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The synthesis and characterization of electrical and magnetic nanocomposite: PEDOT/PSS–Fe_3O_4

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ABSTRACT

The poly(3,4-ethylenedioxythiophene)/poly(styrene sulfonate)–Fe_3O_4 (PEDOT/PSS–Fe_3O_4) nanoparticles have been prepared by using polystyrene sulfonic sodium (NaPSS) as a dispersant and dopant. The characterization of nanocomposites was investigated by transmission electron microscope, X-ray diffraction, UV spectroscopy, electrochemical study, four-probe, thermogravimetric analysis and magnetic property measurement system. XRD revealed the presence of spinel phase of Fe_3O_4 and the average size was calculated to be about 12 nm. The conductivity of nanocomposites at room temperature is excellent and it depends on the Fe_3O_4 content. The thermal stability of composites is outstanding. Higher saturation magnetization of 6.47 emu g^{-1} (20 wt.% Fe_3O_4) was observed at 300 K.

1. Introduction

The electrical and magnetic materials have attracted an increasing interest in recent years because of their applications in the fields of electrical and magnetic shields, molecular electronics, nonlinear optics and microwave absorbing materials [1–4].

Recently, some conducting polymers with nanoparticles of Fe_3O_4 which possess desirable electrical and magnetic properties have been prepared. To date, most of the literatures focused on the composites of polypyrrole (PPY)–Fe_3O_4 and polyaniline (PANI)–Fe_3O_4 [5–9].

The system of PEDOT/PSS has many excellent features such as good film forming properties, high conductivity, high visible light transmissivity, and excellent stability comparing with PPY and PANI. The PEDOT/PSS was prepared by the method of oxidative polymerization, with ammonium persulfate ($(NH_4)_2S_2O_8$) as the oxidant and Fe^{3+} as the catalyst. The PEDOT segments (6–18 repeating units) are much shorter comparing to PSS chains [10] (Fig. 1). Magnetic nanoparticles Fe_3O_4 have already been employed in many advanced technology areas such as biology, pharmacy, diagnostics, *etc*. It is noteworthy that NaPSS was used both as a dispersant and dopant in our aqueous phase polymerization system. The PEDOT/PSS–Fe_3O_4 nanocomposites have been prepared by three steps: (1) Fe_3O_4 ferrofluid was prepared according to previous literature [11]. (2) Then NaPSS was added into Fe_3O_4 ferrofluid and the nanocomposites (PSS–Fe_3O_4) were prepared. (3) Lastly, the EDOT was added into the mixture and the EDOT was polymerized on the PSS chains which act as a dopant.

2. Experimental

2.1. Materials and instrument

3,4-Ethylenedioxythiophene monomer (Bayer AG, Germany) was hermetic and stored in fridge. Polystyrene sulfonic acid sodium (NaPSS 20 wt.%, molecular mass 50,000) was purchased from Xing Zhi Lian Co., China. All other reagents, including $(NH_4)_2S_2O_8$, $FeSO_4{\cdot}7H_2O$, $FeCl_3{\cdot}6H_2O$, ammonia (25%), HCl (35%), $Fe_2(SO_4)_3{\cdot}xH_2O$ are analytical grade and used without further purification. Deionized distilled water was used as the dispersion medium.

The morphology of the composites was observed by FEI-Tecnai 12 TEM. The crystal structure of the composites was examined by XD-3A diffractometer. The UV–vis spectrum was observed at room temperature on a Hitachi U3010 spectrometer. Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) were carried out on a CHI660B electrochemical workstation. A conventional three-electrode configuration cell was employed for all electrochemical measurements, with an Ag/AgCl (Saturated KCl, 0.199 V vs. SHE) electrode as the reference electrode and a platinum wire as the auxiliary electrode. Gold working electrodes used were made from a gold wire (99.995%) of a radius of 1 mm. All potentials quoted were with respect to the Ag/AgCl electrode. Conductivity was measured by DB-4 using the standard four-probe method on pressing pellets of composites under 20 MPa at room temperature. Thermal property of the composites was examined by Q600SDT synchronization heat analyzer. The magnetism measurement was measured at 300 K by using MPMS XL-7 Magnetic Property Measurement System.

2.2. Preparation of Fe_3O_4 ferrofluid

Fe_3O_4 nanoparticles were prepared by chemical precipitation method [11]. $FeCl_3{\cdot}6H_2O$ and $FeSO_4{\cdot}7H_2O$ with 2:1 molar ratio were added into quantitative deionized water. The mixture was stirred slowly under nitrogen atmosphere for 5 min. Then ammonium hydroxide solution was added until the colour of mixture changed to black. The reaction was vigorously stirred for 1 h at room temperature. The resulting magnetic nanoparticles were separated by centrifugation at 5000 rpm for 5 min and the deposits were washed by deionized water for three times.

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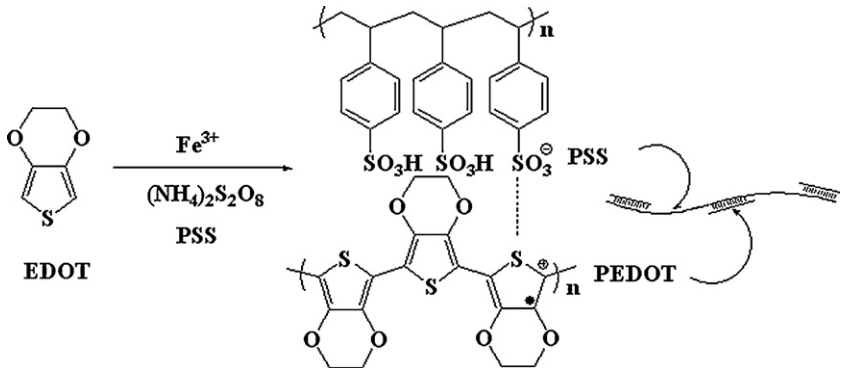

Fig. 1. Schematic representation of the polymer complex between PEDOT and PSS.

2.3. Preparation of PSS–Fe_3O_4 composite

The prepared Fe_3O_4 nanoparticles were added in 250 ml deionized water and 12.5 g NaPSS (20 wt.%) were added in the ferrofluid. The mixture was mechanically stirred at room temperature for 4 h.

2.4. Preparation of PEDOT/PSS–Fe_3O_4 composite

1 g EDOT was added to the prepared PSS–Fe_3O_4 mixture with slowly stirring. Then 2.26 g $(NH_4)_2S_2O_8$ and 25 mg $Fe_2(SO_4)_3$ were added into the reactor. Hydrochloric acid (0.63 M) was added dropwise into the above mixture with vigorous stirring. The pH value of the mixture was adjusted to about 3. The mixture was kept stirring for 30 h at room temperature. After that, the productions were separated by centrifugation at 5000 rpm for 5 min and dried overnight in vacuum oven at 60 °C. The remaining solutions of the reaction were used for electrochemical study. Four kinds of power with different content of Fe_3O_4 in PEDOT/PSS–Fe_3O_4 nanocomposite (1.6 wt.%, 5 wt.%, 10 wt.% and 20 wt.%) were prepared.

3. Results and discussion

3.1. TEM micrograph of PSS–Fe_3O_4 and PEDOT/PSS–Fe_3O_4 nanocomposite

In Fig. 2(a) the TEM micrograph of PSS–Fe_3O_4 nanocomposite, Fe_3O_4 particles with particle size smaller than 10 nm could be found. The small size of Fe_3O_4 particles is attributed to the dispersant (PSS). Fig. 2(b) shows the TEM micrograph of PEDOT/PSS–Fe_3O_4 composite with 5 wt.% Fe_3O_4. The diameter of the particles is in the range of 10–30 nm. These particles are agglomerated due to the decrease of the emulsification (PSS) during the polymerization process and magneto-dipole interactions between the particles. Fig. 2(c) shows the TEM micrographs of PEDOT/PSS–Fe_3O_4 film with 5 wt.% Fe_3O_4. A majority of Fe_3O_4 particles has regular shape and well dispersed in the polymer. The diameter of Fe_3O_4 particles ranges from 10 to 30 nm.

3.2. X-ray diffraction analysis of Fe_3O_4 and PEDOT/PSS–Fe_3O_4 composite

Fig. 3 shows the XRD patterns of different samples. The characteristic diffraction peaks of composite (20 wt.% Fe_3O_4) at $2\theta = 30.0^\circ$, 35.4°, 43.1°, 53.3°, 57.0° and 62.6° are well consistent with the pure Fe_3O_4 nanoparticles (Fig. 3(e)) [12]. The main diffraction peaks of PEDOT/PSS–Fe_3O_4 composites are similar to the pure Fe_3O_4 nanoparticles, indicating the presence of crystalline structure Fe_3O_4 nanoparticles in the composites. There is no obvious chemical interaction between Fe_3O_4 and PEDOT/PSS in the composites. The average size of the Fe_3O_4 nanoparticles for (3 1 1) reflection can be calculated by the Scherrer equation [13].

$$D = \frac{0.89\lambda}{\beta \cos\theta},$$

where D is the grain size, λ is the X-ray wavelength, β is the full-width at half maxima of the X-ray diffraction peak, and θ is the Bragg angle. According to the β value of Fe_3O_4 (3 1 1), the particle size was calculated to be about 12 nm.

It is known that the amorphous nature of the nanocomposite will increase if composites have higher amount of polymer [14]. In Fig. 3 the diffused broad of amorphous peaks ranged from 10° to 30°, indicating the crystalline behavior of Fe_3O_4 is suppressed because of the encapsulation of polymer. This result is also in agreement with other researchers [5,15].

3.3. UV–vis spectra of PEDOT/PSS and PEDOT/PSS–Fe_3O_4 composite

Fig. 4 shows UV–vis spectra of PEDOT/PSS–Fe_3O_4 composite solutions with different Fe_3O_4 content. The absorbance at 250 nm shows the presence of substituted phenyl groups in PSS [16] and the absorbance near 600 nm is assigned to the PEDOT $\pi \rightarrow \pi^*$ absorption [17]. However, there is no obvious evidence to prove the interaction between these two components. The result of XRD supports this conclusion as well.

3.4. Electrochemical behaviors of PEDOT/PSS and PEDOT/PSS–Fe_3O_4 composite

Prior to test in voltammetric experiments, the remaining solutions of the reaction were centrifuged at 5000 rpm for 5 min to eliminate the interference of PEDOT/PSS–Fe_3O_4 composite. Cyclic voltammetry of the solutions (PEDOT/PSS and PEDOT/PSS–Fe_3O_4 composite with 20 wt.% Fe_3O_4) are presented in Fig. 5(a) and (b), respectively. Both of the CVs have two redox peaks at 0.392 V, 0.448 V (Fig. 5(a)) and 0.345 V, 0.470 V (Fig. 5(b)) which are attributed to the redox of Fe(II)/Fe(III) couple [18].

The differential pulse voltammetry of PEDOT/PSS–Fe_3O_4 composite solutions with different Fe_3O_4 content are shown in Fig. 6. The peak current rises as the content of Fe_3O_4 increase, indicating the increase of Fe^{3+} concentration in the solution. This can be attributed to the addition of hydrochloric acid into the mixture. As PEDOT/PSS is a porous matrix [19], a number of Fe_3O_4 nanoparticles could be dissolved into the mixture during the reaction.

3.5. Conductivity of PEDOT/PSS and PEDOT/PSS–Fe_3O_4 composite

The conductivity of PEDOT/PSS–Fe_3O_4 composites containing 1.6 wt.%, 5 wt.%, 10 wt.%, 20 wt.% Fe_3O_4 is in the range of 0.21–1.67 S cm^{-1}, lower than that of PEDOT/PSS powder (4 S cm^{-2}) (Fig. 7). A reasonable explanation for this result is associated with the existence of insulated Fe_3O_4 nanoparticles in the composite that prevent the transfer of charge carrier in the PEDOT/PSS chains.