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RESEARCH ARTICLE

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Synthesis of cross-linked magnetic composite microspheres containing carboxyl groups

Abstract Fe_3O_4 magnetic nano-particles were prepared by a co-precipitation method and were modified using oleic acid. Then, the cross-linked magnetic composite microspheres containing a carboxyl group were prepared by using an improved emulsion polymerization with divinylbenzene (DVB) as the cross-linking agent. The composite microspheres comprised the Fe_3O_4 magnetic nano-particles as cores and the copolymer of styrene and acrylic acid as shells. The morphology and structure of the composite microsphere were characterized by FT-IR, transmission electron microscopy (TEM), X-ray diffraction (XRD), X-ray photoelectron spectrum (XPS) and so on. The results show that the composite microspheres were well dispersed in emulsion with uniform sizes and carboxyl groups on their surface. They were cross-linked and stable in 1 mol/L of HCl and DMF.

Keywords cross-linked, magnetic, composite microspheres

1 Introduction

In the recent decade, polymer composite microspheres with special properties have attracted a lot of attention [1,2]. The synthetic technologies of interpenetrating polymer network (IPN) are of high interest in the field of polymer production. The typical IPN materials have network or cross-linking structures. The network structures can directly be formed by polymerization or a cross-linking method in the presence of another polymer [3].

Cross-linked polymer microspheres, which are often used as the polymer framework of functional materials, have been widely used in many fields, such as ion exchange resins, polymer agents, polymer catalysts, polymer sorbents, polymer materials for biology and medical applications [4]. The mono-dispersed cross-linked polymer microspheres have some good properties, such as large specific area, high absorbability, good condensation behavior. The microspheres have a bright future for application in standard batching, chromatographic technique, biomedicine, microelectronics and in the chemical industry [5–7]. However, the common polymer microspheres have poor heat resistance and solvent resistance and that being so, their applications are limited. So, syntheses of cross-linked composite microspheres have attracted more and more attention.

The magnetic composites microspheres, which are generally consisted of organic and inorganic magnetic substances, are a kind of nano-particle materials with certain magnetic properties and magnetic fields. By modification on the surface of the magnetic composite microspheres or copolymerization, active groups (such as $-COOH$, $-NH_2$, $-OH$, $-CHO$, $-SO_3H$ and $-CH_3Cl$ et al.) can be grafted on the surface of the composite microspheres. At room temperatures these active groups can form Schiff alkali by combining with enzyme, protein, nucleic acid, antibody,antigen and cell active substance, and also can be widely used in magnetic separation, cell separation, nucleic acid separation, immunity detection and in the fields of biochemistry and biomedicine [8]. In the recent decade, the magnetic composites microspheres, as one of the new type functional materials, have exhibited strong vitality in the fields if magnetic materials, biomedicine, cytology, bioengineering, separation engineering, and stealth technique fields.

In this work magnetic cross-linked composite microspheres with monodispersal were prepared by an improved method of emulsion polymerization. Influential factors on the process of preparation were considered. The core is Fe_3O_4 magnetic nano-particles and the shell is copolymer of styrene and acrylic acid. The magnetic cross-linked composite microspheres show uniform particle sizes and have hydroxyl groups. The magnetic cross-linked composite microspheres will have

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great potential in applications, such as for use as magnetic materials, in biomedicine, cytology, bioengineering, separation engineering, and in stealth technique.

2 Experimental

2.1 Materials

Ferrous chloride tetrahydtrate ($FeCl_2 \cdot 4H_2O$): A.R., XiLong chemical plant, Shantou Guandong; Ferric chloride anhydrous ($FeCl_3 \cdot 6H_2O$): A.R., Shenyang fifths chemical plant; sodium carbonate (Na_2CO_3): A.R., Tianjin Tanggu chemical plant; Sodium dodecyl benzene sulfonate (SDBS): C.P., Shanghai chemical agent plant; Oleic acid, Shanghai chemical agent plant; Styrene (Sty): A.R., Tianjin Guangfu fine chemicals industry research institute; Acrylic acid (AA): Shanghai chemical agent plant; 2,2′-azo-bis-(2-methylpropionitrile) (AIBN): A.R., Beijing chemicals industry plant; Divinylbenzene (DVB): A.R., Shanghai Shengzhong fine chemicals industry co.; ammonium hydroxide (25%–28% $NH_3 \cdot H_2O$): A.R., Jilin Longtan chemical agent plant; the second distilled water was our own. Styrene, acrylic acid and divinylbenzene were used after reduced pressure distillation; AIBN was re-crystallized from methanol before being used.

2.2 Synthesis of the cross-linked magnetic composite micro-spheres

2.2.1 Preparation of Fe_3O_4 magnetic nano-particles modified by oleic acid [9–11]

27 g $FeCl_3 \cdot 6H_2O$ and 12 g $FeCl_2 \cdot 4H_2O$ were added into a 500 mL three-necked flask and dissolved in 100 mL distilled water. Then 80 mL ammonium hydroxide (25%–28% $NH_3 \cdot H_2O$) was rapidly added into the solution and agitated. After reaction for 10 min, 11 mL oleic acid were added into the three-necked flask. The system was heated up to 70°C and maintained at that temperature for 30 min. Then, it was heated up to 110°C to get rid of vapor and unreacted ammonia, and cooled to ambient temperature. The products were washed by distilled water multiple times and then dried and stored.

2.2.2 Synthesis of cross-linked magnetic composite microspheres containing carboxyl groups [12]

0.5 g Fe_3O_4 magnetic nano-particles (MP) that was prepared above, 0.4 g SDBS and 0.1 g Na_2CO_3 were dissolved in 60 mL deionized water. It was then subjected to sonication for 30 min. Then the mixture was moved to a 250 mL three-necked flask with a condenser, a nitrogen inlet and a stirrer and adequately stirred and emulsified for 30 min. The temperature was raised to 70°C, and 0.04 g AIBN was added to the flask under N_2 gas protection. The temperature was then raised to 75°C and followed by dropwise addition of 11 mL in an oil phase mixture containing 0.06 g AIBN, 0.5 mL DVB and 10:1 (volume ratio) St/AA into the system. The reaction proceeded for 10 h at a stirring rate of 400 r/min. The obtained emulsion with cross-linked magnetic composite microspheres appeared brown in color.

2.3 Characterization of the cross-linked magnetic composite microspheres

A COULTERLS-230 Grainsize Analyzer was used to determine the size and size distribution of the magnetic composite microspheres. An Infrared Spectra (FT-IR) Analyzer (American) was used to detect the functional groups of Fe_3O_4 magnetic nano-particles and magnetic composite microspheres. A JEM-2000EX transmission electron microscope (TEM) (JAPAN) was used to observe the morphology and structure of the magnetic cross-linked composite microspheres. A D8ADVANCE X-ray diffraction analyzer (Germany) was used to determine the crystalline forms of the Fe_3O_4 nano-particles. A VG ESCA LAB MKII photoelectron energy spectrometer (U.K.) was used to determine the hydroxyl content on the surface of composite microspheres. An EV Vibrating Sample Magnetometer (American) was used to determine the saturation magnetization of the Fe_3O_4 nano-particles and composite microspheres.

3 Results and discussion

3.1 Transmission electron microscopy (TEM)

Figure 1 shows the micrographs of Fe_3O_4 nano-particles (Fig. 1(a)) and Fe_3O_4 nano-particles modified by oleic acid (Fig. 1(b)). Because Fe_3O_4 nano-particles may aggregate with other the particles, the size shown in the TEM images was bigger than that of individual nano-particles.

As shown in Fig. 1(a), unmodified Fe_3O_4 nano-particles exhibit uniform size and very good dispersion, having spherical shape and diameters of about 10 nm. While the modified Fe_3O_4 nano-particles (Fig. 1(b)) show uniform sizes, their dispersion is not as good as the unmodified ones. The modified Fe_3O_4 nano-particles show some conglomeration phenomenon and the apparent diameter is about 12–15 nm.

Figure 2 shows the TEM photographs of Fe_3O_4/P(St-AA) cross-linked magnetic composite microspheres after different treatments. Fig. 2(a) shows the as-prepared Fe_3O_4/P(St-AA) composite microspheres without treatment. Fig. 2(b) shows the Fe_3O_4/P(St-AA) composite microspheres after being soaked in 1 mol/L HCl for 48 h.

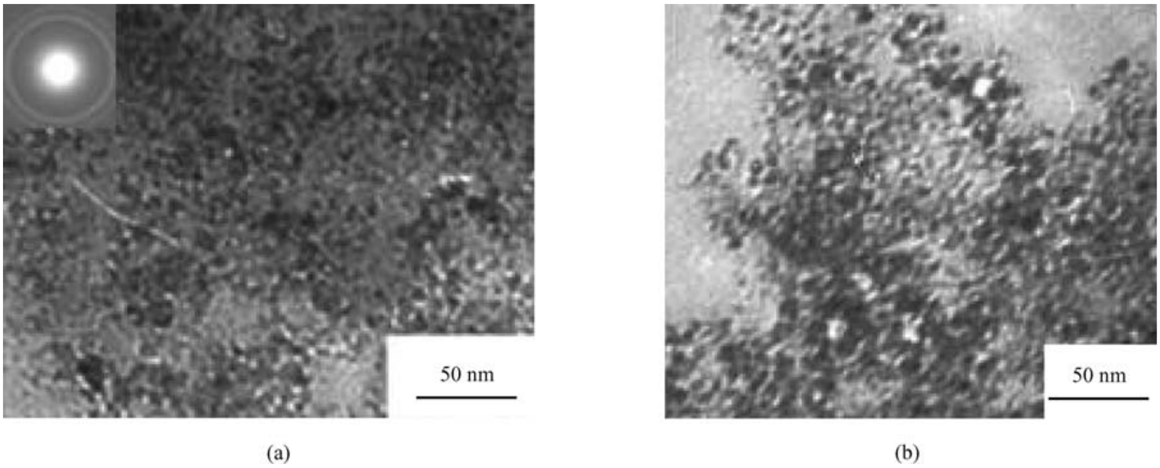


Fig. 1 TEM photographs of Fe_3O_4 before and after modification by oleic acid
(a) Before modification; (b) After modification

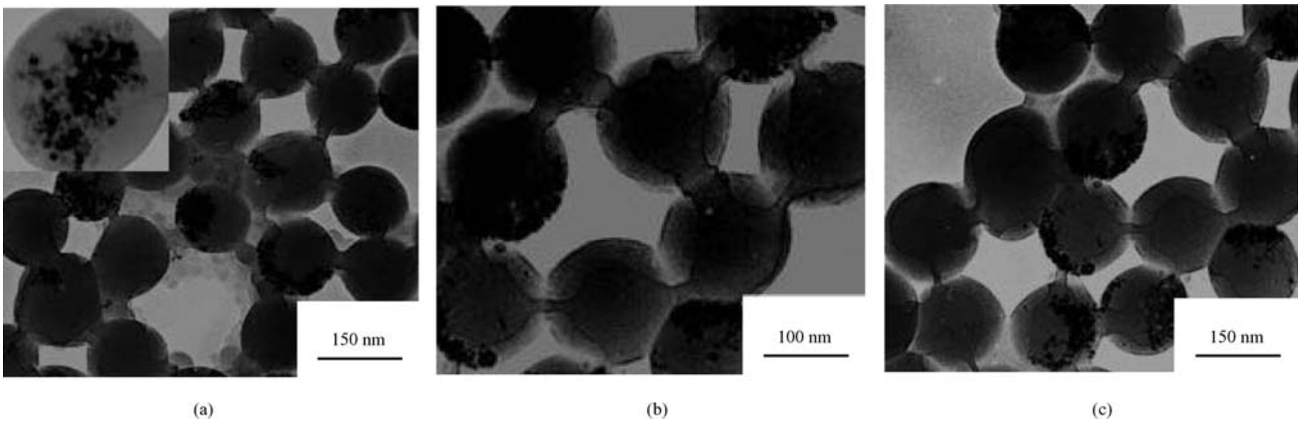


Fig. 2 TEM photographs of Fe_3O_4/ P(St-AA) composite microspheres
(a) Without treatment; (b) Soaked in 1 mol/L HCL for 48 h; (c) Soaked in DMF for 24 h

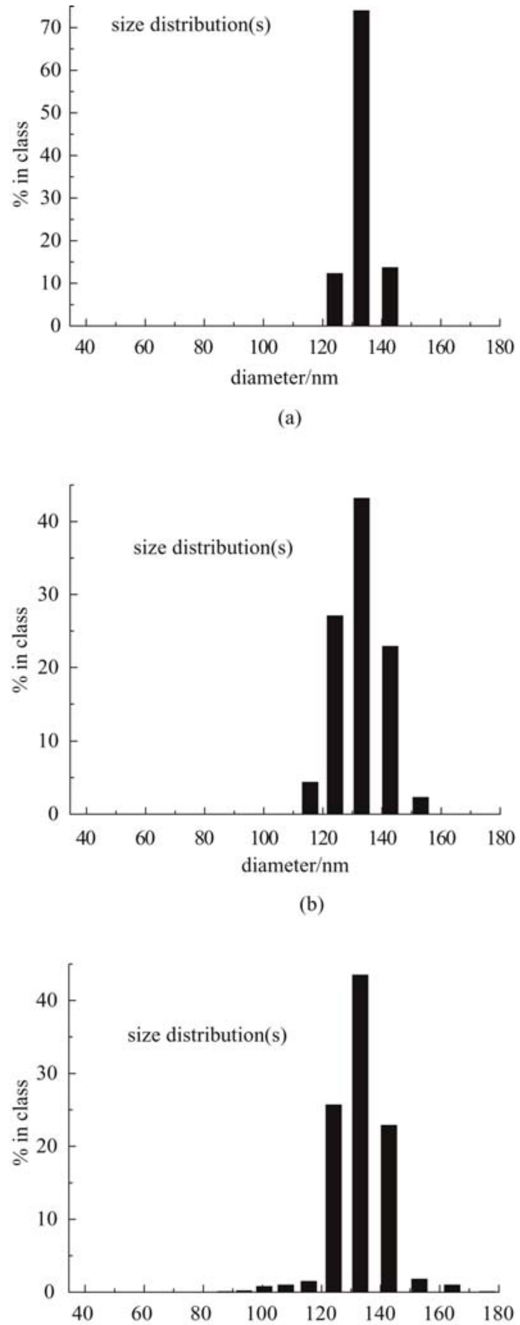
Fe_3O_4/P(St-AA) composite microspheres (shown in Fig. 2(c)) were soaked in DMF for 24 h and were washed for many times. It is clear that Fe_3O_4/P(St-AA) composite microspheres are spherical with uniform size of about 135 nm. The microspheres are well dispersed and there are interconnections among neighboring microspheres. The surface of microspheres in Fig. 2(a) was rough and may have uncoated Fe_3O_4 nano-particles adhering to it. The microspheres in Fig. 2(b) exhibit smooth surface, retaining good dispersion and interconnections. Fig. 2(c) is quite similar to of Fig. 2(b). It can be seen that the magnetic cross-linked composite microspheres show excellent stability in organic (DMF) and inorganic (HCl) solvents which is necessary in many applications.

3.2 Size distribution

Figure 3 shows the size distribution of the composite microspheres under storage. It could be observed that the size distribution of the composite microspheres does not show obvious change in a storage process up to 6 months. The size of most microspheres remains in the range of 125-142 nm. These results are in accordance with those of our TEM studies indicating that the emulsions with magnetic composite microspheres are quite stable.

3.3 X-ray diffraction (XRD)

Figure 4 gives the XRD patterns of modified and unmodified Fe_3O_4 nano-particles. They show the same diffraction peaks at around $2\theta = 30.40^\circ$, 35.62°, 43.46°, 54.06°, 57.34° and 63.00°, respectively, which are consistent with those of Fe_3O_4 standard samples. It means that the black magnetic powders obtained by the reaction are Fe_3O_4 nano-particles; and the sharp diffraction peaks in the images indicate that the modified and unmodified Fe_3O_4 magnetic particles are all good crystals.



(a)

(b)

(c)

Fig. 3 Histograms of particle size distribution of Fe_3O_4/P(St-AA) composite microspheres

3.4 Infrared spectra (FT-IR)

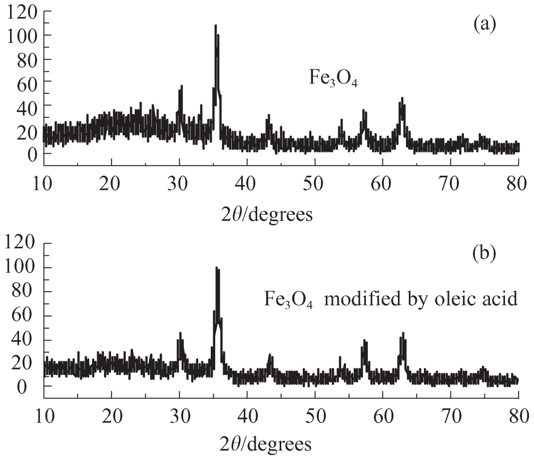


Fig. 4 XRD pattern of Fe_3O_4 nano-particles without (a) and with (b) modification by oleic acid

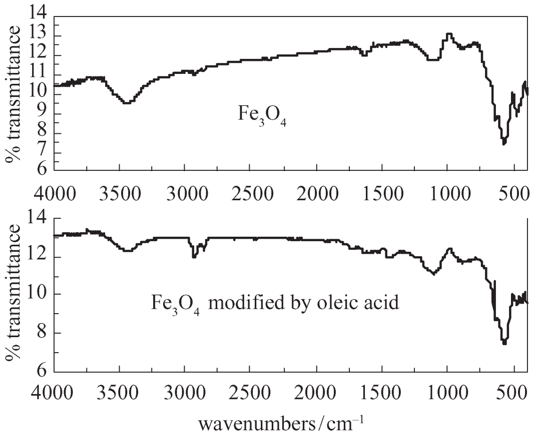


Fig. 5 FT-IR spectra of Fe_3O_4 nano-particles (a) Fe_3O_4; (b) Fe_3O_4 modified by oleic acid

Figure 5(a) shows the Infrared spectra (FT-IR) of Fe_3O_4 nano-particles unmodified and modified by oleic acid. The 580 and 3430 cm^{-1} absorption peaks correspond to Fe_3O_4 absorption and hydroxide group absorption of $Fe(OH)_2$ or $Fe(OH)_3$. The 1450–1650 cm^{-1} absorption peaks may be the symmetry stretching vibration absorption of CO_3^{2-} formed by CO_2 in air in combination with Fe_3O_4 nano-particles. For Fe_3O_4 nano-particles modified by oleic acid, the 1440, 2860 and 2920 cm^{-1} absorptions correspond to absorptions of C=O and −OH, C=, $-CH_2-$ in oleic acid. Because the modified Fe_3O_4 nano-particles were washed by water and ethanol many times, the physical properties of Fe_3O_4 nano-paticles surface were changed by the oleic acid, including its characteristic smoothness and roundness. In the meantime, it is indicative that the surface of Fe_3O_4 nano-particles has very strong adsorption ability.

Figure 6 shows the FT-IR spectrum of Fe_3O_4 composite microspheres. The absorption peaks appearing in the IR spectra at: 580 cm^{-1} (Fe_3O_4), 1065 cm^{-1} and 698 cm^{-1}(deformation vibration of C−H bonds in benzene ring), 1600 cm^{-1} (vibration of benzene ring); 900 cm^{-1}(O−H), 1720 cm^{-1} (C=O), 1315 cm^{-1} (C−O) and so on, show that the composite microspheres are composed of Fe_3O_4 nano-particles and AA /St copolymer molecules.

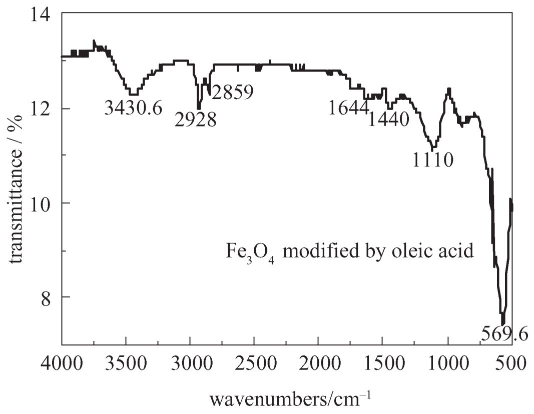


Fig. 6 FT-IR spectra of Fe$_3$O$_4$/ P (St-AA) composite microspheres

3.5 Magnetic analysis

Figure 7 gives the hysteresis loop of Fe$_3$O$_4$ nano-particles and composite micro-spheres at 298 K. It is observed that the hysteresis loop of Fe$_3$O$_4$ nano-particles shows no hysteresis. When the intensity of extra magnetic field is zero, both the magnetization intensity and the coercive force are zero, it indicates that Fe$_3$O$_4$ nano-particles had a good superparamagnetism characteristic. The different magnetic characteristics can be related to the size of the magnetic materials. When the size of ferromagnetic substance is in the nanometer level, the magnetic domains may transform to single magnetic domains. With decreasing material size, the coercive force increases; when the size of materials decreases to 20 nm, the coercive force comes to a max; if the size decreases to 13 nm, the coercive force may come to zero, the materials may exhibit superparamagnetism [13,14]. The size of Fe$_3$O$_4$ nano-particles synthesized in this paper is about 12–15 nm. The Fe$_3$O$_4$ nano-particles show superparamagnetism. However the magnetism of the composite microspheres is not perfect, the decrease in magnetism could be the results of oxidation or agglomeration of Fe$_3$O$_4$ nano-particles in the process of reaction and storage. Moreover, the thickness of the polymer shell might also affect the magnetism of the composite microspheres to a certain extent.

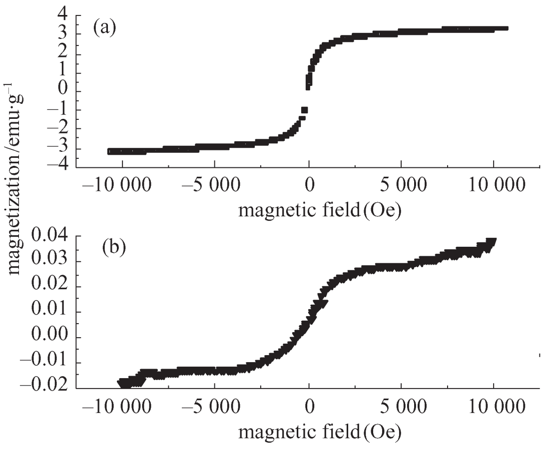
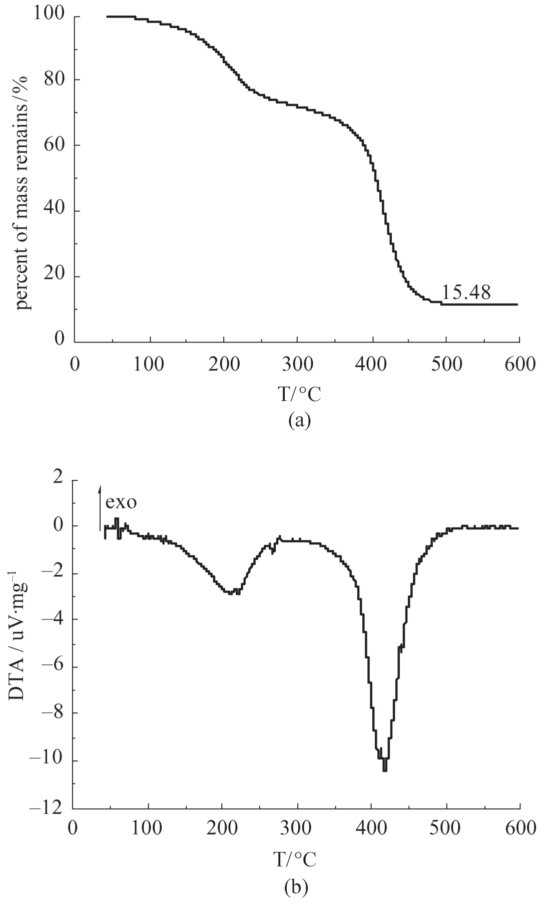


Fig. 7 Hysteresis loop of Fe$_3$O$_4$ nano-particles (a) and Fe$_3$O$_4$/P(St-AA) composite microspheres (b)

3.6 TG-DTA

The content of magnetic nano-particles is an important characteristic of the magnetism of composite microspheres, so the composite micro-spheres were characterized using TG-DTA analysis. Fig. 8(a) shows the TG curve of the magnetic composite microspheres, and Fig. 8(b) gives their DTA results. An exothermal peak around 250°C corresponds to organic combustion. A peak at about 385°C corresponds to partial oxidation Fe$_3$O$_4$ nano-particles. When temperature is up to 600°C, organics are completely denatured and only Fe$_3$O$_4$ magnetic nano-particles remain. This method can expediently determine the content of Fe$_3$O$_4$ magnetic nano-particles in the polymeric magnetic composite microspheres. From Fig. 8 (a), it was found that the remnant mass (%) of magnetic



(a)

(b)

Fig. 8 TG (a) and DTA (b) curves of Fe$_3$O$_4$/P(St-AA) composite microspheres composite micro-spheres at 600°C or their content of Fe_3O_4 magnetic nano-particles was 15.48%.

3.7 X-ray photoelectron spectrum (XPS)

Figure 9 shows the X-ray photoelectron spectra (XPS) of magnetic composite microspheres soaked by hydrochloric acid and DMF. It could be seen that uncoated Fe_3O_4 can hardly be detected at the surface of the composite microspheres.

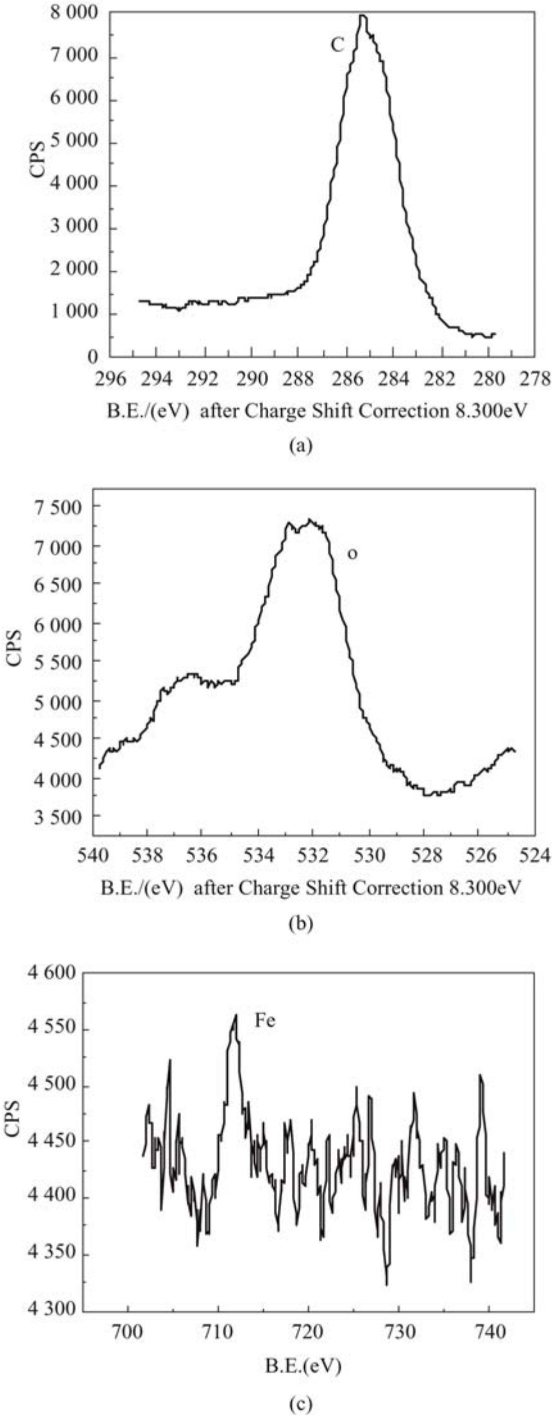


Fig. 9 XPS spectra of Fe_3O_4/P(St-AA) composite microspheres (after Charge Shift Correction 8.300 eV)
(a) spectrum of C; (b) spectrum of O; (c) spectrum of Fe

From the data listed in Table 1, the carboxyl content of the composite microspheres could be calculated according to formula (1).

$$C_x = (A_i/S_i)/(\Sigma A/S) \tag{1}$$

Here, C_x is element content; A_i is area; S_i is sensitivity factor. The content of carboxyl (−COOH) groups in composite microspheres was found to be 12%.

Table 1 Data of photoelectron energy spectra of polymer composite microspheres

element	bind energy/eV	*A*/(CPS·eV)	S	content/%
C(C−H)	285.104	2051.38	0.25	
C(COOH)	288.930	826.55	0.25	12
O(O−Fe)	531.970	8106.87	0.66	
O(C=O)	533.741	2814.53	0.66	
O(O−H)	536.428	2393.48	0.66	

4 Conclusions

The magnetic cross-linked composite microspheres used in this paper has a lot of excellent properties: (1) The size of the composite microspheres is uniform and controllable; (2) Because the composite microspheres have cross-linked structures, they could exhibit high stability in most organic or inorganic solvents for a long time period; (3) The composite microspheres are magnetic with characteristics of polymers and the hydroxyl groups on the surface of the composite microspheres may result in their good biocompatibility.

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