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Facile synthesis of Shell-Core Polyaniline/$SrFe_{12}O_{19}$ Composites and Magnetic Properties

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Polyaniline (PANI)/$SrFe_{12}O_{19}$ (SrM) composites were synthesized by in-situ polymerization and characterized by XRD, FT-IR, SEM, TEM and VSM. The results showed that $SrFe_{12}O_{19}$ particle obtained by hydrothermal method was of uniform hexagonal plate-like structures with diameter ranging from 2-5 μm. PANI/SrM composites with 15wt% PANI displayed shell-core structure. The $SrFe_{12}O_{19}$ particle was embedded in PANI. Magnetic properties results shown that, due to the presence of nonmagnetic PANI layer, the values of M_s, *Mr*, *Hc* were all lower than those of the pure $SrFe_{12}O_{19}$ particle, and indicated the information of "shell-core" structure composite.

Keywords: $SrFe_{12}O_{19}$ ferrite; in-situ polymerization; PANI/SrM composites; magnetic properties

1. Introduction

Polyaniline (PANI) has been intensively investigated as electromagnetic interference (EMI) shielding material and broadband microwave adsorbing material, due to some significant characteristics such as very light weight, flexibility and reasonably facile processibility [1-4]. However, PANI as a microwave-absorbing material has only electrical loss [5, 6], which is not of any help in improving the microwave absorption property and widening the absorption bandwidth [7]. To compensate for this defect, the integration of magnetic materials and conducing polymers has attracted increased interest. Recently, several interesting research projects have focused on the preparation of PANI composites with magnetic and conducting properties. T. H. Ting et al. [8] synthesized PANI/$BaFe_{12}O_{19}$ composite by in situ polymerization with different Ba ferrite content. S. Saima et al reported PANI/$CuFe_2O_4$ composites via in situ polymerization and discussed the photocatalytic properties of PANI/$CuFe_2O_4$ composites [9]. Yavuz et al. reported a novel approach for synthesizing the PANI–ferrite particles with a hybrid structure via an oxidative electrochemical polymerization of aniline [10].

As is well known, M-type ferrites with hexagonal structure can strongly absorb electromagnetic waves by the mechanism of moment precession resonance (MPR) and display a promising application in microwave absorption due to their permittivity and permeability losses in the microwave frequency band [11]. In particular, strontium hexaferrite (SrM) has been widely used in magnetic recording and microwave absorption, due to its high stability, excellent high-frequency response, large magneto-crystalline anisotropy, and large magnetization

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as well [12]. In previous studies, Hessien et al. [13] have synthesized the $SrFe_{12}O_{19}$ nanoparticles from the natural sample. Jean et al. [14] have synthesized $SrFe_{12}O_{19}$ nanoparticles by hydrothermal method accompanied by calcination. Up to now, a great deal of studies has been devoted to choosing the hexaferrite as the magnetic component in polyaniline-based composites. The previous work reported that the morphology and crystalline size have a significant influence on the composite materials' properties and application [15]. Therefore, we attempt to control SrM ferrite crystalline morphology and size to achieve good shielding and wave adsorbing properties.

Herein, the high-purity strontium ferrite particles were synthesized firstly by hydrothermal method, and then the polyaniline (PANI)/strontium ferrite (SrM) composites were synthesized by in-situ polymerization under mechanical stirring after the ultrasonic dispersion of the mixture. Structure, morphology and magnetic properties of the composite materials were characterized by various instruments and investigated. And a possible polymerization mechanism for PANI/$SrFe_{12}O_{19}$ composites was also discussed.

2. Experimental

2.1 Synthesis of $SrFe_{12}O_{19}$ ferrite particles

The $SrFe_{12}O_{19}$ particles were prepared by hydrothermal process using analytical $Fe(NO_3)_3 \cdot 9H_2O$ and $Sr(NO_3)_2$ as starting materials. Firstly, aqueous solutions of $Fe(NO_3)_3 \cdot 9H_2O$ and $Sr(NO_3)_2$ were coprecipitated by NaOH. In this process, the molar ratio of OH^-/NO_3^- ($R_{O/N}$) and the atomic ratio Fe/Sr ($R_{F/S}$) were set as 2 and 5, respectively. This mixture was then poured into a Teflon lined autoclave. The autoclave was closed and heated at 240°C for 5 h. After allowing the autoclave to cool down to room temperature, the precipitate was separated from solution by centrifugation, washed with deionized water, absolute alcohol and dried at 60 °C for 24 h.

2.2 Synthesis of PANI/SrM composite

0.228 ml aniline (An) and 0.03g $SrFe_{12}O_{19}$ were added in 20 ml HCl solution (1 $mol \cdot L^{-1}$) and homogeneously dispersed under 30 min ultrasonic dispersion and mechanical stirring. 0.625g of peroxydisulfate (APS) was dissolved in 20 ml HCl solution, which was used as an oxidizing agent. The APS solution was then slowly added dropwise to initiate the polymerization. The polymerization was allowed to proceed for 24 h, with mechanical stirring. PANI/SrM composite was obtained by filtering and washing the suspension with methanol and deionized water several times, dried under vacuum at 70 °C for 24 h.

2.3 Characterization

The crystal structures of the samples (SrM, PANI, PANI/SrM) were performed by X-ray diffraction analysis (XRD, Rigaku D/Mmax-2500PC, CuKα). The fourier transform infrared spectroscopy (FTIR) spectra were recorded using Nexu670 spectrometer. The surface morphology and particle size were observed using field emission scanning electron microscopy (FE-SEM, JSM-2800LV) and transmission electron microscopy (TEM, JEM-2100). The magnetic properties of the samples were measured by vibrating sample magnetometer (VSM, HH-15) at room temperature.

3. Result and discussion

3.1 X-ray diffraction

Fig.1 shows the XRD patterns of SrM ferrite, PANI and PANI/SrM composite. It is found that for strontium ferrite (Fig. 1a), diffraction peaks are observed at 2θ =22.99°, 30.83°, 32.19°, 34.11°, 40.31°, 42.42°, 55.05°, 56.59°, 63.05°, 72.58°, 75.46°, which correspond to the typical M type $SrFe_{12}O_{19}$ (P63/mmc PDF#33-1340), furthermore, no any secondary phase is detected, which demonstrates the single phase SrM ferrites are synthesized by hydrothermal method. XRD pattern of PANI (Fig.1b) shows one broad diffraction peak centered at 2θ=25.15°,

which can be ascribed to the periodicity parallel and perpendicular to polymer chains of PANI [16]. As seen Fig.1c, diffraction peak positions of PANI/SrM composite are basically similar to the as-prepared $SrFe_{12}O_{19}$ ferrite particles. Simultaneously, there is a wide peak in the range of 15°-30° and the center at 25.15°, which corresponds to characteristic peak of PANI. Furthermore, it is also observed that the intensities of peak for PANI/SrM composite are weaker than those of pure $SrFe_{12}O_{19}$ ferrite, which reveals that presence of PANI coatings layer. These results indicate that PANI/SrM core-shell composite are obtained.

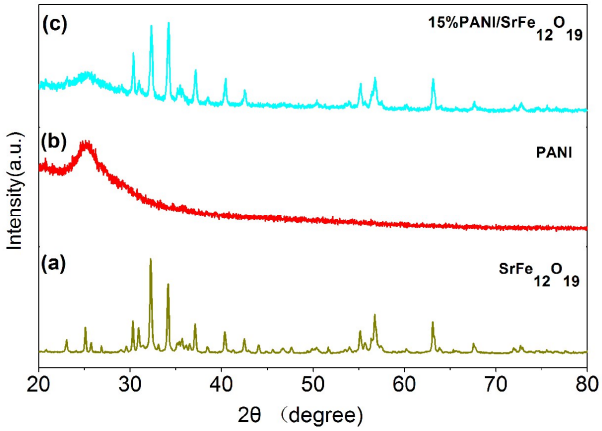

Fig.1 XRD patterns of (a) SrFe12O19, (b) PANI, and (c) PANI/SrFe12O19 composite

3.2 FTIR spectra

The FTIR spectra of the SrM, PANI and PANI/SrM composite are shown in Fig.2. The FTIR spectrum of SrM has been well reported in the literature [17]. In this case, the FTIR spectrum of SrM (Fig.2a) reveals that the peaks at 400-600 cm^{-1} are intrinsic vibrations of the tetrahedral and octahedral sites for the $SrFe_{12}O_{19}$, respectively. The FTIR spectrum of PANI (Fig. 2b) shows that it contains all of the characteristic peaks of PANI. The peaks appeared at 806 cm^{-1}, 1120 cm^{-1}, 1254 cm^{-1}, 1486 cm^{-1} and 1541 cm^{-1}, which represent the C–H out of plane bending vibration of a 1,4-disubstituted aromatic ring, C-H bending mode of a quinoid ring, C-N and $C\text{-}N^{+}$ stretching vibration mode or C-H bending mode of a benzenoid ring, C＝N stretching mode of a benzenoid ring and the C＝C stretching mode of a quinoid ring, respectively [18]. As show in Fig.2c, the FTIR spectrum of PANI/SrM composite is almost identical to that of PANI. However, it is also observed that the characteristic peaks of PANI/SrM composite are slightly shifted towards a higher wave number (1578 cm^{-1}, 1301 cm^{-1}, 1160 cm^{-1}) compared to those of the pure PANI. Hence, these results reveal that there exists an interaction between $SrFe_{12}O_{19}$ particles and PANI chains, and suggests well wrapping of SrM ferrite particles with PANI in PANI/SrM composites.

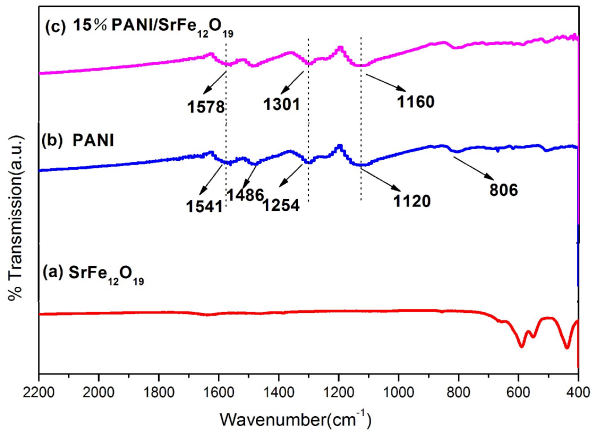

Fig.2 FT-IR spectra of (a) $SrFe_{12}O_{19}$, (b) PANI and (c) PANI/$SrFe_{12}O_{19}$ composite

3.3 Morphology and EDS analysis

The morphology and particle size of strontium ferrite and PANI/SrM composites are determined by SEM and TEM. The SEM and TEM micrographs of strontium ferrite (Figs. 3a and 3c) reveal that the particles are approximately hexagonal in shape with diameter ranging from 2-5 μm. A slight agglomeration is also observed, which is due to the magneto dipole interactions among the magnetic $SrFe_{12}O_{19}$ particles [19]. The EDS spectrum (Fig.3b) of $SrFe_{12}O_{19}$ particle showed that the ration about Fe, Sr and O was corresponded with the chemical formula of $SrFe_{12}O_{19}$, considering the reasonable experimental error. The result confirms that the composition is in agreement with the experiment design. Fig.3d shows the

TEM image of the PANI/SrM composite. It is clearly seen that a net-like structure is formed. The black region is $SrFe_{12}O_{19}$ particles, and the gray colored shell is PANI in the composite. The color difference is attributed to the different electron penetrability. These results indicate the ferrite particles are wrapped by PANI. In addition, it also can be observed that the PANI can minimize the aggregation of ferrite particles, which is due to the repulsive forces between magnetic particles and PANI. Hence, from the results of SEM and TEM, it is clear that synthetic method in this study is applicable to the synthesis of core shell PANI/SrM composites. The results obtained are quite similar to other systems reported elsewhere [20, 21].

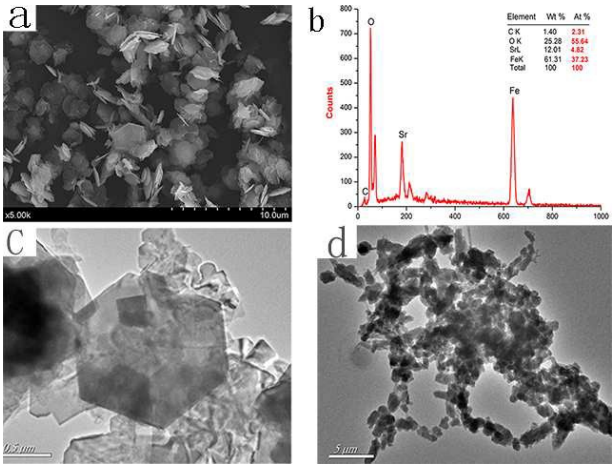

Fig.3 SEM image of (a) $SrFe_{12}O_{19}$, TEM images of (b) $SrFe_{12}O_{19}$ (c) PANI/$SrFe_{12}O_{19}$ composite

3.4 Magnetic properties

Fig.4 shows the hysteresis loops of the pure PANI, $SrFe_{12}O_{19}$ particles and PANI/SrM composites at room temperature. The magnetic parameters such as saturation magnetization (*Ms*), remanence magnetization (*Mr*) and coercivity (*Hc*) of the composites determined by the hysteresis loops are given in Table 1. It can be seen that the *Ms* value of PANI and PANI/SrM composites are much lower than that of the pure $SrFe_{12}O_{19}$ ferrite. The result is obvious, because PANI is nonmagnetic. The existence of nonmagnetic PANI can be envisaged as a magnetic dead layer on the surface, thus affecting the magnitude of magnetization due to quenching of the surface moment. The *Mr* and *Hc* are also less than those of $SrFe_{12}O_{19}$ ferrite. Generally, the coercivity of a material depends upon many factors, such as microstructure, grain shape, composition, magnetic anisotropy etc [22]. For the PANI/SrM composites, in the polymerization process, PANI is deposited on the ferrite surface, crystallite boundaries, which have a healing effect to cover the ferrite surface defects, such as pores and cracks, leading to a decrease in magnetic surface anisotropy of ferrite particles. Consequently, the PANI/SrM composites show lower value of coercivity compared to that of strontium ferrite.

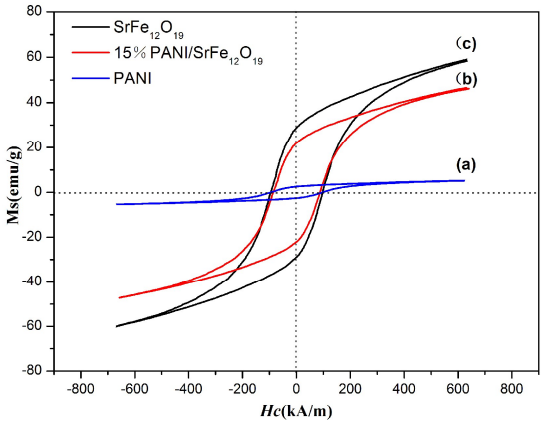

Fig.4 Magnetic hysteresis loops of (a) PANI, (b) PANI/$SrFe_{12}O_{19}$ (c) $SrFe_{12}O_{19}$ particles

Table.1 Saturation magnetization (*Ms*), remnant magnetization (*Mr*) and coercivity (*Hc*) of samples

Sample	*Ms/emu·g*$^{-1}$	*Mr/emu·g*$^{-1}$	*Hc/kA·m*$^{-1}$
PANI	4.95	2.25	96.42
PANI/SrM	46.91	22.35	84.35
$SrFe_{12}O_{19}$	58.63	29.31	98.12

3.5 Mechanism of Polymerization

The polymerization mechanism of PANI/SrM composites are proposed, as shown in Fig.5. According to charge compensation mechanism, due to the polymerization in the acidic conditions, the surface of the ferrite is positively charged. Therefore, adsorption of an

amount of anions such as Cl^- may compensate the positive charges on the ferrite surface. Moreover, in this charge compensation system, extra adsorption of the Cl^- on the ferrite surface would work as the charge compensator for positively charged PANI chains in the formation of PANI/SrM composites. As aniline monomers are shifted to cationic anilinium ions under the acidic condition, the electrostatic interactions occur between anions absorbed on ferrite surface and cationic anilinium ions. In addition, it is also probable that there is hydrogen bonding between the polyaniline chains and the oxygen atoms on the ferrite surface in the core–shell composites. The interactions can ensure ferrite particles to be embedded into the polymer

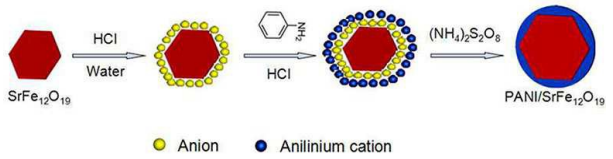

Fig.5 The simple synthesis procedure mechanism of core-shell material of PANI/$SrFe_{12}O_{19}$

chains and form 'core–shell' structural composites.

4. Conclusion

The shell-core structure PANI/$SrFe_{12}O_{19}$ composites are successfully prepared via in-situ polymerization. The synthetic procedure is simple and feasible. The crystallite size of the synthesized $SrFe_{12}O_{19}$ particles can be as fine as 2–5 μm. SEM and TEM results reveal that the $SrFe_{12}O_{19}$ ferrite particles are embedded in to the PANI matrix forming the core-shell structure. The intrinsic magnetic hysteresis loop measurements indicate that the *Ms*, *Mr* and *Hc* are all less than those of pure $SrFe_{12}O_{19}$ ferrite due to the presence of nonmagnetic PANI layer.

Acknowledgements

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