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SHORT COMMUNICATION

Genping Song
Jie Bo
Rong Guo

The characterization and property of polystyrene compounding of α-Fe_2O_3 in the nano-scale

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G. Song · J. Bo · R. Guo (✉)
College of Chemistry and Chemical Engineering, Yangzhou University, 225002 Yangzhou
E-mail: guorong@mail.yzu.edu.cn

Abstract α-Fe_2O_3/polystyrene composite nanoparticles were synthesized in an oil/water microemulsion. Their structure was characterized by transmission electron microscopy, X-ray diffraction and Fourier transform-infrared spectrometry. An Ubbelonde viscometer, a Gouy balance and a model 283 potentiostat/galvanostat measured the molecular weight of the composite nanoparticles and their magnetic and electrical characteristics respectively.

Keywords α-Fe_2O_3 · Composite nanoparticles · Microemulsion · Property characterized

Introduction

In the very important area of composite nano-materials, organic and inorganic composite nanoparticles have developed rapidly in the last 20 years, and their special characteristics are of increasing interest [1]. The composite magnetic micro spheres formed by the monomers of organic substances and ferric oxides can be moved quickly or be separated by the action of a magnetic field after they combine with biological active matter such as enzymes, cells and antibodies [2, 3]. The magnetic micro spheres can eliminate bone marrow cancer cells in a simple, safe, and effective, operation [4, 5]. Now, the magnetic micro spheres have become the new functional polymer materials and they can be applied in catalysts, pigments, fine ceramics, magnetic record materials, biotechnology and many other fields [6]. The composite nanoparticles formed by ferrous oxides and styrene monomers have been widely applied [7, 8, 9]. Thus synthesis of α-Fe_2O_3/polystyrene composite nanoparticles is of great interest to scientists. However, up to now, we have not found any reports on their magnetic and electrical characteristics.

In this work, we prepared polystyrene nanoparticles and α-Fe_2O_3/polystyrene composite nanoparticles, and systematically studied their magnetic and electrical characteristics in order to provide some helpful theoretical information.

Materials and methods

Materials

Sodium dodecyl benzene sulfonate (SDBS) (Fluka), styrene (Fluka), benzene (>99%, Aldrich), ammonium peroxydisulfate (APS) (>99%, Aldrich), ethanol (Fluka), ferrous sulfate (>99%, Aldrich), hydrochloric acid (ShangHai ZhengXing reagent factory), and bidistilled water were used.

Synthesis of polystyrene and α-Fe_2O_3/polystyrene composite nanoparticles

Preparation of α-Fe2O3 ultra fine particles A mixture of $FeCl_3$ (2.8 mol l^{-1}) and HCl (0.1 mol l^{-1}) was diluted to a concentration of 0.018 mol l^{-1} $FeCl_3$ and 0.0010 mol l^{-1} HCl with 85 °C deionic water. The sample was then hydrolyzed in an oven at 105 ± 1 °C for 24 h, and the reaction rapidly stopped using salt-ice refrigeration. The particles were separated by ultracentrifugation (L7–55 Beckman ultracentrifuge) at 20,000 rpm [10].

Synthesis of polystyrene nanoparticles Styrene (10%) was placed in 5% SDBS micelle solution, and the polymerization reaction

initiated by APS (1 mmol l^{-1}). The size of the particles formed varied from 20 to 40 nm [11].

Preparation of α-Fe2O3/polystyrene composite nanoparticles The molar ratio of styrene:α-Fe_2O_3 was kept at 20:1. The appropriate quantity of α-Fe_2O_3 nanoparticles and initiator APS were placed in the oil/water (O/W) microemulsion (SDBS/styrene/ water = 0.1/1/9), and stirred at 85 °C for 8 h. α-Fe_2O_3/polystyrene composite nanoparticles (pink emulsion) were then obtained after centrifuging. The conversion of styrene was about 86%, but the nanoparticles of by-products were not observed using a transmission elctron microscope (TEM).

Structural characterization

A series of different concentrations of benzene solution were spiked with polystyrene nanoparticles, and their [η] values measured by Ubbelonde viscometer at 20 °C. α-Fe_2O_3/polystyrene composite nanoparticles were dissolved in benzene solution, and then α-Fe_2O_3 particles removed by centrifuging. These were carefully added to a series of benzene solutions of different polystyrene concentrations. Their [η] values were measured by Ubbelonde viscometer at 20 °C. The polystyrene molecular weights were calculated using the Mark empirical formula:

$$[\eta] = KM_\eta^\alpha \quad (1)$$

where [η] is the limiting inherent viscosity, M_η is the viscosity-average molecular weight, K and α are the constants, which depend on the solvent and the type of macromolecule. At 20 °C, $K = 1.23\times10^{-4}$, and $\alpha = 0.72$.

The particles' size and morphology were examined using the TECNAI-12 TEM (Philips). The X-ray diffraction (XRD) patterns of α-Fe_2O_3 nanoparticles, polystyrene nanoparticles and α-Fe_2O_3/polystyrene composite nanoparticles were carried out using the Mo3XHF22 X-ray diffractometer (Japan MAC). The infrared spectra of these particles were obtained by using the NICOLET740 Fourier transform infrared spectrometer (America).

Measurement of magnetic and electrical characteristics

The magnetic susceptibilities of α-Fe_2O_3 nanoparticles and α-Fe_2O_3/polystyrene composite nanoparticles were measured by Gouy balance (Fu Dan University machine shop). The capacitance and pure resistance of α-Fe_2O_3 nanoparticles and α-Fe_2O_3/polystyrene composite nanoparticles were measured with Model 283 potentiostat/galvanostat (EG & G, Princeton Applied Research, USA).

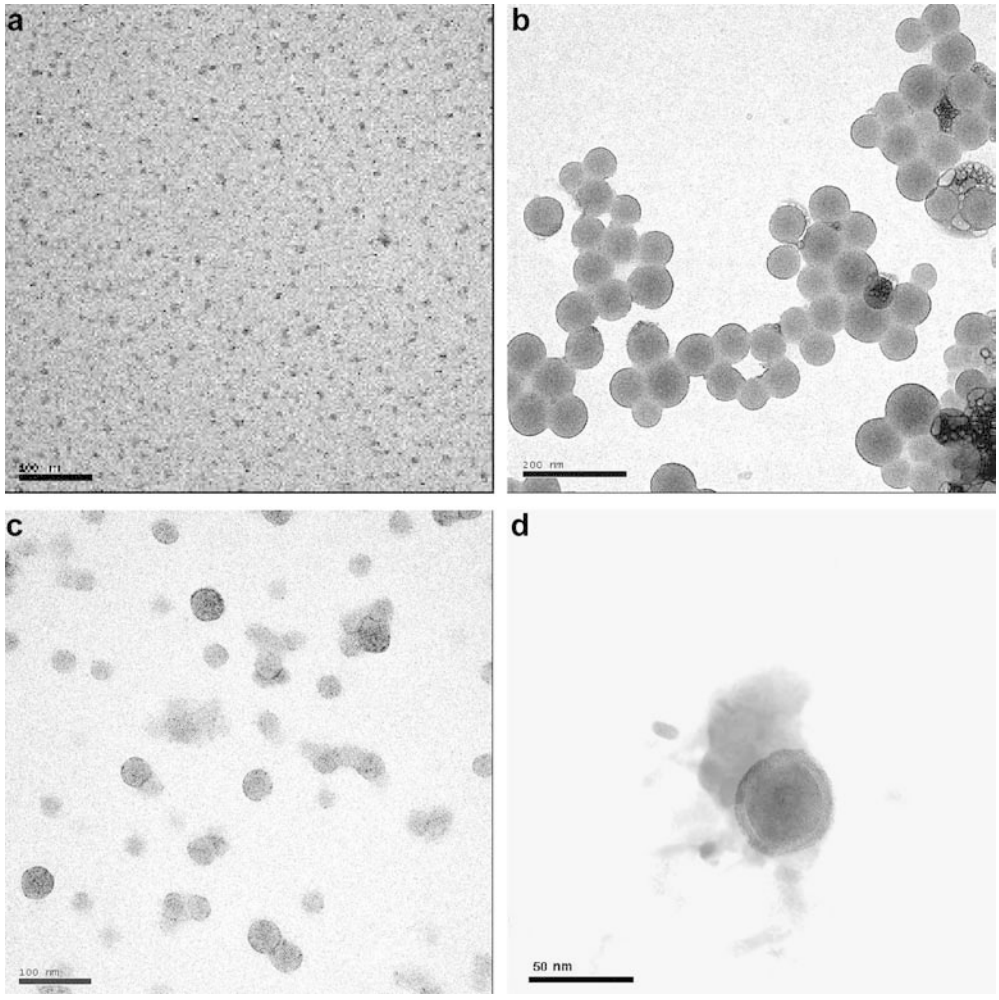

Fig. 1a–d Transmission electron microscope photographs of **a** α-Fe_2O_3, **b** polystyrene, **c** α-Fe_2O_3/polystyrene(×23 K) and **d** α-Fe_2O_3/polystyrene(×46 K)

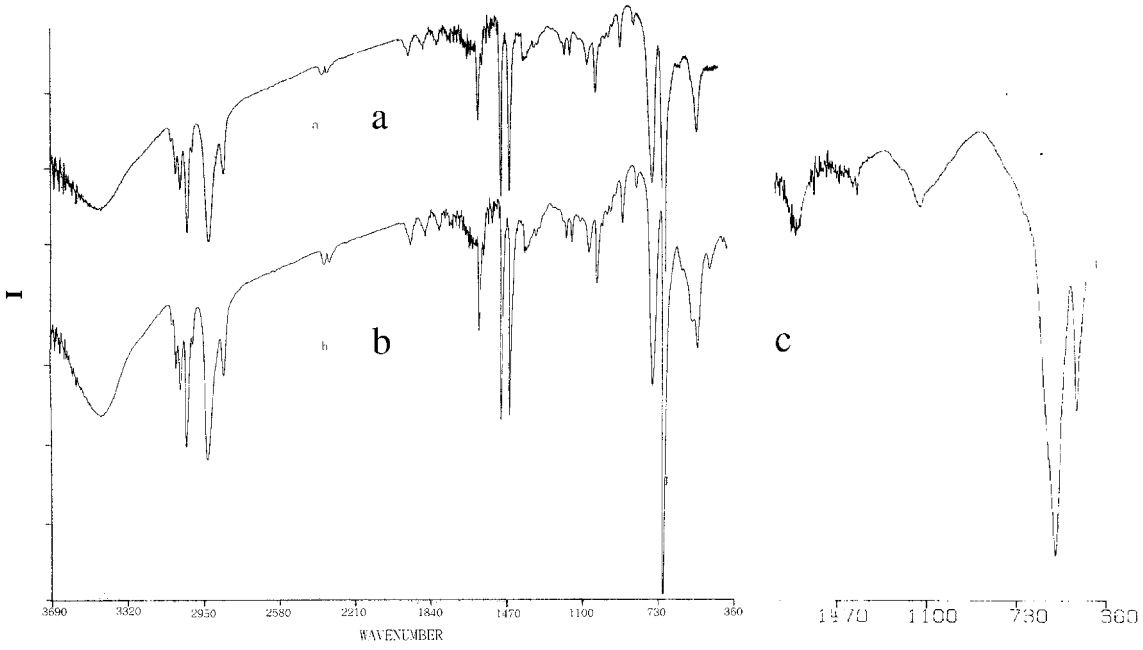

Fig. 2 Fourier transform-infra red spectra of nanoparticles. *a* Polystyrene, *b* α-Fe_2O_3/polystyrene, *c* α-Fe_2O_3

Results and discussion

Structural characterization of α-Fe_2O_3 nanoparticles and α-Fe_2O_3/polystyrene composite nanoparticles

According to Eq. 1, the molecular weight of polystyrene nanoparticles is 6×10^5–9.3×10^5, and the molecular weight of polystyrene in α-Fe_2O_3/polystyrene composite nanoparticles is 6.5×10^5–1×10^6, which agrees approximately with the value 6.3×10^5–9.6×10^5 calculated by the formula $D=0.133\times M^{0.38}$ (D is the diameter of polystyrene nanoparticles in nanometers) [12]. Thus α-Fe_2O_3 is enwrapped by polystyrene.

The TEM photographs of α-Fe_2O_3, polystyrene and α-Fe_2O_3/polystyrene are shown in Fig. 1. From these we can see that the α-Fe_2O_3 nanoparticles size is about 10 nm, the size of polystyrene particles varies from 20 nm to 35 nm, and the diameter of α-Fe_2O_3/polystyrene particles ranges between 20 nm and 40 nm. The distribution of all particle diameters is equal. From Fig. 1d we can observe that the structure of the composite nanoparticles is the shell-core shape.

When the composite nanoparticles are washed with dilute hydrochloric acid, the color of the solution doesn't

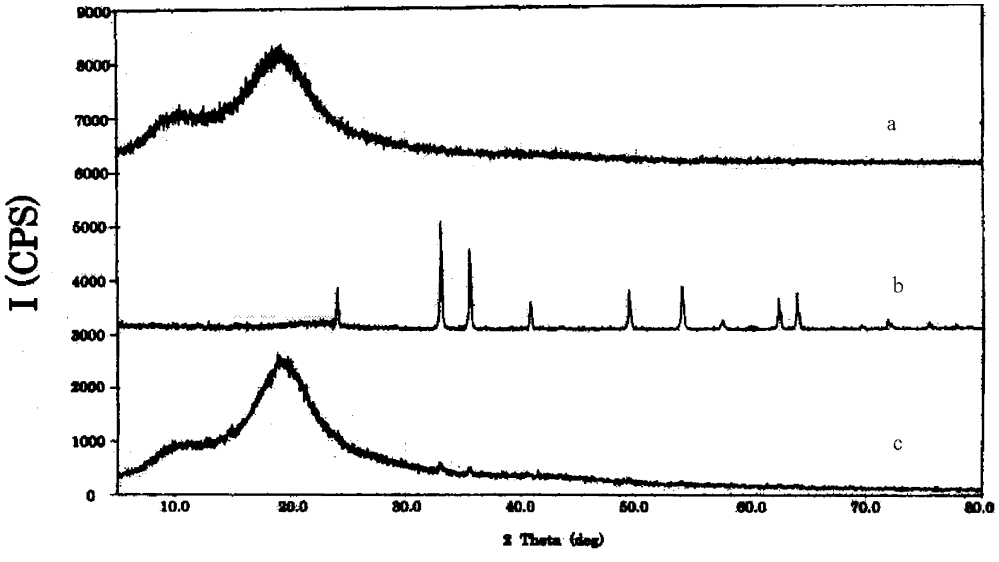

Fig. 3 X-ray diffraction spectra of nanoparticles. *a* Polystyrene, *b* α-Fe_2O_3, *c* α-Fe_2O_3/polystyrene

change. Thus, there is no Fe^{3+} dissolved in the dilute hydrochloric acid, which basically indicates that α-Fe_2O_3 is enwrapped completely by polystyrene. Further, on dropping a solution of $KSCN^-$ into the above system, the color of the system doesn't change to blood red, again indicating that α-Fe_2O_3 is completely enwrapped by polystyrene.

Figure 2 depicts the Fourier transform-infrared spectrometry spectra of the three nanoparticles. The band at 3,040–2,800 cm^{-1} is assigned to =C-H of the aromatic rings stretching. The benzene ring skeletal vibration modes are seen at 1,625–1,575 cm^{-1}, and 1,525–1,475 cm^{-1}. The bending band at 900–750 cm^{-1} is attributable to the C-H bending mode of mono-substituted benzene. Polystyrene and α-Fe_2O_3/polystyrene only contain the structure of mono-substituted benzene, which is evidenced from the peaks at 2,000–1,600 cm^{-1}, 697 cm^{-1} and 750 cm^{-1}. The presence of two characteristic peaks at 583.4 cm^{-1} and 478 cm^{-1} in Fig. 2b suggests that the α-Fe_2O_3 nanoparticles exist in α-Fe_2O_3/polystyrene composite nanoparticles. However, the relative intensity of these two peaks became smaller than those of Fig. 2c because of α-Fe_2O_3 coated by polystyrene. Furthermore, the absorption peak at 1,118 cm^{-1}, ascribable to the Fe-O vibration peak disappearing, also shows that α-Fe_2O_3 nanoparticles exist in α-Fe_2O_3/polystyrene composite nanoparticles [13].

Figure 3a–c shows separately the XRD spectra of the polystyrene nanoparticles, α-Fe_2O_3 nanoparticles and α-Fe_2O_3/polystyrene composite nanoparticles: the characteristic peaks of polystyrene are at 10° and 19°; the peak shapes are broad and lines are not smooth, which shows the nanoparticles are fine and amorphous. The XRD peak of Fig. 3b can superpose completely the standard XRD spectrum of α-Fe_2O_3. By this token, we can conclude that the ferromagnetic substance contained in the magnetic α-Fe_2O_3 nanoparticles is α-Fe_2O_3 particles. By comparing Fig. 3a with Fig. 3c, α-Fe_2O_3 nanoparticles coated by polystyrene still exhibit the characteristics of amorphous particles. From Fig. 3c, we can see the peak points of the α-Fe_2O_3 characteristic peaks at 33° and 35.6°, which indicates that α-Fe_2O_3 doesn't form a phase alone, and that it is coated by polystyrene. This result shows that α-Fe_2O_3/polystyrene composite nanoparticles are stable and take on core-shell structures. Obviously, due to the shielding effect of polystyrene shells, the XRD effect becomes weak, so that Fig. 3c doesn't show all α-Fe_2O_3 characteristic peaks; only the stronger peaks are displayed.

Magnetic characteristics of α-Fe_2O_3 nanoparticles and α-Fe_2O_3/polystyrene composite nanoparticles

Mole magnetic susceptibility of α-Fe_2O_3 nanoparticles, $X_{Fe_2O_3}$, can be described by [14]:

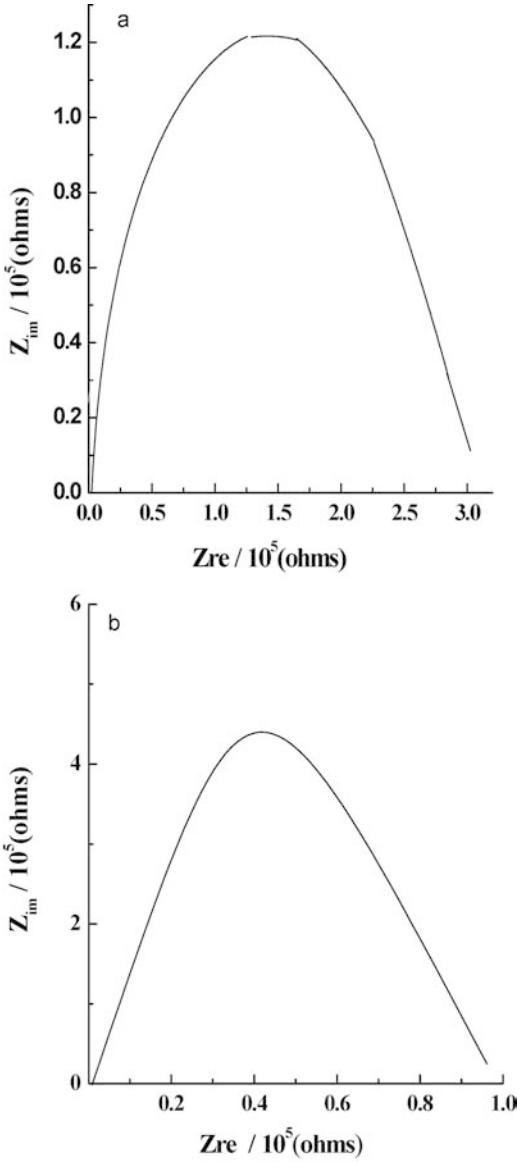

Fig. 4a, b Warburg impedance plots of α-Fe_2O_3 and α-Fe_2O_3/polystyrene nanoparticles. **a** α-Fe_2O_3. **b** α-Fe_2O_3/polystyrene

$$X_{Fe_2O_3} = \frac{2gML_{Fe_2O_3}\Delta W_{Fe_2O_3}}{H_c^2 m_{Fe_2O_3}} \quad (2)$$

Where g is the gravity constant, M is the molar weight, Hc is the magnetic field intensity, L is the length of the standard sample, ΔW is the change of sample weight without magnetic field, and m is the sample mass. Through this function we obtain $X_{Fe_2O_3} = 22.6$. So we can conclude that these nanoparticles have magnetic characteristics.

Mole magnetic susceptibility of α-Fe_2O_3/polystyrene composite nanoparticles, $X_{Fe_2O_3+PS}$ can be described by:

$$X_{Fe_2O_3+PS} = \frac{2gML_{Fe_2O_3+PS}\Delta W_{Fe_2O_3+PS}}{H_c^2 m_{Fe_2O_3+PS}} \quad (3)$$

Through this function, we can measure $X_{Fe_2O_3+PS}$ of the α-Fe_2O_3/polystyrene composite nanoparticles we synthesized: $X_{Fe_2O_3+PS} = 5.42$. After comparing mole magnetic susceptibility of α-Fe_2O_3 nanoparticles and α-Fe_2O_3/polystyrene composite nanoparticles ($X_{Fe_2O_3+PS} \prec X_{Fe_2O_3}$), we can conclude that the mole magnetic susceptibility of α-Fe_2O_3 nanoparticles decreases remarkably for polystyrene-coated α-Fe_2O_3 nanoparticles.

Electrical characteristics of α-Fe_2O_3 nanoparticles and α-Fe_2O_3/polystyrene composite nanoparticles

Warburg complex planar impedance graphs are shown in Fig. 4 [15]. Table 1 indicates the capacitance and pure resistance (The measured system has been corrected through simulating a normal electric circuit).

From Table 1, we see that the composite nanoparticles have greater resistance and smaller capacitance than α-Fe_2O_3 nanoparticles, due to being coated by the insulator polystyrene, and that the distributed heterogeneity of the polystyrene's thickness outer α-Fe_2O_3 nanoparticles results in the incommensurability of the composite nanoparticles' conducting ability. So, the Warburg complex planar impedance graph of the composite nanoparticles is less perfect than that of α-Fe_2O_3 nanoparticles.

Table 1 Values of capacitance and pure resistance

Sample	R (kΩ)	C (pF)
α-Fe_2O_3	24.31	143.8
α-Fe_2O_3/polystyrene	25.75	134.3

In conclusion, α-Fe_2O_3/polystyrene composite nanoparticles synthesized in the O/W microemulsion have the characteristics of a core-shell structure. Compared with α-Fe_2O_3 nanoparticles, the magnetic and electrical characteristics of α-Fe_2O_3/polystyrene composite nanoparticles become weaker, and compared with pure polystyrene nanoparticles, α-Fe_2O_3/polystyrene composite nanoparticles have the greater magnetic and electrical characteristics.

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