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Synthesis and characterization of γ-Fe$_2$O$_3$—polythiophenen nanocomposites

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Recently, inorganic/conducting polymer composites with good electrical and magnetic properties have received tremendous attention, and study on this kind of composites has become one of the most active and promising research fields. What makes inorganic/conducting polymer composites so attractive is their potential application to batteries, electro-chemical display devices, molecular electronics, electromagnetic shields, and microwave-absorbing materials etc. [1, 2]. Until now, the research on this aspect is mainly limited to magnetic polypyrrole nanocomposites [3–5] and magnetic polyaniline nanocomposites [6, 7]. Polythiophene and its derivatives are research hotspots in the conducting polymer area for their easy polymerization and stabilization in air. Chen [8] and Faid [9] *et al.* have doped polythiophene and its derivatives with I_2 and BF_4^- to improve their conductivity. However little research on magnetic polythiophene (PTP) nanocomposites is reported. In this letter, we report a novel chemical synthesis of a γ-Fe$_2$O$_3$ encapsulated PTP (γ-Fe$_2$O$_3$-PTP) conducting nanocomposite.

γ-Fe$_2$O$_3$ nanoparticles were synthesized according to the following procedure: a solution of $FeCl_3{\cdot}6H_2O$ and $FeSO_4{\cdot}7H_2O$ was mixed and stirred at room temperature. Then NaOH solution was added to the mixed solution until the pH values of the reaction mixture reached the range of 13–14. The resulting nanoparticles were put into an oven at 80 °C for 3 hrs, then filtered, washed and dried in air. γ-Fe$_2$O$_3$ nanoparticles prepared from the previous step were modified by polyethylene glycol (PEG-400), then added into a round-bottom flask equipped with a mechanical stirrer. $CHCl_3$ and thiophene monomer were added to the flask. Then anhydrous ferric chloride was added and stirred at 0 °C for 2 hrs. After the ice bath was removed, the mixture was allowed to warm to room temperature and to stir for 3 hrs. $CHCl_3$ was evaporated and the residue was added to 1 M HCl (0 °C). The product was filtered, washed and dried in vacuum. Pure polythiophene was prepared with a similar method as the preparation of γ-Fe$_2$O$_3$-PTP, but γ-Fe$_2$O$_3$ nanoparticles and PEG-400 were not required.

The phase composition of γ-Fe$_2$O$_3$-PTP nanocomposites were characterized by X-ray diffraction (XRD) using a D8 ADVANCE diffractometer employing Cu K_α ($\lambda = 0.154$ nm) radiation. The structure of the samples was analyzed by FTIR PE580-B using samples pressed into pellets with KBr. The morphologies of the γ-Fe$_2$O$_3$-PTP nanocomposites were observed using TEM JEM-100CX. The microstructure of the samples was investigated by Mössbauer spectroscopy using a constant—acceleration spectrometer with a ^{57}Co source in a Pd matrix at room temperature. Hyperfine interaction parameters were derived from the Mössbauer spectra using a least-squares method. The spectrometer was calibrated using a standard 25 μm α-Fe foil.

The TEM photograph of γ-Fe$_2$O$_3$ in Fig. 1a shows an average particle size of 10–20 nm. The TEM photograph of γ-Fe$_2$O$_3$-PTP in Fig. 1b shows that the γ-Fe$_2$O$_3$ nanoparticles are encapsulated by polythiophene successfully.

In the stretching vibration region, for thiophene monomer there are two peaks centered at 3060 and 3100 cm^{-1} due to aromatic C_α-H and C_β-H stretching vibration. However, for polythiophene there is only one broad peak centered at about 3060 cm^{-1} in proportion to the thiophene ring at the end of the polymer, which is very small [10]. Figs 2a and b are the FTIR spectra of PTP and γ-Fe$_2$O$_3$—PTP. As can be seen, in both Figs 2a and b, only one broad peak is present at 3060 cm^{-1}. In the fingerprint region, the absorption peak at 790 cm^{-1} is due to the out-of-plane vibration of the 2,5-substituted thiophene ring created by the polymerization of thiophene monomer. This may prove that thiophene monomer has polymerized in both cases. The peak centered at 1655 cm^{-1} in Fig. 2a is usually ascribed to the vibration of C=O group, suggesting the possibility of polythiophene reacting with O_2, this result is in accordance with the literature [11]. When encapsulating γ-Fe$_2$O$_3$ nanoparticles, this peak moves to 1633 cm^{-1}, which proves that interaction happens between C=O and γ-Fe$_2$O$_3$ nanoparticles. The absorption peak at 698 cm^{-1} was due to the thiophene ring breathing vibration. After encapsulating γ-Fe$_2$O$_3$ nanoparticles this peak is weakened apparently and moves to low wavenumber, indicating that γ-Fe$_2$O$_3$ has an effect on the thiophene ring. The peak in Fig. 2b at 580 cm^{-1} indicates the presence of γ-Fe$_2$O$_3$ nanoparticles [12]. All this proves that strong interaction happens

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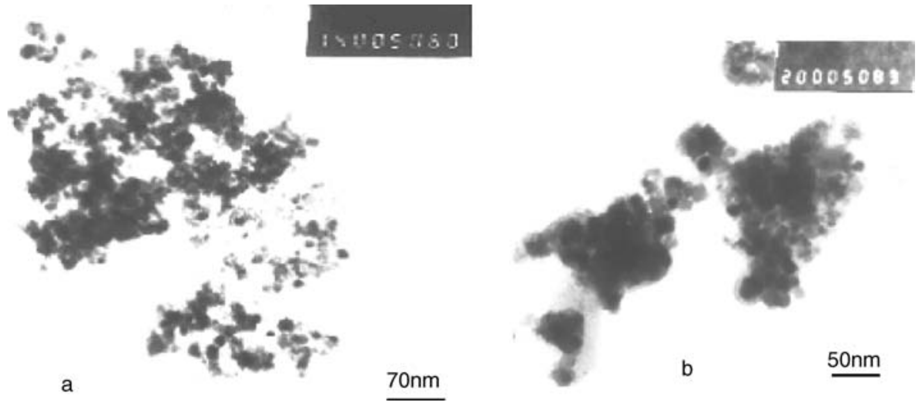

Figure 1 TEM micrographs of γ-Fe_2O_3 nanoparticles and γ-Fe_2O_3—PTP composites: (a) γ-Fe_2O_3 nanoparticles, and (b) γ-Fe_2O_3—PTP composites.

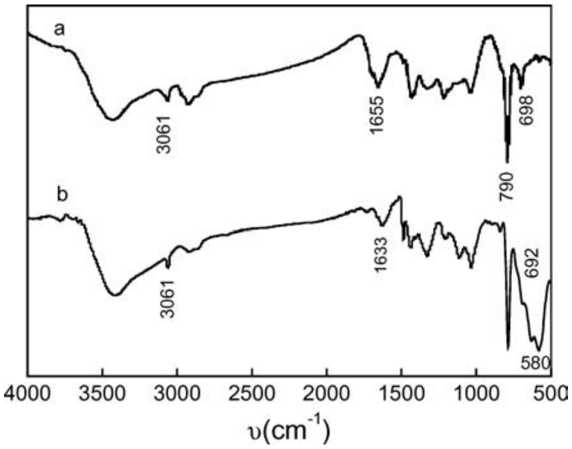

Figure 2 FTIR spectra of PTP and γ-Fe_2O_3—PTP: (a) PTP and (b) γ-Fe_2O_3—PTP.

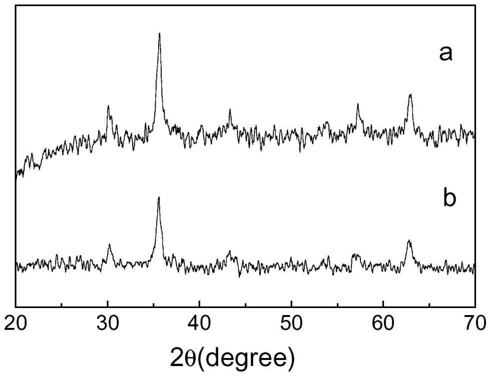

Figure 3 XRD spectra of γ-Fe_2O_3 and γ-Fe_2O_3—PTP: (a) γ-Fe_2O_3 and (b) γ-Fe_2O_3—PTP.

between γ-Fe_2O_3 and polythiophene, making polythiophene as the shell encapsulating on the surface of γ-Fe_2O_3 nanoparticles.

Fig. 3 displays the XRD pattern of γ-Fe_2O_3 and γ-Fe_2O_3—PTP. In Fig. 3a, the diffraction peaks at 30.109, 35.619, 43.335, 57.293, and 62.943 °C are in accordance with standard XRD card (JCPDS: 25-1402) of γ-Fe_2O_3. The diffraction peak in Fig. 3b is consistent with that in Fig. 3a, which means that PTP was amorphous. Most of the literature on preparing PTP reported that it was amorphous [13, 14]. This result indicates that although γ-Fe_2O_3 nanoparticles are encapsulated by PTP, PTP has no evident effect on the crystal structure of γ-Fe_2O_3 and γ-Fe_2O_3 nanoparticle dose not nucleate crystallization of the PTP.

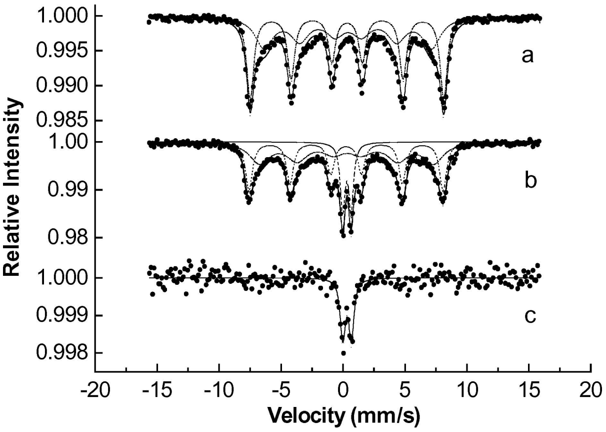

Figure 4 Mössbauer spectra of γ-Fe_2O_3 nanoparticle. γ-Fe_2O_3—PTP and PTP($FeCl_3$): (a) γ-Fe_2O_3 nanoparticle, (b) γ-Fe_2O_3—PTP, and, (c) PTP ($FeCl_3$).

The Mössbauer spectra of γ-Fe_2O_3 and γ-Fe_2O_3—PTP are presented in Fig. 4. The Mössbauer spectrum of γ-Fe_2O_3 nanoparticles (Fig. 4a) shows the asymmetric broadening toward the central peaks of the sextet. We fitted the spectrum with two sextets. The basic parameters are shown in Table I. The parameters of the sextet with large H value are consistent with γ-Fe_2O_3 [15], the sextet with small H value and line broadening is due to a surface effect and a collective magnetic excitation of γ-Fe_2O_3 nanoparticle [16]. These observations prove that the sample before encapsulation consists of γ-Fe_2O_3 nanoparticles. Comparing the Mössbauer spectrum of γ-Fe_2O_3—PTP with that of γ-Fe_2O_3, an

TABLE I Mössbauer spectra parameters of γ-Fe_2O_3 nanoparticle. γ-Fe_2O_3—PTP and PTP($FeCl_3$)

Samples	Sub-spectra	H (kOe)	IS (mm/s)	QS (mm /s)	Γ/2 (mm/s)	Area (%)
γ-Fe_2O_3	Sexlet1	485.71	0.32	0.01	0.28	40.8
	Sexlet2	439.19	0.38	0.04	0.82	59.2
γ-Fe_2O_3—PTP	Sexlet1	485.08	0.25	0.02	0.33	39.8
	Sexlet2	434.31	0.32	0.07	0.97	45.5
	Double1		0.31	0.69	0.21	14.6
PTP ($FeCl_3$)	Double1		0.33	0.7	0.22	100

Note: IS—isomer shift; QS—quadrupole splitting; H—hyperfine field; Γ/2- width of lines.

apparent doublet was detected in γ-Fe_2O_3—PTP. Considering our experiment using $FeCl_3$ as catalyst, we guess the doublet may be caused by the doping of $FeCl_3$ to PTP. So we test the Mössbauer spectrum of pure PTP, which was shown in Fig. 4c. As we can see, there is a doublet in the spectrum of PTP. We analyze these spectra and list the basic parameters in Table I. IS and QS of PTP are in accordance with $FeCl_3$ [17]. Comparing the doublet parameters with those of γ-Fe_2O_3—PTP, there is no apparent difference for IS and QS. In our experiment, the quality of $FeCl_3$ was four times that of thiophene monomer and the reaction was very rapid. So $FeCl_3$ was unavoidably doped in PTP. Herein we think the doublet in γ-Fe_2O_3—PTP is due to $FeCl_3$. Comparing Figs 4a and b, we also find that the asymmetric broadening toward the central peaks of the sextet is still present in γ-Fe_2O_3—PTP. Analyzing the spectra, we find that the area proportion of the two sextets changed greatly. The area ratio of the second sextet to the first sextet changed from 1.45 to 1.14, which shows that after encapsulation with PTP, the surface effect and collective magnetic excitation of γ-Fe_2O_3 nanoparticles are depressed apparently. Together with the FTIR and TEM results, we can see that strong interaction happened between PTP and γ-Fe_2O_3 nanoparticles.

In conclusion, we prepared γ-Fe_2O_3—PTP nanocomposites using monomer polymerization method. FTIR, XRD,TEM and Mössbauer spectra proved that the encapsulation was successful and strong interaction happened between γ-Fe_2O_3 and PTP.

Acknowledgment

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