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Preparation and characterization of electromagnetic functionalized polyaniline/$BaFe_{12}O_{19}$ composites

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ABSTRACT

Electromagnetic functionalized polyaniline/$BaFe_{12}O_{19}$ composites were synthesized by *in situ* polymerization of aniline in the presence of $BaFe_{12}O_{19}$ particles. The structure and morphologies of products were characterized by X-ray diffraction, infrared spectra, scanning electron microscopy and transmission electron microscopy. In the electromagnetic measurements, it was found that the ac conductivity of $BaFe_{12}O_{19}$ particles enhanced while the saturation magnetization and coercivity decreased after polyaniline coating.

1. Introduction

Inherently conducting polymers are attractive materials, as they cover a wide range of functions from insulators to metals and retain the mechanical properties of conventional polymers [1,2]. The considerable electrochemical and physicochemical properties result in conducting polymers having various practical applications [3–6]. Among the conducting polymer, polyaniline (PANI) has received a great deal of attention in recent years due to its easy synthesis, excellent environmental stability, and high electrical conductivity. It is well known that conducting polymers can effectively shield electromagnetic waves generated from an electric source, whereas electromagnetic waves from a magnetic source can be effectively shielded only by magnetic materials [7]. Thus, incorporation of magnetic constituents and conducting polymeric materials opens new possibilities for the achievement of good shielding effectiveness for various electromagnetic sources.

Barium hexaferrite $BaFe_{12}O_{19}$ has been currently magnetic material with great scientific and technological interest, and have been widely used for permanent magnets, magnetic recording media and microwave absorbers, due to its high stability, excellent high-frequency response, large magnetocrystalline anisotropy and large magnetization as well [8]. In recent years, barium hexaferrites have displayed a promising application in microwave absorption due to their dielectric and magnetic losses in microwave frequency band [9–11]. Up to now, many reports have focused on choosing the cubic spinel ferrite as magnetic component in the polyaniline-based composites [12–14]. To our best of knowledge, little work has been reported on the preparation and electromagnetic properties of polyaniline-based hexaferrite composites [15].

In this article, the electromagnetic functionalized PANI/$BaFe_{12}O_{19}$ composites, where $BaFe_{12}O_{19}$ particles were magnetic core obtained by a citrate sol–gel combustion process and PANI was the conducting shell, were synthesized by *in situ* polymerization of aniline in the presence of $BaFe_{12}O_{19}$ particles. The samples were characterized by various experimental techniques, and the electromagnetic properties of composites were investigated.

2. Experimental

2.1. Materials

Aniline was distilled twice under reduced pressure and stored below 0 °C. Citric acid, ammonia, $Fe(NO_3)_3{\cdot}9H_2O$, $Ba(NO_3)_2$, $(NH_4)_2S_2O_8$ (APS) were all of analytical purity and used without further purification.

2.2. Preparation of hexaferrite$BaFe_{12}O_{19}$ (BF) particles

Hexaferrite $BaFe_{12}O_{19}$ was prepared by a citrate sol–gel combustion process. Stoichiometric amounts of $Fe(NO_3)_3{\cdot}9H_2O$ and $Ba(NO_3)_2$ were dissolved in a minimum amount of deionized water

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by stirring on a hotplate at ca. 50 °C with the ratio of iron to barium being set at 11.5. Citric acid was then added to the mixture solution to chelate Ba^{2+} and Fe^{3+}. The molar ratios of citric acid to metal ions used were 1:1. An ammonia solution was added to adjust the pH value to 7. The clear solution was slowly evaporated at 80 °C with constant stirring and then the viscous gels were formed. By increasing the temperature up to 200 °C, the gel precursors were combusted to form the brown-colored loose powders. Finally, the as-burnt powders were calcined at 900 °C for 2 h. The hexaferrite $BaFe_{12}O_{19}$ with particle size in the range of 90–140 nm were obtained.

2.3. Preparation of polyaniline/$BaFe_{12}O_{19}$ composites

Polyaniline/$BaFe_{12}O_{19}$ composites were prepared by *in situ* polymerization of aniline in the presence of $BaFe_{12}O_{19}$ particles. 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 procedure, 1 ml aniline monomer was injected into 35 ml of 0.1 M HCl solution containing a certain amount of $BaFe_{12}O_{19}$ particles under ultrasonic stirring for 30 min 2.49 g APS in 20 ml of 0.1 M HCl solution was then slowly added dropwise to the above mixture. The polymerization was carried out by ultrasonic stirring for 8 h at room temperature. The composites were obtained by filtering and washing the reaction mixture with deionized water and ethanol, and dried under vacuum at 60 °C for 24 h. The PANI/$BaFe_{12}O_{19}$ composites containing different content of $BaFe_{12}O_{19}$ were synthesized by using 10 wt% (PB-1) and 20 wt% (PB-2)of $BaFe_{12}O_{19}$ hexaferrite with respect to aniline monomer.

2.4. Characterization

The XRD patterns of the samples were collected on a Philips X'pert Pro MPD diffractometer with Cu Kα radiation (λ = 0.15418 nm). The working voltage of the instrument was 40 kV, and the current was 40 mA. Infrared spectra were recorded on a Nicolet Avatar 360 spectrometer in the range of 400–4000 cm^{-1} using KBr pellets. The field emission scanning electron microscopy (FESEM) was conducted on a Hitachi S4800 field emission scanning electron microscope. The high-resolution transmission electron microscopy (HRTEM) observations were performed 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 7404) with a maximum magnetic field of 15 kOe. The ac conductivity of samples at room temperature was performed on an Agilent E4991A RF Impedance/Material Analyzer in the frequency range from 1 MHz to 1 GHz.

3. Results and discussions

3.1. Polymerization mechanism

It is known that the surface charge of metal oxide is positive below the pH of the point of zero charge (PZC), while it is negative above that. Since the surface of barium ferrite has PZC of pH ≈4.2 [16], it is positively charged in the acidic conditions. Therefore, adsorption of an amount of the anions may occur and compensate the positive charges on barium ferrite surface. Meanwhile, the specific adsorption of these anions on the barium ferrite surface may also take place. In this approach, aniline monomers are converted to cationic anilinium ions in acidic conditions. Thus, the electrostatic interactions appear between anions adsorbed on the barium ferrite surface and cationic anilinium ions. The aniline monomers electrostatically complexed to the barium ferrite surface are then polymerized by ammonium persulfate as an oxidizing agent at room temperature.

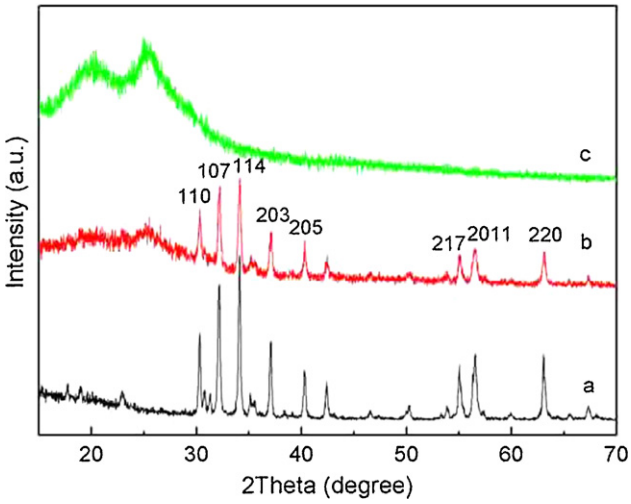

Fig. 1. XRD patterns of (a) $BaFe_{12}O_{19}$ particles, (b) PANI/$BaFe_{12}O_{19}$ composite (PB-1) and (c) PANI.

3.2. Structural characterization

Fig. 1 shows the XRD patterns of the $BaFe_{12}O_{19}$ particles and PANI/$BaFe_{12}O_{19}$ composite (PB-1). As shown in Fig. 1(a), the XRD pattern of the $BaFe_{12}O_{19}$ particles presents the magnetoplumbite structure with no extra reflections, and is perfectly indexed to (1 1 0), (1 0 7), (1 1 4), (2 0 3), (2 0 5), (2 1 7), (2 0 1 1) and (2 2 0) crystal plane of hexagonal $BaFe_{12}O_{19}$ (JCPDS Card No. 84-0757). The typical XRD pattern of PANI (Fig. 1c) shows two broad diffraction peaks centered at $2\theta = 20.4°$ and 25.4°, which can be ascribed to the periodicity parallel and perpendicular to the polymer chains, respectively [17]. Fig. 1(b) shows the XRD pattern of PANI/$BaFe_{12}O_{19}$ composite which contains the characteristic peaks of PANI and $BaFe_{12}O_{19}$ including the peaks at $2\theta = 30.4°$, 32.1°, 34.1°, 37.1°, 40.3°, 55.1°, 56.6° and 63.1°. In addition, the intensities of broad diffraction peaks corresponding to PANI in the composite become weakened with introducing $BaFe_{12}O_{19}$ particles, which indicates that $BaFe_{12}O_{19}$ particles have an effect on the crystallinity of PANI.

Fig. 2 shows the IR spectra of PANI and PANI/$BaFe_{12}O_{19}$ composite (PB-1). The characteristic peaks of PANI occur at 1562, 1479,

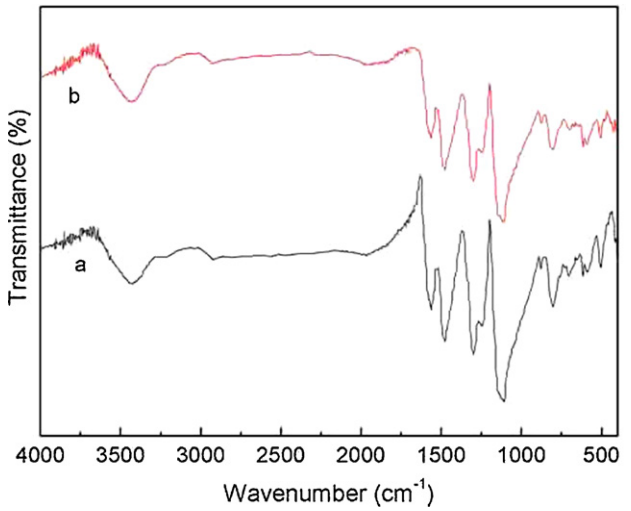

Fig. 2. IR spectra of (a) PANI and (b) PANI/$BaFe_{12}O_{19}$ composite (PB-1).