A brief overview of photocatalytic mechanisms and pathways in water

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Abstract This paper outlines the basic events that occur when a semiconductor, in contact with aerated liquid water containing low concentrations of pollutants, is photoexcited. First, the factors favouring this recombination of photoproduced charges are recalled, and the difficulties in decreasing the recombination are underlined. Second, the formation and identification of the species resulting from charge transfer with O₂, H₂O and pollutants are presented. Third, the reactions involving these species are considered, and methods for assessing their respective importance are critically reviewed. Fourth, on the basis of the view that the photocatalyst surface is covered by tightly bound water layers which hinder the adsorption of many organic pollutants, the hypothesis according to which primary photocatalytic events can take place within the near-surface solution layers is discussed.

Keywords Mechanisms; photocatalysis; pollutant removal; TiO₂

Photonic excitation
A photon, with an energy at least equal to the bandgap and absorbed by a semiconductor, promotes an electron from the filled valence band to the vacant conduction band, which leaves behind a “hole” (i.e. electron vacancy) in the valence band. Unfortunately, this activation process is readily reversible, that is, the out-of-equilibrium electron-hole pairs can recombine either directly (band-to-band recombination) or most often indirectly (viz., via bulk or surface defects) by radiative and nonradiative processes (Figure 1). Charge recombination is the main drawback of heterogeneous photocatalysis; it considerably limits the applications. Foreign cations in substitutional and interstitial positions in the semiconductor lattice behave as recombination centers. Consequently, purer photocatalysts, with otherwise identical structure and texture, should, in principle, be more active. However, as foreign elements originate from the natural minerals used to prepare the semiconductor, their extensive removal is very likely too costly for water treatment, except for very special cases, e.g. space shuttles. A high surface area, which is sought to increase the adsorption of reactants, is linked to both bulk defects and, above all, a high density of surface irregularities, such as steps, kinks, etc. These irregularities correspond to electron energy levels differing from those of a single crystal, and accordingly can act as recombination centres of photoproduced charges. Therefore, there is a tradeoff between reactants adsorption and charge recombination. Despite high expectation, it remains to be proved whether for semiconductors with particle size < 1.5 nm, that is, with a majority of atoms being surface atoms, the surface charge recombination rate can be outweighed by higher rates of interfacial charge transfers.

Also, recombination of photoproduced charges reduces the benefit that could be expected from increasing radiant flux φ. Whereas for low φ values a linear relation between the photocatalytic reaction rate, r, and φ is observed, for higher φ values r
becomes proportional to $\phi^{1/2}$ (e.g. Al-Sayyed et al., 1991) because the recombination rate prevails over $r$.

**Primary reactions involving holes and electrons**

Oxidation of water by the valence-band hole ($h_{VB}^+$) can produce the hydroxyl radical, $\cdot$OH. This is likely the predominant fate of $h_{VB}^+$ in neutral liquid water. At basic pH, reaction with the hydroxide ion can become significant. Recombination of two $\cdot$OH radicals forms H$_2$O$_2$. On the other hand, many organic compounds have a redox potential at a higher energy than the valence band edge of common semiconductor oxides; therefore, when they are in contact with the surface of the photoexcited semiconductor, they can act as electron donors and thus yield a radical cation. The potential role of this reaction pathway is discussed later. Some ions can be oxidised by direct electron transfer. That can be one of the reasons of the unfavourable effect of these anions upon the photocatalytic reaction rates. In the case of SCN$^-$ anions, the absorption of the resulting radical anion ($\text{SCN}^\cdot_2^-$ (Lawless et al., 1991) has even been used to assess the effect of gold particles deposited on colloidal TiO$_2$ on the rate of recombination of electron-hole pairs (Kamat, 2002).

The conduction-band electron ($e_{CB}$) can react with adsorbed dioxygen to form the superoxide radical-anion, O$_2^- \cdot$ or its protonated form, the hydroperoxyl radical, HO$_2^+$ (pK$_A$ = ca.4.7). In water, two HO$_2^+$ or O$_2^-$ radicals can combine if their concentration allows them to react significantly:

$$2\text{HO}_2^+ \text{ (or } 2\text{O}_2^- + 2\text{H}^+ \text{)} \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 \text{ (disproportionation reaction)}$$

The redox potentials of some ions and organics, e.g. halomethanes, permit their reaction by $e_{CB}$ Halomethanes are thus cleaved, giving halide anions (e.g. Calza et al., 1997); the reduction rate is evidently increased in the absence of O$_2$ acting as a competing scavenger of $e_{CB}$.

**Detection of radical species**

Detection of a radical is based on the reaction of this radical with a scavenger, which leads to a stable product that can be identified and, upon accumulation, quantified by an extremely sensitive method (ESR; optical spectroscopies, e.g. chemiluminescence). Demonstrating the selectivity of the scavenger and unambiguously assigning the spectroscopic characteristics are the main issues.

Phthalic hydrazide has been used as a $\cdot$OH-scavenger (Backa et al., 1997). Oxidation of its benzene ring by the $\cdot$OH radical yields principally 3-hydroxyphthalic hydrazide.
which luminesces when further oxidised into the corresponding phthalic acid. It was demonstrated, using the sulphate radical anion, that the competing oxidation pathway via the phthalic hydrazide radical cation, which could be formed by reaction with a hole in the case of photocatalysis, does not lead to 3-hydroxyphthalic acid. However, implementing this method is apparently not straightforward. Thorough calibration and control experiments are needed, since (i) 4-hydroxyphthalic acid is also produced and the resulting chemiluminescence, upon further oxidation, is much weaker than that occurring with the 3-isomer, and (ii) pH and transition metal ions influence the chemiluminescence.

The fast and slow decays of the chemiluminescence of luminol in aqueous suspensions of photoexcited semiconductors have been attributed to superoxide and hydrogen peroxide, respectively (Nosaka et al., 1997). Indeed, several species can play a role, but appropriate control experiments have allowed the authors to validate their interpretation of the decays observed.

Spin-trapping molecules have been added in semiconductor aqueous suspensions to follow the formation and reaction of radicals with various pollutants. However, these experiments are sometimes carried out under conditions distinct from those of photocatalysis (inter alia because of problems due to water), and reliable assignments of the ESR signals require the use of various spin adducts and conditions (pH, added solvent, etc.) (Konaka et al., 1999; Brezova et al., 2005).

Diffuse reflectance flash photolysis has been used to distinguish products of direct electron transfer between the pollutant and TiO$_2$ in aqueous suspensions from those resulting from reaction of the pollutant with OH radicals. It implies unambiguous assignments of the absorption spectra of the radical cation and the OH adduct (Draper and Fox, 1990).

Formation of singlet dioxygen, O$_2$, on photoexcited TiO$_2$ has been suggested on the basis of the observation, in some cases, of products that might stem from oxidation by this species. However, proving that these products could not also be formed through other pathways is difficult, and also O$_2$ traps did not have the expected effect. For TiO$_2$ dispersed in ethanol (Konaka et al., 1999) evidence for O$_2$ was based on ESR, the authors suggesting that O$_2$ might be generated by the energy released by the electron-hole recombination via O$_2$ radicals. Formation of O$_2$ was not confirmed, but not excluded either, in another ESR study (Brezova et al., 2005).

Reactions involving the species issued from direct hole or electron transfers

Regarding the OH radical, the following reactions have been proposed, on the basis of radiochemistry data, for the photocatalytic transformations of aliphatic alkyl radicals:

\[
\begin{align*}
&\text{RH} + ^{\circ}\text{OH} \rightarrow \text{R}^\circ + \text{H}_2\text{O}; \text{R}^\circ + \text{O}_2 \rightarrow \text{ROO}^\circ; \text{RO}_2^\circ + \text{RH} \rightarrow \text{ROOH} + \text{R}^\circ; \text{ROOH} \rightarrow \text{ROO}^\circ + ^{\circ}\text{OH} \\
&\text{RCH}_2\text{O}^\circ + \text{O}_2 \rightarrow \text{RCHO} + \text{HOO}^\circ; \text{RCH}_2\text{O}^\circ + \text{RH} \rightarrow \text{RCH}_2\text{OH} + \text{R}^\circ
\end{align*}
\]

For benzene derivatives, a OH radical is added to the ring, the resulting cyclohexadienyl radical adding dioxygen and eliminating a HO$_2$ radical, the leaving species in all these reactions.

Organic radical cations, R$^\circ^+$, obtained by direct electron transfer (Figure 1) from electron-rich compounds can be transformed by successive hydration and deprotonation, e.g. benzene derivatives with electron-donating substituents can yield cyclohexadienyl radicals, as in the case of the attack by OH radicals. Very acidic R$^\circ^+$ can deprotonate spontaneously and form other products.

Alternatively, the oppositely charged radical ions, R$^\circ^-$ and O$_2^-$, have been assumed to react at a diffusion-controlled rate to form an instable dioxetane (vide infra).
H$_2$O$_2$ can scavenge $e^-_\text{CB}$ or react with superoxide, thereby further reducing O$_2$:

$$\text{H}_2\text{O}_2 + e^- \rightarrow \text{OH}_2^+ + \text{OH}^-; \quad \text{H}_2\text{O}_2 + \text{O}_2^- \rightarrow \text{OH}_2^+ + \text{OH}^- + \text{O}_2$$

Because these reactions are known to occur in aqueous solution, they are believed to take place at the semiconductor surface as well. They represent another way of producing the very oxidising $\cdot$OH radical upon photoexcitation of a semiconductor in water. However, as H$_2$O$_2$ is formed via the recombination of radicals (vide supra), it is a minor pathway. Additionally, it has been shown (Jenny and Pichat, 1991) that H$_2$O$_2$ efficiently decomposes over UV-irradiated TiO$_2$, at least in acidic solution, which is another cause for its concentration to be insignificant.

Respective importance of the various active species

The respective importance, in the chemical steps that transform organic pollutants, of the various species which can exist at the surface (or near the surface) of a photocatalyst is being debated on. Most of the experiments conceived to clarify this topic are based on the chemical analysis of the intermediate products of a given pollutant. Comparisons have been made between the product distributions obtained with and without the addition of a OH$^-$ scavenger (e.g. Minero et al., 2000; Ryu and Choi, 2004) or an enzyme (Pichat et al., 1995) that dismutates either O$_2^-$ or H$_2$O$_2$. The product distribution of the photocatalytic degradation can also be compared to that yielded by processes generating OH radicals in homogeneous phase. These procedures can be criticised since (i) some include the addition of chemicals, (ii) they generally do not discriminate between the effects arising from the existence, in photocatalysis, of species other than $\cdot$OH radicals and the effects related to adsorption phenomena, and (iii) controversies exist about whether the Fenton and photo-Fenton processes involve Fe (IV) ions in addition to $\cdot$OH radicals (Pignatello et al., 1999).

A method for determining the role of surface OH groups was to replace these groups by fluoride ions. Interpretation of the results is complex as this replacement can produce various changes. From careful analysis of the results, it was deduced that phenol reacts predominantly with $\cdot$OH radicals bound to TiO$_2$ relative to free $\cdot$OH radicals (Minero et al., 2000). However, this conclusion does not agree with the facts that phenol is poorly adsorbed and that its removal rate increases when sintered, i.e. lower-surface-area, TiO$_2$ are employed (Agrios and Pichat, 2006).

Two examples are presented here. The first one is that of benzo[b]pyridine (quinoline). It has been shown by comparing the photocatalytic and photo-Fenton degradations that this compound can be attacked by both $\cdot$OH radicals (predominantly on the benzene moiety) and holes (predominantly on the pyridine moiety). By use of superoxide dismutase, the latter mechanism was suggested to involve reaction between superoxide and the N-centered radical cation – resulting from hole transfer – giving rise to a dioxetane whose intermediate formation was supported by the analysis of the products formed from various monohalogenated quinolines (Cermenati et al., 1997; 2000).

Reaction between $\text{RO}^+$ and O$_2^-$ was also invoked for 4-chlorophenol degradation (Li et al., 1999). The second example is that of As(III). Although poorly reactive per se, at least in homogeneous phase, superoxide has been claimed to directly oxidise As(III) in UV-irradiated TiO$_2$ aqueous suspensions; this conclusion was based on rate changes observed upon replacing TiO$_2$ by Pt/TiO$_2$ or dye-sensitised Pt/TiO$_2$ or fluorinated TiO$_2$, or upon adding tert-butyl alcohol or a polyoxometalate (Ryu and Choi, 2004). In contrast, it has been observed that the decay of $\cdot$OH radicals created by pulse radiolysis of colloidal TiO$_2$ was markedly faster in the presence of As(III), whereas it was inferred from the indirect determination, also by pulse radiolysis, of the reaction rate constant $k$ of
As(III) with superoxide in homogeneous phase, that \( k \) was comparatively too low to significantly contribute to the oxidation of As(III) (Xu et al., 2005). This example clearly illustrates the difficulty in drawing definitive conclusions regarding the role of active species.

Nevertheless, using the reactions of the previous section, the extremely numerous case studies (Blake, 1999), without forgetting basic organic chemistry knowledge, it is possible to predict the nature of the main intermediate products of the photocatalytic degradation of any organic pollutant.

**Near-surface solution-phase vs. surface-based reaction events**

Particles of oxides, such as TiO\(_2\), are terminated by hydroxyl groups. In liquid water, the surface coverage is dominated by water molecules which are linked between themselves and to the surface hydroxyl groups by hydrogen bonds. Consequently, the bond lengths between water molecules near the surface are slightly shorter than those between water molecules in the water bulk. The effect of the surface extends to several water layers. That renders difficult the approach of organic molecules to the surface, since these molecules must cleave the hydrogen bonds between the tightly bound water molecules close to the surface. Various factors can intervene regarding the penetration of diluted organics through these water layers, e.g. the polarity, the presence of charged moieties or groups capable of forming hydrogen bonds, and the shape of the molecule (in particular, the steric hindrance of functional groups) (e.g. Brown et al., 1999). Also, a lower amount of surface OH groups, resulting for instance from an increased sintering temperature, can lead to thinner tightly bound surface water layers as was shown by an NMR study (Nosaka et al., 2004). This would facilitate the approach of pollutants to the surface or, at least, reduce the pollutants-surface distance. From this reasoning, it can be deduced that in the case of water purification, the concentration of organic pollutants near or on the surface is most often very low, e.g. for benzene derivatives, it can be below the detection limit (Agrios and Pichat, 2006) or on the order of a few molecules per 100 nm\(^2\) (e.g. Al-Sayyed et al., 1991) for realistic photocatalyst and pollutant concentrations. Added to the recombination of photoproduced charges, these low extents of adsorption account for the relatively low rates of photocatalytic removal of organic pollutants from water.

However, even poorly adsorbed pollutants are eliminated by photocatalysis. A possible explanation would be that the photocatalytic degradations occur via an Eley–Rideal mechanism implying that the residence time of the organic at the surface would be short enough for the adsorbed amount to remain extremely low; but this hypothesis is not in accord with the preceding reasoning which predicts slow rates for migration of organic molecules to and from the surface through the tightly bound water layers. Another interpretation would be that the organic molecules can react not only in the monolayer, but also in the multilayers of water in the neighbourhood of the TiO\(_2\) surface as it has been derived by Cunningham et al. (1994) from a series of experiments, and suggested by Turchi and Ollis (1990) based on an analysis of the kinetic possibilities; in the same line, it has been inferred, from the interpretation of photoelectrochemical measurements, that \( ^{•} \text{OH} \) radicals can migrate from the surface into the aqueous solution (Peterson et al., 1991).

This hypothesis was validated by the results of experiments in which the photocatalytic removal rate of various organics was studied in aqueous suspensions containing an equal mass of various TiO\(_2\) (Agrios and Pichat, 2006; Enriquez and Pichat, 2006). These TiO\(_2\) derived from the same source but differed by the sintering temperature and, accordingly, by the surface area. It was found that for compounds that can react by direct electron transfer (the mechanism believed to be involved, for instance, in decarboxylation and formation of pyridine radical cation), the removal rate decreased with the surface area.
area. By contrast, it was the opposite for compounds prone to react through \( \cdot \)OH radical-mediated attack. In other words, these latter compounds were less sensitive to surface area variation than to the decrease in recombination rate of photoproduced charges due to sintering. These results are consistent with the hypothesis that \( \cdot \)OH radical-mediated attack could occur not only on the surface, but also within the near-surface solution layers. This hypothesis was further checked by comparing the removal rates of some of the probes over powdered TiO\(_2\) to rates over TiO\(_2\) coatings where the accessibility to the TiO\(_2\) surface was restricted by a SiO\(_2\) binder. The decreases in rate due to the decreased accessibility were much more marked for molecules whose main degradation mechanism requires a direct contact with the surface (Enriquez et al., 2004). In practice, one test pollutant does not suffice to quantitatively compare activities, and selection of an optimal photocatalyst depends on the characteristics of the water before and after treatment.

**Conclusions**

To sum up, water treatment by homogeneous AOPs is not fully understood so far. Photo-catalysis on semiconductors adds to the complexity because of the variability brought about by the solid and its interface with pollutants-containing water at various pHs. It should not be overlooked that the surface is dominantly covered by water molecules, so that classical reasoning borrowed from gas-phase (photo)catalysis does not apply. Therefore, though basic phenomena are known, controversies exist. Anyhow, treating each particular case in its entirety – inasmuch that the water contents are themselves totally known – will remain out of reach. The present knowledge allows one to indicate the degradation pathways, but not precisely their respective importance. Cost-effective enhancement of the activity of the photocatalyst appears extremely difficult to achieve because of opposing needs (high surface area vs. low density of structural defects).

**References**


