

Visible-light sensitization of TiO₂ photocatalysts via wet chemical N-doping for the degradation of dissolved organic compounds in wastewater treatment: a review

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Abstract Increased pollution of ground and surface water and emerging new micropollutants from a wide variety of industrial, municipal, and agricultural sources has increased demand on the development of innovative new technologies and materials whereby challenges associated with the provision of safe potable water can be addressed. Heterogeneous photocatalysis using visible-light sensitized TiO₂ photocatalysts has attracted a lot of attention as it can effectively remove dissolved organic compound in water without generating harmful by-products. On this note, recent progress on visible-light sensitive TiO₂ synthesis via wet chemical N-doping method is reviewed. In a typical visible-light sensitive TiO₂ preparation via wet chemical methods, the chemical (e.g., N-doping content and states) and morphological properties (e.g., particle size, surface area, and crystal phase) of TiO₂ in as-prepared resultants are sensitively

dependent on many experimental variables during the synthesis. This has also made it very difficult to provide a universal guidance at this stage with a certainty for each variable of N-doping preparation. Instead of one-factor-at-a-time style investigation, a statistically valid parameter optimization investigation for general optima of photocatalytic activity will be certainly useful. Optimization of the preparation technique is envisaged to be beneficial to many environmental applications, i.e., dissolved organic compounds removal in wastewater treatment.

Keywords TiO₂ · Visible-light sensitive · Photocatalysis · Wastewater treatment · Review · Drinking water

Introduction

Increased pollution of ground and surface water and emerging new micropollutants from a wide variety of industrial, municipal, and agricultural sources has challenged the viability of current water treatment practices on meeting the regulation and increased demand of all water users. There is a clear need for the development of innovative new technologies and materials whereby challenges associated with the provision of safe potable water can be addressed. In recent years, heterogeneous photocatalysis technique by semiconductors has attracted a lot of attention in

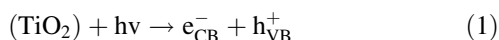
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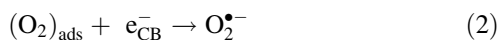
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the water purification of dissolved-organic-compound contained water without generating harmful by-products (Dai and Yin 2014; Han et al. 2014; Yin et al. 2010; Zhang et al. 2012; Xia et al. 2014). Among the available, semiconductive TiO₂ nanoparticles has proven to be the most promising (Graetzel 2001), with reported advantages of low cost and toxicity, greatly enhanced surface area, tunable properties which can be modified by size reduction, doping, or sensitizer, no substantial loss of photocatalytic activity after repeated process cycles, enhanced photo-induced charge transport (Hagfeldt et al. 1992) and no depletion layer formation on the surface (Nazeruddin et al. 1993). Besides, due to the intensive research on the photocatalytic activity of TiO₂, the mechanism of its degradation of dissolved organic compounds is well understood, which can be illustrated as follows (Zou and Zhu 2007; Gaya and Abdullah 2008):

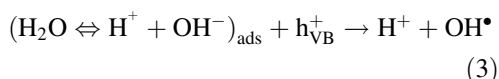
1. Absorption of efficient photons ($h\nu \geq EG = 3.2e$) by TiO₂



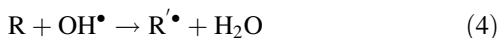
2. Oxygen ionsorption (first step of oxygen reduction; oxygen's oxidation degree passes from 0 to $-1/2$)



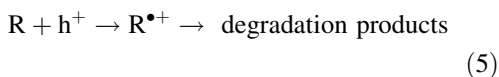
3. Neutralization of OH⁻ groups by photoholes which produces OH[•] radicals



4. Oxidation of the organic reactant via successive attacks by OH radicals



5. Direct oxidation by reaction with holes



However, it is well known that the band gap energy of TiO₂ is intrinsically wide between 3.0 and 3.2 eV (3.0 for rutile and 3.2 for anatase). This means plain TiO₂ semiconductors only absorb a small portion (3.6–5.2 %, depending the weather conditions) of solar spectrum in the UV region. It is of great interests

that if TO₂ photocatalysts could possess the ability of directly utilizing visible sunlight. Early attempts on visible-light sensitization of TiO₂ mainly involved the doping of transition metal elements (Hoffmann et al. 1995; Choi et al. 1994a; Wang et al. 2000), which, however, has the drawbacks of require intensive energy and expensive ion implantation facilities, thermally unstable, increase free charge carrier trapping in bound electron-hole pairs, tend to form charge carrier recombination centers, possible photo-corrosion, and harmful nature of the dopants (Wang et al. 1999; Yamashita et al. 1998; Choi et al. 1994b). More importantly, these cationic dopants only result in limited band gap changes, and in some cases, do increase the light absorption, but not the photocatalytic activity. As a consequence, more significant advances in this field were achieved on doping TiO₂ photocatalyst with non-metallic or anionic elements such as carbon, sulfur, halides, phosphor, and boron (Zhao et al. 2005; Chen et al. 2008a). While the valence band edge of TiO₂ primarily derives from oxygen 2*p* orbitals and the conduction band (CB) edge from titanium 3*d* orbitals, non-metallic doping can result in electronic transitions from the dopant instead of oxygen 2*p* or 3*p* orbitals to the Ti 3*d* orbitals (Chen et al. 2008b). Asahi et al. first recognized the visible-light sensitivity of TiO₂ with a certain amount of nitrogen dopants in 2001, and now nitrogen has proven to be one of the most effective non-metallic dopant due to its similar size to oxygen and low ionization energy (Chen et al. 2011; Park et al. 2002).

In this review, recent literature on N-doped TiO₂ nanoparticles prepared by wet chemical methods, i.e., hydrolysis of a TiO₂ precursor with N-containing solution, are reviewed. Other doping methods reported in the literature include the sputtering and implantation (Batzil et al. 2006; Diwald et al. 2004a; Kitano et al. 2006), high-temperature-sintering TiO₂ under N-containing atmosphere (Diwald et al. 2004b; Nakamura et al. 2004; Irie et al. 2003a), etc. Compared to these methods, wet chemical method can not only avoid the high-temperature-induced surface property change but also have the fine control of the nitrogen-doping level with the possibility of high N-content (reportedly up to 8 %). Other reported advantages include low temperature and energy costs, the simplicity in controlling crystal structure/morphology and particle size by simple variations in experimental conditions, such as hydrolysis rate, solution pH, and

solvents. Up to date, the reported studies on N-doped TiO₂ nanoparticles preparation via wet chemical methods are flourished but still lacking of parametric investigations on experimental preparation variables, and more importantly their influence on the visible-light photoactivity of as-synthesized products. It is evident to speculate that the chemical (e.g., N-doping content and states) and morphological properties (e.g., particle size, crystal phase) of as-prepared resultants are sensitively dependent on the experimental conditions during the synthesis.

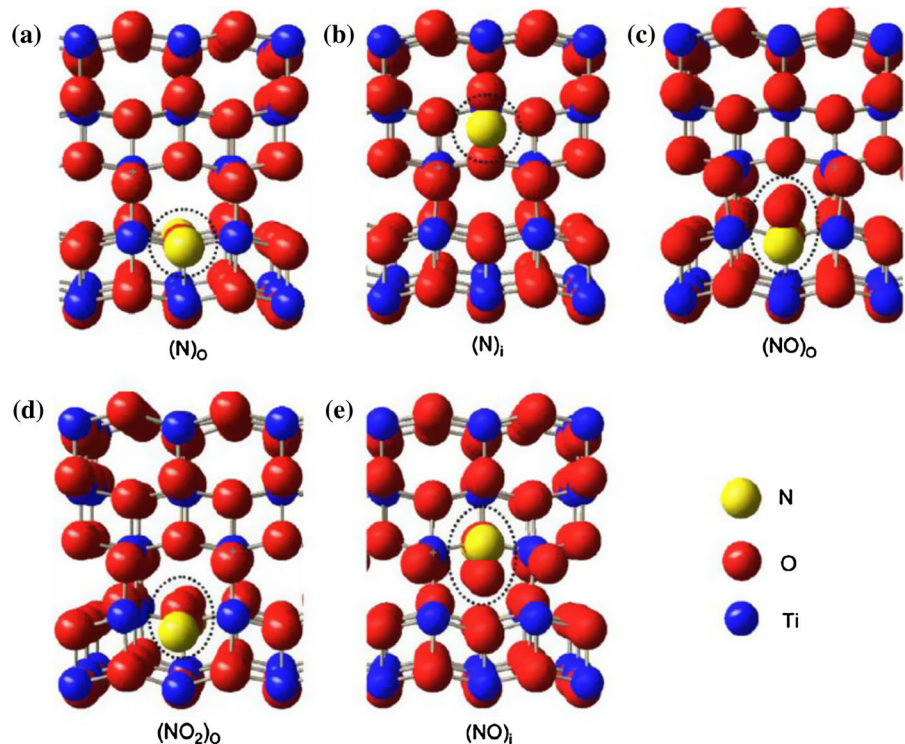
Effects of N-doping on TiO₂ visible-light sensitivity

Despite the viability of TiO₂ visible-light sensitization through wet chemical N-doping, there are still several discrepancies in the literature regarding the promoting effect of N-doping on the visible-light sensitivity of TiO₂:

Firstly, N-dopants in the TiO₂ resultants can exist as either substitutional in form of Ti–N–Ti bond or interstitial in form of Ti–O–N or Ti–N–O bond as illustrated in Fig. 1. For the former, the literature

agreed that the binding energy (BE) of N 1s peaks is fingerprinted at 396–398 eV; for the later, that is 400–406 eV. The discovery of this variance can be dated back to the heated debate over the originality of Asahi's work, as Sato challenged the first discovery of N-doped TiO₂ and its visible-light sensitivity to his credit (Sato 2002). This was later cleared up by the fact that the N-doped TiO₂ obtained by Asahi belonged to substitutional group, whereas the one reported by Sato et al. 15 years earlier was more interstitial like. Based on some theoretical densities-of-states (DOS) calculations of different substitutional doping (i.e., C, N, F, S for O), Asahi maintained the critical role of Ti–N bond on visible-light sensitivity of N–TiO₂ in his work, although their samples in the absence of any Ti–N bond were indicative of visible-light activities as well. Almost at the same time, Sakatani and Koike suggested that the nitrogen atoms were doped at the interstitial sites and that these interstitial nitrogen atoms were responsible for visible-light response (Sakatani et al. 2001). Later on, Peng et al. explained that both interstitial and substitutional N-dopants can enable the visible-light sensitivity of TiO₂ nanoparticles, whereas only the former is higher than the later in

Fig. 1 Schematic models for **a** substitutional N-doping, **b** interstitial N-doping, **c** substitutional NO-doping, **d** substitutional NO₂-doping, and **e** interstitial NO-doping. Each atom of the supercell (16 TiO₂ units) is fully relaxed to stabilize the system (Reprinted with permission from Elsevier.) (Asahi and Morikawa 2007)



terms of visible-light activity (Peng et al. 2008). The nitrogen content in the N-doped TiO₂ reported in the literature, which could be one of major indicators in terms of the doping quality, varies vastly from 0.08 to 8 % along with different degree red-shift towards the visible-light range. Low concentrations of nitrogen have been generally observed to be all interstitial, while higher levels of nitrogen incorporation in titania lattice encourage substitutional doping (Di Valentin et al. 2005a).

It is estimated that the existence of these two N-doping states would also vary according to the different preparation techniques, in many cases, both coexisted (see Fig. 2). However, larger proportion of N-dopants in TiO₂ nanoparticles prepared by wet chemical methods should more likely belong to the interstitial doping group (see Table 1), as it is a consensus that Ti-O bond is quite stable at the mild conditions, which make it very difficult for nitrogen to replace the oxygen sites during the diffusion-controlled wet chemical preparation. Plus, N-containing amino substances would undergo serious oxidation during the calcinations treatment. This could result in the existence of various NO_x species, such as NO, NO₂, NO²⁻, NO₂⁻, NO₂²⁻, NO₃⁻, and N₂O₂²⁻, etc. in N-doped TiO₂ resultants, which has been observed

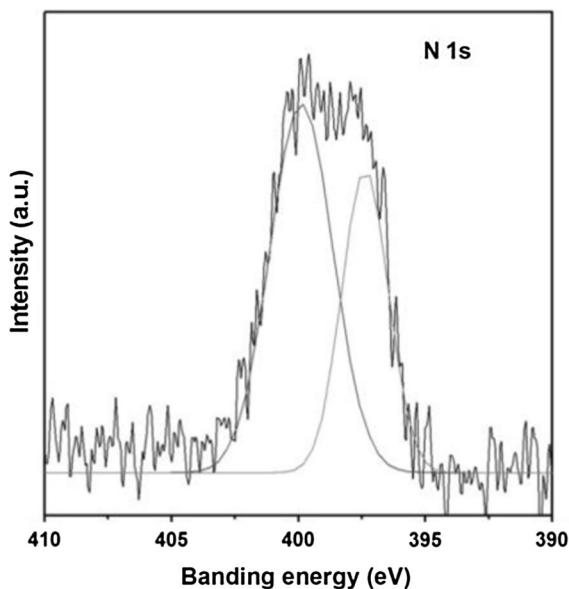


Fig. 2 A typical N 1 s region of the XPS spectra for N-TiO₂ photocatalysts prepared via wet chemical method using titanium butoxide and triethylamine as titanium and nitrogen source, respectively, where two peaks show at around 397 and 401 eV

widely in the literature (Chen et al. 2005; Sakatani et al. 2003; Joung et al. 2006; Livraghi et al. 2006). Finally, it is noteworthy that the radius of these N-containing species are usually too large to dope into the TiO₂ bulk, so they more likely exist at the surface of the catalysts particles through formed chemical bonds or be adsorbed at the meso-pores. This, however, should barely hinder its application of water treatment at all, as the photoactive surface of an N-doped TiO₂ photocatalyst is generally considered to be sufficient during photodegradation of dissolved organic compounds. In addition, N-doping was observed to have promoting effect on the surface area and the number of surface hydroxyl groups (Wang et al. 2005), of which the later would in turn increase the concentration of beneficial free hydroxyl radicals for the TiO₂ photodecomposition in the application of water treatment (Yang et al. 2009).

Secondly, it is still subject to a debate that whether doped nitrogen or oxygen vacancies are responsible for the photocatalytic activity shift towards visible-light range. While most of works in this area agreed upon the necessity of N presence in N-doped TiO₂, Ihara et al. claimed that the visible-light sensitivity of N-TiO₂ nanoparticles arise from the oxygen-deficient sites, as the existence of N-dopants was only necessary to retard the reoxidation of oxygen-deficient TiO₂, which authors considered to be essential for visible-light sensitization (Ihara et al. 2003). The recent development on this subject provided by Lin et al. further suggested that N-dopants can only affect the absorption below 500 nm wavelength, whereas the O vacancies are responsible for the visible-light sensitization at wavelength above 500 nm (Lin et al. 2005). Generally, low concentrations of nitrogen within TiO₂ could promote interstitial doping and cause a large decrease in the formation energy of oxygen vacancies in the anatase from 4.2 to 0.6 eV, as a result of the excess electrons created in the oxygen vacancy being trapped on the nitrogen site (Zhao et al. 2008; Dunnill and Parkin 2011). While some authors attributed resulted color centers and enhanced photocatalytic activity to these oxygen vacancies (Zhao and Liu 2008; Pan et al. 2013), others believe that the presence of oxygen vacancies instead acts as recombination sites for electrons and holes leading to poor performance (Prabakar et al. 2007). It is safe to speculate that an optimal point between visible-light band gap enhancement and increased electron-hole

Table 1 Experimental conditions and properties as-synthesized N-doped TiO₂ via wet chemical methods

Studies	TiO ₂ precursors	N precursors	N-doping conditions		Calcinations T [°C]	N-doped TiO ₂ properties	
			pH	T (°C) solvent		N wt%	N doping state size [nm]
Gole et al. (2004)	Ti[OCH(CH ₃) ₂] ₄	Triethylamine Hydrazine	2	Aqueous isopropanol		5.1, 17.3	Substitutional 10
Sathish et al. (2005)	TiCl ₃	Ammonia	8.5	Na ₂ S solution	400*, 500, 600		Substitutional 14
Ihara et al. (2003)	Ti(SO ₄) ₂	Ammonia 28 %	7		400	0.2	13*
Liu et al. (2005)	Ti[OCH(CH ₃) ₂] ₄	Ammonia	85	Aqueous ethanol	400		
Sakthivel and Kisch (2003)	TiCl ₄	Ammonia Ammonium carbonate Ammonium bicarbonate	5.5		400	0.08-0.13	7-10
Sakthivel et al. (2004)	1) Ti[OCH(CH ₃) ₂] ₄ 2) TiCl ₄	Thiourea		Ethanol	500 600*	0.07 0.3	Interstitial 22 7
Sano et al. (2004)	TiCl ₄	2,2'-bipyridine			300 in air, 380 in N ₂		Interstitial 7.7-8.7
Wang et al. (2007)	Ti(OBu) ₄	Ammonia 25 %		HNO ₃ and ethanol	400-800		Interstitial 13.9-63.7
Kobayakawa et al. (2005)	Ti(OH) ₄	Urea			400		
Ananpattarachai et al. (2009)	Ti[OCH(CH ₃) ₂] ₄	Diethanolamine Triethylamine Urea	4	HNO ₃ and ethanol	800	4.11 0.64	Interstitial 4.11
Wang et al. (2006)	TiCl ₃	Diethylamine Triethylamine Ethylenediamine			140	5.01 0.24-0.29 0.34-0.44 0.23-1.70	Interstitial 7
Sun et al. (2008)	Ti(OBu) ₄	Ammonia	5.5	~0	450	1.76	Interstitial 14
Sun et al. (2009)	TiCl ₄	Mixture of ammonia and hydrazine hydrate* Ammonia			400	0.45 0.21 0.24	Interstitial 9
Xu et al. (2008)	Ti(OBu) ₄	Hydrazine hydrate	1.5	Isopropanol			Substitutional 3.5
Wang et al. (2005)	Ti(OBu) ₄	Ethylamine			350		Interstitial 9
Sato et al. (2005)	1) Ti[OCH(CH ₃) ₂] ₄ 2) TiCl ₄	Ammonia 25 % Ammonia	0	HNO ₃ and ethanol	>330		Interstitial 50
Livraghi et al. (2005)	Ti[OCH(CH ₃) ₂] ₄	NH ₄ Cl		Isopropanol	497	0.03-0.53	Interstitial 50
Belver et al. (2006)	Ti[OCH(CH ₃) ₂] ₄	2-methoxyethylamine N ₁ ,N ₁ ',N ₃ '- tetramethylethyl- enediamine		Isopropanol			
Sathish et al. (2007)	Ti[OCH(CH ₃) ₂] ₄	1,2-phenylenediamine Melamine	50	Aqueous ethanol	400, 500*, 600, 700		Interstitial 25-50

* Indicates the optimum of the variable within reported experimental conditions; Calcinations were carried out in air if not otherwise specified

recombination effects in N-doped TiO₂ may exist by tightly control the N-dopant incorporation (i.e., level and types) (Irie et al. 2003b; Yang et al. 2010).

Thirdly, Asahi ascribed the visible-light absorbance in N-doped TiO₂ to the band gap narrowing effect, which was resulted from the interaction between N_{2p} and O_{2p} states (Asahi et al. 2001). Later on, several other researcher in their follow-up studies on N-doped TiO₂ suggested that the creation of new inter-bands localized within the band gap of TiO₂ is the origin of visible-light activity based on density-functional-theory (DFT) calculations (Di Valentin et al. 2004, 2005a, b; Wang et al. 2006; Lee et al. 2005; Yang et al. 2006). For example, Di Valentin et al. suggested that the single-atom nitrogen impurities form either diamagnetic (N_b⁻) or paramagnetic (N_b[•]) bulk centers. Both types of N_b centers give rise to localized N_{2p} states within the band gap of the oxide, as illustrated in Fig. 3, rather than mixing with O_{2p} states for both rutile and anatase TiO₂. To clarify, Payne and his co-workers further claimed that the hybridization between N_{2p} and O_{2p} states is only possible when the N-doping level exceeds 20 % in anatase TiO₂ (Lin et al. 2005); Yang et al. found that the interaction between N_{2p} and O_{2p} states is less pronounced when N-doping is the substitutional type (Yang et al. 2006). Later on, Sun et al. attempted to correlate the concentration of NO₂²⁻ with the visible-light activity of as-prepared N-doped TiO₂ photocatalysts, as their DFT calculations supported a NO₂²⁻-induced formation of new mid-band energy levels near CB (Sun et al.

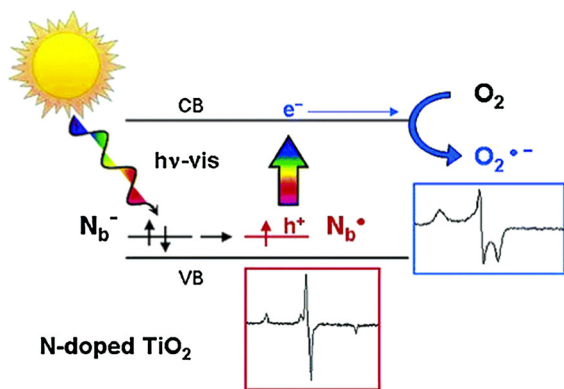


Fig. 3 Sketch of the proposed mechanism for the processes induced by vis-light irradiation of the N-doped sample in O₂ atmosphere (Reprinted with permission from the American Chemical Society.) (Livraghi et al. 2006)

2009). Now it is generally agreed that the substitutional incorporation of nitrogen would result in an increase of ~ 0.14 eV in energy in the valance band of anatase due to the overlap between N_{2p} and O_{2p} states; In the case of interstitial doping, the incorporation of nitrogen creates an inter-band state 0.74 eV above the valence band, as illustrated in Fig. 4 (Di Valentin et al. 2005a, 2007).

To sum up, photocatalytic enhancement and nitrogen content are more likely a more complex indirect correlation of doping types (i.e., substitutional or interstitial), existence of oxygen vacancies and band structure types (i.e., hybridization of N_{2p} and O_{2p} states or creation of a new inter-band). Other factors to the uncertainty could arise from the content of other visible-light-induced dopants (such as C, S, etc.) as impurities from organic precursors or simply the chemisorbed N-containing molecules on as-prepared TiO₂ nanoparticles surface that are non-active, such as NH₃.

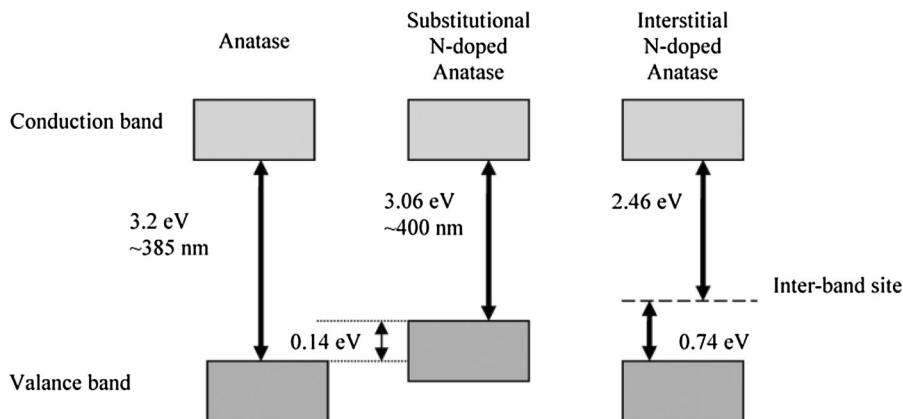
Experimental parameters of wet chemical N-doping method and their effects

An attempt to summarize the recent literature on visible-light sensitive N-doped TiO₂ nanoparticles synthesized by wet chemical methods is undertaken (Table 1), of which key experimental variables are listed for comparison. Optimal values of the experimental parameters in each study are also underlined where possible. The following sections will deal with each variable and its influences on the resulting photocatalytic activity of N-doped TiO₂ nanoparticles.

Influences of TiO₂ precursors

In a typical wet chemical preparation of TiO₂ photocatalysts, TiO₂ precursors were mostly either titanium alkoxides or inorganic titanium, such as TiCl₃, TiCl₄, Ti(SO₄)₂, and Ti(OH)₄. When using inorganic-type TiO₂ precursor, special attention needed to be paid on the effective removal of some ion impurities, as they are potentially harmful to the photoactivity of TiO₂ formation. In their study, Harada et al. observed that the presence of Cl⁻ ions on the surface of AC promotes the aggregation of titanium oxides species, and the formation of rutile TiO₂ phase instead of anatase form. As one of two common TiO₂ species, rutile generates

Fig. 4 Schematic showing the valance and conduction bands of the three different forms of N-doped anatase (Reprinted with permission from the Royal Society of Chemistry.) (Dunnill and Parkin 2011)



fewer charge carriers with lower lifetimes than that of an anatase-type TiO_2 , when in the same nano-sized particles form with the same crystalline quality and reactive surface properties (Colbeau-Justin et al. 2003). As a result, rinsing with water or acids, such as HNO_3 , is essential. On the other hand, some of the ion presence appeared to be beneficial. For example, the SO_4^{2-} presence on TiO_2 surface has been reported to show higher photocatalytic activity than pure TiO_2 (Yamazaki et al. 2001; Kim et al. 2003; Huang et al. 1998).

Ti species in these TiO_2 precursors exist as either Ti^{3+} or Ti^{4+} , which could affect the preparation process as well. Wang et al. claimed that using Ti^{3+} -containing precursors is advantageous for substitutional N-doping, as transformation of Ti^{3+} to Ti^{4+} during the hydrolysis would create an oxygen vacancy, making it easier for nitrogen atoms to occupy the oxygen sites during the crystal growth (Wang and Lewis 2006). Conversely, this process did not enhance N-doping results greatly (the highest sample with 1.7 % N-content) and suggested a majority of interstitial N-doping other than substitutional type. Another interesting TiO_2 precursor seen in the literature is N-containing TiO_2 precursors, such as Ti^{4+} -bipyridine complex. Sano et al claimed its advantages to be the readily existed Ti–N bonds in the precursors, which could ease up the N-doping content increasing at room temperature (Sano et al. 2004). Nevertheless, their XPS results showed that N 1 s peaks at 396 eV (Ti–N) were only recognizable inside the bulk, whereas N 1 s peaks at 400 eV (Ti–O–N or Ti–N–O) were clearly spotted on the N-doped TiO_2 surface. Results in this study confirmed that Ti–N bond does not necessarily related to the quality of

N-doping directly in terms of visible-light sensitivity as they originally thought.

Influences of nitrogen precursors

In the literature, a number of studies used ammonia solution as nitrogen precursors during the hydrolysis preparation of N-doped TiO_2 . Compared with other amino group precursors, one possible drawback using ammonia as N precursors is the chemisorbed NH_3 molecules on TiO_2 surface, which might cover the photoactive sites that served as Lewis bases to capture photo-induced holes; this is detrimental to the oxidative degradation (Young and Desai 1989). This might diminish the overall photoactive promoting effect of the N-doping. Burda and his co-workers published a series of papers on hydrolysis methods using triethylamine as N precursor (Burda et al. 2003; Chen and Burda 2004). They claimed the superiority of their method by achieving up to 8 % N-content in their TiO_2 nanoparticles resultants. Their preparation involved in the excess usage of N precursors and prolonged stirring after its addition into the TiO_2 precursors. Another interesting N precursor reported in the literature is sulfur-containing solvent such as thiourea (Sakhivel et al. 2004), which was originally used to obtain S-doped TiO_2 . Similar to using the $\text{Ti}(\text{SO}_4)_2$ as TiO_2 precursor, it is essential to use ethanol as solvent and use water or acid to wash the particles to remove the sulfur species, i.e., SO_4^{2-} .

Influences of solvents and pH values

Adding some alcohol solvents (such as 2-isopropanol, ethanol, etc.) to the hydrolytic system can make it

more volatile than using water alone. This could facilitate the evaporation and the following drying treatments. Nevertheless, excessive use of alcohol or high alcohol-to-TiO₂ precursor volume ratio should be avoided, as it could shrink the body of colloidal formation and make it denser (Montoya et al. 1992). This could lead to less porosity and poor crystallinity of TiO₂ nanoparticles formation at the later stage. As for using water alone, addition of a certain amount of acid is crucial to obtain a stable colloidal solution and to preserve the particles in their nano-sized form. This catalytic effect is brought about through the electrical charging of the hydroxide particles by proton adsorption, which hinders the gel agglomeration.

Acid addition is also likely to have a potential linkage to the TiO₂ phase transition during the hydrolysis. Zhu et al. reported that high acid concentration (2.0 M) favored the formation of rutile phase TiO₂ during the hydrolysis of TiOSO₄·xH₂O (see Fig. 5) (Zhu et al. 2005). The follow-up investigations on this effect in the presence of N-dopants are still needed. In terms of the acid type, HNO₃ is preferable to HCl due to avoiding of the possible implication of an unfavorable Cl⁻ ion effect on TiO₂ crystal formation. In addition, the pH value of the hydrolytic system is also an important factor on the N-doping quality of nano-sized TiO₂ resultants. In general, high pH values are unfavorable to nitrogen-doping efficiency, as Ti-

bound amine groups are more easily substituted by anion OH⁻ in the solution during the hydrolysis process. Therefore, usage of base in the solvents needs to be controlled in order to avoid any adverse effect on the N-doping efficiency. On the other hand, this might made the inorganic TiO₂ precursors like TiCl₃, TiCl₄, Ti(SO₄)₂ somewhat desirable, as their hydrolysis usually results in an acid environment.

Other than acidity and basicity, addition of certain electrolytes in the solvents could have influences on the formation of Ti, N-containing organic complex. Some particular benefits arising from a certain electrolyte may vary from case to case. Sathish et al. reported the positive effects of Na₂S presence during their N-doped TiO₂ preparation through the hydrolysis of TiCl₃ with aqueous ammonia; it induced the in situ formation of transient (NH₄)_x-TiS_x complex and a reductive solution environment, of which the latter is beneficial for the removal of any dissolved oxygen (Sathish et al. 2005). Gole et al. discovered that the addition of Pd(NO₃)₂ in the hydrolysis of Ti[OCH(CH₃)₂]₄ with triethylamine could increase the N-doping level from 5.1 % to a high level of 17.6 % (Gole et al. 2004), though the detailed explanation of the effect was lacking in the study.

Influences of post N-doping treatments

General wet chemical photocatalysts preparation requires minimum calcinations temperature (around 200 °C) to enable the proper crystallinity of the TiO₂ nanoparticles, which is deeply related to its electronic properties, i.e., charger carrier lifetimes. However, unnecessary high temperature (>500 °C) is to avoid for two reasons. Firstly, high temperatures induce the shrinkage of N-doped TiO₂ surface area due to the grain (i.e., crystallite size) growth or nanoparticles agglomerating effect throughout the treatment process, of which typical results are shown in Fig. 6a. Secondly, high temperatures also favor the TiO₂ phase transition from anatase to rutile. In extreme cases, a complete transition is expected when calcinations temperature is >700 °C in air. They are both detrimental to the resulting photocatalytic activity. Reportedly, some of the ambient gases are likely to affect the calcination temperature on TiO₂ crystal phase transition. For example, using protective hydrogen gas alone reportedly confined the complete anatase-to-rutile phase transition temperature of a TiO₂ between

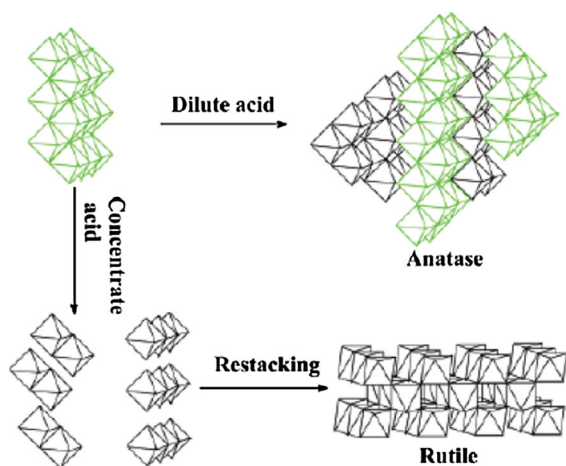


Fig. 5 Structural features of hydrogen-titanate (top left), anatase (top right), and rutile (bottom right), as well as the phase transitions from the hydrogen-titanate to anatase and rutile, in dilute and concentrate acid solutions, respectively (Reprinted with permission from the American Chemical society.) (Zhu et al. 2005)

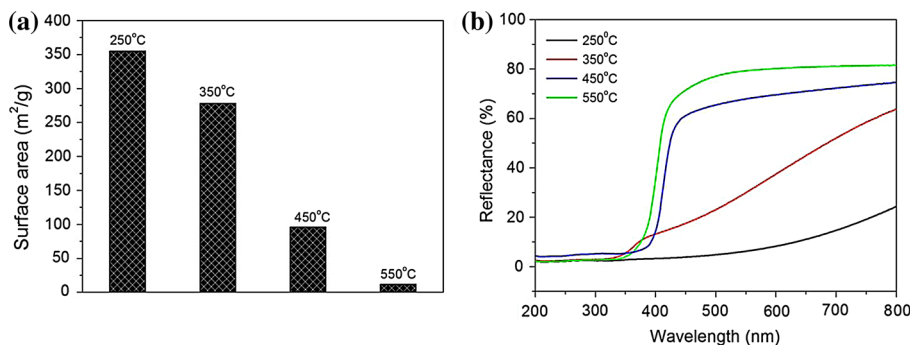


Fig. 6 **a** Surface area of typical N-doped TiO₂ under different calcinations temperatures; **b** the corresponding UV-Vis DRS spectra, where bare TiO₂ was synthesized without any N-dopants (Reprinted with permission from Taylor & Francis,.) (Zhang et al. 2015)

525 and 550 °C, which is much lower than that (700 °C) in the presence of air (Hamasaki et al. 1994). Furthermore, it is also of great interests to know if there are possible N-dopants-related high-temperature effects on the TiO₂ phase transition. For interstitial N-doped TiO₂, Wang et al. observed that the phase transition temperature remains un-affected, which started at around 400 °C (Wang et al. 2005). Most recently, Xu et al. reported that the substitutional doping of nitrogen can inhibit the anatase-to-rutile transformation and confined the transition temperature to around 800 °C under their experimental conditions (Xu et al. 2008).

On the other hand, in terms of retaining sufficiently high N-doping levels in N-doped TiO₂ resultants, literature studies reported that increasing temperature, especially when above 400 °C, could diminish the visible-light absorbance due to the thermal release of the doped nitrogen and its re-substitution by oxygen atoms (see Fig. 6b). This was usually accompanied by the fading of the color intensity of the resultants. Microscopically, high calcinations temperatures (above 600 °C) are unfavorable to the formation of both interstitial and substitutional doped N, while Nosaka et al. reported the calcinations temperatures for maximum amount of two kinds of doped N atoms are 400 and 500 °C, respectively (Nosaka et al. 2005).

Conclusions

It should be noted that there is not yet a clear and direct correlation between N-doping level and overall photocatalytic activity, since the latter can also be affected

by many other factors, such particle size, surface area, and functionalization. This has also made it very difficult to provide a universal guidance at this stage with a certainty for each variable of N-doping preparation. Instead of one-factor-at-a-time style investigation, a statistically valid parameter optimization investigation for general optima of photocatalytic activity will be certainly useful. Optimization of the wet chemical N-doping technique is envisaged to be beneficial to the near-term development of TiO₂ photocatalysts or its nanocomposites for solar-driven environmental clean-up, i.e., dissolved organic compounds removal in wastewater treatment.

To test N-doped TiO₂ photocatalytic activity, some lab-scale investigations on the degradations of dissolved organic compounds under simulated environmental conditions were carried out. It seemed that these efforts firstly aimed at decomposition of organic dyes or colored compounds, such as methylene blue (MB), azo dyes acid, including acid orange 7 (AO7), procion red MX-5B (MX-5B), and reactive black 5 (RB5), etc. However, due to the possibility of TiO₂ visible-light sensitization by dyes, this might give rise to an uncertainty that minor part of photodecomposition may proceed via non-N-doping-induced visible-light photocatalysis (Kisch and Macyk 2002). Accordingly, the latest attempts in this nature have shifted their interests to non-colored dissolved organic compounds, such as 4-chlorophenol, phenol, 2-propanol, benzoic acid, trichloroethylene (TCE), etc. Various decomposition degree and rates were reported, of which most claimed to be satisfactory, and yet not directly comparable between studies. It should also be noted that photocatalytic decomposition of large

molecular weight organics in solution by N-doped TiO₂ nanoparticles has not yet been reported. This is mainly due to the fact that depending on different dissolved organic compounds, the degree and rate of total mineralization, i.e., decomposition of organic pollutants into harmless products, varies (Li et al. 2007). Supposedly, this could be greatly relieved by developing TiO₂/adsorbent composites, as it has a large capability of adsorbing degradation intermediates (Zhang et al. 2009, 2010, 2011). Further investigations in this aspect are certainly of great interests, especially in terms of water treatment applications. At the current stage, the feasibility of their applications is still restricted to dilute solutions.

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