

Fe-doped ZnO synthesized by parallel flow precipitation process for improving photocatalytic activity

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Abstract. ZnO and Fe-doped ZnO photocatalysts with different molar ratio of Fe/Zn (0.25%, 0.50%, 0.75% and 1.0%) were synthesized by a parallel flow precipitation method. The structures and morphologies of as-synthesized samples were tested by the X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM), Brunauer-Emmett-Teller (BET) surface area, respectively. The results reveal that Fe-doped ZnO has higher BET surface area than pure ZnO. XRD spectra of Fe-doped ZnO photocatalysts display merely the characteristic peaks of hexagonal wurtzite structure. The morphologies of ZnO vary from the regular hexagonal prism rod to irregular short rod and flake when Fe is introduced into ZnO particles. For degradation of RhB dye, the 0.50%Fe photocatalyst possesses the most outstanding photocatalytic performance under visible light radiation, which is more than ten times as high as the pure ZnO.

1. Introduction

ZnO is a promising photocatalyst due to its high catalytic efficiency, strong oxidative activity, and no toxicity [1]. However, during the photodegradation process of organic dye pollutants, photoexcited electrons (e^-) and holes (h^+) fast recombination and photocorrosion make ZnO exhibit poor photocatalytic performance. To promote the photocatalytic activity of ZnO, varieties of metal ions have been doped into ZnO, such as Co^{2+} , La^{3+} , Ce^{3+} , etc [2]. Modification of ZnO-based photocatalyst with these metal ions can extend response range of light and promote photo-induced charge carriers to separate, which may improve its photocatalytic activity effectively [3]. Fe-doped ZnO had been synthesized by various approaches, among of which, the parallel flow precipitation technology is an extremely attractive one for mass production in industry and low cost, removing the need for complication equipments [4, 5]. Furthermore, the influence of Fe-doping on photodegradation rate of ZnO photocatalyst synthesized using a parallel flow precipitation method has been seldom concerned. The primary driving force in this study is to concentrate on the influence of Fe-doping on morphology, structure, crystal grain size as well as the relationship between them and photodegradation rate of ZnO samples synthesized using the parallel flow precipitation process. The photocatalytic activity was tested by degradation of Rhodamine B (RhB).



2. Experimental section

All chemical reagents of analytical grade were obtained from Damao Chemical Reagent Factory and used without further purification. Fe-doped ZnO were synthesized in the following parallel flow precipitation process. 7.35 g $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and different amount of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were completely dissolved in 30 mL of deionized water and marked A (molar ratio of Fe/Zn was 0%, 0.25%, 0.50%, 0.75% and 1.0%). With two constant flow pumps, solution A and $\text{NH}_3 \cdot \text{H}_2\text{O}$ (1 mol/L) were simultaneously infused into the same reactor under constant stirring and the pH was controlled at 6.8. After being washed, precipitates obtained were dried by spray and then calcined for 2 h at 673 K in the muffle oven. The photocatalysts with various molar ratio of Fe/Zn were labeled as ZnO, 0.25%Fe, 0.50%Fe, 0.75%Fe and 1.0%Fe, respectively. The Brunauer-Emmett-Teller (BET) surface area was tested using a NOVA 2000e automatic surface analyzer (Quantachrome). The morphologies and dimensions of samples were studied by a Hitachi S-4800 field emission scanning electron microscopy (FE-SEM). X-ray diffraction (XRD) patterns were carried out by a D/max2200VPC diffractometer with Cu-K α (wavelength 0.15406 nm, 30 mA and 40 kV). The photocatalytic activity of photocatalysts (50 mg) prepared was assessed using the degradation of 50 mL RhB solution (10 mg/L).

3. Results and discussion

The XRD patterns of the pure and Fe-doped ZnO photocatalysts are shown in figure 1. All samples obtained have a hexagonal wurtzite structure according to the standard spectrum (JCPDS no. 36-1451). Additionally, no other peaks were observed and the peak positions were not changed greatly with the adding of Fe. However, the full width at half maximum (FWHM) of pure ZnO was narrower than that of Fe-doped ZnO, illustrating the crystal size of ZnO decreased as introducing of Fe. This is because the ionic radius of Fe (0.064 nm) is different from Zn (0.074 nm), and a finite solid solution can be formed when Fe substituted for Zn [6]. Thus, the lattice shrinkage was increased and crystal growth was impeded with the increasing of Fe content. According to the Scherrer equation, the average crystallite size of ZnO, 0.25%Fe, 0.50%Fe, 0.75%Fe and 1.0%Fe is 97 nm, 91 nm, 76 nm, 85 nm and 89 nm, respectively.

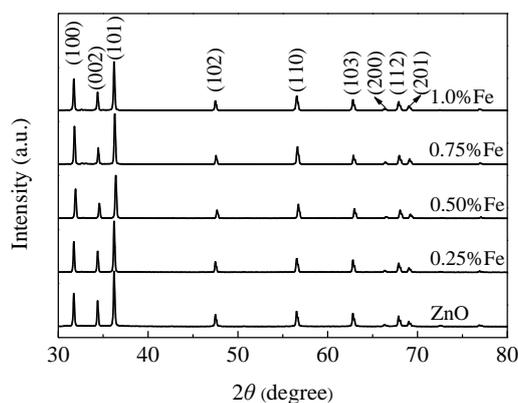


Figure.1 XRD patterns of ZnO and Fe-doped ZnO.

Table 1. Specific surface area of the synthesized photocatalysts.

Photocatalysts	ZnO	0.25%Fe	0.50%Fe	0.75%Fe	1.0%Fe
S_{BET} (m^2/g)	16.9	19.7	30.3	23.6	20.4

The BET surface area of Fe-doped ZnO samples is summarized in table 1. The specific surface area tends to increase firstly and then decline with the adding of Fe, the maximum is $30.3 \text{ m}^2/\text{g}$ of 0.50%Fe, which is almost double of that of the pure ZnO. This may be attributed to Fe substituted for Zn into the

crystal lattice of ZnO and restrained the growth of ZnO. It is generally accepted that the photocatalytic process is mainly related to the adsorption and desorption of pollutant molecules on the surface of photocatalyst [7]. The larger specific surface area can supply the more reactive adsorption and desorption sites for the photocatalytic degradation of organic pollutants.

FE-SEM photographs of the pure and Fe-doped ZnO photocatalysts are shown in figure 2. The images display that undoped ZnO is composed of typical hexagonal prism and average grain size is 2 μm in length and 1 μm in diameter approximately. Compared with undoped ZnO, the crystal size of Fe-doped ZnO decreased and their morphologies varied from regular hexagonal prism rod to irregular short rod and flake when Fe was introduced into ZnO particles. Among these Fe-doped ZnO, average crystal size of the 0.5%Fe was minimum, which was in accordance with the result of XRD.

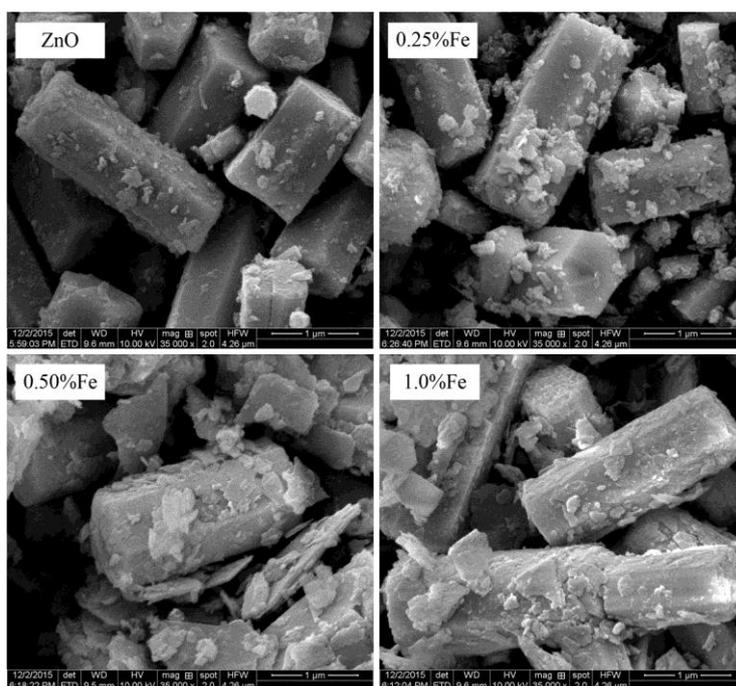


Figure 2. FE-SEM images of ZnO and Fe-doped ZnO.

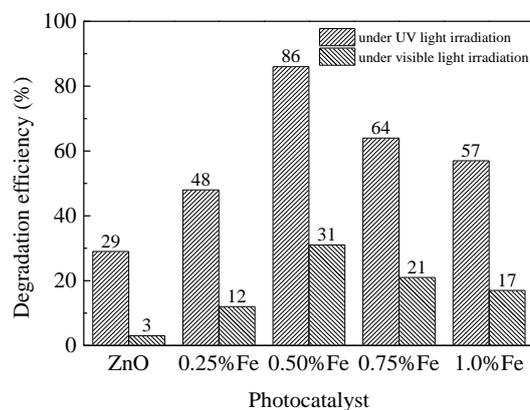


Figure 3. Photocatalytic performance of the synthesized photocatalysts for degradation of RhB.

The photodegradation rate of the pure and Fe-doped ZnO is presented in figure 3. As described in figure 3, all Fe-doped ZnO photocatalysts displayed better photocatalytic activity than that of pure ZnO under both UV and visible light illumination. Furthermore, the 0.50%Fe photocatalyst exhibited the highest photocatalytic performance under visible light radiation, which was more than ten times as high as the undoped ZnO. It is well known that ZnO-based photocatalysts are exposed to the light of energy higher than its band gap, the photoexcited e^-/h^+ pairs can be produced, then further react with O_2 and H_2O to produce the highly reactive superoxide radical anions ($\cdot O_2^-$) and hydroxyl radicals ($\cdot OH$) [8, 9]. These active species (h^+ , $\cdot O_2^-$ and $\cdot OH$) can react with the organic pollutants near or on the surface of photocatalyst, causing the decomposition of pollutants into CO_2 and H_2O . Fe into the ZnO lattice introduced inter-band trap site, which captured photoexcited e^- and reduced the recombination speed of h^+ and e^- , and the charge separation efficiency was improved. High charge separation efficiency enhanced the formation of these active species, which benefited for the photodegradation of RhB dye. Here, the improved photodegradation rate of Fe-doped ZnO material is attributed to the decreased crystal size, the increased specific surface area and the enlarged separating rate of photogenerated charge carriers.

4. Conclusions

Fe-doped ZnO were successfully synthesized by a parallel flow precipitation process. The as-synthesized Fe-doped ZnO photocatalysts were merely comprised of hexagonal wurtzite structure and exhibited much higher photocatalytic performance in degradation of RhB solution under both UV and visible light radiation than pure ZnO. The 0.50%Fe photocatalyst possessed the best photocatalytic activity, which could be ascribed to the decreased crystal size, the increased specific surface area and the enlarged separating rate of photogenerated charge carriers. Doping ZnO with Fe is an effective way for enhancing its photocatalytic activity.

References

- [1] B İkizler and S M Peker 2014 *Thin Solid Films* **558** 149
- [2] W Raza, M M Haque and M Muneer 2014 *Appl Surf Sci* **322** 215
- [3] R Saleh and N F Djaja 2014 *Superlattices Microstruct* **74** 217
- [4] X H Yu, D W Meng, C Z Liu, X W He, Y Q Wang and J Xie 2012 *Mater Lett* **86** 112
- [5] S S Yi, J B Cui, S Li, L J Zhang, D J Wang and Y H Lin 2014 *Appl Surf Sci* **319** 230
- [6] B P Kafle, S Acharya, S Thapa and S Poudel 2016 *Ceram Int* **42** 1133
- [7] J Z Li, J B Zhong, X Y He, S T Huang, J Zeng, J J He and W L Shi 2013 *Appl Surf Sci* **284** 527
- [8] S S Xiao, L Zhao and J S Lian 2014 *Catal Lett* **144** 347
- [9] M Rezapour and N Talebian 2014 *Ceram Int* **40** 3453