

Review Article

TiO₂-Based Photocatalytic Process for Purification of Polluted Water: Bridging Fundamentals to Applications

Chuan Wang, Hong Liu, and Yanzhen Qu

Key Laboratory of Reservoir Aquatic Environment, Chinese Academy of Sciences, Chongqing Institute of Green and Intelligent Technology, Chongqing 401122, China

Correspondence should be addressed to Hong Liu; liuhong@cigit.ac.cn

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Recent years have witnessed a rapid accumulation of investigations on TiO₂-based photocatalysis, which poses as a greatly promising advanced oxidation technology for water purification. As the ability of this advanced oxidation process is well demonstrated in lab and pilot scales to decompose numerous recalcitrant organic compounds and microorganism as well in water, further overpass of the hurdles that stand before the real application has become increasingly important. This review focuses on the fundamentals that govern the actual water purification process, including the fabrication of engineered TiO₂-based photocatalysts, process optimization, reactor design, and economic consideration. The state of the art of photocatalyst preparation, strategies for process optimization, and reactor design determines the enhanced separation of photo-excited electron-hole (e-h) pairs on the TiO₂ surface. For the process optimization, the kinetic analysis including the rate-determining steps is in need. For large-scale application of the TiO₂-based photocatalysis, economics is vital to balance the fundamentals and the applied factors. The fundamentals in this review are addressed from the perspective of a bridge to the real applications. This review would bring valuably alternative paradigm to the scientists and engineers for their associated research and development activities with an attempt to push the TiO₂-based photocatalysis towards industrially feasible applications.

1. Introduction

Heterogeneous photocatalysis based on semiconductors has witnessed rapid progress in the last decades [1–3]. The semiconductor photocatalyst, of which the electrons in the valence band can be promoted to the conduction band when being excited by adequate photoenergy, possesses photogenerated electron-hole (e-h) pairs. The e-h pairs enable a series of reductive and oxidative reactions [4–6], and some of them further result in valuable reactions. This method has been initially put forward for the extraction of hydrogen energy from water via the conversion of photoenergy in the 1970s, when the energy crises has emerged [7]. Later in the 1980s, it has been tested as an environmental purification alternative for water [8, 9] and gas [10] as well. This review focuses on the water purification by addressing the fundamentals that serves as a connection with the real-time application.

Many reports have evidenced that numerous organic toxic compounds often present in water can be removed by the photocatalytic method. Chlorinated compounds, alkenes,

alkanes, aromatics, dyes, and so forth, have been tested as the model pollutants [2, 3, 11, 12]. The rationale for TiO₂ photocatalytic method is predominantly based on the oxidation of pollutants by means of hydroxyl radicals (HO[•]) that feature the advanced oxidation technologies (AOTs) [13, 14]. The HO[•] production can be expressed as follows:



The h (hole) is highly oxidative, and the oxidation of water by h leads to a formation of HO[•] radicals, which are extremely active and nonselective in attacking the substrates in aqueous solution. Meanwhile, the electron (e) needs to be scavenged by an electron acceptor. Accordingly, the photogenerated e-h pairs are separated, leading to the transformation of pollutants. Otherwise, the photogenerated e-h pairs will be self-combined with an undesired release of thermal energy. As desired, the photogenerated e-h pairs should be separated as far as possible to improve the process performance of photocatalysis.

The TiO₂ photocatalysis has attracted great attention as a promising water treatment technology due to quite a few intrinsic advantages. (i) Powerful ability to decompose the pollutants: the organic pollutants can be decomposed and even mineralized due to the dramatic powerful oxidation ability of HO[•]. Consequently, this technique can be utilized widely in the cases once the advanced treatment of water, particularly containing the recalcitrant organic compounds, is demanded. (ii) Ambient operating conditions: the process can be realized under ambient operating conditions, and thus is acknowledged as quite safe. (iii) Low cost: the sunlight can be employed as the energy source, and the oxidant is ambient O₂. Meanwhile, as the TiO₂ photocatalyst can be recycled, the cost can be further cut off to run the process. (iv) Environmentally friendliness: TiO₂ are chemically stable, nearly non-toxic, or relatively safe, even in the harsh conditions. Thus, the TiO₂ photocatalysis is thought as an environmentally-friendly approach, even if recent concerns arise on its environmental risks as it is released into the environment [15].

Many reports available in recent years have evidenced that numerous organic contaminants can be decomposed or even mineralized [16] by photocatalysis, and the mechanism governing the photocatalytic process on the TiO₂ surface has been disclosed in depth [17]. Also, efforts for preparation of photocatalytic materials [7–9, 18–22], which include the modification of the commonly used TiO₂ photocatalyst and the design and preparation of new photocatalysts, are intensively exerted. These efforts inclusively have attempts to accelerate the degradation process of target substrates by enhancing the separation efficiency of e-h pairs or to extend the wavelength of excitation light from ultraviolet (UV) regime to visible regime.

Along with the lab-scale investigation of simulated wastewater, some pilot-scale tests have been performed [23, 24]. It could be understood that, although the results served to demonstrate the technical feasibility for water purification, the TiO₂ photocatalysis is still facing a series of technical challenges for a large-scale installment in wastewater treatment plants (WWTPs). It must be noted that challenges, such as fabrication of active TiO₂ photocatalyst, rapid separation and recycling of TiO₂ after use, and optimization of the overall process, are determined by the fundamentals. In particular, the connection between the fundamentals and the actual scenario should be well understood by both the scientists and engineers as they are performing their own individual tasks.

However, the fundamentals, which have been well established in the literature, are far from being fully understood or sophisticatedly applied in the actual application. Also, the operating parameters optimized in laboratory often suffer a mismatching with the actual scenario. In view of the problem, this review highlights the connection between the two tasks, which is expected to bring valuable information for the academia and industry. Along with this highlight, the economic consideration was covered, which eventually leads to a balance between the various variables working in the TiO₂ photocatalytic process.

2. Water Purification of TiO₂ Photocatalysis

With the increasing demand of the water sources, novel technologies, which serve to purify the polluted water with powerful ability to decompose the pollutants in energy-saving and environmentally-benign manners, are becoming essential. As well known, conventional technologies, such as filtration, coagulation, adsorption, and precipitation, principally serve to transfer the pollutants from one phase to another. The newly emerging membrane separation technology [25] also belongs to such category. Following them, further steps must be taken to treat or dispose the transferred pollutants. In this regard, chemical oxidation, featured by their ability to destroy the molecular structures of pollutants, is an indispensable option. During the processes, the toxicity of the involved organic moieties is likely to extenuate or aggravate, and thus the degree of pollutant degradation should be in control. Moreover, the concept of wastewater will become out of date, since the so-called wastewater is just staying at a stage during the overall recycling of water as a resource. The TiO₂-based photocatalytic process, harnessing the sunlight as an energy source and ambient O₂ as an oxidant for water purification, is capable of exhaustively mineralizing the organic pollutants and eliminating the toxicity. Thus, the TiO₂-based photocatalysis is accepted as an effective tool to purify the polluted water.

As listed in Table 1, the water, which is polluted by textile, pesticides, medicine, and so forth, can be treated by the TiO₂-based photocatalysis. It should be pointed out that the TiO₂-based photocatalysis is just employed as an individual method herein. Actually, however, effluents discharged from industrial processes commonly contain recalcitrant or nonbiodegradable pollutants, and thus an integrated process containing biological and physicochemical units will be more applicable. Basically, in the front of integrated process, the influent can be subjected to a physical unit such as filtration or grilling to separate the solids. Following is a physicochemical unit such as coagulation to remove the colloidal substances. Subsequently, a biological unit including aerobic or anaerobic oxidation serves to degrade most of the biodegradable organic molecules, and thus the water quality is usually improved in terms of the indexes such as chemical oxygen demand (COD) and NH₃-N. Finally, a chemical means, such as the TiO₂-based photocatalytic process, is incorporated to purify the water by finally removing the recalcitrant organic pollutants.

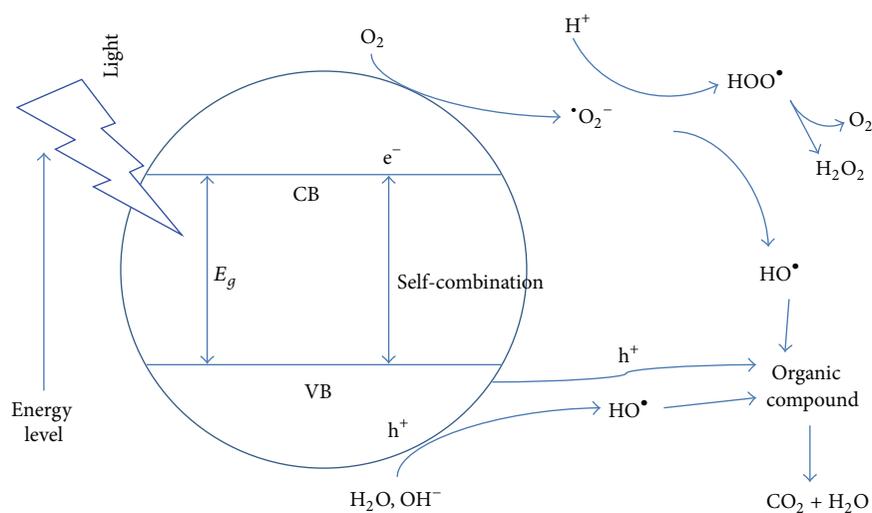
From the technical point of view, the TiO₂-based photocatalytic process is applicable as one prerequisite is satisfied, which is the transparency of water. The transparency ensures the transmission of the light. The TiO₂-based photocatalytic process can be installed as a pretreatment unit or an advanced unit. If the effluent is in need of further purification to destroy the nondegradable organic pollutants, the TiO₂-based photocatalytic process follows the biological unit. Alternatively, the TiO₂-based photocatalytic process is put in front of the biochemical unit to improve biodegradability for a better biological oxidization of the organic substrates.

TABLE 1: Engineered TiO₂, the associated treated targets, reactors and principal operation parameters.

TiO ₂	Water	Reactor	Principal operation parameters investigated	References
TiO ₂ P25	Pharmaceutical wastewater	Sequencing batch biological reactor	H ₂ O ₂ dosage, TiO ₂ dosage, pH, irradiation, time and hydraulic retention time	[73]
TiO ₂ /carbon aerogel	High-concentration dye wastewater	Photocatalysis-enhanced electrosorption reactor	Electrochemical adsorption, potential, temperature, initial pH, and wavelength	[74]
TiO ₂ P25	Wastewater treatment plant effluents	Lab-scale solar photoreactor	Temperature, pH, and light wavelength	[75]
TiO ₂ nanofiber	Hospital wastewater	Batch annular slurry photoreactor (ASP)	Fine bubble aeration, light wavelength, and pH	[76]
Nano TiO ₂	Paper mill wastewater	Solar reactor	TiO ₂ dosage, pH	[59]
C-TiO ₂	Antibiotics wastewater	A computerized Luzchem CCP-4V photochemical reactor	pH, wastewater flow rate	[77]
TiO ₂ P25	Antibiotics wastewater	Capacity cylindrical acrylic photoreactor	pH, gas rate, light intensity, and TiO ₂ dosage	[78]
TiO ₂ /SiO ₂ beads	Organic compounds-containing wastewater	Batch recirculation type photocatalytic reactor	pH, wastewater flow rate	[79]
TiO ₂ P25	Textile wastewater	Pebble bed photocatalytic reactor	TiO ₂ pebbles, water treatment after absorption of reflow exhaust gas	[80]
TiO ₂ P25	Industrial wastewater	A hermetically sealed photoreactor	Pressure, adsorption time, and temperature	[81]
PFT/TiO ₂	Toxic heavy metals wastewater	A column glass photoreactor	Wavelength	[82]
TiO ₂ P25	Secondary effluent	A cylindrical glass reactor	Amount of TiO ₂ loaded, maximum emission peak	[83]
TiO ₂ /Ti anode	Textile wastewater	A thin-film photoelectrocatalytic reactor	pH, lamp position, and light intensity	[84, 85]
TiO ₂ P25	Pharmaceutical and cosmetic wastewater	Common photoreactor	pH, time, catalysts, and H ₂ O ₂ concentration	[86]
TiO ₂ P25	Olive mill wastewater	Common photoreactor	Light wavelength, pH	[87]
TiO ₂ P25	Textile dyehouse wastewater	Immersion well batch-type photoreactor	pH, light wavelength, temperature, and H ₂ O ₂ concentration	[22]
TiO ₂ /SiO ₂	DNP and municipal wastewater	Fixed bed circulation type reactor	Water flow rate, residence time	[88]
Ag-TiO ₂	Seawater	poly (methyl methacrylate) reactors	temperature, dosage of bacterial suspension, and O ₃	[89]
S-TiO ₂	MC-LR in surface water	Borosilicate glass dish	pH, light wavelength	[90]
nano TiO ₂	Drinking water	Tank-style reactor	Permeate flux with a membrane,	[91]
TiO ₂ P25	Surface water	Photovoltaic reactor	Temperature,	[92]
TiO ₂ P25	Benzalkonium chloride	Annular glass reactor	Light wavelength, TiO ₂ dosage	[93]
NF-TiO ₂ -P25 films	Drinking water	Glass vessel reactor	Light intensity, pH	[94]
TiO ₂ microsphere	Organic compounds-containing wastewater	Cylindrical photoreactor	Light wavelength, concentration of TiO ₂ suspensions	[66]
TiO ₂ films	MC-LR in surface water	Sealed round pyrex reactor	Temperature, water flow rate, pH, TiO ₂ coating surface area, and thickness	[95]

TABLE I: Continued.

TiO ₂	Water	Reactor	Principal operation parameters investigated	References
TiO ₂ (P25)-AGS	Toxic heavy metal wastewater	A photocatalytic bath	pH, dosage of catalyst, and temperature	[96]
TiO ₂ P25	Drinking water	Cylindrical Pyrex reaction vessel	Catalyst loading, light wavelength	[97]
TiO ₂ P25	Organic compounds-containing wastewater	A thermostated reactor	Temperature, dissolved oxygen concentration	[60]
TiO ₂ -modified nanofiltration membranes	Organic compounds-containing wastewater	Cell reactor	Light intensity, temperatures	[98]
TiO ₂ P25	Textile wastewater	Immersion well reactor	Dosage of TiO ₂ and H ₂ O ₂ , pH	[99]
TiO ₂ film supported on a porous nickel net	Pesticides	Reactor with ozone generator	pH, ozone dosage, treatment time and temperature	[100]
TiO ₂ nanotubular arrays	Swimming pool water	Cylindrical glass reactor	pH, potential	[101]

FIGURE 1: The scheme of TiO₂ photocatalytic process.

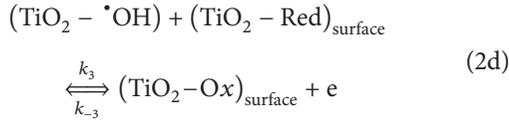
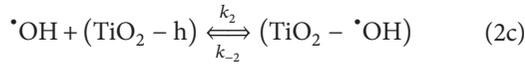
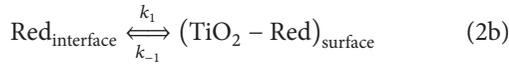
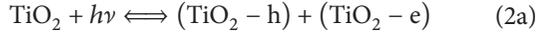
3. Fundamentals

To develop a real TiO₂-based photocatalytic process, optimization of the operating parameters is of importance. However, the fundamentals that have been well established in laboratory are not utilized sophisticatedly or even overlooked in real application. Also, the parameters that are optimized in the laboratory test, which has only one substrate, are not applicable in the full-scale process. The presence of cosubstrates in wastewater may significantly influence the degradation of target substrate. C. Lin and K. S. Lin have observed that the presence of humic acid (HA) retarded the photocatalytic degradation of 4-chlorophenol [26].

Consequently, the fundamentals that closely connect the real scenario should be focused on. Herein, the e-h pair generation and separation, adsorption of organic substrate, and rate determining step (RDS) of the photocatalytic reaction are addressed. These fundamentals are analyzed on how to define a maximized efficiency in real application, whereas any successful and competitive real process should get a balance between efficiency and economics.

3.1. Importance of Photogenerated e-h Pair Separation. The TiO₂ photocatalytic process starts with the generation and separation of e-h pairs, which are illustrated in Figure 1. Based

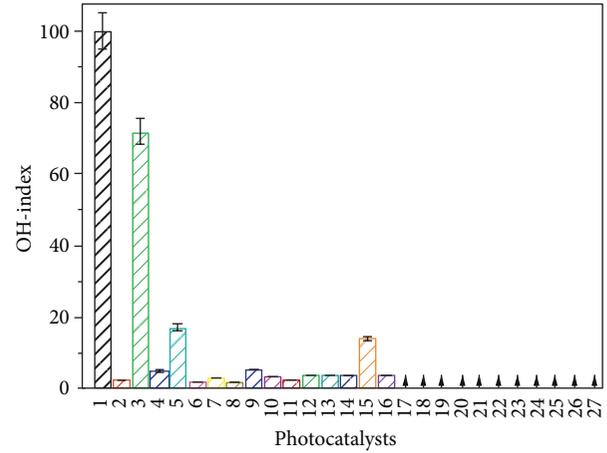
on the mechanism of photocatalytic oxidation proposed by Hoffmann et al., [27] the reactions on the TiO_2 can be correspondingly expressed as follows:



It could be understood that upon the photo-excitation, the electrons on the valence band (VB) jump to the conduction band (CB), generating h left on the VB. As the electrons and holes initially separate and interact with substrates in the solution and then combine together, an effective conversion of substances is thus resulted in. As recombination occurs, there is no any conversion of substances.

Following the generation of holes and electrons, radicals of $\text{HO}\cdot$ are generated and considered to work as the principal oxidative species during the photocatalytic process. Xiang et al. have proposed a concept of “OH-index” to quantitatively characterize the production of $\text{HO}\cdot$ on different photocatalytic systems [28]. Such index, which can be measured easily by photoluminescence technique, is using coumarin as a probe molecule. It appears that this index is quite adequate to explain the activity difference in different systems. For example, P25 TiO_2 , which is a most available commercial photocatalyst, has the highest “OH-index” as illustrated in Figure 2.

The photoenergy plays an important role in the e-h separation. The energy that is sufficient to generate the e-h pairs must surpass the energy of TiO_2 band gap. The equation, $E = h\lambda$, designates the relationship between the energy and the associated light wavelength. TiO_2 (*n*-type) has a band gap of 3.2 eV. Accordingly, the light wavelength must be shorter than 380 nm, which falls into the range of UV light. This requirement determines that a full illumination of the photocatalyst is an indispensable factor when designing a real photocatalytic matrix. First, an artificial lamp must be installed. Lamps with 254 nm and 365 nm as the main wavelength are well commercialized. A more powerful illumination of the photocatalyst certainly accelerates the e-h pair generation. High-pressure mercury lamp is also powerful, whereas its illumination is not stable and thus not recommended for real application. Many lamps can be installed together in the photocatalytic reactor to ensure a full illumination, while the heat release should also be taken into account as the illumination time lasts a long time. Second, the target water must be sufficiently transparent for the transmission of the light. Accordingly, following the pretreatment that serves to remove the particles or species that shadow the light, the TiO_2 -based photocatalytic process can be well employed. Third, only the UV lamps that are made



(1) P25	(10) V_2O_5	(19) BiOBr
(2) Am	(11) Bi_2WO_4	(20) CuO
(3) A	(12) CeO_2	(21) MnO_2
(4) R	(13) CdS	(22) Fe_2O_3
(5) ZnO	(14) CuS	(23) BiVO_4
(6) SnO_2	(15) BiOCl	(24) ZrO_2
(7) SrTiO_3	(16) BiOI	(25) La_2O_3
(8) BaTiO_3	(17) ZnS	(26) NiO
(9) WO_3	(18) Cr_2O_3	(27) Bi_2O_3

FIGURE 2: Comparison of OH-index of various photocatalysts. Arrows represent OH-index = 0. Am, A, and R denote amorphous, anatase, and rutile of TiO_2 , respectively. This figure is taken from the article of Xiang et al. [28].

from quartz glass can be immersed in water. Fourth, even if an immobilization of the TiO_2 photocatalyst serves to recover the TiO_2 , it may bring about a decrease in the e-h generation due to the decrease in the illumination intensity caused by the water shadow. As a result, in real application, the suspended TiO_2 instead of the immobilized TiO_2 is more efficient. Li et al. have reported a type of suspended TiO_2 microsphere, which allows both the TiO_2 suspension and recovery [29].

3.2. Measure for e-h Pair Separation. Following the photogeneration of e-h pairs, a fast recombination of charge carriers is thermodynamically favorable and thus yields a low quantum yield of the reactive species for organic degradation. Obviously, any effort to facilitate the e-h separation and inhibit its recombination is encouraged. Many measures, including TiO_2 modification, scavenger of electrons, and imposition of external force, are allowed to enhance the e-h separation.

3.2.1. TiO_2 Preparation. The TiO_2 is a cornerstone of the photocatalytic process. In laboratory, it is often prepared by methods such as sol-gel method and hydrothermal method. The physical morphology is controllable through hydrothermal preparation, while the TiO_2 is chemically composed of two crystalline types of anatase and rutile. The rutile type

is more stable, and the thermal treatment of anatase type leads to a transformation to rutile. The difference in the distribution of the two types is considered to determine the associated catalytic activity. Basically, pure rutile is found to exhibit a poor activity, while a suitable composition may be more active than the pure anatase type [30]. The preassumed correlation between the composition of crystal phase and the e-h pair separation has been clearly evidenced. Recently, however, Xu and coworkers have found that the anatase and rutile have the same activity in the degradation of 4-chlorophenol, and the difference just lies in their different adsorption ability towards O_2 [31, 32]. Thus, as the TiO_2 with different crystal phases is fabricated, the O_2 adsorption ability on the individual crystal phase needs to be taken into account. The composition of TiO_2 photocatalyst can be adjusted through thermal treatment by means of the increase in temperature.

3.2.2. TiO_2 Doping. To overcome the drawback of low photocatalytic efficiency brought by the e-h self-combination, the bare TiO_2 can be further modified by doping a foreign ion. Table 2 shows that various metal ions, metal oxides, and a few nonmetal elements such as nitrogen, sulfur, fluorine, and silicon can be employed as the dopants.

Gurkan et al. [33] have reported the density function theory (DFT) calculation of the Se(IV)-doping of TiO_2 sample, showing that the doping does not cause a significant change in the positions of the band edges, whereas produces additional electronic states originating from the Se 3p orbitals in the band-gap. Accordingly, the electrons can be excited from the defect state to the conduction band by a relatively lower energy, and thus visible light can be utilized. Further, the benefit of the doped transition metal lies in the improved trapping of electrons to inhibit e-h recombination during irradiation.

In real application for water purification, special attention should be paid to the potential leakage of the doped ions, which may result in a secondary pollution in the treated water. In this regard, the N-doped TiO_2 appears to be a promising method due to the cleanness brought by the nitrogen and has attracted great attention in recent years. In particular, the photocatalytic activity under visible light illumination has been well evidenced [34–40]. However, the unanimity exists for the photocatalytic mechanism. For example, Irie et al. have stated that the irradiation with UV light excites the electrons in both the VB and the impurity energy levels, but illumination with visible light only excites electrons in the impurity energy level [41]. Ihara et al. have concluded that the oxygen-deficient sites formed in the grain boundaries are importantly attributed to the visible light activity, while the doped nitrogen in part of the oxygen-deficient sites is important as a blocker for reoxidation [42].

Also, for the application of the fabricated TiO_2 , the intrinsic advantages brought by the preparation methods should be accurately analyzed, so as to appropriately ascribe the accelerated activities to the e-h separation. For example, Liu et al. [43] have reported that a heat treatment of TiO_2 by hydrogen does not lead to any change in the physical

TABLE 2: Doping of TiO_2 for the enhanced photocatalytic activity.

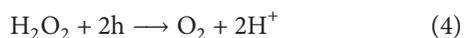
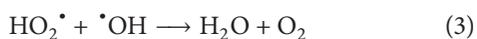
Doped TiO_2	Doping method	References
N-doped TiO_2	Sol-gel method; microwave hydrothermal method	[34–36]
Si-doped TiO_2	Hydrolysis of titanium isopropoxide	[102, 103]
Si-doped TiO_2/ZrO_2	Sol-gel method	[37]
S-doped TiO_2 nanoparticles	Hydrothermal method	[38]
SiO_3^{2-} doped TiO_2 films	Hydrothermal method	[39]
N/S co-doped TiO_2	Manual grinding of thiourea and urea	[104]
S-doped TiO_2/Ti electrode	Anodization method	[105]
S-doped TiO_2-ZrO_2 nanoparticles	Sol-gel method	[40]
C–N-doped TiO_2 nanotube	Chemical vapor deposition (CVD)	[61]
Se(IV) on Degussa P25	Wet impregnation	[33]
Al(III)-doped TiO_2	Sol-gel method	[106]
V-doped TiO_2	Sol-gel method	[107]
Fe-doped TiO_2	Hydrothermal method	[62]
Polypyrrole/Fe-doped TiO_2	Sol-gel method, emulsion polymerization	[108]
Er^{3+} : $YAlO_3/Fe$ - and Co-doped TiO_2	Sol-gel method	[109]
Cu^{2+} -doped TiO_2/SiO_2	Sol-gel method	[110]
$ZnFe_2O_4$ on TiO_2	Sol-gel method	[111]
Ag doped TiO_2	Photoreduction using the sacrificial acid	[112]
Ag/F- TiO_2	Sol-gel method; photoreduction method	[113]
Ag- TiO_2-xNx	Sol-gel method	[114]
Sn-doped TiO_2	Sol-gel method	[115]
Lanthanide ions-doped TiO_2	Sol-gel method	[116]
La^{3+}/Zr^{4+} co-doped TiO_2	Sol-microwave method, oil-bath condition synthesis	[117]
Ce-doped TiO_2	Sol-gel method	[118]
Ce-doped TiO_2 microspheres	solvothermal method	[67]
Nd/F doped TiO_2	Sol-gel method	[119]
W-doped TiO_2	Solvothermal method	[120]
W- TiO_2 films	Liquid phase deposition (LPD)	[121]
W/N co-doped TiO_2 nanoparticles	Sol-hydrothermal method	[122]
Bi-doped TiO_2	Sol-gel method	[123]
C-dope TiO_2 powders	Oxidative annealing of TiC	[41]

properties including the crystal phase, specific surface area, and particle size. However, results of electron paramagnetic

resonance (EPR) detection show that the H₂ treatment leads to formation of oxygen vacancy and Ti³⁺ species on the TiO₂. Moreover, the kinetic constants of phenol degradation increased with the H₂ treatment temperatures lower than 800°C. Therefore, the production of oxygen vacancy and Ti³⁺ species, which are relatively stable as exposure to ambient air, is considered to extend the lifetime of the e-h pairs. The oxygen vacancy and Ti³⁺ species act as holes traps, and oxygen vacancy acts as an electron scavenger. Further, the trapped holes transfer to the organic substrate leading to a degradation reaction and charged defects recover to their original states of oxygen vacancy and Ti³⁺.

3.2.3. Scavenging of the Photogenerated Electrons. To effectively separate the e-h pairs, the electrons need to be scavenged along with the trapping of holes by H₂O to form [•]OH. Otherwise, the electrons will recombine together with the holes without any transformation of pollutants. The most commonly available scavenger is the dissolved oxygen (DO), and thus the TiO₂-based photocatalytic reactions are most often performed in an aerated aqueous system. It has been observed that the reaction rate increases toward a plateau with the partial pressure of O₂ in a gas phase [44]. Actually, before the electron scavenging, an adsorption process of DO occurs, and the adsorption model may be described by a typical Langmuir adsorption.

Besides DO, H₂O₂ is often added as an environmental benign electron scavenger to aid the DO. H₂O₂, being a stronger electron acceptor than oxygen, reacts with the electrons in the valence band of the photocatalyst to generate [•]OH. Chu et al. have observed that the degradation rate of chlorinated aniline can be improved by adding 0.01 mM H₂O₂ to the reaction solution [45]. However, as the H₂O₂ is overdosed at 100 mM, a retardation of approximately 26% rate is caused. The rate retardation can be accounted for as follows. The H₂O₂ does scavenge the valuable HO[•], while the H₂O₂ in excess consumes the oxidative holes on the TiO₂ catalyst surface (3), where the overall oxidation capabilities of the system are significantly reduced [46]:



Additionally, alternative oxidative species such as Cr(VI) ions can be employed as the electron scavenger in the TiO₂-based photocatalysis [47]. The Cr(VI) ions are also a type of pollutant, and the photocatalysis is sometimes employed to remove the Cr(VI) ions as a reductive process using the electrons [48]. As the Cr(VI) ions coexist with organic pollutant, a special supply of DO as the electron scavenger appears to be unnecessary [49]. Compared to the conventional process of Cr(VI) removal using ferrous reduction, the competition of TiO₂-based photocatalysis may be impeded as the economics is taken into account, because the former appears to be a quite rapid process.

3.2.4. Imposition of Bias to Separate the e-h Pairs. External forces such as electric bias can be employed to accelerate

the separation of e-h pairs, which is realized in an electrode system. In this system, the TiO₂ is employed as the anode, where the organic substrate is oxidized by the radicals generated from the interaction between the holes and H₂O. The photogenerated electrons flow through the external circuit and arrive at the cathode where they are scavenged by oxidative species. In this system, an externally imposed anodic bias serves to drive the electrons away from the anode to the cathode, and thus the e-h self-combination of TiO₂ can be efficiently inhibited on the anode. Some reports have shown that a bias of around 0.5 V is efficient to lead to a significant increase in the organic degradation on the anode by means of enhancing the e-h separation [50, 51]. Additional advantage brought by this system leads to the easy recovery of TiO₂ compared to the conventional suspended system.

The lab-scaled prototype of this system, however, may find difficulty in the scale-up for actual water purification, likely because of the utilization of the electrode. As the TiO₂ powder is attached to the anode support, a binder with powerful binding strength is indispensable to anchor the TiO₂ particles on the electrode surface. The binder making of polymer may be degraded after a long-time photocatalytic process, which decreases the lifetime of electrode. Despite this challenge, the photoelectrochemical system can be employed as a powerful platform for the probing of photocatalytic mechanism. In essence, the TiO₂-based photocatalytic process is such one involving electron transfer, which can be exactly investigated by electrochemical means. Liu et al. have employed electrochemical impedance spectroscopy to ascertain the TiO₂-based photocatalytic process, and thus the reaction phenomenon can be accounted for [52]. By means of this powerful tool, the rate-determining steps have been well ascertained.

3.3. Adsorption of Organics onto TiO₂ Surface and Organic Degradation Reaction. Accompanied with the successful e-h separation is the organic degradation reaction. Majority of the reports on the water purification are to investigate the degradation reaction of an individual substrate. The substrate is initially adsorbed onto the TiO₂ surface, and the adsorption ability is often observed to determine the overall degradation efficiency [1]. A large specific surface area of TiO₂ photocatalyst benefits the accumulation of organic substrate on the TiO₂, and thus more active sites are available for the subsequent degradation reaction [53]. Generally, the adsorption behavior can be described by the Langmuir adsorption isotherm, and the kinetic model of organic degradation rate can be described as follows:

$$\frac{dC}{dt} = K_a K_r \frac{C}{1 + K_a C} \quad (5)$$

In (5), K_r designates the contribution of organic degradation and K_a is the contribution of organic adsorption [54]. Obviously, large values of K_a and K_r are beneficial for the acceleration of reaction rate. As the K_a value is small enough

to be neglected, (5) can be considered as the first-order reaction rate as follows:

$$\ln\left(\frac{C_0}{C}\right) = K_{ap}t, \quad (6a)$$

where K_{ap} equals $K_r K_a$ as the apparent reaction rate constant.

In real application, it is noteworthy that the chemisorption, occurring through a formation of chemical bond, contributes to the acceleration of degradation reaction. In some cases, a great number of the organic substrate is adsorbed, while the degradation reaction of organic substrate does not become more rapid just because of the physisorption instead of chemisorption. It has been disclosed by FT-IR that the organic substrate is chemically adsorbed in the form of complex with the TiO_2 [55]. This complex likely leads to a deviation of the first-order rate model of the degradation reaction, because the large K_a value cannot be neglected in (5). In this scenario, the reaction rate can be described as follows [29, 56, 57]:

$$\ln\left(\frac{C_0}{C}\right) + (C_0 - C) = k_{ap}t \quad (6b)$$

Certainly, in real application, the reaction kinetics involving the adsorption should be kept in mind to solve some problems. For example, as the water containing textile as a pollutant is treated, a great number of textile molecules are adsorbed, while physically onto the TiO_2 . Obviously, such type of adsorption does not contribute to the degradation. On the other hand, as the chemisorption predominates with a large K_a value, the first-order rate reaction model that is commonly applied to describe the reaction is not applicable, and (6b) is more adequate to fit the degradation data of target pollutants.

3.4. Rate-Determining Steps. Besides the steps of adsorption and degradation reaction, mass transfer and desorption of the reaction products are also the main steps involved in the heterogeneous catalytic reaction. Among these steps, the slowest step determines the overall reaction rate, while which one is the rate-determining step (RDS)? As the aqueous system is commonly fully stirred by means of air bubbling to form a suspension, the step of mass transfer is generally considered as a fast step, and the adsorption and degradation reactions are potentially the RDS.

In real application, the ascertainment of RDS is of importance. Clearly, only manipulation of the RDS leads to an alteration of the overall reaction rate. For example, as the adsorption step is RDS, increase in the specific surface area to improve the adsorption ability enables the acceleration of the overall reaction rate. Otherwise, the associated efforts are in vain. Liu et al. have employed electrochemical impedance spectroscopy (EIS) to ascertain the RDS of TiO_2 photocatalytic process [52]. Their results show that the surface degradation reaction of organic pollutant is commonly an RDS, while the adsorption step is another RDS once the surface degradation reaction becomes quite rapid. In essence, the acceleration of organic degradation reaction can be considered as the acceleration of the e-h separation. To date,

the TiO_2 photocatalysis is suffering from the low quantum yield, and TiO_2 that has a sufficiently rapid e-h separation is not available. Accordingly, any effort in the acceleration of the e-h separation is valuable.

4. Balance of the Efficacy and Economics

4.1. Economic Estimation of TiO_2 Photocatalysis for Water Purification. The organic pollutants experience an oxidation pathway during the photocatalytic process, and thus a typical TiO_2 -based photocatalytic matrix is composed of four indispensable elements: light source, photocatalyst, oxidant as an electron acceptor, and reactor. The light source supplies energy that excites the electrons on the valence band of TiO_2 to jump to the conduction band, and then holes are left on the conduction band. The TiO_2 -based photocatalyst works as a catalyst, which adsorbs organic substrate onto the surface, and then the degradation reaction occurs. As the oxidative holes are consumed to generate $\cdot\text{OH}$ via the interaction with H_2O , the electrons are left and must be scavenged by an oxidant, mostly, by ambient O_2 . The ambient O_2 has an additional function to buoyant the TiO_2 particles to form a suspension, and thus the mass transfer limit can be precluded. The reactor is the place where the photocatalytic process is realized.

To develop an effective TiO_2 -based photocatalytic process for water purification, the operating parameters should be well optimized for the full utilization of the light illumination, ability of catalyst, and ambient O_2 in the reactor. When doing this work, the fundamentals that have been established in the laboratory should be used sophisticatedly. In addition, since the solution chemistry varies significantly, the experience in one place, even if quite successful, is not applicable in another place. Particular, the optimized parameters cannot be implemented in some real applications due to the limitation of operating cost.

Basically, the operation cost of photocatalytic reaction matrix includes the cost of photocatalytic materials, electricity, and aging of equipment, while the cost of TiO_2 photocatalyst shares the major part and is discussed herein. The cost of TiO_2 photocatalyst depends on its dosage. For example, 0.1–2 wt% TiO_2 , as usually dosed in water treatment, costs too much if it is used one time. It is estimated that the cost of the TiO_2 photocatalyst in treating 1 m^3 of water at this dosage level varies from 3 to 60 USD, under the condition that the price of TiO_2 powders is as low as approximately 3000 USD per ton. This cost is undoubtedly unaffordable for most consumers, particularly in the developing countries [58].

4.2. Recovering of the TiO_2 Photocatalyst. This economic estimation implies that the progress obtained in the reaction efficiency must be balanced by the economic consideration. Thus, the stability of TiO_2 photocatalyst may outweigh its temporary activity, even if quite high. Also, the recycling of the TiO_2 powders, which are commonly employed, is also vital. In particular, the TiO_2 particles are often prepared in a scale of nanosize, and it has been well recognized that the nanosized TiO_2 particles exhibit unique photocatalytic ability

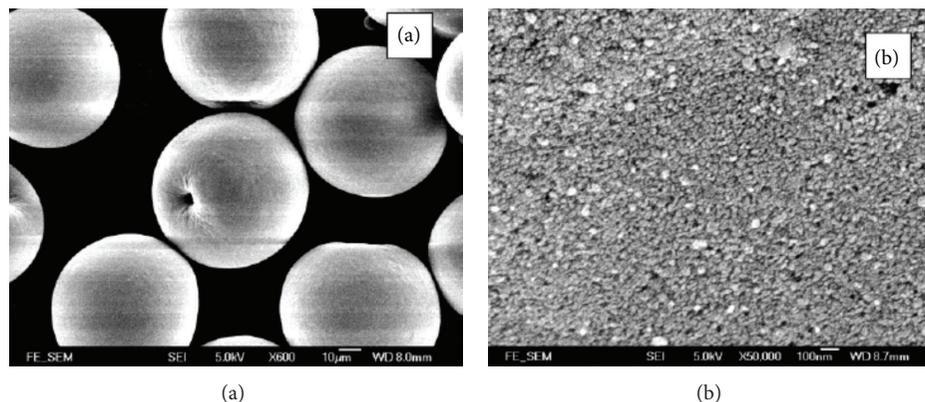


FIGURE 3: SEM image of the TiO₂ microspheres samples ((a) has 600 multiple and (b) has 50,000 multiple magnifications). Taken from [57].

[3, 13, 59–63]. Obviously, these nanosized TiO₂ powders can be well suspended to form a fine contact between the catalyst particles and the substrate, and thus the illumination of the particles is ensured. Accordingly, the organic substrates can be rapidly destroyed in the photocatalytic matrix with nanosized TiO₂ powders.

However, this nanosized TiO₂ is often synthesized through hydrothermal method that demands high temperature and pressure and thus is quite costly once the preparation is practiced in a large scale. In view of the economic consideration as previously mentioned, these TiO₂ particles will encounter a difficulty in separation from the aqueous phase and recycling after use. An addition of a chemical such as coagulant enables the TiO₂ sedimentation and separation, whereas the reuse of TiO₂ becomes impossible due to the TiO₂ fouling. Mostly, the TiO₂ powders are immobilized onto a support [16] to preclude the postseparation, and the TiO₂ can be reused. Moreover, as the TiO₂ powders are immobilized onto a support such as porous nickel [64] or Ti mesh [65] to form an electrode, a bias can be conveniently applied to the anode TiO₂ to enhance the e-h separation. It is noted that in both cases, however, a significant loss in the contact area between the immobilized photocatalyst and the light source exists, which lowers the global efficiency of photocatalytic degradation of organic substrate. Therefore, the efficacy sometimes must be sacrificed for the sake of cost cutting, and a balance between the efficacy of TiO₂ and the running cost is of significance.

This balance requires a novel concept of design of the photocatalyst matrix, in which the advantage of the suspension system should be kept, while the easy recycling of the photocatalyst should be simultaneously realized. Therefore, a microsphere photocatalyst appears to be an ideal option. If the size of microspheres can be designed at a suitable scale in size, they can be well suspended by the air bubbling. The ambient oxygen works as an electron scavenger and thus is inevitably supplied. This way, the suspended TiO₂ can be finely illuminated. Upon the task of photodegradation, the air bubbling stops. Consequently, the microspheres settle at the reactor bottom quickly by the aid of gravity and thus can be readily reused.

Such microsphere photocatalysts have been successfully fabricated [29, 56, 57, 66–70]. For example, as illustrated

in Figure 3, a TiO₂ microsphere photocatalyst with a size regime of 30–160 µm and an average size of around 80 m has been prepared by reconstructing the mixture of TiO₂ sol and TiO₂ nanosized powders with a spray drier [29, 57]. After that, the as-prepared microspheres are thermally treated to obtain the anatase-dominant sample TiO₂ microspheres. The experimental results showed that the photoreaction rate using the TiO₂ microspheres was comparable to that using the TiO₂ powder counterparts. Moreover, the TiO₂ microsphere samples could be reused in the photocatalytic oxidation reaction for more than 50 times, without obvious destruction of the physical structure and significant loss in its activity.

4.3. Coupling of Diverse Technologies. Effluents discharged from industrial processes usually contain various pollutants. Accordingly, diverse technologies, including physical, biological, and chemical ones, are needed to be chosen to treat them in light of such properties. Pollutants in the form of colloids or biodegradable solutes are treated by conventional approaches such as coagulation or biological process. The TiO₂ photocatalyst is specially designed to destroy the recalcitrant pollutants that are nonbiodegradable. The [•]OH involved in the TiO₂ photocatalytic process is extremely powerful to destroy the molecular structures and lead to partial or complete mineralization. Generally, the TiO₂ photocatalysis is particularly fitful for the advance treatment of water, with an attempt of final discharge of the effluent or reuse of the purified water. Clearly, it appears infeasible to purify the seriously contaminated water solely by the TiO₂ photocatalytic process. Without surprise, the TiO₂ photocatalysis has its intrinsic drawbacks in treating actual water. For example, the water should be transparent for the light transmission, and the extremely polluted water often shadows the light. Second, the biological processes are cost effective in the decomposition of a great number of biodegradable pollutants at low concentrations. Therefore, the balance between the efficacy of TiO₂ photocatalytic process and economics requires a smart coupling of it with other conventional process.

In real application, a successful process for water purification is commonly an integrated one including quite a few technologies for the sake of both technical efficacy and cost effectiveness. Basically, a physical unit such as filtration or

grilling unit goes first to separate the solids. Then, a physicochemical process such as coagulation follows to remove the colloidal substances. Further, a biological process is installed to degrade most of the biodegradable organic molecules. Finally, if the effluent requires further purification to destroy the nondegradable organic pollutants, the TiO₂ photocatalytic process is desirable. In addition, TiO₂ photocatalytic process is expected to improve the biodegradability of polluted water as a pretreatment unit by decomposing the recalcitrant pollutants. Anyway, any pilot-scale test is usually extremely necessary to verify the technique and economic feasibility [71], and more fundamental research is also in need to understand the enhancing mechanism of the photocatalytic activity [72], while associated reports are very limited.

5. Concluding Remarks

With the rapid accumulation of reports on the TiO₂-based photocatalysis for water purification, its application becomes a task with great importance. In view of the fact that the fundamentals of the TiO₂-based photocatalysis have been well established, a link with the actual application in water purification should be followed. Analysis in this review shows that it is of significance to keep in mind that the fundamentals, clarified in laboratory, sometimes find it difficult to solve the problems that are encountered in practice. Consequently, some TiO₂-based catalysts, which possess high activity in the degradation of model pollutants in the laboratory, are in great need of further investigation to improve their applicable ability such as separation and recycling. During the further investigation, apart from the fundamentals, economics is believed to play a vital role in actual application, indicating that a balance between the reaction efficiency and the operating cost should also be considered. Moreover, a flexible coupling of TiO₂-based photocatalysis with other technologies is equally important to push it towards real application of water purification.

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