

Photocatalytic water treatment: fundamental knowledge required for its practical application

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Abstract This review attempts to present a state-of-the art overview of the underlying principles of photocatalysis that should not be neglected when designing pilot-scale facilities. In particular, the roles and properties of the primary charge carriers generated upon bandgap illumination within a photocatalyst particle, i.e. valence band hole and conduction band electron, are discussed. The chemical nature of the primary oxidant is critically assessed.

Keywords Photocatalysis; pilot scale; water treatment

Introduction

Photocatalysis, i.e. using semiconductor particles under bandgap irradiation as little microreactors for the simultaneous reduction and oxidation of different redox systems, has been intensively studied during the last 25 years since the pioneering work of Carey *et al.* (1976). The main focus of these studies seems to be the investigation of the principal applicability of photocatalytic systems for the efficient treatment of water and air streams polluted with toxic substances. Several review articles on this topic have recently been published (Bahnemann *et al.*, 1994; Hoffmann *et al.*, 1995; Bahnemann, 1999). In some cases, pilot-scale or even commercially available reactors have already been constructed, especially when titanium dioxide is used as the photocatalyst (Dillert *et al.*, 1999a,b; Alfano *et al.*, 2000).

However, due to the inherent complexity of this minute photoelectrochemical system, details of the underlying reaction mechanisms of photocatalysis are even today still far from being understood. In contrast to an ordinary photoelectrochemical cell which employs an external bias voltage to deliberately separate oxidation and reduction processes in different compartments of the reactor, in photocatalysis both processes occur on the surface of the same semiconductor particle, usually only separated by a distance of a few angstroms. Moreover, as is evident from basic principles, the reaction rate of the overall process will be limited by the slowest reaction step, which in most cases is not known. Consequently, most laboratory studies have in the past been restricted to the measurement of overall degradation kinetics of organic model compounds (Bahnemann, 1999).

This review concentrates on a detailed description of the primary events occurring immediately after the absorption of a photon within a single titanium dioxide particle in an aqueous environment. This restriction was made, because: 1) titanium dioxide seems to be the most active photocatalyst, and 2) the photocatalytic treatment of polluted water seems to be a promising application for an interfacial electron transfer serving the environment.

Primary processes upon bandgap irradiation of semiconductor particles

Absorption of a photon with an energy $h\nu$ greater than or equal to the bandgap energy E^g of the semiconductor (i.e. 3.2 eV for titanium dioxide in its anatase modification) generally leads to the formation of an electron/hole pair in the semiconductor particle (reaction (1)).



where e^-_{cb} represents a conduction band (CB) electron and h^+_{vb} a positive hole in the valance band (VB) of the semiconductor. Ultrafast laser flash photolysis experiments using colloidal titanium dioxide have shown that the generation of these charge carriers happens within a few femtoseconds after the absorption of a photon (Colombo *et al.*, 1995; Colombo and Bowman, 1995, 1996). Immediately after the laser flash very broad featureless transient absorption spectra ranging from 400 nm to 800 nm are obtained (Serpone *et al.*, 1995; Bahnemann *et al.*, 1997). These absorption spectra are generally attributed to trapped electrons and holes.

After their generation according to reaction (1) both, conduction band electrons and valence band holes, are migrating to the surface of the semiconductor particle. The transit time τ needed by these charge carriers to reach the surface of the particle is given by $\tau = R^2/\pi D$ with R being the radius of the particle and D the diffusion coefficient of the excited charge carriers (Grätzel and Frank, 1982). Taking a value of $D = 5 \times 10^{-3} \text{ cm}^2\text{s}^{-1}$ (Wolff *et al.*, 1991) and a particle radius of 2.5 nm (radius of particles typically used in experiments with colloidal titanium dioxide) the average transit time is only 1.3 ps. Even in bigger particles such as those used in photocatalytic systems for water treatment (e.g. 21 nm for Degussa P25 titanium dioxide) the transit time is only some ten picoseconds. Reaching the surface these charge carriers are trapped in subsurface and surface states of the particle (reactions (2) and (3))



where e^-_{tr} and h^+_{tr} represent the trapped electron and trapped hole, respectively.

These trapped charge carriers exhibit strong optical absorptions. The position of the absorption maxima is strongly affected by the presence of suitable electron acceptors and donors in the surrounding aqueous phase. Exploiting this effect it has been shown in early laser flash photolysis studies that the trapped electron exhibits a strong optical absorption around 650 nm while the trapped hole absorbs predominantly at shorter wavelengths, i.e. around 430 nm or even shorter (Bahnemann *et al.*, 1984a,b).

The trapping of the charge carriers is a very fast process. Rothenberger *et al.* performed picosecond and nanosecond transient absorption experiments on titanium dioxide and observed that the electron trapping time was faster than 30 ps, the time resolution of their laser system (Rothenberger *et al.*, 1985). The trapping time for holes was estimated to be <250 ns. In a recent picosecond study by Serpone and co-workers employing colloidal titanium dioxide suspensions with varying particle diameters, both the spectrum of the trapped electrons and that of the trapped holes were found to be fully developed after a laser pulse of 30 ps (Serpone *et al.*, 1995). Another recent picosecond study by Bowmann and co-workers had shown that the time needed for the full development of the spectrum of the trapped electron is approximately 200 fs (Colombo *et al.*, 1995; Colombo and Bowman, 1995, 1996).

Chemical nature of trapped charge carriers

Generally it is assumed, that Ti^{IV} cations at the surface of the titanium dioxide particle are reduced by the light induced electrons forming Ti^{III} cations (Howe and Grätzel, 1985, 1987; Moser *et al.*, 1991; Micic *et al.*, 1993) which can be considered to be intrinsic surface states localised about 0.1 eV below the conduction band edge, i.e. within the bandgap (Schindler and Kunst, 1990; Warman *et al.*, 1991). An equilibrium between these trapped

electrons and free CB electrons is assumed. However, in an acidic medium nearly all electrons are trapped in surface states (Howe and Grätzel, 1985). On the basis of their laser flash photolysis measurements Hoffmann and co-workers have extended this mechanistic picture (Martin *et al.*, 1994a,b). These authors assume that the CB electrons are trapped in two different Ti^{III} sites (reactions (4) and (5)).



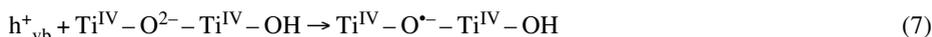
where Ti^{III}OH is a surface-trapped electron while Ti^{III} denotes a bulk trapped electron, respectively. The dynamic equilibrium of reaction (4) represents the reversible trapping of a CB electron in a shallow trap. Hoffmann *et al.* have estimated that these trapped electrons are located in the range of 25 to 50 meV below the conduction band edge of titanium dioxide Degussa P25 (Martin *et al.*, 1994a,b). Reaction (5) represents the irreversible trapping in a deep trap.

Concerning the nature of the electron-trapping centres, several problems arise. Assuming that the absorption of the trapped electrons around 650 nm (1.7 eV) corresponds to a transition between a classical surface state and the conduction band, this surface state should be located close to the middle of the band gap. As pointed out by Bahnemann and co-workers this assignment cannot be correct because it has been found experimentally that the reduction of molecular oxygen occurs *via* transfer of a trapped electron (Bahnemann *et al.*, 1997). This process would not be possible thermodynamically if the electron originated from an energy state being 1.7 eV below the conduction band of titanium dioxide. Accordingly, Bahnemann *et al.* assumed that the absorption is due to an excitation of a trapped electron within a surface molecule (Bahnemann *et al.*, 1997).

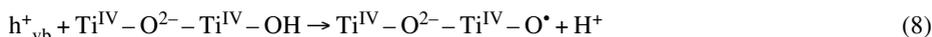
The chemical nature of the trapped holes has not been clearly identified yet. Early reports assume that the holes are trapped at adsorbed hydroxyl groups on the titanium dioxide surface yielding weakly adsorbed hydroxyl radicals (reaction (6)) (Gonzalez-Elipse *et al.*, 1979; Jaeger and Bard, 1979; Anpo *et al.*, 1985; Lawless *et al.*, 1991).



Howe and Grätzel have deduced from esr investigations that the hole is trapped at a subsurface oxygen anion (reaction (7)) (Howe and Grätzel, 1985)



Other authors propose that the trapped hole is an oxygen radical centered at the surface of the titanium dioxide particle, having an energy state lower than the valence band edge of the semiconductor (reaction (8)) (Micic *et al.*, 1993).



On the other hand, an extended model incorporating two different types of traps appears to be much better suited to explaining the experimental observations obtained by Bahnemann and co-workers (Bahnemann *et al.*, 1997). It is envisaged that at least two different trap sites for holes exist on the surface of the TiO₂ particle. While holes which are trapped in energetically deep traps, $h^+_{tr,d}$, can be characterized by their transient absorption around

430 nm, those initially residing in shallow traps, $h^+_{tr,s}$, do not possess such spectral features. Following their generation, all holes are rapidly trapped in either of these energy states (reactions (9) and (10)).



The holes trapped in shallow traps can be excited thermally into the valence band, thus an equilibrium with free holes is indicated in reaction (10). Shallowly trapped holes, $h^+_{tr,s}$, will therefore have a comparable reactivity to detrapped holes, h^+ .

While both types of trapped holes will recombine with the trapped electrons within the first 200 ns after their generation following reaction (1), only holes excited thermally from the shallow traps have the chance to migrate to the energetically more favored $h^+_{tr,d}$ site (*cf.* reaction (11)).



It is assumed that deeply trapped holes, h^+_{tr} , are chemically equivalent to surface-bound hydroxyl radicals. Weakly trapped holes, on the other hand, that are readily detrapped apparently possess an electrochemical potential close to that of free holes and can therefore be considered to be chemically similar to the latter. Their shallow traps are probably created by surface imperfections of the semiconductor nanocrystals. From these traps the charge carriers recombine or they are transferred by interfacial charge transfer to suitable electron acceptors or donors adsorbed at the surface of the semiconductor.

Hole transfer through the intermediate formation of hydroxyl radicals

The detailed analysis of photocatalytic degradation experiments employing acetate as the model pollutant has shown that holes as well as hydroxyl radicals can act as oxidizing species (Wolff *et al.*, 1991). Both, degradation rates and products, were found to depend strongly on the pH of the TiO_2 suspension. While in acidic suspensions (pH 3.0) formate and formaldehyde were detected as the only products of the photocatalytic oxidation of acetate, in alkaline suspension (pH 10.6) the main products were glycolate and formate accompanied by smaller amounts of glyoxylate and formaldehyde. Comparing this product distribution with that obtained in homogeneous solutions upon the oxidation of acetate with hydroxyl radicals or by direct one-electron oxidation, e.g. on a Pt electrode, shows that both oxidizing species contribute to the photocatalytic oxidation of acetate (Schuchmann and von Sonntag, 1984; Schuchmann *et al.*, 1985).

It has been established in detailed radiation chemical investigations that hydroxyl radicals attack acetate ions mainly at the methyl group according to reaction (12) (Neta *et al.*, 1969).



In the presence of air the radicals thus formed react quickly with molecular oxygen leading to the products given in reaction (13) (Schuchmann *et al.*, 1985).



Direct oxidation of acetate results in the well-known Kolbe decarboxylation with the formation of methyl radicals (reaction (14)) (Schuchmann and von Sonntag, 1984).



A considerably different product distribution results when these methyl radicals react with oxygen (reaction (15)) (Schuchmann and von Sonntag, 1984).



The formation of glycolate and glyoxylate during its photocatalytic oxidation can be taken as evidence for the photocatalytic oxidation of acetate *via* hydroxyl radicals. The relative importance of this reaction path seems to be higher with increasing pH. In alkaline suspensions the surface of the TiO_2 particles is negatively charged ($\text{pH}_{\text{ZPC}} = 6.0\text{--}6.4$) and the resulting electrostatic repulsion should hinder the adsorption of the negatively charged carboxyl group of the acetate anion, thus favoring an attack of surface bound hydroxyl radicals onto the methyl group. On the other hand, negatively charged carboxyl groups are directed towards positively charged surface groups of the semiconductor particles at pH values below the pH_{ZPC} and an attack leading to the subsequent decarboxylation of the acetate molecule is favored. Here a different mechanism appears to be operative, probably a direct oxidation of the acetate molecule via holes.

Kinetic isotope work (Cunningham and Srijaranai, 1988; Robertson *et al.*, 1998) also provides evidence for hydroxyl radical attack. Cunningham and Srijaranai observed a primary kinetic isotope effect of 3.3 for the destruction of isopropanol using TiO_2 . A similar effect of 3 was reported by Robertson for the photocatalytic destruction of the cyanotoxin, microcystin-LR. The results of both studies suggest that the formation of the hydroxyl species may be a rate limiting process in the photocatalytic process. It was proposed that the reduced rate of photocatalytic decomposition in D_2O was due to the lower quantum efficiency for the formation of $\bullet\text{OD}$ radicals on the TiO_2 surface (Cunningham and Srijaranai, 1988). This would therefore result in a relatively lower surface concentration of $\bullet\text{OD}$ radicals on the TiO_2 surface for subsequent attack on the target molecules. The lower rate of oxidation may, however, be due to the $\bullet\text{OD}$ radical having a lower oxidation potential compared to the $\bullet\text{OH}$ radical and therefore having a reduced oxidising power. Whatever the reason for the influence of the kinetic isotope effect on the photocatalytic process, Cunningham proposed that such effects strengthened the supposition that the photogeneration of hydroxyl radicals was the rate determining process for the photocatalytic process. It is interesting that the magnitudes of the kinetic isotope effects observed by Cunningham and Robertson were so similar. Robertson *et al.* (1998) proposed that an additional possibility was that the destruction of the substrates may be mediated by hydroxyl radicals generated *via* the superoxide radical anion produced at the conduction band. This is subsequently hydrated or deuterated by the solvent. This may be rate determining since the O_2 has to be generated at the conduction band prior to interaction with the solvent and subsequent formation of OH^\bullet or OD^\bullet species. Therefore the kinetic isotope effect could be due to the interaction of the solvent with the superoxide species rather than the attack on the toxin. If this is the case it was suggested that a similar kinetic isotope effect would be observed no matter what substrate was being destroyed. Further kinetic isotope studies will help elucidate the potential of this proposed mechanism. Interestingly, other workers have also suggested the possibility that species ($\text{O}_2^{\bullet-}$, HO_2^\bullet and H_2O_2) generated following conduction band electron transfer to oxygen were involved in photocatalytic oxidation processes (Okamoto *et al.*, 1985; Anpo *et al.*, 1991).

Richard found evidence that both holes and hydroxyl radicals are involved in the photocatalytic oxidation of 4-hydroxybenzyl alcohol (Richard, 1993). Her results suggest holes and hydroxyl radicals have different regioselectivities in the photocatalytic transformation of this compound: hydroquinone is thought to result from the direct oxidation by a valence-band hole, dihydroxybenzyl alcohol from the reaction with a hydroxyl radical, while 4-hydroxybenzaldehyde is produced by both pathways. In the presence of a hydroxyl radical quencher, the formation of dihydroxybenzyl alcohol is completely inhibited while the formation of 4-hydroxybenzaldehyde is inhibited. The strongest evidence for direct hole oxidation as the principal step in the photooxidation step comes from a recent study performed by Draper and Fox that failed to detect any of the expected intermediate hydroxyl radical adducts following diffuse reflectance flash photolysis of several titanium dioxide/substrate combinations (Draper and Fox, 1990). In each case where the product of hydroxyl radical-mediated oxidation was known to be different from that of direct electron transfer oxidation, the authors observed only the products of the direct electron-transfer oxidation.

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