Review

An overview on limitations of TiO$_2$-based particles for photocatalytic degradation of organic pollutants and the corresponding countermeasures

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ABSTRACT

The pollutants classified as "persistent organic pollutants (POPs)", are being subject to high concern among the scientific community due to their persistence in the environment. TiO$_2$-based photocatalytic process has shown a great potential as a low-cost, environmentally friendly and sustainable treatment technology to remove POPs in sewage to overcome the shortcomings of the conventional technologies. However, this technology suffers from some main technical barriers that impede its commercialization, i.e., the inefficient exploitation of visible light, low adsorption capacity for hydrophobic contaminants, uniform distribution in aqueous suspension and post-recovery of the TiO$_2$ particles after water treatment. To improve the photocatalytic efficiency of TiO$_2$, many studies have been carried out with the aim of eliminating the limitations mentioned above. This review summarizes the recently developed countermeasures for improving the performance of TiO$_2$-based photocatalytic degradation of organic pollutants with respect to the visible-light photocatalytic activity, adsorption capacity, stability and separability. The performance of various TiO$_2$-based photocatalytic processes for POPs degradation and the underlying mechanisms were summarized and discussed. The future research needs for TiO$_2$-based technology are suggested accordingly. This review will significantly improve our understanding of the process of photocatalytic degradation of POPs by TiO$_2$-based particles and provide useful information to scientists and engineers who work in this field.

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1.   Introduction

In recent times, the world faces enormous challenges ahead as drinkable water runs short due to natural disasters, population increase, and water pollution. In view to suppress the worsening of clean water shortage, the possible reuse of onsite rural wastewater or treated municipal wastewater from treatment plants for agricultural and industrial activities may be the best solution for the future of sustainable water management in water-deprived countries (Lapena et al., 1995; Bradley et al., 2002; Xu et al., 2012). Since these wastewaters constitute one of the largest possible water resources, their reuse is anticipated to offset more clean water resource.

Recycling wastewaters is usually associated with the presence of suspended solids, health-threat coliforms and the so-called persistent organic pollutants (POPs, e.g., pharmaceuticals, personal care products and endocrine disrupters) that are both tedious and expensive to treat (Viessman and Hammer, 1998; Miranda-Garcia et al., 2011; Zeng et al., 2013a,b). In particular, the POPs are frequently detected in treated sewage, surface and groundwater and even drinking water, and have been observed to be capable of long-range transport, bioaccumulate in human and animal tissue, biomagnify in food chains, and to have potential significant impacts on human health and the environment (Miranda-Garcia et al., 2011). Development of advanced water treatment technologies with low-cost and high efficiency to treat the POPs contaminated wastewater is desirable. Currently, available water treatment technologies such as adsorption or coagulation merely concentrate the pollutants present by transferring them to other phases, but they are not completely "eliminated" or "destroyed" (Padmanabhan et al., 2006). Other conventional water treatment methods such as sedimentation, filtration, chemical oxidation and biotechnology suffer from some disadvantages such as incomplete removal, high consumption of chemical reagent, high treatment cost, time-consuming and generation of toxic secondary pollutants (H.R. Dong et al., 2011; Oller et al., 2011; Zhou et al., 2014). Effective alternative water treatment technologies are therefore required to improve treated effluent quality.

Photodegradation process of POPs has attracted increasing attention during the past decades due to its effectiveness in rapidly degrading and mineralizing recalcitrant organic compounds (Legrini et al., 1993; Chong et al., 2010; Miranda-Garcia et al., 2011). Various photocatalysts including CdS, SnO$_2$, WO$_3$, SiO$_2$, ZnO, Nb$_2$O$_3$, Fe$_2$O$_3$ were being studied but the nano-TiO$_2$ photocatalyst is well-known among the metal oxides for its high efficiency, low cost, physical and chemical stability, widespread availability, and noncorrosive property (Carp et al., 2004; Herrmann et al., 2007). It can be used to degrade a variety of organic and inorganic pollutants. When nano-TiO$_2$ is irradiated with ultraviolet (UV) light, electrons are promoted from the valence band to the conduction band, resulting in the generation of energized "holes" in the former (Fujishima et al., 2000; Chong et al., 2010). Free electrons react with the oxygen to form superoxide radical anions (O$_2^{\cdot-}$), while energized holes react with water (H$_2$O) or hydroxyl ion (OH$^-$) to form hydroxyl radicals ($^\cdot$OH). To date, the main TiO$_2$ applications are focused on air purification (Ao and Lee, 2003; Zhao and Yang, 2003; Li et al., 2005a,b). Studies in wastewater treatment by TiO$_2$ are still mainly in the stage of laboratory experiments because of some technical barriers. Firstly, the widespread technological use of TiO$_2$ is to some extent constrained by its wide band gap (anatase, ~3.2 eV), which requires ultraviolet irradiation for photocatalytic activation, giving rise to a very low energy efficiency in utilizing solar light (Yin et al., 2003; Zaleska, 2008; Chong et al., 2010). Because UV light accounts for only a small fraction (5%) of the sun's energy compared to visible light (45%), the shift in the optical response of TiO$_2$ from the UV to the

visible spectral range will have a profound positive effect on the practical applications of the material. Besides the inefficient exploitation of visible light, the practical applications were also prohibited due to the following limitations: 1) low adsorption capacity to hydrophobic contaminants; 2) high aggregation tendency; and 3) difficulty of separation and recovery (Bhattacharyya et al., 2004; Gao et al., 2011; Cui et al., 2013).

To improve the photocatalytic efficiency of TiO_2, many studies have been carried out to eliminate the limitations mentioned above. Although some review papers on TiO_2 technologies have been published in recent years, most of them focused on contaminants removal, the reaction mechanisms, preparation methods of TiO_2-based particles, principles of photocatalysis, and effects of operational parameters (Gaya and Abdullah, 2008; Zaleska, 2008; Chong et al., 2010; Lim et al., 2011; Morales-Torres et al., 2012; Pelaez et al., 2012). None of them extensively summarizes the limitations of TiO_2-based technologies and the developed countermeasures in the past years. Therefore, this paper aims to review and summarize the limitations of TiO_2 technologies and the recent works on the modification of TiO_2 photocatalysts with the purpose of improving the photocatalytic degradation of organic pollutants. The existing shortcomings and future research needs to utilize TiO_2 photocatalysis for water treatment are also summarized and discussed.

2. Basic principle of TiO_2 photocatalysis

The semiconductor TiO_2 has been widely utilized as a photocatalyst for inducing a series of reductive and oxidative reactions on its surface. The mechanisms underlying the heterogenous photocatalysis employing the semiconductor TiO_2 catalyst have been intensively reported in many papers (Fujishima et al., 2000; Gaya and Abdullah, 2008; Banerjee et al., 2014). Generally, there are five essential key steps in the heterogenous photocatalysis on the surface of TiO_2, namely, the (1) photoexcitation (light absorption and charge-carriers generation), (2) diffusion, (3) trapping, (4) recombination, and (5) oxidation (Gaya and Abdullah, 2008; Chong et al., 2010; Foo and Hameed, 2010). The key reactions involved in the photocatalysis are listed in Table 1. Upon irradiation of TiO_2 with light energy equivalent to or greater than its band gap energy (anatase, ~3.2 eV), the electron is excited from the valence band (VB) to the conduction band (CB). Fig. 1 depicts the mechanism of the electron–hole pair formation when the TiO_2 particle is irradiated with light of adequate energy. The light wavelength for such photon energy usually corresponds to $\lambda < 400$ nm. The photonic excitation leaves behind an empty unfilled valence band, and thus generates the electron–hole pair ($e^- - h^+$) (Eqs. (2.1)–(2.3)).

The e^-_{TR} and h^+_{TR} in Eq. (2.4) represent the surface trapped valence band electron and conduction-band hole respectively. It was reported that these surface-trapped electrons and holes recombine much more slowly than they do in the bulk (Furube et al., 2001). Serpone et al. (1995) have highlighted the important consequences of surface trapped holes (h^+_{TR}) and electrons (e^-_{TR}) to the photooxidation of organic compounds. In the absence of electron scavengers (Eq. (2.4)), the photoexcited electron recombines with the valence band hole in nanoseconds with simultaneous dissipation of heat energy. Hence, the presence of electron scavengers is vital for prolonging the recombination and successful functioning of photocatalysis.

In most applications, photocatalytic degradation reactions are carried out in presence of water, air, the target contaminant and the photocatalyst. Generally, the positive hole reacts with the surface OH^- groups on the TiO_2 particle to produce surface adsorbed hydroxyl radical ($^{\bullet}OH_{ads}$) (Eqs. (2.5) and (2.6)) depicts how the presence of oxygen prevents the recombination of electron–hole pair, while allowing the formation of superoxide radical anion ($O_2^{\bullet-}$). This $O_2^{\bullet-}$ radical can be further protonated to form the hydroperoxyl radical ($HO_2^{\bullet}$) and subsequently H_2O_2 (Eqs. (2.7)–(2.9)). The $HO_2^{\bullet}$ radical formed was also reported to have scavenging property and thus, the coexistence of these radical species can doubly prolong the recombination time of the h^+_{TR} in the entire photocatalysis reaction. Photogenerated holes and the formed reactive oxygen species (e.g., $^{\bullet}OH$) can participate in the degradation of organic pollutants (Fujishima et al., 2000; Zhao and Yang, 2003; Banerjee et al., 2014) (Eqs. (2.10) and (2.11)).

Since the heterogenous photocatalysis reaction mostly occurs on the photon activated surface of TiO_2, the understanding of the reaction steps involved in the photodegradation of organics is essential in the formulation of kinetic expressions. With increasing irradiation time, the liquid phase organic compounds are degraded to their corresponding intermediates and further mineralized to carbon dioxide, water and inorganic ions (from heteroatoms) (Eq.

Table 1 – The reactions involved in the TiO_2 photocatalysis with the presence of organic pollutant (RH).

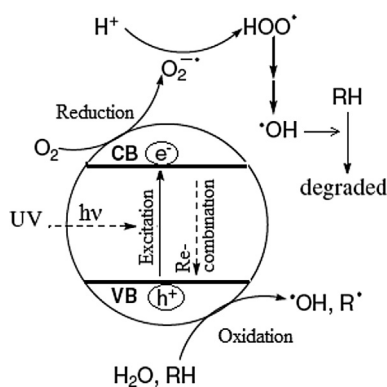| Reactions	Eq. no.
Photoexcitation: $TiO_2 + h\nu \rightarrow e^- + h^+$	(2.1)
Charge – carrier trapping of e^- : $e^-_{CB} \rightarrow e^-_{TR}$	(2.2)
Charge – carrier trapping of h^+ : $h^+_{VB} \rightarrow h^+_{TR}$	(2.3)
Electron – hole recombination : $e^-_{TR} + h^+_{VB}(h^+_{TR}) \rightarrow e^-_{CB} + heat$	(2.4)
Oxidation of hydroxyls: $(OH^-)_{ads} + h^+ \rightarrow {}^{\bullet}OH_{ads}$	(2.5)
Photoexcited e^- scavenging : $(O_2)_{ads} + e^- \rightarrow O_2^{\bullet-}$	(2.6)
Protonation of superoxides : $O_2^{\bullet-} + {}^{\bullet}OH \rightarrow HOO^{\bullet}$	(2.7)
Co – scavenging of e^- : $HOO^{\bullet} + e^- \rightarrow HO_2^-$	(2.8)
Formation of H_2O_2: $HOO^- + H^+ \rightarrow H_2O_2$	(2.9)
Photodegradation by $^{\bullet}OH$: $RH + {}^{\bullet}OH \rightarrow R^{\bullet} + H_2O$	(2.10)
Direct photoholes: $RH + h^+ \rightarrow R^{\bullet} \rightarrow$ Intermediate(s)/Final Degradation Products	(2.11)
$RH \xrightarrow{TiO_2/h\nu} intermediate(s) \rightarrow CO_2 + H_2O +$ inorganic ions (from heteroatoms)	(2.12)

Fig. 1 – **Schematic diagram illustrating the principle of TiO₂ photocatalysis with the presence of water pollutant (RH).**

(2.12)). The overall photocatalysis reaction as depicted by Eq. (2.12) can generally be divided into five independent steps (Herrmann, 1999): 1) mass transfer of the organic contaminants in the liquid phase to the TiO₂ surface; 2) adsorption of the organic contaminants onto the photon activated TiO₂ surface (i.e. surface activation by photon energy occurs simultaneously in this step); 3) photocatalysis reaction for the adsorbed phase on the TiO₂ surface; 4) desorption of the intermediates from the TiO₂ surface and 5) mass transfer of the intermediates from the interface region to the bulk fluid. In terms of rate determination, the overall rate of reaction is equal to the slowest step, which could possibly be either the mass transfer step or the reaction step. Vinodgopal and Kamat (1992) also reported the dependence of the photodegradation rate of the organic surrogate on surface coverage of the photocatalysts used. This outlines the importance of molecules adsorption or surface contact with the catalyst during the photocatalytic degradation. Another factor that greatly restricts the photocatalytic activities of TiO₂ is the low quantum yield of excitons due to the fast electron–hole $(e^- - h^+)$ recombination. The other important factor is the recombination of radical intermediates on the TiO₂ surface. Partially oxidized species could undergo reduction by electrons (and partially reduced ones undergo oxidation by holes and/or surface ·OH) to give back the initial substrate (Vione et al., 2005). Besides, there are other operational parameters that could influence the process of photocatalytic degradation, e.g., light intensity, nature and concentration of substrate (i.e., organic pollutants), nature of photocatalyst (e.g., particle size), concentration of photocatalyst, pH and reaction temperature (Gaya and Abdullah, 2008).

3. Limitations and countermeasures in TiO₂-based photocatalytic processes

TiO₂ photocatalysis is one of the most efficient destructive technologies among advanced oxidation processes (AOPs), because it appears to utilize solar energy to lead to the total mineralization of most of the organic pollutants that exist in air and aqueous systems (Legrini et al., 1993). However, its application is limited because of its narrow photocatalytic region (λ < 400 nm) and ability to absorb a small fraction (<5%)

of incident solar irradiation and indoor light, which results from its relatively large band gap (anatase, ~3.2 eV) (Yin et al., 2003). Hence, any improvement of the photocatalytic efficiency of TiO₂ by shifting its optical response to the visible range will have a profound positive effect.

Since photocatalytic degradation mainly occurs on the surface of TiO₂, mass transfer limitation has to be minimized for effective TiO₂ application in water treatment. However, due to its poor affinity towards organic pollutants (especially the hydrophobic organic pollutants), the adsorption of organic pollutants on TiO₂ surface is relatively low, resulting in slow photocatalytic degradation rates. Therefore, how to concentrate the target pollutants around the TiO₂ nanoparticles to enhance photocatalytic efficiency requires consideration. Besides, during the photocatalytic degradation process, the TiO₂ nanoparticles may undergo aggregation due to the instability of the nanosized particle, which may hamper the light incidence on the active centers and consequently reduce its catalytic activity (Gao et al., 2011; Mallakpour and Nikkhoo, 2014). However, it should be noted that it may well happen that small particles show higher scattering, which can reduce their photocatalytic activity compared to larger ones (Minero and Vione, 2006). Furthermore, for the slurry system, one main practical challenge to overcome is to recover the nanosized TiO₂ particles from the treated water in regards to both the economic concern and safety concern. The above limitations in the application of TiO₂-based particles for photocatalytic degradation of organic pollutants are summarized in Fig. 2.

To overcome those limitations of TiO₂-based photocatalysis, the following countermeasures have been adopted in previous studies: 1) modification of TiO₂ catalyst, in order to achieve the utilization of visible light (Bannat et al., 2009; F. Dong et al., 2011); 2) optimization of catalyst synthesis, in order to obtain catalysts with a defined crystal structure, smaller particle sizes, and high affinity to various organic pollutants (Makarova et al., 2000; Lightcap et al., 2010); and 3) design and development of second generation of TiO₂ catalyst, with high separation ability, which can be recovered and regenerated effectively (Nakayama and Hayashi, 2007; Gad-Allah et al., 2007; Tang et al., 2013). The purposes of these modifications and developments were to improve photocatalytic efficiency, complete degradation of organic pollutants, improve visible light absorption,
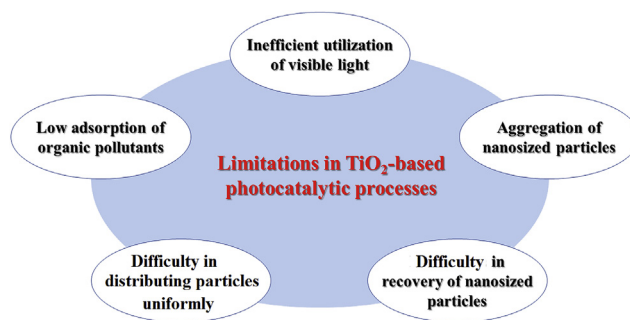

Fig. 2 – **Limitations in application of TiO₂-based particles for photocatalytic degradation of organic pollutants.**

Table 2 – The countermeasures to improve the performance of TiO$_2$-based photocatalytic processes and their respective mechanisms and drawbacks.

Countermeasures		Improvements/mechanisms	Drawbacks	Ref.
Enhancing the visible-light photocatalytic activity of TiO$_2$ particles	Doping of metals	⋄ Narrowing band gap ⋄ Retarding electron–hole recombination ⋄ Enhancing adsorption of contaminants	⋄ Thermal instability ⋄ Dopant concentration dependent ⋄ Costly	Bannat et al., 2009; J. Zhang et al., 2010
	Doping of non-metals	⋄ Narrowing band gap ⋄ Enhancing adsorption of contaminants ⋄ Enhance conductivity of TiO$_2$	⋄ Formation of oxygen vacancies ⋄ Short-term efficiency of photocatalysis ⋄ High temperature for preparation and the procedures are somewhat tedious	Q. Li et al., 2008; F. Dong et al., 2011
	Co-doping technique	⋄ Improved interfacial charge transfer ⋄ Synergistic effect of two elements co-doping	⋄ The dosage level could be an important factor in influencing the photoactivity ⋄ Need multistep experimental process for preparation	Gombac et al., 2007; Huo et al., 2009
	Surface organic modification (dye sensitization/organic coating)	⋄ Enhancing visible light absorption ⋄ Improving electron–hole separation	⋄ Surface coating tend to partially desorb ⋄ Be depressed by the competitive adsorption of other coexisting species ⋄ The sensitizers or coatings are toxic and unstable in aqueous solution	Zhao et al., 2005; Chen et al., 2009
Enhancing adsorption of organic pollutants on TiO$_2$ particles	Surface organic modification	⋄ Hydrogen bonding, n–π and π–π interactions result in stronger adsorption	⋄ Concern on the remobilization of surface coating during the photocatalysis process	Makarova et al., 2000
	Doping of carbon-based nanoparticle	⋄ Provide high surface area, well conductivity and higher visible light absorption intensity ⋄ Suppression of electron–hole recombination (due to the high electrical conductivity) ⋄ Band-gap narrowing resulting from the presence of Ti–O–C bonds	⋄ Concern on the remobilization of carbon-based material during the photocatalysis process	Williams et al., 2008; Lightcap et al., 2010
Stabilization of TiO$_2$ particles	Stabilization by support structures	⋄ Immobilize the TiO$_2$ photocatalyst to prevent aggregation	⋄ Lower activity of supported TiO$_2$ than the unrestricted catalyst	Carp et al., 2004
	Stabilization by surface modification	⋄ Prevent the particle aggregation and disperse homogeneously of TiO$_2$ nanoparticles	⋄ Stability could be decreased in the presence of cations, e.g., Ca^{2+}	Nakayama and Hayashi, 2007
Separation of TiO$_2$ particles	Immobilization on support structures	⋄ Immobilize the TiO$_2$ photocatalyst for easy recovery	⋄ Lower activity of supported TiO$_2$ than the unrestricted catalyst	Mascolo et al., 2007
	Magnetic separation	⋄ This type of composite photocatalyst comprises of a TiO$_2$ shell and a magnetic core, making them recoverable due to their magnetic properties	⋄ The photocatalytic activity of magnetic TiO$_2$ can be influenced by the magnetic core size, calcination temperature, etc.	Gad-Allah et al., 2007; Tang et al., 2013

improve stability and reproducibility, and to improve recycle and reuse abilities of TiO_2. The countermeasures for overcoming these limitations, and the mechanisms and drawbacks of each countermeasure are briefly summarized in Table 2 and are discussed in detail in the following sections.

3.1. Approaches to enhance the visible-light photocatalytic activity of TiO_2 particles

How to improve the photocatalytic activity of TiO_2 in the visible region is the main focus of the recent TiO_2 photocatalysis research. Several approaches for TiO_2 modification have been proposed: metal-ion implanted TiO_2 (e.g., Au) (Anpo, 2000; Fuerte et al., 2001), non-metal doped-TiO_2 (e.g., N) (Ohno et al., 2003; Yu et al., 2003b; Pelaez et al., 2012), composites of TiO_2 with semiconductor having lower band gap energy (e.g. sensitizing of TiO_2 with dyes) (Chatterjee and Mahata, 2001) and TiO_2 doped with upconversion luminescence agent (Zhou et al., 2006; J. Wang et al., 2007). The mechanisms of each modification approach and their advantages and drawbacks are discussed in detail in the following.

3.1.1. Doping with metals
Over the past decades, metal-doped TiO_2 (e.g., Cu, Co, Ni, Cr, Mn, Fe, Ru, Au, Ag, Pt) photocatalysts have been widely studied for improved photocatalytic performance on the degradation of various organic pollutants under visible light irradiation (Anpo, 2000; Fuerte et al., 2001; Arabatzis et al., 2003; Hu et al., 2006; Zang and Farnood, 2008; Zaleska, 2008; Han et al., 2014). TiO_2 particles can be simply substitutionally or interstitially doped with different cations, can form mixed oxides or a mixture of oxides. The dominant parameters include the character and concentration of dopants and the applied thermal treatment (Soria et al., 1991; Palmisano et al., 1994). Many controversial results are reported in the literature since even the method of doping (e.g., impregnation, coprecipitation, and sol–gel methods) leads to different morphological and crystalline properties of the photocatalyst (Zaleska, 2008).

Fig. 3 — Mechanisms of metal-doped TiO_2 photocatalysis: ①: narrowing band gap (hv_1: pure TiO_2; hv_2: metal-doped TiO_2); ②: retarding electron–hole recombination; and ③: enhancing adsorption of contaminants (RH).

The effect of metal ion dopants on the photocatalytic activity is a complex problem. The visible light photoactivity of metal-doped TiO_2 can be explained by a new energy level produced in the band gap of TiO_2 by the dispersion of metal nanoparticles in the TiO_2 matrix. As shown in Fig. 3, electrons can be excited from the defect state to the TiO_2 conduction band by photons with energy equal to hv_2. An additional benefit of transition metal doping is the improved trapping of electrons to inhibit electron–hole recombination during irradiation (Fig. 3). Deposition of metal nanoparticles with a large work function, such as Ag (Tran et al., 2006), Pt (Kowalska et al., 2008), and Au (Subramanian et al., 2001; Wang et al., 2008; Bannat et al., 2009), onto TiO_2 surface has been found to efficiently retard the e^-–h^+ recombination because of the Schottky barrier formed at the metal–TiO_2 interface. Decrease of charge carriers recombination results in enhanced photoactivity. Here, the metal nanoparticles act as a mediator in storing and shuttling photogenerated electrons from the TiO_2 surface to an acceptor. Iliev et al. (2006) demonstrated that deposition of Pt or Ag on the surface of TiO_2 greatly enhanced the photocatalytic degradation of oxalic acid due to the increased separation of e^-–h^+ and higher rate of O_2 reduction. Besides the above causes for the enhanced photoactivity of metal-doped TiO_2, there is another factor that should be taken into account in the photocatalytic process. Since surface sites can also be occupied by metal ion dopants, the surface properties as well as the point of zero charge value of TiO_2 may be altered by doping, depending both on the type and amount of the dopant metal. Consequently, a modification of adsorption properties takes place (Fig. 3). Ranjit et al. (2001a,b) reported that lanthanide ions can form complexes with various Lewis bases (e.g., acids, amines, aldehydes, alcohols, thiols, etc.) through interaction of these functional groups with the f-orbitals of the lanthanides. Xu et al. (2002) found that the metal-doped TiO_2 (e.g., La^{3+}, Ce^{3+}, Er^{3+}, Pr^{3+}, Gd^{3+}, Nd^{3+}, and Sm^{3+}) presents an improved NO_2 adsorption. Li et al. (2004) also reported an enhancement of saturated adsorption capacity and adsorption equilibrium constants of La^{3+} doped TiO_2 compared to bare TiO_2 for 2-mercaptobenzothiazole.

However, it was found that the photocatalytic activity of metal-doped TiO_2 could be influenced by dopant concentration. Ambrus et al. (2008) and Tong et al. (2008) reported an improved photocatalytic performance for the optimum Fe dopant concentration. Beyond the optimum concentration of dopant, the photodegradation rate decreased. It was concluded that the dopant ions below an optimum dosage level can act as electron–hole separation centers, and thus enhance the photocatalytic efficiency, while the dopant ions with dosage level exceeds optimum value, can act as electron–hole recombination centers which are detrimental to the photocatalytic activity (Wu et al., 2009). Besides, metal doping showed other drawbacks: thermal instability of doped TiO_2 and requirement of more expensive ion-implantation facilities (J. Zhang et al., 2010). In addition, although noble metals coupling could be efficient in improving the photocatalytic reactions, the cost-effectiveness needed by industrial application usually causes their replacement by more economical transition or non-metals doping.
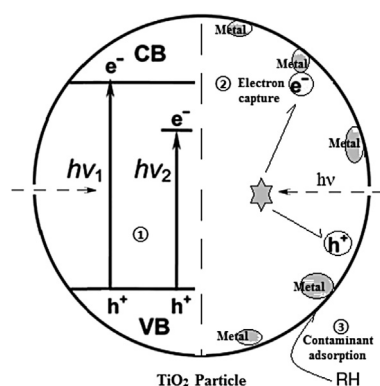
3.1.2. Doping with non-metals

Compared with metal dopants, nonmetal dopants, such as C, N, S, B, P, F and I (Chen et al., 2007), may be more appropriate for the extension of the photocatalytic activity of TiO_2 into the visible region because their impurity states are near the valence band edge, but they do not act as charge carriers, and their role as recombination centers might be minimized. Numerous contributions have been devoted recently to developing effective TiO_2 photocatalysts doped with nonmetal elements to extend the light absorbance of TiO_2 into the visible region (F. Dong et al., 2011; Likodimos et al., 2013; Moustakas et al., 2013; El-Sheikh et al., 2014). Among all nonmetal-doped TiO_2 materials, N- and C-doped TiO_2 nano-materials have been found to exhibit superior photocatalytic activity under visible light irradiation.

Until now, much effort has been focused on the research of N-doped TiO_2 (N–TiO_2). There have been a large number of publications that deal with the preparation of N–TiO_2 by physical or chemical methods, including sol–gel, sputtering, ion implantation, mechanochemical and plasma-enhanced chemical vapor deposition method (Zaleska, 2008). However, different conclusions concerning the state of doped nitrogen in the N–TiO_2 lattice and the mechanism of band gap narrowing have been derived (Fig. 4). For example, Asahi et al. (2001) proposed that substitutional-type doping using N was effective for the band gap narrowing of TiO_2 due to the mixing of N 2p with O 2p states in the valence band based on spin-restricted local density approximation calculations on anatase. The N 2p state hybrids with O 2p states in anatase TiO_2 doped with nitrogen because their energies are very close, and thus the band gap of N–TiO_2 is narrowed and the material becomes able to absorb visible light. However, Irie et al. (2003) and Lindgren et al. (2003) found that interstitial-type doping of N atoms was related to the photo-threshold energy decrease, which induced localized N 2p states within the band gap just above the top of the valence band, facilitating the production of oxygen vacancies. Ihara et al. (2003) reported that oxygen-deficient sites formed in the grain boundaries is important to emerge vis-activity and nitrogen doped in part of oxygen-deficient sites are important as a blocker for reoxidation. Zhao and Liu (2008) concluded that

Fig. 4 – Mechanisms of non-metal doped TiO_2 photocatalysis: ①: narrowing band gap (hυ₁: pure TiO_2; hυ₂: non-metal doped TiO_2); ②: facilitating electron transfer from the bulk of the TiO_2 structure to the surface region (reaction sites); and ③: enhancing adsorption of contaminants (RH).

TiO_2 doped with substitutional nitrogen has shallow acceptor states above the valence state. In contrast, TiO_2 doped with interstitial nitrogen has isolated impurity states in the middle of the band gap. These impurity energy levels are mainly hybridized by N 2p states and O 2p states.

Besides N–TiO_2, the carbon doped TiO_2 (C–TiO_2) has also received special attention (Wu et al., 2013). Sakthivel and Kisch (2003) reported that C–TiO_2 was five times more active than N–TiO_2 in the degradation of 4-chlorophenol by visible light. In the investigation of C–TiO_2, similar to the N–TiO_2, there was also a debate as to whether the doped type of carbon is substitutional or interstitial (Chen et al., 2007). This was accounted for by the crystal form and synthesis method of TiO_2. Valentin et al. (2005) reported that carbon can be doped into TiO_2 lattice and then strongly enhance the visible light absorption of TiO_2 via substituting oxygen sites or getting into the interstitial positions of TiO_2, which is due to the introduction of series of localized occupied states into the band gap of TiO_2 lattice. In addition, some reports suggested that large band gap narrowing could also originate from residual carbon-containing species with complex composition, through incomplete removal of organic compounds in the calcination procedure (Lettmann et al., 2001; Sakthivel and Kisch, 2003). Besides, carbon doping can significantly stabilize the anatase TiO_2 and improve the adsorption of organic pollutant molecules on the catalyst surface (Kang et al., 2008; Hahn et al., 2009). Moreover, carbon doping can enhance the conductivity of TiO_2 (Janus et al., 2006; Xiao and Ouyang, 2009), as it could facilitate the charge transfer from the bulk of the TiO_2 structure to the surface region where the desired oxidation reactions take place (Fig. 4).

In spite of the visible-light photocatalytic performance of nonmetal-doped TiO_2, at the same time, there are some problems with nonmental-doped TiO_2: 1) The doping of nonmetals into the lattice of TiO_2 usually results in the formation of oxygen vacancies in the bulk. These defects can act as massive recombination centers of photo-induced electron–hole pairs, which largely limit the visible light photocatalysis efficiency of nonmental-doped TiO_2 for industrial applications (X.Y. Li et al., 2008; F. Dong et al., 2011). In view of practical application, higher photocatalytic reaction efficiency is required because the photocatalytic efficiency of nonmetal-doped TiO_2 under visible light is still low (Ozaki et al., 2007; Dong et al., 2010). 2) The stability of nonmetal-doped TiO_2 is also a concern in regard to the long-term efficiency of photocatalysis. It is reported that the stability of N–TiO_2 becomes worse after photoelectrolysis of water under visible light irradiation due to a decrease in N concentration at the surface layer (Kitano et al., 2006). Deactivation of N-doped TiO_2 for the oxidation of 2-propanol in aqueous solution under visible light after a reaction of 150 h was also observed, which was related to the liberation of doped N atoms (Nosaka et al., 2005). 3) The preparation method is another crucial factor that should be considered for applications. The doping process of the nonmetal elements always involves thermal treatment at high temperatures (400–850 °C) or a long time of hydrothermal treatment, both of which are unfavorable in energy (F. Dong et al., 2011). Besides, expensive, toxic, or unstable precursors are used; undesirable gaseous byproducts are usually produced in the preparation process; and the procedures are
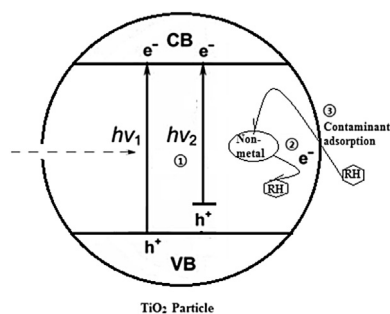
somewhat tedious, which, in all, make the preparation costly and large-scale application difficult (Dong et al., 2009). Therefore, development of new and optimization of existing photocatalysts exhibiting activity under visible light with surface characteristics of improved performance and having high chemical and physical stability are crucial for broader scale utilization of photocatalytic systems in commercial application.

3.1.3. Co-doping technique

More recently, the simultaneous doping of two kinds of atoms into TiO_2 has attracted considerable interest (J. Zhang et al., 2010). These co-doped TiO_2 nanomaterials have been demonstrated to have improved photocatalytic activities compared to those of non-doped TiO_2 or single-ion doped TiO_2, especially in the visible light region. For example, monocrystalline TiO_2 codoped with Eu^{3+} and Fe^{3+} shows synergistic effect, which significantly increases the photocatalytic degradation of chloroform in solution (five times compared to pure nanocrystalline TiO_2 and about two to six times compared to Fe^{3+} or Er^{3+} doped separately, respectively) (P. Yang et al., 2002). It was proposed that Fe^{3+} serves as a hole trap and Eu^{3+} as an electron trap, speeding up the anodic and the cathodic processes, respectively, via improved interfacial charge transfer. Livraghi et al. (2009) investigated the decomposition of methylene blue by N–F-codoped TiO_2 in aqueous phase. It was found that F could activate the active site of N by producing extra electrons to the low energy orbital of $N_b^\cdot$ (a paramagnetic species). Doping with F and N created a synergism in which F improved the incorporation of N photoactive species into TiO_2. Cong et al. (2007) reported that titania co-doped with N and Fe^{3+} (0.5 wt%) decomposed a 50 mL 20 mg L^{-1} rhodamine B solution completely in 4 h under visible light irradiation, faster than N-doped TiO_2 or Fe-doped TiO_2. However, under UV light, the photocatalytic activities of Fe–N co-doped TiO_2 was lower than that of undoped TiO_2. The nitrogen ions and Fe^{3+} dopants could act as the recombination center of electrons and holes, thus decreasing the UV photoactivity. Interestingly, some research reported that co-doped TiO_2 photocatalysts exhibited good photoactivities under both UV and visible light (J. Zhang et al., 2010). For instance, Lin et al. (2007) found that the phosphorus and nitrogen co-doped titania showed high photoactivity in the UV illumination and also in visible light. They suggested that the O–P–N linkage would lead to the high photocatalytic activity.

In the recent studies, the different roles of reactive oxygen species (ROS) were found in doped and co-doped visible-light-active TiO_2 photocatalysts (Rengifo-Herrera et al., 2009; Rengifo-Herrera and Pulgarin, 2010; Banerjee et al., 2014; Zhao et al., 2014). Zhao et al. (2014) showed that N–F co-doped TiO_2 exhibited the best performance to destroy 6-hydroxymethyl uracil (6-HOMU), a model compound for cyanotoxins. Mechanistic investigations carried out in the presence of scavengers for $\cdot O_2^-$, $^1O_2$ (singlet oxygen), $\cdot OH$, and h^+_{vb} have shown that $\cdot O_2^-$ is the prime ROS leading to the photocatalytic degradation of 6-HOMU. Rengifo-Herrera and co-workers proposed that for N–S co-doped TiO_2, photogenerated holes formed under visible light irradiation do not possess suitable reduction potential to generate $\cdot OH$ radical by the oxidation of H_2O (Rengifo-Herrera et al., 2009; Rengifo-Herrera and Pulgarin, 2010). It has also been reported that less oxidative superoxide radical anion $\cdot O_2^-$, and $^1O_2$ species are predominantly responsible for the photocatalytic bacterial inactivation under visible light irradiation, however, highly oxidizing $\cdot OH$ radicals are produced under UV light excitation, which play active roles toward photocatalytic activity (Rengifo-Herrera et al., 2009; Rengifo-Herrera and Pulgarin, 2010).

As discussed in the previous section, the dosage level could also be an important factor in influencing the photoactivity of co-doped TiO_2. Below an optimum dosage level, the dopant ions can act as electron–hole separation centers, promote the charge separation, and thus enhance the photocatalytic efficiency. However, as dosage level exceeds optimum value, the dopant ions can act as electron–hole recombination centers which are detrimental to the photocatalytic activity. Wu et al. (2009) found that 4.0 wt% of Au was found to be the optimum dopant concentration for photodegradation of methyl orange by Au/N-doped TiO_2 under both UV and visible light irradiation. Higher amounts of gold deposition (>4.0 wt% Au) caused decreased photocatalytic activities through an electron–hole recombination process. In addition, the high concentrations of Au may also block the N–TiO_2 from absorbing the incoming photons.

Besides high catalytic activity for photodegradation of organic pollutants, the issue of physiochemical stability and reuse of the synthesized photocatalysts is another main objective in this research area. Unfortunately, only a few papers have reported on the stability and reuse of co-doped TiO_2 (Gombac et al., 2007; Huo et al., 2009). Huo et al. (2009) evaluated the performance of N and F co-doped TiO_2 in methylene blue degradation through ten successive batches. After ten consecutive photocatalytic experiments, the N and F co-doped TiO_2 photocatalyst retained high photocatalytic performance. Gombac et al. (2007) investigated the stability of N–B co-doped TiO_2 for photodegradation of methyl orange and found that after four cycles, a relatively small decrease of the catalyst activity was observed. They suggested that the presence of B allowed a stronger retention of N-containing species. Currently, no report on the changing of concentration or composition of the dopants after long time of reaction is available. It is worthwhile to indicate that research on stability and reuse of these co-doped TiO_2 catalysts is in high demand in both academic and commercial sectors.

3.1.4. Surface organic modification

As mentioned above, those metal/nonmetal-doped TiO_2 materials were generally somewhat difficult to be prepared with the needs of lattice exchange at high temperature and multistep experimental process. In the past decade, surface modification of TiO_2 with organic ligands has drawn much attention.

3.1.4.1. Dye sensitization.
Visible light-induced dye-sensitized TiO_2 photocatalysts can be readily prepared under a mild condition through interfacial adsorption of dye molecules on TiO_2 in an ambient environment (Bae et al., 2004; Chen et al., 2005). Thus, much interest has been shown in surface

modification of TiO_2 with organic dyes for construction of dye-sensitized photocatalytic systems under visible-light irradiation (Jiang et al., 2007). Dyes that are used as sensitizers include erythrosin B (Kamat and Fox, 1983), thionine (Patrick and Kamat, 1992), substituted and unsubstituted bipyridine (O'Regan and Graetzel, 1991; M. Yang et al., 2002) and phthalocyanine (Yu et al., 2003a).

The absorption of TiO_2 sensitized by a proper dye molecule can be extended to visible region because the dye can absorb the visible light to reach an excited state (Eq. (3.1)) (O'Regan and Graetzel, 1991). The dye in the excited state has, in general, a lower redox potential than the corresponding ground state. If the redox potential is lower than the conduction band (CB) of TiO_2, an electron may be injected from the excited state into the CB (Eq. (3.2) and Fig. 5), and consequently the cationic radicals and CB electron are formed. Surface sensitization of TiO_2 by electron transfer via chemisorbed or physisorbed dyes can 1) increase the efficiency of the excitation processes and 2) expand the used wavelength range through excitation of the sensitizer followed by an electron transfer between the excited dye and the CB of TiO_2. Depending on its redox environment, the dye is able to donate (in most cases) or receive an electron improving electron–hole separation (Kiriakidou et al., 1999).

$$Dye + h\nu \rightarrow Dye^* \tag{3.1}$$

$$Dye^* + TiO_2 \rightarrow Dye^{*+} + TiO_2(e^-) \tag{3.2}$$

$$TiO_2(e-) + O_2 \rightarrow TiO_2 + O_2^{\cdot -} \tag{3.3}$$

$$O_2^{\cdot -} + H^+ \rightarrow HO_2^{\cdot} \tag{3.4}$$

$$2HO_2^{\cdot} \rightarrow H_2O_2 + O_2 \tag{3.5}$$

$$H_2O_2 + e^- \rightarrow OH^- + {}^{\cdot}OH \tag{3.6}$$

If the oxidative energy level of the excited dye/complex compound is favorable (i.e., more negative) with respect to the CB level of the semiconductor, the dye molecule can transfer the electron to the CB of the semiconductor. A prerequisite for this electron transfer is a low quantum yield of the redox

Fig. 5 – The mechanism of the photocatalytic decomposition of organic pollutants (RH) over organic ligand (OL) modified TiO_2 under visible light.

process catalyzed by the dye/complex molecule (Fan and Bard, 1979). The injected electron reacts with surface adsorbed O_2 to yield $O_2^{\cdot -}$ (Eq. (3.3)), which produces $HO_2^{\cdot}$ on protonation (Eq. (3.4)) and subsequently $^{\cdot}OH$ (Eqs. (3.5) and (3.6)) leading to the degradation of the organic pollutants (Fig. 5).

Dye-sensitized photocatalysis begins with the light absorption of dye and a subsequent electron transfer from the excited dye to the conduction band of TiO_2. The electron transfer from excited dye to TiO_2 usually depends strongly on the adsorption efficiency of the dye molecule (Zhao et al., 1998). However, in the case of the dye-sensitized TiO_2 photocatalyst, the dye molecules are only absorbed onto the TiO_2 surface by physical/chemical adsorption. No steady chemical bond is formed between TiO_2 and dye molecules. So the dye molecules as sensitizers tend to partially desorb, which can decrease photocatalytic activity during the photocatalytic reaction process; and the activity can be deeply depressed by the competitive adsorption of other coexisting species in the solution. Considering that pollutants usually exist at high concentration in actual wastewaters, dye-sensitized photocatalysis may face difficulties to keep a valuable electron transfer efficiency. In addition, while the dye-sensitized TiO_2 is efficient in the utilization of visible light, all of the known sensitizers are toxic and unstable (i.e., undergo degradation) in aqueous solution, thus making them unsuitable for applications in photocatalysis (Zhao et al., 2005).

3.1.4.2. Organic coating. In the past decades, the modification of TiO_2 nanoparticles with organic chelating ligands has been a key research topic because it does not only induce dramatic changes in the electrical and optical properties of the nanoparticles, but it also results in the occurrence of other desirable properties. For example, Cozzoli et al. (2003) prepared organic-capped anatase TiO_2 nanorods at 80 °C, which can be dispersed in organic solvents to form optically clear concentrated solutions because of oleic acid surface modification. Niederberger et al. (2004) developed a nonaqueous sol–gel method to synthesize water-soluble dopamine-functionalized anatase TiO_2 nanoparticles. X.Y. Li et al. (2008) developed an in situ chemical oxidative polymerization method in hydrochloric acid solutions to synthesize TiO_2 nanoparticles modified by polyaniline. These nanoparticles exhibit significantly higher photocatalytic activity than neat TiO_2 on the degradation of phenol aqueous solution under visible light irradiation.

Jiang et al. (2007) developed a simple surface modification of TiO_2 nanocrystals through a traditional organic reaction between the surface hydroxyls on TiO_2 nanoparticle and the −NCO groups of tolylene diisocyanate (TDI). It is noteworthy that a steady chemical bond is formed in the TDI-modified TiO_2 by the chemical reaction. Due to the existence of the surface complex, the absorption edge of as-prepared TDI-modified TiO_2 nanomaterial extended well into the visible region. It was found that the TDI-modified TiO_2 material could largely absorb visible light and showed improved photocatalytic performance compared with unmodified TiO_2.

Chen et al. (2009) proposed the visible light-induced photocatalytic mechanism of TiO_2–TDI photocatalyst. In the case of TiO_2–TDI, a direct electron transfer from the organic ligand moiety to the conduction band of TiO_2 is achieved upon absorption of visible light. The conduction band electron then
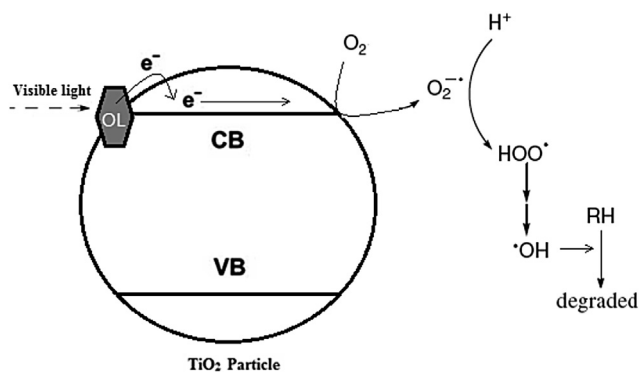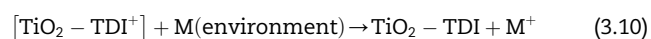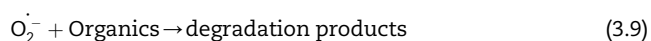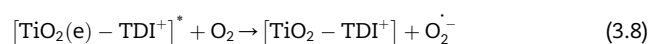
reacts with surface adsorbed oxygen to produce superoxide radical, which subsequently induces the degradation of coexisting organics in the solution. The organic ligand moiety, however, was not cleaved from the surface of TiO_2. It was subsequently recovered by capturing an electron from the environment (e.g. the reductive species generated during the photodegradation of organics), and then carried out another reaction cycle with the absorption of another visible light photon. Thus, the whole visible light-induced photocatalytic process of TiO_2–TDI can be expressed briefly as follows (Eqs. (3.7)–(3.10)) and Fig. 5.

$$TiO_2 - TDI + h\nu(vis) \rightarrow \left[TiO_2(e) - TDI^+ \right]^* \tag{3.7}$$

$$\left[TiO_2(e) - TDI^+ \right]^* + O_2 \rightarrow \left[TiO_2 - TDI^+ \right] + O_2^{\cdot -} \tag{3.8}$$

$$O_2^{\cdot -} + Organics \rightarrow degradation\ products \tag{3.9}$$

$$\left[TiO_2 - TDI^+ \right] + M(environment) \rightarrow TiO_2 - TDI + M^+ \tag{3.10}$$

3.2. Approaches to enhance adsorption of organic pollutants on TiO_2 particles

Adsorption of contaminants in the vicinity of the photocatalytic sites promotes the photodegradation of contaminants that normally do not or in low quantities adsorb on the photocatalyst surface. Thus, improving contaminant adsorption by modifying TiO_2 surface is another way to enhance its photocatalytic activity. Modification of TiO_2 surface using chelating ligands has been investigated to enhance adsorption of organic contaminants (Makarova et al., 2000). Moreover, fullerene or graphene-modified TiO_2 particles also have shown excellent adsorptive and semiconducting properties (Oh et al., 2007; Zhang et al., 2012).

3.2.1. Surface organic modification
The coordination sphere of the surface titanium atoms is incomplete and thus exhibits high affinity to oxygen-containing ligands to form chelating structures. Makarova et al. (2000) investigated the effect of three groups of compounds on adsorption of nitrobenzene (NB): a long chain carboxylic acid (lauryl sulfate) to make the surface of the TiO_2 particles hydrophobic; an amino acid (L-arginine) with a high affinity for hydrogen-bonding and electron-donating properties; and a benzene derivative (salicylic acid) that may form π−π donor−acceptor complexes. It was found that the adsorption of NB increased at all surface-modified TiO_2 specimens as compared with bare TiO_2. The best adsorption was found for arginine-modified and salicylate-modified TiO_2, while adsorption was smaller in lauryl-modified colloids. This suggests that hydrogen bonding, n−π and π−π interactions result in stronger adsorption of NB as compared with its physical adsorption due to the presence of a hydrophobic environment on the particle surface. Moreover, due to strong electron donating properties, arginine provides a stable surface layer with a controlled reductive degradation pathway for NB. Arginine also improves the coupling between NB and TiO_2, and electrons from the conduction band of TiO_2 can be transferred to NB without significant activation energy. These results indicate that surface modification of nanocrystalline TiO_2 with electron-donating chelating agents is an effective route to enhance both adsorption and decomposition of nitroaromatic compounds.

In recent years, molecularly imprinted polymers, owing to their attractive selectivity, have been introduced to improve the selectivity of the TiO_2 photocatalyst (Xu et al., 2014). By using estrone as a template molecule, Xu et al. (2014) prepared molecularly imprinted TiO_2 hybridized magnetic ferroferric oxide (Fe_3O_4) nanoparticles through a semicovalent approach by a liquid phase deposition method, for selective photocatalytic degradation and removal of target estrone with the irradiation of UV light. The obtained Fe_3O_4@SiO_2@imprinted TiO_2 displayed high adsorption capacity, fast kinetics and high selectivity. Also, excellent stability during long-time photocatalysis was exhibited. More importantly, the Fe_3O_4@imprinted TiO_2 provided potential application prospective for photocatalytic removal of trace target organic pollutants in the presence of other high-level pollutants.

3.2.2. Doping with carbon-based nanoparticles
It has been confirmed that TiO_2/carbon composites or carbon-modified TiO_2 could increase the adsorption capacity and improve photodegradation performance in the visible region (Janus et al., 2006; Shao et al., 2010). Composites of TiO_2/C have also been shown to improve the energy and power density of electrochemical cells and enhance the energy-storage capacity (Cheng et al., 2008). Therefore, TiO_2 composited with carbon of different forms, such as fullerene (Oh et al., 2007), activated carbon (W.D. Wang et al., 2007), graphene (Kamegawa et al., 2010) and carbon nanotubes (CNTs) (Woan et al., 2009) have been fabricated to obtain novel structures and properties.

Activated carbon was initially used as a support for TiO_2 in photodegradation studies (Fu et al., 2004). Loading TiO_2 on activated carbon has drawn great attention since the high adsorption capability of activated carbon can help to enrich organic substrate around the catalyst, promoting the pollutant transfer process and hence increasing the photocatalytic efficiency (Y. Li et al., 2008; Xu et al., 2008). The synergistic effect of adsorption by activated carbon and photocatalytic decomposition by TiO_2 has been observed in the degradation of several types of organic pollutants (Matos et al., 2007; Lim et al., 2011). Matos et al. (1998) determined that there is a synergistic effect when using TiO_2 mixed with activated carbon having a surface area of 775 m^2/g. The phenol degradation enhancement was attributed to the strong adsorption of phenol and its intermediate species on the activated carbon followed by subsequent mass transfer of the species to the photocatalytically active TiO_2. Wang et al. (2012) synthesized a high thermal stability C-doped SiO_2/TiO_2 coated with activated carbon nanoporous composites. The as-synthesized nanoporous composites exhibit both much higher absorption capability and better photocatalytic activity for the photooxidation of methylene blue than pure TiO_2. The higher absorption capability and better photocatalytic activity are attributed to their high surface area, well conductivity and higher visible light absorption intensity.

Carbon nanotubes (CNTs) also provide a larger specific surface area similar to activated carbon and thus enhance the

photocatalytic degradation as explained above. Beyond the surface area, CNTs may be tailored to enhance specificity toward adsorbents through the modification of their surface groups (Carp et al., 2004). When purified via acid treatment, CNTs formed alcohol, keto, and acid moieties on their surfaces. These groups can be further modified to improve adsorption of specific species, an advantage over activated carbons that are typically nonselective and have a lower pollutant-degradation rate due to the degradation of all species (benign and pollutant) present (Carp et al., 2004). Thus, CNTs are also excellent candidates to allow deeper insight into the semiconductor junction of TiO_2 with metallic or semiconducting carbons.

Among the same types of carbon supports, fullerene is very promising for synergistic reasons; its energy sensitization improves the quantum efficiency and there is an increase of charge transfer between the fullerene and TiO_2 by acidification of surface groups. Oh et al. (2007) prepared a fullerene/TiO_2 composite and investigated its photocatalytic effect. Since fullerene has absorptive and semiconducting properties, the fullerene/TiO_2 composite revealed a sound photodegradation activity. The results revealed that the excellent activity of the fullerene/TiO_2 composites for organic dye removal could be attributed to the synergistic effect of photocatalysis of the supported TiO_2 and absorptivity of the fullerene.

Graphene is recently emerging as one of the most promising materials to produce next generation photocatalysts (Morales-Torres et al., 2012), with excellent mobility of charge carriers, large specific surface area, flexible structure, high transparency and good electrical and thermal conduction (Geim and Novoselov, 2007). Nguyen-Phan et al. (2011) prepared TiO_2/graphene oxide composites for the photodegradation of methylene blue. Superior adsorption and photocatalysis performance under both UV and visible radiation were achieved in the presence of the composites rather than in pure TiO_2. The good photocatalytic performance on the TiO_2–graphene oxide composite systems irrespective of light sources could be attributed to a synergy effect including the increase in specific surface area in the presence of graphene oxide as well as the formation of both π–π conjugations between dye molecules and aromatic rings and ionic interactions between methylene blue and oxygen-containing functional groups at the edges or on the surfaces of carbon-based nanosheets. Graphene oxide plays the roles of adsorbent, electron acceptor and photosensitizer in order to accelerate photodecomposition.

The photocatalytic activity of reduced graphene oxide (RGO)–P25 composites (1 wt% GO) was also evaluated in the degradation of methylene blue (H. Zhang et al., 2010), a higher conversion of methylene blue being found with these composites in comparison with bare P25. This photocatalytic enhancement was ascribed to (1) the two-dimensional planar grapheme structure favoring dye adsorption, (2) the suppression of electron–hole recombination (due to the high electrical conductivity), (3) enhanced light absorption in longer wavelengths of the visible region, and (4) high transparency and band-gap narrowing resulting from the presence of Ti–O–C bonds. In general, the carboxylic acid functional group of GO facilitates binding of oxide particles. The high dye

adsorption is due to the formation of both π–π conjugations and the interactions between methylene blue molecules and oxygenated surface groups at the edges or on the surfaces of GO. Moreover, electron consumption occurs simultaneously, in which GO is partially reduced to RGO under UV assistance and electrons are regenerated, resulting in the partial restoration of the conjugated π–π network (Williams et al., 2008; Lightcap et al., 2010). This phenomenon leads to an efficient charge separation and to the possibility of more π–π interactions between the composite and the organic compounds.

3.3. Approaches for the stabilization of TiO_2 particles

A large surface area can be the determining factor in certain photodegradation reactions, as a large amount of adsorbed organic molecules promotes the reaction rate (Carp et al., 2004). However, one problem that needs to be addressed with nanosized photocatalysts is the difficulty in distributing single particles uniformly and reducing particle aggregation (Nakayama and Hayashi, 2007). Two approaches are possible: i) embedding them into a support structure or ii) modifying their surface using organic coating to reduce particle aggregation.

3.3.1. Stabilization by support structures

Since photocatalytic degradation mainly occurs on the surface of TiO_2, mass transfer limitation has to be minimized for effective TiO_2 application in water treatment. It is well recognized that the slurry form in which TiO_2 powder is well dispersed in suspension is more effective than the systems with fixed support (Mascolo et al., 2007). However, during the photocatalytic degradation process, the TiO_2 particles may undergo coagulation due to the instability of the nanosized particle, which will hamper the light incidence on the active centers and consequently reduce its catalytic activity (Yu and Zhao, 2001; Cho et al., 2005). Furthermore, for the slurry system, one main practical challenge to overcome is to recover the nanosized TiO_2 particles from the treated water (which is discussed in detail in the following section). How to concentrate the target pollutants around the TiO_2 particles to enhance photocatalytic efficiency also requires consideration. These challenges may be realized by mounting the nanosized TiO_2 particles on much larger particulates which should also serve as a good pollutant adsorbent to attain synergistic pollutant removal and degradation.

In the past decade, an intense effort has been devoted to loading TiO_2 on different supports (Carp et al., 2004), such as glass beads, fiber glass, glass pellets, glass sheets, silica, organo-clays, stainless steel, Al_2O_3 fiber textile, c-Al_2O_3, quartz beads, polyethene and polypropylene films, fabrics (cotton and polyester), activated carbon, and zeolites are used. Generally, the strategies focused on supported TiO_2 are developed in order to: 1) immobilize the TiO_2 photocatalyst; 2) increase the illuminated specific catalyst area; 3) increase the adsorption capacity and surface area of the photocatalyst; and 4) influence the selectivity of the photocatalytic reaction. The first demand originates from the requirement to use photocatalysts in continuous processes where the utilization of TiO_2 powder is technologically impracticable. Unfortunately, a

small particle size leads to high filtration costs of catalyst removal, hindering its industrial application. For this reason, the synthesis of photocatalysts with high activity and effective separation properties simultaneously is a priority topic.

A photocatalyst surface is active only if it is illuminated. It is difficult to illuminate all the catalyst particles in suspended systems, because the particles further away from the light sources are shielded from radiation by those near the light source. Hence, the penetration depth of light into suspensions is limited. In immobilized systems, it is possible to obtain a configuration in which all catalyst particles are illuminated, e.g., a thin layer coated on a tube surrounding a tube light (Dijkstra et al., 2001).

Several attempts have been made to obtain hybrid photocatalysts, which are expected to induce synergism because of the adsorption properties of organic molecules (Carp et al., 2004). The basic concept is based on the physisorption of reactants on inert substrates followed by their surface diffusion to the interface between the adsorptive sites and photocatalytic sites (Chen et al., 1999; Tang et al., 2014a). The first step is achieved by using supports with large surface areas for adsorption and high adsorption capacity for the target substances, while the second is achieved only if the adsorption strength is moderate enough to allow diffusion of adsorbed substrates to the loaded TiO$_2$ (Yoneyama and Torimoto, 2000; Ao and Lee, 2003). Adsorbents such as silica (Vohra and Tanaka, 2003), alumina (Tanaka et al., 2002), zeolites (Reddy et al., 2003), mesoporous molecular sieves, clays (Ooka et al., 2003) (TiO$_2$ incorporated into the interlayer space of the clays), and activated carbon (Arana et al., 2003) have been used. In the recent studies, Athanasekou et al. (2012, 2014) and Moustakas et al. (2014) developed a highly efficient hybrid photocatalytic/ultrafiltration process for water purification using visible light. The process relies on the development of partially reduced graphene oxide/TiO$_2$ composite membranes and their incorporation into an innovative water purification device that combines membrane filtration with semiconductor photocatalysis. Composites consisting of graphene oxide sheets decorated with TiO$_2$ nanoparticles were deposited and stabilized into the pores of ultrafiltration mono-channel monoliths using the dip-coating technique. These studies offer an immobilization alternative permitting scale-up ability and photoreactor based water treatment industrial applications.

However, in spite of so many efforts, it is still unclear which supports are most suitable in terms of mechanical stability and selectivity. Besides, the activity of supported TiO$_2$ is normally lower than the unrestricted catalyst. This is most likely the immobilization reduces TiO$_2$'s active surface area-to-volume ratios and decreased mass-transfer rate, in addition to the hindrance in light harvesting that is caused by the massive inactive supports (Mascolo et al., 2007).

3.3.2. Stabilization by surface modification

TiO$_2$ particles suffer from severe aggregation during photocatalytic reactions, which would reduce their active sites and light harvesting capability. As a result, the photocatalytic activity would be decreased (Liu et al., 2012). Moreover, TiO$_2$ particles have little affinity for organic matrix because of the low particle size and high surface energy. For useful applications, especially for the treatment of hydrophobic organic

pollutants, many studies have been made on surface modification of TiO$_2$ particles.

Carboxylic acids are most widely used as modifiers, with a coordination of carboxylic groups (COOH) to surface Ti atoms (Weng et al., 2003). Mallakpour and Nikkhoo (2014) modified the surface of TiO$_2$ nanoparticles via grafting with amino acid containing diacids. This surface modification prevented the aggregation and allowed a homogenous dispersion of TiO$_2$ nanoparticles. Nakayama and Hayashi (2007) prepared poly(L-lactic acid)-TiO$_2$ nanoparticle nanocomposite films by incorporating surface modified TiO$_2$ nanoparticles into polymer matrices. In the process of preparing the nanocomposite films, severe aggregation of TiO$_2$ nanoparticles could be reduced by surface modification by using carboxylic acid and long-chain alkyl amine. As a result, the TiO$_2$ nanoparticles of 3–6 nm in diameter were uniformly dispersed in polymer matrices.

Li et al. (2015) investigated the stability and the sorption of phenanthrene on nano-TiO$_2$ coated with humic acid (HA). The nano-TiO$_2$ sedimentation experiments indicated that the presence of aromatic-rich HA was more capable of stabilizing nano-TiO$_2$ particles than was the presence of aliphatic-rich HA. This result is because the deionized phenolic groups in the HAs were preferentially adsorbed on the nano-TiO$_2$ surfaces, which generated a higher charge density on the nano-TiO$_2$ surfaces and caused stronger repulsive forces among particles. Furthermore, the aromatic-rich TiO$_2$-HA complexes exhibited a greater sorption capacity than the aliphatic-rich TiO$_2$–HAs complexes and nonlinear phenanthrene sorption because of their higher affinity and for the substrate. Romanello and Fidalgo de Cortalezzi (2013) studied the aggregation rates, aggregate size and aggregate morphology of Nano TiO$_2$ under the presence of inert electrolytes, divalent cations, and these two combined with natural organic matter (NOM). NOM adsorbed to the nanoparticles and made their zeta potential more negative, hence stabilizing them by lowering the pH of maximum aggregation (Dong and Lo, 2013a; Tang et al., 2014). Divalent cations partially neutralized the adsorbed NOM, and at high concentrations aggregation was observed with Ca^{2+}, suggesting the presence of specific Ca^{2+}-NOM bridges (Dong and Lo, 2013b, 2014). Li and Sun (2011) studied the aggregation/sedimentation potentials of TiO$_2$ nanoparticles in the presence of Suwannee River fulvic acids (SRFA) at different pH values. The results showed that SRFA adsorption significantly enhanced the stability of TiO$_2$ nanoparticles at pH 4, 6 and 8, mainly due to the dramatic increase in negative surface charges. Note that the organic surface modifiers or NOM, in aquatic environments can not only increase the stability of nanoparticles but can also influence the adsorption of hydrophobic organic compounds and the number of available reactive sites on TiO$_2$ particles. Besides, the organic ligands (e.g., humic acids) can be degraded by TiO$_2$ (Uyguner and Bekbolet, 2009), so they are not necessarily stable under photocatalytic conditions. Presumably, not all the methods used to obtain stable particle suspensions will lead to photoactive TiO$_2$. Therefore, future work should be carried out to investigate the effects of surface modifiers or NOM on the stability and photocatalytic activity of TiO$_2$ particles.

3.4. Approaches for the separation of TiO₂ particles

Finely dispersed TiO_2 has large reactive surface area, but it is difficult to separate and recover these particles from liquid phase. Thus, the recovery and reusability of the TiO_2 particles is crucial and decides their further applications. The way to effectively immobilize or separate the TiO_2 particles is still a challenge in the photocatalytic system. In order to solve the problem of separation, two potential approaches have been studied, i.e., immobilized TiO_2 onto various supports and preparation of magnetic photocatalyst for magnetic separation (Carp et al., 2004; Gad-Allah et al., 2007).

3.4.1. Immobilization on support structures

Some researchers immobilized TiO_2 onto various supports, such as glass fibers, glass, quartz, stainless steel, etc. (Carp et al., 2004). This has been illustrated in detail in Section 3.3.1. As discussed in the previous part, although these studies provided a facile way to solve the particle aggregation and separation problem, the photochemical reactivity of supported TiO_2 is normally reduced due to the reduction of TiO_2's active surface area-to-volume ratios, the decreased mass-transfer rate, and the inactive support's hindrance in light harvesting. Thus, although this approach provides a solution to the solid–liquid separation problem, slurry-type reactors offer significant advantages over immobilized catalyst-type reactors because of the catalyst surface availability and superior mass-transfer properties (Matthews, 1990).

3.4.2. Magnetic separation

Another solution to the separation problem is the utilization of magnetic separation which provides a very convenient approach for separating, recovering and reusing the fine photocatalytic magnetic particles by external magnetic field (Gong et al., 2009; He et al., 2012; Tang et al., 2014b). Some authors prepared composite nanoparticles with magnetic core and photoactive shell using magnetic granules and TiO_2 (Wang and Zhou, 2010). They confirmed that magnetic TiO_2 photocatalysts present enhanced separation properties from slurry photoreactors when an external field is applied. In general, this type of composite photocatalyst comprises of a TiO_2 shell and a magnetic core, making it recoverable due to its magnetic properties such as superparamagnetism, high field magnetic irreversibility and high saturation magnetization (Wang and Zhou, 2010; He et al., 2012).

A number of materials with different elemental compositions have been used as the magnetic core, such as Fe_3O_4, γ-Fe_2O_3, $NiFe_2O_4$, $CoFe_2O_4$, FeCo, and Co_3O_4. Among these, Fe_3O_4 has drawn a lot of attention due to its remarkable magnetic properties, low toxicity, and biocompatibility (Deng et al., 2008; Zhang et al., 2011; Zhang and Zhu, 2012). However, a direct deposition of TiO_2 onto the surface of magnetic oxide particles leads to high levels of photodissolution (i.e., dissolution under influence of illumination) of the magnetic core. It has been proven that the addition of a silica layer between the magnetic core and the TiO_2 shell promotes the photocatalytic activity of the catalyst by abating the adverse impact of the magnetic core and stabilizing the anatase form of TiO_2 (Martyanov and Klabunde, 2004). The presence of a silica membrane provides magnetic nanoparticles with a chemically inert surface, helping to inhibit the oxidation of the Fe_3O_4 core by the holes photogenerated in the outer layer TiO_2 (Fu et al., 2006; Wang et al., 2009). However, the photocatalytic activity of magnetic TiO_2 is also influenced by the magnetic core size, content of the silica layer and calcination temperature (Gad-Allah et al., 2007).

Recently, research work is devoted to fabricating multi-component photocatalysts with enhanced visible light photoactivity and ability to be recycled (Li et al., 2011; Guo et al., 2011; Wu et al., 2012). Magnetic visible photocatalysts were investigated for overcoming the two fundamental drawbacks, i.e. photocatalyst recovery and visible light utilization, hindering catalyst application and development in the fields of environmental pollutants and energy sources (Li et al., 2011; Wu et al., 2012). Multi-component photocatalysts with magnetic and photoactive properties provide a way of achieving this. Guo et al. (2011) reported that the Ag halides such as AgBr and AgI (which are photoactive to visible light) immobilized on $SiO_2@Fe_3O_4$ magnetic supports exhibited faster degradation rates for 4-chlorophenol than N–TiO_2. However, the Ag halides are easily photo-reduced and quickly lose their stability. Liu et al. (2013) prepared the magnetic AgBr–TiO_2/$SiO_2@Fe_3O_4$ photocatalyst by solvothermal and sol–gel methods, in which photoactive AgBr–TiO_2 was seeded on the $SiO_2@Fe_3O_4$ shell–core magnetic support. The catalyst exhibited excellent photocatalytic degradation of methylene blue under visible light, and was easily separated and reused in five successive runs, using an external magnetic field. Tang et al. (2013) designed a new photocatalyst, magnetic TiO_2–graphene, which integrates the functions of: (1) TiO_2 photocatalysis, (2) excellent electron-capture ability and high adsorptivity of graphene, (3) magnetic separation, and (4) high stability through suppressing photodissolution of the magnetite by SiO_2 (Wang et al., 2009). Taking advantages of graphene and TiO_2, the catalyst exhibited strong light absorption in the visible region and high adsorption capacity to organic pollutants, resulting in almost 100% photocatalytic removal efficiency of typical herbicide 2,4-dichlorophenoxyacetic acid (2,4-D) from water under simulated solar light irradiation, far higher than 33% on commercial P25. Furthermore, the catalyst can be rapidly recovered with highly stable photocatalytic performance. After 8 successive cycles, the removal efficiency of 2,4-D maintained 97.7%, and particularly, 99.1% 2,4-D removal efficiency came back at the ninth recycle when the catalyst was re-treated by ultrasonication.

3.5. Future challenges in TiO₂-based photocatalytic processes

Despite the increased use and development in the past decades, TiO_2-based photocatalytic technology still suffers from some technical barriers that impede its commercialization. Further research and development in this area are necessary to overcome or mitigate these shortcomings and to expand the use of the TiO_2-based particles for photocatalytic degradation. Based on this review, the key areas for future research are proposed as follows:

1) Although many investigations have been carried out concerning the modification of the TiO_2 surface to improve its photocatalytic activity, little work has been reported on the enhancement of photocatalytic activity of magnetic TiO_2 particles under visible light through doping or/and surface modification. Besides, the physicochemical stability and sustainability of non-metal doped or surface-modified TiO_2 particles for repetitive use have not been studied. It is necessary to design a multifunctional photocatalyst that integrates the characteristics of excellent visible-light photocatalytic activity, high adsorption capacity, high stability, and magnetic separability.

2) A complete photodegradation of some POPs by the photocatalysts is still difficult to achieve. More studies should be carried out with the aim of enhancing the reactivity of photocatalysts. Additionally, it is necessary to explore the possibility of combined use of TiO_2-based technologies with other technologies (e.g., biological means and electrodynamics) to expand the scope of application. Besides, the final or the intermediate products of photocatalytic degradation may not be innocuous substances. The degradation products can be more dangerous than the parent compound. Harmful by-products may cause decrease in reaction rate and secondary pollution. There has been scanty literature on the toxicity of the photocatalyst or the overall photocatalytic process, especially for the modified photocatalysts. Fundamental characterization and quantification of the reactivity, toxicity and fate of different modified photocatalysts are needed.

3) TiO_2 photocatalyzed reactions are non-selective oxidations. Since they are governed by a free radical mechanism, the degradation rate of a large variety of molecules is found to be approximately the same. On the one hand, this lack of sensitivity may be advantageous, but a poor selectivity also implies that the catalyst does not differentiate between highly hazardous contaminants and contaminants of low toxicity. The low toxicity contaminants can be easily degraded by biological means, while many of the highly hazardous materials are non-biodegradable. Therefore, it is necessary to develop a photocatalyst system that can selectively degrade pollutants utilizing visible and/or solar light irradiation, acting as a complement to biological techniques.

4) The previous work mainly focused on batch scale of photocatalytic degradation and magnetic separation for pollutant removal and particle recovery, but lack of application in a larger scale. Thus, there is a need for the design of a prototype for the convenience of both photocatalytic degradation of organic pollutants and particles recovery so that it can be applied in real practice.

4. Conclusions

Photodegradation process of POPs by TiO_2-based particles has attracted increasing attention during the past decades. However, its application is limited due to some main practical challenges: i) the inefficient exploitation of visible light, ii) low adsorption capacity for hydrophobic contaminants, iii) uniform dispersion in aqueous suspension and iv) post-recovery of the TiO_2 particles after water treatment. This review summarized the recently developed countermeasures for improving the performance of TiO_2-based photocatalytic degradation of organic pollutants with respect to the above limitations. Several approaches for enhancement of visible-light photocatalytic activity of TiO_2 have been developed: metal-doped TiO_2, non-metal doped-TiO_2, co-doped TiO_2 (i.e., the simultaneous doping of two kinds of elements into TiO_2), sensitizing of TiO_2 with dyes and TiO_2 doped with upconversion luminescence agent. To enhance adsorption of organic pollutants onto TiO_2 particles, two approaches have been proposed: surface modification of TiO_2 with organic ligands and doping with carbon-based nanoparticles. Two approaches are possible in distributing TiO_2 particles uniformly in suspension: embedding TiO_2 particles into a support structure or modifying their surface using organic coating to reduce particle aggregation. The separation of TiO_2 particles from aqueous phase can be achieved via immobilization on support structures or magnetic separation. However, each countermeasure still suffers from some technical barriers that impede its commercialization. Further research and development in this area are required to overcome these shortcomings and to expand the application of the TiO_2-based particles for photocatalytic degradation.

REFERENCES

Ambrus, Z., Balasz, N., Alapi, T., Wittmann, G., Sipos, P., Dombi, A., Mogyorosi, K., 2008. Synthesis, structure and photocatalytic properties of Fe(III)-doped TiO₂ prepared from TiCl₃. Appl. Catal. B 81, 27–37.

Anpo, M., 2000. Use of visible light. Second-generation titanium dioxide photocatalysts prepared by the application of an advanced metal ion-implantation method. Pure Appl. Chem. 72, 1787–1792.

Ao, C.H., Lee, S.C., 2003. Enhancement effect of TiO₂ immobilized on activated carbon filter for the photodegradation of pollutants at typical indoor air level. Appl. Catal. B: Environ. 44, 191–205.

Arana, J., Dona, R.J.M., Rendon, E.T., Cabo, C.G., Gonzalez, D.O., Herrera, M.J.A., Perez, P.J., Colon, G., Navio, J.A., 2003. TiO₂ activation by using activated carbon as a support. Part I. Surface characterisation and decantability study. Appl. Catal. B: Environ. 44, 161–172.

Arabatzis, I.M., Stergiopoulos, T., Bernard, M.C., Labou, D., Neophytides, S.G., Falaras, P., 2003. Silver-modified titanium dioxide thin films for efficient photodegradation of methyl orange. Appl. Catal. B: Environ. 42, 187–201.

Asahi, R., Morikawa, T., Ohwaki, T., Aoki, K., Taga, Y., 2001. Visible-light photocatalysis in nitrogen-doped titanium dioxides. Science 293, 269–271.

Athanasekou, C.P., Romanos, G.E., Katsaros, F.K., Kordatos, K., Likodimos, V., Falaras, P., 2012. Very efficient composite

titania membranes in hybrid ultrafiltration/photocatalysis water treatment processes. J. Membr. Sci. 392–393, 192–203.

Athanasekou, C.P., Morales-Torres, S., Likodimos, V., Romanos, G.E., Pastrana-Martinez, L.M., Falaras, P., Dionysiou, D.D., Faria, J.L., Figueiredo, J.L., Silva, A.M.T., 2014. Prototype composite membranes of partially reduced graphene oxide/TiO$_2$ for photocatalytic ultrafiltration water treatment under visible light. Appl. Catal. B: Environ. 158–159, 361–372.

Bae, E., Choi, W., Park, J., Shin, H.S., Kim, S.B., Lee, J.S., 2004. Effects of surface anchoring groups (carboxylate vs. phosphonate) in ruthenium-complex-sensitized TiO$_2$ on visible light reactivity in aqueous suspensions. J. Phys. Chem. B 108, 14093–14101.

Bannat, I., Wessels, K., Oekermann, T., Rathousky, J., Bahnemann, D., Wark, M., 2009. Improving the photocatalytic performance of mesoporous titania films by modification with gold nanostructures. Chem. Mater. 21, 1645–1653.

Banerjee, S., Pillai, S.C., Falaras, P., O'Shea, K.E., Byrne, J.A., Dionysiou, D.D., 2014. New insights into the mechanism of visible light photocatalysis. J. Phys. Chem. Lett. 5, 2543–2554.

Bhattacharyya, A., Kawi, S., Ray, M.B., 2004. Photocatalytic degradation of Orange II by TiO$_2$ catalysts supported on adsorbents. Catal. Today 98, 431–439.

Bradley, B.R., Daigger, G.T., Rubin, R., Tchobanoglous, G., 2002. Evaluation of onsite wastewater treatment technologies using sustainable development criteria. Clean Technol. Environ. Policy 4, 87–99.

Carp, O., Huisman, C.L., Reller, A., 2004. Photoinduced reactivity of titanium dioxide. Prog. Solid State Chem. 32, 33–177.

Chatterjee, D., Mahata, A., 2001. Demineralization of organic pollutants on the dye modified TiO$_2$ semiconductor particulate system using visible light. Appl. Catal. B: Environ. 33, 119–125.

Chen, D.M., Jiang, Z.Y., Geng, J.Q., Wang, Q., Yang, D., 2007. Carbon and nitrogen co-doped TiO$_2$ with enhanced visible-light photocatalytic activity. Ind. Eng. Chem. Res. 46, 2741–2746.

Chen, F., Deng, Z., Li, X.Z., Zhang, J., Zhao, J., 2005. Visible light detoxification by 2,9,16,23-tetracarboxyl phthalocyanine copper modified amorphous titania. Chem. Phys. Lett. 415, 85–88.

Chen, F., Zou, W.W., Qu, W.W., Zhang, J.L., 2009. Photocatalytic performance of a visible light TiO$_2$ photocatalyst prepared by a surface chemical modification process. Catal. Commun. 10, 1510–1513.

Chen, H., Masumoto, A., Nishimija, N., Tsutsumi, K., 1999. Preparation and characterization of TiO$_2$ incorporated Y-zeolite. Colloids Surfaces A: Physicochem. Eng. Aspects 157, 295–305.

Cheng, H.S., Chen, L., Cooper, A.C., Sha, X.W., Pez, G.P., 2008. Hydrogen spillover in the context of hydrogen storage using solid-state materials. Energy Environ. Sci. 1, 338–354.

Cho, H.I., Park, H.J., Kim, G.Y., 2005. Oxidative degradation and toxicity reduction of trichloroethylene (TCE) in water using TiO$_2$/solar light: comparative study of TiO$_2$ slurry and immobilized systems. J. Environ. Sci. Health, Part A 40, 1033–1044.

Chong, M.N., Jin, B., Chow, C.W.K., Saint, C., 2010. Recent developments in photocatalytic water treatment technology: a review. Water Res. 44, 2997–3027.

Cong, Y., Zhang, J.L., Chen, F., Anpo, M., 2007. Preparation, photocatalytic activity, and mechanism of nano-TiO$_2$ co-doped with nitrogen and iron (III). J. Phys. Chem. C 111, 10618–10623.

Cozzoli, P.D., Kornowski, A., Weller, H., 2003. Low-temperature synthesis of soluble and processable organic-capped anatase TiO$_2$ nanorods. J. Am. Chem. Soc. 125, 14539–14548.

Cui, J., He, T., Zhang, X., 2013. Synthesis of Fe$_3$O$_4$@SiO$_2$@Ption-TiO$_2$ hybrid composites with high efficient UV–visible light photoactivity. Catal. Commun. 40, 66–70.

Deng, Y., Qi, D., Deng, C., Zhang, X., Zhao, D., 2008. Superparamagnetic high-magnetization microspheres with an Fe$_3$O$_4$@SiO$_2$ core and perpendicularly aligned mesoporous SiO$_2$ shell for removal of microcystins. J. Am. Chem. Soc. 130, 28–29.

Dijkstra, M.F.J., Michorius, A., Buwalda, H., Panneman, H.J., Winkelman, J.G.M., Beenackers, A.A.C.M., 2001. Comparison of the efficiency of immobilized and suspended systems in photocatalytic degradation. Catal. Today 66, 487–494.

Dong, F., Guo, S., Wang, H.Q., Li, X.F., Wu, Z.B., 2011. Enhancement of the visible light photocatalytic activity of C-doped TiO$_2$ nanomaterials prepared by a green synthetic approach. J. Phys. Chem. C 115, 13285–13292.

Dong, F., Wang, H.Q., Wu, Z.B., 2009. One-step "green" synthetic approach for mesoporous C-doped titanium dioxide with efficient visible light photocatalytic activity. J. Phys. Chem. C 113, 16717–16723.

Dong, F., Wang, H.Q., Wu, Z.B., Qiu, J.F., 2010. Marked enhancement of photocatalytic activity and photochemical stability of N-doped TiO$_2$ nanocrystals by Fe^{3+}/Fe^{2+} surface modification. J. Colloid Interface Sci. 343, 200–208.

Dong, H.R., Guan, X.H., Wang, D.S., Li, C.Y., Yang, X., Dou, X.M., 2011. A novel application of H$_2$O$_2$–Fe(II) process for arsenate removal from synthetic acid mine drainage (AMD) water. Chemosphere 85 (7), 1115–1121.

Dong, H.R., Lo, I.M.C., 2013a. Influence of humic acid on the colloidal stability of surface-modified nano zero-valent iron. Water Res. 47 (1), 419–427.

Dong, H.R., Lo, I.M.C., 2013b. Influence of calcium ions on the colloidal stability of surface-modified nano zero-valent iron in the absence or presence of humic acid. Water Res. 47 (7), 2489–2496.

Dong, H.R., Lo, I.M.C., 2014. Transport of surface-modified nano zero-valent iron (SM-NZVI) in saturated porous media: effects of surface stabilizer type, subsurface geochemistry, and contaminant loading. Water Air Soil Pollut. 225, 2107–2118.

El-Sheikh, S.M., Zhang, G.S., El-Hosainy, H.M., Ismail, A.A., O'Shea, K.E., Falaras, P., Kontos, A.G., Dionysiou, D.D., 2014. High performance sulfur, nitrogen and carbon doped mesoporous anatase–brookite TiO$_2$ photocatalyst for the removal of microcystin-LR under visible light irradiation. J. Hazard. Mater. 280, 723–733.

Fan, F.R., Bard, A.J., 1979. Spectral sensitization of the heterogeneous photocatalytic oxidation of hydroquinone in aqueous solution at phthalocyanine-coated TiO$_2$ powders. J. Am. Chem. Soc. 101, 6139–6140.

Foo, K.Y., Hameed, B.H., 2010. Decontamination of textile wastewater via TiO$_2$/activated carbon composite materials. Adv. Colloid Interface Sci. 159, 130–143.

Fu, P.F., Luan, Y., Dai, X.G., 2004. Preparation of activated carbon fibers supported TiO$_2$ photocatalyst and evaluation of its photocatalytic reactivity. J. Mol. Catal. A: Chem. 221, 81–88.

Fu, W.Y., Yang, H.B., Bala, H., Liu, S.K., Li, M.H., Zou, G.T., 2006. Preparation and characteristics of core–shell structure cobalt/silica nanoparticles. Mater. Chem. Phys. 100, 246–250.

Fuerte, M.D.H.A., Maira, A.J., Martinez-Arias, A., Fernadez-Garcia, M., Conesa, J.C., Soria, J., 2001. Visible light-activated nanosized doped-TiO$_2$ photocatalysts. Chem. Commun. 24, 2718–2719.

Fujishima, A., Rao, T.N., Tryk, D., 2000. Titanium dioxide photocatalysis. J. Photochem. Photobiol. C: Photochem. Rev. 1, 1–21.

Furube, A., Asahi, T., Masuhara, H., Yamashita, H., Anpo, M., 2001. Direct observation of a picosecond charge separation process in photoexcited platinum-loaded TiO_2 particles by femtosecond diffuse reflectance spectroscopy. Chem. Phys. Lett. 336, 424—430.

Gad-Allah, T.A., Kato, S., Satokawa, S., Kojima, T., 2007. Role of core diameter and silica content in photocatalytic activity of $TiO_2/SiO_2/Fe_3O_4$ composite. Solid State Sci. 9, 737—743.

Gao, B., Yap, P.S., Lim, T.M., Lim, T.T., 2011. Adsorption-photocatalytic degradation of Acid Red 88 by supported TiO_2: effect of activated carbon support and aqueous anions. Chem. Eng. J. 171, 1098—1107.

Gaya, U.I., Abdullah, A.H., 2008. Heterogeneous photocatalytic degradation of organic contaminants over titanium dioxide: a review of fundamentals, progress and problems. J. Photochem. Photobiol. C 9, 1—12.

Geim, A.K., Novoselov, K.S., 2007. The rise of graphene. Nat. Mater. 6, 183—191.

Gombac, V., De Rogatis, L., Gasparotto, A., Vicario, G., Montini, T., Barreca, D., Balducci, G., Fornasiero, P., Tondello, E., Graziani, M., 2007. TiO_2 nanopowders doped with boron and nitrogen for photocatalytic applications. Chem. Phys. 339, 111—123.

Gong, J.L., Wang, B., Zeng, G.M., Yang, C.P., Niu, C.G., Niu, Q.Y., Zhou, W.J., Liang, Y., 2009. Removal of cationic dyes from aqueous solution using magnetic multi-wall carbon nanotube nanocomposite as adsorbent. J. Hazard. Mater. 164 (2—3), 1517—1522.

Guo, J.F., Ma, B.W., Yin, A.Y., Fan, K.N., Dai, W.L., 2011. Photodegradation of rhodamine B and 4-chlorophenol using plasmonic photocatalyst of $Ag—AgI/Fe_3O_4@SiO_2$ magnetic nanoparticle under visible light irradiation. Appl. Catal. B: Environ. 101, 580—586.

Hahn, R., Schmidt-Stein, F., Salonen, J., Thiemann, S., Song, Y., Kunze, J., Lehto, V., Schmuki, P., 2009. Semimetallic TiO_2 nanotubes. Angew. Chem. Int. Ed. 48, 7236—7239.

Han, C., Likodimos, V., Khan, J.A., Nadagouda, M.N., Andersen, J., Falaras, P., Rosales-Lombardi, P., Dionysiou, D.D., 2014. UV—visible light-activated Ag-decorated, monodisperse TiO_2 aggregates for treatment of the pharmaceutical oxytetracycline. Environ. Sci. Pollut. Res. 21, 11781—11793.

He, Z.Q., Hong, T.M., Chen, J.M., Song, S., 2012. A magnetic TiO_2 photocatalyst doped with iodine for organic pollutant degradation. Sep. Purif. Technol. 96, 50—57.

Herrmann, J., Duchamp, C., Karkmaz, M., Hoai, B., Lachheb, H., Puzenat, E.G., 2007. Environmental green chemistry as defined by photocatalysis. J. Hazard. Mater. 146, 624—629.

Herrmann, J.M., 1999. Heterogeneous photocatalysis: fundamentals and applications to the removal of various types of aqueous pollutants. Catal. Today 53, 115—129.

Hu, C., Lan, Y., Qu, J., Hu, X., Wang, A., 2006. $Ag/AgBr/TiO_2$ visible light photocatalyst for destruction of azodyes and bacteria. J. Phys. Chem. B 110, 4066—4072.

Huo, Y., Jin, Y., Zhu, J., Li, H., 2009. Highly active $TiO_{2-x-y}N_xF_y$ visible photocatalyst prepared under supercritical conditions in $NH_4F/EtOH$ fluid. Appl. Catal. B: Environ. 89, 543—550.

Ihara, T., Miyoshi, M., Iriyama, Y., Matsumoto, O., Sugihara, S., 2003. Visible-light-active titanium oxide photocatalyst realized by an oxygen-deficient structure and by nitrogen doping. Appl. Catal. B: Environ. 42, 403—409.

Iliev, V., Tomova, D., Bilyarska, L., Eliyas, A., Petrov, L., 2006. Photocatalytic properties of TiO_2 modified with platinum and silver nanoparticles in the degradation of oxalic acid in aqueous solution. Appl. Catal. B: Environ. 63, 266—271.

Irie, H., Watanabe, Y., Hashimoto, K., 2003. Nitrogen-concentration dependence on photocatalytic activity of $TiO_{2-x}N_x$ powders. J. Phys. Chem. B 107, 5483—5486.

Janus, M., Inagaki, M., Tryba, B., Toyoda, M., Morawski, A.W., 2006. Carbon-modified TiO_2 photocatalyst by ethanol carbonisation. Appl. Catal. B: Environ. 63, 272—276.

Jiang, D., Xu, Y., Hou, B., Wu, D., Sun, Y.H., 2007. Synthesis of visible light-activated TiO_2 photocatalyst via surface organic modification. J. Solid State Chem. 180, 1787—1791.

Kamat, P.V., Fox, M.A., 1983. Photo-sensitization of TiO_2 colloids by Erythrosin-B in acetonitrile. Chem. Phys. Lett. 102, 379—384.

Kamegawa, T., Yamahana, D., Yamashita, H., 2010. Graphene coating of TiO_2 nanoparticles loaded on mesoporous silica for enhancement of photocatalytic activity. J. Phys. Chem. C 114, 15049—15053.

Kang, I.C., Zhang, Q., Yin, S., Sato, T., Saito, F., 2008. Improvement in photocatalytic activity of TiO_2 under visible irradiation through addition of $N—TiO_2$. Environ. Sci. Technol. 42, 3622—3626.

Kiriakidou, F., Kondarides, D., Verykios, X.E., 1999. The effect of operational parameters and TiO_2-doping on the photocatalytic degradation of azo-dyes. Catal. Today 54, 119—130.

Kitano, M., Funatsu, K., Matsuoka, M., Ueshima, M., Anpo, M., 2006. Preparation of nitrogen-substituted TiO_2 thin film photocatalysts by the radio frequency magnetron sputtering deposition method and their photocatalytic reactivity under visible light irradiation. J. Phys. Chem. B 110, 25266—25272.

Kowalska, E., Remita, H., Colbeau-Justin, C., Hupka, J., Belloni, J., 2008. Modification of titanium dioxide with platinum ions and clusters: application in photocatalysis. J. Phys. Chem. C 112, 1124—1131.

Lapena, L., Cerezo, M., Garcia-Augustin, P., 1995. Possible reuse of treated municipal wastewater for *Citrus* spp. plant irrigation. Bull. Environ. Contam. Toxicol. 55, 697—703.

Legrini, O., Oliveros, E., Braun, A.M., 1993. Photochemical process for water treatment. Chem. Rev. 93, 671—698.

Lettmann, C., Hildenbrand, K., Kisch, H., Macyk, W.F., 2001. Visible light photodegradation of 4-chlorophenol with a coke-containing titanium dioxide photocatalyst. Appl. Catal. B: Environ. 32, 215—227.

Li, D., Haneda, H., Hishita, S., Ohashi, N., 2005a. Visible-light-driven N—F-codoped TiO_2 photocatalyst. 2. Optical characterization, photocatalysis, and potential application to air purification. Chem. Mater. 17, 2596—2602.

Li, D., Haneda, H., Hishita, S., Ohashi, N., 2005b. Visible-light-driven N—F-codoped TiO_2 photocatalysts synthesis by spray pyrolysis and surface characterization. Chem. Mater. 17, 2588—2595.

Li, F.B., Li, X.Z., Hou, M.F., 2004. Photocatalytic degradation of 2-mercaptobenzothiazole in aqueous $La^{3+}—TiO_2$ suspension for odor control. Appl. Catal. B: Environ. 48, 185—194.

Li, Q., Li, Y.W., Wu, P.G., Xie, R.C., Shang, J.K., 2008. Palladium oxide nanoparticles on nitrogen-doped titanium oxide: accelerated photocatalytic disinfection and post-illumination catalytic "memory". Adv. Mater. 20, 3717.

Li, S., Sun, W., 2011. A comparative study on aggregation/sedimentation of TiO_2 nanoparticles in mono- and binary systems of fulvic acids and Fe(III). J. Hazard. Mater. 197, 70—79.

Li, X.Y., Wang, D.S., Cheng, G.X., Luo, Q.Z., An, J., Wang, Y.H., 2008. Preparation of polyanilinemodified TiO_2 nanoparticles and their photocatalytic activity under visible light illumination. Appl. Catal. B: Environ. 81, 267—273.

Li, Y., Dong, X.F., Li, J.P., 2011. Synthesis and characterization of super para-magnetic composite photocatalyst—titania/silica/nickel ferrite. Particuology 9, 475—479.

Li, Y., Ma, M., Sun, S., Wang, X., Yan, W., Ouyang, Y., 2008. Preparation, photocatalytic activity of TiO_2—carbon surface composites by supercritical pretreatment and sol—gel process. Catal. Commun. 9, 1583—1587.

Li, Y.J., Yang, C., Guo, X.T., Dang, Z., Li, X.Q., Zhang, Q., 2015. Effects of humic acids on the aggregation and sorption of nano-TiO$_2$. Chemosphere 119, 171–176.

Lightcap, I.V., Kosel, T.H., Kamat, P.V., 2010. Anchoring semiconductor and metal nanoparticles on a two dimensional catalyst mat. storing and shuttling electrons with reduced graphene oxide. Nano Lett. 10, 577–583.

Lim, T.T., Yap, P.S., Srinivasan, M., Fane, A.G., 2011. TiO$_2$/AC composites for synergistic adsorption–photocatalysis processes: present challenges and further developments for water treatment and reclamation. Crit. Rev. Environ. Sci. Technol. 41, 1173–1230.

Lin, L., Zheng, R.Y., Xie, J.L., Zhu, Y.X., Xie, Y.C., 2007. Synthesis and characterization of phosphor and nitrogen co-doped titania. Appl. Catal. B: Environ. 76, 196–202.

Lindgren, T., Mwabora, J.M., Avendano, E., Jonsson, J., Hoel, A., Granqvist, C.-G., Lindquist, S.-E., 2003. Photoelectrochemical and optical properties of nitrogen doped titanium dioxide films prepared by reactive DC magnetron sputtering. J. Phys. Chem. B 107, 5709–5716.

Liu, J.J., Zuo, S.L., Yu, L.M., Yu, Y.C., Li, B.S., Chen, P.W., 2013. Visible light photodegradation of methylene blue by AgBr–TiO$_2$/SiO$_2$@Fe$_3$O$_4$ magnetic photocatalysts. Particuology 11, 728–731.

Liu, K., Zhu, L.J., Jiang, T.F., Sun, Y.G., Li, H.B., Wang, D.J., 2012. Mesoporous TiO$_2$ micro-nanometer composite structure: synthesis, optoelectric properties, and photocatalytic selectivity. Int. J. Photoenergy 2012, 1–9.

Livraghi, S., Elghniji, K., Czoska, A.M., Paganini, M.C., Giamello, E., Ksibi, M., 2009. Nitrogen-doped and nitrogen–fluorine-codoped titanium dioxide. Nature and concentration of the photoactive species and their role in determining the photocatalytic activity under visible light. J. Photochem. Photobiol. A 205, 93–97.

Likodimos, V., Han, C., Pelaez, M., Kontos, A.G., Liu, G.L., Zhu, D.W., Liao, S.J., de la Cruz, A.A., O'Shea, K., Dunlop, P.S.M., Byrne, J.A., Dionysiou, D.D., Falaras, P., 2013. Anion-doped TiO$_2$ nanocatalysts for water purification under visible light. Ind. Eng. Chem. Res. 52, 13957–13964.

Makarova, O.V., Rajh, T., Thurnauer, M.C., 2000. Surface modification of TiO$_2$ nanoparticles for photochemical reduction of nitrobenzene. Environ. Sci. Technol. 34, 4797–4803.

Mallakpour, S., Nikkhoo, E., 2014. Surface modification of nano-TiO$_2$ with trimellitylimido-amino acid-based diacids for preventing aggregation of nanoparticles. Adv. Powder Technol. 25, 348–353.

Martyanov, N., Klabunde, J., 2004. Comparative study of TiO$_2$ particles in powder form and as a thin nanostructured film on quartz. J. Catal. 225, 408–416.

Mascolo, G., Comparelli, R., Curri, M.L., Lovecchio, G., Lopez, A., Agostiano, A., 2007. Photocatalytic degradation of methyl red by TiO$_2$: comparison of the efficiency of immobilized nanoparticles versus conventional suspended catalyst. J. Hazard. Mater. 142, 130–137.

Matos, J., Laine, J., Herrmann, J.M., 1998. Synergy effect in the photocatalytic degradation of phenol on a suspended mixture of titania and activated carbon. Appl. Catal. B: Environ. 18, 281–291.

Matos, J., Laine, J., Herrmann, J.M., Uzcategui, D., Brito, J.L., 2007. Influence of activated carbon upon titania on aqueous photocatalytic consecutive runs of phenol photodegradation. Appl. Catal. B: Environ. 70, 461–469.

Matthews, R., 1990. Purification of water with near-UV illuminated suspensions of titanium dioxide. Water Res. 24, 653–660.

Miranda-Garcia, N., Suarez, S., Sanchez, B., Coronado, J.M., Malato, S., Maldonado, M.I., 2011. Photocatalytic degradation of emerging contaminants in municipal wastewater treatment plant effluents using immobilized TiO$_2$ in a solar pilot plant. Appl. Catal. B: Environ. 103, 294–301.

Minero, C., Vione, D., 2006. A quantitative evaluation of the photocatalytic performance of TiO$_2$ slurries. Appl. Catal. B: Environ. 67, 257–269.

Morales-Torres, S., Pastrana-Martínez, L.M., Figueiredo, J.L., Faria, J.L., Silva, A.M.T., 2012. Design of graphene-based TiO$_2$ photocatalysts – a review. Environ. Sci. Pollut. Res. 19, 3676–3687.

Moustakas, N.G., Kontos, A.G., Likodimos, V., Katsaros, F., Boukos, N., Tsoutsou, D., Dimoulas, A., Romanos, G.E., Dionysiou, D.D., Falaras, P., 2013. Inorganic–organic core–shell titania nanoparticles for efficient visible light activated photocatalysis. Appl. Catal. B: Environ. 130–131, 14–24.

Moustakas, N.G., Katsaros, F.K., Kontos, A.G., Romanos, G.Em., Dionysiou, D.D., Falaras, P., 2014. Visible light active TiO$_2$ photocatalytic filtration membranes with improved permeability and low energy consumption. Catal. Today 224, 56–69.

Nakayama, N., Hayashi, T., 2007. Preparation and characterization of poly(L-lactic acid)/TiO$_2$ nanoparticle nanocomposite films with high transparency and efficient photodegradability. Polym. Degrad. Stab. 92, 1255–1264.

Nguyen-Phan, T.D., Pham, V.H., Shin, E.W., Pham, H.D., Kim, S., Chung, J.S., Kim, E.J., Hur, S.H., 2011. The role of graphene oxide content on the adsorption-enhanced photocatalysis of titanium dioxide/graphene oxide composites. Chem. Eng. J. 170, 226–232.

Niederberger, M., Garnweitner, G., Krumeich, F., Nesper, R., Colfen, H., Antonietti, M., 2004. Tailoring the surface and solubility properties of nanocrystalline titania by a nonaqueous in situ functionalization process. Chem. Mater. 16, 1202–1208.

Nosaka, Y., Matsushita, M., Nishino, J., Nosaka, A.Y., 2005. Nitrogen-doped titanium dioxide photocatalysts for visible response prepared by using organic compounds. Sci. Technol. Adv. Mater. 6, 143–148.

O'Regan, B., Graetzel, M., 1991. A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO$_2$ films. Nature 353, 737–740.

Oh, W.C., Jung, A.R., Ko, W.B., 2007. Preparation of fullerene/TiO$_2$ composite and its photocatalytic effect. J. Ind. Eng. Chem. 13, 1208–1214.

Ohno, T., Mitsui, T., Matsumura, M., 2003. Photocatalytic activity of S doped TiO$_2$ photocatalyst under visible light. Chem. Lett. 32, 364–365.

Oller, I., Malato, S., Sánchez-Pérez, J.A., 2011. Combination of advanced oxidation processes and biological treatments for wastewater decontamination—a review. Sci. Total Environ. 409, 4141–4166.

Ooka, C., Yoshida, H., Horio, M., Suzuki, K., Hattori, T., 2003. Adsorptive and photocatalytic performance of TiO$_2$ pillared montmorillonite in degradation of endocrine disruptors having different hydrophobicity. Appl. Catal. B: Environ. 41, 313–321.

Ozaki, H., Iwamoto, S., Inoue, M., 2007. Marked promotive effect of iron on visible-light-induced photo-catalytic activities of nitrogen- and silicon-codoped titanias. J. Phys. Chem. C 111, 17061–17066.

Padmanabhan, P.V.A., Sreekumar, K.P., Thiyagarajan, T.K., Satpute, R.U., Bhanumurthy, K., Sengupta, P., Dey, G.K., Warrier, K.G.K., 2006. Nano-crystalline titanium dioxide formed by reactive plasma synthesis. Vacuum 80, 11–12.

Palmisano, L., Schiavello, M., Sclafani, A., Martin, C., Martin, I., Rives, V., 1994. Surface properties of iron-titania

photocatalysts employed for 4-nitrophenol photodegradation in aqueous TiO_2 dispersion. Catal. Lett. 24, 303–315.

Patrick, B., Kamat, P.V., 1992. Photoelectrochemistry in semiconductor particulate systems. J. Phys. Chem. 96, 1423–1428.

Pelaez, M., Nolan, N.T., Pillai, S.C., Seery, M.K., Falaras, P., Kontos, A.G., Dunlop, P.S.M., Hamilton, J.W.J., Byrne, J.A., O'Shea, K., Entezari, M.H., Dionysiou, D.D., 2012. A review on the visible light active titanium dioxide photocatalysts for environmental applications. Appl. Catal. B: Environ. 125, 331–349.

Ranjit, K.T., Willner, I., Bossmann, S.H., Braun, A.M., 2001a. Lanthanide oxide-doped titanium dioxide photocatalysts: novel photocatalysts for the enhanced degradation of p-chlorophenoxyacetic acid. Environ. Sci. Technol. 35, 1544–1549.

Ranjit, K.T., Wilner, I., Bossmann, S.H., Braun, A.M., 2001b. Lanthanide oxide doped titanium dioxide photocatalysts: effective photocatalysts for the enhanced degradation of salicylic acid and t-cinnamic acid. J. Catal. 204, 305–313.

Reddy, E.P., Davydov, L., Smirniotis, P., 2003. TiO_2-loaded zeolites and mesoporous materials in the sonophotocatalytic decomposition of aqueous organic pollutants: the role of the support. Appl. Catal. B: Environ. 42, 1–11.

Romanello, M.B., Fidalgo de Cortalezzi, M.M., 2013. An experimental study on the aggregation of TiO_2 nanoparticles under environmentally relevant conditions. Water Res. 47, 3887–3898.

Rengifo-Herrera, J.A., Pulgarin, C., 2010. Photocatalytic activity of N, S co-doped and n-doped commercial anatase TiO_2 powders towards phenol oxidation and E. coli inactivation under simulated solar light irradiation. Sol. Energy 84, 37–43.

Rengifo-Herrera, J.A., Pierzchała, K., Sienkiewicz, A., Forro, L., Kiwi, J., Pulgarin, C., 2009. Abatement of organics and Escherichia coli by N, S co-doped TiO_2 under UV and visible light. Implications of the formation of singlet oxygen ($^1O_2$) under visible light. Appl. Catal. B: Environ. 88, 398–406.

Sakthivel, S., Kisch, H., 2003. Daylight photocatalysts by carbon-modified titanium dioxide. Angew. Chem. Int. Ed. 42, 4908–4911.

Serpone, N., Lawless, D., Khairutdinov, R., Pelizzetti, E., 1995. Subnanosecond relaxation dynamics in TiO_2 colloidal sols (particle sizes $Rp = 1.0$–13.4 nm). Relevance to heterogeneous photocatalysis. J. Phys. Chem. 99, 16655–16661.

Shao, G.S., Liu, L., Ma, T.Y., Wang, F.Y., Ren, T.Z., Yuan, Z.Y., 2010. Synthesis and characterization of carbon-modified titania photocatalysts with a hierarchical meso-/macroporous structure. Chem. Eng. J. 160, 370–377.

Soria, J., Conesa, J.C., Augugliaro, V., Palmisano, L., Sciavello, M., Scalfani, A.J., 1991. Dinitrogen photoreduction to ammonia over titanium dioxide powders doped with ferric ions. J. Phys. Chem. 95, 274–282.

Subramanian, V., Wolf, E., Kamat, P.V., 2001. Semiconductor–metal composite nanostructures. To what extent do metal nanoparticles improve the photocatalytic activity of TiO_2 films? J. Phys. Chem. B 105, 11439–11446.

Tanaka, T., Teramura, K., Yamamoto, T., Takenaka, S., Yoshida, S., Funabiki, T., 2002. TiO_2/SiO_2 photocatalysts at low levels of loading: preparation, structure and photocatalysis. J. Photochem. Photobiol. A: Chem. 148, 277–281.

Tang, L., Yang, G.D., Zeng, G.M., Cai, Y., Li, S.S., Zhou, Y.Y., Pang, Y., Liu, Y.Y., Zhang, Y., Luna, B., 2014a. Synergistic effect of iron doped ordered mesoporous carbon on adsorption-coupled reduction of hexavalent chromium and the relative mechanism study. Chem. Eng. J. 239, 114–122.

Tang, L., Fang, Y., Pang, Y., Zeng, G.M., Wang, J.J., Zhou, Y.Y., Deng, Y.C., Yang, G.D., Cai, Y., Chen, J., 2014b. Synergistic adsorption and reduction of hexavalent chromium using

highly uniform polyaniline-magnetic mesoporous silica composite. Chem. Eng. J. 254, 302–312.

Tang, Y.H., Zhang, G., Liu, C.B., Luo, S.L., Xu, X.L., Chen, L., Wang, B.G., 2013. Magnetic TiO_2–graphene composite as a high-performance and recyclable platform for efficient photocatalytic removal of herbicides from water. J. Hazard. Mater. 252–253, 115–122.

Tang, W.W., Zeng, G.W., Gong, J.L., Liang, J., Xu, P., Zhang, C., Huang, B.B., 2014. Removal of heavy metals from aqueous solutions using nanomaterials affected by humic/fulvic acid: a review. Sci. Total Environ. 468–469, 1014–1027.

Tran, H., Scott, J., Chiang, K., Amal, R., 2006. Clarifying the role of silver deposits on titania for the photocatalytic mineralisation of organic compounds. J. Photochem. Photobiol. A 183, 41–52.

Tong, T., Zhang, J., Tian, B., Chen, F., He, D., 2008. Preparation of Fe^{3+}-doped TiO_2 catalysts by controlled hydrolysis of titanium alkoxide and study on their photocatalytic activity for methyl orange degradation. J. Hazard. Mater. 155, 572–579.

Uyguner, C.S., Bekbolet, M., 2009. Application of photocatalysis for the removal of natural organic matter in simulated surface and ground waters. J. Adv. Oxid. Technol. 12, 87–92.

Valentin, C.D., Pacchioni, G., Selloni, A., 2005. Theory of carbon doping of titanium dioxide. Chem. Mater. 17, 6656–6665.

Vione, D., Minero, C., Maurino, V., Carlotti, M.E., Picatonotto, T., Pelizzetti, E., 2005. Degradation of phenol and benzoic acid in the presence of a TiO_2-based heterogeneous photocatalyst. Appl. Catal. B: Environ. 58, 79–88.

Viessman Jr., W., Hammer, M.J., 1998. Water Supply and Pollution Control, sixth ed. Addison Wesley Longman Inc, California, USA.

Vinodgopal, K., Kamat, P.V., 1992. Photochemistry on surfaces: photodegradation of 1, 3-diphenylisobenzofuran over metal oxide particles. J. Phys. Chem. 96, 5053–5059.

Vohra, M.S., Tanaka, K., 2003. Photocatalytic degradation of aqueous pollutants using silica-modified TiO_2. Water Res. 37, 3992–3996.

Wang, C., Yin, L., Zhang, L., Kang, L., Wang, X., Gao, R., 2009. Magnetic (γ-Fe_2O_3@SiO_2)n@TiO_2 functional hybrid nanoparticles with actived photocatalytic ability. J. Phys. Chem. C 113, 4008–4011.

Wang, J., Ma, T., Zhang, G., Zhang, Z.H., Zhang, X.D., Jiang, Y.F., Zhao, G., Zhang, P., 2007. Preparation of nanometer TiO_2 catalyst doped with upconversion luminescence agent and investigation on degradation of acid red B dye using visible light. Catal. Commun. 8, 607–611.

Wang, S.H., Zhou, S.Q., 2010. Titania deposited on soft magnetic activated carbon as a magnetically separable photocatalyst with enhanced activity. Appl. Surf. Sci. 256, 6191–6198.

Wang, W.D., Silva, C.G., Faria, J.L., 2007. Photocatalytic degradation of Chromotrope 2R using nanocrystalline TiO_2/activated-carbon composite catalysts. Appl. Catal. B: Environ. 70, 470–478.

Wang, X., Mitchell, D.R.G., Prince, K., Atanacio, A.J., Caruso, R.A., 2008. Gold nanoparticle incorporation into porous titania networks using an agarose gel templating technique for photocatalytic applications. Chem. Mater. 20, 3917–3926.

Wang, Y.B., Zhang, J.Z., Liu, X., Gao, S.M., Huang, B.B., Dai, Y., Xu, Y.B., 2012. Synthesis and characterization of activated carbon-coated $SiO_2/TiO_{2-x}C_x$ nanoporous composites with high adsorption capability and visible light photocatalytic activity. Mater. Chem. Phys. 135, 579–586.

Weng, Y.X., Li, L., Liu, Y., Wang, L., Yang, G.Z., 2003. Surface-binding forms of carboxylic groups on nanoparticulate TiO_2 surface studied by the interface-sensitive transient triplet-state molecular probe. J. Phys. Chem. B 107, 4356–4363.

Williams, G., Seger, B., Kamat, P.V., 2008. TiO$_2$–graphene nanocomposites. UV-assisted photocatalytic reduction of graphene oxide. ACS Nano 2, 1487–1491.

Woan, K., Pyrgiotakis, G., Sigmund, W., 2009. Photocatalytic carbon-nanotube–TiO$_2$ composites. Adv. Mater. 21, 2233–2239.

Wu, C.L., Shen, L., Zhang, Y.C., Huang, Q.L., 2012. Solvothermal synthesis of Cr-doped ZnO nanowires with visible light-driven photocatalytic activity. Mater. Lett. 65, 1794–1796.

Wu, X.Y., Yin, S., Dong, Q., Guo, C.S., Li, H.H., Kimura, T., Sato, T., 2013. Synthesis of high visible light active carbon doped TiO$_2$ photocatalyst by a facile calcination assisted solvothermal method. Appl. Catal. B: Environ. 142–143, 450–457.

Wu, Y.M., Liu, H.B., Zhang, J.L., Chen, F., 2009. Enhanced photocatalytic activity of nitrogen-doped titania by deposited with gold. J. Phys. Chem. C 113, 14689–14695.

Xiao, Q., Ouyang, L.L., 2009. Photocatalytic activity and hydroxyl radical formation of carbon-doped TiO$_2$ nanocrystalline: effect of calcination temperature. Chem. Eng. J. 148, 248–253.

Xu, A.W., Gao, Y., Xu, H.Q., 2002. Preparation, characterization, and their photocatalytic activities of rare earth doped TiO$_2$ nanoparticles. J. Catal. 207, 151–157.

Xu, J., Ao, Y., Fu, D., Yuan, C., 2008. Synthesis of fluorine-doped titania-coated activated carbon under low temperature with high photocatalytic activity under visible light. J. Phys. Chem. Solids 69, 2366–2370.

Xu, P., Zeng, G.M., Huang, D.L., Feng, C.L., Hu, S., Zhao, M.H., Lai, C., Wei, Z., Huang, C., Xie, G.X., Liu, Z.F., 2012. Use of iron oxide nanomaterials in wastewater treatment: a review. Sci. Total Environ. 424, 1–10.

Xu, S.F., Lu, H.Z., Chen, L.X., Wang, X.C., 2014. Molecularly imprinted TiO$_2$ hybridized magnetic Fe$_3$O$_4$ nanoparticles for selective photocatalytic degradation and removal of estrone. RSC Adv. 4, 45266–45274.

Yang, M., Thompson, D.W., Meyer, G.J., 2002. Charge-transfer studies of iron cyano compounds bound to nanocrystalline TiO$_2$ surfaces. Inorg. Chem. 41, 1254–1262.

Yang, P., Lu, C., Hua, N., Du, Y., 2002. Titanium dioxide nanoparticles co-doped with Fe^{3+} and Eu^{3+} ions for photocatalysis. Mater. Lett. 57, 794–801.

Yin, S., Zhang, Q., Saito, F., Sato, T., 2003. Preparation of visible light-activated titania photocatalyst by mechanochemical method. Chem. Lett. 32, 358–359.

Yoneyama, H., Torimoto, T., 2000. Titanium dioxide/adsorbent hybrid photocatalysts for photodestruction of organic substances of dilute concentrations. Catal. Today 58, 133–140.

Yu, J., Zhao, X., 2001. Effect of surface treatment on the photocatalytic activity and hydrophilic property of the sol–gel derived TiO$_2$ thin films. Mater. Res. Bull. 36, 97–107.

Yu, J.C., Xie, Y., Tang, H.Y., Zhang, L., Chan, H.C., Zhao, J., 2003a. Visible light-assisted bactericidal effect of metal phthalocyanine-sensitized titanium dioxide films. J. Photochem. Photobiol. A: Chem. 156, 235–241.

Yu, J.C., Zhang, L., Zheng, Z., Zhao, J., 2003b. Synthesis and characterization of phosphated mesoporous titanium dioxide with high photocatalytic activity. Chem. Mater. 15, 2280–2286.

Zaleska, A., 2008. Doped-TiO$_2$: a review. Recent Pat. Eng. 2, 157–164.

Zang, Y., Farnood, R., 2008. Photocatalytic activity of AgBr/TiO$_2$ in water undersimulated sunlight irradiation. Appl. Catal. B: Environ. 79, 334–340.

Zeng, G.M., Chen, M., Zeng, Z.T., 2013a. Risks of neonicotinoid pesticides. Science 340 (6139), 1403.

Zeng, G.M., Chen, M., Zeng, Z.T., 2013b. Shale gas: surface water also at risk. Nature 499 (7457), 154.

Zhang, H., Lü, X.J., Li, Y.M., Wang, Y., Li, J.H., 2010. P25-graphene composite as a high performance photocatalyst. ACS Nano 4, 380–386.

Zhang, H., Zhu, G.Q., 2012. One-step hydrothermal synthesis of magnetic Fe$_3$O$_4$ nanoparticles immobilized on polyamide fabric. Appl. Surf. Sci. 258, 4952–4959.

Zhang, J., Wu, Y., Xing, M., Leghari, S.A.K., Sajjad, S., 2010. Development of modified N doped TiO$_2$ photocatalyst with metals, nonmetals and metal oxides. Energy Environ. Sci. 3, 715–726.

Zhang, X., Wu, F., Deng, N., 2011. Efficient photodegradation of dyes using light-induced self-assembly TiO$_2$/β-cyclodextrin hybrid nanoparticles under visible light irradiation. J. Hazard. Mater. 185, 117–123.

Zhang, Y.C., Zhang, N., Tang, Z., Xu, Y., 2012. Improving the photocatalytic performance of graphene–TiO$_2$ nanocomposites via a combined strategy of decreasing defects of graphene and increasing interfacial contact. Phys. Chem. Chem. Phys. 14, 9167–9175.

Zhao, C., Pelaez, M., Dionysiou, D.D., Pillai, S.C., Byrne, J.A., O'Shea, K.E., 2014. UV and visible light activated TiO2 photocatalysis of 6-hydroxymethyl uracil, a model compound forthe potent cyanotoxin cylindrospermopsin. Catal. Today 224, 70–76.

Zhao, J., Wu, T., Wu, K., Oikawa, K., Hidaka, H., Serpone, N., 1998. Photoassisted degradation of dye pollutants. 3. Degradation of the cationic dye rhodamine B in aqueous anionic surfactant/TiO$_2$ dispersions under visible light irradiation: evidence for the need of substrate adsorption on TiO$_2$ particles. Environ. Sci. Technol. 32, 2394–2400.

Zhao, J., Yang, X., 2003. Photocatalytic oxidation for indoor air purification: a literature review. Build. Environ. 38, 645–654.

Zhao, J.C., Chen, C.C., Ma, W.H., 2005. Photocatalytic degradation of organic pollutants under visible light irradiation. Top. Catal. 35, 269–278.

Zhao, Z., Liu, Q., 2008. Mechanism of higher photocatalytic activity of anatase TiO$_2$ doped with nitrogen under visible-light irradiation from density functional theory calculation. J. Phys. D: Appl. Phys. 41, 1–10.

Zhou, Y.Y., Tang, L., Zeng, G.M., Chen, J., Cai, Y., Zhang, Y., Yang, G.D., Liu, Y.Y., Zhang, C., Tang, W.W., 2014. Mesoporous carbon nitride based biosensor for highly sensitive and selective analysis of phenol and catechol in compost bioremediation. Biosens. Bioelectron. 61, 519–525.

Zhou, W., Zheng, Y., Wu, G., 2006. Novel luminescent RE/TiO$_2$ (RE = Eu, Gd) catalysts prepared by in-situation sol–gel approach construction of multi-functional precursors and their photo or photocatalytic oxidation properties. Appl. Surf. Sci. 252, 1387–1392.