

Modified TiO₂ For Environmental Photocatalytic Applications: A Review

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Supporting Information

ABSTRACT: This paper summarizes recent research dealing with development of titanium dioxide (TiO₂) used for environmental applications. TiO₂ plays the most important role owing to its excellent chemical and physical properties. However, the TiO₂ band edge lies in the UV region that makes them inactive under visible irradiation. In this regard, considerable efforts have been made to increase the visible light activity of TiO₂ via the modification of its electronic and optical properties. Doping TiO₂ using either anions or cations is one of the typical approaches that has been largely applied. Coupling TiO₂ with a narrow band gap semiconductor (M_xO_y/TiO₂ or M_xS_y/TiO₂) represents another approach. This work aims to encompass the new progress of TiO₂ for an efficient application in water and wastewater treatment under visible light, emphasizes the future trends of TiO₂ in the environment, and suggests new research directions, including preparation aspects for the development of this promising material.

1. INTRODUCTION

Over the past few years, the abusive use of pharmaceutical and personal care products (PPCPs), pesticides, surfactants, industrial chemicals, and combustion byproducts have resulted in their undesirable accumulation in the environment. Several pollutants are soluble in water and have been detected in surface water, groundwater, sewage water, and drinking water. The excessive occurrence of these residues in the environment has received a great attention as emerging contaminants due to persistent characters. The complex mixture of these compounds and their non-biodegradable character make conventional wastewater treatment methods (physical, chemical, and biological methods) unable to completely remove them.¹

Advanced oxidation processes (AOPs) have been proposed as alternative methods for the elimination of many toxic organic compounds in wastewaters, air, and soil. The principle of AOPs (including O₃/H₂O₂, UV/O₃, UV/H₂O₂, H₂O₂/Fe²⁺, and UV-TiO₂) is to produce hydroxyl radical in water, a very powerful oxidant capable of oxidizing a wide range of organic compounds with one or many double bonds.² In spite of the good oxidation of refractory organic pollutants, the complexity of these methods (AOPs), the high chemical consumption, and the relatively high treatment costs constitute the major barriers for large scale applications.³

Nowadays, a photocatalytic process using a semiconductor as photocatalyst (ex. TiO₂) under UV irradiation has been extensively applied for the oxidation of various refractory organic compounds such as bisphenol A, tetracycline, sulfamethazine, etc.^{4–6} Nonetheless, the fast recombination of the photogenerated electron/hole (e[−]/h⁺) reduces the photonic efficiency and represents the major drawback of photocatalytic applications.^{7,8} A renewed interest in photocatalysis has been spurred by the search for reliable, cost-

effective water treatment processes. From this point of view, the photo-electrocatalytic oxidation (PECO) technique combining photocatalytic and electrolytic processes represents an alternative method.^{8,9} Recently, this photo-electrocatalytic process has received increasing attention in the environmental field because of its ability to destroy undesirable organic compounds in the aqueous phase and to remove traces of organic species that are stable and difficult to oxidize by means of conventional water treatments methods.^{8,10–12}

The combination of electrochemical and photocatalysis technologies offer the opportunity to promote the separation between the electron–hole photogenerated (e[−]/h⁺) and to prevent their recombination. According to the previous research,¹³ the applied external potential is a key factor in the photo-electrocatalytic technique because it accelerates the photocatalytic reactions. The basic of such process consists of ejecting an electron from the valence band (VB) to the conduction band (CB) of the semiconductor, thereby creating an “h⁺” hole in the valence band. This is due to the UV irradiation of TiO₂ with an energy equal or superior to the band gap (>3.2 eV for TiO₂ photocatalyst). These charge carriers (e[−]/h⁺) can migrate to the surface of the catalyst, where they are then available to undergo redox reactions with substrates.¹⁴ This is followed by the formation of extremely reactive oxygen species (OH[•], O₂^{•−}, H₂O₂, O₃, etc.) at the surface of the semiconductor and/or a direct oxidation of the polluting species (R).

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Table 1. Common Semiconductors Used in Photocatalysis Processes

semiconductor	band gap (eV)	wavelength (nm)	light absorption	valence band (V vs NHE)	conduction band (V vs NHE)
TiO ₂	3.2	387	UV	+3.1	−0.1
SnO ₂	3.8	318		+4.1	+0.3
ZnO	3.2	387		+3.0	−0.2
ZnS	3.7	335		+1.4	−2.3
WO ₃	2.8	443	visible	+3.0	+0.4
CdS	2.5	496		+2.1	−0.4
CdSe	2.5	729		+1.6	−0.1

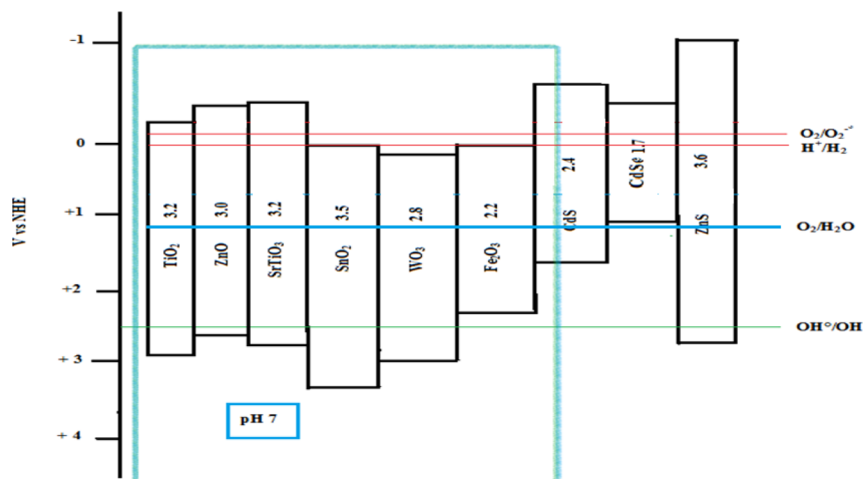


Figure 1. Band gap and redox potential for different semiconductors using the normal hydrogen electrode (NHE).

Most of the materials used for photo-electrocatalytic degradation of pollutants are titanium dioxide (TiO₂) and zinc oxide (ZnO).^{15–18} TiO₂ and ZnO are considered as semiconductors with a wide band gap ($E_g = 3.2$ and 3.4 eV for TiO₂ anatase and ZnO, respectively). Titanium dioxide remains one of the most promising materials due to its high oxidation efficiency, nontoxicity, high photostability, chemical inertness, and environmentally friendly nature.^{1,19,20} Another advantage of TiO₂ is its low cost, owing to the abundance of Ti (0.44% of Earth's crust).^{21,22} With worldwide reserves in excess of 600 million tons, the annual production of Ti metal is approximately 90 000 tons and the annual production of TiO₂ is around 4.3 million tons.²² Previous research^{8,23–25} has shown that the TiO₂ semiconductor is an excellent photocatalyst that can under UV irradiation mineralize a large range of refractory organic pollutants such as herbicides, dyes, pesticides, and phenolic compounds, among others. TiO₂ could be activated under UV irradiation having a wavelength lower than 387 nm due its large band gap (3.0 – 3.2 eV). Such an oxide absorbs only a small fraction of solar light (less than 5% of solar energy is emitted as UV irradiation).²⁶ This major drawback limits the TiO₂ application for large scale. Owing to the successful results at the laboratory scale, TiO₂ material merits further research, in particular concerning the better environmental applications at large scale.

Recently, the development of a new TiO₂ photocatalyst by extending the absorption of the wavelength range into the visible light region has received a great interest.^{19–21,27,28} The scientists are exploring methods to modify titanium dioxide by shifting its optical response to the visible range. Impurities doping of TiO₂ (either cations or anions) is one of the typical approaches that has been applied by several research groups to extend the spectral response to visible light region.^{16,20,29–31}

For example, the doping of carbon,^{32–34} nitrogen,^{35–37} and sulfur^{38,39} in TiO₂ can lower its band gap and shift its optical response to the visible light range. Another approach is to couple TiO₂ with a narrow band gap semiconductor (M_xO_y/TiO_2 or M_xS_y/TiO_2) possessing a higher conduction band than that of TiO₂.^{19,21,40,41} The common semiconductors used in photocatalyst process are shown in Table 1. These new photocatalyst materials (TiO₂/ZnO; TiO₂/CdS; TiO₂/WO₃; TiO₂/CdSe, etc.) ensure the extension of light absorption toward visible light and prevent the fast recombination of exited electron/holes during photocatalytic and photo-electrocatalytic processes.¹⁹

Despite the extensive knowledge assembled by the scientists around the world showing the importance of the topic, there are a number of key questions that need to be answered: (i) the electronic structure of doped TiO₂ or coupled TiO₂ with others materials; (ii) the advantages and the drawbacks of each one, their efficiency; and (iii) their expansive environmental applications at large scale. To this end, the present review aims to provide a comprehensive analysis of the electronic and structural properties of the TiO₂ photocatalyst, review the recent progress of the photocatalytic efficiency of doped TiO₂ or coupled TiO₂ semiconductors, and evaluate their potential applications in environmental field.

2. ELECTRONIC AND STRUCTURAL PROPERTIES OF TiO₂

Due to its excellent chemical and physical properties, titanium dioxide has gained a great success for environmental applications.^{42–44} In 1972, Fujishima and Honda⁴⁵ were the first to propose the photocatalytic splitting of water on TiO₂ electrode. Since this discovery, TiO₂ has become the most suitable semiconductor, and research works increasingly

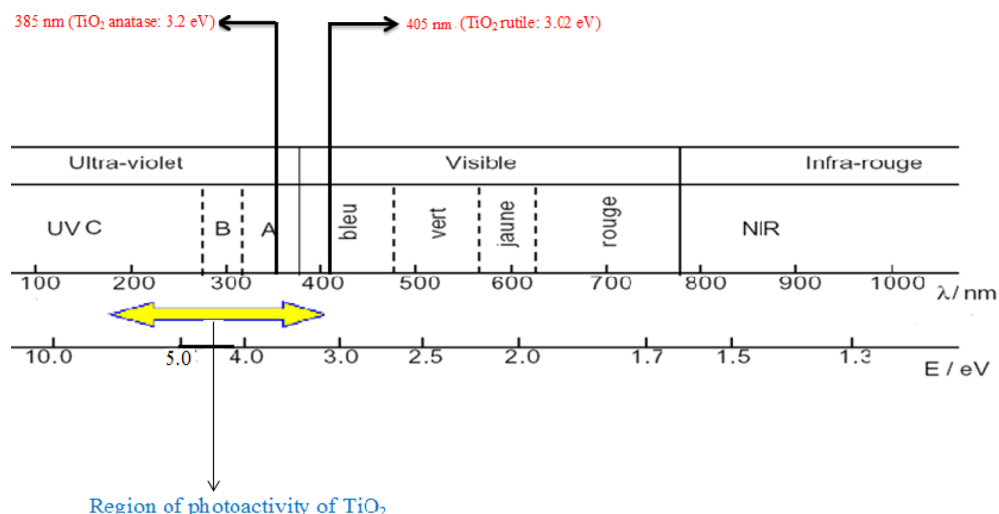


Figure 2. UV region for photoactivity of TiO_2 .

focused over the years on enhancing its efficiency in environmental applications.^{45,46} Belonging to the family of semiconductors, TiO_2 is classified as photocatalyst, where two reactions were occurred simultaneously: (a) oxidation reactions from the photogenerated holes on the valence band and (b) reduction reactions from photogenerated electrons on the conduction band.⁴⁷ Among other semiconductors, one of the key advantages of the TiO_2 is that it allows simultaneously the reduction of the protons ($E_{\text{NHE}}(\text{H}^+/\text{H}_2) = 0.0 \text{ eV}$) and the oxidation of water ($E_{\text{NHE}}(\text{O}_2/\text{H}_2\text{O}) = 1.23 \text{ eV}$) (Figure 1).⁴⁸ More specifically, the redox potential of the donor species ($E^\circ(\text{O}_2/\text{H}_2\text{O}) = 1.23 \text{ V}$) adsorbed on the TiO_2 photocatalyst is more negative than the potential of the TiO_2 valence band (+2.5 V/ENH at pH 7), whereas the redox potential of the acceptor molecules ($E^\circ(\text{O}_2/\text{O}_2^\bullet) = -0.33 \text{ V}$) is more positive than the potential of the TiO_2 conduction band (-0.52 V/ENH at pH 7).^{48,49}

The presence of a small amount of oxygen vacancies, which are compensated by the presence of Ti^{3+} centers, classifies TiO_2 as an n-type semiconductor.⁴⁸ In the TiO_2 material, the lower part of the conduction band is formed by the 3d orbitals of Ti^{4+} , while the valence band is mainly formed by the overlapping of the oxygen 2p orbitals. Titanium dioxide exists in three different crystal forms: anatase, rutile, and brookite.^{50,51} Anatase and rutile are the most studied forms of nanostructured TiO_2 , whereas brookite forms are still scarce.^{52–55} In fundamental studies, the rutile TiO_2 is the most explored, whereas the anatase TiO_2 is the most investigated form in the applied studies.⁴⁶ According to previous research,^{56,57} TiO_2 anatase form plays a central role in the industrial applications such as photonic crystals, photocatalytic process, photovoltaic cells, and photo/electrochromics, among others. It has been found by Ohtani⁵⁸ that the anatase structure has higher photocatalytic activity than the rutile one. Most researchers in the field argue that the physical properties of TiO_2 such as crystal structure (anatase or rutile), crystal size distribution, surface hydroxyl group density, surface roughness, and so on, influence the photocatalytic activity.^{58,59} In the morphology of TiO_2 rutile, the dominant faces are (110), (100), and (101), whereas (011) and (001) are the dominant faces in the morphology of TiO_2 anatase.²⁷ Rutile is the thermodynamically most stable phase.⁶⁰ The (110) face of TiO_2 rutile has the lowest energy and it is the most intensely studied surface.⁵⁰ By

comparison, theoretical studies⁶¹ show that the surface (001) of anatase TiO_2 is much more reactive, since it largely affects the stability, the adsorptive properties, and the catalytic reactivities of TiO_2 anatase form. Upon heating, the TiO_2 anatase is transformed into rutile.⁵⁵ Anatase form can be easily synthesized at lower temperature (below 400°C), whereas rutile form is frequently synthesized at moderate temperature (from 400 to 600°C).^{48,56} Besides, the crystalline structure of rutile and anatase TiO_2 are both tetragonal. The tetragonal anatase structure contains 12 atoms per conventional unit cell compared to the tetragonal rutile structure which contains only 6 atoms per conventional unit cell.²⁷ According to Fujishima,⁶² the octahedral of TiO_2 rutile are slightly orthorhombic and each octahedron is connected to 8 surrounding octahedrons, while those of TiO_2 anatase are distorted orthorhombic and each octahedron is connected to 10 surrounding octahedrons. These differences in lattice structures are responsible for the different mass densities and electronic band structures between the two forms of TiO_2 (anatase and rutile) and, consequently, could contribute to higher photocatalytic efficiency for anatase form under UV irradiations.^{46,63}

The most significant reason for the low conversion efficiency of TiO_2 under visible light is due to the width of the band gap, which is 3.2 and 3.0 eV for the anatase and rutile phase, respectively.⁴⁷ This relatively wide band gap means that both TiO_2 forms could be stimulated only under UV irradiation. According to Egerton and Christensen,⁶⁴ the rutile form of TiO_2 absorbs until 405 nm, while the anatase form absorbs until 385 nm (Figure 2). Thus, the development of TiO_2 photocatalyst able to adsorb visible light region of the spectrum requires (i) engineering the band gap to less than 3.0 eV; (ii) suitable potentials of the conduction and/or valence band edges; and (iii) higher mobility of the charge carriers within in the valence and the conduction bands.⁶⁵

3. DOPING TiO_2

To extend the spectral response of TiO_2 into the visible region and to enhance its photocatalytic activity, several strategies have been developed.^{66,67} Doping pure TiO_2 with either anions or cations is one ways for sensitizing TiO_2 to visible light.^{16,27,68} This route promotes the use of the main part of the solar spectrum and also to ensure the charge traps to keep electron–hole photogenerated separate.⁵⁷ The recent photocatalytic

applications using TiO_2 -doped with cations and anions are summarized in Table SM1 and Table SM2 (Supporting Information), respectively.

3.1. Cation-Doped TiO_2 . Titanium dioxide doped with cations such as rare earth metals, noble metals, poor metals, and transition metals have been widely investigated.^{68,69} According to previous research,^{21,41,69} the metallic ions-doped TiO_2 widen the light absorption range, increase the redox potential of the photogenerated radicals, and enhance the quantum efficiency by inhibiting the recombination of the electrons and holes photogenerated on the conduction and valence bands, respectively. However, the nature and the concentration of dopant, the length of the induced space charge layer, as well as photocorrosion process change the properties at the surface of the materials and consequently influence the photocatalytic activity.⁴⁹ This phenomenon has been demonstrated for example by Karakitsou and Vervikios.⁷⁰ The concentration and the valence of the doping cations (In^{3+} , Zn^{2+} , W^{6+} , Nb^{5+} , Li^+ , etc.) influenced the enhancement or the reduction of the photocatalytic activity.

Although there is a large amount of research^{71,72} that demonstrates how metal ion doping of TiO_2 improves the visible light absorption properties of the material, it should be also mentioned that the increase of the visible light absorption is not a sufficient condition to promote the photoactivity of doped TiO_2 .^{41,60,73} Indeed, during the implantation of cations, a certain amount of defects could be created and act as recombination centers, which decrease the photocatalytic activity. This adverse effect could be avoided by reannealing the doped TiO_2 .⁴¹

Besides, another feature of TiO_2 -doped with metals cations has been mentioned by Dunnills.⁶⁰ Doping TiO_2 with cations having either higher or lower oxidation state promotes the increase in the electrical conductivity. For instance, in the case of doping TiO_2 with metallic cations having lower oxidation state (Fe^{3+} in low concentration), the electroneutrality was achieved by removing electrons from the valence band.⁷⁴ The hopping of the electrons creates holes in the valence band of the system and increases the electrical conductivity (conduction p-type). By comparison, in the case of doping TiO_2 with metallic action having higher oxidation rate such as Nb^{5+} , electroneutrality in the system was achieved by injection of the electrons into the conduction band already empty.⁷⁵ These electrons that passed into the conduction band increase the electrical conductivity (conduction n-type).

3.1.1. Doped TiO_2 with Rare Earth Metals. Rare earth metals, including scandium (Sc), yttrium (Y), and the 15 lanthanoids, are a group of 17 chemical elements in the Periodic Table. According to Teh and Mohamed,⁶⁸ these metals, having incompletely occupied 4f and empty 5d orbitals, could be used as catalysts or to promote catalysis. Various studied have extensively incorporated rare earth elements into the TiO_2 matrix for improving the photoactivity.^{76–78}

Research carried out by Fan⁷⁹ showed that the cerium (Ce)-doped TiO_2 (mixture of anatase and rutile) is able to retard the development of the grain size of TiO_2 to decrease its crystallite size (increase the specific surface area), hence improving the photocatalytic activity. Besides, the redox pair of Ce ($\text{Ce}^{3+}/\text{Ce}^{4+}$) could act as an electron scavenger that traps the bulk electrons into TiO_2 and leads to an increase in the performance of the photocatalytic activity.⁶⁸ It was also concluded that the amount of Ce significantly influences the photocatalytic activity. When the content of doping is excessively high, the space

charge region becomes narrow and the penetration depth of light exceeds the space charge layer. Thus, the recombination of the photogenerated electron–hole pairs becomes easier, which lead to reduce the photocatalytic activity.⁷⁶ Higher photocatalytic activity of gadolinium (Gd)-doped TiO_2 has been also recorded by El-Bahy⁷⁸ compared with pure TiO_2 . Results recorded by El-Bahy⁷⁸ show also that $\text{Gd}^{3+}/\text{TiO}_2$ prepared by sol-gel method has lowest band gap and particle size and highest surface area and pore volume. It was found by Teh and Mohamed⁶⁸ that a higher surface area promotes the adsorption of more reactant molecule on the surface of the photocatalyst and consequently avoids the recombination of the electron–hole photogenerated. The lowest crystallite size increases the specific surface area of the photocatalyst, promotes the shifting of photogenerated carriers to the surface of the photocatalyst and enhances the interaction with reactant molecules.⁸⁰

Others rare earth elements such as neodymium (Nd)^{76,77} and holmium (Ho)⁸⁰ have been also used for doping TiO_2 . According to Stengl,⁷⁶ the higher photocatalytic activity in rare earth metals was mainly due to the transition of 4f electrons, which led to decrease the energy band gap by allowing the transfer of charge between the TiO_2 valence/conduction band and the 4f level in rare earth ions.⁷⁷

3.1.2. Doped TiO_2 with Noble Metals. Nobel metals including osmium (Os), palladium (Pd), ruthenium (Ru), rhodium (Rh), silver (Ag), iridium (Ir), platinum (Pt), and gold (Au), have high resistance to corrosion and oxidation in moist air, unlike most base metals.⁶⁸ Their precious nature derives from their rarity in Earth's crust. It has been reported by Grabowska⁸¹ that noble metals such as platinum, palladium, silver, and gold ions allow to extend the light absorption of TiO_2 band gap semiconductor to the visible light. The effect of noble metal (Pt and Au)-doped TiO_2 photocatalyst has been recently investigated by Dozzi⁸² for the degradation of formic acid. Kisch et al.⁸³ also investigated the photocatalytic degradation of 4-chlorophenol under visible irradiation of TiO_2 modified with chloride complexes of Pt. The presence of noble metals nanoparticles contributes in increasing the separation of photogenerated charge carriers, and consequently improves the photocatalytic performances on the surface and bulk modified photocatalyst systems. According to Yoon,⁸⁴ the surface of noble metal serves as visible light absorbing sensitizers and centers of charge separation.

In addition, the effect of silver (Ag)-doped TiO_2 has been largely studied by several researchers.^{85–87} The addition of silver enhances the photocatalytic activity of TiO_2 and, thus, increases the rate of degradation of rhodamine 6G dye,⁸⁵ methylene blue,⁸⁶ and methyl orange.^{87,88} The photocatalytic activity improvement of silver (Ag)-doped TiO_2 was mainly attributed to the increase of specific surface area, which promotes more reactive sites available to take part in photoreactions.⁶⁸ On the other hand, doping TiO_2 with Ag retards the recombination rate of electron–hole pair by enhancing the charge carrier separation and hence improves the photocatalytic activity.^{85,86} It has been reported by Sobana⁸⁹ and Xin⁹⁰ that Ag nanoparticles deposited on TiO_2 act as electron traps, enhance the electron–hole separation, and ensure afterward the transfer of the trapped electron to the adsorbed O_2 acting as an electron acceptor.

3.1.3. Doped TiO_2 with Transitions Metals. According to the IUPAC definition, a transition metal is an element whose atom has an incomplete d subshell or which can give rise to cations with an incomplete d subshell. A number of research

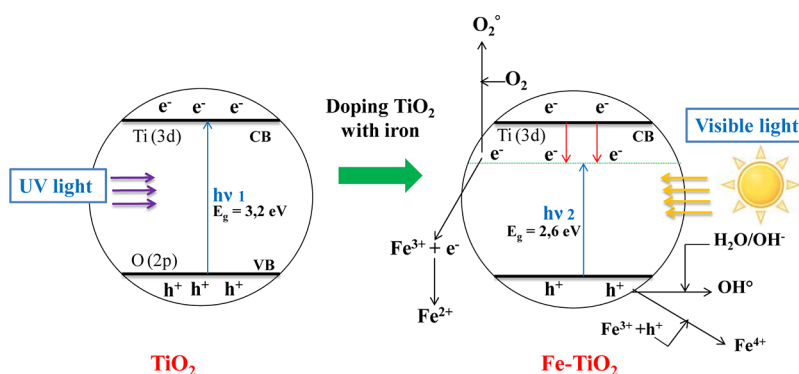


Figure 3. Schematic energy level of iron doping TiO_2 .

groups have doped TiO_2 with transition metals such as iron,⁹¹ cobalt,⁹² nickel,⁹³ manganese,⁹⁴ chromium,⁹⁵ vanadium,⁹⁶ copper,⁹⁷ zinc,⁹⁸ and zirconium,^{99,100} among others, in the attempt to create shift of the band gap energy and to extend the spectral response of the TiO_2 to the visible light region. According to previous studies,^{16,101,102} doping TiO_2 with transition metals tunes the electronic structure and shifts the light absorption region from UV to visible light, thus enhancing the photocatalytic activity of TiO_2 . The shift of the absorption edge to the visible light region is caused by the charge-transfer transition between the d electrons of the transition metals and the conduction or the valence band of TiO_2 .⁶⁸ Such a metal creates a new electron state inside the electronic structure of TiO_2 , which can capture the excited electrons from the TiO_2 valence band and prevent the recombination of charge carriers.^{103,104}

However, the type of the transition metal, its concentrations, and the microstructural characteristics of the catalyst are the main factors that influence the photocatalytic degradation of various substrates under visible region.¹⁰³ It has been found by He¹⁰⁵ that there is a critical doping concentration that influences the photocatalytic activity. The further increase in dopant concentration could increase the recombination of the charge carriers (e^-/h^+), thus lowering the photoactivity of TiO_2 . For instance, it has been reported by He¹⁰⁵ that a suitable amount of dopant Ag (2–4 mol %) could effectively increase the photocatalytic activity of the TiO_2 film. It also has been shown by Karakitsou and Vervikios⁷⁰ that doping TiO_2 with transition metals having a valency higher than +4 could increase the photoreactivity, while others studies¹⁰⁶ showed that doping TiO_2 with trivalent or pentavalent metal ions decrease the photoreactivity of TiO_2 even under UV irradiation. The transition metals that exhibit two or more oxidation states usually ensure an enhancement in the TiO_2 photocatalytic activity.¹⁰⁷ For instance, iron (Fe) with different ion forms (Fe^{4+} , Fe^{3+} , and Fe^{2+}) acts as a trap for the electron–hole pairs and consequently inhibits their recombination (Figure 3).⁶⁸ On the other hand, the radius of Fe^{3+} (0.79 Å) is similar to that of Ti^{4+} (0.75 Å). This trait promotes the easy incorporation of Fe^{3+} ions into the crystal lattice of TiO_2 .^{108,109} Asilturk et al.¹¹⁰ studied also the effect of Fe^{3+} -doped TiO_2 photocatalyst. It was found that Fe^{3+} doping TiO_2 prevents the agglomeration of the particles, forming well nanocrystalline particles with high surface area and, thus, ensuring high photocatalytic efficiency. Among a great variety of transition metal ion dopant investigated previously,^{111–113} Fe^{3+} having band gap of 2.6 eV has been found to be the best candidate to enhance the photocatalytic activity, while some research groups^{114,115} have

found that the presence of this cation in TiO_2 is detrimental for the photocatalytic degradation reactions of organic pollutants in aqueous systems. Due to the widely varying experimental conditions, it remains difficult until this time to make direct comparison between metal transitions doping TiO_2 and to unify conclusions.

3.1.4. Doped TiO_2 Poor Metals. Poor metals, also known as post-transition metals, are the metallic elements in the p-block of the Periodic Table, situated between the metalloids and the transition metals (including groups 13, 14, and 15). A characteristic of the poor metals is that they have lower melting and boiling points than the transition metals; they are also softer and have a higher electronegativity. Compared to the metalloids in the same row (boron (B), silicon (Si), germanium (Ge), arsenic (As), etc.), post-transition metals have significantly higher boiling points. Post-transition metals, including aluminum (Al), gallium (Ga), indium (In), tin (Sn), thallium (Tl), lead (Pb), and bismuth (Bi), are a group of seven chemical elements in the Periodic Table.⁶⁸ Aluminum is a silvery-white chemical element and is one of the most abundant metal found in Earth's crust. In nature, it does not occur in metallic form but is found with soils, clays, and rocks. It can be found also in vegetation and in all of Earth's water. According to research studies conducted by Choi and Depero,^{116,117} doping TiO_2 with aluminum shows retardation of TiO_2 phase transformation from anatase to rutile by stabilizing the surface state of TiO_2 particles and also inhibits grain growth. Liu and co-workers¹¹⁸ also studied the effect of Al-doped TiO_2 photocatalysts. They found them to be promising photocatalyst, where they show (Al-doped TiO_2) excellent photo-degradation behavior for Congo Red.

Bismuth (Bi) is another example of post transition metal that has received great attention for doping TiO_2 .^{119–121} Compared to the undoped TiO_2 , Bi doping TiO_2 can enlarge the wavelength response range and also intrinsically narrow the band gap transition of the catalyst, hence enhancing the photocatalytic activity under visible light for degradation of methylene blue.¹¹⁹ Bi-doped TiO_2 has proved an effective way to increase the photocatalytic activity for the degradation of different organic pollutants. Under visible light, higher mineralization of sulforhodamine-B (61.6% of TOC removal) and higher degradation rate of rhodamine B (more than 90% at 0.25% of Bi- TiO_2) have been recorded by Jiang¹²² and Li,¹²³ respectively. The incorporation of Bi induces the $\text{Bi}^{4+}/\text{Bi}^{3+}$ species, which trap the electrons and thus ensure the separation of the electron–hole pairs.¹²³ Besides, research conducted in the last years^{124–126} shows that a suitable amount of tin (Sn) doping TiO_2 could be an effective way to increase the

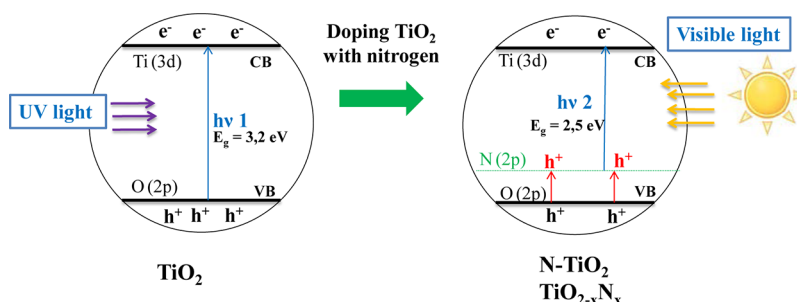


Figure 4. Schematic energy level of nitrogen doping TiO_2 .

photocatalytic activity. For example, as reported by Zheng,¹²⁷ the photocatalytic activity of TiO_2 thin film in the degradation of rhodamine B dye was efficiently improved by Sn implantation, whereas the photocatalytic activity of Sn-doped TiO_2 was doubled for the degradation of toluene in the gas phase.¹²⁸ The incorporation of Sn into the TiO_2 lattice has been shown to be very effective because of the similar ionic radius of the two metals ($\text{Sn}_{(\text{IV})} = 0.71 \text{ \AA}$; $\text{Ti}_{(\text{IV})} = 0.68 \text{ \AA}$).¹²⁵ Doped Sn^{4+} inhibits the phase transformation of TiO_2 from anatase to rutile, decreases the diameter of TiO_2 photocatalyst, and enhances significantly the photocatalytic activity. According to Sui,¹²⁵ the Sn^{4+} -doped into TiO_2 exerts a synergistic effect on their photocatalytic activity.

3.2. Drawbacks of Cations Doping of Titanium Dioxide. As discussed in the previous section, doping TiO_2 with metallic cations has shown positive effects on photocatalysis. However, several authors^{27,129–131} have reported that metal doping TiO_2 have also considerable drawbacks. The photocatalytic activities of a cation-doped TiO_2 decrease even under UV irradiation. The metal-doped materials have been shown to suffer from thermal instability, and the metals centers act as an electron traps, which encourage the recombination of the photogenerated electrons/holes pairs.^{36,132} It has been reported by Lu,¹³³ that the cationic dopant could be localized in the d-level deep of TiO_2 band gap, which serve as carriers recombination centers leading to decrease the photocatalytic activity. For instance, gallium (Ga^{3+}), chromium (Cr^{3+}), and aluminum (Al^{3+}), known as acceptor centers (p-type doping agents), act as a trap for photogenerated electrons and promote the easy recombination with the positive holes. On the contrary, n-type doping agents such as niobium (Nb^{5+}), antimony (Sb^{5+}), and tantalum (Ta^{5+}), known as donor centers, act as traps for photogenerated holes, ensuring the attraction of the electrons and thus promoting the recombination of e^-/h^+ .^{68,134} In noble metals, the difference between the Fermi level of noble metals and that of titania is ascribed to the electron–hole pairs separation. Yet, once the metal centers become negatively charged, hole will be attracted especially for highly loaded samples (more than 5%) and the recombination is favored. Current research supports the conclusion that the desired TiO_2 band gap narrowing of TiO_2 can be better achieved using anionic dopant rather than cationic dopant.^{35,36,135}

4. ANION-DOPED TiO_2

Various approaches have been made in the bid to hinder the recombination of the photogenerated electron–hole pairs. Doping TiO_2 with anionic nonmetals such as carbon (C),^{29,32–34} nitrogen (N),^{20,35,136–138} sulfur (S),^{38,39,139} and iodine (I)¹⁴⁰ have received much attention. Compared to

cation doping, their role as recombination centers might be minimized.^{27,30} Tan¹⁴¹ showed that nonmetal dopants have the ability to improve the morphology and the photocatalytic performance of TiO_2 , whereas Ren²⁶ showed that the anionic metal doping of TiO_2 can lower its band gap and shift its optical response to the visible light region. Over the last several years, it has been demonstrated by many researchers that TiO_2 doped with nonmetal elements (carbon, sulfur, fluorine, nitrogen, etc.) show positive effects in the visible region and higher photocatalytic activity. The impurity states are near to the valence band edge but do not act as charge carriers.^{26,29,135,142} Among all the anions, the doping of TiO_2 with carbon or nitrogen has been found to ensure higher photocatalytic activity under visible light irradiation.³⁰

Significant attention has been directed toward the carbon doping of TiO_2 .^{47,143,144} The substitution of carbon atoms in the TiO_2 photocatalyst introduces new states (C 2p) close to the valence band edge of TiO_2 (O 2p). Accordingly, the conduction band edge shifts to narrow the band gap. The incorporation of carbon into TiO_2 may form carbonaceous species at the surface of the photocatalyst, which are reported to facilitate the absorption in the visible light.^{143,145} Furthermore, the high surface area of the doped sample is another factor that increases the photocatalytic activity of the C-doped TiO_2 .⁶⁸ The higher surface area provides more reactive sites and promotes the adsorption of more target pollutants. Shen and co-workers¹⁴⁴ reported that C-doped TiO_2 appears to be much efficient to degrade trichloroacetic acid under visible light irradiation than pure TiO_2 . The electron excited from these surface states (C-doped TiO_2) had the ability to form sufficient of $\text{O}_2^{\cdot-}$ and OH^\cdot radicals under visible irradiation and, consequently, to ensure higher degradation and mineralization of pollutants.

On the other hand, doping TiO_2 with nonmetals such as nitrogen has received specific attention nowadays.^{143,146–151} The photocatalytic proprieties of N-doped TiO_2 under visible light show a promising extension for environmental application where the conventional TiO_2 is not used.¹⁵⁰ Doping nitrogen into titania changes the refraction index, hardness, electrical conductivity, elastic modulus, and the photocatalytic activity toward visible light absorption.^{68,147,152,153} The nitrogen species resulting from the TiO_2 doping could be either a substitutional or an interstitial N atom in the TiO_2 matrix. The substitutional species are mostly localized above the valence band, whereas the interstitial form is present at 0.73 eV above the valence band.¹⁴⁶ By comparison to ZnO, nitrogen has the ability to simultaneously substitute both O and Ti sites in TiO_2 to form $\text{Ti}_{1-y}\text{O}_{2-x}\text{N}_{x+y}$ instead of $\text{TiO}_{2-x}\text{N}_x$.^{143,147} According to Guo,¹⁵⁴ it is so difficult to make the substitution of O by N because the ionic radius of N (1.71 Å) is so much greater compared to that

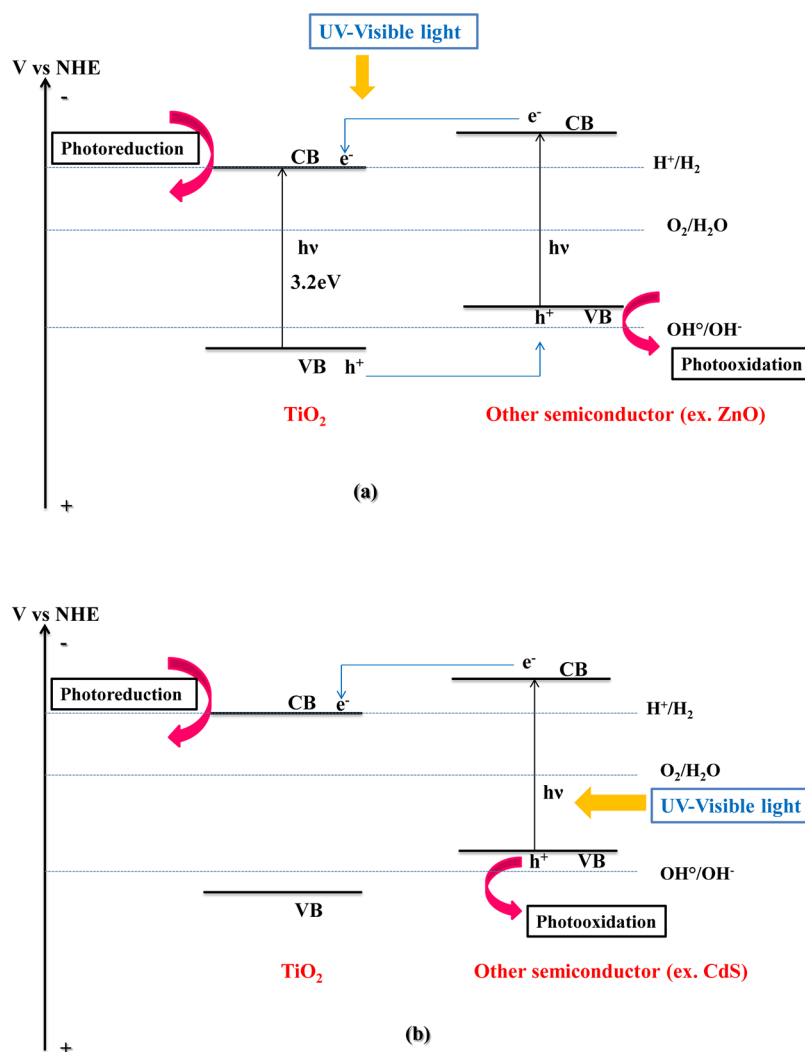


Figure 5. Vectorial transfer of electrons–holes (e^-/h^+) in coupled semiconductor system.

of O (1.4 \AA). Thus, to maintain the electroneutrality and to form an oxygen vacancy, three oxygen atoms should be replaced by two nitrogen atoms. In the presence of nitrogen impurities in titania, the energy of oxygen vacancies is reduced from 4.2 to 0.6 eV , indicating that nitrogen favors the formation of oxygen vacancies.^{20,155} As shown in Figure 4, these oxygen vacancies promote the absorption in the visible region (from 400 to 600 nm) and ensure the activation of N-doped TiO_2 ($E_g = 2.5\text{ eV}$) under visible light. For instance, research of Peng¹⁴⁷ and Ao¹⁵³ showed that N-doped TiO_2 has a narrower energy band gap and can be activated under visible irradiations. Under visible light, more electrons and holes are generated and promote the photocatalytic redox reactions.

The Asahi research group suggested that the N_{2p} level could mix with O_{2p} which results in the narrowing of the band gap and enhancing the photocatalytic activity.³⁵ However, recent experimental and theoretical research shows that the formation of the localized midgap state above the top of the valence band is responsible for increasing the photoactivity of TiO_2 in the visible region.¹ Yet, the localized midgap would decrease the oxidation power of the photogenerated hole compared to that of pure TiO_2 . Likewise, the formation of oxygen vacancies in the bulk usually resulting from the doping of N into the lattice of TiO_2 , could act as recombination centers for carriers that

decrease the photocatalytic efficiency.¹ Another problem with N-doped TiO_2 is the low concentration of nitrogen used for doping TiO_2 . Compared to carbon-doped TiO_2 , there is no significant energy shift ($<0.05\text{ eV}$) in the valence band edge for higher concentration of nitrogen (5.2%). The significant shift of band gap (2.55 eV) is only observed in the lower nitrogen doping concentration (0.52%).²⁷ At the same time, the decrease in N concentration at the surface layer after photoelectrolysis of water under visible light irradiation could worsen the stability of N-doped TiO_2 and consequently decrease the photocatalytic activity.¹⁵⁶ A deactivation of N-doped TiO_2 has been observed by Nosaka¹⁵⁷ during the oxidation of 2-propanediol under visible irradiation. This is mainly due to the loss of N concentrations.

Furthermore, it has been also observed that the techniques or the preparation methods employed for doping N into TiO_2 influence the state of N in titania and its effectiveness in the visible light absorption.^{143,150} Thus, it is very important to choose the appropriate preparation methods for N doping TiO_2 , which promote extending the light absorption and ensuring higher photocatalytic efficiency.

In addition to nitrogen and carbon doping, sulfur and fluorine have been successfully used for TiO_2 doping.^{135,139,158} Fluorine atoms (1.33 \AA for F^-) could easily substitute for O

atoms (1.4 Å for O^{2-}) owing to their similar ionic radius.¹⁴³ Fluoride ions have been detected not only at substitutional sites in the lattice but also physically adsorbed on the surface of nanoparticles doped TiO_2 .^{135,159}

By comparison, sulfur can be used as anion for doping TiO_2 by substituting O sites³⁸ and also as cation by replacing Ti^{4+} in the bulk¹⁶⁰ or at the surface.^{161,162} The substitutional doping of S into the TiO_2 distorts the crystal lattice because the ionic radius of S (1.8 Å) is so greater compared to that of O (1.4 Å).^{41,143} The incorporation of an S_{3p} band above the valence band edge shifts the band gap and ensures higher photocatalytic efficiency.¹⁴³ Furthermore, it was found that S-doped TiO_2 is able to extend the photocatalytic activity to the visible region and to ensure excellent photocatalytic degradation of organic pollutant under visible irradiation.^{139,142} For instance, higher degradation of trichloroethylene (80%) and methyl-tertiary butyl ether (75%) have been recorded by Jo and Yang¹⁶³ when S-doped TiO_2 (weight of S = 2.6 mg cm⁻²) has been used under daylight irradiation (1.8 mW cm⁻²). By incorporating sulfur into TiO_2 , it is also possible to modify the ratio of anatase and rutile and to improve the photocatalyst efficiency of doped TiO_2 under visible irradiation.^{164,165} According to Tian,¹⁶⁶ the anatase/rutile phase composition ratio was strongly influenced by the amount of sulfur. By increasing the amount of S (doping TiO_2 with 1.5% of sulfur), the phase composition ratio is enhanced.

Despite the several advantages achieved by doping TiO_2 with nonmetal anions, researchers have found that the content of dopant would decrease during the annealing process, thus reducing the photoactivity under visible radiation.⁶⁸ This major drawback limits the incorporation of nonmetallic anions for doping TiO_2 . Other research focuses on the coupling of two semiconductors as one way to compensate the drawbacks of doped TiO_2 . This approach will be discussed in the following section.

5. COUPLED SEMICONDUCTOR PHOTOCATALYSTS

Coupling between different semiconductors with different energy levels is another interesting approach, which has received great interest in the past decade.^{21,41,48,167} In photocatalytic systems, coupling TiO_2 with others semiconductors was designed to extend the absorption wavelength range into the visible light region and to alleviate the charge carrier recombination in individual photoelectrodes.^{19,41} It has been reported by Zhang⁴¹ that the good matching of the conduction band and valence band of the two semiconductors could ensure an efficient transfer of the charge carriers from one to another. When the large band gap of TiO_2 is coupled with a small band gap semiconductor having more negative conduction band level, the electron can be injected from the small band gap of the semiconductor used as a sensitizer to the TiO_2 . The energy gap between corresponding band levels ensures the transfer of charge carriers from one particle to its neighbor and promotes the separation between the electron–holes photogenerated.⁴¹ Figure 5 presents semiconductors configuration in which a vectorial transfer of electron–hole photogenerated between corresponding band levels ensures a spatial separation between them. The efficient transfer of electrons and holes photogenerated between TiO_2 and the sensitizer depends on the difference between the conduction band and the valence band potentials of the two semiconductors.¹⁶⁸ According to Robert,²¹ the efficient transfer of electron between TiO_2 and the sensitizer was occurred when

the conduction band of TiO_2 is more anodic than the corresponding band of the sensitizer. Under visible irradiation, only the sensitizer is excited and the electrons photogenerated will flow into the conduction band of the adjacent TiO_2 (Figure 5a). On the other hand, if the valence band of the sensitizer is more cathodic than that of TiO_2 one, the holes photogenerated behind in the valence band of the sensitizer (Figure 5b). As mentioned in certain number of studies, the photocatalytic activity of TiO_2 coupled with metal oxides such as CdS,¹⁶⁹ SnO_2 ,¹⁷⁰ WO_3 ,¹⁷¹ and FeO_3 ,¹⁷² Bi_2S_3 ,¹⁶⁸ among others, has been largely used for improving the process under visible irradiation. For photocatalytic application intended for water and wastewater treatment, the systems M_xO_y/TiO_2 and M_xS_y/TiO_2 are the most widely used.²¹ The different photocatalytic and photo-electrocatalytic applications using photosensitization system (TiO_2/M_xO_y or TiO_2/M_xS_y) are shown in Table SM3 (Supporting Information). TiO_2/CdS is an example of TiO_2/M_xS_y system, which has been applied by Zyou¹⁷³ to ensure the degradation of 75% of phenazopyridine after 60 min of treatment time and using solar simulator lamp (400–800 nm; 0.0212 W/cm²). By comparison, SnO_2/TiO_2 and ZnO/TiO_2 are examples of a TiO_2/M_xO_y system, which have been applied by Zhang⁴¹ and Ge,¹⁷⁴ respectively. Higher degradation rate of methyl orange (95% and 98.13%) have been recorded using SnO_2/TiO_2 and ZnO/TiO_2 , respectively.

5.1. Photosensitization of TiO_2 by M_xS_y Nanoparticles.

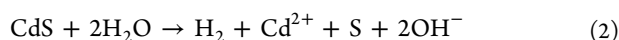
Coupling TiO_2 with cadmium sulfide (CdS) is highly promising approach in the field of research.^{21,175} Cadmium sulfide, with a narrow band gap of 2.4 eV, is one of the very well-known semiconductors.¹⁷⁶ Both the conduction band and the valence band of CdS are higher than their counterparts in TiO_2 .⁴¹ The conduction band potentials of TiO_2 and CdS versus Normal Hydrogen Electrode (NHE) at pH 7 are –0.5 and 0.95 V, respectively.¹⁴³ Such appropriate alternation in the energy levels of the valence and conduction bands allows CdS to act as photosensitizer to absorb visible irradiation and to generate electrons and holes. Subsequently, the electrons are injected into the conduction band of the inactivated TiO_2 leaving the holes behind in the valence band of CdS (eq 1). The TiO_2 accepts photoelectrons generated from the CdS, which could effectively inhibits the recombination of photoelectrons and holes in CdS.^{177,178} Owing to this charge separation under visible light illumination, the couple TiO_2/CdS has been widely applied to enhance the degradation of organic pollutants (Acid Orange II; organic dye Drimaren red, phenazopyridine, methyl orange, etc.) by photocatalytic and photo-electrocatalytic reactions.^{173,179–181}



A small amount of CdS dispersed in the TiO_2 matrix can absorb visible light making the photocatalyst TiO_2/CdS sensitive to visible light. Bassekhouad¹⁷⁹ prepared TiO_2/CdS by a sol–gel method with a CdS loading varied from 5 to 50%. Higher photocatalytic activity of TiO_2/CdS containing low proportion of CdS (from 5 to 10%) has been recorded toward the degradation of Acid Orange II (removal more than 50% of Acid Orange II) under visible (less than 20% of Acid Orange II degradation) light irradiation ($\lambda > 400$ nm) compared to pure TiO_2 or CdS. This higher activity is mainly due to the electron transfer from CdS to TiO_2 , which prevents the recombination of charge carriers.⁴¹ The same trend has been also reported by Tristao¹⁸¹ while studying the photodegradation of organic dye Drimaren red using the same catalyst. The photocatalytic

efficiency of the couple TiO_2/CdS is highly dependent on the proportion of CdS. For instance, higher degradation of organic dye Drimaren red (more than 95%) has been recorded when the TiO_2/CdS system containing lower amounts of CdS (only 5%).¹⁸¹ In water, organic compounds are adsorbed on the CdS surface than the TiO_2 , and the suitable level suggests that the transfer of the electrons from the dye to CdS contributes to the degradation mechanism.^{21,179}

Another interest of the structured couple is that the surrounding TiO_2 matrix can protect the CdS against photocorrosion, which represents the major problem of CdS photocatalyst in environmental application.¹⁷⁹ Photoanodic corrosion occurs when the photogenerated holes do not react quickly with the water molecular or with organic pollutants.²¹ According to Colmenares,¹⁸² the S^{2-} in the CdS photocatalyst is easily oxidized by photogenerated holes, which is accompanied by the release of Cd^{2+} into the solution and the formation of the elemental sulfur layer on the surface of the CdS (eq 2). This phenomenon could negatively affect the photocatalytic reactions.²¹



Compared to other sulfide semiconductor such as Bi_2S_3 , the visible light activity of CdS/TiO_2 is reported to be much lower.¹⁶⁸ Bi_2S_3 is able to absorb light up to 800 nm, whereas CdS adsorb visible light only at 600 nm.¹⁶⁸ Owing to its narrow band gap (1.3 eV), Bi_2S_3 photocatalyst appears to be a good for photocatalytic application.¹⁸³ The conduction band and the valence band potentials of TiO_2 is more negative and less positive, respectively, than the corresponding band of the Bi_2S_3 used as sensitizer.¹⁸⁴ However, the conduction band position of Bi_2S_3 (−0.76 V) is lower than the conduction band position of CdS (−0.95 V). It has been reported by Rehman¹⁴³ that the extent of the visible light absorption of the sensitizer, in addition to the location of the band edges of the two coupled semiconductors are the main factors that determine the photocatalytic activity under visible irradiation. The $\text{Bi}_2\text{S}_3/\text{TiO}_2$ junction has been studied by Bessekhouad¹⁶⁸ at different concentrations of Bi_2S_3 onto TiO_2 for photocatalytic degradation of organic pollutants (4 hydroxybenzoic acid, Orange II). It has been reported in this work that the Bi_2S_3 absorbs a large part of visible light and when the junction contains 10 wt % of Bi_2S_3 , the absorbance started at 800 nm. By performing photocatalytic test, Bi_2S_3 (10 wt %)/ TiO_2 demonstrate high ability to remove more than 60% of 4 hydroxybenzoic acid and 100% of Orange II in both visible light and UV–vis light.

Furthermore, a new approach has been developed by Ho¹⁸⁵ for the fabrication of visible light photocatalysts using molybdenum and tungsten dichalcogenides (MoS_2 and WS_2). The major interests in using these semiconductors are their photostability against corrosion and their narrow band gaps (1.1–1.7 eV) that closely match the solar spectrum.¹⁸⁶ Unfortunately, the conduction band energy levels of bulk MoS_2 and WS_2 are also less negative than that of TiO_2 . This structure avoids the transfer of electrons from the potential of sensitizer to titanium dioxide. Accordingly to same research group,¹⁸⁵ MoS_2 and WS_2 exhibited quantum confinement effects. Owing to this confinement, the band gaps of MoS_2 and WS_2 can be increased significantly, leading to a change in their redox potentials. Such appropriate energy levels of the valence and conduction bands edge promote MoS_2 and WS_2 to act as photosensitizer under visible irradiation in the heterogeneous

semiconductor systems. Under visible light irradiation ($\lambda > 400$ nm), both $\text{MoS}_2/\text{TiO}_2$ and WS_2/TiO_2 are efficient in the degradation of methylene blue and 4-chlorophenol.

Cadmium selenide (CdSe) is another material that has been widely used as photosensitizer in the CdSe/TiO_2 system. CdSe has a lower band gap ($E_g = 1.74$ eV) and has been considered as potential material to form a composite semiconductor with TiO_2 .¹⁶⁵ More than 30% of 4-chlorophenol degradation and more than 20% of total organic carbon were achieved under visible light irradiation using CdSe/TiO_2 as photocatalyst.¹⁶⁵ By comparison, a similar study by Lo¹⁸⁷ used CdSe/TiO_2 for photocatalytic degradation of 4-chlorophenol under 420 nm irradiation. Only 10% of 4-chlorophenol photodegradation was obtained using CdSe/TiO_2 under visible irradiation. This lower result is mainly due to the insufficient amount of CdSe on the TiO_2 (only 27.6% of CdSe). Until this date, the photocatalytic properties of CdSe/TiO_2 have not been extensively investigated compared to the CdS/TiO_2 . According to Lo,¹⁸⁷ the use of CdS to couple with TiO_2 seems to be most favorable than CdSe.

5.2. Coupling TiO_2 by M_xO_y Nanoparticles. The TiO_2/WO_3 hybrid system has received much attention in the field of photo-electrochemistry.^{167,188,189} TiO_2/WO_3 is a system of semiconductor-semiconductor coupled material, which has been widely used as a photocatalyst for decades.¹⁸³ The band gap of WO_3 is lower (2.8 eV), and both the upper edge of the valence band and the lower edge of the conduction band of WO_3 are lower than those of TiO_2 .¹⁸³ Thus, WO_3 can be excited by visible light, and the photogenerated holes can be transferred from WO_3 to TiO_2 .¹⁹⁰ The electron in the conduction band of TiO_2 could be easily accepted by WO_3 because the standard reduction potential between W(VI) and W(V) is only −0.03 V.¹⁸³ The electrons in WO_3 would then be transferred to the oxygen molecules adsorbed on the surface of TiO_2 . The increase of the photocatalytic activity of TiO_2 was confirmed by several research groups as a result of coupling with WO_3 for the decomposition of benzene,¹⁹¹ methylene blue,¹⁹¹ butyl acetate,¹⁹² and dichlorobenzene.¹⁹³ Higher rates of pollutant degradation were recorded owing to the increase of electron transfer from TiO_2 to WO_3 via the formation of an intermediate W(V) species, together with the increased surface acidity in the TiO_2/WO_3 couple. It has been reported by Papp¹⁹⁴ that the surface acidity and the protonated surface hydroxyl groups promote the transfer of electron from the conduction band of TiO_2 to the adsorbed oxygen molecules and hence increase the photocatalytic activity. However, the TiO_2/WO_3 coupling does not always enhance the photocatalytic activity of TiO_2 . Too much loading of WO_3 could act as a center of charge recombination (eqs 3 and 4).⁴¹ Furthermore, the preparation technique of coupled semiconductor TiO_2/WO_3 remains a critical parameter that influences the band structure properties and, consequently, the photocatalytic activity.⁴¹



As mentioned in previous works,^{41,183,195,196} the tin dioxide (SnO_2) semiconductor attracts much interest because it possesses interesting electrochemical and photo-electrochemical properties. Traditionally, SnO_2 has been viewed as a poor candidate for photocatalytic application, even under UV illumination as a

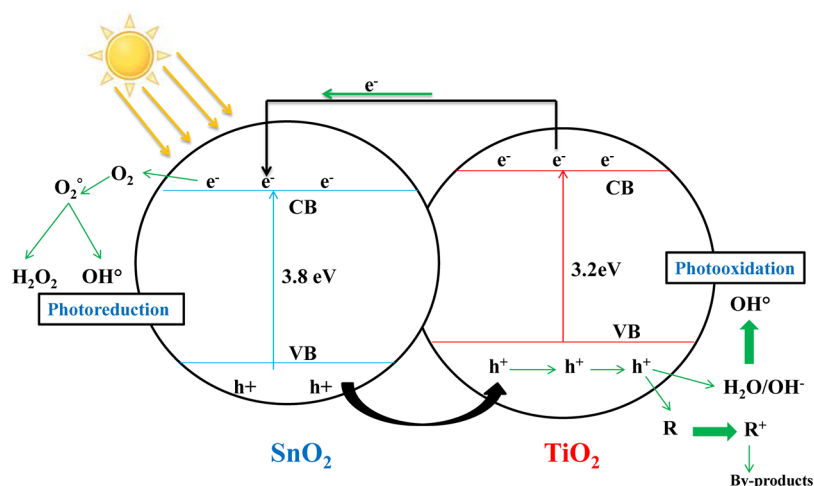


Figure 6. $\text{TiO}_2/\text{SnO}_2$ photocatalyst configuration.

result of its very large band gap (3.8 eV) and its instability to reduce oxygen.^{41,195} To overcome such limitations and achieve efficient charge separation, systematic research was conducted to use SnO_2 as a coupled semiconductor. The couple system $\text{SnO}_2/\text{TiO}_2$, where TiO_2 play the role of photosensitizer for SnO_2 has received a great attention.^{188,195,197,198} The conduction band of SnO_2 is more positive (0.5 V) than that of TiO_2 and could act as a sink for the photogenerated electrons.^{21,41,195} Using SnO_2 coupled to TiO_2 , the photogenerated electrons can accumulate on the SnO_2 and the photogenerated holes can accumulate on the TiO_2 owing to the formation of a heterojunction at the $\text{SnO}_2/\text{TiO}_2$ (Figure 6). According to Yu,⁴¹ Zhang,¹⁹⁹ and El-Maghraby,²⁰⁰ the $\text{SnO}_2/\text{TiO}_2$ system avoids the recombination rate of photogenerated charge carriers, ensuring higher quantum efficiency and better photocatalytic efficiency in organic pollutant degradation. For instance, more than 15% of 4-chlorophenol removal has been recorded by Lin¹⁸⁹ using $\text{TiO}_2/\text{SnO}_2$ under 369 nm of UV irradiation compared to single TiO_2 and SnO_2 system (around 5% of degradation rate of 4-chlorophenol). Besides, higher decolorization of Acid Orange 7 (more than 97%) has been recorded after 60 min of photo-electrocatalytic treatment at 0.83 V and using the similar system ($\text{TiO}_2/\text{SnO}_2$) as photocatalyst.¹⁹⁵

Despite the higher photocatalytic and the photo-electrocatalytic performance of $\text{TiO}_2/\text{SnO}_2$ configuration under UV irradiation, the incorporation of this system for environmental applications at a large scale remains limited due to the large band gap of both TiO_2 and SnO_2 . Recently, a new approach toward the improvement of photocatalytic activity of TiO_2 under visible illumination moves to the substitution of Sn for Ti in the TiO_2 lattice. This substitution enhances the absorption of visible light by the doped Sn- TiO_2 and leads to better separation of charge carriers.^{196,201}

Cuprous oxide (Cu_2O) is another interaction metal oxide p-type semiconductor. Owing to its lower band gap (2.0 eV),²⁰² Cu_2O is a promising material for the conversion of solar energy into chemical energy.²⁰³ Nevertheless, the application of Cu_2O as photocatalyst is very limited due to the fast recombination of charge carriers. Combining Cu_2O with TiO_2 represent a promising way because the absorption of sunlight was achieved and the separation of the e^-/h^+ was ensured.⁵¹ Compared to TiO_2 , Cu_2O possess higher conduction band (−1.4 eV) and valence band edge.²⁰⁴ Under visible light, the photogenerated

electrons in the conduction band of Cu_2O were transferred to the conduction band of TiO_2 and the photogenerated holes in the valence band of TiO_2 were transferred to the valence band of Cu_2O .²⁰³ As the result, high concentrations of electrons and holes were obtained in the conduction band of TiO_2 and valence band of Cu_2O , respectively. Thus, Ti^{3+} electron centers could be formed, which may lead to enhance the photocatalytic efficiency of $\text{Cu}_2\text{O}/\text{TiO}_2$. More than 90% of photocatalytic degradation efficiency of methylene blue²⁰³ and dye brilliant red x-3B²⁰⁵ have been recorded using $\text{Cu}_2\text{O}/\text{TiO}_2$ as photocatalyst.

However, it well-known that the photocatalytic activity is closely related with the surface area. It has been reported²⁰⁶ while studying the photocatalytic activity of $\text{Cu}_2\text{O}/\text{TiO}_2$, that the physical chemical properties and the structure of the photocatalyst influence the performance of the process. Some other oxides, such as ZnO ,¹⁷⁴ Bi_2O_3 ,²⁰⁶ ZrO_2 ,²⁰⁷ among others, have been used in previous research for enhancing the photoactivity of titanium dioxide. Yet, the application of these different photocatalysts in coupling with TiO_2 remains limited in the photocatalytic treatment of water.²¹

6. OTHERS PHOTOSENSITIZING TiO_2

The photocatalytic activity of TiO_2 under visible light could be also enhanced by coupling of organic and inorganic dyes to TiO_2 surface.^{208,209} Dye sensitized TiO_2 has been widely and successfully applied to the degradation of pollutants. Various electron transfer steps are involved in this process. The physical adsorption of dyes occurs through the weak van der Waals interaction between dye molecule and the TiO_2 surface. The photochemical process is initiated by photoexcitation of dye molecules upon illumination by visible light, followed by the transfer of the electrons from the excited dye to the conduction band of TiO_2 . Subsequently, in the presence of suitable electron donors (e.g., EDTA, organic acids, water, alcohols, etc), the oxidized dye is regenerated. The injection of electron into the conduction band of TiO_2 is favorable due to the more negative potential of the lowest unoccupied molecular orbital (LUMO) of the dye molecules as compared to the potential of the TiO_2 conduction band.²⁰⁹ The electrons injected by dye molecules to the surface of titania are scavenged by molecules of oxygen to promote the generation of superoxide radical $\text{O}_2^{\cdot-}$ and hydrogen peroxide radical $^{\cdot}\text{OOH}$. These radicals attack the aromatic rings of organic pollutants forming intermediates and

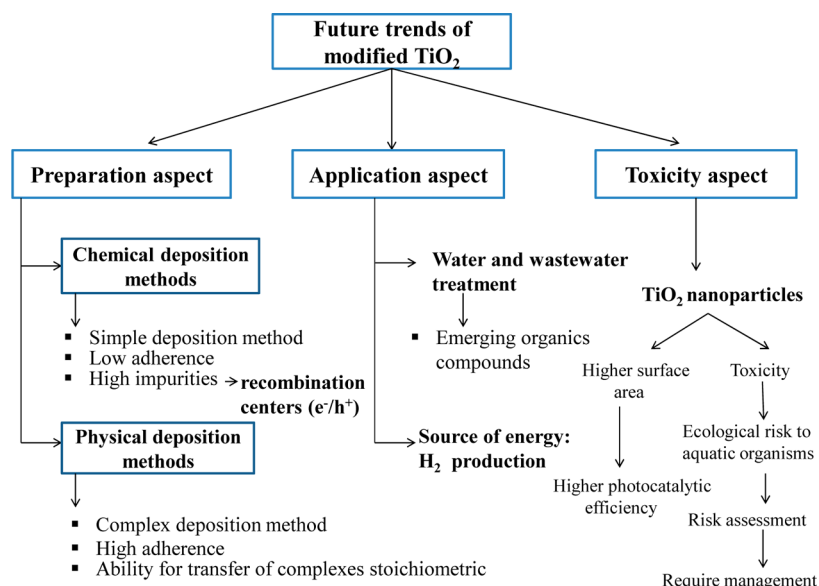


Figure 7. Future trends of modified TiO₂ for environmental applications.

mineralizing them to carbon dioxide and water. Despite the popular utilization of dyes as sensitizers of TiO₂, the quantity of the dye adsorbed on the TiO₂ surface is a crucial parameter because only this amount contributes to photocatalytic process. The frequent desorption of dye molecules reduces significantly the potential use of this technique for practical applications. The extent of dye adsorption depends on the initial concentration of dye, the nature of dye, the surface of the photocatalyst and the pH of the solution.^{210,211} Besides, the photochemical properties of dyes and the interfacial transfers of electrons between dyes and TiO₂ are very important parameters to ensure high photocatalytic efficiency.²⁰⁸

Another mechanism of sensitizing TiO₂ by visible light is the direct charge transfer between surface adsorbate and TiO₂. In the charge transfer sensitization, the electron is photoexcited directly from the ground state adsorbate to the conduction band of TiO₂. The formation of the charge transfer complex on the surface of TiO₂ usually accompanies the appearance of a visible light absorption band, which is not seen in either adsorbate or TiO₂ alone.²⁰⁸ Aromatic compounds having hydroxyl or carboxyl anchoring group are the common examples of formation of charge transfer complex on TiO₂ surface. The TiO₂–catechol complex is a classical example of charge transfer complex.²⁰⁸ According to Wang et al.²¹² the formation of a complex between catechol and TiO₂ creates a broad new band centered at 390 nm, which is extended into the visible region at 600 nm. The excitation of visible light induces the direct transfer of electron from the organic substrates into the conduction band of TiO₂. The application of such mechanism could be a promising alternative for the development of visible light active photocatalysts.

7. FUTURE TRENDS OF TiO₂ FOR ENVIRONMENTAL APPLICATIONS

This review has emphasized some key areas concerning the electronic properties and structure of TiO₂, doping TiO₂ with cationic and anionic metals, and coupling TiO₂ with other semiconductors. Its efficiency in the degradation of pollutants using photocatalytic or photo-electrocatalytic process also has been discussed. Metal doping of TiO₂ has been extensively

explored as a way to improve the photoactivity under visible light.⁴⁹ However, foreign cations could act as a recombination center, and therefore, significant separation between e[−]/h⁺ is only possible at low concentrations of dopants.⁴⁸ Moreover, doping TiO₂ with anionic metals or coupling TiO₂ with other semiconductors represent another approaches to increase the photonic efficiency and the photocatalytic activity of TiO₂. On one hand, doping TiO₂ with anionic nonmetals (such as nitrogen, carbon, etc.) or the increase of its photosensitization in the presence of others semiconductors (such as CdS, WO₃, etc.) make it more suitable for environmental applications. On the other hand, it also makes it potentially significant as promising photocatalyst due to its higher chemical and physical properties (high oxidation efficiency, nontoxicity, high photostability, and chemical inertness, among others).

Despite these achievements and remarkable improvements in TiO₂ structure (doping TiO₂ or coupling TiO₂), several challenges (toxicity and preparation aspects) have to be considered for practical environmental applications, as illustrated in Figure 7.

7.1. Preparation Aspect of TiO₂. It is well-known that photocatalytic activity remains an inconclusive area for all the TiO₂ investigations. The photocatalytic activity is mainly related with surface morphology.¹⁸² The provision of sufficient high specific area of catalyst remains one of the major difficulties. Evidently, there is a clear relation among the surface properties, the rational development of improved synthesis ways, and the potential usefulness of the material prepared for specific applications.^{50,213} Thus, various methods including physical and chemical deposition techniques (hydrothermal synthesis, chemical vapor deposition, pulsed laser deposition, magnetron sputtering, nitrogen plasma, sol–gel) have been adopted to achieve photocatalysts exhibiting desirable physical properties and high activity and stability for photocatalytic applications under visible irradiation using a main part of solar spectrum. For instance, doping transition metals into titania lattice has been mostly carried out using chemical sol–gel technique,^{214,215} whereas doping TiO₂ with nitrogen as an example of anionic metals was mostly conducted under gaseous flow of molecular nitrogen (N₂),^{143,146} nitrous

oxide,¹⁵⁴ and ammonia.²¹⁶ Besides, the pulsed laser deposition (PLD) method is one of the techniques that was used by Peng¹⁴⁹ to prepare nitrogen-doped TiO₂ thin films. Results showed a significant visible light response at 595 nm and a decrease of the band gap as evidence of 3% N doping. The same method has been successfully conducted by Dabney²¹⁷ and Zhao²¹⁸ to prepare Nb-doped TiO₂ and N-doped TiO₂, respectively. Different molecules, different operating conditions, and different methods of analysis make the comparison between deposition techniques so difficult. Compared to the common and available synthesis methods, PLD has become a widely used technique for the deposition of thin films due to its several advantages.²¹⁸ Among the advantages of the PLD method, one can mention the high density of the deposited film with their enhanced adhesion to the substrate because of the rather energetic species involved in the ablation.²¹⁹ It also offers the possibility to achieve nanostructured coating, which is known for high specific area.^{149,220} Compared to other plasma deposition techniques, the PLD method offers a quite independent control of the growth parameters while making deposits in a wide range of pressures and temperatures. The PLD technique is well-known not only for its versatility but, more importantly, for its unique ability to transfer of complexes stoichiometric.^{149,221,222} Magnetron sputtering is also among the very powerful techniques that have been used for the synthesis of TiO₂ materials for photocatalytic applications.^{223–225} As reported by Abdollahi Nejand,²²⁶ magnetron sputtering is a suitable method for doping the metal and nonmetal elements. This technique allows the deposition of well adherent, uniform, mechanical, durable, and transparent films with a controllable density.^{226,227}

Until now, it has been very difficult to assess which of the many deposition techniques is the most effective for photocatalytic application at large scale. The choice of one method over another should take into consideration the cost, the effectiveness, and the operation for large scale. Thus, extensive research should be more conducted to achieve this objective.

7.2. Application Aspect of TiO₂. Nowadays, the presence of emerging organic pollutants such as hormones, phenolic compounds, pharmaceutical compounds, personal care products, and pesticides, among others, in the aquatic environment has received much attention. The application of photocatalytic or photo-electrocatalytic processes using a new TiO₂ photocatalyst structure could be a good alternative to avoid the major drawbacks of conventional treatment methods. Up to now, the application of these new technologies using doped TiO₂ or coupled TiO₂ as photocatalyst for water and wastewater treatment were carried out at the laboratory scale. Thus, the industrial implementation of photocatalytic process using modified TiO₂ under solar irradiation must take into consideration parameters such as the illumination of the photocatalyst. To the best of our knowledge, conventional photocatalytic processes have been tested in large reactors for practical applications by using a wide variety of photoreactor designs (e.g., parabolic trough, inclined plate, fixed/fluidized bed, packed bed, corrugated plate, and falling film photoreactors). This was discussed in detail by Braham and Harris²²⁸ and McCullagh et al.²²⁹ The commercial development of photocatalytic technologies using modified TiO₂ photocatalyst should take into account these designs of the photoreactor in order to promote contact between solar irradiation and the surface of the photocatalyst and, consequently, to ensure higher efficiency of photocatalytic process.

It is worth noting that, during the photocatalytic reaction, the surface of the doped photocatalyst may be covered with organic substances that reduce its active surface. This may affect the treatment performance in long-term experiments. To circumvent these major drawbacks, the use of doped photocatalyst in the form of expanded metal (titanium covered with doped titania) and the application of a high recycling flow rate during the treatment could be one of the easier and more feasible regeneration methods of the photocatalyst surface. Such a structure of photocatalyst provides a good mechanical strength and promotes higher turbulence near the catalyst for increasing the mass transfer coefficient at the electrode–electrolyte interface. Moreover, the high recycling flow rate could be benefit to decrease the thickness of the diffusion layer near the photocatalyst and, consequently, to increase the performance of the photocatalytic process. Likewise, the polarity reversal could be also used to maintain the longevity of doped TiO₂ photocatalyst.

Future research should be also focused to combine this novel technology with biological processes when treating effluents containing refractory organic compounds. Coupling a biodegradation process with a physicochemical process transforms the nonbiodegradable organic pollutants into biodegradable compounds, which contributes to increase the depurative efficiency of the subsequent biological process. Besides, when a biological process was installed downstream, the residence time and reaction volume for the biological treatment could be significantly reduced. In this way, the operating cost of treatment will be decreased.

Although extensive studies have emphasized the TiO₂ semiconductor for photocatalytic and photo-electrocatalytic oxidation of persistent organic pollutants present in water and wastewater,^{13,63,65,149} other potential environmental uses of TiO₂ photocatalyst as source of energy have gathered a great deal of interest.^{48,230,231}

Hydrogen energy is a storable, clean, and environmentally friendly fuel for the future.^{223,225} Fujishima and Honda⁴⁵ have discovered the hydrogen production from photo-electrochemical water splitting using TiO₂ photocatalyst. Subsequently, scientific interests have been focused in enhancing the photocatalytic H₂ production for energy generation. For hydrogen production, the conduction band level should be more negative than the hydrogen production level (E_{H_2/H_2O}), while the valence band should be more positive than the water oxidation level (E_{O_2/H_2O}) for efficient oxygen production from water by photocatalysis. Unfortunately, the photocatalytic production efficiency of H₂ on a bare TiO₂ is very low due to the following reasons: (i) the rapid recombination of e^-/h^+ photogenerated, (ii) the large H₂ production overpotential, and (iii) the fast backward between hydrogen and oxygen.^{232–234} Likewise, the inability use of visible light is another drawback that limits the efficiency of solar photocatalytic for hydrogen production at large scale.²³⁰ However, to overcome the above listed problems and make solar photocatalytic hydrogen production feasible, more efforts have been made to the deposition method such as metal cation doping,²³⁵ carbon and nitrogen doping,^{32,35} etc. Thus, the development of novel TiO₂ photocatalyst merits further research for environmental applications. The future challenge should more focus on the development of novel TiO₂ photocatalyst, which would be able to ensure simultaneously the generation of H₂ and the oxidation of refractory organic pollutants.

7.3. Toxicity Aspect. The development of TiO₂ nanocrystalline photocatalyst is another emerging area where considerable interest has been shown.^{236–238} Such a nanometric grain size (range from a few tens up to a few hundreds of nanometers) is expected to have an important effect on the photocatalytic activity of the TiO₂ coating.²³⁹ Indeed, with the decrease in particle size, the catalytic activity is enhanced due to the huge increase in the surface area of the material.¹³ Nevertheless, nanomaterials can be an important emerging class of contaminants,^{240–242} which have a wide ecological impacts within marine and estuarine ecosystems.²⁴³ TiO₂ uses include different areas such as medical applications,²⁴⁴ catalyst for water and air purification,^{245,246} energy storage,^{247,248} and antimicrobial applications,²⁴⁹ among others. In 2005, the global production of TiO₂ nanoscale was estimated to be 2000 ton, whereas in 2010 the production had increased to 5000 ton.²⁵⁰ According to Westerhoff,²² nanomaterials engineering could pose an ecology risk to aquatic organisms. Among the most commonly used nanoparticles, higher concentrations of TiO₂ have been reached in surface water and pose a significant problem to aquatic ecosystems.²⁴³ During the photocatalytic process, the TiO₂ nanoparticles could diffuse in the aquatic environment. These nanomaterials are then released to surface waters, where they can interact with living organisms. This major drawback limits the use of nanostructured TiO₂ for photocatalytic applications at large scale.

The development of modified TiO₂ photocatalyst by introducing anions or cations could pose an ecological risk to aquatic ecosystem. Indeed, the release of these anionic or cationic compounds in aquatic systems could lead to adverse impacts on the target organisms. For example, the presence of nitrogen as an example of anionic compounds contribute mainly to eutrophication of water bodies, in addition to the risks associated with toxicity and bad odors.²⁵¹ The presence of sulfide compounds in water is also very toxic for many microorganisms because the reaction of sulfide with iron from cytochromes inhibiting the respiration.²⁵² Besides, the release of cation compounds (such as Pb, Ni, Cr, Zn, and Cu, among others) in the aquatic environment are still very toxic and can cause several problems such as extermination of aquatic organisms, as well as risks to human health.^{253,254} Metals are persistent compounds, toxic and absolutely nonbiodegradable.²⁵³ Thus, they can accumulate in the environment and increase their toxicity. To avoid these major drawbacks, research should be focused on the development of preparation techniques in order to increase the photostability of the material.

8. CONCLUSION

This research highlights the importance of TiO₂ photocatalyst for environmental applications. As it has been stated in this review, a number of research studies have focused on the development of a new TiO₂ photocatalyst able to absorb visible light as a main part of solar spectrum. The limitations of pure TiO₂, which require the use of UV light and its high photogenerated electrons and holes recombination rate, can be overcome by introducing foreign species into the titanium dioxide matrix. The doping of TiO₂ with either cationic or anionic metals and coupling TiO₂ with other semiconductors are the major approaches that have been reviewed. Up to now, the successful applications of TiO₂ photocatalyst under visible light for water and wastewater treatment were carried out at the laboratory scale. Future research should be focused on the use

of novel TiO₂ photocatalyst (doped TiO₂ or photosensitization TiO₂) for large scale applications.

■ ASSOCIATED CONTENT

Supporting Information

Additional tables as described in the text. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

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