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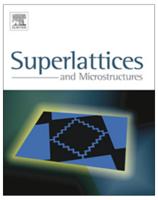

Preparation and photocatalytic application of Zn—Fe_2O_4@ZnO core–shell nanostructures

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ABSTRACT

In this study, nanohallow Zn—Fe_2O_4 microspheres were synthesis by $ZnCl_2$, $FeCl_3{\cdot}6H_2O$ and ammonium acetate using the hydrothermal method. Then, Zn—Fe_2O_4@ZnO core–shell structured spheres were prepared by using immobilization of ZnO nanoparticles on the surface of Zn-ferrite spheres via sol–gel rout. SEM and TEM images showed morphology and core–shell structure of particles. Results of VSM illustrate that Zn—Fe_2O_4 and Zn—Fe_2O_4@ZnO particles are superparamagnetic. Photocatalytic activity studies confirm that synthesised Zn—Fe_2O_4@ZnO core–shell sphere with molar ratio of 1:1 had excellent photodegradating behavior to methylene blue (MB) as compared to other core–shell ratios, pure Zn—Fe_2O_4 and pure ZnO.

1. Introduction

Pigments are one of the most common pollutants in waste water of many industries such as textiles and chemicals [1]. One of these pigments is methylene blue, a hazardous cationic pigment being a mutagen, carcinogen and resistant to biological decomposition [2]. There are different techniques to eliminate this pollutant, for example, electrochemical treatment [3,4], floatation and coagulation [5], chemical oxidation [6], liquid–liquid extraction [7] and surface adsorption [8–11]. Another way of eliminating this pollutant is photocatalytic analysis. Variety of semiconductors is employed for this process. Nowadays, to increase the performance of the photocatalyst, a combination of two metal oxides as composite or core–shell system is employed. Immense amount of work has been performed with CuO/ZnO and Fe_3O_4/ZnO combination [12–16]. Utilization of a combination with magnetite is more economical, due to the ease of separation and recovery of the catalyst after the elimination of the pollutant. Many researchers have addressed use of core–shell system for better performance in the environment. Since the photocatalytic activity of semiconductor ZnO is only in the range of UV light [17,18], the use of magnetite core which is active in visible light [19], enhances the efficiency of the catalyst under the sun. Naturally a catalyst that has the ability to remove contaminants in visible light is more desired.

In this work, for the first time, synthesis of ZnO core–shell combination with the Zn—Fe_2O_4 spheres with nanopores, the catalyst was used for photocatalytic degradation of methylene blue under visible light LED lamp. The nanoscale pores in addition to the photocatalytic degradation process, causing part of the contaminants to be removed from the environment by adsorption. Replacing magnetite with zinc ferrite increased the magnetism of the combination under similar conditions. The presence of zinc in the magnetic combination enhances the compatibility between Zn—Fe_2O_4 as its core and ZnO as its shell, which eases the core–shell synthesis process and increases its efficiency.

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2. Experimental

2.1. Materials

In this study, iron (III) chloride ($FeCl_3$), zinc chloride ($ZnCl_2$), ammonium acetate, ethylene glycol ($C_2H_6O_2$), zinc acetate ($Zn(C_2H_3O_2)_2{\cdot}6H_2O$) and ethanol were used to prepare the samples.

2.2. Preparation of $Zn{-}Fe_2O_4$ nanoparticles

A mixture of 70 mL ethylene glycol, iron (III) chloride and zinc chloride was stirred in a mechanic stirrer to achieve a clean solution. Then, the above solution was added during stirring 2.312 g NH_4Ac. With continued practice of mixing, the color turns to dark yellow and palms appeared. This solution for 40 min was sonicated. The solution is then placed in an oven at 215 °C for 4 h to obtain a black precipitate.

2.3. Preparation of $Zn{-}Fe_2O_4$@ZnO core–shell

The resulting black precipitation was re-dispersed in deionized water before $Zn{-}Fe_2O_4$ was added to it, then sonicated for 2 h and freeze–thaw action of ammonia added drop wise until the pH reached 11. The precursor solution was transferred into a round-bottom flask and kept at 120 °C for 3 h. After cooled to room temperature, the precipitate was placed in an oven at temperature of 80 °C for 24 h and then placed into a vacuum oven at 80 °C for 24 h.

2.4. Characterization of $Zn{-}Fe_2O_4$@ZnO core–shell

The particle morphologies of the ZnO powder were observed by an AIS2100 (Seron Technology) scanning electron microscopy (SEM) and a JEOL 2010F transmission electron microscopy (TEM). The FT-IR analyses were carried out on a Shimadzu FTIR-8400S spectrophotometer using a KBr pellet for sample preparation. DRS spectra were prepared via a Shimadzu (MPC-2200) spectrophotometer. Furthermore, the structure of particles were analyzedby powder X-ray diffractometer (XRD, Bruker AXS D8 advance). Also a commercial HH-15 model vibrating sample magnetometer (VSM, Lake Shore 7410) was used at room temperature to characterize the magnetic properties of $Zn{-}Fe_2O_4$ particles and $Zn{-}Fe_2O_4$@ZnO nanohallow spheres.

2.5. Photocatalytic experiments

Photocatalytic activity studies of the prepared $Zn{-}Fe_2O_4$@ZnO core–shells were evaluated by the degradation MB solution. In a typical process, the catalytic reaction was carried out in a 100 mL photoreactor, which contains 50 mL of MB dye (10 mgL^{-1}) solution and 0.05 g of catalyst. Before irradiation, the solution was stirred in the dark (15 min) for obtaining an equilibrium point of initial physical adsorption of MB over the surface of samples. Irradiation was carried out using a 5 W LED visible light (with emission wavelength about 460–490 nm). All photocatalytic experiments were accomplished at the same conditions. For determination of MB decolorization at specified periods, the lamps were turned off and 3 mL of each sample was collected and separated from the photocatalyst by centrifugation. The photocatalytic performance was indirectly monitored by relating the optical absorbance to the MB degradation amount using a double beam UV–Vis spectrophotometer at a wavelength of 664 nm.

3. Results and discussion

3.1. Morphology study

The SEM images of $Zn{-}Fe_2O_4$, ZnO and $Zn{-}Fe_2O_4$@ZnO are shown in Fig. 1A–C, respectively. For $Zn{-}Fe_2O_4$ and $Zn{-}Fe_2O_4$@ZnO, the morphology is clearly similar with spheres, but ZnO particles do not have specific morphology.

Also, the morphology of $Zn{-}Fe_2O_4$@ZnO core–shell investigated by TEM images as shown in Fig. 1D. It is illustrated that a layer of ZnO with 30 nm thickness coated on $Zn{-}Fe_2O_4$ core.

3.2. FT-IR spectroscopy

FT-IR spectra of ZnO, $Zn{-}Fe_2O_4$ and $Zn{-}Fe_2O_4$@ZnO indicated in Fig. 2 in the range 400–4000 cm^{-1}. In the spectra of $Zn{-}Fe_2O_4$, the strong and sharp absorption band appeared at 575 cm^{-1} is in good agreement with vibration of Fe—O as typical band of spinel ferrite. In the spectra of ZnO, the observed peak at 563.53 cm^{-1} that related to Zn—O bonding. Strong absorption at 3325.04 cm^{-1} associated to O—H tensile vibration. In the spectra of $Zn{-}Fe_2O_4$@ZnO and ZnO, the peaks at 1417.58 cm^{-1} and 1627.81 cm^{-1} to attributed to the symmetric and asymmetric stretchings of COO^-, respectively. On the other hand, the disappearance of C=O stretching modes of the carboxylic acid functionality in the range of 1700–1725 cm^{-1}