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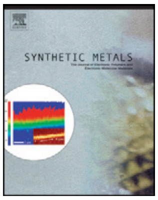

Preparation and characterization of polypyrrole/nano-$SrFe_{12}O_{19}$ composites by in situ polymerization method

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ABSTRACT

Polypyrrole (PPY)/nano-$SrFe_{12}O_{19}$ composites were synthesized by in situ polymerization method. The samples were characterized by TEM, SEM, XRD and IR technology. Spherical, conglobulation-like and arborization-like polypyrrole/$SrFe_{12}O_{19}$ composites were synthesized in an emulsion polymerization system for the first time. It was found that the morphology of PPY/nano-$SrFe_{12}O_{19}$ composites depended on the $SrFe_{12}O_{19}$ content of the reaction system. A possible mechanism for the formation of the different morphologic composites had been proposed. It was found that the saturation magnetization (M_S) and remanent magnetization (M_r) for the composites decreased with the decrease of the nano-$SrFe_{12}O_{19}$ content. The coercivity force (H_c) for the composites increased with the increase of PPY content when the PPY content was at a low value, and then decreased with the increase of PPY content. The possible mechanism for the phenomenon had been proposed. The conductivity was measured, and the variation mechanism of the composites conductivity was analyzed in the paper.

1. Introduction

Recently, conducting polymer composites with both electrical and ferromagnetic properties have received tremendous attention, and study on this kind of composites has becoming one of the most active and promising research area [1–3]. What makes conducting polymer composites so attractive is their potential applications in batteries [4], electro-chemical display devices [5], molecular electronics [6], electrical–magnetic shields, and microwave-absorbing materials [7], etc.

Polypyrrole (PPY) is one of the most promising conducting polymers due to unique properties, excellent environmental stability and potential application in electronic devices [8,9]. Among the inorganic magnetic nano-particles, $SrFe_{12}O_{19}$ nano-particles had received great attention because of their excellent magnetic properties as well as extensive potential applications in the field of permanent magnetic material [10–12]. Recently, PPY composites containing ferrite nano-particles were mostly studied. Many methods had been reported for producing PPY/ferrite composites.

Xue et al. [13] obtained PANI–Fe_3O_4 nano-composites through mechanical mixing the DBSA–PANI powder and the HCl–PANI–Fe_3O_4 powder. Wan's group [14–16] prepared the PANI nano-composites containing Fe_3O_4 nano-particles by blending the PANI in N-methyl-2-pyrrolidone (NMP) with iron(II) sulfate aqueous solution, and precipitating Fe^{2+} into magnetite, and allowing the monomer to react with $FeCl_2{\cdot}4H_2O$ and $FeCl_3{\cdot}6H_2O$, following by treatment with KOH aqueous solution. However, the most general method was by direct polymerization of aniline monomers in an aqueous solution in the presence of dispersed iron oxide particles with different surfactants. Deng et al. [17] reported the preparation of PANI/Fe_3O_4 nano-particles with core–shell structure via an in situ polymerization of aniline monomer in an aqueous solution, which contained Fe_3O_4 nano-particles and surfactant NaDS. He and Yu [18] and He [19–21] obtained sub-micrometer polyaniline/nano-silica, polyaniline/nano-ZnO and polyaniline/nano-CeO_2 composites by using nano-silica, nano-ZnO and nano-CeO_2 as the stabilizer for the Pickering emulsion, respectively. Yuan-Xun Li et al. [22] obtained tubular polyaniline–barium ferrite composite by in situ polymerization of aniline.

In this work, PPY/nano-$SrFe_{12}O_{19}$ composites were prepared in the phase of an emulsion polymerization system. The morphology of PPY/nano-$SrFe_{12}O_{19}$ composites could be modified by the amount of $SrFe_{12}O_{19}$. A possible formation mechanism of PPY/nano-$SrFe_{12}O_{19}$ composites was also discussed. The samples were characterized by various experimental techniques and magnetic properties and the conductivity of PPY/nano-$SrFe_{12}O_{19}$ composites were investigated.

2. Experimental

2.1. Preparation of $SrFe_{12}O_{19}$ nano-particles

$SrFe_{12}O_{19}$ nano-particles were prepared by sol-gel method. The detailed process could be described as follows. $Fe(NO_3)_3{\cdot}9H_2O$ and

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$Sr(NO_3)_2$ (as the molar ratio of Sr/Fe equal to 1:12) were dissolved in 120 ml distilled water, then the entire mixture was stirred at 80 °C until $Fe(NO_3)_3 \cdot 9H_2O$ and $Sr(NO_3)_2$ were completely dissolved. Citric acid (as the molar ratio of acid/metal ion equal to 1:1) was added to the solution. The pH value of the solution was then adjusted to 6 with $NH_3 \cdot H_2O$. This solution was evaporated at 80 °C until the gel formed. This gel was dried at 90 °C to obtain dry-gel. Then, the dry-gel were heated in a oven in air atmosphere at 850 °C for 2 h. The $SrFe_{12}O_{19}$ sample A was obtained.

2.2. Synthesis of PPY/nano-$SrFe_{12}O_{19}$ composites

PPY/nano-$SrFe_{12}O_{19}$ composites were prepared in the phase of sodium lauryl benzene sulfate (DBS) emulsion polymerization system. The detailed process could be described as follows. Some account of $SrFe_{12}O_{19}$ was dissolved into sodium lauryl benzene sulfate solution, and dispersed in supersonic wave atmosphere for 30 min. The pyrrole was added into the above solution, the mass ratio of pyrrole to $SrFe_{12}O_{19}$ were kept at 10:1, 15:1, 20:1, 0, respectively, to obtain sample B, C, D and E. Then the solution was agitated under the atmosphere of nitrogen for 60 min. Then $K_2S_2O_8$ (the mol ratio of pyrrole to $K_2S_2O_8$ was 1:1) was added to the pyrrole mixture. Then the mixture was agitated for 24 h at the temperature between 0 °C and 5 °C. All the reaction solutions were put into a 200 ml beaker and irradiated with ultrasonic wave using a SK2200-LH ultrasonic cleaning bath. The precipitates were washed with ethyl alcohol, HCl and water respectively for many times. Finally, the product was dried under vacuum at 60 °C for 10 h. Thus the PPY/nano-$SrFe_{12}O_{19}$ composites B, C, D and E were obtained.

2.3. Characterization

The crystalline structure of the samples was determined by α D/max-A diffractometer (Cu Kα radiation, $\lambda = 0.154056$ nm) studies. Fourier transform infrared spectroscopy (FTIR) spectra of the samples were taken in dried KBr powder on Nexus 670 spectrometer (Nicolet, USA). The morphology of as-prepared PPY/nano-$SrFe_{12}O_{19}$ composite was investigated by transmission electron microscopy (TEM) and scanning electron microscope (SEM). The magnetic properties were measured at room temperature using a vibration sample magnetometer (VSM) with a maximum field of 10 KOe. The conductivity was measured on a SDY-4 four-probe instrument at room temperature.

3. Results and discussion

3.1. X-ray diffraction analysis

The XRD patterns of $SrFe_{12}O_{19}$ and PPY/$SrFe_{12}O_{19}$ composite nano-particles were shown in Fig. 1. As shown in Fig. 1, the XRD spectra showed diffraction peaks of $SrFe_{12}O_{19}$ (1 1 0), $SrFe_{12}O_{19}$ (1 0 7), $SrFe_{12}O_{19}$ (1 1 4), $SrFe_{12}O_{19}$ (2 0 3), $SrFe_{12}O_{19}$ (2 0 5) and $SrFe_{12}O_{19}$ (2 0 6) were all observed in each curve. The relative peak value of Fig. 1a was lower. That was because the relative PPY mass of sample C was higher than the other samples. But there was a wide peak observed in the ranges between $2\theta = 20°$ and 30° in Fig. 1a–c, which corresponded to the peaks of polymer. It indicated there was the PPY crystal in the composites and the composite nano-particles were obtained.

3.2. FTIR spectral analysis

The FTIR spectra of the PPY/nano-$SrFe_{12}O_{19}$ composites and PPY sample without $SrFe_{12}O_{19}$ nano-particles under the same conditions were shown in Fig. 2. It was observed from Fig. 2(2)–(3) that there was the peak at the 600 cm^{-1} (correspond to vibrations of the tetrahedral and octahedral sites for $SrFe_{12}O_{19}$) in each curve. But there was no peak in the curve of Fig. 2(1). The peaks at 1560 cm^{-1} and 1470 cm^{-1} attributed to the characteristic C=C stretching of the quinoid and benzenoid rings, the peaks at 1299 cm^{-1} and 1240 cm^{-1} correspond to N–H bending and asymmetric C–N stretching modes of the benzenoid ring were also observed in each curve of Fig. 2. The peak around 1134 cm^{-1} was associated with vibrational modes of N=Q=N (Q refers to the quinonic-type rings), indicating that PPY formed in our sample. The peak at 818 cm^{-1} was attributed to the out-of-plane deformation vibration of the p-disubstituted benzene ring. In addition, the peak located at about 3439 cm^{-1} corresponds to N–H stretching mode. The IR spectrum of PPY–$SrFe_{12}O_{19}$ composite was almost identical to that of PPY. However, the characteristic peaks of $SrFe_{12}O_{19}$ can be observed in Fig. 1c and shifted to lower wave numbers (580 cm^{-1}). These results indicated that there was interaction

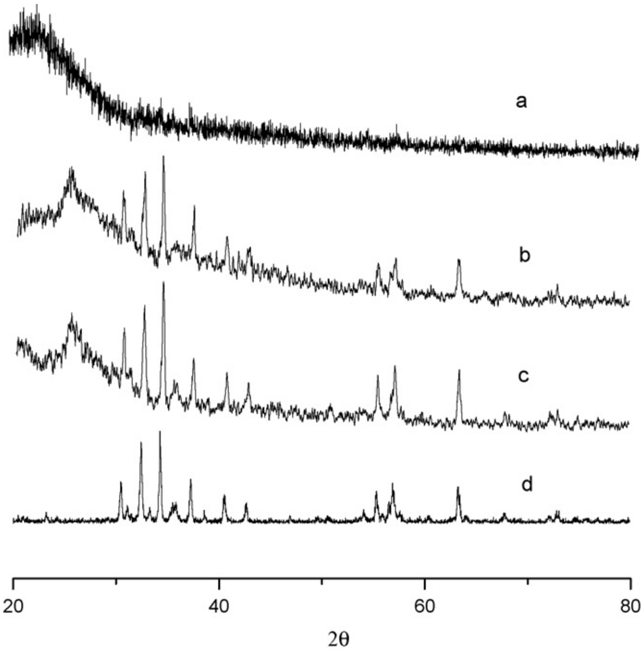

Fig. 1. The XRD patterns of samples prepared as the pryrrole/$SrFe_{12}O_{19}$ mass ratios: (a) 20:1; (b) 15:1; (c) 10:1; (d) 0.

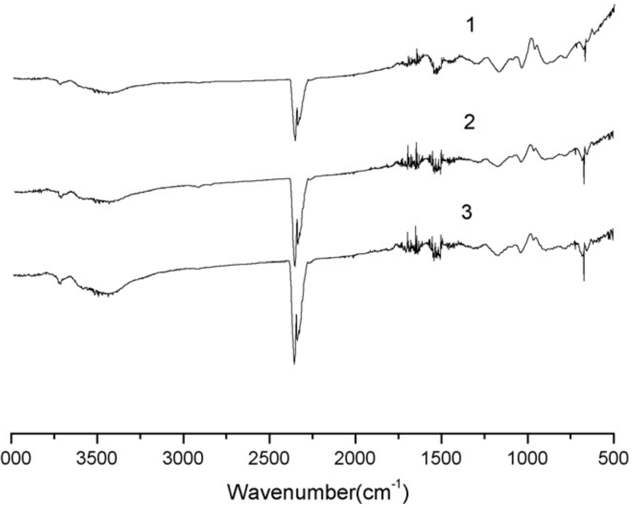

Fig. 2. FTIR spectra of prepared with different $SrFe_{12}O_{19}$/pryrrole mass ratios: (1) 0; (2) 1:10; (3) 1:15.