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Synthesis and ferrimagnetic properties of novel Sm-substituted LiNi ferrite–polyaniline nanocomposite

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Abstract

Polyaniline (PANI)–$LiNi_{0.5}Sm_{0.08}Fe_{1.92}O_4$ nanocomposite was synthesized by an *in situ* polymerization of aniline in the presence of $LiNi_{0.5}Sm_{0.08}Fe_{1.92}O_4$ ferrite. The products were characterized by powder X-ray diffractometer (XRD), Fourier transform infrared (FTIR) and UV–visible absorption spectrometer, thermogravimetric analyser (TGA), atomic force microscope (AFM) and vibrating sample magnetometer (VSM). The results of XRD, FTIR and UV–visible spectra confirmed the formation of PANI–$LiNi_{0.5}Sm_{0.08}Fe_{1.92}O_4$ composite. AFM study showed that ferrite particles had an effect on the morphology of the composite. TGA revealed that the incorporation of ferrite improved the thermal stability of PANI. The nanocomposite under applied magnetic field exhibited the hysteresis loops of ferrimagnetic nature at room temperature. The bonding interaction between ferrite and PANI in the nanocomposite had been studied.

Keywords: Magnetic materials; Nanocomposite; Polyaniline; Ferrite; Magnetic properties

1. Introduction

Conducting polymers have attracted considerable attention for their potential applications in various fields, such as electromagnetic interference (EMI) shielding [1], rechargeable batteries [2,3], electrodes and sensors [4,5], corrosion protection coatings [6] and microwave absorption [7]. Among the known conducting polymers, polyaniline (PANI) has been extensively studied in the last two decades due to its unique electrochemical and physicochemical behavior, good environment stability and relatively easy preparation [8,9].

Conducting polymer–inorganic composites possess not only the nature of the flexibilities and processability of polymers but also the mechanical strength and hardness of inorganic components. Recently, several interesting research has focused on PANI–inorganic composites to obtain the materials with synergetic or complementary behavior between polyaniline and inorganic nanoparticles [10,11].

Polymer–inorganic composites with an organized structure provide a new functional hybrid between organic and inorganic materials [12,13]. Up to date, the preparation of polyaniline with ferromagnetic properties has been studied [14,15]. Deng et al. have studied the synthesis of magnetic and conducting Fe_3O_4–cross-linked polyaniline (CLPANI) nanoparticles with core–shell structure by using a precipitation–oxidation technique [16]. Yang et al. have reported the preparation of conducting and magnetic PAn/γ-Fe_2O_3 nanocomposite by modification–redoping method [17].

The soft magnetic spinel ferrites have been widely used in microwave devices [18,19]. The electromagnetic properties of ferrites can be tailored by controlling the different types and amounts of metal ions substitution. Recently, the fabrication of spinel MnZn or NiZn ferrite–polyaniline composites has been reported [20–22], but polyaniline–ferrite systems fabricated by incorporating Sm-substituted LiNi ferrite into polyaniline has not been reported. We attempted to introduce a relatively small amount of rare earth ions into spinel ferrites to improve the electromagnetic properties of spinel ferrites [23,24] by the occurrence of 4*f*–3*d* couplings. In the present work, we prepared PANI–$LiNi_{0.5}Sm_{0.08}Fe_{1.92}O_4$ nanocomposite by an *in situ* polymerization in aqueous

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solution. The samples were characterized by various experimental techniques, and the magnetization and coercivity of the composite were measured.

2. Experimental

2.1. Materials

Aniline monomer was distilled under reduced pressure and stored below 0 °C. Ammonium peroxydisulfate ($(NH_4)_2S_2O_8$, APS), ferric oxide (Fe_2O_3), lithium carbonate (Li_2CO_3), nickel sulfate ($NiSO_4{\cdot}6H_2O$), samarium oxide (Sm_2O_3) and oxalic acid ($H_2C_2O_4{\cdot}2H_2O$) were all of analytical reagent grade and used as received. All reagents were purchased from Shanghai Chemical Agents Ltd Co. in China.

2.2. Preparation of $LiNi_{0.5}Sm_{0.08}Fe_{1.92}O_4$ ferrite

Sm-substituted LiNi ferrite $LiNi_{0.5}Sm_{0.08}Fe_{1.92}O_4$ was prepared by a novel rheological phase reaction method [25]. In a typical procedure, stoichiometric amounts of Li_2CO_3 (0.01 mol), $NiSO_4{\cdot}6H_2O$ (0.01 mol), Sm_2O_3 (0.0008 mol), Fe_2O_3 (0.0192 mol) and $H_2C_2O_4{\cdot}2H_2O$ (0.084 mol) were thoroughly mixed by grinding in an agate mortar for 30 min, about 15 ml anhydrous ethanol was then added to form the mixture in rheological state. The mixture was sealed in a teflonlined stainless-steel autoclave and maintained at 120 °C for 48 h in an oven. The obtained precursor was washed several times with deionized water and ethanol, dried at 60 °C for 12 h, and sintered at 1000 °C for 2 h in air, followed by cooling in a furnace to room temperature with 5 °C/min cooling rate.

2.3. Synthesis of PANI–$LiNi_{0.5}Sm_{0.08}Fe_{1.92}O_4$ composite

PANI–$LiNi_{0.5}Sm_{0.08}Fe_{1.92}O_4$ composite was prepared by an *in situ* polymerization in aqueous solution. In a typical procedure, a certain amount of $LiNi_{0.5}Sm_{0.08}Fe_{1.92}O_4$ particles was suspended in 35 ml 0.1 M HCl solution and stirred for 30 min to get well dispersed. 1 ml aniline monomer was then added to the suspension and stirred for 30 min. 2.49 g APS in 20 ml 0.1 M HCl solution was then slowly added dropwise to the suspension mixture with a constant stirring at room temperature. After 12 h, the polymerization was achieved and the suspension was in dark green. The composite was obtained by filtering and washing the suspension with 0.1 M HCl and deionized water, and dried under vacuum at 60 °C for 24 h.

2.4. Characterization

X-ray diffraction patterns of the samples were recorded on a Philips-Pw3040/60 X-ray diffractometer (XRD) with a Ni-filter and graphite monochromater, and Cu Kα radiation (λ=0.15418 nm) at a scanning speed of 4°/min in the range of 2θ=15–80°. The infrared spectra of the products were determined on a Nicolet Nexus 670 Fourier transform infrared spectrometer in the range of 4000–400 cm^{-1} using KBr pellets. The UV–vis spectra of the samples dissolved in *N,N*-dimethylformamide (DMF) were recorded on a Shimadzu UV-2501PC spectrophotometer in the range of 300–800 nm. The TG curves of the samples were recorded on a Shimadzu model DT-40 thermal analyser in N_2 (flow rate 40 ml/min) at a heating rate of 10 °C/min from room temperature to 800 °C. The magnetic properties of the composite were measured at room temperature by using a vibrating sample magnetometer (VSM, Lakeshore 7403).

3. Results and discussion

3.1. X-ray diffraction analysis

Fig. 1 shows X-ray diffraction patterns of $LiNi_{0.5}Sm_{0.08}Fe_{1.92}O_4$ ferrite, PANI and PANI–$LiNi_{0.5}Sm_{0.08}Fe_{1.92}O_4$ composite. The XRD pattern of $LiNi_{0.5}Sm_{0.08}Fe_{1.92}O_4$ ferrite in Fig. 1(a) shows the single phase spinel structure with the characteristic reflections of the *Fd3m* cubic spinel group, which confirms the formation of Sm-substituted LiNi ferrite. These results indicate that Fe^{3+} is replaced by Sm^{3+} on the octahedral sites in spinel ferrite, and obey the Vegard's law [26]. The typical XRD pattern of PANI (curve c) shows the broad diffraction peaks at about 15.35° and 25.39°, and suggests an amorphous nature, which is consistent with the results obtained by other research groups [27,28].

Fig. 1(b) shows the main diffraction for PANI–$LiNi_{0.5}Sm_{0.08}Fe_{1.92}O_4$ composite, which contains the characteristic peaks of the $LiNi_{0.5}Sm_{0.08}Fe_{1.92}O_4$ ferrite (curve a) at 2θ=18.44°, 30.31°, 35.66°, 37.27°, 43.35°, 53.75°, 57.33°, and 62.81°. However, the intensities of the peaks for the composite are weaker than that of the pure ferrite, which reveals that the polyaniline coating layer has an effect on the crystallinity of $LiNi_{0.5}Sm_{0.08}Fe_{1.92}O_4$ ferrite. In addition, a characteristic amorphous PANI peak can be observed in XRD pattern of the composite (curve b), which indicates the formation of PANI–$LiNi_{0.5}Sm_{0.08}Fe_{1.92}O_4$ composite.

The average crystallite size of PANI–$LiNi_{0.5}Sm_{0.08}Fe_{1.92}O_4$ composite can be calculated by the Debye–Scherrer formula [29]

$$\beta = \frac{k\lambda}{D\cos\theta} \tag{1}$$

where λ is the wavelength of Cu Kα radiation (0.15418 nm), k is the shape factor taken as 0.9, D is the average crystallite size, θ is the Bragg's angle, and β is the full width at half-maximum (FWHM) of the diffraction peaks. The average crystallite size of PANI–$LiNi_{0.5}Sm_{0.08}Fe_{1.92}O_4$ composite is 87.3 nm, estimated from the XRD peak broadening of the (311) peak.

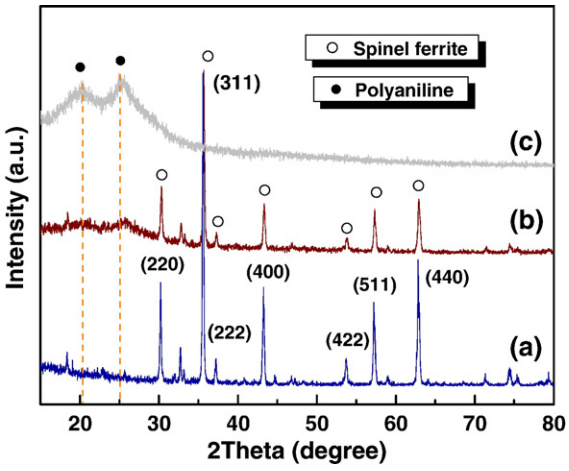

Fig. 1. XRD patterns of $LiNi_{0.5}Sm_{0.08}Fe_{1.92}O_4$ (a), PANI–$LiNi_{0.5}Sm_{0.08}Fe_{1.92}O_4$ composite (b) and PANI (c).