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# Photocatalytic degradation of methylene blue on Fe<sup>3+</sup>-doped TiO<sub>2</sub> nanoparticles under visible light irradiation

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**Abstract** Fe<sup>3+</sup>-doped TiO<sub>2</sub> composite nanoparticles with different doping amounts were successfully synthesized using sol-gel method and characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM) and ultraviolet-visible spectroscopy (UV-Vis) diffuse reflectance spectra (DRS). The photocatalytic degradation of methylene blue was used as a model reaction to evaluate the photocatalytic activity of Fe<sup>3+</sup>/TiO<sub>2</sub> nanoparticles under visible light irradiation. The influence of doping amount of Fe<sup>3+</sup> ( $\omega$ : 0.00%–3.00%) on photocatalytic activities of TiO<sub>2</sub> was investigated. Results show that the size of Fe<sup>3+</sup>/TiO<sub>2</sub> particles decreases with the increase of the amount of Fe<sup>3+</sup> and their absorption spectra are broaden and absorption intensities are also increased. Doping Fe<sup>3+</sup> can control the conversion of TiO<sub>2</sub> from anatase to rutile. The doping amount of Fe<sup>3+</sup> remarkably affects the activity of the catalyst, and the optimum efficiency occurs at about the doping amount of 0.3%. The appropriate doping of Fe<sup>3+</sup> can markedly increase the catalytic activity of TiO<sub>2</sub> under visible light irradiation.

**Keywords** Fe<sup>3+</sup>-doped, TiO<sub>2</sub> nanoparticles, nature light, methylene blue, photocatalytic activity

## 1 Introduction

It has shown a capacious prospect to generate clean environment using photocatalyst. Particularly, TiO<sub>2</sub> is known to be one of the most effective photocatalysts because of its nontoxicity, low cost and high photocatalytic activities, etc. However, the large band gap ( $E_g = 3.2$  eV) in TiO<sub>2</sub>, activated

only by ultraviolet (UV) light, low efficiency in utilizing solar energy and high recombination rate of the photo-generated electron/hole pairs result in the low efficiency in utilizing photon and hinder its further application in industry. In order to solve these problems, many methods have been applied to the modification of TiO<sub>2</sub>, such as modification by noble metal [1], semiconductor junctions [2], polymer- [3] and transition metal-doping [4]. Among these methods, transition metal-doping has been studied extensively, and this technology has been applied to the degradation of dye, nitric oxide, polythene film and organic pollutants, etc. However, there are no agreements on the mechanism and effects of the dopants on photocatalytic activities about transition metal-doping till now [5–7], even for the same metal-doping the results are different under different experimental conditions. For example, the optimal amount of Fe<sup>3+</sup> is 3.0%, 0.5% and 0.0% respectively in the works of Gao et al. [8], Choi et al. [4] and Yu and Cheng [9]. Actually, it is impossible to make a comparison between the results under different experimental conditions because of the effects on the catalytic performance of numerous factors, such as synthesis conditions, work up processes, reaction conditions, surface states and electron quality, etc.

In this paper, Fe<sup>3+</sup>-doped TiO<sub>2</sub> composite nanoparticles with different doping amounts ( $\omega$ : 0.00%–3.00%) were successfully synthesized by a sol-gel method and characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM) and ultraviolet-visible spectroscopy (UV-Vis) diffuse reflectance spectra (DRS). The influence of the doping amount of Fe<sup>3+</sup> on photocatalytic activities was also investigated by the degradation of methylene blue (MB) dye solution under nature light.

## 2 Experimental

### 2.1 Materials

All chemicals were of analytical grade and were used as received without further purification: tetrabutyl titanate, anhydrous ethanol, ferric nitrate, methylene blue (MB) and deionized water.

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## 2.2 Characterizations

The crystal structures, morphologies and spectral properties of the Fe<sup>3+</sup>-doped TiO<sub>2</sub> composite nanoparticles were characterized and analyzed by BD-86 X-ray diffraction (XRD, Japan), JEM-1200EX transmission electron microscope (TEM, Japan) and Shimadzu 754 UV-Vis spectrophotometer. The TEM samples were prepared by dispersing the Fe<sup>3+</sup>-doped TiO<sub>2</sub> composite nanoparticles in ethanol under ultrasonic, dropping them onto a carbon coated copper grid, and then drying them in the air.

## 2.3 Preparation of photocatalysts

Tetrabutyl titanate was added to anhydrous ethanol to form a clear solution, and then a solution of ferric nitrate containing hydrochloric acid solution was added dropwise to the above solution with vigorously stirring, thus resulting in a stable sol. The sol was then aged for several days and dried to gel. The gel was sintered at 500°C for 2 h to obtain Fe<sup>3+</sup>-doped TiO<sub>2</sub> nanoparticles. By changing the concentration of ferric nitrate solution, Fe<sup>3+</sup>-doped TiO<sub>2</sub> composite nanoparticles with different doping amounts ( $\omega$ : 0.00%–3.00%) were successfully prepared.

## 2.4 Measurement of photocatalytic activity

The Photocatalytic activities of the Fe<sup>3+</sup>-doped TiO<sub>2</sub> composite nanoparticles were evaluated by the photocatalytic degradation of MB. Then, 50.0 mg of sample was added to 50.0 mL of MB solution with a concentration of 10.0 mg/L in a 100.0 mL beaker and the system was stirred under sunlight. After a certain time, 5 mL of suspension solution was centrifuged to remove the photocatalyst and the absorption value ( $A_t$ ) of the solution at 664 nm (the maximum absorption wavelength of MB) was determined. The degradation efficiency ( $D_t$ ) of MB solution was calculated as follows:  $D = (A_0 - A_t) / A_0 \times 100\%$ , in which  $A_0$  is the absorption value of 10.0 mg/L MB solution. The photocatalytic activities of these samples were evaluated by the changes of  $D_t$  with the reaction time ( $t$ ).

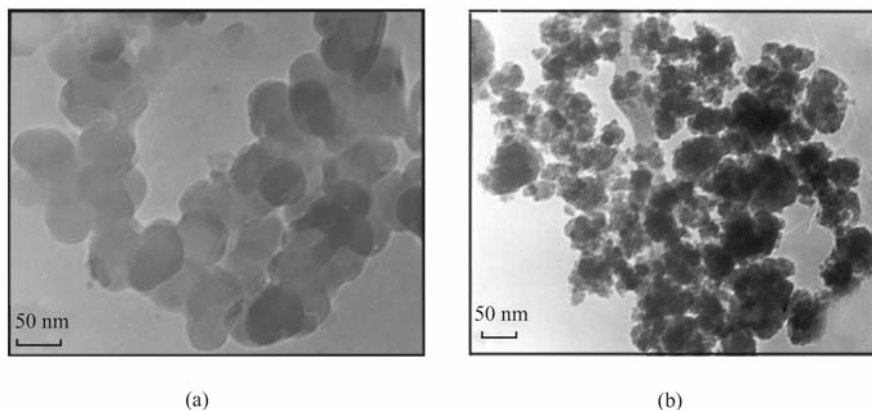
## 3 Results and discussion

### 3.1 TEM observation

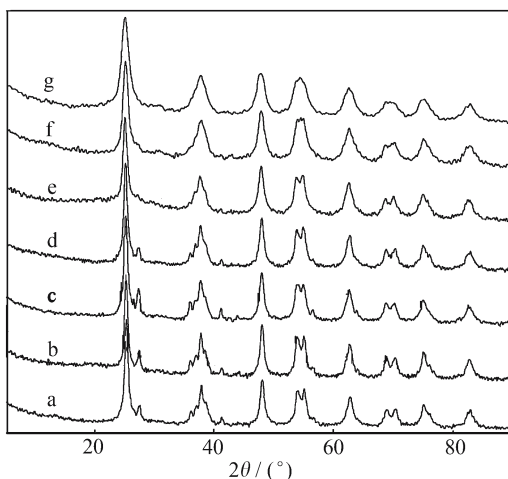
From Fig. 1(a) and (b), the average particle sizes can be seen at different doping amounts of Fe<sup>3+</sup> which are respectively about 40 and 10 nm when the amounts are 0.3% and 3.0%. The sizes obviously decrease with the increase of the doping amount of Fe<sup>3+</sup> and a few films exist while the amount is about 3.0%. These results reveal that the Fe<sup>3+</sup> doping restrains the growth of the TiO<sub>2</sub> crystal grains, resulting in a decrease in particle size [10] and an increase in the surface energy, which may cause agglomeration between the crystal grains.

### 3.2 XRD analysis

Figure 2 shows the XRD patterns of TiO<sub>2</sub> nanoparticles with different doping amounts of Fe<sup>3+</sup> ( $\omega$ : 0.00%–3.00%). It can be seen that (1) TiO<sub>2</sub> is a mixture of anatase and rutile phases while the doping amount of Fe<sup>3+</sup> is lower than 0.5%, and rutile phase disappears with the further increase of doped Fe<sup>3+</sup>. In the range of 0.0–0.5%, the percentage of rutile phase increases with the increase of the doping amount of Fe<sup>3+</sup> and reaches a maximum value (14.9%) when the amount is about 0.3%, and then decreases with the further increase of the amount. These results reveal that the doping Fe<sup>3+</sup> controls the crystalline conversion of TiO<sub>2</sub> from rutile to anatase phase. (2) The diffraction peaks are remarkably broadened. There are some factors affecting the broadening of diffraction peaks, such as the grain size, the defect of the crystal, and so on. From the results of the sample's TEM, it can be concluded that the small grain size is one of the factors resulting from the broadening of diffraction peaks. (3) The characteristic peaks of Fe<sub>2</sub>O<sub>3</sub> are not observed in the studied range of doping amount of Fe<sup>3+</sup>. One of the reasons may be the homogeneous dispersion of Fe<sup>3+</sup> in the TiO<sub>2</sub> lattice because of the similar ion radii of Fe<sup>3+</sup> and Ti<sup>4+</sup>, and the other is that the amount of doped Fe<sup>3+</sup> is so low that it can not be detected by XRD or the weak diffraction peaks of Fe<sub>2</sub>O<sub>3</sub> are shielded by the broadened diffraction peaks of TiO<sub>2</sub>.



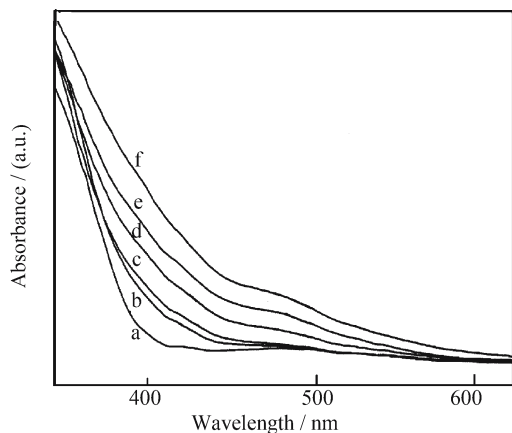
**Fig. 1** TEM images of TiO<sub>2</sub> composite nanoparticles containing (a) 0.3% and (b) 3.0% Fe<sup>3+</sup>



**Fig. 2** XRD patterns of  $\text{TiO}_2$  nanoparticles with different amounts of  $\text{Fe}^{3+}$ -doped a) 0.0%; b) 0.1%; c) 0.3%; d) 0.5%; e) 1.0%; f) 2.0%; g) 3.0%

### 3.3 UV-Vis analysis

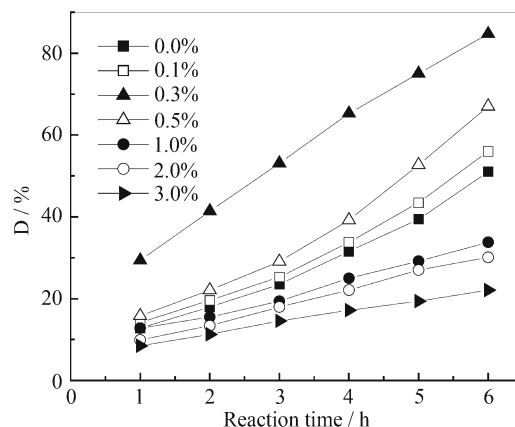
Figure 3 shows the UV-Vis spectra of  $\text{Fe}^{3+}/\text{TiO}_2$  nanoparticles with different doping amounts of  $\text{Fe}^{3+}$ . The absorption edge of these samples shows a remarkable shift to the visible range and the intensity increases with the increase of the amount. This is mainly due to that  $\text{Fe}^{3+}$  inserts into the structure of titanium dioxide, locates at interstices or occupies some of the  $\text{Ti}^{4+}$  lattice sites because of diffusion and transfer of the ions, and forms impurity interim levels between valence and conduction bands in  $\text{TiO}_2$ . The impurity interim levels form impurity energy band, which overlaps with the  $\text{TiO}_2$  conduction band as the amount of impurity increases [11], consequently the transition of the photo-generated electron in the semiconductor to the conduction band requires a lower energy than the transition to the intrinsic absorption band and a lower energy of the photon may excite the transition of the photo-generated electron. Therefore, the semiconductor may absorb the light energy of long wavelength, produce the red shift and broaden the range of the absorption spectra.



**Fig. 3** UV-Vis spectra of  $\text{Fe}^{3+}/\text{TiO}_2$  nanoparticles with different doping amounts of  $\text{Fe}^{3+}$ -doped a) 0.1%; b) 0.3%; c) 0.5%; d) 1.0%; e) 2.0%; f) 3.0%

### 3.4 Photocatalytic activity

Figure 4 shows decolorization efficiencies of MB solution on the  $\text{Fe}^{3+}/\text{TiO}_2$  complex particles with different doping amounts of  $\text{Fe}^{3+}$  as a function of reaction time. It can be found that the photocatalytic activity firstly increases with the increase of the doping amount of  $\text{Fe}^{3+}$ , reaches a maximum activity at about the amount of 0.3% and then decreases with the further increase of the amount. The photocatalytic activity is lower than pure  $\text{TiO}_2$  when the doping amount of  $\text{Fe}^{3+}$  increases to 1.0% upwards. These results indicate that the photocatalytic activity of  $\text{TiO}_2$  can be improved by doping an appropriate amount of  $\text{Fe}^{3+}$  into  $\text{TiO}_2$ . The photocatalytic activity of  $\text{TiO}_2$  is improved most effectively when the doping amount of  $\text{Fe}^{3+}$  is about 0.3%, and the decolorization efficiency of MB solution reaches 84.9% when the reaction time is 6 h, which showed a 34% increase as compared to the pure  $\text{TiO}_2$  with a decolorization efficiency of 51.2%, and is 1.67 times of that of the pure  $\text{TiO}_2$ . It was reported in a similar system by Yan et al. [12] that the photocatalytic activity had only a 13.5% increase as compared to the un-doped  $\text{TiO}_2$ . To summarize the experimental results above, the main factors affecting the photocatalytic activity in our experimental conditions may be the crystal and electron structures. This result is consistent with the study of Gao et al. [13], whose study indicated that the separation between photo-generated electron and hole in the anatase crystal could be accelerated effectively when a thin layer of rutile crystal grows on the surface of anatase crystal, and this may improve the photocatalytic activity. Hence, the photocatalytic activity is optimal when the doping amount of  $\text{Fe}^{3+}$  is 0.3%.

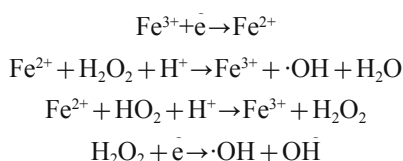


**Fig. 4** Decolorization efficiencies of MB solution on the  $\text{Fe}^{3+}/\text{TiO}_2$  complex particles with different amounts of  $\text{Fe}^{3+}$ -doped

Choi et al. [4] considered that the transition from  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$  corresponds to the transition from  $d^5$  to  $d^6$ , and  $\text{Fe}^{2+}$  is relatively unstable due to the loss of exchange energy and tends to return to  $\text{Fe}^{3+}$ , resulting in the release of the trapped electron becoming easy. However, the  $\text{Fe}^{2+}/\text{Fe}^{3+}$

energy level lies close to  $Ti^{3+}/Ti^{4+}$  level. As a consequence of this proximity, the trapped electron in  $Fe^{2+}$  can be easily transferred to a neighboring surficial  $Ti^{4+}$  and combines with oxygen molecule adsorbed on the surface to form  $O_2^-$  and finally  $\cdot OH$ , thus the number of active groups is increased and the photocatalytic activity is improved correspondingly.

Furthermore,  $H_2O_2$  may be produced in the photocatalytic reactions on  $TiO_2$  as well. According to Fenton reactive mechanism, the coexistence of  $Fe^{2+}$  and  $H_2O_2$  in an acidic condition may produce  $\cdot OH$ , which has strong oxidizing power. Hence, it can be inferred that the following reactions may exist simultaneously in the reactive system.



However, the photocatalytic activity of  $TiO_2$  does not increase linearly as the doping amount of  $Fe^{3+}$  increases, so the reactions above are unlikely the decisive rate processes.

The experimental results indicate the particle size of the photocatalyst decreases as the amount of doped  $Fe^{3+}$  increases under the same processing temperature, and the absorption range of the UV-Vis spectrums becomes broader with the increase of the doping amount of  $Fe^{3+}$ . However, the photocatalytic activity of  $TiO_2$  does not show a linear increasing relationship simply as the doping amount of  $Fe^{3+}$  increases. Therefore, the main factor influencing the variety of the activity is not the particle size of and absorption range of the spectrums. It was reported on the basis of electron spin resonance (ESR) spectrum in the literature [6] that the promotion of the photocatalytic activity of  $TiO_2$  by doping  $Fe^{3+}$  should attribute to the effect of  $Fe^{3+}$  as an irreversible hole trappers.

We consider that the vacancies introduced in the crystal lattice by  $Fe^{3+}$  make the surface charges unbalanced. To keep the electro-neutrality, the surfaces of  $TiO_2$  should adsorb more  $OH^-$  ions, which may react with photo-generated hole  $h^+$  and form active  $\cdot OH$ , and hence promote the photocatalytic efficiency. Therefore, the concentration of hole carrier may increase under visible light irradiation with increasing doping amount of  $Fe^{3+}$  and the photocatalytic efficiency may be improved accordingly. However, on one hand, when the dopant concentration reaches a definite level, the excessive doping of  $Fe^{3+}$  which acts as an acceptor impurity will make the concentration of the hole in the valence band increase, the surface barrier energy reduce, the transition layer thicker, the ability of separating hole and electron weaker, the electron-hole combination easier and eventually the photocatalytic efficiency decrease. On the other hand, when the doped  $Fe^{3+}$  is excessive, the  $Fe^{3+}$  entered into the crystal lattice has become saturated, so the surplus  $Fe^{3+}$  combines with  $TiO_2$  as a separate phase and decreases the photocatalytic activity of  $TiO_2$ . Thus, it can be inferred from our experimental results

the vacancies in the above crystal play an important role in the improvement of the photocatalytic activity.

## 4 Conclusion

$Fe^{3+}$ -doped  $TiO_2$  composite nanoparticles with different doping amounts ( $\omega$ : 0.00%–3.00%) are successfully synthesized using sol-gel method under the same condition. The results indicate that the size of the  $TiO_2$  nanoparticles decreases as the doping amount of  $Fe^{3+}$  increases, the doping of  $Fe^{3+}$  can control the conversion of  $TiO_2$  from anatase to rutile, broaden the width of the diffraction peaks of  $TiO_2$ , and produce a red shift in the band gap transition and an increase of absorption in visible range. It is important that an appropriate doping of  $Fe^{3+}$  (about 0.3% in our experiment) can markedly improve the catalytic activity of  $TiO_2$  under sunlight irradiation, and the catalytic activity is 1.67 times of that of the pure  $TiO_2$ . The main factors affecting the catalytic activity in our experimental conditions are concluded to be the phase and electron structures of  $TiO_2$ . It is of great significance for using solar energy as the irradiation source to improve the catalytic activity of  $TiO_2$  obviously by appropriately doping  $Fe^{3+}$  into  $TiO_2$ . The introduction of  $Fe^{3+}$  ions in  $TiO_2$  nanoparticles is responsible not only for reducing the photo-generated hole-electron recombination rate but also for utilizing solar energy sufficiently. Hence, it is hopeful to use  $Fe^{3+}$ -doped  $TiO_2$  as an effective photocatalyst in the degradation of organic contaminants, cleanup of aqueous contaminants especially the aqueous contaminants of dye and so on in the fields of environmental decontamination.

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