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Facile fabrication and characterization of $NiFe_2O_4$/ZnO hybrid nanoparticles

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ABSTRACT

Ferromagnetic $NiFe_2O_4$/ZnO hybrid nanoparticles were successfully synthesized by the hydrolysis of zinc acetate in the presence of $NiFe_2O_4$ colloidal suspension in water-in-oil (w/o) microemulsion under ultrasonic irradiation. The structure and morphology of samples were characterized by X-ray diffraction, infrared spectra and transmission electron microscopy. The microstructure studies revealed that the ZnO nanolayer were deposited on the surface of $NiFe_2O_4$ nanoparticles. The magnetic properties of the resulting hybrid nanoparticles were investigated by vibrating sample magnetometer. Magnetic measurements showed that the saturation magnetization and coercivity decreased upon nonmagnetic ZnO coating.

1. Introduction

A spinel structure which is formed by a nearly closepacked fcc array of anions with holes partly filled by the cations can be represented by the formula AB_2O_4 [1], where A represents metallic ions located in A interstitial (tetrahedral) sites and B metallic ions located in B (octahedral) sites. Due to the large electronegativity of oxygen, the ionic type of bonds prevails in almost all oxide spinels [2]. Ferrites of the type MFe_2O_4 ($M = Co^{2+}$, Ni^{2+}, Zn^{2+}, Mn^{2+}, etc.) possess the spinel structure. In recent years, there has been a growing interest in magnetic ferrite nanoparticles, owing to both the broad practical applications in several important technological fields such as ferrofluids, magnetic drug delivery, magnetic high-density information storage [3–5] and fundamental understanding of unusual properties of nanoparticles compared to those of bulk materials.

Encapsulating magnetic nanoparticles in nonmagnetic matrix is a promising and important approach in the development of magnetic nanoparticles in the technological and biomedical application [6], and also may help to understand the magnetic behavior of nanoparticles due to new possible surface, interparticles, and exchange interactions in magnetic/nonmagnetic matrix [7]. Up to date, many efforts have been devoted to fabricating magnetic composites. Xu and co-workers synthesized magnetic composites with silica being coated on Fe_3O_4 cores using a template-assisted approach [8]. Fu and co-workers reported the synthesis and microwave absorbing properties of core–shell structured $MnFe_2O_4$–TiO_2 nanocomposites through the hydrolysis of titanium butoxide precursor [9]. In our previous study, we have reported the synthesis of core–shell structured $Zn_{0.5}Cr_{0.5}Fe_2O_4/TiO_2$ nanocomposites through the hydrolysis of titanium tetrabutyloxide in water-in-oil (w/o) microemulsions assisted by ultrasonic irradiation [10].

ZnO-based magnetic semiconductors (MS) have initiated enormous scientific interests in recent years because of their unique properties with possible technological applications utilizing both the semiconductor physics and the ferromagnetism. However, there are still many difficult problems in ZnO-based MS, including the technique for crystal growth and film fabrication, the quality of materials, p-type doping and so on [11]. Alternatively, ZnO-based MS could also be achieved by fabricating hybrid nanoparticles. However, within the limits of our knowledge, the studies focused on this area have been rarely reported.

In the present work, we first report the preparation of $NiFe_2O_4$/ZnO hybrid nanoparticles by the hydrolysis of zinc acetate in the presence of $NiFe_2O_4$ nanoparticles in w/o microemulsion under ultrasonic irradiation. The ferromagnetic behaviors of $NiFe_2O_4$/ZnO hybrid nanoparticles are discussed on the basis of the structure characterization and morphology analysis.

2. Experimental

2.1. Materials

All the reagents were of analytical grade and used as received without further purification, including $Ni(NO_3)_2{\cdot}6H_2O$, $Fe(NO_3)_3{\cdot}9H_2O$, NaOH, $Zn(CH_3CO_2)_2{\cdot}2H_2O$, cyclohexane, *n*-pentanol and cetyltrimethylammonium bromide (CTAB).

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2.2. Preparation of $NiFe_2O_4$ colloidal suspension

An aqueous $NiFe_2O_4$ colloidal suspension was synthesized via a simple refluxing route in alkaline solution. In a typical procedure, a stoichiometric amount of $Fe(NO_3)_3{\cdot}9H_2O$ and $Ni(NO_3)_2{\cdot}6H_2O$ were dissolved in distilled water and a 50 mL metal nitrate aqueous solution was prepared. The solution was poured as quickly as possible into the boiling alkaline solution (200 mL, 5.0 g NaOH). The mixture solution was then refluxed at 100 °C for 2 h. A stable $NiFe_2O_4$ colloidal suspension was obtained.

2.3. Preparation of $NiFe_2O_4$/ZnO hybrid nanoparticles

$NiFe_2O_4$/ZnO hybrid nanoparticles were prepared by the hydrolysis of zinc acetate in the presence of $NiFe_2O_4$ in w/o microemulsion, using CTAB as the surfactant, *n*-pentanol as the cosurfactant, cyclohexane as the oil phase. The whole experiment was operated in an ultrasonic apparatus (Model KQ-250DB, Kunshan Ultrasonic Instrument Co. Ltd.), using a power of 100 W and operated at 50 kHz. In a typical experimental procedure, 0.1 g $Zn(CH_3CO_2)_2{\cdot}2H_2O$ and 2.0 g CTAB was added to 5 ml distilled water, then 2 ml *n*-pentanol and 30 ml cyclohexane were introduced. The mixture was stirred and the system became transparent immediately; thus, a clear and transparent microemulsion system was obtained. After that, a certain amount of $NiFe_2O_4$ colloidal suspension was added to the above microemulsion solution. After ultrasonic stirring for 8 h, the resulting products formed within the water pools of the reverse micelles were collected by centrifugation, washed repeatedly with ethanol and water, and dried at 60 °C for 24 h in air.

2.4. Characterization

X-ray diffraction patterns of the samples were collected on a Philips X'pert Pro MPD diffractometer with Cu Kα radiation (λ = 0.15418 nm). Infrared spectra were recorded on a Nicolet Avatar 360 spectrometer in the range of 400–1000 cm^{-1} using KBr pellets. The composition was determined by using a Hitachi S4800 scanning electron microscope equipped with an energy dispersion spectrometer (EDS). TEM images and the electron diffraction (ED) patterns were carried out on a JEOL JEM-2010 transmission electron microscope at an accelerating voltage of 200 kV. Magnetic measurements were carried out at room temperature using a vibrating sample magnetometer (VSM, Lakeshore 7407) with a maximum magnetic field of 10 kOe. The samples were weighed and fixed in the sample holder in the magnetic field of the coils of VSM.

3. Results and discussion

Fig. 1 shows the XRD patterns of $NiFe_2O_4$ (a), $NiFe_2O_4$/ZnO hybrid nanoparticles (b) and ZnO (c). The diffraction peaks in Fig. 1(a) are well indexed as cubic spinel phase with a lattice parameter of $a = 0.836$ nm (JCPDS card file no.86-2267), and no impurities are detected. The peaks appeared at 30.1°, 35.6°, 37.3°, 43.4°, 53.7°, 57.4° and 62.8° can be assigned to scattering from the (2 2 0), (3 1 1), (2 2 2), (4 0 0), (4 2 2), (5 1 1) and (4 4 0) planes of the spinel crystal lattice, respectively. Using Debye–Scherrer formula: $D = 0.9\lambda/\beta\cos\theta$ where D is the average crystallite size, λ is the wavelength of Cu Kα, β is the full width at half maximum (FWHM) of the diffraction peaks, and θ is the Bragg's angle, the average sizes are estimated to be about 22 nm. As shown in Fig. 1(b), besides the characteristic diffraction peaks of the spinel phase $NiFe_2O_4$, the peaks at 31.8° (1 0 0), 34.4° (0 0 2), 47.6° (1 0 2), 56.6° (1 1 0), 66.4° (2 0 0) and 68.1° (1 1 2) corresponding to hexagonal wurtzite phase ZnO with lattice parameters of $a = 0.325$ nm and $c = 0.521$ nm (JCPDS card file no. 79-0206) also can be observed. In addition, the EDS spectra of $NiFe_2O_4$/ZnO hybrid nanoparticles shown in Fig. 2 indicate the presence of Zn, Ni, Fe and O elements.

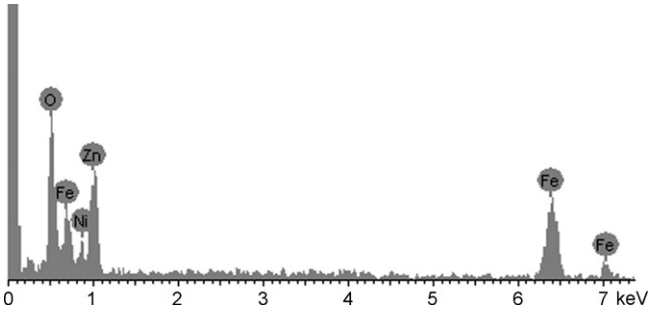

Fig. 2. EDS spectra of $NiFe_2O_4$/ZnO hybrid nanoparticles.

Fig. 3 shows the FT-IR spectra of $NiFe_2O_4$ (a), $NiFe_2O_4$/ZnO hybrid nanoparticles (b) and ZnO (c). In ferrites the metal ions are situated in two different sublattices, designated tetrahedral and octahedral according to the geometrical configuration of the oxygen nearest neighbors. Waldron [12] and Hafner [13] studied the vibrational spectra of ferrite and attributed high frequency band ν_1 (610–580 cm^{-1}) to the intrinsic vibration of the tetrahedral sites and low frequency band ν_2 (440–400 cm^{-1}) to the octahedral site. It is observed from Fig. 3(a) that the peaks at 598 and 411 cm^{-1} are intrinsic vibration of the tetrahedral and octahedral sites, respectively. In the FT-IR spectrum of ZnO (Fig. 2(c)), the broad band in the vicinity of 460–500 cm^{-1} is assigned to the Zn–O vibration [14]. As shown in Fig. 3(b), the characteristic peaks of spinel $NiFe_2O_4$ and wurtzite ZnO appear in the infrared spectrum of $NiFe_2O_4$/ZnO hybrid nanoparticles.

Fig. 4 shows the morphology of the as-prepared $NiFe_2O_4$/ZnO hybrid nanoparticles. It indicates that the quasi-spherical $NiFe_2O_4$ particles (Fig. 4(a)) with some agglomeration are a consequence of the preparation method and nanoparticle surface properties. The crystallite size of $NiFe_2O_4$ is estimated to be in the range of 20–25 nm, which is very consistent with the results of XRD analysis. The ED rings corresponding to $NiFe_2O_4$ in Fig. 4(c) are well indexed as (1 1 1), (2 2 0), (3 1 1), (4 0 0), (4 2 2), (5 1 1) and (4 4 0) reflections

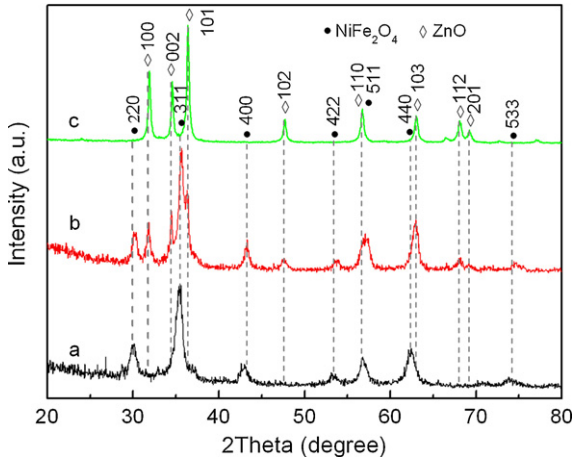

Fig. 1. XRD patterns of $NiFe_2O_4$ (a), $NiFe_2O_4$/ZnO hybrid nanoparticles (b) and ZnO (c).

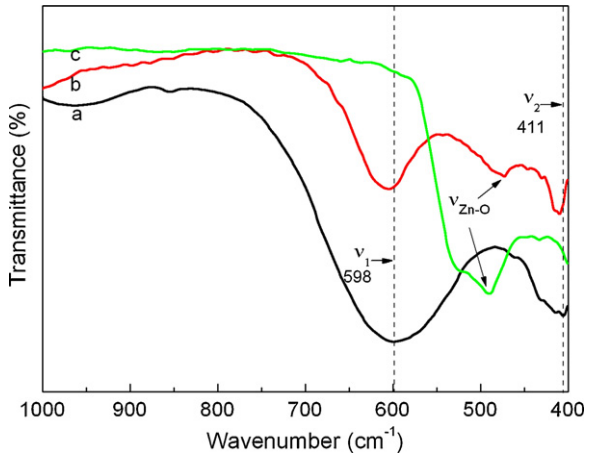

Fig. 3. FT-IR spectra of $NiFe_2O_4$ (a), $NiFe_2O_4$/ZnO hybrid nanoparticles (b) and ZnO (c).