CHAPTER 3

Current Issues Concerning the Mechanism of Pristine TiO_2 Photocatalysis and the Effects on Photonic Crystal Nanostructures

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3.1 Photocatalysis and Sustainability

The development of human society, with advances in technology, has the merit of many ingenious devices, materials, and methods that have contributed undoubtedly to large improvements in the quality of human life.

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However, together with the progress achieved so far, undesired wastes, byproducts and toxins have also been produced, damaging our planet, and putting in danger to some extent our sustainability.

Human beings have proven to be able to use nature beyond any thinkable limitation. The drawback of such behavior is that we collectively have not yet learnt to control, among other undesired consequences, ecological disasters caused by contaminants and pollutants in the atmosphere and the water body of our planet, both of which are absolutely essential for life.

Since public support of necessary initiatives and changes is the basis for the creation of a sustainable society, the work of scientists is of profound importance in educating the industrial and academic communities to address workforce training and global involvement. The number of projects devoted to sustainable chemistry has constantly been increasing over recent years and, among other techniques and methods, semiconductor photocatalysis, in particular TiO_2-based photocatalysis, has been receiving particular attention as a promising way to treat specific environmental problems of air and water purification, disinfection, and as a possibility for fuel production and alternative synthetic pathways in the framework of green chemistry.

Interestingly, in recent decades, the development of new technologies has gained an enormous momentum that appears to have already overtaken that of the feasibly produced scientific knowledge. Such a situation is reached usually by relying on the successful results of performed tests, while a potential danger hides behind the lack, in many cases, of a true comprehension of the processes involved. In this sense we might be at risk of failing to create a sustainable future. One illustrative example is the interaction between photocatalysis and water. Water is a fundamental substance for life. And photocatalysis plays a very delicate in-between role: while it can be useful for cleaning polluted water, it can also be used for cleaving water (water splitting) to produce hydrogen and consequently store energy as a fuel. In other words, photocatalysis can improve the water quality but can also destroy the water molecule itself. A sensible human approach towards these two issues is therefore indispensable, and keeping a proper ethical and correct balance when using both technologies. For this reason and upon such a scenario, the understanding of the underlying mechanisms of photocatalysis is undoubtedly essential.

Hence the question "What is photocatalysis?" needs to be answered first. In principle, it is the *simple* arrangement of a semiconducting material in contact with a compound, organic or inorganic, either gaseous or in solution, to which light with an energy matching that of the semiconductor's bandgap is provided for its excitation. However, a *complex* series of mechanisms turning on a variety of reactions that yield oxidized and reduced species are initiated in this "simple" system.[1]

Semiconductor photocatalysis offers two main challenging areas of remarkable complexity to those researchers dedicated to revealing the secrets of nature. A challenge of great interest to material scientists and chemical engineers is the design and realization of optimal materials with high efficiency and special and/or tunable properties to be used in systems for particular purposes. Several reviews on materials employed for semiconductor photocatalysis can thus be found describing in depth the different developed approaches.[2–6]

A second challenge traditionally taken up by physical chemists, physicists, and chemists is the task of elucidating and proving the mechanisms involved.

Since both challenges are intimately connected, progress achieved in one area helps to initiate new findings in the other, and *vice versa*. Furthermore, the restriction to only one of these two approaches appears to be almost impossible, *i.e.*, multidisciplinary work is usually the most successful approach for fruitful present and future research in semiconductor photocatalysis.

Initiated by the findings of Honda and Fujishima in 1972,[7] who used TiO_2 for the photo-assisted electrochemical splitting of water, much effort has been invested in the study of this reaction. There are numerous reviews on photocatalytic and photoelectrochemical water splitting, focusing on photocatalytic materials, reactor set-ups, or mechanistic aspects.[8–16] In addition, other uses of photocatalysis, such as photocatalytic organic synthesis,[17–20] are regarded as emerging topics.

In more detail, semiconductor photocatalysis is based on the fundamental reaction in which an electron–hole pair is created upon the absorption of light. Linked to this event, further reactions of low or high complexity proceed to build up the entire photocatalytic process. While many attempts can be combined to enhance and improve the efficiency, photonic photocatalysis[21] has emerged as an innovative method that only introduces structural, but not chemical, modifications.

A critical overview of various currently discussed mechanisms in pristine TiO_2 photocatalysis is presented here, pointing out numerous open questions and the effects, beneficial or not, which they may have on TiO_2 photonic systems.

Hence, we hope to be able to inspire scientists and all types of researchers to eventually focus on fundamental issues for a deeper understanding of the chemical processes, placing our society definitively on a safer route to a sustainable future.

3.2 The Basic Principle of TiO_2 Photocatalysis

The basic principle of photocatalysis relies on the formation of an electron–hole pair upon the absorption of a photon with an energy equal or greater than the semiconductor's band-gap. These two highly reactive entities are consequently involved in all subsequent coupled reactions oxidizing and reducing the suitable species in the system concomitantly.

The photogeneration of an exciton is a well-established process both in direct and in indirect semiconductors.[22] Photogenerated electrons need to react with a proper acceptor, which is normally assumed to be O_2 (in particular when referring to environmental photocatalysis), forming initially a superoxide radical and finally ending up as H_2O. The photogenerated holes, depending on their oxidizing power, are transferred to the target molecule (usually an organic compound that functions as a pollutant) thus inducing its oxidation. If the oxidation results in its entire degradation with the final products being CO_2, H_2O and eventually ionized halides, the compound is said to be mineralized.[8] Inorganic pollutants can also be converted into less toxic or less dangerous compounds[23,24] by oxidation (reaction with holes) or reduction[25] (reaction with electrons), while biological entities, *e.g.*, macromolecules, bacteria and viruses, can be eliminated for disinfection.[15]

The photocatalyst is therefore involved in the production of an oxidative and a reductive species. Initially, these are a photogenerated hole created in the valence band, h^+_{VB}, and a photogenerated electron formed in the conduction band, e^-_{CB}:

$$\text{Photocatalyst} \xrightarrow{h\nu} e^-_{CB} + h^+_{VB} \tag{3.1}$$

Depending on how the h^+_{VB}s, free and delocalized in the crystal lattice, move to the surface and are transferred to the corresponding chemical species for oxidation, direct or indirect photocatalysis can proceed. The diffusion of h^+_{VB} to the surface, or at what velocity they travel through the solid matrix, or in which crystallographic direction their mobility is hindered or favored are questions that are currently a matter of debate with no consensus to date. However, independently of how h^+_{VB}s reach the surface, two different mechanisms may take place: (1) they are either transferred to the adsorbed pollutant, causing its immediate oxidation (eqn (3.2)), or (2) they are first transferred to adsorbed water molecules, generating hydroxyl radicals (${}^{\bullet}OH$), which upon reaction with the pollutant will produce the respective oxidation products (eqn (3.3)):

$$h^+_{VB} + \text{Pollutant}_s \rightarrow {}^{\bullet}\text{Pollutant}^+_s \tag{3.2}$$

$$h^+_{VB} + OH_s \rightarrow {}^{\bullet}OH_s \tag{3.3}$$

In eqn (3.3), the suffix "s" in ${}^{\bullet}OH_s$ indicates the formation of surface groups and can thus be interpreted as surface trapped holes.

Mechanism 1 is normally regarded as direct oxidation or direct photocatalysis, while mechanism 2 is called indirect oxidation or indirect photocatalysis. Mechanism 1 is associated with systems where the pollutant adsorbs strongly at the photocatalyst surface, establishing a good electronic contact, while mechanism 2 will be dominant in systems with a weak target molecule (pollutant) adsorption.

The pollutant's photo-oxidation *via* mechanism 2 will therefore be mediated by the action of ${}^{\bullet}OH_s$ – and depending on how long the ${}^{\bullet}OH_s$ needs to migrate to meet the pollutant or how fast the latter can reach it the photocatalytic oxidation rate will vary considerably. In principle, mechanism 2 can be as fast as mechanism 1. It may also be slower, but it is most unlikely to be faster.

The photogenerated hydroxyl radicals can react either while adsorbed at the photocatalyst surface, $^{\bullet}OH_s$ (eqn (3.4)), or after desorption, *i.e.*, act as free hydroxyl radicals in solution, $^{\bullet}OH_{free}$ (eqn (3.5)):

$$^{\bullet}OH_s + \text{Pollutant} \rightarrow \text{Oxidation products} \tag{3.4}$$

$$^{\bullet}OH_s \xrightarrow{\text{desorption}} {}^{\bullet}OH_{free} \tag{3.5a}$$

$$^{\bullet}OH_{free} + \text{Pollutant} \rightarrow \text{Oxidation products} \tag{3.5b}$$

Systems in which the target molecule is weakly adsorbed at the photocatalyst surface are likely to be dominated by photocatalytic reactions such as shown in eqn (3.4) or (3.5). Oxidation products will therefore be formed either in the bulk liquid or gas phase, with a low probability of adsorption. In this case, the eventual blocking or poisoning of the photocatalyst surface is rather unlikely. The situation will be considerably different in systems where pollutants can strongly adsorb. On the one hand, photo-oxidation reactions involving two adsorbed species, *i.e.*, $^{\bullet}OH_s$ and Pollutant$_s$, require high surface mobility of the species. But, on the other hand, they cannot be disregarded since surface diffusion is considerably faster than diffusion from the bulk to the surface. Moreover, an average distance between $^{\bullet}OH_s$ and Pollutant$_s$ on nanoparticles may be small enough to allow electron transfer through a tunneling mechanisms.

Interestingly, Monllor-Satoca *et al.* suggest a model, based on TiO$_2$ photocatalysis studies, that takes into account both mechanisms and, additionally, these authors introduce the possibility of an adiabatic or inelastic hole transfer,[26] meaning that a hole is transferred either to a dissolved species following the rate defined by the Marcus–Gerischer[27,28] model or to an adsorbed species with good electronic interaction to the surface, respectively. In Monllor-Satoca *et al.*'s model the concept of direct or indirect hole transfer is based on the status of the hole: a free and delocalized valence band hole, h^+_{VB}, or a hole that has migrated to the surface and has been trapped (h^+_{surf}), will account for a direct or for an indirect mechanism, respectively, disregarding the existence of $^{\bullet}OH_{free}$ as a result of the desorption of $^{\bullet}OH_s$. According to their mechanistic approach, $^{\bullet}OH_s$ radicals are intrinsic surface states formed by protonation of terminal O_s^{2-} at the location where h^+_{VB}s are trapped, and $^{\bullet}OH_{free}$ can only arise from the desorption of extrinsic $^{\bullet}OH_s$ formed on terminal Ti atoms. Bahnemann *et al.*, by means of time-resolved laser flash photolysis,[29] also identified two types of traps for holes: deep traps that are long-lived and unreactive and shallow traps in thermally activated equilibrium with h^+_{VB} exhibiting a high oxidation potential. According to Monllor-Satoca *et al.* the unreactive deep traps might correspond to the intrinsic $^{\bullet}OH_s$. In this case, the reactive shallow traps can be assigned to h^+_{VB} and, in a similar manner as the direct hole transfer to adsorbed pollutants occurs, extrinsic $^{\bullet}OH_s$ will be generated, since in both cases the adsorption occurs at unsaturated Ti surface atoms (eqn (3.2) and (3.3)). Compounds that adsorb strongly on the surface of metal oxide particles usually form covalent bonds employing one, two or three O atoms (to form mono-, bi- or tri-dentate complexes), as is the case for alcohols[30] and organic acids.[31–34] The reaction can be schematically described:

$$\mathrm{Ti_s} + \mathrm{HO{-}R} \xrightarrow{\text{adsorption}} \mathrm{Ti_s{-}OR^-} + \mathrm{H^+_{aq}}, \quad \mathrm{R} = \text{organic moeity} \tag{3.6}$$

By the simultaneous protonation of a terminal O_s^{2-}, electroneutral inner-sphere adsorption is achieved with a strong and stable interaction with the lattice, either for the case of a proper organic compound or water, *i.e.*, R = H. The hole transfer mechanism in these cases is still not completely understood, but presumably it may occur *via* the newly formed Ti–O bond in which the O atom can be partially considered as part of the lattice. Investigations of the TiO_2–water interface reveal that the electron transfer is possible *via* a so-called wet electron state resembling an unoccupied electronic state 2.4 eV above the Fermi level with a lifetime of ≤15 fs for its decay to the conduction band.[35] A comprehensive overview of the different time scales for some elementary reactions in TiO_2 can be found in ref. 36.

Different methods, *e.g.*, spin-trap electron paramagnetic resonance and radical-induced fluorescence, have been used to identify the radical intermediates.[37–39] Notably, however, the formation of $^{\bullet}OH$ can also follow a reductive pathway:[40]

$$e^-_{CB} + O_2 \rightarrow O_2^{\bullet-} \xrightarrow{e^-,2H^+} H_2O_2 \xrightarrow{e^-} {}^{\bullet}OH + {}^{-}OH \tag{3.7}$$

with the e^-_{CB} converting the oxidant species, *i.e.*, O_2, into H_2O_2 which is then further reduced to yield hydroxyl radicals. Although H_2O_2 should be formed as a rather stable product by the further reduction of $O_2^{\bullet-}$, it is only found in traces when working with TiO_2 powders,[41] since by its subsequent reduction, very likely, $^{\bullet}OH$ is formed. Peroxo-complexes on the TiO_2 surface are rather stable – thus the likelihood of detecting free H_2O_2 is small. Two recent studies, *i.e.*, laser-induced fluorescence measurements of two types of UV irradiated photocatalysts, Pt/TiO_2 and WO_3/TiO_2,[42] and photocatalytic degradation experiments in the aqueous phase using Pt/WO_3 systems,[43] led to the suggestion of the importance of the photo-reductive path for $^{\bullet}OH$ formation. Interestingly, Nakamura and Nakato suggest that the photogenerated H_2O_2 at the surface of TiO_2 may also be attacked by h^+_{VB} producing O_2.[44] In this manner it will be competing for holes with the pollutant or water molecules thus short-circuiting the photocatalytic cycle.

In some systems mechanism 1 (eqn (3.2)) appears to be uniquely responsible for the photocatalytic reaction, *e.g.*, in the case of the photocatalytic degradation of formic acid,[26] acetic acid[26] and oxalic acid.[45] Such a direct hole transfer mechanism has been proposed based upon experimental evidence from illuminated semiconductor systems tested by a fluorescence technique using terephthalic acid and iodide oxidation.[37] Of particular interest is the case of dichloroacetic acid (DCA), which has also been attributed to follow direct oxidation on TiO_2.[29] DCA adsorption isotherms on different nanoparticulate TiO_2 powders do not show a strong interaction with the surface, as supported by ATR-FTIR spectra of the interface between an aqueous DCA solution and these materials.[46] The ATR-FTIR spectra corresponding to surface TiO_2–DCA complexes show very weak signals slowly disappearing with time, very likely indicating desorption and a weak attachment to the surface.[46]

Mechanism 2 (eqn (3.3)) is found to be dominant in other photocatalytic systems, *e.g.*, the photo-oxidation of methanol,[26] chloroform,[26] methylviologen,[26] 2-propanol[26] and phenol.[26] In some cases, both mechanisms can take place at the same time, for instance, depending on the illuminating photon flux, some systems may experience a transition from an indirect to a direct mechanism, where a low photon flux favors an indirect mechanism and a high photon flux a direct one.[26]

In general, regardless of the reaction in which the photogenerated electrons and holes are involved, they undoubtedly lead to a complex set of subsequent reactions, resulting in total in the so-called semiconductor photocatalytic activity. The photocatalytic reaction as a whole can proceed *via* several different mechanisms, which may take place all at once, or one after another. The following sections condense a description of some selected mechanisms that are currently being discussed in the scientific community.

3.3 Current Mechanisms

3.3.1 Antenna Mechanism

This mechanism involves the transfer of photogenerated charge carriers, *i.e.*, the initially formed electron/hole pair (or exciton), the photogenerated hole or the photogenerated electron from the semiconductor nanocrystallite where it originates to another nanocrystallite, both belonging to a chain of nanocrystallites topotactically attached.[47,48] This is the case of two attaching faces that have the same crystallographic orientation. Therefore, the electronic coupling is expected to be much more efficient for electron transfer processes than in a conventional attachment because the overall atomic arrangement resembles that of an extended single crystallite. For suspended powders the chains of nanocrystalline photocatalyst particles can also be arranged three-dimensionally, forming small aggregates electronically well coupled.

In a chain of topotactically attached crystallites the excitation may occur at one crystallite at any position in the chain, while, upon migration of the photogenerated hole and/or electron within the chain, the respective oxidation and reduction is finally realized at another crystallite. Such a phenomenon resembles the function of an antenna, *i.e.*, converts electromagnetic waves into current or *vice versa*. These chains of nanocrystallites can therefore receive the electromagnetic waves from the UV irradiation source and transform them into an electric current in which the photogenerated charge carriers are transported to other crystallites where they induce the photocatalytic reaction (Figure 3.1).

The antenna mechanism was suggested for first time to explain the high photonic efficiencies of photocatalytic methanol degradation using Fe(III)-doped anatase nanoparticles with diameters between 2 and 4 nm in aqueous suspensions.[47,49] Experimental support for this mechanism was found when Ag deposition on anatase colloidal nanoparticles was studied by time-resolved laser flash photolysis.[50] Moreover, the antenna mechanism delivers a plausible explanation for the enhanced activity observed during methanol photo-oxidation over mesoporous Au/TiO_2 nanocrystals as photocatalysts.[51] Notably, the topotactic attachment working as the basis of this mechanism has been employed to explain the mechanism of the crystal growth of anatase and iron oxide nanoparticles,[52] as well as of single crystalline ZnO nanorods from quasi-spherical ZnO nanoparticles.[53]

The antenna mechanism should lead directly to an enhancement of the overall photocatalytic activity because the chance of using more photons arriving at the nanoparticles is higher. This is reflected in the fact that those photons arriving at particles without adsorbed target species will not end up in mere recombination but will still be useful by means of the present mechanism which permits the delivery of the photogenerated species for reaction

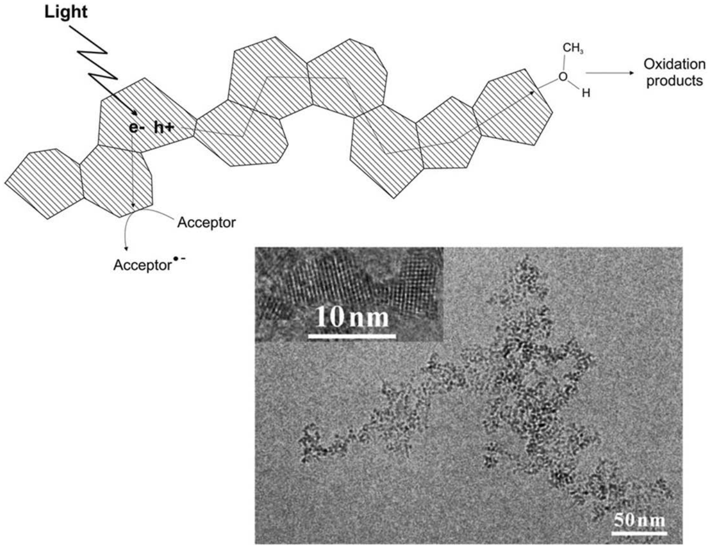

Figure 3.1 Schematic representation of the antenna mechanism. The photogenerated charge carriers can be transferred due to the topotactic attachment of the particles represented in the scheme by the alignment of the lattice fringes. Cryo-TEM and HRTEM (inset) of a 0.5 at% Fe(III)-doped TiO_2 sample showing the topotactic attachment between the particles. (Adapted with permission of Elsevier, ref. 57.)

at another particle within the chain. In other words, the physical and energetic interconnection among TiO_2 nanoparticles can be regarded as ensuring an enhanced charge separation and a consequent reduced recombination. In this sense, the charge carrier diffusion length is markedly increased.[54]

Recently, Park *et al.*[55] provided support for this mechanism, by means of decoupling the light absorbing moiety from the active catalytic center. This was achieved by monitoring the H_2 production under visible light of an ensemble of two different modified TiO_2 nanoparticles systems, *i.e.*, dye-sensitized and Pt loaded, mediated by bare TiO_2 nanoparticles. In dye-sensitized systems, an electron is injected into the TiO_2 conduction band upon light absorption, while noble metals at the nanoparticles ensure the H_2 production localized at the surface of the metal. The presence of the bare TiO_2 nanoparticles mediating both different modified systems is aimed at facilitating the charge separation and the electron migration from the dye-sensitized part of the agglomerate to the Pt loaded one across the grain boundaries. Retarded recombination on the dye-sensitized part was confirmed by transient laser spectroscopy. Additional effects of a diminishing H_2 production may be caused by the increase of pH resulting from H^+ consumption at the reduction reaction. Deficient proton diffusion from the bulk media may impact on the rate of neutralization in terms of keeping pH constant, meaning that local pH changes (increase) near the metal surface could result in a reduced H_2 production.

An engineering challenge for more direct proof of such a mechanism would be, for instance, the realization of spatially resolved experiments involving the construction of chains of topotactically attached crystallites with different lengths. Then, the illumination should be provided to a crystallite at one end of the chain, while the electron and/or the hole should be collected at the other end. Another major technological challenge will be the construction of a proper experimental setup for measuring the photocatalytic degradation of the crystallite at the end of the chains, taking into account the very small dimensions of the systems, *i.e.*, the surface area of one crystallite, the amount of adsorbed pollutant at the specific surface area, *etc.*, for the application of analytical or electrochemical techniques. In this sense, Park's work is independent of these needs, albeit the technique is sensitive to pH. Its control at a nanoparticle scale spatial resolution is a technological challenge that would enlighten not only these types of experiments but plenty of others in which protons – for instance, as main contributors to the surface charges of the nanoparticles – play a most important role.

3.3.2 Deaggregation of Particle Agglomerates

This mechanism was first suggested by Pagel.[56] Laser pulse-induced optoacoustic calorimetry (LIOAC) measurements of suspensions of 2–4 nm anatase nanoparticles in water in the presence of halide ions, $X^- = Br^-$ or Cl^-, showed that the formation of the corresponding radical anions, $X_2^{\bullet -}$, was unexpectedly exothermic rather than endothermic. Hence, a model invoking newly formed surface area at the particles was suggested. The model proposes a partial deaggregation of the aggregates described above by the effect of light, thus producing additional photocatalyst surface area. The subsequent establishment of the thermodynamic protonation equilibrium induces additional halide adsorption and the formation of the respective electrochemical double layer, all of which are exothermic processes explaining the exothermal LIOAC observations during $X_2^{\bullet-}$ formation (Figure 3.2).

The enthalpy of deaggregation was estimated to be around 30 kJ $\mathrm{mol_{TiO_2}}^{-1}$, corresponding to the cleavage of hydrogen bonds that stabilize the particle aggregates. Rigorously, this energy lies in the range of the binding energy of one hydrogen bond, implying a rather weak particle–particle interaction within the nanoparticulate clusters. However, this is not the case for all particles in all agglomerates. As shown in the HRTEM image presented in Figure 3.1 at least some particles appear to be in very close contact and hence strongly bounded (likely bonded by topotactic attachments), leading to the optimal situation for the antenna mechanism to take place (see above).

According to the deaggregation mechanism the energy liberated non-adiabatically upon recombination of a photogenerated electron–hole pair can be used by the system to break the bonds that had “glued” some particles together. The deaggregation mechanism thus requires the existence of some particles weakly bounded to the overall agglomerate which are preferentially attached to its outer part where the incoming photons are absorbed. Figure 3.2 schematically illustrates the deaggregation of the first particle from the cluster of nanoparticles.

In analogy to the dissolution of a solid, the agglomerates may deaggregate stepwise by losing particles from outside to inside upon consecutive photon absorption. Furthermore, this process will stop when reaching a region within the agglomerate where the particles are more strongly bound to each other.

Since the deaggregation mechanism requires the consumption of photons, it competes with the photocatalytic reaction under consideration leading to a decrease of the photocatalytic activity of the system. However, this

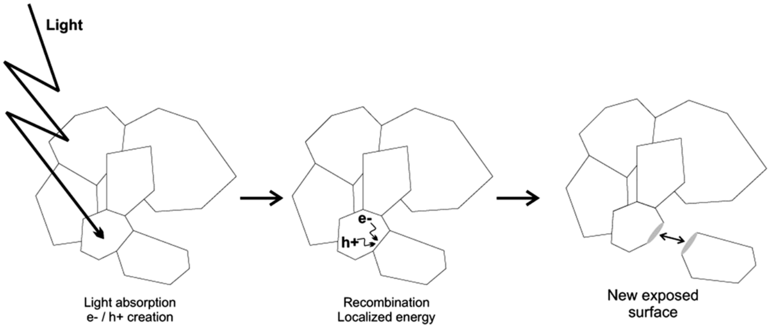

Figure 3.2 Deaggregation scheme illustrating the separation of an outer particle from the agglomerate following the absorption of light.

model was applied to explain a remarkable increase in the quantum yield of photocatalytic methanol oxidation observed upon repetitive laser pulse illumination.[57,58] In this case, based upon the calculation of the energetic requirement for deaggregation, it was concluded that the energy supplied by the first 200 laser pulses was likely to be sufficient for the supposedly stepwise deaggregation of even larger agglomerates than a tetramer, as explicitly suggested by Pagel's model.[56] The quantum yields were compared to those of continuous illumination photocatalytic experiments, and remarkably higher yields were obtained by laser pulsed illumination. Since in continuous illumination experiments the absorption of a photon by a single nanoparticle appears to be a rare event as compared with the high-intensity laser pulse illumination, it was concluded that the aggregation remains intact in the former case because there is sufficient time for the redistribution of the photon energy among the many vibrational modes before the same aggregate absorbs a second photon. Experiments conducted under chopped illumination (10 s light on/1 s light off) using $Pt^{x-}/TiO_{2}-_{y}B_{y}$ as a photocatalyst revealed a slightly higher rate for hydrogen evolution than under continuous illumination.[59] It was suggested that the period of darkness favored the capture of electrons from the electrolyte while under its absence an accumulation of photogenerated electrons and holes at the interface enhanced their recombination, which was identified as a major back reaction decreasing the hydrogen evolution at the photocatalyst.

Recently, experiments under continuous illumination at rather low intensities (0.6 mW cm^{-2}) with TiO_2 layers in contact with acidic water solutions containing Cl^- showed that the infrared bending mode of water only develops in the presence of light and not after longer dark periods.[60] The nanoparticles are packed forming a thin film that is in contact to the solution. The space in between the particles is filled with water molecules, the spectrum of which is subtracted as a blank. Only after illumination is the bending mode of water visible, indicating that additional water has been incorporated in between the particles, and that is possible if the thin film expands due to the deaggregation of some agglomerates. Such observations indicate that the phenomenon may still proceed under continuous illumination and not only under pulsed irradiation. The energetic requirements may be easily met due to the high density of agglomerates as compared with the colloidal dispersions employed by Pagel *et al.*

Indirect proofs of such an apparently simple mechanism are always welcome; a more conclusive proof would include thermodynamic measurements of the exact energy requirements for a quantitative energy and mass balance.

3.3.3 Band-Gap Coupling: Z-Scheme and Heterojunctions

Cooperative effects between different photocatalyst particles are also found to occur in dimers rather than involving extended arrangements such as agglomerates or chains as in the deaggregation or the antenna mechanisms. One example of such systems is the combination of two semiconductors the band-gaps of which are indirectly coupled *via* a reversible donor/acceptor pair. Depending upon the appropriate positioning of the band-gap energies the two-step photoexcitation of these systems have been shown to efficiently split water in the absence of any sacrificial reagents.[61–63] The photocatalytic decomposition of water thus operates under a mechanism similar to the so-called Z-scheme reaction (Figure 3.3). In this manner, O_2 and H_2 gases are formed over the two different photocatalysts by the photo-oxidation of H_2O and the concurrent photoreduction of H^+. These systems also consist of a reversible donor/acceptor pair, *i.e.*, redox mediator. Among the O_2 evolution photocatalysts and redox mediators examined, Pt-loaded WO_3 (Pt/WO_3) and the IO_3^-/I^- pair, respectively, were found to be the most active components.[63] Furthermore, the combination of these two components with Pt-loaded ZrO_2/TaON allowed stoichiometric water splitting into H_2 and O_2 under visible light.[63] The high activity of this non-sacrificial visible-light-driven water splitting system which utilizes the so-called Z scheme is due to the efficient reaction of electron donors (I^- ions) and acceptors (IO_3^- ions) on the Pt/ZrO_2/TaON and Pt/WO_3 photocatalysts, respectively, which suppresses undesirable reverse reactions.

The idea of avoiding or at least retarding the electron–hole recombination, thus enhancing the photocatalytic activity, has been thoroughly investigated by many researchers. The employed approaches involved the direct electronic coupling of the band-gaps from two different semiconductors,[64–66] or of one band of the photocatalyst to the electronic levels of a noble metal catalyst particle[66,67] (Figure 3.4). These systems are complex and there are many parameters to control and tune. For example, the adsorption of the target compound to be oxidized needs to occur totally or at least preferentially at the particle where the holes are available. Additionally, the electron

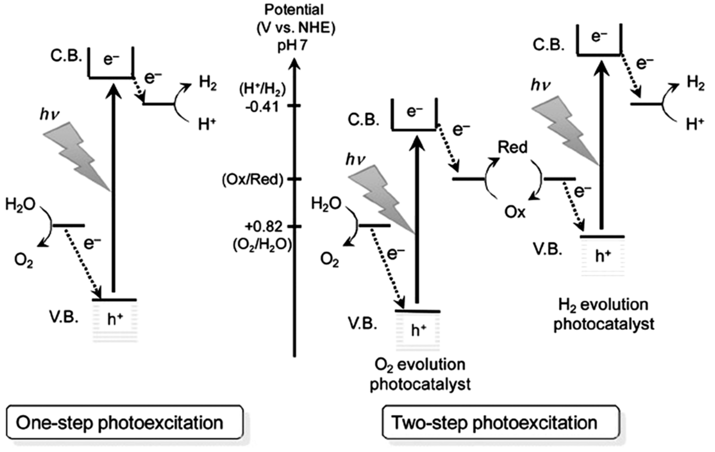

Figure 3.3 Schematic energy diagrams of photocatalytic water splitting for one-step and two-step photoexcitation systems. (Reprinted with permission from ref. 63. Copyright 2010 American Chemical Society.)

acceptor needs to adsorb or pick up the electron from the attached particle which can be either a semiconductor or a metal. In the opposite situation, in which a selective adsorption is not achieved, either no enhancement or even a partial or total suppression of the photocatalytic activity will be observed. The scenario is therefore delicate, since instead of avoiding recombination its facilitation may even be induced.

Immediately upon their creation, the photogenerated electrons and holes need therefore to move across the particle to arrive to their corresponding reaction sites. However, if the particles are small, the charge carriers will feel the influence of surface modifications. The attachment of another semiconductor material may produce depletion or accumulation regions and, consequently, the electronic properties may be modified or altered. In this case,

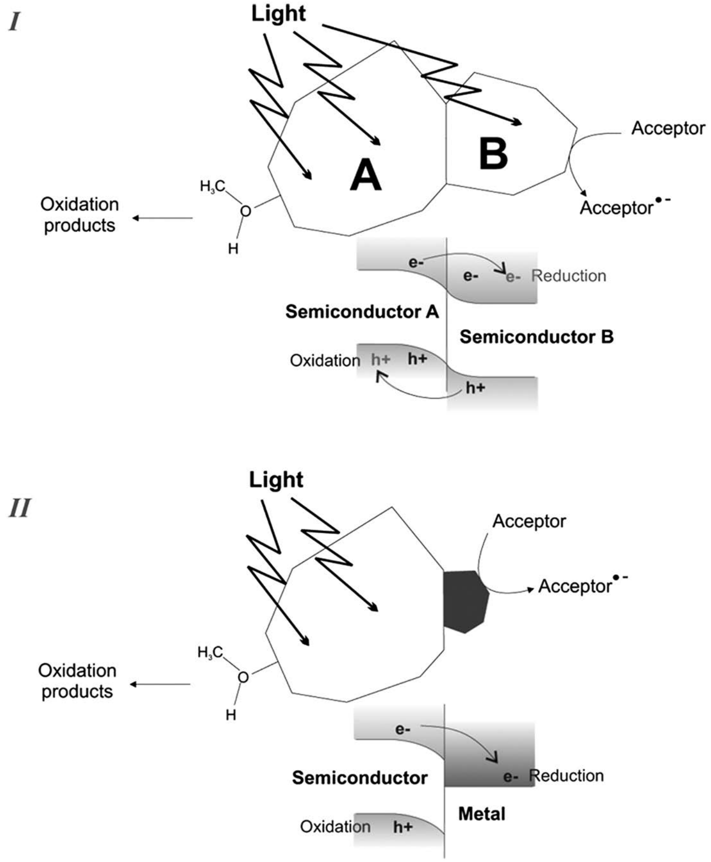

Figure 3.4 Band-gap coupling schemes for electron–hole separation. (I) Coupling of two semiconductor particles with different positions of conduction and valence band. (II) Metal particle or cluster attached and electronically connected to a semiconductor particle. In both cases the photocatalytic oxidation of methanol has been arbitrarily chosen as the illustrative example.

due to the electronic coupling in the heterojunctions, as a band bending is to be generated, the resulting local electric fields acting on the photogenerated charge carriers may be responsible for establishing the direction of migration to their corresponding reaction sites.

It must be remarked that not any combination of two different semiconductors physically attached and in good electronic contact will serve as a proper system for the electron–hole separation. Those with an ohmic contact (Figure 3.4), and not a rectifying contact (Schottky barrier), between the semiconductors and/or the semiconductor and the metal constitute an optimal scenario for avoiding recombination through an efficient charge separation. A minimal energy loss is also desired. The application of external electric fields may serve to enhance the mobility of the carriers, but its application in the nanometer size range remains an engineering challenge.

The combination of different semiconductors with noble metals and/or redox couples in an electrolytic matrix, as well as the establishment of heterojunctions, represent an important and promising issue for the future of photocatalysis.

3.3.4 Wettability

Wettability, highly hydrophilic conversion, or superhydrophilicity is a phenomenon observed on UV irradiated surfaces in which a drop of water spreads to reach a contact angle of 0°. On illuminated TiO_2 surfaces this phenomenon was first observed by Kume and Nozu and documented in a patent application[68] and later published by Fujishima and coworkers.[69] Intensive research is nowadays being performed on this topic.[70–75] Several models have been proposed to explain the underlying mechanism[9,76–78] and will be briefly described below.

3.3.4.1 Creation of OH Surface Groups

The atomistic model proposed by Fujishima, Hashimoto and coworkers incorporates the participation of photogenerated electron–hole pairs for the creation of new OH surface groups and consequently of evenly distributed hydrophilic nanosized domains.[79–81] While the photogenerated electrons reduce surface Ti(IV) atoms to the Ti(III) state, the holes oxidize bridging O atoms, which are subsequently ejected from the lattice. Water molecules will then occupy these oxygen vacancies producing adsorbed bridging OH groups. Such highly reactive doubly coordinated OH groups further proceed to trap a second hole, weakening the bond to one of the Ti atoms. Subsequent dissociative water adsorption finally yields two OH groups singly coordinated to two Ti atoms (Figure 3.5).[80]

This mechanism was originally suggested based on results from UV irradiated rutile single crystal (110) surfaces (Figure 3.5) containing bridging O atoms. Supporting this mechanism, high resolution images showed

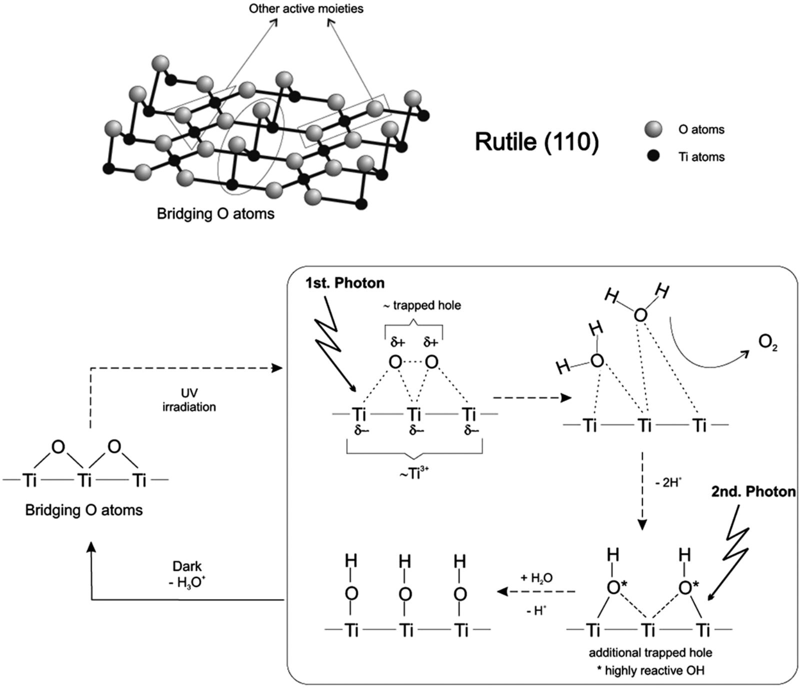

Figure 3.5 Atomistic model for the explanation of the photo-induced hydrophilic effect on TiO_2 according to Fujishima, Hashimoto and coworkers on the rutile (110) surface.[79–81]

hydrophilic domains photogenerated preferentially along the [001] direction of the (100) plane.[69] Contradictorily, Mezhenny *et al.* showed a negligible or the lack of an effect on the appearance of rutile (110) surfaces upon irradiation with reasonable light intensities by means of scanning tunneling microscopy.[82] Identical experiments exploring the wettability on rutile (100) surfaces that possess a different distribution of bridging O atoms yielded similar results, while those on (001) surfaces with no bridging O atoms showed superhydrophilicity only upon extended UV irradiation. This was interpreted assuming that bridging O atoms are slowly created by proper surface reconstructions.[83]

The existence of dangling bridging O atoms as a starting step requires non-hydrated surfaces, which experimentally is rather difficult to realize unless freshly cleaved single crystals are used or the material is heated in vacuum to high temperatures. Supporting this fact, temperature programmed desorption (TPD) experiments show that at least one single monolayer of water is always present at TiO_2 surfaces under ambient conditions.[84] Although the type of adsorption of water molecules is still a matter of discussion, *e.g.*, dissociatively or associatively, bridging O atoms appear to be fully involved in both adsorption modes.[85–87]

The model depends on the action of a second photogenerated hole on already highly active OH groups to break the bridging bond (Figure 3.5). Experimental evidence demonstrating the apparently different nature of these highly active OH groups as compared with other OH groups formed, for instance, upon surface hydration is, however, still not available.

Photo-induced hydrophilicity was subsequently reported by the same authors to also occur on a polycrystalline anatase thin film.[83] Similar investigations with single crystals of anatase would surely be desirable to elucidate the mechanism operative for this polymorph.

Interestingly, an enhancement of the photoinduced superhydrophilicity is found by introducing tensile stress.[88] To explain this phenomenon it has been suggested that the surface reconstruction underlying the superhydrophilicity involves a volume expansion occurring exclusively near the surface[89] and the tensions created upon the lattice distortions lead to the observed increase of surface hardness.[76] However, White *et al.*[90] studied the phenomenon using rutile (110) surfaces prepared with or without oxygen vacancies, by means of high-temperature annealing in ultra-high vacuum and healing with O_2 at 220 K, respectively, and found that the wetting behavior is independent of the presence or absence of surface oxygen vacancies.

Even though the creation of a hydrophilic surface competes for electron–hole pairs with the photocatalytic conversion of pollutants,[9] the overall photocatalytic process can still be favored due to the increase of the adsorption capacity of the semiconductor *via* the creation of OH groups as new adsorption sites for pollutant molecules. Additionally, the formation of the highly reactive OH radicals may also enhance the photocatalytic activity by increasing the oxidizing power of the photogenerated holes.[91]

3.3.4.2 Impurities Removal

A simple mechanism, totally extrinsic to the atomic structure of TiO_2 and involving the photocatalytic oxidation of adsorbed organic impurities to yield free surface for the spreading of water droplets, has been suggested to be responsible for its photo-induced hydrophilicity property. Yates and coworkers have shown that low water contact angles at the UV irradiated single crystal rutile (110) surface correlate with the photocatalytic removal of non-wetting hydrocarbons.[92] Hence, these authors argue that the clean TiO_2 surface is inherently hydrophilic (Figure 3.6). Mills and Crow have also concluded that pristine surfaces of plain glass and titania, which are intrinsically superhydrophilic, lose this property due to contamination by hydrophobic organic compounds, as indicated by a noticeable increase in the measured contact angle.[73]

An induction time for the surface cleaning preceding the photocatalytically induced hydrophilicity is therefore expected. Moreover, interferences due to the presence of reaction products of such degraded impurities may

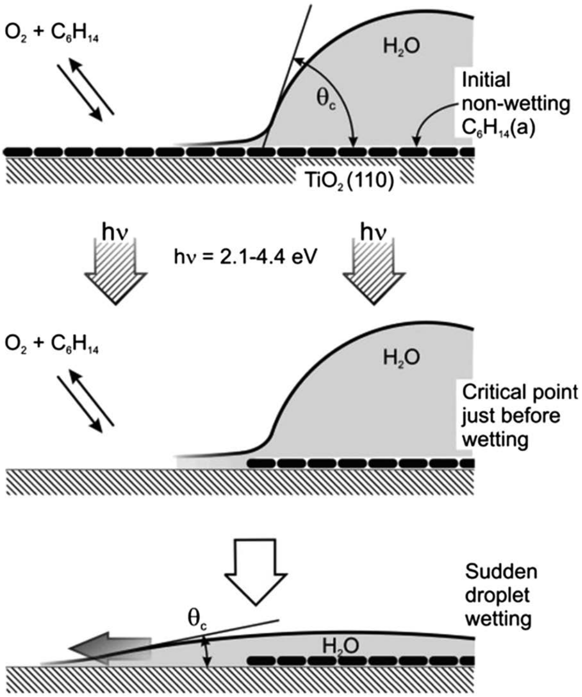

Figure 3.6 Impurity removal allowing a water droplet to spread on the clean rutile (110) face. (Reprinted with permission from ref. 92. Copyright 2005 American Chemical Society.)

catalyze, *i.e.*, accelerate, or more likely retard the creation of a hydrophilic surface. The level of impurities is known to be variable, depending upon the type of photocatalyst used as well as the storage or working conditions. It is common for both mechanisms ("OH surface group creation" and "impurities removal") that the superhydrophilic surface of the photocatalyst increases its adsorption capacity, and should consequently lead to an enhancement of its photocatalytic activity. This will, in particular, be true for hydrophilic pollutants, while the more hydrophobic ones should be degraded with a lower efficiency.

More evidence supporting this mechanism was provided by Ishida and Fujita[93] who showed that superhydrophilic TiO_2 can be obtained without UV irradiation. The treatment of TiO_2 surfaces with reactive oxygen species generated by air plasma removes all surface organic contaminants thus leading to almost 0° for the contact angle of water.

Another recent work by Foran *et al.*[94] in which the time dependence of some surface coverages of organic compounds on TiO_2 were modeled showed that the value of the contact angle for water prior to illumination is close to 4°.

The results of Ishida and Fujita and those of Foran *et al.* support the fact that clean TiO_2 surfaces are inherently superhydrophilic.

3.3.4.3 Adsorbed and Desorbed Water

An alternative atomistic model, not directly intrinsic to the TiO_2 structure, but involving interactions of water molecules at the UV irradiated TiO_2 surface, has been suggested by Anpo and coworkers to explain the photoinduced superhydrophilicity of TiO_2.[78] These authors envisage a combined process of (a) desorption of H_2O molecules by the effect of heating due to the infrared portion of the light and (b) the partial elimination of hydrocarbons by photocatalytic decomposition under UV irradiation. Process (b) resembles the impurities removal mechanism suggested by Yates (see above).

With a decrease of adsorbed H_2O molecules at the surface, the distribution of H bonds within adsorbed water clusters decreases, resulting in a decrease in the surface tension. This is suggested to be the driving force for the water cluster to spread out, forming a thin water layer (Figure 3.7).

To a certain extent, the model suggested by Anpo and coworkers does not compete with the photocatalytic reaction since it includes the residual heat produced by the illumination source. On the one hand, by water spilling the pollutant can be delivered to other parts of the surface for adsorption and further photocatalytic removal. On the other hand, some electron–hole pairs are expected to be consumed for the removal of the impurities present at the surface, thus reducing the efficiency of the photocatalytically induced superhydrophilicity.

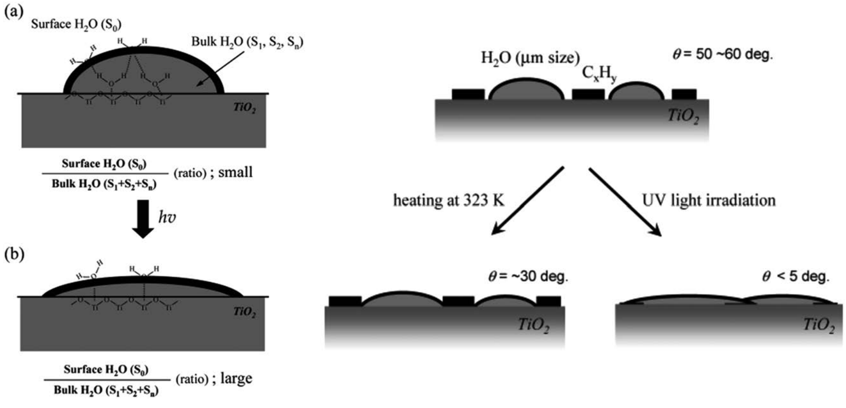

Figure 3.7 Mechanism suggested by Anpo and coworkers. The two diagrams on the left show the shapes of H_2O clusters on TiO_2 surfaces: (a) before and (b) after UV light irradiation. The chemical states of water are represented by S_0, H_2O molecules without any active hydrogen bonds; S_1 and S_2, H_2O molecules with one or two active hydrogen bonds, respectively; S_n, polymeric chained H_2O clusters. On the right-hand side, the mechanism for improvement of surface wettability of TiO_2 photocatalyst surfaces under UV light irradiation is shown: the water clusters spread by absorption of residual heat from the irradiation source and the removal of organic impurities (C_xH_y) results in a contact angle change from 50–60° to less than 5°.[78] (Adapted with permission from ref. 78. Copyright 2005 American Chemical Society.)

3.3.4.4 Some Remarks About Wettability

The wettability property of UV irradiated TiO_2 has initiated a new discussion about the underlying mechanism and the impact on the photocatalytic activity of the semiconductor. The models suggested to describe the phenomenon are based on atomic surface reconstructions that lead to the creation of additional OH groups, photocatalytic oxidation and removal of organic impurities which hinder the inherent surface hydrophilicity of the semiconductor, and rearrangements of H bond distributions within adsorbed water clusters upon evaporation of some water molecules due to residual heat from the illumination source. On the one hand, wettability appears to be a competitive reaction consuming electron–hole pairs intended to act on the pollutant that needs to be eliminated by photocatalytic degradation. On the other hand, by water spilling, pollutants with high water affinity can be delivered to other parts of the surface for adsorption and further photocatalysis. It might be as well possible that the wettability phenomenon is simply the sum of all these suggested processes. In this sense one could say that a still undiscovered mechanism of wettability "hides" behind a change of paradigm challenging current knowledge.

3.3.5 Photo-Thermal Desorption of Water

The model of the photo-thermal desorption of water used to explain the increase of the TiO_2 adsorption capacity for oxalic acid under UV irradiation is based on the results from *in situ* attenuated total reflection-Fourier-transform infrared (FTTR-FTIR) experiments.[95] The creation of new adsorption sites upon UV illumination of the TiO_2 surface by means of a photo-thermal-desorption of water molecules has been suggested (Figure 3.8). The "photo-" part is supported by similar experimental observations in which water molecules are desorbed from the TiO_2 surface by direct action of the UV irradiation.[96] The "thermal-" part is based on the concept that the thermal energy (non-radiative) released upon recombination of photogenerated

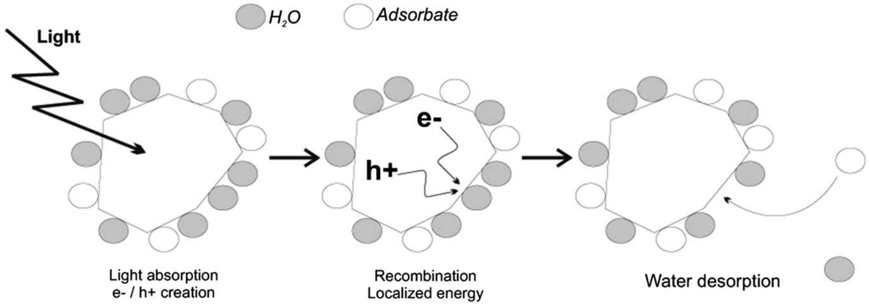

Figure 3.8 Photo-thermal desorption of water creating additional adsorption sites under band-gap illumination.

electron–hole pairs may be used by the system to desorb water molecules. UV induced local heating effects in TiO_2 nanocrystals have been reported by Berger *et al.*[97] This mechanism suggests that the stronger chemisorption of water as compared to other ligands can be reverted by the effect of light under non-equilibrium conditions.

Two effects that play in opposite directions coexist in this mechanism resulting in the detriment or enhancement of the photocatalytic activity of the semiconductor. On the one hand, the consumption of electron–hole pairs to form new adsorption sites previously occupied by water molecules impacts negatively on the photocatalytic activity towards the target pollutant, while, on the other hand, the enlarged adsorption capacity of the photocatalyst obtained by water desorption will definitively lead to an increase in the photocatalytic activity of the adsorbed pollutant. As compared to the impurities removal mechanism (see above), which also provides new sites for the adsorption of target molecules and hence a predictable albeit small enhancement of the photocatalytic activity correlating to the surface concentration of the impurities, perturbation of the adsorption equilibrium under irradiation exchanging adsorbed water into educt molecules may produce drastic changes in adsorption capacity and consequently in photocatalytic efficiencies since the amount of adsorbed water is much higher than that of adsorbed impurities.

Direct proofs for the operation of this suggested mechanism, in systems where the photocatalysts are immersed or in contact with a water bulk phase containing the pollutant, are highly challenging because the assessment of the surface, at an atomic or molecular level, is drastically limited. Theoretical calculations are usually an interesting tool with which to explore mechanistic possibilities. Spatially resolved thermodynamic measurements may lead to the findings of further hints crucial to elucidate the true division between the “photo-” and “thermal-” parts of this mechanism.

3.4 TiO_2 Photonic Crystal Nanostructures

An interesting concept in photocatalysis was suggested some years ago and is based on the idea of combining the properties of photonic crystals with the photocatalytic power of the semiconductor. Such an approach is commonly called photonic photocatalysis. Photonic crystals are periodic arrangements of dielectric contrast in the length scale of the wavelength of light.[98] Upon interaction with light, coherent Bragg diffraction forbids photons of certain energies to propagate through the material in a particular crystallographic direction giving rise to a stop-band reflection, the energy range of which depends on the periodicity and the dielectric contrast of the photonic crystal. At the frequency edges of these stop bands photons propagate with a reduced group velocity. These photons are called slow photons. Such systems can be constructed using semiconductor materials; of particular interest is the dielectric contrast between that of the semiconductor and that of air. The photocatalytic activity of the semiconductor can thus be expected to increase if it is conveniently structured as a photonic crystal. In that case, the energy of the slow photons must overlap with the absorbance edge of the semiconductor. Due to the increased effective optical path length of the slow photons, an enhancement of the light absorption is to be expected resulting in the generation of additional electron–hole pairs that would have not been produced in the unmodified semiconductor.

The concept of photonic photocatalysis has been investigated experimentally by Ozin and coworkers[21,99–101] employing sacrificial closed packed polystyrene sphere templates which upon infiltration with a TiO_2 precursor and subsequent calcination yielded inversed anatase opal structures supported on a glass substrate (Figure 3.9). These periodic arrangements of air spheres in a TiO_2 matrix show enhanced photocatalytic properties as compared with non-structured TiO_2 for the degradation of the model compound methylene blue when the size of the spheres was about 300 nm.[21] Aqueous phase photocatalysis is therefore expected to be highly efficient because the accessible surface area for the pollutant within these systems is considerably higher than that in dispersed powder systems,[99] or at least comparable to those systems that are porous, micro-porous and multi-size-porous. One advantage of these high-surface

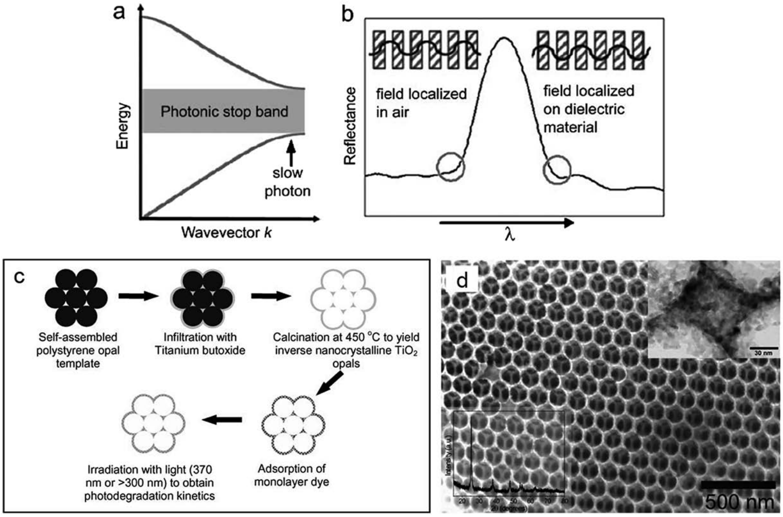

Figure 3.9 (a) Photonic band diagram of a photonic crystal. Slow photons are associated to the reduced group velocity propagating light near the photonic stop-band. (b) Stop-band reflection with the position of the slow photons being indicated by the circles. (c) Scheme showing the fabrication of a TiO_2 inverse opal and the solid-state photocatalytic degradation experiments using a dye as model compound. (d) Scanning and transmission electron microscopy images, and powder X-ray diffraction pattern (lower left-hand corner), of an inverse TiO_2 opal. (Reproduced from ref. 101 with permission of The Royal Society of Chemistry.)

area photocatalytic materials is that after the reaction for treating waste water, the photocatalyst can be easily removed, especially when compared to the situation in which a powdered material has been suspended in the aqueous system.

The influence of the structure of the semiconductor on the improvement of its photocatalytic activity has been reviewed by Aprile *et al.*[102] showing that physical modifications without changes in the chemical composition of the semiconductor can have a considerable impact. Photonic crystal structures, encapsulation inside the micropores and cavities of zeolites, structured periodic mesoporous materials with high specific surface area and well-defined porosity, and nanotubes of micrometric length with a long diffusion length of charge carriers along the nanotube axis are examples of such physical modifications. In general, such modifications of the system are the target of many engineering approaches for extending the photocatalytic activity of UV absorbing semiconductors into the visible region. Interestingly, Meseguer *et al.*[103] have expanded this concept to the so-called photonic sponge. In this case an appropriate distribution of air spheres of different sizes in a TiO_2 matrix prepared using a commercial TiO_2 powder is fabricated to obtain films with highly scattering properties over a very wide wavelength range in the visible spectral region. The resulting photonic sponge exhibited a 3.3-fold higher initial photocatalytic degradation rate for succinonitrile than analogous films of the same thickness made of unstructured P25 TiO_2 nanoparticles.[103]

A remarkable enhancement of the photocatalytic activity under visible light irradiation was also achieved by coupling inverse TiO_2 opal photonic crystals to a TiO_2/poly(3-hexylthiophene) heterojunction photocatalyst.[104] Moreover, systems involving the presence of metal particles to suppress the electron–hole recombination, such as inverse TiO_2/Pt opal Schottky structures on a Ti substrate, have been investigated, yielding kinetic constants for the degradation of the model compound phenol that are 1.5 times larger than that of disordered inverse TiO_2/Pt opals, and 3.3 times higher than that of nanocrystalline pristine TiO_2 films on the Ti substrate.[105]

Until now, one of the limitations of these photonic photocatalytic systems is that large sizes of the photonic semiconductor crystals could not be prepared. Moreover, the preparation procedures developed till now yield materials in which the concentration of defects is high enough to suppress or at least hinder the desirable properties. Hence, promising materials should ideally be large and defect-free.[98] But, is it the only challenge behind photonic photocatalysis? Is it that the improved photocatalytic efficiency of TiO_2 nanostructured as a photonic crystal just relies on the control of the synthesis and preparation parameters? This is, surely, a vast field for future improvement, but the mechanisms of photocatalysis should also be revised in relation to the effects on such special systems. Are all the suggested mechanisms in TiO_2 photocatalysis beneficial for the expected improved efficiency in photonic photocatalysis?

A close view of a TiO_2 photonic crystal in an inverse opal structure (Figure 3.10) shows that the structure of the systems is formed by attached nanoparticles of *circa* 20–30 nm size, independently of the employed method to produce them.[106] Such an arrangement of particles turns the system into a good candidate for the operation of the discussed mechanisms in TiO_2 photocatalysis.

While an antenna mechanism would work in favor of enhancing the photocatalytic efficiency, in general, and specifically in TiO_2 photonic crystals, the effect of the deaggregation mechanism will work to the detriment of it. By means of the antenna mechanism, the effect of light can act in the system beyond the upmost surface. On the other hand, light induced deaggregation will provide additional surface area by breaking the agglomerates that in the case of the photonic systems are essential to keep the structure that ensures the existence of slow photons. Such a mechanism would therefore be undesired for photocatalytic systems with an enhanced efficiency based on structural modifications. Not only the structure would be broken, but also part of the material from the inverse opal would be lost in the surrounding media due to the deaggregation mechanism.

As TiO_2 photonic crystals are structures with large and interconnected pores, strong adsorption of reactant, products or intermediates far from the surface leads to "encapsulation" of species. Hindered diffusion in this type of system, when very small polymeric spheres are used as templates, also plays an important role which deserves close attention. Hence, gas or aqueous phase photocatalytic applications of TiO_2 photonic crystals may lead to different results as compared to non-structured TiO_2 systems. It is therefore a matter of which compound is to be degraded in order to find an appropriate photocatalytic design. As the nature of the compound is important, specific studies for each target are necessary.

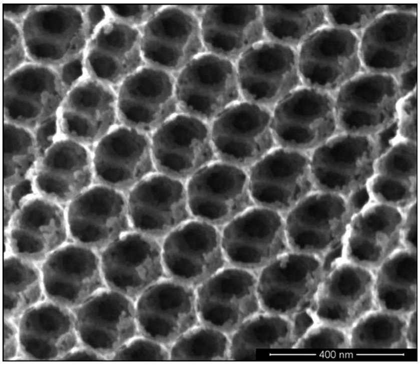

Figure 3.10 Field emission scanning electron microscopy (FE-SEM) of a TiO_2 photonic crystal in an inverse opal structure. TiO_2 nanoparticles of 20–30 nm form the structure. The sample was not covered by any thin layer of gold but inspected under the microscope without any further treatment.

3.5 Concluding Remarks

The many different and ingenious mechanisms that try to model and to explain the various processes involved in TiO_2 photocatalysis lack rigorous experimental evidence in order to proof their validity or to decide among different alternatives for any particular case or system. Novel and very challenging experimental designs for their validation will therefore have to be developed. And in this sense, will TiO_2 photonic crystals be a key element in the proof of a proposed mechanism?

Whether direct hole oxidation or indirect OH radical reactions take place has not yet been answered for many systems; furthermore, a unifying concept taking into account all initial electron and hole transfer steps is missing as well. The control, the monitoring and the capability to tune the very first step in which the electron–hole pair is created is extremely important. It must be remarked that the question of where and to what extent the photogenerated charge carriers are localized in the semiconductor is a very difficult issue to solve. Will it require the development of more advanced theories or other types of experiments yielding new physical–chemical insights, or rather the combination of both?

Direct proof of the antenna mechanism strongly requires advances in characterization tools for the materials. A proper description and understanding of electron and energy transfer processes occurring between two or more particles is still missing. Moreover, a detailed characterization of the particle–particle interface remains a key question to be solved. This includes a detailed understanding of the electronic coupling of two semiconductor particles, of a semiconductor and a metal particle as well as of an array of particles in agglomerates able to work as an antenna. The dynamics of the formation of these interfacial attachments need to be studied as well as their detailed structure and the penetration depth of the interfacial properties into the bulk of the particles.

On the other hand, the relative importance of the bulk of the particle in comparison with its surface needs to be assessed. Perhaps, the photocatalytic reaction can be well described just using surface properties. Moreover, atomistic models can clearly make a great contribution to this point and computational sciences will find a good opportunity to provide useful tools. However, the difficulties in comparing the predictions of an atomistic model with the results of macroscopic experiments prevents a general consensus from being reached. That is, for example, the case for the wettability.

The determination of surface energies can also open new doors for further interpretations, although such measurements are difficult for nanoparticles. In principle, the clean surface of, for example, a metal oxide in vacuum is fully hydrophilic. The unsaturated bonds of the most exposed atoms, determining the surface energy, will therefore relax successfully binding water molecules. Dissociative water adsorption in such a situation is thus the expected form of adsorption since it can electroneutrally satisfy all dangling bonds at the surface. The fundamental question of how water adsorbs on the metal oxide surface has not been answered unanimously yet, deserving undoubtedly challenging investigations.

The mechanism through which newly available adsorption sites are provided by photodesorption of water molecules is one example of what for water adsorption. Other key-factors for a better understanding of the role of surficial water entail the characterization of surface topographies as well as good theoretical models describing the localization of photogenerated charge carriers and the destination of recombinations not yielding any photocatalytic reaction. Particles in the nanometer size range are in general difficult to characterize and it is still very uncertain whether their bulk properties are the same or at least similar to those of the same material with a macroscopic size. Surface indexing of nanoparticles is therefore a need for the understanding of surface reaction mechanisms at an atomic level.

Regarding the energetics, the deaggregation of the agglomerates under light irradiation involves the consideration of non-adiabatic thermal processes which are often not considered in photocatalysis. In general, the rates of a photocatalytic process are calculated by monitoring the compound's concentration during its photocatalytic degradation and/or the concentration of the products formed.

When the exact absorbed light energy is known, the ratio of reaction rate to the absorbed photon flux will give the quantum yield (for monochromatic illumination) or the quantum efficiency (for polychromatic illumination). In most cases, however, only the total amount of incoming radiation is known, leading to values of photonic yield or photonic efficiencies, respectively. In most cases the thus determined photonic efficiencies values do not exceed 1%, *i.e.*, 99% of all available photons are not utilized by the process. The fate of the remaining photons not leading to any photocatalytic conversion is usually not considered. But, what about them? What about their trajectories, activities, reactions, participation in combined reactions, destinations, energies, their dissipation as heat or radiation, recombinations, *etc.*? What about the fate of the photon energy that is absorbed without being involved in the studied photocatalytic conversion process? A better understanding of these "majority" processes can be expected to have an enormous impact on the understanding (and the eventual improvement!) of the minority processes. These kinds of investigations will surely yield some very unexpected results, *i.e.*, it is very likely that the major part of photocatalysis is still undiscovered.

Structural modifications by means of the construction of photonic crystals with semiconductor materials, *e.g.*, photonic photocatalysis, is an interesting and promising approach not only for extending the absorption of light to spectral regions where the semiconductor absorbs poorly but as a suitable material for the study of the mechanisms of TiO_2 photocatalysis.

The use of TiO_2 photonic crystals opens a door for both new approaches in material synthesis, as well as for advanced engineering technologies. An indisputable interweave of technological developments and basic science will certainly provide the necessary experimental data for understanding the processes taking place in the system. However, such a dependable experimental basis is also required for the postulation of models explaining the existence or absence of intermediate compounds, the nature of the products, and other characteristic or special features of the photocatalytic reactions. Albeit TiO_2 photocatalysis promises attractive technological applications, further important advances will surely be realized if careful attention is paid to the fundamental unknowns. In addition, it will be knowledge about the processes and the underlying mechanisms that will enable us to produce and control the photocatalytic reactions needed for a sustainable world.

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