Enhanced photocatalytic property of Fe doped ZnO nanoparticles prepared by sol-gel

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Abstract. Fe doped ZnO nanoparticles with different Fe concentrations 0.5%-2% were synthesized by sol-gel route. X-ray diffraction (XRD) results revealed that the prepared nanoparticles presented the hexagonal wurtzite structure. No impure peaks were found. Scanning electron microscope (SEM) and transmission electron microscopy (TEM) confirmed the nanoparticle morphology of Fe doped ZnO. UV-vis spectrophotometer showed the high absorption both in UV and visible region. Photocatalytic activity was calculated by degrading methyl orange (MO) aqueous solution under solar light. ZnO with 0.5 at% Fe showed the highest photocatalytic performance. It was observed that MO dyes undergo 91% photodegradation under 4 h solar irradiation. The results show that the prepared Fe doped ZnO nanoparticles can be effectively helpful for the photocatalytic applications.

1. Introduction

With increasing drinking water supplies being contaminated by organic compounds, human health is in grave danger. So an eco-friendly and sustainable solution is urgently required. At this point, many advanced researches have been focused on the photocatalytic degradation [1-3]. ZnO, with a direct bandgap, possesses chemical and physical stability, low cost and powerful oxidation strength [4]. However, ZnO has not yet acted as an ideal photo catalyst due to its wide bandgap energy (3.37 eV) and rapid recombination of photogenerated electron-hole pairs [5]. Hence how to reduce its bandgap energy is the major goal to achieve.

Numerous studies have been reported that doping transition metal element plays an important role in extending the absorption of ZnO in visible region [6], such as Cu [7], Mn [8], Co [9, 10], Ag [11] and Pd [12] doped ZnO. Compared to these relatively expensive or toxic transition metals, Fe is superior to them thanks to its economical and eco-friendly traits [6]. Hui et al. [13] found that Fe doped ZnO nanoparticles exhibited higher photo activity than undoped ZnO. Kayani et al. [14] confirmed that Fe doped ZnO can effectively decrease ZnO band gap to enhance its photocatalytic performance.

In this study Fe doped ZnO nanoparticles were synthesized by sol-gel route which includes a doping concentration of Fe (0.5, 1, 2%) for the fabrication of Fe doped ZnO nanoparticles. Fe doped ZnO nanoparticles were characterized by X-ray diffraction (XRD), field emission scanning electron microscope (SEM), transmission electron microscopy (TEM) and UV-vis spectrophotometer. The obtained results were used to analyse the photocatalytic activity. The different percentages of Fe doped ZnO all present remarkable photocatalytic efficiency. The 0.5% Fe doped ZnO almost photodegrades MO entirely under 4 h sunlight exposure with 91% photodegradation.
2. Experimental section

2.1. The fabrication of Fe-ZnO
In a typical synthesis procedure, Zn(NO₃)₂·6H₂O and Fe(NO₃)₃·9H₂O were added into distilled water with molar ratio in 0.5, 1 and 2 at %, respectively. C₆H₈O₇·H₂O was then added into the ion solution with pH adjusted at 8. The mixed solution was then stirred in 80°C water bath until the formation of a sol. The sol was preheated in an oven at 100°C for 12 h to evaporate the solvent and remove the organic residuals. The dried sol was then annealed at 600°C for 3 h at ambient air to obtain Fe₀.₀₀₅Zn₀.₉₉₅O, Fe₀.₁Zn₀.₉₀O and Fe₀.₂Zn₀.₉₈O.

2.2. Characterization
The structure of the samples was characterized by X-ray diffraction (XRD) using a Dmax-β diffractometer with nickel-filtered Cu Kα radiation. The surface morphology was taken on a Model SU8010 field emission scanning electron microscope (FESEM). Transmission electron microscopy (TEM) images were taken via a TF20. The absorption spectra of samples were investigated by UV–vis diffuse reflectance spectra (DRS) with a UV–vis spectrophotometer (Shimadzu UV-2550) swept on a scale from 200 to 600 nm with BaSO₄ as the reference.

2.3. Photo catalysis
The degradation of MB and MO under sunlight was served as the photocatalytic performance of the prepared samples. Experiments were carried out in a sprightly sunshine day. In each test, 60 mg of the photo catalysts was added into 60 mL of 10 mg/L MO and MB aqueous solutions, respectively. The above suspension was then magnetically stirred in the dark for 30 min to reach the adsorption-desorption equilibrium. During the outdoor irradiation, about 4 mL of the suspension was taken out for every 0.5 h and centrifuged before being measured at 464 and 664 nm according to the maximum absorption wavelengths of MO and MB, respectively. The decolorization efficiency (%) is calculated as the following the equation: Degradation rate (%) = (A₀ − A)/A₀ × 100 [15], where A₀ and A are initial absorbance and changed absorbance of dye after sunlight irradiation, respectively.

3. Result and discussion
The crystallinity and crystal phases of the synthesized nanoparticles were examined by X-ray diffraction (XRD). As shown in Fig. 1, the well-defined diffraction peaks at 31.8°, 34.5°, 36.2°, 47.6°, 56. 8° are well consistent with crystal planes of ZnO (100), (002), (101), (102) and (110), respectively. The above diffraction peaks are well matched with the quartzite hexagonal phase of ZnO and are in accordance with JCPDS No. 03-0888. No other peaks, like Fe₂O₃, Fe₃O₄ and Zn-ferrite, are found in the obtained pattern, which indicated that Fe did not change the crystal structure of host material and Fe has successfully been doped in the lattices of ZnO.
The morphologies of synthesized Fe doped ZnO nanoparticles were characterized by FESEM and TEM. It is observed in Fig. 1(a), (b) and (c) that all kinds of Fe doped ZnO show the structure of nanoparticles, which are termed as NPs. These NPs were grown in very high density with varying sizes. With the increase of Fe content, the NPs seem to gather together. Especially, Fe$_{0.02}$Zn$_{0.98}$O, the highest Fe content, exhibits some small bulks compared to Fe$_{0.005}$Zn$_{0.995}$O with separated nanoparticles. In Fig. 1, the sizes of these NPs are about 250 nm, and some little particles are attached to the surface of Fe doped ZnO. Fig.1 (d) shows the EDS spectrum of Fe$_{0.005}$Zn$_{0.995}$O. Except oxygen, iron and zinc elements, no other undesirable elements are detected, which confirmed the purity of the prepared Fe doped ZnO. The TEM images of Fe$_{0.005}$Zn$_{0.995}$O are shown in Fig. 3(a) and (b). The observed structure is consistent with SEM results. Due to the growth of high density, some agglomeration and overlapping of NPs are observed in TEM micrograph.

**Figure 1.** XRD pattern of pure ZnO and Fe doped ZnO nanoparticles

**Figure 2.** SEM morphologies of (a) Fe$_{0.005}$Zn$_{0.995}$O, (b) Fe$_{0.01}$Zn$_{0.99}$O and (c) Fe$_{0.02}$Zn$_{0.98}$O, (d) EDS spectrum of Fe$_{0.005}$Zn$_{0.995}$O.
Figure 3. TEM morphologies of Fe_{0.005}Zn_{0.995}O.

The optical activity of Fe doped ZnO NPs is characterized by UV-vis spectroscopy at room temperature. As shown in Fig. 4(a), the synthesized Fe doped ZnO nanoparticles remain the high absorption in UV region. While compared to ZnO with little response to visible light, all the prepared Fe-ZnO/ZnS nanoparticles exhibit remarkable absorption in visible region, which contributes to the enhanced photocatalytic activity. In addition, the bandgap energy ($E_g$) of Fe doped ZnO NPs, shown in Fig. 4(b) was calculated from the plot between ($\alpha h\nu$) $^2$ versus $h\nu$ according to Tauc’s equation [16]. In the amplified image, the $E_g$ Fe doped ZnO nanoparticles are all about 3.05 eV, compared to the bigger one of reported ZnO (3.37 eV) [17].

Figure 4. UV–vis spectrum of Fe-doped ZnO nanoparticles

In order to evaluate the photocatalytic performance of the prepared samples, the degradation of MO under solar light irradiation was provided. As is shown in Fig. 5(a), all Fe doped ZnO photo catalysts possessed considerable degradation when exposed to sunlight. it can be seen in the picture that the Fe_{0.005}Zn_{0.995}O exhibited the highest photo efficiency, which degraded about 91% MO after 4 h exposure, compared to Fe_{0.01}Zn_{0.99}O (89.4%) and Fe_{0.02}Zn_{0.98}O (67.4%). Considering the evaporation of the solvent in the sweltering day, the final photocatalytic degradation tends to be better. Moreover, by fitting the experimental data with Langmuir–Hinshelwood model, the degradation kinetics of MO was investigated and is expressed in equation $\ln \frac{A}{A_0} = kt$ where k was the rate constant. As shown in Fig. 6(b), the apparent rate constants by degrading MO of Fe_{0.005}Zn_{0.995}O, Fe_{0.01}Zn_{0.99}O, and Fe0.02Zn0.98O were 0.6241, 0.5858 and 0.2984 min$^{-1}$, indicating that Fe_{0.005}Zn_{0.995}O runs faster during photocatalytic process, while the excess doping Fe is blaming for reducing the photocatalytic active sites on the surface of ZnO. The results are consistent with the former spectra.
Figure 5. (a) Photodecolorization and (b) reaction kinetics of MO under solar illumination by Fe doped ZnO particles

The photocatalytic mechanism of Fe doped ZnO has been widely discussed. Under the solar irradiation, the process of photocatalytic process can be discussed as followings [18]:

\[
\text{ZnO} + h\nu \rightarrow e^- + h^+
\]

\[
\text{Fe}^{3+} + e^- \rightarrow \text{Fe}^{2+}
\]

\[
\text{Fe}^{2+} + \text{O}_2^- \rightarrow \text{Fe}^{3+} + \text{O}_2
\]

\[
\text{Fe}^{3+} + h^+ \rightarrow \text{Fe}^{4+}
\]

\[
\text{Fe}^{4+} + \text{OH}^- \rightarrow \text{Fe}^{3+} + \text{OH}^-
\]

Under solar irradiation, the photo-induced electron hole pairs were generated, the photogenerated electrons are partly transported into Fe$^{3+}$ to form Fe$^{2+}$, and Fe$^{3+}$ ions receive the holes to form Fe$^{4+}$. This process largely suppresses the combination of electron hole pairs. Thus, the photo activity of ZnO is effectively enhanced. However, neither Fe$^{4+}$ or Fe$^{2+}$ ions are stable, so Fe$^{4+}$ or Fe$^{3+}$ will be captured by OH$^-$ and O$_2^-$ radicals to generate OH$^-$ and O$_2^-$, which can degrade the organic pollutant effectively. However, with the increase of Fe concentration, the electrons will migrate to Fe$^{4+}$ ions instead of Fe$^{3+}$ ions. So Fe$^{3+}$ ions will act as the recombination centers resulting in depreciating the photocatalytic activity of ZnO nanoparticles.

4. Conclusion
Fe doped ZnO nanoparticles were successfully synthesized by sol-gel route and the effect of Fe doping concentration 0.5%-2% on photo activity was discussed. All the Fe doped ZnO nanoparticles exhibit remarkable absorption in visible light region and show excellent degradation of MO under solar irradiation. Moreover, the Fe$_{0.005}$Zn$_{0.995}$O reaches the highest photodegrading rate (91%), which benefits from the suppressive recombination of electron-hole pairs and enhanced absorption.

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