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Preparation and photocatalytic properties of magnetically reusable Fe₃O₄@ZnO core/shell nanoparticles



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HIGHLIGHTS

SEVIEI

- Fe₃O₄@ZnO core/shell nanoparticles were successful synthesized.
- The core/shell nanoparticles show excellent photocatalytic activity.
- Fe₃O₄ core ensures core/shell nanoparticles reuse easily in waste water treatment.

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G R A P H I C A L A B S T R A C T

Magnetically reusable $Fe_3O_4@ZnO$ core/shell nanoparticles were synthesized by a simple two-step chemical method. Almost no decrease in photocatalytic efficiency was observed even after recycling six times.



ABSTRACT

Fe₃O₄@ZnO binary nanoparticles were synthesized by a simple two-step chemical method and characterized using various analytical instruments. TEM result proved the binary nanoparticles have core/ shell structures and average particle size is 60 nm. Photocatalytic investigation of Fe₃O₄@ZnO core/shell nanoparticles was carried out using rhodamine B (RhB) solution under UV light. Fe₃O₄@ZnO core/shell nanoparticles showed enhanced photocatalytic performance in comparison with the as prepared ZnO nanoparticles. The enhanced photocatalytic activity for Fe₃O₄@ZnO might be resulting from the higher concentration of surface oxygen vacancies and the suppressing effect of the Fe³⁺ ions on the recombination of photoinduced electron–hole pairs. Magnetization saturation value (5.96 emu/g) of Fe₃O₄ @ZnO core/shell nanoparticles is high enough to be magnetically removed by applying a magnetic field. The core/shell photocatalytic can be easily separated by using a commercial magnet and almost no decrease in photocatalytic efficiency was observed even after recycling six times.

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1. Introduction

* Corresponding authors. Fax: +86 434 3294566. E-mail addresses: jhyang1@jlnu.edu.cn (J. Yang), lixiuyan@126.com (X. Li). In the last two decades, photocatalysis in the presence of semiconductors caused a wide range of concern because it can be used in environmental protection [1-4]. Among those



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semiconductors, ZnO is well-known as an excellent candidate for photocatalytic reaction owing to its high photocatalytic activity, environmental compatible feature and relatively low cost [5,6].

Due to photocatalytic process mainly occurs on surface of ZnO photocatalysts, powder ZnO which have large specific surface area were utilized in wastewater treatment usually [3,7,8]. However, an imperative problem to be solved in industry applications of powder ZnO photocatalysts is efficient separation of these fine ZnO micro/nanoparticles from treated water. Traditional separation methods always cost too much and may result in secondary pollution caused by photocatalyst loss [9]. Magnetic carriers provide a very efficient and convenient method for separating and recycling catalysts by using external magnetic fields [10]. Up to now, most magnetic photocatalysts have two functional parts at least: a magnetic component (γ -Fe₂O₃ or Fe₃O₄) with the separation function via an external magnetic field; the second part is the photocatalytic component with a photocatalytic function, such as SnO₂, ZnO or TiO₂ nanoparticles [11–13]. These heterogeneous catalysts have been proved to be efficient in both separation and recycle [14]. For instance, Fe₃O₄/Ag/SnO₂ core-shell structured particles can be removed using an external magnetic field and their photocatalytic efficiency can still be maintained at 95.74%, even after eight cycles of use [11]. Thus, develop magnetic photocatalysts with efficient reusability became a hot research subject in photocatalytic area [15].

In addition, the introduction of magnetic carriers may result in the catalytic activity decrease attribute to the decrease of active ingredient in photocatalyst system [16]. Therefore, semiconductor shells with high photocatalytic performance were synthesized to counteract the negative effect of inactive magnetic core [17]. Deposition of noble metal can enhance photocatalytic activity of magnetically reusable photocatalyst obviously [16,18,19]. Li et al. reported RhB in solution can be removed completely by Fe₃O₄@SiO₂@TiO₂@Pt after 20 min UV irradiation while Fe₃O₄@SiO₂@TiO₂ spent 25 min under the same condition [19]. But expensive cost for noble metal restricted it application in industry. To decrease the running cost, increase the concentration of surface defect can enhance activity of ZnO photocatalytic efficiently and was considered as an economic method [20,21]. Wang et al. reported that the oxygen vacancies can facilitate the photodecomposition of 2,4-dichlorophenol under visible light irradiation by ZnO photocatalyst [22]. Enlightened by former studies, it could be an effective route to obtain high photocatalytic performance catalyst by introducing oxygen defects.

Herein, we report our recent research on the synthesis of Fe_3O_4 @ZnO core/shell nanoparticles. The photocatalytic activities of the binary composites were evaluated using the degradation of RhB as a model reaction. It is found that Fe_3O_4 @ZnO core/shell nanoparticles show excellent photocatalytic activity for degrading RhB in comparison with as prepared ZnO. The enhanced photocatalytic activity was attributed to the high concentration of oxygen vacancies and the presence of Fe^{3+} ions in the core/shell catalyst.

2. Experimental

2.1. Materials and chemicals

Ferric chloride hexahydrate (FeCl₃• 6H₂O), ferrous chloride tetrahydrate (FeCl₂• 4H₂O), sodium hydroxide (NaOH), zinc acetate dihydrate (Zn(Ac)₂• 2H₂O), ethylalcohol (C₂H₅OH) were purchased from Sinopharm Chemical Reagent Co. Ltd and used as received. Deionized water (resistivity > 18.0 M Ω cm) was using throughout the experiment.



Scheme 1. Schematic illustrations of the fabrication of Fe_3O_4 (a), ZnO (b) and Fe_3O_4 (@ZnO (c).



Fig. 1. XRD patterns of synthesized Fe₃O₄ (a) (the line in below), ZnO (b) (the middle line), and Fe₃O₄@ZnO (c) (the upper line); the inset image is magnifying image of the select area in curve (c).

2.2. Synthesis of Fe_3O_4 nanoparticles

Fe₃O₄ nanoparticles were synthesized through a coprecipitation method. The fabrication process was depicted in Scheme 1a. As shown in Scheme 1a, FeCl₃• 6H₂O (6 mmol, 1.622 g) and FeCl₂• 4H₂O (3 mmol, 0.597 g) were dissolved in deionized water (200 ml). After stirring for 40 min at 55 °C, 100 ml NaOH solution (0.24 mol L⁻¹) was added to the resulting complex dropwise. Then the reaction mixture was heated at 60 °C for 1 h under mechanical



Fig. 2. SEM images of Fe_3O_4 (a), ZnO (b) and $Fe_3O_4@ZnO$ (c); TEM images of Fe_3O_4 (d), ZnO (e) and $Fe_3O_4@ZnO$ (f); SEAD image of Fe_3O_4 (g) and $Fe_3O_4@ZnO$ (h); HRTEM images of Fe_3O_4 (i, j), ZnO (k) and $Fe_3O_4@ZnO$ (l).

stirring, producing a black suspension. The $\rm Fe_3O_4$ were magnetically collected, washed with ethanol and deionized water, and then dried.

2.3. Synthesis of ZnO nanoparticles

As illustrated in Scheme 1b, ZnO nanoparticles were synthesized by a hydrothermal method. Briefly, $Zn(Ac_2) \cdot 2H_2O$ (10 mmol, 2.195 g) and NaOH (20 mmol, 0.8 g) were dissolved in 30 ml deionized water respectively at first. Then the NaOH solution was added into the $Zn(Ac_2) \cdot 2H_2O$ solution dropwise under stir. The mixture solution was transferred into a Teflon-lined reactor maintained at 170 °C for 10 h. Subsequently, the system was cooled to room temperature. The obtained precipitation after cooling down to room temperature was filtered off, washed three times by deionized water and ethanol, and dried at 60 °C for 10 h.

2.4. Synthesis of Fe₃O₄@ZnO core/shell nanoparticles

As shown in Scheme 1c, $Fe_3O_4@ZnO$ core/shell nanoparticles were prepared based on the synthesis of ZnO. For the preparing of $Fe_3O_4@ZnO$ core/shell nanoparticles, Fe_3O_4 (2 mmol, 0.463 g) was added into the precursor in the process of hydrothermal synthesis ZnO. The following steps are the same with the procedure for preparing ZnO nanoparticles described in 2.3.



Fig. 3. (a) PL spectra of the synthesized ZnO (a-I) and Fe₃O₄@ZnO (a-II) core/shell nanoparticles; Gaussian fit results of the 420–750 nm emissions of ZnO nanoparticles (b), Fe₃O₄@ZnO core/shell nanoparticles (c) with the original curves in black, the Gaussian fit showing in red, and the green lines showing the fitted peaks. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

2.5. Characterization

XRD (MAC Science, MXP18, Japan), FESEM (Hitachi S4800), TEM (JEOL JEM-2100HR, 200 kV), PL (Renishaw inVia micro-PL spectrometer, 325 nm, He–Cd laser), VSM (Lake Shore 7407) and UV– vis spectrophotometer (UV-5800PC, Shanghai Metash Instruments Co., Ltd) were used to characterize the crystal structure, morphologies, magnetic and optical properties of the synthesized samples.

2.6. Photocatalytic degradation of RhB

At the beginning, 60 mg of the synthesized products were dispersed in 60 mL of the RhB aqueous solution (7 mg L^{-1}) and the mixed solution was stirred in the dark for 15 min until reaching the adsorption equilibrium. Then, the mixture solutions were irradiated under a high-pressure Hg lamp (250 W, wavelength centered at 365 nm). The concentration reduction of RhB during photocatalytic experiment was recorded by UV–vis spectrophotometer.

3. Results and discussion

The crystalline phase and structure of Fe_3O_4 , ZnO, and Fe_3O_4 @ZnO are studied by XRD analysis. As shown in Fig. 1a, all of the identified peaks in the XRD pattern can be attributed to magnetite Fe_3O_4 , based on the standard data for magnetite (JCPDS no. 19-0629). All the diffraction peaks in the Fig. 1b belong to the wurtzite phase ZnO (JCPDS no. 36-1451), indicating that ZnO have a wurtzite structure. The blue curve (Fig. 1c) and it magnifying image of



Fig. 4. (a) Adsorption changes of RhB aqueous in the presence of Fe₃O₄@ZnO, (b) Degradation efficiency versus reaction time for ZnO and Fe₃O₄@ZnO.



Scheme 2. A proposed photocatalytic reaction mechanism of the Fe₃O₄@ZnO.

the select area shows two sets of diffraction peaks for $Fe_3O_4@ZnO$ well indexed to hexagonal wurtzite ZnO and magnetite Fe_3O_4 . No additional peaks are observed, which confirms that the sample only contained nanocrystalline ZnO and Fe_3O_4 . But only base on the XRD result we can not confirm the combination mode of the



Fig. 5. Room-temperature magnetic hysteresis loops of Fe_3O_4 (a) –I, $Fe_3O_4@ZnO$ (a) –II; the inset image in (a) is the magnetic separation and redispersion process of $Fe_3O_4@ZnO$, (b) six cycles of the removal of RhB over $Fe_3O_4@ZnO$ samples under UV irradiation.

binary compound.

To investigate the morphology, particle size and crystalline structure of the as synthesized samples, SEM images of Fe₃O₄, ZnO and Fe₃O₄@ZnO together with TEM images and the corresponding HRTEM and SAED are shown in Fig. 2. From SEM and TEM images of three samples (Fig. 2a-f), we can observe the average particle sizes of Fe₃O₄, ZnO and Fe₃O₄@ZnO are 7 nm, 50 nm and 60 nm, respectively. The SAED image (Fig. 2g) and HRTEM image (Fig. 2j) further prove the synthesized Fe₃O₄ have a magnetite structure. The HRTEM (Fig. 2k) for ZnO shows clear crystal lattice distance which belong to (100) planes of wurtzite phase ZnO (JCPDS no. 36-1451). The selected area electron diffraction (SAED) pattern of Fe₃O₄@ZnO core/shell structure is presented in Fig. 2h. The diffraction dot displayed in the SAED patterns supports the presence of ZnO in the synthesized core/shell structure. It index to the (100) plane of hexagonal ZnO corresponding to JCPDS Card no. 36-1451. The SAED pattern also show the diffraction rings of different planes of magnetite Fe₃O₄ (JCPDS 16-0629) confirming the existence of Fe_3O_4 in the nanostructures. The HRTEM image (Fig. 21) of Fe₃O₄@ZnO shows a core/shell structure and the crystal lattice distances of the core and shell belong to magnetite Fe₃O₄ and wurtzite phase ZnO, respectively. Combining with the result of XRD characterization, we can confirm the final obtained binary compound were $Fe_3O_4@ZnO$ core/shell nanoparticles.

In order to study the feature of electron-hole pairs on the surface of photocatalysts, photoluminescence spectra (PL) of as synthesized ZnO and Fe₃O₄@ZnO core/shell nanoparticles (λ_{ex} =325 nm) were illustrated in Fig. 3. Both PL spectra in Fig. 3a consisted of a sharp UV emission peak ($\lambda = 380$ nm) and one broad peak in the visible region (λ =450–700 nm). The sharp UV emission band generally assigned as a near-band-edge emission band and the position agrees well with the literature [23,24]. The broad emission in the visible-light region is associated to ZnO surface detects, in which oxygen vacancies are the most accepted defects [25–27]. Changes in the green emission intensity have been associated to changes in the concentration of the oxygen vacancies reported in the literature. In our study, by using Gaussian Fitting the visible emission in spectra can be fitted into green emission $(\lambda = 543 \text{ nm})$ and yellow emission $(\lambda = 588 \text{ nm})$ as shown in the Fig. 3b and c. The intensity of green emission for Fe₃O₄@ZnO core/ shell nanoparticles is obviously stronger in comparison with ZnO nanoparticles. It means more oxygen vacancies existed on the surface of Fe₃O₄@ZnO core/shell nanoparticles. Wang et al. reported that the increased surface oxygen vacancies decreased the surface recombination centers, and improved the charge separation efficiency [21].

The results of photodegradation RhB are shown in Fig. 4b. Without any catalyst, only a slow decrease in the concentration of RhB was detected under UV irradiation. When $Fe_3O_4@ZnO$ was added as photocatalyst, 99.3% RhB in aqueous solution could be eliminated after 60 min of UV irradiation (Fig. 4b-III). ZnO can eliminate 92.6% RhB in aqueous solution under the same UV irradiation time (Fig. 4b-II).

In many researches on semiconductor photocatalysis, bigger particle sizes always lead to weaker photocatalytic activity [28]. But in our case Fe₃O₄@ZnO with bigger particle size shows enhanced photocatalytic activity compare with ZnO. That might result from two reasons. The concentration of surface oxygen vacancies was considered as a vital factor to determine the photocatalytic performance of ZnO photocatalyst [21,29,30]. Surface oxygen vacancies can trap photoinduced electrons during the photocatalytic process and then prevent the recombination of photogenerated electron–hole pairs. In addition, oxygen species (such as O_2 , OH^-) could be adsorbed by surface oxygen vacancies easily. After reacting with photogenerated carriers, those oxygen species were transformed into $\bullet O_2^-$ and $\bullet OH$ which can accelerate the photocatalysis process.

The enhanced photocatalytic activity of Fe₃O₄@ZnO is also related to the presence of Fe³⁺ ions in the hybrid nanoparticles. Ambrus' work proved Fe³⁺ ions in Fe₃O₄ can act as a photogenerated electron-trapping site to prevent the fast recombination of photoinduced charge carriers and prolong their lifetime [31]. As shown in Scheme 2, the photoinduced electron in the conduction band of ZnO can be captured by Fe³⁺ ions in this study. This will result in the formation of Fe²⁺ ions, which are more active in comparison with Fe³⁺ ions. Then Fe²⁺ ions would react with the O₂ dissolved in the reaction solution to generate Fe³⁺ ions and \bullet O₂⁻ radicals. These \bullet O₂⁻ radicals can destroy the structure of various organic pollutants, degrading them into non-toxic carbon dioxide and water [32].

Easy magnetic separation and recycle are vitally important for the application of photocatalyst in industry. To investigate magnetic property of as synthesized samples, magnetic hysteresis loops of Fe₃O₄ and Fe₃O₄@ZnO measured at 300 K are presented in Fig. 5a. Both samples have superparamagnetic behavior because almost no remanence or coercivity was observed from the magnetic hysteresis loops. After coated with ZnO, the magnetization saturation value (M_S) of Fe₃O₄@ZnO (Fig. 5a-II) decreases. The decrease in M_S value can be attributed to the influence of grain boundary on the properties of nanograined polycrystals [13]. As shown in the inset of Fig. 5a, the M_S value of Fe₃O₄@ZnO (5.96 emu/g) (Fig. 5a-II) is still high enough to be magnetically separated by applying a magnetic field. It indicates that the core/ shell photocatalyst can be separated and reused in waste water treatment easily.

To study the reusability of the synthesized $Fe_3O_4@ZnO$ core/ shell nanoparticles further, the $Fe_3O_4@ZnO$ was separated by applying a magnetic field after the photodegradation of RhB in aqueous solution. The core/shell photocatalyst was recycled for another five times under the same conditions after simple washing and drying. As shown in Fig. 5b, no obvious decrease was detected in all recycling experiments. It indicates that the as synthesized $Fe_3O_4@ZnO$ core/shell photocatalyst have excellent stability and reusability.

4. Conclusions

In summary, Fe₃O₄@ZnO core/shell nanoparticles were prepared by a simple two-step chemical method. The magnetization saturation value of the core/shell nanoparticles (5.96 emu/g) is sufficient high for magnetic separation when applied as reusable catalyst in waste water treatment. Fe₃O₄@ZnO exhibited enhanced photocatalytic activities than those of the pure ZnO nanoparticles. Surface oxygen vacancies and the presence of Fe³⁺ ions in binary composite codetermine final photocatalytic activity of Fe₃O₄@ZnO core/shell nanoparticles.

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