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Phthalocyanines: Alternative Sensitizers of TiO$_2$ to be Used in Photocatalysis

William A. Vallejo Lozada, Carlos Diaz-Uribe,
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Additional information is available at the end of the chapter

Abstract

Currently, titanium dioxide is a most researched semiconductor in photocatalysis field; however, practical applications of TiO$_2$ are limited due to high band gap (3.2 eV). In last decades, researchers implemented several strategies to improve photoactivity of TiO$_2$ in visible electromagnetic spectrum. Titanium dioxide (TiO$_2$) sensitization for absorption of naturals and/or synthetics organic dyes is an important research subject in the field, and it is an efficient method to develop practical application in waste treatment. In this chapter, we review main theoretical aspects of sensitization process of TiO$_2$ by phthalocyanines and its effect in photocatalytic properties. In the last section, we review reports of photocatalytic systems.

Keywords: phthalocyanines, sensitization, TiO$_2$, photocatalysis, reactive oxygen species.
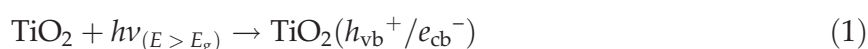
1. Introduction

Photocatalytic process has received great attention as it is one of the most promising technologies within renewable energy technology projects [1]. Treatment of recalcitrant compound and solar recovery of polluted water is an intensive field of research around world laboratories. Currently, titanium dioxide (TiO$_2$) is one of the most important photocatalytic materials for environmental purification; this material is inexpensive, it is available in abundance on earth surface, it is environmental safe, its energy band limits are identical to redox level of water. However, despite so many features, TiO$_2$ has drawbacks such as fast recombination rate of photogenerated electron-hole pair, low quantum yield in the photocatalytic reactions in

aqueous solutions, and it has a high band gap value (3.2 eV, only photocatalytic active under UV irradiation), these drawbacks limit its practical applications [2, 3]. Different methodologies improve TiO$_2$ properties in visible range of electromagnetic spectrum: (a) metal and non-metal doping [4, 5], (b) ion implantation [6], (c) composites with others semiconductors (e.g., CdS, ZnO ZrO$_2$, V$_2$O$_5$, and WO$_3$) [7–10], quantum dots sensitization [11], and (d) TiO$_2$ sensitization by physical and/or chemical adsorption of synthetics and/or naturals organic dyes, this strategy improves the TiO$_2$ photophysical properties in the visible range of the electromagnetic spectrum, and it is considered to be one of the most efficient methods to develop practical applications [12–14].

Through this chapter, we review theoretical aspects of photocatalytic process, information about TiO$_2$, sensitization process, physical and chemical properties of phthalocyanines, and last section presents reports of phthalocyanines as sensitizers in photocatalytic systems.
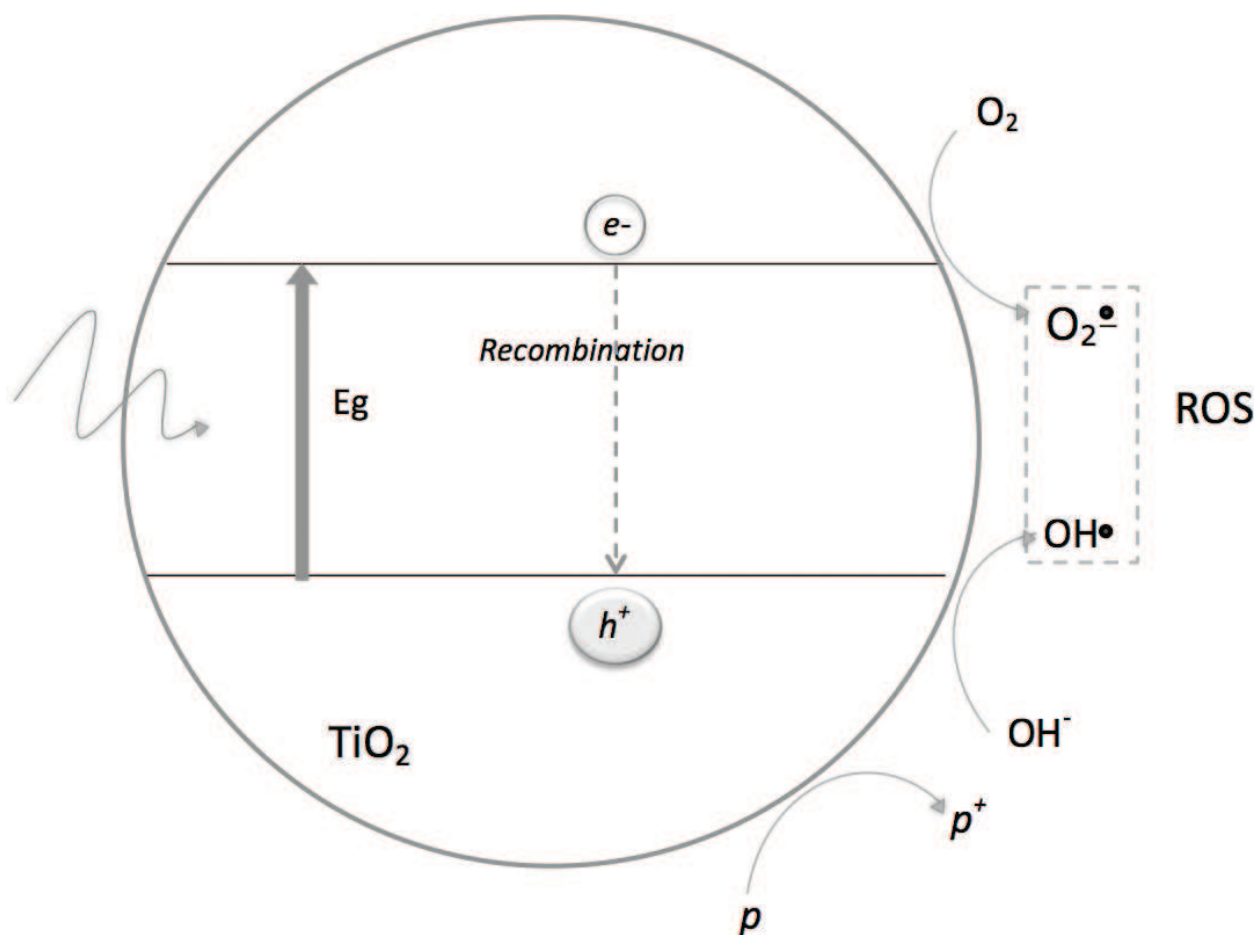
2. Photocatalytic process

Since pioneer work of Fujishima on photochemical water splitting [15], several fields on renewables energy application have been greatly developed and photocatalysis has emerged as one of the most promising approach for the sustainable organic pollutants decomposition in both water and air [16]. The basic photocatalytic principle relies on five steps: (a) reactants diffusion to the surface of semiconductor, (b) adsorption of reactants on semiconductor surface, (c) reaction on the surface of semiconductor (electromagnetic radiation absorption with electrical excitation, charge transfers of photogenerated charge carriers and both direct electronic transfer to pollutant, and reactive oxygen species), (d) desorption of products from semiconductor surface, and (e) diffusion of products from the surface of the semiconductor [17]. **Figure 1** shows general photocatalytic process, the schematic reactions are as follows:

$$\text{TiO}_2 + h\nu_{(E > E_g)} \rightarrow \text{TiO}_2(h_{vb}^+ / e_{cb}^-) \tag{1}$$

$$\text{TiO}_2(h_{vb}^+ / e_{cb}^-) \rightarrow \text{TiO}_2 + \text{Heat}; \text{ bulk or surface recombination} \tag{2}$$

$$\text{TiO}_2(h_{vb}^+ / e_{cb}^-) \rightarrow \text{TiO}_2 + h\nu; \text{ bulk or surface recombination} \tag{3}$$

where (vb) and (cb) are valence and conduction bands of semiconductor, respectively, and P is the pollutant. Under correct electromagnetic irradiation (.), semiconductor absorbs this radiation and one electron can be excited from (vb) to (cb), in this stage one electron-hole pair (charge carriers) is generated (Eq. (1)), after that, charge carriers may recombine through both bulk and surface recombination. In the absence of electric field, recombination process is very fast (nanoseconds) and the extra energy is released as phonon (heat) or some times photons are emitted (Eqs. (2) and (3)). Furthermore, after the charge transfer, inverse process charge transfer from the adsorbed species on TiO$_2$ surface can occur.
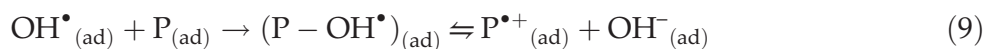
$$(e_{cb}^-) + \text{O}_{2(ad)} \rightarrow \text{O}_2^{\bullet-}{}_{(ad)} \tag{4}$$

$$\text{O}_2^{\bullet-}{}_{(ad)} + \text{H}_2\text{O} \rightarrow \text{OH}^{\bullet}{}_{(ad)} + \text{OH}^-{}_{(ad)} + \text{O}_{2(ad)} \tag{5}$$

Figure 1. General photocatalityc process: absorption of electromagnetic radiation, charge pair genetarion, bulk and surface recombination, ROS generation.

Electron-hole pair separation follows different ways, oxygen prevents recombination by trapping electrons, and it generates superoxide radical anions, after that hydroxyl radicals are produced according to Eqs. (4) and (5). If the oxygen molecules are previously adsorbed on TiO$_2$ surface, it supports the electron transfer process.

$$(h_{vb}{}^{+}) + H_2O_{ad} \rightarrow OH^{\bullet}{}_{(ad)} + H^{+} \tag{6}$$

$$(h^{+}) + OH^{-}{}_{(ad)} \rightarrow OH^{\bullet}{}_{(ad)} \tag{7}$$

Furthermore, oxidation by holes yields more hydroxyl radicals molecules (Eqs. (6) and (7)). Hydroxyl radicals are powerful oxidizing species, they are considered as important species in the photocatalytic processes.

$$(h^{+}) + P_{(ad)} \rightarrow P^{\bullet+}{}_{(ad)} \tag{8}$$

$$OH^{\bullet}{}_{(ad)} + P_{(ad)} \rightarrow (P-OH^{\bullet})_{(ad)} \leftrightharpoons P^{\bullet+}{}_{(ad)} + OH^{-}{}_{(ad)} \tag{9}$$

The photodecomposition of pollutant proceeds through both parallel and consecutive reactions. Hydroxyl radicals can react directly with all organic pollutant (Eq. (9)). Some authors
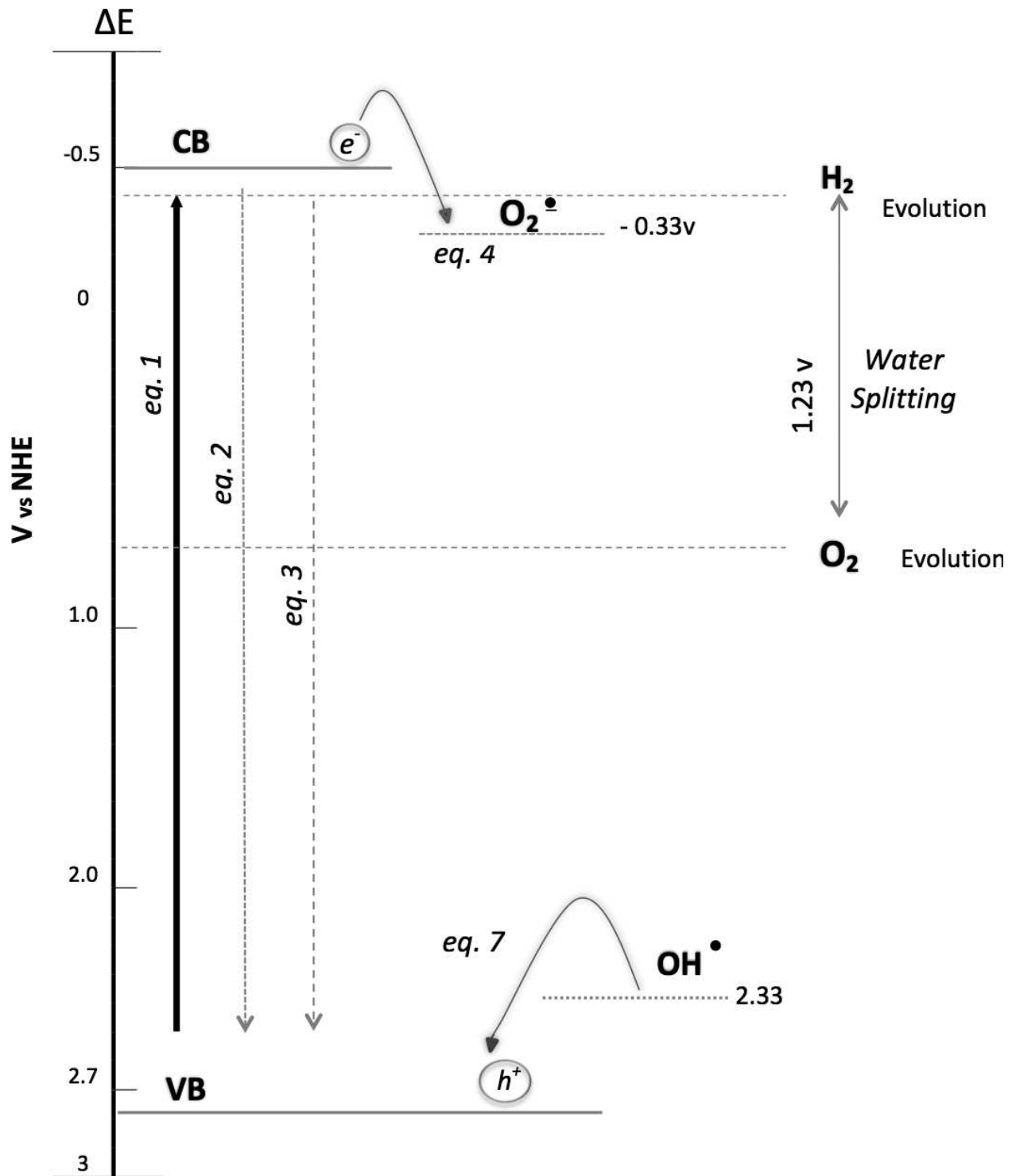
Figure 2. TiO$_2$ potential energy and ROS reaction generation to normal hydrogen electrode at pH = 7.0 (NHE) [20–22].

reported that photogenerated holes play a major role in TiO$_2$ photocatalysis. The redox potential of holes is thermodynamically suitable to oxidize almost any organic molecule [18]. Charge carrier trapping would suppress recombination and increase the lifetime of the separated electron and hole, other factors like e.g., surface area, crystallinity, trap density, etc. can affect photocatalytic performance of semiconductor [19].
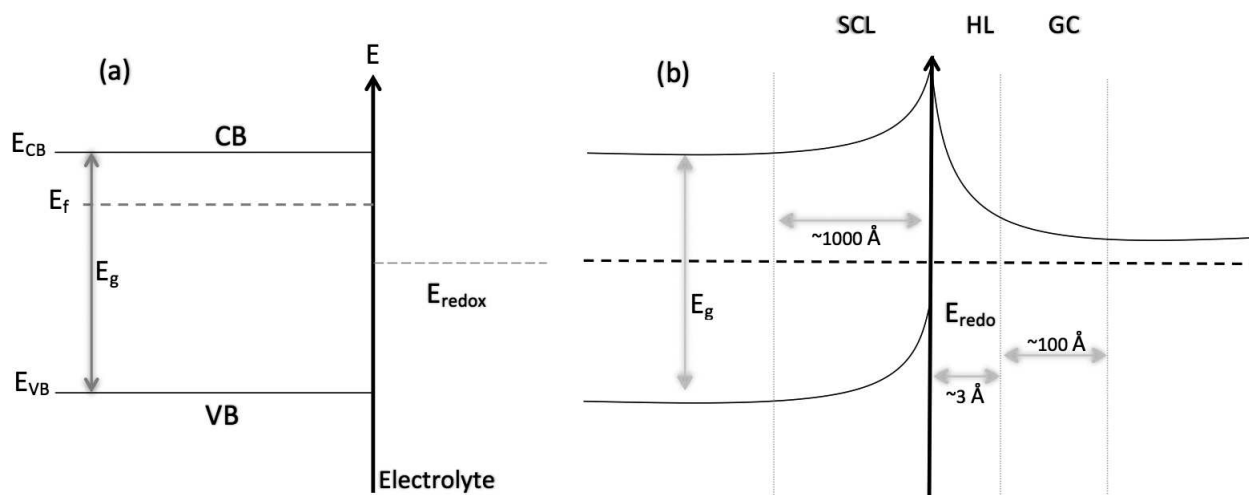
Figure 3. Energy band diagram for an n-type semiconductor before (a) and after (b) the equilibration of Fermi levels at the interface of semiconductor/electrolyte (inside, SCL: spatial charge region, HL: Helmholtz layer, GC: Gouy Chapman space). Adapted from Ref. [23].

Driving force of the photocatalytic process is the energy difference between position of band edges for the conduction/valence bands and the redox potential levels of solution. It determines the probability of the charge transfer processes. **Figure 2** shows band edge positions of TiO$_2$ and redox potential of different reactions of ROS generation. Furthermore, this figure shows TiO$_2$ potential energy related with normal hydrogen electrode at pH = 7.0 (NHE), in this scale, band gap of anatase-TiO$_2$ (3.2 eV) is located in a range −0.5 to 2.7 eV. Within this range, we can assign reactions (Eqs. (1)–(8)) in terms of energetic levels (redox potentials). Energy valence band of semiconductor must be lower than oxidant species (donor) and energy conduction band of semiconductor must be higher than reductant species (acceptor) [20–22].

Band bending in semiconductor occurs near to the junction due to the difference between potential redox of electrolyte and Fermi level (chemical potential) of semiconductor, **Figure 3** shows semiconductor/electrolyte junction. Helmholtz layer (Armstrong thickness) is generated on the semiconductor surface, this layer is generated by ions and/or molecules adsorbed on semiconductor surface, inside semiconductor as such as heterojuntion in solar cells, depletion zone is generated. Equilibrium between semiconductor surface and electrolyte is reached through flow of charge from one phase to another, and a band bending is formed within the semiconductor side; differences between Fermi levels of semiconductor and redox potential electrolyte determine band-bending in semiconductor. Space charge layer (SCL) is the region where bending band occurs and is characterized by the accumulation of charge at the surface. The extension of the SCL depends on the dielectric constant of the material and the concentration of donor impurities [23].

3. Titanium dioxide

Advantages of TiO$_2$ (e.g., it is a photocatalytic activity under UV irradiation, resistant to photocorrosion, innocuous to the nature, and inexpensive) have permitted to implement

photocatalytic applications. Nowadays, TiO_2 is the most investigated material as a photocatalyst and a better understanding and improvement of catalytic reactions are main driving forces for surface investigations on TiO_2. **Figure 4** shows a comparison between TiO_2 and some photocatalysts with respect to NHE. Several semiconductors have reported photocatalytic activity or water splitting (e.g., Fe_2O_3 [24], CdS [25], Cu_2O [26], WO_3 [27], SnO_2 [28], ZnO [29]). Currently, more than 190 semiconductors have been assayed as suitable photocatalysts [30].

Titanium dioxide (TiO_2) has three polymorphs: (a) anatase, (b) rutile, and (c) brookite structures. In **Table 1**, some physical and chemical properties for these three polymorphs are
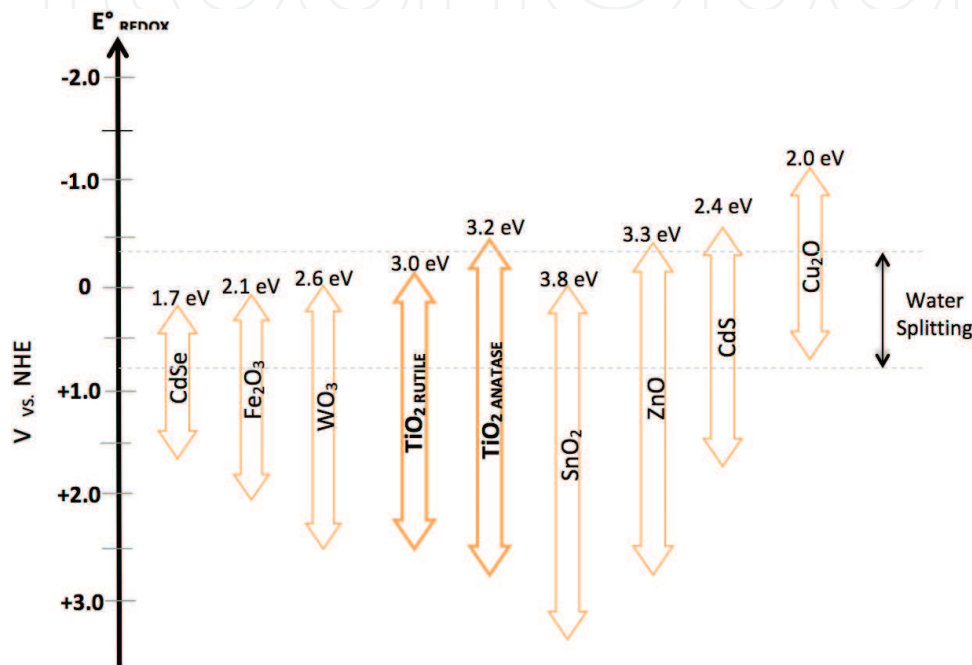
Figure 4. Band gap of some photocatalysts compared to the redox potential of different chemical species measured at 1 M, pH 7. Adapted from Ref. [22].

Crystal structure	System	Space group	Lattice constant (nm)			
			A	b	c	c/a
Rutile	Tetragonal	$D_{4h}^{14} - P4_2/mnm$	0.4584	–	0.2953	0.644
Anatase	Tetragonal	$D_{4h}^{19} - I4_1/amd$	0.3733	–	0.937	2.51
Brookite	Rhombohedral	$D_{2h}^{15} - Pbca$	0.5436	0.9166	0.5135	0.944
Density (kg/m^3)		Band gap energy (eV)		Standard heat capacity (J/mol °C)		
Rutile	4240	3.0 indirect		55.06		
Anatase	3830	3.2 indirect		55.52		
Brookite	4170	–		298.15		

Adapted from Ref. [31].

Table 1. TiO_2 bulk properties.

summarized. The thermodynamic most stable structure is brookite, while anatase is a meta-stable phase, it becomes rutile at high temperatures. All three polymorphs have octahedral structures that are differ in distortion of octahedron. In both anatase and brookite structures, octahedron is more distorted as oxygen atoms are very close. In rutile, the unit cell contains two TiO$_2$ units and the Ti and O coordination numbers are six and three, respectively. **Figure 5** shows the unit cells anatase and rutile [31, 32].

Titanium dioxide (TiO$_2$) is an n-type semiconductor, oxygen vacancies and Ti interstitials have been studied in rutile and anatase polymorphs, rutile-TiO$_2$ has an indirect band gap at 3.0 eV and anatase-TiO$_2$ has an indirect band gap at 3.2 eV [31]. The optical properties of TiO$_2$ can be determined by diffuse reflectance measurements that can be analyzed by Kubelka-Munk remission function [33]:

$$F(R_\alpha) = \frac{(1 - R_\alpha)^2}{2R_\alpha}$$

(10)

where R_α is the reflectance; $F(R_\alpha)$ is an indicative of the absorbance of the sample at particular wavelength value, it is proportional to the absorption constant of the material. The optical band gap by extrapolating the linear portion of the $(F(R_\alpha)hv)^2$ versus hv plot on the x-axis according to:

$$(F(R_\alpha)hv)^2 = A(hv - E_g)$$

(11)

where E_g is the band gap energy and A is a constant depending on the transition probability. Anatase polymorph has high photocatalytic activity; however due to high band gap value, TiO$_2$ is photoactive under UV irradiation. Currently, several strategies are used to improve the photoactivity of TiO$_2$ in the visible electromagnetic spectrum: metal doping, non-metal
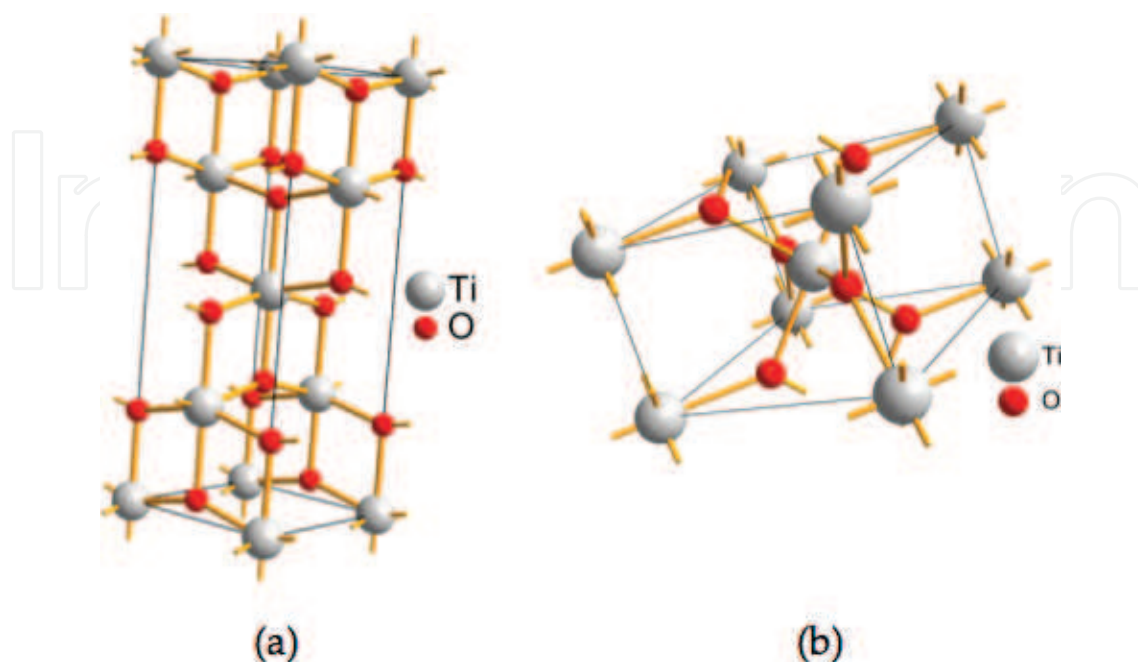
Figure 5. Crystal structures of TiO$_2$ polymorphs: (a) anatase and (b) rutile.

doping, composites with semiconductors having lower band gap energy, quantum dots, dye sensitization. In the next section, we shall delve into sensitization method [34].

4. Sensitization process

Currently, one of the main topic research on photocatalytic technologies is directed to use visible region of electromagnetic spectrum as source radiation its implementation allows to clean and cheap photochemical technologies are employed in wastewater treatment [35]. Titanium dioxide is photocatalytic active under UV radiation and sensitization improves the TiO_2 photoactivity in visible range of electromagnetic spectrum. In sensitization process, a molecular entity (sensitizer) alters other molecule (semiconductor) by energy transfer or electronic transfer from sensitizer to semiconductor after radiation absorption [36]. In this process, phthalocyanine absorbs the visible light, after that, it is excited to a state of greater energy leaving an electron in the lowest energy unoccupied molecular orbital (LUMO) orbital. This electron can be transferred to the conduction band of TiO_2, from where it is transferred to an oxygen molecule to produce superoxide anion (Eq. (4)). It begins degradation processes of contaminants such as dyes or even treatments of bacteria in water samples. **Figure 6** shows TiO_2 photosensitization for phthalocyanine through an ester bond. Several experimental works have confirmed that these phthalocyanines can be adhered on the TiO_2 surface if they are substituted by groups such as –COOH or –SO_3 which are capable of forming strong bonds on the surface of the semiconductor [37–39].

A photosensitizer (FS) is a molecule (e.g., organic or inorganic dyes), which induces photochemical and photophysical reactions after its excitation under electromagnetic radiation. Some requirements for FS are as follows [40–43]:
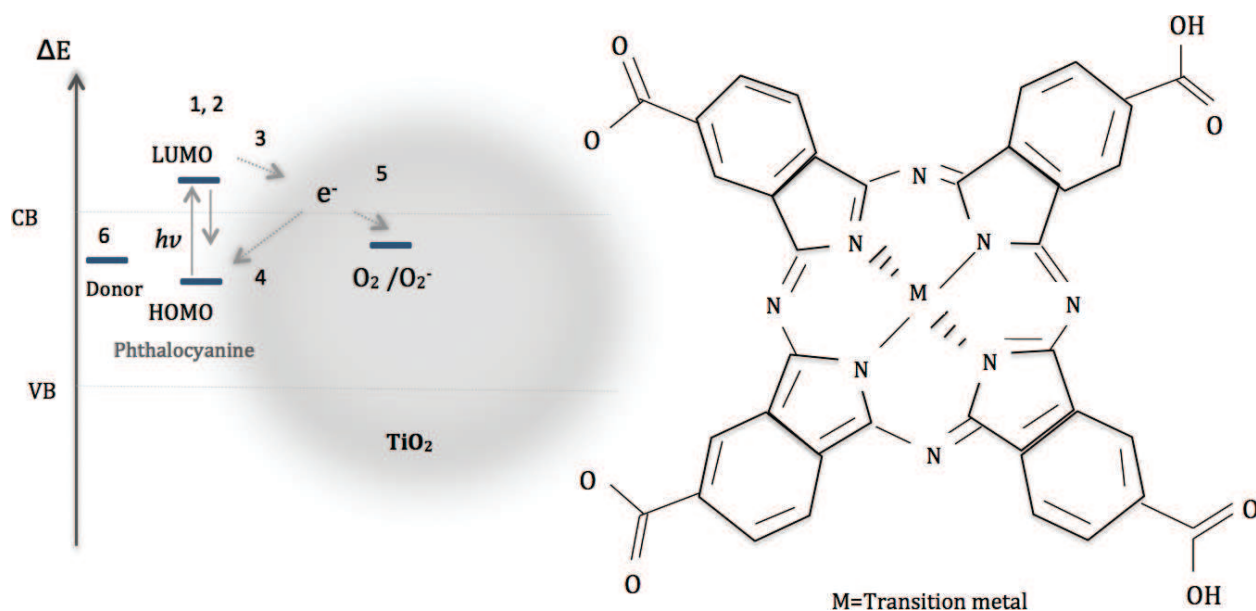

Figure 6. General scheme of TiO_2 photosensitization for phthalocyanines: metallic tetra carboxy phthalocyanines bonds to TiO_2 through carboxylate group (—CO^{2-}). Sensitization mechanism: (1) sensitizer excitation, (2) decay to basal state, (3) electron transfer, (4) recombination, (5) ROS generation, and (6) sensitizer is regenerated by electron donors (e.g., pollutant) [38].

- Intense visible light (400–750 nm) absorption, molar absorption coefficients greater than $10^4 \, M^{-1} \, cm^{-1}$.

- High efficiency intersystem crossing singlet excited state (S^1) to the triplet excited state (T^1) and energy $T^1 > 95 \, kJ \, mol^{-1}$ (energy singlet oxygen).

- Long life of excited states.

- High quantum yield of singlet oxygen production.

- High photostability.

Different organic dyes have been less investigated for sensitization of wide TiO$_2$ such as porphyrins, several transition-metal complexes and organic dyes (e.g., porphyrins and phthalocyanines) have been successfully employed as sensitizers in photocatalysis. After irradiation, photo-sensitizer in its basal state (^0FS) absorbs a photon of visible light ($10^{15} \, s^{-1}$), immediately it excites to singlet state ($^1FS \, ^*$) and returns to ground state by emitting fluorescence (10^6–$10^9 \, s^{-1}$) or phosphorescence (10^{-2}–$10^4 \, s^{-1}$). However, it could decay through intersystem crossing triplet state ($^3FS^*$) that can react with a fundamental oxygen molecule through two types of reactions that lead to the generation of reactive oxygen species (ROS) that are highly cytotoxic for bacteria, fungi, organic pollutants, etc., such as (a) reaction type I yields superoxide and hydroxyl radical and (b) reaction type II yields singlet oxygen [44–46]. **Figure 7** shows general scheme of excitation and decay to sensitizer after irradiation absorption.

Phenalenone, bengal rose, methylene blue, ruthenium complexes, porphyrin derivatives, and phthalocyanines are the most used organic dyes as FS. **Table 2** shows the quantum yields to singlet oxygen production. Furthermore, **Figure 8** shows the typical structures of these sensitizers.

Reactive oxygen species (ROS) is the term applied to molecules more reactive than molecular O$_2$, oxygen disruption and excitation or/and sequential reduction of oxygen can generate these
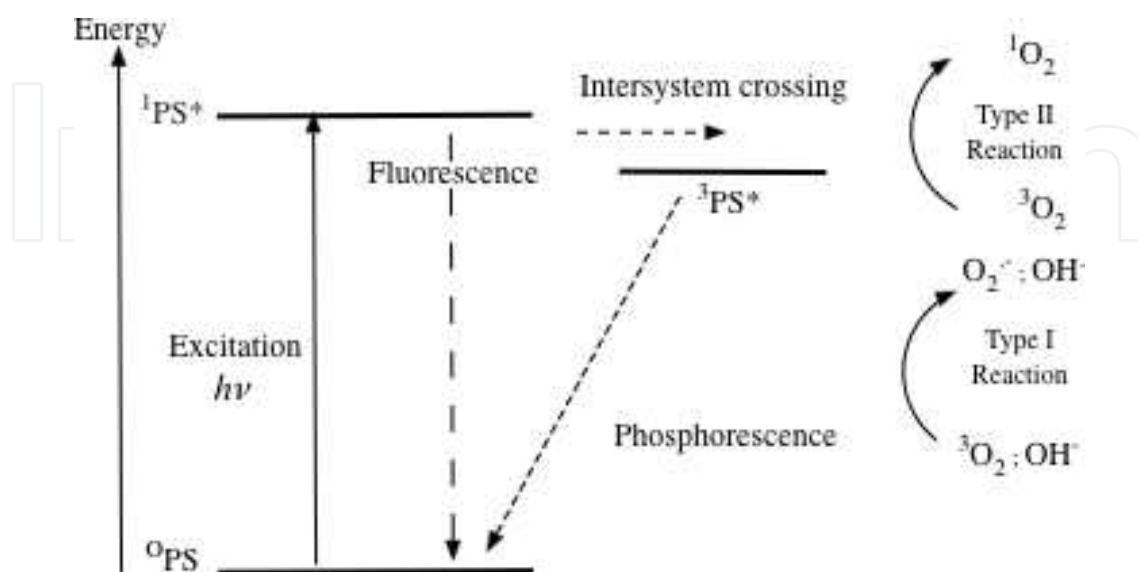

Figure 7. General scheme of excitation and decay of sensitizer after irradiation absorption. Adapted from Ref. [45].

Chemical compound	Quantum yield $^1O_2$ (ϕ_Δ)
Phenalenone	1.0
Bengal rose.	0.75
Methylene blue	0.50
Ruthenium complexes*	0.20–1.00
Phthalocyanines	0.60
Porphyrins	0.70

* For 2,2′-bipyridine chelating polyaceticheterocyclic ligands or 1,10-phenanthroline and their derivatives.

Table 2. List of several organic compounds and oxygen singlet quantum yield each one [42].
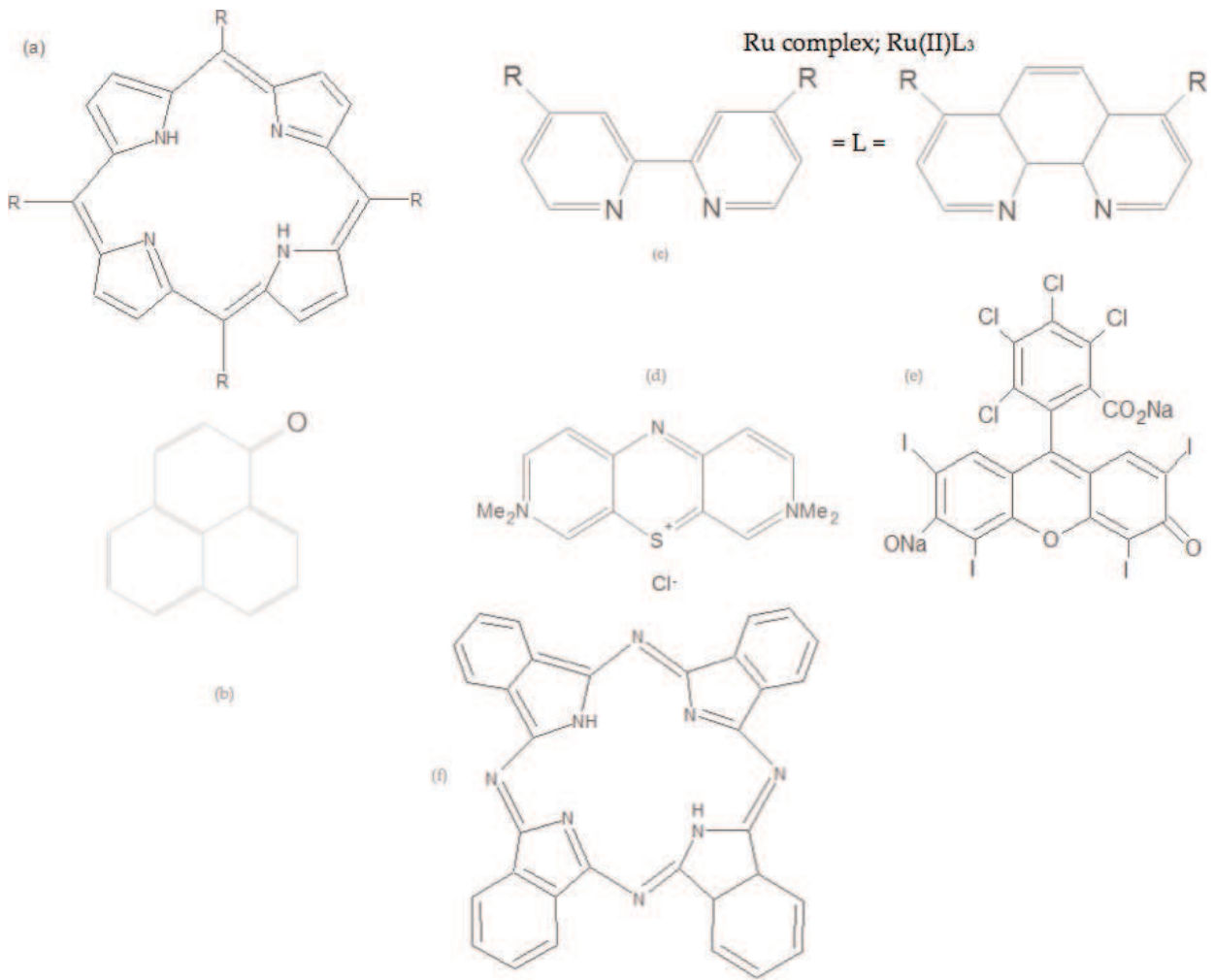
Figure 8. Chemical structures of typical sensitizers: (a) porphyrin, (b) phenalenone, (c) ruthenium complex, (d) methylene blue, (e) bengal rose, and (f) phthalocyanines [40].

species. **Figure 9** shows the sequence of reaction to ROS generation such as (a) O_2 can transforms into singlet oxygen ($^1O_2$) after electromagnetic radiation, (b) O_2 also can produce superoxide anion electron transfer and (c) in presence of ion hydronium anion, superoxide generates
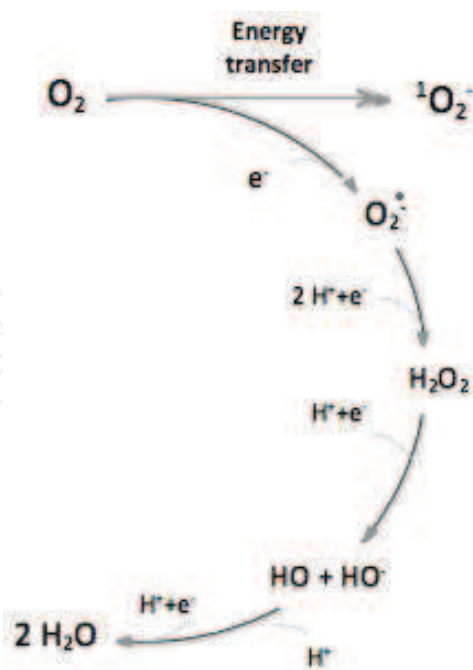
Figure 9. Scheme of cycle of main ROS generation. Adapted from Ref. [45].

peroxide hydrogen which produces hydroxyl radical and the hydroxyl ion, the latter can be protonated to form water [46, 47]. Reactive oxygen species (ROS) are highly reactive and they react to recalcitrant organic compounds and even bacteria [48].

# 5. Phthalocyanines: physical and chemical properties

Braun and Tcherniak synthesized phthalocyanines in 1907 (dark and insoluble solid known as acid phthalocyanines). **Figure 8** shows typical structure of phthalocyanines. Phthalocyanines are macrocycles composed by four isoindole groups; benzene and a pyrrole each form an isoindole group. The isoindole groups are linked together by four nitrogen atoms, thus phthalocyanines have eight nitrogen atoms and eight alternating carbon atoms with conjugated double bonds. Furthermore, four nitrogen atoms can act as ligands and coordinate an atom of some element (e.g., Zn, Cu, Ni, Fe, Co, etc.) to obtain metal complex phthalocyanines. Also, the benzene rings located at the periphery of the structure can be substituted with several functional groups to obtain several substituted phthalocyanines [49–55].

Metal phthalocyanines with carboxylic substituents (called metal tetra carboxy phthalocyanines), which are attractive for the sensitization process, exhibit high absorption coefficients in the visible region of the electromagnetic spectrum, high photo-stability to minimize photo-bleaching effects, and bound to TiO$_2$ surface through the carboxylate groups [56, 57]. Synthesis of metal phthalocyanines is usually carried out by transmetalation of acid phthalocyanines for using quinoline and 1-chloronaphthalene. Furthermore, Achar method is used in the synthesis of metal tetra carboxy phthalocyanines; it uses urea, anhydride trimethyl ether, and ammonium

tetrathiomolybdate as catalyst. **Figure 10** shows Achar synthesis to Zn and Cu tetra carboxy phthalocyanines (TcPcZn and TcPcCu) [58].

Phthalocyanines properties have been extensively explored in several research fields, due to their 18 aromatic π electrons macrocycle phthalocyanines, similar to natural prophyrin, have high thermal and chemical stability and prominent electronic properties, and poor solubility in alcohols, ketones or ethers. Suitable solvents are those having high boiling points such as quinoline, trichlorobenzene, and some strong acids, however, their solubility is limited to a maximum amount 1 mg L^{-1} of solvent. Furthermore, for the metal-phthalocyanines, the solubility varies depending on the central atom; the TcPcCu and TcPcZn presented appreciable solubility in concentrated sulfuric acid and dimethylsulfoxide (DMSO) [59, 60]. Several phthalocyanines and their derivatives produce large quantities of singlet oxygen ($^1O_2$) and other reactive oxygen species (ROS) in the presence of light and molecular oxygen [57, 58]. They have been used to implement TFA and potential applications in photocatalysis in conjunction with TiO_2.

Optical properties are one of the most important physical chemistry characterizations of tetra carboxy phthalocyanines (TcPc). Typical UV-Vis absorption spectrum of TcPc in solution shows two bands: (a) Q bands located at near IR (600–800 nm), free-metal phthalocyanines shows four Q bands, and (b) soret band located at near UV (300–400 nm), both Q and soret bands correspond to $\pi \rightarrow \pi^*$. Phthalocyanines can be derived form dimmers even in dilute solutions, the self-associations are detected by the appearance of new absorption bands at higher energies. **Figure 11** shows absorption of UV-Vis spectrum of zn-tetra carboxy phthalocyanine dissolved in concentrated H_2SO_4. The Q-band of M-PCs has bathochromic effects through an extension of the
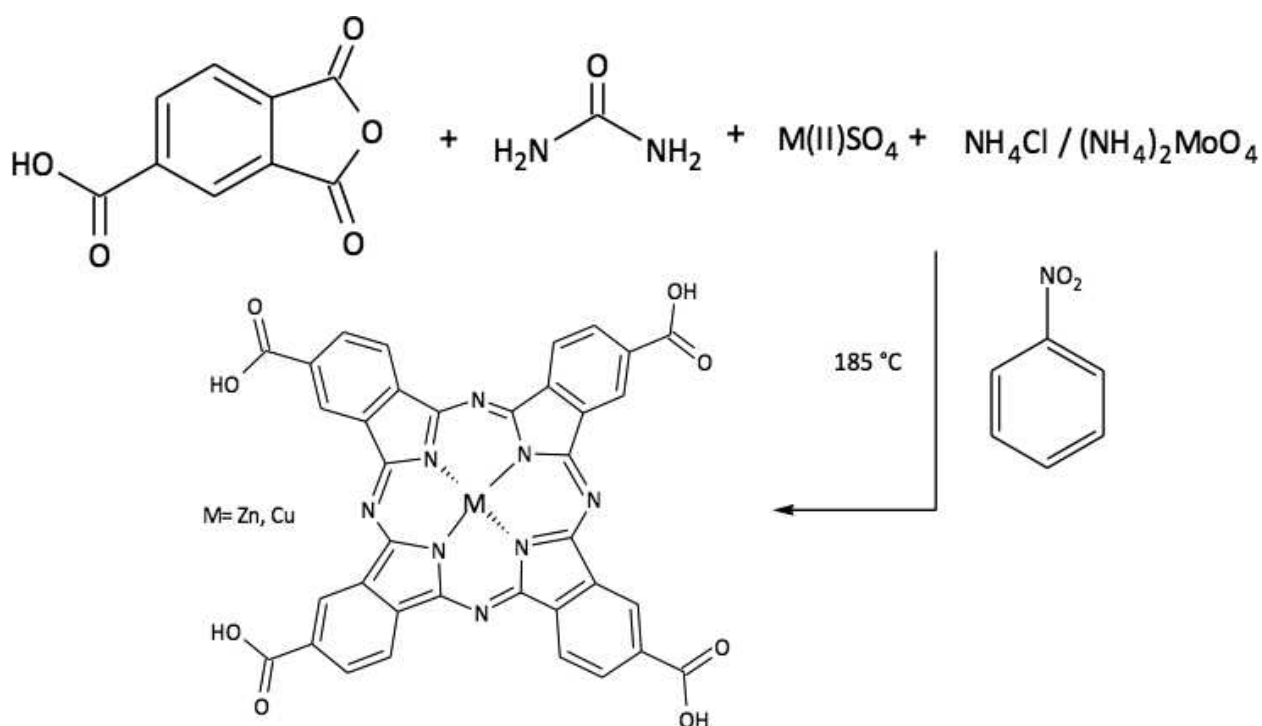
Figure 10. Synthesis of Zn and Cu tetra carboxy phthalocyanines (Method of Achar) [58].
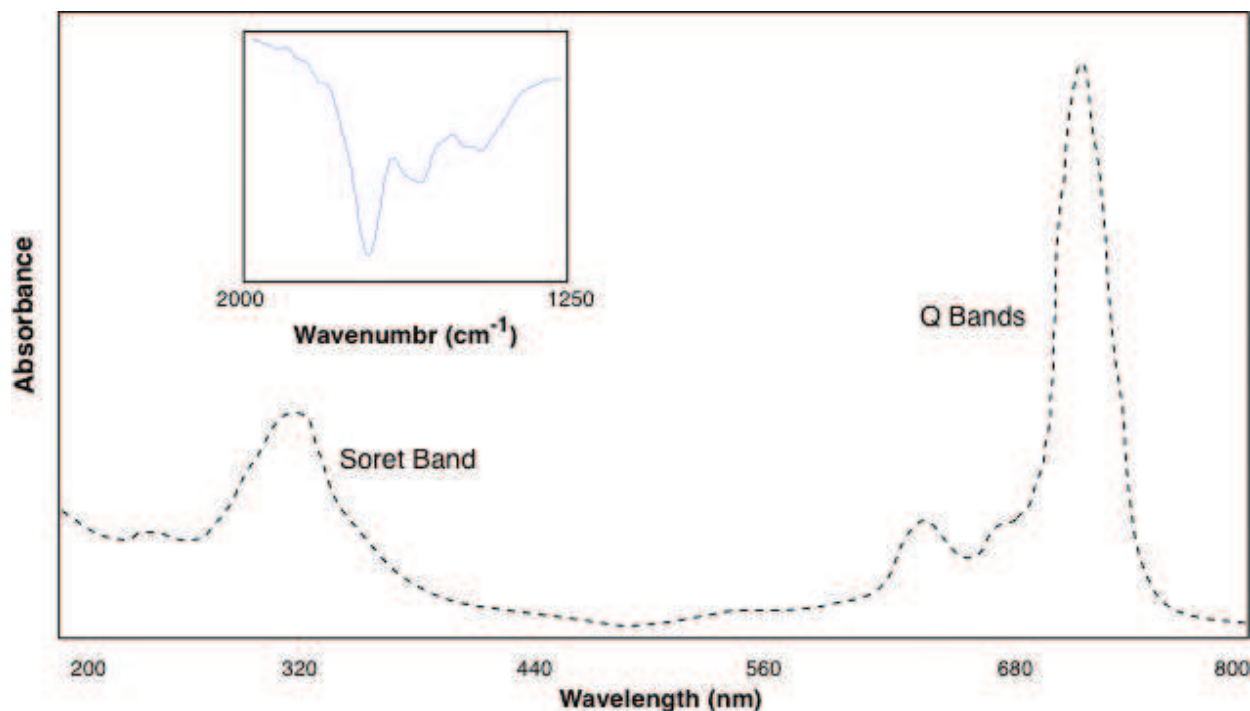
Figure 11. Absorption UV-Vis spectrum of zn-tetra carboxy phthalocyanine dissolved in concentrated H$_2$SO$_4$, (inside: shows carboxylates IR-signals to sensitization on TiO$_2$ thin films).

π conjugation system. Furthermore, shift of absorption maxima depends on change in electron distribution in the phthalocyanine macrocycle by the substituents [61, 62].

IR-spectra of tetracarboxyl phthalocyanines shows typical signals associated to —OH, —CH2, C—O, and beside specific signals located near 1650 cm^{-1} (C—N) and 3023 cm^{-1} (N—H), furthermore symmetric and asymmetric stretching furthermore signals associates to (—CO^{2-}) are reported to tetracarboxyl phthalocyanines [63]. The tetracarboxyl phthalocyanines can interact on TiO$_2$ surface by two ways, first through a very strong physical adsorption and second through chemical adsorption of reaction of carboxylic acids with group Ti—OH on TiO$_2$ surface; phthalocyanines could be absorbed as carboxylates on the semiconductor surface (**Figure 11**, shows carboxylates IR-signals) [64, 65].

6. Photocatalytic efficiency and perspectives

In typical photocatalytic test, visible and/or UV lamps are used as radiation source, catalyst is used in suspension and/or thin film form, temperature and pH maintain constant values. Sometimes O$_2$ is bubbling into solution and some authors incorporate ultrasonic bath. Prior to irradiation, the suspension is magnetically stirred in the dark to reach dye adsorption–desorption equilibrium on TiO$_2$ surface, photodegradation progress is followed by spectrophotometric methodology.

First-order decay in kinetic describes profile of photocatalytic degradation and others dyes [66]. Previous studies have showed that photocatalytic degradation rate of textile dyes in

heterogeneous photocatalytic oxidation systems under UV-light illumination followed the Langmuir-Hinshelwood (L-H) kinetics model [67–69]:

$$v = -d[C]/dt = \frac{kK[C]}{1 + K[C]} \tag{12}$$

where v is the rate of dye mineralization, k is the rate constant, C is the pollutant concentration, and K is the adsorption coefficient. Eq. (12) can be solved explicitly for t by using discrete changes in pollutant from the initial concentration to a zero reference point. However, apparent first-order model is used when the concentration of substrate is in the scale of millimoles $1 \gg K\,[C]$:

$$v - d[C]/dt = k_{app}[C] \tag{13}$$

$$[C]_t = [C_o]e^{k_{app}t} \tag{14}$$

where time (t) at minutes and k_{app} is the apparent reaction rate constant ($k_{app} = k^*K$; min^{-1}); the assumption of a pseudo first-order model was used in several studies to characterize the effect of different experimental conditions on the degradation rate [70–72]. **Table 3** lists k_{app} values to several photocatalytic studies. Langmuir-Hinshelwood kinetics permits to compare different photocatalytic yield, and it is a reference methodology to analyze several conditions of photocatalytic tests to develop pilot and industrial applications.

Basic applications in photocatalysis comprise: (a) hydrogen production, (b) cleaning (e.g., filter to gas phase), (c) water waste treatment, (d) self-cleaning systems, and (e) emerging application (e.g., medical, mechanical, self-cooling, and others). Reports indicate that more than 1000 companies are interested in photocatalytic applications. Nowadays, the global market for photocatalyst material and products reach nearly to \$1.5 billion in 2014 and forecast to reach nearly \$2.9 billion in 2020. **Figure 12** shows photocatalytic products and their distribution in market. Main application includes exterior building materials, since 1990s several industries have installed photocatalytic filters with UV lamps inside air purifiers; applications in deodorization are implemented in hospitals and officers. Last year, both exterior and road materials have been increased [76–81].

Photocatalyst	Pollutant	k_{app} (min^{-1}) $\times 10^{-3}$	Efficiency (%)
Degussa P-25-TiO$_2$ [72]	Styrene	44.5	95
PEG-2000 TiO$_2$ [73]	Rhodamine	0.93	–
Nanotubes arrays-TiO$_2$ /Ag nanoparticles [74]	Ethylene	0.32	–
Natural rubber-TiO$_2$ [75]	Methylene Blue	38.3	90
Iron (III) Tetracarboxyphthalocyanine-TiO$_2$ [58]	Methylene blue	27.9	30

Table 3. Langmuir-Hinshelwood (L-H) kinetics model to photocatalytic treatments.
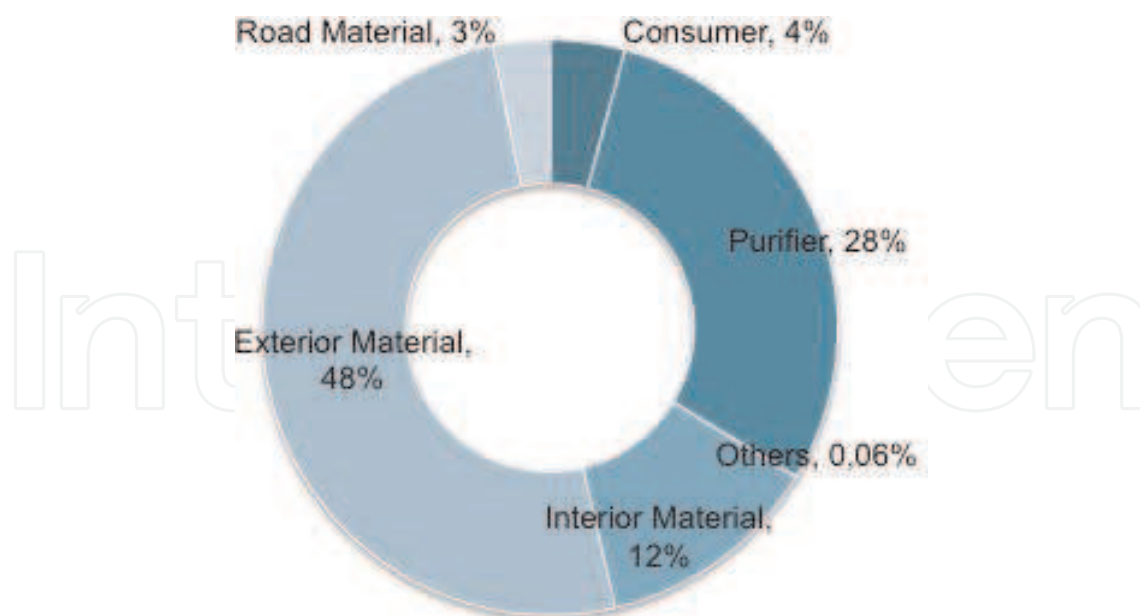
Figure 12. Photocatalytic products and their distribution in market [80].

Photocatalytic applications report suitable photodegradation efficiency in several systems (e.g., TiO$_2$, sol-gel, thin films, TiO$_2$/active carbon, TiO$_2$/sensitizer and others), intense research around world impulse this growing and currently several application in both industrial and pilot-scale have been developed to treatment different pollutants (e.g., hard metals, herbicides, dyes, drugs and others); several reports indicate photocatalytic system continue to grow as part of environmental technology developments based on renewable energies.

7. Conclusions

Titanium dioxide (TiO$_2$) is most used semiconductor for wastewater treatment and several strategies (e.g., quantum dots, noble metal deposition, coupled semiconductor, ion modification, doping sensitization, etc.) and allows improving photocatalytic activity in a visible range. In this chapter, we review some physical and chemical properties of phthalocyanines as sensitizers in photocatalytic systems. We present different aspects of basic principle and development of these systems. Sensitization is an economic and technological option to improve photo-activity of TiO$_2$ in visible range of electromagnetic spectrum. Photocatalytic technology has several advantages over its homologues in wastewater treatment, and nowadays, high efficiency of different systems has been developed in both laboratory and pilot-scale. Furthermore, industrial applications can be address to develop photocatalytic system treats several pollutants (two or more pollutants simultaneously). Finally, photocatalytic applications are a real option in the field of renewable energy technologies, and today, these are one of the most important environmental technologies around the world.

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