

Chapter 2

Principles of TiO₂ Photocatalysis

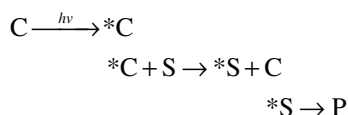
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2.1 Definition of Photocatalysis

A substance can be thought to be a *catalyst* when it accelerates a chemical reaction without being consumed as a reactant; that is to say, it appears in the rate expression describing a thermal reaction without appearing in the stoichiometric equation [49]. A catalyst is a compound that lowers the free activation enthalpy of the reaction. Then, *photocatalysis* can be defined as the acceleration of a photoreaction by the presence of a catalyst [38, pp. 362–375]. This definition, as pointed out in [29, pp. 1–8], includes *photosensitization*, a process by which a photochemical alteration occurs in one molecular entity as a result of initial absorption of radiation by another molecular entity called the photosensitizer [13], but it excludes the photo-acceleration of a stoichiometric thermal reaction irrespective of whether it occurs in homogeneous solution or at the surface of an illuminated electrode. Otherwise, any photoreaction would be catalytic [29, pp. 1–8]. Depending on the specific photoreaction, the catalyst may accelerate the photoreaction by interaction with the substrate in its ground or excited state and/or with a primary photoproduct.

When the light is adsorbed by the catalyst C, the system represents a sensitised photoreaction which may occur through two different ways:

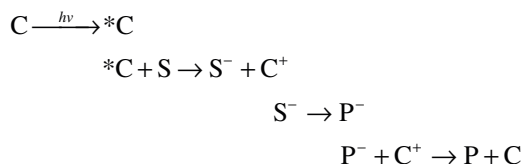
1. via energy transfer, by forming an activated state of the reactant of interest, S, which is more easily oxidized than their ground state:



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2. via electron transfer, by acting either as an electron donor or acceptor.



In the case of energy transfer, the product P is formed from the activated substrate along the potential energy curve, while a new reaction path is opened when the photosensitizer transfers an electron to the substrate [29, pp. 1–8]. In considering excited-state redox reactivity, particularly that involved in organic photocatalysis, the direct occurrence of electron transfer will be of greater concern than involving energy transfer.

Due to the fact that the difference between a sensitised and a catalysed photoreaction is somewhat arbitrary, due to the different and complex mechanisms involved (static and dynamic sensitisation, interaction with a photoproduct, photoinduced reactions,...), the term, photocatalysis has therefore been defined as broad as possible without the specific implication of any special mechanism, and refers then to the action of a substance whose function is activated by the absorption of a photon. A photocatalyst can be described as one involved in the quantum yield expression for a photochemical reaction without its stoichiometric involvement; or more precisely, it appears in the quantum yield expression for reaction from a particular excited state to a power greater than its coefficient in the stoichiometric equation [14].

2.2 Oxidation of Organic Molecules by Photocatalysis

When the light of the appropriate energy illuminates the sensitizer, an electron from the valence band promotes to the conduction band, leaving an electron deficiency or hole, h^+ , in the valence band and an excess of negative charge in the conduction band, e^- , which are oxidizing and reducing equivalents respectively and can participate in redox reactions.

The most important group of reactions photocatalysed by TiO_2 in construction materials are the oxidation of organic molecules. The redox potential needed to oxidize an organic substrate is determined by the position of the valence band and the redox potential of the organic substrate with respect to a standard electrode. If the organic substrate has a more negative redox potential than the redox level of the photogenerated hole, it may reduce h^+ giving the cation radical of the organic substrate, S^+ . Subsequent reaction of S^+ , that is faster than back electron transfer, leads to product formation. On the other hand, if the hole is reduced by water or adsorbed OH^- ions, $\text{HO}\cdot$ and/or other radicals are formed, able to oxidize organic matter. The electron is taken up by an oxidizing agent, normally the adsorbed oxygen.

In environmental chemistry, from a functional point of view, the photocatalysis is one of the so-called Advanced Oxidation Technologies (AOT's). The concept of AOT's was initially established by Glaze and coworkers [20], who defined the

AOT's as the process involving the generation and use of powerful redox transient species, mainly the hydroxyl radical (HO·). This radical can be generated by different procedures, and is very effective in the oxidation of different species, mainly organic matter.

Among the nonphotochemical AOT's, one can distinguish the oxidation with O₃/OH⁻, O₃/H₂O₂, Fenton's processes, electrochemical oxidation, radiolysis, plasma, ultrasonic treatment, etc. Among the photochemical processes, we can find the oxidation in subcritical and supercritical water, photolysis of water in UVV, UV/H₂O₂, UV/O₃, UV/H₂O₂/O₃, Photo-Fenton's processes, and heterogeneous photocatalysis.

The hydroxyl radical, OH·, exhibits the main characteristic of being able to attack to every organic compound; after the fluorine, it is the most powerful oxidizing agent and reacts 10⁶–10¹² times faster than alternative agents, as O₃ [8]. That gives an idea of the oxidation potential of the photocatalysis.

2.3 Other Chemical Concepts of Interest

In the field of heterogeneous photocatalysis, there are several fields of the chemistry that are of great importance. Among them, the solid state chemistry [22, 35, 45], with the knowledge on crystal structure, nonstoichiometry and defect chemistry, electronic properties of solids, chemical bonds, structures and arrangements of atoms, electronic conductivity, are remarkable. In addition, the knowledge of surface chemistry is very important, especially the structures, compositions, dynamics of atoms and molecules, and the electronic properties of surfaces. The adsorption and bonding of gas atoms and molecules on surfaces are also needed for understanding the mechanisms in heterogeneous photocatalysis [1, 28, 46].

2.4 Principles of TiO₂ Photocatalysis

Titanium dioxide (TiO₂) is an excellent photocatalyst with applications in various fields. The main advantages of TiO₂ are its high chemical stability when exposed to acidic and basic compounds, its nontoxicity, its relatively low cost and its highly oxidizing power, which make it a competitive candidate for many photocatalytical applications [5, 9, 16, 17, 41]. TiO₂ exists in three different crystalline modifications: anatase, brookite and rutile, where anatase exhibits the highest overall photocatalytic activity. Basic physical properties of the anatase-type TiO₂ are listed in Table 2.1 [16, p. 125].

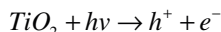
Table 2.1 Basic physical properties of anatase-type titanium dioxide

Crystal form	Tetragonal system
Density (g/cm ³)	3.90
Refractive index	2.52
Permittivity	31
Thermal stability	Change to rutile type at high temperature

The highly oxidizing effect of TiO_2 makes it suitable for decomposition of organic and inorganic compounds at very low concentrations ranging from 0.01 to 10 ppm [16]. The photocatalytic effect of TiO_2 can be used for self-cleaning surfaces, decomposing atmospheric pollution and self-sterilization [9, 17]

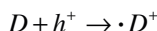
2.4.1 Oxidation-Reduction Reactions

TiO_2 is a semiconductive material that during illumination acts as a strong oxidizing agent lowering the activation energy for the decomposition of organic and inorganic compounds. The illumination of the surface of the TiO_2 induces the separation of two types of carriers: (1) an electron (e^-) and (2) a hole (h^+). To produce these two carriers, sufficient energy must be supplied by a photon to promote an electron (e^-) from the valence band to the conduction band, leaving a hole (h^+) behind in the valence band. The recombination of holes and electrons is relatively slow in TiO_2 compared to electrically conducting materials, i.e., metals where the recombination occurs immediately.

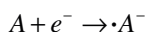


The required energy that has to be supplied by the photons for the promotion of the electrons depends on the band gap for the specific material. The band gap is the difference in energy between the highest permitted energy level for the electron in the valence band and the lowest permitted energy level in the conduction band. The band gap is the minimum energy of light required to make the material electrically conductive [5]. The band gap energy, E_g of TiO_2 (anatase) is 3.2 eV, which corresponds to photons with a wave length of 388 nm [16].

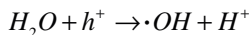
The photoinduced hole can oxidize a donor molecule (D) adsorbed on the TiO_2 surface.



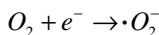
The electron in the conduction band can reduce an acceptor molecule (A).



The strong oxidation power of the hole enables a one-electron oxidation step with water to produce a hydroxyl radical ($\cdot\text{OH}$).



Oxygen can act as an electron acceptor, and be reduced by the promoted electron in the conduction band to form a superoxide ion ($\cdot\text{O}_2^-$). The superoxide ion is a highly reactive particle, able to oxidize organic materials. The oxidation-reduction process is shown in Fig. 2.1.



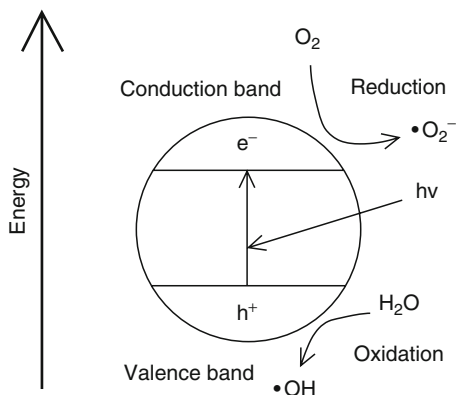


Fig. 2.1 Photopromotion of an electron, reduction of oxygen and oxidation of water

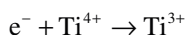
2.4.2 Development of Superhydrophilicity

The degree of water repellence on a surface of a specific material can be measured by the water contact angle. A hydrophobic surface has a water contact angle that is higher than a hydrophilic surface. For glass and other inorganic materials, the water contact angle is between 20° and 30°. Almost no surface is known with a water contact angle less than 10°, compared to the water contact angle of the illuminated surface of titanium dioxide being less than 1° [16].

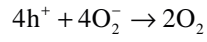
The fogging effect that can be experienced on the bathroom mirrors and the windows of cars is caused by the condensation of water damp that forms small droplets on the surfaces. Until now, the main approach to prevent this type of fogging has been to create a hydrophobic surface that repels the water molecules. This method still leads to creation of water drops that have to be removed from the surfaces for example by blowing or shaking.

The superhydrophilic effect of TiO₂ is formed when the surface is exposed to UV light, and after a certain time of moderate illumination the water contact angle approaches zero [17]. When the illumination stops, the superhydrophilic effect disappears. If the surface is prepared with a water-retaining material like silicone dioxide or silica gel, the superhydrophilic effect can be maintained even after the light is turned off [16]. On the surface of a hydrophilic material, the condensation of water damp forms a uniform film, which flattens out instead of fogging the surface with water drops.

The superhydrophilic effect is also caused by to the production of holes because the electrons tend to reduce the Ti(IV)-cations to Ti(III)-ions



and the holes oxidize the O₂⁻ -anions.



This process leads to ejection of oxygen atoms and creation of oxygen vacancies at the TiO_2 surface. These vacancies are covered by water molecules that are forming OH-groups that create the superhydrophilic effect.