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Composites of nanotubular polyaniline containing Fe_3O_4 nanoparticles*

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Results of charge-transport and magnetic measurements of nanotubular polyaniline (PANI) composites containing Fe_3O_4 nanoparticles (∼10nm) synthesized by a "template-free" method are reported. The $T^{-1/2}$ resistivity has been observed, and dc magnetic susceptibility data are fitted to an equation $\chi = \chi_P^* + C/T$. With increasing weight ratio of Fe_3O_4, the electrical conductivity and temperature-independent susceptibility χ_P^* increase, and the Curie-type susceptibility is suppressed at low temperatures. Further discussions have been given. The PANI-H_3PO_4/Fe_3O_4 composite containing 27wt% of Fe_3O_4 nanoparticles is superparamagnetic, exhibiting very little hysteresis even at 5K.

Keywords: polyaniline, nanotube, resistivity, magnetic susceptibility
PACC: 7360R, 7540C, 7530C, 7280T

1. Introduction

Among the conducting polymers, polyaniline (PANI) has been of particular interest because of its electrical, electrochemical and optical properties. At the same time, magnetic nanoclusters also show unusual phenomena. Recently, to realize the full potential of technological applications of magnetic nanomaterials and organic polymers, composites of conducting polymers containing magnetic nanoclusters have attracted much attention, because the resultant nanocomposites may good possess magnetic and electrical properties. For example, Wan and co-workers[1,2] reported a composite of PANI containing Fe_3O_4 nanoparticles[3] with both conducting and unusual paramagnetic properties, which showed a high saturated magnetization with a lower coercive force (H_c=0). In particular, Tang *et al*[4] have prepared γ-Fe_2O_3/PANI free standing nanocomposite films which are macroscopically processable, high electrically conductive (82–237S/cm) and superparamagnetic (no hysteresis loop at room temperature). However, composites of nanotubular conducting polymers containing magnetic nanoclusters have not been reported yet, and its physical properties, such as the temperature dependences of conductivity and dc magnetic susceptibility have not been explored sufficiently.

In this paper, the nanotubular H_3PO_4 doped PANI composites containing Fe_3O_4 nanoparticles with an average diameter of 10nm have been prepared by a "template-free" method,[5–7] and their dc magnetic susceptibility and resistivity have been studied.

2. Experimental

In a typical polymerization, firstly, aniline monomer and H_3PO_4 were mixed in the presence of Fe_3O_4 (average diameter is about 10nm) for the given ratio at low temperatures. Secondly, ammonium persulfate (APS) as the oxidant dissolved in deionized water and was added slowly into the previously cooled mixture. After all the oxidant was added, the reaction mixture was stirred for 24h. Thirdly, the precipitate was then washed with deionized water, methanol, and ethyl ether several times, and finally dried at room temperature in a dynamic vacuum for 24h.

Three samples with the same molar ratio of aniline to H_3PO_4 (1:0.5) have been prepared; the weight percentages of Fe_3O_4 are 0 (pure PANI-

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H_3PO_4), 5.9 and 27 wt%, respectively. Figure 1 shows the typical scanning electron microscopic (SEM) and transmission–electron microscopic (TEM) images of nanocomposites. With increasing weight per cent of Fe_3O_4, the inner diameter of nanotubes decreases, and nanorods of PANI increase (as shown in Fig.1 (b) and (c)). Particularly, Fe_3O_4 nanoparticles with ~10nm in diameter embedded in the nanorods are obviously observed.

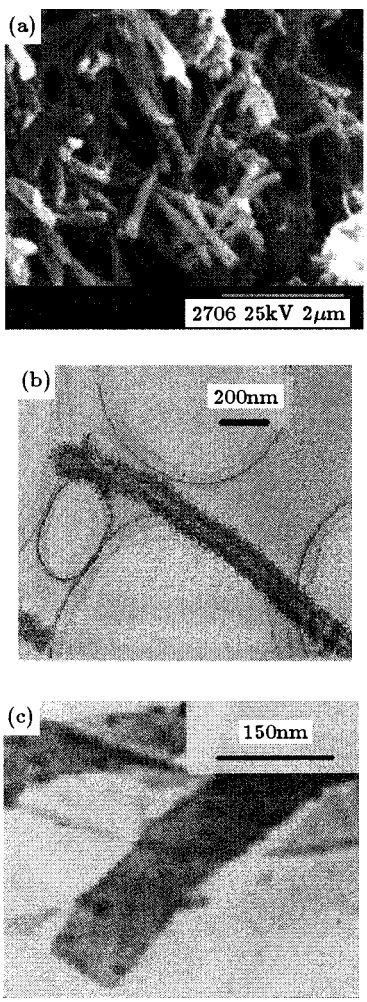


Fig.1. (a) The typical SEM images of PANI-H_3PO_4/Fe_3O_4 nanocomposites; (b) The typical TEM images of PANI-H_3PO_4/Fe_3O_4 nanotubes (the content of Fe_3O_4 is small); (c) The typical TEM images of PANI-H_3PO_4/Fe_3O_4 nanorods (the content of Fe_3O_4 is large).

The electrical resistivities of powder pellets of composites were measured by a standard four-probe method using Keithley 220-programmable current source and 181-nanovoltmeter. DC magnetic susceptibility was measured using a MagLabEXA magnetometer (OXFORD INSTRUMENTS) with dc magnetic field of 1T from 4.2 up to 250K. Dependence of magnetization on the applied magnetic field at 5K was also measured using the same magnetometer.

3. Results and discussion

3.1. DC magnetic susceptibility and superparamagnetism

The dc magnetic susceptibility (χ) of PANI-H_3PO_4/Fe_3O_4 composites for a two-ring-repeat unit is shown as a function of the absolute temperature in Fig.2. It is obvious that the total magnetic susceptibility, χ, can be written as a sum of a temperature-independent susceptibility χ_P^* and a Curie-type susceptibility χ_C[8−10]

$$\chi = \chi_P^* + \chi_C = \chi_P^* + C/T, \tag{1}$$

where C is the Curie constant. The values of χ_P^* and C can be obtained from Fig.2. For PANI-H_3PO_4 nanotubes, the temperature-independent susceptibility $\chi_{P-\mathrm{PANI}}$ is 3.9×10^{-4} emu·mol^{-1}·2rings^{-1}, the Curie constant is C=2.1×10^{-1} K·emu·mol^{-1}·2rings^{-1}. For PANI-H_3PO_4/Fe_3O_4 composites, in fact, χ_P^* includes the contributions of PANI-H_3PO_4 and Fe_3O_4, so χ_P^* can be expressed as

$$\chi_P^* = \chi_{P-\mathrm{PANI}} + \chi_{\mathrm{Fe_3O_4}}, \tag{2}$$

where $\chi_{P-\mathrm{PANI}}$ is the Pauli-type susceptibility of PANI-H_3PO_4 and $\chi_{\mathrm{Fe_3O_4}}$ is the susceptibility of Fe_3O_4 nanoparticles. When the weight per cent of Fe_3O_4 increases, χ_P^* increases dramatically: for PANI-H_3PO_4/Fe_3O_4 composites containing 5.9 and 27wt% of Fe_3O_4, χ_P^* is 1.8×10^{-2}, 1.3×10^{-1}emu·mol^{-1}·2rings^{-1}, respectively. This may be due to increasing $\chi_{\mathrm{Fe_3O_4}}$, because $\chi_{P-\mathrm{PANI}}$ is small, only about 3.9×10^{-4}emu·mol^{-1}·2rings^{-1}. It is noticed that the magnetization of Fe_3O_4 nanoclusters should be nearly saturated in the magnetic field of 1T (as shown in Fig.3); therefore $\chi_{\mathrm{Fe_3O_4}}$ will certainly be temperature-independent and increase with increasing weight of Fe_3O_4.

In Fig.2, it is evident that with increasing weight per cent of Fe_3O_4, the Curie-type susceptibility of PANI-H_3PO_4/Fe_3O_4 composites is gradually suppressed, for example, the curve of the temperature dependence of the susceptibility becomes much flatter and flatter at low temperatures, the Curie constant C decreases from 2.1×10^{-1} to 1.2×10^{-1}, 4.6×10^{-2} K·emu·mol^{-1}·2rings^{-1}, and the number of singly occupied states N_S (N_S can be calculated from Eq.(5)) also decreases from 4.3×10^{17} to 2.4×10^{16}, 0.9×10^{16}

(per mole two rings of PANI). These can be ascribed to the contribution of increasing magnetic nanoclusters of Fe_3O_4. Firstly, as is known, both polaron in PANI and electron in Fe_3O_4 have spins; since Fe_3O_4 nanoclusters are doped into nanocomposites (as shown in Fig.1 (c)), the spins in PANI-H_3PO_4 chains and Fe_3O_4 nanoclusters will interact with one another, which may decrease the number of singly occupied states at low temperatures. Secondly, from Fig.4 we can see that with increasing the content of Fe_3O_4 the resistivity of the composites decreases. This also indicates the weakening of electron localization, which decreases the average intra-site electron–electron Coulomb interaction U (see the following section of this paper) and suppresses the Curie-type susceptibility of PANI-H_3PO_4 at low temperature.

In Fig.2, for pure PANI-H_3PO_4 nanotubes, it is also evident that at around T_t ~45K there is a crossover from temperature-independent susceptibility to Curie-type behaviour, this may be attributed to the diagonal correlation effects in Anderson-localized states,[11] which gives rise to the occurrence of singly occupied states below the Fermi energy E_F and results in a Curie-type susceptibility at low temperatures. Kaminura[11] has given the general formula for the static spin susceptibility in the Anderson localized regime:

$$\chi(T) = 2\mu_B^2/k_BT \sum_{\alpha} \{2 + \exp[\beta(\mu - \varepsilon_\alpha - U)] + \exp[-\beta(\mu - \varepsilon_\alpha)]\}^{-1}, \quad (3)$$

where $\beta = 1/k_BT$, μ is the chemical potential, ε_α are the energies of the localized states labelled by α, and U is the average intrasite electron–electron Coulomb interaction (or the mean value of the diagonal correlation energy). The numerical solution of the above equation shows that at low temperatures the susceptibility obeys the Curie law,

$$\chi(T) = \mu_B^2 N_S/k_BT, \quad (4)$$

where N_S is the number of singly occupied states. Since the total density of states at E_F is finite, the Curie-type behaviour of susceptibility can be ascribed to the diagonal correlation on the spin susceptibility. According to Eq.(3), the Curie constant C can be expressed as:

$$C = N_S\mu_B^2/k_B. \quad (5)$$

The value of N_S can be calculated from the above equation. For nanotubular PANI-H_3PO_4, the number of singly occupied states N_S is 4.3×10^{17} (per mole two rings).

Kamimura also has denoted,[11], when W (W is an energy width, Kamimura assumed that W equals the mobility edge E_C) is much larger than U ($W/U \gg 5$), the temperature dependence of the susceptibility gradually changes from a Curie-type behaviour to a temperature-independent susceptibility with increasing temperature. The occurrence of this change indicates that at around crossover temperature T_t, $k_BT_t \approx U$.[11,12] So we can estimate that U is about 4×10^{-3}eV. Below the crossover temperature T_t, the susceptibility shows a Curie-type behaviour; while above T_t, the susceptibility mainly shows a temperature-independent behaviour. In Fig.2, we can also see that with increasing weight per cent of Fe_3O_4 the crossover temperature T_t decreases, which may indicate that U decreases and the value of W/U increases.

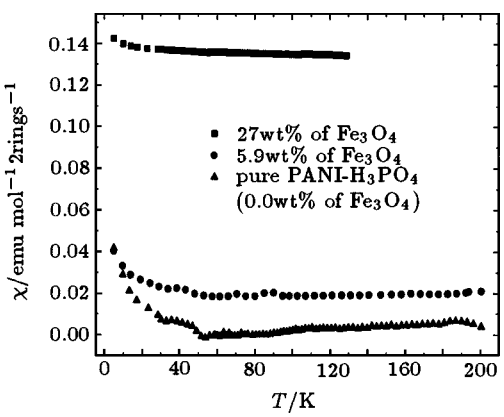


Fig.2. The temperature dependence of the dc magnetic susceptibility of PANI-H_3PO_4/Fe_3O_4 nanocomposites measured under a 1T dc magnetic field.

At 5K, the plots of the magnetization versus the applied magnetic field (between ±5T) of PANI-H_3PO_4/Fe_3O_4 composites are shown in Fig.3. The PANI-H_3PO_4 sample exhibits paramagnetism. With increasing Fe_3O_4 content, the superparamagnetism of Fe_3O_4 nanoclusters exhibits clearer and clearer. There is only a little hysteresis for PANI-H_3PO_4/Fe_3O_4 composite containing 27wt% of Fe_3O_4 even at 5K. Based on the results shown in Fig.3, the saturated magnetization (M_s) and coercive force (H_c) have been estimated to be M_s=6emu/g and H_c ≈0.044T, respectively.

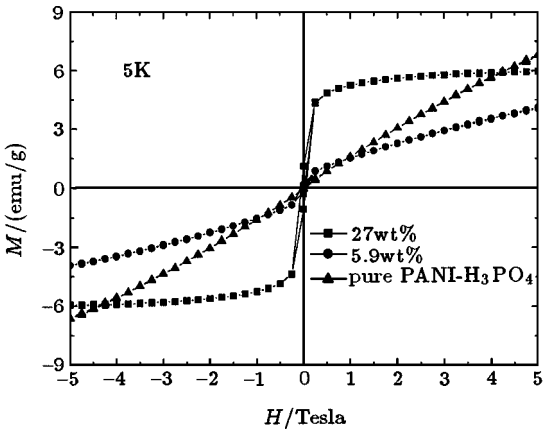


Fig.3. Magnetization versus applied field plots at 5K for PANI-H_3PO_4/Fe_3O_4 nanocomposites.

3.2. DC electrical resistivity (ρ)

Figure 4 shows the temperature dependence of the resistivity of PANI-H_3PO_4/Fe_3O_4 composites having different contents of Fe_3O_4. It is obvious from Fig.4 that: (1) the resistivity data can be well fitted with the relation $\ln\rho(T)=A+B\cdot T^{-1/2}$, that is to say, $\ln\rho(T)$ is linear with $T^{-1/2}$; (2) the resistivity decreases with increasing content of Fe_3O_4. This indicates that the nanocomposites still possess higher conductivity (the room-temperature conductivity is about 0.5S/cm).

On the basis of analysis of the SEM and TEM images of PANI-H_3PO_4 nanotubes and other experimental results,[13−15] we suppose that the nanotube can be described as a bundle of coupled parallel curled chains. Due to the disorder of nanotubes and the weak coupling between nanotubes, the contact resistance in the intertubular regions determines mainly the resistance of nanotubular PANI-H_3PO_4. This leads to $T^{-1/2}$ resistivity,[16] which can be interpreted by quasi-one-dimensional (1D) variable-range hopping (VRH) conduction model. For quasi-1D VRH model,[17] the temperature dependence of resistivity follows the relation:

$$\rho(T) = \rho_0 \exp(T_0/T)^{-1/2}, \qquad (6)$$

where T_0 is the energy needed for the charge carriers' hopping conduction. From Fig.4, we can calculate T_0, as shown in Table 1. From Table 1, we can see that, when the content of Fe_3O_4 increases from 0 to 5.9, 27wt%, T_0 decreases from 15630 to 14980, 13360K. This indicates that magnetic nanoclusters of Fe_3O_4 in PANI-H_3PO_4 may reduce the energy needed for charge carriers' hopping conduction, and enhance the conductivity.

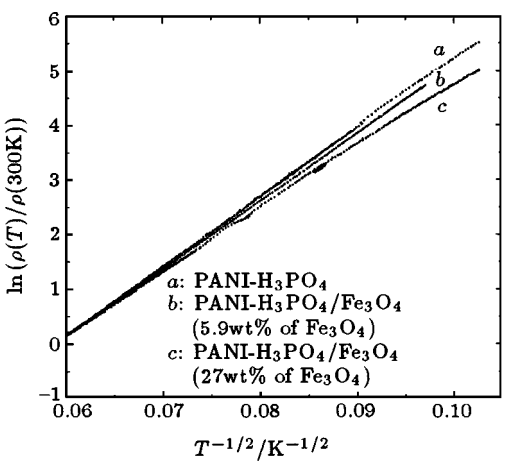


Fig.4. Variation of resistivity of PANI-H_3PO_4/Fe_3O_4 nanocomposites with $T^{-1/2}$ ($80 < T < 300$K). The resistivities are normalized by ρ(300K).

Table 1. Related data for PANI-H_3PO_4/Fe_3O_4 composites. χ_P^* is the temperature-independent susceptibility (including the contribution of $\chi_{Fe_3O_4}$); C is the Curie constant; N_S is the number of singly occupied states; T_0 is the energy needed for charge carriers' hopping conduction.

wt% of Fe_3O_4 in composite	0	5.9	27
χ_P^* (emu·mol^{-1}·2rings^{-1})	3.9×10^{-4}	1.8×10^{-2}	1.3×10^{-1}
C (K·emu·mol^{-1}·2rings^{-1})	2.1×10^{-1}	1.2×10^{-1}	4.6×10^{-2}
N_S (per mole two rings)	4.3×10^{17}	2.4×10^{16}	0.9×10^{16}
T_0 (K)	15630	14980	13360

4. Conclusion

PANI-H_3PO_4/Fe_3O_4 composites that are both electrically conductive and magnetically susceptible have been prepared and studied. The main results obtained in this paper are summarized as follows:

1. DC magnetic susceptibility includes the temperature-independent contribution and the Curie-like contribution. With increasing weight per cent of Fe_3O_4 in the composites, the temperature-independent susceptibility (χ_P^*) increases due to the nearly saturated magnetizations from increasing $\chi_{Fe_3O_4}$.

2. With increasing content of Fe_3O_4, the Curie-type susceptibility is suppressed at low temperatures, and the crossover temperature (T_t ~45K) from the temperature-independent susceptibility to Curie-like behaviour decreases, which may be attributed to the weakening of electron localization in PANI chains.

3. The PANI-H_3PO_4/Fe_3O_4 composite containing 27wt% of Fe_3O_4 is superparamagnetic, exhibiting a very small hysteresis even at 5K (the saturated magnetization M_s=6emu/g and coercive force H_c ≈0.044T).

4. The intertubular contact resistance is dominant due to the disorder of the sample. The $T^{-1/2}$ resistivity has been observed and interpreted by quasi-1D VRH model. With increasing content of Fe_3O_4, the energy needed for charge carriers' hopping conduction T_0 decreases. The nanocomposites room-temperature conductivity is about 0.5S/cm.

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