

Catalytic performance and room temperature ferromagnetism of TiO₂ doped with non-metallic elements

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Abstract

Titanium dioxide (TiO₂) is regarded as one of the important semiconductor materials for the wide applications in the field of the solar water splitting, sewage disposal and spin electronics and so on. Therefore, doping with proper elements to improve and extend its scope of applications has become the focus of recent research fields. Comparatively speaking, the nonmetal elements can improve the performance of TiO₂ by reducing the band gap, improving the light absorbing capacity, and reducing the electron and hole recombination rates. In this paper, we mainly summarize the change of room temperature ferromagnetism and catalytic performance of TiO₂ doped with nonmetal elements via various preparation techniques. The review may contribute to the further studying and wider application of TiO₂.

Keywords: Titanium dioxide, ferromagnetism, catalytic performance.

1. Introduction

Titanium dioxide (TiO₂), as one of the most important metal oxides, which exhibits excellent photochemical activities such as ultraviolet absorption properties, photocatalysis, and acid catalysis properties, has attracted extensive attention. In 1972, Fujishima and Honda ^[1] reported that as a catalyst TiO₂ can decompose water to produce hydrogen in the first time. Then, the research work of preparations, structures, properties and applications of nano TiO₂ has a long-term development and becomes one of the hot topics in the semiconductor research field. At the same time, as a kind of diluted semiconductor materials with semiconducting and ferromagnetic properties at room temperature ^[2], TiO₂ nano materials attract great attention in the scientific research field, especially the potential application on the multifunction and spin electronic devices ^[3]. However, the band gap of intrinsic TiO₂ is about 3.2 eV,

and can only absorb ultraviolet light (<380 nm), unable to make full use of the energy of the visible light (400-750 nm) for about 43% of the solar spectrum ^[4].

Therefore, it is quite necessary to modify TiO₂ and enhance its characteristics. The early-stage research is about doping with transition metals to shrink the energy band. After the metal ions are doped, the conduction band of d orbital of the Ti atom and d orbital of the metal atom are overlapped, which reduces the band gap of TiO₂ (See as Fig.1.(b)), and TiO₂ becomes a catalyst by visible light irradiation ^[5]. Equally, nonmetal doping and metal doping have similar effects which can introduce an impurity level above the valence band. By visible light irradiation, the electrons can be excited from the impurity level to the conduction band, so that the catalytic performance and room temperature ferromagnetism of TiO₂ are improved ^[6] (See as Fig.1.(c)).

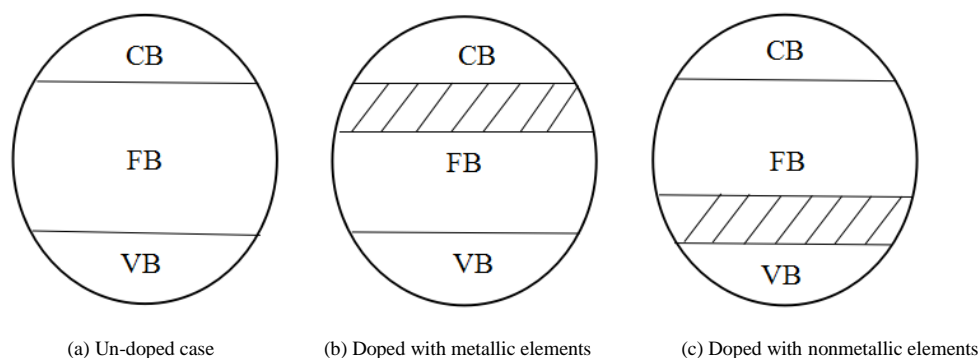


Figure 1. Diagram of energy band of TiO₂

However, metal elements could cause thermal instability and the electron trap which can reduce the photocatalytic efficiency of TiO₂ ^[4, 7]. Consequently, researchers start to consider some nonmetallic elements such as H, B, C, N, S,

P, and F etc. to sensitize TiO₂, which may bring unexpected results. This paper mainly reviews the development process and current research progress of TiO₂ doped with non-metal elements.

2. Catalytic performance

There is a large amount of literatures about the application of TiO₂ as photocatalysts, and it has been proved that doping with light factors can expand the absorption range of TiO₂ in the visible light. In terms of the doping mode, there are three kinds of ways to add the non-metallic atoms into crystal lattices. The first is to substitute the non-metallic atoms into O lattices, because the light elements with smaller atomic radius will not affect the stability of the TiO₂ crystal structure. The second is that the Ti atoms are replaced by non-metallic atoms. The third possibility is that the non-metallic atoms may be located at the interstitial sites.

The substitution of N is extensively studied and regarded as a relatively good effective dopant. For example, in 2001, Asahi et al.^[8] reported that an orbital hybridization phenomenon is observed after a small amount of N elements replace O in the lattices, which will shorten the band gap of TiO₂. Therefore, the rate of the photodegradation of methylene blue and gaseous acetaldehyde under sunlight irradiation is distinctly improved comparing to no-doped TiO₂. Nakamura et al.^[9] firstly proposed that the N-TiO₂ can cause the visible light response which is attributed to the formation of the intermediate band gap. Irie's work also supported the idea of forming intermediate band gap in N-TiO₂^[6]. Following the deepening of the field, the researchers began to propose different ideas, Diwaid et al.^[10] considered the interstitial N rather than substitutional N to produce the visible light response, interstitial N leads to the reduction of the threshold photon energy

for photochemistry from 3.0 eV to 2.4 eV. In contrast, substitutional nitrogen is inactive for lowering the photochemical threshold energy below the band-gap energy of rutile TiO₂. Additionally, Chen et al.^[11] prepared TiO₂ doped with C, N, and S by the high temperature oxidation method, which indicated that N-doping can change the crystal structure of TiO₂, and the band-edge absorption of N-TiO₂ is estimated as 415 nm (3.0 eV) which is close to the rutile-phase, but different to the pristine TiO₂ (390 nm).

Except nitrogen, Cristiana et al.^[12] used the DFT calculations to discuss TiO₂ doping with carbon. They considered that the oxygen environment affects on the doping effects, and concluded that under poor oxygen conditions and low carbon concentrations, the substitution of O with C and oxygen vacancies is favored. Whereas, under oxygen rich conditions, interstitial and substitutional (to Ti) C atoms are preferred. Furthermore, the carbon impurities can induce several localized occupied states in the band gap, which may interpret the red shift of the absorption edge under the visible light irradiation. Lin et al.^[13] have similar ideas that they prepared C-doped mesoporous by sol-gel method and found that the absorbance spectra of C-doped porous TiO₂ film exhibited a significant red shift to the visible region. Furthermore, the high photocatalytic activity of C-doped mesoporous TiO₂ film is a result of the size of mesopores in TiO₂.

The reviews in the above are all focused on the anatase and rutile phase of TiO₂ polymorphy. Actually, the brookite phase is proved possessing excellent photochemical activity, and for the F-doped

TiO₂, the sample which is composed of anatase and brookite phases shows a significant red shift [14]. Hui et al. [15] systematically studied the effects of the doping H, N, and the both on the electronic properties of TiO₂ via first-principles calculations. They found that the effect of the doping is phase-dependent. The interstitial H is superior to the substitutional H in reducing the band gap, while the N prefers the substitutional state. However, for rutile-TiO₂, the interstitial N atoms narrow the band gap to 1.76 eV. Moreover, for the case of N and H codoping, the substituted N and interstitial H are the best combination to enhance the electronic properties of codoped TiO₂, and can widely apply in water decomposition. Similar conclusions are also reported by Lan Mi [16] in 2007.

As a matter of fact, the research on the hydrogen production from the decomposition of TiO₂ has made great progress. Frites et al. [17] incorporated hydrogen to N-TiO₂ by electrochemically generating hydrogen gas under cathodic polarization in room temperature. With the increasing of the photocurrent density, the photoresponse towards water splitting reaction increases gradually. Recently, the research [18] concerned with H-brookite TiO₂ reported that comparing to the pristine brookite, the calculated density of states of H-brookite shows a narrowed bandgap and an increased electron density. It found that Ti₃⁺ plays an important role to enhance the photocatalytic activity under visible light in TiO_{2-x}. Therefore, Feng et al. [19] generated the stable and effective Ti₃⁺ substances in the TiO₂ surface layer by introducing interstitial B via sol-gel synthesis method. They found that interstitial B leads to the formation of

abundant and stable Ti₃⁺ species and forms two new groups of mid-gap states, which can promote acceleration of the photogenerated electron mobility to improve the solar-light photocatalytic activity of B-TiO₂ eventually. Xue et al. [20] studied B and N co-doped anatase TiO₂ and concluded that the presence of Ti–O–B–N and O–Ti–B–N are conducive to optimize the pore structure and enhance the photo response capacity.

In addition, doping with Fluorine, sulfur and phosphorus has also been investigated for years. For example, the fluorination of TiO₂ leads to the increase of the absorption coefficient for ultraviolet light and the high photo reactivity can expand its application to the use of window glass of buildings and automobiles [21, 22]. On the other hand, in the field of catalytic degradation, Periyat et al. [23] modified TiO₂ with sulfur via a simple methodology to extend the anatase phase stability. The sunlight photocatalytic activity is reflected in kinetic analysis who indicated that the rate constant values of S-doped TiO₂ have 10-fold greater photocatalytic activity compared to the undoped sample. As well as sulfur (S) dopant, the modified titania also has high activities for degradation of methylene blue in aqueous solution under irradiation of the wavelengths longer than 440 nm [24, 25]. Meanwhile, the S-doping can cause the photo-to-carrier conversion and narrowing of the energy band gap [26]. Hassiain Basha et al. [27] successfully prepared P-doped TiO₂ photocatalysts via sol-gel method and investigated the photocatalytic activity under visible light irradiation. As a result, it is found that the P-doped TiO₂ have outstanding photo-

catalytic properties under visible light irradiation^[28].

Recently, Kamani et al.^[29] reported the sonocatalytic degradation with N doped TiO₂ could remove refractory pollutants like humic acid from aqueous solution. They concluded that the lower band gap energy and well-structured anatase phase are important for high photocatalytic degradation. The sonocatalytic activity for humic acid degradation of synthesized N-doped TiO₂ is about 1.86 times higher than the pristine TiO₂. In addition, Huang et al.^[30] reported that the fluorinated TiO₂ significantly improved the degradation efficiency of formaldehyde. They revealed that the increase of degradation rate is due to the addition of F, which could improve the crystallinity and adsorption of particles significantly. Lin et al.^[31] prepared C-TiO₂ nano particles by a simple hydrothermal procedure, and the degradation of methylene blue demonstrated that the photocatalytic performance of C-TiO₂ is enhanced significantly.

3. Room temperature ferro-magnetism

The room temperature ferromagnetism (RTFM) of TiO₂ doped with transition metals is studied extensively. The samples exhibited semiconductor characteristics and ferromagnetic behavior at the room temperature. Meanwhile, the discovery of ferromagnetism of TiO₂ doped with nonmagnetic elements at the room temperature overthrows the possible influence of extrinsic ferromagnetism stemming from the formation of magnetic secondary phases.

Abduleziz et al.^[32, 33] prepared synthetic TiO₂ doped with nonmagnetic elements (N and C) via the low temperature hydrothermal method. The experimental results have significant M-H hysteresis loops for doped-TiO₂, and conclude that the doped-TiO₂ has a strong RTFM. Meanwhile, the reduction of saturation magnetization (Ms) after annealing indicated that the defect concentration is not the only magnetic source of ferromagnetic behavior of TiO₂ at the room temperature. However, Valentin et al.^[34] combined characterization methods and computer simulation to characterize the paramagnetic species present in N-doped anatase TiO₂ powders. Owing to the different preparation conditions, there are two kinds of structurally different nitrogen impurities: substitutional and interstitial N atoms in the TiO₂ anatase matrix. Also, Gomez-Polo et al.^[35] synthesized TiO₂ doped with N and C elements via sol-gel procedure. They found that the maximum values of Ms and remnant magnetization (Mr) is raised for the post-annealed sample in the vacuum and decreased for the N and C doping cases. The results indicate that the N-doped nanoparticles display ferromagnetic features at the room temperature. Sudhir et al.^[36] reported that they used ab initio electronic structure calculations to synthesize TiO₂ doped with N or F to analyse the electronic and magnetic properties. The results showed a robust magnetic ground state for N- and F- doped TiO₂ which possess a significant magnetic moment.

By radio frequency sputtering and DFT calculations, Drera et al.^[37] studied the effect of N-doping on the magnetic of TiO_{2-x} rutile thin films. The M-H hysteresis loop

showed that the Ms of N-doped sample is estimated as 30 emu/cm³, which is six times larger than no-doped samples. The results also showed that TiO₂ doped with N may form an impurity level as acceptor or donor level which leads to the reduction of energy gap in the rutile TiO₂. In addition, Bao et al.

[38] have successfully fabricated N-TiO₂ films with RTFM under N₂O atmosphere by pulse laser deposition. The results showed that N states in TiO₂ film strongly affect the ferromagnetism of the samples, and the results indicated that the replacement of O with N is the origin of ferromagnetism.

Table 1. Performances of TiO₂ doped with N, C and H by different preparation methods

Doped elements	Methods	Performances			References	Phase
		Parameters	Pristine	Doped		
N	Hydrothermal	Ms	0.007 emu/g	0.042	[33]	Anatase
		Hc	100 Oe	215		
	High temperature oxidation	Absorption edge	390 nm	415	[11]	
	Sol-gel	Band gap energy	3.09 eV	2.91	[29]	
	Radio-frequency sputtering	Saturation	5 emu/cm ³	30	[37]	
First-principle	Band gap energy	2.52 eV	1.76	[15]	Brookite	
C	Sol-gel	Size	3.0 nm	5.6	[13]	Anatase
	One-step "Green" synthetic	Band gap energy	3.10 eV	2.78	[40]	
	Temperature-programmed carbonization	Absorption wavelength	470 nm	700	[41]	
			400 nm	800	[42]	
Chemical modification						
H	Electro-chemically	Photo current Density	0.35 mA/cm ²	2.2	[17]	Brookite
	Hydrothermal	Photo current density	130 μA/cm ²	650	[18]	
		Band gap energy	3.35 eV	3.05		
	First-principle	Band gap energy	2.96 eV	2.81	[15]	Anatase
			2.91 eV	2.79		Rutile
			2.52 eV	2.39		Brookite

Based on the above analysis, in Table 1, we selected three representative non-metallic elements prepared via different methods and compared the change of the

performances before and after doping. From the table, we can clearly conclude that the room temperature ferromagnetism and photocatalytic properties of TiO₂ are

significantly improved after doping. For example, the property of the RTFM is connected to the increase of M_s and M_r ; the variation of the band gap and absorption wavelength reflect that the nonmetal elements doping improves the photocatalytic properties and photo degradation of TiO₂; the increase of photocurrent density implies the enhancement of hydrolysis ability of TiO₂ under the irradiation of sunlight. Furthermore, the changed size of the mesopores indicates nonmetal elements can form a new state which lies just above the valence band, which narrows the band gap of TiO₂ and makes the catalyst to absorb visible light efficiently^[13, 20].

In Fig.2, we compared the band gap energies for the before and after doping cases. Obviously, no matter of which element is doping, the band gap of the doped material will be reduced, which may be the reason for the improvement of TiO₂'s performances. Generally, in the process of doping, one "intermediate level" will be formed between the valence band and the conduction band, which will greatly diminish the band gap width of the doped-TiO₂ (See as Fig.1). On the other hand, this "intermediate level" will also prolong the residence time of the photo-generated electrons and holes to reduce the recombination rate to enhance the visible light response of the material eventually^[39].

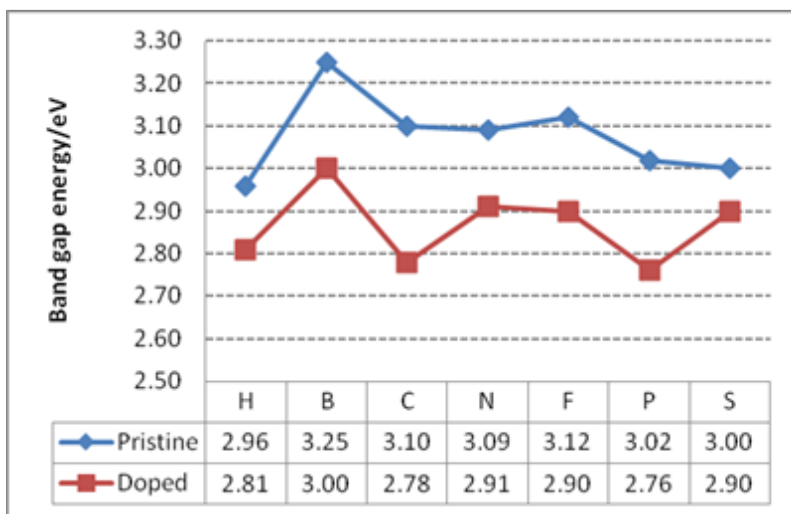


Figure 2. Energy band gap of pristine TiO₂ and doped TiO₂ with H^[15], B^[19], C^[39], N^[29], F^[14], P^[28] and S^[26]

4. Conclusions

This paper mainly investigated different non-metallic elements doped into TiO₂ via varieties of non-synthetic methods. In general, the form of performance changing is associated with the dopants,

preparations and the structures. Furthermore, the formation of spin-polarized states in the band gap enhances the magnetic performance while the formation of mid-gap states accompanied by a significant reduction of the band gap improves the photocatalytic activity and photocatalytic

property under the irradiation of sunlight.

In summary, the non-metal or nonmagnetic elements can significantly enhance the RTFM and catalytic performances. To obtain doped TiO₂ photocatalytic materials with the characteristics of high specific surface area, low recombination rate, high photocatalytic efficiency and thermal stability will be a new research interest in the future.

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References

- [1]. Fujishima A, Honda K. *Nature*. 238(1972):37–38.
- [2]. Kulkarni J S, Kazakova O, Holmes J D. *Applied Physics A*. 85(2006):277-286.
- [3]. Zhao Y, Feng P, Hui L, et al. *Journal of Physical Chemistry C*. 117(2013):21718-21723.
- [4]. Kisch H, Zang L, Lange C, et al. *Angewandte Chemie International Edition*. 37(2010):3034-3036.
- [5]. Yamashita H, Harada M, Misaka J, et al. *Catalysis Today*. 84(2003):191-196.
- [6]. Irie H, Watanabe Y, and Hashimoto K. *Journal of Physical Chemistry B*. 107(2003):5483-5486.
- [7]. Macyk W, Kisch H. *Chemistry*. 7(2001):1862-1867.
- [8]. Asahi R, Morikawa T, Ohwaki T, et al. *Science*. 293(2001):269-271.
- [9]. Nakamura R, Tomoaki Tanaka A, Nakato Y. *Journal of Physical Chemistry B*. 108(2004):10617-10620.
- [10]. Diwald O, Thompson T L, Zubkov T, et al. *Cheminform*. 35(2004):219-221.
- [11]. Chen X, Burda C. *Journal of the American Chemical Society*. 130(2008):5018-5029.
- [12]. Valentin C D, Gianfranco P A, Selloni A. *Chemistry of Materials*. 17(2006):6656-6665.
- [13]. Lin X, Rong F, Ji X, et al. *Microporous and Mesoporous Materials*. 142(2011):276-281.
- [14]. Yu J C, Yu J, Ho W, et al. *Cheminform*. 33(2002):3808-3816.
- [15]. Pan H, Zhang Y W, Shenoy V B, et al. *Journal of Physical Chemistry C*. 115(2011):12224-12231.
- [16]. Mi L, Xu P, Shen H, et al. *Applied Physics Letters*. 90(2007):171909-1-3.
- [17]. Frites M, Khan S U M. *Electrochemistry Communications*. 11(2009):2257-2260.
- [18]. Choi M, Lee J H, Jang Y J, et al. *Scientific Reports*. 6(2016):36099-1-12.
- [19]. Feng N, Liu F, Huang M, et al. *Scientific Reports*. 6(2016):34765-1-19.
- [20]. Xue H, Jiang Y, Yuan K, et al. *Journal of Computational and Theoretical Nanoscience*. 18(2016):213-220.
- [21]. Yamaki T, Sumita T, Yamamoto S. *Journal of Materials Science Letters*. 21(2002):33-35.
- [22]. Hattori A, Tada H. *Journal of Sol-Gel Science and Technology*. 22(2001):47-52.
- [23]. Periyat P, Pillai S C, McCormack D E, et al. *Journal of Physical Chemistry C*. 112(2008):7644-7652.
- [24]. Ohno T, Mitsui T, Matsumura M. *Chemistry Letters*. 32(2003):364-365.
- [25]. Umebayashi T, Yamaki T, Tanaka S, et al. *Chemistry Letters*. 32(2003):330-331.

- [26]. Umebayashi T, Yamaki T, Yamamoto S, et al. *Journal of Applied Physics*. 93(2003):5156-5160.
- [27]. Natori H, Kobayashi K, Takahashi M. *Journal of Oleo Science*. 58(2009):389-394.
- [28]. Shi Q, Yang D, Jiang Z, et al. *Journal of Molecular Catalysis B Enzymatic*. 43(2006):44-48.
- [29]. Kamani H, Nasserri S, Khoobi M, et al. *Journal of Environmental Health Science and Engineering*. 14(2016):1-9.
- [30]. Huang D, Liao S, Quan S, et al. *Journal of Materials Science*. 42(2007):8193-8202.
- [31]. Lin C, Song Y, Cao L, et al. *Nanoscale*. 5(2013):4986-4992.
- [32]. Ablat A, Wu R, Mamat M, et al. *Solid State Communications*. 243(2016):7-11.
- [33]. Ablat A, Wu R, Jian J, et al. *Materials Letters*. 132(2014):86-89.
- [34]. Valentin C D, Pacchioni G, Selloni A, et al. *Journal of Physical Chemistry B*. 109(2005):11414-11419.
- [35]. Gomez-Polo C, Larumbe S, Pastor J M. *Journal of Applied Physics*. 113(2013):17B511-1-3.
- [36]. Pandey S K, Choudhary R J. *Journal of Physics Condensed Matter An Institute of Physics Journal*. 23(2011):276005-1-11.
- [37]. Drera G, Mozzati M C, Galinetto P, et al. *Applied Physics Letters*. 97(2010):012506-1-3.
- [38]. Bao N N, Fan H M, Ding J, et al. *Journal of Applied Physics*. 109(2011):127201-1-4.
- [39]. Pan L, Zou J J, Liu X Y, et al. *Industrial and Engineering Chemistry Research*. 51(2012): 12782-12786.
- [40]. Dong F, Wang H, and Wu Z. *Journal of Physical Chemistry C*. 113(2009):16717-16723.
- [41]. Li Y, Hwang D S, Lee N H, et al. *Chemical Physics Letters*. 404(2005):25-29.
- [42]. Lee S, Yun C Y, Mi S H, et al. *Korean Journal of Chemical Engineering*. 25(2008):892-896.