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Letter

Synthesis and properties of Ni/ZnS magnetic luminescent bifunctional nanocomposites

Yongbo Li[a], Ran Yi[a], Xiaohe Liu[a,b,*]

[a] Department of Inorganic Materials, Central South University, Changsha, Hunan 410083, People's Republic of China
[b] State Key Laboratory of Powder Metallurgy, Central South University, Changsha, Hunan 410083, People's Republic of China

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ABSTRACT

Ni/ZnS core/shell nanocomposites with both magnetic and luminescent properties were prepared via a two-step approach with an initial synthesis of Ni nanoparticles and then as templates for the deposition of ZnS nanoparticles. The structure and properties of as-synthesized samples were characterized by XRD, TEM, VSM and PL. Studies indicate that typical nanocomposites consist of Ni (core) with 80–130 nm diameter and adjacent ZnS (shell) with a thickness of about 30–50 nm. The value of magnetization saturation of nanocomposites significantly decreases after coating with ZnS as a result of the nonmagnetic coating affecting. The emission spectrum of nanocomposites shows a small red shift as compared with that of pure ZnS. The possible reason for this phenomenon may be ascribed to the change of size, morphology and crystallinity of ZnS sample after coating.

1. Introduction

Recently, there has been a great deal of interest in the fabrication of core/shell composite materials [1,2], because the physical and chemical properties of these composite materials can be tuned by controlling their compositions and the relative sizes of the core and shell. The composite materials not only combine properties of the original components but also possess novel and collective performances not seen in the original components. For example, Wang et al. have prepared Ag/ZnO nanocomposites through a facile hydrothermal method; the nanocomposites enlarged the application of single constituent and showed potential applications in photodegradation of organic dye pollutants and destruction of bacteria [2].

As an important magnetic functional material, nickel has attracted extensive attention with various applications, including magnetic storage and catalytic fields [3,4]. However, Ni nanoparticles are prone to be oxidized and unstable in acid or base due to their large specific surface area and natural properties. A suitable coating is essential to overcome these limitations and widen its scope of application. Zinc sulfide, a unique material for its semiconducting and optical properties, has gained wide attention for applications in light-emitting diodes and luminescence devices [5,6]. So far, various approaches have been developed to synthesize magnetic fluorescent bifunctional nanocomposites. For example, Bala et al. prepared Ni/ZnS core/shell nanostructure by a sol–gel route [7]. Liu and co-workers synthesized Fe_3O_4/CdSe/ZnS magnetic fluorescent bifunctional nanocomposites by depositing heterogeneous semiconductor on magnetic nanoparticles [8]. Therefore, ZnS is an

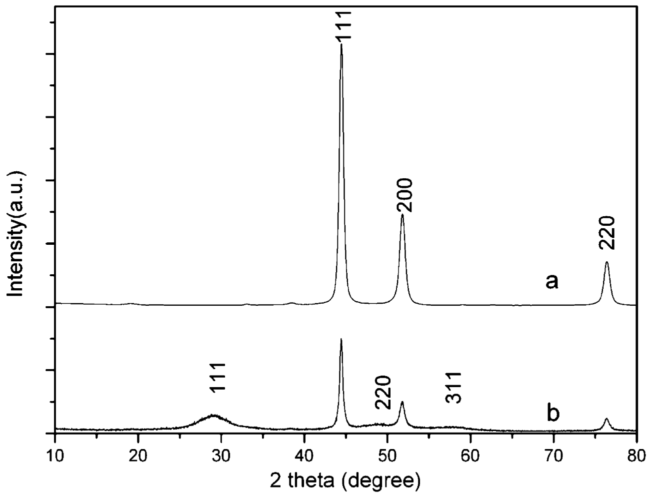

Fig. 1. XRD spectra of as-prepared samples: Ni nanoparticles (a) and Ni/ZnS nanocomposites (b).

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* Corresponding author at: Department of Inorganic Materials, Central South University, Room 236, Heiping Building, Changsha, Hunan 410083, People's Republic of China. Tel.: +86 731 8830543; fax: +86 731 8879815.
E-mail address: liuxh@mail.csu.edu.cn (X. Liu).

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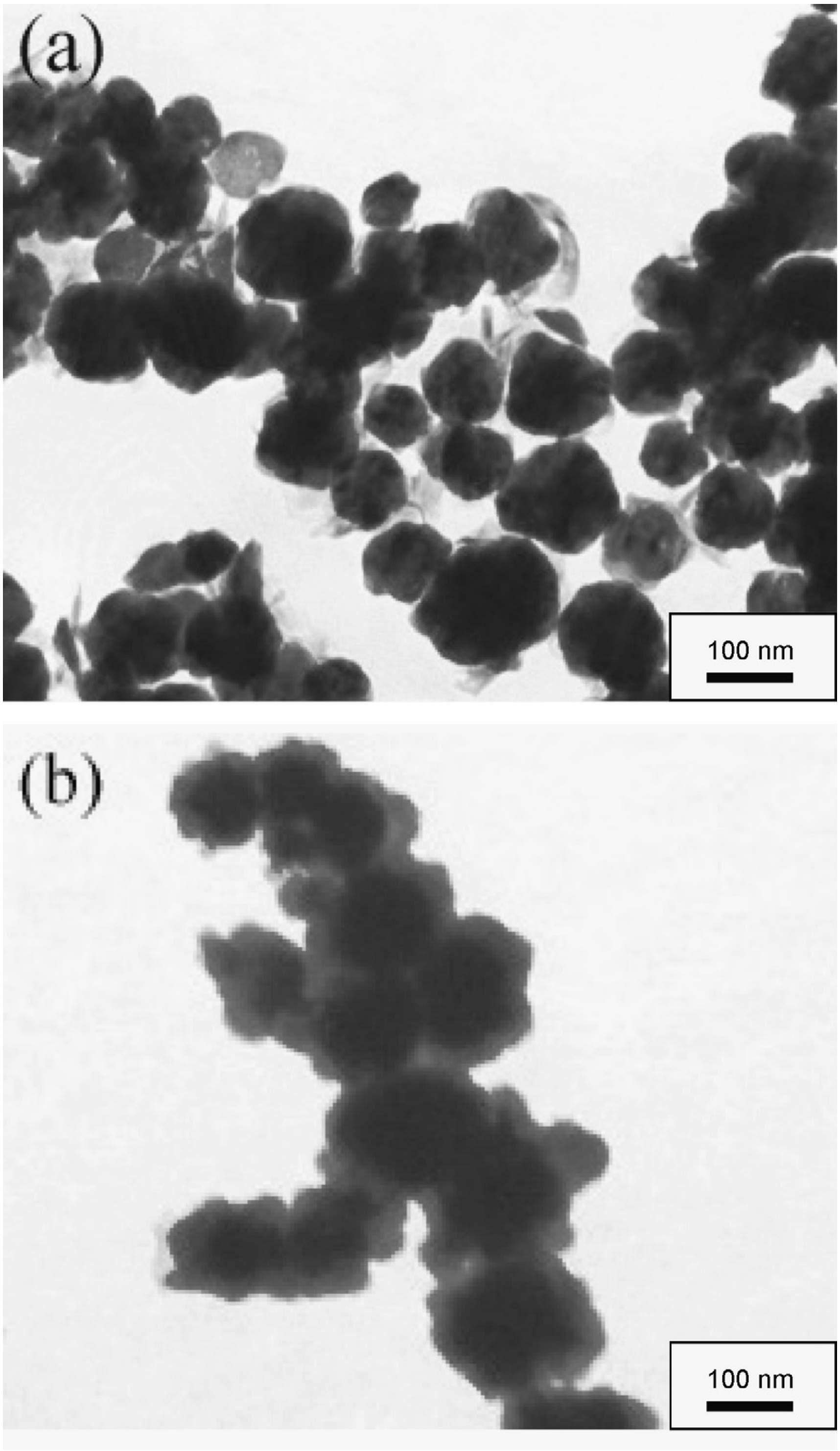

Fig. 2. Typical TEM images of as-prepared Ni nanoparticles (a) and Ni/ZnS nanocomposites (b).

excellent and promising coating material and we select it for the encapsulation of Ni nanoparticles to prepare magnetic fluorescent nanocomposites.

In the present work, we have succeeded in preparing Ni/ZnS nanocomposites and the synthesis procedure involve an initial synthesis of magnetic material and then ZnS encapsulated on the surface of Ni nanoparticles. The preparation process required a relative low temperature, and no surface pretreatments were needed to introduce new surface functional groups or additional covalent for the deposition of ZnS onto Ni nanoparticles in our experiments. The Ni/ZnS core/shell nanocomposites are discussed according to the structural and morphological characterization and property measurement including XRD, TEM, VSM and PL.

2. Experimental details

2.1. Synthesis

$NiCl_2{\cdot}6H_2O$ (0.2377 g), poly(vinyl pyrrolidone) (0.5 g), absolute ethanol (1 ml) and $N_2H_4{\cdot}H_2O$ (8 ml 80 wt%) and NaOH (2 g) were all added into deionized water (20 ml). The above mixture was heated to 80 °C and the reaction lasted for 1 h. Then a simple two-step chemical solution reaction was employed to build core/shell nanostructure, which was similar to the work of Shim and co-workers [9]. Firstly, the obtained Ni (0.5 mmol) nanoparticles and thioacetamide (4 mmol) were put into deionized water (20 ml) under vigorous mechanical stirring under 60 °C for 2 h. Subsequently, $Zn(AC)_2{\cdot}H_2O$ (2 mmol) was added to the above solution and the mixture was irradiated by ultrasonic waves under 60 °C for 30 min. The final products were centrifuged and washed with absolute ethanol and distilled water several times respectively, and dried in a vacuum at 60 °C for 4 h.

2.2. Characterization

The obtained samples were characterized by X-ray powder diffractometer (XRD) with Cu Kα radiation ($\lambda = 1.5418$ Å). The size and morphology of the products were characterized by a JEM-200CX transmission electron microscope (TEM) at 160 kV. Magnetic properties of the samples were carried out by using a LDJ-9600 vibrating sample magnetometer (VSM). Photoluminescence (PL) measurements were carried out at room temperature using 260 nm as the excitation wavelengths with a luminescence spectrometer (Hitachi F-4500).

3. Results and discussion

During the sample preparation, the molar ratio of $Zn(AC)_2{\cdot}H_2O$ to thioacetamide was selected to be 0.5 in order to obtain the better density of ZnS particles on the surface of Ni nanoparticles, which was testified by a literature report [10]. Fig. 1 shows the XRD spectra of as-prepared samples. The diffraction peaks at $2\theta = 44.4^\circ$, 51.8° and 76.4° can be well indexed to the (1 1 1), (2 0 0), and (2 2 0) planes of cubic fcc-type Ni crystals (JCPDS 65-2865). As for nanocomposites, the diffraction peaks of ZnS phase can be clearly distinguished and the data matches well those for pure cubic phase ZnS (JCPDS 80-0020), which indicates that the ZnS phase exists in the nanocomposites. The crystallite size of ZnS sample can be calculated according to the Scherrer equation ($d = 0.89\lambda/\beta\cos\theta$), and the average size is about 2.1 nm.

Typical TEM micrographs of the pure Ni nanoparticles and Ni/ZnS nanocomposites are shown in Fig. 2(a) and (b). As revealed by TEM images, the Ni nanoparticles are almost spherical with 80–130 nm diameter. From Fig. 2(b), it can be seen that Ni nanoparticles are completely encapsulated in a ZnS shell with a thickness of about 30–50 nm.

The magnetic properties of nanocomposites were examined and compared with the magnetic properties of Ni nanoparticles. Fig. 3 shows magnetic properties of as-obtained products measured with a VSM at room temperature. The value of magnetization saturation (M_s) of Ni nanoparticles is 53.6 emu/g, which is higher than that of 49 emu/g reported in [7]. This variation may be as a result of anisotropy of nanoparticles and dipolar interaction among nanoparticles. The M_s of Ni/ZnS nanocomposites is about 47.8 emu/g, lower than that of Ni nanoparticles. The reasonable explanation for this phenomenon is that the nonmagnetic coating layer on the surface of magnetic nanoparticles reduced the magnetism of magnetic materials. It can be found that the M_s of Ni/ZnS nanocomposites is larger as compared to the previous report, this result may be related to the larger M_s of core material and the shell thickness. The covercivity (Hc) of magnetic nanoparticles is determined by the strength of magnetic dipoles in magnetic domains, as well as the relations between adjacent magnetic domains [11]. However, it can be found that the value of Hc has almost no change after ZnS coating from Fig. 3, indicating that the encapsulation has no effect on the structure of Ni nanoparticles.

PL study is a powerful tool to investigate the optical properties of magnetic luminescent bifunctional nanostructures. We have performed the room-temperature PL to show the optical properties of nanocomposite over its individual component (ZnS). The preparation procedure of ZnS nanoparticles was similar to that of Ni/ZnS nanocomposites. The only difference was that there was no Ni nanoparticles as seeds involved during the preparation. The room-temperature luminescence spectra of samples are presented in Fig. 4. In Fig. 4, ZnS nanoparticles have a strong emission band at 397 nm which is similar to other reports [12,13]. For nanocomposites, a strong emission is observed at 399 nm and the maximum emission peaks of two samples are so close and show a small red shift as compared with pure ZnS, and the similar phenomenon is also observed in Tang's work [14]. However, it is different from Bala's work in which Ni/ZnS nanocomposites present a lager blue shift compared to pure ZnS [7]. The possible reason of the small red shift is that the size, morphology and crystallinity of ZnS sample may change after Ni nanoparticles as seeds in synthesis procedure of nanocomposites, and the alteration may make PL properties of two samples relatively approach because PL property of ZnS nanomaterials is generally sensitive to the synthetic conditions, crystal size, and shape. Furthermore, compared to pure ZnS nanoparticles, the nanocomposite particles become larger after the coating so as to result in a red shift of emission band. Compared with pure ZnS, it is noted that the fluorescent intensity of nanocomposite decreases obviously, this significant decrease indicates that the presence of Ni nanoparticles in nanocomposite strongly reduces the fluorescence

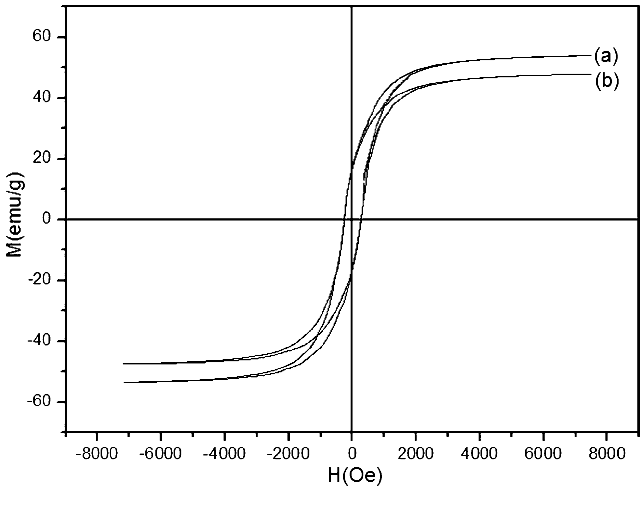

Fig. 3. Magnetization versus applied magnetic field for Ni nanoparticles (a) and Ni/ZnS nanocomposites (b).

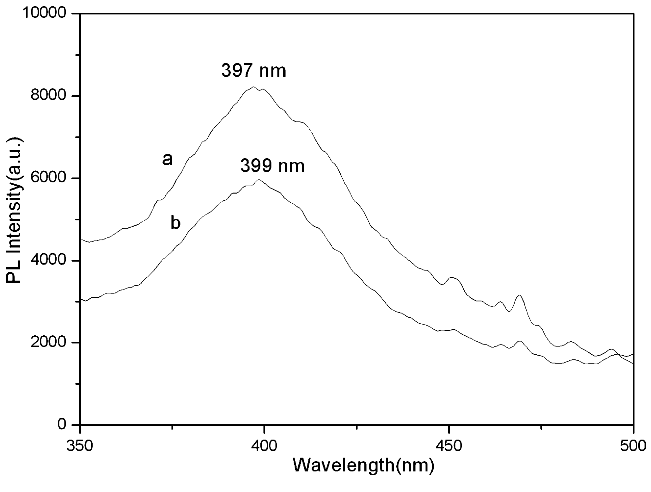

Fig. 4. PL spectra of the samples: ZnS sample (a) and Ni/ZnS nanocomposites (b).

intensity. The reason may be due to absorption of Ni nanoparticles, the so-called quantum dots and static quenching [15].

4. Conclusions

In conclusion, we have prepared Ni/ZnS core/shell nanocomposites by a simple, additive-free procedure that involves the hydrothermal synthesis of Ni nanoparticles and deposition of ZnS nanoparticles. The typical nanocomposites consist of Ni (core) with 80–130 nm diameter and adjacent ZnS (shell) with a thickness of about 30–50 nm. The value of M_s of nanocomposite is lower than that of pure ZnS as a result of the nonmagnetic coating. As compared with that of pure ZnS, the emission spectrum of nanocomposites shows a small red shift due to the change of size, morphology and crystallinity of ZnS sample after coating. It can be clearly observed that the PL intensity of nanocomposites decreases obviously. Maybe the reason is attributed to absorption of Ni nanoparticles, the so-called quantum dots and static quenching.

Acknowledgements

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