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Photocatalytic degradation of methylene blue on Fe³⁺-doped TiO₂ nanoparticles under visible light irradiation

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Abstract Fe³⁺-doped TiO₂ 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 Fe³⁺/TiO₂ nanoparticles under visible light irradiation. The influence of doping amount of Fe³⁺ (ω : 0.00%–3.00%) on photocatalytic activities of TiO₂ was investigated. Results show that the size of Fe³⁺/TiO₂ particles decreases with the increase of the amount of Fe³⁺ and their absorption spectra are broaden and absorption intensities are also increased. Doping Fe³⁺ can control the conversion of TiO₂ from anatase to rutile. The doping amount of Fe³⁺ remarkably affects the activity of the catalyst, and the optimum efficiency occurs at about the doping amount of 0.3%. The appropriate doping of Fe³⁺ can markedly increase the catalytic activity of TiO₂ under visible light irradiation.

Keywords Fe³⁺-doped, TiO₂ nanoparticles, nature light, methylene blue, photocatalytic activity

1 Introduction

It has shown a capacious prospect to generate clean environment using photocatalyst. Particularly, TiO₂ 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 TiO₂, 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 TiO₂, 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 Fe³⁺ 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, Fe³⁺-doped TiO₂ composite nanoparticles with different doping amounts (ω : 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 Fe³⁺ 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^{3+} -doped TiO_2 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^{3+} -doped TiO_2 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^{3+} -doped TiO_2 nanoparticles. By changing the concentration of ferric nitrate solution, Fe^{3+} -doped TiO_2 composite nanoparticles with different doping amounts (ω : 0.00%–3.00%) were successfully prepared.

2.4 Measurement of photocatalytic activity

The Photocatalytic activities of the Fe^{3+} -doped TiO_2 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^{3+} 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^{3+} and a few films exist while the amount is about 3.0%. These results reveal that the Fe^{3+} doping restrains the growth of the TiO_2 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_2 nanoparticles with different doping amounts of Fe^{3+} (ω : 0.00%–3.00%). It can be seen that (1) TiO_2 is a mixture of anatase and rutile phases while the doping amount of Fe^{3+} is lower than 0.5%, and rutile phase disappears with the further increase of doped Fe^{3+} . In the range of 0.0–0.5%, the percentage of rutile phase increases with the increase of the doping amount of Fe^{3+} 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^{3+} controls the crystalline conversion of TiO_2 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_2O_3 are not observed in the studied range of doping amount of Fe^{3+} . One of the reasons may be the homogeneous dispersion of Fe^{3+} in the TiO_2 lattice because of the similar ion radii of Fe^{3+} and Ti^{4+} , and the other is that the amount of doped Fe^{3+} is so low that it can not be detected by XRD or the weak diffraction peaks of Fe_2O_3 are shielded by the broadened diffraction peaks of TiO_2 .

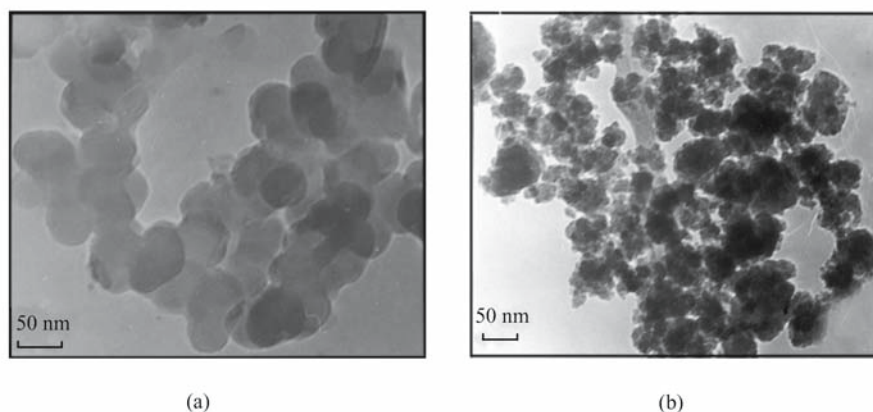


Fig. 1 TEM images of TiO_2 composite nanoparticles containing (a) 0.3% and (b) 3.0% Fe^{3+}

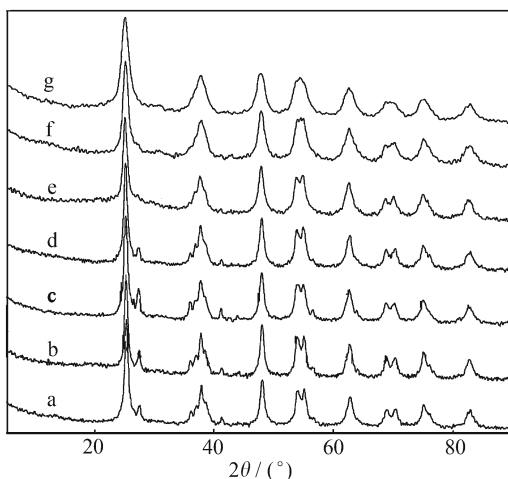


Fig. 2 XRD patterns of TiO_2 nanoparticles with different amounts of Fe^{3+} -doped a) 0.0%; b) 0.1%; c) 0.3%; d) 0.5%; e) 1.0%; f) 2.0%; g) 3.0%

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 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 Fe^{3+} inserts into the structure of titanium dioxide, locates at interstices or occupies some of the Ti^{4+} lattice sites because of diffusion and transfer of the ions, and forms impurity interim levels between valence and conduction bands in TiO_2 . The impurity interim levels form impurity energy band, which overlaps with the 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.

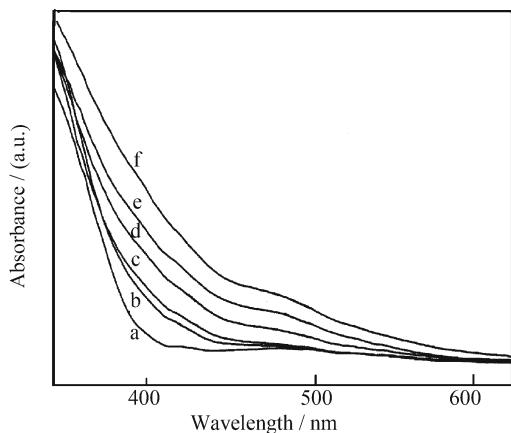


Fig. 3 UV-Vis spectra of $\text{Fe}^{3+}/\text{TiO}_2$ nanoparticles with different doping amounts of Fe^{3+} -doped a) 0.1%; b) 0.3%; c) 0.5%; d) 1.0%; e) 2.0%; f) 3.0%

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 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 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 TiO_2 when the doping amount of Fe^{3+} increases to 1.0% upwards. These results indicate that the photocatalytic activity of TiO_2 can be improved by doping an appropriate amount of Fe^{3+} into TiO_2 . The photocatalytic activity of TiO_2 is improved most effectively when the doping amount of 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 TiO_2 with a decolorization efficiency of 51.2%, and is 1.67 times of that of the pure 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 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 Fe^{3+} is 0.3%.

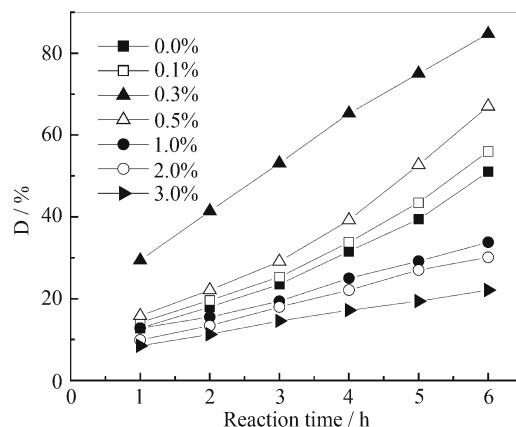
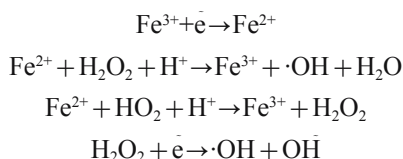


Fig. 4 Decolorization efficiencies of MB solution on the $\text{Fe}^{3+}/\text{TiO}_2$ complex particles with different amounts of Fe^{3+} -doped

Choi et al. [4] considered that the transition from Fe^{3+} to Fe^{2+} corresponds to the transition from d^5 to d^6 , and Fe^{2+} is relatively unstable due to the loss of exchange energy and tends to return to 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 $\text{Ti}^{3+}/\text{Ti}^{4+}$ 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 $\cdot\text{OH}$, 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 $\cdot\text{OH}$, 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 $\cdot\text{OH}$, 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 (ω : 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 contaminates, cleanup of aqueous contaminates especially the aqueous contaminates of dye and so on in the fields of environmental decontamination.

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