process assuming that titania surface OH groups act as catalysts (Eq. 12-13) [92]. Thus, melamine could be produced according to the over-all reaction depicted in Equation 14 [92].

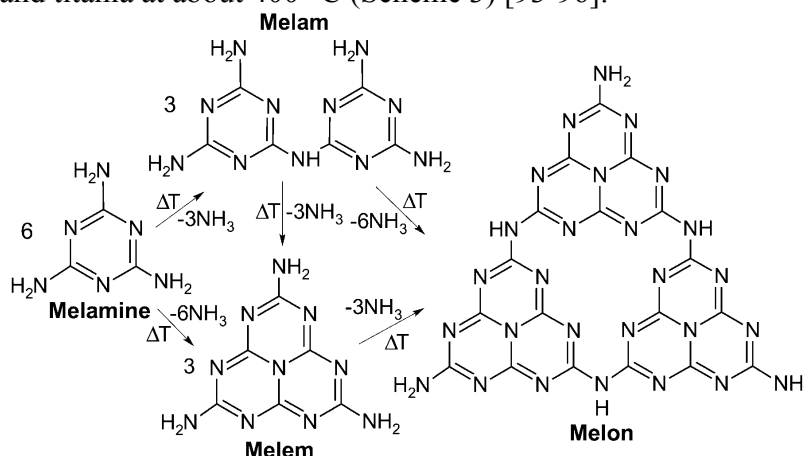
In agreement with this rationalization efficient photocatalysts were obtained also when urea was replaced by melamine in the modification procedure. Highest photocatalytic activity was achieved, when the calcination was performed at 400 °C, whereas only an inactive material was afforded at 600 °C, resembling the temperature dependence of urea modification.



(12)



Since at 400 °C melamine undergoes polycondensation to white melam, white-beige melem, and yellow melon, it appeared likely that melem and melon are present in “N-doped” photocatalysts obtained from urea and titania at about 400 °C (Scheme 3) [93-96].

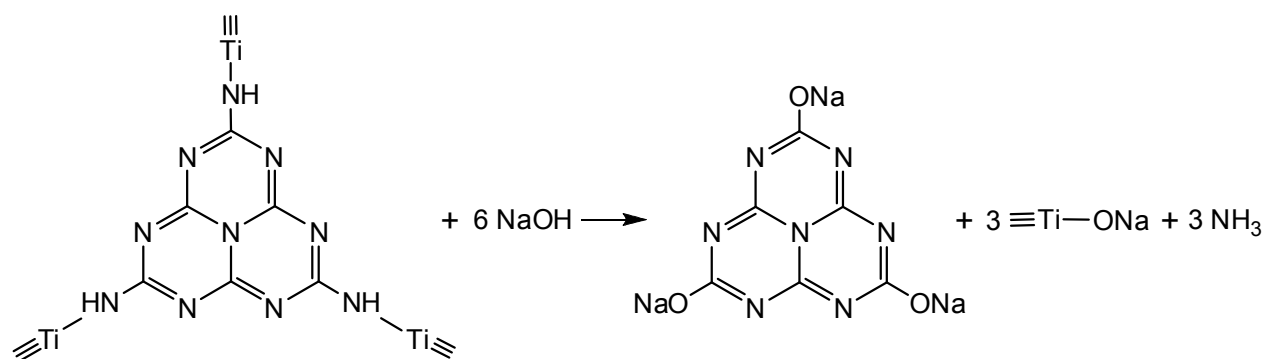


**Scheme 3.** Condensation products of melamine produced at 350 – 500 °C in the absence of titania [93, 95].

To further test this hypothesis, melamine was heated at 450 °C producing a yellow mixture of melem and melon as indicated by FTIR and elemental analysis which did not change when kept in air for 1h at 400 °C. The mixture before and after calcination at 400 °C was inactive in visible light induced formic acid degradation. However, when the mixture was treated at 400 °C in the presence of an equal amount of titania, the resulting yellowish powder *TiO<sub>2</sub>-N,C/melem,melon* exhibited 80% degradation, as also observed for *TiO<sub>2</sub>-N,C* obtained from urea (**Fig. 11**). It is noted that grinding the *melem/melon* mixture with titania at room temperature produced only an inactive material.

The results presented above strongly suggest that during the preparation of nitrogen-modified visible light photocatalysts from titanium dioxide and urea a key step is the titania-catalyzed formation of melamine. Subsequent condensation affords a mixture of oligonuclear aromatic amines, predominantly melam, melem, and melon. Thereafter, condensation between the triazine amino and titania OH groups generates Ti-N bonds. Thus, the visible light absorbing triazine derivative becomes covalently attached to the semiconductor.

Since it is known that the amino groups in melem can be replaced by OH through nucleophilic attack of hydroxide [97], *TiO<sub>2</sub>-N,C/melamine* was treated with sodium hydroxide at 100 °C. In fact, the expected cyamelurate and ammonia were obtained (Scheme 4). Both the residue and the evaporated extract did not photocatalyze visible light mineralization of formic acid. As expected, the material obtained by heating titania and the extract at 400 °C afforded a photocatalyst of only low activity (19% degradation in 3h).



**Scheme 4.** Extraction of cyamelurate from  $TiO_2-N,C/melamine$ .

The chemical results discussed above clearly indicate that the same photocatalyst is obtained irrespective of using urea or melem/melon as the modifier. To further support this conclusion the following physical measurements were performed.

Various XPS N1s binding energies for urea-derived  $TiO_2-N$  were reported in the literature. Peaks at 396-397 eV were assigned to nitridic nitrogen like in titanium nitride (N-Ti-N) [85-89, 98], peaks at 399 eV assumed to originate from nitridic nitrogen in modified titania (O-Ti-N) [72], signals at 400-401 eV may be due to N-N, N-O or N-C groups [72, 73, 85, 86, 90, 98], and chemisorbed  $N_2$  [88,89], and peaks at 407-408 eV were proposed to correspond to nitrite [74]. The binding energies of 399.2 and 400.5 eV for  $TiO_2-N,C$  and of 399.1 and 400.6 eV for  $TiO_2-N,C/melem,melon$  compare well with corresponding data of carbon nitrides (399-400 eV, C=N-C) [99, 100], of similar graphite-like phases (400.6 eV, N-C  $sp^2$ ) [96, 101], and of polycyanogen (399.0 eV, 400.5 eV,  $(-C=N-)_x$ ) [102]. Corresponding values for the as obtained mixture of melem/melon are 399.2 eV and 398.4 eV.

Analogous to the XPS data, also the optical absorptions of  $TiO_2-N,C$  and  $TiO_2-N,C/melem,melon$  are very similar. Assuming the materials to be indirect semiconductors, as is  $TiO_2$ , a plot of the modified Kubelka-Munk-Function  $[F(R_\infty)E]^{1/2}$  vs.  $h\nu$  (**Fig. 12**) afforded the bandgap energies summarized in **Table 3** together with other basic data.

**Table 3.** Nitrogen to carbon atomic ratio (N/C)<sup>a</sup>, quasi-Fermi energies ( $nE_F^*$ )<sup>b</sup>, bandgap energies ( $E_{bg}$ ), and initial mineralization rates ( $r_i$ ) of formic acid for various  $TiO_2-N/C$  samples.

| photocatalyst           | N/C  | $E_{bg}$<br>(eV) | $nE_F^*$<br>(V,<br>NHE) | $r_i$<br>( $10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$ ) |
|-------------------------|------|------------------|-------------------------|----------------------------------------------------------|
| $TiO_2$                 | 0    | 3.23             | -0.56                   | 0.12                                                     |
| $TiO_2-N,C/CA, NH_3$    | 1.80 | 2.90             | -0.48                   | 2.44                                                     |
| $TiO_2-N,C$             | 1.66 | 2.90             | -0.48                   | 1.37                                                     |
| $TiO_2-N,C/melamine$    | 1.67 | 3.02             | -0.48                   | 0.58                                                     |
| $TiO_2-N,C/melem,melon$ | 1.53 | 3.07             | -0.51                   | 0.65                                                     |
| $TiO_2-N,C/CA$          | 1.50 | 3.07             | -0.51                   | 2.34                                                     |

<sup>a</sup>Elemental analysis. <sup>b</sup>Measured according to ref. [34] and calculated for pH = 7.

As compared to unmodified titania the new materials exhibit a bandgap-narrowing of 0.16-0.33 eV and a slight anodic shift of the quasi Fermi level of 0.05-0.08 V. In the presence of  $TiO_2-N,C/CA,NH_3$ ,  $TiO_2-N,C/CA$ ,  $TiO_2-N,C$ ,  $TiO_2-N,C/melem,melon$ ,  $TiO_2-N,C/melamine$ , and  $TiO_2$  relative initial rates ( $r_i$ , relative to the  $TiO_2$  rate) of 6, 4, 4, 4, 3, and 1, respectively, were found for formic acid degradation.

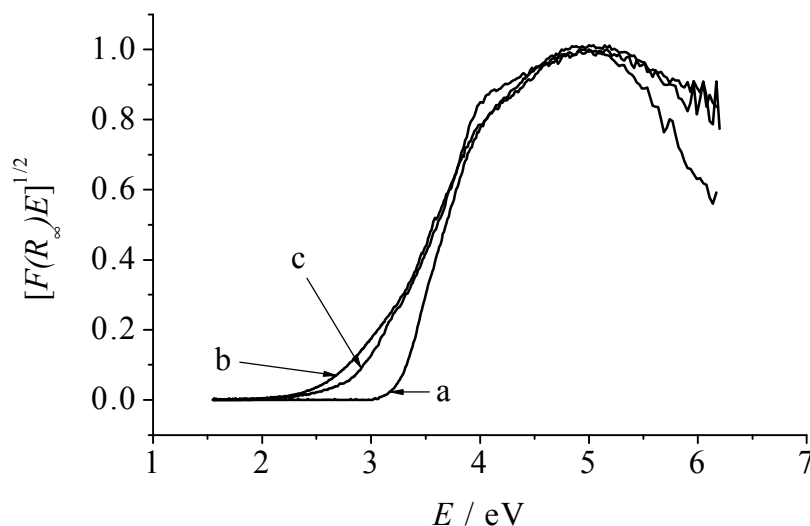


**Fig. 12** Plot of transformed Kubelka-Munk function vs. energy of light for (a)  $\text{TiO}_2$ , (b)  $\text{TiO}_2\text{-N/C}$ , (c)  $\text{TiO}_2\text{-N,C/melem,melon}$ .

Although the results presented above exclude the possibility that urea derived so-called “ $\text{TiO}_2\text{-N}$ ” exhibits visible light activity due to the presence of oxygen vacancies [76-78], they do not exclude the possibility that non-stoichiometric titania of visible light activity may be formed when titania is calcined in vacuo at 400 °C in the *absence* of urea. The generation of surface defects by annealing in vacuo is well documented in the literature [6,103, 104]. However, both the resulting  $\text{TiO}_{2-x}$  and the material obtained from it by calcining with urea or melamine at 400 °C were inactive in formic acid mineralization. The inactivity of the latter materials is understandable, as the as prepared  $\text{TiO}_{2-x}$  should have a surface OH group concentration too low to enable the crucial addition of isocyanic acid according to Eq. 12 or condensation with aminotriazine groups. As established above, without this pre-calcination titania and urea or melamine afford highly active  $\text{TiO}_2\text{-N,C}$  photocatalysts.

In summary, these findings clearly reveal that calcining a mixture of urea and  $\text{TiO}_2$  at 400 °C produces amino-tri-*s*-triazine derivatives covalently attached to the semiconductor. Therefore, and contrary to previous reports, visible light photocatalytic activity of “N-doped” or “N-modified” titania prepared from urea does not originate from the presence of nitridic, amidic, and nitrogen oxide species or color centers. Contrary to most other visible light photocatalysts this dye-sensitized titania enables also an efficient oxidation of formic acid.

### III.2 Carbon-modified Titania

Recently, we have reported on a carbon modified titania ( $\text{TiO}_2\text{-C}$ ) prepared from  $\text{TiCl}_4$  and tetrabutylammonium hydroxide [54, 105, 106]. Thereafter a technical process was developed rendering this visible light photocatalyst (VLP) commercially available. It consists of calcining titania in the presence of an organic compound as carbon source [106]. Several reports concerned with this type of modification employing solid, liquid or gaseous carbon sources have been published in the mean time [107, 108, 109, 110, 111, 112]. Alternatively, also the organic substituent in a titanium alcoholate may serve as carbon precursor [111, 113-115]. In all cases calcination temperatures were in the range of 250 – 500 °C. Carbon modified titania was obtained also by annealing titanium carbide at about 600 °C [116]. All these so called “C-doped” titania materials exhibit a weak absorption shoulder between 400 and 800 nm, the intensity of which increases with increasing carbon content [54, 113]. However, maximum photocatalytic activity is observed at intermediate carbon concentrations. Thus, in the case of  $\text{TiO}_2\text{-C}$  the absorbance steadily

increases with carbon contents of 0.03%, 0.42%, and 2.98%, whereas the reaction rate of 4-chlorophenol oxidation exhibits a maximum at 0.42% [54].

Most of these carbon modified anatase materials are active in visible light photo-oxidations of various organic pollutants. In addition to 4-chlorophenol [108, 117] also isopropanol [116], gaseous benzene [112] and nitrogen oxides [107, 111, 115] were photo-oxidized by visible light irradiation of “C-doped” titania. It was generally proposed that the presence of some carbon species in titania is necessary for the observation of visible light activity. Contrary to this common opinion it was proposed that not carbon species itself but oxygen vacancies, generated only in the presence of a carbon source, are responsible for visible light activity [76-78]. To allow a decision between these two contrary proposals, some simple chemical experiments were conducted with the commercial VLP material [118].

Heating an alkaline suspension of the beige VLP powder at 90 °C afforded a brown extract ( $\text{SENS}_{\text{ex}}$ ) and an almost white residue ( $\text{VLP}_{\text{res}}$ ). This suggested that  $\text{SENS}_{\text{ex}}$  contained a molecular sensitizer which may be re-assembled to VLP upon treating it with  $\text{VLP}_{\text{res}}$ . In fact, treating a suspension of  $\text{VLP}_{\text{res}}$  in the extract  $\text{SENS}_{\text{ex}}$  at 90 °C and subsequent calcination of the brown solid at 200 °C afforded a slightly brownish powder  $\text{VLP}_{\text{reas}}$ . The latter as well as VLP and  $\text{VLP}_{\text{res}}$  all have anatase structure with crystallite sizes of 13, 10, and 12 nm, respectively, as indicated by XRD analysis.

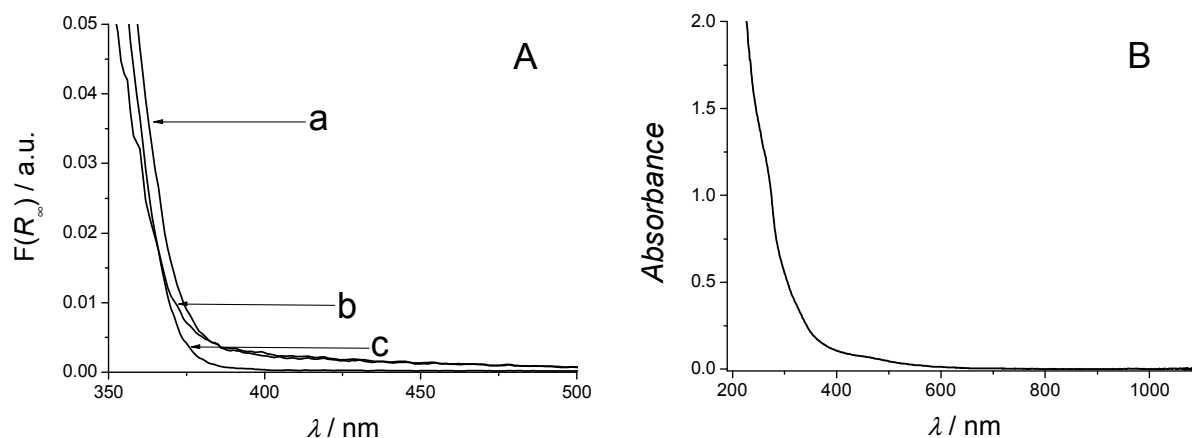


**Fig. 13.** A) Diffuse reflectance spectra of a) VLP, b)  $\text{VLP}_{\text{reas}}$ , and c)  $\text{VLP}_{\text{res}}$ . B) Absorption spectrum of the as obtained extract solution  $\text{SENS}_{\text{ex}}$ .

Diffuse reflectance spectra of VLP and  $\text{VLP}_{\text{reas}}$  exhibit a weak but significant absorption in the visible, which is absent in the case of  $\text{VLP}_{\text{res}}$  (**Fig. 13A**). Assuming that all three materials are indirect semiconductors like anatase, optical bandgaps of 3.22, 3.21, and 3.27 eV are obtained for VLP,  $\text{VLP}_{\text{reas}}$ , and  $\text{VLP}_{\text{res}}$ , respectively, from a plot of transformed Kubelka-Munk function vs. the energy of the exciting light. The extract solution exhibits a weak absorption shoulder in the visible (**Fig. 13B**).

Although the similar diffuse reflectance spectra of VLP and  $\text{VLP}_{\text{reas}}$  suggested that the re-assembling reaction between  $\text{VLP}_{\text{res}}$  and extract  $\text{SENS}_{\text{ex}}$  has reformed VLP, XPS experiments, photoelectrochemical measurements, and photocatalytic activity tests were performed to prove or disprove this assumption.

It was generally proposed that the presence of some carbon species in titania is responsible for the visible light activity. However, the chemical nature of the “carbon dopant” is still a matter of controversial discussion. In general the C1s binding energy, as easily obtained by XPS, was taken as diagnostic tool for the type of carbon present. From corresponding values of 284.8 – 285.7 eV [54, 105, 109, 116, 117, 119, 120, 121] the presence of elemental carbon and graphitic or coke-like carbon was proposed [113, 121]. It is noted that the binding energies of carbidic carbon of 281.8 – 284.3 eV [107, 116, 119, 120, 122, 123] and aromatic ring carbon atoms of 284.3 – 284.7 [124-126]

fall in the same range and therefore assignments may be ambiguous. Also surface carbonates were proposed as relevant species 286.5 – 289.4 eV [54, 89, 105, 112, 121, 127]. But it was shown that their presence is not responsible for visible light activity [65]. Binding energies of 288.6 and 288.9 eV were thought to arise from structural fragments like Ti-O-C [109] and Ti-OCO [128]. Density functional theory calculations suggest that substitutional (of lattice oxide) and interstitial carbon atoms are present [129]. Contrary to the common opinion it was proposed that not carbon species itself but oxygen vacancies, generated only in the presence of a carbon source, are responsible for visible light activity [76]. It is noted that the relevant species may be different, depending on the nature of the carbon source.

In anatase powders prepared from alcoholates as carbon source a symmetric paramagnetic signal was observed at  $g = 2.005$  by EPR spectroscopy, assigned to an aromatic coke like species [113]. Similar results were obtained for the commercial VLP product revealing that signal intensity increases with carbon content [105]. Although the intensity increased upon Vis irradiation, it could not be concluded that the corresponding radical is involved in the photocatalysis process since the concentration of radicals was about five to six orders of magnitude lower than the total carbon content [105]. Contrary to this, it was proposed that in carbon modified titania prepared from gaseous cyclohexane this paramagnetic signal arises from an electron trapped at an oxygen vacancy [112].

XPS analysis of VLP<sub>reas</sub> and VLP revealed the presence of three peaks in the range of C1s binding energies (**Fig. 14**). Curve fitting analysis affords almost identical values of 284.8, 286.5, 288.4 eV and 284.8, 286.3, 288.8 eV for VLP<sub>reas</sub> and VLP, respectively. The only significant difference is the higher intensity of the 286.5 eV peak in VLP<sub>reas</sub>. This excellent agreement further supports the success of the re-assembling reaction. Peaks at 284.8 eV are assumed to arise predominantly from adventitious carbon, although aromatic and graphitic carbon have similar binding energies in the range of 284.3 – 284.7 eV [120, 124-126]. Peaks at the higher binding energies may originate from carbonate or carboxylate groups. Presence of the former seems unlikely since in the FTIR spectrum no corresponding absorption can be observed at 1720-1740  $\text{cm}^{-1}$ ; it is known that carbonate does not induce visible light activity [65, 113]. More likely is that these peaks arise from two types of carboxylates. From the fact that benzoate bridging two titanium centers exhibits a binding energy of 288.6 eV [126], the peaks 288.4 and 288.6 eV can be assigned to an arylcarboxylate group. The remaining peaks at 286.5 and 286.3 eV are tentatively assigned to a bidentately bound arylcarboxylate, which should have a slightly lower C1s binding energy. A symmetrical surface binding of the arylcarboxylate is also supported by the O1s binding energies. The two peaks at 530.0 and 531.5 eV can be assigned to oxygen atoms in titania and in the coordinated carboxylate, respectively. Corresponding values of 529.9 and 531.3 [130]/531.5 eV [126] were reported for benzoic acid coordination.

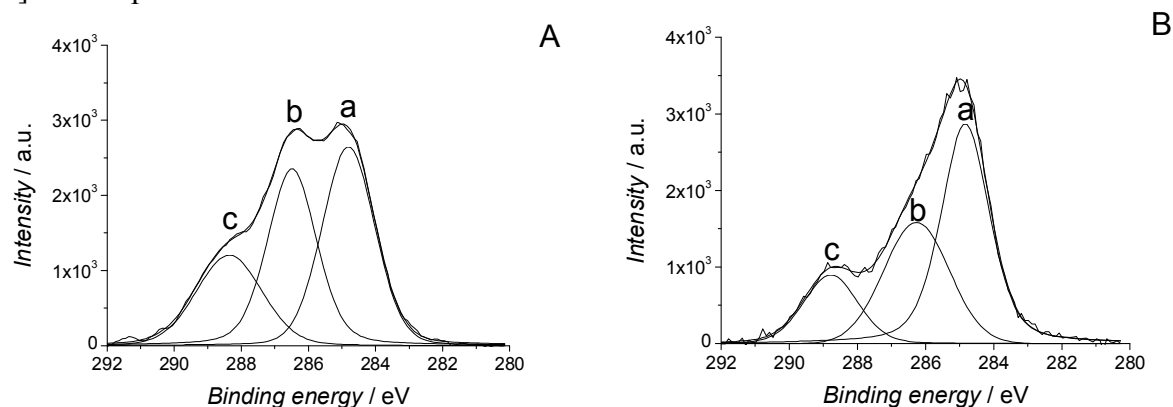


**Fig. 14.** XPS C1s spectra of VLP<sub>reas</sub>: 284.8 (a), 286.5 (b), 288.4 (c) eV (A) and of VLP: 284.8 (a), 286.3 (b), 288.8 (c) eV (B).

Although both diffuse reflectance and XPS data further corroborate the similarity of VLP and  $\text{VLP}_{\text{reas}}$ , it is at least of equal importance comparing also their photoelectrochemical properties. This was performed by measuring the quasi-Fermi level of electrons ( $nE_F^*$ ) for all three powders through recording the photovoltage of a powder suspension as a function of pH value (**Fig. 15**) [34]. Again VLP and  $\text{VLP}_{\text{reas}}$  exhibited the same result, which was in this case one unique  $nE_F^*$  value of  $-0.50$  V (NHE), whereas  $-0.56$  V was obtained for  $\text{VLP}_{\text{res}}$  at pH 7. The latter value suggests that the powder remaining after extraction consists of unmodified anatase, in accordance with the XRD data, whereas the anodically shifted value is significant of carbon-doped titania [54]. Assuming that the energy difference between Fermi level and conduction band edge is negligible for these n-type powders, the valence band edge potentials of VLP and  $\text{VLP}_{\text{reas}}$  were obtained as 2.72 and 2.71 V, respectively, by adding the bandgap energy to the quasi-Fermi energy.

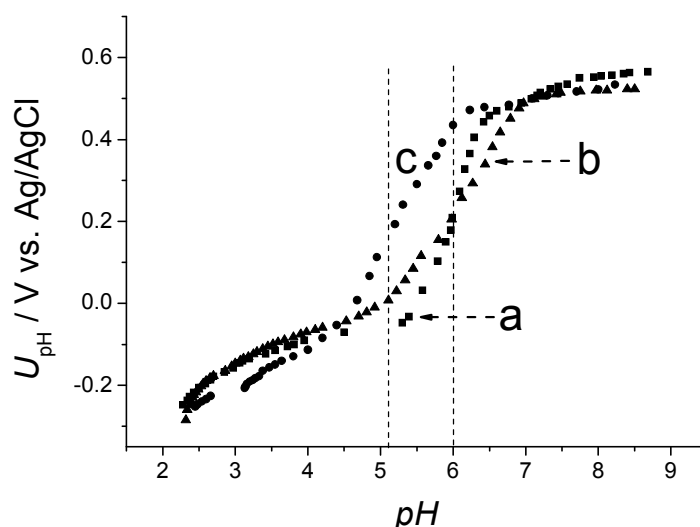


**Fig. 15.** Variation of photovoltage with pH value for the suspension of various photocatalysts in the presence of methylviologen dichloride. a) VLP, b)  $\text{VLP}_{\text{reas}}$ , c)  $\text{VLP}_{\text{res}}$ . Dashed lines indicate pH values of inflection points from which the quasi-Fermi level can be calculated.

The results presented above suggest that the alkali extract  $\text{SENS}_{\text{ex}}$  contains carboxylic groups, which during the re-assembling reaction, undergo esterification with titania surface hydroxyl groups. This is corroborated by FTIR analysis of the brown residue obtained from  $\text{SENS}_{\text{ex}}$  after the removal of water from the basic solution (pH 12). The sample exhibited intense peaks at  $1580$  and  $1420\text{ cm}^{-1}$ , assignable to asymmetric and symmetric stretching vibrations of an arylcarboxylate group. Corresponding values of e.g. free sodium benzoate are  $1552/1414\text{ cm}^{-1}$  (KBr). Unfortunately no corresponding peaks could be obtained in the FTIR spectra of VLP and  $\text{VLP}_{\text{reas}}$ , both measured conventionally or by the ATR technique. This failing suggests that the sensitizer is present as thin surface layer of too low concentration to be detected by FTIR spectroscopy. The fact that the significant carbon peaks at  $286.3\text{ eV}$  and  $288.8\text{ eV}$  in the XPS spectrum completely disappear after sputtering with argon for 3 min, what is sufficient to remove a 4 nm thin surface layer, corroborates this explanation.

The excellent agreement between the physical properties of VLP and  $\text{VLP}_{\text{reas}}$  as reported above, suggests that also the photocatalytic activities may be very similar. In fact, visible light photodegradation experiments with 4-CP revealed that after 3 h irradiation time VLP and  $\text{VLP}_{\text{reas}}$  induced mineralizations of 70% and 77%, respectively. Contrary to this,  $\text{VLP}_{\text{res}}$  exhibited only 18% mineralization (**Fig. 16**).

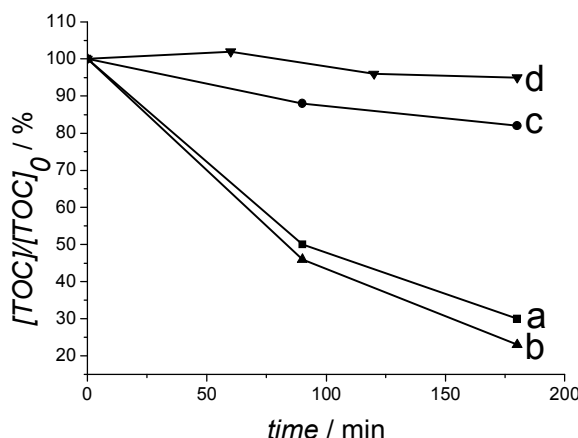


**Fig. 16.** Photomineralization of 4-CP with visible light ( $\lambda \geq 455$  nm) in the presence of (a) VLP, (b) VLP<sub>reas</sub>, (c) VLP<sub>res</sub>, (d) SENS<sub>ex</sub>. Suspensions (a) and (b) exhibited pH  $\sim 5.8$ , whereas suspension (c) and solution (d) needed addition of acid to obtain this pH value.

It is noted that the photodegradation rate strongly depends on the pH value at which the re-assembling reaction was conducted. At 3 h of irradiation time the VLP<sub>reas</sub> prepared at pH $\sim 12$  afforded only 13% mineralization, whereas 44% were obtained at pH $\sim 7$ . Noteworthy is also that suspensions of VLP and VLP<sub>reas</sub> in 4-CP exhibit the same pH value of 5.8 suggesting a similar surface structure.

To exclude a mutual homogeneous photosensitized degradation a blank experiment was carried out employing only the extract SENS<sub>ex</sub>, which exhibits absorption shoulders at 460 and 260 nm. However, no photodegradation of 4-CP was observable (**Fig. 16d**). To check the possibility if oxygen defects may also induce visible light activity, VLP<sub>res</sub> was heated in vacuo for 1 h at 150 °C. Under the standard experimental conditions this material enabled within 3 h a 4-CP mineralization of 20%.

The results presented above indicate that the commercial visible light photocatalyst VLP contains an organic sensitizer which can be extracted with alkaline water. Both the extract and the remaining solid do not exhibit significant activity in the photomineralization of 4-chlorophenol. However, when these two components are re-assembled, the activity, quasi-Fermi level, diffuse reflectance spectrum, and XPS data are almost identical with those of original VLP. Thus, the visible light activity of VLP and probably of many previously reported so-called "C-doped" titania powders is not due the presence of lattice carbon atoms or oxygen defects as generally reported. However, the present findings do not exclude the presence of defects in VLP but there is no experimental evidence that they are involved in the visible light induced charge separation at the sensitizer modified anatase surface.

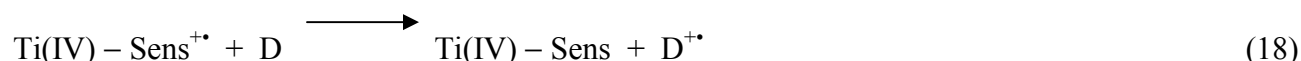
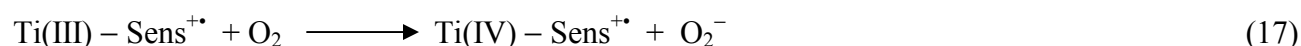
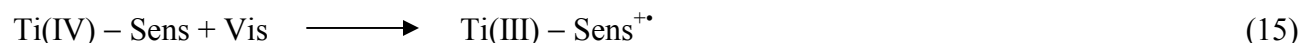
#### IV) Summary

As discussed in Chapter II for the inorganic sensitizers the photoactive species of the corresponding photocatalysts can be considered as a surface transition metal halide complex, i.e. a metal complex sensitizer, having titania as a semiconducting "inorganic ligand" bound via oxygen to a platinum(IV) or rhodium(III) center. In the case of the platinum complex visible light irradiation results in a platinum centered excitation followed by homolytic Pt-Cl bond cleavage and electron injection of Pt(III) into the titania conduction band. Thus, the reducing and oxidizing surface sites can be described as an trapped electron, i.e. a Ti(III) center, and a loosely bound chlorine atom. In the case of the rhodium surface complex the excitation is of the rhodium-to-titanium charge-transfer type resulting in a Ti(III) center and a Rh(IV) species.

For the photocatalysts modified by organic sensitizers the situation can be considered as complementary to the inorganic sensitizers. Now the sensitizer is an organic ligand bound by Ti-N



or Ti-O bonds to a titanium surface center. Vis light induced charge separation resembles the mechanism operating in dye-sensitized solar cells.



Excitation within a sensitizer absorption band or a sensitizer-to-titanium charge-transfer band affords Ti(III) and the radical cation of the sensitizer (Eq. 15). Subsequent standard reaction steps produce reactive oxygen species ROS ( $\text{OH}$ ,  $\text{HO}_2$ ,  $^1\text{O}_2$ ,  $\text{H}_2\text{O}_2$ ) and finally induce a complete oxidation of the pollutant D (Eq. 16-20). In this very simplified proposal competitive reaction steps like charge recombination and oxidative degradation of the sensitizer are omitted for the sake of clarity. The latter seems to be of minor importance as indicated by the excellent long term stability of both types of surface-modified titania photocatalysts during the photooxidation of 4-chlorophenol.

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## Titanium Dioxide Photocatalyst. Unresolved Problems

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**Abstract.** The present work considers the performance of TiO<sub>2</sub>-based photosensitive oxide semiconductors as photocatalysts for water purification. This paper brings together the concepts of solid state chemistry for nonstoichiometric compounds and the concepts of photocatalysis in order to discuss the reactivity between TiO<sub>2</sub> and water including microorganisms (bacteria and viruses). The performance of TiO<sub>2</sub> photocatalysts are considered in terms of a model of photoelectrochemical cell. The experimental data on photocatalytic removal of microorganisms from water are considered in terms of the effect of several properties, including pH, dispersion, light intensity, and temperature. It is argued that correct understanding of the performance of TiO<sub>2</sub> photocatalysts requires recognition that properties of TiO<sub>2</sub>, which is a nonstoichiometric compound, are determined by defect disorder and the related ability to donate or accept electrons. The photocatalytic properties of TiO<sub>2</sub> are considered in terms of the reactivity of both anodic and cathodic sites with water and the related charge transfer at the TiO<sub>2</sub>/H<sub>2</sub>O interface. It is shown that the formation of well defined photocatalysts requires knowledge of mass and charge transfer during processing and performance, respectively. The main hurdles in the development of high-performance photocatalysts are discussed.

### Introduction

Access to clean water is essential for mankind to survive. However, the recent development of industry has converted many rivers and lakes into toxic dumps. Water reserves in many areas have been polluted by increasingly intensive release of sewage and industrial wastes. In consequence, water is polluted to the extent that it is unsafe to drink. Therefore, the development of new water purification technologies in an environmentally friendly manner is the matter of increasing importance and urgency. A range of approaches have been applied to decontaminate waste water, including filtration, biological processing and chemical treatment. There have been increasing efforts to develop photocatalysts, which can be used to recycle contaminated water photocatalytically by using solar energy as the only driving force of the process [1–6]. This process allows to decompose toxic contaminants in water (bacteria and toxic organic compounds) into harmless substances (mineralization).

Oxide semiconductors are promising candidates as photocatalysts for water purification due to their low cost and the ability to absorb solar energy [3]. While there have been an accumulation of reports on photocatalysis, at present the research aims to overcome the hurdles required for commercialisation.

The most prominent candidate for high-performance photocatalysts is titanium dioxide,  $\text{TiO}_2$  [4, 7]. Its main advantage over other oxide semiconductors is relatively high reactivity with both light and water as well as organic solutes dissolved in water. At the same time,  $\text{TiO}_2$  exhibits an outstanding resistance to corrosion and photocorrosion in aqueous environments.

The most recent studies indicate that properties of  $\text{TiO}_2$  and its reactivity are closely related to defect disorder and the related semiconducting properties [7]. Therefore, defect engineering may be used for the processing of  $\text{TiO}_2$ -based oxide semiconductors, which exhibit properties that are critical for photoreactivity. These critical properties include electronic structure, charge transport and surface properties [7].

Intensification of research on photocatalysis resulted in an accumulation of a substantial amount of data on the performance of  $\text{TiO}_2$ -based photocatalysts. Platinum, due to its high cost, is unlikely to be the component of commercial photocatalysts. However, many reports on  $\text{TiO}_2$  photocatalysis are still concentrated on the effects of Pt on photocatalytic performance [8–12].

Most of the studies reported in the literature are based on a "trial and error" approach. At the same time, there is no clear strategy for the development of high-performance photocatalysts methodically. Moreover, most of the reported experimental data are not well defined as the studied systems are commonly not reproducible [7]. In other words, the reported photocatalytic systems do not exhibit reproducible properties. Therefore, the data reported by different authors are frequently not compatible and cannot be compared.

So far, little is known about the reactivity of  $\text{TiO}_2$  with water and, specifically, the effect of hydrogen on the properties of  $\text{TiO}_2$ . There is a need to understand the reactivity of hydrogen ions (protons) that is present in water, with  $\text{TiO}_2$  and their effect on surface and bulk properties of  $\text{TiO}_2$ . While it is clear that such effect is substantial, so far little is known in this matter.

The aim of the present work is to present an overview of the main research approaches in the development of  $\text{TiO}_2$ -based photocatalysts for water disinfection (removal of bacteria and viruses). Several unresolved problems will be discussed and the key questions, that need to be addressed, will be formulated.

## Titanium Dioxide Photocatalysis

**Light-induced reactions** The concept of photocatalysis by using semiconductors is based on their ability to absorb light resulting in enhanced reactivity with water and its solutes. A simple model of  $\text{TiO}_2$ -based semiconductors, showing light-induced ionisation over band gap, is shown in Figure 1 [3].

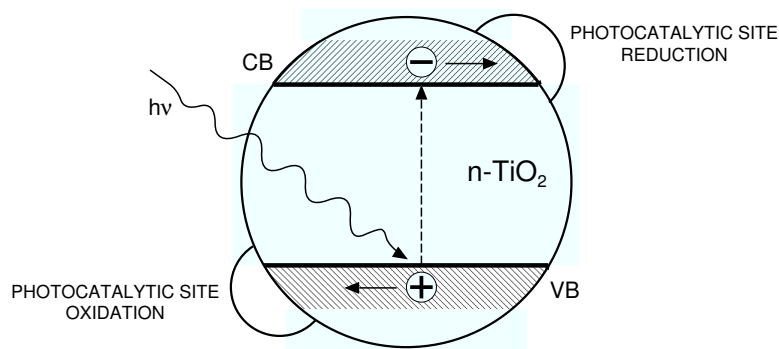


Fig. 1: Model of a  $\text{TiO}_2$  semiconducting photocatalyst.



The space charge, which is formed at the  $\text{TiO}_2$ /water interface, and the related electric fields, lead to the separation of electrons and electron holes that are transferred to cathodic and anodic sites, respectively. This, consequently, results in an increase of the reactivity of these sites. The properties of the sites and selected anodic and cathodic reactions are outlined in Figure 2.

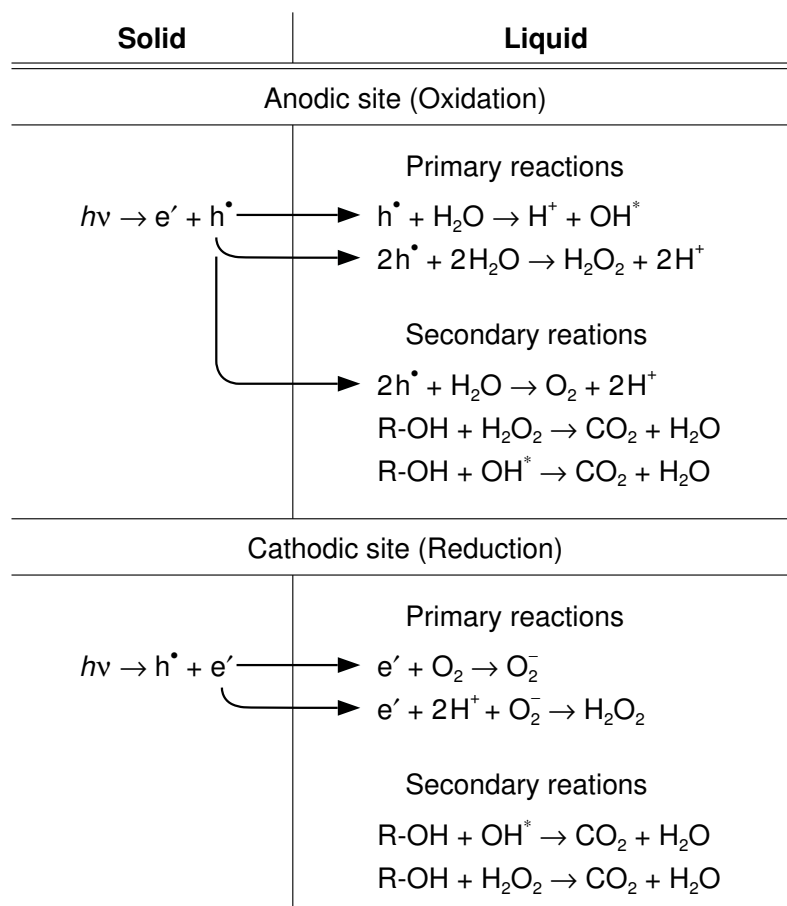


Fig. 2: Light-induced reactions at anodic and cathodic sites for n-type  $\text{TiO}_2$  (R–OH represents organic compounds, such as alkanes, alkenes or alcohols).

Stable performance requires that the amount of the charge transferred during light-induced reactions is identical at both anodic and cathodic sites. At the same time, the charge transfer at the cathodic sites becomes rate determining. Therefore, appropriate engineering is required to increase the reactivity of the cathodic sites.

The effect of light on the semiconducting properties for n-type semiconductors may be represented by the split of the Fermi level into two quasi-Fermi levels related to electrons and holes as represented in Figure 3 [13]. While the light-induced concentrations of electrons and holes are the same, the effect of light on the quasi-Fermi levels related to electrons and holes are different. As seen in Figure 3, the effect of light on the concentration of the minority type charge carriers for n-type  $\text{TiO}_2$  (electron holes) is substantial and, at the same time, the increase of the quasi-Fermi level related to electrons is insignificant.

The light-enhanced reactivity of anodic sites is shown in Figure 4a, where the upward band bending is due to the surface charge at the  $\text{TiO}_2/\text{H}_2\text{O}$  interface. The primary photo-induced reaction at anodic sites is the oxidation of adsorbed water molecules leading to the formation of  $\text{OH}^*$  radicals

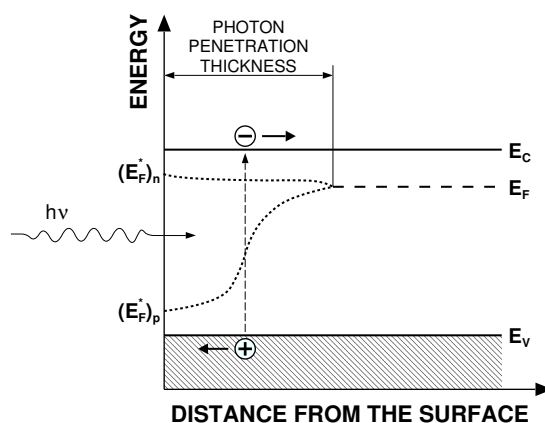


Fig. 3: Representation of light-induced split of the Fermi level,  $E_F$ , into the quasi-levels related to electrons,  $(E_F^*)_n$ , and electron holes,  $(E_F^*)_p$ , for n-type  $\text{TiO}_2$ .

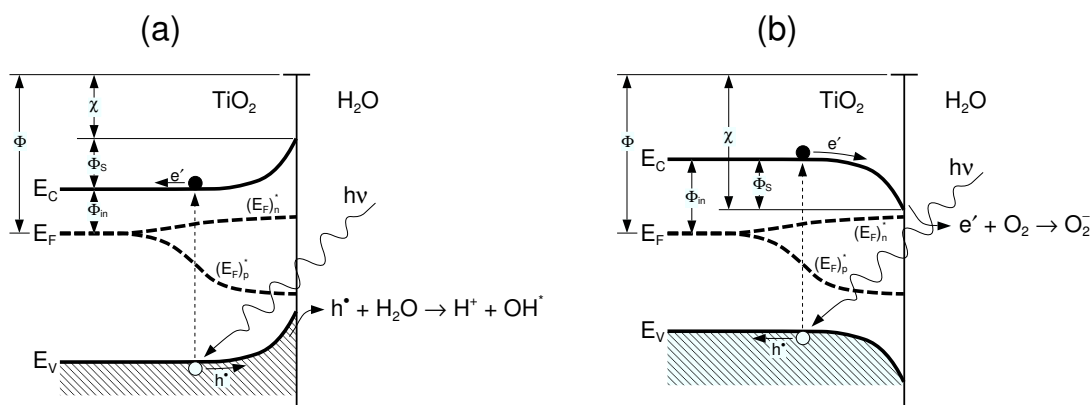


Fig. 4: Photoreactivity of  $\text{TiO}_2$  at the anodic (a) and cathodic (b) sites, along with the related charge separation and charge transfer.

and protons [1–7]. Therefore, the progress of the anodic reactions requires a supply of electron holes. As seen in Figure 3, the light-induced enhancement of the chemical potential of holes results in a substantial increase of the oxidation power (the ability to donate holes or accept electrons) of the anodic sites. The increased concentration of hydroxyl radicals,  $\text{OH}^*$ , results in oxidation of organic compounds [14]. The rate of anodic reactions may be further enhanced by deposition of islets of solids with a low work function, such as  $\text{ReO}_2$ , which have the tendency to enhance the charge transfer [1,3].

The primary photo-induced reaction at cathodic sites is the reduction of molecular oxygen (Figure 4b) [3, 15]. Therefore, the progress of the cathodic reaction is determined by the supply of both oxygen to the surface of  $\text{TiO}_2$  as well as electrons from the solid phase.

*Conclusions. Performance of oxide photocatalysts involves the reactions at both anodic and cathodic active sites. Stable performance requires that the charge transfer at both sides is identical. Therefore, maximization of the performance for n-type semiconductors, such as  $\text{TiO}_2$ , requires that the performance at the cathodic sites is enhanced.*

**Supply of oxygen** Supply of oxygen to the cathodic site is the rate determining step of the cathodic reaction. Therefore, oxygen supply is critical for the performance of the photocatalyst [16].

The amount of oxygen dissolved in water depends on the surface area of the water/gas phase interface and the concentration of oxygen in the gas phase. Consequently, enhanced oxygen dissolution in water may be achieved by passing a gas rich in oxygen through the electrolyte (aeration). The rate of oxygen exchange across the water/gas phase interface may be enhanced by increasing the rate of passing the purge gas and its turbulency. Alternatively, enhanced oxygen supply may be achieved by adding an oxidant to the electrolyte.

*Conclusion. Oxygen supply to the cathodic site is critical for the performance of photocatalysts based on n-type semiconductors, such as n-type  $\text{TiO}_2$ .*

**Deposition of noble metals** A substantial amount of reports have been accumulated on the effect of noble metals, such as platinum, on the performance of  $\text{TiO}_2$  [8–12]. The data on the effect of Pt indicate that the photocatalytic activity is sensitive to the dispersion of Pt on the surface and the related ratio of the Pt/ $\text{TiO}_2$  areas.

Sakhvitol et al. [12] reported the effect of the irradiation time on the extent of the rate of photocatalytic oxidation of dichloroacetic acid at different Pt content (the studies also included Au and Pd). The data reported by Sakhvitol et al., in terms of normalised concentration, are shown in Figure 5.

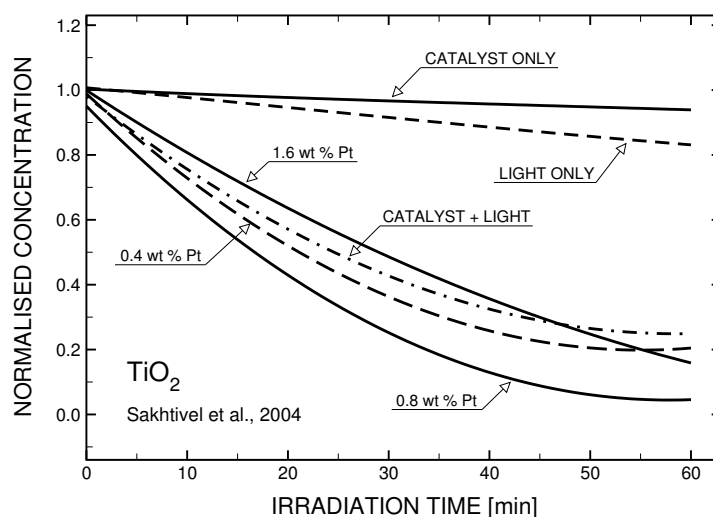


Fig. 5: Effect of irradiation on photocatalytic degradation of acid green 16 (leather dye) in terms of normalised concentration versus time for  $\text{TiO}_2$  decorated with platinum islets, according to Sakhvitol et al. [12].

The effect of Pt on photocatalytic properties is represented in Figure 6 showing that Pt-activated  $\text{TiO}_2$  catalysts exhibit an optimum of performance. This optimum depends on the rates of the respective electrode reactions and their surface areas:

$$k_A S_A = k_C S_C \quad (1)$$

where  $k_A$  and  $k_C$  are the rates of the anodic and cathodic reactions, respectively, expressed in the amount of the photodecomposed compound per time unit, and  $S_A$  and  $S_C$  are the respective surface areas. The optimum is expected to be dependent on the photoactivity of the individual phases forming the photocatalyst and the nature of the organic compounds to be decomposed.

*Conclusions. While the effect of noble metals on photocatalytic performance of  $\text{TiO}_2$  is relatively well established, these metals are unlikely to be the components of commercial photocatalysts due to their costs.*

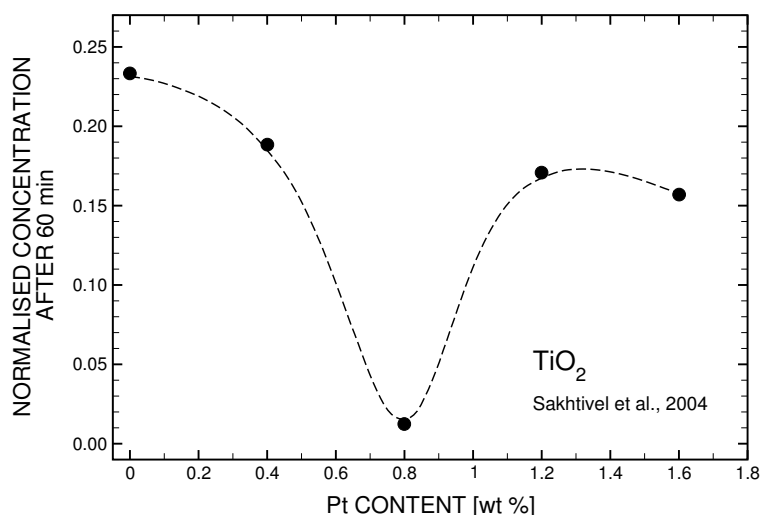


Fig. 6: Effect of platinum content on photocatalytic degradation of acid green 16 (leather dye) according to Sakhtivel et al. [12].

**Doping with aliovalent ions** The main strategy of research on the development of  $\text{TiO}_2$  photocatalysts with enhanced performance is to reduce their band gap through incorporation of aliovalent ions [17–21]. The aim of band gap reduction is to increase the amount of the solar energy that can be absorbed [3, 7, 18]. These studies include doping with anions, like nitrogen, fluorine and carbon, as well as a wide range of cations. While the cathodic performance may be enhanced by oxygen supply and deposition of noble metals, the incorporation of aliovalent ions leading to band gap reduction results in enhanced light absorption and, therefore, enhanced performance of both sites.

Liu et al. [20] reported that doping  $\text{TiO}_2$  with nitrogen leads to enhanced photocatalytic activity in inactivation of *E. coli* bacteria and decolorisation of acid orange. Their studies on N-doped  $\text{TiO}_2$  (>20 at% N) were compared to that of Degussa P25. They assumed that nitrogen doping is limited to the surface layer. The observed enhancement in inactivation of the *E. coli* bacteria is shown in Figure 7. The result is considered in terms of the effect of nitrogen on the reduction of band gap and increased light absorption (Figure 8). Similar effect was observed by Nakamura et al. [19]. Kim and Choi [21] reported the effect of F-doping on photocatalytic oxidation of acetaldehyde (Figure 9). These data indicate that the incorporation of fluorine into  $\text{TiO}_2$  results in reduction of the band gap.

Doping of  $\text{TiO}_2$  with aliovalent ions is expected to be the major research strategy in the development of high-performance photocatalysts. However, there is an urgent need to recognise that reproducible systems may only be achieved when the processing procedure is well defined. The formation of well defined (reproducible) systems requires knowledge of propagation kinetics of dopants. It is important to realise that doping with aliovalent ions results in changes in a range of performance-related properties, including band gap, charge transport, flat band potential and surface properties. While all these properties, which are interrelated, have an effect on photocatalytic activity, their individual contributions are different.

*Conclusions. Doping with aliovalent ions is a promising way to increase photocatalytic activity of  $\text{TiO}_2$ . However, doping procedures must be well defined in order to ensure that all related properties are modified in a controlled manner.*

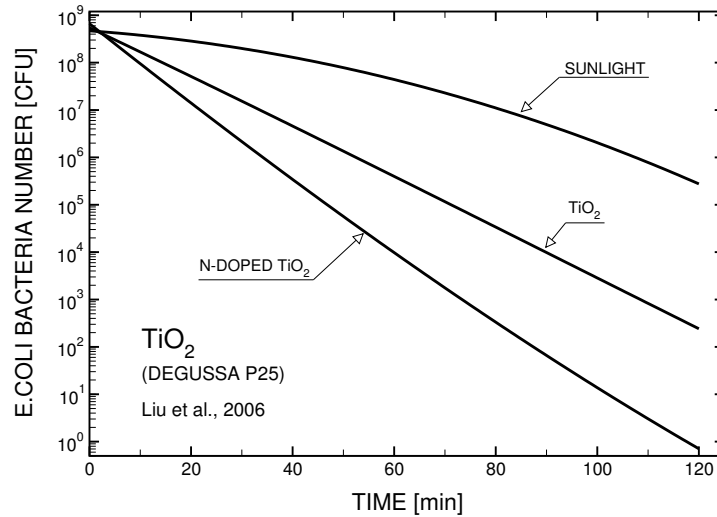


Fig. 7: The kinetics of E.coli bacteria disinfection for undoped and nitrogen-doped  $\text{TiO}_2$  according to Liu et al. [20].

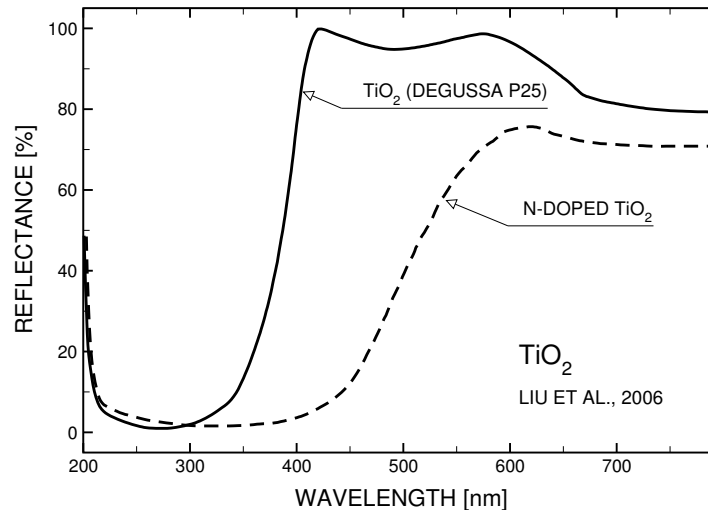


Fig. 8: Reflectance spectra for undoped and nitrogen-doped  $\text{TiO}_2$  according to Liu et al. [20].

### Water Disinfection by $\text{TiO}_2$ Photocatalyst

The aim of the present section is to discuss the research strategy on water disinfection by  $\text{TiO}_2$  photocatalysts, including the effect of the processing conditions on water purification.

There is general agreement that  $\text{TiO}_2$  is the best candidate for high-performance photocatalysts for the removal of toxic organic compounds from water and water disinfection (removal of microorganisms, such as bacteria and viruses). There is an increasing number of papers reporting the effect of several properties on photocatalytic performance of  $\text{TiO}_2$ . These include (i) acidity/alkalinity and the related pH [22–26], (ii) dispersion and the surface area [14, 27–30], (iii) light intensity and light energy [23, 24, 31–34], and (iv) temperature [23].

Alhakimi et al. [22] reported that maximum degradation of potassium hydrogen phthalate was observed at  $\text{pH} < 5$  (Figure 10). The effect of pH on photocatalytic performance may be considered

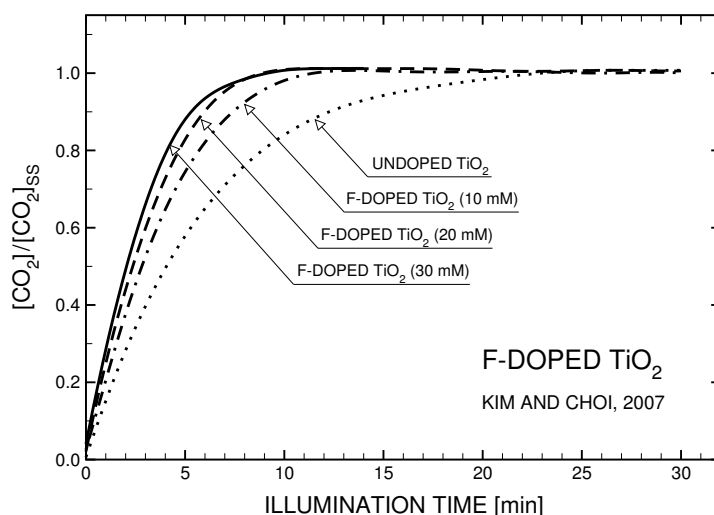


Fig. 9: Effect of fluorine doping on photodegradation of acetaldehyde by  $\text{TiO}_2$  thin films (normalised scale) according to Kim and Choi [21].

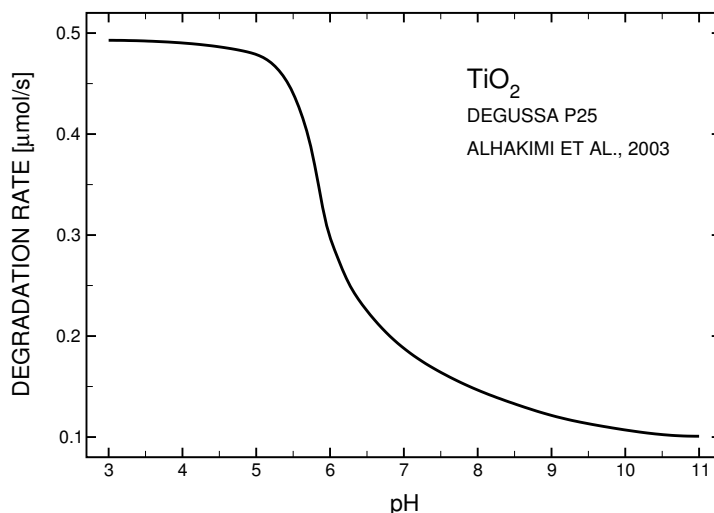
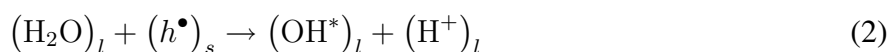


Fig. 10: Effect of pH on photodegradation of potassium phthalate on  $\text{TiO}_2$  according to Alhakimi et al. [22].

in terms of photocatalyst's dispersion and the related area of the water/ $\text{TiO}_2$  interface.

According to Galvez [27] the  $\text{TiO}_2$  particles aggregate at  $\text{pH} = 6.9$ , forming large clusters, which sediment quickly (Figure 11). This effect, however, is not consistent with the data reported by Alhakimi [22]. Consequently, there is a need to better understand the effect of pH on photocatalytic performance, which appear to be related to the effect of hydrogen on properties of  $\text{TiO}_2$ .

A step forward in this direction has been made by Rincon and Pulgarin [24]. They reported the photocatalytic inactivation of *E. coli* bacteria by  $\text{TiO}_2$ . They observed that the light-induced disinactivation process is accompanied by decrease of pH from 7 to about 4 (Figure 12). This effect was considered in terms of the light-induced water decomposition:



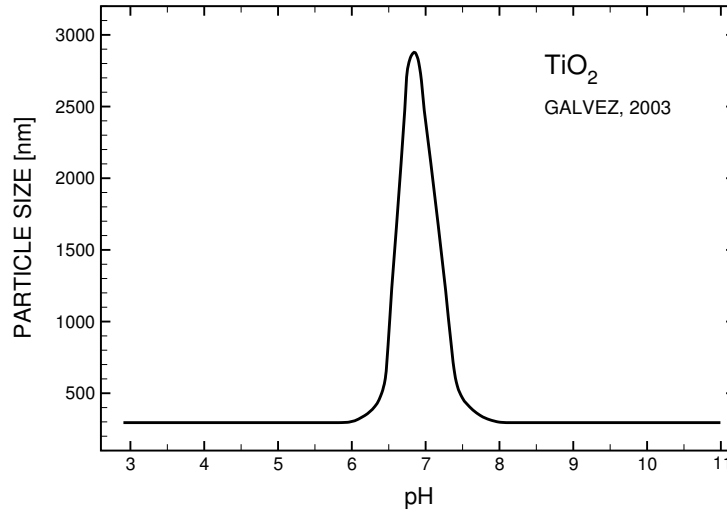


Fig. 11: Effect of pH on the mean particle size of  $\text{TiO}_2$  suspended in water according to Galvez [27].

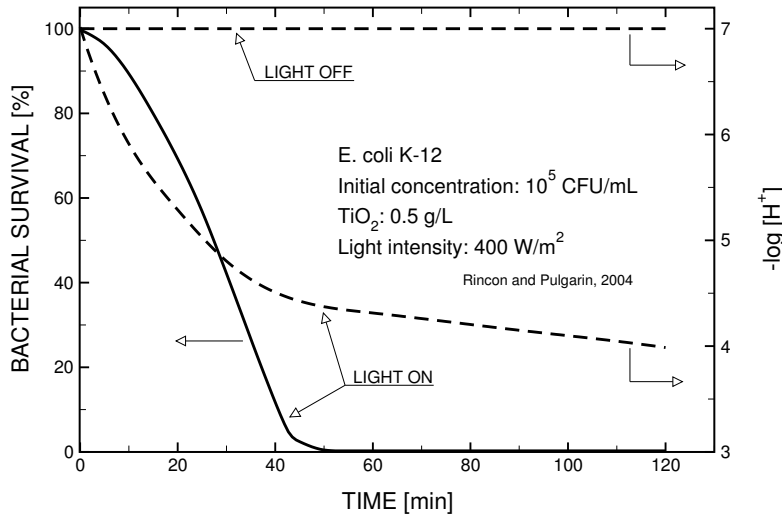
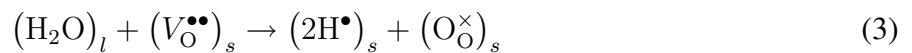
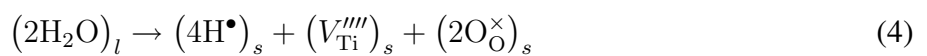


Fig. 12: Effect of light on water disinfection from *E. coli* bacteria for  $\text{TiO}_2$  photocatalyst, and the accompanying change of pH according to Rincon and Pulgarin [24].

Alternative explanation is the formation of protons as a result of the reactivity between water and  $\text{TiO}_2$ , represented by the following reaction:



where protons in the  $\text{TiO}_2$  lattice are associated with lattice oxygen. Hydrogen incorporation may also lead to the formation of negatively charged titanium vacancies:



In reactions (2)–(4) subscripts  $l$  and  $s$  denote the liquid and solid phases, respectively. Assuming that protons incorporate into the lattice of n-type  $\text{TiO}_2$  in dark conditions (when the predominant electronic charge carriers are electrons) the effect of light results in the formation of electron holes,

which then become the predominant electronic charge carriers within the light penetration distance. Subsequently, the reaction (3) is shifted leftwards leading to the removal of protons from the lattice, what leads to the decrease of pH (Figure 12).

Increased dispersion of particles results in an increase in the catalytically active surface area. At the same time, however, the increase in dispersion results in a decrease of light penetration through the suspension. Kim et al. [28] observed that an optimum of disinfection from some food pathogenic bacteria is at 1 mg/mL for  $\text{TiO}_2$  of the surface area  $2.95 \text{ m}^2/\text{g}$ . Saito et al. [29] reported similar findings.

The increase of light intensity leads to an increased rate of killing bacteria. According to Wei et al. [31] the cell's killing rate increases proportionately with an increase in incident light intensity from 180 to  $1660 \mu\text{Es}^{-1}\text{m}^{-2}$ . It is essential to note, however, that quantitative assessment must take into account the intensity of the light at the photocatalyst surface rather than at the light source. The difference between the two may be substantial as the light intensity at the liquid/solid interface is reduced due to light dispersion by the suspension. Rincon and Pulgarin [34] reported that in the presence of  $\text{TiO}_2$  the process of disinfection continues for some time even in the dark, after the light was switched off.

The part of solar energy spectrum with photon energy smaller than that of the band gap is converted into heat, if absorbed. This leads to temperature increase in the reactor. Rincon and Pulgarin [23] reported a significant enhancement of water disinfection (removal of coliform bacteria) when the temperature increases. The reaction time required to achieve 100% inactivation of *E. coli* for 0.5 g/L of  $\text{TiO}_2$  (anatase,  $50 \text{ m}^2/\text{g}$ ) was 120 and 35 min. at  $23^\circ \text{C}$  and  $45^\circ \text{C}$ , respectively.

### Data Compatibility

The data reported by different authors may be compared only when these data are well defined in terms of the quantities that have an effect on photocatalytic properties, such as:

1. Structure, microstructure (nanostructure) and the related surface area
2. Nonstoichiometry and the related defect disorder
3. Chemical composition and related concentration gradients
4. Impurity level
5. Light source, light intensity and its spectrum
6. Liquid phase composition, temperature, pH

**Structure and microstructure** Studies are reported mainly for commercial specimens, such as Degussa P25, which is a mixture of both rutile and anatase phases. However, there is a wide range of other commercial titania products on the market, including Millennium PC 500, Hombikat UV 100, and Kerr-McGee, which differ in terms of grain size and phase composition.

While structure and microstructure are essential properties of solids in general, the performance of photocatalysts is determined by their electronic structure and surface properties rather than their crystalline structure [7].



**Nonstoichiometry** Titanium dioxide is a nonstoichiometric compound [35]. Its nonstoichiometry may be considered in terms of the presence of point defects, including oxygen vacancies, titanium vacancies and titanium interstitials, which exhibit a wide range of valencies [7]. The concentration of these defects depends on oxygen activity in the lattice as well as the concentration of impurities and the concentration of dopants. It has been shown that annealing of  $\text{TiO}_2$  in extremely reduced conditions leads to the imposition of n-type semiconducting properties, while the imposition of high oxygen activity results in insulating or p-type properties [7]. The studies on semiconducting properties indicate that oxygen nonstoichiometry of  $\text{TiO}_2$ , and the related defect disorder, have a strong impact on its properties and reactivity.

**Chemical composition and related concentration gradients** The most frequently applied procedure to change photocatalytic properties is to change chemical composition by the incorporation of aliovalent ions (doping). The doping procedure usually consists of annealing of co-precipitated mixtures of oxides, including  $\text{TiO}_2$  and oxide phases of dopants. The annealing takes place at elevated temperatures that allow the incorporation of the dopant ions into the host lattice. However, selection of the time and the temperature required for the formation of either homogeneous solid solution or desired concentration gradients requires knowledge of the diffusion rates of the species involved. Frequently reported doping procedures fail to recognise that homogeneous distribution of some ions within the  $\text{TiO}_2$  at elevated temperatures may require weeks rather than hours. If the annealing time is not sufficiently long, the doping process may lead to the imposition of ill defined concentration gradients within specimens or the formation of heterogeneous systems. Efficient distribution of dopants may also be achieved by sol-gel techniques. It is important to note that the effect of doping on properties depends on oxygen activity [7].

**Impurity level** The properties of photocatalysts are usually assessed in terms of their basic chemical composition. At the same time, most of reports fail to recognise the effect of impurities (unintentional dopants) on properties. However, the effect of impurities, especially of aliovalent ions, on semiconducting properties may be substantial even at the level of several parts per million [36].

**Light source and light intensity** Light sources exhibit a wide range of spectral distribution, which are different from that of sunlight. Therefore, the data can be compared only for the same light source and the same light intensity. Such assessment may be difficult for dispersed systems, which affect the transport of light from the light source to the surface of the photocatalyst.

## Hurdles to Commercialisation

While several reports indicate that water disinfection by  $\text{TiO}_2$  leads to complete removal of bacteria [31, 34], the performance of  $\text{TiO}_2$ -based photocatalysts is still below the level required for commercialisation. The progress of research in this area requires more empirical data, which are well defined and can be used for derivation of theoretical models describing the effect of light on photocatalytic reactions. These models may then be used to establish correlations between different properties and photocatalytic performance. There is also an increasing need to establish standards that may be used to compare photocatalytic activities of different systems. While such standards are not available yet, there have been efforts to propose such standards under auspices of the International Organisation for Standardisation [37]. While  $\text{TiO}_2$  of Degussa (P25) in many cases is considered as such standard, its processing conditions and the related oxygen activity, are unknown.

The most frequently studied properties include the band gap, which has a critical effect on light absorption, and charge separation. It is essential to recognise, however, that performance is also af-

fectured by the energy losses related to charge transport, and surface properties. Consequently, high-performance photocatalysis may be achieved through the optimisation of the entire system (maximised light absorption and minimised energy losses).

It has been shown that all performance-related properties are closely related to nonstoichiometry and the related defect disorder [7]. Therefore, the photocatalytic systems may be optimised by using defect engineering, which allows to achieve the desired properties by imposition of controlled defect disorder.

An important issue in the development of commercial photocatalytic systems for water purification is the understanding of the effect of hydrogen ions (protons) on catalytic activity. So far, these ions have been considered in terms of reactions in the aqueous electrolyte. Recent studies indicate, however, that hydrogen also reacts with the  $\text{TiO}_2$  lattice leading to changes in its composition, defect disorder, and reactivity [38].

In summary, there is an urgent need to answer the following questions:

- How to process photocatalysts that are well defined and reproducible?
- Which are the specific performance-related properties of  $\text{TiO}_2$ -based oxide semiconductors?
- What are the relationships between the performance-related properties and nonstoichiometry of  $\text{TiO}_2$ ?
- How can the performance-related properties be optimised in order to achieve maximised activity?
- What is the reactivity mechanism of water with the  $\text{TiO}_2$  surface and its lattice?

## Conclusions

While there is a large body of evidence that water may be purified by solar energy, there is an increasingly urgent need to bring this technology to commercial maturity. Intensive studies aim to develop such technology, and awareness is growing that progress in this area requires to combine the concepts of several scientific disciplines and engineering, including photocatalysis, photoelectrochemistry, solid state chemistry, surface science and microbiology.

The present work considers photocatalytic removal of microorganisms from water in terms of specific effects of several properties, including pH, dispersion, light intensity, temperature, on photocatalytic performance. The analysis of the experimental data reported so far, indicate that the development of high-performance photocatalysts requires the optimisation of the properties, which are directly related to performance, such as charge transport, surface properties and near-surface properties.

## Acknowledgments

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## Tayloring the Photocatalytical Activity of Anatase TiO<sub>2</sub> thin Film Electrodes by three-dimensional Mesoporosity

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**Keywords:** sol-gel processes, self-assembly, mesoporous materials, photocatalysis, 3D-structured photoelectrodes, light induced water-splitting

**Abstract.** Mesoporous titanium dioxide (m-TiO<sub>2</sub>) thin film electrodes were synthesized by evaporation-induced self-assembly (EISA), utilizing a novel type of amphiphilic block copolymer as template. The ordered network of pores shows an accessible inner volume that results in a huge BET-surface and a distinct transparency. According to X-ray diffraction analyses the mesoporous films are highly crystalline after calcination at 550°C. 1D and 2D small-angle X-ray scattering and transmission electron microscopy investigations prove the high quality of the mesopore texture over micrometer-sized areas. These well-defined, crystalline m-TiO<sub>2</sub> films show an increased photoactivity for overall water splitting and oxidation of formic acid as compared to porous films prepared in the same manner without a template. The performance of the electrodes was analyzed by measuring the photocurrent and the mass signal of liberated gas by electrochemical mass spectroscopy (EMS). These experiments reveal that film morphology have a great influence to the I-V characteristic of photoelectrodes. An appropriate crystallization temperature is indispensable to obtain an optimum between crystallinity, morphology and photoactivity and to prevent collapse of the mesopore architecture.

### Nomenclature.

|               |                                                                         |
|---------------|-------------------------------------------------------------------------|
| $\alpha$      | - absorption coefficient                                                |
| $\beta$       | - angle of incidence                                                    |
| $\Delta$      | - typically used to explain the difference between start- and end-value |
| $\epsilon$    | - permittivity of the medium xy                                         |
| $\epsilon_0$  | - permittivity of free space                                            |
| $\theta$      | - Scattering angle (XRD)                                                |
| $\lambda$     | - wave length                                                           |
| $\mu_e$       | - mobility of electrons                                                 |
| $\mu\text{m}$ | - micrometer                                                            |
| $\mu_p$       | - mobility of defect electrons (holes)                                  |
| $\nu$         | - frequency                                                             |
| $\Omega$      | - resistivity (Ohm)                                                     |
| APCE          | - absorbed photon to current exchange efficiency                        |

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|                                   |                                                                   |
|-----------------------------------|-------------------------------------------------------------------|
| bcc                               | - body centered cubic                                             |
| BET                               | - Brunauer-Emmet-Teller analysis method                           |
| BJH                               | - Barret-Joiner-Halenda analysis method                           |
| °C                                | - grad celsius                                                    |
| cm                                | - centimeter                                                      |
| cps                               | - counts per second                                               |
| D                                 | - diffusion coefficient                                           |
| E                                 | - energy                                                          |
| $E_{\text{Rev}}^0$                | - standard redox potential of the water-splitting reaction        |
| EISA                              | - evaporation induced self assembling                             |
| $E_{\text{Measure}}$              | - potential applied to the photoelectrode                         |
| EMS                               | - electrochemical mass spectroscopy                               |
| $E_{\text{OC}}$                   | - open circuit/ maximum photovoltage of the photoelectrode        |
| eV                                | - electron volt                                                   |
| $f_s$                             | - exponential fit-factor of surface recombination                 |
| g                                 | - gramm                                                           |
| $g_{\text{Cat}}$                  | - gramm of catalyst                                               |
| h                                 | - Planck constant                                                 |
| I                                 | - light intensity                                                 |
| $I_0$                             | - initial light intensity                                         |
| $I_{\text{light}}$                | - amount of absorbed light                                        |
| $I_{\text{ph}}$                   | - photo current                                                   |
| $I_s$                             | - current of charge carrier to the surface                        |
| $I_{\text{SR}}$                   | - surface recombination current                                   |
| I-V                               | - current-voltage curve                                           |
| $j_{\text{ph}}, j_{\text{photo}}$ | - photocurrent density                                            |
| k                                 | - Boltzman constant                                               |
| $k_T$                             | - charge transfer rate constant                                   |
| kV                                | - kilo volt                                                       |
| L                                 | - diffusion length of charge carrier                              |
| $L_D$                             | - Debye lenght                                                    |
| m                                 | - meter                                                           |
| mA                                | - milli ampere                                                    |
| mV                                | - milli volt                                                      |
| m/z                               | - molar mass – charge ratio (mass spectroscopy)                   |
| NHE                               | - normal hydrogen electrode                                       |
| nm                                | - nanometer                                                       |
| PEC                               | - photoelectrochemical cell                                       |
| $p_s$                             | - surface concentration of photogenerated minority charge carrier |
| q                                 | - charge                                                          |
| s                                 | - second                                                          |
| $s_R$                             | - surface recombination velocity                                  |
| SAXS                              | - small angle X-Ray scattering                                    |
| SEM                               | - secondary electron microscopy                                   |
| T                                 | - temperature                                                     |
| U                                 | - potential                                                       |
| $U_{\text{fB}}$                   | - flat band potential                                             |
| V                                 | - Volt                                                            |
| $V_{\text{OC}}$                   | - open circuit voltage, maximal photovoltage                      |
| W                                 | - depletion zone width                                            |
| W                                 | - Watt                                                            |

WAXS- wide angle X-ray scattering

XRD - X-ray diffraction

∞ - endless

## 1. Introduction

For tomorrow's society it is of major interest to extend the use of solar energy based processes to accomplish a more sustainable use of resources and energy. Thereby, photocatalysis and photoelectrochemical cells (PEC) can contribute significantly to that strategy [1-3]. The application of titanium dioxide ( $\text{TiO}_2$ ) as a photocatalyst for solar selfcleaning surfaces is one example of a more sustainable use of resources. Since the discovery of photocatalytic splitting of water on  $\text{TiO}_2$  electrodes by Honda und Fujishima [4], this material has been extensively studied for photocatalytic applications [5-7]. It benefits from high corrosion stability, a high oxidation-potential and from an inexpensive availability. Potent applications are solar self cleaning of surfaces, solar driven water- or gas-purification and its use for anti-fogging and anti-bacterial films [8-10]. An additional application may be the use of thermodynamically stable and semi-conducting  $\text{TiO}_2$  films as a matrix for water splitting catalysts.

Because the overall functionality and efficiency of a catalyst depends strongly on its surface and interface properties, nanotechnology is an effective tool to vary and optimize the types of precondition in a molecular scale [11]. In general, catalysis of chemical or photochemical reactions demand large surfaces to yield high turnover-rates of reagents. Yet, in the case of photocatalysis, a more precise point of view is necessary. Morphology of the photocatalyst influences not only the pathway and distribution of incoming light, but also the charge carrier generation rate inside the film, the range of the external applied electrical field, the extension of the particle's depletion zone and the amount of photogenerated charge carriers that are able to reach the particle's surface within their lifetime will be affected [12]. The advantage of an ordered, highly porous three-dimensional photoelectrode structure would therefore be: (1) an increase in active surface area, (2) good connectivity of the constituting  $\text{TiO}_2$  nanocrystals, (3) an improvement of educt/product transport capabilities, together with a (4) better penetration of light into deep bulk layers. In addition, with the right nanotechnology technique, the pore size could be designed to fit well to the semiconductors character, like specific charge carrier diffusion length and charge carrier lifetime. Although the generation of well-defined mesoporosity within a crystalline matrix was frequently postulated as prerequisite for an optimum performance, there is surprisingly only a small number of studies on the photocatalytic activity of such materials.

Several methods have been established to structure  $\text{TiO}_2$  films on a nanometer-scale. The most common ones are template based methods, in that the metal-oxide precursor hydrolyzes in presence of structure forming agents [13-18]. Other strategies for structuring photoelectrodes are electrochemically etching of titanium metal sheets [19] and the adsorptively crystallization of  $\text{TiO}_2$  on already structured architectures, like those of carbon or Mordenite [20]. The electrodes investigated in this article were prepared by the EISA process (evaporation induced self assembling), which belongs to the template based methods. Here, the formation of structure providing micells and the hydrolysis of the titanium based precursor occur simultaneously during the dipcoating process [21], while the final crystallization of the titaniumoxide is induced in a subsequent heat-treatment step over  $600^\circ\text{C}$ . The body centered cubic pore structure (bcc) solidifies after an appropriate annealing. Due to the mesoporosity, the BET-surface of such m- $\text{TiO}_2$  films increase to quantities about  $200 \text{ m}^2/\text{g}$  [18], what is 2.5 times higher than for undeposited  $\text{TiO}_2$ -P25 powder for example. A main hurdle towards such highly structured materials is the untimely collapse of the mesostructure, often caused by too fast annealing and crystallization of  $\text{TiO}_2$  and also affected by the type of template chosen, like Pluronic based polymers for instance. As recently demonstrated, the use of special block copolymers, like KLE-22, prolongates its existence to annealing temperatures that enable the formation highly crystalline films [18].

The present study demonstrates the improved photocatalytic activity of these well-defined, ordered, and highly mesoporous  $\text{TiO}_2$  film electrodes compared to their low porous counterparts with non-organized porosity.

For this reason, two series of photoelectrodes were prepared and analyzed by measuring the current-voltage characteristics and the gas evolution ( $\text{O}_2/\text{CO}_2$ ) for the water-splitting reaction and the photooxidation of formic acid respectively. In series 1, the electrodes differ in structure and crystallinity (table 1). The electrode with the long range 3-dimensional (3-D) network of pores is called Ti-1(b), and the electrode prepared in the same way but without using the structure-giving template is named as Ti-2. Electrode Ti-3 was prepared with the same template used for processing the Ti-1(b)-photoelectrode, but the final annealing temperature was kept below  $300^\circ\text{C}$  to prevent a complete crystallization.

**Table 1:** Classification and preparation conditions of electrodes investigated in this article.

| Series | Sample name | Template | Annealing/<br>( $^\circ\text{C}$ ) | Morphology                       |
|--------|-------------|----------|------------------------------------|----------------------------------|
| 1      | Ti 1(b)     | yes      | 650                                | mesoporous + crystalline         |
|        | Ti 2        | no       | 650                                | nonregular-porous + crystalline  |
|        | Ti 3        | yes      | <300                               | mesoporous + amorph              |
| 2      | Ti 1a       | yes      | 600                                | mesoporous + crystalline         |
|        | Ti 1b       | yes      | 650                                | mesoporous + crystalline         |
|        | Ti 1c       | yes      | 700                                | partial mesoporous + crystalline |

In series 2, the photoelectrodes differ in morphology only. The relation of crystal growth and crystallization grade to the film morphology and the photoelectrochemical properties were investigated relative to different annealing temperatures – Ti-1a:  $600^\circ\text{C}$ ; Ti-1b:  $650^\circ\text{C}$ ; Ti-1c:  $700^\circ\text{C}$ .

All experimental results, including a calculation of absorbed photon to current conversion efficiency (APCE) plus a time- and mass-related formic acid decomposition rate are described in chapter 3.1 to 3.4. In chapter 4.1 to 4.3, an overview of  $\text{TiO}_2$  specific surface reactions and a model to predict I-V curves theoretically is given and discussed. The conclusions made from the experiments and the I-V-modelling in chapter 5 complete this article.

## 2. Experimental Section

The diblock copolymer  $(\text{CH}_2\text{CH}_2\text{CH}_2(\text{CH})\text{CH}_2\text{CH}_3)_{89}(\text{OCH}_2\text{CH}_2)_{79}\text{OH}$ , “KLE22”) used in this study was synthesized at the Max-Planck-Institute Golm/Potsdam in the department colloids and interfaces. Details in the synthetic procedure is shown elsewhere [18, 22]. All other chemicals were purchased from ALDRICH and used as received without further purification.

*Synthesis of mesoporous  $\text{TiO}_2$  films:* To 600 mg titanium tetrachloride ( $\text{TiCl}_4$ ) in 3 ml ethanol (EtOH), 500 mg of water ( $\text{H}_2\text{O}$ ) was added. After 24 h, 100 mg “KLE22” dissolved in 3 ml EtOH was added to the sol. Thin films were prepared by dip-coating arbitrary, flat substrates (silicon wafer, ITO/FTO-covered glass etc.) at constant withdrawal rate ( $6 \text{ mm s}^{-1}$ ) and constant relative humidity (20 %). After dip-coating, the films were transferred into an oven and treated successively at  $100^\circ\text{C}$ ,  $200^\circ\text{C}$  and  $300^\circ\text{C}$  for 12 hours to solidify and dehydrate the mesostructured  $\text{TiO}_2$  network. Transformation of the thitherto amorphous framework into polycrystalline mesoporous anatase was achieved by a subsequent annealing by using a heating-up ramp of  $5^\circ\text{C min}^{-1}$  in air.

*Analytical methods:* 1D-SAXS and WAXS measurements were performed in symmetric reflection using a D8 diffractometer from Bruker instruments ( $\text{Cu-K}_\alpha$  radiation,  $\lambda = 0.154 \text{ nm}$ ). 2D-



SAXS measurements were carried out using a Nonius rotating anode setup (Cu-K $\alpha$  radiation) featuring a 3-pinhole collimation system and a MAR CCD area detector with a sample-detector distance of 750 mm. Ultrathin silicon wafers (thickness 40 micrometer) were covered with a mesoporous TiO $_2$  thin layer and used for these measurements. TEM images were taken with a Zeiss EM 912 $\Omega$  at an acceleration voltage of 120 kV. Samples were ground in a ball mill and taken up with acetone. One droplet of the suspension was applied to a 400 mesh carbon-coated gold grid and left to dry. Surface morphology of films was studied by SEM using a LEO440 instrument equipped with an In-Lens detector (acceleration voltage: 2.0 kV). Current voltage measurements were done in a three electrode compartment, which was connected to a quadrupole mass spectrometer (Balzers, QMI 420). A platinum wire and a mercury sulfate reference electrode (+0.630 V vs. NHE) was used as counter and reference electrode, respectively. All potentials are given versus the natural hydrogen electrode (NHE). Throughout the measurements, the electrolyte (0.5M H $_2$ SO $_4$  or 0.5M H $_2$ SO $_4$  + 0.5M formic acid) was purged with nitrogen. Illumination took place from the electrode backside with a 150W Xe-arc lamp (full range 0.7 Wcm $^{-2}$ ). Thereby, the light absorption of each electrode was measured with a Power/Energy meter (Melles Griot 13 PEM 001).

### 3. Results

#### 3.1. Mesoscale structure and chemical composition

The mesoporous TiO $_2$  films were prepared using the mentioned EISA process according to a recent study [18]. Compared to this previous study, the now modified recipe generated an even better mesostructural order, especially upon crystallization of TiO $_2$  into the anatase phase. Aside from a slightly different concentration of the block copolymer, the main difference was an optimized temperature ramp. SAXS measurements were carried out using two different setups. In order to verify that the films used for the photocatalytic studies were indeed well-structured and in order to characterize the mesostructure, a rotating anode setup was equipped with a 2D detector and a suitable sample holder specially constructed for thin films. As described above, with such a SAXS laboratory setup thin films (prepared on ultrathin Si wafers) can be well characterized, particularly because a specially designed sample holder allowed measurements under different angles  $\beta$  of incidence between the x-ray beam and the film surface. Such 2D SAXS patterns (Fig. 1,  $\beta$  ca. 7.5°) showed well-defined interference maxima, which could be assigned to a deformed BCC structure of mesopores in [110] orientation with respect to the substrate. The SAXS pattern indicated significant unidirectional shrinkage of the mesostructure normal to the substrate (in z-direction) between 450°C and 600°C compared to an ideal BCC structure of spherical mesopores due to the stresses upon evaporation of the solvent, crosslinking and rearrangement of oxo-titanate species during heat-treatment. An isotropic ring was observed in 2D SAXS measurements in transmission mode ( $\beta$  = 90°), revealing that the films consisted of domains being randomly oriented to each other parallel to the substrate. Measurements in symmetric reflection ( $\theta$ -2 $\theta$ -scans) were performed using a 1D-detector, thus providing scans in z-direction (Fig. 1). These curves showed two pronounced equidistant interference maxima, being attributable to the (110) and (220) reflections. Heat-treatment resulted in a shift in the positions, being in conformity with the shrinkage observed from 2D SAXS measurements. In conclusion, the deformed mesostructure was characterized by an in-plane lattice parameter of approximately 19 nm and a repeat unit in z-direction of  $d_{110}$  = 8 nm at 550°C, corresponding to a shrinkage of over 50%. The SAXS study confirmed that the mesostructure was still well-defined and intact even after the onset of crystallization within the pore walls. Compared to our previous study, the mesostructure showed higher mesostructural order at high annealing temperatures, which we attribute to the different heating procedure: In the present case, various subsequent heat treatment steps (at 100°C, 200°C and prolonged heating at 300°C) kept the mesostructure up to high temperatures prior to the start of crystallization at ca. 500°C. As

shown in a case study on  $\text{HfO}_2$ , the mesostructure can only be maintained upon crystallization, if a highly condensed, water-free amorphous oxidic matrix is created first, which is then converted into the crystallization form upon further heating. The mesostructure collapsed at temperatures above  $700^\circ\text{C}$ .

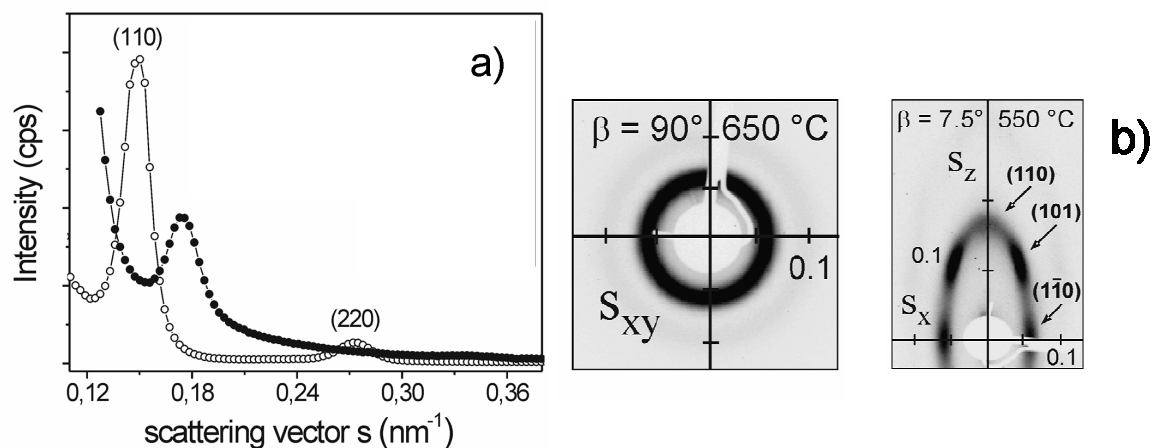


**Fig. 1:** SAXS analysis of  $\text{TiO}_2$  mesoporous ordered networks after different steps of the heat-treatment. 1D-SAXS patterns of a thin film calcined at  $300^\circ\text{C}$  (hollow circles) and  $550^\circ\text{C}$  (filled circles), respectively. The scattering curves are slightly shifted by a scaling factor for better visualization. Insets: 2D-SAXS patterns of a  $\text{TiO}_2$  thin film after crystallization, taken with a laboratory rotating anode at an angle of incidence  $\beta = 7.5^\circ$  and  $90^\circ$ , respectively (scattering vector  $s$  components in  $\text{nm}^{-1}$ ). The presence of second order reflections underlines the high degree of mesopore ordering after crystallization of the  $\text{TiO}_2$  framework at elevated temperatures.

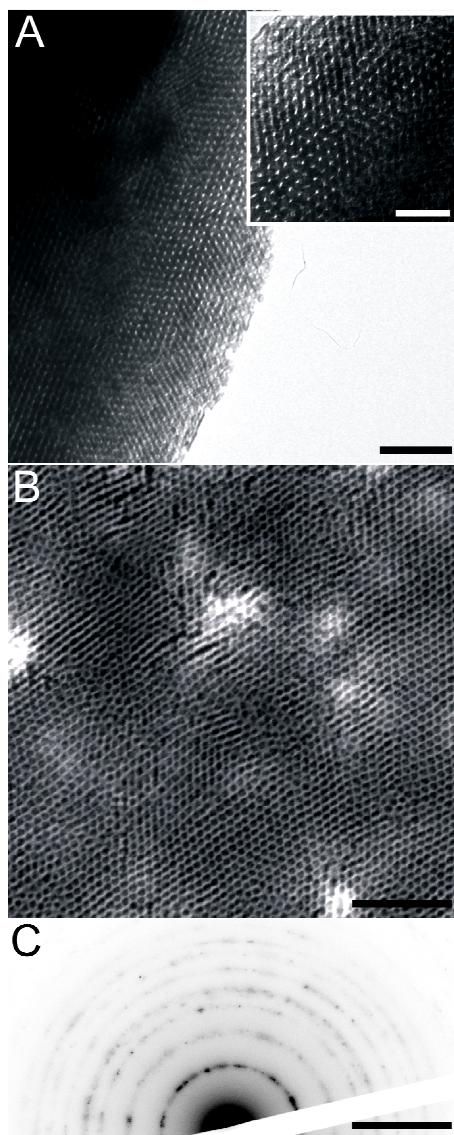


**Fig. 2:** Electron microscopy study of a highly-ordered  $\text{TiO}_2$  thin film after crystallisation at  $650^\circ\text{C}$ . **A** TEM image (inset is a magnification as specified below) and **B** SEM image, both showing the distinct shape of the well-defined mesopores and walls without larger structural defects. SAED pattern (corresponding to **A**) revealing characteristic diffraction rings of pure-phase anatase. Scale bars: (A) 100 nm and inset 50 nm, (B) 200 nm, (C)  $4\text{ nm}^{-1}$ .

The structural information derived from SAXS was confirmed by transmission electron microscopy (TEM) and scanning electron microscopy (SEM) (Fig. 2). Highly ordered domains of mesopores were observable, being uniform over large domains of up to micrometers. From these microscopic techniques an average pore-to-pore distance of ca. 20 nm (centre to centre) and an average mesopore dimension of ca. 14-15 nm were obtained. In conclusion, the pore wall thickness must be 5-6 nm. Electron diffraction, performed on such meso-structured domains, indicated the presence of the anatase phase and a high degree of crystallinity. The evolution of crystallinity was monitored by wide-angle x-ray scattering (WAXS) taken at different annealing temperatures, revealing an onset of crystallization at ca.  $500^\circ\text{C}$  with increase in crystallinity up to  $650^\circ\text{C}$  (Fig.3). Using the Scherrer equation an average crystallite size of ca. 14 nm was determined from the (101) reflection of a sample treated at  $600^\circ\text{C}$ . The porosity was determined on material scratched off the films by  $\text{N}_2$  physisorption at 77 K. The BET-surface ranged between  $180\text{--}230\text{ m}^2/\text{g}$ . The pore-size distribution analysis that was carried out (BJH-method) gave an average mesopore diameter of 7 nm.

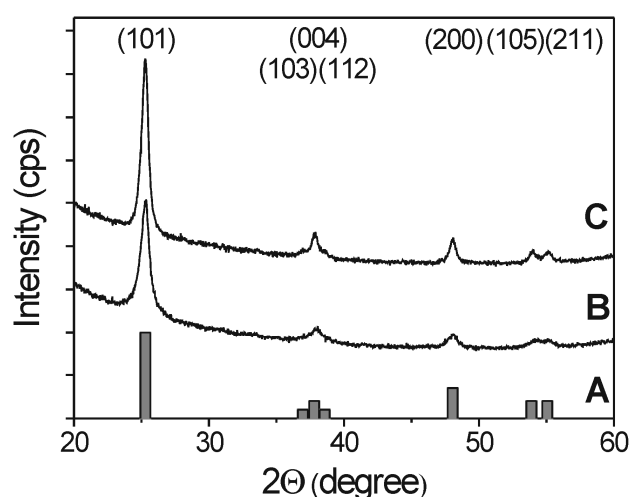


**Fig. 3:** X-ray diffraction study of a well-defined mesoporous  $\text{TiO}_2$  thin film. **A:** reference pattern from the JCPDS database ([21-1272] tetragonal anatase). **B** and **C:** experimental WAXS patterns of a film heat-treated at 500 °C and 650 °C, respectively, showing characteristic reflections of anatase.

Transmission and reflection measurements revealed a transparency of ~85% for the mesoporous film (d: 200 nm,  $\lambda > 430$  nm, Fig.4). The indirect bandgap of anatase, estimated from the absorption coefficient (Lambert-Beer) and its square-root plot against the photon energy, is about 3.31 eV, which coincides with energies published in literature (3.2 – 3.4 eV) [23].

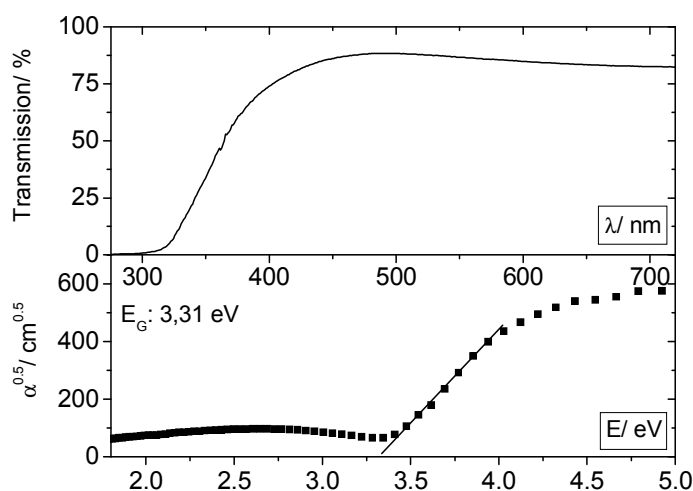


**Fig. 4 top:** Transmission spectra of a crystalline, mesoporous  $\text{TiO}_2$  film (quartz substrate, d: 200 nm). **Fig. 4 bottom:** Plot of the square root of the absorption coefficient  $\alpha$  versus light energy. Both, transmission and reflection were used for its calculation.

Thereby, diverse analytical techniques revealed that the  $\text{TiO}_2$  films used for the catalytic studies were indeed crystalline and mesostructured with well accessible mesoporosity.

### 3.2 The water- splitting reaction with mesoporous $\text{TiO}_2$ -photoelectrodes

The current-voltage characteristic of electrodes of series 1 is shown in Fig. 5. The dark-current was low ( $< 4 \mu\text{A}/\text{cm}^2$ ) for all investigated electrodes. In UV-light, the electrodes differed in their I-V characteristics clearly. At low potentials the photocurrents started to increase linearly ( $j_{\text{photo}} > 10 \mu\text{A}/\text{cm}^2$ : Ti-1(b): +0.07 V; Ti-2: +0.10 V; Ti-3: +0.2 V/ NHE). At more positive potential, the

photocurrent increase became smaller. Ti-1 continued with the best performance, in that the photocurrent continued to rise to  $0.26 \text{ mA/cm}^2$  at  $0.5 \text{ V (NHE)}$  and finally to  $0.46 \text{ mA/cm}^2$  at  $1.4 \text{ V/NHE}$ .

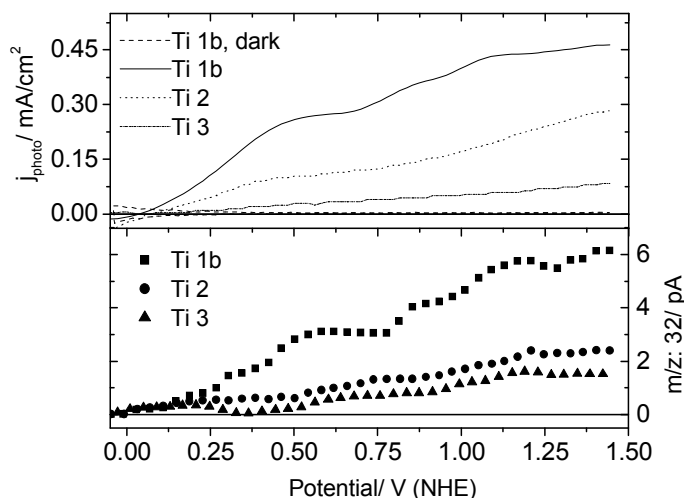


**Fig. 5 top:** Photocurrent-voltage characteristic of series1-electrodes obtained for the water splitting reaction in 0.5M sulfuric acid. **Fig. 5 bottom:** Plot of the oxygen mass-signal ( $m/z$ : 32 pA) corresponding to the photocurrent-potential scan above.

With the two other electrodes much lower photocurrents and lower smaller slopes of photocurrent increase were observed: Ti-2 (crystalline, not porous)  $0.10 \text{ mA/cm}^2$ ; Ti-3 (porous, not crystalline)  $0.03 \text{ mA/cm}^2$  at  $0.5 \text{ V/NHE}$ . Interestingly, a clearly plateau formation of photocurrent was observed for the crystalline electrodes only. The differences in photocurrent were highest for low potentials and decreased with increasing applied potential (table 2).

**Table 2:** Photocurrent ratios of “series 1”-electrodes at 0.5 and 1.3 V/NHE, respectively.

| $j_{\text{Ph}}$ ratio at 0.5 V | Ti 2 | Ti 3 | $j_{\text{Ph}}$ ratio at 1.3 V | Ti 2 | Ti 3 |
|--------------------------------|------|------|--------------------------------|------|------|
| Ti 1b                          | 2.5  | 8.6  | Ti 1b                          | 1.8  | 6    |
| Ti 2                           | 1    | 3.4  | Ti 2                           | 1    | 3.3  |
| Ti 3                           | 0.3  | 1    | Ti 3                           | 0.29 | 1    |

At low reversed bias ( $<0.5 \text{ V/NHE}$ ) electrode Ti-1(b) produced 8.6 times and 2.5 times more photocurrent compared with electrodes Ti-3 and Ti-2 respectively, whereas the ratios decreased to 6 and 1.8 at higher voltages ( $1.3 \text{ V/NHE}$ ). Apparently, high positive potentials reduced the advantages of morphology and crystallinity to a certain degree. The influence of the applied voltage on the semiconductor/electrolyte interface will be explained in chapter 3.3 and 3.4.

Simultaneously with the measurement of the I-V curve, the oxygen liberation rate was determined with help of a mass spectrometer ( $^{16}\text{O}_2$ ,  $m/z$ : 32; bottom of Fig. 5). The mass signal followed the trend of the current-voltage graph, but in general, the mass-signal onset was shifted to slightly higher potentials ( $+40 \text{ mV}$ ) due to the retarding effect of gas migration through the mass-spectrometer inlet-membrane ( $\sim 100 \text{ }\mu\text{m}$ ). In conformity with the I-V characteristic above, the structured, mesoporous electrode Ti-1(b) showed the highest  $\text{O}_2$  liberation rate. Significant lower rates of oxygen evolution were obtained with the electrodes Ti-2 and Ti-3.

To sum up these observations so far, the electrode's water splitting activity, reflected by photocurrent, slope of photocurrent and mass signal of evolved oxygen, was improved clearly for the morphologically structured, crystalline electrode Ti-1(b), especially at low potentials.

### 3.3 The oxidation of formic acid with mesoporous TiO<sub>2</sub>-photoelectrodes

In presence of formic acid the photocurrent increased for the electrodes in series 1 and the photocurrent onset shifted negatively, relative to the onset in pure aqueous sulfuric acid (fig.6). No water electrolysis reaction was observed in darkness ( $j_{\text{dark}} < 3.6 \mu\text{A}$  for all electrodes). Similar to the trend of the behaviour observed for the water splitting, the crystalline, mesoporous electrode Ti-1(b) showed the earliest onset ( $-0.03 \text{ V/NHE}$ ,  $0.05 \text{ mA/cm}^2$ ) and the highest photocurrent ( $>0.80 \text{ mA/cm}^2$ ,  $>0.5 \text{ V/NHE}$ ) of electrodes in series 1. In presence of formic acid, the onset of the two other electrodes shifted more positively relative to Ti-1(b) than without (Ti-2  $+50 \text{ mV}/0.02\text{V/NHE}$ ,  $0.04 \text{ mA/cm}^2$ ; Ti-3  $+350 \text{ mV}/0.30\text{V/NHE}$ ,  $0.03 \text{ mA/cm}^2$ ). This corresponded to an increase of +60% and +50%.

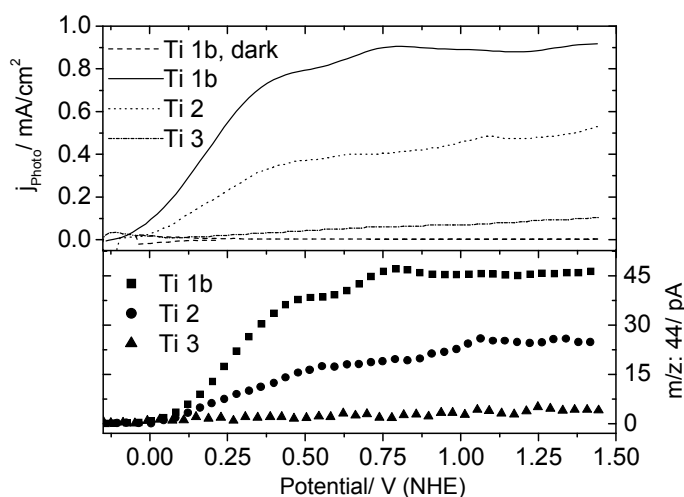


**Fig. 6 top:** Current-voltage characteristic of series1-electrodes obtained for formic acid oxidation under darkness and illumination with UV-light. **Fig. 6 bottom:** The corresponding mass-signal of carbon dioxide ( $m/z$ : 44, pA) to the photocurrent-potential scan.

The photocurrent increased for all crystalline electrodes (Ti-1(b), Ti-2) approximately by the factor of 3 compared to the water splitting reaction (Fig.5, 6, Table 2, 3). But it did much less for the amorphous electrode Ti-3 (+1.4 times).

Once again, the differences between the series 1 electrodes were smaller at high potential (table 3). At low reversed bias ( $<0.5\text{V/NHE}$ ), electrode Ti-1(b) produced 15.6 times and 1.8 times more photocurrent than electrode Ti-3 and Ti-2, respectively. At high anodic potentials, these ratios fell to 7.6 and 1.5.

**Table 3:** Ratios of photocurrent observed during the oxidation of formic acid in acidic aqueous solution at 0.5 V and 1.3 V vs. NHE, respectively.

| $j_{\text{Ph}}$ ratio at 0.5 V | Ti 2 | Ti 3 | $j_{\text{Ph}}$ ratio at 1.3 V | Ti 2 | Ti 3 |
|--------------------------------|------|------|--------------------------------|------|------|
| Ti 1b                          | 1.8  | 15.2 | Ti 1b                          | 1.5  | 7.6  |
| Ti 2                           | 1    | 8.4  | Ti 2                           | 1    | 5.2  |
| Ti 3                           | 0.12 | 1    | Ti 3                           | 0.19 | 1    |

At the bottom of Fig. 6, the mass signal of liberated carbon dioxide ( $^{12}\text{C}^{16}\text{O}_2$ ,  $m/z$ : 44) is plotted versus the applied potential. The  $\text{CO}_2$  liberation trend was: Ti-1b (38.0 pA) > Ti-2 (16.3 pA) and Ti-3 electrode (2 pA). It is worth to note that the  $\text{CO}_2$  mass signal of electrode Ti-3 did not rise significantly with increasing potential like it did for the water splitting reaction (bottom, Fig.5). Consequently, the low photocurrent cannot be explained by a worse charge transport this time. In addition one may conclude that the oxidation of organic substances was apparently more affected by absent crystallinity than the water splitting reaction. The photocurrent observed in an amperometric experiment with electrode Ti-1a is presented in Fig. 7. Immediately after illumination with UV-light, the current appeared and the formic acid was oxidized continuously over a period of minutes.

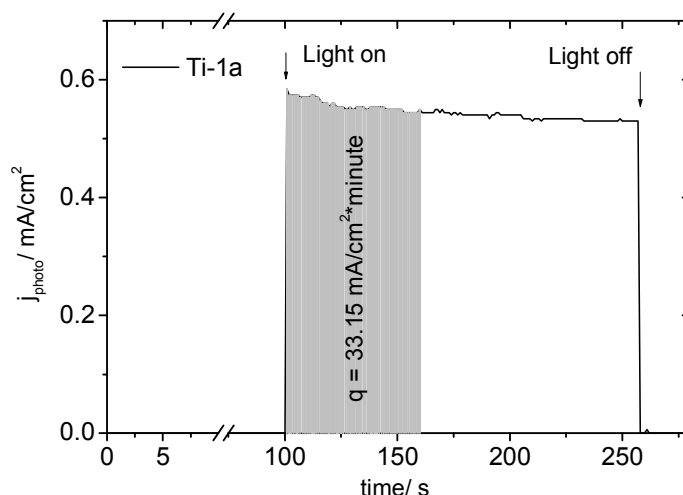


**Fig. 7:** Photocurrent of electrode Ti-1a observed at a constant potential (+0.32 V/NHE) in formic acid solution plotted versus the time. The estimated charge flux was 33.15 mA/cm<sup>2</sup> per minute (integration of the grey marked area).

The loss of current was below 2% in a two minute illumination period, which shows that the transport of oxidant into the film is in equilibrium. The charge flux was about 33.15 mA/cm<sup>2</sup> per minute, correlated to a formic acid decomposition rate of 5  $\mu\text{mol}$  per hour and a decomposition rate of 0.065 mol per hour and gramm of catalyst (mol/h\*g). In chapter 3.4 the calculation is discussed and presented in more detail.

### 3.4. APCE calculation

The absorbed photon to current conversion efficiency (APCE) is an important quantity relating the electrode's performance to the light intensity consumed. The APCE was calculated by using equation (Eq. 1), where  $j_{\text{Photo}}$  is the photocurrent measured,  $E_{\text{Rev}}^0$  the thermodynamic potential of water splitting,  $E_{\text{Measure}}$  is the potential applied,  $E_{\text{OC}}$  is the electrode's open circuit potential and  $I_{\text{light}}$  is the absorbed amount of light [20a,24]. The thermodynamic potential of watersplitting (+1.23 V) [25] was used to calculate the total power output. The light power input ( $I_{\text{light}}$ ) was determined by measuring the transmission for each electrode.

$$APCE(\%) = j_{\text{Photo}} * \left[ \frac{E_{\text{Rev}}^0 - |E_{\text{Measure}} - E_{\text{OC}}|}{I_{\text{light}}} \right] * 100 \quad (1)$$

The electrode's open circuit potentials ( $E_{OC}$ , light) are listed in table 4. The  $V_{OC}$  values of all crystalline electrodes (Ti-1a-c, Ti-2) were close to each other in pure sulfuric acid and in aqueous formic acid solution, but the one of the amorphous, mesoporous electrode Ti-3 was not ( $\Delta V_{OC}$ : - 20 mV in sulfuric acid, -100 mV in formic acid solution).

**Table 4:** Open circuit potentials and potential related APCE maxima obtained by structured and unstructured electrodes, in 0.5M sulfuric acid and acidified formic acid solution.

| Sample | Oven Temp./<br>(°C) | $V_{OC}/H_2SO_4$ ,<br>(V vs. NHE) | $V_{OC}/HCOOH$ ,<br>(V vs. NHE) | $\frac{APCE_{Max}}{(H_2SO_4, \%)}$ | $\frac{APCE_{Max}}{(HCOOH, \%)}$ |
|--------|---------------------|-----------------------------------|---------------------------------|------------------------------------|----------------------------------|
| Ti 1a  | 600                 | -0.05                             | -0.11                           | 0.4                                | 1.78                             |
| Ti 1b  | 650                 | -0.074                            | -0.12                           | 0.7                                | 2.13                             |
| Ti 1c  | 700                 | -0.074                            | -0.13                           | 0.56                               | 1.70                             |
| Ti 2   | 600                 | -0.074                            | -0.11                           | 0.04                               | 0.15                             |
| Ti 3   | <300                | -0.055                            | -0.01                           | 0.012                              | 0.02                             |

In Fig. 8, the calculated conversion efficiencies are plotted versus the potential applied. Fig. 8A belongs to the watersplitting reaction and Fig. 8B belongs to the formic acid decomposition. The APCE maxima are compiled in table 4. In an ideal case, a photocurrent-onset and an APCE maximum should be located at low potentials.

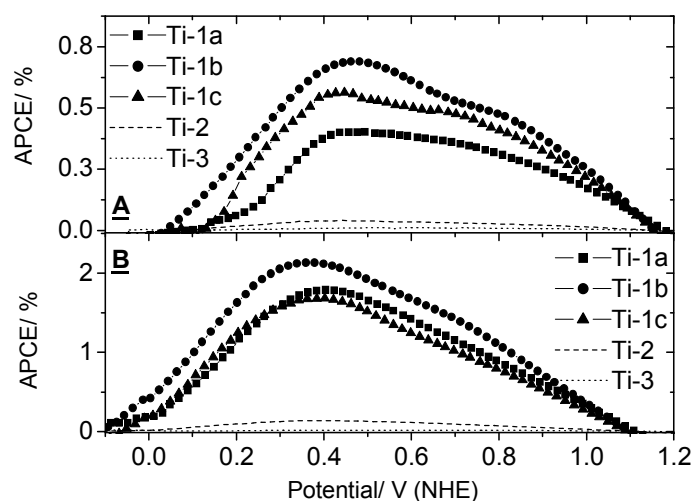


**Fig. 8 A+B:** The absorbed photon to current conversion efficiency (APCE), obtained for electrodes of both series is plotted versus the applied potential. The Fig. 8A refers to the watersplitting reaction, whereas the Fig. 8B refers to the oxidation of formic acid.



A huge difference was determined between the mesoporous electrodes Ti-1(a-c) and the electrodes Ti-2 and Ti-3. This may be related to their structure-related high transparency of the first group of materials (the amount of absorbed light was ten times lower) and the high photocurrent of these electrodes. The APCE spectra of electrodes of series 2 differed more between each other in aqueous, sulfuric acid solution than they did in aqueous, formic acid solution. Electrode Ti1-b showed the highest APCE maxima in aqueous sulfuric acid and in aqueous formic acid solution. It split water with an overall efficiency of 0.7% (0.45 V/NHE) and it oxidized formic acid with an efficiency of 2.1% (0.35 V/NHE).

## 4. Discussion

This study has shown that the same  $\text{TiO}_2$  prepared as mesoporous and non-mesoporous material largely differs significantly with respect to the photo-electrochemical performance. In the following the differences should be critically analyzed and theoretically explained on the basis of existing concepts.

### 4.1 Mesoporous $\text{TiO}_2$ in catalysis

In recent years, the number of publications dealing with morphology and its consequences for the performance of photoelectrodes [17, 26] and semiconductor devices (e.g. dye-solar cells) [27] has continuously been increasing. One has to carefully distinguish between reports that deal with changes in electrode morphology when they are still characterized by an unordered network of sintered  $\text{TiO}_2$  particles and those that describe changes in long range order and synthesis of new shaped 3-D structures (Fig. 2).

Photocatalytic properties of mesoporous  $\text{TiO}_2$  have been investigated by Stucky [14], Yu [15] and Day [17] so far. The last group experimented with mesoporous  $\text{TiO}_2$  powder and reported an enhanced degradation of red dye (X-3B). Stucky and Yu et al. prepared thin layered electrodes by dipcoating the substrates in a triblock polymer (Pluronic P123) based solution of titanium compounds. But Stucky et al. were focused on electrochromic properties and Yu et al. did not measure I-V curves. The decomposition rate of acetone in UV light which they estimated was not very high (0.0031 mol/g<sub>cat</sub>\*h). Both publications lack parallel experiments done with films prepared in the same way but without using the template.

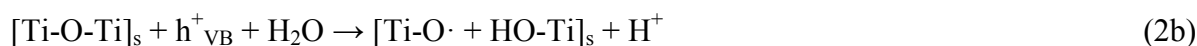
Coming back to the experiments and results presented in the preceding chapter, we can argue that the positive influence of morphology on photoelectrochemical reactions has clearly been demonstrated (Fig. 5-8). The ordered mesoporous electrodes surpass the electrodes prepared without template in photocurrent density, in the steepness of the slope of photocurrent density as a function of electrode potential, in the APCE value and in the mass signal of evolved  $\text{O}_2$  and  $\text{CO}_2$ .

### 4.2 Light induced surface reactions at $\text{TiO}_2$ particles

The oxidation of adsorbates at the  $\text{TiO}_2$  surface is assumed to be initiated by radicals, which are formed after a bond cleavage between titanium and oxygen lattice atoms ( $\text{Ti-O-Ti} + h\nu \rightarrow \text{Ti-O}\cdot$ ). This bond cleavage is caused by the excitation of an electron from the oxygen 2p valence band into the titanium 3d conduction band. According to recent mechanistic theories, the photogenerated defect electron ( $h\nu_{\text{VB}}$  equivalent to  $\text{Ti-O}\cdot$ ) at the valence band edge can react with both, adsorbed hydroxy-groups (-OH) to form surface near hydroxy-radicals ( $\cdot\text{OH}$ ) [28] or with the surface to form titanium-peroxo species ( $\text{TiO}\cdot$ ,  $\text{TiOO}\cdot$ ) [29].

If organic material is present, its reaction with surface bonded titanium-peroxide and titanium-peroxo radicals, together with the known reaction pathway via hydroxyl radicals and hydrogen peroxide formation is to be expected [30-32]. The formation of superoxide ( $\text{O}_2^{\cdot-}$ ) via the reduction of dissolved oxygen with electrons from the  $\text{TiO}_2$  conduction band can not be neglected, but it is

assumed that its concentration is low due to measurements in nitrogen gas saturated electrolytes and the applied positive potential. The following mechanism is based on a proposal by Nakato et al. [33]. It relies on the silent assumption that photo-generated holes diffusing to the TiO<sub>2</sub> surface are trapped near oxygen vacancies forming surface states. In this case the chemical nature of these states is not well defined and is not expected to be an oxygen p-state. It follows the reaction sequence [33]:



After the light induced formation of charge carrier pairs in bulk and surface (Eq. 2a), the defect electrons near the surface can react rapidly with adsorbed species or defect states at the surface (Eq. 2b). Additional defect electron trapping leads to the formation of a Ti-O-O-Ti peroxy-complex (Eq. 2c), which finally decomposes by evolving oxygen and restoring the TiO<sub>2</sub> lattice (Eq. 2d). The subtitle *s* denotes the presence of surface near reactions. In case of formic acid oxidation two defect electrons have to be consumed at the catalyst surface to form gaseous carbon dioxide and two protons (Eq. 2f) [32].



The model for photocatalytic water oxidation described by equations (Eq. 2a) to (Eq. 2d) [33] is not the only possible. Recently, an alternative mechanism has been proposed which is based on the interfacial reactivity of Ti-vacancies [34]. In this case surrounding oxygen vacancies would serve as surface states and oxygen p states could get involved in interfacial reactions with water. Such a reaction would seem to be much more specific. But more studies are necessary.

### 4.3 Model for the I-V characteristic of TiO<sub>2</sub> thin film photoelectrodes

In order to understand the different shapes and intensities of the photocurrent – voltage characteristics obtained for mesoporous and template-free prepared TiO<sub>2</sub>, theoretical models for such curves have to be considered. From our experience up to now we may however already conclude that such a theoretical model must include both kinetical parameters describing the bulk material and interfacial properties. This is clearly to be derived from the different shapes of the current – voltage curves concerned, as to be shown below.

A first theoretical description of the I-V characteristics and their dependence on semiconductor properties, like conductivity, doping level and diffusion length of charge carriers, was done by Gärtner for a solid-solid Schottky contact in 1959 [35].

In the well known Gärtner equation, the photocurrent is calculated by the sum of photogenerated charge carriers in the space charge layer and the charge collection of carriers diffused into that layer within their lifetime. Gärtner's equation is given by:

$$I_{ph} = qI_0 \left( 1 - \frac{e^{-\alpha W}}{1 + \alpha L} \right) \quad (3)$$

where  $q$  is the electrical charge,  $I_0$  the light intensity,  $\alpha$  is the absorption coefficient,  $W$  the width of the depletion zone and  $L$  is the diffusion length of minority charge carriers. Interfacial charge transfer- and surface recombination rates were not considered in this approximation, assuming them infinite and negligible, respectively. But, especially for polycrystalline metal oxide surfaces and the known strong interaction with aqueous solutions, interfacial rate constants are expected to be very relevant.

Several approaches considering these constants have been provided so far [36], but the resulting equations turned out to be so complicated that they can only be analyzed numerically. In order to understand the role of kinetic parameters an analytic formalism is highly desirable. Therefore model we use here is based on publications by Tributsch et al. [37]. If one assumes a proportional relation between the photocurrent and the product of the interfacial charge transfer rate times the potential dependent surface concentration of minority carriers, one will obtain the following equation:

$$I_{ph} = qk_T \Delta p_s (\Delta U) \quad (4)$$

where  $q$  is the elementary charge,  $k_T$  is a charge transfer rate constant,  $\Delta p_s$  is the surface concentration of photogenerated minority carriers (holes in case of a n-semiconductor) and  $\Delta U = U - U_{FB}$  stands for the potential applied. A surface recombination is considered in that model by defining a surface recombination current ( $I_{SR}$ ), which is similar derived like the approach before (Eq. 5).

$$I_{SR} = qs_R \Delta p_s (\Delta U) \quad (5)$$

For the reason of charge conservation, the sum of photocurrent and surface recombination current equals the minority carrier current ( $I_s$ ) towards the surface.

$$I_s = I_{ph} + I_{SR} \quad (6)$$

The flux of minority carriers to the surface ( $I_s$ ) was calculated by solving the continuity equation of the diffusion region in the 1-dimensional case, including boundary conditions and a charge carrier generation rate that depends on the thickness of the space charge layer (Eq. 7). For more details we refer to the former mentioned publication [37].

$$I_S = qI_0 \left( 1 - \frac{e^{-\alpha W}}{1 + \alpha L} \right) - \frac{qD}{L} * \Delta p_S * e^{-\Delta U q / kT} \quad (7)$$

After rearranging equation (Eq. 5) to  $s_R$  and inserting of  $I_{ph}$  (Eq. 4) into it, one obtains equation (Eq. 8). Equation (Eq. 9) relates the overall hole-flux to the surface and to the kinetic parameters  $k_T$  and  $s_R$ :

$$s_R = (I_S - I_{ph}) / q\Delta p_S = \frac{(I_S - k_T q \Delta p_S)}{q\Delta p_S} \quad (8)$$

$$\Delta p_S = \frac{I_S}{q * (k_T + s_R)} \quad (9)$$

Insertion of (Eq. 7) in (Eq. 9) gives equation (Eq. 10):

$$\Delta p_S = \frac{I_0 \left( 1 - \frac{e^{-\alpha W}}{1 + \alpha L} \right)}{k_T + s_R + \frac{D e^{-\Delta U q / kT}}{L}} \quad (10)$$

Finally, the substitution of  $\Delta p_S$  into equation (Eq. 4) leads to equation (Eq. 11), out of which the photocurrent-voltage characteristic of the semiconductor can be calculated theoretically.

$$I_{ph} = k_T q I_0 \frac{1 - \frac{e^{-\alpha W}}{1 + \alpha L}}{k_T + s_R + \frac{D}{L} e^{-\Delta U q / kT}} = q I_0 \frac{1 - \frac{e^{-\alpha W}}{1 + \alpha L}}{1 + s_R / k_T + \frac{D}{k_T L} e^{-\Delta U q / kT}} \quad (11)$$

If we compare this relation (Eq. 11) with the Gärtner formula (Eq. 3) one realizes, that it is very similar and still reasonably simple, but it considers in addition a denominator, which contains the additionally required bulk solid state and interfacial kinetic constants. They concern the bulk material properties expressed by diffusion coefficient  $D$  and diffusion length  $L$ , and the surface recombination rate constant  $s_r$  and the interfacial charge transfer rate  $k_r$  respectively. These constants are definitively needed to describe the observed differences between mesoporous and non mesoporous  $TiO_2$  materials. Basically, equation (Eq. 11) , first term, expresses a photo-generated hole current towards the interface, limited by an interfacial rate constant  $k_r$  as a multiplication factor, and modified by a denominator, which considers hole fluxes via the interfacial charge

transfer ( $k_r$ ), via surface recombination ( $s_r$ ), and via a potential dependent back diffusion from the interface ( $(D/L)e^{\Delta U_q/kT}$ ).

Some calculated I-V curves for different parameter constellations are given in Fig. 9. In general, the photocurrent depends on the applied voltage ( $\Delta U$ ), the width of the depletion zone  $W$  (itself a function of  $\Delta U$ ,  $W=(2\epsilon_0\epsilon\Delta U/eN_D)^{1/2}(\Delta U)^{1/2}$ ), the absorption coefficient for the incident light ( $\alpha$ ), the light intensity ( $I_0$ ), the diffusion length of minority carrier ( $L$ ), the hole diffusion coefficient ( $D$ ) and on the charge transfer rate ( $k_T$ ) and the surface recombination rate ( $s_R$ ).

It should be noted that in case of an infinite interfacial charge transfer rate ( $k_T = \infty$ ) and in absence of any surface recombination ( $s_R=0$ ), this relation transforms back to Gärtner's approach. The fact that the recombination velocity decreases with increasing band bending (caused by the external potential) is considered during the calculations by describing  $s_R$  as an exponential function of the applied voltage ( $s_R=s_R(0)*\exp(-f_s*\Delta U)$ ). All parameters used for the calculation were taken from literature: absorption coefficient  $\alpha=10^4 \text{ cm}^{-1}$ , relative permittivity (anatase)  $\epsilon_{HL}=31$ , doping density  $N_D=1*10^{17} \text{ 1/cm}^3$  and diffusion coefficient of holes  $=4*10^{-5} \text{ m}^2/\text{s}$  [35a-b, d, 37]. The electron transfer rate is assumed to be first order and its quantity is taken from a publication by Bahnemann et al. ( $k_T \sim 6*10^5 \text{ 1/s}$ ) [39]. The surface recombination velocity given in literature and observed in own time resolved surface photovoltage measurements can vary by more than six orders of magnitude (nanoseconds to milliseconds). In this approach,  $s_R$  was chosen to be smaller than  $k_T$  one time, and greater the next. The hole diffusion length used ( $20 \text{ nm} < L < 250 \text{ nm}$ ) is more comparable to a typical Debye length, present in that material ( $L_D=(\mu_p/(\mu_p+\mu_e))^{1/2}*(\epsilon_0\epsilon_{HL}k_B T/4\pi e_0^2 N_D)$ ,  $L_D=5.8 \text{ nm}$  with  $N_D=1*10^{17} \text{ 1/cm}^3$ ;  $\epsilon_{HL}=31$ ;  $D=4*10^{-5} \text{ m}^2/\text{s}$ ,  $T=295 \text{ K}$ ,  $\mu_e=0.4*10^{-4} \text{ m/Vs}$ ;  $\mu_p=1.6*10^{-3} \text{ m/Vs}$ ) [36b,38,44], than to the values reported in literature ( $L_{p+} \sim 1 \mu\text{m}$ ) [34, 35b]. But the given polycrystallinity of the electrodes together with the existence of many grain boundaries may justify this. The diffusion length  $L$  is comparable to the width of the depletion zone used in the model-calculations.

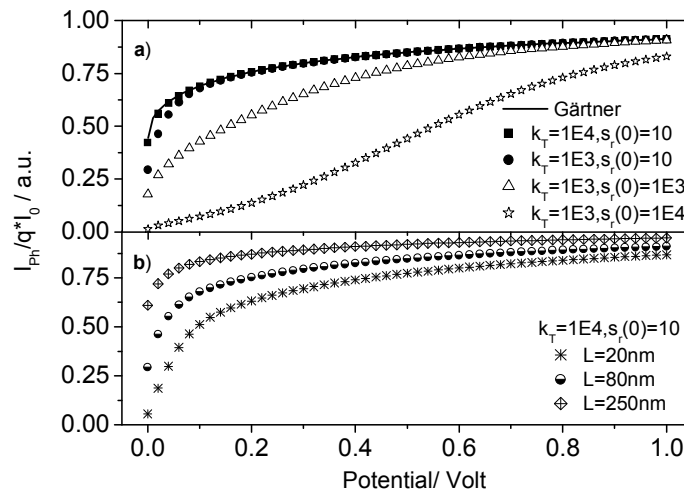


**Fig. 9:** Shape of  $\text{TiO}_2$  electrodes I-V curves calculated by using formula (10) under the conditions:  $\alpha=10^4 \text{ cm}^{-1}$ ,  $N_D=1*10^{17} \text{ cm}^{-3}$ ,  $\epsilon=31$ ,  $f_s=5$ ,  $D_{h+}=4.0^{-5} \text{ m}^2/\text{s}$ ,  $L=80 \text{ nm}$ . a) variation of charge transfer rate ( $k_T$ ) and surface recombination rate ( $s_R$ ); b) variation of the hole diffusion length  $L$ .

The plots in Fig. 9 emphasize the dominant influence of the kinetic parameters ( $k_T$ ) and ( $s_R$ ) on the I-V curve's shape. The charge transfer rate  $k_T$  is varied between  $\infty$  and  $1000 \text{ 1/s}$ . For high values of  $k_T$  ( $<10000 \text{ 1/s}$ ) the I-V curve is, of course, similar to the curve obtained using Gärtner's model, which stands for an ideal behavior of the semiconductor (flat solid interface, no

surface recombination, infinite charge transfer rate). When the charge transfer rate decreases and the surface recombination rate increases the ratio of  $s_R/k_T$  rises, which causes a reduction of the photocurrent. In addition, the current-onset gradually shifts to more positive potentials seen with more drastic parameter changes. A high surface recombination rate causes a complete quenching of charge carrier generated at low potentials (near the flat band position). High potentials are necessary to overcome the recombination process and to collect a photocurrent at the back-contact. The fact that all generated I-V curves tend towards one common photocurrent value for high potentials is attributed to the function of  $s_R$  that decreases exponentially with increasing potential. The influence of the holes diffusion length ( $L$ ) is highlighted in Fig. 9b. With increasing  $L$  the current onset starts at lower potentials and the photocurrent rises. This trend is reasonable. When the diffusion length increases, the number of photogenerated holes that have a possibility to reach and to react at the catalyst's surface within their lifetime increases too. The shift in photocurrent onset is caused by better availability of charge carriers. The I-V curve observed in the experiment (fig. 5, 6) is a superposition of curves shaped by different parameters (fig. 9), which do not have to be constant in time and location within the electrode surface

In conclusion, a catalyst used for photoelectrocatalysis should have a high charge transfer rate, a low surface recombination rate and an appropriate charge carrier diffusion length to generate an advantageous relation between energy input (light, potential) and energy output (photocurrent). If a catalyst is used with a marginally low diffusion length, nanostructuring of the electrode can partially overcome this drawback. By introducing a regular network of pores, the distance between the particle centers and the particles surfaces can be reduced and finally matched to the given diffusion length. A schematic diagram of two different electrode morphologies is presented in Fig. 10. The left handed scheme shows a side view of the 3D mesoporous electrode (bcc, 100face), the right handed scheme shows a view of an electrode prepared by irregular sintering of porous particles. The comparison between both highlights the importance of the diffusion length of minority carriers. A quantity named as electrolyte/semiconductor/electrolyte distance (E/S/E distance) is introduced, describing the volume of a catalyst that actively contributes to the photocatalysis. The E/S/E distance should be low as possible to mimic the advantages present in catalysis with powders, in that the distance bulk-surface is the particle's diameter and no grain boundaries play a role for the charge carrier transport.

The electrodes investigated in this article were polycrystalline and they were illuminated with polychromatic light, which actually impedes a quantitative comparison of theoretical and experimental I-V curves, because of the wide spectrum of absorption constants ( $\alpha$ ) in play. Nevertheless the model was chosen to emphasize the importance of the kinetic constants ( $k_T$ ,  $s_R$ ) and of the electrode morphology (as expressed by  $L$ , the diffusion length, in relation to the width  $W$  of the depletion layer) for the I-V characteristic of semiconductor electrodes. It can be used to understand the different I-V characteristics observed in experiment (Fig. 5, 6) qualitatively. Furthermore, the empiric observation that an externally applied potential and an increased surface results in an increased photocurrent and/or an increased catalyst's activity can now be explained theoretically. Also, the involved processes can be understood with a deeper insight, and it is clear, why mesoporous materials allow a more efficient collection of photo-generated minority carriers. the  $\text{TiO}_2$  material layers are significantly thinner than the width of the space charge layer

Some limitations of the model should be mentioned. No trap- or grain boundary limited electron transport (to the backcontact) [39, 40] is considered yet. The porosity of the investigated electrodes will cause a complete penetration of electrolyte into the film, which will affect both the range of the depletion zone and the range of the external applied electrical field [12]. Models designed for compact semiconductor materials would probably be valid for the first layers only (on top of back-contact where the potential drop is confined). Furthermore the experimental I-V curves were influenced by serial- and parallel-resistances and the Helmholtz-layer can deplete in presence of certain components (e.g. formic acid) in certain potential regions. All mentioned points have an impact on the measured photocurrent [41] and could be responsible for additional affects on the I-V

curves. All these mechanisms could be considered and the formula further optimized. But the consequence would be its drastic complication.

#### 4.4 General discussion of experimental findings

All of the investigated  $\text{TiO}_2$  electrodes were able to split water and to oxidize formic acid (fig. 5-8). Both the degree of crystallinity (series 1 and 2) and the electrode morphology (series 1) influence the I-V characteristic. In the following section, the background of these impacts will be discussed and linked to the theoretical predictions in chapter 4.3.

According to the chosen preparation method, in which the precursor  $\text{TiCl}_4$  is hydrolyzed, the crystallite size and the degree of crystallinity depend on the annealing temperature. A high degree of crystallinity is important to obtain a minimized number of lattice defects (bulk, surface) and to narrow the energetic distribution of interfacial electron trap states. Consequently, the recombination of photogenerated charge carriers is reduced in the bulk and at the surface. In addition, the annealing secures a sintering between the  $\text{TiO}_2$  particles and supports the formation of an interparticle network. Two parameters, the effective diffusion coefficient and the migration velocity of charge carriers are influenced strongly by the number of grain boundaries and their energetic properties, e.g. deep or shallow trap states. Both will affect the charge carrier diffusion length ( $L$ ) and subsequently the surface concentration of minority carriers (Eq.9).

A comparison of the I-V spectra obtained for the mesoporous but not crystalline electrode (Ti-3) with spectra obtained for the crystalline ones (Ti-1a-c, Ti-2) supports the points mentioned above. Despite the non-crystalline nature of sample Ti-3, the surface is reactive (checked by mass-spectroscopy, Fig.5), but the measured photocurrent and slope of photocurrent are quite low in comparison to Ti-1 and Ti-2 (Fig.5). The photocurrent observed for Ti-2 and Ti-1a-c for the watersplitting reaction is 3 times and  $>8$  times higher, respectively (Table 2). The additional improvement shown with the long range 3-D structured electrodes relative to the non-regular porous electrodes, present in form of a photocurrent onset at lower positive potentials, in form of an improved slope of current-onset and in form of an increased photocurrent-maximum (Fig.: 5-7, Table: 2-4), leads to the conclusion that both crystallinity and 3-D structuring of electrodes play an important role in supporting photoelectrocatalysis.

We believe that several facts contribute to the differences observed. First, the more open structure of the mesoporous electrodes and their thinner pore-walls secure a deeper penetration of light into the film. As a result, the overall number of generated charge carriers in the film increases. Second, the increased active surface area (BET-surface) provides additional space for charge transfer reactions at the catalyst/solution interface. The porosity brings about an improved educt/product transport capability. And third, thin pore walls create appropriate conditions for low  $E/S/E$  distances (compare fig.10), which finally allow more holes, generated in the bulk, to reach the surfaced reaction sites within their lifetime. The typical thickness of a pore-wall in the mesoporous electrodes (Ti1 a-c) is about 4-5 nm (SEM), whereas the average particle size (SEM) present for the non-regular porous electrode (Ti-2) is about 200nm. The diffusion length  $L$  ( $20 \text{ nm} < L < 250 \text{ nm}$ ) will consequently always exceed the distance from the site of photogeneration of a hole to a pore-wall surface (compare fig.10). All these factors will cause an increasing photocurrent, as was observed in the experiments. And the given theory provides an adequate qualitative explanation and indicates the lines along which the photocatalytic properties of the  $\text{TiO}_2$  material could still further be improved.

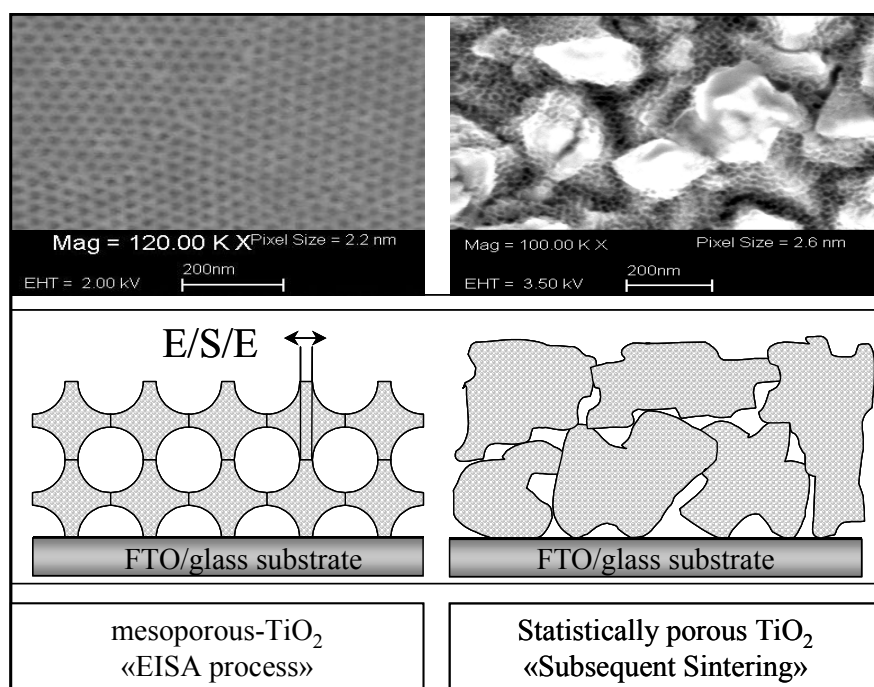


**Fig. 10:** Scheme of two different electrode morphologies – 3-D porous electrodes (100face) prepared by the EISA process (left) and porous electrodes prepared by making porous  $\text{TiO}_2$  particles first together with subsequent sintering (right). The E/S/E distance indicates the lowest distance of electrolyte-semiconductor-electrolyte. A low E/S/E distance is equivalent to a highly “active” volume of the semiconductor.

Assuming that a decreased E/S/E distance functions like an increased hole diffusion length in the material, the shifts in photocurrent onset and the increased photocurrent, observed for the mesoporous electrodes, can be explained with the model presented in chapter 4.3 and Fig. 9. Interestingly, the porous structure, made by the EISA process, did not lower the diffusion coefficient, like it was described by A.J. Frank et al. [42]. Otherwise, the I-V characteristic of the mesoporous electrodes (Ti-1a-c) would be disadvantageously related to the electrodes with less porosity (Ti-2). Frank et al explained their results of a decreasing diffusion coefficient with increasing porosity by an increase of dead ends formations. This is reasonable when highly porous  $\text{TiO}_2$  particles were prepared first and sintered together afterwards. In contrast to that procedure the implementation of porosity and the formation of the interparticle network via sintering were achieved together in one step in the EISA process.

The presence of favourable kinetic parameters for the mesoporous electrodes (high  $k_T$ , low  $s_R$  in relation to the other electrodes) can be assumed on the basis of our theoretical interpretation. The presence of favourable crystal sites, which would also explain the increased activity, could not be deduced from XRD measurements.

The influence of morphology can, however, can be derived from a second experiment. Mesoporous electrodes which were annealed at temperatures between 600 and 700°C differ in their I-V characteristics (table 4, fig.8). Samples annealed at 600°C and 700°C showed lower photocurrents and a more positive photocurrent-onset potential than samples annealed at 650°C. An explanation can be the observed growth of crystallite size. One the one hand the number of grain boundaries decreases, whereas on the other hand the BCC lattice of pores starts to collapse for a heat-treatment above 700°C.

The explanation of other experimental findings, like the stepwise increase of the photocurrent during the water splitting reaction can only be presumed. A different potential dependent activation



of available crystal sites and of related  $k_T$  and  $s_R$  may be responsible for the stepwise increase of photocurrent. The obtained I-V curve can be understood to be the result of a superposition of photocurrent curves of different crystal sites. Another possibility may be the presence of localized energetic barriers at the  $\text{TiO}_2/\text{FTO}$  interface, which need additional potential to be activated.

The amperometric experiment (fig 7) shows the continuous oxidation of formic acid with a mesoporous electrode. Assuming a complete suppressing of the water splitting reaction, an absence of charge trapping and charge injection [45], two defect electrons have to be consumed to produce a carbon dioxide molecule and a proton (Kolbe reaction, formula f). A charge of some  $33 \text{ mA/cm}^2$  per minute was obtained by integrating the photocurrent-time graph. Out of that, a formic acid decomposition rate of  $0.08 \text{ } \mu\text{mol}$  per minute ( $5 \text{ } \mu\text{mol/h}$ ) and square centimetre electrode area (macroscopic surface) was calculated with help of Faraday's law. The amount of catalyst present at  $1 \text{ cm}^2$  electrode area was about  $74 \mu\text{g}$ , so that the mass related decomposition rate would be  $0.065 \text{ mol/h} \cdot g_{\text{cat}}$  formic acid per hour and gram catalyst. This quantity is clearly greater than the rate published by Yu et al. ( $0.0031 \text{ mol/g}_{\text{cat}} \cdot \text{h}$ ).

## 5. Conclusions

The modified recipe used for the EISA process generated a well structured, long range 3D BCC lattice of spherical pores in a  $\text{TiO}_2$  film. The advantages of this structure with respect to (electro)-photocatalysis were shown in experiments and in theoretical calculations. The electrodes, with a defined, long range 3-D porosity, showed favourable shifts in photocurrent onset, an increased photocurrent maximum and an increased APCE value in photodecomposition of water and formic acid, compared with conventional (irregularly porous) sintered electrodes. The analysis of the two series of electrodes revealed empirically that both crystallinity and porosity have a deep impact on the photocatalytic performance and the I-V characteristic. Besides the use of a sufficient template, the appropriate annealing temperature is the major key to achieving the optimal balance between crystallinity and mesoporous structure. In the system presented here, the optimum was located at  $650^\circ\text{C}$ . SAXS patterns indicated a unidirectional shrinkage of the mesostructure between  $450^\circ\text{C}$  and  $600^\circ\text{C}$ , whereas the mesoporous structure started to collapse for temperature above  $700^\circ\text{C}$ .

The theoretical model presented in chapter 4.3 (Fig.: 9) can explain the empiric observations and provides a deeper insight into the involved processes behind changes in the catalyst's surface and morphology. It seems worth considering, how to design the electrodes morphology appropriately for the catalyst involved. Template based preparation methods can serve this purpose. The importance of this topic ranges from applications in classical and photo assisted catalysis to applications in solar cell- and sensor-devices.

## 6. Literature

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# Surface Science Approach to Photochemistry of TiO<sub>2</sub>

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## Abstract

Surface science studies of photochemistry on titanium dioxide (TiO<sub>2</sub>) were reviewed. In the studies, photochemical processes were investigated in relation to atomic-scale surface structures by applying surface-sensitive analytical methods to single crystal TiO<sub>2</sub> surfaces with well-defined structures. It is demonstrated that a surface science approach is promising for full description of the photochemical processes on TiO<sub>2</sub>.

## Why a Surface Science Approach?

The present paper focuses on photochemistry studies of titanium dioxide (TiO<sub>2</sub>) single crystal surfaces, in which photoreaction kinetics and dynamics were investigated using surfaces with atomically well-defined structures. TiO<sub>2</sub> has been widely studied in the field of surface science in order to reveal origins of its properties which are suitable to industrial applications including photochemical devices such as photocatalysts and photoelectrodes. The surface science studies of TiO<sub>2</sub> have been featured in the pioneering book of metal oxide surfaces written by Henrich and Cox published in 1994 [1] and reviewed in the paper written by Diebold in 2003 [2]. Photochemistry studies of TiO<sub>2</sub> were reviewed by Linsebigler et al. in 1996 with detailed instructions on surface photochemistry [3].

Titanium dioxide is a wide band gap metal oxide with a band gap of approximately 3 eV and becomes an n-type semiconductor when donor-like O vacancies are formed by reduction treatment. Irradiation by ultraviolet (UV) light causes band gap excitation to form conduction band electrons and valence band holes. A major factor showing that TiO<sub>2</sub> has an excellent performance as a photochemical device is the conduction and valence band edge energies appropriate for exchange of electrons with adsorbates [4]. The band bending in the vicinity of the semiconducting TiO<sub>2</sub> surface

contributes to the photochemistry of  $\text{TiO}_2$  by promoting the separation of the photogenerated electrons and holes. In addition to such collective properties, atomic-scale surface structures are thought to be closely related to photochemical properties of the  $\text{TiO}_2$  [5]. Distribution of photogenerated electrons and holes should be sensitive to the local electrostatic potential influenced by arrangement of ionic Ti and O atoms. Electron transfer between adsorbates and  $\text{TiO}_2$  surface through the overlapping orbitals should be affected by the geometric and electronic structures of the adsorbate- $\text{TiO}_2$  interface. Examining photochemical properties of  $\text{TiO}_2$  surfaces in relation to their atomic-scale structures would provide unequivocal understanding of the photochemical processes. Surface science studies, where single crystal surfaces with well-defined structures are examined in controlled environments, could provide such information about the atomic-scale surface structures.

### Rutile $\text{TiO}_2$ (110) Surface; A Prototype for Surface Science Studies of $\text{TiO}_2$

Titanium dioxide has three natural crystal phases, anatase, brookite, and rutile. Surface science studies of  $\text{TiO}_2$  have concentrated on the rutile crystal [2], because a large size and high quality rutile crystal is commercially available. Among the low index surfaces of the rutile  $\text{TiO}_2$ , the (110) surface has been most widely used in surface science studies. The (110) surface exhibits a simple truncation of the bulk structure by conventional cleaning procedures in ultra-high vacuum (UHV), i.e., repetition of  $\text{Ar}^+$  sputtering and annealing at 900 K [6]. The cleaning operation gives rise to the O vacancies and thereby raises bulk conductivity, which is beneficial for surface-sensitive analytical methods using charged particles such as electrons and ions as probes. The studies introduced here were all performed in UHV using the rutile (110) surface except for one. A brief look at the non-reconstructed ( $1\times 1$ ) structure of the (110) surface would help us to review the studies.

Fig. 1(a) shows the unit cell of the rutile crystal. The lattice constants of the tetragonal unit cell,  $a$  and  $c$ , are 0.46 and 0.30 nm, respectively. Each Ti atom is coordinated to six O atoms, and each O atom is coordinated to three Ti atoms. Figure 1(b) shows the structure of the  $\text{TiO}_2$ (110)-( $1\times 1$ ) surface with a unit cell of 0.65 nm $\times$ 0.30 nm. The topmost O atoms are bound to two 6-fold-coordinated Ti atoms in a bridging coordination (bridging O atoms) and form rows along the [001] direction. Between the bridging O atom rows, Ti atoms coordinated to five O atoms (5-fold-coordinated Ti atoms) are exposed. A few percent of the bridging O atoms are missing [7], whereas removal of the in-plane O atoms is less probable [8]. The removed bridging O atom leaves two electrons, and the bridging O vacancies are recognized as a  $\text{Ti}^{3+}$  shoulder at the low binding energy side of the Ti  $2p_{3/2}$  X-ray photoelectron spectroscopy (XPS) peak [9, 10]. In an electron energy loss (EEL) spectrum, an energy loss peak attributed to electron excitation from the O vacancy state to the conduction band appears at around 0.8 eV [10, 11]. Hydrogen atoms, possibly formed by dissociation of residual water molecules in a vacuum chamber, reside on some of the bridging O atoms and form surface hydroxyl (OH) groups [12]. The surface free from the bridging O vacancy can be prepared by 1000 K annealing in  $\text{O}_2$  and subsequent cooling to room temperature in  $\text{O}_2$  of the sputter-annealed ( $1\times 1$ ) surface [9].

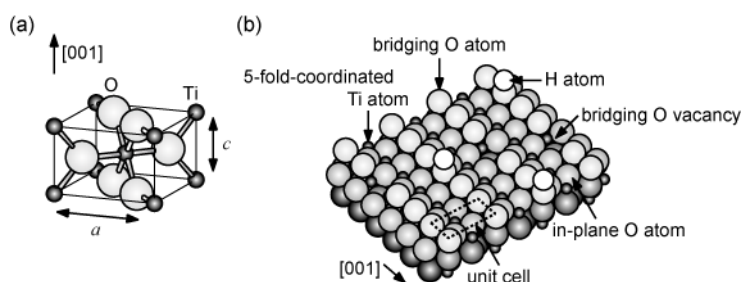


**Fig. 1** (a) A unit cell of the rutile  $\text{TiO}_2$ . Small and large balls represent Ti and O atoms, respectively. The lattice constants of the tetragonal unit cell,  $a$  and  $c$ , are 0.46 and 0.30 nm, respectively. (b) A ball model of the rutile  $\text{TiO}_2(110)-(1 \times 1)$  surface prepared by sputter-anneal cycles in UHV. Oxygen atoms are shaded according to their depth. The size of the unit cell is 0.65 nm  $\times$  0.30 nm.

### Atomic-Scale Observation of a $\text{TiO}_2(110)-(1 \times 1)$ Surface

The atomic-scale structure of the  $(1 \times 1)$  surface can be visualized by using a scanning probe microscope (SPM). Figure 2 shows a typical (a) scanning tunneling microscope (STM) image [13] and (b) a noncontact atomic force microscope (NC-AFM) image of the  $(1 \times 1)$  surface obtained in UHV [7]. The empty state STM image shows atomically flat terraces separated by single steps. The bright rows extending to the  $[001]$  direction correspond to the positions of the 5-fold-coordinated Ti atoms [14, 15]. The electron tunneling to the empty states derived mainly from the Ti 3d orbitals is responsible for the image contrast. The spot indicated by the circle A between the neighboring Ti atom rows is the bridging O vacancy. The surface OH groups are occasionally observed as spots between the Ti atom rows [12, 16], possibly depending on the tip condition, though they are not observed in Fig. 2(a). The depression in the Ti atom rows B was assigned to subsurface defects in ref. 13. The NC-AFM, a scanning probe microscope which regulates the tip-sample distance by detecting weak attractive force [17], visualizes the geometrically higher bridging O atom rows as bright rows as shown in Fig. 2(b). The depressions in the rows are the bridging O vacancies. The surface OH groups are occasionally observed as protrusions or depressions on the rows dependent on the polarity of the tip end [18, 19].

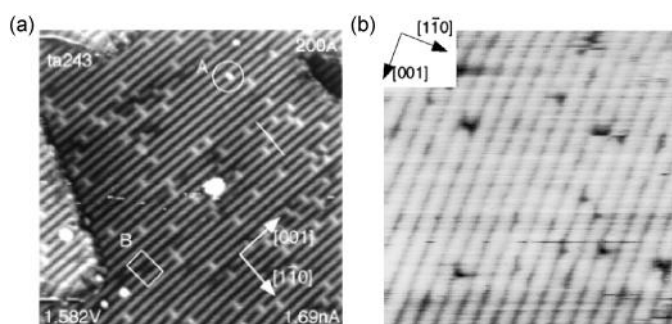


**Fig. 2** (a) An empty state STM image of the rutile  $\text{TiO}_2(110)-(1 \times 1)$  surface (20 nm  $\times$  20 nm) [13]. Sample bias voltage ( $V_s$ ) = +1.582 V, tunneling current = 1.69 nA. (b) An NC-AFM image of the  $\text{TiO}_2(110)-(1 \times 1)$  surface (10 nm  $\times$  10 nm) [7]. Frequency shift ( $\Delta f$ ) = -80 Hz,  $V_s$  = 0 V.

## Photochemistry of Oxygen

Surface species derived from the  $O_2$  molecule such as superoxide anion radical ( $O_2^-$ ) and atomic oxygen play key roles in the photoreactions on powdered  $TiO_2$  [20, 21]. The possible roles of the oxygen species include an oxidizer, a trap for photogenerated electrons, and maintaining of the stoichiometry of the  $TiO_2$  surface. Clarifying the behaviors of the oxygen species is prerequisite for understanding photochemical processes on  $TiO_2$  surfaces.

The first report examining photochemistry of oxygen species on the rutile  $TiO_2(110)-(1\times1)$  surface was by Lu et al. [22, 23]. The surface was exposed to  $O_2$  at 105 K, and photodesorbed species were examined. Irradiation by UV light with energy larger than the band gap of the  $TiO_2$  (3.1 eV) induced desorption of  $O_2$  molecules, whereas thermal desorption of  $O_2$  did not occur at the temperature between 100 and 500 K. The maximum yield of  $O_2$  was comparable to the number of the bridging O vacancies titrated by low energy ion scattering techniques. An equivalent amount of  $^{16}O_2$  and  $^{18}O_2$  was desorbed from the surface exposed to an equivalent mixture of  $^{16}O_2$  and  $^{18}O_2$ . The authors concluded that the  $O_2$  molecules were adsorbed at the bridging O vacancies and were desorbed by capturing photogenerated holes. The molecularly adsorbed oxygen species were designated as  $\alpha-O_2$ . From detailed analysis of the photodesorption spectra, the  $\alpha-O_2$  was distinguished between two species with different desorption cross sections,  $\alpha_1-O_2$  and  $\alpha_2-O_2$  [24]. The  $\alpha_1-O_2$  and  $\alpha_2-O_2$  were assigned to the molecular oxygen species in different types of O vacancies. Heating the surface to 200 K with the  $\alpha-O_2$  gave rise to a new component with a faster desorption rate in the  $O_2$  photodesorption spectra. This was attributed to the conversion of the  $\alpha-O_2$  to another molecular species,  $\beta-O_2$ . Superoxide anion radical and peroxide anion ( $O_2^{2-}$ ) formed by electron transfer from the reduced Ti atoms to the  $O_2$  molecules were proposed as candidates for the  $\alpha-O_2$  and the  $\beta-O_2$ . Photodesorption of the  $\beta-O_2$  decreased as the heating temperature was raised and completely ceased by heating to temperatures above 400 K, which indicated dissociation of the  $\beta-O_2$  to O atoms. One O atom filled the vacancy, and the other resided on the Ti atom rows [16, 25, 26]. The transition of the oxygen species on the  $TiO_2(110)-(1\times1)$  surface is illustrated in Fig. 3(a).

Perkins et al. reported the photochemical property of the O adatoms on the  $TiO_2(110)-(1\times1)$  surface [27]. Fig. 3(b) shows the temperature programmed desorption (TPD) spectra of  $H_2O$  from the surface. Spectrum a obtained on the surface exposed to  $H_2O$  at 115 K showed two peaks at 270 and 520 K. The peak at 270 K arose from  $H_2O$  molecularly adsorbed on the 5-fold-coordinated Ti atoms [25], and the peak at 520 K was assigned to the  $H_2O$  produced by recombination of two OH groups which were formed by dissociative adsorption of  $H_2O$  molecules at the bridging O vacancies [28]. Spectrum b was obtained on the surface exposed to  $O_2$  and then to  $H_2O$  at 115 K. The shoulder on the high temperature side of the peak at 270 K originated from  $H_2O$  produced by recombination of two OH groups on the 5-fold-coordinated Ti atoms, and indicates the presence of the O adatoms. A  $H_2O$  molecule reacts with the O adatom to form two OH groups [25]. The peak at 520 K in spectrum a disappeared because the bridging O vacancies were filled by the  $O_2$  dose. Spectrum c was obtained on the surface which was exposed to  $O_2$  at 115 K, irradiated by UV light ( $h\nu$

= 4.13 eV), and then exposed to H<sub>2</sub>O. The existence of the shoulder indicated that the O adatoms remained on the surface after UV irradiation.

In summary, molecular oxygen and atomic oxygen are possible oxygen species on the TiO<sub>2</sub>(110)-(1×1) surface. The molecular species  $\alpha$ -O<sub>2</sub> is formed in the bridging O vacancy at 105 K, and is converted to other oxygen species,  $\beta$ -O<sub>2</sub> and O adatoms, at higher temperatures. The  $\alpha$ -O<sub>2</sub> and  $\beta$ -O<sub>2</sub> are desorbed with the band gap excitation of TiO<sub>2</sub> at temperatures higher than 105 K. The O adatoms remain on the surface after UV irradiation at 115 K.

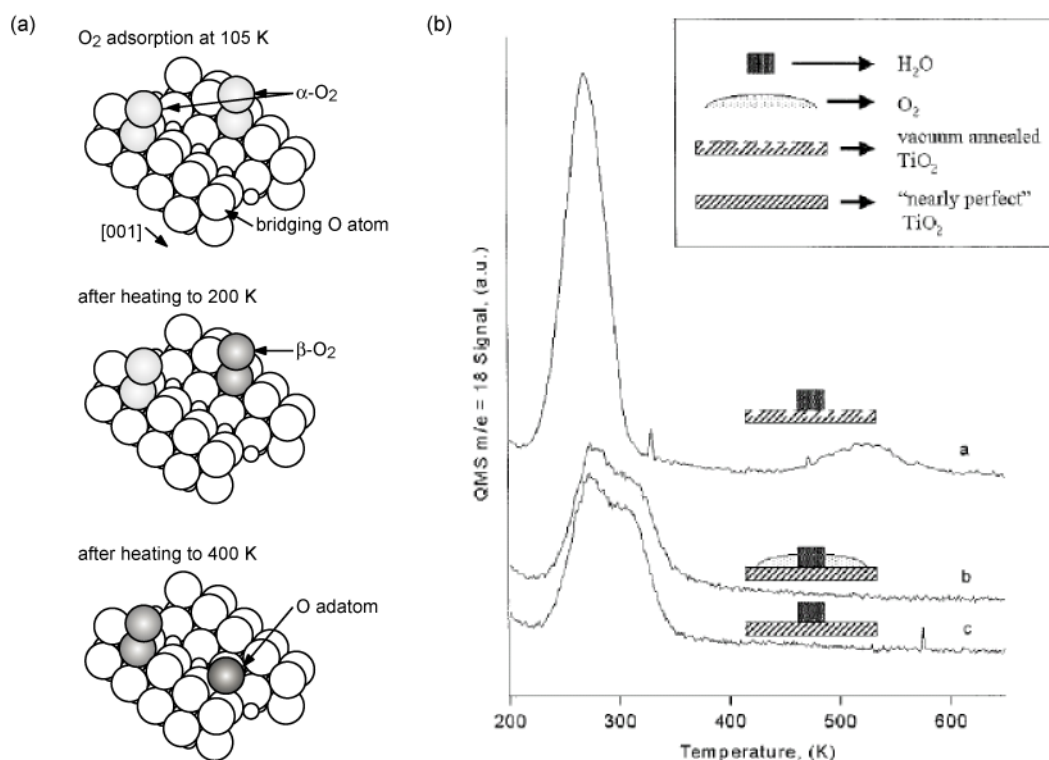


**Fig. 3** (a) A schematic illustration representing the oxygen species on the TiO<sub>2</sub>(110)-(1×1) surface. (b) The TPD spectra of H<sub>2</sub>O from the TiO<sub>2</sub>(110)-(1×1) surfaces. a: The surface exposed to H<sub>2</sub>O at 115 K. b: The surface exposed to O<sub>2</sub> and then to H<sub>2</sub>O at 115 K. c: The surface exposed to O<sub>2</sub>, irradiated by UV ( $h\nu = 4.13$  eV), and then exposed to H<sub>2</sub>O [27].

### Photooxidation of Carbon Monoxide

Oxidation of carbon monoxide (CO) is a prototypical model reaction widely studied in the field of surface science [29] due to its relative simplicity and importance from the view point of industrial applications such as air pollution control catalysts, gas sensors, and fuel cells.

Linsebigler et al. examined photooxidation of C<sup>18</sup>O on the rutile TiO<sub>2</sub>(110)-(1×1) surface [23, 24, 30]. The surface was exposed to <sup>18</sup>O<sub>2</sub> and then C<sup>18</sup>O at 105 K, and desorption of C<sup>18</sup>O<sub>2</sub> induced by UV irradiation ( $h\nu = 3.9$  eV) was monitored. C<sup>18</sup>O<sub>2</sub> was desorbed when the vacancy-free (1×1) surfaces were annealed at temperatures higher than 400 K prior to the exposure to <sup>18</sup>O<sub>2</sub>, and the yield of C<sup>18</sup>O<sub>2</sub> increased with the temperature of the pre-annealing. The C<sup>18</sup>O<sub>2</sub> desorption was not



observed when the vacancy-free surfaces were not annealed or were  $\text{Ar}^+$  sputtered. The results indicated that the bridging O vacancy was needed for the  $\text{CO}_2$  production. The exponential decay constant for the  $\text{CO}_2$  desorption was identical to that of the  $\alpha\text{-O}_2$  photodesorption, and the yield of  $\text{CO}_2$  decreased with the conversion of the  $\alpha\text{-O}_2$  to the  $\beta\text{-O}_2$ . Exclusive production of  $\text{C}^{18}\text{O}_2$  from  $\text{C}^{18}\text{O}$  and  $^{18}\text{O}_2$  excluded the involvement of the lattice O of the  $\text{TiO}_2$  in the reaction, and exclusive production of  $\text{C}^{18}\text{O}^{16}\text{O}$  from  $\text{C}^{18}\text{O}$  and  $^{16}\text{O}_2$  excluded the dissociation of CO in the reaction. The authors concluded that the  $\text{CO}_2$  was produced by photochemical reaction of the  $\alpha\text{-O}_2$  with the CO molecularly adsorbed on the 5-fold-coordinated Ti atom [31]. The CO photooxidation was a minor process compared to that of the  $\text{O}_2$  photodesorption.

Linsebigler et al. reported the effect of Pt loading on the CO photooxidation as well [32]. It is known that loading nanometer-sized Pt clusters is effective for enhancing the photocatalytic activity of powdered  $\text{TiO}_2$  [33]. After Pt evaporation using a Pt wire as a source, the  $\text{TiO}_2(110)\text{-(1}\times\text{1)}$  surface was annealed at 600 K to promote clustering of Pt and to generate the bridging O vacancies. The surface was exposed to  $^{18}\text{O}_2$  and then to  $\text{C}^{18}\text{O}$  at 105 K, and photodesorption of  $\text{C}^{18}\text{O}_2$  was monitored. The left-hand panels in Fig. 4 show the photodesorption spectra of  $\text{C}^{18}\text{O}_2$  from the surface containing different amounts of Pt under UV irradiation ( $h\nu = 3.9$  eV). The initial rate of  $\text{C}^{18}\text{O}_2$  production (height of the initial peak of the desorption spectrum) and yield of the  $\text{C}^{18}\text{O}_2$  (peak area) were both reduced with the amount of Pt, which was attributed to a decrease of the bare  $\text{TiO}_2$  surface providing bridging O vacancies. The exponential decay constants for the  $\text{C}^{18}\text{O}_2$  desorption were independent of the Pt loading as shown in the right-hand panel. Thus the Pt loading was ineffective on CO photooxidation on the  $\text{TiO}_2(110)$  surface at a low temperature where thermal processes are quenched.

It was shown that  $\alpha\text{-O}_2$  was the active species for CO photooxidation on the  $\text{TiO}_2(110)\text{-(1}\times\text{1)}$  surface at 105 K and that the kinetics of the photooxidation was insensitive to the Pt loading at that temperature. The activity of O adatoms on CO photooxidation and the role of Pt clusters at higher temperatures would be an interesting subject for further investigation.

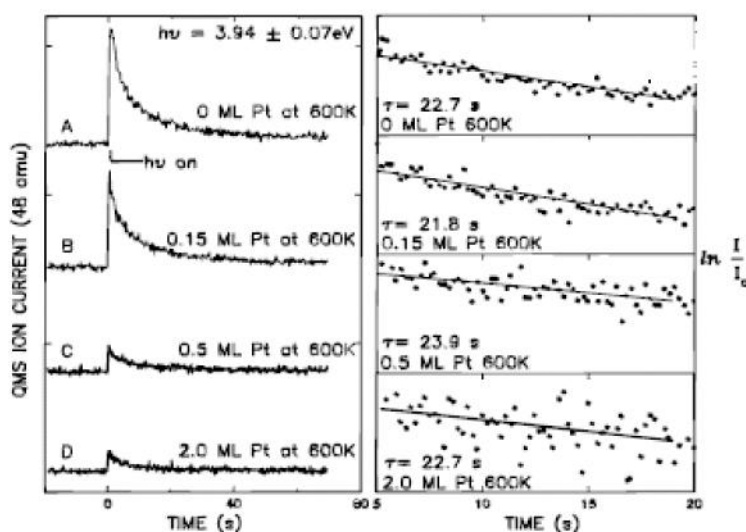


**Fig. 4** Kinetics of CO<sub>2</sub> production for CO+O<sub>2</sub> layers on Pt-loaded TiO<sub>2</sub>(110)-(1×1) surfaces. Left panel: photodesorption spectra of CO<sub>2</sub>. Right panel: decay times for CO<sub>2</sub> formation rate derived from the spectra in the left panel. One monolayer (ML) of the Pt was defined to be  $1.5 \times 10^{15} \text{ cm}^{-2}$  [32].

### Photochemistry of Halomethanes

Halomethanes (CH<sub>4-n</sub>X<sub>n</sub>, X=F, Cl, Br) are frequently used in photochemical studies [34, 35]. The molecules have a strong absorption in the UV region, and their simple structures are beneficial for identifying reaction intermediates and products.

Weitz and co-workers studied the photochemistry of deuterated iodomethane (CD<sub>3</sub>I) on the rutile TiO<sub>2</sub>(110)-(1×1) surface [36, 37]. A vacancy-free (1×1) surface with 1 ML (1 ML =  $3.8 \times 10^{14} \text{ cm}^{-2}$ ) of CD<sub>3</sub>I was prepared by exposing the surface to CD<sub>3</sub>I gas at 100 K and was irradiated by UV light with the wavelengths of 257–351 nm. Analysis of photodesorbed species by time-of-flight mass spectroscopy showed that dissociation was predominant over the molecular desorption of the CD<sub>3</sub>I. Complete loss of the C 1s XPS peak by UV irradiation indicated that the CD<sub>3</sub> fragments were expelled to the gas phase and did not remain on the surface. The dissociation cross section was estimated from the intensities of C 1s and I 3d<sub>5/2</sub> XPS peaks originating from the CH<sub>3</sub>I molecules on the surface. The I 3d<sub>5/2</sub> peak originating from the CD<sub>3</sub>I molecule exhibits higher binding energy than that from I adatoms by 1.6 eV. The estimated cross section was equivalent to the photodissociation cross section of gas phase CD<sub>3</sub>I when the wavelength of UV light was shorter than 302 nm. The authors concluded that the contribution of the photogenerated electrons and holes to the CD<sub>3</sub>I dissociation was limited due to poor overlap of electronic states between the adsorbed CD<sub>3</sub>I molecules and the TiO<sub>2</sub> surface, and that the CD<sub>3</sub>I molecules were directly excited by the UV irradiation. When the wavelengths of UV light were longer than 334 nm, the photodissociation cross

sections on the  $\text{TiO}_2$  surface exceeded that in the gas phase. This was explained by the contribution of  $\text{TiO}_2$  becoming relatively large due to reduced UV absorption by the  $\text{CD}_3\text{I}$  molecule.

Yates, Jr. and co-workers reported photooxidation of chloromethane ( $\text{CH}_3\text{Cl}$ ) on the  $\text{TiO}_2(110)-(1\times 1)$  surface [38, 39]. The surface was exposed to reactant gases at 105 K, and the species remaining on the surfaces after UV irradiation was identified by TPD. Figure 5 shows the yield ratios of the species. No species except for  $\text{CH}_3\text{Cl}$  was desorbed from the vacancy-free surfaces and the surfaces exposed only to  $\text{D}_2^{18}\text{O}$  (upper scheme). When the surface was exposed to  $^{18}\text{O}_2$  prior to the  $\text{CH}_3\text{Cl}$  exposure,  $\text{H}_2^{18}\text{O}$ ,  $\text{C}^{18}\text{O}$ , and formaldehyde (70%  $\text{H}_2\text{C}^{18}\text{O}$  and 30%  $\text{H}_2\text{C}^{16}\text{O}$ ) were detected with a decrease of  $\text{CH}_3\text{Cl}$  (middle scheme). When the surface was exposed consecutively to  $\text{D}_2^{18}\text{O}$ ,  $^{16}\text{O}_2$ , and  $\text{CH}_3\text{Cl}$ , the desorption yield ratio of the  $\text{H}_2\text{C}^{18}\text{O}$  and  $\text{H}_2\text{C}^{16}\text{O}$  was reversed, and  $\text{C}^{16}\text{O}$  was not detected (lower scheme). Hydrogen chloride ( $\text{HCl}$ ) was another product which showed a delayed increase after the photooxidation experiments due to its low yield and high sticking probability on the chamber walls. Neither desorption nor fragmentation of the  $\text{CH}_3\text{Cl}$  occurred during the UV irradiation in each experiment. The authors concluded that the bridging O vacancies and  $\text{O}_2$  exposure were essential to the photooxidation of  $\text{CH}_3\text{Cl}$  and that the surface OH groups derived from  $\text{H}_2\text{O}$  were not. Direct reaction of the oxygen species with the  $\text{CH}_3\text{Cl}$  to produce CO was proposed on the basis of the fact that the O atoms of CO were derived exclusively from  $\text{O}_2$ . The oxygen species is possibly the  $\alpha\text{-O}_2$ . The  $\text{O}_2$ ,  $\text{H}_2\text{O}$ , and  $\text{TiO}_2$  were all possible sources of the O atom in  $\text{H}_2\text{CO}$ , which indicated that the reaction path to produce  $\text{H}_2\text{CO}$  was different from that for the CO production.

Contribution of the vacancy-free  $\text{TiO}_2$  surface to the  $\text{CD}_3\text{I}$  photodissociation seems important. The step edges are possible surface structures which enhance dissociation. Coordination to the 4-fold-coordinated Ti atoms exposed at the step edges [13] might allow better electronic overlap for the  $\text{CD}_3\text{I}$  molecules compared to the 5-fold-coordinated Ti atoms on the flat terraces. Employing high index surfaces with high density of steps [40] would clarify the contribution of the steps to the photooxidation.

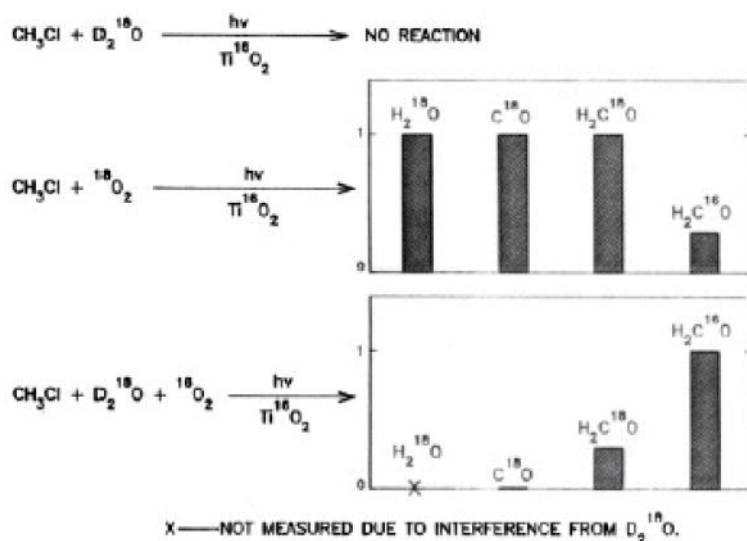


**Fig. 5** The isotope distribution in the photochemical products on  $\text{TiO}_2(110)-(1\times 1)$  surface [38].

## Photooxidation of Acetone

Acetone ( $\text{CH}_3\text{COCH}_3$ ), often used as ingredients in household products such as glues, paints, and varnishes, potentially causes headaches, fatigue, and nausea, and is one of the volatile organic chemicals which should be reduced by  $\text{TiO}_2$  photocatalysts.

Henderson examined photooxidation of acetone on the  $\text{TiO}_2(110)-(1\times 1)$  surface [41]. The surface was exposed to acetone at 95 K, and TPD analysis was performed on surfaces with 0.25 and 1 ML (1 ML =  $5.2\times 10^{14} \text{ cm}^{-2}$ ) of acetone to examine the species remaining on the surface. After irradiation with a Hg arc lamp in  $\text{O}_2$  at 95 K, the peak of the TPD of a ketene ( $\text{CH}_2=\text{C}=\text{O}$ ) grew with the decrease of the peak of acetone as the irradiation time was extended. Desorption of the ketene indicated the presence of acetate ( $\text{CH}_3\text{COO}^-$ ) which is thermally decomposed to ketene during the TPD. In the photodesorption spectra on surfaces with 0.75 ML of acetone at 200 K, desorption of methyl radicals ( $\text{CH}_3$ ) was confirmed. The cross section of the  $\text{CH}_3$  desorption was equivalent to the depletion cross section of the adsorbed acetone estimated from its coverage determined from the TPD peak intensities. The conversion of acetone to the acetate with a cleavage of the C-C bond was concluded. The left panel of Fig. 6 shows  $\text{CH}_3$  photodesorption spectra obtained on the surfaces covered by 0.25 ML of acetone at 105 K. The  $\text{CH}_3$  was not detected on the surface exposed only to acetone as shown in spectrum (a). When the surface was exposed to  $\text{O}_2$  at 95 K and heated to room temperature prior to the exposure to acetone,  $\text{CH}_3$  desorption was observed as shown in (b). Heating the surface used in (b) up to 243 K before UV irradiation gave rise to an over 4-fold increase of the initial yield of the  $\text{CH}_3$  (a component with a faster desorption rate forming the initial spike) as shown in (c). The results indicated the need of  $\text{O}_2$  and the presence of thermal activation barrier in the acetone photooxidation process. The author proposed a process via the intermediate formed by thermal reaction of the acetone and active oxygen species (either O adatom or  $\text{O}_2$  molecules). A linear chain of acetone molecules anchored to the 5-fold-coordinated Ti atom rows and ended by an O adatom was presented as a candidate for the complex [42]. The photooxidation process is illustrated in the right panel of Fig. 6.

Lateral distribution of the complex and its conversion to acetate might be visualized by scanning probe microscopes. The STM [43] and NC-AFM [44] offer sufficiently high spatial resolution to identify individual carboxylate molecules ( $\text{R-COO}^-$ , R = H,  $\text{CH}_3$ ,  $(\text{CH}_3)_3\text{C}$ ,  $\text{HC}\equiv\text{C}$ ,  $\text{CF}_3$ ,  $\text{CF}_2\text{H}$ ) on the  $\text{TiO}_2$  surface as spots with different image heights.

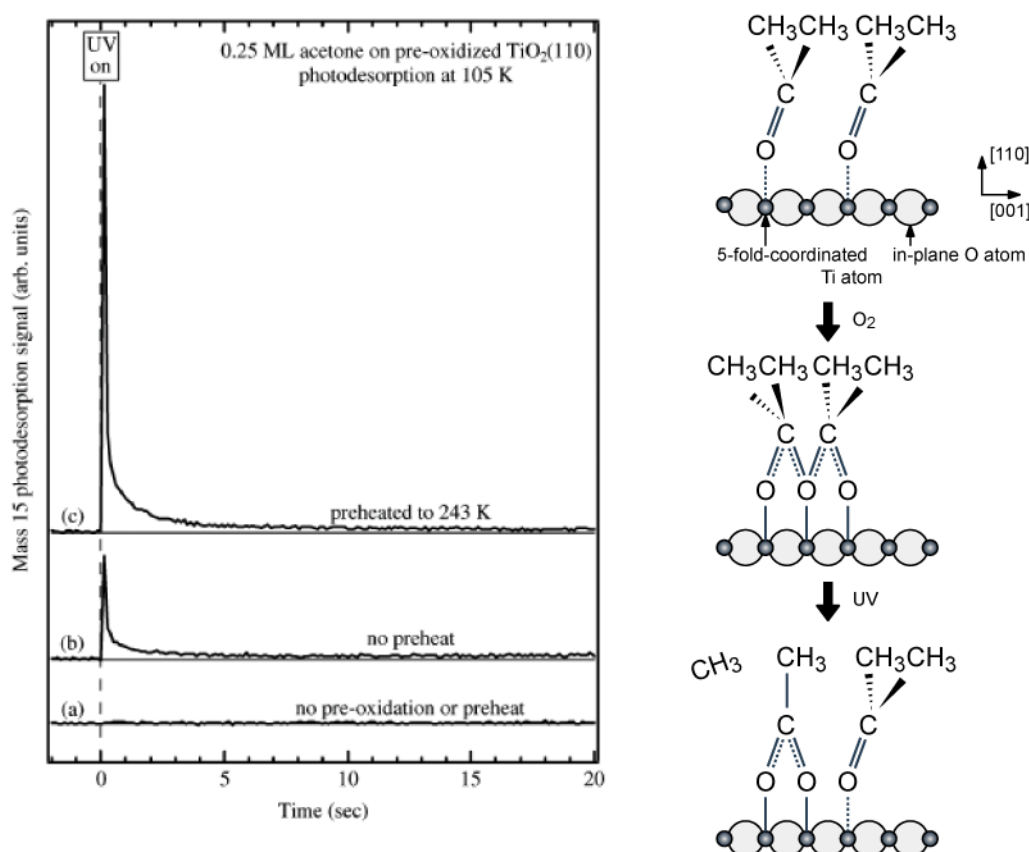


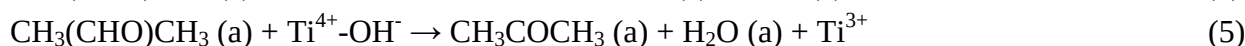
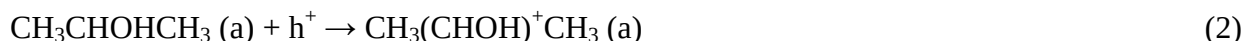
**Fig. 6** Left panel: photodesorption spectra of methyl radical on the  $\text{TiO}_2(110)$  surfaces at 105 K. (a) Surface exposed only to acetone at 105 K. (b) Surface exposed to  $\text{O}_2$  at 95 K, heated to room temperature, and cooled to 105 K for acetone adsorption. (c) Surface (b) heated to 243 K and cooled to 105 K after the acetone adsorption [41]. Right panel: a schematic illustration representing photooxidation of acetone on the  $\text{TiO}_2(110)$  surface.

### Photodehydrogenation of 2-Propanol

2-propanol is one of the probe molecules used to assess catalytic activity and examine reaction dynamics [45, 46]. A rich store of knowledge from previous catalysis research is beneficial when examining the reaction dynamics on model surfaces.

Brinkley et al. examined photoreaction of 2-propanol ( $\text{CH}_3\text{CHOHCH}_3$ ) on the  $\text{TiO}_2(110)-(1\times 1)$  surface [47, 48]. Mixed gas of 2-propanol and  $\text{O}_2$  was introduced to the  $\text{TiO}_2$  surface, and the products in the reflected gas were examined. When the surface was irradiated by UV light ( $h\nu = 3.1\text{--}4.1$  eV), acetone and  $\text{H}_2\text{O}$  were produced with a ratio of 1:1. The reaction probability per collision of the 2-propanol was 0.15. The authors proposed a process in which the trap of the photogenerated electrons by adsorbed  $\text{O}_2$  molecules (Eq. 1) initiated the dehydrogenation of the 2-propanol. The holes were efficiently trapped by the 2-propanol, which reduced the barrier to remove H atoms of the OH group to produce the reaction intermediate  $\text{CH}_3(\text{CHO})\text{CH}_3$  (Eq. 2, 3).

The intermediate was dehydrogenated by OH groups including the bridging O atoms or those on 5-fold-coordinated Ti atoms (Eq. 4, 5).



The designation “(a)” and the bracket stand for an adsorbed species and the bridging O vacancy, respectively. The reaction probability of the 2-propanol increased when the (1×1) surface was annealed prior to the reaction. The increase of the reaction probability was attributed to an enhanced adsorption of O<sub>2</sub> and 2-propanol in the bridging O vacancies. Fig. 7 shows the reaction probability on the surface pre-annealed at 800 K as a function of exposure time to the mixed gas. The reaction probability decreased from 0.15 to 0.09 when O<sub>2</sub> exposure reached 5×10<sup>3</sup> ML (1 ML = 5.2×10<sup>14</sup> cm<sup>-2</sup>). The authors concluded that the decrease of the reaction probability was due to healing of the bridging O vacancies and that the vacancy-free surface was active for the dehydrogenation of the 2-propanol. The surface defects insensitive to the oxidation such as steps and subsurface O vacancies were proposed as possible active sites.

Contribution of subsurface O vacancies to the photochemical reactions, as well as the activity of step edges which was mentioned also in the sections about halomethanes, is an issue to be examined. Titanium dioxide wafers with a controlled dopant concentration might provide some insights into the influence of subsurface defects [49].

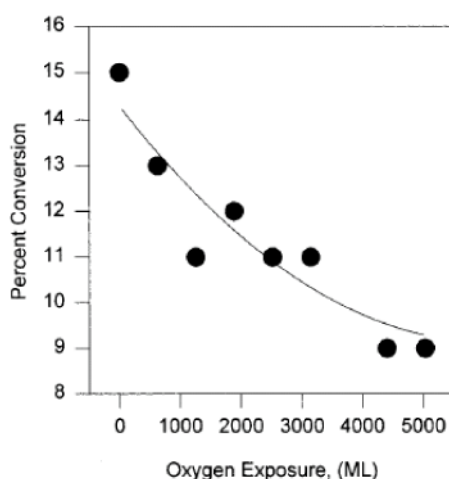


**Fig. 7** Reaction probability of 2-propanol to acetone in a steady state as a function of exposure time to 2-propanol and O<sub>2</sub> flux under UV irradiation at 350 K. 2-propanol = 0.1 ML s<sup>-1</sup>, O<sub>2</sub> = 0.7 ML s<sup>-1</sup> [48].

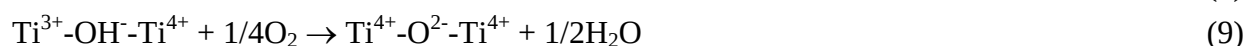
### Photodecomposition of Pivalate

Lateral charge distribution on TiO<sub>2</sub> surface is an important issue closely related to photochemical processes which involve transfer and trapping of photogenerated electrons. Scanning probe microscopes, which detect tip-sample interaction such as tunneling current and atomic force, are powerful analytical tools for atomic-scale surface analysis.

Henderson et al. examined photodecomposition of pivalate ((CH<sub>3</sub>)<sub>3</sub>CCOO<sup>-</sup>) adsorbed on the TiO<sub>2</sub>(110)-(1×1) surface at 280 K [50-52]. A sequence of the STM image at each experimental stage is presented in the left panel of Fig. 8. Image (a) shows the (1×1) surface with the bridging O vacancies of 0.12 ML (1 ML = 5.2×10<sup>14</sup> cm<sup>-2</sup>). The bright lines diagonally crossing the image from the top left to the bottom right are the Ti atom rows, and the spots between the rows are the bridging O vacancies. After exposure to O<sub>2</sub>, 0.09 ML of the vacancies disappeared in the image, and an equivalent number of spots appeared on the Ti atoms rows as shown in image (b). The spots were assigned to O adatoms. Image (c) shows the surface (b) exposed to pivalic acid ((CH<sub>3</sub>)<sub>3</sub>CCOOH) gas at room temperature. Individual spots arranged in a (2×1) periodicity (0.60 nm × 0.65 nm) are the pivalates. The pivalic acid molecule dissociates to the pivalate anion and H<sup>+</sup> on the TiO<sub>2</sub>(110)-(1×1) surface. The pivalates are anchored to two 5-fold-coordinated Ti atoms in a bridge form and are saturated at 0.5 ML. The accompanying H<sup>+</sup> forms a surface OH group on the bridging O atom [53].



A model of the pivalate-adsorbed surface is represented in the right panel of Fig. 8. After irradiation by a Xe arc lamp for 1 hour, 0.33 ML of the pivalates disappeared, and faint spots of 0.17 ML appeared between the Ti atom rows as shown in images (d) and (e). The faint spots were assigned to OH groups bound to 6-fold-coordinated Ti<sup>3+</sup> cations which resulted from trapping of the photogenerated electrons. The increase of the Ti<sup>3+</sup> was monitored by the growth of a broad feature with a maximum at around 0.8 eV in EEL spectra. During the irradiation, an equivalent amount of CO<sub>2</sub> and isobutene ((CH<sub>3</sub>)<sub>2</sub>C=CH<sub>2</sub>) was yielded. After re-exposure to O<sub>2</sub>, the faint spots in STM images disappeared as shown in image (f), and the broad range in the EEL spectra was reduced. The reaction process was proposed as follows:



Uetsuka et al. examined the effect of the Pt loading on the photodecomposition of the pivalate on the TiO<sub>2</sub>(110)-(1×1) surface [54]. Nanometer-sized Pt clusters were prepared on the surface by Pt

evaporation followed by annealing at 920 K. On Pt-free surfaces, the initial rate of the pivalate decomposition, which was estimated from the coverage of adsorbed pivalates in the STM images, was  $0.4 \text{ ML h}^{-1}$  ( $1 \text{ ML} = 2.6 \times 10^{14} \text{ cm}^{-2}$ ) at 280 K. The decomposition stopped when 0.4 ML of the pivalates was consumed. The decomposition rate and the maximum consumption of the pivalate increased with the amount of Pt, and reached  $1.2 \text{ ML h}^{-1}$  and 0.8 ML, respectively, with the Pt clusters of  $8 \times 10^{11} \text{ cm}^{-2}$ . The enhanced decomposition was attributed to the electron trapping of the Pt clusters. Hiehata et al. reported an increase of the work function on the Pt clusters on the  $\text{TiO}_2(110)-(1 \times 1)$  surface after the photodecomposition of the pivalate by using a Kelvin probe force microscope (KPFM) [55]. The KPFM is an applied method of the NC-AFM and provides a lateral distribution of the work function with the surface topography [17, 56, 57]. The work function increase was attributed to the enhanced dipole moment component directed from the vacuum to the surface by electron accumulation to the Pt clusters.

The studies demonstrated that the photogenerated electrons and holes can be tracked in relation to atomic-scale surface structures on the well-defined  $\text{TiO}_2$  surfaces. Controlling the charge distribution on the basis of surface structures such as surface defects, metal cluster sizes, and intercluster distances might be one possible way to optimize the performance of photochemical devices.

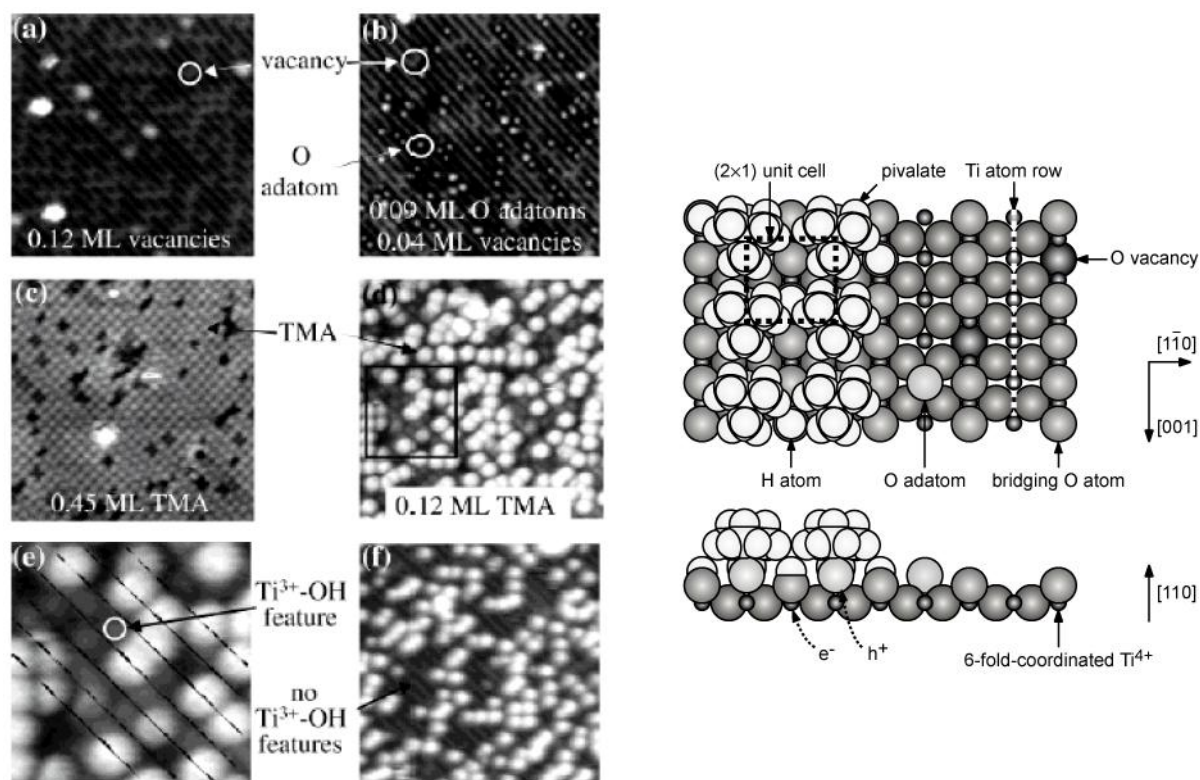


**Fig. 8** Left panel: STM images of  $\text{TiO}_2(110)$  surfaces at 280 K. (a) The  $\text{TiO}_2(110)-(1 \times 1)$  surface. (b) The surface in (a) exposed to 100 L of  $\text{O}_2$ . (c) The surface in (b) after exposure to pivalic acid gas. (d) The surface in (c) after UV irradiation in UHV for 1 h. (e) Close up of the region indicated by a square in (d). (f) The surface shown in (d) after exposure to 100 L of  $\text{O}_2$ . Size of the images is  $16 \text{ nm} \times 16 \text{ nm}$  with exception of image (e) [50]. Right panel: Schematic illustration representing the pivalate-covered surface.



### Electron Transfer from Dye Molecule to TiO<sub>2</sub>

Anodes of dye-sensitized solar cells are one of the major applications of TiO<sub>2</sub> [58, 59]. Electron transfer through overlapping molecular orbitals of the dye and TiO<sub>2</sub> surface is a key step in the solar-to-electricity conversion process and should be controlled by how and where the dye is adsorbed on the surface. However, there has been no way of examining the electron transfer for individual dyes.

Ikeda et al. performed work function measurement on Ru(4,4'-dicarboxy-2,2'-bipyridine)<sub>2</sub>(NCS)<sub>2</sub> (N3) dye-adsorbed TiO<sub>2</sub>(110) surfaces by using the KPFM [60]. The TiO<sub>2</sub>(110)-(1×1) surface was removed from the vacuum chamber after exposure to pivalic acid gas and was immersed in the solution of the N3. The pivalate monolayer protects the (1×1) surface against contaminants from the laboratory air [61]. The set of images in Fig. 9(a) shows the topography and simultaneously obtained work function map of the N3-adsorbed surface in the dark. Bright particles in the topographic images were assigned to the N3 molecules and the aggregates which replaced the pivalates. In the work function map, the areas with larger work function were presented brighter. The work function on the N3 was larger than that on the surrounding pivalate-covered TiO<sub>2</sub> surface by 0.07 V on average. Under visible light irradiation, the work function on 44% of the N3 became smaller than that on the pivalate monolayer by 0.14 eV on average as shown in the images of Fig. 9(b). The authors claimed that the work function decrease was due to the enhancement of dipole moment component directed to the vacuum side, which was caused by the electron injection from the N3 to the TiO<sub>2</sub>. A schematic illustration representing the dipole moments originating from the adsorbed molecules is shown in the right panel of Fig. 9. Trapping of the injected electrons at the 6-fold-coordinated Ti atom bound to the bridging O atoms was assumed. Otherwise, the injected electrons would have been immediately recombined with the cationized N3 molecules.

It was demonstrated that the electron transfer properties of individual dyes can be examined. Correlating the electron transfer to the atomic-scale structure of TiO<sub>2</sub> surfaces and adsorbed dyes may offer clues leading to enhancement of the electron injection efficiency from the dyes on the basis of the electrode surface structures and thereby improve solar cell performance.

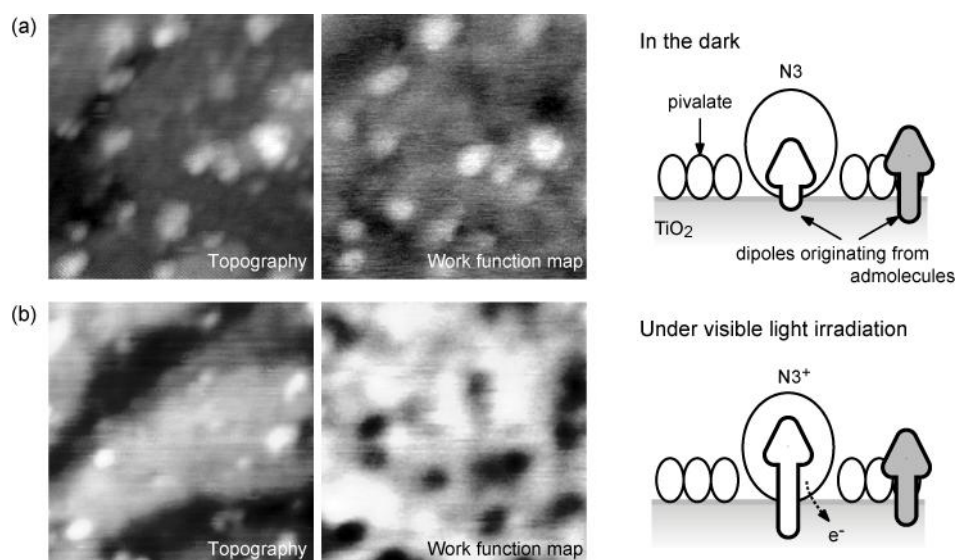


**Fig. 9** Left panels: Sets of topographic images and work function maps of the N3-adsorbed TiO<sub>2</sub>(110) surfaces obtained (a) in the dark and (b) under visible light (30 nm×30 nm). Right panels: Schematic illustration representing the change of dipole moments originating from adsorbed molecules.

### Photodecomposition of Acetic Acid

Band bending in the vicinity of the surface is one of the factors determining the photochemical property of semiconducting TiO<sub>2</sub>. In the band-bending region, the photogenerated electrons and holes are separated by the electric field, and the electron-hole recombination is suppressed.

Idriss et al. examined photodecomposition of acetic acid (CH<sub>3</sub>COOH) on a rutile TiO<sub>2</sub>(001) surface [62, 63]. Two kinds of TiO<sub>2</sub>(001) surfaces with different structures, the {011}-faceted surface and {114}-faceted surface [64], were prepared by flashing to 750 and 900 K in O<sub>2</sub>, respectively, following cleaning by cycles of Ar<sup>+</sup> sputtering and annealing. Models of the (001), (011), and (114) surfaces assuming bulk termination are shown in Fig. 10(a). The three surfaces have different arrangements of the Ti and O atoms in the topmost layer. The surface Ti atoms are all coordinated to four O atoms on the (001) surface, but to five O atoms on the (011) surface. The (114) surface consists of both 4-fold and 5-fold coordinated Ti atoms. A steady flow of acetic acid gas was introduced to the {011}-faceted and {114}-faceted surfaces under UV irradiation ( $h\nu = 3.4$  eV) at 320 K, and products in the gas phase were examined. Ethane (C<sub>2</sub>H<sub>6</sub>), methane (CH<sub>4</sub>) and CO<sub>2</sub> were produced on both surfaces. The formation of C<sub>2</sub>H<sub>6</sub> showed a sharp initial increase due to the consumption of the lattice O atoms of TiO<sub>2</sub>. Fig. 10(b) shows the initial yield of the ethane as a function of the pressure of the acetic acid gas. The {011}-faceted surface provided a larger yield than the {114}-faceted surface did. The authors attributed the difference in activity of the two surfaces to collective properties. Assuming that the identical reaction products on the two surfaces suggested the identical reaction pathway, local arrangement of surface Ti and O atoms was thought to be insufficient to explain the difference in activity. The difference in width of the band-bending

region was proposed as the origin of the different activity. The widths of the band-bending region estimated from the quantum yields of the acetic acid photodecomposition were 18.2 and 6.6 nm for the {011}-faceted and the {114}-faceted surfaces, respectively.

It was shown that the studies on well-defined surfaces highlight the contribution of the band bending to the photochemical processes on  $\text{TiO}_2$  surface. Closer consideration of the effects of the adsorbates and the dopants as well as the arrangement of the ionic Ti and O atoms on the band bending would promote better understanding of the photochemical properties of  $\text{TiO}_2$ .

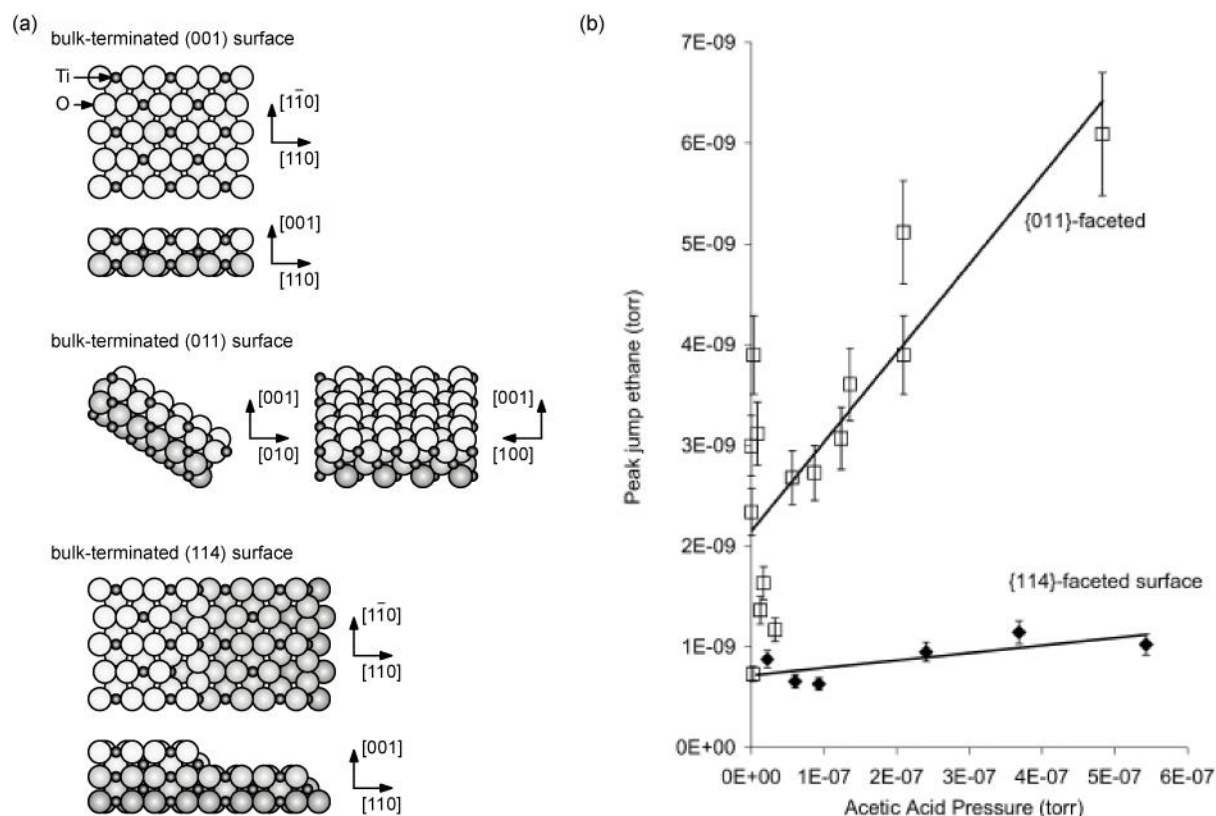


**Fig. 10** (a) Ball models of the rutile  $\text{TiO}_2$ (001) surface, (011) surface, and (114) surfaces. Small and large balls represent Ti and O atoms, respectively. Oxygen atoms are shaded according to their depth. (b) Formation of ethane in steady-state conditions on the {011}-faceted and {114}-faceted  $\text{TiO}_2$ (001) surfaces as a function of acetic acid pressure in an ultrahigh vacuum [63].

## Outlook

The studies introduced here demonstrated that the surface science approach offers deeper insights into the photochemical processes on the  $\text{TiO}_2$  surfaces in relation to atomic-scale surface geometry and local electronic structure. The motivations for the studies originate from the importance of the  $\text{TiO}_2$  in industrial applications as well as pure scientific interest. A future subject is to bridge the fundamental research and industrial applications more firmly by reducing the material gap (differences between the model surfaces and the surfaces of  $\text{TiO}_2$  in industrial uses) and the pressure

gap (difference between UHV for surface science analysis and high-pressure gaseous/liquid environments for industrial application).

The use of epitaxially grown single crystalline anatase TiO<sub>2</sub> films [65-68] would reduce the material gap. Anatase generally shows higher performance as photocatalysts and photoelectrode in comparison to rutile. Preparation of model surfaces in accordance with surface modification methods for photochemical devices may provide novel insights. Photocatalytic activity is sensitive to preparation conditions such as metal-loading methods and redox treatments as well as loaded metals and the loading amount [3, 69, 70]. To reduce the pressure gap, the NC-AFM is one of the promising analytical tools. Atomic scale imaging has been attained in water [71] as well as in an atmospheric pressure gas [72]. In addition to the high spatial resolution, the NC-AFM has potential to derive various tip-surface interactions. Interface-selective nonlinear optical spectroscopy [73] is another powerful analytical method for detailed description of the interface structures.

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# Composite Titanium Dioxide Photocatalysts and the "Adsorb & Shuttle" Approach: A Review

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**Abstract.** Composite photocatalysts, made of titanium dioxide and high surface area adsorbents become more and more common. To large extent, this is due to the phenomenon of "Adsorb & Shuttle", i.e. the adsorption of molecules on the inert, adsorptive, domains, followed by diffusion to the photocatalytic domains.

This manuscript reviews the published literature on composite photocatalysts, and analyzes the various aspects affecting their performance. One of these aspects is the enhancement of the degradation rate of pollutants, which is governed by a variety of factors including surface area, adsorptivity, strength of interaction, the loading of photocatalyst in the composite, and operation parameters (such as temperature, humidity and pH). Other aspects include a reduction in the emission of intermediate products and a different distribution of end-products.

Care was taken to describe the possibility of using the inert adsorptive domains to enhance the degradation of specific species, as well as to discuss the effect of composite photocatalysts on deactivation phenomena, and the interrelation between "Adsorb & Shuttle" phenomena and out-diffusion of oxidizing species from the TiO<sub>2</sub> domains, known as the "remote degradation" phenomenon.

## Nomenclature

### Abbreviations

|                                |                                                                              |
|--------------------------------|------------------------------------------------------------------------------|
| AC                             | : Activated carbon                                                           |
| A&S                            | : Adsorb & Shuttle                                                           |
| BET surface area               | : Specific surface area as measured by the Brunauer, Emmett, Teller isotherm |
| BTEX                           | : Benzene, toluene, ethylbenzene, xylene                                     |
| CNTs                           | : Carbon Nanotubes                                                           |
| CO                             | : Carbon oxide                                                               |
| CO <sub>2</sub>                | : Carbon dioxide                                                             |
| C <sub>s</sub>                 | : Concentration of propionaldehyde in the gas phase                          |
| CB                             | : Chicago Blue Sky 6                                                         |
| D <sub>app</sub>               | : Diffusion coefficient                                                      |
| DIMP                           | : Di-isopropyl methylphosphonate                                             |
| f <sub>ads</sub>               | : Fraction of initial adsorption                                             |
| FTIR                           | : Fourier Transform Infrared spectroscopy                                    |
| HF                             | : Hydrofluoric acid                                                          |
| H <sub>2</sub> O <sub>2</sub>  | : Hydrogen peroxide                                                          |
| H <sub>3</sub> PO <sub>4</sub> | : Phosphoric acid                                                            |
| Hg                             | : Mercury                                                                    |
| ICB                            | : Ionized Cluster Beam                                                       |
| IEP                            | : Iso- Electric Point                                                        |
| IR                             | : Infrared                                                                   |

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|                  |                                                                         |
|------------------|-------------------------------------------------------------------------|
| $K_{ad}$         | : Adsorption coefficient                                                |
| $k_{obs}$        | : Apparent decomposition rate                                           |
| $k_{photo}$      | : Actual rate constant of the photodecomposition reaction               |
| $k_{max}$        | : Maximum apparent rate constant                                        |
| $k_{CO_2}$       | : Mineralization rate constant                                          |
| L-H              | : Langmuir- Hinshelwood                                                 |
| LIF              | : Laser Induced Fluorescence                                            |
| 2MNQ             | : 2-methyl-1,4-naphtoquinone                                            |
| MRS              | : Molecular recognition sites                                           |
| MUA              | : 1,1-mercaptoundecanoic acid                                           |
| MUACu            | : 1,1-mercaptoundecanoic acid whose proton was substituted by $Cu^{+2}$ |
| $N_2$            | : Nitrogen                                                              |
| N                | : The number of $TiO_2$ particles in the film                           |
| NO               | : Nitrogen oxide                                                        |
| $NO_2$           | : Nitrogen dioxide                                                      |
| P25              | : Titanium dioxide, Degussa                                             |
| $P_{ads}$        | : The amount of adsorbed propionaldehyde                                |
| $S_{ads}^{init}$ | : Amount of adsorbed propylamide prior to UV exposure                   |
| SAMs             | : Self-Assembled Monolayers                                             |
| $S_{ad}$         | : Amount of adsorbed propionaldehyde                                    |
| $S_{ad}^{max}$   | : Maximal amount of adsorbed propionaldehyde                            |
| $SiO_2$          | : Silicon dioxide                                                       |
| SA&S             | : Specific Adsorb and Shuttle                                           |
| TEM              | : Tunneling Electron Microscopy                                         |
| $TiO_2$          | : Titanium dioxide                                                      |
| TCE              | : Trichloroethylene                                                     |
| UV               | : Ultraviolet                                                           |
| UV-VIS           | : Ultraviolet-Visible                                                   |
| $V_{film}$       | : The volume of the film                                                |
| XPS              | : X-ray Photoelectron Spectroscopy                                      |

### List of Units

|              |                                   |
|--------------|-----------------------------------|
| $^{\circ}C$  | : Temperature in Celsius degree   |
| $\mu m$      | : Micrometer                      |
| Min          | : Minutes                         |
| $\mu mole$   | : Micromole                       |
| $mW/cm^2$    | : Milliwatt per square centimeter |
| $m^2 g^{-1}$ | : Square meters per gram          |



## 1. Introduction

Photocatalysis is a promising scientific field, whose technological aspects include treatment of contaminants in aqueous solutions, gas phase or even on solid surfaces.[1] The general scheme for the photocatalytic destruction of organics by titanium dioxide, considered to be the photocatalyst of choice, involves the excitation of the photocatalyst by irradiation with supraband gap photons, charge separation and migration of the electrons and holes to the surface of the photocatalyst. There, the holes are trapped by  $\text{H}_2\text{O}$  or  $\text{OH}^-$  adsorbed at the surface, thus forming hydroxyl radicals.[2] For most organic materials, destruction occurs through an oxidation mechanism where the hydroxyl radicals attack the organic compound to give organo radicals that undergo secondary reactions to form  $\text{CO}_2$  and water,[3] although reductive mechanisms are possible in the case of perhalogenated compounds.

A major obstacle for large scale implementation of photocatalysis stems from the fact that photodegradation kinetics depends to large extent on the adsorption coefficient of the contaminants on the photocatalyst surface, such that it is extremely difficult to photodegrade molecules that hardly adsorb on the polar  $\text{TiO}_2$ . Unfortunately, many hazardous contaminants, in particular contaminants of low polarity, belong to this category. Moreover, in practice, the effluents that are needed to be treated contain several contaminants that compete on the adsorptive sites of the photocatalyst, thus limiting the validity of laboratory scale, single component experiments, for practical use. These problems can be aggravated by lack of control on the formation of harmful by-products and toxic intermediates.

Attaching photocatalyst particles to inert domains may assist in improving the efficiency of the photocatalytic process. The basic concept, termed as “Adsorb & Shuttle” (A&S), is based on using the inert domains for adsorbing target compounds that otherwise hardly adsorb on the photocatalyst. That way, a reservoir of the contaminants within a small distance from the photocatalytic sites is formed. Once adsorbed in the vicinity of the photocatalyst, the target molecules may surface-diffuse to the photocatalytic sites as shown schematically in Fig. 1.

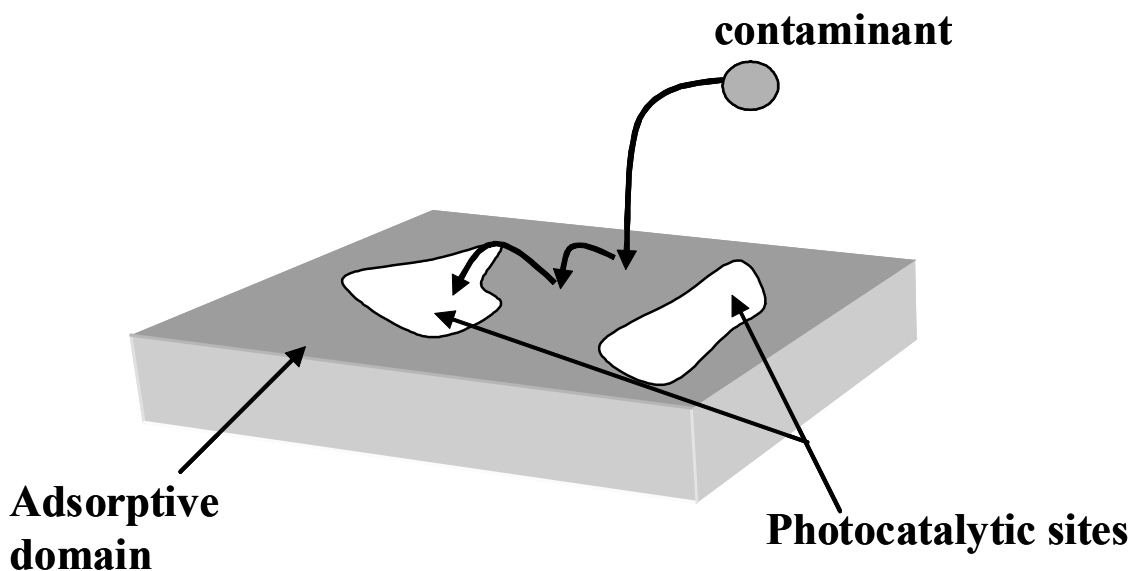


**Figure 1.** The concept of Adsorb and Shuttle

Composite photocatalysts as a means for overcoming mass transport problems have become popular in recent years both in the academia and in the industry. A demonstration of this trend is presented in Fig. 2, which depicts the ratio of the number of articles on composite materials containing titanium dioxide that were used for photocatalysis versus the total number of publications on photocatalysis with titanium dioxide. The results presented in this Figure were

acquired by counting hits upon using SciFinder as our search engine, having "Titanium Dioxide", "Photocatalysis", and "Composites" as keywords. It is likely that other search engines might give different number of hits. Yet, regardless of the actual numbers, the monotonically increase in the popularity of this approach cannot be denied. Taken the vast increase in the scientific interest on titanium dioxide photocatalysis in the last two decades, this continually growing percentage reflects an impressive growth in the number of manuscripts dedicated to the use of inert supports in photocatalysis. It is for this reason that we have decided to discuss this issue at length.

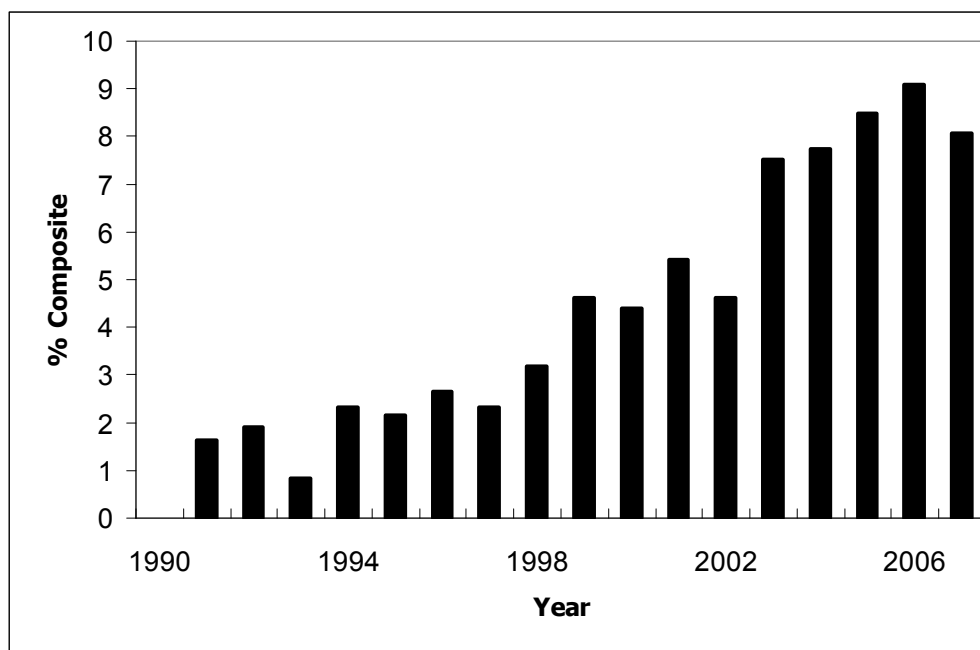


**Figure 2.** The percentage ratio of manuscripts on  $\text{TiO}_2$  photocatalysis by composite materials to that of the total number of manuscripts on titanium dioxide and photocatalysis.

The following review paper summarizes the work done so far on the interplay between inert domains and photocatalytic domains. Accordingly, it concentrates on cases where it is possible to define specific domains of the inert materials. Thus, it does not refer to the massive research done on doping of titanium dioxide, which is characterized by low content of dopants, delicate spread of these constituents and, for most cases, by electronic and photoelectronic effects rather than mass transport effects.

The manuscript is divided into the following sections:

2. Preparation and characterization of composite photocatalysts
  - 2.1 Type of inert supports
  - 2.2 Preparation methods
  - 2.3 Surface area and its effect on adsorptivity
  - 2.4 Film thickness
3. Photocatalytic experiments
  - 3.1 Compounds used as model contaminants
  - 3.2 Enhancement of degradation rate
    - 3.2.1 adsorptivity and surface area
    - 3.2.2. loading
    - 3.2.3 domain size
    - 3.2.4 crystallinity of the inert support
    - 3.2.5 temperature of operation
    - 3.2.6 humidity

- 3.2.7 pH
- 3.3 Formation of intermediate products
- 3.4 Formation of end-products
- 3.5 Preferential degradation
- 3.6 Deactivation
- 3.7 Effects on the inert adsorbents
- 4. "Adsorb & Shuttle" versus "Remote Degradation"
- 5. "Adsorb and Shuttle" with visible light
- 6. Practicality aspects
- 7. Conclusions

This scheme represents our will to try to generalize the large number of papers dedicated to composite photocatalysts, in a manner that will assist the readers to engineer the right material for their end-use. To large extent, this review is a snap-shot of the current situation in the field, a situation that if examined by the current intensive work can change quite rapidly.

## 2. Preparation and Characterization of Composite Photocatalysts

The type of inert supports used in composite photocatalysts as well the preparation procedure govern the photocatalytic properties of the composite photocatalyst. Although these two factors are often coupled we will try to discuss them separately.

**2.1 Type of inert supports.** The number of materials used as inert adsorbents in composite photocatalysts is remarkably low, taken the large number of manuscripts on composite photocatalysts. These materials can be classified into four main groups, namely carbonaceous materials, oxides, metals and polymers. Among the various carbonaceous materials, often used for treating chlorinated compounds, one may find activated carbon (AC)[4],[5] (probably the most common adsorbent), fullerenes, graphite, and carbon nanotubes.[6] Historically, activated carbon was one of the first adsorbents to demonstrate the concept of "Adsorb & Shuttle" [5],[7]. Moreover, it was found that a slurry containing activated carbon particles together with titanium dioxide may show enhanced degradation rates, even when no active measures are taken to assure good adherence between the two components, due to a strong interaction inferred from a reduction in the overall accessible area for adsorption.[8]

The group of oxides includes mainly zeolites[9],[10], silica,[11] and alumina,[10] out of which zeolites are probably the most abundant. Fig. 3 presents the number of manuscripts on composite photocatalysts utilizing activated carbon and zeolites as a function of the year of publication. The data for this Figure was collected by using SciFinder as a database source. Both inert substrates are the most abundant within their classes. It is evident that the interest in both has grown significantly since the beginning of the nineties. Some stagnancy in the scientific interest in photocatalytic composites containing zeolites over the last seven years is noticed, which is in contrast to the continuing growth in the scientific and technological interest in AC composites. Generally speaking, carbonaceous materials are characterized by relatively high surface area and high adsorption energy but poor adherence to the photocatalyst, whereas the oxides tend to adhere well to the photocatalyst, however, at certain cases, at the expense of lower absorbability of the model contaminants. As will be discussed at length in part 3.2, high adsorption energy, leading to high adsorbed amounts of model contaminants does not guarantee a high photodegradation rate. In that sense, the constantly growing interest in AC composites may reflect their low cost on one hand and the development of means to improve the adherence between the two components on the other.

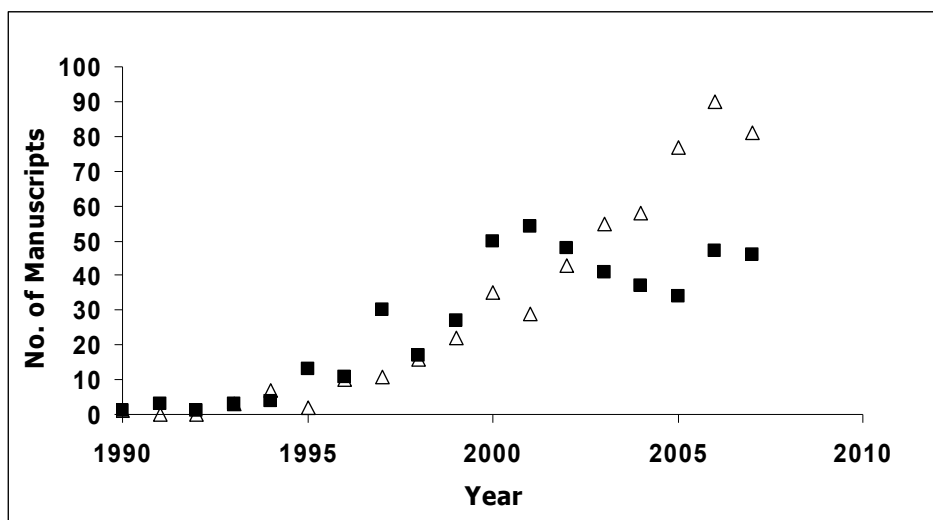


**Figure 3.** The number of manuscripts on composite photocatalysts utilizing activated carbon (empty triangles) or zeolites (filled squares) as inert adsorbents as a function of the year of publication.

If one omits cases where metals were used as dopants (cases that are beyond the scope of this review, as mentioned above), it will be noticeable that metals are utilized almost solely in the context of preferential degradation (see part 3.5). Here, they are not used to directly adsorb the model contaminants but rather for the irreversible chemisorption of Self-Assembled Monolayers (SAMs) which serve as physisorption sites for the contaminants.

Particles of titanium dioxide partially coated with a hydrophobic organo-silicone layer were found to be very efficient in the photocatalytic destruction of permethrin, a water insoluble pesticide. The use of polymers as inert substrates has many prospects but at the same time suffers from severe limitations.[12] Organo-silanes and polymers may provide an easy way to load the photocatalyst particles. Their adsorptive performance, in terms of surface area and specific affinity, can be controlled and even "tailored" to large extent, and above all, they may provide an adequate solution in cases where an irregular shape is needed or in cases where low-temperature preparative procedures are required. A major drawback of polymers and other organics attached directly to the photocatalyst to increase the sticking coefficient of contaminants is their tendency to be degraded by photocatalysis. One way to overcome this problem is to maintain a physical barrier between the photocatalyst particles and the polymeric supports. For example, magnesium carbonate microtubes, onto which titanium dioxide particles were loaded, served as barriers between photocatalyst particles and an outer polyvinyl alcohol matrix.[13] Accordingly, it was possible to decompose 2-propanol without any significant degradation of the outer matrix.

**2.2 Preparation methods.** The preparation of the composite photocatalysts requires proper procedures that will assure good adherence between the photocatalyst and the inert substrate, while maintaining a high surface area. For most cases this is achieved by in-situ preparation (by a sol-gel method, for example) of one of the constituents, usually the photocatalyst. Such processes may include thermal treatment at appropriate temperatures (usually between 300 °C and 650 °C), needed in order to displace solvents and commonly used chelating agents (such as acetylacetone), and, more important, to form the active anatase phase. An interplay between the inert substrates and the nascent titanium dioxide is expected, as indeed observed by Jung et al.[14], who reported that fixation of amorphous silica with titanium dioxide increased the thermal stability of the photoactive anatase phase. It is noteworthy that in the sol-gel preparation methods, the calcination step, which is essential in order to get the photoactive anatase phase, might reduce the surface area of the inert component. However, this reduction in the surface area is often balanced by the improved

crystallinity of the photocatalyst, provided that the temperatures of calcination remain below the anatase to rutile phase transition temperature. A nice demonstration of this claim was presented by Harada et. al.[15], where the activity of activated carbon loaded with sol-gel prepared titanium dioxide was measured as a function of the calcination temperature in the 300 °C – 450 °C range.

A relatively easy way to obtain good adherence between the photocatalyst and activated carbon is by an in-situ hydrothermal preparation of the titanium dioxide. That way, a Ti-O-C bond was claimed to be formed.[16] Supercritical treatment with isopropanol was also used in a quest for a way to get good coupling between the photocatalyst and activated carbon, but the mineralization rates compared with those of a mixture made of AC and TiO<sub>2</sub> were better by no more than 50%.[17] Alternatively, it is possible to prepare a thin layer of inorganic carbon in-situ, for example by thermal carbonization of poly(vinyl alcohol) under N<sub>2</sub> environment.[18]

Even when pre-prepared titanium dioxide particles are being used, thermal treatment is often done to improve the adherence between the two components. One of the ways to reduce the temperature needed for adherence between the photocatalyst and the inert support is by using the Ionized Cluster Beam (ICB) method, where a cluster beam of ionized titanium is oxidized by gaseous oxygen at a temperature as low as 250 °C and deposited in-situ on inert substrates such as activated carbon fibers and porous silica.[19]

The preparation method of the activated carbon was found to be an important parameter governing the enhancement ratio. High enhancement ratios (as high as 2.5 in the degradation of phenol and 4-chlorophenol)[20] were obtained with ACs that were prepared by physical treatment (CO<sub>2</sub> or steam) whereas no synergism (and in fact a detrimental effect) was found with ACs that were prepared by chemical treatments with H<sub>3</sub>PO<sub>4</sub>. Here, a correlation between low dry ash content and enhancement was found, suggesting the existing of a detrimental doping effect. No correlation could be found between the BET surface area of the various ACs and their enhancement factor.

It is noteworthy that in certain cases the presence of the inert constituent (or its precursor) affects the properties of the nascent photocatalyst. For example, fixation of amorphous silica within the titanium dioxide domains[14] increased the thermal stability of the anatase phase, such that the phase transition from anatase to rutile was retarded even at temperatures as high as 800 °C. Likewise, it was found that the crystalline phase of the titanium dioxide was affected not only by the type of precursor (using titanium ammonium oxalate led to the formation of pure anatase whereas using titanium trichloride directed towards the formation of an anatase - rutile mixture) but also by the type of activated carbon that was used.[15]

Another means to form composites fibers containing titanium dioxide is electrospinning, a relatively simple method, based on electrostatic surface charging of a viscous solution, drawing a jet moving at a high speed towards a grounded stationary or rotating surface. This technique has already been used to fabricate TiO<sub>2</sub> nanofibers,[21] and was extended to the formation of fibers containing both titanium dioxide and polymers such as poly(vinyl alcohol)[22] or poly(acrylonitrile).[6]

**2.3 Surface area and its effect on adsorptivity.** Loading high surface area adsorbents with photocatalytic titanium dioxide decreases significantly the surface area of the adsorbent even at low loading, due to clogging of nano-pores at their necks.[23] Accordingly, adsorptivity is also reduced in comparison with the adsorptivity of the bare adsorbent (see Fig. 6). The extent of reduction in the surface area is usually higher when the titanium dioxide is formed in-situ from a viscous liquid phase, for example by a sol-gel process, as the high viscosity of the liquid helps in bridging over small cavities.

In theory, the connection between surface area and adsorptivity (and eventually enhanced degradation rates) is clear and sensible, and yet a systematic reading of the data that appears in the literature reveals a much complex situation. Surface area is usually measured by BET isotherm, using small molecules such as nitrogen that are quite different in size and shape from the model contaminants used in the photocatalytic measurements. Unlike the almost spherical nitrogen molecules, the model contaminants are usually non-symmetrical, hence their area per molecule

depends heavily on their packing and orientation relative to the surface. This, in turn, is a function of the chemical and physical properties of the surface. It is difficult to expect that a nearly planar aromatic molecule will adsorb on a graphitic substrate in the same orientation as it does on alumina, for example. For this reason, not only that the calculated BET surface area cannot serve to get an accurate estimation of the number of adsorbed model contaminants but in fact it cannot provide it even on a relative scale. This problem is aggravated in porous substrates, manifested through BET isotherms of types IV or V and a noticeable hysteresis during an adsorption – desorption cycle.

**2.4 Film thickness.** In a non-composite film of  $\text{TiO}_2$  the absorption of UV light takes place over 0.5-2  $\mu\text{m}$ , depending on the type and porosity of the medium, as well as on the wavelength that is used. The efficiency of the photocatalytic process depends to large extent on the odds that the charge carriers will reach the surface, where the contaminants are adsorbed. These odds are expected to become smaller as the diffusion length is increased.

The deleterious effect of thickness might be aggravated when composites, made of photocatalyst particles embedded in an inert adsorptive matrix, are being used, since the matrix might prevent the migration of the charge carriers to the film surface. The situation is obviously worsened if the inert support itself absorbs UV light in a dissipative manner, thus reducing the number of photons available for photocatalysis, to the extent that might eliminate the effect of the A&S mechanism. For this reason, it is expected that the optimal thickness of a photocatalytic film made of a composite material would be lower than the optimal thickness of a film consisting solely titanium dioxide. Indeed, an adverse effect of the film thickness on the degradation kinetics of gaseous pyridine was observed with a  $\text{TiO}_2$  / mordenite composite film.[9]

### 3. Photocatalytic experiments

The photocatalytic activity of the composite photocatalysts was assessed by probing degradation kinetics and product distribution of model contaminants in air or in water. It was established that composite photocatalysts affect not only the degradation rates, but also the distribution of intermediate products as well as the end products. The extent by which these effects are manifested is governed by a large number of factors such as the surface area, the adsorptivity of the surface, the loading, the domain size and even operational parameters of the experiments such as humidity or temperature. In the following part the various factors will be analyzed, based on the partial data that was gathered so far. It is noteworthy that in most cases the comparison was made between the composite and titanium dioxide that was prepared in the same manner as the composite photocatalyst. While this may provide a good impression on the basics of the various effects it does not tell much on the actual benevolent effect, since for a commercial use the comparison should be made against a benchmark product.

Several works put their focal point not at the photocatalytic degradation pre-se but on the inert adsorptive substrates, while using photocatalysis as a means to regenerate the adsorptive substrates. [24],[25] Distinguishing between regenerating and the enhanced efficiency is not just a semantic matter, as it has definitive practical implications. One of these implications is the development of systems in which adsorption takes place continuously, whereas exposure to UV light is done periodically. Such periodic photocatalysis step can be achieved either by using the natural day-night cycles, or by the use of shorter, artificially controlled, cycles, found to increase the quantum photoefficiency of titanium dioxide.[26]

To date, most of the attention put into the photocatalytic “adsorb & shuttle” approach was concentrated in enhancing the photodegradation efficiency, and not into analyzing whether the introduction of inert supports affects other aspects, such as the appearance of intermediates, the distribution of products, and the differentiation between co-existing contaminants. However, the introduction of adsorbents into the system may alter the performance also in these aspects, as will be discussed in parts 3.3-3.5

**3.1 Compounds used as model contaminants.** The number of compounds served as model contaminants in comparative experiments with composite photocatalysts is quite large. Among the model contaminants one may find propionaldehyde[27], pyridine[9], dye stuff[16], herbicides[5] and insecticides, ions of heavy metals like mercury[28] and chromium[16], simulants of nerve gases, chlorinated compounds such as 1,2-Dichloroethane[19] and many more classes. Some of these model contaminants were selected based on previous knowledge about the difficulty they have to be adsorbed on titanium dioxide (rhodamine 6G and per-chlorinated compounds, for example), while others were selected without any clear (or at least declared) reason. It is very rare to find manuscripts where the subject of research was the different behavior of various contaminants that were degraded under the same conditions on the same composite photocatalyst. Still, some information can be achieved from the few cases where streams containing several contaminants were studied (these few cases are reviewed below). At any case, although a detailed comparison is therefore unlikely to be achieved with present data, some useful comparative information can still be obtained and is presented implicitly in the various sections of this manuscript.

**3.2 Enhancement of degradation rate.** Based on an analysis of the published literature it can be claimed that the most popular benefit of using composite photocatalysts is an enhancement in the degradation rate of contaminants, as deduced by measuring the concentration of the contaminants either directly or indirectly. This enhancement is often analyzed quantitatively by using an enhancement factor (also called enhancement ratio) defined (for an apparent first order kinetics) as the ratio between the rate constant with the composite photocatalyst to the reaction rate constant with titanium dioxide having the same weight as the  $\text{TiO}_2$  in the composite. Under this definition, the enhancement factor given in the literature is usually between 2 to 7. One of the systems found to have high enhancement factor is that of Park et. Al., who used ordered mesoporous carbon, attached to titanium dioxide.[29] Here, the ordered mesoporous structure was prepared by HF etching of a silica-rods template, around which active carbon was formed from furfuryl alcohol. A pseudo first order constant larger by a factor of 5 than that of P25 was found in the degradation of Rhodamine 6G, known to have very low adsorption on titanium dioxide. It is noteworthy that some of the effect could be attributed to the presence of fluorine ions which remained on the surface of the activated carbon from the preparative step of silica etching. Another highly efficient composite photocatalyst is that of Ao et. Al., where the removal efficiency for multiple indoor air pollutants with  $\text{TiO}_2/\text{AC}$  was (under certain operational conditions, such as high humidity and short contact time) 7 times higher than that with  $\text{TiO}_2$ . [30]

The enhancement ratio depends on a large number of parameters, some of which reflect the characteristics of the photocatalyst, while other reflect the experimental conditions. This way of dividing is somehow arbitrary, as the two classes of factors are often coupled. Among the governing parameters one may outline the adsorptivity difference (per unit of area) between the inert domains and the photocatalyst, the specific area of the inert part, the relative loading (gram per gram) of the photocatalyst versus that of the inert constituent, the diffusivity of contaminants on the inert substrates (and / or the diffusivity and life-time of light-induced active oxidizing species), and, in connection to that and to the loading, also the average diffusion distance that the contaminants (or any other active species) have to travel in order to reach the photocatalyst' domains. Operational parameters include for example, temperature, humidity, pH, and contact time. The following parts summarize the current knowledge on the effect of these parameters on the extent of enhancement.

**3.2.1 Adsorptivity and surface area.** The adsorption isotherms on composite particles, as well as photodegradation kinetics on these substrates, behave quite often in a Langmuir-Hinshelwood (L-H) manner. Although L-H kinetics do not necessarily imply a surface reaction[31], such a behavior is usually considered to be an indication for a surface reaction.

**Table 1:** The various photocatalysts used in the degradation of propyzamide, amount of adsorbed propyzamide prior to UV exposure ( $S_{\text{ads}}^{\text{init}}$ ), and the fraction of carbons in un-decomposed propyzamide, photoproducted intermediates and the final product  $\text{CO}_2$ , as measured at a time corresponding to production of 50% of the propyzamide's carbon. [based on ref. [32]].

| photocatalyst                   | $S_{\text{ads}}^{\text{init}}$<br>( $\mu\text{mol g}^{-1}$ ) | Irradiation<br>time (min) | Fraction of carbons contained in<br>given species (%) |               |               |
|---------------------------------|--------------------------------------------------------------|---------------------------|-------------------------------------------------------|---------------|---------------|
|                                 |                                                              |                           | propyzamide                                           | Intermediates | $\text{CO}_2$ |
| Naked $\text{TiO}_2$            | 0.44                                                         | 480                       | 0                                                     | 49.0          | 51.0          |
| $\text{TiO}_2/\text{mordenite}$ | 4.41                                                         | 110                       | 13                                                    | 38.5          | 48.5          |
| $\text{TiO}_2/\text{SiO}_2$     | 7.53                                                         | 100                       | 12.1                                                  | 35.8          | 52.1          |
| $\text{TiO}_2/\text{AC}$        | 27.9                                                         | 85                        | 34.9                                                  | 14.6          | 50.5          |

One of the first works on the correlation between adsorptivity and A&S effects is that of Torimoto et. al.[32], who calculated the adsorption coefficients of propyzamide (Table 1), based on a measured L-H behavior. As presented in the Table, the amount of adsorbed propyzamide prior to UV exposure ( $S_{\text{ads}}^{\text{init}}$ ), which roughly represents the relative adsorptivity, was inversely correlated with the time needed to mineralize 50% of the propyzamide's carbon to  $\text{CO}_2$ ; the higher the adsorptivity was, the lower was the time needed for this extent of recovery.

A seminal work on the relation between adsorptivity and the enhancement factor was performed by Takeda et. Al.[33] who measured the apparent diffusion coefficient of propionaldehyde on composite films made of  $\text{TiO}_2/\text{mordenite}$ ,  $\text{TiO}_2/\text{silica}$ ,  $\text{TiO}_2/\text{ferrierite}$ ,  $\text{TiO}_2/\text{alumina}$ ,  $\text{TiO}_2/\text{activated carbon}$ , and four composites made of  $\text{TiO}_2$  and zeolites. An apparent diffusion coefficient ( $D_{\text{app}}$ ) was calculated by measuring the degradation rate of the contaminant upon irradiating one tenth of a  $\text{TiO}_2$ - loaded film onto which the contaminant was pre-adsorbed. As presented in Table 2,  $\text{TiO}_2/\text{ferrierite}$  and  $\text{TiO}_2/\text{activated carbon}$  possessed high adsorbability ( $f_{\text{ads}}$ ) for propionaldehyde, yet their  $D_{\text{app}}$  was much smaller than that of  $\text{TiO}_2/\text{mordenite}$ , which had a lower adsorbability, thus supporting the notion that too high adsorption energies might act to reduce surface diffusion. On the other hand, there were cases ( $\text{TiO}_2/\text{zeolites}$ , for example), in which the adsorbability was low, and yet not only that  $D_{\text{app}}$  was not high, but in fact was quite low. This suggested that  $D_{\text{app}}$  was not governed solely by adsorbability but rather by a variety of factors (including adsorbability).



**Table 2:** Fraction of initial adsorption of propionaldehyde ( $f_{\text{ads}}$ ), apparent decomposition rate based on exposure of the total area ( $k_{\text{obs}}$ ), and apparent diffusion coefficient ( $D_{\text{app}}$ ) for various composite  $\text{TiO}_2$  photocatalysts [based on ref. [33]]

| Photocatalyst                     | $f_{\text{ads}}$ | $k_{\text{obs}}$ | $D_{\text{app}}$ |
|-----------------------------------|------------------|------------------|------------------|
| $\text{TiO}_2$ / mordenite        | 0.92             | 1.5              | 2.5              |
| $\text{TiO}_2$ ./ silica          | 0.83             | 1.3              | 1.9              |
| $\text{TiO}_2$ / ferrierite       | 0.98             | 0.77             | 1.0              |
| $\text{TiO}_2$ / alumina          | 0.84             | 0.97             | 0.96             |
| $\text{TiO}_2$ / activated carbon | 0.95             | 0.68             | 0.91             |
| $\text{TiO}_2$ / zeolite X        | 0.83             | 0.33             | 0.40             |
| $\text{TiO}_2$ / zeolite A(4)     | 0.84             | 0.25             | 0.28             |
| $\text{TiO}_2$ / zeolite A(3)     | 0.65             | 0.22             | 0.26             |
| $\text{TiO}_2$ / zeolite A(5)     | 0.66s            | 0.15             | 0.25             |

Under the assumption that round particles of  $\text{TiO}_2$  are evenly spread within the adsorbent matrix a model was developed, connecting the apparent decomposition rate based on exposure of the total area ( $k_{\text{obs}}$ ), the fraction of initial adsorption of propionaldehyde ( $f_{\text{ads}}$ ), the diffusion coefficient ( $D$ ), the actual rate constant of the photodecomposition reaction on the  $\text{TiO}_2$  particle ( $k_{\text{photo}}$ ), the number of  $\text{TiO}_2$  particles in the film ( $N$ ), and the film volume ( $V_{\text{film}}$ ). According to this model

$$\frac{f_{\text{ads}}}{k_{\text{obs}}} = \frac{1}{k_{\text{max}}} + \frac{V_{\text{film}}}{4\pi RND} \quad (1)$$

where  $k_{\text{max}}$  is the maximum apparent rate constant, obtained when all contaminants are adsorbed on the adsorbent, and given by

$$k_{\text{max}} = \frac{4\pi R^2 N k_{\text{photo}}}{V_{\text{film}}} \quad (2)$$

Quite impressively, plotting  $f_{\text{ads}}/k_{\text{obs}}$  versus  $1/D_{\text{app}}$  for the set of adsorbents, reflecting a wide range of adsorbate – adsorbent interactions, gave a high fidelity straight line, in accordance with the model. It is noteworthy that the way the experiments were done could not, in principle, negate the possibility that the observed diffusion- controlled degradation rates were not due to diffusion of contaminants from the darkened area to the exposed area but rather due to diffusion of oxidizing species from the exposed area to the darkened one (see below, part 4). Nevertheless, if this was the case here, and the degradation was indeed governed by out-diffusion of oxygenating species, one could have expected the correlation between  $f_{\text{ads}}$ ,  $k_{\text{obs}}$  and  $D_{\text{app}}$  to be very different from the one predicted by the propionaldehyde diffusion model, which was found to be so successful.

The same group has studied later [34] also the degradation of propionaldehyde over a variety of hybrid photocatalysts. A Langmuir- Hinshelwood kinetics manifested by

$$\frac{C_s}{S_{ad}} = \frac{C_s}{S_{ad}^{max}} + \frac{1}{K_{ad} S_{ad}^{max}} \quad (3)$$

was observed. Here,  $C_s$  is the concentration of propionaldehyde in the gas phase,  $S_{ad}$  is the amount of adsorbed propionaldehyde,  $S_{ad}^{max}$  is the maximal amount of adsorbed propionaldehyde, and  $K_{ad}$  is the adsorption constant. Fig. 4 presents the first order mineralization rate constant ( $k_{CO_2}$ ), normalized by the amount of adsorbed propionaldehyde ( $P_{ads}$ ), versus the adsorption coefficient ( $K_{ad}$ ). Each point in the graph represents a different inert co-substrate. It is evident that the mineralization rate constant increases with the adsorption constant up to a maximal value and then decreases when the adsorption coefficient is too high. To explain these results it was proposed that in cases where the adsorption constant was low, the decomposition rate was determined by the amount of adsorbed contaminant, while in cases where the adsorption constant was very high, plenty of adsorbed molecules could be found on the support, yet, the degradation rates were low due to insufficient mobility. For this specific case the highest mineralization rates were obtained with composites having inert substrates of mordenite and silica, onto which the apparent diffusion coefficient of propionaldehyde was app.  $2.5 \times 10^{-4} \text{ cm}^2 \text{ s}^{-1}$ .

As mentioned before, too strong interaction between the adsorbate and the adsorbent might harm the diffusibility of the contaminant, thus canceling any synergistic effect. This was exactly what was found to happen when the photodegradation of dichloromethane on a composite photocatalyst consisting of titanium dioxide and activated carbon was studied.[4] Here, the rate of  $CO_2$  production was found to decrease monotonically with the increasing of the mass ratio of activated carbon in the composite photocatalyst, even when the comparison was made on an equal amount of  $TiO_2$  basis. In other words, not only that adding the inert adsorbent did not have any benevolent effect on the degradation rate, but, in fact, it competed against the photocatalyst, thus reducing the mineralization rate instead of enhancing it. It is noteworthy that the mineralization rate with a suspension made of a mixture of  $TiO_2$  particles and activated carbon particles gave worse results, thus suggesting that part of the decrease in the mineralization rate incurred by the competitive adsorption was removed upon adhering the activated carbon and the titanium dioxide.

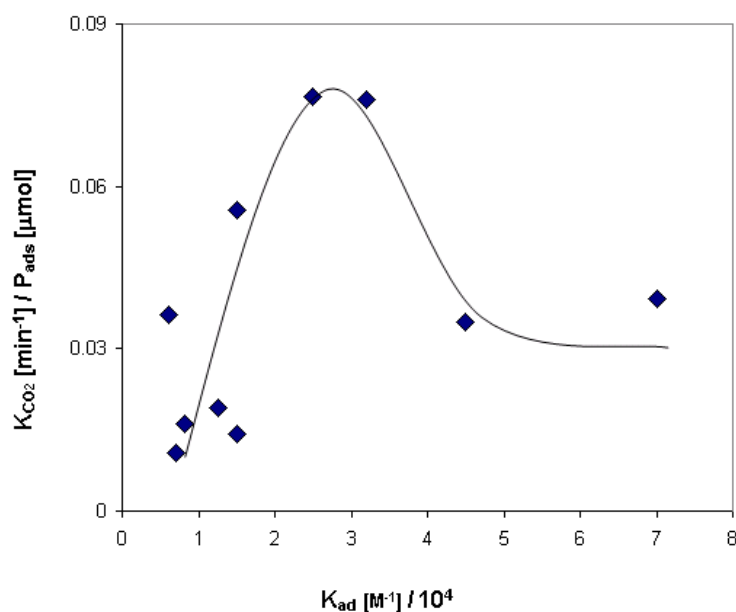


**Figure 4:** The mineralization rate constant ( $k_{CO_2}$ ) of propionaldehyde on a variety of composite photocatalysts, normalized by the amount of adsorbed propionaldehyde ( $P_{ads}$ ), versus the adsorption coefficient ( $K_{ad}$ ) [based on data from ref. [34]].

**3.2.2. Loading.** As can be expected, the A&S effects vary significantly with the loading, as the loading has an impact both on the surface area and on the averaged diffusion distance (at a constant domain size). The optimal values span quite widely. For example, in the case of photodegradation of acetophenone by a composite consisting of  $\text{TiO}_2$ -Zeolite A, the rate constant under UV without a cutoff filter was found to be constant so far as the loading of titania was above a few percents.[10] In contrast, the optimal loading of titania in a  $\text{SiO}_2$ - $\text{TiO}_2$  composite used for degrading Rhodamine 6G was as high as 30% [11], or even 50% as was found for the degradation of propionaldehyde by a composite consisting of mordenite and titania.[27].

We are not aware of any systematic work which tried to correlate between the optimal loading and the type of contaminant. Nevertheless, it is sensible that the optimal value depends not only on the type of inert support but also on the type of contaminant. Strong interaction between the adsorbate and the adsorbent are likely to push the optimum loading towards low loading, since high loading of the inert material might require a diffusion distance which is too large for a strong adsorbate.

The effect of loading is not only through a possible change in the required diffusion distance but can occur through changes in the structure or morphology of the composite photocatalyst. In this context, it is worth mentioning that the optimal loading of silica in a composite photocatalyst used to photodegrade trichloroethylene (30%), was attributed to the fact that at this loading the average pore size and pore volume were the highest.[14] Apparently, the surface area played here a less important role, since the BET surface area was found to increase monotonically within the range of measurements, i.e. 0-50%.

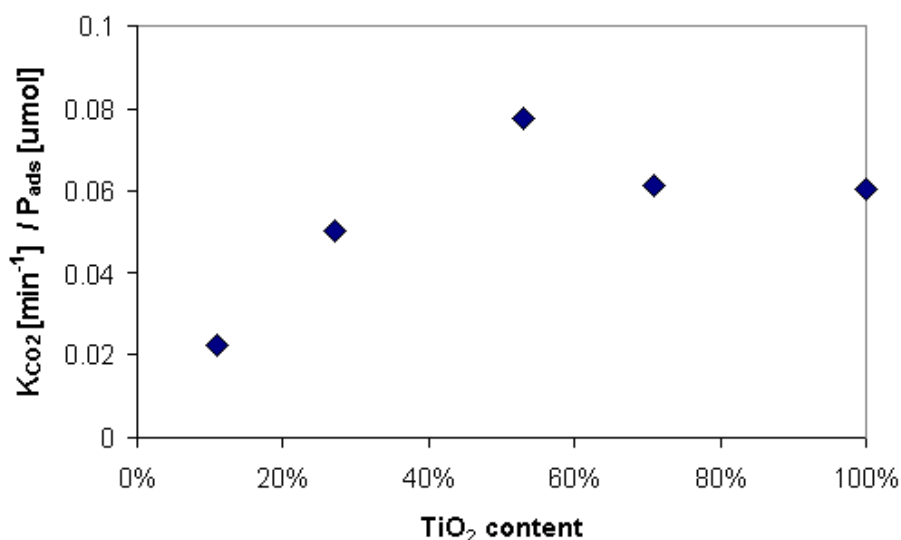


**Figure 5:** The rate constant for  $\text{CO}_2$  evolution during the photodegradation of propionaldehyde, normalized by the amount of adsorbed propionaldehyde versus the  $\text{TiO}_2$  loading. [based on data from ref.[34]].

**3.2.3 Domain size.** The rate constant for the evolution of  $\text{CO}_2$  during the photodegradation of propionaldehyde was shown to increase up to a  $\text{TiO}_2$  loading of 50% and then was found to decrease.[34] This is not altered significantly when the rate is normalized by the amount of contaminant adsorbed on the surface of the composite photocatalyst, as presented in Fig. 5, which demonstrates that below 50% the situation is reaction- rate limited (lack of photocatalyst), whereas above this point it is mass-transport limited.

It is expected that at constant loading, the smaller the domains are, the larger the A&S effects will be, due to a shorter length that the contaminants have to diffuse through (see Fig. 9).

Shorter diffusion length is beneficial also in cases where spill-over of oxidizing species is the dominant mechanism of degradation (see chapter 4). On the other hand, for preferential degradation by means of Specific Adsorb & Shuttle (see chapter 3.5), such enhanced spill-over of oxidizing species might be quite destructive for organic molecular recognition sites chemisorbed on the inert domains.

Quite rationally, it was often claimed, that the maximal effect on the degradation rate is obtained when the adsorption energies between the inert adsorbent and the contaminant are of medium strength. Low adsorption energies may lead to low sticking probabilities of the contaminants on the adsorbents, whereas adsorption energies that are too high might prevent surface diffusion (see part 3.1). A thorough work that will quantify this statement and will provide the optimal energy as a function of average diffusion distance is yet to be done.

**3.2.4 Crystallinity of the inert support.** The effect of crystallinity of zeolite A within a composite photocatalyst was tested for the photodegradation of acetophenone.[10] It was found that the apparent first order rate constant increased monotonically with the extent of crystallinity. According to the author's report, no photocatalytic activity was observed when less of half of the inert zeolite substrate was crystalline. While it is understandable that the structure of the inert substrate plays a role in the photoactivity enhancement, it is quite difficult to explain why low crystallinity of the zeolite substrate had such a dramatic effect on the measured rate constant, taken into account that the zeolite was an inert substrate that was supposed only to assist in the mass transport of the contaminants to the photoactive sites. Hence, it is plausible that, at least in this case, the inert domains played an active role in the photocatalytic process, either by serving as stabilizers for reactive species such as OH radicals or superoxide anions, or by adsorbing oxygen molecules that are spilt off to the photocatalytic domains, where they strip photoinduced electrons, thus reducing recombination rates.

**3.2.5 Temperature of operation.** It is often claimed that the role of temperature in photocatalytic processes on TiO<sub>2</sub> is quite minor, however this claim is not necessarily accurate. With respect to composite photocatalysts, it is expected that increasing the temperature will increase diffusivity (at the expense of lowering the adsorption constant). Hence, degradation processes with high adsorption energies adsorbents are expected to benefit from raising the temperature, while degradation processes with low adsorption energy adsorbents are likely to become less efficient.

The amount of data on the effect of temperature on the efficiency of composite photocatalysts is quite meager. One of the few works, which put some attention to temperature effects studied the degradation of propyzamide on a composite photocatalyst consisting of titanium dioxide and activated carbon (Table 3).[5] As presented in the Table, the rate constant with the composite photocatalyst at 40 °C was considerably higher than at 25 °C, however the enhancement ratio was reduced from 5.6 to 4.4, somehow against the expectation. The fact that the data in Table 3 was calculated based on mineralization rates instead of degradation rates may explain this difference, at least partially.

**Table 3:** The rate constant of mineralization of propyzamide on composite and non-composite photocatalyst at two temperatures: 25 °C and 40 °C [data taken from ref. [5]].

| Temperature (°C) | Rate Constant [m. <sup>-1</sup> ]<br>TiO <sub>2</sub> | Rate Constant [m. <sup>-1</sup> ]<br>TiO <sub>2</sub> / activated carbon | Enhancement Ratio |
|------------------|-------------------------------------------------------|--------------------------------------------------------------------------|-------------------|
| 25               | 0.25 *10 <sup>-4</sup>                                | 1.4*10 <sup>-4</sup>                                                     | 5.6               |
| 40               | 0.75*10 <sup>-4</sup>                                 | 3.3*10 <sup>-4</sup>                                                     | 4.4               |

**3.2.6 Effect of humidity.** Water adsorbed on TiO<sub>2</sub> is the source for hydroxyl radicals needed to initiate photocatalytic reactions. On the other hand, water competes with the model contaminants on adsorptive sites. It is for this reason that one expects to find the optimal relative

humidity at some intermediate level, which depends on the adsorptivity of the contaminants as well as on the reaction pathway. In general, this optimal point is obtained already at a very low relative humidity, such that within the practical range of use, water act to reduce the photodegradation rates of most contaminants. For composite photocatalysts having large surface area, and in particular for those whose inert adsorbents hardly adsorb water, it can be said that the problem of competition for adsorption sites between water vapor and the organic substances is solved, at least partially. In this case it is expected that the optimal relative humidity will be shifted towards higher values, practically reducing the detrimental effect of humidity. One may further expect this specific virtue of composite photocatalysts to be more pronounced with contaminants that hardly adsorb on titanium dioxide, hence cannot compete successfully with water for titania sites.

The experimental data on humidity effects comparing bare titanium dioxide to composite titanium dioxide are not too many. One of the few relevant works is that of Ao et. Al., who studied the effect of humidity on the photodegradation of mixtures of pollutants, such as nitric oxide, BTEX and SO<sub>2</sub> by a TiO<sub>2</sub>-AC photocatalyst.[35] As explained above, it was found that the competition with water in the removal of NO as well as that of BTEX was reduced upon using the composite, such that the adverse effect of humidity was much less pronounced. This finding was not altered in the presence of other co-pollutants such as benzene, toluene, p-xylene, ethylbenzene, or SO<sub>2</sub>. Generally speaking, the higher the humidity level was, the higher was the enhancement factor (up to 7-8!!!) achieved with the TiO<sub>2</sub>-AC composite. One may add also a recent publication on the photocatalytic oxidation of toluene on activated carbon- loaded TiO<sub>2</sub>, showing a positive correlation with humidity (albeit without a comparison with bare photocatalyst).[36]

**3.2.7 pH effect.** The adsorption of pollutants, in particular charged pollutants, depends to large extent on the pH, which governs the surface charge on the photocatalyst. Taken that the isoelectric point of TiO<sub>2</sub> is around 7 (actually 6.2 -7.5 depending on the preparation procedure), acidic pH will positively charge the photocatalyst while basic pH will negatively charge it. Whether amphoteric molecules will be adsorbed on the surface or not will then be dictated by their tendency to be charged at these operational conditions. Accordingly, it is understandable that the addition of an adsorbent, having a different point of zero charge, may cause the material to respond to acidity variations in a manner that is not necessarily the same as the host's. As a consequence, it can be expected that the dependence of the pollutants' adsorption and degradation rate on the pH will be altered upon introducing of inert adsorbents.

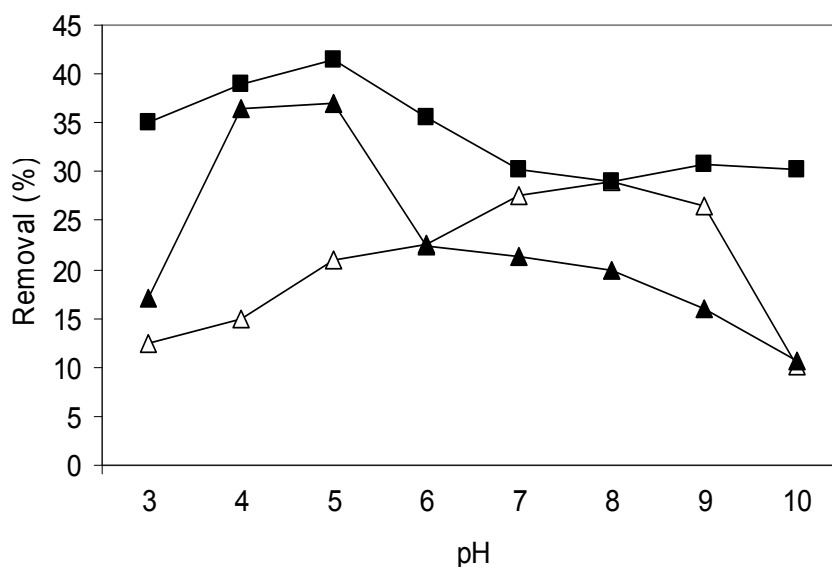


**Figure 6:** Removal efficiency of hydroquinone as a function of pH, for bare TiO<sub>2</sub> (empty triangles), a TiO<sub>2</sub>-AC composite (filled triangles), and activated carbon (filled squares). The same weight of TiO<sub>2</sub> was used for bare and composite photocatalyst. The loading of TiO<sub>2</sub> in the composite photocatalyst was 0.46% by weight and the AC weight was 2 gr. in both cases [based on data from ref. [37]]

Hydroquinone is known to have, apart from its neutral form at its isoelectric point (IEP) of 4.2, another two charged forms (positive and negative), which become more and more dominant as the acidity is swept away from the IEP. Results on its removal with bare titanium dioxide and with a composite photocatalyst containing activated carbon are given as a function of pH in Fig. 6, following ref. [37]. Here, the removal efficiency reflected both adsorption and photodegradation, which could not be differentiated under the experimental conditions. Another important factor was the possible blocking of light by the activated carbon particles, especially under the low loading (0.46%) of the composite. The high weight of AC used in these experiments does not help to get a precise impression of the photocatalytic effect, nevertheless, the results clearly indicate that the behavior of the composite differs at large from that of each of its constituents. The Figure further shows that below a pH of 6 the composite structures performs better than the bare titanium dioxide particles, despite the partial blocking of light. This was not the case at an intermediate pH region, where the TiO<sub>2</sub> particles were still uncharged, and could attract the negatively charged hydroquinone. As expected, at very high pH (pH 10) and at very low pH (pH 3) the removal efficiency decreases since both the photocatalyst and the contaminant have the same charge.

It should be noted that the point of maximal adsorption of composite photocatalysts might be different from that of the bare photocatalyst. Nevertheless, reports in the literature usually make their calculations of the benevolent effect under a fixed pH. Such calculations should therefore be taken with some cautious, since the comparison is not made at the point of maximal adsorption (or maximal quantum efficiency), but rather at a specific pH that might favor one type of catalyst over the other.

**3.3 Formation of intermediate products.** In many cases the photodegradation process goes through the production of intermediate products that might be released into the media. These chemicals should be of concern, as they are not necessarily benign. Two good examples are the photocatalytic degradation of trichloroethylene (TCE) in the gas phase, which produces phosgene and dichloroacetyl chloride,[38] and the photodegradation of the pesticide diuron.[39] In that sense,

one of the benevolent effects of using composite photocatalysts is the reduced rate by which intermediate products are released. This effect is rationalized in most cases, as originating from secondary adsorption of the intermediate products on the inert surfaces, followed by their subsequent degradation. Along this line, only minute amounts of the intermediate products hydroquinone and benzoquinone were found in the degradation of phenol[8] and 4-chlorophenol[40] by a suspension made of P25 particles and activated carbon. Similarly, a clear difference in the ratio between intermediates and CO<sub>2</sub> during the degradation of propyzamide at a given mineralization extent (50% of the total carbon) can serve as another demonstration for the specific effect on the production of intermediates.[32]

Likewise, it was found that the release of NO<sub>2</sub>, an intermediate formed during the oxidation of nitric oxide, is reduced upon immobilizing the titanium dioxide on activated carbon.[41] It was claimed that the mechanism of NO oxidation involves two steps. In the first step the NO is attacked by OOH to form NO<sub>2</sub> and hydroxyl radical, whereas in the second step the OH radical oxidizes the NO<sub>2</sub> thus forming HNO<sub>3</sub>. The role of the AC, is therefore, to adsorb the NO<sub>2</sub> and to shuttle it to the photocatalytic domains.

Another example is the use of anatase nanoparticles made by low temperature (75 °C) hydrolyzation of titanium butoxide and loaded on activated carbon in a rotary evaporator.[42] The composite photocatalyst was used for the photodegradation of phenol. No details were given as for the strength of adherence between the two components, however repetitive measurements showed that six cycles of use yielded a decrease of more than 40 % in the amount of adsorbed phenol and a decrease of no more than 17% in the removal of phenol. This reduction was ascribed by the authors to intermediates adsorbed on the surface of the photocatalyst rather than to detachment of the TiO<sub>2</sub> nanoparticles from the activated carbon substrate.

The release of different type of intermediate products is often taken as indicative for a change in the reaction mechanism. However, the appearance of different types of intermediates does not necessarily imply such a change in the reaction pathway. For example, the first detected intermediate in a TiO<sub>2</sub> -mediated degradation of 4-chlorophenol was hydroquinone, whereas the first detected intermediate in the degradation with a zeolite-TiO<sub>2</sub> composite was benzoquinone. Yet, this difference was explained in terms of different local pH (pH 10 in the zeolite case) and not by the reaction having a different pathway.[10]

**3.4 Formation of end-products.** Adsorptive domains can serve not only for the adsorption of reagents or intermediate products but also as a means to catch end-products, thus removing them from the streams to be cleaned. It is known that Hg(II) can be reduced on titanium dioxide to Hg(0), whose adsorption on titanium dioxide is quite meager. At the same time, the adsorbability of Hg(II) on AC is lower than that of Hg(0). A substantial increase in mercury removal, found upon using a combination of the two, was attributed to a reductive process on the photocatalyst, followed by trapping of the metallic mercury on the activated carbon surface.[28] Another route, albeit not mentioned explicitly, could also be a spill-over of electrons from the photocatalyst to the inert surface, where mercury ions had been pre-adsorbed.

Another case in which composite photocatalysts had an impact on the (relative) distribution of products is demonstrated in Fig. 7. Here, the ratio between CO and CO<sub>2</sub> production during the photodegradation of rhodamine 6G is given for two bare photocatalysts (Degussa P25 and a sol-gel made anatase), for a composite made of the sol-gel made anatase loaded on activated carbon and for a suspension containing a mixture of sol-gel made TiO<sub>2</sub> particles and activated carbon. From the Figure it is quite evident that the relative amount of CO production was considerably lower than that produced by the bare photocatalysts. This difference was most noticed upon comparing with P25, where the relative amount of CO produced by the composite particles was approximately half the amount produced with P25.

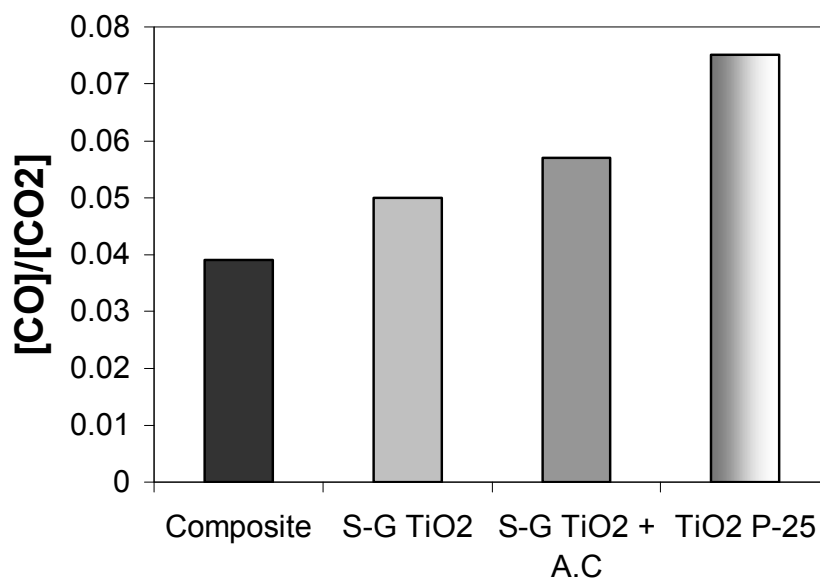


**Figure 7:** CO/CO<sub>2</sub> production ratio during the photodegradation of rhodamine 6G by several types of photocatalysts: a bare commercial photocatalyst (Degussa P25), a bare photocatalyst made by a sol-gel method, a suspension containing of a mixture of the bare sol-gel photocatalyst and activated carbon particles, and a composite photocatalyst consisting of the same sol-gel-made photocatalyst particles loaded on activated carbon particles.[23]

It was earlier mentioned that one of the effects of introducing an inert constituent is channeling the photodegradation pathway towards less intermediate products and more mineralized end products. This was not the case for a silica matrix containing titanium dioxide nanoparticles. Here, an enhanced selective epoxidation of styrene into styrene oxide was observed.[43] This tendency was explained in terms of formation of F-centers sites (possibly at the TiO<sub>2</sub>-SiO<sub>2</sub> interface), which, upon UV exposure and especially under non-humid conditions, produced active oxygen species instead of hydroxyl radicals. It is noteworthy here that no detailed information regarding the exact effect of the inert silica matrix was given, nevertheless, results differed at large from those obtained with TiO<sub>2</sub> particles (P25) in the absence of the silica matrix.

An interesting effect of low loading of titanium dioxide within a zeolite matrix can be the production of end products that differ significantly from those produced at high loading. This effect was demonstrated with the use of MCM-41 matrix, hosting 0.6% by weight of TiO<sub>2</sub>. [44] Here, photocatalytic removal of NO led to the formation of reductive products (N<sub>2</sub> and O<sub>2</sub>) instead the usual oxidative products (NO<sub>2</sub>, HNO<sub>3</sub>). Results were explained in terms of the formation of isolated titanium dioxide, having a lower coordination number. The same reasoning was given for the photocatalytic reduction of carbon dioxide with water to produce a mixture of methane and methanol.[45]

**3.5 Preferential degradation.** Photocatalytic oxidation is known to be governed by a free radical mechanism, hence operates in a manner that hardly differentiates between different contaminants, provided that these molecules adsorb on the photocatalyst's surface. The lack of sensitivity to the type of contaminants seems to be benevolent at first glance, since it means that there is no need to pre-design the photocatalyst for a certain contaminant. Nevertheless, a second thought alters this picture. Mixed streams may contain hazardous contaminants together with organic contaminants of low toxicity. In many cases, the toxic stuff is in low concentration, whereas the less toxic is the majority. It is obvious that in such cases, it is preferable to degrade the more toxic stuff, even at the expense of lower degradation rates for the less harmful components.[46] Moreover, many low-toxicity contaminants can be degraded by biological means, whereas many of the highly hazardous materials are non-biodegradable, due to their high toxicity.



The use of composite photocatalysts may provide a way to promote preferential degradation of specific contaminants. In a straight forward manner, the fact that the synergy effect varies from one pollutant to another (for example: a synergy factor of 2.4 for 4-chlorophenol, but only 1.3 for 2,4- dichlorophenoxyacetic acid for the same system[47]) may provide such a means, in particular if one takes into consideration that the specific synergetic effect varies also with the type of activated carbon that is used (i.e. hydrophobic AC made by high temperature activation, versus hydrophilic AC, made by low temperature activation).

Grafting of organo-silane molecules to obtain preferential degradation of hydrophobic molecules was proposed by several groups.[48][12][49][50] Likewise, the modification of titanium dioxide nanoparticles with the electron-donating chelating agent arginine [51] resulted in enhanced specific adsorption of nitrobenzene due to interaction of the  $\pi$ - system of the nitrobenzene ring with the arginine amino group, leading to a faster reductive photodecomposition. Nevertheless, although grafting of organic adsorbents on the photocatalyst may indeed serve to enhance the photodegradation of specific contaminants, it definitively suffers heavily from the fact that the grafted molecules themselves also degrade.

A few years ago, it was suggested [52] to introduce immobile organic molecular recognition sites (MRS) on inert domains, located not on the photocatalyst but rather in its vicinity. These pre-designed molecular recognition sites physisorbed selectively target molecules, that surface-diffused from site to site towards the interface between the inert domains and the photocatalytic domains, where they were destroyed (Fig. 8).

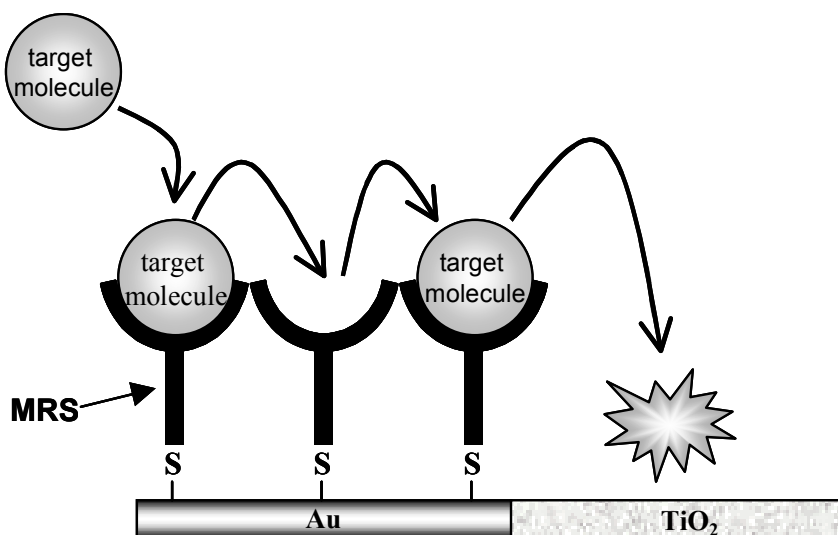


**Figure 8:** Schematic scheme of the specific "Adsorb & Shuttle" approach [53].

Since the molecular recognition sites were organic, care had to be taken to prevent their destruction by oxidizing species that could spilt-over from the photocatalytic domains, as indeed was observed with self- assembled monolayers (SAMs) chemisorbed on silicon dioxide, next to  $\text{TiO}_2$ . [54] Fortunately, it was found that SAMs anchored through a thiol functional group to metallic stripes did not suffer from this instability.[55]

The first system demonstrating this Specific Adsorb and Shuttle (SA&S) approach used thiolated  $\beta$ -cyclodextrin as the molecular recognition host, and 2-methyl-1,4-napthoquinone (2MNQ) as the model contaminant.[56] The host molecules were chemisorbed on micrometer- sized gold stripes located next to microns-sized titanium dioxide stripes on silicon wafers. This molecule was chosen to demonstrate the "SA&S" approach based on the well-known size-selective affinity with a variety of apolar guests, due to its cyclic structure, consisting of 7 glucopyranose units forming a torus-like structure. An increase of more than 10 times in the ratio between the degradation rate of 2MNQ to that of benzene was found upon comparing solutions containing one contaminant at a time, and an

increase of 6 times was found upon comparing solutions containing a mixture of the two contaminants.

Fig. 9 presents the kinetics of the photocatalytic degradation of 2MNQ physisorbed on the thiolated cyclodextrin, as deduced from the reduction in the area of its  $1666\text{ cm}^{-1}$  IR peak, for structures having adsorptive domains of different sizes. As shown in the Figure, the smaller the domain width was, the faster the photodegradation of the 2-methyl-1,4-naphtoquinone was. For example, 20% degradation was obtained with the  $5\text{ }\mu\text{m}$  width structures after 5 minutes, whereas the same extent of degradation with the  $40\text{ }\mu\text{m}$  width structures required 90 minutes. This effect of the domain size was in line with the notion that the 2MNQ molecules were adsorbed on the molecular recognition sites, from where they had to diffuse to the photocatalytic titanium dioxide domains. That the degradation was due to 2MNQ diffusion from the MRS to the  $\text{TiO}_2$  domains and not due to OH diffusion was supported by the observation that the degradation of the 2MNQ was not accompanied by the degradation of the molecular recognition sites.

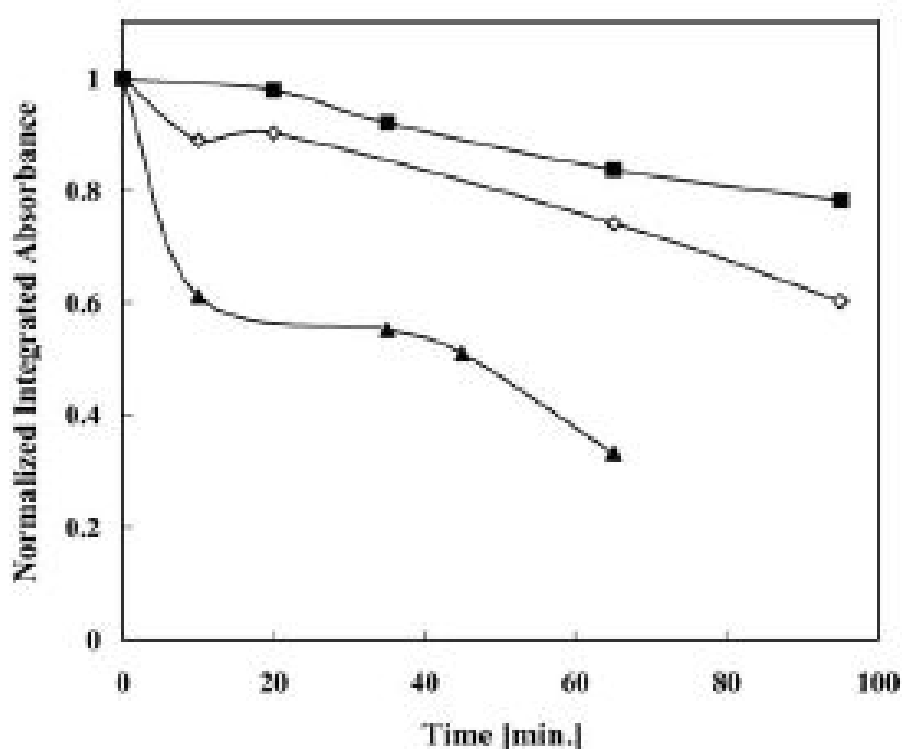


**Figure 9:** The photodegradation kinetics of 2-methylnaphtoquinone on substrates containing  $\text{TiO}_2/\text{Au}$  stripes of different width, onto which thiolated cyclodextrin was chemisorbed. In all samples, the width of the gold stripes was equal to that of the  $\text{TiO}_2$  stripes. Filled triangles represent stripes of  $5\text{ }\mu\text{m}$  in width, empty diamonds represent stripes of  $20\text{ }\mu\text{m}$  in width, and filled squares represent stripes of  $40\text{ }\mu\text{m}$  in width.[46]

Another model contaminant that showed enhanced rate of photodegradation with the same host system was the dye-stuff Chicago Blue Sky 6 (CB).[56] Here, an aqueous solution containing a mixture of  $0.01\text{ mM}$  of CB and  $0.01\text{ mM}$  of the dye-stuff Rhodamine 6G was exposed to  $365\text{ nm}$  UV light ( $0.09\text{ mW/cm}^2$ ). The degradation of the CB dye and that of Rhodamine was calculated based on changes in their UV-VIS spectra, as reflected in their  $625\text{ nm}$  and  $527\text{ nm}$  peaks, respectively. It was found that the degradation of the CB was 70% faster when using the MRS-containing samples. This enhancement was not observed for Rhodamine 6G.

A second published system was based on 1,1-mercaptoundecanoic acid (MUA), whose proton was substituted by  $\text{Cu}^{+2}$  (MUACu).[53] This system was designed for the photodegradation of the semi-volatile compound di-isopropyl methylphosphonate (DIMP), known as a stimulant for

the nerve agent sarin. FTIR studies showed that the photodegradation process of DIMP yielded acetone as an intermediate product. It was further shown that the molecular recognition sites enhanced specifically the degradation of DIMP but not that of acetone. This process occurred simultaneously with desorption of DIMP from the reactor's walls, which partially compensates for the loss of DIMP from the gas phase. A model, taking into account desorption from the reactors walls, as well as generation and degradation of acetone, was developed and fitted to the experimental results (Fig 10). Based on this model, the enhancement in the reaction rate constant for the degradation of DIMP could be calculated. Improvement factors of app. 4-10 were obtained for a structure, made of alternating stripes of titanium dioxide and MUACu, both having 5  $\mu\text{m}$  in width. Unlike the thiolated  $\beta$ -cyclodextrin system, some degradation of the organic part of the MRS upon irradiation was observed in this case. This could put an apparent limitation on the use of these structures in practical devices. Nevertheless, repeated measurements done following a two hours recovery time in air did not find any long-term reduction in the photoefficiency of DIMP degradation, in comparison with the first run. XPS measurements suggested that in that case, the thiol part of the MRS remained attached to the metal and was connected to the copper ion, which was the binding site for the DIMP.

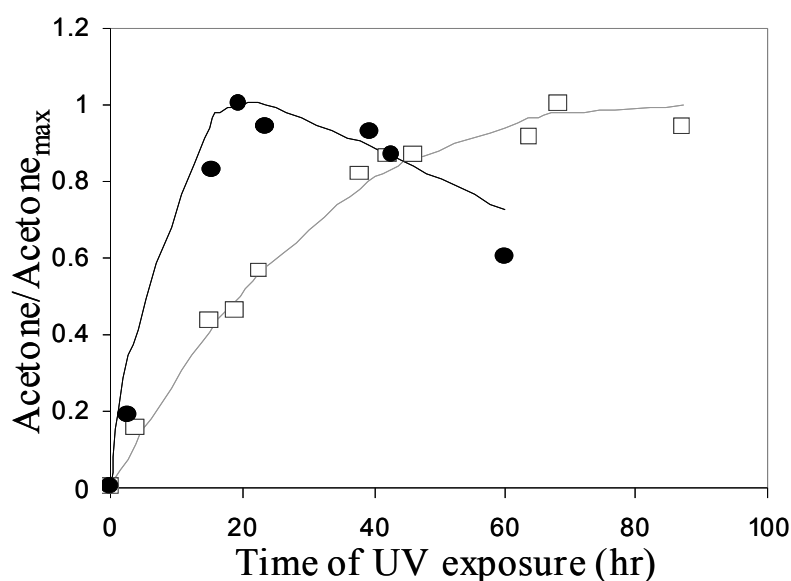


**Figure 10:** Changes in the concentration of the intermediate product acetone during the photodegradation of DIMP. Data is fitted according to a model that takes into account adsorption and desorption on reactor walls (connecting lines). €:  $\text{TiO}_2/\text{Au}$  stripes without MRS; ●:  $\text{TiO}_2/\text{Au}$  stripes with MRS. [based on ref. [53]]

The fact that the benevolent effect of the MUACu was noticed with DIMP, but not with acetone (in the absence of DIMP), evidently showed that MRS may serve not only to increase degradation rates but also to induce preferential photodegradation. Such selectivity is of great importance in particular in systems where the intermediate products are far less hazardous than the initial reactants, as indeed happens in this system, and may also happen in the photodegradation of many chemical warfare agents. Nevertheless, there was still a need for better protection of the molecular recognition sites from photodegradation, and for better understanding of the kinetics and energetics of the surface diffusion of the guests.

**3.6 Deactivation.** Another effect, claimed to be connected with that of reduced emission of intermediate products, was the prevention of deactivation, often related to the production of intermediates that block the active sites. For example, no deactivation was observed, regardless of relative humidity, upon using a composite consisting of TiO<sub>2</sub>-supported activated carbon fibers to degrade toluene,[36] known, like many other aromatics, to induce deactivation on bare titanium dioxide.[57] Here, it was claimed that the strong adsorption of the intermediates, which blocks the surface of the titanium dioxide, was far less important under conditions where the reactants adsorb onto the inert domains. Such a mechanism may imply, in our eyes, that the strong adsorption of the intermediates on the photocatalyst surface does not effect charge recombination, and that the observed deactivation on bare titania was simply due to reduced adsorption. Unfortunately, the data was silent with respect to possible alternative mechanisms, for example reaction on the activated carbon, induced by spill-over of photo-generated species from the photocatalyst to the inert support. Another possibility could be a reduction in the importance of competition between the pollutants and water on the adsorptive sites.

**3.7 Effects on the inert adsorbents.** An interesting effect was observed in composite photocatalysts made of P25 particles co-loaded with Carbon NanoTubes (CNTs) on poly(acrylonitrile) nanofibers prepared by electrospinning.[6] The photocatalytic activity of the composite fibers was measured in the absence of contaminants as well as with acetone, or with the dye rhodamine 6G. TEM images, as well as FTIR measurements, showed that the presence of carbon nanotubes reduced the extent by which the polymeric matrix was degraded upon exposure to UV light. At the same time, no adverse effect on the ability of the photocatalyst to degrade organic molecules was observed,[58] and in the case of rhodamine 6G, an enhanced degradation rate was observed. These apparently contradicting results were explained by a mechanism that was based on the transport of photoinduced charge carriers from the photocatalyst particles to the carbon nanotubes, which may induce a variety of effects, depending on the degradation mechanism and on reaction loci.[59]

#### 4. "Adsorb & Shuttle" versus "Remote Degradation"

A second mechanism by which the photodegradation rate of contaminants is enhanced by using inert domains in the vicinity of photocatalytic domains relies not on the surface diffusion of the contaminants, but rather on the diffusion of active species from the titanium dioxide, where they are formed, to the inert domains, onto which the contaminants are adsorbed. This second mechanism, named in the literature as "remote degradation"[60] was first mentioned in the case of photodegradation of rhodamine 6G on composite particles comprising of silica and titania microdomains and made by a sol-gel method,[11] and later confirmed by following the degradation kinetics of cross-linked self-assembled monolayers chemisorbed on silicon.[54],[55] Here, a diffusion length as long as 80 micrometer was observed. By comparing the degradation kinetics of monolayers chemisorbed on a thick dielectric layer it was deduced that the remote degradation is likely to occur through oxidizing chemical species and not directly by mobile charge carriers. These findings were corroborated independently in a study reporting on the remote degradation of soot.[61]

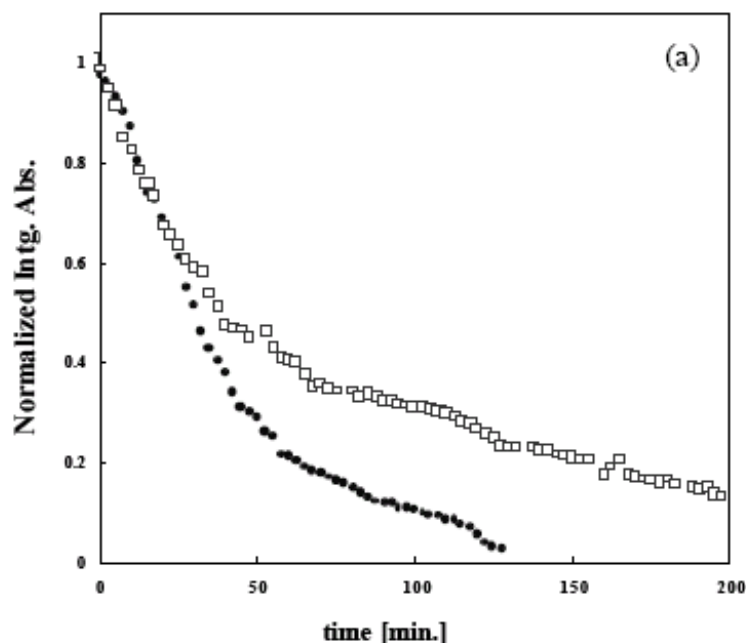


**Figure 11:** Changes in the normalized integrated absorbance of the C-H stretch bands of a C18 aliphatic monolayer anchored on long inert domains in the vicinity of titanium dioxide domains following UV exposure (a) results with inert domains made of silicon ●: domain width of 40 μm, □: domain widths of 80 μm. (b) results with inert domains made of gold ●: domain width of 2.5 μm, ○: domain width of 40 μm. [following ref. [56]]

The stability of the oxidizing species depends to large extent on the inert substrate. This was demonstrated by the effect of the crystallinity of inert zeolites on the photocatalytic efficiency of the composite structure,[10] which was claimed to affect the lifetime of the oxidizing radicals, or, alternatively, to affect the adsorption of oxygen, a major player in the stripping of electrons, on the zeolite surface. Another example for the importance of the inert substrate on the lifetime of the mobile active species is the fast remote degradation kinetics of aliphatic SAMs anchored on silicon dioxide, compared with the high stability of similar SAMs anchored to metals, such as platinum or gold (Fig. 11).

The nature of the active species responsible for the remote photodegradation phenomena was, and still is, under debate. Laser Induced Fluorescence (LIF) measurements have traced OH radicals away from the titanium dioxide surface,[62] suggesting that either the OH radicals are capable of leaving the titanium dioxide surface into the gas phase, or that H<sub>2</sub>O<sub>2</sub> formed on the TiO<sub>2</sub> surface diffuse in the gas phase and subsequently disintegrated into hydroxyl radicals.

## 5. "Adsorb & Shuttle" with visible light

The A&S effect can promote photocatalytic reactions not only under UV light but also under visible light. Composite particles, made by hydrolyzing TiCl<sub>4</sub> under controlled conditions together with commercial AC powder were treated with ammonia and calcined at 500 °C to form N-doped TiO<sub>2</sub>-AC composite.[63] The photoactivity was tested based on removal rates of phenol, without monitoring the production of CO<sub>2</sub> or any other end- or by-products. Under these conditions, a complete disappearance of phenol signal was obtained within 40 minutes. For comparison, the same time of exposure yielded no more than 5% removal with undoped P25 and 10% with undoped TiO<sub>2</sub>-AC (reflecting probably adsorption rather than true degradation). Unfortunately, no data was given regarding doped titanium dioxide in the absence of activated carbon, although some

estimation of performance can be obtained from results under solar irradiation, where removal of doped  $\text{TiO}_2$  w/o AC was approximately half of that of the composite photocatalyst. It is noteworthy that the specific surface area of the composite photocatalyst was reported to be only twice that of non-composite photocatalyst ( $91\text{-}96\text{ m}^2\text{ g}^{-1}$  and  $49\text{ m}^2\text{ g}^{-1}$ , respectively).

## 6. Practicality aspects

The use of composite photocatalysts has a large potential if one takes into consideration their benefits, mainly overcoming the problem of uncontrollable intermediate products and handling of contaminants that hardly adsorb on the polar photocatalyst. To this, one may add the fact that the technology of adsorption of contaminants on activated carbon is a mature technology, capable of handling a large number of contaminants, with high loading-per-weight ratio[64], so that photocatalysis with composite photocatalysts can be marketed as an upgrade of existing adsorptive measures. We believe that composite photocatalysts have particular potential for indoor air treatment as this is characterized by the need to reduce the level of contaminants within a single pass operation acting with a very short contact time, which is favorable for composite photocatalysts.[65]

It seems that there is a gap of knowledge between laboratory scale experiments and field scale experiments with composite photocatalysts. Nevertheless, one may find some comfort in a series of pilot plant experiments showing that the same enhancement factor of 2.4 was found upon scaling up a system that was designed to handle 4-chlorophenol by a volume factor of 12000.[40] Another work, which might be relevant, measured the performance of cementitious materials containing  $\text{TiO}_2$  in a pilot street configuration, however there was no specific information on A&S phenomena.[66]

It is impossible, within the framework of this manuscript, to describe all the patents that include composite photocatalysts. One example mentioned the use of activated carbon as a part of a "UV- activated odor filtration device".[67] A second example described a two layer structure, where the top layer was made of porous titanium dioxide and the bottom, compact layer, was made of a mixture of  $\text{TiO}_2$  and a thermocatalyst (such as manganese oxide) to handle materials that were difficult to treat by photocatalysis.[68] To these, one may add numerous patents, which utilize substrates (such as paper, cloth, plastics and the like) onto which titanium dioxide and adsorbents (usually activated carbon) are introduced.

In spite of all this, one cannot detour a feeling that whenever one finds a patent mentioning a composite made of an adsorbent and a photocatalyst, the function of the adsorbent, according to most inventors, is no more than to supply the necessary high surface area needed for the photocatalyst. In that sense, the full potential of composite photocatalysts and their unique properties are far from being fully recognized.

## 7. Conclusions

There is strong evidence that composite materials comprised of inert domains in close vicinity to photocatalytic titanium dioxide may affect significantly the photocatalytic performance of the photocatalyst. The most important effect is an apparent enhancement in the degradation rate, due to the adsorption of the contaminants in adsorptive sites on the surface of the inert domains, followed by diffusion towards the photoactive domains (the Adsorb & Shuttle effect). As shown above, the extent of enhancement depends on a large number of parameters including the surface area, the adsorptivity of the inert domains, the ratio between the inert component and the photocatalytic component, the size of the domains, and operational conditions such as temperature, humidity, and type of contaminant.

Another, yet no less important, virtue of using composite photocatalysts is the ability to alter the chemical species that are released during the photocatalytic process. Here, the existence of

adsorptive sites in close proximity facilitates secondary cycles of adsorption – diffusion – degradation, which reduce the release of intermediate species, some of which could be more harmful than the parent pollutants.

Of specific importance is the possibility of utilizing the "Adsorb & Shuttle" approach to obtain preferential degradation of contaminants, i.e., to increase the relative disappearance rate of a specific pollutant relative to the disappearance rate of other pollutants, co-existing in the medium. This can be achieved either by selecting the most appropriate adsorbent for the specific contaminant, or alternatively, by "tailoring" the surface of the inert component to increase the affinity between the adsorptive domains and the target pollutant.

Taking all these advantages, it is no wonder that composite photocatalysts draw an increasing attention, which eventually is transformed (and will continue to be transformed) into patents and products.

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## X-Ray Photoelectron Spectroscopy of Anatase-TiO<sub>2</sub> Coated Carbon Nanotubes

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**Keywords:** Carbon Nanotubes, Anatase, X-Ray Photoelectron Spectroscopy, Photocatalysis.

**Abstract.** A high efficiency nanocomposite photocatalyst is reported. Multiwall carbon nanotubes (MWNTs) were coated with titania. Two distinct types of nanocomposites were synthesized with variation in the synthetic procedure. One of the nanocomposites is based on a core of arc-discharge synthesized multiwall carbon nanotubes; whereas the other is based on a core of chemical vapor deposition (CVD) grown MWNTs. The nanocomposites have a similar appearance in transmission electron microscopy pictures in that they have a core of MWNTs that are chemically bonded to a few nanometer thick layer of pure anatase phase of titania. Yet they show a dramatically different photocatalytic behavior when they are compared on the basis of rates of photocatalytic decomposition of an organic dye in aqueous media following the Langmuir-Hinshelwood mechanism. This article focuses on the analysis of the differences in the nanocomposites using X-Ray Photoelectron Spectroscopy (XPS). XPS spectra of these materials indicate that there are distinct differences. However, they also show that both share C-O-Ti bonds that transform the carbon in the carbon nanotubes into a dopant for the anatase titania. This doping seems to be essential for long wavelength, i.e. visible light induced photocatalysis.

| Abbreviation   | Explanation                                             |
|----------------|---------------------------------------------------------|
| CNT            | Carbon nanotubes                                        |
| MWNT           | Multiwall carbon nanotubes                              |
| SWNT           | Single wall carbon nanotubes                            |
| l-NTs          | Long Carbon nanotubes (CVD grown)                       |
| s-NTs          | Short Carbon nanotubes (Arc-discharge)                  |
| l-ANTs         | Long anatase coated carbon nanotubes (CVD grown)        |
| s-ANTs         | Short anatase coated carbon nanotubes (Arc-discharge)   |
| I              | Intensity (XPS or adsorption)                           |
| $\lambda$      | Wavelength                                              |
| $\tau$         | Time for 1/e reduction on the contaminant concentration |
| $\sigma$       | Breadth of the XPS peak                                 |
| VT             | Voigt lineshape function                                |
| s <sub>l</sub> | Weight of Lorentz peak                                  |
| s <sub>g</sub> | Weight of Gauss peak                                    |

### Introduction

Titanium dioxide is widely used and is recently of interest for photocatalytic applications, like sterilization and in energy generation as in solar cells [1, 2]. In this article the main focus is to describe the photocatalytic properties of titania in respect to deactivation of hazardous materials, be it bioparticles such as viruses, spores, bacteria or chemical warfare agents. In principle every

semiconductor can be used as photocatalyst, but titania has a significant number of advantages over other competing materials [3-5]. Titania has a band-gap in the shallow UV [6]; it has the highest photocatalytic efficiency among all photocatalysts, is environmentally safe, is inexpensive, and can be synthesized in a variety of forms (particles, fibers, thin films, coatings) [4]. There are, however, significant limitations for the application of titania in sterilization since its efficiency was always lower than that of chemical agents like chlorine [4, 5]. The photocatalytic reactions of titania have been studied with much detail. One major factor that reduces its efficiency is the rapid recombination of the UV induced formed holes and electrons in the lattice. Since this recombination has the fastest reaction rate, it limits significantly the amount of free holes and electrons that can migrate to the surface before recombination. On the surface the holes typically generate hydroxyl radical species that are amongst the strongest oxidizers known. The combination of two semiconductors or a semiconductor and a metal have been successfully applied before. The metal or secondary semiconductor is typically designed to pull electrons into its lattice and act as a receptor. This scavenging of electrons yields retardation for the recombination. The first efforts towards this approach were reported for dispersed mixtures of anatase nanoparticles with noble metal particles, usually Ag, Au or Pt [7-10].

In this article multi-wall carbon nanotubes (MWNTs) replace the noble metals in the role of the electron receptor. The novel nanocomposites were synthesized by nucleating and growing titania as coating on the surface of MWNTs. The composite material is designed to contact the titania coating with the MWNT core by chemical bonds instead of van der Waals interactions. Earlier publications have already established that some of the novel nanocomposites are superior in dye destruction and spore destruction than the commercially available Evonik's Aerioxide<sup>®</sup> P25 which is typically used in photocatalytic studies to establish a standard for comparison. Furthermore, we already showed that nanocomposites are superior in photocatalytic destruction of dyes or bacterial spores to a simple colloidal suspension of nanotubes and titania particles. The purpose of this article is to specifically look at the interface that TiO<sub>2</sub> and MWNTs form in order to get a better understanding of the unexpected, significant enhancement that occurred in the nanocomposite material. Since the interface is buried only a few nm below the anatase a surface sensitive technique with a penetration depth of few nanometers was selected. X-ray photoelectron spectroscopy (XPS) was chosen, even though it summarizes over a large area and such summaries the contributions from multiple nanocomposite nanoparticles. The advantage of this method is that there is literature data available for both MWNTs and anatase. XPS spectra of anatase are characterized by the major peaks for oxygen as in O<sub>1s</sub> at 531.5 eV. A secondary peak at 527-529 eV appears, too. That peak is attributed to lattice oxygen, while the first one is attributed to surface oxygen. The lattice oxygen is very sensitive to the size of the crystal grain.

The characterization of nanomaterials and especially nanocomposites provides challenges. In order to investigate the XPS spectra for nanosized particles the use reference materials with similar size is recommended. This allows determining the exact position of the lattice peak. The next peaks that are significant are the titanium peaks Ti<sub>2p1/2</sub> and Ti<sub>2p3/2</sub>. The Ti<sub>2p1/2</sub> peak appears at 464.2 eV and only minor deviations have been noted in the literature or databases. The Ti<sub>2p3/2</sub> is located at 458-459 eV [11-15]. Sharp and intense peaks are a good indication that the TiO<sub>2</sub> consists only of Ti<sup>+4</sup> ions in the lattice. If Ti<sup>+3</sup> lattice ions are present a shift of the binding energy to lower values has been observed. In this article, the analysis is based on three nanomaterials: equiaxed  $\alpha$ -TiO<sub>2</sub> (anatase) nanoparticles with a Feret diameter of 5 nm and anatase coated MWNTs with variation in MWNT synthetic conditions. The XPS spectra of single wall and MWNTs have been studied extensively. Key information can be collected in the vicinity of the original elemental carbon peak at 284.6 eV. This article will use XPS spectra to better understand the surprising properties that MWNT-anatase nanocomposites demonstrate which includes superior photocatalytic decomposition of organic pollutants and bacterial spores. Furthermore, they show photocatalytic activity in visible light as well as in the dark after exposure to UV light for few minutes.

## Materials and methods

Two distinct composites were synthesized; both had  $\text{TiO}_2$  in anatase phase as nanometer thick coating; one was based on chemical vapor deposition (CVD) grown MWNTs (containing  $\text{Fe}_2\text{O}_3$  as catalyst, 6% by weight, as received), whereas the other one was based on arc discharge synthesized MWNTs. The arc discharge MWNTs were purchased from Alfa-Aesar (product #: 42886 in 2006 catalog) in soot form with a median length of 3  $\mu\text{m}$ . CVD MWNTs were purchased from Nanostructured & Armor Material Inc., USA (product #: 1236YJS) and were delivered in powder form. Their mean length was reported by the manufacturer as 700 nm. Due to their significant length difference the CVD grown MWNTs will be referred to as short nanotubes (s-NTs) and the arc discharge MWNTs as long nanotubes (l-NTs). The nanocomposites were characterized with Raman spectroscopy

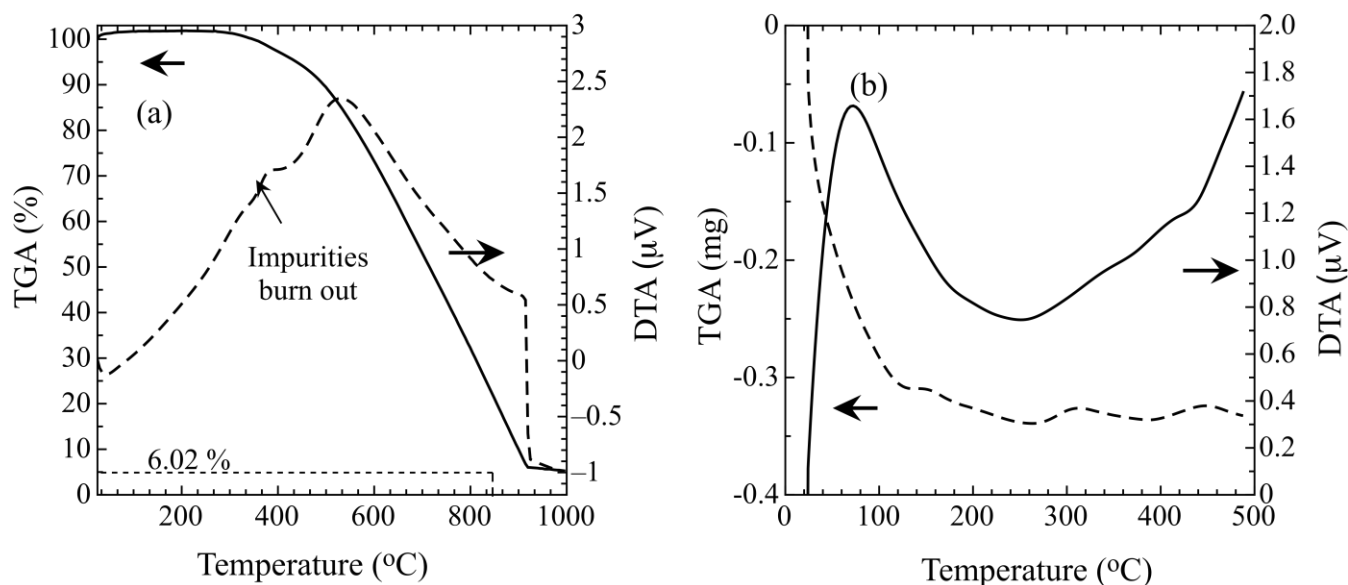


**Figure 1:** (a) The TGA/DTA data for s-NTs in air. The peak at 600 $^{\circ}\text{C}$  indicates the burning temperature of the s-NTs. About 6% of the initial mass is retained, which is assigned to the Fe catalyst. (b) The TGA/DTA data for s-ANTs. At approximately 250 $^{\circ}\text{C}$  the crystallization starts and continues up to 500 $^{\circ}\text{C}$ .

and XRD for structural properties; with dye and spore degradation for their photocatalytic reactivity; and the interface between the  $\text{TiO}_2$  coating and the MWNTs with Raman and XPS spectroscopy. The photocatalytic activity and structural characterization will only be described briefly since the main focus of this article is the XPS spectroscopic analysis.

**Synthesis of the anatase coated nanotubes.** The coating was done via sol-gel route. Various precursors and various methodologies have been used, in order to optimize the process of the coating. The objective was to achieve a uniform coating around the MWNT, while minimizing the number of free particles. Among the precursors that were used it was shown that titanium isopropoxide, had the best results for the short carbon nanotubes, in regards to the minimum number of free titania particles and the coating uniformity. Similarly for the long nanotubes the titanium sulfate was used. Hence, although the methodology was the same, there were variations to accommodate the differences of the shape and size of the carbon nanotubes, and the difference in the precursor reaction rates.

Prior to the coating the carbon nanotubes were treated in 60% (10 N) nitric acid ( $\text{HNO}_3$ ) at elevated temperature to purify and chemically functionalize them. Although the most common way for purifying the NTs is the 1:3  $\text{HNO}_3$  to  $\text{H}_2\text{SO}_4$  this method was not used here since the S impurities can be poisonous for the photocatalysis. 50 mg of the tubes were added in 200 ml of acid, which by

the end of the process yields 30 mg of tubes after the washing for both types of nanotubes. The *l*-NTs were kept under those conditions for approximately 10h at 140°C, while the *s*-NTs were held for 6h at 100°C. The nanotubes were then washed three times with DI water (for the *l*-NTs) or absolute ethanol (for the *s*-NTs). The functionalization will create surface groups such as -COOH -OH and >C=O critical for the sol-gel process since they can be used as initiation sites for the sol-gel chemistry. In addition they will significantly enhance the dispersion of the tubes in the medium where the coating will take place. After the final washing of the *l*-NTs suspension (30 mg of *l*-NTs in 300 ml of water), it was placed in a three-way 300 ml flask. The flask was placed in an oil bath at 40°C and was refluxed under constant stirring speed. After the temperature was stabilized the pH was fixed at approximately, ~3 with 0.1N HNO<sub>3</sub>. 106 µl of solution that contains 45 wt Ti<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> in dilute H<sub>2</sub>SO<sub>4</sub> (Sigma-Aldrich, product #:495182) was injected and the reaction was carried for 1 hour. The coated NTs were washed three times 3 times with DI water and left to dry at 40°C for two days. The process for *s*-NTs is similar to the process followed for the *l*-NTs. The solvent in this case was ethanol and the pH that was fixed at approximately 4. 11.68 µl of water was added along with 58 µl of Ti(OC<sub>3</sub>H<sub>7</sub>)<sub>4</sub> (Sigma-Aldrich, product #:377996).

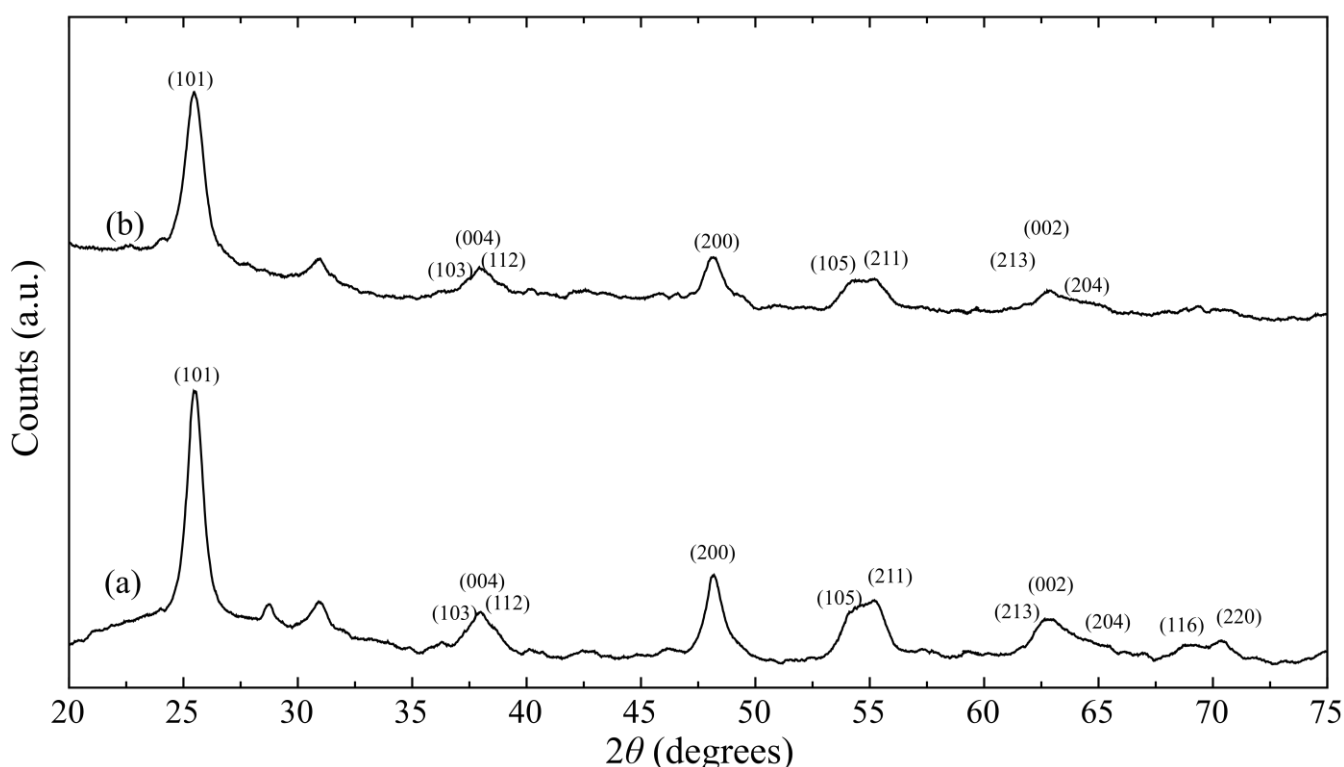


**Figure 2:** X-Ray diffraction pattern for the (a) *l*-ANTs and (b) *s*-ANTs. For both materials the major anatase peaks are present and named.

TGA/TDA showed that the nanotubes could tolerate temperatures up to 600°C without any substantial damage Fig. 1 (a), denoted by the small mass loss. The coated nanotubes showed an exothermic reaction starting at 250°C that continues up to 500°C without any significant mass loss, which denotes the crystallization of the anatase. Both samples were then heat-treated at 500°C for 3h with ramping temperature at 10 K/min.

## Characterization

The characterization of the nanocomposites was performed with scanning electron microscopy (SEM) (FEG-SEM JEOL JSM-6335F), transmission electron microscopy (TEM) (JEOL TEM 2010F), Fourier transform infrared spectroscopy (FTIR) (Nicolet MAGNA 760 Bench), Zeta Potential (Brookhaven ZetaPlus), particle sizing (Coulter Multisizer III), thermal gravimetric analysis (TGA) (Netzsch STA 449C Jupiter), X-ray photoelectron spectroscopy (XPS) (KRATOS XSAM 800) and X-ray diffraction (XRD) (XRD Philips APD 3720). Measurements with these techniques were performed at three stages of the process (before and after the functionalization and after the coating). The FTIR, Zeta Potential and particle sizing was used prior to the coating process to verify the formation of functional groups on the MWNTs and ensure dispersibility of the modified MWNTs. TEM and SEM were used to characterize the coating for coherence and thickness. The chemical composition was measured with X-ray photoelectron spectroscopy (XPS) and the crystal structure was confirmed by XRD. Brunauer, Emmett and Teller theory was used (BET) to calculate the specific surface area of the particles from gas adsorption. The BET specific surface areas of the materials were used as the grounds to calculate reaction constants for the photocatalytic reactions. All comparisons in this article are based on the BET specific surface area and not on a weight basis.

## Results

**Structural Characteristics and Surface Chemistry:** Figure 2 shows the XRD spectra of the l-ANTs and s-ANTs. All characteristic peaks of anatase are visible in addition to two peaks that are attributed to the MWNTs. The anatase coating thickness and grain size observed by TEM shows some variation for the two nanocomposites. The s-ANTs have an anatase coating with varying thickness

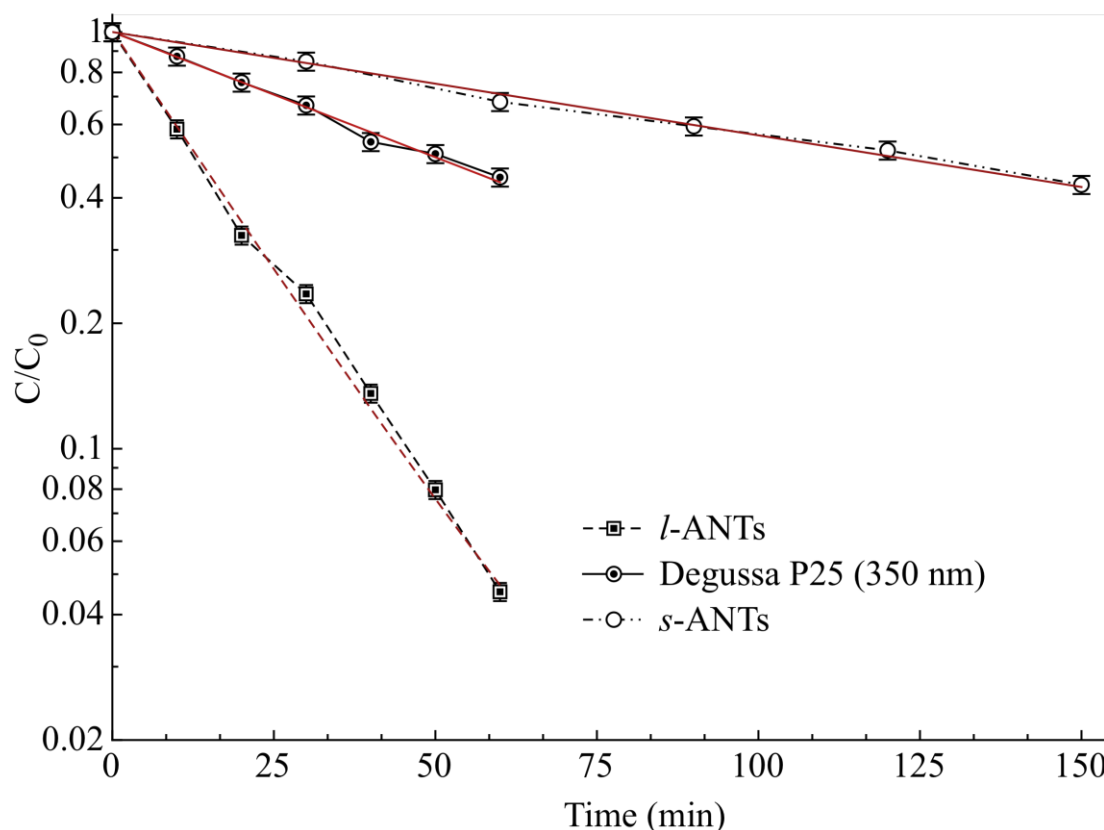


**Figure 3:** The photocatalytic activity of the two types of coated tubes, in comparison with Aeroxide® P25.

from 3 to 10 nm yielding an average value of 6 nm; whereas the l-ANTs have a uniform coating. It is also found that the coating on the s-ANTs does not always completely cover the entire MWNTs. The XRD clearly confirmed the anatase phase for both nanocomposites with no indication of the rutile phase. This is in accordance with the heat treatment that was used to favor pure anatase formation. Scherrer's formula was used to calculate an average grain size of 5.3 nm. This was found to be in agreement with the TEM analysis (Fig. 4).

**Photocatalytic Dye Destruction:** For detailed presentation and results the reader is advised to look elsewhere [16]. Due to the significance of these results for this discussion a short summary is introduced. 1 mg of particles was dispersed in 50 ml 5 pmm Procion Red MX-5B<sup>®</sup> dye. The solution was then placed in a dark chamber and irradiated with the UV with peak wavelength 375 nm. Every 10 minutes 1.5 ml of solution was removed in a plastic cuvette. The samples were left for 2 days for the particles to settle and the absorption intensity of the dye was measured with UV-VIS spectrophotometry. It was assumed that the UV-VIS adsorption intensity is proportional to the concentration, therefore  $I(\lambda)/I_o(\lambda) = C/C_o$ . The Langmuir-Hinshelwood model was used to fit the data to  $C/C_o = e^{-t/\tau}$  where the parameter  $\tau$  is the time required for 67% dye reduction and was used to compare the results. All experiments were repeated three times and with three different wavelengths (513, 524 and 537 nm). The time for 67% destruction was found to be significantly different with  $\tau_{l\text{-}ANTs}=19.1$  min and the  $\tau_{s\text{-}ANTs}=177.5$  min, while Aeroxide<sup>®</sup> P25 yielded  $\tau_{P25}=25$  min. The complete photocatalytic data is presented in Fig. 3. The most important result is that although the arc-discharge nanotubes–titania nanocomposites were more active than Degussa P25, the CVD nanotubes–titania nanocomposites did not perform as expected. On the contrary this nanocomposite appears to underperform Degussa P25 by one order of magnitude. This is a surprising result considering the fact that the materials for the nanocomposite are similar in chemical composition. Therefore, it is necessary to consider the internal structure of the nanotubes. For this purpose XPS and Raman spectroscopy was applied. XPS is a highly surface sensitive technique and the Raman is a tool that has extensive literature available for CNTs.



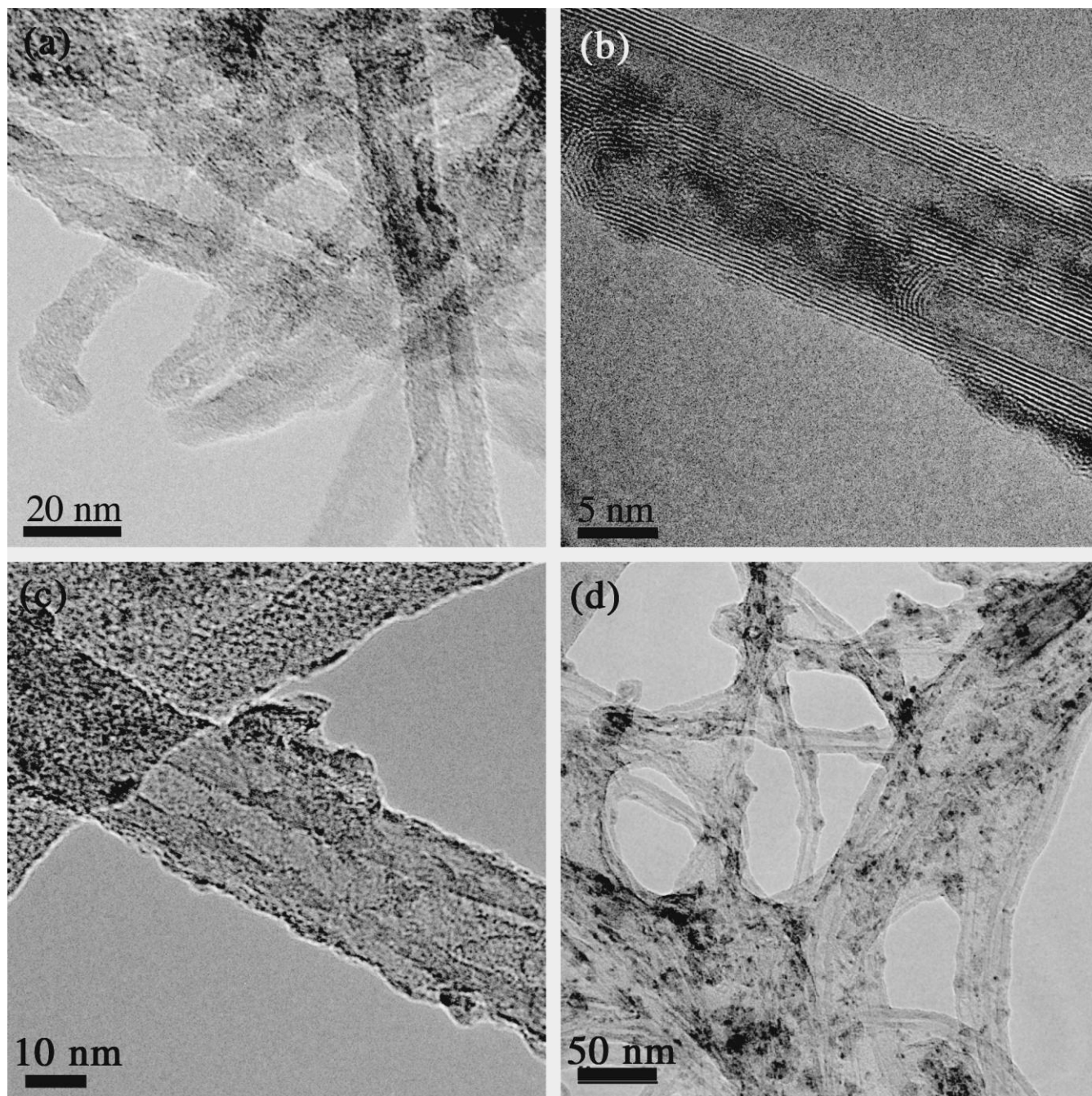


**Figure 4:** TEM images of the s-MWNTs. (a) The s-MWNTs after the acid treatment. The cavity of the tubes is visible. (b) High magnification of acid oxidized *l*-MWNTs where concentric tube layers are visible. (c) The s-ANTs. (d) The *l*-ANTs.

**Raman analysis.** The Raman analysis is discussed elsewhere in detail so here only a small, summary will be given [16]. The main finding is that the MWNTs have differences in their electronic properties. Long MWNTs were found to be good electrical conductors; whereas the short MWNTs correlated to poor electric conductors at room temperature. These conclusions were derived after the analysis of the Raman peaks and their shifts before and after the coating. Table 1 summarizes the results of the Raman data. It is worth noting that all peaks (both titania and NTs) were significantly shifted from before to after coating. Furthermore, all peaks have a different shift: not only in magnitude but in direction, too. This eliminates the possibility that the shift may occur due to a miss-calibration of the instrument. Furthermore, even though the two nanocomposites exhibit major differences in photocatalytic reactivity yet they have similar results for bonding to

titania according to their Raman spectra. This means that the splitting of the G Band that is seen for the *l*-NTs (excellent photocatalytic properties) and which is not available for the *s*-NTs (poor photocatalytic properties) becomes important for the interpretation of the Raman data. The split for the *l*-MWNTs yielded almost similar peak intensity and G<sup>+</sup> peak was fitted better with the Breit-Wigner-Fano lineshape compared to Lorentz.

**Table 1:** Summary of the Raman result. Here the major peaks are listed along with their shift for both, *l*-ANTs and *s*-ANTs.

| <i>l</i> -ANTs  |                           |                     |                           | <i>s</i> -ANTs  |                           |                     |                           |
|-----------------|---------------------------|---------------------|---------------------------|-----------------|---------------------------|---------------------|---------------------------|
| Titania         |                           | Carbon Nanotube     |                           | Titania         |                           | Carbon Nanotube     |                           |
| Band            | Shift [cm <sup>-1</sup> ] | Band                | Shift [cm <sup>-1</sup> ] | Band            | Shift [cm <sup>-1</sup> ] | Band                | Shift [cm <sup>-1</sup> ] |
| E <sub>g</sub>  | +5                        | D Band              | -5                        | E <sub>g</sub>  | +5                        | D Band              | -5                        |
| E <sub>g</sub>  | -                         | G <sup>-</sup> Band | -4                        | E <sub>g</sub>  | -                         | G <sup>-</sup> Band | -4                        |
| B <sub>1g</sub> | +10                       | G <sup>+</sup> Band | -6                        | B <sub>1g</sub> | +10                       | G <sup>+</sup> Band | -6                        |
| A <sub>1g</sub> | -                         |                     |                           | A <sub>1g</sub> | -                         |                     |                           |
| B <sub>1g</sub> | -10                       |                     |                           | B <sub>1g</sub> | -10                       |                     |                           |
| E <sub>g</sub>  | -                         |                     |                           | E <sub>g</sub>  | -                         |                     |                           |

The Raman spectroscopic analysis allows us to conclude that:

- a bond exists between the titania coating and the carbon nanotubes and
- *l*-ANTs that performed better in photocatalytic dye destruction tests contain cores of metallic carbon nanotubes; whereas *s*-ANTs contain cores of MWNTs with non-metallic properties.

**XPS analysis.** For all cases 3 mg of powder was mixed with 300 µl iso-propanol to form a thin paste that was placed on a Si wafer (100). Since the studied materials with the exception of the α-TiO<sub>2</sub> nanopowder have a high content of carbon the Si wafer will be used in addition with the advantageous carbon to calibrate the peaks. All the materials (*l*-ANTs and *s*-ANTs) showed no detectable impurities. The measured peaks did not indicate any impurities, however, non-stoichiometric TiO<sub>2</sub> is confirmed, which may be formed due to the presence of SiO<sub>2</sub> at the surface of the Si wafer.

The energy was calibrated with the Carbon 1s peak. Here, the Silicon 1s peak was also used for calibration. This is necessary due to the Raman spectroscopic findings that indicate that the MWNTs are bonded to the titania. The bond energy of carbon (C1s) might thus been influenced. The commercial software that came with the instrument was used to smooth the data. The peaks were fit with Gauss lineshape (eq. 1);

$$I(E) = \frac{I_0}{\sigma\sqrt{2\pi}} e^{-\frac{(E-E_0)^2}{2\sigma^2}} \quad (1)$$

where  $I_0$  is the intensity ( $N(E)$ ),  $E$  is the binding energy  $E_0$  the binding energy where the peak appears and  $\sigma$  a parameter related with the width of the peak. In certain cases in order to fit the tail of the peaks the Voigt peak (eq. 3) is used, which is a mix of Lorentz (eq. 2) and Gauss peaks:

$$I(E) = \sqrt{\frac{\pi}{2}} I_0 \frac{s_l}{s_g} VT \left( \frac{E - E_0}{s_g \sqrt{2}}, \frac{s_l}{s_g \sqrt{2}} \right). \quad (2)$$

where,

$$VT(y, x) = \frac{y}{\pi} \int_{-\infty}^{+\infty} \frac{e^{-t^2}}{y^2 + (x - t)^2} dt. \quad (3)$$

again  $E$  is the binding energy,  $E_0$  is the energy where the peak appears,  $s_g$  and  $s_l$  are fitting parameters. The default equation is the Gauss if not stated differently. The fitting algorithms used are the Levenberg-Marquardt, Monte-Carlo and Robust. The peak recognition was done based on literature [11-13, 15, 17-20] and on the commercial software (ProFit by QuantumSoft).

**XPS of the Reference Material.** The first material that was analyzed by XPS was the anatase nano powder ( $\alpha$ -TiO<sub>2</sub>). Since the particle diameter of these equiaxed particles is 5 nm it is expected that the lattice oxygen will have a slight shift that comes from the size constrain while the surface oxygen will not be affected. However, no changes are expected for the titanium. The titanium atom shows two distinct peaks at 458.4 eV for the Ti2p<sub>1/2</sub> and at 464.2 eV for the Ti2p<sub>3/2</sub>, both in good agreement with the database (Fig 5). [21] The O1s peak for this nanopowder appears with a split (Fig. 5). The peak is at

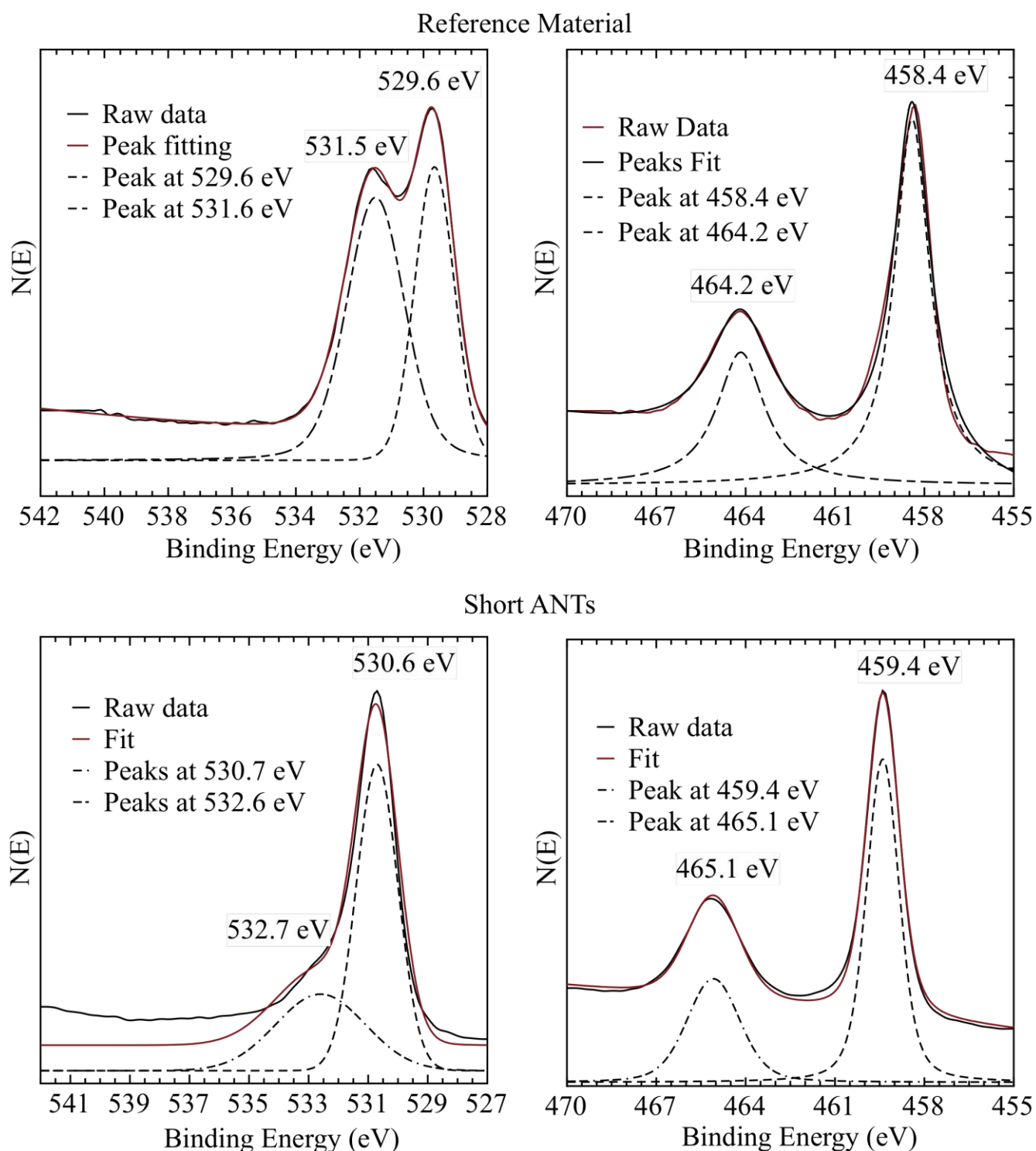


**Figure 5:** Collective representation of the XPS data regarding the s-ANTS. The upper row gives the Ti2p and O1s peaks of the reference material and the lower row is the data obtained by the s-ANTS. The shifts in both peaks are summarized in table 2.

529.6 eV and represents the lattice oxygen. It is shifted slightly compared to database values [21] It is assumed that this shift is caused by the particle diameter of 5 nm. Another O1s peak appears at 531.5 eV and is attributed to the surface oxygen. In this case the energy is higher compared to the bulk since there are open bonds. Since this material is of nanometer-size, it has a large specific surface area which increases the ratio of surface to bulk oxygen. This is reflected in the peak intensity. It has been argued that the ratio between the two peaks can be correlated to the surface area of the material [13]. However, another contribution has to be considered, for example the ratio

between bulk and surface oxygen also depends on the crystal orientation. Certain crystallographic orientations are richer in oxygen. So the relative ratio of the two peaks will be a function of both the specific surface area and the

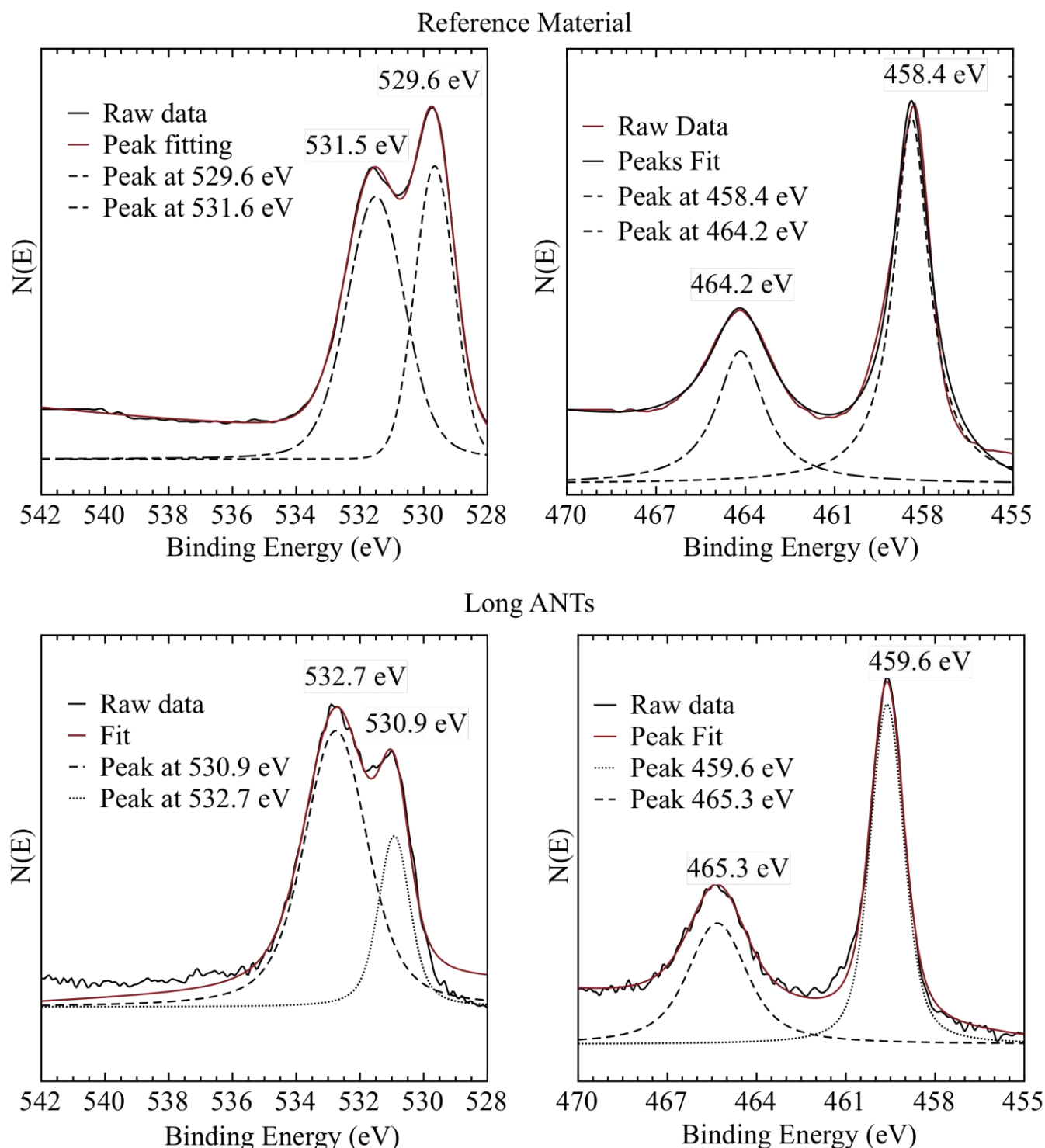


**Figure 6:** Collective representation of the XPS data regarding the coated long carbon nanotubes. The upper row gives the Ti2p and O1s peaks of the reference material and the lower row is the data obtained from the s-ANTs. The shifts in both peaks are summarized in table 2.

crystallographic orientation. The O1s peaks were fitted well with the Gaussian lineshape. The fitting results may be used to calculate the ratio of the surface to bulk oxygen (RSB), which will be discussed later.

**XPS of the s-ANTs.** The C1s was used as calibration in addition to the Si2p which was very weak and could not be used exclusively. Examining the C1s peak of the coated short carbon nanotubes (Fig 7) shows that there are two distinct peaks at 284.6 eV and 285.9 eV. The 284.6 eV is the peak that is being attributed primarily to the elemental carbon secondarily to the graphite structure. The 285.9 eV peak is attributed to the C=O, -COOH and -OH bonds [19, 20, 22]. Those groups are expected to be present as a consequence of the acid treatment. Furthermore, they were confirmed by

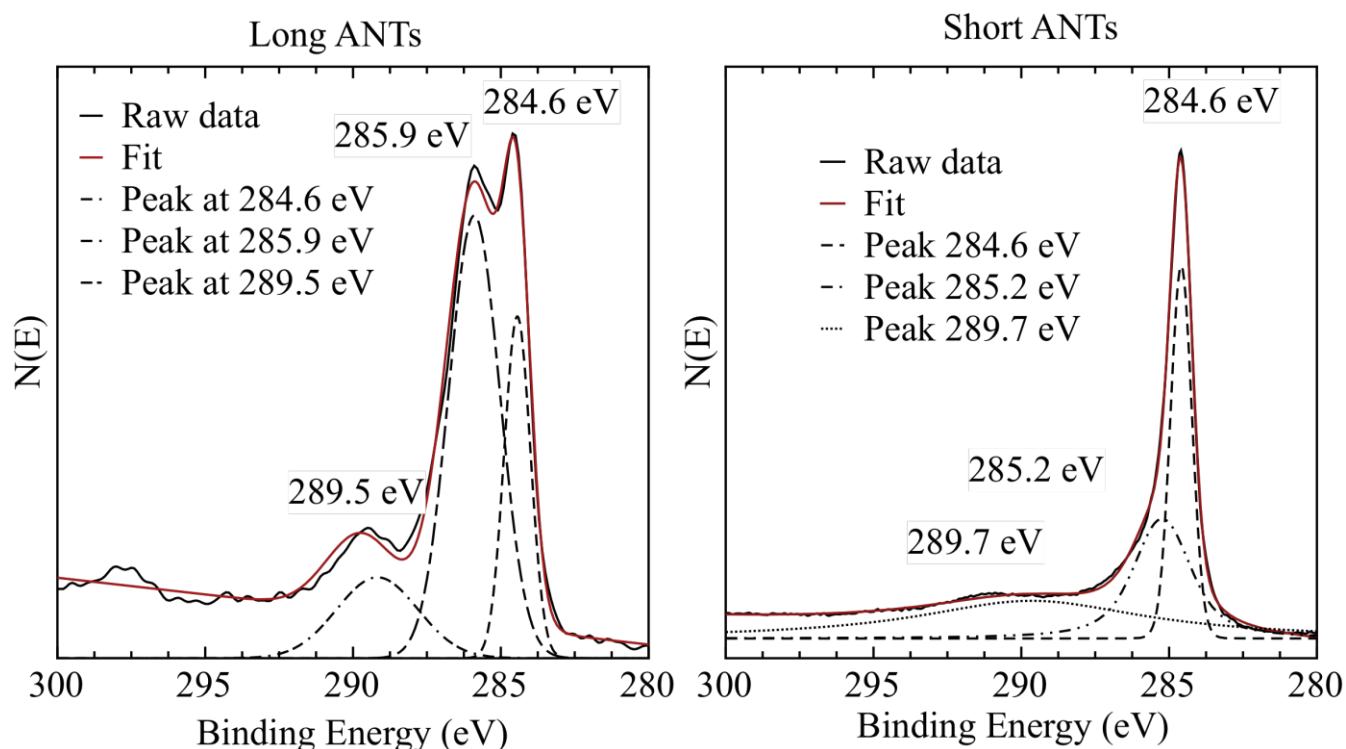


**Figure 7:** Collective representation of the XPS data regarding the carbon section of the s-ANTs, l-ANTs.

zeta-potential data and used in processing to achieve a colloiddally stable MWNT suspension. These groups were also confirmed by FTIR.

One new carbon peak appeared at 289.7 eV. This peak is far from the elemental carbon region and is assigned to the bond of carbon to another element. In the literature there are many references for this peak, however most are about fluoride bonded directly to carbon [17] or metals like Na and Li that may directly bond to carbon [23]. But there are also references that reported this peak as an oxygen bond. However, none of the previous publications gives a satisfactory explanation. Therefore, a new, more detailed explanation has to be considered. The coating process after the acid treatment is set-up to generate bonds between the MWNTs and the nucleating TiO<sub>2</sub>. It is assumed that this peak is originated from that bond. Carbon can be bonded to titanium through an O (C-O-Ti) or it can be directly bonded to titanium (C-Ti), which, however appears at 281.3 eV.

Let us discuss these results in light with the oxygen XPS data, especially with the RBS ratio. As mentioned above, there are two O1s peaks at 530.6 eV peak and at 532.7 eV, one representing surface and the other one bulk oxygen. Their  $I_{\text{Surface}}/I_{\text{bulk}}$  ratio is calculated to be 0.2526 for l-ANTs; whereas the reference anatase nanopowder has a ratio of 0.8307. This gives the reference anatase nanoparticles a higher surface oxygen amount, which seems to be in contradiction with the results from specific surface area measurements. The BET specific surface area for the s-ANTs was three fold above the reference material of the titania nanoparticles. This apparent contradiction may be explained by the impact of crystallographic orientation, which in the case of the s-ANTs seems to expose surfaces less oxygen rich.

The most important result however, is the shift (compared to the reference material values) that has occurred in both peaks. The first peak at 530.6 eV, regarding the lattice oxygen, is shifted by +1.0 eV (original value 529.6 eV) and the second peak that is at 532.7 eV, surface oxygen, has been shifted by +1.1 eV (original value at 531.5 eV). This shift again points to bonding oxygen to a non-anatase element which in this case may be carbon.

Finally, there are two titanium peaks in s-ANTs at energies 459.4 eV and 465.1 eV for Ti2p<sub>1/2</sub> and Ti2p<sub>3/2</sub> respectively. When comparing those peaks with the peaks of the reference material, both appear to be shifted. The Ti2p<sub>1/2</sub> is shifted by 1.0 eV and the Ti2p<sub>3/2</sub> is shifted by 1.1 eV. This means that the analysis of the XPS spectra for the s-ANTs gives strong evidence for a bond between titania and the MWNTs. Due to the absence of a characteristic peak for C–Ti the bond is interpreted as C–O–Ti.

**Table 2:** Summary of the XPS peaks

| Peak                    | Reference<br>anatase<br>nanopowder | s-ANTs    |            | l-ANTs    |            |
|-------------------------|------------------------------------|-----------|------------|-----------|------------|
|                         | Peak [eV]                          | Peak [eV] | Shift [eV] | Peak [eV] | Shift [eV] |
| C1s <sub>Graphite</sub> | 284.6                              | 284.6     | 0.0        | 284.6     | 0.0        |
| C1s <sub>C–O, C=O</sub> | N/A                                | 285.9     | –          | 285.7     | –          |
| C1s <sub>C–O–Ti</sub>   | N/A                                | 289.7     | –          | 289.7     | –          |
| O1s <sub>Surface</sub>  | 531.5                              | 532.7     | 1.2        | 532.7     | 1.2        |
| O1s <sub>Bulk</sub>     | 529.6                              | 530.6     | 1.0        | 530.9     | 1.3        |
| Ti2p <sub>1/2</sub>     | 458.4                              | 459.4     | 1.0        | 459.6     | 1.2        |
| Ti2p <sub>3/2</sub>     | 464.2                              | 465.1     | 0.9        | 465.3     | 1.1        |

**XPS of the l-ANTs.** Again the C1s peak was used to calibrate the spectra in addition to the Si peak which was very weak. The MWNTs used in this sample are different. Since the analysis of the XPS peaks yields similar results as for s-ANTs, only the key differences will be discussed. In this case the C1s peak at 285.2 eV is shifted compared to the previous case (285.9 eV). This shift is related to the amount of –COOH groups. Since the scale is in arbitrary units the peaks cannot be compared directly but the relative height to the main carbon peak can. In the case of the s-ANTs that ratio is  $I_{1Cs}/I_{C=O, -COOH}=1.1026$  and for the l-ANTs that ratio becomes  $I_{1Cs}/I_{C=O, -COOH}=0.3273$ .

These ratios will correlate directly with the number of the –COOH groups. This is evidence that the arc discharge synthesized longer tubes have been attacked less by the oxidative treatment and formed fewer carboxylic acid groups on the surface. Titanium also shows the specific peak at 289.7 eV. This peak is therefore assigned to the same origin by the C–O–Ti bond. However, the peak appears broadened and is less intense. This fits well to the earlier finding that there are fewer –COOH groups available on L-ANTs and the conclusion that the 289.7 eV is indeed a peak that comes from the C–O–Ti bond.

The other two peaks for titanium and oxygen in the XPS of l-ANTS appear at a lower intensity than for the s-ANTs. This is apparent in the signal to noise ratio, which is lower. Furthermore, the peaks appear to be significantly shifted compared to the reference material. The surface oxygen peak is at 532.7 eV located at the same energy as the surface oxygen peak for the s-ANTs. The second peak, regarding the lattice oxygen, is at the 530.9 eV and is very close where the respective peak for the s-ANTs is (530.6 eV). The relative intensity of the two peaks, i.e. the ratio  $I_{Surface}/I_{Bulk}$  ratio is calculated as 1.5636. This is very different from the anatase reference material ratio of 0.8307 and the s-ANTs ratio of 0.2526.

The last peaks for discussion are the Ti2p. The major peaks appear at 459.6 eV for Ti2p<sub>1/2</sub> and 465.2 eV for Ti2p<sub>3/2</sub>. These values are close to the respective values of the s-ANTs (459.4 eV and 465.1 eV respectively). Again, it is worth to note that the noise is increased compared to the



reference material due to the relative less amount of titania in the *s*-ANTs. As for the *s*-ANTs the *l*-ANTs XPS spectra show overall peak shifts, 1.2 eV for the Ti2p<sub>1/2</sub> and 1 eV for the Ti2p<sub>3/2</sub>. This confirms that the bond between TiO<sub>2</sub> and MWNTs is based on C-O-Ti and not C-Ti.

**XPS Result.** The XPS revealed that there is a bond among the Ti and the C linked via an oxygen atom. This is important, since it is the first report of such a bond. Furthermore, it is concluded that this bond will impact the photocatalytic performance. Beyond the earlier interpretation of the XPS for the bonds, a further observation is the shift towards higher energies. Higher energies denote a slightly more positive energy that is in turn evidence that the holes on the surface of the composites are more numerous than the holes of the reference sample. Although there was no UV exposure, this might come from quantum mechanics where the transition of electrons with thermal energy is allowed.

## Conclusions

In the present work two different composites based on a CNT core were synthesized and their photocatalytic results were reported. Although the composites had similar chemical composition the two composites displayed drastically different photocatalytic results. The composite with the CVD carbon nanotubes, underperformed the benchmark Degussa P25 while the arc-discharge nanotube based composite outperformed the benchmark. Raman spectroscopy and XPS was used to analyze molecular differences in the nanocomposites. The XPS analysis of the *l*-ANTs and *s*-ANTs confirms those both are nanocomposites and consist of MWNT cores with TiO<sub>2</sub> coatings. All peaks show displacement compared to the reference material. Since the grain size was not significantly different as confirmed by Scherrer analysis and TEM picture analysis, those shifts may be attributed to the bond of titanium via an oxygen bridge with a carbon on the MWNT. In addition to the shift, a new peak that is not explained reasonably from the databases appears at approximately 289.7 eV. It is feasible to attribute this peak to the C-O-Ti bond. Therefore, we conclude that the anatase coating is chemically bonded to the MWNTs. Furthermore, the bond must be in the form of C-O-Ti. This is expected from the synthesis conditions. The -COOH and -OH groups have been successfully used as anchoring points during the *sol-gel* process.

In addition the majority of the peaks was shifted to higher energies that suggests that the specific elements have a lack of electrons. In the fundamental theory of the composites the concept was to use the carbon nanotubes as an electron sink when the material is irradiated with light. Even in the absence of light however, a finite number of electron and holes have been generated, and those electrons can migrate to the MWNT core leaving behind an electron deficiency. The deficiency is the main reason for the shift observed for the XPS peaks.

Overall the XPS results in combination with the photocatalytic reaction rates showed the validation of the original concept. We therefore conclude that electrically conductive MWNTs can act as an electron sink. Furthermore, it shows the creation of a bond between the MWNTs and the titania shell.

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## Efficient Photoelectrochemical Splitting of Water to H<sub>2</sub> and O<sub>2</sub> at Nanocrystalline Carbon Modified (CM)-n-TiO<sub>2</sub> Thin Films

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**Abstract.** The carbon modified n-type titanium oxide (CM-n-TiO<sub>2</sub>) thin films were synthesized by flame oxidation of Ti metal sheets both flat and grooved and also by using combination of spray pyrolysis and flame oxidation of flat surface. Also undoped reference n-TiO<sub>2</sub> samples were also synthesized in an electric oven for comparison. Photoresponse of CM-n-TiO<sub>2</sub> and n-TiO<sub>2</sub> were evaluated by measuring the rates of water splitting to hydrogen and oxygen, in terms of observed photocurrent densities. Under the white light illumination of intensity of 100 mW cm<sup>-2</sup> from the xenon lamp the photocurrent densities were found to be 1.60, 9.17, 11.44 and 14.68 mA cm<sup>-2</sup> for optimized oven made n-TiO<sub>2</sub> (sample 1), flame made on flat surface (sample 2), on grooved surface (sample 3) and spray pyrolysis-flame made CM-n-TiO<sub>2</sub> (sample 4) thin films at 0.477 V, 0.240 V, 0.242 V and 0.215 V biases respectively. The corresponding maximum photoconversion efficiencies for these thin films were found to be 1.2 %, 9.08 %, 11.31 % and 14.04 % for samples 1-4 respectively. Under monochromatic light illumination from the xenon lamp the maximum photoconversion efficiencies for samples 1-4 were found to be 0.94 %, 8.86 %, 11.16 % and 13.79 % respectively. However, under actual natural global AM 1.5 sunlight illumination of 1 sun, the maximum photoconversion efficiencies reduced to 0.67 %, 5.63 %, 7.62 % and 12.26 % for samples 1, 2, 4 and 3 respectively. These values compared well with those found under monochromatic light illumination from the xenon lamp. The increasing efficiencies were found consistent with lowering of band gaps from 2.9 eV for sample 1 to 2.65 eV and generation of mid-gap band at 1.6 eV for both samples 2 and 3 and 1.4 eV above the valence band for sample 4. Carbon contents were found to be 0.0, 17.60, 19.38 and 23.23 atom % for samples 1, 2, 3 and 4 respectively.

### Definitions of Terms:

|                                      |                                                                                                            |
|--------------------------------------|------------------------------------------------------------------------------------------------------------|
| $E_{\text{meas}}$                    | Measured working electrode potential with respect to a reference electrode                                 |
| $E_{\text{aoc}}$                     | Working electrode potential measured with respect to a reference electrode at open circuit condition (aoc) |
| $E_{\text{app}}$                     | Applied potential = $E_{\text{meas}} - E_{\text{aoc}}$                                                     |
| $j_p$                                | Photocurrent density                                                                                       |
| $j_p(\lambda)$                       | Wavelength of light, $\lambda$ dependent photocurrent density                                              |
| $E_{\text{rev}}^0$                   | Reversible potential at the standard state                                                                 |
| $E_{\text{app}}(\lambda)$            | Wavelength of light, $\lambda$ dependent applied potential = $E_{\text{meas}} - E_{\text{aoc}}(\lambda)$   |
| $E_{\text{aoc}}(\lambda)$            | Wavelength of light, $\lambda$ dependent electrode potential measured at open circuit condition (aoc)      |
| $P_o$                                | Power Density of incident Light, for example, in milli watt per cm <sup>2</sup> per sec.                   |
| $P_o(\lambda)$                       | Wavelength, $\lambda$ dependent power density of incident light                                            |
| % $\epsilon_{\text{photo}}$ (total)  | Percent total photoconversion efficiency                                                                   |
| % $\epsilon_{\text{photo}}(\lambda)$ | Wavelength of light, $\lambda$ dependent Percent photoconversion efficiency                                |

|                                                            |                                                                                                                                                                                         |
|------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| $\eta(\nu)$                                                | Frequency, $\nu$ of light dependent quantum efficiency                                                                                                                                  |
| $E_g$                                                      | Band gap energy                                                                                                                                                                         |
| SCE                                                        | Saturated Calomel Electrode (acts as a reference electrode)                                                                                                                             |
| XRD                                                        | X-ray diffraction                                                                                                                                                                       |
| SEM                                                        | Scanning electron Microscope                                                                                                                                                            |
| EDS                                                        | Energy dispersive spectroscopy                                                                                                                                                          |
| CM                                                         | Carbon modified                                                                                                                                                                         |
| CM-n-TiO <sub>2</sub>                                      | Carbon modified negative type titanium oxide                                                                                                                                            |
| AM 1.5                                                     | Air Mass when sun is in zenith and sunlight falls perpendicularly on the surface of the earth                                                                                           |
| Monochromatic Light                                        | Wavelength, $\lambda$ dependent light                                                                                                                                                   |
| UV light                                                   | Ultra violet light                                                                                                                                                                      |
| Semiconductor Materials                                    | Materials having partial electrical conductivity in which higher energy conduction band is separated from lower energy valence band by an energy gap called band gap.                   |
| Calcinations                                               | Heating materials in an electric oven at elevated temperature                                                                                                                           |
| IPCE                                                       | Incident photon conversion efficiency or quantum efficiency or quantum yield                                                                                                            |
| Action spectra                                             | Plots of IPCE (or quantum efficiency) versus wavelength of light.                                                                                                                       |
| NREL                                                       | National Renewable Energy Laboratories                                                                                                                                                  |
| Mid-gap bands                                              | Extra bands produced inside the main band gap in a semiconductor.                                                                                                                       |
| Quantum Efficiency or quantum yield                        | Wavelength dependent conversion efficiency                                                                                                                                              |
| Photoconversion efficiency for water splitting to hydrogen | Power output from combustion of H <sub>2</sub> gas produced per second and per unit surface area of photoelectrode divided by power input from sun per second and per unit surface area |

## Introduction

Sunlight can ultimately become an unlimited source of clean and renewable energy if it could be efficiently harnessed to split water to hydrogen and oxygen. Numerous studies have focused on the semiconductor photoelectrodes for their applications for water splitting reaction [1-23]. Most of these studies were in search for highly stable and low cost semiconductor materials for efficiently harvesting the solar energy. Among the photoelectrode materials, titanium dioxide (n-TiO<sub>2</sub>) was recognized to be the most promising because of its low cost, chemical inertness, non-toxicity, and photostability. However, its wide band gap (3.0-3.2 eV) limits its photoresponse in the ultraviolet region which is only a small fraction (~ 5 %) of the sun's energy compared to visible light from 400 nm to 750 nm (~ 49 %). Hence, any shift in the optical response of n-TiO<sub>2</sub> from the UV to the visible spectral range will have a profound positive effect on the photocatalytic efficiency of the material. Several attempts were made to lower the band gap of n-type titanium oxide (n-TiO<sub>2</sub>) by transition metal dopants [24, 25] but no noticeable change in band gap energy of n-TiO<sub>2</sub> was observed. Visible light absorption by the transition metal doped n-TiO<sub>2</sub> was found to be due to d-d transition of electrons in the transition metal dopants but not due to band gap lowering. The transition metal dopants acted adversely on photocatalytic activity of n-TiO<sub>2</sub> because they acted as recombination centers for the photogenerated carriers.

However, recent studies involved doping of n-TiO<sub>2</sub> by carbon [1, 15-23, 26-31] nitrogen [32, 33], sulfur [34], also fabricating the carbon modified (CM)-n-TiO<sub>2</sub> in mesoporous [35, 36], and nanostructure [37, 38] forms. Photocatalytic activity of sulfur doped n-TiO<sub>2</sub> was found to diminish under UV and visible light illuminations due to catalytic poisoning induced by oxidation of sulfur to

SO<sub>2</sub> and SO<sub>4</sub><sup>2-</sup>. Photocatalytic activity of nitrogen doped n-TiO<sub>2</sub> was reported to be much lower than carbon doped n-TiO<sub>2</sub> [31]. Furthermore, no studies on photosplitting of water by nitrogen doped n-TiO<sub>2</sub> were reported as of yet.

It was found that carbon modification of n-TiO<sub>2</sub> photocatalyst synthesized by thermal oxidation of Ti metal in a natural gas flame lowered the band gap energy of n-TiO<sub>2</sub> to 2.32 eV and exhibited water-splitting to hydrogen and oxygen with a photoconversion efficiency of 8.35 % [1] under artificial light illumination from a xenon lamp. This progress stimulated further investigation into carbon modified n-TiO<sub>2</sub> (CM-n-TiO<sub>2</sub>) as visible light active photocatalysts [26-31] and also as photoelectrodes [15-23] for water splitting reaction with enhanced photoconversion efficiency.

Sakthivel and Kisch [31] observed visible light absorption by carbon-doped n-TiO<sub>2</sub> nanoparticles synthesized by hydrolysis of TiCl<sub>4</sub> with tetrabutylammonium hydroxide (C<sub>16</sub>H<sub>36</sub>NOH) followed by calcinations of the precipitates. They observed five fold increase in photocatalytic activity of carbon doped n-TiO<sub>2</sub> compared to nitrogen doped ones. Irie *et al.* [26] observed visible light response for carbon-doped n-TiO<sub>2</sub> synthesized by partial oxidation of titanium carbide powder. Xu *et al.* [29] reported that the carbon modified n-TiO<sub>2</sub> nanoparticles, synthesized by wet process using glucose (C<sub>6</sub>H<sub>12</sub>O<sub>6</sub>) solution as the carbon source, absorbed well into the visible to near infrared region up to 800 nm. These CM-n-TiO<sub>2</sub> samples showed thirteen fold increase in photocatalytic activity compared to regular undoped n-TiO<sub>2</sub> due to band gap lowering from 3.2 to 2.78 eV and generation of a mid-gap band at 1.45 eV above the valence band.

Xu and Khan [16] also showed enhanced rate of water splitting at spray pyrolytically synthesized visible light active carbon doped n-TiO<sub>2</sub> thin films. Enhanced photoresponse for water splitting at nanocrystalline carbon doped n-TiO<sub>2</sub> thin films were also reported by Xu *et al.* [17]. Argon was found to be the most effective calcining ambient to enhance the carbon doping of n-TiO<sub>2</sub> films. The resultant carbon modified n-TiO<sub>2</sub> thin film calcined in Ar at the optimum temperature of 700 °C contained 3.8 at % carbon and showed higher photoresponse in both UV and visible regions compared to those calcined in air at the optimum temperature of 500 °C that contained 2.3 at % carbon. Carbon content in these samples calcined in presence of oxygen in air reduced due to removal of some carbon in the forms of CO and CO<sub>2</sub>. This wet process synthesis allowed molecular scale mixing of the carbon source with precursor of TiO<sub>2</sub> for improved doping homogeneity and is capable of tuning the carbon content in the film.

Importantly, Mohaputra *et al.* [18] synthesized CM-n-TiO<sub>2</sub> thin films by flame oxidation of Ti metal sheet and reported photoconversion efficiency of 8.5 % for water splitting which is slightly higher than earlier results [1]. Carbon doping was considered to be responsible for the lowering of the band gap of n-TiO<sub>2</sub> and consequent high photocatalytic activity under visible light illumination. Noworyta and Augustynski [19] observed shift in the spectral response (up to 425 nm) during water splitting reaction for carbon doped n-TiO<sub>2</sub> film electrodes formed in the flame of a burner fed with various gas mixtures. Shanker *et al.* [39] investigated the effect of flame annealing on the spectral photoresponse of titania nanotubes and demonstrated the enhancement of the visible light absorption and the photocurrent for water splitting due to annealing in the flame. However, in their study, the flame annealing was carried out at 1020 °C which is much higher than the optimum temperature of 850 °C observed earlier [1]. Such high temperature generally removes considerable amounts of carbon from the sample and thus reduces the photoresponse. Given the sensitivity of CM-n-TiO<sub>2</sub> to flame temperature, Xu *et al.* [40, 41] prepared highly ordered n-TiO<sub>2</sub> nanotube array films by electrochemical anodization of Ti metal sheet followed by calcinations in an electric oven and further oxidation in natural gas flame at optimum temperature to incorporate carbon into it. Significant enhancement of the photoresponse of these carbon modified (CM)-n-TiO<sub>2</sub> nanotube films for water splitting was also reported [40, 41].

Hahn *et al.* [42] prepared carbon doped self-organized TiO<sub>2</sub> nanotubes layers formed by electrochemical anodization of Ti in a HF/Na<sub>2</sub>HPO<sub>4</sub> electrolyte. The tubes were treated at 500 °C under a mixed flux of N<sub>2</sub> and acetylene (C<sub>2</sub>H<sub>2</sub>). The acetylene treated carbon doped nanotubes

showed a significant photoresponse over the whole range of visible light up to the near-IR region (827 nm).

Nakano *et al.* [43] prepared  $\text{TiO}_2\text{:C}$  films by oxidative annealing of sputtered TiC films. They reported three bands having energies 0.86 eV, 1.30 eV, and 2.34 eV below the conduction band of carbon doped n- $\text{TiO}_2$ . They attributed the 0.86 eV level to the intrinsic nature of  $\text{TiO}_2$ , whereas the 1.30 eV and the 2.34 eV levels were newly introduced by C-doping and behaved as deep-level bands. In particular, the pronounced 2.34 eV band contributed to band gap narrowing by mixing C 2p with the O 2p valence bands. Therefore, the 2.34 eV level played a significant role for the visible-light sensitivity in  $\text{TiO}_2\text{:C}$ . Ren *et al.* [44] synthesized a visible-light-active  $\text{TiO}_2$  photocatalyst by carbon doping using glucose as carbon source. The preparation was performed by a hydrothermal method at temperature as low as 160 °C. The carbon-doped n- $\text{TiO}_2$  showed absorption in the 400–450 nm range with a red shift in the band gap transition.

In an important theoretical study, Nie and Sohlberg [45] reported the lowering of the band gap of n- $\text{TiO}_2$  to 2.32 eV (535 nm) due carbon incorporation and predicted that the band gap value of 1.58 eV may be possible to achieve by some complex carbon doping. Interestingly, it was found experimentally that enhanced carbon doping lowered the band gap of n- $\text{TiO}_2$  up to 1.45 eV [16]. Wang and Lewis [46, 47] addressed theoretically the effects of carbon dopants concentration on the photoresponse of n- $\text{TiO}_2$  in the visible-light region. They found that the substitutional and interstitial carbon dopants incorporated into  $\text{TiO}_2$  drastically affected the electronic structure of the material, thus improving its photoactivity. They predicted the low band gap of 2.35 eV for carbon doped  $\text{TiO}_2$  as it was experimentally observed earlier [1]. The theoretical findings of Valentin *et al.* [48] revealed the presence of substitutional and interstitial carbon in carbon modified (CM)-n- $\text{TiO}_2$  which were found to be responsible for the lowering of its main band gap and as well as generating a mid-gap band.

In this article we summarized our studies on thin film photoelectrodes of oven-made n- $\text{TiO}_2$ , flame made flat and grooved carbon modified CM-n- $\text{TiO}_2$  and CM-n- $\text{TiO}_2$  synthesized by using combination of spray pyrolysis and flame oxidation method. The results of photocurrent density on these photoelectrodes for water splitting reaction to  $\text{H}_2$  and  $\text{O}_2$  and the maximum photoconversion efficiencies under both xenon lamp and natural sunlight of global AM 1.5 were also provided. These samples were characterized in terms of band gap energies, x-ray diffraction pattern, scanning electron micrograms and carbon contents to correlate with their photoresponse.

## Experimental details

**Synthesis of Reference n- $\text{TiO}_2$  Films in an Electric Oven (oven made).** Titanium (0.25 mm thick, 99.5 % from Alfa Co.) metal sheets were cut, cleaned, and dried as described in section 2.1. Ti metal sheets were oxidized by using an electric oven (Multiple Unit, Series C4497 WEO). A digital thermocouple (Thermolyne Corp K-type Thermocouple (PM-20700)) was used to measure and maintain the temperature of the oven. The oxidation temperature and the oxidation time were varied from 800 °C to 950 °C and from 5 to 30 minutes, respectively.

**Synthesis of CM-n- $\text{TiO}_2$  Films by Thermal Flame Oxidation Method (flame made).** Titanium (0.25 mm thick, 99.5 % from Alfa Co) metal sheets were cut to an area of  $\sim 1.0 \text{ cm}^2$ . For the grooved samples, grooves were made on the surface of Ti samples as horizontal and vertical lines with different depths of 0.001, 0.003 and 0.005 inch. The distance between each grooved line was kept at about 1 mm apart. Ti metal samples (grooved and non-grooved) were cleaned in a sonicator for three fifteen-minute intervals with: (i) acetone; (ii) acetone: double de-ionized water (1:1); and then with (iii) double de-ionized water. After drying in air, these metal sheets were thermally oxidized by using custom designed large flame (Knight, Model RN 3.5 x a WC) under controlled natural gas and oxygen flows. Most importantly, the flame must be kept facing

downward to minimize the excess air flow from the surrounding. The same oxidation temperature range and oxidation times mentioned in section 2.1 were utilized. Each flame oxidation temperature was kept constant for the duration of oxidation by controlling the flow rates of oxygen (1.5 L/min to 2.0 L/min) and the natural gas (2.0 L/min).

The flow rates of both natural gas and oxygen were measured using the flow meter (OMEGA Engineering Inc., Model FL-1806). The digital thermocouple (Thermolyne Corp K-type Thermocouple, PM-20700) was used to measure and maintain the temperature of the flame. The oxide layers on the top of front and back sides of the Ti, Fe and W samples were removed using a file. This area was used to make electric contact using a copper clip. The back side and part of the front side were covered with a non-conducting epoxy adhesive. The uncovered area of the photoelectrode which was exposed to incident light was calculated using an Image J computer program.

**Synthesis of CM-n-TiO<sub>2</sub> Films by the Combination of Spray Pyrolysis and Thermal Flame Oxidation (spray-flame made).** Spray pyrolytic synthesis of thin films of semiconductors were described earlier in detail [4, 7]. The spray solution consisted of 0.175 M TiCl<sub>4</sub> in ethanol. Titanium metal sheets from Alfa (0.25 mm thick, 99.5% pure) were used as substrates. A custom made Pyrex 250 mL round-bottom flask with two spray attachments on the glassware was used to spray the solution as shown in Figure 2.2. These attachments consist of two burette like tips that point at each other at a 90° angle. The lower burette was used to deliver the ethanolic solution and the other burette tip acted as the point at which the carrier gas flows to atomize the ethanolic solution.

The spray pyrolysis was carried out at a substrate temperature of 460°C for a total of 20 s. The pressure of the carrier gas (oxygen) was maintained at 20 PSI. Five minute breaks were allowed between each spray period of 10 s to maintain a constant temperature on the substrate surface. A Thermolyne Corp. K-type Thermocouple (PM20700, Series 405) was used to measure and maintain the temperature of Ti metal substrate placed on a Fisher Scientific hotplate. Thermal flame oxidation for 16 min at 825 °C (as described in section 2.1) was then performed.

**Measurements of Photocurrent Density.** The measurement of photocurrents were performed in a single compartment three-electrode photoelectrochemical cell using CM-n-TiO<sub>2</sub> or n-TiO<sub>2</sub> as the working electrode; platinum as a counter electrode and saturated calomel electrode (SCE) as a reference electrode. An electrolyte solution of 5 M KOH was used. The surface of photoelectrodes was illuminated with light intensity of 100 mWcm<sup>-2</sup> from a 150 Watt xenon arc lamp (Kratos Model LH 150/1). The spectral irradiance of xenon lamp was measured by using a silicon detector (UDT Sensors. Inc., Model 10DP/SB). The photocurrent,  $j_p$ , as a function of measured potential,  $E_{meas}$ , versus Saturated calomel electrode (SCE) was determined using an EG & G Princeton Applied Research model 362 scanning potentiostat and plotted using an EG & G Princeton Applied Research (Houston Model RE 0092) X-Y recorder. The photocurrent  $j_p$  was obtained by subtracting dark current from current under illumination of light. A Keithley multimeter was used to measure the electrode potential at open circuit conditions prior to scanning each sample.

The photocurrents under monochromatic light illumination,  $j_p(\lambda)$ , as a function of wavelength,  $\lambda$ , were measured using 362 EC&G scanning potentiostat, a Spectra Physics monochromator, model 77250 and a Keithley multimeter.

**UV-Vis Spectroscopic Measurements.** UV-Vis absorption spectra of CM-n-TiO<sub>2</sub> and n-TiO<sub>2</sub> were recorded using a Varian Cary 1E UV-Visible Spectrophotometer with a Varian GRID 36is-25 microprocessor and a Dell Optiplex PC. Labsphere (Model DRA-Ca-30I) with a reflectance standard (I.D.USRS-99-010) was used. The UV-Vis absorption spectra were measured for the wavelength range between 190 and 800 nm by means of double reverse reflectance.

**X-ray Diffraction (XRD) Measurements.** X-ray diffraction (XRD) data were collected using PANalytical Xpert-Pro MPD X-ray diffractometer. The scans having angles from  $18^\circ$  to  $70^\circ$  ( $2\theta$ ) were carried out using a Copper  $K\alpha$  radiation ( $\lambda = 1.544 \text{ \AA}$ ) operating at 40 mA and 45 kV. Samples were run with a continuous scan at a rate of 0.100 degrees per minute with a recording period of 0.017 degrees.

**Scanning Electron Microscopic (SEM) Measurements.** Scanning electron micrograms (SEM) were taken using a Cam Scan series 4 microscope operating at 50 kV with a tungsten filament on specimens upon which conductive carbon tape was used to make a contact with the conductive titanium surface with the aluminum sample deck.

**Energy Dispersive Spectroscopic (EDS) Measurements.** An electron microprobe attached to the scanning electron micrograms (SEM) unit (Model Cam Scan series 4) used in energy dispersive spectroscopy (EDS) mode was employed to obtain quantitative information of the amounts of carbon in CM- n-TiO<sub>2</sub>. Furthermore, this EDS system did not use carbon grid as a sample holder. The samples were placed directly on an aluminum sample deck. X-ray detector with an ultra thin window was used to facilitate the detection of light element like carbon. The EDS was performed using a Princeton Gamma Tech. Inc. Integrated Microanalyzer software package.

## Results and Discussion

**Dependence of Photocurrent Density on Measured Electrode Potential.** Plots of photocurrent density ( $j_p$ , mA cm<sup>-2</sup>) as a function of measured potential,  $E_{\text{meas}}$  (V/SCE) for oven-made n-TiO<sub>2</sub> synthesized at 825°C for 16 min (sample 1); CM-n-TiO<sub>2</sub> synthesized by only thermal flame oxidation of Ti at 825°C for 16 min (sample 2); grooved CM-n-TiO<sub>2</sub> synthesized by only thermal flame oxidation of Ti (0.005 inch groove depth) at 820°C for 18 min (sample 3); CM-n-TiO<sub>2</sub> synthesized by spray pyrolysis of 0.175M TiCl<sub>4</sub> in ethanol at substrate temperature of 460 °C for 20 sec at carrier gas (oxygen) pressure of 20 psi followed by thermal flame oxidation at 825°C for 16 min (sample 4) are shown in Fig. 1.

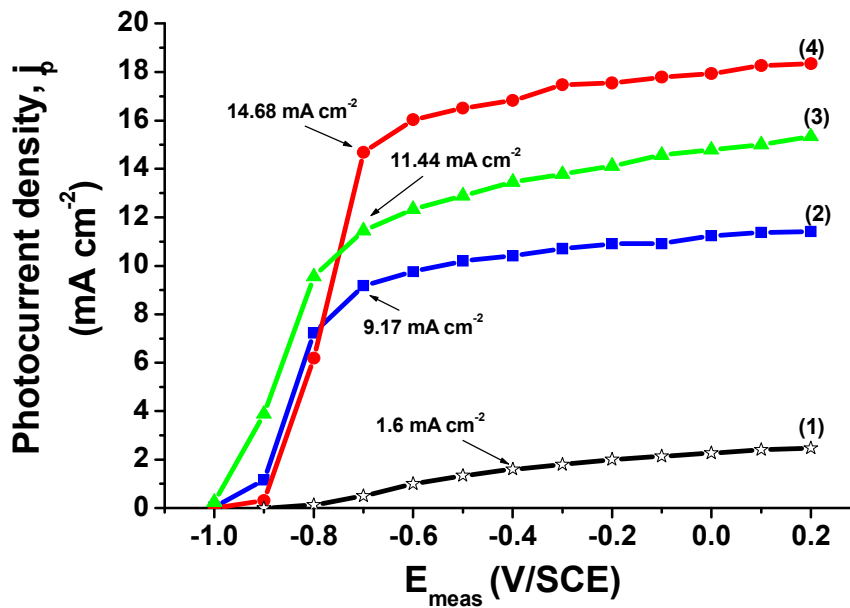


**Fig. 1:** Photocurrent density,  $j_p$  (measured under light intensity of  $100 \text{ mW cm}^{-2}$  from a 150 Watt xenon lamp) as a function of measured potential,  $E_{\text{meas}}$  (V/SCE), for oven-made n-TiO<sub>2</sub> synthesized at 825°C for 16 min (sample 1); CM-n-TiO<sub>2</sub> synthesized by only thermal flame oxidation of Ti at 825°C for 16 min (sample 2); grooved CM-n-TiO<sub>2</sub> synthesized by only thermal flame oxidation of Ti (0.005 in groove depth) at 820°C for 18 min (sample 3); CM-n-TiO<sub>2</sub> synthesized by combination of spray pyrolysis of 0.175M TiCl<sub>4</sub> in ethanol at substrate temperature of 460 °C for 20 sec at carrier gas (oxygen) pressure of 20 psi followed by thermal flame oxidation at 825°C for 16 min (sample 4); electrolyte solution of 5 M KOH was used. The electrode potentials at open circuit condition under illumination,  $E_{\text{aoc}}$ , were found to be -0.977 V/SCE (sample 1), -0.940 V/SCE (sample 2), -0.942 V/SCE (sample 3), and -0.915 V/SCE (sample 4).

Sample 1 shows the lowest photocurrent density of  $1.6 \text{ mA cm}^{-2}$  measured at  $-0.4 \text{ V/SCE}$ . The observed low photocurrent density for sample 1 was due to absence of carbon and as well as lower thickness in such electric oven made samples. Sample 4 generated the highest photoresponse compared to samples, 1, 2 and 3. Photocurrent density, measured at  $-0.7 \text{ V/SCE}$  increased significantly from  $9.17 \text{ mA cm}^{-2}$  for sample 2 to  $11.44 \text{ mA cm}^{-2}$  for sample 3. The surface grooving of Ti metal increased the effective surface area of oxide layer in sample 3 and consequently generated higher photocurrent density. A sharp increase in photocurrent density to  $14.68 \text{ mA cm}^{-2}$  measured at  $-0.7 \text{ V/SCE}$  for sample 4 can be attributed to increased the thickness of the oxide layer synthesized by combination of spray pyrolysis and flame oxidation methods. This is because increased thickness allows absorption of more light to generate more electron-hole pairs (excitons).

**Dependence of Photoconversion Efficiency on Applied Potential.** The calculation of total percent photoconversion efficiency ( $\% \epsilon_{\text{photo}} (\text{total})$ ) of light energy under white light illumination to chemical energy in the presence of an external applied potential ( $E_{\text{app}}$ ) was carried out using the equation given earlier [1, 4] as,

$$\% \epsilon_{\text{photo}} (\text{total}) = j_p (E_{\text{rev}}^{\circ} - |E_{\text{app}}| / P_o) \times 100 \quad (1)$$

where  $j_p$  is the photocurrent density ( $\text{mA cm}^{-2}$ ),  $E_{\text{rev}}^{\circ}$  is the standard reversible potential (which is 1.23 V for water splitting reaction),  $P_o$  is the power density of incident light ( $\text{mW cm}^{-2}$ ),  $|E_{\text{app}}|$  is the absolute value of the applied potential which is obtained as [1],



$$E_{app} = (E_{meas} - E_{aoc}) \quad (2)$$

where  $E_{meas}$  (vs. SCE) is the potential at which the photocurrent density was measured,  $E_{aoc}$  (vs. SCE) is the electrode potential at open circuit condition in the same electrolyte solution under the same illumination intensity at which the photocurrent density was measured. The values of  $E_{aoc}$  (vs. SCE) were found to be  $-0.847$  V,  $-0.940$  V,  $-0.942$  V,  $-0.915$  V for samples 1, 2, 3, 4 respectively.

The corresponding maximum photoconversion efficiencies (see Fig. 2) were found to be 1.2 % at 0.447 V bias, 9.08 % at 0.240 V bias, 11.31 % at 0.242 V bias, and 14.04 % at 0.215 V bias for samples 1, 2, 3, and 4, respectively.

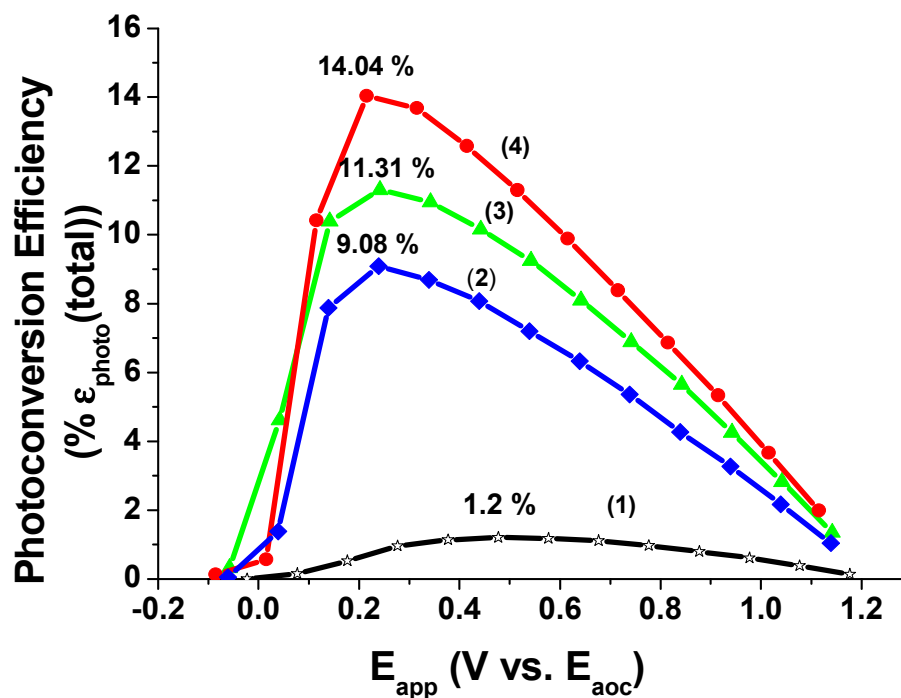


**Fig. 2:** Dependence of photoconversion efficiency, %  $\epsilon_{photo}(\text{total})$ , on applied potential  $E_{app}$  (V vs.  $E_{aoc}$ ), for samples 1, 2, 3 and 4.

**Monochromatic Photocurrent Density - Wavelength Dependence.** The plots of monochromatic photocurrent density,  $j_p(\lambda)$ , as a function of wavelength of light,  $\lambda$ , for samples 1, 2, 3 and 4 are shown in Fig. 3.

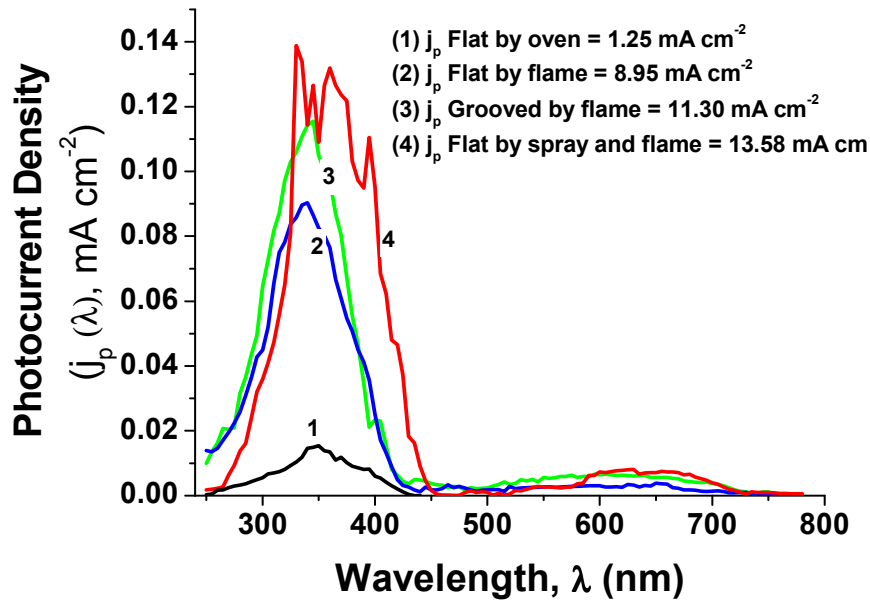


**Fig. 3:** The monochromatic photocurrent density,  $j_p(\lambda)$ , as a function of wavelength of light,  $\lambda$ , for samples 1, 2, 3 and 4 respectively.

The monochromatic photocurrent density,  $j_p(\lambda)$ , was measured (at measured potentials corresponding to applied potential at which maximum %  $\epsilon_{\text{photo}}(\text{total})$  was observed (see Fig. 2) under white light illumination. The values of  $E_{\text{app}}$  used were 0.477 V, 0.240 V, 0.242 V and 0.215 V for samples 1, 2, 3 and 4 respectively. Performing integration under the curve, total photocurrent densities of 1.25 mA cm<sup>-2</sup>, 8.95 mA cm<sup>-2</sup>, 11.30 mA cm<sup>-2</sup> and 13.58 mA cm<sup>-2</sup> were found for samples 1, 2, 3, and 4, respectively. These values are a little lower than the corresponding photocurrent density values under white light illumination from the xenon lamp because of loss of some light passing through the monochromator.

**Photoconversion Efficiency from Monochromatic Photocurrent Density.** Alternatively, the percent total photoconversion efficiency (%  $\epsilon_{\text{photo}}(\text{total})$ ) of light energy to chemical energy can be obtained by using the following equation [20, 21, 49, 50]:

$$\% \epsilon_{\text{photo}}(\text{total}) = \frac{\int_{\lambda_{\min}}^{\lambda_g} j_p(\lambda) [E_{\text{rev}}^o - |E_{\text{app}}(\lambda)|] d\lambda}{\int_{\lambda_{\min}}^{\infty} P_o(\lambda) d\lambda} \times 100 \quad (3)$$

where  $j_p(\lambda)$  is wavelength dependent photocurrent density under monochromatic light illumination (mA cm<sup>-2</sup> nm<sup>-1</sup>) and  $P_o(\lambda)$  is the power density of incident monochromatic light (mW cm<sup>-2</sup> nm<sup>-1</sup>). Note that the applied potential,  $E_{\text{app}}(\lambda)$  was found to be wavelength dependent and can be expressed as,

$$E_{\text{app}}(\lambda) = E_{\text{meas}} - E_{\text{aoc}}(\lambda) \quad (4)$$

where  $E_{\text{aoc}}(\lambda)$  is the electrode potential in volts at open circuit conditions under monochromatic light illumination.  $\lambda_{\min} = 250$  nm for light from xenon lamp and 300 nm for sunlight, and  $\lambda_g =$

$1239.85/E_g$  is the threshold wavelength corresponding to band gap energy,  $E_g$  of the sample in electron volt unit.

Note that wavelength dependent percent photoconversion efficiency,  $\% \epsilon_{\text{photo}}(\lambda)$  can be expressed as [20, 21],

$$\% \epsilon_{\text{photo}}(\lambda) = \frac{j_p(\lambda)[E_{\text{rev}}^\circ - |E_{\text{app}}(\lambda)|]}{\int_{\lambda_{\text{min}}}^{\infty} P_0(\lambda) d\lambda} \times 100 \quad (5)$$

The plot of  $\% \epsilon_{\text{photo}}(\lambda)$  versus wavelength,  $\lambda$ , using Eq. 5 is given in Fig. 4 where total intensity in the denominator of Eq. 5 was taken as  $100 \text{ mW cm}^{-2}$ .

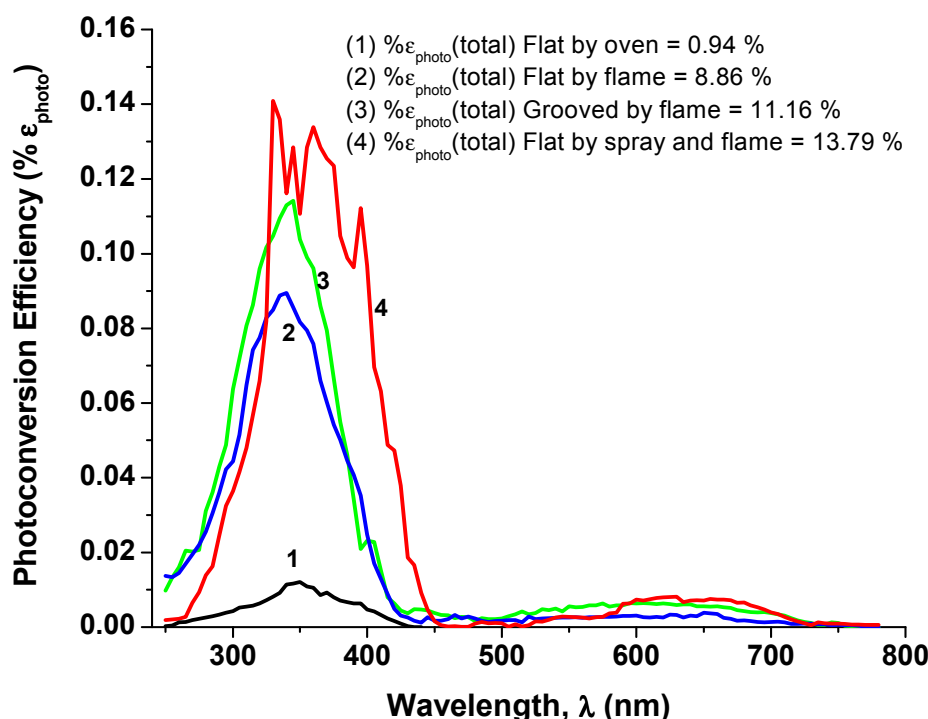


**Fig. 4:** The photoconversion efficiency,  $\% \epsilon_{\text{photo}}(\lambda)$ , as a function of wavelength of light,  $\lambda$ , for samples 1, 2, 3 and 4.

Performing the integration (as given in Eq. 3) from  $\lambda_{\text{min}} = 250 \text{ nm}$  (for xenon lamp white light) to  $\lambda_g$  nm or determining the area under the curve in Fig. 4 obtained using Eq. (5), total photoconversion efficiencies of 0.94 %, 8.86 %, 11.16 % and 13.79 % were obtained for samples 1, 2, 3 and 4 respectively. These values are little lower but comparable to 1.2 %, 9.08 %, 11.31 % and 14.04 % (when calculated using equation 1 under white light illumination of intensity  $100 \text{ mW cm}^{-2}$  from a 150 W xenon lamp) for samples 1, 2, 3, and 4, respectively.

It is observed in Fig. 3 that higher photocurrent response and consequent higher photoconversion efficiency of CM-TiO<sub>2</sub> samples was determined by the unusually higher ability of the material to use the absorbed UV-photons to convert OH<sup>-</sup> ions to O<sub>2</sub> gas. Such unusual behavior of CM-n-TiO<sub>2</sub> samples mainly in the UV regions may be explained in terms of following effects. One is the possible multi electron-hole pairs (excitons) generation (MEG) by absorption of single

high energy photons in the UV-region across multiple low energy band gaps (see Fig. 5) in the CM-n-TiO<sub>2</sub> nanocrystals (*Ncs*) as it is observed in its scanning electron micrograph (see Fig. 6).

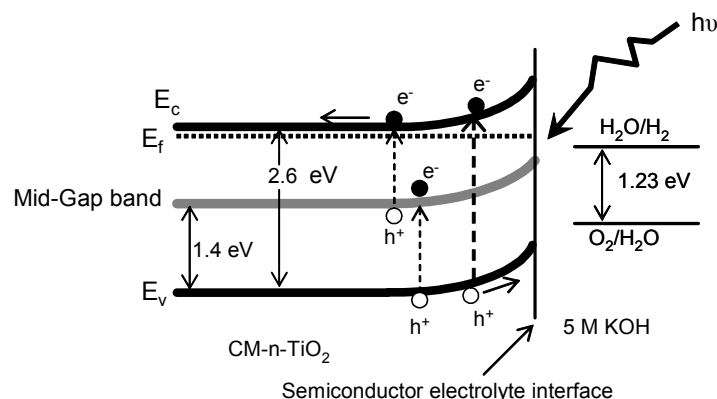


**Fig. 5:** A schematic diagram of valence, conduction and mid-gap bands to show the band gaps in CM-n-TiO<sub>2</sub> films synthesized by thermal flame oxidation of Ti metal sheet.

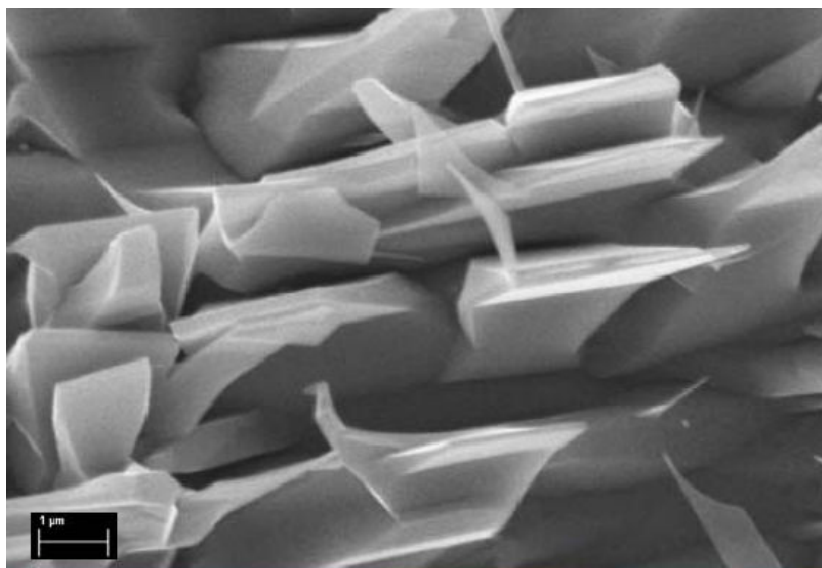


**Fig. 6:** SEM images for a CM-n-TiO<sub>2</sub> (sample 4).

The multi- exciton generation (MEG) by a single photon was observed earlier [51-53] in *Ncs* and explained theoretically in terms of impact ionization [54-56]. Such MEG by a single photon can be explained also by other physical process, such as generation of multiple excitons by absorption of light when excess energy of photogenerated electrons by high energy UV photons is lost as radiation re-absorbed.

Furthermore, the microscopic nanocrystalline and rough nanowall surface of CM-n-TiO<sub>2</sub> (see Fig. 6) could have temporarily trapped microscopic oxygen gas bubbles that may have acted as tiny lenses and spherical mirrors that helped to concentrate the incident light on the electrode surface, augmenting the photoresponse for water splitting by an order of magnitude.

**Band gap Energy Determination.** The band gap energy,  $E_g$ , can be determined from the frequency of light,  $\nu$ , dependent quantum efficiency,  $\eta(\nu)$ , using the following equation [4, 5, 7]:

$$\eta(\nu) h\nu = A (h\nu - E_g)^n \quad (6)$$

where  $A$  is a constant,  $n$  equals either 0.5 for allowed direct transition or 2 for allowed indirect transitions,  $h\nu$  is the photon energy of frequency,  $\nu$ . The wavelength,  $\lambda$  dependent quantum efficiency,  $\eta(\lambda)$  or incident photon conversion efficiency, IPCE ( $\lambda$ ) can be expressed as [20, 21],

$$\eta(\lambda) = \text{IPCE}(\lambda) = j_p(\lambda) / [e I_0(\lambda)]$$

$$= [1239.85 (\text{V nm}) J_p(\lambda) (\text{mA cm}^{-2} \text{ nm}^{-1})] / [\lambda (\text{nm}) P_o(\lambda) (\text{mW cm}^{-2} \text{ nm}^{-1})] \quad (7)$$

where  $e$  is the electronic charge and the incident photon flux and the wavelength dependent photon flux,  $I_0(\lambda)$  ( $\text{cm}^{-2} \text{ nm}^{-1} \text{ s}^{-1}$ ) was expressed as [20, 21],

$$I_0(\lambda) = P_o(\lambda) \lambda / hc$$

$$= [P_o(\lambda) (\text{mW cm}^{-2} \text{ nm}^{-1}) \lambda (\text{nm})] / [1239.85 (\text{V nm}) e] \quad (8)$$

where  $h$  is the Planck's constant and  $c$  is the velocity of light

Fig. 7 shows  $[\eta(\lambda) h\nu]^{1/2}$  vs.  $h\nu$  plot for samples 1, 2, 3 and 4 respectively.

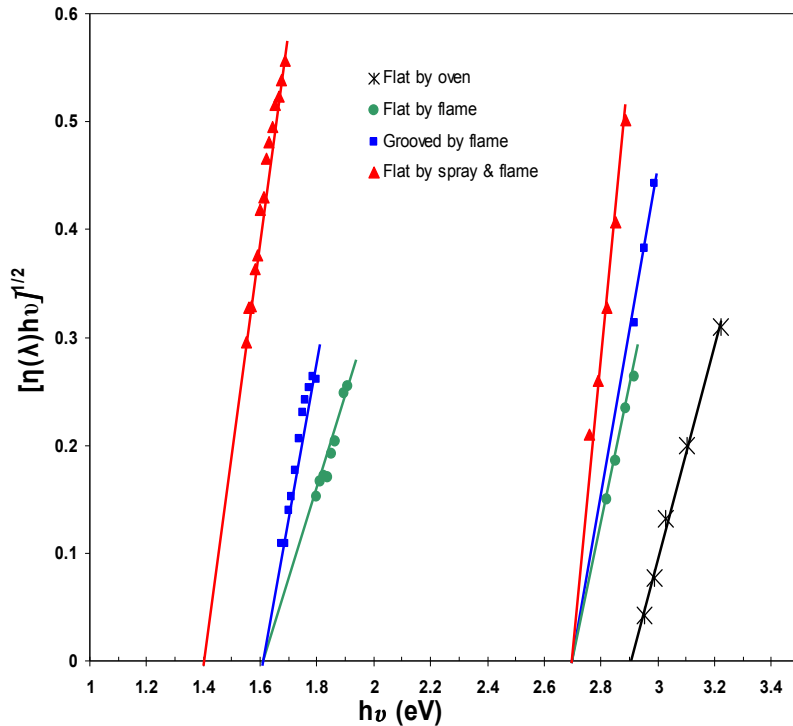


**Fig. 7:** The respective plots of  $[\eta(h\nu)]^{1/2}$  vs.  $h\nu$  to determine the band gap for samples 1, 2, 3 and 4.

From the intercepts of the straight lines the band gaps were obtained. It shows two indirect band gap energies for all CM-n-TiO<sub>2</sub> photoelectrodes. The first band gap energy of 2.65 eV corresponds to lowering of original band gap (samples 2, 3 and 4) and second band gap with values of 1.6 eV and 1.4 eV can be attributed to mid-gap band generated by carbon doping (see schematic diagram in Fig. 5). Theoretical analysis [45-38] and experimental findings [38] also showed multiple band gaps in CM-n-TiO<sub>2</sub>. Oven-made n-TiO<sub>2</sub> showed only one band gap of 2.9 eV, and as a result, poor photoresponse was obtained. Note that the first band gap energy values for all CM-n-TiO<sub>2</sub> samples were found equal. The slopes of band gap plots for sample 4 were found to be the highest, which is in accordance with the highest observed photoresponse generated by this sample.

**Spectral Distribution of Light for Global AM 1.5 Natural Sunlight (1 sun) and Xenon lamp Light (100 mW cm<sup>-2</sup>).** It is important to compare the spectral distribution of light from both xenon lamp light and sunlight. Fig. 8 compares the spectral distribution of these two lights.

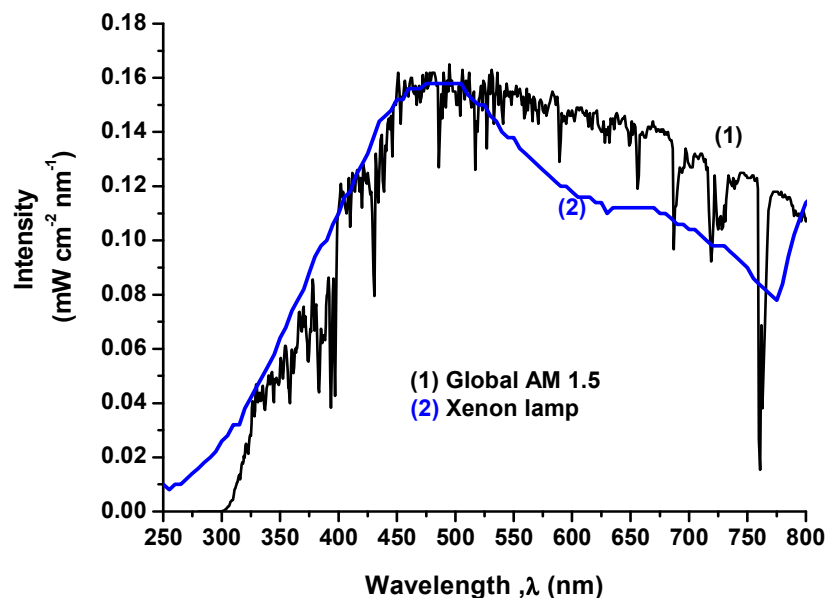


**Fig. 8:** The wavelength dependent intensity of light from a 150 W xenon lamp at intensity of 100 mW cm<sup>-2</sup>, measured by using silicon photon detector (UDT Sensors. Inc., Model 10DP/SB), compared to the wavelength dependent intensity of natural global AM 1.5 sunlight in the wavelength range from 300 to 800 nm obtained from NREL website [51].

The integrated value of the intensity from 300 up to 800 nm for global sunlight AM 1.5 (1 sun = 100 mW cm<sup>-2</sup> measured by NREL [51]) was found to be 59.00 mW cm<sup>-2</sup>. This clearly indicates that the contribution from remaining light from 800 nm to 4100 nm present in global sunlight will be 41.00 mW cm<sup>-2</sup> [= (100 – 59) mW cm<sup>-2</sup>]. Hence, total xenon lamp light comparable to sunlight (1sun) will be 97 mW cm<sup>-2</sup> [= (56 + 41) mW cm<sup>-2</sup>] where 56.00 mW cm<sup>-2</sup> is the integrated value of intensity from 250 nm to 800 nm for xenon lamp light.

Note that the spectral distribution of xenon lamp light begins below 250 nm compared to global AM 1.5 sunlight that begins at 300 nm. Furthermore, the spectral distribution of xenon lamp light is higher in the UV region, but in the visible region it is lower than that of sunlight. Hence, one will expect comparable photocurrent density and photoconversion efficiencies for CM-n-TiO<sub>2</sub> samples for water splitting under actual global sunlight illumination of AM 1.5 (1 sun) and the xenon lamp illumination of intensity of 100 mW cm<sup>-2</sup>. However, relatively higher values for photocurrent density and photoconversion efficiency under xenon lamp illumination will be expected compared to those under sunlight for CM-TiO<sub>2</sub> due to higher spectral distribution of the former in the UV region than in the visible region (see Fig. 9) and that the absorption coefficient of light of CM-TiO<sub>2</sub> in UV region is much higher compared to that in the visible region.

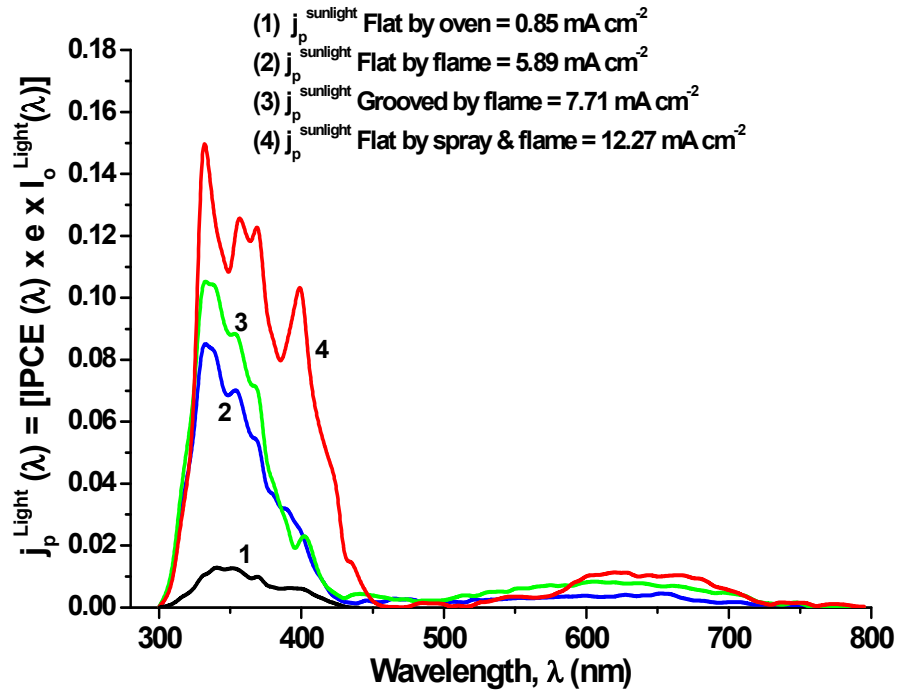


**Fig. 9:** Wavelength dependent photocurrent density under global sunlight illumination,  $j_p^{\text{sunlight}}(\lambda) = [\text{IPCE}(\lambda) \times e \times \text{global sunlight intensity, } I_o^{\text{sunlight}}(\lambda)]$ , versus wavelength of incident Xenon lamp,  $\lambda$ , for samples 1, 2, 3 and 4.

**Photocurrent Density and Photoconversion Efficiency from IPCE ( $\lambda$ ) using Illumination intensity,  $I_o(\lambda)$  of Natural global AM 1.5 Sunlight.** Utilizing the values of the wavelength dependent incident photon conversion efficiency IPCE ( $\lambda$ ) or quantum efficiency,  $\eta(\lambda)$  of these samples it is possible to determine the photocurrent density,  $j_p^{\text{sunlight}}(\lambda)$ , under natural global AM 1.5 sunlight illumination as [20, 21],

$$j_p^{\text{sunlight}}(\lambda) = \text{IPCE}(\lambda) e I_o^{\text{sunlight}}(\lambda) \quad (9)$$

where  $I_o^{\text{sunlight}}(\lambda)$  is the wavelength dependent photon flux of incident global AM 1.5 sunlight which can be obtained using Eqs. 7 and 8 in which photon power density of sunlight  $P_o^{\text{sunlight}}(\lambda)$  was used from the tabulated data given in National Renewable Energy Laboratory (NREL) web site [51].

The plots of  $j_p^{\text{sunlight}}(\lambda)$  [data obtained from Eq. 9] versus the wavelength of light,  $\lambda$ , for samples 1 - 4 are given in Fig. 9. The integrated values of total current density under sunlight illumination were found to be  $0.85 \text{ mA cm}^{-2}$ ,  $5.85 \text{ mA cm}^{-2}$ ,  $7.71 \text{ mA cm}^{-2}$  and  $12.27 \text{ mA cm}^{-2}$  for sample 1, 2, 3 and 4 respectively.

The total photocurrent density,  $j_p^{\text{sunlight}}(\text{total})$ , under sunlight illumination can be expressed as [20, 21],

$$j_p^{\text{sunlight}}(\text{total}) = \int_{\lambda_{\min}}^{\lambda_g} \text{IPCE}(\lambda) I_o(\lambda) d\lambda \quad (10)$$

The total photoconversion efficiency under natural sunlight illumination can be expressed as [20, 21],

$$\% \epsilon_{\text{solar}}^{\text{sunlight}} (\text{total}) = \frac{\int_{\lambda_{\min}}^{\lambda_g} j_p^{\text{sunlight}}(\lambda) [E_{\text{rev}}^o - |E_{\text{app}}(\lambda)|] d\lambda}{\int_{\lambda_{\min}}^{\infty} P_o^{\text{sunlight}}(\lambda) d\lambda} \times 100 \quad (11)$$

where the denominator was taken as  $100 \text{ mW cm}^{-2}$  for actual natural global AM 1.5 sunlight (1 sun).

Hence, using Eq. 10 and the denominator in Eq. 11 as  $100 \text{ mW cm}^{-2}$  for global AM 1.5 sunlight one can express the simplified form of Eq. 11 as,

$$\% \epsilon_{\text{solar}}^{\text{sunlight}} (\text{total}) = [j_p^{\text{sunlight}} (\text{total}) \text{ mA cm}^{-2} (1.23 - E_{\text{app}}) \text{ volt} / 100 \text{ mW cm}^{-2}] \times 100 \quad (12)$$

Where  $E_{\text{rev}}^o = 1.23$  volt was used for water splitting reaction.

Photoconversion efficiencies under sunlight illumination were obtained using Eqs. 11 or 12. Fig. 10 shows the calculated wavelength dependent percent photoconversion efficiencies under sunlight illumination,  $\% \epsilon_{\text{solar}}^{\text{sunlight}}(\lambda)$  as a function of wavelength of incident light,  $\lambda$ .

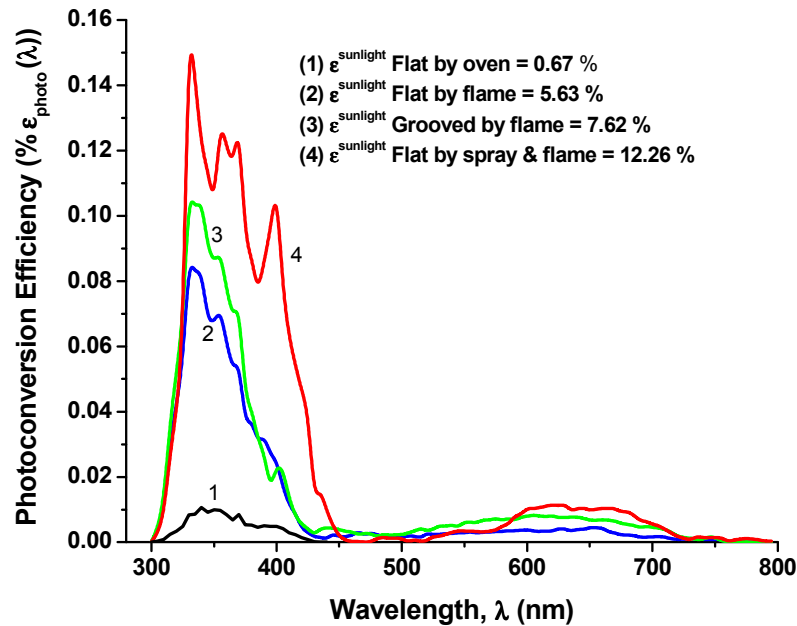


**Fig. 10:** Wavelength dependent photoconversion efficiency under sunlight illumination,  $\% \epsilon_{\text{solar}}^{\text{sunlight}}$ , versus wavelength of incident light,  $\lambda$ , for samples 1, 2, 3 and 4.

Performing the integration under the curve from 300 nm to  $\lambda_g$ , photoconversion efficiencies of 0.67 %, 5.63 %, 7.62 and 12.26 % were found for samples 1, 2, 3 and 4, respectively. These results indicate that CM-n-TiO<sub>2</sub> thin films synthesized by combination of spray pyrolysis and natural gas flame oxidation (sample 4) can be expected to split water with  $\geq 10$  % even under actual sunlight illumination. The photoconversion efficiency values for these 4 samples under different illumination conditions are summarized in Table 1.



**Table 1:** Maximum Photoconversion Efficiencies (%) under xenon lamp light and actual natural sunlight illumination conditions for reference electric oven made (n-TiO<sub>2</sub>), flame made and spray–flame made CM-n-TiO<sub>2</sub> samples and their band gap and mid-gap Energies.

| Titanium<br>Oxide, TiO <sub>2</sub><br>Samples              | % maximum<br>Photoconversion<br>efficiency under<br>white light<br>illumination<br>from Xenon<br>Lamp Light<br>[%] | % maximum<br>Photoconversion<br>efficiency under<br>monochromatic light<br>illuminations from<br>Xenon lamp |                                     | % maximum<br>Photoconversion<br>efficiency under<br>monochromatic<br>actual natural<br>sunlight<br>illuminations<br>(integrated from<br>300 nm present<br>in sunlight)<br>[%] | Band gap<br>Energies          |                               |
|-------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------|-------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------|-------------------------------|
|                                                             |                                                                                                                    | Integrated<br>from 250<br>nm<br>[%]                                                                         | Integrated<br>from 300<br>nm<br>[%] |                                                                                                                                                                               | Band<br>gap<br>Energy<br>[eV] | Mid-<br>gap<br>Energy<br>[eV] |
| 1. Oven made                                                | 1.2                                                                                                                | 0.94                                                                                                        | 0.84                                | 0.67                                                                                                                                                                          | 2.9                           | None                          |
| 2. Flame made                                               | 9.08                                                                                                               | 8.86                                                                                                        | 7.62                                | 5.63                                                                                                                                                                          | 2.65                          | 1.6                           |
| 3. Flame made<br>on grooved Ti<br>surface (from<br>ref. 21) | 11.31                                                                                                              | 11.16                                                                                                       | 8.41                                | 7.62                                                                                                                                                                          | 2.65                          | 1.6                           |
| 4. Spray<br>pyrolysis and<br>Flame made                     | 14.04                                                                                                              | 13.79                                                                                                       | 12.89                               | 12.26                                                                                                                                                                         | 2.65                          | 1.4                           |

**UV-Vis Spectra.** The UV-Vis absorption spectra of n-TiO<sub>2</sub> (sample 1) and CM-n-TiO<sub>2</sub> (samples 2-4) are shown in Fig. 11.

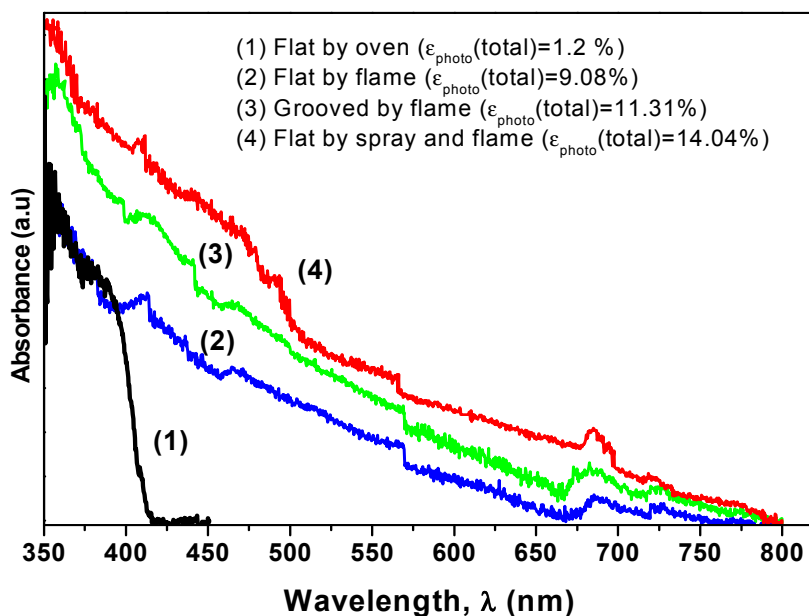


Fig. 11: UV-Visible spectra of Samples 1- 4.

The absorption spectra of CM-n-TiO<sub>2</sub> samples 2, 3 and 4 demonstrate a wide absorption in the UV and visible regions with a tail extending to the near-infrared region up to 800 nm. This indicates low band gap energy values for these samples. The reference oven-made n-TiO<sub>2</sub> (sample 1) shows absorption only up to 415 nm which corresponds to band gap energy of 3.0 eV. The lower band gaps of CM-n-TiO<sub>2</sub> samples can be attributed to carbon incorporation during the flame oxidation of the Ti metal sheet. The UV-Vis spectroscopic results show higher absorption in UV, as well as in the visible regions for CM-n-TiO<sub>2</sub> films synthesized by a combination of spray pyrolysis and flame oxidation (sample 4) compared to sample 2 and 3. Also, these UV-Vis spectra are consistent with the higher photocurrent densities at the CM-n-TiO<sub>2</sub> thin film electrodes prepared by the combination of the two methods. Importantly, this observation conforms to the hypothesis that the spray pyrolysis increased the thickness of the visible light active CM-n-TiO<sub>2</sub> films. Consequently, these films absorbed more light.

However, the UV-Vis spectra do not match well with the monochromatic photocurrent density-wavelength dependent plot (see Fig. 3). The UV-Vis spectra represent the excitation of electrons from a lower energy state (to generate holes in this state) to higher energy state by absorption of light. However, to have photocurrent, photogenerated holes will have to be (1) transported to the interface and (2) undergo transition across the interface to available (thermally distributed) hole acceptor states (e.g., OH<sup>-</sup> ions) in solution. These two extra processes are responsible for the mismatch between the UV-Vis spectra and the monochromatic photocurrent density-wavelength dependent plots.

The electrons that are excited to conduction band from the shallow mid-gap band in CM-n-TiO<sub>2</sub> (see Fig. 5) by light of wavelength around 500 nm shows absorption in the UV-Vis spectra. However, the holes generated in the mid gap band (see Fig. 7) are lost by recombination due to very low availability acceptor states of holes in solution. Consequently negligible photocurrent density was generated (see Fig. 5). However, absorption of light in the UV-Vis spectra around 500 nm was observed because such absorption does not require the availability of acceptor states of holes in solution. Furthermore, the light around 500 nm (2.48 eV) having sub-band gap energy cannot be absorbed by CM-n-TiO<sub>2</sub> to generate electron-hole pairs in its valence band. However, the light

around 600 nm to 700 nm can excite electrons from the valence band to mid-gap band states of CM-n-TiO<sub>2</sub> (see Fig. 6); these electrons move to the counter electrode. The corresponding holes generated in the valence band undergo transition to available acceptor states of holes in solution (OH<sup>-</sup> ions). Consequently, some photocurrents are observed in this wavelength region (see Fig 3).

**Scanning Electron Microscopy (SEM).** The surface characterization of a CM-n-TiO<sub>2</sub> film (sample 4) was performed by employing a scanning electron microscope (SEM) and the image is shown in Fig. 6. The surface looks extremely rough and nanocrystalline area to absorb incident light, multiple absorption and reflection to absorb more light and consequently generated enhanced photoresponse. Furthermore, the microscopic rough surface could temporarily trap microscopic oxygen gas bubbles on rough surface that may have acted as tiny lens and spherical mirrors that helped to concentrate the incident light on the electrode surface and hence augmented the photoresponse for water splitting by an order of magnitude. Generation of multi electron-hole pairs (excitons) by absorption of single high energy photon in UV-region in nanocrystals (Ncs) as was explained theoretically in terms of impact ionization [52-57].

**X-ray diffraction (XRD).** X-ray diffraction (XRD) measurements were carried out to characterize the structure of n-TiO<sub>2</sub> and CM-n-TiO<sub>2</sub> samples. Fig. 12 shows the XRD patterns for oven-made n-TiO<sub>2</sub> (S1 for sample 1); CM-n-TiO<sub>2</sub> synthesized by only thermal flame oxidation (S2 for sample 2) and the CM-n-TiO<sub>2</sub> synthesized by combination of spray pyrolysis and thermal flame oxidation (S3 for sample 4).

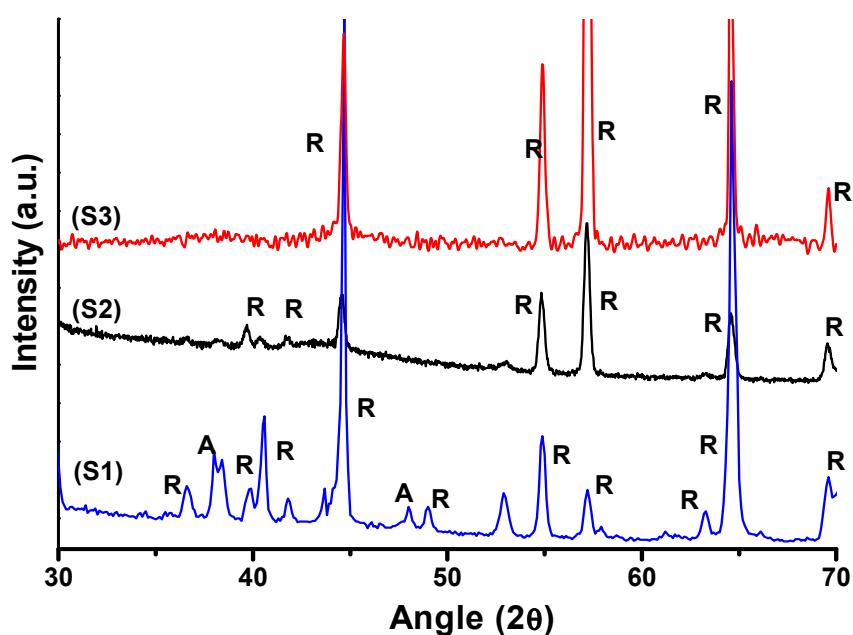


Fig. 12: X-ray diffraction (XRD) patterns for samples 1, 2 and 4 and identified as S1, S2 and S3 respectively.

The peaks of these XRD spectra of both CM-n-TiO<sub>2</sub> photoelectrodes (S2 and S3) are consistent with the rutile structure. The XRD results demonstrate that the crystal structure of oven-made n-TiO<sub>2</sub> (S1) is of mixture of anatase and rutile forms. It is important to note that some peaks of rutile structure are missing in both CM-n-TiO<sub>2</sub> samples (S2 and S3) compared to those in oven-made n-TiO<sub>2</sub> (S1). This indicates the marked influence of carbon modification on the structure of n-TiO<sub>2</sub>.

**Energy Dispersive spectroscopy (EDS).** Fig. 13 shows the Pattern of Energy Dispersive Spectroscopic (EDS) data for samples 1, 2, 3 and 4.

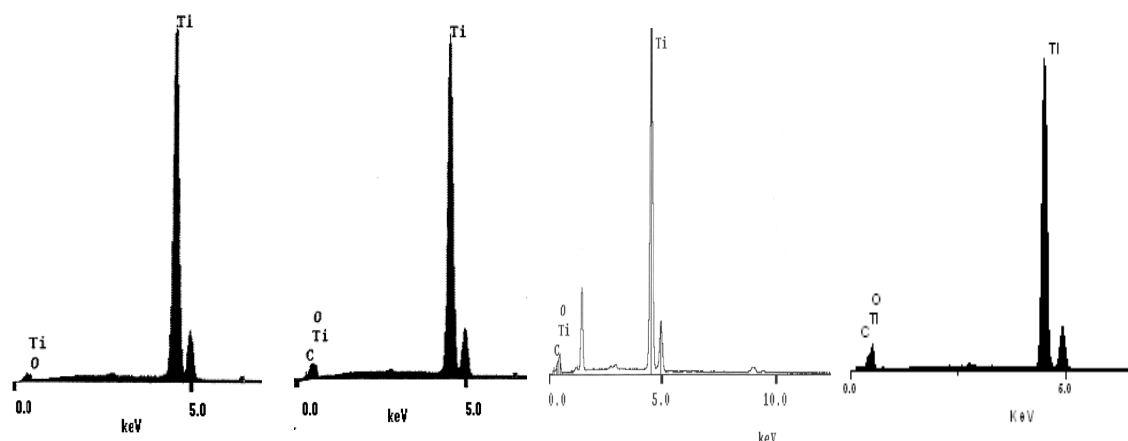


**Fig. 13:** Pattern of Energy Dispersive Spectroscopy (EDS) of samples 1, 2, 3 and 4.

The carbon contents increased significantly from 17.60 atom % for CM-n-TiO<sub>2</sub> synthesized by only thermal flame oxidation to 23.23 atom % for CM-n-TiO<sub>2</sub> synthesized by combination of spray pyrolysis and thermal flame oxidation (see Table 2 for detail).

**Table 2.** Atomic percent of elements, Ti, O and C in n-TiO<sub>2</sub> and CM-n-TiO<sub>2</sub> films from EDS data.

| Element | [Atomic %]              |                                        |                                           |                                                     |
|---------|-------------------------|----------------------------------------|-------------------------------------------|-----------------------------------------------------|
|         | Flat n-TiO <sub>2</sub> | Flat CM-n-TiO <sub>2</sub><br>By flame | Grooved CM-n-TiO <sub>2</sub><br>by flame | CM-n-TiO <sub>2</sub><br>by spray and<br>flame made |
| Ti      | 33.33                   | 15.73                                  | 13.96                                     | 10.10                                               |
| O       | 66.66                   | 66.67                                  | 66.67                                     | 66.67                                               |
| C       | 0                       | 17.60                                  | 19.38                                     | 23.23                                               |

The results in Table 1 were obtained from EDS data which are considered semi-quantitative. Furthermore, Carbon atoms that may be present as substitutional, interstitial and on the surface are all included in the EDS data. Also, from powder X-ray data (see Fig. 12) one cannot identify the type of carbon (graphitic C, C<sub>60</sub> or C<sub>n</sub> etc) present in the sample. For such identification detail XAFS and XANES studies must be carried out. Since all different types of carbon are included in the EDS data, it is not imperative that 50 % of Ti has been replaced by carbon. Hence, the EDS data in Table 1 provides mainly qualitative information concerning the presence of carbon and its relative amounts in these three samples.

**Reproducibility of Synthesis of CM-n-TiO<sub>2</sub>.** Reproducibility is one of the critical aspects in thin film fabrication. The reproducibility of synthesis of the best performing CM-n-TiO<sub>2</sub> (sample 4) electrodes synthesized at the same optimum conditions was tested. Fig. 14 shows photocurrent

density,  $j_p$ , vs. measured potential ( $E_{\text{meas}}$ , V/SCE) of three CM-n-TiO<sub>2</sub> photoelectrodes synthesized by combination of spray pyrolysis and thermal flame oxidation of Ti metal (0.25 mm thick Ti) under the same spray pyrolysis of 0.175M TiCl<sub>4</sub> in ethanol at substrate temperature of 460 °C for 20 sec at carrier gas (oxygen) pressure of 20 psi followed by thermal flame oxidation at 825°C for 16 min (identical conditions used for sample 4).

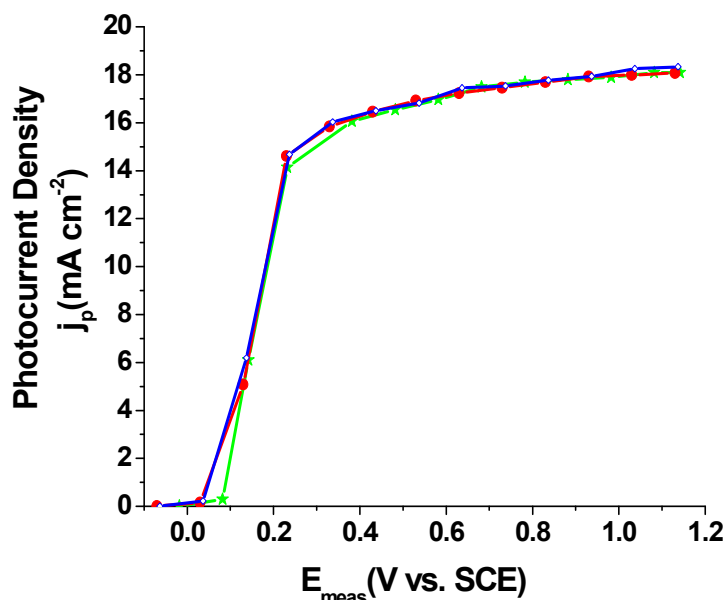


**Fig. 14:** Reproducibility test of synthesis of CM-n-TiO<sub>2</sub> (sample 4) synthesized by combination of spray pyrolysis and flame oxidation in terms of photocurrent density. All three CM-n-TiO<sub>2</sub> thin films electrodes were prepared at the same optimum conditions used for sample 4. The electrode potentials at open circuit condition under illumination,  $E_{\text{aoc}}$  were found to be  $-0.915 \pm 0.02$  V/SCE for all three films.

At open circuit conditions, all three CM-n-TiO<sub>2</sub> samples were found to have almost the same value of  $E_{\text{aoc}}$  such as  $-0.915 \pm 0.02$  V vs. SCE under the same illumination condition. The three samples demonstrate approximately consistent values of photocurrent densities at all measured potentials with standard deviation of  $0.01 \text{ mA cm}^{-2}$  at measured potential of  $-0.7$  volt/SCE at which photoconversion efficiency was found to be maximum.

## Conclusions

It is essential to optimize the temperature and the time of thermal flame oxidation process to synthesize CM-n-TiO<sub>2</sub> films of best photoresponse having highest photoconversion efficiency. The surface grooving increased the surface area of the CM-n-TiO<sub>2</sub>; consequently more visible light was absorbed and higher photocurrent density and photoconversion efficiency were obtained. A spray pyrolysis process increased the thickness of the CM-n-TiO<sub>2</sub>; consequently more visible light was absorbed and higher photocurrent density and photoconversion efficiency were obtained.

Multiple absorption-reflection of light, generation of multi-electron-hole pairs (excitons) by a single energetic photon across mid-gap bands, impact ionization by excitons generated by high energy photons in the nanocrystalline CM-n-TiO<sub>2</sub> [52-57], and incident photon concentration by few order of magnitude [58] by temporarily trapped oxygen gas bubbles on the porous CM-n-TiO<sub>2</sub> surface acted as tiny lens and spherical mirrors helped to augment the photoresponse for water splitting. The combination of spray pyrolysis and flame oxidation process helped to increase the

thickness of the CM-n-TiO<sub>2</sub> films which facilitated the absorption of more light and consequently enhanced the photoresponse and the photoconversion efficiency to a considerable extend to 12.26 % under actual natural sunlight illuminations as summarized in Table 1. A correlation was found between the atom % of carbon content and the amount of visible light absorption and the consequent higher photoconversion efficiency.

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## Structure-Reactivity Relationships of Anatase and Rutile TiO<sub>2</sub> Nanocrystals Measured by In Situ Vibrational Spectroscopy

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**Keywords:** TiO<sub>2</sub>, anatase, rutile, nanocrystal, Fourier transform infrared, spectroscopy, formic acid, formate.

**Abstract.** A comprehensive analysis of structural-reactivity relations on TiO<sub>2</sub> nanocrystals is presented. Using an interplay between TEM, X-ray diffraction and vibrational spectroscopy of well-defined anatase and rutile TiO<sub>2</sub> nanocrystals correlations between the adsorbate structure of formic acid and the corresponding photo-induced decomposition rate are described. It is demonstrated that the detailed bonding configuration determines the decomposition rate. Generalizations and implications of the findings are discussed.

### Introduction

Photocatalysis is a broad research field which lies at the heart of modern sustainable technologies such as air and water cleaning, solar hydrogen production, wet solar cells, self-cleaning and antibacterial surface coatings. A detailed understanding of photocatalytic processes is not possible without explicit model studies of the detailed photocatalyst structure, adsorbate structures and surface reaction mechanisms. The most common crystal modifications of TiO<sub>2</sub> are anatase and rutile. They have different electronic properties with slightly different energy band dispersion with different band gaps and symmetries of band gap interband transitions. The surface atomic arrangement and free energy of a crystal vary with the crystallographic orientation. Therefore, the electronic properties and reactivity as well as other physical and chemical properties of crystals depend on their shape. The {101} and {001} crystal faces of TiO<sub>2</sub> are reported to have the lowest surface energy of anatase, while the {110} crystal faces of rutile have much lower surface energy than other faces [1-4]. Thus different families of crystal planes are expected to terminate anatase and rutile nanoparticles to minimize the particle surface energy. Anatase which has several low index crystal faces with similar surface energy exhibits different crystal morphologies exposing different fractions of low index faces. The minimum free energy morphology of an anatase crystal calculated by the Wulff construction exhibits a truncated tetragonal bipyramidal structure exposing {101} and {001} faces, where more than 90 per cent of the surface are {101} faces [1]. Recent reports suggest that there is an intimate coupling between the particle morphology, the exposed surface faces and the particle reactivity [5-7]. Hence it is of utmost importance to be able to control and modify the morphology of crystals to tune their reactivity.

The (101) surface of anatase is reported to be quite unreactive and do not promote dissociative water, methanol and formic acid adsorption [8-10]. In contrast it has been reported that the (001) surface is reactive: It spontaneously reconstruct under ultra-high vacuum conditions and water spontaneously dissociated on the non-reconstructed (001) surface [11]. The photocatalytic activity of anatase TiO<sub>2</sub> crystal with different morphologies, face distribution and surface atomic arrangements other than that dictated by thermodynamics have been the subject of only few reports.

Yang et al [12] reported on a method to synthesize 1.6  $\mu\text{m}$  sized anatase crystals with a large fraction of  $\{001\}$  faces by using fluorine-terminated surfaces to change the relative stability of  $\{101\}$  and  $\{001\}$  surfaces. They synthesized uniform anatase  $\text{TiO}_2$  crystals with a high percentage (47 per cent) of  $\{001\}$  faces using hydrofluoric acid as a morphology controlling agent. Moreover, they showed that fluorinated surface of anatase single crystals can easily be cleaned using heat treatment to render a fluorine-free surface without altering the crystal structure and morphology. Byun et al [13] reported on a CVD method to prepare anatase  $\text{TiO}_2$  thin films with preferred  $\langle 112 \rangle$  orientation. The  $\langle 112 \rangle$  orientated films resulted in the larger surface area for photocatalytic reaction by forming columnar structure with deeper voids on the film surface. Among the films they prepared those that exhibited  $\langle 112 \rangle$  orientation showed the highest photocatalytic reaction rate for benzene decomposition and was attributed to columnar structure and larger surface area of these films. In a later study Kim et al [14] compared SEM micrographs of the surface morphology and cross sectional images of  $\langle 112 \rangle$  and  $\langle 001 \rangle$ -oriented anatase  $\text{TiO}_2$  films. They concluded that surface of the  $\langle 001 \rangle$  oriented film was denser than that of the  $\langle 112 \rangle$  oriented film. The  $\langle 112 \rangle$  oriented film was reported to consist of  $\{100\}$  and  $\{004\}$  faces and exhibited an open columnar structure perpendicular to the substrate surface, while the  $\langle 001 \rangle$  oriented film exhibited densely aggregated columns. Jhin et al [15] reported a CVD method for preparation of anatase  $\text{TiO}_2$  films with enhanced  $\langle 112 \rangle$  orientation on soda-lime glass by plasma pretreatment of the substrate. Tokita et al [16] prepared anatase films on non-epitaxial substrates by a CVD method. The films exhibiting  $\langle 110 \rangle$ ,  $\langle 100 \rangle$ ,  $\langle 112 \rangle$  and  $\langle 001 \rangle$  crystal orientation showed high photocatalytic activity for methylene blue reduction. Among them the  $\langle 112 \rangle$  oriented film had the highest reactivity.

Ohno et al [17] studied the crystal face dependent photocatalytic reactivity of 1  $\mu\text{m}$  large rutile and anatase crystals obtained from Toho Titanium Company. The truncated tetragonal bipyramidal shaped anatase particles in this study exposed predominantly  $\{101\}$  and  $\{001\}$  faces. Photocatalytic reduction of hexachloroplatinate resulted in Pt deposits on all faces of the anatase crystals only when isopropanol was added to the solution. By monitoring the amount of deposits on various crystal surfaces they showed that the anatase  $\{001\}$  faces pre-coated with Pt were more reactive for  $\text{Pb}^{2+}$  oxidation to  $\text{PbO}_2$  than the  $\{101\}$  faces. They thus concluded that the  $\{001\}$  and  $\{101\}$  faces provide oxidative and reductive sites, respectively. In another study Taguchi et al [18] etched the micro-sized anatase particles. By comparing the structure determined by SEM before and after etching they showed that by this process the edge between two  $\{101\}$  faces is selectively etched thus forming new  $\{112\}$  faces. Large  $\text{PbO}_2$  deposits are observed in SEM on the  $\{112\}$  faces when  $\text{Pb}^{2+}$  was photocatalytically oxidized on the Pt-deposited  $\text{TiO}_2$  particles. The oxidative activity of the  $\{112\}$  face was considered to be stronger than that of the  $\{001\}$  face, which acts as the oxidative site on the  $\text{TiO}_2$  particles before etching because no  $\text{PbO}_2$  deposits were seen on the  $\{001\}$  face of the etched particles.

In this paper we combine in situ vibrational spectroscopy with solution based nanofabrication methods to probe the adsorbate structure of formic acid on  $\text{TiO}_2$  nanoparticles with different structure and particle size. We show that the  $\text{TiO}_2$  surface structure strongly affects the bonding and photo-reactivity. There are hitherto no reports available that describes the photocatalytic reactivity of the  $(112)$ ,  $(100)$  and  $(111)$  anatase surfaces for organic molecules. In particular, there are no reports that treats the photocatalytic activity of anatase  $\text{TiO}_2$  nanoparticles in the 10-60 nm size range that exposes  $\{112\}$ ,  $\{111\}$ , and  $\{100\}$  faces. Even though reports of large anatase crystals and minerals exhibiting a truncated ditetragonal bipyramidal terminated by  $\{100\}$ ,  $\{112\}$  or  $\{001\}$  faces have published elsewhere [12, 17, 18], these studies are not related to catalysis, in particular photocatalysis, nor to the particle size regime below 100 nm. Our results suggest that even though  $\text{TiO}_2$  photocatalysis has been studied extensively during the past decades, the understanding of the bonding and reactivity of even the simplest organic molecules with  $\text{TiO}_2$  is still very much rudimentary and there are plenty of room for improvements in many applications. Advanced

Infrared (IR) surface spectroscopy is an important characterization technique in this context that provide information of adsorbate structures, and mechanism of molecular surface processes occurring on metal oxides. IR spectroscopy allows for studies under a wide range of experimental conditions: from ultra-high vacuum to high pressures, from cryogenic temperatures to ~800 K, in gas or liquids, on single crystals, powders, thin films, or colloidal solutions. This allows for true in situ or operando studies, which can provide valuable information that can help bridge pressure and structure gap problems known to hamper our understanding of e.g. catalytic reactions on solid surfaces, including photocatalytic reactions [6, 19-22].

## Experimental

Nanoparticles were prepared by solution based methods employing alkoxide precursors [23, 24] or hydrothermal treatments of microemulsions [25, 26] as described in detail elsewhere. The particles thus obtained were all well-crystallized, mono-disperse and spectroscopically contaminant free. The anatase samples are denoted “A25”, “A40” and “A60”, respectively. The latter is the commercially available anatase obtained from BDH Ltd. Sample “P25” is the commercially available TiO<sub>2</sub> powder sample P25 provided by Degussa AG which is typically used as a reference photocatalyst. P25 is not phase pure; it contains 70-80 wt.% anatase primary particles mixed with rutile primary particles. The sample denoted “Rutile 6x80” is pure rutile TiO<sub>2</sub> nanoparticles [25, 26].

Structural, optical and chemical properties of the synthesized materials were characterized by a range of different techniques as described in detailed elsewhere [24, 25, 27]. Briefly, phase analysis was made by the powder X-ray diffraction patterns obtained with a Guiner-Hägg focusing camera employing Cu K $\alpha_1$  radiation and Si as internal standard using a Siemens D5000 instrument. The X-ray diffraction patterns all showed that the materials were of the tetragonal anatase or rutile modification, respectively, with characteristic 2 $\Theta$  diffraction peaks. The particle diameter determined from a Scherrer analysis of the (101) diffraction peak are shown in Table 1. Scanning electron microscope (SEM) images were obtained with a FEG-SEM Leo 1550 Gemini instrument. Transmission electron microscopy (TEM) was done with a Jeol 2000 FXII instrument equipped with an EDS module (Link AN 1000). High-resolution transmission electron microscopy (HR-TEM) and selected area diffraction (SAED) were performed with a transmission electron microscope JEOL JEM 3010 operated at 300 kV (LaB6 cathode) giving a point resolution of 0.17 nm [28]. A copper grid coated with a holey carbon support film was used to prepare samples for the TEM observation. The grid was coated by dispersing powder samples in ethanol and subsequent treatment of the suspension in ultrasound for 10 minutes. The TEM analyses showed that the entire sample was crystalline with well developed crystal faces [7].

Morphology analysis of the particles was done by orienting a computer simulated crystal morphology (tetragonal symmetry, point group 4/mm) according to the orientation deduced from the HRTEM and SAED analysis of TEM micrographs and subsequently fitting the crystal surface energy (vectorial distance from crystal origin to surface plane) to yield a best two-dimensional fit with the experimental images. This procedure was made for typically 2-4 different particles from each batch with sufficient data quality. For consistency validation, morphology analysis was also made on TEM images of particles where no a priori knowledge of particle orientation was available. Complementary validation of the particle dimensions was made by comparing the size,  $d_{hkl}$ , of the particles from XRD data calculated from the Scherrer equation, viz.  $d_{hkl}=0.9\lambda/B_{hkl}\cos\theta$ , by analysis of the full-width at half maximum of the reflection from the (101), (004) and (200) planes for anatase and the (110) from rutile, respectively. The major exposed surface faces determined from the morphology analyses are presented in Table 1 (see Results section below). Visualization of the crystals was made with the WinMorph software [29]. The accuracy of the dimensions determined from this analysis is estimated to be better than 15%. Sufficient HRTEM data of the A25 particles

with appropriate orientation with respect to the electron beam prevents however an unambiguous determination of (112) planes, whose existence can only be inferred indirectly from low magnification TEM data and XRD dimensions.

| Sample | Phase           | Particle size [nm] <sup>§</sup> | Major exposed surfaces <sup>*</sup> |
|--------|-----------------|---------------------------------|-------------------------------------|
| A25    | anatase         | 25                              | {101}, {001}, {100}, ({112})        |
| A40    | anatase         | 40                              | {101}, {112}, {111}, {100}          |
| A60    | anatase         | 66                              | {101}, {001}                        |
| R6x80  | rutile          | 20                              | {110}, ({101})                      |
| P25    | anatase/ rutile | 21                              | n.a.                                |

**Table 1** Physical properties of the TiO<sub>2</sub> nanoparticles used in the present study [21, 24, 25, 27]. <sup>§</sup>) Particle size determined from Scherrer analysis of (101) peak. <sup>\*</sup>) Exposed surfaces are listed in order of relative abundance. Surfaces in parenthesis are not conclusively evidenced from morphology analysis of HR-TEM images.

The HCOOH adsorbate structures were determined by in situ Fourier transform infrared (FTIR) spectroscopy employing a vacuum pumped spectrometer (Bruker IFS66v/S) equipped with a LN<sub>2</sub> cooled narrow band HgCdTe detector. All FTIR measurements were performed in modified transmission (Specac) or diffuse reflectance, DRIFT, (Praying-Mantis, Harrick) gas reaction cells allowing for *in situ* reaction studies with simultaneous gas deposition, light illumination and FTIR spectroscopy of the thin solid films or powders [24, 28]. For DRIFT spectroscopy of adsorbates on TiO<sub>2</sub> nanoparticles dilution of the solid by e.g. KBr is not necessary since IR absorption by TiO<sub>2</sub> is negligible above 1000 cm<sup>-1</sup> where most necessary spectral information is located. The ionic character of the Ti-O bonds in TiO<sub>2</sub> is manifested in the strong IR absorption below ca. 950 cm<sup>-1</sup>. IR spectroscopy of adsorbed species on metal oxide surfaces is therefore in general prohibited below ca. 1000 cm<sup>-1</sup>. It should be noted that even though the particle size is in general much smaller than the irradiation wavelength for nanoparticles the IR spectrum of TiO<sub>2</sub> (and metal oxides in general) is still not independent of particle size. Field-induced polarization effects and state of aggregation may have strong influence on the M-O vibrational stretching modes and must be considered on a case by case basis [30].

Formic acid (GC grade, Merck) was adsorbed on the various TiO<sub>2</sub> nanoparticles by means of a homebuilt gas generator [24, 28]. The independently calibrated formic acid concentrations in the gas feed were ca. 7900 ppm. No other gases than formic acid were detected by mass spectrometry analysis of the gas effluent from the reaction cells. FTIR spectra were recorded with 4 cm<sup>-1</sup> resolution and 135 scans (corresponding to 30 sec measurement time per spectra) and 30 sec dwell time between consecutive spectra. Prior to each measurement the samples were annealed at 673 K in synthetic air and subsequently cooled to 299 K in the same feed. After dosing the sample was kept in the gas feed for ca 15 minutes prior to illumination (except when otherwise stated). FTIR backgrounds were collected on clean samples (265 scans) in synthetic air or N<sub>2</sub> feed at 299 K. FTIR spectra were smoothed with a Savitzky-Golay algorithm using a 9 point window. Absorbance peak areas were obtained after appropriate base line corrections and Lorentzian curve fitting of the spectral region of interest.

Photo-induced degradation of HCOOH and surface reactions were measured by in situ FTIR spectroscopy by monitoring the mode resolved surface products and adducts as a function of time during illumination. Repeated FTIR spectra were measured with 4 cm<sup>-1</sup> resolution as a function of time consisting typically of 135 scans and 30 sec dwell time between consecutive spectra. The samples were held at 299 K in a 100 ml min<sup>-1</sup> gas flow of synthetic air (20% O<sub>2</sub> and 80% N<sub>2</sub>) during measurements.

Photon irradiation was made with simulated solar light generated by a Xe arc lamp source operated at 200W employing air mass filters AM1.5 [24, 28]. Briefly light was admitted to the reaction cells through a quartz fibre bundle and focused through a lens onto the sample surface such that the whole film or powder surface was illuminated (typically 7-10 mm illuminated area). The photon power on the sample was determined to be  $166 \text{ mW cm}^{-2}$  for wavelengths between 200 and 800 nm, corresponding to ca  $12 \text{ mW cm}^{-2}$  for  $\lambda < 390 \text{ nm}$ .

## Results

**Particle structure and morphology.** In Fig. 1 are shown TEM micrographs, SAED pattern and corresponding particle shape of the A25 and A40 anatase particles, respectively, obtained from the structure and morphology analysis. Corresponding data for the rutile R6x80 and the anatase A60 particles have been published elsewhere [25, 26]. Fig. 2 depicts the most probable particle shapes deduced from morphology analyses of TEM data from each batch. The crystal face distribution and centre-to-face distance in the geometrical construction of the crystals that simultaneously fits the observed particles with bright-field TEM and XRD data are presented in Table 2. Each sample contains some degree of heterogeneity, but the majority of particles may be classified as follows: Sample A60 is associated with structure AI; sample A40 to AIII; sample A25 contains both AII and AIII type particles; and sample R6x80 is associated with RII. Structures AI and RI represents morphologies typically found in macroscopic mineral crystals (order of mm), even though samples with tabular forms (AII) and richer distribution of surfaces faces (AIII) occasionally have been found in nature and may depend on the specific mineral inclusion (typically quartz). It should be noted that structures AII and AIII have to our knowledge not been reported for synthetically fabricated nanocrystals in the size range 10-100 nm.

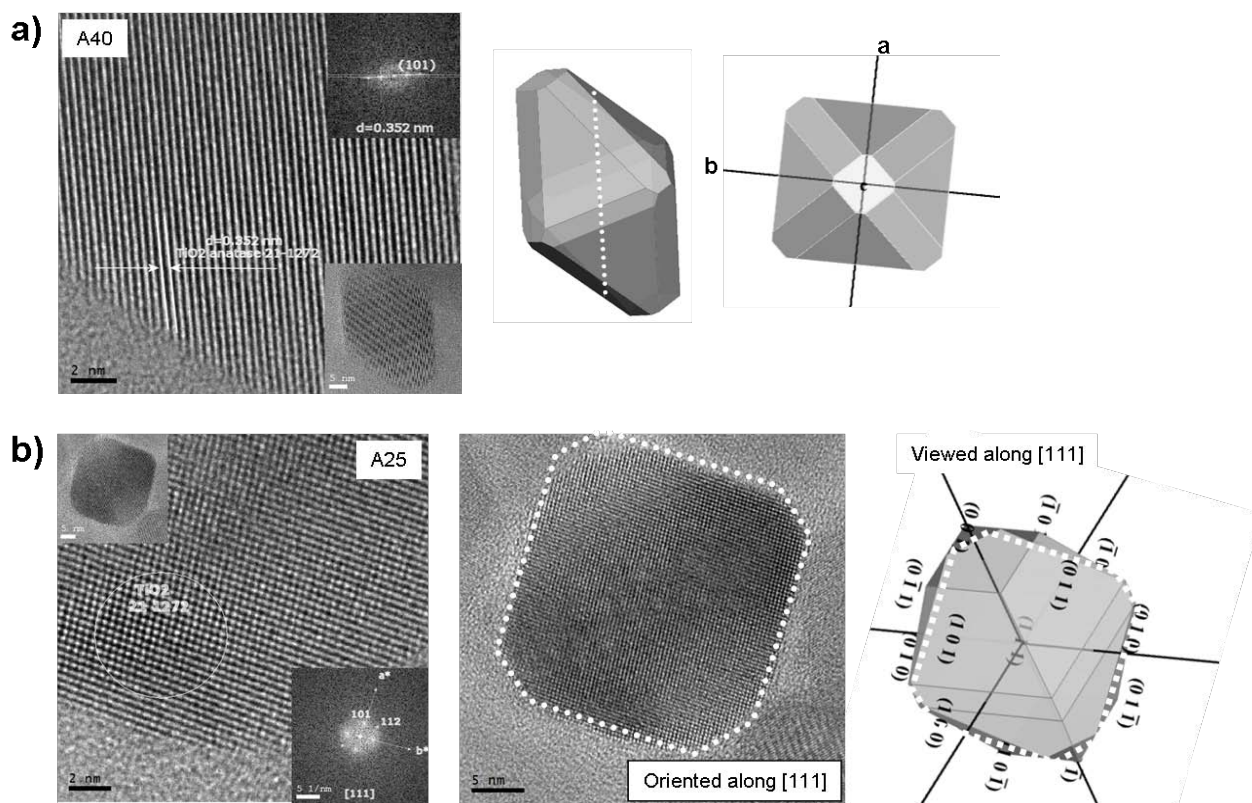


**Fig. 1** HR-TEM and SAED images (inset) of (a) A40 and (b) A25 anatase particles, respectively. Corresponding particle morphologies with appropriate crystal orientation with respect to associated HR-TEM micrographs are shown to the right.

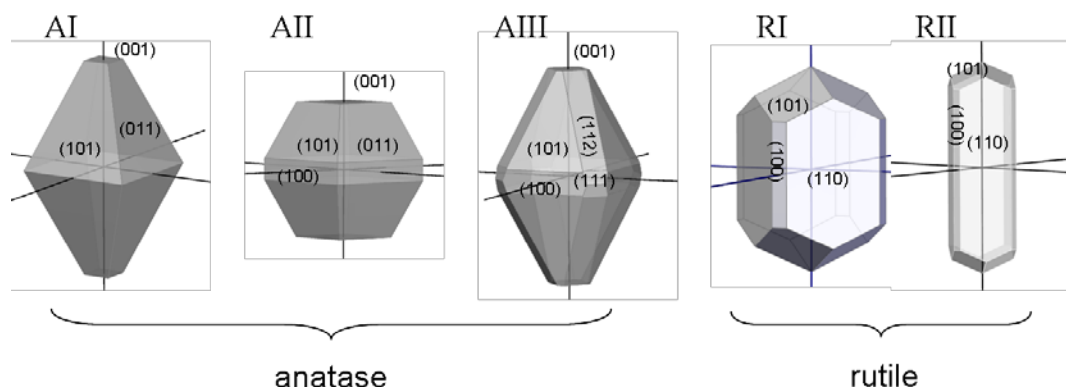


**Fig. 2** Compilation of the most probable  $\text{TiO}_2$  particle shapes deduced from morphology analyses of TEM and SAED data.

The anatase particles expose families of  $\{101\}$ ,  $\{111\}$ ,  $\{112\}$ ,  $\{100\}$  and  $\{001\}$  crystal faces to varying extent. The A40 sample exhibits a clear dominance of structure AIII shown in Fig. 2. The  $\{101\}$ ,  $\{100\}$ ,  $\{112\}$  and  $\{001\}$  faces must all be present to describe the A60 morphology (Fig. 1a). The existence of  $\{111\}$  faces is however not conclusive from the experiments. We include this face to comply with reported mineralogical data on large anatase crystals and construct the most general shape. In Table 2 both results - with and without  $\{111\}$  faces are included. Sample A60 is the commercial anatase particles obtained from BDH and typically expose  $\{101\}$  faces with small fractions of  $\{001\}$  faces. A60 exhibits the well-known morphology associated with the truncated bipyramidal structure shown in Fig. 2 (structure AI) exposing mainly  $\{101\}$  faces and small areas of  $\{001\}$  surfaces [4]. In TEM some of the A60 particles exhibit a more tabular form [7]. Sample A25 reveal a more heterogeneous particle morphology distribution. Our analysis show that the A25 sample is mainly composed of primary particles with dominant particle shapes described by structures AII and AIII in Fig. 2. The HR-TEM micrograph shown in Fig. 1b is associated with structure AII. We note that the observed anatase crystal shapes summarized in Fig. 2 are all special cases of structure AIII.

| Sample             | face index | Center-to-face distance<br>(arb. units) <sup>*</sup> | No. faces | Face area ratio<br>$\{hkl\}/\Sigma_{abc}\{hkl\}^{\S}$ |
|--------------------|------------|------------------------------------------------------|-----------|-------------------------------------------------------|
| A25                | {101}      | 0.5                                                  | 8         | 0.75                                                  |
|                    | {001}      | 0.7                                                  | 2         | 0.10                                                  |
|                    | {100}      | 0.5                                                  | 4         | 0.15                                                  |
| A40                | {101}      | 0.5                                                  | 8         | 0.44-0.52 (0.51)                                      |
|                    | {001}      | 0.85-0.90                                            | 2         | 0.03-0.04 (0.03)                                      |
|                    | {100}      | 0.5                                                  | 4         | 0.09-0.11 (0.12)                                      |
|                    | {112}      | 0.55-0.58                                            | 8         | 0.30-0.32 (0.34)                                      |
|                    | {{111}}    | (0.55-0.60)                                          | 8         | (0.03-0.11)                                           |
| A60                | {101}      | 0.44                                                 | 8         | 0.98                                                  |
|                    | {001}      | 0.9                                                  | 2         | 0.02                                                  |
| R6x80 <sup>†</sup> | {110}      | n.a                                                  | 4         | >0.90                                                 |

**Table 2** Compilation of structural parameters obtained from morphology analysis of the anatase crystals used in the present study. <sup>\*</sup>) The centre-to-face distance is the radial distance between the centre of the crystal to the surface plane labelled {hkl} employed in the Wulff construction of the particles. This number is proportional to the surface energy of face {hkl}. <sup>§</sup>) The face area ratio is defined as  $[(\text{face surface area} \times \text{no. faces}) / (\text{total surface area of the nanocrystals})]$ . The numbers in parenthesis show the result if the {111} faces are included in the analysis. <sup>†</sup>) The face index of exposed surface planes and face area ratio is taken from Refs. [25, 26].

The face distribution of the different particles depicted is summarized in Table 2. It is seen that the fraction of {101} faces, which typically is the most abundant crystal face (AI), significantly decreases for AII (75%) and AIII (ca. 50%), while simultaneously the area of the {112}, {100} and to a lesser extent {001} faces increases. The rutile R6x80 nanoparticles expose mainly {110} surfaces in agreement with the much lower surface energy of this face compared to the other low index faces. We [25] and others [31] have shown that more than >90% of the exposed surfaces can be attributed to {110} planes. The latter particles are therefore excellent model systems to compare data obtained on single crystal TiO<sub>2</sub>(110) surfaces and thus provide a rationale to associate typical adsorption structures with observed vibrational spectra and reaction kinetics. We have previously adopted this approach to interpret reaction kinetic of formic acid, formate, acetone and propane on TiO<sub>2</sub> nanoparticles [6, 7, 32]. In the following we extend this approach and use it to associate vibrational spectra and adsorption structure to specific crystal face distributions.

**Formic acid adsorption structure.** In Fig. 3 is shown FTIR spectra obtained after HCOOH adsorption and subsequent solar light irradiation in synthetic air, respectively. The FTIR spectra are normalized to the initial surface coverage and the relative surface concentrations are thus inter-comparable between the different TiO<sub>2</sub> particles. Based on the measured uptake kinetics from in situ FTIR spectroscopy and considering that minor desorption may take place during evacuation of the reaction cell prior to irradiation (see below), we estimate that in all cases the HCOOH/HCOO coverage is close to saturation. In the following we simply assume that the surface coverage prior to irradiation is 1 ML without quantifying how many molecules per unit area this corresponds to. The reported desorption rates are therefore reported in units of ML min<sup>-1</sup>. Table 3 summarizes the observed vibrational frequencies and corresponding mode assignments.

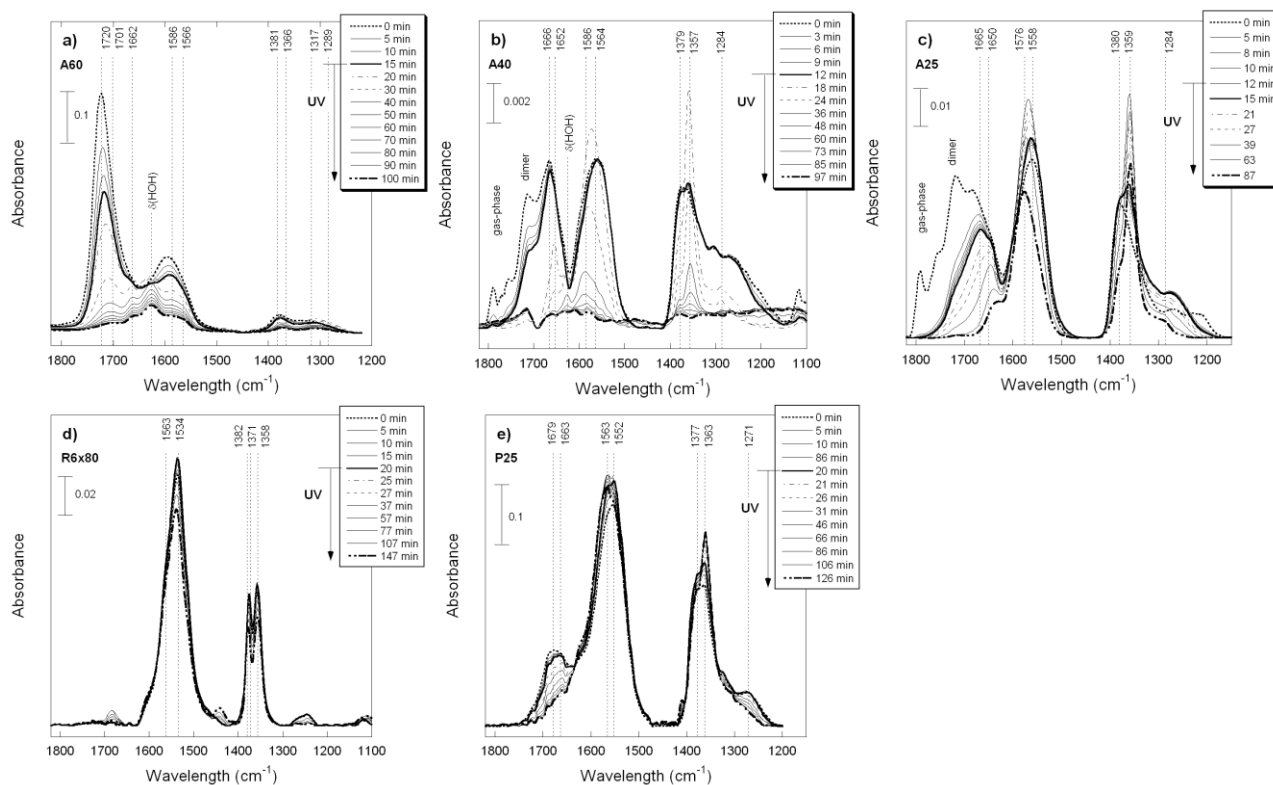


**Fig. 3** FTIR spectra obtained after dosing formic acid on anatase and rutile nanoparticles and subsequent photo-induced decomposition.



| TiO <sub>2</sub> substrate    | Mode assignment               |                              |                   |                  |                           | Ref.               |
|-------------------------------|-------------------------------|------------------------------|-------------------|------------------|---------------------------|--------------------|
|                               | $\nu_{\text{as}}(\text{OCO})$ | $\nu_{\text{s}}(\text{OCO})$ | $\nu(\text{C=O})$ | $\nu(\text{CO})$ | $\Delta\nu_{\text{as-s}}$ |                    |
| <i>Single crystal (UHV)</i>   |                               |                              |                   |                  |                           |                    |
| Rutile TiO <sub>2</sub> (110) |                               |                              |                   |                  |                           | [33]               |
| $\mu$ -formate                | 1566 (Specie B) <sup>*</sup>  | 1393 (Specie B)              |                   |                  | 173                       |                    |
| $\mu$ -formate                | 1535 (specie A) <sup>*</sup>  | 1363 (Specie A)              |                   |                  | 172                       |                    |
| $\mu$ -formate                |                               | 1365                         |                   |                  |                           | [34]               |
| <i>Nanoparticles</i>          |                               |                              |                   |                  |                           |                    |
| Anatase A25                   |                               |                              |                   |                  |                           | This work          |
| $\mu$ -formate                | 1558                          | 1359                         |                   |                  | 199                       |                    |
| HCOOH(a)                      |                               |                              | 1665, 1650        | 1270             |                           |                    |
| HCOOH (liq)                   | 1717                          |                              |                   |                  |                           |                    |
| Anatase A40                   |                               |                              |                   |                  |                           | This work          |
| $\mu$ -formate                | 1564                          | 1366                         |                   |                  | 198                       |                    |
| HCOOH(a)                      |                               |                              | 1662              | 1260             |                           |                    |
| HCOOH (liq)                   | 1714                          |                              |                   |                  |                           |                    |
| HCOO <sup>−</sup>             | 1586                          | 1346                         |                   |                  | 240                       |                    |
| Anatase A60                   |                               |                              |                   |                  |                           | This work          |
| $\mu$ -formate                | 1566                          | 1366                         |                   |                  | 200                       |                    |
| HCOOH(a)                      |                               |                              | 1662              | 1289             |                           |                    |
| HCOOH (liq)                   | 1720                          |                              |                   |                  |                           |                    |
| HCOO <sup>−</sup>             | 1586                          |                              |                   |                  |                           |                    |
| P25                           |                               |                              |                   |                  |                           | This work          |
| $\mu$ -formate                | 1563, 1552                    | 1363                         |                   |                  | 200, 189                  |                    |
| HCOOH(a)                      |                               |                              | 1679, 1663        | 1271             |                           |                    |
| P25                           |                               |                              |                   |                  |                           | [35]               |
| $\mu$ -formate                | 1553                          | 1379                         |                   |                  | 174                       |                    |
| HCOOH(a)                      |                               |                              | 1682,             | 1277             |                           |                    |
| Rutile R6x80                  |                               |                              |                   |                  |                           | This work,<br>[25] |
| $\mu$ -formate                | 1562 (Specie B)               | 1371 <sup>s</sup>            |                   |                  | 191                       |                    |
|                               | 1536 (Specie A)               | 1358 (Specie A)              |                   |                  | 178                       |                    |

**Table 3** Vibrational frequencies and mode assignment of formic acid and formate adsorbed on TiO<sub>2</sub>. \*) Note the mixing of mode assignments in Ref. [33]: 1566  $\leftrightarrow$  1535 cm<sup>-1</sup>. §) Unambiguous assignment of peak not possible due to mixing with  $\delta(\text{CH})$  and possible other  $\mu$ -formate species [25].

The FTIR spectra clearly demonstrate that the adsorbate structure is very different on the various anatase and rutile nanoparticles. In particular it is evident that no significant dissociation of HCOOH occurs on A60 upon adsorption. The vibrational signature is instead associated with liquid-like (H-bonded) HCOOH which gradually desorbs as a function of time while the sample is held in synthetic air. The evaporation rate is determined to be 0.02 ML min<sup>-1</sup> by monitoring the decay of the  $\nu(\text{C=O})$  mode associate to the liquid-like specie.

The other extreme situation occurs on rutile which exhibit spectra typical for formate adsorbed on single crystal TiO<sub>2</sub>(110) [33]. In this case HCOOH dissociates according to [33, 36, 37]:



Here O<sub>B</sub> denotes the two-fold coordinated, bridging O atoms that form ridges along the [001] direction on the (110) surface. On the perfect (110) rutile surface the formate molecule adsorbs with

the molecular axis along the [001] direction with the O atoms bonded to four-fold coordinated Ti atoms thus forming a bridging bidentate specie ( $\mu$ -formate A). Missing  $O_b$  atoms (O vacancies) have been shown to lead to another type of formate specie associated with a different vibrational structure [33]. In this case one O atom in the formate molecule interacts with the O vacancy and fill that site thus “completing” the defective (110) surface; the formate molecular axis is in this case perpendicular to the [001] direction. This specie is denoted  $\mu$ -formate B. The two species co-exist under atmospheric conditions and give rise to a double  $\nu(\text{OCO})$  peak structure in FTIR spectra as shown in Fig. 4d [7, 25]. Smaller rutile particles exposing larger areas of minority surface planes can have additional formate structures; again with slightly different vibrational signatures [25].

Turning now to the smaller anatase particles A25 and A40 which exhibit more elaborate surface structures containing mixtures of crystal faces (AII and AIII in Fig. 2), we see that the vibrational adsorbate structure in Fig. 4 also becomes more complex. The smaller size also generally leads to a larger fraction of defect sites (apart from O vacancies) due to edges, corners and steps. Following the  $\text{HCOOH}$  uptake we have previously shown [7] that on small anatase particles formate first adsorbs on c.u.s. atoms associated with defect sites ( $\nu_{\text{as}}(\text{COO}) \approx 1570 \text{ cm}^{-1}$ ), which is associated to bidentate coordinated species based on comparisons with related published data and Deacon’s rules (whether it is chelating or bridging cannot be deduced based on FTIR data alone [31]). With increasing coverage these adsorption sites becomes populated. We attribute the absorption band at  $\sim 1550 \text{ cm}^{-1}$  that gradually appears in the spectra to bridging bidentate coordinated to minority anatase faces ( $\{112\}$ ,  $\{100\}$ ,  $\{001\}$ , and possibly also  $111$ }), since this band is absent on the A60 particles which mainly expose (101) faces. Furthermore, there is a clear correlation with water formation and the absorption band at  $1586 \text{ cm}^{-1}$  on the A40 and A60 samples (Fig. 3). This band occurs at similar frequency as aqueous formate [31] and is therefore attributed to the  $\nu_{\text{as}}(\text{OCO})$  in  $\text{HCOO}^-$  ions.

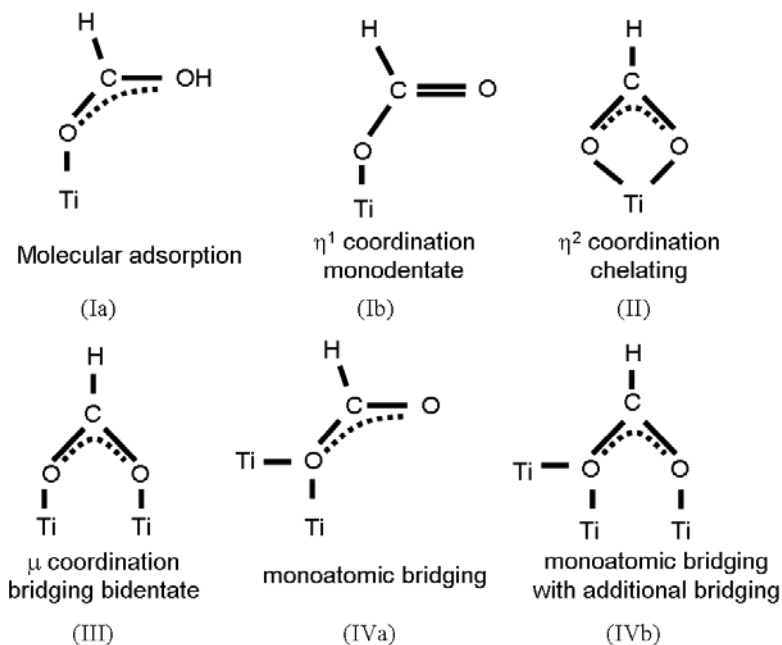


**Fig. 4** Schematic drawing of possible formic acid and formate coordination to Ti metal atoms.

The vibrational bands occurring around  $1640\text{--}1660 \text{ cm}^{-1}$  can be attributed to either an adsorbed  $\text{HCOOH}$  specie ( $\text{HCOOH(a)}$ , type Ia in Fig. 4) or hydrogen bonded monodentate  $\text{HCOO}^-$  specie (type Ib in Fig. 4). The distinction between these two species is ambiguous when adsorbate-adsorbate interactions and hydrogen to water and hydroxyls bonding is included in the interaction scheme. It is reasonable to assume that some of the faces with higher surface energy contained

within the smaller anatase particles present in A40, A25 and P25 samples exhibit an open surface structure and reactive (basic) surface O atoms that may promote dissociation. Theoretical considerations suggest that it is the basicity of adjacent O atoms that determines whether HCOOH dissociates or not and the proton is transferred to the surface forming a  $\text{HO}_b$  species [5]. It is likely that there is an intermediate state with the H atom bonded to both the HCOO moiety and the  $\text{O}_b$  surface atom (Fig. 5). For the same reasons adsorbate-adsorbate interactions and interactions with water molecules and surface hydroxyls can lead to similar mixtures of species that may account for the broad vibrational signature at  $1640\text{--}1660\text{ cm}^{-1}$ . In Table 2 we label this specie HCOOH(a) having these considerations in mind. The monodentate character of the O-C-O bonding of these species agrees with rules proposed by Deacon et al [38] on splitting and positions of  $\nu_{\text{as}}(\text{COO})$  and  $\nu_{\text{s}}(\text{COO})$  for a large number of acetato complexes, as well as previous reports on the HCOOH/ $\text{TiO}_2$  adsorption system [31, 39]. It is clear from the spectra in Fig. 2 that the A40 sample presents a bonding environment that is intermediate between the two extreme adsorbate structures seen on the A60 and R6x80 samples, respectively, i.e. it favours monodentate coordination and HCOOH dissociation according to the scheme outlined in Fig. 5 but not bidentate HCOO coordination. The A25 sample and even more so P25 contain significantly more bidentate formate species. We attribute this to bidentate or higher metal coordination of HCOO bonded to c.u.s. sites, e.g. edges, steps and lattice defects which to a larger extent (than the larger particles) are present on the smaller particles (species II, III or IVb in Fig. 4).

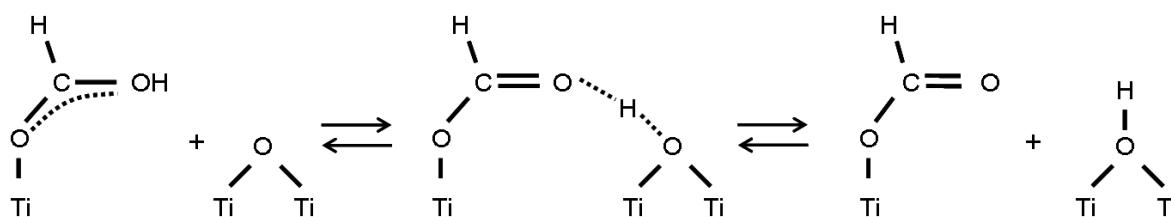


**Fig. 5** Reaction scheme depicting the conversion of specie Ia and Ib in Fig. 4 and the intermediate hydrogen bonded specie.

To summarize the rutile R6x80 particles have a distinct spectral profile characteristic of a bridging bidentate HCOO adsorption structure (or more precisely mixtures of  $\mu$ -formate A and B species). The A60 particles is mainly associated with liquid-like HCOOH, while the smaller A25 and A40 particles show a heterogeneous distribution of co-existing adsorbed HCOO and HCOOH species, each with its own spectral signature. The detailed surface structure on A25 and A40 manifested in a distribution of surface faces (Fig. 2 and Table 2) dictates whether dissociation occurs or not as depicted by the reaction scheme in Fig. 5. The role of c.u.s. sites becomes more pronounced for the smaller A25 (and P25) particles and can be attributed to distinct vibrational signatures associated with  $\mu$ -formate species.

**Photo-degradation of formic acid.** In Fig. 6 the concentration of adsorbed HCOOH and HCOO molecules as a function of irradiation time is shown. The surface concentration was determined by the integrated absorbance originating from the  $\nu(\text{OCO})$  and  $\nu(\text{C=O})$  bands for HCOO and HCOOH, respectively, given by the assignments in Table 3. It is clearly seen that the photo-reactivity is highest on the A40 anatase particles, while it is lowest on the R6x80 rutile and P25 particles. In the former case the photo-induced decomposition (PID) rate is determined to be  $0.08\text{ ML min}^{-1}$  taking into account a minor contribution from molecular HCOOH desorption. In the latter cases only very slow degradation of HCOO occurs. On the P25 particles the monodentate species associated with the  $1660\text{--}1680\text{ cm}^{-1}$  absorption bands on the anatase phase rapidly decomposes, while the bidentate species coordinated to both anatase and rutile phase particles are only slowly decomposed. Based on

comparisons with data on anatase particles exposing a high fraction of {101} faces (A60) and rutile particles exposing mainly (110) planes (R6x80) as well as rutile sample containing about equal ratios of (110) and (101) planes [6, 25], we find a correlation between the high photocatalytic reactivity of the A40 sample to the presence of minority {112}, {111}, {001} and {100} planes exposed on these particles. We have previously shown that monodentate HCOO/HCOOH species are more easily decomposed during UV irradiation than bidentate species on rutile nanoparticles [25]. It is therefore likely that bonding to minority surfaces on the A40 favors monodentate HCOOH/HCOO coordination (Fig. 5), which co-exist with adsorbed HCOOH species present on {101} surfaces. Thus the larger photo-reactivity is correlated to the concentration of monodentate HCOO/HCOOH species (species Ia and Ib in Fig. 2). On the A25 sample, a significantly larger portion of HCOOH dissociates to form bidentate coordinated HCOO species due to coordination to c.u.s. sites; these species exhibit a much smaller PID rate which is evident by comparison with the R6x80 rutile sample that almost exclusively exhibit bidentate HCOO bonding. The PID rates are summarized in Table 4.

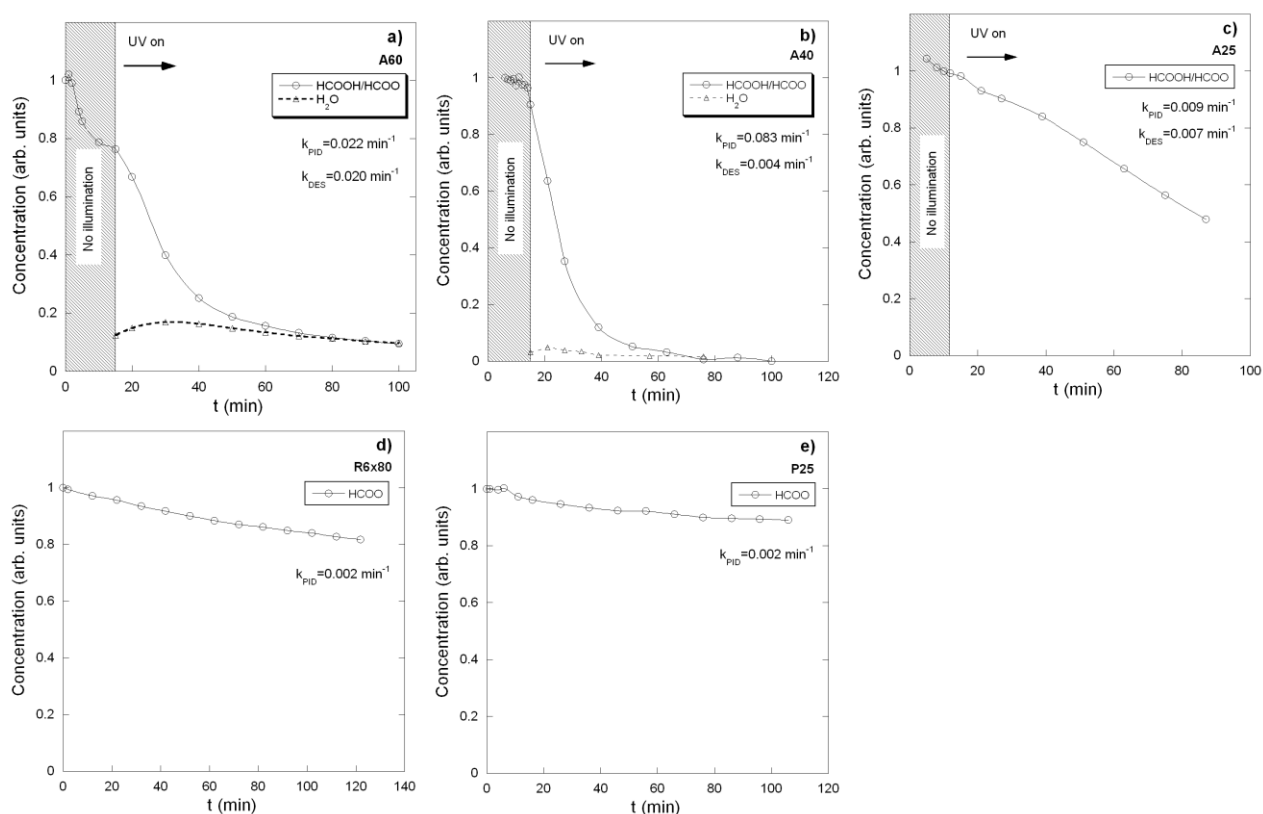


**Fig. 6** The concentration of adsorbed HCOOH and HCOO molecules on anatase and rutile TiO<sub>2</sub> as a function of irradiation time. The photo-induced decomposition (PID) rate determined from the first 20 min of illumination assuming first-order kinetics is indicated in the figures. The desorption rate (DES) was determined from control experiments with the samples held in dark.

## Discussion

Coordinatively unsaturated surface atoms (c.u.s.) are generally more reactive than the corresponding saturated atoms, since their valence number make them prone for additional coordination. The c.u.s. Ti<sup>n+</sup> cations at the TiO<sub>2</sub> surface are acidic (Lewis acids sites) and want to form bonds with basic molecules, while the c.u.s. O<sup>n-</sup> anions are basic (Lewis bases) and adsorb acidic molecules. While the acidic sites have proven to be fairly straightforward to characterize, the basic surfaces sites of

oxides have proven to be more elusive. Davydov [40] suggested that reactive adsorption of CO<sub>2</sub> forming surface carbonates is a suitable molecule to probe the basic properties of oxide surfaces. In particular, the splitting of the asymmetric and symmetric carbonate stretching vibrations,  $\Delta\nu_{\text{as-s}} \equiv \nu_{\text{as}}(\text{COO}) - \nu_{\text{s}}(\text{COO})$ , of the carbonate molecule has been correlated to the strength of the basic sites. For example, the M-O covalency of a lattice O atom involved in monodentate coordinated carbonate is lower than that for a bidentate carbonate. According to Nakamoto  $\Delta\nu_{\text{as-s}}$  is about 300 cm<sup>-1</sup> for bidentate carbonate [41]. This value increases with increasing covalent character of the M-O bond, i.e. decreasing basicity of the O atom. Since the surface atoms on TiO<sub>2</sub> nanoparticles are expected to deviate from stoichiometry to a larger degree than bulk terminated samples, e.g. with excess oxygen possessing different valency, the above considerations predict that  $\Delta\nu_{\text{as-s}}$  for CO<sub>2</sub> adsorbed such that it forms a bidentate carbonate molecule should be higher if it is coordinated to a three-fold coordinate O atom than a two-fold O atom. Similarly, the surface properties should be influenced by O adatoms with comparably strong basic character. In analogy with metal-carbonate coordination, Deacon et al [38] have analyzed  $\Delta\nu_{\text{as-s}}$  and the positions of  $\nu_{\text{as}}(\text{COO})$  and  $\nu_{\text{s}}(\text{COO})$  for a large number of acetato complexes. By comparing  $\Delta\nu_{\text{as-s}}$  of the free aqueous state (“ionic”) and metal coordinated complexes (“metal coordinated”), respectively, they observed the following correlations (Deacon’s rules):

$\Delta\nu_{\text{as-s}}$  (metal coordinated) >  $\Delta\nu_{\text{as-s}}$  (ionic): monodentate coordination

$\Delta\nu_{\text{as-s}}$  (metal coordinated) <  $\Delta\nu_{\text{as-s}}$  (ionic): bidentate chelating or bridging coordination

$\Delta\nu_{\text{as-s}}$  (metal coordinated) <<  $\Delta\nu_{\text{as-s}}$  (ionic): bidentate chelating coordination

The first correlation has strong experimental support as well as its converse, i.e. monodentate coordinated complexes always exhibit  $\Delta\nu_{\text{as-s}}$  (metal coordinated) >  $\Delta\nu_{\text{as-s}}$  (ionic). In our case we have  $\Delta\nu_{\text{as-s}}$  (ionic)=240 cm<sup>-1</sup> (Table 2). However, the inverse of other two correlations are not always obeyed, and it is not straightforward to distinguish the bidentate chelating from the bridging coordination solely based on the magnitude of  $\Delta\nu_{\text{as-s}}$ . In general, these empirical rules should be complemented by additional structural data. This was also concluded in a recent spectroscopic and theoretical study of formate and acetate adsorption on (large) rutile TiO<sub>2</sub> nanoparticles [31]. Moreover, when studying adsorption of carboxylic acid on oxide surfaces interpretation of vibrational spectra may be complicated from a practical viewpoint by formation of surface esters and condensation products of carboxylate ions, since these have spectral features close to the carboxylate surface complexes. Additional complications arise due to the heterogeneity of possible carboxylate species discussed above (cf. Fig. 4).

The above empirically based findings have recently been rationalized by A. Selloni and co-workers using density functional calculations [5, 42]. Scrutinizing their findings and translating them into the context above the following general features governing the bonding and reactivity of HCOOH on anatase TiO<sub>2</sub> surfaces can be discerned: (i) Surfaces with a large density of coordinatively unsaturated surface sites promote dissociation and bidentate bonding due to interactions with basic surface O atoms present on these surfaces. (ii) Surface planes exhibiting strained configuration of surface atoms, i.e. large Ti-O-Ti bond angles within the surface plane [42] make the surface O atom become more or less basic, and hence more or less reactive. The in-plane Ti-O-Ti bond angles differs however considerably among the (101), (111), (100), (112) and (001) surfaces, with the (101) exhibiting the lowest Ti-O-Ti bond angle within the surface plane (along the  $[10\bar{1}]$  direction), while the others have a strained angle (102 vs. 155 degrees for the bulk terminated structures, respectively). (iii) Small nearest-neighbour (nn) Ti-Ti distances [5] promote bridging bidentate coordination. The nn Ti-Ti distance in bulk terminated (un-reconstructed) anatase (101) is 3.783 Å, and it is the same in the anatase (001), (100) and (112) surfaces, while it is much shorter (2.953 Å) in rutile (110), and also between rows of mirror reflected domains in brookite

(210). From the data in Table 2, Fig. 2 and 6 we find that there is a correlation between crystal face distributions, nn Ti-Ti distance, in-plane Ti-O-Ti bond angles on exposes crystal faces. The data are presented in Table 4. Possible surface reconstructions will of course modify these predictions, but they do give an indication of the importance of the basicity of surface O atoms and nn Ti-Ti distance on the various crystal faces. In particular we see that a short nn Ti-Ti atoms present on the {110} surfaces correlates with a smaller  $\Delta\nu_{\text{as-s}}$  value, formation of bridging bidentate formate and a small PID rate. We note that it previously has been shown that a shorter nn Ti-Ti distance present also on brookite  $\text{TiO}_2(210)$  in the narrow gaps along the [001] direction in the herringbone structure separating mirror reflected rows [5], stabilizes HCOO bonded in bidentate configurations. The spectra shown in Fig. 2 clearly demonstrate that the vibrational structure and  $\Delta\nu_{\text{as-s}}$  vary significantly among the various anatase particles (cf. Table 2 and 4). The morphology analysis suggests that the different anatase nanoparticles have different face distribution. In fact, there are strong indications that the small particles expose A40 and A25 expose surface planes not present at all on A60. Moreover, the smaller particles inevitably expose a larger fraction of c.u.s. atoms due to edges, corners, surface defects than the larger particles. Moreover from the FTIR data and the corresponding reactivity measurements (Fig. 3 and 6) it is evident that the reactivity increases in the order of increasing  $\Delta\nu_{\text{as-s}}$  towards monodentate bonding of HCOO/HCOOH(a) (Table 4). Thus we may propose that a decreasing basicity of the oxygen surface atoms favours a monodentate bonding scheme of adsorbed HCOO/HCOOH species. We conjecture that it is beneficial for a high photo-reactivity to maintain moderate bonding of adsorbed HCOO/HCOOH, which is intermediate between anatase (101) which is non-reactive, and rutile (110) which is too reactive and form stable bidentate HCOO species. On A40, and to some extent on the A25 particles this is accomplished by exposing suitable combinations of reactive {112}, {111}, {100} and {001} faces of anatase. In contrast on the {101} planes on anatase molecular adsorption of HCOOH occurs forming hydrogen-bonded, liquid-like clusters whose decomposition is limited by diffusion of photo-generated oxygen radicals. Face communication by means of surface diffusion between the different crystal faces (and the non-reactive {101} faces) may also contribute to the observed reactivity thus providing an explanation for an optimum particle size which correlates with an effective diffusion length on the nanocrystals [43]. At present we cannot ambiguously correlate the inferior activity on A25 and P25 to unfavourable crystal faces or a relatively larger concentration of c.u.s. atoms. Whatever the cause, our data do however show the intrinsic difficulties of preparing small size ( $d < 25$  nm) photo-reactive  $\text{TiO}_2$  nanoparticles; i.e. smaller is not always better.

| Sample | $\mu$ -formate                                   |                                 | $\eta^1$ -formate/<br>HCOOH(a)*          |                                 | In-plane Ti-O-Ti angle<br>on majority face [°] <sup>†</sup> | nn Ti-Ti distance<br>[Å]** | PID rate<br>[ML min <sup>-1</sup> ] |
|--------|--------------------------------------------------|---------------------------------|------------------------------------------|---------------------------------|-------------------------------------------------------------|----------------------------|-------------------------------------|
|        | $\Delta\nu_{\text{as-s}}$<br>[cm <sup>-1</sup> ] | Relative conc. [%] <sup>§</sup> | $\nu(\text{C=O})$<br>[cm <sup>-1</sup> ] | Relative conc. [%] <sup>§</sup> |                                                             |                            |                                     |
| A25    | 199                                              | 64                              | 1650,<br>1665                            | 36                              | 102, 155                                                    | 3.783                      | 0.009                               |
| A40    | 198                                              | 43                              | 1652,<br>1666                            | 41                              | 102, 155                                                    | 3.783                      | 0.083                               |
| A60    | 200                                              | 11                              | 1662                                     | 14                              | 102                                                         | 3.783                      | 0.022                               |
| R6x80  | 200, 189                                         | 100                             | 1663,<br>1679                            | 0                               | 97                                                          | 2.953                      | 0.002                               |
| P25    | 191, 178                                         | 79                              |                                          | 21                              | n.a.                                                        | n.a                        | 0.002                               |

**Table 4** Compilation of data on  $\Delta\nu_{\text{as-s}}$ , relative concentration of  $\mu$ -formate and  $\eta^1$ -formate species/HCOOH(a) species, in-plane Ti-O-Ti angles, nn Ti-Ti distance and photo-induced HCOO/HCOOH decomposition (PID) rate for the various  $\text{TiO}_2$  particles employed in the present study. \*) Vibrational frequency of peaks associated with various monodentate coordinated

HCOO/HCOOH species. <sup>s)</sup> The relative concentration of  $\mu$ -formate or monodentate formate or HCOOH(a) species to the total concentration of HCOO/HCOOH surface species. <sup>†)</sup> The shortest angle between a c.u.s. O surface atom and neighbouring coordinated Ti atoms on any of the exposed crystal faces. <sup>\*\*)</sup> Shortest nearest neighbour (nn) Ti-Ti distance on any of the exposed crystal faces.

We can conclude that a monodentate HCOO/HCOOH bonding configuration is the most susceptible adsorbate structure for photo-stimulated radical attack of the carbon atom ( $O_2^{\cdot -}$  species in our experiments) and subsequent molecular decomposition. The exact mechanistic pathway is at present not clear, but our results indicate that both  $H_2O$  and  $CO_2$  formation takes place during PID reaction (Fig. 6). This suggests that both dehydration ( $HCOOH \rightarrow CO + H_2O$ ) and dehydrogenation ( $HCOOH \rightarrow CO_2 + H_2$ ) of formate occurs. This is consistent with the amphoteric nature of the  $TiO_2$  surface exposing both acid and basic sites, which in general favour dehydration and dehydrogenation, respectively. For example the occurrence of the 1680 and 1442  $cm^{-1}$  bands on rutile may be associated with carbonate formation.

Even though the above assignments of adsorbate structures are qualitatively consistent with the proposed correlation of Ti-O bonding character with reported positions of the carboxylate stretching vibrations [7, 21, 25, 31, 33, 35, 38, 44] and reported ab initio calculations [5, 10, 36, 37, 45], we stress that without independent structural data of both the particles and adsorbate the formate adsorption structure cannot be unambiguously deduced from the infrared data alone. By the comparative approach presented here employing well-characterized nanoparticles we are however able to provide qualitative support for our assertions and present a consistent picture that determines the bonding and reactivity of HCOOH on  $TiO_2$ .

The results presented here have implications also on ligand- $TiO_2$  bonding in general. The results show ways to modify the coordination of carboxylic groups to  $TiO_2$  surfaces by appropriate selection of  $TiO_2$  nanocrystals with appropriate size that exhibit large fractions of minority {112}, {111}, {100} and {001} faces. This can as described above facilitate either dissociative adsorption leading to bridging bidentate coordination, monodentate coordination or non-dissociated carboxylic acid adsorption. This opens ways to modify and optimize e.g. metal-organic dye attachments to  $TiO_2$  nanoparticles used in e.g. wet solar cells and biomaterials and bio-imaging applications. The findings that the particle morphology and hence the distribution of exposed surface planes strongly affects their reactivity may also have implications for their biological response in general. We have recently demonstrated that living lung epithelial cells respond very different to anatase and rutile  $TiO_2$  nanoparticles. Interestingly the results indicates that primary bronchial epithelial cells can indirectly affect blood vessels when stimulated with  $TiO_2$  nanoparticles, but also that the responsiveness depends on the specific size and crystalline structure [46].

## Summary

We have shown that the specific surface structure and crystal face distribution of  $TiO_2$  nanoparticles in the 10-70 nm size regime strongly affects the bonding configuration and photo-reactivity of adsorbed formic acid. In particular we have discussed the photocatalytic oxidation of formic acid on anatase  $TiO_2$  nanoparticles prepared by solution based methods that expose large areas of {112}, {111}, {100} and {001} crystal faces co-existent with {101} crystal faces. The principle mechanisms responsible for their reactivity are outlined and methods to tune the reactivity by modifying the size and face distribution are described. In detail we have shown that (i) the relative amount of metal coordinated formate is significantly smaller on the large A60 anatase particles than the small anatase and rutile particles, (ii) on anatase particles exposing large fraction of {112}, {100} and/or {001} faces HCOOH dissociates to form monodentate HCOO/HCOOH species, (iii)  $\mu$ -formate (bi-coordinated HCOO) is the dominant specie on rutile particles exposing {110} faces, and on small anatase particles having a large fraction of c.u.s. sites associated with edges, steps and

lattice defects (this includes e.g. P25). The principle reasons responsible for the different HCOO/HCOOH bonding configuration is proposed to be due to the presence of basic O surface atoms and the nn Ti-Ti distance. The existence of strained Ti-O-Ti bonds and O atoms with basic chemical character favors dissociation of the H atom on the HCOOH molecule and the formation of surface OH species. This situation is realized on all surfaces except the anatase {101} surfaces, which do not promote HCOOH dissociation. The nearest neighbor Ti-Ti distance is similar on all anatase surfaces, while it is considerably shorter on rutile (110); this favors stable bi-coordination on rutile nanoparticles. In terms of photo-reactivity the importance of the {112}, {111}, {100} and {001} faces is to increase the formic acid dissociation rate and promote bonding of monodentate coordinated species. It is argued that the C atom on monodentate coordinated species is readily attacked by oxygen radicals thereby providing an explanation for the high reactivity on the A40 sample. On {101} faces clusters of HCOOH molecules form. Oxidation of these clusters is slow due to diffusion of oxidizing agents. On rutile particles and small anatase particles the chemistry is mainly governed by bidentate coordinated species, which both are energetically more stable and less reactive towards oxygen radicals.

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## Sol-Gel Titania and Titania-Silica Mixed Oxides Photocatalysts

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**Abstract.** This paper presents a review of the work published by the authors on the synthesis, characterization and evaluation of the photocatalytic activity of TiO<sub>2</sub>/SiO<sub>2</sub> materials. The use of titania-silica mixed oxides photocatalysts is proposed basically as a process improvement to overcome the difficulties of recovering titania from the slurries after the photocatalytic treatment of contaminated waters. To understand the mechanism governing the photocatalytic activity of these materials, several titania-silica photocatalysts have been prepared through a sol-gel method that allows controlling the main variables to obtain materials with different textural properties, degree of titania incorporation, dispersion of the photoactive phase and crystallinity of titanium dioxide. The samples have been characterized in depth, looking for correlations between the main physicochemical properties (TiO<sub>2</sub> crystallite size, band gap energy and titania surface area) and the activity shown in the photocatalytic oxidation of cyanide, selected as model pollutant. The results suggest that the photocatalytic activity is strongly influenced by the quality of the titania crystal network, which in turn is improved by the use of a hydrothermal crystallization procedure. Additionally, the evaluation of the fraction of the total surface area corresponding to titania is mandatory for comparing the catalytic activity of different materials in processes in which titanium dioxide is the only phase catalytically active and silica behaves as an inert support.

### Nomenclature

|           |                                                                       |
|-----------|-----------------------------------------------------------------------|
| $D_{XRD}$ | average crystallite size, nm                                          |
| $E_g$     | semiconductor bandgap energy, eV                                      |
| $r_V$     | volume-based reaction rate, mol L <sup>-1</sup> s <sup>-1</sup>       |
| $r_S$     | surface-based reaction rate, mol m <sup>-2</sup> s <sup>-1</sup>      |
| $S_{BET}$ | specific surface area of the catalyst, m <sup>2</sup> g <sup>-1</sup> |
| $V_P$     | pore volume, cm <sup>3</sup> g <sup>-1</sup>                          |

### Introduction

The preparation and characterization of titania-silica mixed oxides have been extensively reported in the literature due to their large number of applications in catalysis [1]. These materials could be synthesized following many different strategies such as flame hydrolysis, impregnation, coprecipitation, chemical vapour deposition, sol-gel, etc., leading to mixed oxides with different physicochemical properties depending on the composition, the dispersion of the titania phase, etc. Among them, the sol-gel method has been shown to be a very versatile way of controlling the bulk and surface properties of the oxides [2].

At low titanium contents, sol-gel TiO<sub>2</sub>/SiO<sub>2</sub> materials can be prepared with a high dispersion of the Ti atoms located in tetrahedral positions of the silica network, minimizing the Ti-O-Ti bonds. These catalysts show a high activity in redox processes such as epoxidation [3]. At higher titanium

contents, formation of  $\text{TiO}_2$  clusters in which titanium atoms adopt an octahedral coordination cannot be avoided. These  $\text{TiO}_2/\text{SiO}_2$  materials have been proposed for their application as catalysts in heterogeneous photocatalytic processes for the degradation of pollutants [4], in which pure titanium dioxide materials are commonly used [5].

To minimize the reactor volume a high specific surface area for the catalyst is required which leads to the development of photoactive nanocrystalline titania particles. Such a small particle size involves high filtration costs to recover the catalyst from the aqueous phase once the reaction is completed. For that reason many efforts have been devoted to the preparation of supported  $\text{TiO}_2$  immobilized on diverse materials [6,7]. Among the possible support materials, silica is usually the choice due to its high specific surface area, chemical inertness and transparency to the UV-A radiation used in the photocatalytic processes.

Although the crystalline properties of titania-based catalysts are commonly related to their photocatalytic activity, there is no complete agreement in the literature about the mechanism of the photocatalytic reactions on  $\text{TiO}_2/\text{SiO}_2$  materials. Some authors attribute their activity to the formation of quantum crystalline species stabilized on the silica matrix but working under a conventional semiconductor photocatalysis mechanism [8,9] whereas others propose a different mechanism based on the formation of excited states of charge transfer complexes located in the tetrahedral  $\text{Ti}^{4+}$  species isolated in the silica network [10]. This point is obviously connected with the radiation absorption behaviour of the materials, as the band gap energy dramatically increases when the  $\text{TiO}_2$  cluster size is below few nanometers. This enhancement is even higher for mixed oxide materials with low titanium content, where  $\text{Ti}^{4+}$  atoms in tetrahedral coordination are present (if the concept of band gap energy would be applicable to these materials).

The specific surface area has been recognized to be one of the most important factors affecting the photocatalytic efficiency, due to the heterogeneous nature of the process [5]. However, several research groups have found no direct correlation between the photoactivity and the B.E.T. specific surface area values for different  $\text{TiO}_2$  samples [11,12]. The reason of this discrepancy is that photocatalytic processes also require materials with a high degree of crystallinity, usually being the optimum a commitment between both factors [13].

The effective  $\text{TiO}_2$  surface area can be increased through the appropriate dispersion on a silica support [7]. The comparison of the activity between supported and unsupported materials or among different supported systems should be based on the true titania surface area of the materials. The distribution of two different phases in  $\text{TiO}_2/\text{SiO}_2$  mixed oxide materials can be investigated through powder X-ray diffraction, transmission electron microscopy, Raman spectroscopy, UV-Vis diffuse reflectance spectroscopy, etc. However, indirect methods must be used to establish the fraction of the total surface area corresponding to each oxide, such as temperature-programmed desorption (TPD) of 2-propanol coupled with thermogravimetric and mass spectrometry detection (TGA-MS) [14] or selective functionalization with phenylphosphonic acid [15].

This paper presents a review of the work carried out by the authors on the synthesis, characterization and evaluation of the photocatalytic activity of  $\text{TiO}_2/\text{SiO}_2$  materials. Materials were prepared controlling the main variables of the sol-gel route to obtain materials with different textural properties, degree of incorporation and dispersion of titanium species, and crystallinity of titanium dioxide. Additionally a procedure for the evaluation of the fraction of the total surface area corresponding to the titania phase is presented, being used these values to estimate comparable surface-based reaction rates for the oxidation of model pollutants.

## Experimental

**Synthesis of the photocatalysts.** Fig. 1 outlines the synthesis procedure of the materials, based in a two stages sol-gel method with acid hydrolysis and basic condensation at room temperature. As the hydrolysis of the silicon source is much slower than that corresponding to the titanium species, one

of the main variables affecting the degree of incorporation and dispersion of titanium atoms in the silica network is the extension of the silicon alcoxide prehydrolysis. For this step, a solution of tetraethylorthosilicate ( $\text{Si}(\text{OC}_2\text{H}_5)_4$ , 98 wt.%, Alfa Chemicals; TEOS) in ethanol (molar ratio ethanol/TEOS = 2) was hydrolyzed with a 0.05 N HCl solution (molar ratio  $\text{H}_2\text{O}/\text{TEOS}$  = 1.2) at room temperature for 90 minutes.

Prior to the addition and hydrolysis of the titanium source, the mixture was cooled in an ice-water bath. To favour the titanium-silicon heterocondensation, the solution of titanium tetraisopropoxide ( $\text{Ti}(\text{OC}_3\text{H}_7)_4$ , 97 wt%, Alfa Chemicals; TTIP) in isopropanol (mass ratio i-PrOH/TTIP = 1) was added dropwise to the synthesis medium and stirred for 45 minutes. Later, the formation of the mixed oxide gel was induced by increasing the pH with an aqueous solution of  $\text{NH}_3$  1 N.

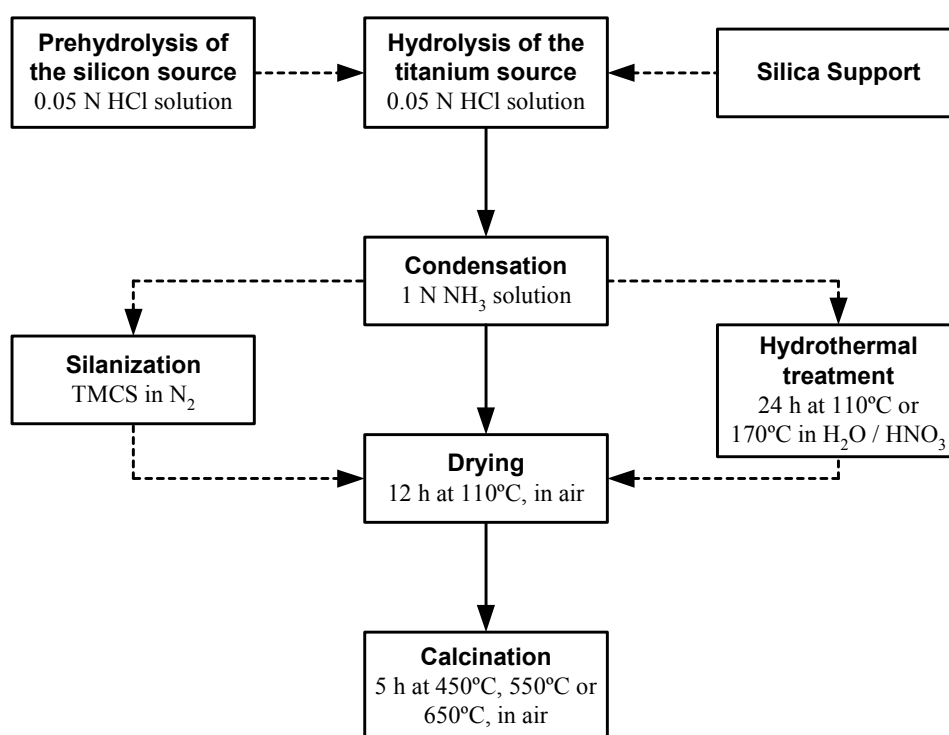


**Fig. 1.** Outline of the procedure for the synthesis of the  $\text{TiO}_2$  /  $\text{SiO}_2$  materials (dashed lines indicate optional steps).

In some cases, before drying and calcination, the gels were hydrothermally treated in autoclave reactors at autogenous pressure or silanized to prevent the collapse of the porous structure during the thermal treatment, thus maintaining high specific surface areas. The silanization procedure was based in that reported by Sotelo et al. [16] by reacting the surface hydroxyl groups with trimethylchlorosilane ( $(\text{CH}_3)_3\text{SiCl}$ , 98%, Aldrich; TMCS) in boiling n-hexane under  $\text{N}_2$  flow.

The different materials presented in this work can be grouped into five categories:

- i) *Pure titania xerogels*, used for reference purposes together with commercial  $\text{TiO}_2$  samples. All the pure titania materials were synthesized in the absence of the prehydrolysis stage, as the silicon source was not incorporated.
- ii)  *$\text{TiO}_2/\text{SiO}_2$  xerogels synthesized with prehydrolysis of the silicon source*. These materials were prepared with and without the silanization step, in order to investigate the influence on the enhancement of the specific surface area of the materials.

- iii) *TiO<sub>2</sub>/SiO<sub>2</sub> xerogels synthesized without prehydrolysis of the silicon source.* For these materials, the hydrolysis of both the titanium and the silicon sources was conducted simultaneously, in order to increase the degree of homocondensation of the titanium dioxide.
- iv) *Hydrothermally treated TiO<sub>2</sub>/SiO<sub>2</sub> xerogels.* This treatment improves the crystallinity of the materials achieved by this process.
- v) *Silica-supported TiO<sub>2</sub> xerogels.* For these materials, the hydrolysis and condensation of the titanium alcoxide took place in the presence of the silica particles previously suspended in the solution, growing the TiO<sub>2</sub> phase inside the porous structure of the support. Two different silica materials were used as supports: a commercially available non-structured silica with a wide pore size distribution (Grace Sylopol 2104, GrSiO<sub>2</sub>,  $S_{BET} = 317 \text{ m}^2 \text{ g}^{-1}$ ,  $V_P = 1.59 \text{ cm}^3 \text{ g}^{-1}$ ), and the so-called SBA-15 silica ( $S_{BET} = 640 \text{ m}^2 \text{ g}^{-1}$ ,  $V_P = 0.96 \text{ cm}^3 \text{ g}^{-1}$ ), a mesostructured material with a very well defined pore size in the range of the mesopores ( $D_P = 6.0 \text{ nm}$ ), prepared in our laboratory according to the original method of Zhao et al. [17].

**Characterization of the photocatalysts.** X-ray diffraction (XRD) patterns of the samples were recorded on a Philips X'PERT MPD diffractometer using Cu K $\alpha$  radiation. To obtain a good signal-to-noise ratio a step size of 0.02° and a step time of 2 s were used. The main diffraction peaks of anatase 1 0 1 ( $2\theta \sim 25.3^\circ$ ) and rutile 1 1 0 ( $2\theta \sim 27.4^\circ$ ) planes were used for the estimation of the average crystal size through the Scherrer's equation, using the calcite 1 0 4 signal ( $2\theta \sim 29.4^\circ$ ) as internal standard to calculate the instrumental width.

Diffuse reflectance UV–VIS spectra were acquired in a Varian Cary 500 Scan UV–VIS–NIR spectrophotometer provided with an integrating sphere accessory. The spectral data in the UV–A range were used to calculate the band gap of the materials.

Textural properties of the materials were determined from the nitrogen adsorption–desorption isotherms at 77K obtained in a Micromeritics Tristar 3000 sorptometer. Surface areas were estimated according to the BET (Brunauer–Emmett–Teller) method, whereas pore size distributions were calculated applying the BJH (Barrett–Joyner–Halenda) model, assuming cylindrical geometry of the pores.

The fraction of titania accessible of the total surface area was estimated by selective functionalization of the materials with phenylphosphonic acid according to the procedure reported by Mutin et al. [18]. 500 mg of the mixed oxide powder were added to a flask containing 500 mL of a 4 mM solution of phenylphosphonic acid in a 4:1 CH<sub>3</sub>OH:H<sub>2</sub>O v/v mixture. After 24 hours of vigorous stirring at room temperature, the solids were filtered and washed several times with a methanol-water solution and finally dried at 110°C for 24 h. The phosphorus content of the materials was determined by inductively coupled plasma atomic emission spectroscopy (ICP–AES) in a Varian Vista AX instrument. Before the analysis, the samples were dissolved with hydrofluoric acid and rinsed with water. The phosphorus concentration in the aqueous solution was quantified through its emission line at 213.618 nm after calibration with certified standards.

**Photocatalytic experiments.** The photocatalytic activity of the materials was evaluated using the photooxidation of potassium cyanide as test reaction. Experiments were carried out at room temperature in a 1 liter batch photoreactor irradiated by a 150 W medium pressure mercury lamp (Heraeus TQ-150) placed axially inside a quartz jacket externally cooled with a 0.01 M CuSO<sub>4</sub> aqueous solution to maintain the reaction media at 25°C and cut-off the radiation below 325 nm. The catalyst was maintained in suspension by a magnetic stirrer placed at the bottom of the vessel. A gas bubbling system provided the oxygen required for the oxidation reaction.

The cyanide solution with the amount of catalyst in suspension corresponding to 0.5 g TiO<sub>2</sub> L<sup>-1</sup> was equilibrated in the dark for 30 minutes and in the meantime the lamp was switched on to stabilize the emission power and spectrum. This catalyst concentration was previously selected from

studies with Degussa P25 titania to guarantee a total absorption of the UV-A incident photon flow, whose value, determined by ferrioxalate actinometry, was  $1.37 \cdot 10^{-5}$  Einstein  $L^{-1} s^{-1}$ .

The initial concentration of potassium cyanide (KCN, Panreac, reagent grade) in all the experiments was 3.85 mM. The pH value was adjusted to 11.0 by addition of NaOH (Scharlab, reagent grade). Once the reaction started, samples were taken at regular time intervals, removing the catalyst by filtering through a 0.22  $\mu m$  nylon syringe filter. The decrease in cyanide concentration along the catalytic test was followed by the pyridine-barbituric standard colorimetric method [19]. A Merck Spectroquant VEGA 400 spectrophotometer was used for the absorption measurements. Finally, the oxidation products, mainly cyanate but also nitrite and nitrate, were analysed by ion chromatography (Metrohm Separation centre 733) using an aqueous solution of  $NaHCO_3$  (2.0 mM) and  $Na_2CO_3$  (1.3 mM) as eluent.

## Results and Discussion

**TiO<sub>2</sub> photocatalysts.** Table 1 summarizes the materials based exclusively on titania used as reference standards. Three different commercial samples were used as provided, without further treatment. The first one is the well known P25-TiO<sub>2</sub> material, catalyst often used in photocatalytic processes which is constituted by a mixture of the two most common titania crystalline phases, anatase and rutile. Additionally two commercial samples of each crystalline phase were also used as references. TiO<sub>2</sub>-1 to TiO<sub>2</sub>-6 materials were synthesized in our laboratory to check the effect of the calcination temperature and the influence of the temperature and acidity of the solution used in the hydrothermal treatment.

**Table 1.** Commercial brands and synthesis conditions of the studied TiO<sub>2</sub> materials.

| Material             | Commercial Brand | Hydrothermal Treatment    | Calcination |
|----------------------|------------------|---------------------------|-------------|
| P25 TiO <sub>2</sub> | Degussa          | -                         | -           |
| Anatase              | Acros            | -                         | -           |
| Rutile               | Alfa             | -                         | -           |
| TiO <sub>2</sub> -1  | -                | -                         | 450°C       |
| TiO <sub>2</sub> -2  | -                | -                         | 650°C       |
| TiO <sub>2</sub> -3  | -                | 110°C H <sub>2</sub> O    | -           |
| TiO <sub>2</sub> -4  | -                | 110°C H <sub>2</sub> O    | 550°C       |
| TiO <sub>2</sub> -5  | -                | 170°C H <sub>2</sub> O    | 550°C       |
| TiO <sub>2</sub> -6  | -                | 110°C HNO <sub>3</sub> 1N | 550°C       |

The materials were characterized by X-ray diffraction, diffuse reflectance UV-Vis spectroscopy, nitrogen adsorption at 77 K and they were tested in the photocatalytic oxidation of cyanide at a TiO<sub>2</sub> concentration of 0.5 g  $L^{-1}$ . The main results obtained are summarized in Table 2.

**Table 2.** Characterization and photoactivity results of the reference TiO<sub>2</sub> materials.

| Material             | Specific Surface Area, $S_{BET}$ (m <sup>2</sup> g <sup>-1</sup> ) | Bandgap, $E_g$ (eV) | Average Crystal Size, $D_{XRD}$ (nm) | Relative photocatalytic activity |
|----------------------|--------------------------------------------------------------------|---------------------|--------------------------------------|----------------------------------|
| P25 TiO <sub>2</sub> | 52                                                                 | 3.7                 | 31 (A); 54 (R)                       | 1.00                             |
| Anatase              | 7.0                                                                | 3.4                 | > 1 μm (A)                           | 0.26                             |
| Rutile               | 4.2                                                                | 3.1                 | > 1 μm (R)                           | 0.07                             |
| TiO <sub>2</sub> -1  | 2.7                                                                | 3.2                 | 42 (A)                               | 0.19                             |
| TiO <sub>2</sub> -2  | 0.3                                                                | 3.0                 | 300 (R)                              | 0.04                             |
| TiO <sub>2</sub> -3  | 200                                                                | 3.5                 | 7.1 (A)                              | 0.28                             |
| TiO <sub>2</sub> -4  | 17                                                                 | 3.4                 | 46 (A)                               | 0.46                             |
| TiO <sub>2</sub> -5  | 21                                                                 | 3.3                 | 57 (A)                               | 0.26                             |
| TiO <sub>2</sub> -6  | 21                                                                 | 3.2                 | 73 (R)                               | 0.10                             |

The activity results have been expressed in relative terms using the initial rate of reaction shown by the material P25-TiO<sub>2</sub>, estimated with a zero order kinetics, as reference ( $9.87 \times 10^{-7}$  mol L<sup>-1</sup> s<sup>-1</sup>). It can be noticed the lower activities showed by all the materials, being the goal of this work the elucidation of the effect of the synthesis route on the physicochemical properties of the materials and their correlation with the photocatalytic activity.

**Textural properties.** Although it is widely assumed that the photocatalytic activity is favored by high specific surface areas, the values of  $S_{BET}$  shown in Table 2 do not present a clear correlation with the activity. Generally speaking it is true that the materials with very low  $S_{BET}$  are the less active, but the material TiO<sub>2</sub>-3 that has an specific surface area of 200 m<sup>2</sup> g<sup>-1</sup> shows a much lower activity than the material TiO<sub>2</sub>-4 with only 17 m<sup>2</sup> g<sup>-1</sup>.

Concerning the influence of the synthetic route on the textural properties, the results point out that the hydrothermal route leads to materials with higher specific surface areas, but the values are drastically reduced after the thermal treatment, being in any case higher than those obtained without being hydrothermally processed. As for the effect of the thermal treatment, it is observed that the decrease in the  $S_{BET}$  is more pronounced as the temperature increases. Finally, it must be noticed that all samples could be considered as non-porous materials, for which the measured surface area corresponds to the external surface of particles and aggregates.

**Bandgap energy.** Fig. 2 shows the diffuse reflectance spectra of selected TiO<sub>2</sub> materials in terms of the Kubelka-Munk function,  $F(R)$ , that can be considered proportional to the absorption of radiation [8]. Values of the bandgap energy,  $E_g$ , displayed in Table 2 were derived from the spectra by plotting  $(F(R) \cdot h\nu)^2$  against  $h\nu$  and extrapolating the linear part of the transformed curve [20], as also shown in Fig. 2 for some of the materials.  $E_g$  values in the range 3.0 to 3.7 were obtained, therefore showing great differences depending on the sample.

Although, no clear correlation is found between the  $E_g$  values of the different materials and their activity for the photocatalytic oxidation of cyanide, in general terms it is observed that the materials with absorption edges at higher wavelength values, such as the commercial rutile and the synthetic materials TiO<sub>2</sub>-2 and TiO<sub>2</sub>-6, present the lowest activities. On the contrary, the most active material, P25-TiO<sub>2</sub>, exhibits the more energetic absorption edge. This would indicate that even though the sample P25-TiO<sub>2</sub> requires a more energetic radiation to be activated, the redox potential of the electron-hole pairs leads to a higher activity. The materials with intermediate bandgap values, that is

TiO<sub>2</sub>-3, TiO<sub>2</sub>-4 and TiO<sub>2</sub>-5, do not follow, however, this trend being TiO<sub>2</sub>-4 much more active than the commercial anatase despite both have comparable threshold wavelengths for absorption of radiation.

**Crystalline phase and average crystallite size.** Fig. 3 shows the X-ray diffraction patterns of P25-TiO<sub>2</sub> and the six synthesized TiO<sub>2</sub> materials. As it was expected, the P25-TiO<sub>2</sub> material presents two clear diffraction signals attributed to anatase (2 $\theta$ ~25.3°) and rutile (2 $\theta$ ~27.5°) confirmed by the analysis of the anatase and rutile commercial samples (not shown). Concerning the materials TiO<sub>2</sub>-1 and TiO<sub>2</sub>-2, both prepared following the same method and calcined at 450°C and 650°C respectively, they show the existence of a thermal transition from the metastable anatase phase crystallized at low temperature to the thermodynamically stable rutile phase at higher temperatures. Moreover, the crystal size of TiO<sub>2</sub>-2 is substantially higher, what confirms the hypothesis that the transition of anatase to rutile requires the growth of the crystals to reach a critical size [21], phenomenon influenced by solid state diffusion and thus activated by temperature.

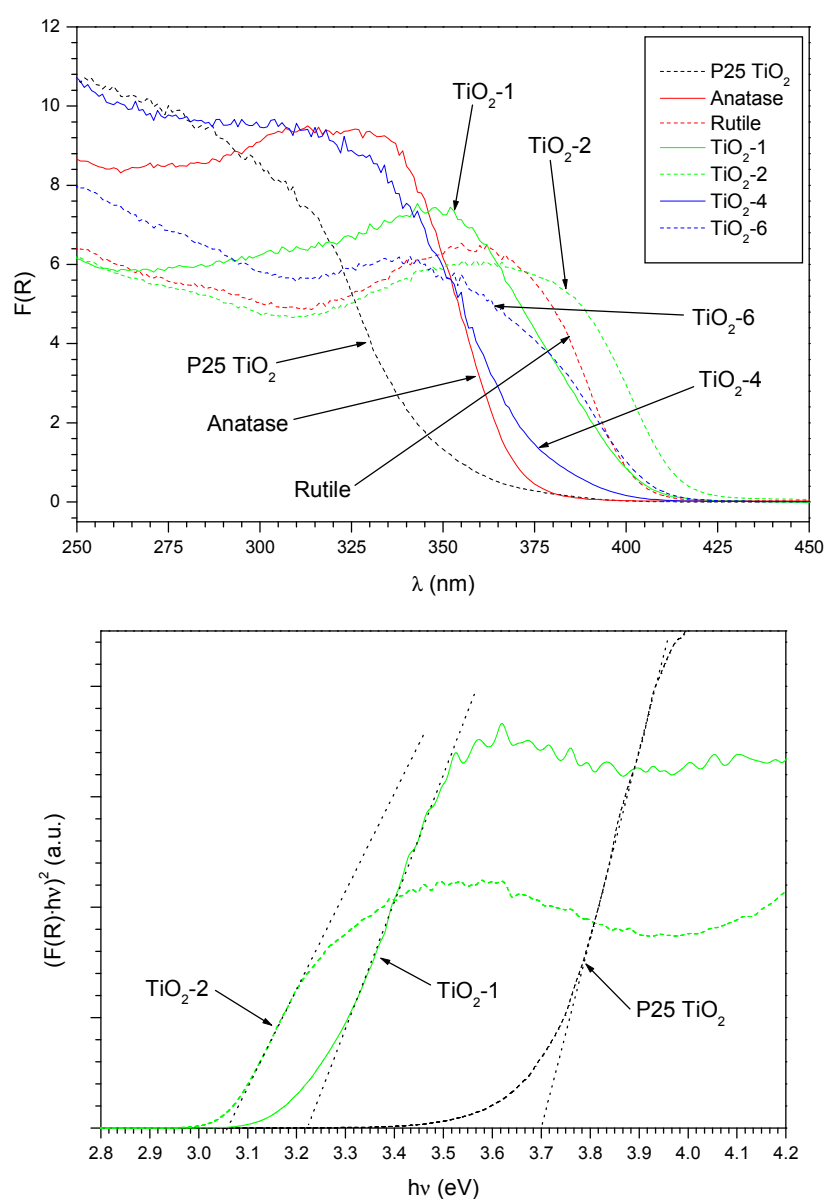


**Fig. 2.** Diffuse reflectance UV-vis spectra of selected TiO<sub>2</sub> materials expressed in terms of the Kubelka-Munk function (top) and examples of band-gap energy calculations from the derived plots (bottom).



This thermal transition from anatase to relatively big crystals of rutile can be avoided if the  $\text{TiO}_2$  gel obtained after condensation is hydrothermally treated in 1M  $\text{HNO}_3$  medium before being calcined, as confirmed by the XRD pattern of the  $\text{TiO}_2$ -6 material, which supports the presence of rutile crystals of comparable size to those of anatase-based materials. In contrast, the use of a hydrothermal treatment in pure  $\text{H}_2\text{O}$  leads to anatase crystals with very low average crystal size even after thermal treatment (46 nm for  $\text{TiO}_2$ -4). As for the influence of the temperature of the hydrothermal treatment, the diffraction patterns show the very similar crystalline properties exhibited by  $\text{TiO}_2$ -4 and  $\text{TiO}_2$ -5 samples, prepared at 110°C and 170°C, respectively.

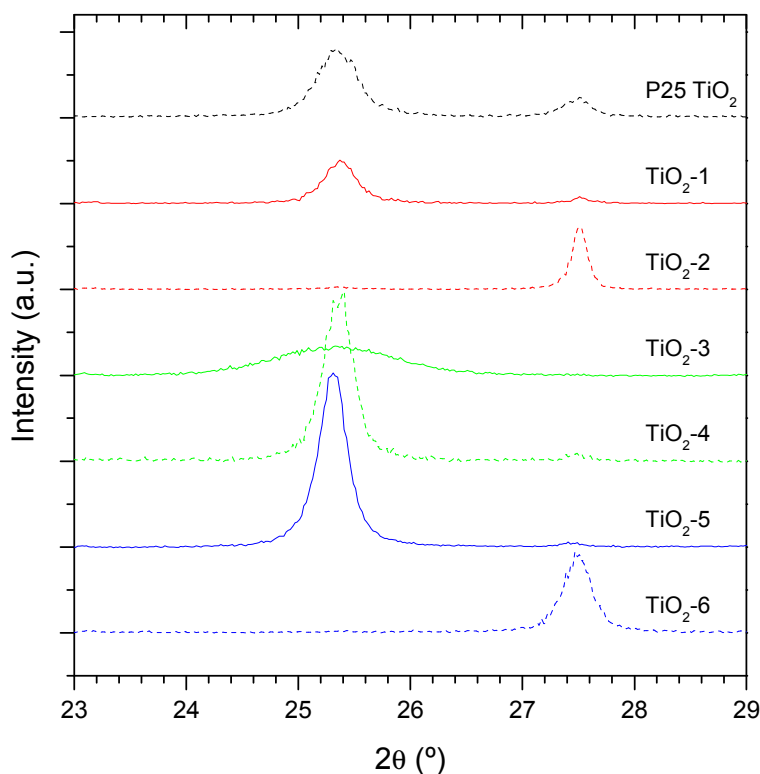


**Fig. 3.** X-ray diffraction patterns of selected  $\text{TiO}_2$  materials.

The results shown in Table 2 suggest a correlation between the crystalline properties of the materials and their activity. In general, anatase containing materials are more active than rutile materials, as confirmed not only by the comparison of both commercial crystalline phases, but also between synthetic materials  $\text{TiO}_2$ -1 and  $\text{TiO}_2$ -2 on one side, and  $\text{TiO}_2$ -4 and  $\text{TiO}_2$ -6 on the other. This higher activity observed for anatase is in agreement with the conclusions of other researchers being attributed to its higher capacity for  $\text{O}_2$  photoadsorption, the lower charge recombination rate [22], and the higher adsorption capabilities for hydroxyl anions and water molecules in comparison to rutile [23].

The crystallographic characterization of the synthetic materials is in good agreement with the specific surface area measurements. Materials with lower crystal sizes clearly exhibit higher values of  $S_{\text{BET}}$ , due to the relative increase in the external surface of the particles and aggregates. From that point of view, the activity of nanocrystalline materials should be higher than that of the commercial samples with crystals in the micrometer range. This is confirmed in the case of materials  $\text{TiO}_2$ -4 and  $\text{TiO}_2$ -6, but not for the remaining samples.

On the other hand, there is a clear relationship between the detected crystalline phase and the band gap energy of the material, showing all the anatase containing materials higher  $E_g$  values than

the rutile based samples, with the only exception of P25 TiO<sub>2</sub> that presents the highest band gap energy despite its approximately 20 wt% of rutile phase [24]. The value of  $E_g$  however not only depends on the crystalline phase but also on the average crystal size, being reported that very small crystals cause a blue-shift in the absorption spectra [25]. This is confirmed by the decrease in the band gap energy of materials TiO<sub>2</sub>-3, TiO<sub>2</sub>-4 and TiO<sub>2</sub>-5 where the anatase average crystal size increases.

From the activity results of Table 2, it is concluded that the hydrothermal treatment leads to much more active materials than the simple thermal treatment, corresponding the highest activity (apart from P25 TiO<sub>2</sub>) to the TiO<sub>2</sub>-4 material, hydroprocessed at 110°C in distilled water and subsequently calcined. In any case, calcination should not be omitted, as it increases the activity of the hydrothermally treated materials. The most plausible explanation for these results is that the hydrothermal treatment favors the low temperature nucleation of anatase crystals. However, the amount of titanium dioxide that remains amorphous after the treatment could be high, as suggested by the X-ray diffraction pattern of TiO<sub>2</sub>-3. Calcination promotes the crystallization and crystal growing of anatase, but the resulting materials are more active if they grow from hydrothermally crystallized nucleus of anatase than directly from amorphous titania. Consequently, although the differences in the physicochemical properties of hydrothermal and non-hydrothermal materials are not very significant, the activity of the former ones is substantially increased.

In any case, it must be recognized that all the synthesized materials are less active than P25 TiO<sub>2</sub>. The high photoactivity of this material has been attributed to its extremely high specific coefficient for radiation absorption [26], to the enhancement in the magnitude of the space-charge potential created by contact between the different phases present and the localized electronic states in the remaining amorphous phase [27], and also to the reduced recombination rate in comparison with a relatively high charge transfer rate [28]. In relation to the latter, Martin et al. [29] have suggested that the high activity of P25 TiO<sub>2</sub> is the result of a very low amount of crystalline defects resulting from its preparation by the Aerosil method at high temperature, whereas sol-gel materials show a much higher density of crystalline defects where the recombination of the charge carriers take place.

Assuming the hypothesis of Martin et al. [29] for the high activity of P25 TiO<sub>2</sub>, it is proposed that the improvement in the activity achieved for sol-gel materials synthesized through a hydrothermal route can be due to the decrease in the density of crystalline defects induced by the hydrothermal crystallization. Consequently, despite the similar physicochemical properties of both types of sol-gel materials, the catalysts hydrothermally processed show much higher photocatalytic activities.

**TiO<sub>2</sub>/SiO<sub>2</sub> photocatalysts.** Table 3 summarizes the preparation procedure of the synthesized TiO<sub>2</sub>/SiO<sub>2</sub> materials, which can be classified into the following different categories:

- i) Materials TiO<sub>2</sub>/SiO<sub>2</sub>-1 to TiO<sub>2</sub>/SiO<sub>2</sub>-6 are TiO<sub>2</sub>/SiO<sub>2</sub> xerogels with three different titania loadings (pure SiO<sub>2</sub> materials for comparison) synthesized with prehydrolysis of the silicon source to favor the heterocondensation of both oxides and maximize the homogenous dispersion of Ti atoms in the silica network, calcined at two different temperatures.
- ii) Materials TiO<sub>2</sub>/SiO<sub>2</sub>-7 to TiO<sub>2</sub>/SiO<sub>2</sub>-12, equivalent to the previous ones but including a silanization step to improved the textural properties of the materials.
- iii) Materials TiO<sub>2</sub>/SiO<sub>2</sub>-13 to TiO<sub>2</sub>/SiO<sub>2</sub>-16 are TiO<sub>2</sub>/SiO<sub>2</sub> xerogels prepared without prehydrolysis of the silicon source to increase the degree of homocondensation of the titanium dioxide.

**Table 3.** Synthesis conditions of the studied TiO<sub>2</sub>/SiO<sub>2</sub> materials.

| Material                               | %TiO <sub>2</sub> | Pre-hydrolysis | Silica Support     | Silanization | Hydrothermal Treatment | Calcination |
|----------------------------------------|-------------------|----------------|--------------------|--------------|------------------------|-------------|
| TiO <sub>2</sub> /SiO <sub>2</sub> -1  | 0                 | Yes            | -                  | -            | -                      | 450°C       |
| TiO <sub>2</sub> /SiO <sub>2</sub> -2  | 0                 | Yes            | -                  | -            | -                      | 650°C       |
| TiO <sub>2</sub> /SiO <sub>2</sub> -3  | 20                | Yes            | -                  | -            | -                      | 450°C       |
| TiO <sub>2</sub> /SiO <sub>2</sub> -4  | 20                | Yes            | -                  | -            | -                      | 650°C       |
| TiO <sub>2</sub> /SiO <sub>2</sub> -5  | 40                | Yes            | -                  | -            | -                      | 450°C       |
| TiO <sub>2</sub> /SiO <sub>2</sub> -6  | 40                | Yes            | -                  | -            | -                      | 650°C       |
| TiO <sub>2</sub> /SiO <sub>2</sub> -7  | 0                 | Yes            | -                  | Yes          | -                      | 450°C       |
| TiO <sub>2</sub> /SiO <sub>2</sub> -8  | 0                 | Yes            | -                  | Yes          | -                      | 650°C       |
| TiO <sub>2</sub> /SiO <sub>2</sub> -9  | 20                | Yes            | -                  | Yes          | -                      | 450°C       |
| TiO <sub>2</sub> /SiO <sub>2</sub> -10 | 20                | Yes            | -                  | Yes          | -                      | 650°C       |
| TiO <sub>2</sub> /SiO <sub>2</sub> -11 | 40                | Yes            | -                  | Yes          | -                      | 450°C       |
| TiO <sub>2</sub> /SiO <sub>2</sub> -12 | 40                | Yes            | -                  | Yes          | -                      | 650°C       |
| TiO <sub>2</sub> /SiO <sub>2</sub> -13 | 20                | -              | -                  | -            | -                      | 450°C       |
| TiO <sub>2</sub> /SiO <sub>2</sub> -14 | 20                | -              | -                  | -            | -                      | 650°C       |
| TiO <sub>2</sub> /SiO <sub>2</sub> -15 | 40                | -              | -                  | -            | -                      | 450°C       |
| TiO <sub>2</sub> /SiO <sub>2</sub> -16 | 40                | -              | -                  | -            | -                      | 650°C       |
| TiO <sub>2</sub> /SiO <sub>2</sub> -17 | 20                | -              | -                  | -            | 110°C H <sub>2</sub> O | 550°C       |
| TiO <sub>2</sub> /SiO <sub>2</sub> -18 | 40                | -              | -                  | -            | 110°C H <sub>2</sub> O | 550°C       |
| TiO <sub>2</sub> /SiO <sub>2</sub> -19 | 40                | -              | GrSiO <sub>2</sub> | -            | -                      | 550°C       |
| TiO <sub>2</sub> /SiO <sub>2</sub> -20 | 20                | -              | GrSiO <sub>2</sub> | -            | 110°C H <sub>2</sub> O | 550°C       |
| TiO <sub>2</sub> /SiO <sub>2</sub> -21 | 40                | -              | GrSiO <sub>2</sub> | -            | 110°C H <sub>2</sub> O | 550°C       |
| TiO <sub>2</sub> /SiO <sub>2</sub> -22 | 60                | -              | GrSiO <sub>2</sub> | -            | 110°C H <sub>2</sub> O | 550°C       |
| TiO <sub>2</sub> /SiO <sub>2</sub> -23 | 20                | -              | SBA-15             | -            | 110°C H <sub>2</sub> O | 550°C       |
| TiO <sub>2</sub> /SiO <sub>2</sub> -24 | 40                | -              | SBA-15             | -            | 110°C H <sub>2</sub> O | 550°C       |
| TiO <sub>2</sub> /SiO <sub>2</sub> -25 | 60                | -              | SBA-15             | -            | 110°C H <sub>2</sub> O | 550°C       |

- iv) Materials TiO<sub>2</sub>/SiO<sub>2</sub>-17 and TiO<sub>2</sub>/SiO<sub>2</sub>-18 consist on mixed oxides synthesized without prehydrolysis of the silicon source and processed through a hydrothermal treatment in water at 110°C and further calcination. These conditions were selected from the previous results reported for pure TiO<sub>2</sub> materials.
- v) Materials TiO<sub>2</sub>/SiO<sub>2</sub>-19 to TiO<sub>2</sub>/SiO<sub>2</sub>-25 are silica-supported TiO<sub>2</sub> xerogels in which the hydrolysis and condensation of the titanium alcoxide took place mainly inside the porous structure of silica particles, being used two different supports and three titania wt% of loading. In contrast with the other materials, TiO<sub>2</sub>/SiO<sub>2</sub>-19 was prepared without hydrothermal treatment, in order to evaluate the influence of this step.

Table 4 summarizes the main results of the textural properties, UV radiation absorption and crystalline character of these materials, together with their photocatalytic activity (relative to P25 TiO<sub>2</sub>) for the oxidation of cyanide at a concentration equivalent to 0.5 g TiO<sub>2</sub> L<sup>-1</sup>.

**Table 4.** Characterization and photoactivity results of the studied TiO<sub>2</sub>/SiO<sub>2</sub> materials.

| Material                               | Specific Surface Area, $S_{BET}$ (m <sup>2</sup> g <sup>-1</sup> ) | Pore Volume, $V_P$ (cm <sup>3</sup> g <sup>-1</sup> ) | Bandgap, $E_g$ (eV) | Avg. Crystal Size, $D_{XRD}$ (nm) | Relative photocatalytic Activity |
|----------------------------------------|--------------------------------------------------------------------|-------------------------------------------------------|---------------------|-----------------------------------|----------------------------------|
| TiO <sub>2</sub> /SiO <sub>2</sub> -1  | 685                                                                | 1.05                                                  | -                   | -                                 | -                                |
| TiO <sub>2</sub> /SiO <sub>2</sub> -2  | 599                                                                | 0.89                                                  | -                   | -                                 | -                                |
| TiO <sub>2</sub> /SiO <sub>2</sub> -3  | 594                                                                | 0.44                                                  | 4.2                 | -                                 | -                                |
| TiO <sub>2</sub> /SiO <sub>2</sub> -4  | 423                                                                | 0.33                                                  | 4.1                 | -                                 | 0.001                            |
| TiO <sub>2</sub> /SiO <sub>2</sub> -5  | 461                                                                | 0.32                                                  | 3.8                 | -                                 | -                                |
| TiO <sub>2</sub> /SiO <sub>2</sub> -6  | 234                                                                | 0.18                                                  | 3.7                 | -                                 | 0.003                            |
| TiO <sub>2</sub> /SiO <sub>2</sub> -7  | 892                                                                | 3.50                                                  | -                   | -                                 | -                                |
| TiO <sub>2</sub> /SiO <sub>2</sub> -8  | 728                                                                | 2.73                                                  | -                   | -                                 | -                                |
| TiO <sub>2</sub> /SiO <sub>2</sub> -9  | 283                                                                | 0.70                                                  | 4.3                 | -                                 | -                                |
| TiO <sub>2</sub> /SiO <sub>2</sub> -10 | 222                                                                | 0.64                                                  | 4.2                 | -                                 | 0.003                            |
| TiO <sub>2</sub> /SiO <sub>2</sub> -11 | 279                                                                | 0.56                                                  | 4.1                 | -                                 | -                                |
| TiO <sub>2</sub> /SiO <sub>2</sub> -12 | 127                                                                | 0.29                                                  | 4.0                 | -                                 | 0.004                            |
| TiO <sub>2</sub> /SiO <sub>2</sub> -13 | 312                                                                | 0.73                                                  | 4.2                 | -                                 | -                                |
| TiO <sub>2</sub> /SiO <sub>2</sub> -14 | 164                                                                | 0.61                                                  | 4.1                 | -                                 | 0.008                            |
| TiO <sub>2</sub> /SiO <sub>2</sub> -15 | 199                                                                | 0.76                                                  | 4.0                 | -                                 | -                                |
| TiO <sub>2</sub> /SiO <sub>2</sub> -16 | 165                                                                | 0.47                                                  | 3.9                 | -                                 | 0.015                            |
| TiO <sub>2</sub> /SiO <sub>2</sub> -17 | 453                                                                | 1.03                                                  | 3.8                 | 5.8 (A)                           | 0.09                             |
| TiO <sub>2</sub> /SiO <sub>2</sub> -18 | 230                                                                | 1.02                                                  | 3.7                 | 12 (A)                            | 0.13                             |
| TiO <sub>2</sub> /SiO <sub>2</sub> -19 | 220                                                                | 0.97                                                  | 3.7                 | 11 (A)                            | 0.20                             |
| TiO <sub>2</sub> /SiO <sub>2</sub> -20 | 299                                                                | 1.16                                                  | 3.7                 | 8.0 (A)                           | 0.49                             |
| TiO <sub>2</sub> /SiO <sub>2</sub> -21 | 246                                                                | 0.94                                                  | 3.7                 | 11 (A)                            | 0.55                             |
| TiO <sub>2</sub> /SiO <sub>2</sub> -22 | 179                                                                | 0.67                                                  | 3.6                 | 12 (A)                            | 0.64                             |
| TiO <sub>2</sub> /SiO <sub>2</sub> -23 | 532                                                                | 0.78                                                  | 3.8                 | 6.2 (A)                           | 0.67                             |
| TiO <sub>2</sub> /SiO <sub>2</sub> -24 | 442                                                                | 0.68                                                  | 3.7                 | 6.7 (A)                           | 0.72                             |
| TiO <sub>2</sub> /SiO <sub>2</sub> -25 | 349                                                                | 0.60                                                  | 3.7                 | 6.8 (A)                           | 0.85                             |

The activity results of Table 4 show that despite all the materials present activities lower than P25 TiO<sub>2</sub>, some of them reach values between 49% and 85% of its activity, what is very significant specially considering the advantages of these materials due to the improvement in the separation step [30]. The goal of the following section is the elucidation of the synthesis route and the subsequent physicochemical properties of the materials that maximize the activity.

**Textural properties.** The homogeneous dispersion of titania on a silica support as been proposed as a way of increasing the effective  $\text{TiO}_2$  surface area [7]. Materials prepared after prehydrolysis of the silicon source show a significant decrease of the specific surface area and specially of the pore volume as the titania content and temperature of calcination increases. However, the materials with the lowest  $S_{\text{BET}}$  value of the group ( $\text{TiO}_2/\text{SiO}_2$ -4 and  $\text{TiO}_2/\text{SiO}_2$ -6) are the only ones that show activity, although the value could be considered as negligible. Although the presence of a silanization step increases the specific surface area and pore volume of the pure silica materials ( $\text{TiO}_2/\text{SiO}_2$ -7 and  $\text{TiO}_2/\text{SiO}_2$ -8 in comparison to  $\text{TiO}_2/\text{SiO}_2$ -1 and  $\text{TiO}_2/\text{SiO}_2$ -2), this is not the case for the mixed oxides for which lower  $S_{\text{BET}}$  and higher pore volumes are observed compared than the non-silanized materials. However, once again the silanized materials with lower specific surface areas compared to the non-silanized ones are the most active, although the increase in activity is not really significant.

Materials prepared without prehydrolysis of the silicon source and calcined at  $650^\circ\text{C}$  ( $\text{TiO}_2/\text{SiO}_2$ -14 and  $\text{TiO}_2/\text{SiO}_2$ -16) show a substantially higher activity, despite their  $S_{\text{BET}}$  values are relatively low, confirming that there not seems to be a correlation between the surface area of the materials and their activity. This is also corroborated by the hydrothermal xerogels calcined at  $550^\circ\text{C}$ ,  $\text{TiO}_2/\text{SiO}_2$ -17 and  $\text{TiO}_2/\text{SiO}_2$ -18, that present a difference between activities far away from the comparison of their surface areas..

The most active catalysts are clearly the silica-supported  $\text{TiO}_2$  xerogels, materials that present intermediate to high  $S_{\text{BET}}$  values. However, once again the activity increases as the titanium loading does, even though the reactions have been performed at the same  $\text{TiO}_2$  concentration. This increase in activity is opposite to the decrease in the specific surface area of the supported materials, what lead to conclude that the *total* surface area of the  $\text{TiO}_2/\text{SiO}_2$  materials do not directly determine their photocatalytic activity.

**Bandgap energy.** Fig. 4 depicts the diffuse reflectance spectra of the most representative  $\text{TiO}_2/\text{SiO}_2$  materials. First of all, it must be noticed the null absorption exhibited by the all the pure silica materials, including both silica supports, in the whole wavelength range studied (only  $\text{TiO}_2/\text{SiO}_2$ -1 is shown for clarity purposes), confirming that all the absorption of radiation is exclusively due to the titania contribution, and justifying the use of silica as supporting material for the  $\text{TiO}_2$  active phase.

From the spectra represented in Fig. 4 it is also remarkable that the absorption at wavelengths below 300 nm shown by all the  $\text{TiO}_2/\text{SiO}_2$  materials is much higher than that of all the  $\text{TiO}_2$  samples. Whereas the absorption of pure titania samples is associated to the crystalline and semiconducting properties of this oxide, in this case the more energetic absorption is attributed to the presence of non-octahedral titanium species, specially titanium atoms bonded to the tetrahedral silica network [31]. According to Uguina et al [32] the maximum incorporation of isolated titanium atoms in the silica network is close to 2 wt%. Consequently, higher titania contents lead to an increase in the  $\text{TiO}_2$  aggregates shifting the absorption band to higher wavelengths, as shown in the spectra of  $\text{TiO}_2/\text{SiO}_2$ -5 and  $\text{TiO}_2/\text{SiO}_2$ -6 in comparison with  $\text{TiO}_2/\text{SiO}_2$ -3 and  $\text{TiO}_2/\text{SiO}_2$ -4. Moreover, the calcination at higher temperatures of mixed oxides results in a shift of the absorption band to even less energetic wavelengths, together with a clear decrease in the absorption below 300 nm (see spectra of  $\text{TiO}_2/\text{SiO}_2$ -6) what probably means that aggregates of  $\text{TiO}_2$  with a weaker interaction with the silica network have been formed.

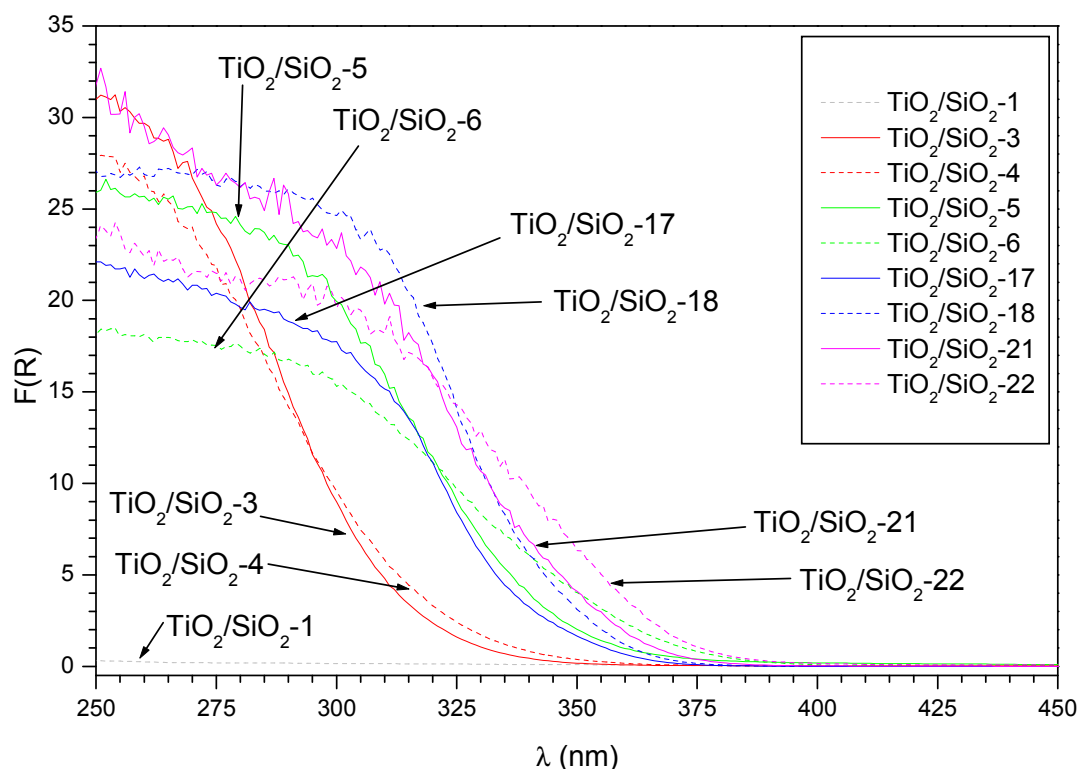


**Fig. 4.** Diffuse reflectance UV-vis spectra of selected  $\text{TiO}_2/\text{SiO}_2$  materials.

The diffuse reflectance spectra of silanized materials (not shown) are equivalent to the corresponding non-silanized materials which confirms that the effect of this step is exclusively the modification of the textural properties. Moreover, materials prepared without hydrolysis of the silicon source neither show significant differences in the absorption threshold, as reveal the  $E_g$  values shown in Table 4.

Concerning the hydrothermal xerogels, the bandgap energy of the  $\text{TiO}_2/\text{SiO}_2$ -17 sample is much lower than all the previously studied mixed oxides with the same titania loading. In contrast,  $\text{TiO}_2/\text{SiO}_2$ -18 presents similar threshold wavelength than other 40 wt% titania loaded materials.

Finally, silica-supported  $\text{TiO}_2$  xerogels seems to present a red-shift of the absorption edge compared to the samples where the silica network is assembled during titania particle formation, more significant as the titania loading increases, as shown the diffuse reflectance spectra of samples  $\text{TiO}_2/\text{SiO}_2$ -21 and  $\text{TiO}_2/\text{SiO}_2$ -22 (Fig. 4).

According to the results included in Table 4, it seems that, exists an acceptable correlation between the photocatalytic activity of the  $\text{TiO}_2/\text{SiO}_2$  materials and their values of  $E_g$ . The most active materials are those with the lower values of the bandgap energy, that is, in the order of 3.6 to 3.8 eV ( $\text{TiO}_2/\text{SiO}_2$ -17 to  $\text{TiO}_2/\text{SiO}_2$ -25), but there are also important differences in activity among them, even for samples with similar  $E_g$  values. These results do not support the extremely high activity (even higher than that of Degussa P25) reported by Yamashita et al. [9] for low titanium containing  $\text{TiO}_2/\text{SiO}_2$  samples, attributed to the formation of excited states of charge transfer complexes located in the tetrahedral  $\text{Ti}^{4+}$  species isolated in the silica network in materials.

Comparing with the values corresponding to pure  $\text{TiO}_2$  materials, all the band gap energies of the  $\text{TiO}_2/\text{SiO}_2$  materials are much higher, in agreement with previous results reported in the literature [2]. Surprisingly, the best  $\text{TiO}_2/\text{SiO}_2$  photocatalysts present the same value of  $E_g$  than the highly active P25  $\text{TiO}_2$  (3.7 eV). That means that the value of the threshold wavelength of absorption must be sufficiently high to show activity (lower  $E_g$  values), but the more energetic the better. This effect is obviously connected with the emission spectrum of the irradiation source used in photocatalytic experiments (usually centered in 355 to 365 nm), which means that the optimum  $E_g$  should depend

on the lamp. In any case, the results prove that the value of the band gap is not the only parameter that determines the photocatalytic activity, as demonstrates the much higher activity of the catalyst  $\text{TiO}_2$ -4 ( $E_g = 3.4$  eV) in comparison with materials  $\text{TiO}_2/\text{SiO}_2$ -17 to  $\text{TiO}_2/\text{SiO}_2$ -19 ( $E_g = 3.7$ -3.8 eV).

**Crystalline phase and average crystallite size.** Fig. 5 illustrates the X-ray diffraction patterns of the most representative  $\text{TiO}_2/\text{SiO}_2$  materials. All the materials from  $\text{TiO}_2/\text{SiO}_2$ -1 to  $\text{TiO}_2/\text{SiO}_2$ -16 do not show any diffraction signal corresponding to titania crystalline phases, independently of the temperature of the thermal treatment (only  $\text{TiO}_2/\text{SiO}_2$ -4 and  $\text{TiO}_2/\text{SiO}_2$ -6 are represented for the sake of clarity). The rest of materials from  $\text{TiO}_2/\text{SiO}_2$ -17 to  $\text{TiO}_2/\text{SiO}_2$ -25 show broad signals corresponding to very small anatase crystals in the range of few nanometers, whose average sizes (Table 4) increase with the  $\text{TiO}_2$  wt% loading.

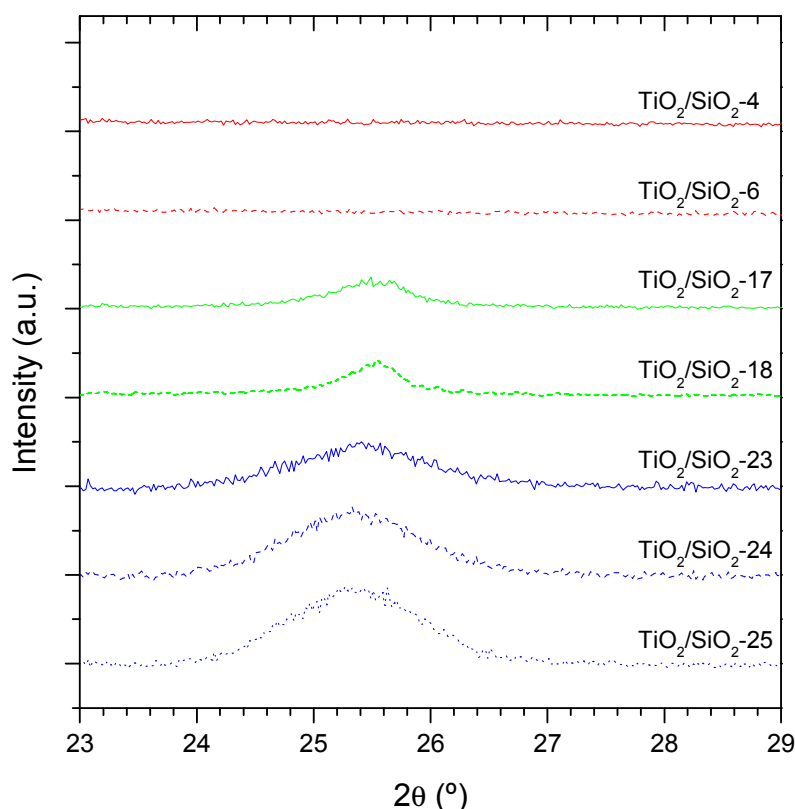


**Fig. 5.** X-ray diffraction patterns of selected  $\text{TiO}_2/\text{SiO}_2$  materials.

The correlation between the crystalline properties and the results of the photocatalytic experiments clearly show that formation of anatase crystals is required to achieve significant activities, although once again materials with similar average crystal sizes showed very different activities.

Materials synthesized with prehydrolysis of the silicon source (with or without silanization) in which titanium atoms are ideally homogeneously distributed onto the support, do not show neither diffraction signals nor photocatalytic activity. Considering the favourable textural properties of these materials and their apparently adequate band gap energy values (at least of the 40 wt%  $\text{TiO}_2$  loaded samples), the absence of crystalline titania seems to be the most plausible explanation for their inactivity, discarding again the proposed photocatalytic mechanism of tetrahedral  $\text{Ti}^{4+}$  charge transfer complexes [9].

The formation of titania clusters is favored in materials  $\text{TiO}_2/\text{SiO}_2$ -13 to  $\text{TiO}_2/\text{SiO}_2$ -16, synthesized without hydrolysis of the silicon source. However, the absence of diffraction signals implies that anatase crystallization remains limited by the segregation of the titania aggregates from the silica network. It is noteworthy that the activity of materials calcined at higher temperature could

be related to the formation of very small quantum-sized anatase crystals not-detectable by powder X-ray diffraction.

Concerning the hydrothermal treatment step, it promotes the growing and crystallization of titania aggregates, probably through a redissolution mechanism in which diffusion is favored. However, despite their crystallinity, the activity of materials  $\text{TiO}_2/\text{SiO}_2$ -17 and  $\text{TiO}_2/\text{SiO}_2$ -18 is not very different from that of non-hydrothermal materials  $\text{TiO}_2/\text{SiO}_2$ -14 and  $\text{TiO}_2/\text{SiO}_2$ -16. A possible explanation to support these results is that titania crystals could be covered by the silicon oxide due to the lower hydrolysis and condensation rate of the latter. This hypothesis is in agreement with the higher activity values observed for silica-supported  $\text{TiO}_2$  xerogels in which the anatase crystals grow over the silica surface and consequently are more accessible. For supported materials the hydrothermal treatment drastically increases the activity of the catalysts, as it is shown by the comparison of samples  $\text{TiO}_2/\text{SiO}_2$ -19 and  $\text{TiO}_2/\text{SiO}_2$ -20, materials with the same wt% of titania loading and equivalent average crystal size but very different activity. This is in complete agreement with the results obtained for pure  $\text{TiO}_2$  materials and supports the hypothesis of the lower density of crystalline defects induced by the hydrothermal crystallization. However, the experimental verification of the lower number of bulk defects of the crystal network in which recombination of the electron-hole pairs could take place should be determined by refining the diffraction patterns using the Rietveld method, which is very difficult to accomplish for such a small crystallite size.

**Effective  $\text{TiO}_2$  surface-based reaction rate.** As it has been shown above, some hydrothermal silica-supported  $\text{TiO}_2$  xerogels achieve a high photocatalytic performance, although the significant differences among the activities of samples  $\text{TiO}_2/\text{SiO}_2$ -20 to  $\text{TiO}_2/\text{SiO}_2$ -25 at equal  $\text{TiO}_2$  cannot be satisfactorily justified through the comparison of the characterization data summarized in Table 4. For that reason, and considering that the *total* surface area of the materials do not correlate their activity, the next question to answer is which is the fraction of the *total* surface area that corresponds to accessible  $\text{TiO}_2$ , that is, the effective  $\text{TiO}_2$  surface area.

The procedure used for determining the  $\text{TiO}_2$  surface area is based on the selective reaction of phenylphosphonic acid with titanium oxide and further quantification of the phosphorus atoms content of the material following two assumptions:

i) The number of phenylphosphonic molecules incorporated to the material only depends on the titania surface area accessible to the reaction with phenylphosphonic acid, being the negligible the differences attributed to the crystalline phase or the surface properties, such as degree of hydroxylation. This hypothesis is confirmed by the results obtained for three different titania materials, showing that the amount of phenylphosphonic acid incorporated to the material is equivalent to  $2.8 \pm 0.2$  atoms of phosphorus per square nanometer of titania surface [15], value in agreement with the grafting density of 3 phenylphosphonic acid molecules per nanometer reported by Mutin et al. [18].

ii) The incorporation of phosphorus by reaction of phenylphosphonic acid with any kind of silica surface could be considered as negligible. This hypothesis is confirmed by the results obtained with two different pure silica materials [15]

Based on these considerations, the accessible  $\text{TiO}_2$  specific surface area of  $\text{TiO}_2/\text{SiO}_2$  materials can be determined through the quantification of phosphorus atoms after reaction with phenylphosphonic acid. The results obtained for materials  $\text{TiO}_2/\text{SiO}_2$ -20 to  $\text{TiO}_2/\text{SiO}_2$ -25 are summarized in Table 5, showing that the specific surface area of titanium dioxide increases with the  $\text{TiO}_2$  loading of the material with both supports, but in all cases the *accessible*  $\text{TiO}_2$  surface is higher when using  $\text{GrSiO}_2$  as support.

Once the  $\text{TiO}_2$  specific surface area is estimated, the surface-based reaction rate,  $r_s$ , can be determined as the ratio between the volumetric reaction rate,  $r_v$ , and the  $\text{TiO}_2$  surface available in the suspension considering the catalyst concentration, as shown also in Table 5. From the results, the surface-based activity of  $\text{TiO}_2$ -4 and also of  $\text{TiO}_2/\text{SiO}_2$ -25 is even higher than that of P25  $\text{TiO}_2$ . Considering that the six  $\text{TiO}_2/\text{SiO}_2$  materials have been synthesized following the same procedure,



they exhibit similar average titania crystal sizes, and the reaction has been carried out with the same titania mass concentration, the expected values for the surface reaction rate would be essentially the same. However, the materials supported on SBA-15 always show higher activities than their correspondent GrSiO<sub>2</sub>-based materials, either in terms of the volumetric or surface reaction rate. Assuming that the characteristics of the titania nanocrystals of the six materials should be very similar, the intrinsic kinetics of the oxidation reaction and the electron-hole recombination rate should be more or less the same. Consequently, differences in activity should be due to differences in the physical steps of the photocatalytic reaction mechanism, such as differences in the radiation absorption coefficients, in the adsorption of the reactants or in the diffusion through the porous structure, being all these aspects more dependent on the properties of the silica support than on the titanium dioxide crystal itself.

**Table 5.** TiO<sub>2</sub> surface based reaction rate of selected studied materials.

| Material                               | Total Specific Surface Area (m <sup>2</sup> g <sup>-1</sup> ) | TiO <sub>2</sub> Specific Surface Area (m <sup>2</sup> g <sup>-1</sup> ) | Catalyst loaded in the reactor (g L <sup>-1</sup> ) | TiO <sub>2</sub> Surface (m <sup>2</sup> L <sup>-1</sup> ) | Reaction rate, $r_V$ (mol L <sup>-1</sup> s <sup>-1</sup> ) | Reaction rate, $r_S$ (mol m <sup>-2</sup> s <sup>-1</sup> ) |
|----------------------------------------|---------------------------------------------------------------|--------------------------------------------------------------------------|-----------------------------------------------------|------------------------------------------------------------|-------------------------------------------------------------|-------------------------------------------------------------|
| P25 TiO <sub>2</sub>                   | 52                                                            | 52                                                                       | 0.5                                                 | 26.0                                                       | $9.87 \times 10^{-7}$                                       | $3.80 \times 10^{-8}$                                       |
| TiO <sub>2</sub> -4                    | 17.2                                                          | 17.2                                                                     | 0.5                                                 | 8.6                                                        | $4.57 \times 10^{-7}$                                       | $5.31 \times 10^{-8}$                                       |
| TiO <sub>2</sub> /SiO <sub>2</sub> -20 | 299                                                           | 14.6                                                                     | 2.5                                                 | 36.4                                                       | $4.82 \times 10^{-7}$                                       | $1.32 \times 10^{-8}$                                       |
| TiO <sub>2</sub> /SiO <sub>2</sub> -21 | 246                                                           | 22.1                                                                     | 1.25                                                | 27.5                                                       | $5.47 \times 10^{-7}$                                       | $1.99 \times 10^{-8}$                                       |
| TiO <sub>2</sub> /SiO <sub>2</sub> -22 | 179                                                           | 35.0                                                                     | 0.87                                                | 30.2                                                       | $6.31 \times 10^{-7}$                                       | $2.09 \times 10^{-8}$                                       |
| TiO <sub>2</sub> /SiO <sub>2</sub> -23 | 532                                                           | 10.0                                                                     | 2.5                                                 | 24.8                                                       | $6.60 \times 10^{-7}$                                       | $2.66 \times 10^{-8}$                                       |
| TiO <sub>2</sub> /SiO <sub>2</sub> -24 | 442                                                           | 16.2                                                                     | 1.25                                                | 20.2                                                       | $7.14 \times 10^{-7}$                                       | $3.54 \times 10^{-8}$                                       |
| TiO <sub>2</sub> /SiO <sub>2</sub> -25 | 349                                                           | 24.8                                                                     | 0.87                                                | 21.5                                                       | $8.37 \times 10^{-7}$                                       | $3.89 \times 10^{-8}$                                       |

## Conclusions

The physicochemical properties of sol-gel TiO<sub>2</sub> and TiO<sub>2</sub>/SiO<sub>2</sub> mixed oxides and consequently their photocatalytic activity are strongly influenced by the preparation procedure. Slight changes in the synthesis route modify the textural properties, absorption spectra and crystalline structure of the catalysts, what have an important impact on the reaction rate for the oxidation of pollutants. For a good photoactivity, suitable textural properties are essential but a good accessibility of the reactant to the titania surface must be also provided. X-ray diffraction patterns and diffuse reflectance spectra show that formation of anatase nanocrystals of suitable size and band gap energy is absolutely required. No evidences of activity based on the formation of tetrahedral Ti<sup>4+</sup> charge transfer complexes, suggested by other authors have been found. Consequently, this work evidences that semiconductor photocatalysis is the only mechanism responsible for the photoactivity of titania-silica materials.

The best photocatalytic activities have been obtained for those catalysts where very small TiO<sub>2</sub> nanocrystals are directly supported onto silica particles. Additionally, a drastic improvement in the photoactivity of the materials is achieved when introducing a low-temperature hydrothermal crystallization step before the calcination. This effect could be related to a decrease in the density of defects in the crystal network that causes a reduction in the recombination rate of the charge carriers.

Additionally, it is shown that the evaluation of the fraction of the total surface area corresponding to titania is the correct way for comparing the catalytic activity of different materials in processes in which titanium dioxide is the only phase catalytically active and silica behaves as an inert support. However, the results of the titanium surface-based reaction rates suggest that the photocatalytic activity is also very affected by the rate of the physical steps of the process, strongly influenced by the silica support.

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# **An Overview of Semi-Conductor Photocatalysis: Modification of TiO<sub>2</sub> Nanomaterials**

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## **1. INTRODUCTION**

### **1.1 General Background on Photocatalysis**

Since the beginning of life on earth, the environment has been polluted by waste, both natural as well as synthetic (man-made). In the case of natural waste however, the environment by itself controls the effect of contamination. But in the case of synthetic materials, the pollution is higher even in trace concentration and this may go on accumulating, leading to disastrous effects on the environment and ecology. Industrial wastes containing heavy metals and pesticide residues fall in this category. The major point sources of pesticide pollution are wastewater from agricultural industries and pesticide manufacturing and formulating plants. Hence the waste from these sources must be removed or destroyed before discharge to the environment. There have been several methods practiced for the treatment of wastewater. However many of them are not able to achieve hundred percent satisfaction.

Environmental pollution and destruction on a global scale as well as lack of sufficient clean and natural energy sources have drawn much attention and concern to the vital need for ecologically clean chemical technology, materials and processes. This is one of the most urgent challenges facing chemical scientists. Recently, light-induced photocatalytic reactions have gained a lot of attention for the purification of wastewater.

### **1.2 Definition of Photocatalysis**

The phenomenon connecting photochemistry and catalysis is referred to as photocatalysis. It implies that light and a catalyst are necessary to bring about or to accelerate chemical transformations<sup>1</sup>.

### **1.3 Photocatalytic Processes**

Organic chemicals which may be found as pollutants in wastewater effluents from industrial or domestic sources must be removed or destroyed before discharge to the environment. Such pollutants may also be found in ground and surface water, which also require treatment to achieve acceptable drinking water quality<sup>2</sup>. The increasing public concern with these environmental pollutants has prompted the need to develop novel treatment methods, in which photocatalysis is gaining considerable attention in the field of pollutants degradation<sup>3</sup>. The utilization of colloidal semiconductors and the introduction of catalysts to promote specific redox processes on semiconductor surfaces were developed in the last two decades<sup>4</sup>. Since the discovery of the photosensitization effect of TiO<sub>2</sub> electrodes on the electrolysis of water into H<sub>2</sub> and O<sub>2</sub> by Fujishima and Honda<sup>5</sup>, photocatalysis by semiconducting TiO<sub>2</sub> has been widely studied with the aim of efficiently converting light energy into reliable and effective chemical energy<sup>6-13</sup>. Laboratory studies have confirmed that naturally occurring semiconductors could enhance this solar driven purification process<sup>14</sup>.

Photocatalytic detoxification of wastewater is a process that combines heterogeneous catalyst and solar energy<sup>15</sup>. Semiconductor photocatalysis, with a primary focus on TiO<sub>2</sub>, has been applied to a variety of problems of environmental interest in addition to water and air purification. The application of illuminated semiconductors for degrading undesirable organics dissolved in air or water is well documented and has been successful for a wide variety of compounds<sup>16</sup>. Organic compounds such as alcohols, carboxylic acids, amines, herbicides and aldehydes have been

photocatalytically destroyed in laboratory and field studies. The photocatalytic processes can mineralize the hazardous organic chemicals to carbon dioxide, water and simple mineral acids<sup>17</sup>.

Current treatment methods such as adsorption and air stripping are merely transferring these contaminants into non-toxic wastes. Thus one of the major advantages of photocatalytic process over existing technologies is that there is no further requirement for secondary disposal methods. Another advantage of this process is that when compared to other advanced oxidation technologies especially those using oxidants such as hydrogen peroxide and ozone, expensive oxidizing chemicals are not required as ambient oxygen is the oxidant<sup>17</sup>. Photocatalysts are also self-regenerated and can be reused or recycled. Finally, the solar photocatalytic process can also be applied to destroy nuisance odour, taste and odour compounds and naturally occurring organic matter which contain precursors for trihalomethanes formed during chlorine disinfection step in drinking water treatment<sup>18</sup>.

#### 1.4 Mechanism of Photocatalysis

During the photocatalytic process, the illumination of a semiconductor photocatalyst with ultraviolet (UV) radiation activates the catalyst, establishing a redox environment in the aqueous solution<sup>15</sup>. Semiconductors act as sensitizers for light induced redox processes due to their electronic structure, which is characterized by a filled valence band (VB) and an empty conduction band (CB)<sup>16</sup>. The energy difference between the valence and conduction bands is called the band gap. The semiconductor photocatalyst absorbs photons with energies equal to or higher than its band gap or threshold energy. Each photon of requisite energy (i.e. wavelength) that hits an electron in the occupied valence band of the semiconductor atom can elevate that electron to the unoccupied conduction band leading to excited state conduction band electrons and positive valence band holes<sup>19</sup>. The fate of these charge carriers may take different paths (Fig.1). Firstly, they can get trapped either in shallow traps (ST) or in deep traps (DT). Secondly, they can recombine non-radiatively or radiatively, dissipating the input energy as heat. Finally, they can react with electron donors or acceptors adsorbed on the surface of the photocatalyst<sup>16</sup>. In fact, it was recently shown that any photo-redox chemistry occurring at the particle surface emanates from trapped electrons and trapped holes rather than from free valence band holes and conduction band electrons<sup>20</sup>.

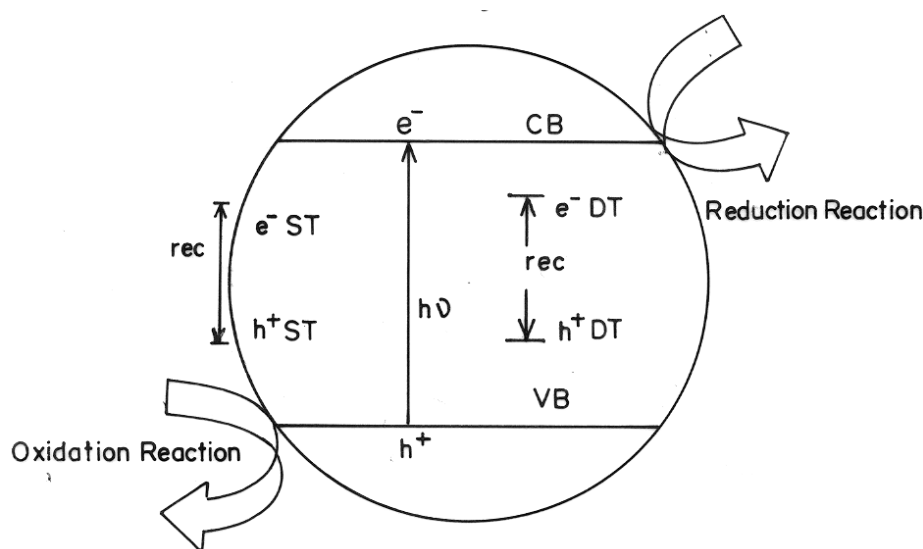


Fig.1: The process involved in semiconductor particles upon bandgap excitation

#### 1.5 Semiconductors as Photocatalysts

Semiconductors (e.g.  $\text{TiO}_2$ ,  $\text{ZnO}$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{WO}_3$ ,  $\text{SnO}_2$ ,  $\text{ZrO}_2$ ,  $\text{CdS}$  and  $\text{ZnS}$ ) can act as sensitizers for light-induced redox process due to their electronic structure which is characterized by a filled valence band and an empty conduction band<sup>21</sup>. Absorption of a photon with an energy greater than the band gap energy leads to the formation of an electron-hole pair. In the absence of

suitable scavengers, the stored energy is dissipated within a few nanoseconds by recombination<sup>22</sup>. If a suitable scavenger is available to trap the electron or hole, recombination is prevented and subsequent redox reactions may occur. The valence band holes are powerful oxidants (+1.0 to +3.5 V vs normal hydrogen electrode (NHE) depending on the semiconductor and pH) while the conduction band electrons are good reductants<sup>23</sup> (+0.5 to -1.5 V vs NHE). Most organic photodegradation reactions utilize the oxidizing power of the holes either directly or indirectly. In bulk semiconductor electrodes, only one species, either the hole or electron, is available for reaction due to band bending<sup>24</sup>. However in very small semiconductor particle suspensions both species are present on the surface. Hence both oxidative and reductive pathways are possible in semiconductor particle suspensions.

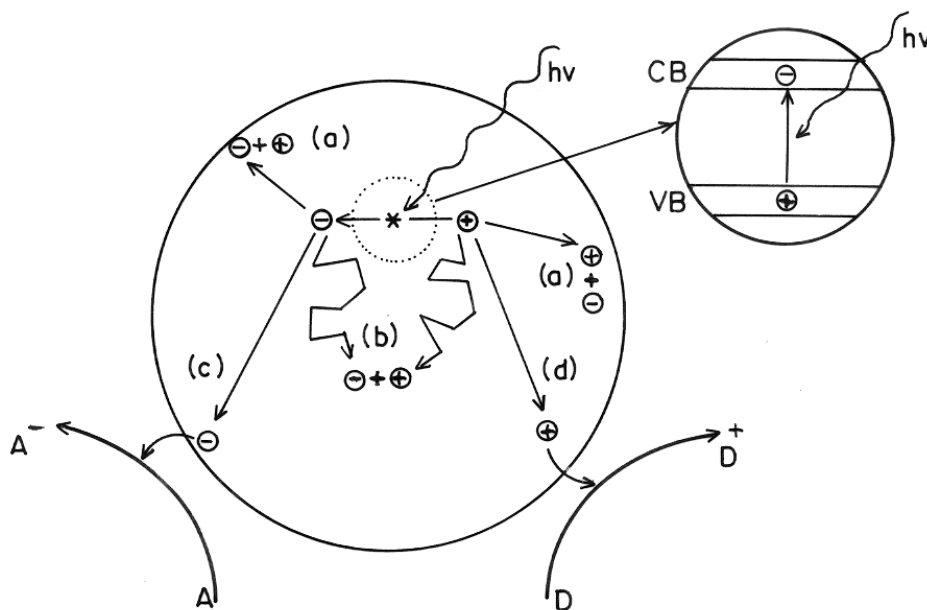
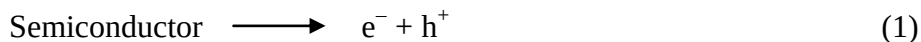


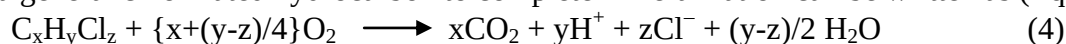
Fig.2: Illustration of major processes occurring on a semiconductor particle following the electron excitation (Electron-hole recombination can occur on the surface [reaction (a)] or in the bulk [reaction (b)] of the semiconductor. At the surface of the particle, photogenerated electrons can reduce an electron acceptor A [reaction (c)] and photogenerated holes can oxidise an electron donor D [reaction (d)]. The combination of reactions (c) and (d) represents the semiconductor sensitisation of the general redox reaction<sup>22</sup>.

Fig. 2 illustrates the typical photocatalytic process<sup>22</sup>. It consists of a superposition of the energy bands of semiconductors and the geometrical image of a spherical particle. Photoexcitation with light of energy greater than the band gap energy ( $E_g$ ) promotes an electron from the valence band to the conduction band, thus creating an electronic vacancy or hole ( $h^+$ ) at the valence band edge. The hole can also be identified as a chemical entity. This hole can initiate further interfacial electron transfer or other chemical reactions to an adsorbate, or with surface-bound  $OH^-$  ions can itself diffuse into the bulk solvent. The photo-generated electron ( $e^-$ ) is usually in the conduction band edge and the hole in the valence band edge. The catalyst deactivation by electron-hole recombination may be difficult, if there is mismatch of energies of the electron and hole. Unlike metals, semiconductors lack a continuum of interband states to assist the recombination of electron-hole pairs. This assures an electron-hole pair lifetime sufficiently long enough to allow these species to participate in interfacial electron transfer<sup>25</sup>. Thus, the act of photo-excitation usually generates an electron-hole pair poised respectively at the conduction band and valence band edges (Equation 1). The components of this activated pair, when transferred across the interface, are capable of reducing and oxidizing a surface-absorbed substrate, forming on a common surface a singly oxidized electron donor (D) and singly oxidized electron acceptor (A) (Equations 2 and 3).



If a photogenerated hole reaches the surface of the semiconductor, it can react with an adsorbed substrate by interfacial electron transfer, assuming that the adsorbate possesses a redox potential appropriate for a thermodynamically allowed reaction. Thus, an adsorbed electron donor can be oxidized by transferring an electron to a photogenerated hole on the surface, and an adsorbed acceptor can be reduced by accepting an electron from the surface. Hole trapping generates a cation radical,  $[D^{\bullet}]^{+}$  (Equation 2) and electron trapping generates an anion radical,  $[A^{\bullet}]^{-}$  (Equation 3). These radical ions can participate in several pathways. They may react chemically with themselves or other adsorbates. They may recombine by back electron transfer to waste the excitation energy through a non-radiative pathway. They may also diffuse from the semiconductor surface and participate in chemical reactions in the bulk solution<sup>12</sup>.

The photocatalysis is chemically productive when the electron-hole pair recombination is suppressed. This can be accomplished by trapping either the photogenerated electron or the photogenerated hole or both. The general stoichiometric-heterogeneously-photocatalysed oxidation of a general chlorinated hydrocarbon to complete mineralization can be written as (Equation 4).



The exact nature of the main oxidizing species formed on the surface of the semiconductor particles following the absorption of a photon is as yet unclear. However, literature studies reveal that the initial oxidation of a pollutant molecule may occur either by indirect oxidation via a surface-bound hydroxyl radical (i.e. a trapped hole at the particle surface) or directly via the valence band hole before it is trapped either within the particle or at the particle surface. In support of the hydroxyl radical being the principal reactive oxidant in photocatalysis, the intermediates detected during photocatalytic degradation of halogenated aromatic compounds are typically of a hydroxylated nature<sup>26-28</sup>. These intermediates are consistent with those found when similar aromatics are reacted with a known source of hydroxyl radicals. In addition, ESR studies have verified the existence of hydroxyl and hydroperoxyl radical in aqueous solutions of illuminated  $TiO_2$ <sup>29</sup>. Over the years, the field of photo-induced electron transfer reactions in heterogeneous systems has witnessed a number of new discoveries, particularly the use of semiconductor particles as photocatalysts in the degradation of organic hazardous pollutants in an aqueous environment.

The particulate semiconductor photocatalysts have several interesting features. Each photocatalyst functions as a micro photoelectrode or as photochemical diode for a metal loaded semiconductor particle. They possess large surface area which is advantageous for surface reactions. Their low cost and ease of fabrication make them attractive in several practical applications. The band gap energy of  $TiO_2$  is large ( $>3.0$  eV) thus it becomes a good photocatalyst despite its poor catalytic activity towards electron transfer reactions. The large band gap semiconductors prove to be better photocatalysts than low band gap materials<sup>30</sup>. These principles have found extensive applications in the field of environmental chemistry and pollution control<sup>31</sup>. Considerable attention has been focused on the photocatalytic mineralization of toxic chemicals present in wastewater. Several reviews have recently been published discussing the underlying reaction mechanisms and illustrative examples<sup>12,16,32-38</sup>.

### 1.6 Type of Semiconductors

The energy level of the lower edge of the conduction band of a semiconductor can be considered to be a measure of the reducing power of photo-excited electrons whereas the upper edge of valence band is a measure of oxidation strength of the holes. Band energies of various semiconductors versus the electrochemical potential of hydrogen and oxygen are depicted in Fig.3.

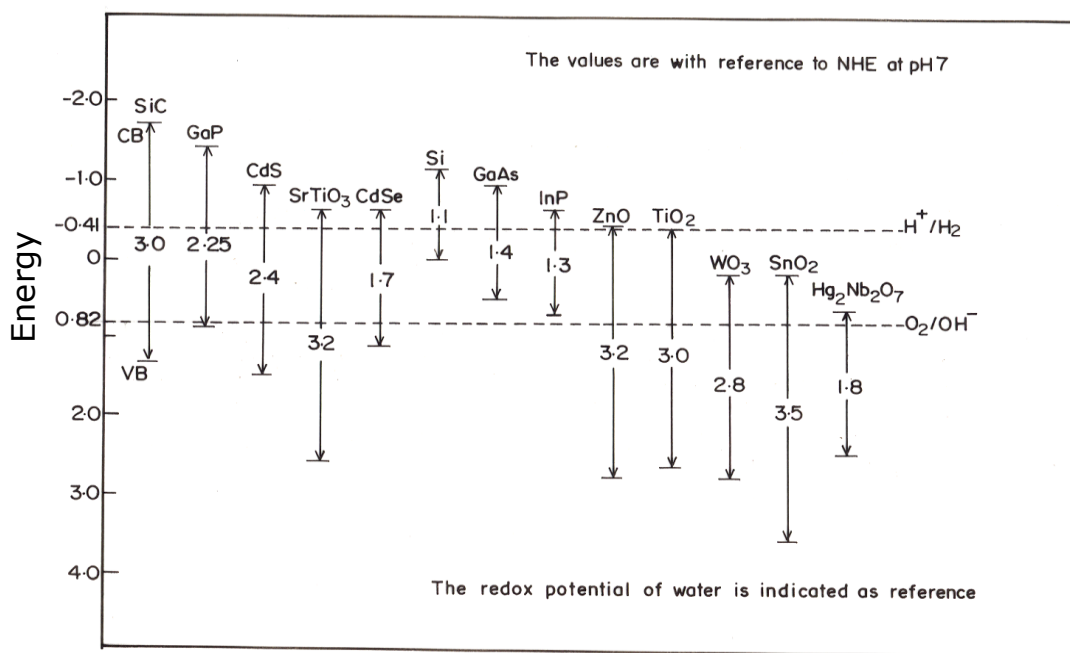


Fig. 3: Bandgap energies of various semiconductors (summarized from M.Fujii, T. Kawai, S. Kawai, Chem. Phys. Lett., 106 (1984) 83-98)

An ideal photocatalyst should be stable, inexpensive, non-toxic and of course highly photoactive. Another primary criteria for the degradation of organic compounds is that the redox potential of  $\text{H}_2\text{O}/\cdot\text{OH}$  couple ( $\text{OH}^- \rightarrow \cdot\text{OH} + e^-$ ,  $E^0 = -2.8 \text{ V}$ ) lies within the band gap of the semiconductor<sup>16</sup>. Several semiconductors have band gap energies sufficient for catalyzing a wide range of chemical reactions. These include  $\text{TiO}_2$ ,  $\text{ZnO}$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{WO}_3$ ,  $\text{SnO}_2$ ,  $\text{ZrO}_2$ ,  $\text{CdS}$ ,  $\text{SrTiO}_3$  and  $\text{ZnS}$ .

Titania, the most thoroughly investigated semiconductor in the literature, seems to be the most promising for photocatalytic destruction of organic pollutants<sup>39</sup>. This semiconductor provides the best compromise between catalytic performance and stability in aqueous media<sup>40</sup>. The anatase phase of titanium dioxide is the material with high photocatalytic detoxification<sup>41</sup>.  $\text{ZnO}$  as a photocatalyst has received much attention due to its low cost and its high photoactivity in several photo-chemical and photo-electro-chemical process<sup>42-44</sup>. The biggest advantage of  $\text{ZnO}$  is that it absorbs a large fraction of solar spectrum<sup>45</sup> and possesses greater quantum efficiency<sup>46</sup> than  $\text{TiO}_2$ . The low cost is another important advantage of  $\text{ZnO}$ . Binary metal sulphide semiconductors such as  $\text{CdS}$ ,  $\text{CdSe}$  or  $\text{PbS}$  are regarded as insufficiently stable for catalysis, at least in aqueous media as they readily undergo photoanodic corrosion<sup>39,47</sup>. These materials are also known to be toxic. The iron oxides are not suitable semiconductors as they readily undergo photo-cathodic corrosion<sup>16</sup>.

## 2. CATALYST MODIFICATION

Among the various semiconductors employed,  $\text{TiO}_2$  and  $\text{ZnO}$  are known to be good photocatalysts for the degradation of several environmental contaminants due to their high photosensitivity and large band gap. Despite the positive attributes of these photocatalysts, there are some drawbacks associated with their use: (i) charge carrier recombination occurs within nano seconds<sup>22,32</sup> and (ii) the band edge absorption threshold does not allow the utilization of visible light<sup>48</sup>. To circumvent these limitations, a number of strategies have been proposed to improve the light absorption features and lengthen the carrier life time characteristics of the catalyst. The long wavelength absorption can be achieved by dye sensitization<sup>49</sup>, external surface modification<sup>50</sup> or band gap tailoring.



Dye sensitization of  $\text{TiO}_2$  with a number of organic dyes extends the sensitivity of  $\text{TiO}_2$  into the visible region by the injection of electrons from an excited level of the dye into the semiconductor conduction band. Bandgap tailoring by doping is the most efficient and frequently used approach. Doping, with certain limits, serves to prolong the lifetime of charge carriers if the dopants have energy levels just below the conduction band or just above the valence band of  $\text{TiO}_2$  to realize shallow charge carrier trapping. Bandgap narrowing also becomes possible if the electronic coupling effect between dopant and semiconductor is strong enough to change the band structure. The band gap narrowing can cause a small reduction of the photo-redox potential energy of  $\text{TiO}_2$  but the increased photon absorption efficiency or generation rate of charge carriers can compensate for this negative effect and largely enhance the overall photo-reactivity as long as the redox potential of  $\text{H}_2\text{O}/\bullet\text{OH}$  couple ( $\sim -2.8$  V) lies within the band gap. Doping with various metal and non-metal ions has been attempted to improve the photocatalytic activity and optical absorption of  $\text{TiO}_2$ . Another main approach to increase the efficiency of charge separation involves the coupling of semiconductor particles with another semiconductor. The quantum yield of  $\text{TiO}_2$  and  $\text{ZnO}$  will increase by supporting the photocatalyst on an adsorbent like zeolites. A few examples are given in the following sections to illustrate the large body of work conducted in photocatalytic modifications.

## 2.1 Metal Ion Dopants

Deposition or incorporation of metal ion dopants into titanium dioxide particles can influence the performance of these photocatalysts. This affects the dynamics of electron-hole recombination and interfacial charge transfer. The largest enhancement of photoactivity through doping was found in nanosized particles, in which the dopant ions are located within 1-2 nm of the surface<sup>51</sup>. The high surface area characteristic of nanoparticles ( $100\text{--}500\text{ m}^2/\text{g}$ ) also appears to enhance the deposition process and resulting activity of the catalyst<sup>52</sup>.

The work of Choi et al<sup>51</sup> involved a systematic study of the effects of 21 different metal ion dopants on nanocrystalline  $\text{TiO}_2$ . Chloroform oxidation and carbon tetrachloride reduction were used as photo-reactivity tests. Their results showed that some doped quantum sized- $\text{TiO}_2$  particles had much greater photoactivity than their undoped counterparts. Doping with Fe (III), Mo(V), Ru(III), Os(III), Re(V), V(IV), and Rh (III) at 0.5 wt% level in the  $\text{TiO}_2$  matrix significantly improved the photo-reactivity for both oxidation and reduction.

Choi et al<sup>51</sup> used laser flash photolysis and time-resolved microwave conductivity measurements to correlate the effects of metal ion dopants and life time of the photo-excited electron. In the case of Fe(III), V(IV), Mo(V) and Ru(III) doped samples, the lifetime of the generated electron was found to increase to 50 ms compared to  $< 200\text{ }\mu\text{s}$  with undoped quantum sized - $\text{TiO}_2$ . There was also an apparent linear correlation between the oxidation quantum yield (of chloroform) and the reduction quantum yield (of carbon tetrachloride) regardless of the nature of the dopant. Ion doping of large band gap semiconductor colloids might not always be effective in lengthening the lifetime of photo-generated charge carriers. Recently, Smith et al<sup>53</sup> showed that in Ru(III) doped  $\text{TiO}_2$  colloids, the electronic decay was as fast as or even faster than undoped  $\text{TiO}_2$ . The difference between the studies carried out by Smith et al<sup>53</sup> and those carried out by Choi et al<sup>51</sup> was the higher dopant level of Ru(III) of 3 wt% used by Smith et al<sup>53</sup> compared to 0.5 wt% dopant level used by Choi et al<sup>51</sup>.

There could be several reasons for variations in the reported effects of dopant ions. One reason for these variations is the location and co-ordination of the dopant ions. These depend critically on the methods of sample preparation and pre-treatment as well as concentration of the dopant ions. The dopant ions may be adsorbed on the surface or they may be incorporated into the interior of the particle on firing or they may form separate oxide phases<sup>39</sup>. The dopant ions can function as both hole and electron traps or they can mediate interfacial charge transfer<sup>51</sup>. Once incorporated into the interior of  $\text{TiO}_2$ , the dopant ions may occupy either lattice (substitutional) or interstitial sites. Their ability to function as trap sites and/or to mediate interfacial charge transfer will depend on these factors<sup>39</sup>.

When the dopant is incorporated in the interior of the particles, the d-electronic configuration of the dopant and its energy level within the  $\text{TiO}_2$  lattice also seem to influence the photoactivity significantly<sup>54</sup>. Finally, the site where the electron gets trapped greatly influences the

redox chemistry of doped semiconductors. A dopant ion might act as an electron trap and this might lead to a lengthening of the lifetime of the generated charge carriers, resulting enhanced in photoactivity. However if an electron is trapped in a deep trapping site, it will have a longer lifetime, but it may also have a low redox potential. This may result in a decrease in the photo-reactivity<sup>16</sup>.

In our earlier studies<sup>55-57</sup>, a series of La-doped ZnO with different La loadings were prepared and unambiguously characterized by various techniques. The XRD and UV-Vis results revealed that the particle size of La-doped ZnO is much smaller as compared to that of pure ZnO and decreases with increasing La loading. HRSEM image of ZnO<sup>56</sup> nanoparticles illustrates that the morphology is well ordered and the size of the particles are in the range 100 -500 nm, suggesting a wide range of band gap values in the ZnO crystals. The HRSEM image of La-doped ZnO<sup>56</sup> demonstrates that lanthanum oxide clusters are formed on the clear smooth surface of ZnO and show aggregations. The photocatalytic activity of La-doped ZnO for the degradation of monocrotophos (MCP) was studied and the results are compared with ZnO and TiO<sub>2</sub>. It was observed that the rate of degradation of MCP over La-doped ZnO showed higher value compared to pure ZnO and TiO<sub>2</sub>. The total organic carbon (TOC) results demonstrated that La-doped ZnO requires shorter irradiation time for the complete mineralization of MCP than pure ZnO for the light of wavelengths 254 nm and 365 nm<sup>56</sup>. The relative photonic efficiencies and the photocatalytic activity of the 0.8 wt% La-doped ZnO are much higher as compared to those of pure ZnO and TiO<sub>2</sub>. The plot of experimentally and theoretically derived values of (MCP<sub>t</sub>) / (MCP<sub>0</sub>) versus time for ZnO and La-doped ZnO catalysts are calculated. The experimentally derived points are exactly coinciding with the theoretical curve illustrating that the reaction follows first-order kinetics. It has been concluded that higher adsorption capacity, smaller particle size, and increase in the band gap value of ZnO upon La loading have a significant influence on the enhanced photocatalytic activity of La-doped ZnO catalysts.

The work carried out by Zhang et al<sup>58</sup> shed a new light on the role of dopant ions and their effect on photoactivity. Firstly, these authors provided further support for the existence of an optimum dopant concentration. Their main finding however that was this optimum concentration is particle- size dependent and decreases with an increasing in size. The system they studied was Fe<sup>3+</sup> doped TiO<sub>2</sub> for the photocatalytic degradation of CHCl<sub>3</sub>. They observed that for 6 nm particles, the optimum Fe<sup>3+</sup> concentration was 0.2 wt% while for 11 nm particles the optimum concentration was 0.05 wt%. They provided the following explanation for their observations. Their first explanation was with regard to the existence of an optimal Fe<sup>3+</sup> dopant concentration. Fe<sup>3+</sup> ions serve as shallow trapping sites for the charge carriers and increase the photocatalytic efficiency by separating the arrival time of e<sup>-</sup> and h<sup>+</sup> at the surface. If Fe<sup>3+</sup> can act as a trap for both e<sup>-</sup> and h<sup>+</sup> at high dopant concentrations, the possibility of charge trapping is high, and as such the charge carriers may recombine through quantum tunneling. If Fe<sup>3+</sup> acts as a h<sup>+</sup> trap only, the recombination of the charge carriers is not of great concern at low dopant concentrations. At high concentrations, however, h<sup>+</sup> may be trapped more than once as it tries to make its way to the surface. This hole which had been 'held back' might then recombine with an electron which is generated by a subsequent photon before it can reach the surface. Thus there exists an optimum Fe<sup>3+</sup> concentration whether the Fe<sup>3+</sup> acts as an e<sup>-</sup> and h<sup>+</sup> traps or as h<sup>+</sup> trap only. With regard to the optimum concentration depending on the particle size, Zhang et al<sup>58</sup> suggested that when the particle size becomes larger, the average path length of a charge carrier to the surface is longer. Thus, for a constant dopant concentration, the longer the path length in which the charge carrier needs to travel, higher the probability of meeting a dopant ion, and hence greater the chance of multiple trappings. This multiple trapping leads to increased volume recombination. A low dopant concentration reduces the chance of multiple trappings for a large particle. Thus the optimal Fe<sup>3+</sup> dopant concentration should decrease with increasing TiO<sub>2</sub> particle size.

## 2.2 Supported Photocatalysts

The photocatalytic efficiency of TiO<sub>2</sub> is greatly influenced by crystal structure, particle size, surface area and porosity. Since the concentration of pollutants to be decomposed is in ppm level or less in many cases, their low frequent collision with TiO<sub>2</sub> photocatalyst makes the reaction rate of

mineralization very low. Some of the limitations of titania are its poor adsorption of the pollutant and recombination of electron-hole pairs. These can be overcome by using titania/zeolite supported photocatalyst. Combining the photocatalytic activity of  $\text{TiO}_2$  with the utility of zeolites as supports for degradation of pollutants, there has been only limited reports in the literature<sup>59</sup>.

The merits of  $\text{TiO}_2$ /zeolite photocatalysts are (i) the adsorbent support makes a high concentration environment of the pollutants around the loaded  $\text{TiO}_2$  by adsorption and hence the rate of photo-oxidation is enhanced appreciably, (ii) the pollutants are oxidized on the photocatalytic surface with adsorbed states and the resulting intermediates are also adsorbed and then further oxidized. Toxic intermediates, if formed, are not released in the air, atmosphere and/or in the solution phase and thereby preventing secondary pollution, (iii) since the adsorbed pollutants in the adsorbent support are oxidized completely to give  $\text{CO}_2$ , the catalytic activity is restored for a long time and (iv) electric field present in the zeolite is capable of accepting electrons, thus avoiding electron-hole recombination, making the holes available to oxidation reactions for longer time.

Xu and Langford<sup>60</sup> studied the photocatalytic activity of  $\text{TiO}_2$  supported on different zeolites for the oxidation of 4-chlorophenol and acetophenone in aqueous solution. The results revealed the highest photoactivity at low titania content of  $< 2\%$  due to the large adsorption of pollutants. Torimoto et al<sup>61</sup> studied the effect of adsorbent as a support for  $\text{TiO}_2$  loading on the photocatalytic degradation of propylamide. The use of adsorbent supports such as zeolites, silica and activated carbon was found to enhance the rate of mineralisation of propylamide due to adsorption of the pollutant in the vicinity of the  $\text{TiO}_2$ . The intermediates were also retained on the adsorbent support and subsequently decomposed, thereby reducing the concentration of possibly toxic intermediates in the bulk solution. Xu and Langford<sup>62</sup> found that the support with low Si/Al ratio in the zeolite framework and large pore size shows the highest photoactivity among the supported catalysts. Takeda et al<sup>63</sup> studied the photodecomposition of propionaldehyde on  $\text{TiO}_2$  loaded adsorbent (zeolites, silica, alumina and activated carbon). They observed that supports having moderate adsorbability forms fairly high concentration environments of the adsorbate around the loaded  $\text{TiO}_2$  and allows a fairly easy supply from the support to the loaded  $\text{TiO}_2$ .

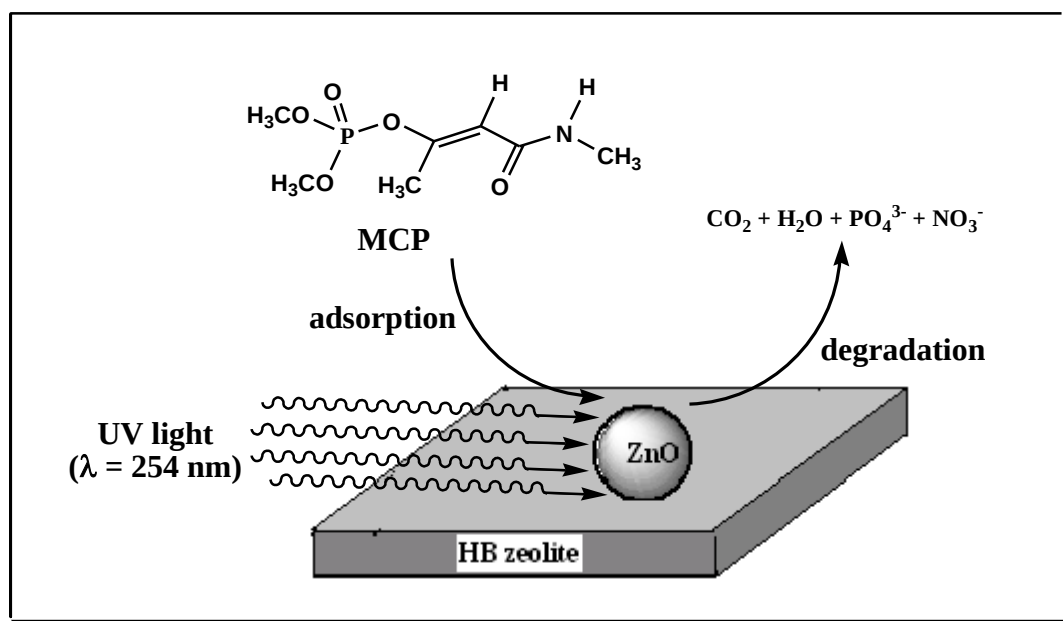


Fig.4: The photocatalytic degradation of MCP in aqueous solution using ZnO and zeolite supported ZnO

Recently we studied<sup>64-66</sup>, the photocatalytic degradation of monocrotophos (MCP) acid in aqueous solution using zeolite supported semiconductors<sup>64</sup> (Fig. 4) using low pressure mercury

lamps. The rate of degradation over pure  $\text{TiO}_2/\text{ZnO}$  and  $\text{TiO}_2/\text{ZnO}$  supported catalysts revealed that neither the support nor the catalyst alone exhibits any influence independently, but there is a mutual synergistic influence on the degradation of MCP. The higher activity of supported  $\text{TiO}_2/\text{ZnO}$  is due to improved adsorption of MCP and the efficient delocalization of photo-generated electrons by the zeolite  $\text{H}\beta$  support. The photocatalytic activity of  $\text{ZnO}$  in the oxidative degradation of MCP can be enhanced with zeolite support by the following pathways. In  $\text{ZnO}$  impregnated  $\text{H}\beta$ , the excited electron is delocalised over the zeolite and hence the electron-hole separation is enhanced as shown in Equations 5 to 8. Thus  $\text{H}\beta$  zeolite assists the availability of the hole for a long time during the oxidative degradation of MCP. Hence the presence of zeolite favors delocalization

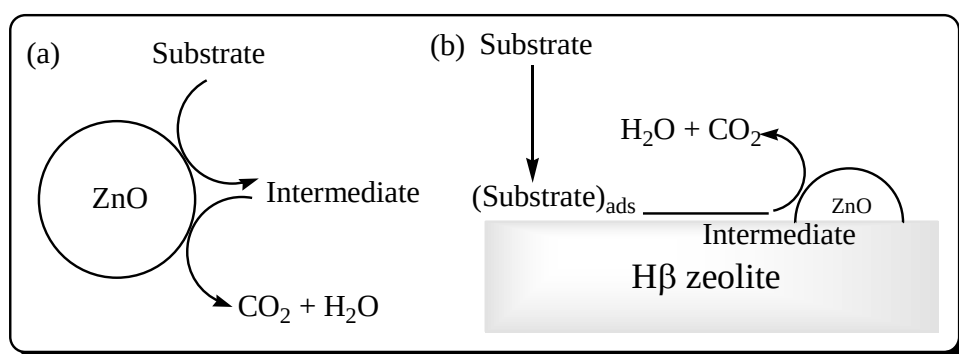
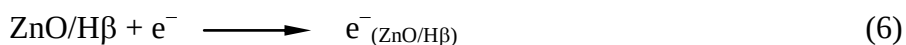


Fig.5a: Plausible photocatalytic mineralisation of MCP over  $\text{ZnO}$  and  $\text{ZnO}/\text{H}\beta$

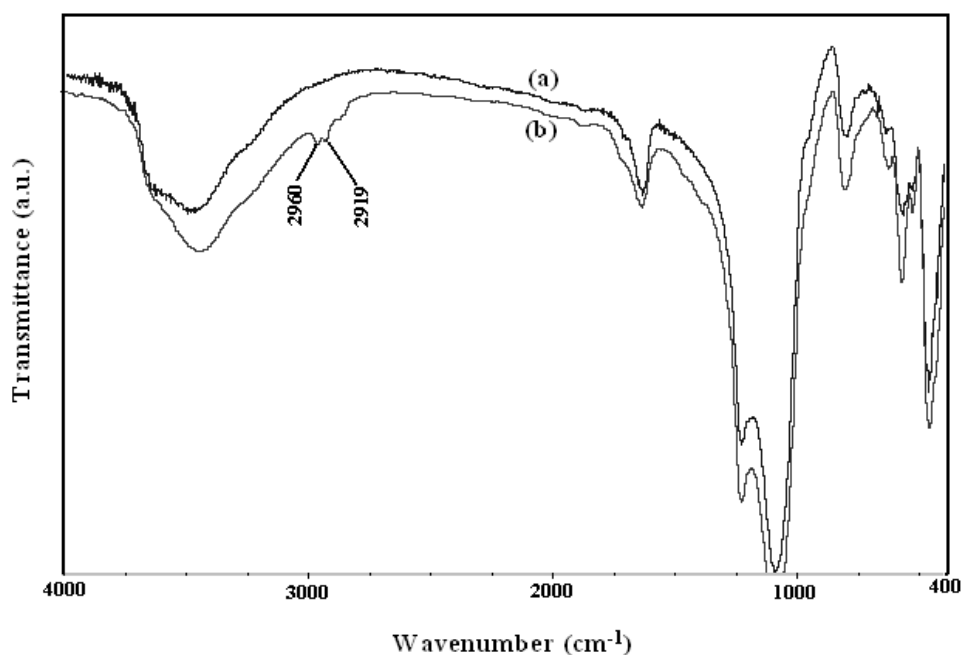


Fig.5b: FT-IR spectra of  $\text{ZnO}/\text{H}\beta$  catalyst (a) before and (b) during photocatalytic degradation of MCP

of photo-produced electrons, thus improving the electron-hole separation. In addition to this role for zeolites, the plausible photocatalytic reaction on the surface of zeolites may be visualized as shown in Fig. 5a. From the figure, it is observed that when ZnO alone is used, reaction intermediates are mostly dissolved in the solution phase whereas a large fraction of intermediates are adsorbed on the support when ZnO/H $\beta$  is used. It is concluded that the adsorbent (zeolite support) has high capability of collection of degradation intermediates as well as the target substrate from the solution phase, thereby preventing dissolution of toxic substances in the solution. In contrast, the use of ZnO alone allows the dissolution of intermediates in the solution due to low absorbability. The dissolved MCP and intermediates are further oxidized to give a variety of other intermediates when they collide with ZnO. The experimental results demonstrate that ZnO needs longer time than the supported ZnO in achieving complete mineralization of MCP. Therefore in the supported system, the support H $\beta$  might help in transporting MCP and its intermediates rapidly towards the ZnO surface as depicted in Fig. 5a. In order to establish the reaction sequence, FT-IR analysis of ZnO supported H $\beta$  during photocatalytic degradation was carried out and the spectrum is shown in Fig. 5b. The spectrum of the parent ZnO/H $\beta$  is also given in the same figure for comparison. There is significant difference between the two spectra. The spectrum of the catalyst obtained during irradiation shows peaks just below 3000 cm<sup>-1</sup> which are characteristics for the adsorbed MCP and its fragments. Thus during photocatalysis, the support is established to adsorb MCP and its fragments in order to transport the same to ZnO.

### 2.3 Dual Semiconductor Systems

The other approach to modify the surface of semiconductor in order to improve charge separation and minimize or inhibit charge-carrier recombination is the use of coupled semiconductors. Excitation of dual semiconductors results in an electron injection into the lower lying conduction band of the second semiconductor. In the composite nanoparticles, electric field is not necessary as the charge separation is achieved by the tunneling of electrons<sup>67</sup>. Recent studies indicate that the inter-particle electron transfer occurs within 500 fs-2ps<sup>68</sup>.

Henglein<sup>69</sup> presented the first example of composite particles when he found that the small amount of Cd<sup>2+</sup> was added to ZnS, resulted in the band gap fluorescence of ZnS being quenched<sup>69</sup>. Since then there have been many papers published relating the optical properties of mixed systems. Some of the systems include ZnS-CdS<sup>70</sup>, CdS-Ag<sub>2</sub>S<sup>71</sup>, CdS-Ag<sub>2</sub>S<sup>72</sup>, mixed crystals of Zn<sub>x</sub>Cd<sub>1-x</sub>S, CdS-ZnS<sup>73</sup>, AgI – Ag<sub>2</sub>S<sup>74</sup>, ZnS-CdSe<sup>75</sup> and CdS-PbS systems<sup>76</sup>.

Reber and Rusek<sup>77</sup> reported that modifying the surface of platinized CdS powders with silver ions could activate these photocatalysts, which are otherwise inactive with respect to H<sub>2</sub> formation. The activation was attributed to the formation of a heterojunction between CdS and Ag<sub>2</sub>S. It was also observed that the fluorescence of CdS was quenched by Ag<sup>+</sup> ions and the spectral response for H<sub>2</sub> formation was extended to wavelengths upto ~ 600 nm where CdS itself does not absorb. Recently, emphasis has been placed on the development of coupled and capped semiconductor systems and their application in photocatalysis. Many papers have been published on coupled semiconductor systems. These include CdS-TiO<sub>2</sub>, CdS-ZnO<sup>78</sup>, CdS-Ag<sub>2</sub>S<sup>72</sup>, ZnO-ZnS<sup>79</sup>, ZnO-ZnSe<sup>80</sup> and AgI-Ag<sub>2</sub>S<sup>74</sup>.

The charge separation mechanism in both capped semiconductor systems and coupled semiconductor systems involves the photogenerated electrons in one semiconductor being injected into the lower lying conduction band of the second semiconductor. However, the interfacial charge transfer is significantly different<sup>81</sup>. The charge-transfer processes involved in coupled and capped semiconductor systems are shown in Figs. 6a and 6b respectively<sup>81,82</sup>. In a coupled semiconductor system the two particles are in contact with each other and both holes and electrons are accessible on the surface for selective oxidation and reduction processes. Capped semiconductors on the other hand have a core and shell geometry. The electron gets injected into the energy levels of the core semiconductor (provided it has a conduction band potential which is lower than that of the shell). Hence the electron gets trapped within the core particle and it is not readily accessible for the reduction reaction. Bedja and Kamat<sup>81</sup> synthesized TiO<sub>2</sub> - capped SnO<sub>2</sub> (SnO<sub>2</sub> at TiO<sub>2</sub>) and TiO<sub>2</sub> -capped SiO<sub>2</sub> (SiO<sub>2</sub> at TiO<sub>2</sub>) nanocrystallites. The photocatalytic properties of the capped semiconductor systems

were tested for the oxidation of  $\text{I}^-$  and  $\text{SCN}^-$ . The  $\text{SnO}_2$  at  $\text{TiO}_2$  colloids were 8-10 nm in diameter and exhibited improved photocatalytic efficiency compared to the uncapped  $\text{TiO}_2$  colloid. The quantum efficiency for  $\text{I}^-$  oxidation was improved by a factor of two to three times upon capping  $\text{SnO}_2$  colloids with  $\text{TiO}_2$ . The improved charge separation in  $\text{SnO}_2$  at  $\text{TiO}_2$  system was confirmed by laser flash photolysis experiments. The photocatalytic properties of  $\text{SiO}_2$  at  $\text{TiO}_2$  colloids were found to be similar to those of uncapped  $\text{TiO}_2$  colloids<sup>81</sup>. Similar work was carried out in the development of two novel photocatalysts. The first photocatalyst is  $\alpha\text{-Fe}_2\text{O}_3$  at  $\text{TiO}_2$  with the aim to expand the catalysts photoresponse into the visible region of the solar spectrum<sup>83</sup>. The second is  $\text{Fe}_3\text{O}_4$  at  $\text{TiO}_2$  with an aim to enhance the catalysts separation properties from the treated water by imparting magnetic properties onto the photocatalyst<sup>84</sup>.

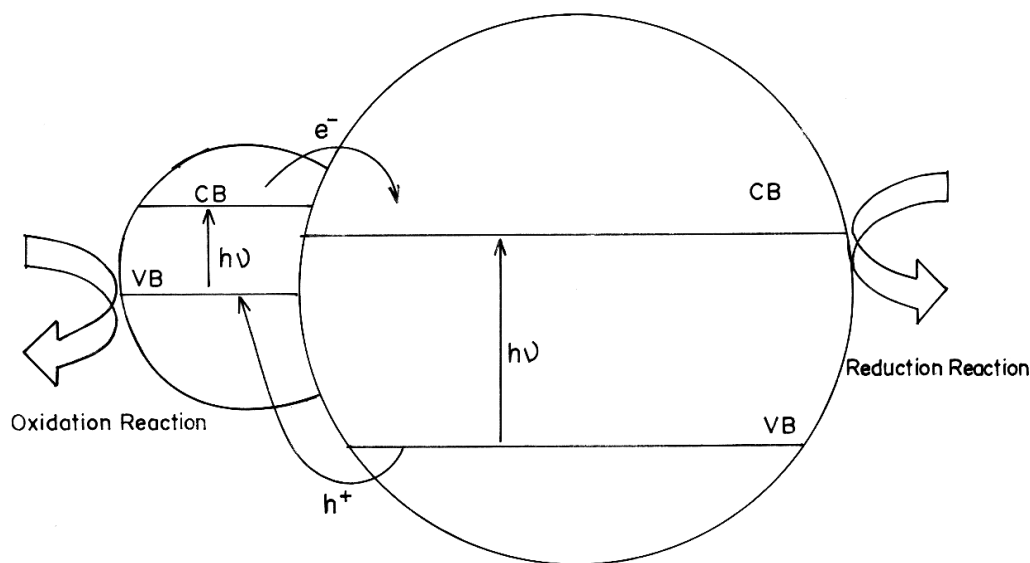


Fig.6a: Charge transfer in coupled semiconductor system

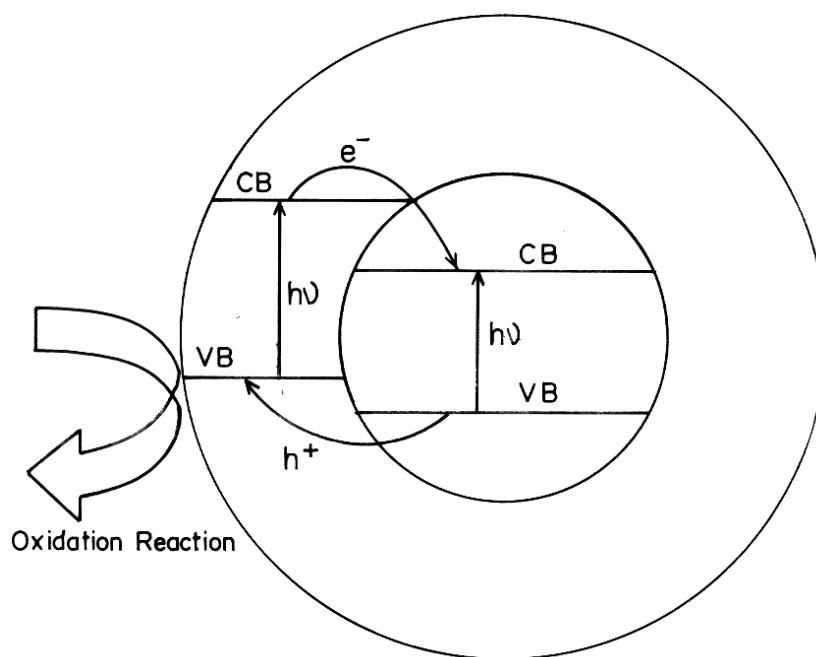


Fig.6b: Charge transfer in capped semiconductor system (Bedja I. and Kamat P.V. *J. Phys. Chem.*, 99 (1995) 9182-9188)

The development of heterogeneous semiconductors system is very promising and has the potential to contribute significantly to the area of photocatalysis. By changing certain parameters such as the thickness of the shell or the particle radius of the core, this approach may allow the tailoring of important properties such as photocatalytic, optical and magnetic properties of the photocatalyst. It may also be important to address problems such as photo-dissolution, which might otherwise occur in an 'unprotected' photocatalysts such as iron oxide<sup>16</sup>.

In a capped system, if the thickness of the deposited shell is sufficiently thick, relative to the core radius, the individual identity of the two semiconductors can be maintained<sup>81</sup>. In these systems, the holes are only accessible at the surface of the photocatalyst. This allows for selective interfacial charge transfer and improves the efficiencies of the oxidation reactions. However, one disadvantage of this approach is the fact that the reducing charge carriers (the electrons) are not utilized during the photocatalytic reaction since they are being accumulated within the core semiconductor. Therefore these photocatalysts cannot be used for photo-reduction reactions or reactions in which super oxide radicals (formed by the reduction of oxygen molecules) play an important role. Three-layered colloidal particles are another development in the field of surface modified semiconductor nanoparticles. They consist of a quantum- sized semiconductor particle as the core, covered by several layers of another semiconductor material, onto which several layers of the core material are then deposited and act as the outermost shell. These particles are called quantum dots or wells<sup>85</sup>. The first example described in the literature is CdS-HgS-CdS system<sup>86</sup>.

Another recent development in the application of nanoparticles in photocatalysis has been the emergence of organic-inorganic nanostructured composites. The interaction between organic and inorganic molecules is being used to generate a range of materials for catalytic applications. Braun et al<sup>87</sup> described the synthesis of stable semiconductor-organic superlattices based on cadmium sulphide and cadmium selenide. The incorporation of organic molecules in an inorganic lattice can tailor the electronic properties of the materials. Therefore, these novel organic-inorganic nanostructured composites may be suitable for photocatalytic applications. Tenne<sup>88</sup> has worked on the preparation of inorganic compounds, namely, WSe<sub>2</sub> and PtS<sub>2</sub> having crystal structures similar to graphite. These compounds can be used to construct fullerene-like structures and nano-tubes with potential applications in photocatalysis and nanoelectronics.

## 2.4 Sensitization of Photocatalysts

The sensitization of TiO<sub>2</sub> with a second component to enhance activity and shift the wavelength of irradiation into the visible region is a goal that has been actively pursued and several approaches have been taken. Sensitizing with dyes that absorb strongly in the visible spectrum has been one approach to extend the photo-response of TiO<sub>2</sub>. In a porous film consisting of nanometer-sized TiO<sub>2</sub> particles, the effective surface area can be enhanced 1000 fold, thus making light absorption efficient even with only a dye monolayer adsorbed on each particle<sup>89</sup>. Once photo-excited, the dye molecules inject electrons into the semiconductor conduction band. Efforts of O'Regan and Graetzel<sup>90</sup> led to the development and commercialization of a device capable of harvesting 46% of the incident solar energy flux. It was based on a 10 µm thick, optically transparent semiconductor film consisting of nanocrystalline TiO<sub>2</sub> particles coated with a monolayer of a Ru-based sensitizer dye. The absorption onset was shifted to 750 nm with the light harvesting efficiency almost 100% in the whole visible region below 550 nm. Recently Salafsky et al<sup>91</sup> found that the presence of an electron donor to the dye cation (I/I<sup>3+</sup> redox couple) prevented the injected charge from directly recombining with the cation and thus the charge has a longer life time. However, this technique is less likely to succeed in photocatalysis due to their instability<sup>39</sup>.

Another approach has been to utilize narrow band gap semiconductors to photosensitize TiO<sub>2</sub>. Nanocrystalline and narrow-band gap semiconductors can be used as sensitizers. These semiconductors can be tailored to suit specific purposes since changing their size can shift their electronic bands (Q-size effects). This concept is a more attractive alternative for TiO<sub>2</sub> sensitization since they are more stable than organic dyes<sup>39</sup>. The sensitizer has a high cross section for absorption of visible light and injects electrons into the lower conduction band of the wide-band gap semiconductor.

The separated charge carriers can be used to initiate the chemical reactions. This principle has been used to construct photoactive layers, in which charge separation is achieved with an efficiency of 80%<sup>67</sup>.

Sensitization of TiO<sub>2</sub> with Q-sized narrow-band gap semiconductors, PbS and CdS, was carried out by Vogel et al<sup>92</sup>. These systems, however, demonstrated a loss in efficiency with photo-corrosion of the narrow-band gap semiconductors in aqueous media. Howe<sup>39</sup> suggested the possibility of using such semiconductor sensitized nanocrystalline TiO<sub>2</sub> for gas phase photocatalysis. A different approach was taken by Bahnemann et al<sup>41</sup> in order to synthesize particles which utilize parts of the visible solar spectrum when acting as a photocatalyst. This approach involved the preparation of a mixed Ti(IV)/Fe(III) oxide catalyst. This photocatalyst has not only increased the activity for destruction of DCA (dichloroacetic acid) but also showed photoresponse to 450 nm light. The prepared particles contained between 0.05 and 50 wt% Fe(III) in their matrix and particle diameters between 4 and 6 nm. The photoresponse shifted to longer wavelengths with increasing content of ferric ions. However this novel photocatalyst also suffered from the problem of partial reductive dissolution upon illumination. This cathodic corrosion competes with the electron transfer to oxidants such as oxygen, found in the system. In order to alleviate the problem of photo-dissolution, the authors suggested the introduction of H<sub>2</sub>O<sub>2</sub> as an electron acceptor into the system. Since, hydrogen peroxide being a better electron acceptor than O<sub>2</sub>, this can be used to compete more efficiently with the photocatalyst dissolution<sup>41</sup>.

### 3. SECOND GENERATION PHOTOCATALYTIC NANOPARTICLES: ANION DOPED TiO<sub>2</sub>

TiO<sub>2</sub> has several advantages due to its high chemical stability, excellent functionality, non-toxicity, and relatively low price, but a serious disadvantage is that it can absorb only UV light ( $\lambda < 380$  nm), therefore it is widely recognized that the development of photocatalysts should allow the main part of the solar spectrum, and even poor illumination of interior light, to be used. Only about 3% of the solar spectrum can be utilized for its photocatalytic capabilities. Since UV light makes up of less than 3% solar spectrum that reaches the earth's surface, the commercial application of these processes has been retarded<sup>93</sup>. Hence much effort has been devoted to prepare a TiO<sub>2</sub> photocatalyst that is capable of efficient utilization of the visible light constituting the main part of the solar spectrum<sup>94</sup>. Many techniques have been examined to extend the spectral response of TiO<sub>2</sub> into the visible region and enhance its photocatalytic activity. Impurity doping is one such approach to extend the spectral response of a wide band gap semi-conductor to visible light. If the photocatalytically active region is expanded to the visible light region, sunlight or indoor light can be used more efficiently. The doping of cations, such as Cr, W, and V, into TiO<sub>2</sub> nanoparticles by wet methods or implantation methods has been conducted to improve the visible light response<sup>93,95,96</sup>. However these techniques involved each of the following problems: the primary ultraviolet activity of TiO<sub>2</sub> photocatalyst tends to decrease, the absorbance around 480 nm (~ peak of solar spectrum) is low, the activity under visible light is much lower than that under UV light, or the doped ion is harmful. In the field of photocatalytic water splitting, the utilization of non-TiO<sub>2</sub> photocatalysts, such as ion-exchangeable layered niobates<sup>97</sup>, tantalum nitride<sup>98</sup> (TaN<sub>5</sub>), and tantalum oxynitride<sup>99</sup> (TaON), under visible light have been studied and developed. However, practical applications of these compounds would be limited to highly productive reactions, since these compounds are often rare and expensive. Apart from this, several strategies including the doping of TiO<sub>2</sub> with transition metals<sup>100-102</sup>, the synthesis of reduced forms with TiO<sub>2-x</sub> structure by the plasma treatment<sup>103,104</sup>, anchoring organic dyes onto the surface of TiO<sub>2</sub><sup>105,106</sup>, and the doping of TiO<sub>2</sub> with anionic non-metals such as C<sup>107,108</sup>, N<sup>109-111</sup>, S<sup>112,113</sup>, P<sup>114</sup>, and halogen atoms<sup>115-117</sup> have been investigated. Among those modifications the photocatalytic activity of cation doped TiO<sub>2</sub> decreased even in the UV region. This was either because of thermal instabilities or an increase in the recombination centers of the charge carriers introduced by the dopant's localized d-states deep in the band gap of TiO<sub>2</sub>, which may decrease the photocatalytic efficiency. Non-metal dopants may



be more appropriate for the extension of photocatalytic activity of  $\text{TiO}_2$  into the visible region than other methods because their impurity states are near the valence band edge, but they do not act as charge carriers, and their role as recombination centers might be minimized compared to metal cation doping<sup>118</sup>. Recently non-metal doped  $\text{TiO}_2$  nanoparticles also named as second-generation photocatalysts have demonstrated to have improved photocatalytic activities compared to those for pure  $\text{TiO}_2$  nanoparticles, especially in the visible light region. Among various dopants, the modification of  $\text{TiO}_2$  with N-dopant seems a powerful way to extend the absorption of light from the UV to visible region, since the substitution of lattice oxygen with nitrogen might narrow the band gap.

### 3.1 Nitrogen (N)-doped $\text{TiO}_2$

Many researchers have recently proposed that nitrogen-doped  $\text{TiO}_2$  is a promising second generation photocatalytic material. The origin and correct identification of nitrogen doped  $\text{TiO}_2$  was discovered by Shinri Sato in 1985<sup>119</sup> and he obtained N-doped  $\text{TiO}_2$  by calcining mixtures of  $\text{Ti}(\text{OH})_4$  and ammonium salts which leads to  $\text{TiO}_2$  based materials that can be activated under visible light. Furthermore, Sato reported that high calcination temperatures of the doped  $\text{TiO}_2$  decreased the visible light absorption and concluded that this loss of activity in the visible region is due to the volatile nature of the dopant. Although the origin of N-doped  $\text{TiO}_2$  is attributed to Sato, more than 15 years prior to that Che and Naccache<sup>120</sup> reported an electron paramagnetic resonance (EPR) in  $\text{TiO}_2$  samples that had been treated with ammonia and then calcined at 300 to 450°C. They concluded from the EPR analysis that  $\text{NO}_2^{2-}$  radicals existed and were on the surface of  $\text{TiO}_2$  and not within the lattice. Since the first report by Sato in 1985, considerable research has been done with respect to the preparation, characterization, photocatalytic activity and mechanism of N-doped  $\text{TiO}_2$  in visible light. However it took almost fifteen years from then until nitrogen doped  $\text{TiO}_2$  again was considered for photocatalytic applications.

In 2001, Asahi et al<sup>109</sup> reported visible light photocatalytic degradation of methylene blue and acetaldehyde by  $\text{TiO}_2$  films doped with nitrogen by sputtering methods. They have accomplished N-doping by reactive sputtering of  $\text{TiO}_2$  film targets in  $\text{N}_2/\text{Ar}$  gas mixtures by high temperature treatment of  $\text{TiO}_2$  powders in  $\text{NH}_3/\text{Ar}$  atmospheres, and by oxidative annealing of  $\text{TiN}$  powder. In these cases, a noticeable new absorption range for light at energies less than the band gap energy of 3.0 eV has been observed and the films and powders of  $\text{TiO}_{2-x}\text{N}_x$  showed a dramatic improvement over pure titanium dioxide under visible light in their optical absorption and the level of photocatalytic activity. They concluded that the substitution of oxygen is anticipated to lower the band gap energy of  $\text{TiO}_2$  as the 2p states of dopant mix with the oxygen 2p states, contributing to a net band gap narrowing. The doping of nitrogen in  $\text{TiO}_2$  has been done by many techniques such as direct amination of  $\text{TiO}_2$ , sputtering, spray pyrolysis, sol-gel, chemical vapor deposition, mechano-chemical reaction and hydrolyzing Ti-containing precursor in ammonia solution<sup>110,121-138</sup>. Experimental results for doping with nitrogen indicate that there is a significant red shift in the absorption spectra, which yields photoactivity in the visible region<sup>109</sup>. The photocatalytic activities of such N-doped systems have been studied<sup>131-133</sup>. There is some debate as to whether nitrogen dopant in  $\text{TiO}_2$  are interstitial or substitutional<sup>109,111</sup>. The experiments by Diwald et al<sup>105</sup> show that the interstitial nitrogen dopant is effective in reducing the threshold photon energy for photochemistry from 3.0 to 2.4 eV, which is a shift of 0.6 eV into the visible region. Their results disagree with the results of Asahi et al<sup>109</sup>, who concluded that nitride ion that substituted for  $\text{O}_2^-$  ions in the  $\text{TiO}_2$  lattice are the necessary dopant species for  $\text{TiO}_2$  photocatalysis in the visible region. In parallel, some theoretical calculations have also been performed to suggest that anion doping of  $\text{TiO}_2$  has considerable effect on the band gap alteration<sup>109</sup>.

In our recent study<sup>139</sup>, we report for the first time, the synthesis of highly crystalline novel mesoporous nitrogen/carbon (C/N), co-doped  $\text{TiO}_2$  (MCNT) using ethylene diamine and carbon tetrachloride as the source for nitrogen and carbon, KIT(Korean Institute of Technology)-6 as the template, and titanium tetra-isopropoxide as  $\text{TiO}_2$  source<sup>139</sup>. The obtained material has been unambiguously characterized by various sophisticated techniques. XRD and TEM analysis<sup>139</sup>

revealed that MCNT material possess highly crystalline 3D structure with continuous network of mesoporous channels as well as structure corresponds to  $\text{TiO}_2$ . UV-DRS analysis<sup>139</sup> indicated that light absorption shifted to lower energy and a stronger absorption in the visible-light region. XPS spectra<sup>139</sup> revealed that C and N were doped effectively and C or N dopants might be present in the chemical environment of Ti-O-N or Ti-O-C. Owing to its textural characteristics and its light absorption in the visible region, it could be very useful for various applications under visible light, such as photocatalysis, fuel cells, bulky bio-molecules adsorption and nanotechnology.

### 3.2 Carbon (C) and Sulfur (S)-doped $\text{TiO}_2$

Narrowing of the band gap has been reported in  $\text{TiO}_2$  nanoparticles doped with many anions (N, C and S), with carbon doped  $\text{TiO}_2$  as one of the best in terms of band gap width. The most common method used for preparing a carbon doped  $\text{TiO}_2$  is by direct oxidation of the Ti metal in the flame of a burner<sup>140-145</sup>. In 2002 Khan et al<sup>140</sup> reported quantitative results on a new carbon-doped rutile photoanode for the photo splitting of water, but there is still disagreement about its solar-to-hydrogen conversion efficiency<sup>146-148</sup>. The resulting photocatalyst could adsorb UV and most of the visible light below 535 nm. Following Khan's work Irie and co-workers<sup>141</sup> prepared a carbon-doped anatase  $\text{TiO}_2$  powders by oxidative annealing of TiC under  $\text{O}_2$  flow at 600°C. Their catalyst showed photocatalytic activities for the decomposition of 2-propanol to  $\text{CO}_2$  via acetone under visible light irradiation<sup>140</sup> (400-530 nm). Sakthivel and Kisch<sup>142</sup> synthesized carbon doped  $\text{TiO}_2$  by the hydrolysis of titanium tetrachloride with tetrabutylammonium hydroxide followed by calcination at 400 and 500°C. In the degradation of 4-chlorophenol by artificial light ( $\lambda \geq 455$  nm) the catalyst powders have a high photocatalytic activity<sup>142</sup>. Recently, a carbon doped titania with high surface area (204  $\text{m}^2/\text{g}$ ) was prepared by temperature programmed carbonization of K-contained anatase titania under a flow of cyclohexene at temperatures between 450 and 500°C<sup>149</sup>. This carbon doped titania has much better photocatalytic activity for gas-phase photo-oxidation of benzene under irradiation of artificial solar light than pure titania. As far as the investigation of  $\text{TiO}_2$  doped with carbon, similar to the N doping, there was also a debate as to whether the doped type of carbon is substitutional<sup>150</sup> or interstitial<sup>151</sup> which was accounted for by the crystal form and the synthesis method of  $\text{TiO}_2$ . In addition, some reports<sup>152</sup> suggested that large band gap narrowing could also originate from residual carbon-containing species with complex composition, through incomplete removal of organic compounds in the calcination procedure. Very recently many researchers synthesized carbon doped  $\text{TiO}_2$  by the reduction of glucose on  $\text{TiO}_2$ <sup>153</sup> and incorporation of carbon by heating with CO at higher temperature<sup>154</sup> and they found that C-doped  $\text{TiO}_2$  showed enhanced photocatalytic activity than pure  $\text{TiO}_2$  under visible light. C-doped  $\text{TiO}_2$  nanoparticles also displayed high photocatalytic activity in the degradation of trichloroacetic acid under visible light<sup>155</sup>.

Substitution of sulfur (S) atoms at the O sites of  $\text{TiO}_2$  could significantly modify the electronic structures of  $\text{TiO}_2$  because S has a larger ionic radius compared to other anions (N, F). S-doped  $\text{TiO}_2$  nanomaterials were synthesized by mixing TTIP with ethanol containing thio-urea<sup>156-158</sup> or by heating sulfide powder<sup>159,160</sup> or by using sputtering or ion-implanting techniques with  $\text{S}^+$  ion flux<sup>161-163</sup>. Different doping methods can induce the different valence states of the dopants. For example, the incorporated S from thio-urea had  $\text{S}^{4+}$  or  $\text{S}^{6+}$  state<sup>156-158</sup>, while direct heating of  $\text{TiS}_2$  or sputtering with  $\text{S}^+$  induced the  $\text{S}^{2-}$  anion<sup>158-163</sup>. There is some debate as to whether sulfur dopants in  $\text{TiO}_2$  are cationic or anionic. The experiments by Ohno et al.<sup>157,158</sup> show that sulfur was incorporated as cationic  $\text{S}^{6+}$  and suggested the  $\text{S}^{6+}$  replaces  $\text{Ti}^{4+}$  ions in the  $\text{TiO}_2$  lattice. Furthermore, these powders absorb visible light more strongly than the N- $\text{TiO}_2$  and other anionic S-doped  $\text{TiO}_2$ . Their results disagree with Umebayashi et al<sup>159-161</sup>, who reported that the nature of S is an anion and replaces the oxygen atom in the  $\text{TiO}_2$  lattice. Various experimental and theoretical studies have also implied that the doping of hetero atoms into the  $\text{TiO}_2$  lattice shifts the light absorption onset to higher wavelengths by reducing the energy difference between the highest occupied and lowest unoccupied states<sup>164,165</sup>. This red shift in optical absorption occurs due to the overlap of 2p and 3p

orbitals of N and S respectively, with the valence band of  $\text{TiO}_2$  and results in the formation of additional energy levels just above the valence band<sup>166</sup>.

### 3.3 Halogen atoms doped $\text{TiO}_2$

Doping of halogen atoms was found to be most effective because the impurity states of halogen ions are near the valence band edge, but they do not act as charge carriers, and their role as recombination centers might be minimized compared to metal cation doping. Very recently, many researchers have reported several improved kinds of non-metal doped  $\text{TiO}_2$  and in particular  $\text{TiO}_2$  doping with halogen atoms such as F<sup>167</sup>, Cl and Br<sup>168</sup> showed higher photocatalytic activity under UV as well as visible light irradiation. F-doped  $\text{TiO}_2$  nanomaterials were synthesized by mixing TTIP with ethanol containing  $\text{H}_2\text{O}-\text{NH}_4\text{F}$ <sup>167-169</sup>, or by heating  $\text{TiO}_2$  under hydrogen fluoride<sup>170,171</sup>, or by spray pyrolysis from an aqueous solution of  $\text{H}_2\text{TiF}_6$ <sup>172,173</sup>, or using ion-implanting techniques with  $\text{F}^+$  ion flux<sup>174</sup>. In 1991 Kuhn et al<sup>175</sup> have pointed out that iodine was promising for n-type doping. Recently Cai and Liu<sup>176, 177</sup> synthesized iodine doped  $\text{TiO}_2$  by hydrothermal treatment using iodic acid and tetrabutyltitanate. According to Cai and Lu iodine existed as  $\text{I}^{5+}$  in the iodine doped  $\text{TiO}_2$  and showed higher visible light photocatalytic activities in the decomposition of phenol<sup>176</sup> and methylene blue<sup>177</sup>. Very recently Su et al<sup>178</sup> synthesized multivalency I-doped  $\text{TiO}_2$  by a combination of a deposition-precipitation process and hydrothermal treatment. They studied both theoretical and experimental aspects and concluded that some iodine energy bands appear in the band gap of  $\text{TiO}_2$  which plays a key role to the visible light activity of I-doped  $\text{TiO}_2$ .

## 4. CONCLUSION

Electronic modification of the catalyst by deposition of metal particles, supported photocatalyst, sensitizer molecules, or other semiconductor particles has a strong effect on the photoactivity of the system. The wavelength tuning of the photo-response, the efficiency of electron-hole separation, and the dynamics of interfacial electron transfer, can be dramatically influenced. This review demonstrates the effectiveness of using nanoparticles of  $\text{TiO}_2$  in developing efficient visible light activated photocatalysts through anion doping. Furthermore, the anion doped  $\text{TiO}_2$  could provide a pathway for the production of environmentally benign photocatalysts that exceed the efficiency of conventional catalysts, particularly for visible light activation.

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## 6. NOMENCLATURE

UV- ultraviolet

VB- valence band

CB- conduction band

ST- shallow traps

DT- deep traps

V- electrical potential

E<sub>g</sub>- band gap energy

$h^+$  - electron holes

e<sup>-</sup> - electrons

NHE- normal hydrogen electrode

D- donor

A- acceptor

[D<sup>•</sup>]<sup>+</sup> - cation radical

[A<sup>•</sup>]<sup>-</sup> - anion radical

ESR- electron spin resonance

EPR- electron paramagnetic resonance

•OH- hydroxyl radical

MCNT- mesoporous- carbon and nitrogen doped titanium dioxide

TTIP- titanium tetraisopropoxide

Wt%- weight percentage

μs- micro second

fs- femto second

ps- pico second

XRD- x-ray diffraction

UV-vis- ultraviolet visible

UV-DRS- ultraviolet-diffuse reflectance spectra

XPS- x-ray photoelectron spectroscopy

HR-SEM- high resolution-scanning electron microscope

TEM- transmission electron microscope

MCP- monocrorphos

DCA- dichloro aceticacid

TOC- total organic carbon

FT-IR- fourier transform- infra red

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## Controlled Synthesis of Titanium dioxide nanostructures

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### Abstract:

Recent interest in nanostructured titanium dioxide (TiO<sub>2</sub>) has been driven by the excellent photocatalytic and optical properties exhibited by the anatase and rutile phases. This article highlights the relationship between reaction conditions and the resultant nanostructured TiO<sub>2</sub> and is primarily focused on wet chemical synthetic methods. We show that solvothermal syntheses of nano-TiO<sub>2</sub> can be rationalised by making use of a diffusion-controlled model accounting for physical properties of the solvent such as the vapour-pressure, allowing the prediction and control the phase, size and type of nanostructured TiO<sub>2</sub> product. This *external* control makes it possible for the systematic synthesis of TiO<sub>2</sub> nanostructures via parameters such as the solvent chain length, the reaction temperature and time, and also by the addition of surfactants, providing the ability to design and tailor the nanostructured TiO<sub>2</sub>, which is vital for the optimal application of these nanostructures in photocatalytic or optical applications.

## 1. Introduction

Recent interest in nanostructured titanium dioxide (TiO<sub>2</sub>) has focused on the vast range of potential applications due to the unique electronic and photocatalytic properties of TiO<sub>2</sub>, including water purification/air deodorization [1, 2], self-cleaning [3], anti-corrosion and self-sterilizing coatings[4, 5], smart windows and the enhancement in performance of dye-sensitized solar cells[6, 7]. TiO<sub>2</sub> is widely used as pigment and whitening agent due to a high brightness and refractive index, which is surpassed by only a few materials. This makes TiO<sub>2</sub> ideal for applications in products such as paints, coatings, plastics, papers, inks, foods and toothpaste, providing both whiteness and opacity. Recently TiO<sub>2</sub> has been used in cosmetics and sunscreens, acting as a physical block to ultra-violet radiation, due to it having a high refractive index and resistance to discolouration under UV light.

Existing methods of producing nano-TiO<sub>2</sub> include direct oxidation of titanium, physical/chemical vapour deposition, sol-gel and hydrothermal methods; however all suffer from a lack of precise control over the final product. Relatively simple solvothermal routes may be preferable to some of the alternative methods, due to the absence of complex equipment and high temperature heat post-treatment processes, making it readily suited to up-scaling for mass production. The nano-morphology of TiO<sub>2</sub> has been found to have a major influence on its suitability in potential applications and a variety of TiO<sub>2</sub> nanostructures have been reported, including nanoparticles, nanofibres, nanowires, nanorods and thin films. Selectivity between these morphologies has been achieved by variation of the experimental technique, external conditions and reaction parameters.

## 2. Properties of Titanium Dioxide

### 2.1. Crystalline Phase Structure.

Rutile is the most abundant phase of TiO<sub>2</sub> found in nature and has a tetragonal structure with a prismatic habit. It finds widespread use in pigments, as a cosmetic ingredient and as catalyst supports, mainly due to its high refractive index. Anatase in contrast, has high a photocatalytic activity, and whilst having a tetragonal structure, displays a bipyramidal habit. The least well-characterised phase, brookite, has an orthorhombic structure and is metastable, making it difficult to produce in large and pure quantities.[8]

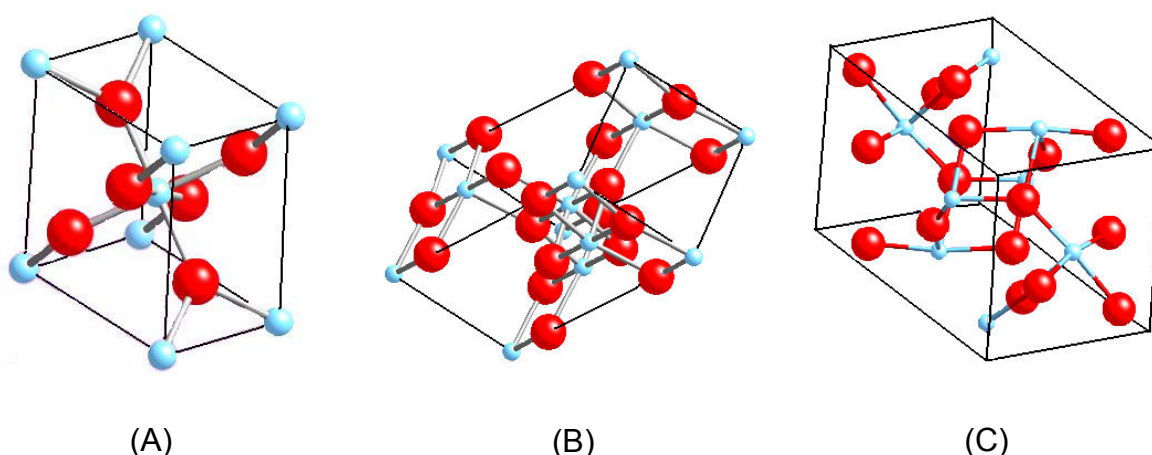


Figure 1 - Crystal Structure; (A) unit cell of rutile (tetragonal), (B) unit cell of anatase (tetragonal) & (C) unit cell of brookite (orthorhombic). Red atom: O & blue atom: Ti

Close inspection of the crystal structures of the three phases highlights the inherent structural similarities, especially between rutile and anatase; in all three, the titanium atom is coordinated to six oxygen atoms in an octahedral environment. Anatase and rutile phases have very similar interatomic distances, the bond lengths of Ti-O in anatase are reported to lie in the range of 1.949-1.980 Å and in rutile of 1.937-1.965 Å.[9] Brookite has a lower symmetry structure, with eight TiO<sub>2</sub>

units included in the orthorhombic cell, the Ti-O bond lengths show a greater range of values, lying over the range of 1.87-2.04 Å.[9]

|                              | <i>Rutile</i>          | <i>Anatase</i>         | <i>Brookite</i>                     |
|------------------------------|------------------------|------------------------|-------------------------------------|
| Atomic Spacing (Å)           | a = 4.596<br>c = 2.958 | a = 3.784<br>c = 9.515 | a = 9.184<br>b = 5.447<br>c = 5.145 |
| Molecule/unit cell           | 2                      | 4                      | 8                                   |
| Density (g/cm <sup>3</sup> ) | 4.13                   | 3.79                   | 3.99                                |
| Bond length Ti-O (Å)         | 1.949 (4)<br>1.980 (2) | 1.937 (4)<br>1.965 (2) | 1.87-2.04                           |
| Bond Angle O-Ti-O (°)        | 81.2°<br>90.0°         | 77.7°<br>92.6°         | 77.0-105°                           |

Table 1 - Crystal Structure Parameter of rutile, anatase & brookite phase of titanium dioxide. [9]

## 2.2. Electronic Properties.

The photocatalytic activity of nanostructured TiO<sub>2</sub> is greatly influenced by the electronic properties, which are known to differ between the different crystalline phases.[9] Whilst relatively little is currently known about the electronic properties of brookite, rutile and anatase have been well characterised and are known to have distinct electronic properties, despite the similarities in their crystal structures. Firstly, the respective electronic/optical valence-conduction band gaps are different; being 3.02 eV in rutile and 3.23 eV in anatase. Mogyorosi *et al.* [10] have proposed that this is due to a higher effective electron mass, a higher Fermi energy level and a greater charge mobility in anatase, which then gives rise to a larger band gap.

## 2.3. Photocatalytic Properties.

The phenomenon of photocatalytic activity in TiO<sub>2</sub> was first demonstrated by Fujishima and Honda in 1972, with the photocatalytic splitting of water, producing molecular hydrogen.[11] The photo-activity in TiO<sub>2</sub> is preceded by the absorption of light in the UV spectral region (peak absorption bands occur at wavelengths of 385 and 411 nm in anatase and rutile, respectively). When the photonic energy is larger or equal to the band gap (3.02-3.23 eV), an electron is promoted from the valence band into the conduction band. Once this happens, the separation of electrons and holes is facilitated by electron trapping sites on the TiO<sub>2</sub> surface. This allows for the electrons and holes to be incorporated into redox reactions with chemical species adsorbed at the surface, resulting in the degradation of the chemical species. If the electron:hole pair is allowed to recombine on the TiO<sub>2</sub> surface, then both will need to be re-generated once again for further photocatalytic activity. Figure 2 is an outline of the photocatalytic mechanism in TiO<sub>2</sub>. [5]

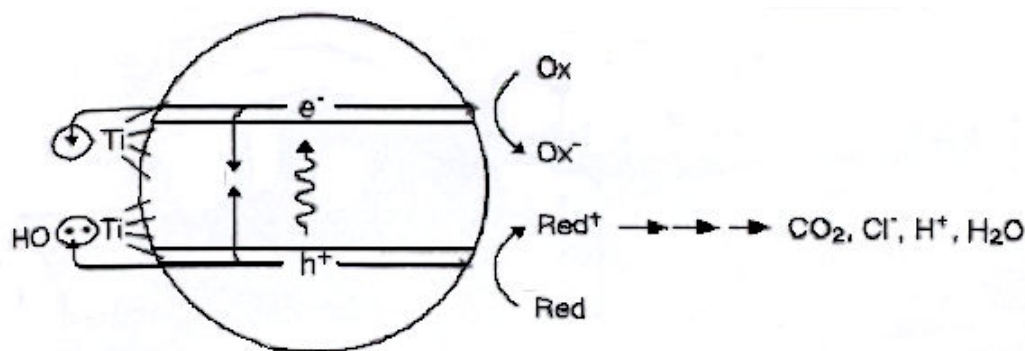


Figure 2 – Schematic of photocatalytic mechanism of titanium dioxide

When moving to nanoscale particles the surface area is greatly enhanced and so  $\text{TiO}_2$  nanoparticles have very high photocatalytic activities, that are then further enhanced by surface defects and quantum size effects. Nanoscale  $\text{TiO}_2$  has a larger ratio of surface area:bulk and so photocatalytic reactivity occurs more readily due to the restricted electron-hole recombination. The synthetic routes to nanoscale  $\text{TiO}_2$  also provide a means to enhance the density of surface defects, which can act as reactive sites for the adsorption, and subsequent degradation and dissociation, of the organic species.[12]

Fox and Dulay have shown that of the pure phases, anatase has a higher photocatalytic activity than rutile.[8] This is mainly due to the fact that rutile suffers more recombination events of the photogenerated electrons and holes. However recent research has suggested that a mixed phase nano- $\text{TiO}_2$  has a greater photocatalytic activity than pure anatase.[8] One of the main arguments for the increased photocatalytic activity is a greater separation of charge carriers, electron-hole pairs, in the mixed phase, than in anatase.[13] However, it has also been suggested that rutile has a faster initial rate of photoactivation, despite anatase having a better overall rate; thus the combined particle displays an overall enhancement.[14] Yet another possible reason for the mixed-phase to show a greater photocatalytic activity is the introduction of defect sites at the crystallite interfaces, which would naturally result in more photocatalytically active sites.[8] Duan and Shi have discussed the enhancement of photoactivity in mixed-phase particles, suggesting that there are two dominant effects that contribute synergistically; the *antenna effect* caused by the presence of rutile which increases the probability of electron excitation, and *surface band bending*, which makes electron injection from rutile to anatase more probable.[15] In this respect, mixed phase  $\text{TiO}_2$  nanostructures are believed to encompass the advantages of the inherent photocatalytic activity in both rutile and anatase, resulting in greater overall efficiencies.

An alternative method of increasing the photocatalytic activity of  $\text{TiO}_2$  is to shift the absorption band into the visible region by chemically doping with group XIV or XV elements. Many research groups have proceeded down this path of anion doping in  $\text{TiO}_2$  nanostructures in order to make optimal use of the visible solar spectrum. Anion doping with nitrogen [16-19], and carbon [20-22] are most commonly reported and usually incorporate the doping agent with the precursor solution, or alternatively titanium precursors containing the dopant moiety have also been used.[9]

Doping of different metallic centres into nanostructured  $\text{TiO}_2$  has resulted in greater efficiencies in the metal-metal charge transfer and in so doing, it has been found to improve the electronic transport and overall photocatalytic activity. Metal doping has other additional advantages, such as improving electron trapping and lowering the extent of charge carrier recombination. A host of metals have been successfully incorporated into the  $\text{TiO}_2$  framework, including silver,[23, 24] palladium,[25] gold,[26] bismuth,[27] tungsten [28] and niobium.[29]

Another area that has recently been addressed with chemical modification of  $\text{TiO}_2$  is aimed at improving the adsorption of organic molecules in applications relating to photocatalytic degradation. One approach has been the complexing of organic molecules onto the  $\text{TiO}_2$  surface and Hong *et al.*[30, 31] have suggested that there is even a synergy between the  $\text{TiO}_2$  and adsorbed species, resulting in a shift of the absorption band into the visible region in the absence of any direct  $\text{TiO}_2$  doping. In this way, the physical and chemical characteristics of the undoped material are maintained.

### 3. Synthetic Methods

Many methods of synthesizing  $\text{TiO}_2$  nanostructures have been investigated over the last fifteen years. However, only in recent years has research into nanoscale  $\text{TiO}_2$  become of wide-spread interest, mostly focused on the photocatalytic properties. There are numerous of methods of synthesizing  $\text{TiO}_2$  on the nanoscale, from the simple direct oxidation of titanium to more complex methods such as sol-gel chemistry. To date, physical/chemical vapour deposition, sol-gel, hydrothermal and solvothermal methods have been the most widely used synthetic routes.

#### 3.1. Physical/Chemical Vapour Deposition.

The use of physical/chemical vapour deposition (PVD/CVD) is the most extensive of the four general synthetic methods, in terms of necessary infrastructure. CVD and PVD also usually incur high levels of heating in order to deposit the decomposed precursor onto the substrate. This results in the  $\text{TiO}_2$  nanostructures mostly consisting of rutile as a phase transition from anatase to rutile

occurs between 500 and 600°C.[32] The synthesis of materials using PVD or CVD involves a vacuum chamber holding an inert atmosphere, within which the deposition occurs. The chamber contains the substrate and the precursor, which can be either liquid or gas phase. Once the precursor is in the chamber, the precise method of deposition varies depending on the required product. Methods of deposition include electrostatic spray or ultrasonic-assisted hydrolysis and pyrolysis reactions such as diffusion flame, thermal plasma, ultrasonic spray and laser-induced pyrolysis.[33] All of these methods have been found to influence the final product in terms of size, orientation and crystalline structure,[33] however samples obtained from CVD/PVD often require further annealing in order to increase the crystallinity. The over-riding advantage of using CVD or PVD methods is the ability to make well formed crystalline nanostructures, enabling highly uniform thin films of  $\text{TiO}_2$  to be prepared; these are ideal for many photocatalytic applications.[32, 34] Goto *et al.* [32] were able to synthesize uniformly thin mixed phase, anatase/rutile, films via CVD, using Nd:YAG laser pyrolysis. Figure 3(A) is a schematic of the LCVD synthesitic method used with the resultant film shown in figure 3(B). On other hand Sheel *et al.* [34] used CVD to produce thin films purely of anatase or rutile by changing the reaction temperature from 400-500°C to 500-650°C. Yates *et al.* managed to grow a thin film of anatase made up of nanoparticles, controlling the diameter of the nanoparticles over 37-84 nm by decreasing the furnace temperature from 900°C to 500°C, with the diameter of the nanoparticles decreasing with increased furnace temperature. The rationale behind this thermal control is that at high temperatures, the residence time of the nanoparticles within the reaction zone is much shorter, thus having less tendency to undergo growth via direct single particle mechanisms, or even coagulation, in the laying down of the film.[35]

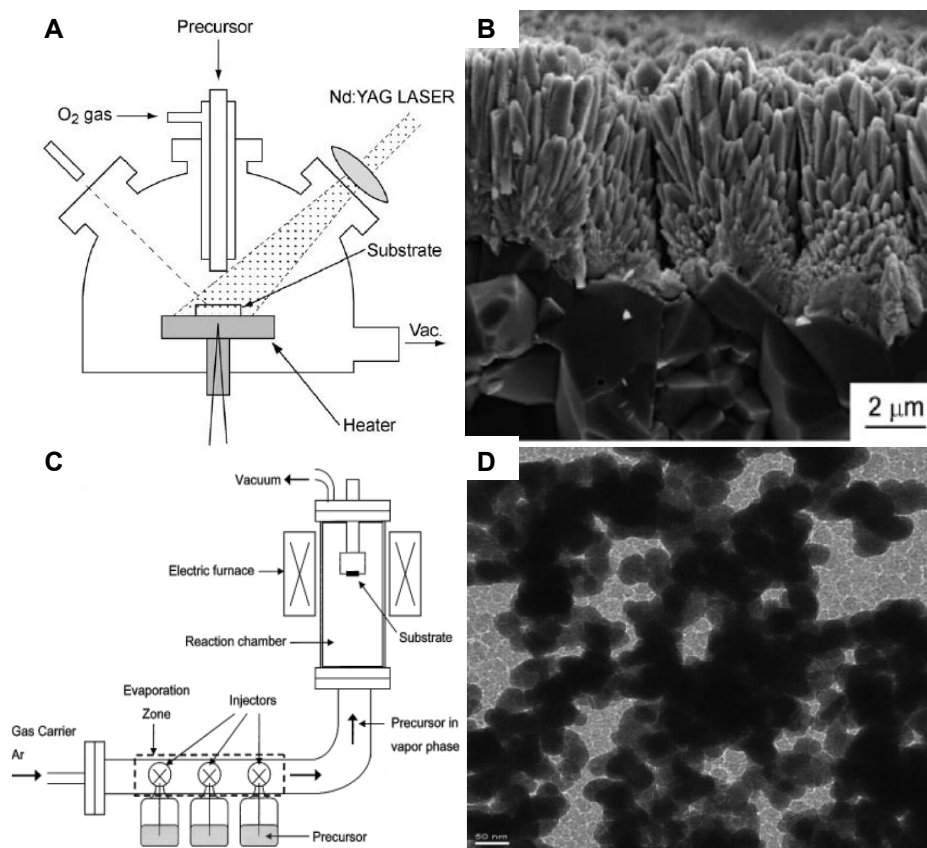


Figure 3 – (A) - A schematic diagram of LCVD apparatus. [32], (B) - Cross-section of YSZ film at  $T = 953\text{ K}$  [32], (C) - Schematic drawing of the pulsed liquid injection metal-organic chemical vapour deposition apparatus [36], (D) - High-resolution transmission electron microscopy image of Titania nanoparticles.[36]

PVD and CVD methods have been demonstrated of effectively synthesizing  $\text{TiO}_2$  nanoparticles, nanotubes and even nanowires, with slight modification of PVD/CVD methodologies being devised in order to synthesise these different nanostructures. For example, Apatiga *et al.* [36] used pulsed liquid injection metal-organic chemical vapour deposition (PI-MOCVD) shown in figure 3(C), with a supersaturated titanium precursor solution, to obtain nanoparticles having an average size of 60 nm in diameter, shown in figure 3(D). At temperatures exceeding  $\sim 600^\circ\text{C}$  they obtained crystalline phases of anatase and rutile, whilst at temperatures below  $600^\circ\text{C}$  only amorphous titania particles were obtained.

The drive to introduce dopants such as carbon,[37] nitrogen and boron in  $\text{TiO}_2$  nanostructures in order to shift the absorption band of the  $\text{TiO}_2$  film into the visible region and transparent thin films of  $\text{TiO}_2$  with nitrogen dopant levels of 1.5% to 5% have been synthesized by Yates *et al.*[19] They found that high temperatures, above  $650^\circ\text{C}$ , are required to ensure adequate incorporation of the nitrogen into the films. Increased concentration of ammonia gas in the injection process was found



to have a dramatic effect on the morphology, reducing both the crystallinity and the grow rate of the films. Meanwhile, Lei *et al.*[38] were able to dope boron into TiO<sub>2</sub> nanotubes by annealing the anodized tubes in-situ with boron at 400, 550 and 700 °C. The temperature of annealing was found to have a pronounced effect upon the photocatalytic efficiency, generally increasing with temperature, whilst the boron dopants were found to increase the anatase to rutile phase transition to higher temperatures.

**3.2. Sol-gel and Templating Methods.** The sol-gel route is the most widely used synthetic method produce TiO<sub>2</sub> nanostructures, probably due to it being a relatively simple procedure that does not require complex equipment. Another second advantage of the sol-gel route is the ability to control the product simply by modification of the precursor solution. However, titania synthesised via sol-gel routes is often amorphous, which then leads to post synthetic heat treatments such as annealing or refluxing, in order to form crystalline phases. Sol-gel routes involves a hydrolysis reaction of titanium alkoxide or halide precursors, followed by a condensation reaction, to form TiO<sub>2</sub>. [33] The hydrolysis reaction is usually acid (typically nitric or sulfuric acid) or base (most commonly sodium hydroxide) catalysed, in a sequential condensation reaction. However, the hydrolysis and condensation reactions often suffer from other competing reaction pathways such as alcoxolation, oxolation, and ololation.[39] The extent of these side-reactions during the sol-gel formation has major consequences on the resultant product and so the amount of water present in the precursor must be carefully monitored, as it will alter the final structure by influencing the reaction pathways. Just as for PVD/CVD, the sol-gel route has been shown to produce many types of nanostructures, from nanoparticles to thin films. Oliveira *et al.* [40] used an acid-catalysed sol-gel route with titanium tetra-isopropoxide (TTIP) as a Ti precursor, resulting in a dry TiO<sub>2</sub>-xerogel which was then heat treated, yielding nanocrystallites in sizes, ranging with temperature, from 4.8 to 8.9 nm. The crystalline phases were mainly anatase at lower temperatures but at higher temperatures only rutile formed. This is shown in figure 4, with the Raman spectra showing the increased presence of rutile as a function of temperature.

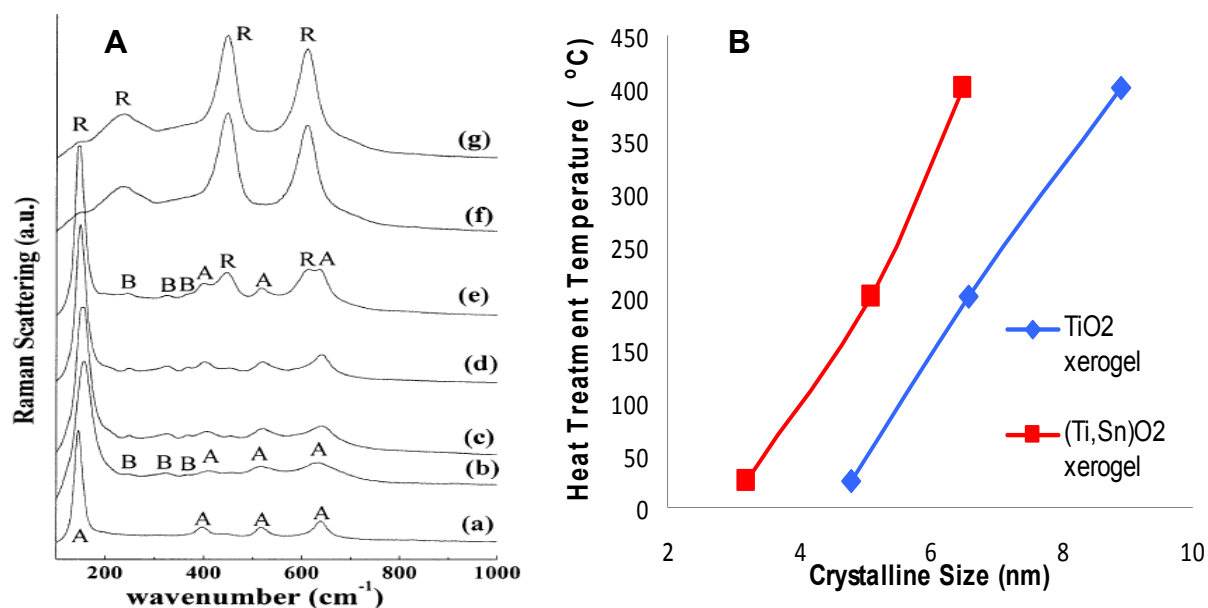


Figure 4 – (A): Raman spectra of commercial anatase  $\text{TiO}_2$  [38] (a),  $\text{TiO}_2$  xerogel (b), and  $\text{TiO}_2$  xerogel heat-treated at 200 °C (c), 400 °C (d), 600 °C (e), 800 °C (f), and 1000 °C (g), (B): Adapted graph from the XRD data table 1 from [40]

More recently, nanotubes and nanowires have been synthesized by Shyue *et al.* [41] using a sol-gel templating process at near-ambient temperature. These workers used anodic-aluminium oxide with embedded nanoholes or nanopores acting as a template. The template was then immersed in the titanium precursor solution for either 6 or 24 h. From this, nanotubes with a diameter of ~240 nm and wall thickness of ~20 nm (figure 6b) and nanowires with a diameter of ~60-260 nm were produced (figure 5a & c).[41]

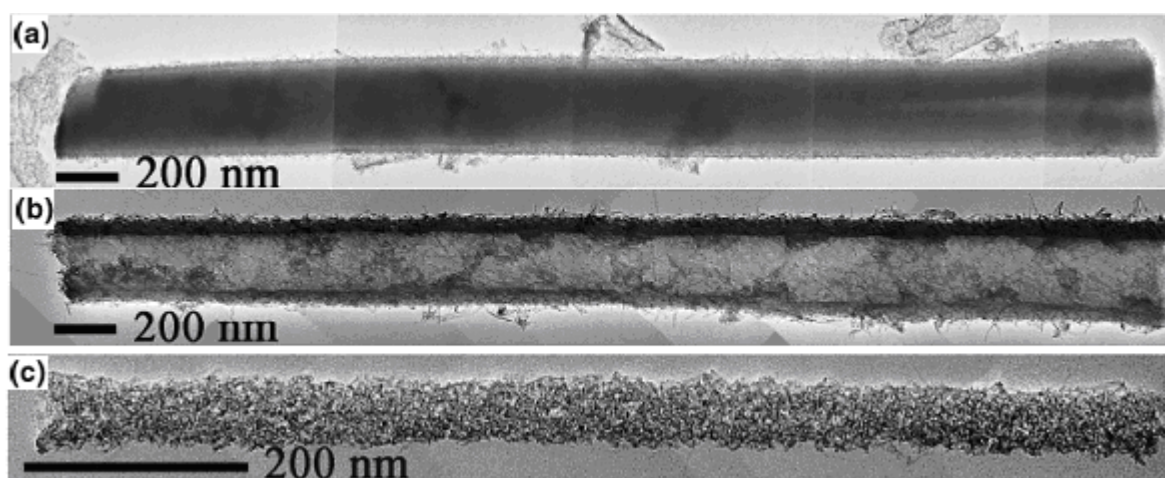


Figure 5 - TEM images of titania: (a) nanowire and (b) nanotube synthesized inside commercial AAO templates; (c) nanowire synthesized inside a prepared AAO template. [41]

Other templating methods have made use of anodic alumina membranes (AAMs) as templates to synthesize highly ordered films, nanowires and nanotubes. Sander *et al.* used an AAM template in sequential atomic layer deposition cycles of titanium tetrachloride (TC) and  $\text{H}_2\text{O}$  at  $105^\circ\text{C}$ . Once the deposition was complete the AAM was etched away, leaving a highly ordered array of  $\text{TiO}_2$  nanotubes.[42] Liu *et al.* electrodeposited  $\text{TiO}_2$  into the pores of alumina membrane which has undergone a two-step anodization process. The anatase nanowires were easily fabricated into the porous alumina membrane and remain highly ordered even upon removal of the AAM template[43].

**3.2.1 Sol Gel Thin Films.** Other groups such as Hagen *et al.* [44] have used sol-gel processing to obtain thin films of  $\text{TiO}_2$  consisting of  $\sim 100$  nm particles (figure 6a & b). They found that the  $\text{TiO}_2$  films produced via the sol-gel route performed as well as commercially produced films in photovoltaic tests, even though the sol-gel film was somewhat thicker, due to difficulties in the control of the method of deposition. This was mainly due to the high porosity of the anatase film, which allowed greater electrolyte diffusion between the layers, thus compensating for the reduced surface area. A room temperature sol-gel process involving the mixing over 30 min. of a  $\text{SiO}_2$  sol, TTIP, ethanol and polyethylene glycol (PEG) mixture, followed by spin coating onto glass substrates concluded that the presence of PEG and/or heat treatment, changed the surface structure, resulting in the enhancement of the photocatalytic activity of the film [45]. The presence of PEG bound to  $\text{TiO}_2$  surface may serve as an effective pathway to transport the active radical species from the  $\text{TiO}_2$  interface to the organic dye which supports the theory of complex-assisted enhancement of photocatalysis[30].

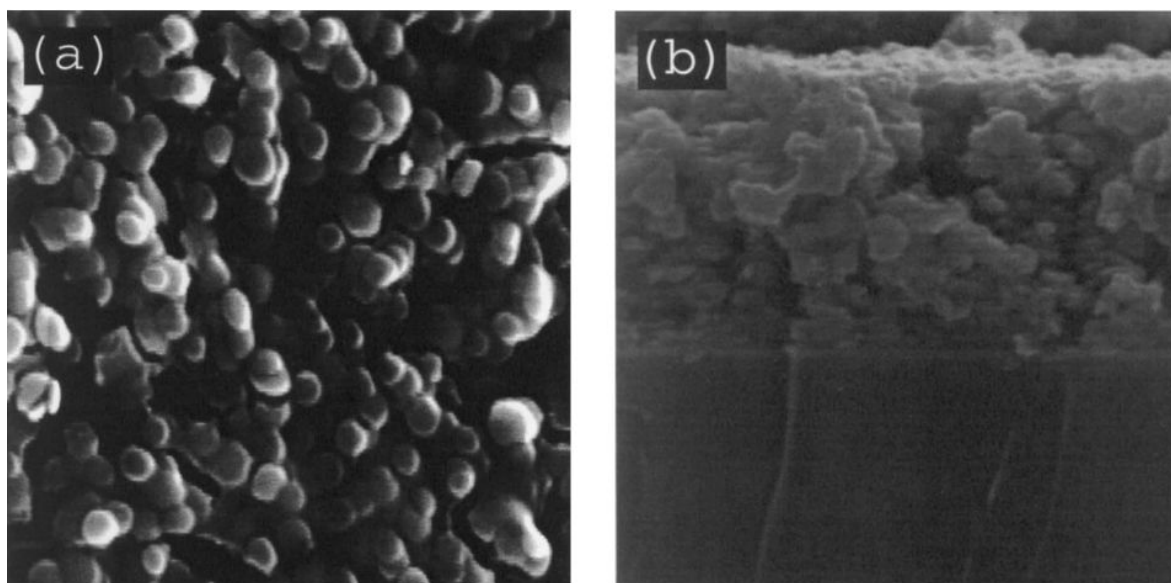


Figure 6 - SEM micrographs of a sol-gel TiO<sub>2</sub> layer with a thickness of 5  $\mu\text{m}$  on an ITO glass substrate. (a) surface (x 15000). (b) cross section (x 9000). [44]

Thin film doping via sol-gel processing is a common and easy approach as the dopant can be incorporated into the preparation stage of the sol-gel. Cheng *et al.* have introduced carbon as the dopant within the sol-gel mixture, with calcination at temperatures ranging between 150 and 500°C. They found that the inclusion of carbon assisted in the transformation of amorphous material to crystalline rutile at 200°C and led to a red-shift in the absorption of samples calcined at 150 and 200°C. Concurrently, samples heated at 500°C displayed lower visible light absorption due to the desorption and leaching of the carbon at higher temperatures.[22]

### 3.3. Hydrothermal Routes.

Hydrothermal synthesis is widely used in industry to manufacture ultra-fine powders and particles. The process is usually conducted in stainless steel autoclaves, either with and without Teflon or glass liners, and often in aqueous solutions. A major advantage of using a hydrothermal route in the synthesis of TiO<sub>2</sub> nanomaterials is the ability to produce different crystalline phases of without the need for further heat treatment processing as it provides the capacity to grow good-quality crystals and to control the crystalline composition simultaneously. The autoclave provides an almost perfect

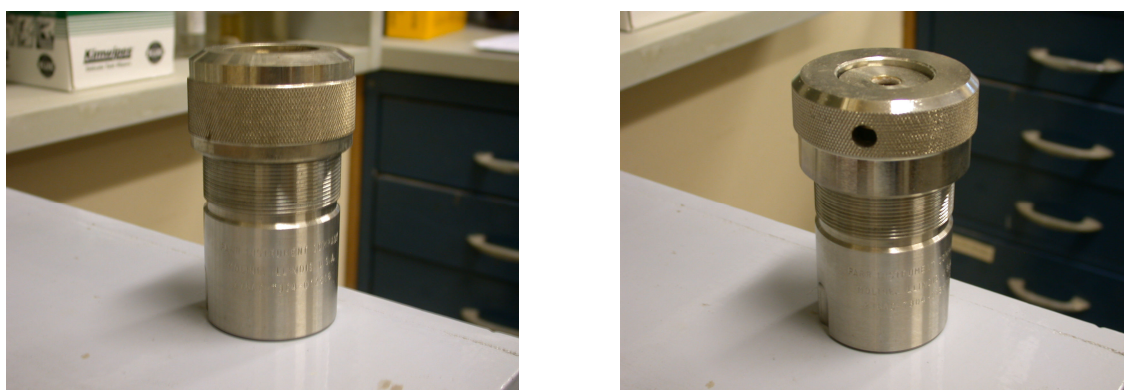


Figure 7 – Stainless Steel Autoclave

reaction environment; it has a uniform temperature gradient, between the solvent and the head-space that allows for the higher temperature region to dissolve the nutrients, with the cooler region suited to enhanced crystal growth.

The initial step in a given hydrothermal reaction is the preparation of the precursor solution, usually consisting of titanium alkoxide or halide. This is mixed into an aqueous solution, possibly with the addition of a surfactant. The selection of the precise precursor solution mixture has been found to have a great effect on the outcome of the final product. The precursor solution is then placed into an autoclave and heated to a given temperature over some period of time. The precipitate formed is then collected either by filtration or centrifugation, washed with an appropriate solvent and dried. With this relative simplicity, hydrothermal reactions can lead to the synthesis of various  $\text{TiO}_2$  nanomaterials simply by varying the experimental parameters. Andersson *et al.* [14] employed a micro-emulsion technique that incorporated a hydrothermal treatment to produce nanoparticles of both rutile and anatase of  $\sim 3\text{-}5$  nm in size. They propose that the precise crystalline phase obtained depends upon the acid used in the hydrothermal treatment. They found that anatase was obtained when using nitric acid and rutile with hydrochloric acid. Other groups, such as Reddy *et al.*, [46] have also produced nanoparticles from hydrothermal reactions, proposing that the crystalline phase is dependent on the pH of the precursor solution. They obtained nanoparticles of size 10-35 nm, with rutile produced under highly acidic conditions and anatase at a pH of around 8. However, it remains uncertain whether pH has a direct effect on the crystalline phase, as both Andersson *et al.* [14] and Reddy *et al.* [46] obtained both rutile and anatase, but not at the same pH. Sun *et al.*, [47] using similar procedures, also produced rutile and anatase powders of 3-9 nm in size by the addition of either water or ammonium sulfate solution to TC and then hydrolysing at  $70^\circ\text{C}$  for 1 h. The product was then left to dry at  $110^\circ\text{C}$  and calcined at  $400^\circ\text{C}$ .

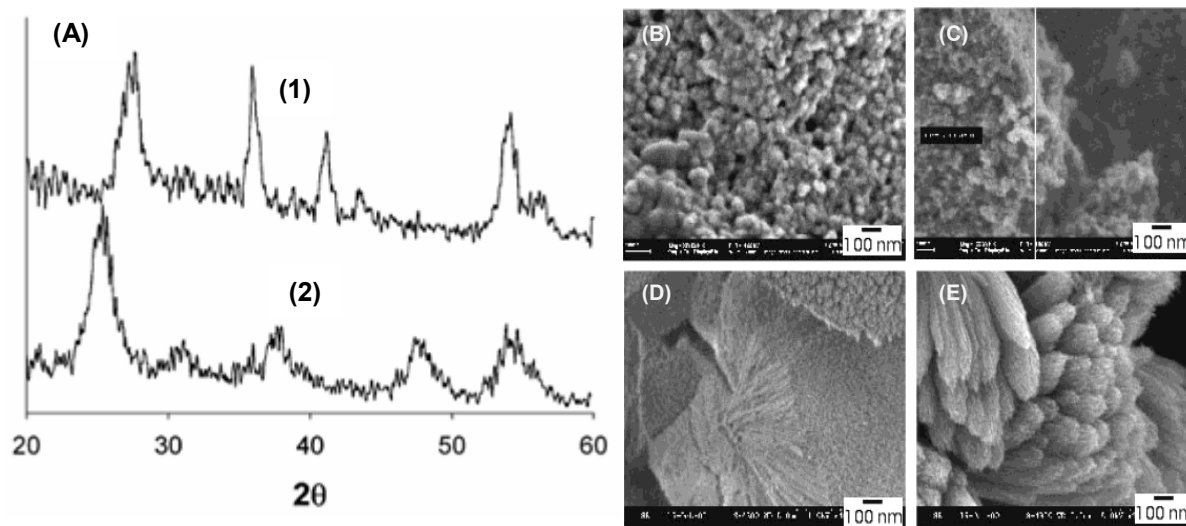


Figure 8 - (A) X-ray powder diffraction spectra of (1) anatase prepared from microemulsion containing  $\text{HNO}_3$  and (2) rutile prepared from microemulsion containing  $\text{HCl}$ . SEM micrograph of titania nanoparticles. (B) & (C) anatase prepared by microemulsion containing  $\text{HNO}_3$ ; (D) & (E) rutile prepared by microemulsion containing  $\text{HCl}$  [22]

The hydrothermal synthesis of  $\text{TiO}_2$  nanotubes has been achieved by the hydrolysis of commercially-available  $\text{TiO}_2$  nanoparticles (Degussa P25) with a sodium hydroxide solution in an autoclave at  $150^\circ\text{C}$  for 50 h., figure 9.[48] Similarly Zhang *et al.* [49] reacted anatase, rutile and mixed phase titania powders with sodium hydroxide under hydrothermal conditions to produce nanotubes, figure 10. From this, the growth of nanotubes from nanoparticles depends greatly on the crystalline phase and size of the particles in the titania powder used as the starting material.

3.4.

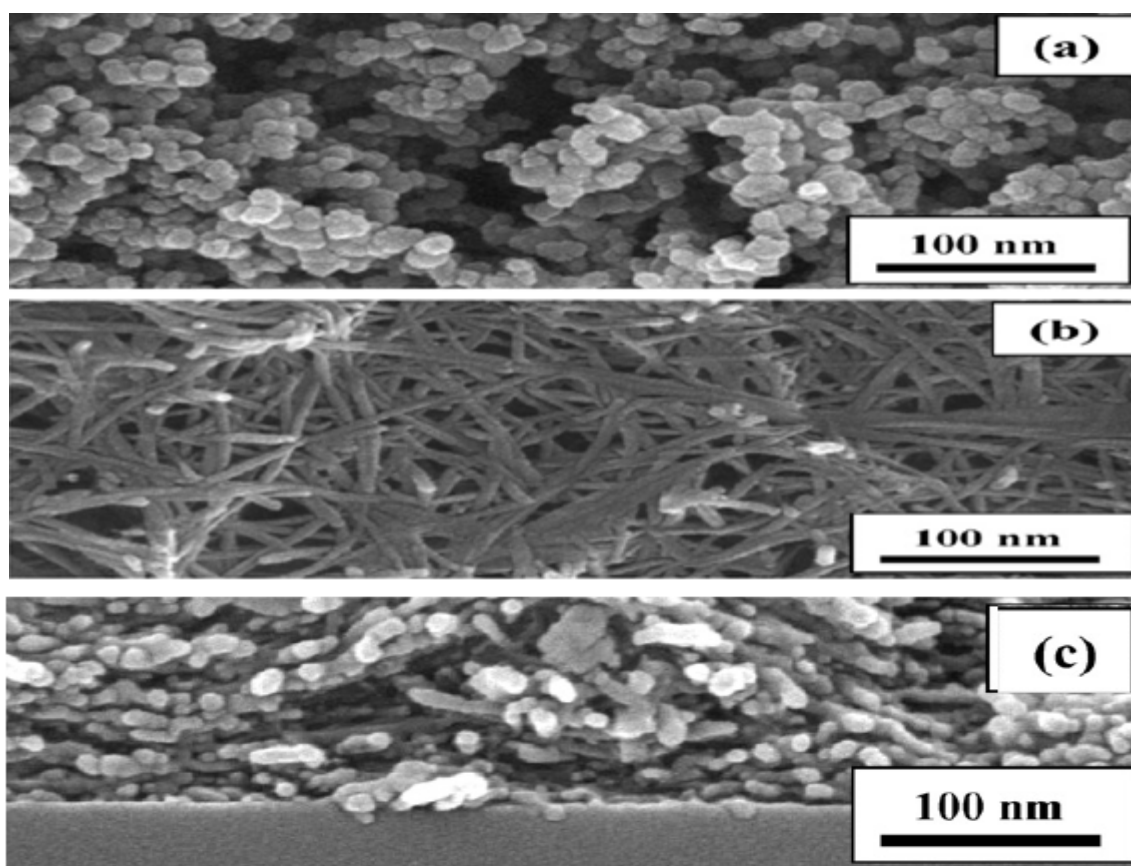


Figure 9 - High resolution SEM micrographs showing morphologies of (a) commercial titania powder, (b) hydrothermally synthesized titania nanotube powder & (c) cross-sectional view of titania nanotube coating. [49]

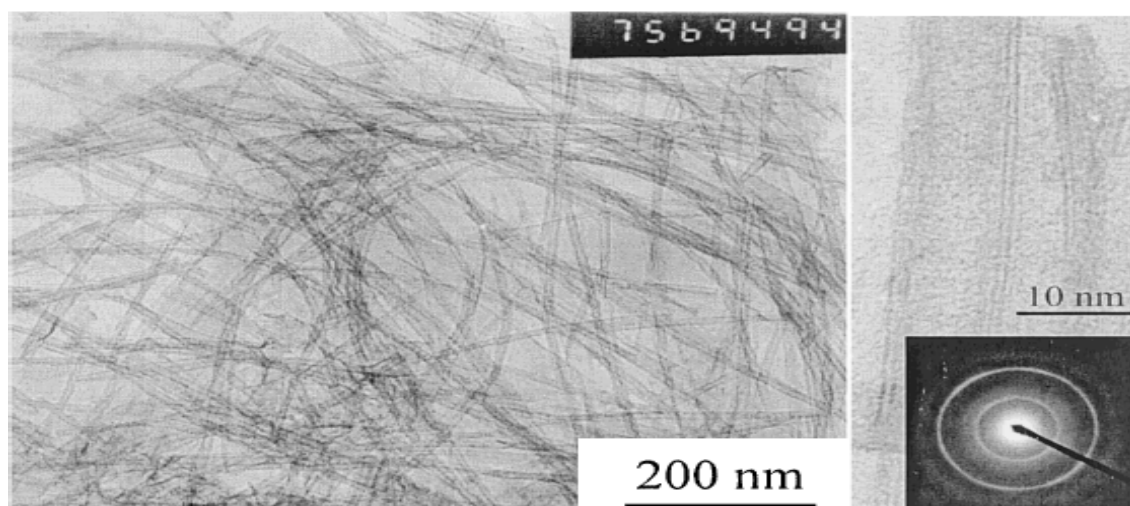


Figure 10 - TEM and HREM (right) images of TiO<sub>2</sub> nanotubes derived from R1. the rings of electron diffraction in the inserted electron diffraction patterns was attribute to 101 and 200 diffraction plane of anatase. [48]

### Solvothermal Routes.

Solvothermal reactions are very similar to hydrothermal reactions, the only difference being that the reaction medium is a non-aqueous solvent; however, it should be noted that this is not always the case in all literature uses of the expression. As with hydrothermal methods, solvothermal synthesis

is conducted in stainless steel autoclaves and simple variation of reaction variables has established that differing shapes, types, sizes, and size distributions, in addition to differing crystalline phases, of nanostructured TiO<sub>2</sub> can be produced. Experimentally the variable parameters include reaction temperature and time, solvent, the presence or not of a surfactant, titanium precursors, *etc.* Therefore, it is essential to determine how these factors affect the properties of the resulting TiO<sub>2</sub> if it is to be of any potential use as a means of mass production for real-world applications. Many groups have used solvothermal syntheses to make a variety of TiO<sub>2</sub> nanostructures, using a range of different experimental parameters and conditions.

**3.4.1. Size and Size Dispersion of Nanostructures.** The size, size distribution and morphology is known to greatly influence the optical and electronic properties. The size of the particles, rods, etc. directly relates to the surface area available for photocatalytic reactions and will determine whether or not quantum size effects assist in the photo-activity. A uniform size distribution is advantageous as it provides a consistent photocatalytic reaction pathway and allows the performance of the nanostructured TiO<sub>2</sub> to be readily characterised. The size and size distribution are influenced by the rates of nucleation and growth under solvothermal conditions; it is generally understood that increasing the reaction temperature and prolonging the reaction time, will increase both the size and size distribution, as was first suggested by Pan *et al.* [50]. This is also supported by other workers,[12] who have observed that upon increasing the reaction temperature, the grain size increased with a resulting decrease in the specific surface area, figures 11 and 15b. Work done by Xu *et al.* [51] found that increasing the reaction temperature from 80°C to 100°C led to an increase in crystallite size from 5.6 to 6.2 nm. These results match current theories about grain growth, especially with respect to the ripening process of nanoparticles.[52, 53] In order to reduce grain growth, reactions should therefore be performed at lower temperatures and shorter reaction times.



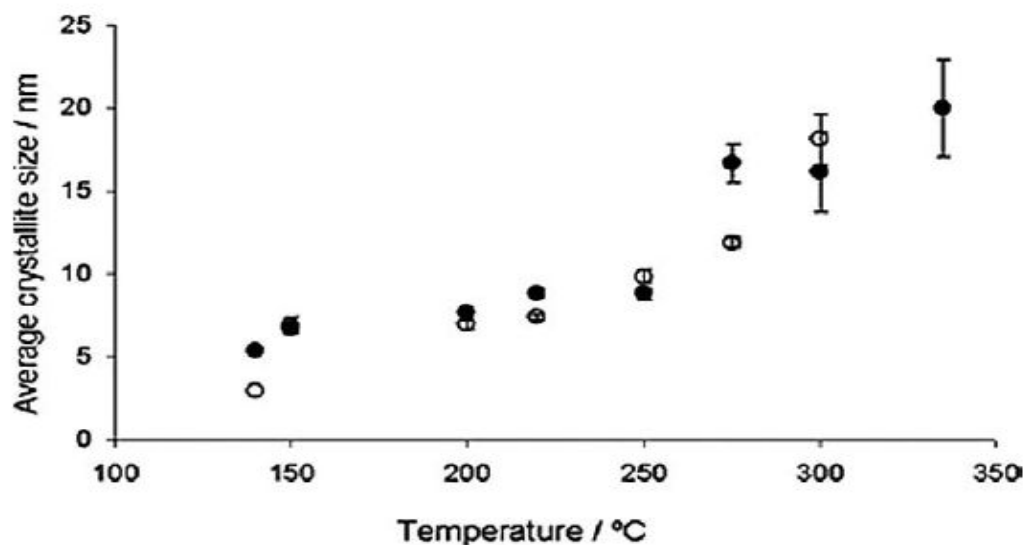


Figure 11 - Effect of reaction temperature on average grain size of solvothermally prepared anatase for hydrolysis ratios of  $r = 20$  (●) and  $r = 5$  (○). Samples were prepared using a  $\text{Ti}(\text{OEt})_4$  concentration of  $0.02 \text{ mol L}^{-1}$  and a total reaction time of 2 h. [52]

Both Kim *et al.* [54] and Kongsuebchart *et al.* [12] have proposed that the concentration of titanium in the reaction mixture directly influences the size of the resulting nanostructure. Kim *et al.* have shown that an increased ratio of titanium:solvent tended to increase the nanoparticle size, but there was a limit on the smallest amount of precursor that could be used to make the nanoparticles, figure 12a, thus an optimum concentration of titanium isopropoxide precursor could be determined. Xu *et al.* [51] showed that increasing the ratio of TC:acetone from 1:30 to 1:15 resulted in crystallite sizes of 6.2 and 8.6 nm respectively. Additional studies by Moon *et al.* [55] and Dutta & Rao [56] also confirm that an increase of crystallite size results with increasing titanium concentrations in the reaction mixture. It is therefore generally accepted that having relatively large amounts of titanium precursor allows for more pronounced growth and nucleation of the crystallites, leading to an increase in size.

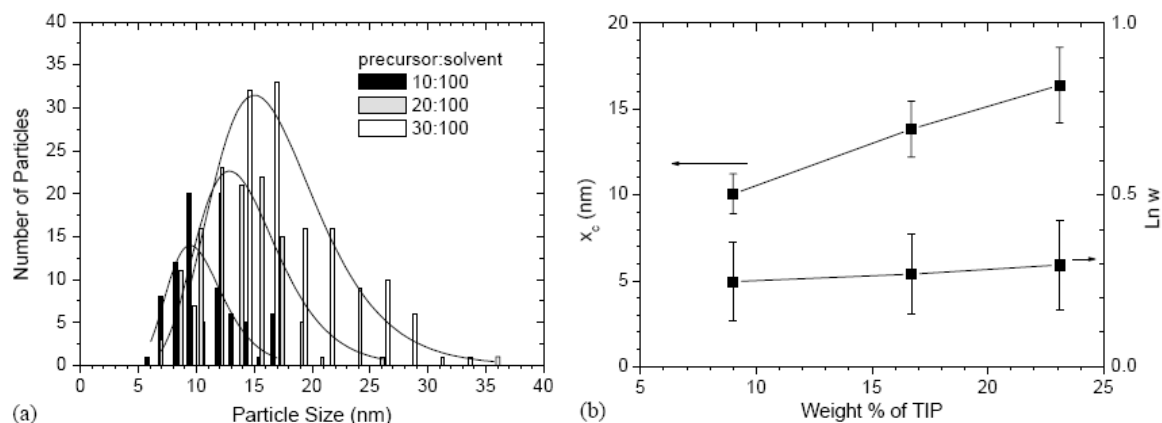


Figure 12 - (a) Distribution of particle size of  $\text{TiO}_2$  particles synthesized by solvothermal route in solutions with different composition of precursor, which is measured by a ruler from TEM images. (b) Fitted parameters with the lognormal function as a function of weight percentage of TIP in the solution. [56]

During solvothermal treatments, the addition of surfactants to the solvent mixture has also been shown to influence the size and the size distribution of the resultant nanoparticles; for example, by increasing the amount of surfactant (tert-butylamine) used in their solvothermal synthesis, Pan *et al.* [50] demonstrated a clear increase in the particle size. On the other hand, Yin *et al.* [57] found that changing the solvent from water (hydrothermal) to methanol (solvothermal) led to a decrease in the nanoparticle size. Both acidic and basic conditions have also been used in an attempt to manipulate crystallite size, table 2, with Gray *et al.* [16] using various nitric acid concentrations to control the size, obtaining a crystallite size of 9 nm using 45 mmol nitric acid solution.

| Volume of tert-butylamine<br>(ml) | Size of $\text{TiO}_2$ nanocrystals<br>(nm) |
|-----------------------------------|---------------------------------------------|
| 0.01                              | 3.6                                         |
| 0.1                               | 4.5                                         |
| 0.8                               | 7.2                                         |

Table 2 – Table shows synthesized nanocrystal with varying amount of tert-butylamine [51]

**3.4.2. Effect of Crystalline Phase.** The different characteristics and stability of each of the  $\text{TiO}_2$  phases, means that obtaining a single pure crystalline phase can be quite difficult. Solvothermal syntheses in essence provide the means to finely control the experimental conditions and thus to isolate specific phases; however in practice mixed phase products are often obtained. This has been investigated by various groups, leading to claims that reaction temperature, pH, precursor

concentrations and solvent all directly affect the nature of the TiO<sub>2</sub> product. However, there remains wide-spread opinion as to which parameters of the parameters dominate the selection for crystalline phase, or indeed the combination of factors thereof, calling upon further work to identify a general mechanism which truly reflects the formation of each particular phase. Whilst most solvothermal syntheses of TiO<sub>2</sub> nanomaterials has resulted in mixed-phase products, there have been some examples in which single, pure crystalline phases were obtained. Yang & Gao [58] obtained rutile particles using two titanium precursors, TC and titanium tetrabutoxide (TB) and went on to suggest that to increase the yield of rutile in a mixed-phase product, the ratio of titanium tetrachloride to titanium tetra-butoxide should be increased, table 3.[58]

| Sample | TC : TB | Temperature (°C) | Phase | Diameter (nm)    |
|--------|---------|------------------|-------|------------------|
| A      | 1:4     | 140              | A+R   | 7.5 (A), 10 (R)  |
| B      | 1:3     | 180              | R+A   | 63.1 (R), 25 (R) |
| C      | 1:2     | 180              | R     | 11.5             |
| D      | 1:1     | 180              | R     | 63.1             |
| E      | 1:2     | 110              | A+R   | 6.7 (A), 4.9 (R) |
| F      | 1:2     | 140              | R     | 31.7             |
| G      | 1:2     | 220              | R     | 34.4             |

Table 3 – Result obtained by [60] from XRD result

Rutile formation is thought to be influenced by the acidity of the precursor solution; in the studies conducted by Yang & Gao,[58] TC acts as a Lewis acid, whilst Li & Gray,[59] varied the acidity of the precursor solution by the addition of hydrochloric acid. During the preparation of the precursor solution, increased HCl:Ti ratios resulted in an increased tendency to form rutile. This idea of acidity favouring rutile formation has also been observed by other workers; Yin *et al.* [60] found that rutile is favoured at pH < 2 and with long chain alcohols, whilst Li & Gray [59] suggested that chloride ions and water molecules may act as charge-shielding agents, inhibiting the growth of the rutile phase, which conflicts somewhat with the idea of pH being a direct means to control the formation of rutile.

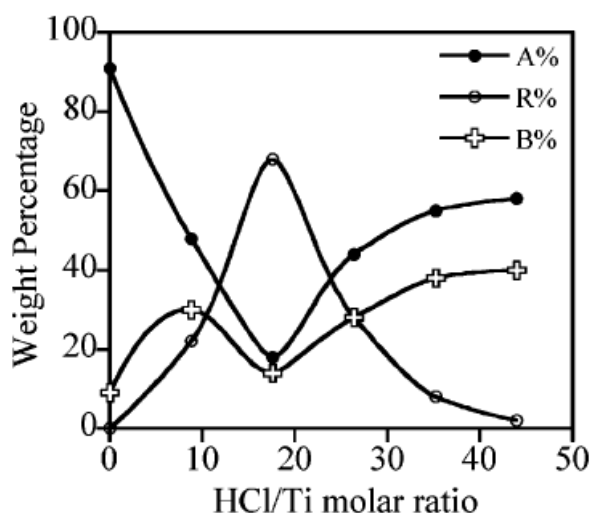


Figure 13 - Crystal structure of mixed-phase  $\text{TiO}_2$  nanocomposites after sintering at 773 K as a function of HCl/Ti ratio during solvothermal processing. (A) anatase, (R) rutile, (B) brookite). [61]

Li & Gray [59] also reported that the competition between the precipitation of brookite and anatase is dependent upon the ratio of water:Ti in the precursor solution, whilst Yin *et al.* [57] found that anatase was promoted by increasing the solubility of titanium precursor in the solvent, prior to solvothermal treatment. In addition to this, they also found that the formation of anatase is linked to the presence of methanol and high concentrations of ammonia; the ammonia is believed to delay the phase transformation from anatase to rutile, whilst brookite is favoured by the suppression of the rutile and anatase with the use of methanol.[60]

It is known that the solvothermal reaction temperature plays a great role in determining the phase of the  $\text{TiO}_2$ , with the thermodynamic transformation of anatase to rutile occurring at around 650°C.[32] Accordingly, it has been found that anatase and brookite phases generally form at lower solvothermal reaction temperatures and that as the reaction temperature is increased, the fraction of rutile in the mixed phase samples tends to increase. Bottcher *et al.*[25] attempted solvothermal syntheses at 100°C and 120°C but were unable to form any crystalline phases, whilst Yang & Gao [58] found that temperatures below 140°C yielded mixed-samples of anatase and rutile. At reaction temperatures above 140°C however, only rutile was obtained, figure 14.

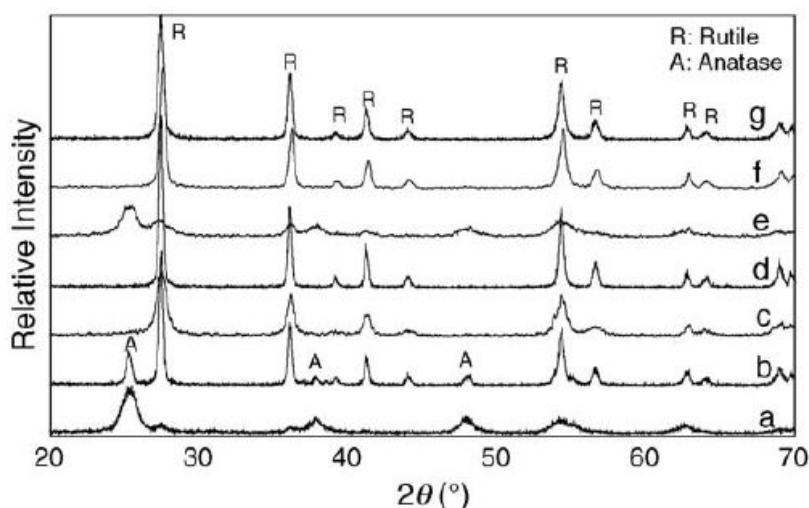


Figure 14 - XRD patterns of (a) sample A ( $r = 1:4$ ,  $140^{\circ}\text{C}$ ), (b) sample B ( $r = 1:3$ ,  $180^{\circ}\text{C}$ ), (c) sample C ( $r = 1:2$ ,  $180^{\circ}\text{C}$ ), (d) sample D ( $r = 1:1$ ,  $180^{\circ}\text{C}$ ), (e) sample E ( $r = 1:2$ ,  $110^{\circ}\text{C}$ ), (f) sample F ( $r = 1:2$ ,  $140^{\circ}\text{C}$ ), and (g) sample G ( $r = 1:2$ ,  $220^{\circ}\text{C}$ ). [60]

**3.4.3. Types of Solvothermal  $\text{TiO}_2$  Nanostructure.** Nanostructures such nanoparticles, nanorods, nanowires/nanofibres and thin films of  $\text{TiO}_2$  have been reportedly synthesised from the solvothermal route, along with others. It is unknown whether all these  $\text{TiO}_2$  nanostructures have the same physical properties or not and so their relative merits for potential use in photocatalytic applications remains unknown. One way to overcome this is to selectively synthesise each of these nanostructural types, in order to assess the relative merits of each under application-specific conditions.

**3.4.3.1. Nanoparticles.** Spherical  $\text{TiO}_2$  nanoparticles obtained via solvothermal routes have been widely investigated, often as a result of the ease of synthesis. Many groups have devised methods to synthesize  $\text{TiO}_2$  by using typical titanium precursors such TTIP, TB and TC under various experimental conditions. Kim *et al.* [54] used TTIP and toluene as the solvent in solvothermal reactions at  $250^{\circ}\text{C}$  over 3 h., resulting in anatase nanoparticles with diameters of 11-19 nm, figure 15a. Kongsuebchart *et al.* [12] used TB in toluene at  $300^{\circ}\text{C}$ , with varying reaction times, obtaining anatase nanoparticles, having diameters ranging from 9-15 nm, figure 15c. Li & Gray [59] used an unconventional solvothermal procedure in which TTIP and a weakly acidic ethanol mixture was refluxed at  $100^{\circ}\text{C}$  for 22 h. to obtain nanoparticles, whilst Rao & Dutta [61] concluded that in order to favour the formation of nanoparticles, low reaction temperatures, short reaction times or low precursor ratio are required.

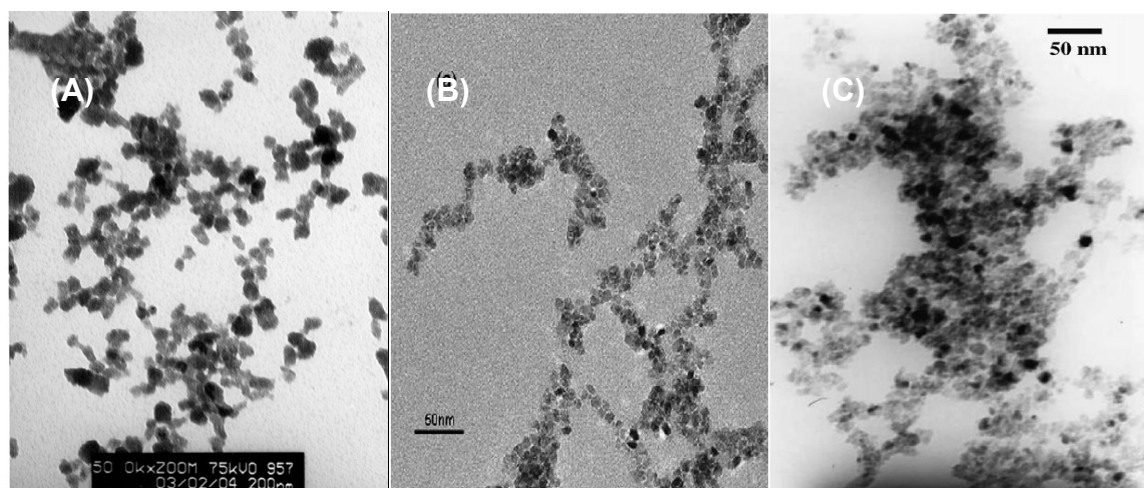


Figure 15 – (A) TEM micrograph of nanoparticle from [54], (B) TEM images of anatase nanoparticles from [52] & (C) TEM micrograph of nanoparticles prepared by [14]

More recently, doped  $\text{TiO}_2$  nanoparticles have been synthesised with the aim of improving the photocatalytic activity by lowering the band-gap, or to increase the superhydrophilicity. Reports of  $\text{TiO}_2$  doping with group III (Al), group V (N) and lanthanide ions are aimed to perturbing the electronic bands, altering the photo-absorption spectrum.[60, 62, 63] One advantage of using a solvothermal approach is that the doping can be performed in-situ and not as a discrete step, as the dopant is one of the reagents added in to the precursor solution prior to treatment. Kang [62] made up precursor solutions consisting of ethanol, TTIP, aluminium isopropoxide and nitric acid (to control pH), which were then solvothermally treated at  $200^\circ\text{C}$  for 10 h., resulting in nanoparticles with diameters of 47-53 nm and exhibiting a contact angle of  $60^\circ$ , figure 16. After UV irradiation, the contact angle was found to be less than  $1^\circ$ , indicating a very high degree of superhydrophilicity.

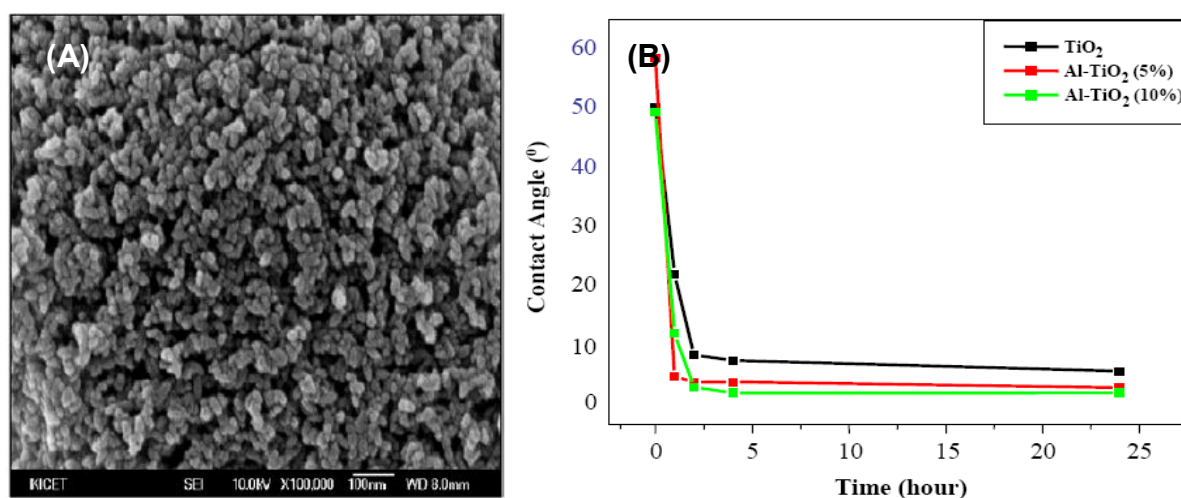


Figure 16 – (A) FESEM image of 10 wt% Al- $\text{TiO}_2$ , (B) Contact angle for water droplet on Al- $\text{TiO}_2$  [63]

Nitrogen doping in solvothermal reactions has been achieved by Yin *et al.*[60] with a urea-alcohol system in which TC, urea and various alcohols were treated in a two-step heating process, 90°C for 1 h. and then 190°C for 2 h. Meanwhile, lanthanide doping has been performed by both Falcomera *et al.*[63] and Moon *et al.*[64] Falcomera *et al.* used lanthanide ions ( $\text{Eu}^{3+}$ ,  $\text{Er}^{3+}$  or  $\text{Sm}^{3+}$ ) in ethanol, with acetic acid and TB in a reaction at 150°C for 3 h., resulting in nanoparticles with an average size of 16 nm. The doping led to a distorted and disordered octahedral Ti environment in the spherical anatase particles. Moon *et al.* by contrast, used terbium nitrate pentahydrate as the dopant precursor, producing nanoparticles having diameters of 6.7-10.2 nm. The prevalence of nanoparticles resulting from solvothermal reactions indicates that a variety of different solvent systems, titanium precursors, reaction times and solvothermal temperatures can be used and that spherical particles are relatively stable across a large range of conditions.

**3.4.3.2. Nanorods.** The solvothermal synthesis of nanorods has been reported by several groups; however the mechanism of formation is still not fully understood. Despite this, research continues to investigate the potentially unique properties and may yet lead to potential applications. Kim *et al.*, [65] used a similar solvothermal method to that used in the synthesis of nanoparticles, but upon the addition of a surfactant such as oleic acid, it resulted in the formation of nanorods. They found that certain conditions must be met before nanorods are formed; these conditions are that the molar ratio of precursor:surfactant needs to be more than 1:3 and the weight ratio of precursor:solvent should be in excess of 1:10. These workers were also able to obtain dumbbell shaped nanorods, preferentially orientated along the [001] axis. Yang and Gao [58] have made nanorods by using two titanium precursors, TC and TB, mixed with distilled water and benzene. The reagents were placed into an autoclave and held at a range of temperatures between 111 and 220°C for 22 h. They found that at 180°C, nanorods were produced that were arranged in a petal-like arrays, figure 17b. However, at higher temperatures such as 250°C, the same reaction mixture resulted in free-standing nanorods, figure 17a.

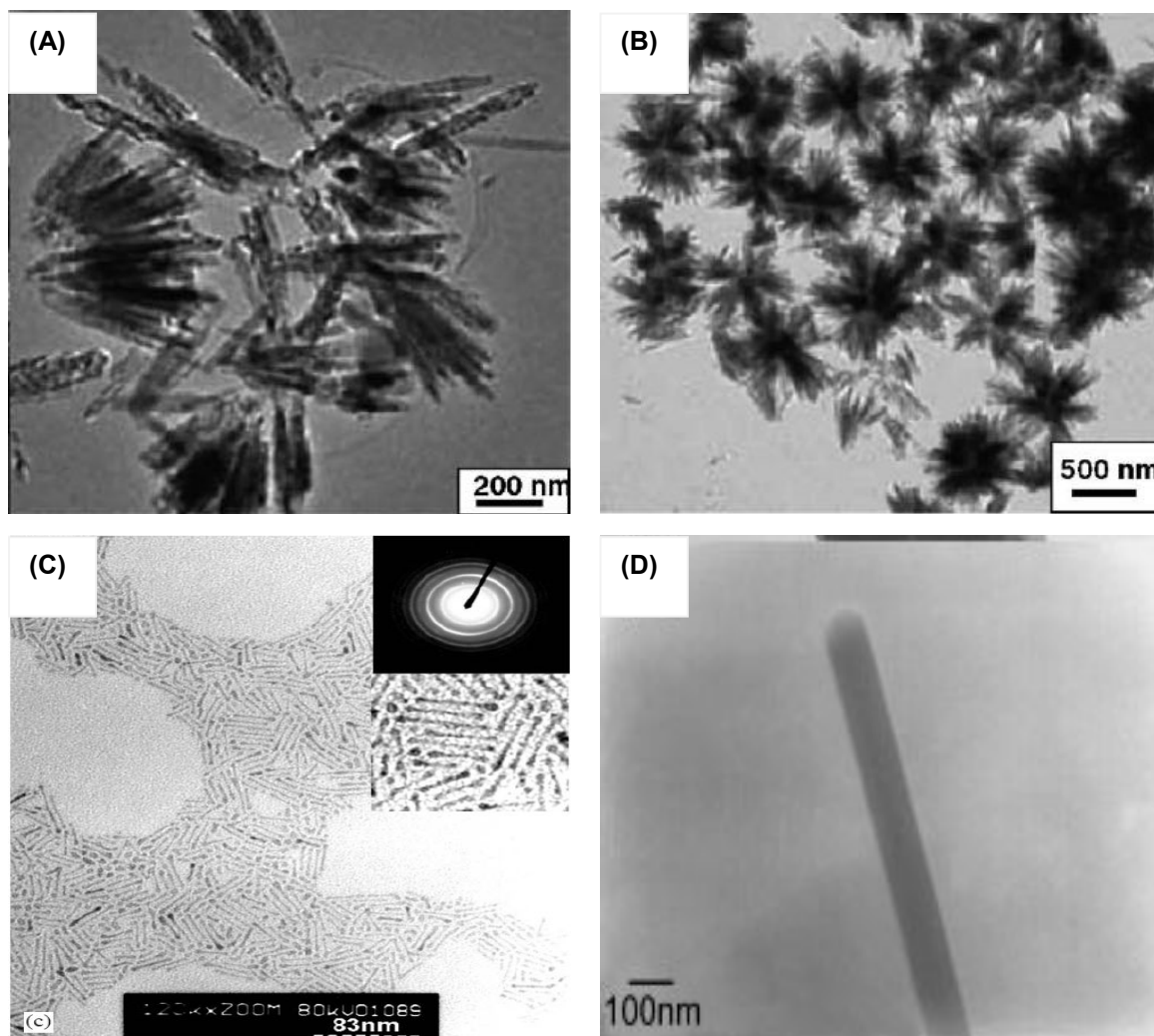


Figure 17 – (A) TEM micrograph of free-standing nanorods, (B) TEM micrograph of nanorods in flowerlike structure [58], (C) TEM micrograph & electron diffraction pattern of dumbbell nanorods [66], (D) LR-TEM micrograph of titania nanorods [67]

In contrast, Wen *et al.*[66] used commercially-available Degussa P25  $\text{TiO}_2$  powder, mixed with aqueous sodium hydroxide and an organic reagent (ethanol, diethanolamine or glycerol). These were placed in an autoclave at 170-200°C for between 12 and 24 h., producing nanorods with an interplanar spacing of about 0.35 nm, with the growth directed along the [001] direction, figure 17d. A single-phase anatase nanorod was synthesized by Xu and Yu [67] by the hydrothermal treatment of H-titanate fibres; this reaction was controlled by altering the reaction temperature and acidic pH. Repeated photocatalytic testing showed that these nanorods can be cycled 15 times and to have a high photocatalytic activity due to the high aspect ratio of the nanorod.

**3.4.3.3. Nanowires/Nanofibres.**  $\text{TiO}_2$  nanowires or nanofibres maybe of interest for use in the semiconductor industries and so optimisation of the bulk synthesis of such nanowires of may be considered to hold specific application-led interests. Yin *et al.*[57] used tetratitanate ( $\text{H}_2\text{Ti}_4\text{O}_9 \cdot 0.25\text{H}_2\text{O}$ ) as the titanium precursor dispersed in methanol or water, placed in an autoclave



and heated for 1 h. The resultant nanofibres were about 200 nm in diameter in both water and methanol solvents. Meanwhile, Wang *et al.*[68] used TC dissolved in primary alcohols, sealed in autoclaves at 100 or 160°C for 24 h. From the primary alcohols tested, n-butanol gave fibres of rutile and isopropanol produced tenuous anatase fibres, at 100°C. More recent research by Wen *et al.*[23] has led to the doping of TiO<sub>2</sub> nanowires with silver to make heterojunctions; by mixing TB, ethanol, aqueous sodium hydroxide and trace amounts of silver nitrate and solvothermally treated in an autoclave at 200°C for 24 h. The TEM images and selected area electron diffraction patterns indicate that the nanowires had diameters of 50-100 nm and lengths of up to few millimeters and consisted of anatase and polycrystalline silver. In addition TEM micrographs showed that the nanowires appeared to contain knots and even to resemble a bamboo-like structure, figure 18b.

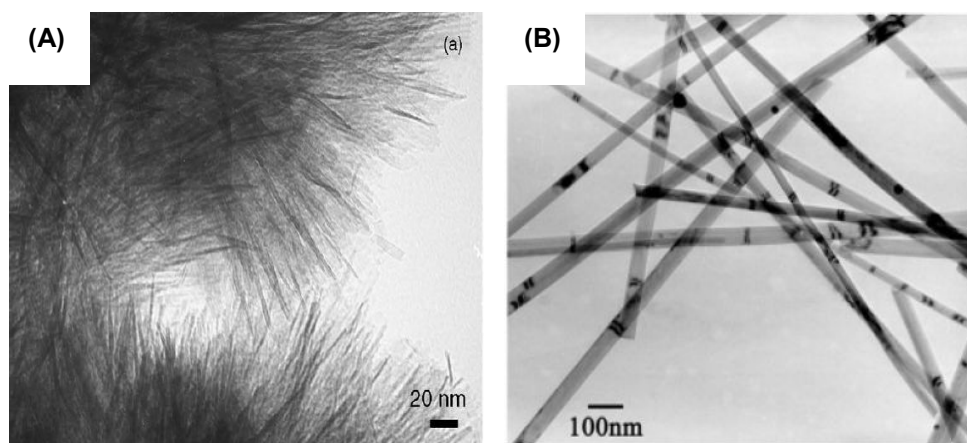


Figure 18 – (A) TEM micrograph nanowires from [59], (B) TEM micrograph of bamboo-shaped Ag-doped TiO<sub>2</sub> nanowire [23]

Xie and Shang [69] have been able to control the morphology of the nanostructures by using ethylenedamine (EDA) as a growth inhibitor, alongside the reaction temperature. Increasing the concentration of EDA with respect to the TTIP led to the synthesis of thinner nanowires, nanorods and fibres with mesoscale ordering. By increasing the temperature and EDA concentration, 2-D and 3-D structures could be synthesized as the nanostructure thermodynamically acts to minimise its surface area.

**3.4.3.4. Thin Films.** Thin films of TiO<sub>2</sub> nanomaterials show promise in applications such as solar panels and other photocatalytic applications such as self-cleaning surfaces. Again, solvothermal reactions leading to films may be beneficial due to the manufacturing process potentially being much lower cost than some other methods. However, thin films produced for these applications must be obtained with precise control over the thickness and uniformity of the film. Lee *et al.*[70] produced thin films by dip coating pyrex glass slides into a colloidal TiO<sub>2</sub> solution prepared via a solvothermal route in which TTIP was mixed with water, hydrochloric acid and butanol and then

heated at 200°C for 50 minutes. In a comparison between films formed by sol-gel and solvothermal routes, these workers reached the conclusion that the solvothermal method produced an anatase thin film of greater uniformity, lower thickness and greater stability.[70] Template-assisted [42, 43] and electrochemical [71] methods of synthesizing thin films of highly ordered nanostructured TiO<sub>2</sub>, such as arrays of aligned tubes, are very advantageous. However, these approaches suffer from the fact that high temperature annealing process are usually required, which can then significantly alter the crystalline phase of the TiO<sub>2</sub>. Despite some notable successes, solvothermally synthesized titania thin films have not been widely investigated to date, and so definitive conclusions on the relative benefits of the approach in this area are very difficult to make.

**3.4.3.5. Mesoporous Nanostructures.** Many research groups have investigated the use of mesoporous nanostructures in order to obtain large surface areas leading to high photocatalytic activities. Li *et al.* [72] have synthesized mesoporous titania spheres from the solvothermal treatment of titanium sulphate in various solvents in calcination reactions at 550°C over 3h. The resulting spheres have an urchin-like morphology which was found to enhance the photocatalytic activity by the multiple reflection of the UV-light within the voids of the complex morphology. Liu *et al.* [73] obtained mesoporous and microporous TiO<sub>2</sub> by ultrasonically treating the solvothermal product of tetrabutyltitanate with octadecylamine as a surfactant template. Despite the mesoporous nanostructures being shown to be poorly crystalline, they were found to exhibit superior photocatalytic activity due to the increased specific surface areas. Stroyuk *et al.* [74] synthesized mesoporous TiO<sub>2</sub> with the incorporation of copper, nickel and silver dopants having surface areas of 130-140 m<sup>2</sup>/g and pore diameters 5-9 nm.

## 4. Systematic Study of Growth Mechanisms

We have performed systematic studies of the reaction characteristics in the solvothermal synthesis of TiO<sub>2</sub> nanostructures. The aim has been to arrive at a detailed understanding of the mechanistic pathways present under the reaction conditions, which should then lead to a means of tailoring the synthesis to specific morphologies. We have noted a number of dependencies in our reactions that are highlighted below.

#### 4.1. Size of Nanoparticles

**4.1.1. Solvent.** A clear relationship has been established between the average crystallite size of the nanostructured material and the length of the alcohol hydrocarbon chain used as a solvent in the solvothermal synthesis, figures 19 and 20. The use of methanol resulted in average crystallite size of 6.45 nm, which was found to increase to 16.7 nm upon changing the solvent to decanol, with intermediate alcohols leading to crystallite sizes between these limits. This provides a clear demonstration that the average crystallite size of the nanostructure is directly related to the chain-length of the solvent. The rationale for this behaviour is that the solvent acts to restrict the diffusion of nucleating Ti-O particles, which then inhibits the growth of large particles in the presence short-chain alcohols. The shorter alcohols achieve this by effectively surrounding the Ti-O nucleation sites, which due their size, form a compact interface to further growth; the polarity of the solvent aids the formation this barrier, or solvation shell, around the proto-TiO<sub>2</sub> lattice. The solvent thereby acts to restrict seeded growth of TiO<sub>2</sub> crystallites, or particle ripening growth mechanisms. The longer chain solvents are both relatively more bulky and significantly less polar as a result of the increased length of the hydrophobic component. These aspects result in a lower affinity for the solute, or a more diffuse and weakly-bound solvation shell. A consequence of this is that the longer chain solvents do not form an effective barrier for the crystallite growth mechanisms, leading to larger overall crystallite sizes.

**4.1.2. Reaction Time and Temperature.** A range of reaction times (3-48 h.) and temperatures (150-230°C) have been investigated and found to have significant effects on the extent of crystallite growth and particle size. It can be clearly seen in figures 19 and 20 that increased temperatures and reaction times tend to increase the average TiO<sub>2</sub> crystallite size. As more energy is applied to the solvothermal reaction, either through higher temperatures and/or longer reaction times, particle growth is favoured as it acts to reduce the integrated surface interfacial energy, which thermodynamically offsets the decrease in entropy on moving to larger crystallites. This observation is in accord with established models of particle growth such as Ostwald and digestive ripening.[53]

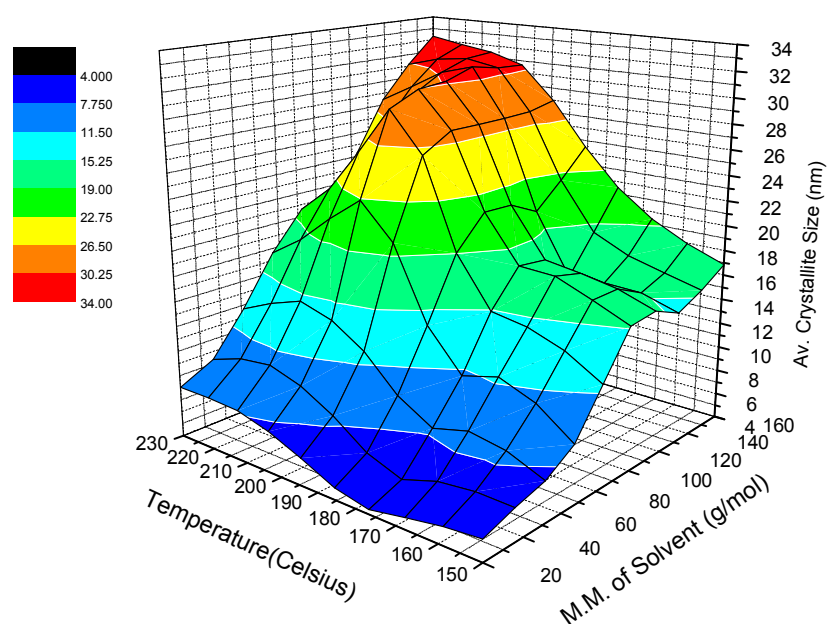


Figure 19.  $\text{TiO}_2$  synthesized with variation of alcoholic solvent and temperature

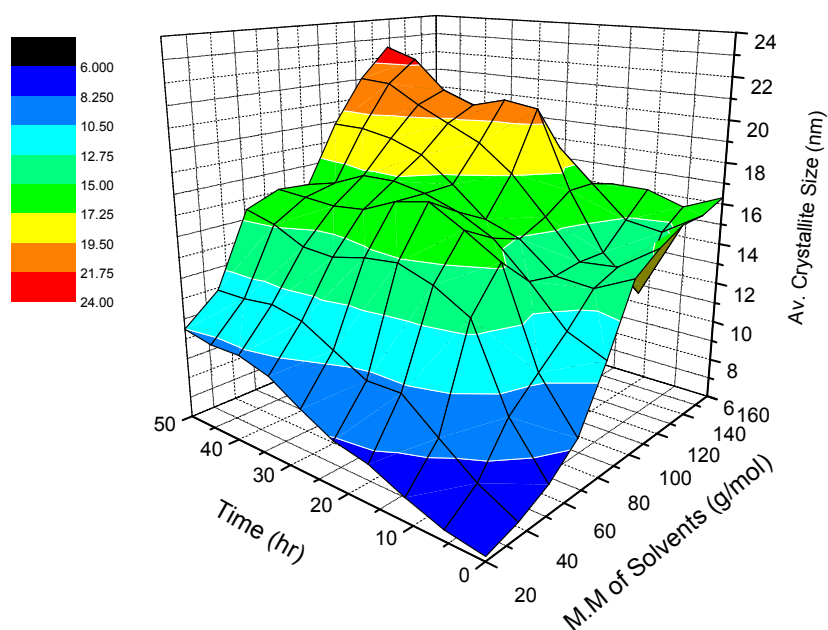


Figure 20.  $\text{TiO}_2$  synthesized with variation of alcoholic solvent and time

#### 4.2. Crystalline Phase.

Just as with the crystallite size, a definite relationship between the alcohol chain length, reaction temperature and reaction time are important parameters in determining the crystalline phase of the nanostructured material, figures 22 and 23. Clearly reactant diffusion is a crucial aspect of phase

determination; in this case it is the diffusion of both solvent molecules and charged species that act as shielding, or blocking agents in the  $\text{TiO}_2$  nucleation processes. Longer solvent chains were found to lead to an enhancement of rutile formation over anatase; the opposite was found to be the case with short-chain solvents. Chloride ions, which are formed in-situ from the decomposition of the TC precursor, act as charge-shielding agents which suppress rutile formation. Of the two dominant phases, anatase, having the lower-density structure, is favoured by mechanisms that directly perturb nucleation, i.e. small charged species such as chloride ions and small solvent molecules. Meanwhile the lower diffusion rates of chloride ions in long-chained solvents, reduces the extent of charge-shielding, permitting the  $\text{Ti}^{\text{m}+}$  and  $\text{O}^{\text{n}-}$  species to diffuse together and nucleate. Thus, the ensuing growth of the titania lattice is less strained, promoting the formation of rutile, the higher density phase. Upon formation of the anatase lattice, hydrogen ions are liberated from the alcohol groups which then undergo acid attack of the Ti-O bonds in the nucleating anatase phase, leading to reactive vacant coordination sites on the Ti atoms within the lattice, figure 21. Depending upon the chain length of the solvent molecules, these vacant coordination sites are then susceptible to solvent attack, with shorter chained solvents being sufficiently small to enter into the reactive pocket, forming the di-hydroxide intermediate. With subsequent dehydration, this then leaves to the anatase structure intact. However, longer-chained solvents are too large to access the reactive vacant coordination sites and so the Ti-O bonds undergo conformational change upon relaxation from the protonated intermediate hydroxide, resulting in the formation of the higher density phase, rutile.

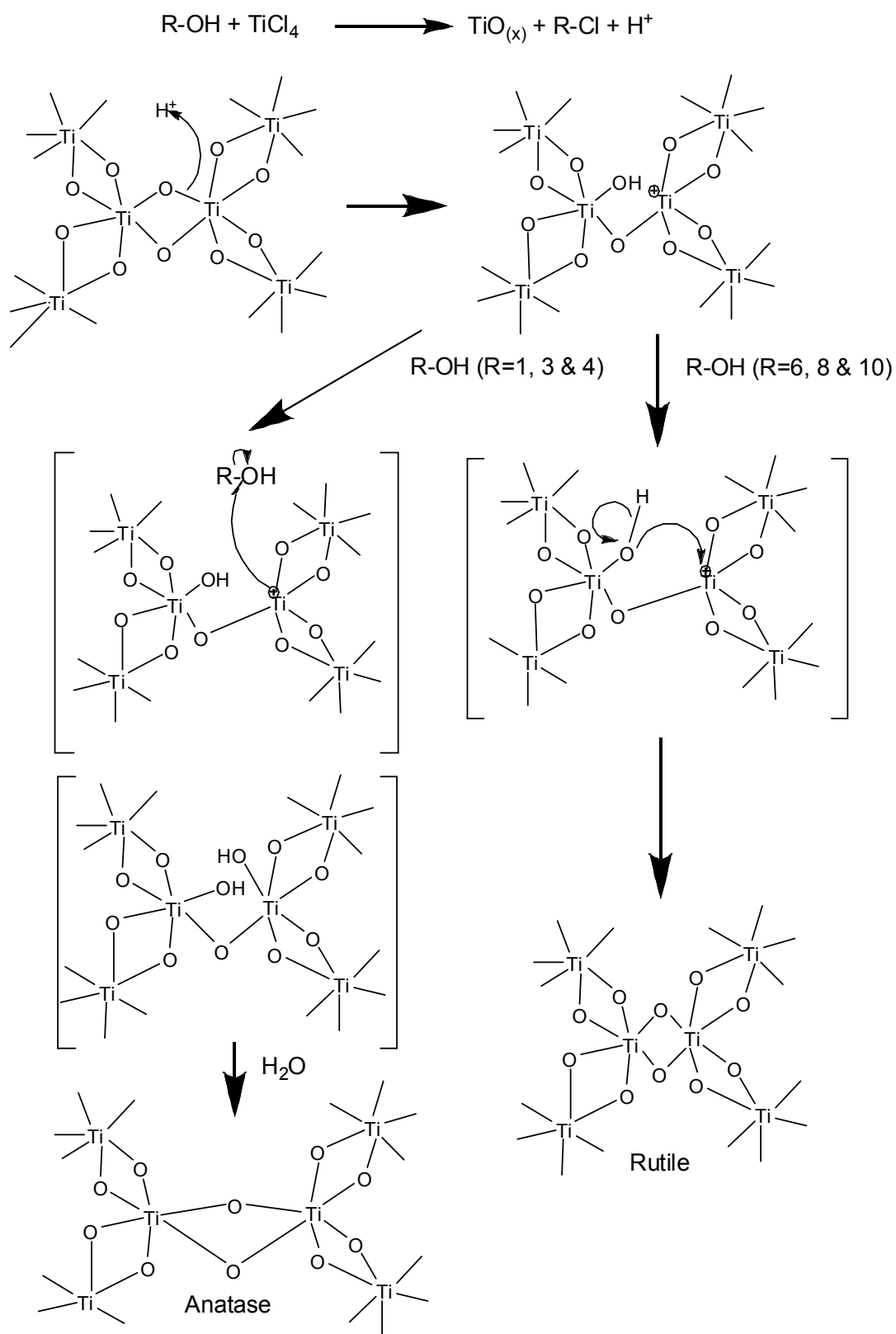


Figure 21 – Mechanism of formation of anatase and rutile with varied solvent length

Higher reaction temperatures and times have been observed to favour the formation of the more thermodynamically stable rutile phase, with anatase favoured at lower temperatures and short reaction times. This observation is also accounted for by the diffusion controlled nucleation of charge shielding agents and precipitation of  $\text{TiO}_2$ . As a result of greater degrees of diffusion (either via higher temperatures or extended times), the increased diffusion of the chloride ion limits its interference with Ti-O bond formation or reformation, resulting in a less strained crystal structure. This would then favour the formation of densely packed rutile structure rather than the strained anatase structure, as observed.

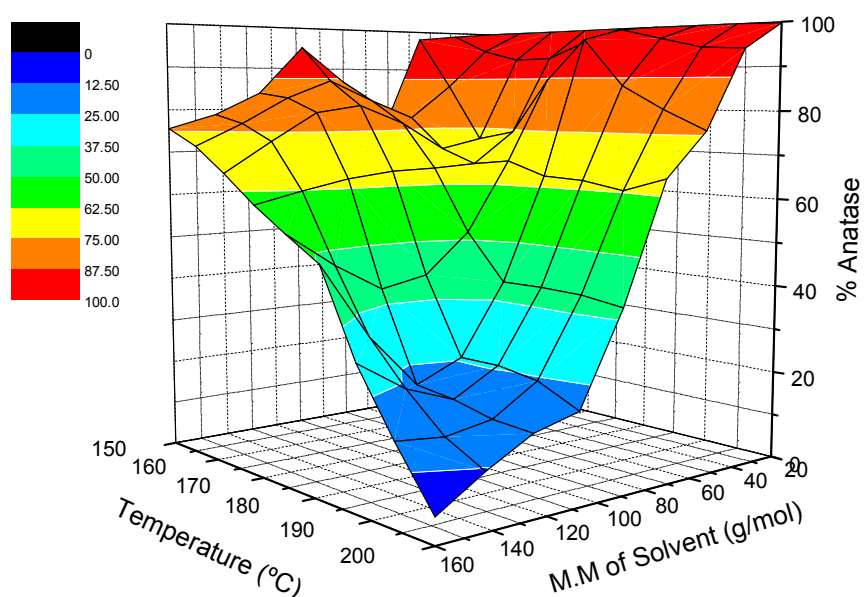


Figure 22. Percentage anatase formation with variation in alcoholic solvent and temperature

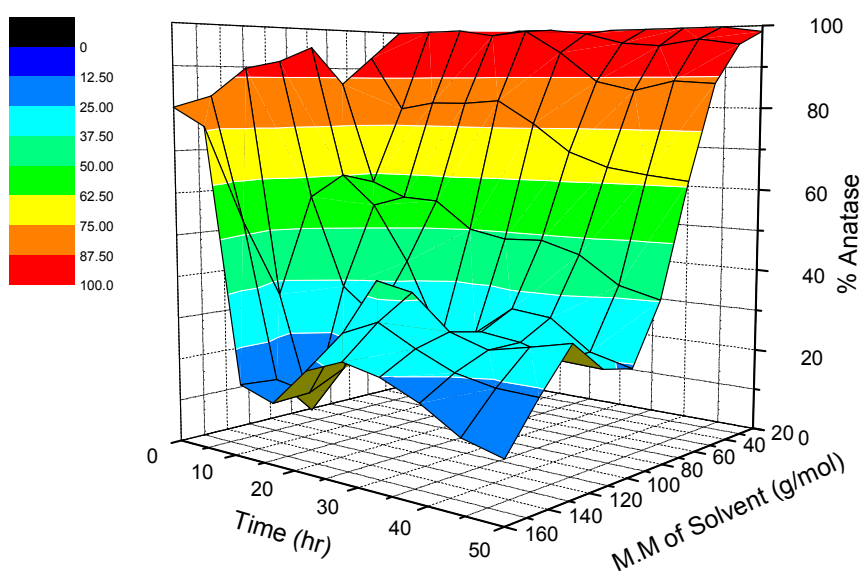


Figure 23. Percentage anatase formation with extended period of reaction time and alcoholic solvent

### 4.3. Nanostructured Morphology

We have found that control of the nanomorphology can be achieved simply by altering the chain-length of the solvent, the reaction temperature, or the reaction time. The formation of spherical nanoparticles is promoted when the  $\text{TiO}_2$  particles have restricted diffusion, either energetically or physically. Nanostructures of higher dimensionality then form when  $\text{TiO}_2$  nanoparticles come together in ripening processes. The relationship between the observed morphology and solvent chain length, suggests that an increase of the solvent chain length results in higher dimensionality of the nanostructures. The use of short chain-solvents, leading to increased solvation trapping of  $\text{TiO}_2$  particles, inhibits particle ripening and so only low dimensional structures such as nanoparticles and nanocubes are obtained. Longer solvents however, promote the formation of higher dimensionality; in this case,  $\text{TiO}_2$  particles are allowed agglomerate and hence the formation of structures such as nanorods and nanofibres. At lower temperatures and decreased reaction times, the products are predominantly low-dimensional nanoparticles and nanocubes. The rationale here is at these lower temperatures and shorter reaction times, the diffusion of  $\text{TiO}_2$  particles is restricted, thus favouring the formation of smaller nanostructures. With respect to thermodynamics, smaller nanostructures are favoured due to lower energy reaction pathways meaning that isolated nanoparticles will have less energy to nucleate together to form higher-order nanostructures. Solvothermal reactions at higher temperatures and over longer reaction times were found to generally result in large clusters of nanoparticles, nanorods and nanofibres. The higher energy pathway in this case, allows for a greater probability for the  $\text{TiO}_2$  nanoparticles to coalesce, forming higher dimensional nanostructures. In addition, the formation of nanorods and nanofibres is energetically favoured by the reduction of surface interfacial energies.

## 5. Conclusion

From the literature review it is evident that whilst, the synthesis of  $\text{TiO}_2$  nanostructures via solvothermal synthesis may be a simple experimental procedure, precisely controlling the resultant product remains problematic. Numerous experimental conditions still need to be refined before commercially viable solvothermal routes to  $\text{TiO}_2$  of prescribed nanostructures can be realised, as the morphology, whether it be nanoparticles, nanowires, nanorods or even thin films, is directly linked to the experimental parameters. In addition to this, further research is also required in the application of  $\text{TiO}_2$  nanomaterials, that may then lead to their application in processes incorporating the oxidative, electrical or photocatalytic properties of this remarkable material.



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## Photocatalytical Properties of TiO<sub>2</sub> Nanotubes

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### Abstract

Titanium dioxide (TiO<sub>2</sub>) nanotubes have been reported one decade ago and have proven to be of a great interest in photocatalytic water splitting, as well as gas sensing and anti-bacterial/cancer treatment. This paper presents an overview on general preparation approaches (chemical treatment, template method and anodic oxidation) of tubular TiO<sub>2</sub> nanoarchitectures and their characterization. Current applications of the nanotubes as photocatalysts are also reviewed.

### 1. Introduction

Since the discovery of photocatalytic water splitting on titania (TiO<sub>2</sub>) by Fujishima and Honda in 1972, the interest in TiO<sub>2</sub> as a photocatalyst for purification of groundwater and wastewater is growing [1-6]. The effective photoexcitation of TiO<sub>2</sub> photocatalysts requires the application of light with energy higher than its band-gap energy [7,8], thus resulting in the formation of electrons (e<sup>-</sup>) in the conduction band and positive holes (h<sup>+</sup>) in the valence band. Excited state electrons and holes can recombine and then dissipate the input energy as heat, get trapped in metastable surface states, and react with electron donors/acceptors. If a suitable reductant (electron donor) or oxidant

(electron acceptor) is available to trap the hole or electron, recombination is prevented and subsequent photocatalytic reactions may occur efficiently on the semiconductor surface. Actually, photocatalytic reactions may occur by either directly via the valence-band hole or indirect oxidation via the surface-bound hydroxyl radicals (i.e., a trapped hole at the particle surface reacts with  $\text{HO}^-$  or  $\text{H}_2\text{O}$  to be transformed into  $\bullet\text{OH}$ ) [9]. The  $\bullet\text{OH}$  radicals produced by  $\text{TiO}_2$  are one of the most powerful oxidizing species with an oxidation potential of 2.80 V [10,11]. Unlike other radicals, hydroxyl radicals are non-selective and thus readily attack a large group of organic chemicals to be hydroxylated or form partially oxidized intermediates. At sufficient contact time and proper operation conditions, it is practically possible to mineralize the target pollutants to  $\text{CO}_2$ . The remarkable advantage of semiconductor photocatalysis over all chemical and biological processes is that they are totally “environmentally friendly” as they neither transfer pollutants from one phase to the other (as in chemical precipitation, adsorption and volatilization) nor produce massive amounts of hazardous sludge [12].

In this general mechanism, electron transport is a limiting factor in the photocatalytic performance of  $\text{TiO}_2$  materials, while the structure of  $\text{TiO}_2$  is a crucial factor in the influence of electron transport. The structural disorder at the contact between two crystalline nanoparticles leads to enhanced scattering of free electrons, thus reducing electron mobility [13]. In contrast, an ordered and strongly interconnected nanoscale architecture offers the potential for improved electron transport leading to higher photoefficiency. This has resulted in one-dimensional  $\text{TiO}_2$  materials, such as nanowires, nanorods and hollow nanotubes, receiving a great deal of attention in recent years [14,15]. Among these materials, hollow  $\text{TiO}_2$  nanotubes that have surface area-related properties can further improve photocatalytic properties because they demonstrate a superior electron transport.

## 2. Definition of $\text{TiO}_2$ nanotubes

$\text{TiO}_2$  nanotubes (TNTs) are tubular nanomaterials and exhibit unusual strength, unique optical properties and interesting semiconducting properties. The defined geometry results in special diffusion paths not only for entering the tubular depth (e.g., reactants to be transported into tubes)

but also for species to be transported through the tube wall (e.g., electrons, holes and ions). Also, the hollow structure can potentially enhance electron percolation and light conversion, as well as the improved ion diffusion at the semiconductor-electrolyte interface [14,16]. Therefore, the nanotubular  $\text{TiO}_2$  materials are expected to great potential applications in electronics, optics, catalysis, energy storage/conversion, and biomedicine. A timeline showing the development and application of TNTs is shown in Fig. 1.

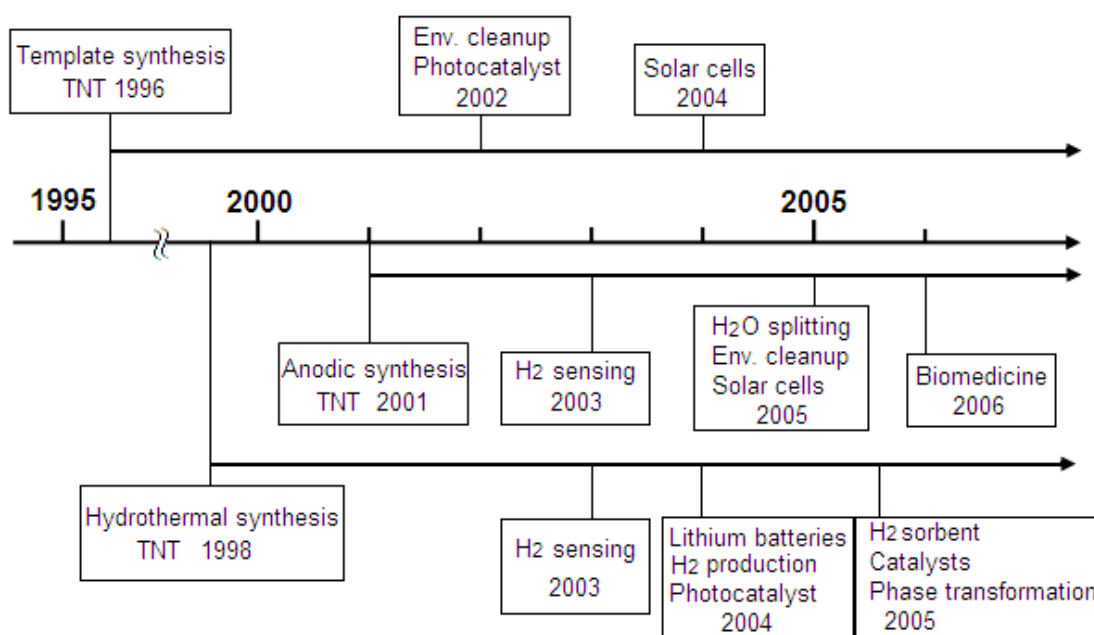


Figure 1. Timeline describing the development of  $\text{TiO}_2$  nanotubular structures.

Due to the wide range of applications, the feasibility to produce self-organized TNT nanostructures has received huge scientific and also significant technological interest. In this paper, we therefore attempt to give an overview of some of the underlying principles governing TNT-photocatalysis (the known properties and surface modifications) and to review the current literature in terms of potential environmentally friendly applications.

## 2. Fabrication of TNTs

To date considerable efforts have been devoted to the preparation of various nanotubular  $\text{TiO}_2$  catalysts by mainly the template-assisted method, chemical treatments of fine  $\text{TiO}_2$  particles and electrochemical anodic oxidation of pure titanium sheet. There are respective advantages and limitations in each of the above-mentioned methods.

### 2.1 Alkaline hydrothermal synthesis

TiO<sub>2</sub> nanotubes can be easily fabricated by hydrothermal treatment of crystalline TiO<sub>2</sub> (anatase, rutile, brookite or their mixture) with highly concentrated NaOH. This method generally produces the nanotubes as small as 10 nm (see Fig. 2) and can derivate different crystal structures apart from the formation of anatase TiO<sub>2</sub> nanotubes. For example, some titanate structures, such as A<sub>2</sub>Ti<sub>2</sub>O<sub>5</sub>•H<sub>2</sub>O [18], A<sub>2</sub>Ti<sub>3</sub>O<sub>7</sub> [19], H<sub>2</sub>Ti<sub>4</sub>O<sub>9</sub>•H<sub>2</sub>O [20], and lepidocrocite titanates [21], have been assigned as nanotube constituents (A = Na and/or H). Such discrepancy demonstrates the need for further investigation on this subject although many groups have tried to analyze the structure of the resulting nanotubes. The mechanism of nanotube formation is also under debate, however, there is a common agreement that after breaking of chemical bonds in the starting tridi- mensional TiO<sub>2</sub> structure, layered entities (2-D) are formed and converted into nanotubes (1-D) through a sheet folding mechanism [22,23].

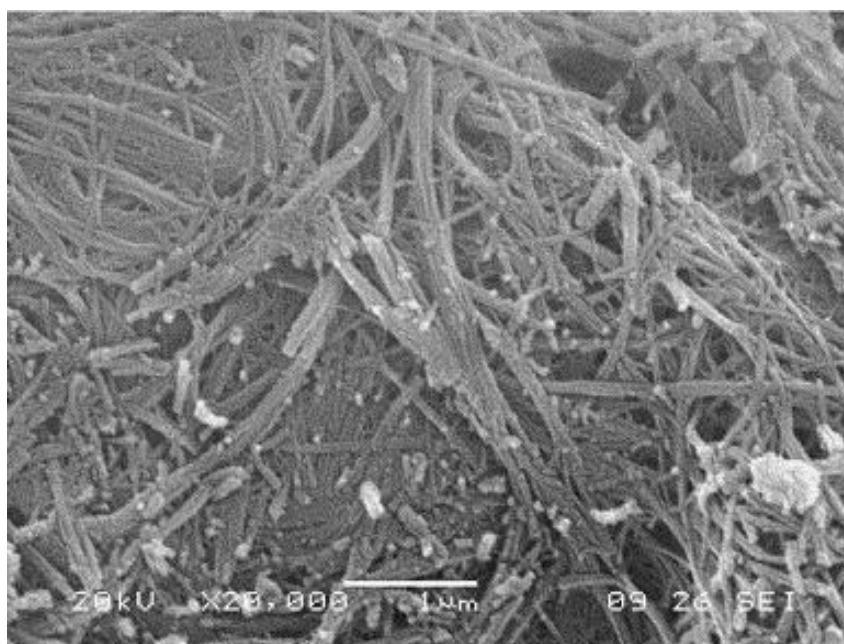


Figure 2. SEM image of the hydrothermal-synthesized nanotube product. Reprinted from ref [17].

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On the other hand, it is widely recognized that the NaOH treatment and post-treatment washing seem to significantly affect the formation and transformation of nanotubes. Knowledge of this transformation could significantly extend the application of this specifically featured material. Table

1 summarizes the nanotube structures proposed by different preparation conditions, which generally involved NaOH treatment, followed by post-treatment washing. The data suggest that the post-treatment was a critical step for nanotube formation. For example, Nakahira et al. [20] characterized the hydrothermal TNT sample as a tetratitanic acid  $H_2Ti_4O_9 \cdot H_2O$ . However, Jin and co-workers [18] proposed the following crystal structure of titanate nanotubes:  $H_2Ti_2O_4(OH)_2$  with an orthorhombic unit cell. Both protons of the bititanic acid could be ion exchanged with sodium ions. These results indicate that the acidity in the post-treatment washing plays a key role in determining the structure of the nanotubes.

Table 1. Nanotube structures prepared from different processes [24].

| Precursor                                                                      | NaOH treatment <sup>a</sup> | Post-treatment  | Refs. |
|--------------------------------------------------------------------------------|-----------------------------|-----------------|-------|
| <i>Nanotube Structure: Anatase <math>TiO_2</math></i>                          |                             |                 |       |
| anatase                                                                        | hydro/110/20                | HCl + water     | [25]  |
| rutile                                                                         | chem/110/20                 | HCl + water     | [26]  |
| anatase                                                                        | chem/150/12                 | water           | [27]  |
| anatase                                                                        | hydro/110/20                | $HNO_3$ + water | [28]  |
| anatase/rutile                                                                 | hydro/130/24                | HCl             | [24]  |
| <i>Nanotube Structure: Anatase <math>TiO_2/H_2Ti_3O_7 \cdot 0.5H_2O</math></i> |                             |                 |       |
| rutile                                                                         | chemi/110/4 <sup>b</sup>    | $HNO_3$ + water | [29]  |
| <i>Nanotube Structure: <math>A_2Ti_2O_5 \cdot H_2O</math></i>                  |                             |                 |       |
| $TiO_2$ powder                                                                 | chem/110/20                 | HCl + water     | [30]  |
| anatase                                                                        | chem/110/20                 | HCl + water     | [18]  |
| <i>Nanotube Structure: <math>A_2Ti_3O_7</math></i>                             |                             |                 |       |
| anatase                                                                        | hydro/130/72                | HCl + water     | [19]  |
| anatase                                                                        | hydro/130/72                | HCl + water     | [31]  |
| any crystals                                                                   | hydro/130/72                | water           | [32]  |
| anatase                                                                        | hydro/180/24                | HCl + water     | [33]  |
| rutile                                                                         | hydro/150/72                | HCl + water     | [23]  |
| <i>Nanotube Structure: <math>H_2Ti_4O_9 \cdot H_2O</math></i>                  |                             |                 |       |
| anatase/rutile                                                                 | hydro/110/96                | HCl + water     | [20]  |
| <i>Nanotube Structure: Lepidocrocite Titanates</i>                             |                             |                 |       |
| anatase                                                                        | hydro/150/48                | HCl + water     | [22]  |

<sup>a</sup> Treatment conditions refer to chemical or hydrothermal processes, temperature (°C) and duration (h), respectively.

<sup>b</sup> Sonication at 280 W before chemical treatment.



## 2.2 Template-assisted synthesis

Template replication technique has been widely used to produce nanoscopic pieces of material in a particular shape [34]. This method utilizes the morphological properties of characterized template materials to construct other materials with a similar morphology by methods including reactive deposition and dissolution. In principle, this approach is a versatile method for synthesizing nanomaterials with controllable size, morphology and structure. The tubule of the desired material is obtained within the pores of templates. However, the template material has to be sacrificial and generally needs to be removed after synthesis. Anodically formed porous alumina oxide (AAO) usually is used as a template due to the uniform pore size, high pore density together with relative ease of their preparation [35-37]. The synthesis of TNTs by AAO-templating usually involves the sol-gel hydrolysis of  $\text{Ti}^{4+}$ -containing compounds in the presence of templating agents, followed by deposition of  $\text{TiO}_2$  into or onto the template aggregates. Further reaction causes bonds to form between the sol particles and the gel is then typically heated to yield the desired material. In fact, the important part of the tubes is the free space in their interior. It is evident that the size of sol particles is smaller than that of the pore of AAO template for successfully extending into the  $\text{TiO}_2$  deposition. However, the irregular deposition and poor penetration of sol particles generally occurs. This is related to the surface charge of sol particles, when template pores establish surface charges impeding sol particles entering the pores. The next stage is selective removal of the templating agent. The AAO template can be partially or completely removed by chemical etching with acid or alkaline. After selective removal of alumina, the external diameter of the  $\text{TiO}_2$  hollow fibers corresponds to the diameter of the pores in the alumina.

It is worth noting that by the sol-gel template method, generally the tubular and fibrillar nanostructures within the template pores can be synthesized simultaneously and even an ensemble of nanostructures that protrude from a surface like the bristles of a brush could also be obtained [38]. For example, Martin and co-workers [39] reported that TNTs were obtained if the membrane is immersed into the sol for a brief period (5 s, Fig. 3a), whereas solid  $\text{TiO}_2$  fibrils were obtained after

long immersion times (60 s, Fig. 3c). Intermediate immersion times yield tubules with very thick walls (25 s, Fig. 3b).

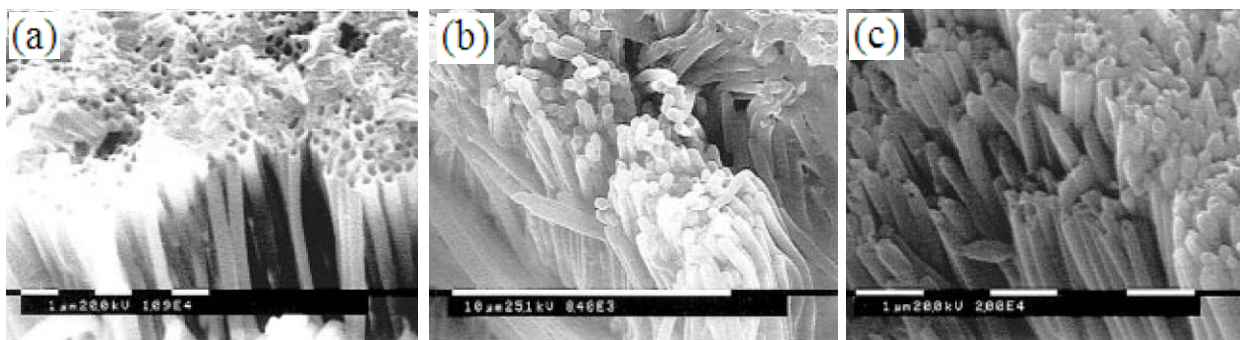


Figure 3. SEM images of  $\text{TiO}_2$  tubes and fibrils prepared in the alumina membrane. The sol was maintained at 15 °C, and the immersion time was varied from 5 to 60 s. (a) Immersion time) 5 s; (b) Immersion time) 25 s; (c) Immersion time) 60 s. Reprinted from ref [39]. Copyright 1997 American Chemical Society.

### 2.3 Anodic oxidation process

In 1991, Zwilling et al. [40] first reported the porous surface of  $\text{TiO}_2$  films electrochemically formed in fluorinated electrolyte by titanium anodization. A decade later Grimes and co-workers [41] synthesized the uniform and highly-ordered TNT arrays by anodic oxidation of a pure titanium sheet in a hydrofluoric acid (HF) aqueous electrolyte. The obtained nanotubes directly grew on the Ti substrate and were oriented in the same direction perpendicular to the surface of the electrode, forming a highly ordered nanotube-array surface architecture.

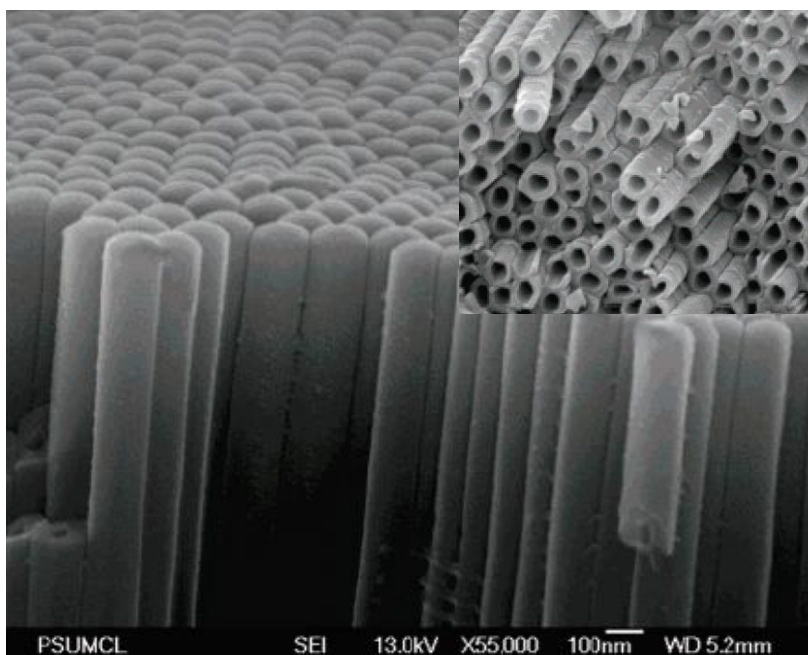


Figure 4. FESEM cross-sectional images of TNT samples. Sample was fabricated at 60 V in 0.25 wt %  $\text{NH}_4\text{F}$  ethylene glycol solution. Reprinted from ref [45]. Copyright 2006 American Chemical Society.

In the anodic oxidation process, the electrolyte composition is a critical determinant with regard to the resulting surface morphology, and hence properties of the anodic films. Besides the above-mentioned  $\text{HF}/\text{H}_2\text{O}$  electrolyte, other aqueous electrolytes ( $\text{KF}/\text{NaF}/\text{H}_2\text{O}$ ,  $\text{NH}_4\text{F}/\text{CH}_3\text{COOH}$  and  $\text{NH}_4\text{F}/\text{H}_3\text{PO}_4$ , etc) and nonaqueous electrolytes (fluorinated dimethyl sulfoxide (DMSO)/ethanol,  $\text{NH}_4\text{F}$ /glycerol, etc) have been developed to prepare TNT arrays [42-45]. In aqueous electrolytes, the length of obtained nanotube arrays is usually less than 500 nm while in nonaqueous organic polar electrolytes,  $\text{TiO}_2$  nanotubes can reach a 134  $\mu\text{m}$  of length and generally have a smooth outer tubewall (see Fig. 4).

To have a better understanding in anodic TNTs, Mor et al. [16] proposed a mechanistic model for the nanotube array formation, as shown in Fig. 5. With the onset of anodization, a thin oxide layer is developed on the titanium surface (Fig. 5a) and then undergoes the localized dissolution to form

small pits (Fig. 5b). The localized dissolution behavior not only produces a thinner barrier layer at the bottom of the pits but also permits the barrier layer further pore growth (Fig. 5c). The electric field distribution in the curved bottom surface of the pore causes pore widening, as well as the pore deepening. As the pores become deeper the electric field in these protruded metallic regions increases enhancing the field-assisted oxide growth and oxide dissolution, hence simultaneously with the pores well-defined inter-pore voids start forming (see Fig. 5d). Thereafter, both voids and tubes grow in equilibrium. The nanotube length increases until the electrochemical etch rate equals the chemical dissolution rate of the top surface of the nanotubes.

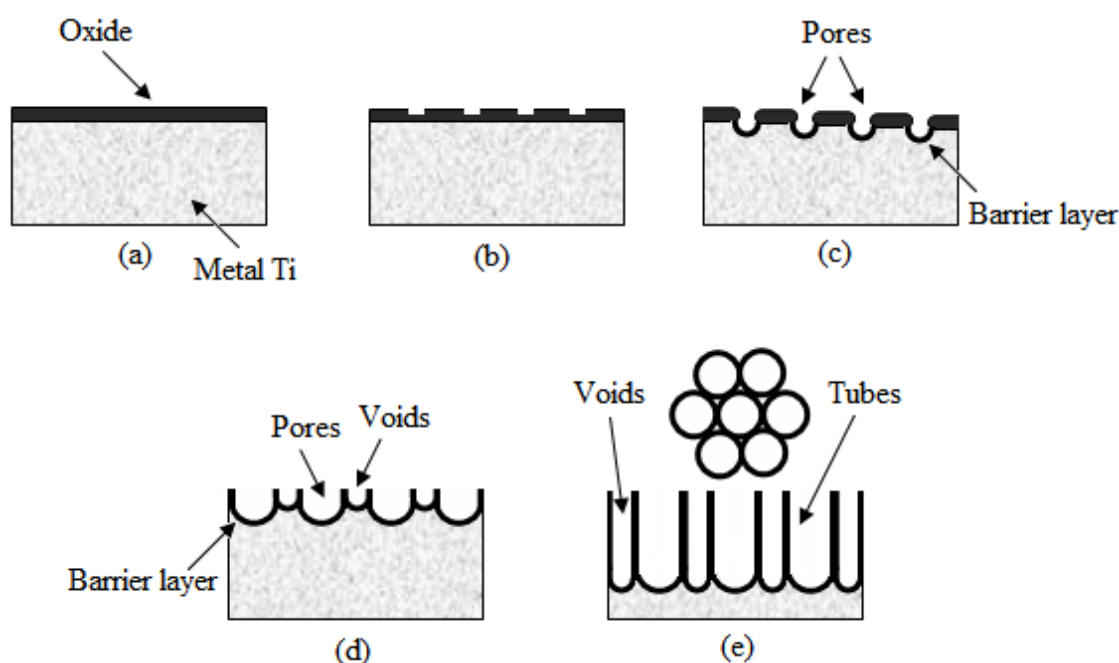


Figure 5. Schematic diagram of the evolution of nanotube arrays at constant anodization voltage: (a) oxide layer formation, (b) pit formation on the oxide layer, (c) growth of the pit into scallop shaped pores, (d) metallic part between the pores undergoes oxidation and field assisted dissolution, and (e) fully developed nanotube arrays with a corresponding top view. Reprinted from ref [16]. Copyright 2006 Elsevier.

## 4. Characteristics of TNTs

### 4.1 Textural properties

It is widely accepted that photocatalytic reactions occur on the surface of catalyst in contact with substrates, where reactant molecules must be first adsorbed by photocatalysts. This indicates that photocatalytic efficiency is significantly influenced by the physicochemical properties of photocatalysts like crystalline structure, surface area, surface acidity, and surface functional groups. Among these factors, a high surface area can be one of the most important factors in certain photocatalytic reactions, as a large adsorption capacity of photocatalysts can promote the reaction rate [46-48]. When compared to  $\text{TiO}_2$  powders, TNT catalysts have a higher specific surface area making a higher photoactivity.

Table 2 summarizes the pore structures and special surface area of various TNT catalysts with comparison of Degussa P25  $\text{TiO}_2$ . The commercial P25 powder is known to be very fine with a particle size of 25–30 nm, a porous surface of 0.092 pore volume and have a special surface area of  $\sim 50 \text{ m}^2 \text{ g}^{-1}$ , while the lab-made TNT catalysts generally present a big difference in these textural properties. For example, the hydrothermal-synthesized TNT samples (TNT-H) the BET specific surface areas range from 200 to  $400 \text{ m}^2 \text{ g}^{-1}$ , 4-8 times higher than that of P25; pore volume is also significantly greater than that observed for Degussa P25. In addition, these specimens usually have a very small tubewall thickness of 2-3 nm, which can be thought to be a key factor for achieving the higher activity of the nanotube samples due to the feasibility of quantum size effect. Instead of, TNT-T and TNT-A samples show higher BET surface area (usually  $> 200 \text{ m}^2 \text{ g}^{-1}$ ) but thicker tubewall ( $\sim 20 \text{ nm}$ ). The different characteristic parameters of these samples to some extent reflect their intrinsic reaction behavior and respective photocatalytic performance.

Table 2. Comparison of textural properties between various TNTs and Degussa P25.

| Samples <sup>a</sup> | Pore volume<br>(cm <sup>3</sup> g <sup>-1</sup> ) | Pore size<br>(nm) | Thickness<br>(nm) | S <sub>BET</sub><br>(m <sup>2</sup> g <sup>-1</sup> ) | Ref. |
|----------------------|---------------------------------------------------|-------------------|-------------------|-------------------------------------------------------|------|
| Degussa P25          | 0.092                                             | 8.3               | 25-30             | ~50                                                   | [49] |
| TNT- H               | 0.89                                              | 10.3              | ~2                | 350.4                                                 | [50] |
|                      | 0.67                                              | 6.7               | ~2                | 404                                                   | [51] |
|                      | --                                                | ~5                | ~3                | 246                                                   | [52] |
|                      | --                                                | 6                 | ~2                | 200                                                   | [53] |
| TNT-T                | 0.16                                              | 3-11              | 20-60             | 95                                                    | [54] |
|                      | --                                                | 50-150            | 10-20             | 100-140                                               | [55] |
| TNT-A                | --                                                | 20-70             | ~22               | 285                                                   | [56] |

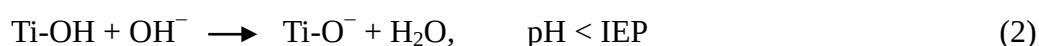
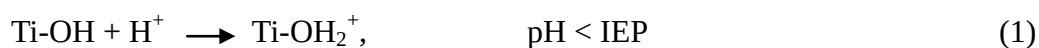
<sup>a</sup> Sample TNT-H, TNT-T and TNT-A was denoted as the material prepared by hydrothermal, template-assisted and anodic technique, respectively.

#### 4.2 Surface hydroxyl groups and surface charges

The surface hydroxyl (OH) groups of TiO<sub>2</sub> have been recognized to play an important role in the photocatalytic behavior, because they not only undertake the adsorption of reactant molecules but also directly participate in the reaction mechanism by trapping of photogenerated holes to form hydroxyl radicals [57-59]. However, there are quite limited reports in the determination of OH groups on the surface of TNTs. In 2006, Qian et al. [60] investigated the IR spectra of hydrothermally synthesized TNTs. They suggested that two sharp absorption bands at 1618 and 3423 cm<sup>-1</sup> were contributed to the deformation and stretching vibrations of OH group of physisorbed water in TiO<sub>2</sub>, respectively, while the shoulder at 3208 cm<sup>-1</sup> from Ti-OH bonds was ascribed to the strong interaction between Ti ions and OH groups. Actually, the defect structure of TNTs formed by oxygen vacancies favors the adsorption of water on the surface and then dissociates water into hydroxyl groups and protons [61-63]. This dissociation behavior leads to the charged surface of TNTs due to the loss or gain of protons and complexation reactions of surface hydroxyl groups [64,65]

Electrophoretic mobility is the most common technique for investigating the surface charges of the metal oxide/electrolyte solutions [66,67]. With this technique, the migration of suspended

particles is quantified under an electric field. The isoelectric point (IEP) position of  $\text{TiO}_2$  depends on the alkali–acid character of surface hydroxyl groups. At the IEP, there are no excess surface charges on  $\text{TiO}_2$  and the electrostatic interaction is minimum at this point. The dissociation reactions of surface hydroxyl groups are pH dependent and the acidity of the oxide can be related to the dissociation constants of the reactions. For example, when pH in the aqueous solution is lower than IEP,  $\text{Ti-OH}_2^+$  forms and the surface possesses positive charge, while if pH is higher than IEP,  $\text{Ti-O}^-$  forms and the surface possesses negative charge (see Eqs. 1 and 2). The lower isoelectric point in terms of the pH value means a higher concentration of hydroxide ions on the surface of the catalyst.



A lower isoelectric pH is associated with a more acidic surface, i.e., a higher affinity for protons and a more negatively charged surface. Table 3 listed that the IEP value of P25 presented in many papers is often divergent and mainly ranges from 6.2 to 6.9, while TNTs samples have an IEP value of 5.3–5.5. These results mean that the total amount of hydroxyl groups on the surface of TNTs is higher than that of P25. This hypothesis has been confirmed by comparing the FTIR spectroscopy and surface acidity of P25 and TNT materials [68–70].

Table 3. Comparison of Isoelectric point (IEP) between various TNTs and Degussa P25.

| Sample      | Isoelectric point | Ref.    |
|-------------|-------------------|---------|
| Degussa P25 | 6.2–6.9           | [71–73] |
| TNT-H       | 5.3–5.5           | [74,75] |
| TNT-T       | --                | --      |
| TNT-A       | ~5.3              | [76]    |

#### 4.2 Electrical properties

The photocatalytical properties of  $\text{TiO}_2$ , including TNT, are closely related to their reactivity and photoreactivity with water and, in some cases solutes in water. While the reactivity and photoreactivity are related to the commonly measured properties of photocatalysts, such as surface area, structure, microstructure, and chemical composition, these are determined by the ability of photocatalysts to donate or accept electrons during the photocatalytic reaction. The latter is related by the chemical potential of electrons,  $\mu_e$ :

$$\mu_e = \mu_e^0 + kT \ln[e^-]$$

where  $\mu_e^0$  denotes  $\mu_e$  in standard conditions,  $[e^-]$  is the concentration of electrons and  $kT$  have their traditional meaning.

The key quantities in the characterisation of photoelectrochemical performance of photoelectrochemical devices include the current-voltage characteristics and the efficiency of photocurrent-to-incident photon,  $E_{ff}$  (for specific wavelength). The latter may be determined from the following equation:

$$\text{Equation 2: } E_{ff}[\%] = \frac{i_{ph} E}{qP}$$

where  $i_{ph}$  is photocurrent density,  $E$  is photon energy,  $q$  is the elementary charge and  $P$  is the light density. The plots of  $E_{ff}^2$  vs  $E$  for the TNTs at different stages of the formation are presented in Fig. 6. This plot, indicating the effect of the procedure on  $E_{ff}$  allows to determine the band gap ( $E_g = 3.15$  eV), which appears to be independent of the experimental procedure and the related morphology.



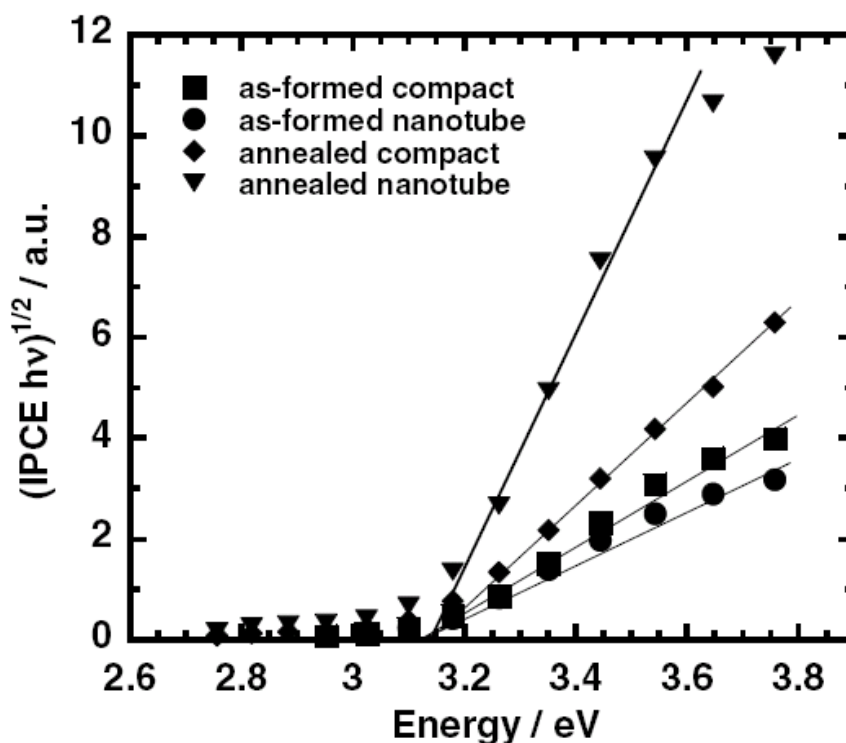


Figure 6.  $(\text{IPCE } h\nu)^{1/2}$  vs.  $h\nu$  plots for as-anodized compact and nanotube  $\text{TiO}_2$  and annealed nanotube  $\text{TiO}_2$ . Reprinted from ref [77]. Copyright 2006 Elsevier.

While the measurement of electrical properties done under static conditions (or in equilibrium) that may allow to assess the effect of processing on the concentration of electronic charge carriers (assuming that the mobility term remains constant), the transient measurement of photocurrent generated under light pulse may be used to assess the life time of the light-induced charge carriers [77].

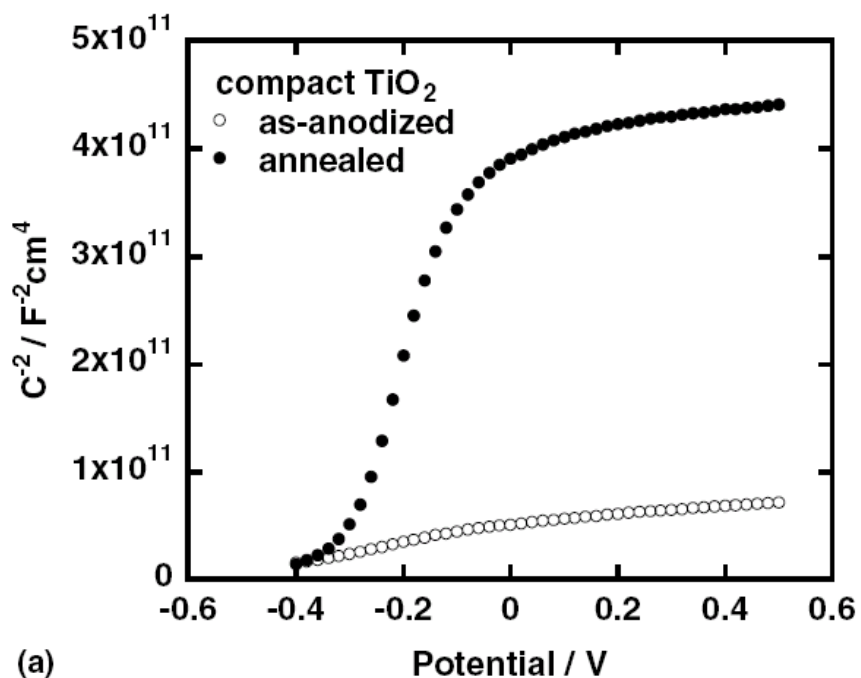
Essential information concerns the effect of processing on the flat band potential, FBP, which may be determined by the Mott-Schottky formula:

$$\text{Equation 3: } \frac{1}{C^2} = \frac{2}{\epsilon\epsilon_0 q N_{\text{sub}} D} \left( U - U_{\text{FBP}} - \frac{kT}{q} \right)$$

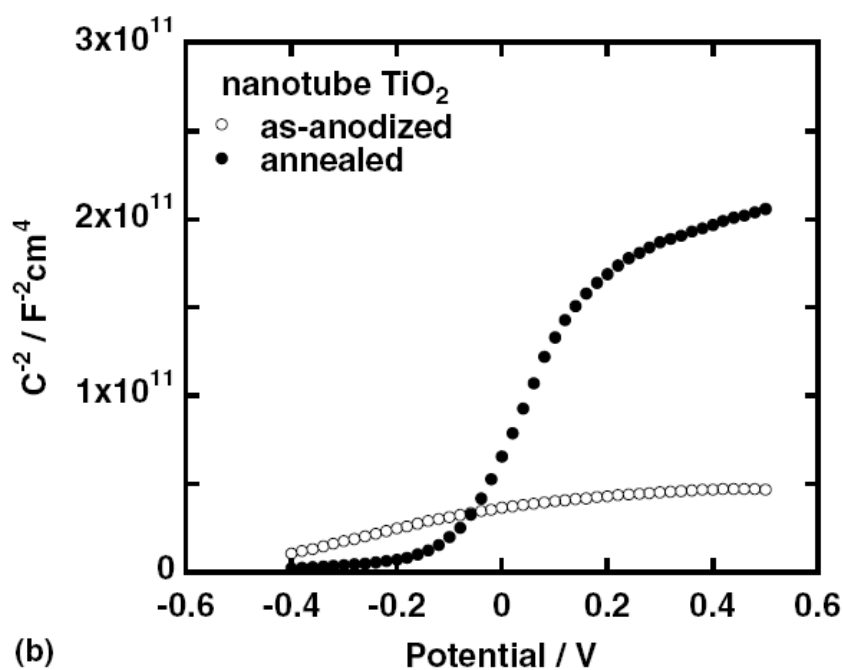
where  $C$  is the space charge capacitance ( $C'' = -1/\omega Z''$ ),  $\epsilon$  and  $\epsilon_0$  denote the dielectric constant in air and in vacuum, respectively,  $U$  and  $U_{\text{FBP}}$  is the applied potential and the FBP, respectively,  $N_D$  is

the concentration of donors (for n-type semiconductor), and the  $kT/q$  term assumes 25 mV at room temperature. The Mott-Schottky plots for  $\text{TiO}_2$  and TNTs (ignoring the capacitance of the Helmholtz layer) are shown in Fig. 7.

In summary, knowledge of electrical properties is essential in the interpretation of photocatalytic properties of  $\text{TiO}_2$ . The TNT is not an exception.



(a)



(b)

Figure 7. Mott-Schottky plots for (a) compact  $\text{TiO}_2$  and (b) nanotube  $\text{TiO}_2$  layer. Reprinted from ref [77]. Copyright 2006 Elsevier.

### 4.3 Optical properties

TNTs are achieved over a wide range of pore size, wall thicknesses, tube-lengths, and chemical composition, leading to different light absorption and photocatalytic properties [78,79]. The optical behavior of TNTs can be studied by measuring their UV-vis absorption, in which the characteristic absorption band of TNTs should be assigned to the intrinsic transition from the valence band (VB) to the conduction band (CB). In general, the TNT samples exhibit a similar absorption band shape in their UV-vis absorption spectra, as shown in Fig. 8. This phenomenon may be identified to be the sub-band gap states of TNTs due to the special nanotube structure. Their onset absorption always starts from 350-400 nm, corresponding the band gap energy of 3.1-3.5 eV when calculated with Kubelka-Munk function [80].

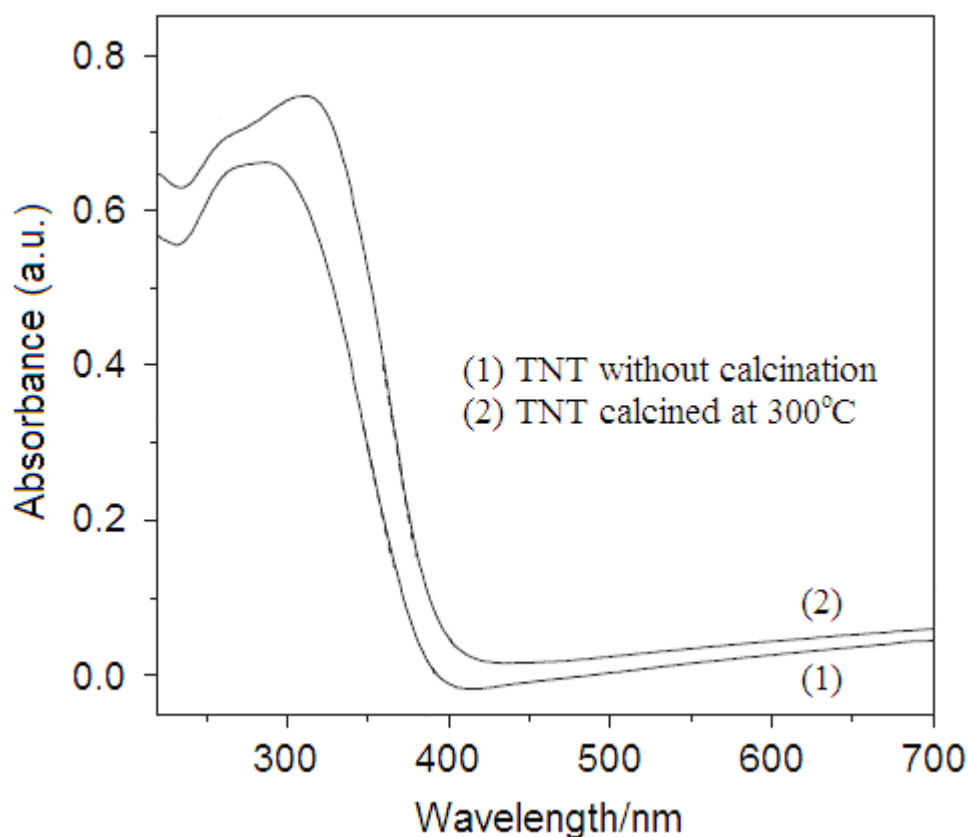


Figure 8. UV-visible absorption spectra of TNTs prepared by hydrothermal treatment. Reprinted from ref [81]. Copyright 2008 Springer.

Table 4 summarizes the onset absorption of TiO<sub>2</sub> P25 and TNTs with corresponding band gap energy. Compared the absorbance of bulk Degussa P25 (at over 400 nm), a blue shift of absorption<sub>onset</sub> with higher band energy (370-380 nm) for TNTs was clearly observed. The interpretation of the blue-shift is not clear so far. Many have attributed the blue-shift in the TNTs to a quantum-size effect [16,88]. However, others suggest that the absorption blue-shift observed for nanoparticles with diameters > 2 nm may be due to direct interband transitions in this indirect semiconductor [89]. Quan et al. [90] proposed that the significant blue-shift with higher band energy of TNTs compared with the TiO<sub>2</sub> particles may be due to the method of material preparation, crystal structure and the surface state. Comparison with the theory is difficult and proper understanding of the absorption behavior requires further study.

Table 4. Comparison of UV-vis absorption<sub>onset</sub> and band gap energy ( $E_g$ ) between various TNTs and Degussa P25.

| Sample      | Absorption <sub>onset</sub><br>(nm) | $E_g^a$<br>(eV) | Ref. |
|-------------|-------------------------------------|-----------------|------|
| Degussa P25 | 425                                 | 2.92            | [82] |
|             | 400                                 | 3.10            | [83] |
|             | 400                                 | 3.10            | [84] |
| TNT-H       | ~370                                | 3.35            | [85] |
|             | ~370                                | 3.35            | [84] |
| TNT-T       | ~370                                | 3.35            | [86] |
|             | ~375                                | 3.30            | [82] |
| TNT-A       | ~380                                | 3.26            | [77] |

<sup>a</sup> The band gap energy ( $E_g$ ) of materials was calculated according to the equation [87]:  $E_g = hc/\lambda \approx 1239/\lambda$ , where  $h$  is Planck's constant,  $c$  is the velocity of light (m/s) and  $\lambda$  is the wavelength of onset absorption (nm).

## 5. Surface modification of TNTs

Low-dimensional TNTs, since they naturally provide a direct path for electron transport, are suitable for an ideal photocatalyst under irradiation of UV light with wavelength shorter than that corresponding to its band gap energy (> 3.26 eV). However, the photocatalytic process using UV

radiation requires substantial electrical power input, leading to the increasing cost and complexity of practical application. From a viewpoint of solar energy utilization, developing photocatalysts capable of using more abundant visible light [4,91,92], which accounts for about 43% of the incoming solar energy, is indispensable.

In recent years considerable effort has been invested in improving the response of TNTs to visible light, mainly including the sensitization with dye [93,94] or polymer [95], loading with noble metal atom [96,97], and coupling with narrow band gap semiconductor [98,99]. In sensitized cases, charge injection from the CB of the narrowband gap semiconductor to that of TNTs can lead to efficient and longer charge separation by minimizing the electron–hole recombination. In noble metal doping cases, a p-n junction is formed between metal and semiconductor, which results in the decreasing electron–hole recombination and meanwhile produces more oxidizing species to undertake the photocatalysis. Another alternative approach is to couple TNTs by using a narrow band gap semiconductor, which absorbs light in the visible region and may be able to transfer electrons to the large band gap  $\text{TiO}_2$  semiconductor. Here, we review various types of modified TNTs so that the material responds more fully to visible light while maintaining the excellent charge transfer properties and chemical stability.

### 5.1 Dye or polymer-sensitization

Recently, many different sensitizers, including organic dyes and conductive polymers, were widely used in the research of dye-sensitized solar cells (DSSCs) [94,100,101]. This technique can lead to a substantial increase of light-to-electric energy conversion efficiency. Among a wide variety of dyes, polypyridyl complexes of Ru and Os with four pendant carboxyl groups, such as N719 dye ( $\text{N719} = [\text{tetrabutylammonium}]_2[\text{Ru}(\text{4-carboxylic acid-4'-carboxylate-2,2'-bipyridyl})_2(\text{NCS})_2]$ ) are the most efficient dyes [93, 102]. In 2007, Zhu et al. [103] found that the TNT-based DSSCs sensitized with N719 dye have a significantly higher light-harvesting efficiency than that of  $\text{TiO}_2$  particle-based DSSCs. However, so far there is quite limited literature involving

the use of dye-sensitized TNTs as photocatalysts in water treatment due to the nonstability of dye molecules in aqueous environment.

The conjugated polymers as photosensitizers such as polyaniline, polythiophene, polypyrrole, and their derivatives have shown excellent stability due to their extending  $\pi$ -conjugated electron systems. In a conjugated polymer/TiO<sub>2</sub> system, the polymer, bound to TiO<sub>2</sub>, can actively harvest the visible light matching the semiconductor energy levels, and then inject electrons into the conduction band (CB) of TiO<sub>2</sub>. A schematic diagram for the charge transfer processes of conjugated polymer and TiO<sub>2</sub> is illustrated in Fig. 9. Here, when the conjugated polymer harvests visible light, an absorbed photon promotes an electron from the ground state of the polymer located in the semiconductor energy gap into an excited state that is in resonance with the CB. The polymer  $\pi$ -orbital becomes the highest occupied molecular orbital (HOMO) in the combined system. Since the lowest unoccupied molecular orbital (LUMO) levels of the polymer are energetically higher than the conduction band edge of TiO<sub>2</sub> [104,105], the electron transfer paths in Fig. 9 are possible. Efficient electron injection into the edge of the CB avoids the energy loss by relaxation to the CB edge [106]. As a result, it should be a vital prerequisite for photosensitization that the interfacial charge transfer between the photosensitizer and the semiconductor takes place, being capable of responding to visible light.

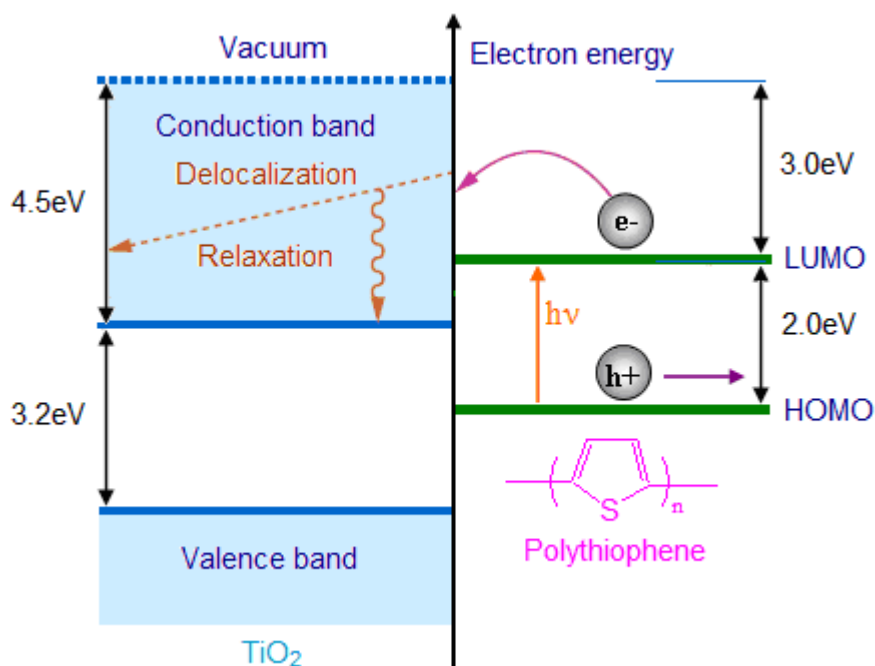


Figure 9. Schematic diagram of conjugated polymer/TiO<sub>2</sub> nanocomposites; detailed view on the polymer-TiO<sub>2</sub> junction and free charge carrier photogeneration mechanism is shown. The conjugated polymer is denoted as polythiophene in the present paper.

## 5.2 Semiconductor coupling

Semiconductor coupling is another method to utilize visible light for TiO<sub>2</sub> photocatalysis. When a large bandgap TiO<sub>2</sub> semiconductor is coupled with a small bandgap semiconductor with a more negative conduction band level, CB electrons can be injected from the small bandgap semiconductor into the TiO<sub>2</sub> semiconductor. This mechanism is similar to that of dye/polymer-sensitized TiO<sub>2</sub> system (see Fig. 9). Since CdS has narrow bandgap (2.4 eV) and its conduction band is ca. 0.5 eV more negative than that of TiO<sub>2</sub> [98], the coupling of the semiconductor should have a beneficial role not only in sensitizing TiO<sub>2</sub> to visible photoresponse but also in improving charge separation. Early studies concentrated on the formation of CdS/TiO<sub>2</sub> combination by depositing CdS microcrystals (4–20 nm) onto TiO<sub>2</sub> particles or highly porous thin films [107–109]. Recently, CdS/TiO<sub>2</sub> nanotubes were successfully prepared using layer-by-layer deposition [110], chemical bath deposition [111] and electrodeposition methods [98]. For example, Hsu et al. [111] synthesized a novel CdS@TNT coaxial nanocables using wet chemical bath deposition with porous

AAO as templates (see Fig. 10). Using this method, the thickness of the TNT sheaths could be controlled precisely by adjusting the reaction conditions. Sequentially, the continuous and polycrystalline CdS nanotubes were deposited onto TNTs by in order to form the coaxial CdS@TNT nanocables. The capability to construct composite nanotubes with functional interior and exterior layers is an important progress.

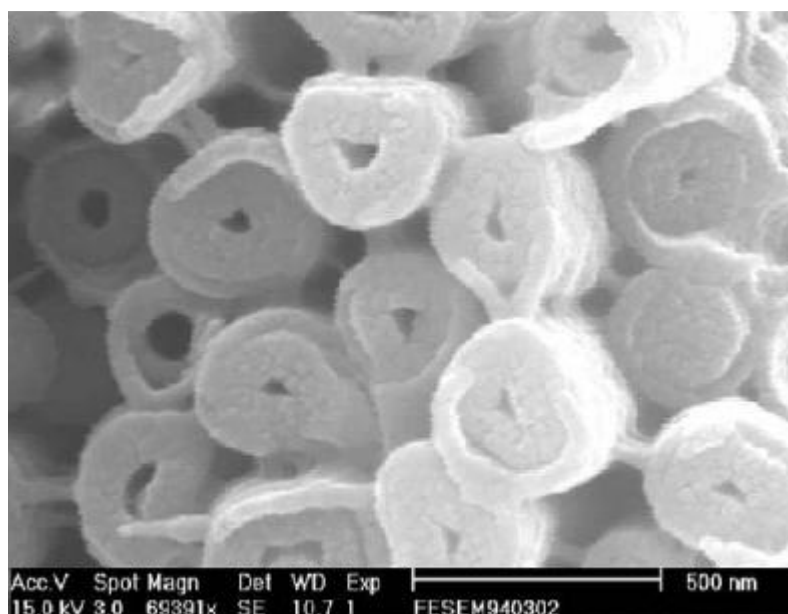


Figure 10. SEM images of CdS@TNT at high magnification. Reprinted from ref [111]. Copyright 2005 Elsevier.

In 2007, Hou and co-workers [99] fabricated a core/sheath heterostructure CdS/TNT electrode by ac electrodeposition of CdS to anodic TNT arrays and used them in photoelectrochemical cells. The core/sheath architecture enhances the photocurrent and efficiency of water photocleavage by allowing for more contact areas of CdS and TNTs. In this case, charge collection efficiency and light harvesting efficiency may be higher than in a planar heterojunction, which will result in higher cell efficiency.

As we know, the key point of the efficient photocatalysis for  $\text{TiO}_2$  catalyst is the combination of carrier generation by light absorption and charge separation. In the case of CdS coupling,



researchers seek to combine the excellent photochemical properties of the crystalline TNTs with the excellent visible absorption properties of CdS nanoparticles, thereby shifting the absorption characteristics of the material architecture into the visible light spectrum. Unfortunately, photocatalysis with CdS/TiO<sub>2</sub> still cannot be applied in real water treatment because of the easy photocorrosion of CdS and its high toxicity.

### 5.3 Noble metal deposition

Other research efforts related to the deposition of noble metals (mainly include Pt, Pd, Au, and Ag) in/on TNT structures has been in progress. A considerable increase of the photocatalytic activity have been reported, in particular, with platinum deposited on TNTs for water splitting and degradation of organic pollutants [96,97,112]. The deposition of Pt metal on n-type TiO<sub>2</sub> semiconductor is similar to those semiconductor-semiconductor p-n junctions [14]. At a p-n junction of Pt/TiO<sub>2</sub> system, electrons diffuse from the TiO<sub>2</sub> (n-type) into the Pt (p-type) region, creating an accumulation of negative charges in the p-type region in the vicinity of the junction. Simultaneously, holes diffuse from the p-type to the n-type region, creating a positive section in the n-type region in the vicinity of the junction. For this situation, the Pt metal must have a higher work function (5.6 eV) than that of the TiO<sub>2</sub> semiconductor (~3.9 eV) [8,113], which renders to form a Schottky barrier between the metal and semiconductor. Fig. 11 schematically illustrates the electron capture properties at the Schottky barrier of the metal in contact with a semiconductor surface. When the two species come in contact the Fermi levels of the metal and semiconductor align causing electrons to flow to the metal from the semiconductor. The decrease in electron density within the semiconductor causes the holes to freely diffuse to the semiconductor surface where oxidation of organic species can occur. Actually, many reseachers have identified that the p-n junction nanotube catalyst shows a much higher photocatalytic activity than that of TNT catalysts that did not contain a p-n junction [14,114]. Summarily, the main enhancing effect of noble metal loading seems to be a higher rate of production of oxidizing species, but care must be taken to conduct a metal-modified semiconductor with the optimum photocatalytic efficiency.

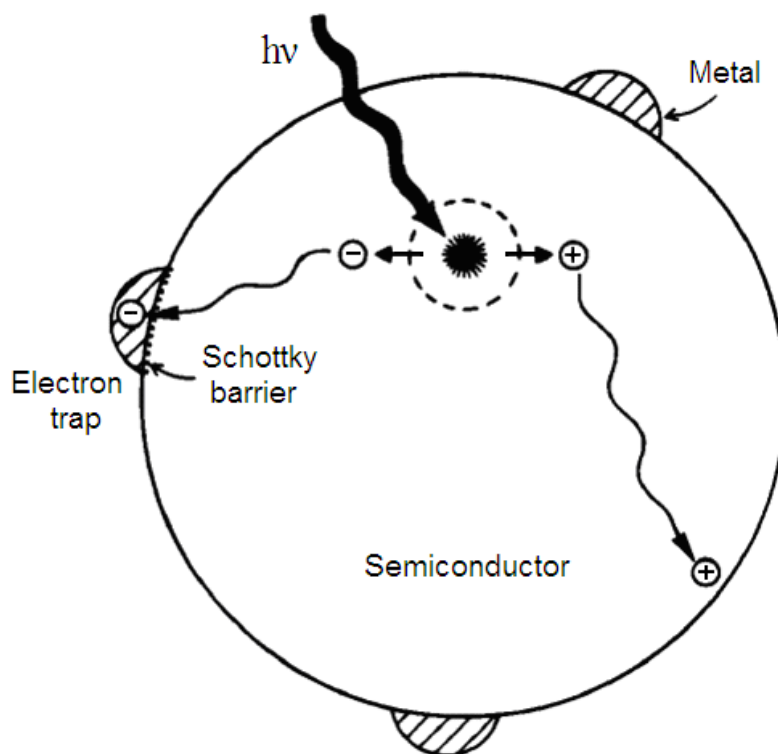


Figure 11. Metal-modified  $\text{TiO}_2$  semiconductor photocatalyst particle. Reprinted from ref [4]. Copyright 1995 American Chemical Society.

#### 5.4 Non-metal doping

Earlier studies on  $\text{TiO}_2$  particles doped with non-metal atoms, including N, C, F, S and P, etc., have been subject to optical absorption in visible region and visible-driven photocatalytic activity. Asahi and co-workers claimed that among these atoms, the most effective substitutional dopant was N for the bandgap narrowing of  $\text{TiO}_2$  [115]. In such doping, the p states (from N dopants) mix with O 2p states (from  $\text{TiO}_2$ ) to narrow the bandgap and then transfer the photogenerated charge carriers to the reactive sites of  $\text{TiO}_2$  surface. Although doping by S shows a similar bandgap narrowing, its ionic radius is too big to enable it to be substituted into the  $\text{TiO}_2$  lattice [116]. The states introduced by C and P are energetically too deep in the bandgap of  $\text{TiO}_2$  to promptly transfer the charge carriers to the surface reactive sites. In F-doped  $\text{TiO}_2$  photocatalysts, the main reason for the improved light absorption was the color centers formed upon F incorporation [117].

Although band-gap engineering of  $\text{TiO}_2$  particles by non-metal doping has received much attention, doping non-metal atoms into TNTs is quite limited. The preparation methods generally used to form non-metal doped  $\text{TiO}_2$  particles, such as high-temperature calcination and chemical vapor deposition, can not be performed to obtain the doped TNTs due to their poor stability. In 2006, Schmuki and co-workers reported the N-doping of anodic TNTs for the first time by N-ion implantation [118] technique and presented a chemically bonded state in  $\text{TiO}_{2-x}\text{N}_x$ . Such dopants give rise to the bandgap narrowing by overlapping between N 2p and O 2p orbitals, creation of oxygen vacancies, or generation of intra-bandgap surface states [115,117,119]. It is worth noting that the ion implantation process is often accompanied by undesired radiation defects introduced in the  $\text{TiO}_2$ , which can act as recombination centres for the photogenerated charge carriers. In the same year, Park et al. [120] reported the carbon doping of the  $\text{TiO}_2$  nanotubular layers by reduction of carbon monoxide, where oxygen vacancies were also said to be responsible for the visible-light activity of C-doped  $\text{TiO}_2$ .

However, in practice, the distribution and amounts of dopants within the TNT materials, which is closely related to the preparation methods, should never be ignored. Too much non-metal atom loading results in the formation of  $\text{TiN}$ , which is not transparent in the visible region, and more recombination centres, which leads to the poorer photoactivity.

## 6. Applications of TNT-photocatalysis

The unique physicochemical properties of TNTs, together with their open mesoporous morphology and high specific surface area, make TNTs as photocatalysts very promising for water purification, water-splitting, anti-bacterial/anti-virals, self-cleaning.

### 6.1 Water purification

TNT is photoactive in the UV region ( $< 400 \text{ nm}$ ) and is currently considered one of the most promising photocatalysts for water photocatalytic decontamination due to their high specific surface

area and efficient interfacial charge-transfer. Application of TNT-photocatalysis to water purification is expected to destroy the unwanted and harmful organic compounds in contaminated water. In photocatalytic reactions with TNT/UV, two modes of TNT (suspended and immobilized) can be adopted, and dissolved oxygen molecules are considered necessary, TNTs obtained by the hydrothermal and template-assisted methods are usually in a powdery form, and in liquid-soil systems the catalysts require to remove from the treated water. In contrast, TNTs obtained by anodic oxidation are in an immobilized film since they grow directly from the titanium metal substrate. The TNT films used as photocatalysts for the removal of organic and inorganic contaminants in water is coming of age. For example, in 2005 Quan et al. [90] for the first time employed the TNT film as a photoelectrode to degrade pentachlorophenol in aqueous solution. In 2007, Pan et al. [121] reported the COD removal of landfill leachate solution by using the system of  $O_3$ /UV/TNT, where TNTs were prepared by the hydrothermal method. This could be interesting for industrial applications. In summary, the development of  $TiO_2$  films with large pore morphology, high mechanical robustness, good structural integrity and high surface area, is undoubtedly becoming an important topic in photocatalysis. The system of TNTs combined with other advanced oxidation technologies is potentially applicable to the remediation of industrial effluents, groundwater, surface water and drinking water.

## 6.2 Water splitting to produce hydrogen

Hydrogen produced from water using solar light is a clean, renewable, and sustainable energy, which will be a critical breakthrough with respect to the rising concern of environmental pollution caused by the use of fossil fuels. Intensive efforts have been made to achieve this goal for the last 30 years. Its technique relies on using a light sensitive material to harness the power of the sun to split water into oxygen and hydrogen gas. Semiconducting materials used as electrodes can absorb solar radiation and make charges, where the charges have energy enough to produce hydrogen. Among them, the TNT array photoanode presents several advantages for the production of

molecular hydrogen. For example, (1) due to light scattering within a porous structure, incident photons are more effectively absorbed than on a flat electrode; (2) the tubular nanoarchitecture results in a large effective surface area in close proximity with the electrolyte, thus enabling diffusive transport of photogenerated holes to oxidizable species in the electrolyte; (3) the relevant structure sizes of the TNT arrays, i.e., half the wall thickness, are about 20 nm, which is less than the retrieval length of crystalline  $\text{TiO}_2$  [122], hence bulk recombination is greatly reduced and the quantum yield enhances.

Grimes and co-workers first reported the water photocleavage with highly ordered  $\text{TiO}_2$  nanotube arrays under ultraviolet irradiation [79]. They found that the nanotube wall thickness is a key parameter influencing the magnitude of the photoanodic response and the overall efficiency of the water-splitting reaction. Mohapatra et al. [123] for the first time reported the double-side illuminated TNT arrays for high volume hydrogen generation by water splitting. These double-sided TNT/Ti/TNT materials are used as both photoanode (carbon-doped  $\text{TiO}_2$  nanotubes) and cathode (Pt nanoparticles dispersed on TNTs; Pt-TNT/Ti/Pt-TNT) in a specially designed photoelectrochemical cell to generate hydrogen by water splitting, as shown in Fig. 12. The experimental results showed that the double-sided TNT photoanode possesses good photoactivity to generate a high volume of hydrogen ( $38 \text{ mL h}^{-1}$ ) under the illumination of a solar spectrum on both sides of the photoanode. However, improving the quantum efficiency for photocatalytic water splitting for solar  $\text{H}_2$  production is still a key research challenge. Reported quantum efficiencies are to date relatively modest.

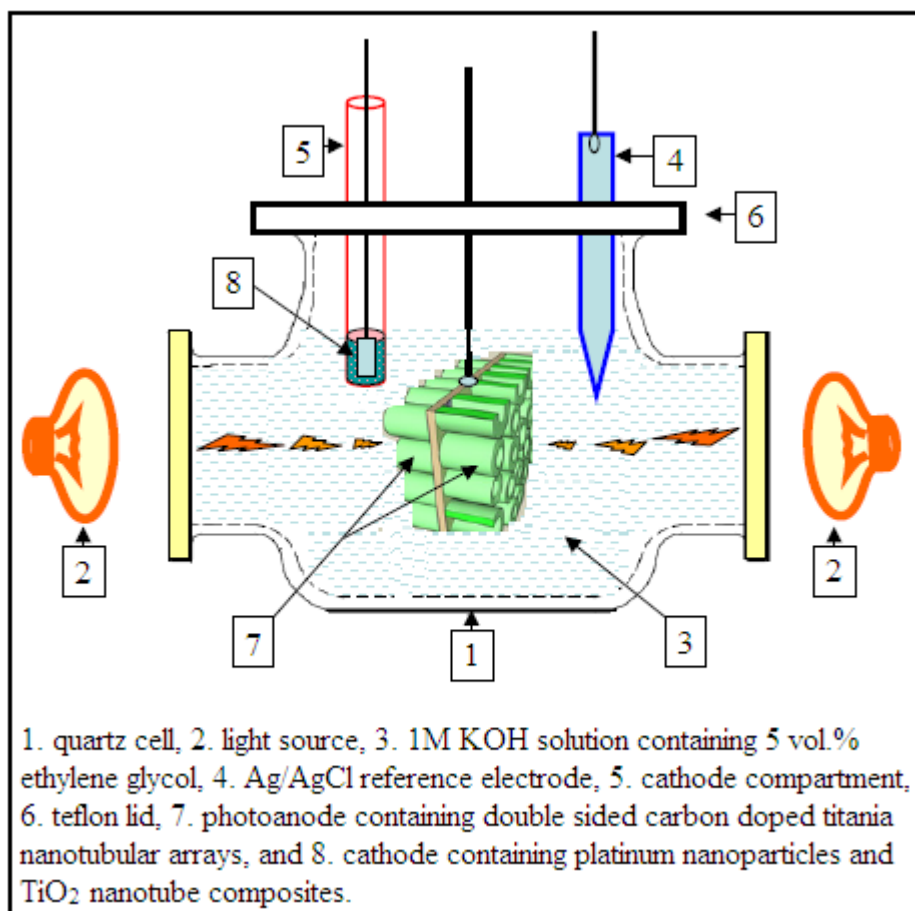


Figure 12. A schematic diagram of the photoelectrochemical cell to generate hydrogen by water splitting using double-side illuminated TiO<sub>2</sub> nanotube arrays. Reprinted from ref [123]. Copyright 2007 American Chemical Society.

### 6.3 Chemical sensors

Chemical sensors are of critical importance for industrial process control, medical diagnosis, and helping to ensure a safe environment. For example, hydrogen sensors have been widely used in the chemical, petroleum and semiconductor industries, also used as diagnostic tools to monitor certain types of bacterial infections in infants. Since hydrogen has the potential for burning and explosion, sensors are needed to detect hydrogen leaks. However, one problem often found in sensors is that the sensors become contaminated, or poisoned, limiting their useful lifetime and creating the potential for spurious measurements; typically the more sensitive the sensor, the more susceptible it is to contamination. A sensor need be able to self-clean and recover from environmental insult.

In 2003, Grimes and co-workers reported a self-cleaning, room-temperature TNT hydrogen gas sensor for the first time [124], and the sensor measurement geometry is shown in Fig. 13. This sensor can be able to self-clean with exposure to UV light, fully recovering its initial properties after being contaminated by either motor oil and/or stearic acid. Considering the nature of gas sensing via the interaction of a semiconducting surface with adsorbed gas molecules, it is thought that TNT arrays, with the characteristics of highly ordered open tubes and large specific surface area, can provide abundant sites and channels for gas adsorption, diffusion and chemical reactions. Besides as the hydrogen sensor, anodic TNT arrays have also attracted great interest in their sensing behavior for other gases, such as oxygen, carbon monoxide, carbon dioxide and even ammonia [125-127].

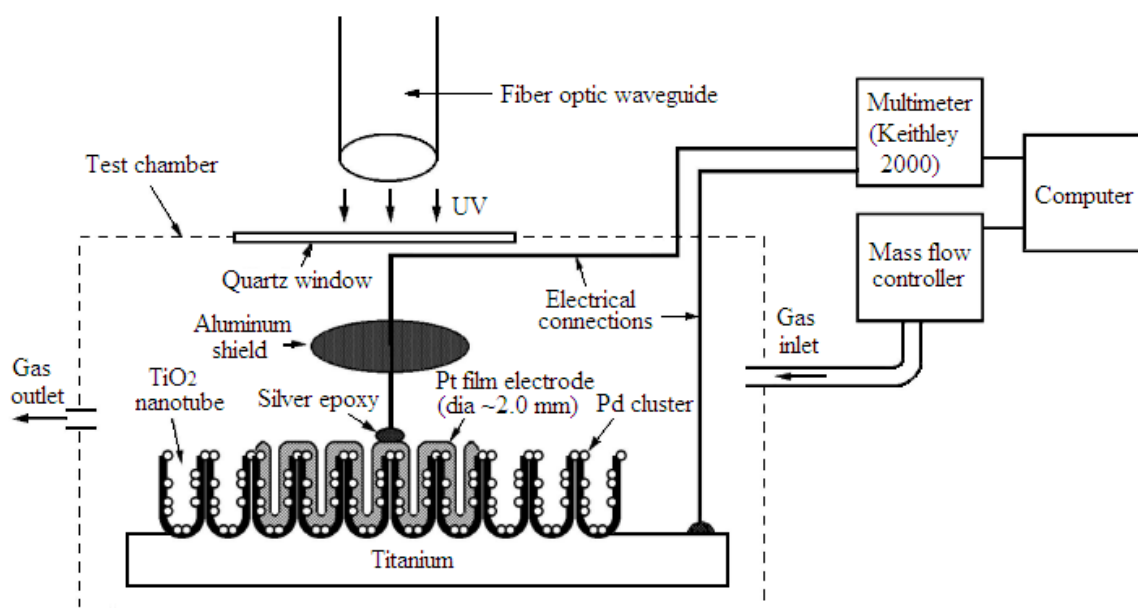


Figure 13. Schematic diagram of experimental geometry used for investigating the self-cleaning capability of the TNT-based room temperature hydrogen gas sensor. Reprinted from ref [124]. Copyright 2003 American Scientific Publishers.

#### 6.4 Anti-bacterial and cancer treatment

Bacterial infection is one of the most common problems after orthopedic implant surgery. If not prevented, bacterial infection can result in serious and life threatening conditions such as

osteomyelitis [128]. Thus, antibiotic treatment is usually prescribed to patients to prevent any complications that may arise after implant surgery. In 1985, Matsunaga et al. showed for the first time the ability of UV-irradiated platinized TiO<sub>2</sub> nanopowder to kill bacterial cells in an aqueous environment [129]. Up to 2005, the antibacterial performance of titanate nanotubes was first evaluated by *Escherichia Coli* and *staphylococcus aureus* [130], where the nanotubes were prepared by alkaline hydrothermal method. In 2007, Popat et al. [129] also investigated the ability to control antibiotic release from the anodic TNTs to prevent bacterial adhesion. They demonstrated that nanotubular surfaces enhance matrix production from osteoblasts.

Recently, the feasibility to use the TNT layer as a photocatalyst for the photo-induced cancer cell killing has been investigated [131]. The cancer cells in contact with TNTs can be triggered upon UV light irradiation. Cancer cells reduce their size and a significant amount of them are killed. Furthermore, Sakai et al. [132] found the possibility for selectively killing a single cancer cell using a polarized, illuminated TiO<sub>2</sub> microelectrode. In practice, there are still some problems to be solved before such a device can be put into practical use, because the photocatalytic reactions only occur under UV illumination. Whether the UV light probably causes mutations in normal cells is also unclear and need further study.

## 7. Conclusions

In this work the pertinent literatures in relation to the scope of TNTs, including the preparation methods, properties, surface modification and photocatalysis applications were comprehensively reviewed. TiO<sub>2</sub> nanotubes usually with a large special surface area can be achieved by simple hydrothermal treatment, template-assisted synthesis, or anodic oxidation. Different preparation methods can significantly influence the nanotube morphodology, surface functional groups, even the crystal structures. To effectively utilize the visible light, surface modification of TNTs is usually carried out by sensitizing with dye/polymer molecules, doping with noble metals, and semiconductor coupling. These modifications can dramatically alter the surface and bulk electronic



structure, not only offering the advantages of photoresponse to visible light region but the decrease of electron-hole recombination leading to the improvement of photocatalytic efficiency. The employment of these fundamental modification methods is a rich area for both basic scientific research and technological development. Further studies are necessary to elucidate the photocatalytic behavior and mechanism of TNTs for their applications in the fields of water purification, water splitting to generate hydrogen gas, self-cleaning, anti-bacterial, and even cancer cell killing.

## Nomenclature

|               |                                               |
|---------------|-----------------------------------------------|
| IEP           | Isoelectric point                             |
| $\mu_e$       | Chemical potential of electrons               |
| $\mu_e^0$     | $\mu_e$ in standard conditions                |
| $k$           | Reaction rate constant                        |
| $T$           | Reaction temperature                          |
| $E$           | Photon energy                                 |
| $E_{ff}$      | Efficiency of photocurrent-to-incident photon |
| $E_g$         | Band gap energy                               |
| $q$           | Elementary charge                             |
| $i_{ph}$      | Photocurrent density                          |
| $P$           | Light density                                 |
| $c$           | Velocity of light                             |
| $C$           | Space charge capacitance                      |
| $\varepsilon$ | Dielectric constant                           |
| $U$           | Applied potential                             |
| $N_D$         | Concentration of donors                       |
| $h$           | Plank's constant                              |
| $\lambda$     | Wavelength of onset absorption                |
| CB            | Conduction band                               |
| HOMO          | Highest occupied molecular orbital            |
| LUMO          | Lowest unoccupied molecular orbital           |

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# Titanium Dioxide Photocatalysts: Performance-Related Properties

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**Abstract.** The present work considers the performance-related properties of TiO<sub>2</sub>-based photosensitive semiconductors as photocatalysts for water purification and photoelectrodes for water splitting. These properties, including electronic structure, charge transport, surface properties, and near-to-surface properties, have an effect on light absorption and its conversion into chemical energy, and are closely related to defect disorder. Therefore, defect chemistry may be used as a framework for their modification in order to achieve enhanced performance. The present work considers the relationships between these specific performance-related properties and defect disorder.

## Introduction

Intensive research aims to develop TiO<sub>2</sub>-based photosensitive materials with enhanced performance in water purification (photocatalyst) and photoelectrochemical water splitting (photoelectrode) [1–11]. The studies aim to establish the effect of selected properties, such as structure, microstructure, surface area and the concentration of foreign ions (dopants), on the performance.

There is a general perception that the band gap energy is the critical performance-related quantity in solar-to-chemical energy conversion [2–11]. This perception is correct as the matching value of the band gap is critical for the amount of solar energy being absorbed and, therefore, available for conversion. At the same time, the energy conversion efficiency (*ECE*) also depends on the energy losses, which are related to (i) charge transfer (determined by ohmic resistance), (ii) recombination of light-induced charge carriers, and (iii) charge transfer between the reacting molecules and the surface of photoelectrode [12]. The aim of the present work is to consider these properties for TiO<sub>2</sub>-based photosensitive semiconductors.

## Energy Conversion Efficiency

The *ECE*,  $\eta_c$ , for photoelectrochemical cells (PECs), has been defined by Parkinson [13]:

$$\eta_c = \frac{I (E_{dec} - V_{bias})}{I_r A} \quad (1)$$

where:  $E_{dec}$  — Nernst's decomposition potential of the cell's redox species (for water  $E_{dec} = 1.23$  eV),  $V_{bias}$  — voltage across the cell,  $I$  — current within the cell,  $I_r$  — incidence of solar irradiance, which depends on geographical location, time, and weather conditions,  $A$  — irradiated area. The relation (1) was derived assuming that the energy stored in the form of chemical energy (hydrogen) can be totally recovered in a hypothetical ideal fuel cell. All quantities in Equation (1) may be determined experimentally, so it can be used for evaluation of the overall efficiency  $\eta_c$ .

The term  $I_r$  can be measured directly or calculated. The latter requires knowledge of the air mass  $AM$ . It has been proposed that the standard level of  $I_r = 970 \text{ W/m}^2$  corresponds to an  $AM$  of 1.5 [14].

The overall energy conversion efficiency  $\eta_c$  ( $ECE$ ) can be expressed as the following function of the property-related components [13, 14]:

$$\eta_c = \eta_{SI}\eta_{CH}\eta_{QE} \quad (2)$$

where  $\eta_{SI}$  is the solar irradiance efficiency,  $\eta_{CH}$  is the chemical efficiency and  $\eta_{QE}$  is the quantum efficiency. The key performance indicator of PEC's performance,  $ECE$ , may also be defined as the ratio of the energy output,  $E_{out}$ , to the total energy input (the amount of light energy striking the surface of photoelectrode),  $E_{in}$ :

$$ECE = \frac{E_{out}}{E_{in}} \quad (3)$$

In Equation (3) the energy output is the difference between energy input and all kind of energy losses,  $E_{loss}$ :

$$E_{out} = E_{in} - E_{loss} \quad (4)$$

These energy losses are related to a range of properties/phenomena, including:

- Electrical resistance,  $E_R$
- Charge transfer,  $E_{CT}$
- Charge recombination,  $E_{REC}$
- Heat generation,  $E_H$
- Optical losses,  $E_{OPT}$

The present work considers the performance-related properties in terms of these energy components that are essential for the  $ECE$ .

## Functional Properties

**Band gap** The ability of a semiconductor to absorb the light energy is closely related to its electronic structure. The band gap is the smallest energy difference between the top of the valence band and the bottom of the conduction band. In the case of direct transitions, light is effectively absorbed by semiconductors when the photon energy is equal or higher than the forbidden energy gap. Then light absorption leads to effective light-induced ionisation over the band gap. The width of the band gap may be determined experimentally by optical reflection spectra and the temperature dependence of the electrical conductivity corresponding to the n–p transition point [12]. Since the energy required for water splitting is 1.23 eV, the optimum value of the desired band gap energy for photoelectrodes is the sum of 1.23 eV and the amount of energy losses (approximately 0.5–1 eV). Therefore, the desired band gap of semiconductors used as photoelectrodes for water splitting remains between 1.8 eV and 2.2 eV, depending on the energy losses.

The band gap of the most commonly available form of  $\text{TiO}_2$ , rutile, is 3.05 eV (Table 1) [15–24]). Therefore, the  $ECE$  may be enhanced when the band gap is reduced. The main research strategy in the processing  $\text{TiO}_2$  with reduced band gap, includes two following approaches:

1. Elevation of the top of the valency band energy (Figure 1a) [25]

2. The imposition of a mid-gap band located  $\sim 2$  eV below the conduction band (Figure 1b) [26]

Figure 2 represents an estimated effect of  $E_g$  on the  $ECE$  for a single photoelectrode PEC at the assumption that the procedures applied in the modification of the band gap do not lead to changes in the energy losses. It has been shown that electronic structure of oxides, including  $\text{TiO}_2$ , is closely related to defect disorder [12]. Therefore, electronic structure may be modified by oxygen content as well as through doping with aliovalent ions.

The reports on the effect of doping on electrochemical properties of  $\text{TiO}_2$  are conflicting. For example, Philips et al. [27] have observed that, although the addition of 30 mol% of vanadium to  $\text{TiO}_2$  single crystal results in band gap reduction to 1.99 eV, the formation of  $\text{Ti}_{0.7}\text{V}_{0.3}\text{O}_2$  had a detrimental effect on photo-activity due to a substantial increase in the flat band potential by about 1 V. On the other hand, Zhao et al. [28, 29] observed that increased amounts of vanadium in  $\text{TiO}_2$  thin films resulted in an increase in the energy conversion efficiency.

There were several attempts to reduce band gap by reduction of grain size. However, Wang et al. [30] observed that the bandgap of the 2.7 nm grain size  $\text{TiO}_2$ , rutile is 3.32 eV, while the band gap for  $\text{TiO}_2$  single crystal is 3.05 eV (Table 1). Also Hoffmann et al. [2] reported that below a certain critical grain size ( $\sim 10$  nm) the band gap increases.

Karakitsou and Veryklos [31] have shown that the anatase form of  $\text{TiO}_2$  exhibits hydrogen production rate higher than that of rutile by the factor of 7 despite the fact that its band gap is larger ( $E_g = 3.2$  eV).

In summary, the above evidences indicate that there is no simple relationship between the width of band gap of a semiconducting photoelectrode and the  $ECE$  of photoelectrochemical cell. Apparently,

| Authors                    | Band gap [eV] | Method | Experiment                                                        |
|----------------------------|---------------|--------|-------------------------------------------------------------------|
| Cronemeyer [15]            | 3.05          | EC     | Single crystal, 773 K–1223 K                                      |
|                            | 3.05          | EC     | Single crystal, 623 K–1123 K                                      |
|                            | 3.03–3.06     | OPT    | Single crystal, room temperature                                  |
| Rudolph [16]               | 3.12          | EC     | Ceramic specimen, 1125 K–1300 K                                   |
| Frova <i>et al.</i> [17]   | 3.0           | OPT    | Single crystal, room temperature                                  |
| Vos & Krusemeyer [18]      | 3.026         | OPT    | Parallel to <i>c</i> axis, room temperature                       |
|                            | 3.059         | OPT    | Perpendicular to <i>c</i> axis, room temperature                  |
| Pascual <i>et al.</i> [19] | 3.031         | OPT    | Parallel to <i>c</i> axis, 1.6 K                                  |
|                            | 3.031         | OPT    | Perpendicular to <i>c</i> axis, 1.6 K                             |
| Daude <i>et al.</i> [20]   | 2.91          | THC    | Parallel to <i>c</i> axis                                         |
|                            | 3.05          | THC    | Perpendicular to <i>c</i> axis                                    |
| Vos [21]                   | 3.03          | THC    | Parallel to <i>c</i> axis, 1.6 K                                  |
|                            | 3.07          | THC    | Perpendicular to <i>c</i> axis, 1.6 K                             |
| Gupta & Ravindra [22]      | 3.0329        | OPT    | Single crystal (both perpendicular and parallel to <i>c</i> axis) |
| Khan <i>et al.</i> [23]    | 3.06          | THC    | Single crystal (both perpendicular and parallel to <i>c</i> axis) |
| Nowotny [24]               | 3.16          | EC     | High purity single crystal, 1073 K–1323 K                         |
| Average                    | 3.05          |        |                                                                   |

Table 1: Band gap energy values reported in literature (EC — electrical conductivity, OPT — optical method, THC — theoretical calculations).



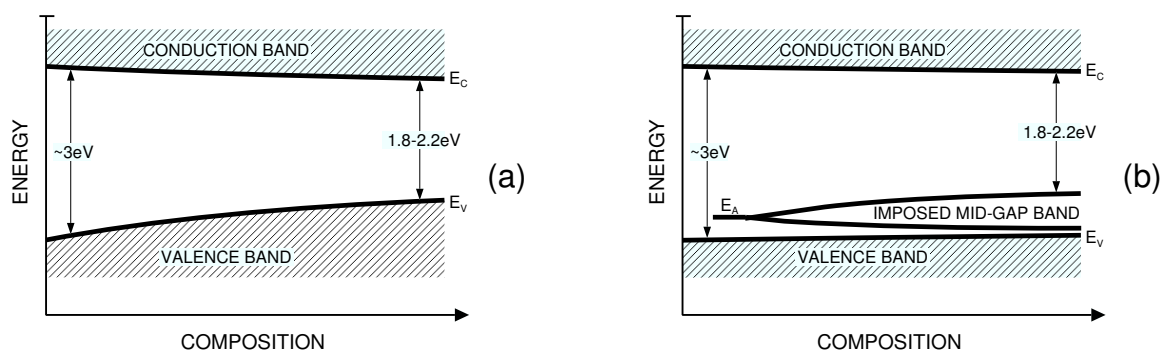


Fig. 1: Schematic representation of band gap reduction by (a) elevation of the edge of valence band, and (b) imposition of a mid-gap band.

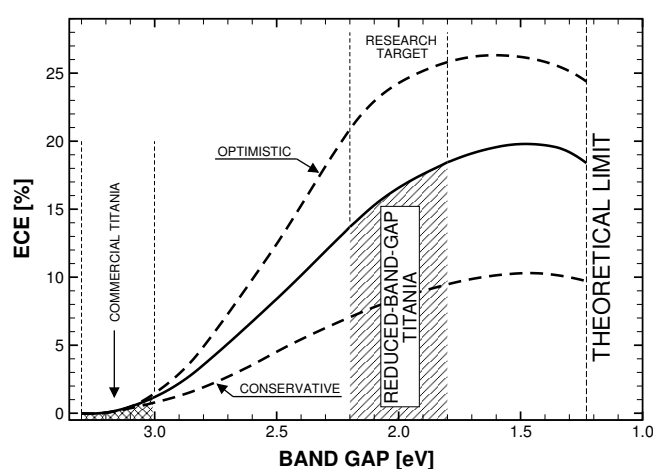


Fig. 2: Expected effect of band gap reduction on  $ECE$  assuming that other energy losses remain unchanged.

the increased solar energy absorption for narrower band gap material can be counterbalanced by increased energy losses related to other effects.

**Recombination** The electron-hole pairs formed as a result of light-induced ionisation have a tendency to recombine, resulting in energy losses. The  $E_{REC}$  component may be reduced by the imposition of an electric field leading to effective charge separation and an increase of the lifetime of photogenerated charge carriers. Such field is formed spontaneously in the space charge layer at the liquid/solid interface between  $\text{TiO}_2$  and a water solution. Recent studies indicate that the electric field may be modified by the imposition of chemically-induced electric field, using the phenomena of segregation and diffusion [12]. However, the effect of segregation in oxide materials is still not well understood, therefore more experimental data is needed before any quantitative models can be formulated.

**Charge transport** The optimal performance of photocatalysts and photoelectrodes requires efficient charge transport in order to minimise the electrical resistance-related energy losses and to maximise the  $ECE$ . This may be achieved by minimisation of the internal resistance through the increase of the concentration of electronic charge carriers and their mobility. Doping is the most commonly

applied procedure to enhance charge transport. It was shown that the resistance of  $\text{TiO}_2$  may even be reduced to the level of metallic-type conduction [32].

**Reactivity and the related charge transfer** An important issue in the development of high-performance photoelectrodes and photocatalysts is the enhancement of charge transfer between adsorbed species and the surface of photoactive semiconductor. In a photoelectrochemical cell both electrodes are physically separated and connected electrically via an external circuit, hence anodic and cathodic processes occur on the surfaces of different solids. In the simple case of a PEC composed of n-type  $\text{TiO}_2$  photoanode and metallic cathode the transfer of light-induced electron holes to water molecules is already efficient, since electron holes are minority charge carriers and even small changes in their concentration lead to a large change in the position of the respective quasi-Fermi level and the associated oxidising power. Therefore, the enhanced charge transfer may be achieved by optimisation of the population of the active surface sites, which are able to form active complexes with the adsorbed reacting molecule, such as water molecules. This model assumes that charge transfer takes place preferentially at the active complexes, while the activation energy of the charge transfer is much higher when the molecules are adsorbed elsewhere. It has been shown that the surface active sites for water oxidation are titanium vacancies [33]. Consequently, energy losses associated with charge transfer are determined by the defect disorder of the outermost surface layer of the photoelectrode.

The performance of photocatalysts, used for example for water decontamination, can be described by a slightly different model. In this case each single grain of photocatalyst is represented by micro-PEC [12], where anodic and cathodic sites are formed on the surface of the same solid, at the local areas of low and high work function, respectively. The formation of  $\text{OH}^*$  radicals at the anodic sites is relatively easy, as these active sites are associated with high charge transfer. However, the transfer of electrons at the cathodic sites is rate controlling [7]. Because anodic and cathodic currents are always equal, the cathodic reaction rate should be enhanced in order to increase the performance of the photocatalyst. This may be achieved by scavenging electrons from cathodic sites, by the supply of oxygen or other oxidants that allows efficiently remove electrons.

**Sub-band absorption** Ultimately, all lost energy is converted into heat, increasing the temperature of the PEC. However, the  $E_H$  component is related to the large part of the solar spectrum with the energy of photons lower than the band gap energy. Such photons, if absorbed, cannot result in ionisation over the band gap and are converted into heat.

**Reflection of light** Due to its high refraction index a substantial amount of incident light is reflected from the surface of  $\text{TiO}_2$ . The reflected photons are not converted into any useful form of energy and, therefore, their energy contribute to  $E_{OPT}$ . In the case of a thin film photoelectrode some photons might also pass through instead of being absorbed. Such effect increases the optical energy losses but can easily be avoided by ensuring sufficient thickness of the film.

### Interdependence of Functional Properties

The modification of functional properties of oxide semiconductors may be achieved, for example, by doping leading to a change in chemical composition of either cationic or oxygen sublattices. Essentially, the process of doping consists of the introduction of the element A at the concentration  $x$  into the  $\text{TiO}_2$  lattice. Therefore,  $x_A$  may be considered as an independent variable. Since the element A has an effect on defect disorder [12], which affects all performance-related properties, these properties must be considered as interdependent. Therefore, the procedure leading to the modification of one property, also affects other properties. For example, while a particular dopant may lead to reduction

of the losses related to component  $E_R$ , the same dopant may lead to an increase of the losses related to the component  $E_{CT}$ . Consequently, several points should be made:

- The single independent variable (dopant), which has an effect on defect disorder, result in changes of all performance related properties. Therefore, studies of the effect of a single variable on the individual performance-related property, such as the band gap energy, can not be simply related to the  $ECE$  without understanding of the effect of other performance-related properties.
- The effect of the independent variable on the  $ECE$  depends on the combined effect of all performance related properties and the balance of energy losses.
- The studies on the effect of independent variables on the  $ECE$  include two stages:
  - The effect of the independent variable on each performance-related components:  $E_R$ ,  $E_{CT}$ , and  $E_{REC}$ .
  - The effect of all performance-related components on the  $ECE$ .

Therefore,  $ECE$  should be maximised by using a multivariant approach to all functional properties, which are closely related to defect disorder. In consequence, the research strategy in the development of high-performance oxide semiconductors should lead to minimization of the energy losses by a multifactorious approach:

$$\nabla E_{loss}(x_1, x_2, \dots, x_n) = 0 \quad (5)$$

where  $x_1, x_2, x_n$  are independent variables, such as dopant concentration, oxygen activity and grain size.

## Conclusions

It has been postulated that the performance of semiconducting photocatalysts is closely related to specific properties, including electronic structure, flat band potential, charge transport and surface properties. These properties, which have been considered for  $\text{TiO}_2$ -based oxide semiconductors, are directly related to defect disorder of  $\text{TiO}_2$  and its solid solutions. Therefore, defect chemistry may be used as a framework for processing of photocatalysts with controlled properties, which are desired for specific applications.

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