

Preparation and Properties of Magnetic Polystyrene Microspheres

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ABSTRACT: Magnetic polystyrene nanospheres were efficiently prepared by using a new indirect process based on miniemulsion polymerization of styrene. The samples were characterized by X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy, transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), and vibrating-sample magnetometry (VSM), respectively. The experimental results clearly show that the 3-methacryloxypropyltrimethoxy silane was anchored onto the surface of the magnetic particles to form the vinyl end.

The size of the magnetic particle is about 6–30 nm. The size of the magnetic particle capped with polystyrene is about 1–2 μm . The magnetic polystyrene spheres exhibit multidomain character, whereas the pure magnetic particles show single domain character. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 3660–3666, 2007

Key words: magnetite nanoparticles; miniemulsion grafting polymerization; 3-methacryloxypropyltrimethoxysilane; magnetic polystyrene microspheres

INTRODUCTION

Monodispersed magnetic particles with specific polymer coatings are of great interest in information science and technology. Because of the relatively rapid and easy magnetic separation, polymer-coated nanomagnetic particles have been used in biomedicine and bioengineering fields, such as immobilized enzyme,¹ cell separation,² protein purification,^{3–5} drug delivery,^{6–8} etc. The polymer-coated magnetic particles can be prepared using various strategies. A simple method is to coat magnetic particles with selected polymers. Physical adsorption and/or chemical reaction of either the magnetic particles onto the polymer surface^{9–11} or the polymer onto the magnetic core^{12–14} could result in particle composites with magnetic properties. Another pathway of obtaining magnetic composites is the *in situ* precipitation of magnetic particles in the presence of polymer. Winnik et al.¹⁵ obtained superparamagnetic composite particles by *in situ* precipitation of magnetic oxides within the porous network of preformed sulfonated macroporous poly(divinylbenzene) microspheres. To achieve the encapsulation of inorganic particles, other suitable methods

have been developed, including conventional suspension dispersion and emulsion polymerization in the presence of magnetic nanoparticles.^{16–20} In those polymerization processes, the magnetic particles are dispersed in an aqueous or emulsion solution of monomer and polymerization is carried out on the surface of inorganic particles by oil or water-soluble initiators.

In this article, we describe a method of preparing stable magnetic polystyrene microspheres using miniemulsion polymerization. We used an efficient water-soluble multisurfactant [sodium dodecyl benzene sulfonate (SDBS) and polyethylene glycol (PEG, $M_n = 6000$)] and a monomer-soluble-longchain-alcohol costabilizer hexadecanol for stabilizing the styrene/water miniemulsion against coalescence (with SDBS/PEG 6000). We chose the oil-soluble initiator benzoyl peroxide (BPO) for initiating the polymerization reaction. The surface-treated magnetic nanoparticles were dispersed in the styrene in the presence of initiator by ultrasound to homogenize the magnetic/styrene dispersion. The preparation of the miniemulsion was carried out by vigorous stirring. Polymerization was performed by blending the two solutions in a three-necked flask.

EXPERIMENTAL

Materials

The following chemicals were purchased from different sources: ferric chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, 99%, Tianjin

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East China Factory of Reagents, China), ferrous sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, 99%, Tianjin Deen Chemical Reagents, China), sodium hydroxide (NaOH , 96%, Shandong Laiyang Chemistry and Chemical Engineering Factory, China), methanol (CH_3OH , 99.5%, Suzhou Chemical Reagents Factory, Anhui, China), absolute ethanol ($\text{C}_2\text{H}_5\text{OH}$, 99.7%, Tianjin Fuchen Chemical Reagents Factory, China), 3-methacryloxypropyltrimethoxysilane ($(\text{CH}_2\text{C}(\text{CH}_3)\text{COOC}_3\text{H}_6\text{Si}(\text{OC}_2\text{H}_5)_3$), 3-MPS, Nanjing Crompton Shuguang Organosilicon Specialties, China), sodium dodecyl benzene sulfonate (SDBS, 90%, Tianjin Fuchen Chemical Reagents Factory, China), polyethylene glycol 6000 (PEG 6000, $M_n = 6000$, Tianjin Kaitong Chemical Reagents, China), hexadecanol (CA, Zhengzhou Paini Chemical Reagent Factory, China), polyvinyl alcohol 124 (PVA 124, Shanghai Chemical Reagents Factory, China Medicine Association), benzoyl peroxide (BPO, 98%, Shanghai Jingxi Chemical Science and Technology Co, China), styrene (St, 99%, Tianjin Kermel Chemical Reagent Development Center, China). Styrene was purified by distillation under reduced pressure prior to use and BPO was recrystallized twice from methanol and then vacuum dried. All other reagents were used as received. Deionized water was used for all experiments.

Synthesis of magnetite nanoparticles

The magnetite nanoparticles were prepared by the conventional coprecipitation method.²¹ 2.705 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, and 1.857 g of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ were dissolved

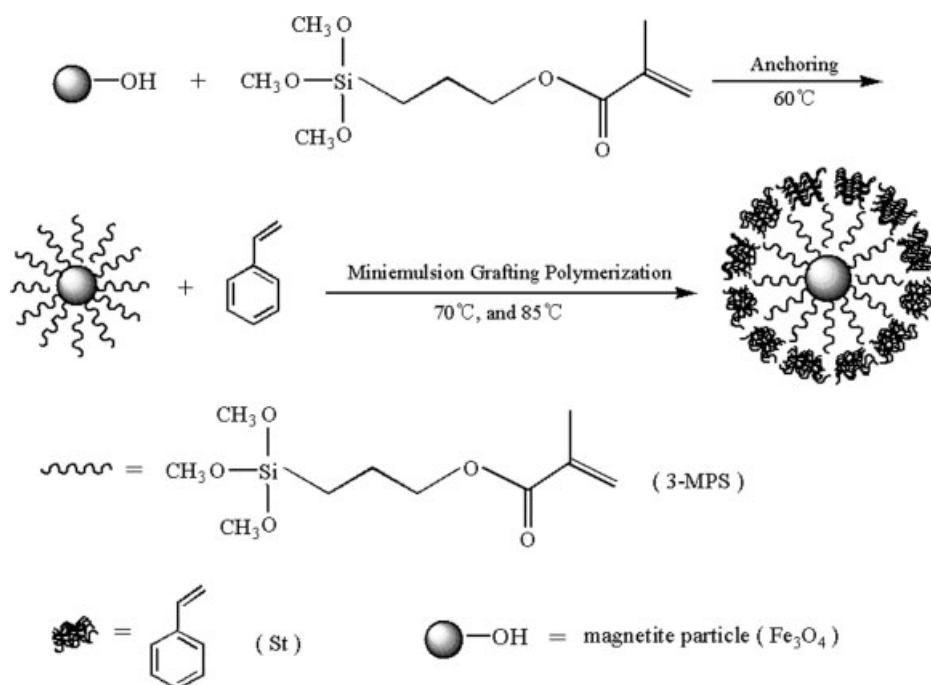
in 150 mL deionized water and heated to 30°C . Then, sodium hydroxide aqueous solution (0.4 mol L^{-1}) was slowly added dropwise into the solution with violent stirring until the pH of the solution raised to 11–12. After aging for 3 h at 50°C , a black powder was formed. The formed black powder was repeatedly washed with deionized water until neutrality was achieved. Finally, the magnetite particles were obtained by magnetic separation process and dried at 60°C in vacuum.

3-MPS-coated magnetite nanoparticles

The preparation procedure of magnetic particles capped with 3-MPS molecules is shown in Scheme 1. The dried magnetite particle (0.8 g) was added in 100 mL of ethanol/water (volume ratio = 1), then the mixture was treated by ultrasonic wave for 30 min to allow a uniform suspension of magnetic particles in the solution. 3-MPS of 1 mL was added dropwise into the solution with the suspension of magnetic particles. The solution was heated at 60°C with rapid stirring for 6 h. The product was washed with absolute ethanol three times and with deionized water twice to remove the physisorption of 3-MPS and dried at 60°C in vacuum.

Preparation of magnetic polystyrene microspheres (miniemulsion process)

The procedure of miniemulsion polymerization of grafting styrene onto the surface of magnetic par-



Scheme 1 Schematic representation for the synthesis of magnetic PS microspheres.

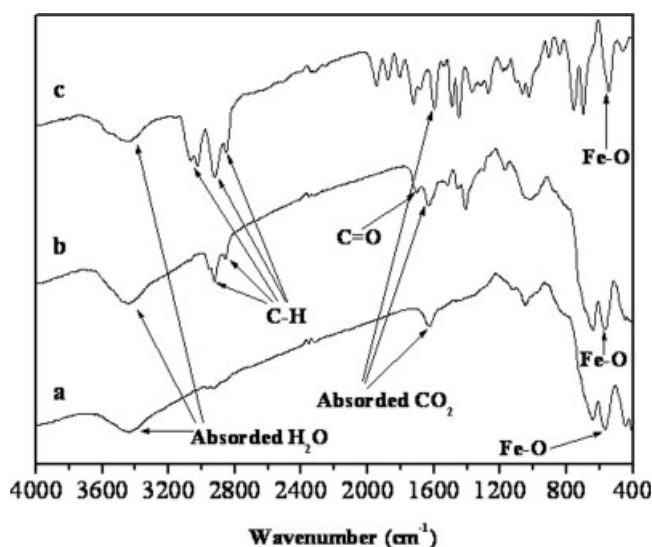


Figure 1 The FTIR spectrum of magnetic particles: (a) unmodified, (b) modified by 3-MPS (c) PS-coated magnetite.

ticles is shown in Scheme 1 that involves three steps: (1) 3-MPS-coated magnetite particles were added into 20 mL of styrene containing 0.3 g of BPO. Then the mixture was subjected to sonication for 10 min and stirred for 12 h to form a stable ferrofluid for further use. (2) 0.1 g of the hydrophilic agent hexadecanol and 20 mg of PVA124, which was used as a dispersing medium, were added to a multisurfactant solution (0.1 g of SDBS/PEG6000, mass ratio = 3/2, in 100 mL of deionized water). The miniemulsion was obtained after stirring for 30 min at 70°C. (3) The obtained miniemulsion and the ferrofluid were mixed and stirred for 3 h in a 250-mL 3-necked flask equipped with a condenser, heated at 70°C for 3 h and at 85°C for 2 h with continual stirring to allow the grafting polymerization of the polystyrene layer on the surface of magnetic particles. The brown product was washed with excess amount of methanol and toluene to remove the physioabsorbed polystyrene and was separated by the magnetic separation process. The magnetite polystyrene microspheres were dried at room temperature in vacuum.

Characterization

Fourier transform infrared (FTIR) spectra were obtained using a TENSOR FTIR spectrometer with a resolution of 1 cm^{-1} by diffusion reflectance spectroscopy. X-ray photoelectron spectra (XPS) were recorded with an AXIS ULTRA electron spectrometer using nonmonochromatic Al $K\alpha$ radiation at 150 W. An overall scan from 0 to 1100 eV with the average of 1 scan was conducted. The average size of the magnetic particles and the PS microspheres was

determined by transmission electron microscopy (TEM) with a JEM-200CXII (JEOL) microscope at 200 kV. Crystals of magnetic particles and 3-MPS coated particles were analyzed by means of X-ray diffraction (XRD) using an X'Pert Pro MPD diffractometer operated at 40 kV and 40 mA with Cu $K\alpha$ ($\lambda = 1.54056 \text{ \AA}$). The mean crystallite size of the Fe_3O_4 powder was determined by the XRD-Scherrer formula (mean crystallite size = $0.9\lambda/(\beta \cos \theta)$, where β is the half width of the diffraction peak and θ is the Bragg angle).²² The vibrating-sample magnetometer (VSM, LS7307-9309) was used to study the magnetic properties of magnetite particles.

RESULTS AND DISCUSSION

Preparation of magnetic polystyrene microspheres

The key step in Scheme 1 is how to anchor the 3-MPS molecules onto the surface of magnetic particle for the subsequent miniemulsion polymerization of styrene onto the surface of magnetic particles. To prove if the 3-MPS molecules are anchored onto the surface of the magnetic particle or not, the FTIR spectroscopy was used. Figure 1 shows the FTIR spectra of unmodified magnetic particle (spectrum a), 3-MPS modified magnetic nanoparticles (spectrum b), and magnetic polystyrene microspheres (spectrum c). The peak at 540–570 cm^{-1} is generally attributed to the vibration of Fe–O bond of Fe_3O_4 , such as 567 cm^{-1} in spectrum a, 565 cm^{-1} in spectrum b, and 545 cm^{-1} in spectrum c. A red shift corresponding to Fe–O vibration is obvious in spectrum c, which could be caused by a steric effect origi-

TABLE I
FTIR Data for Various Samples Shown in Figure 1

Sample	Bond	Wavenumber (cm^{-1})	Mode of vibration
a	Fe–O	567	Stretching vibration
b	Fe–O	565	Stretching vibration
	Si–O,	1300	Stretching vibration
	C–O–C		
c	C=O	1700	Stretching vibration
	C–H	2927, 2858	Stretching vibration
	Fe–O	545	Stretching vibration
	C–H ^a	3028, 3067	Stretching vibration
	C–H ^b	2924, 2856	Stretching vibration
	C–H ^c	700, 756	Out-of-plane bending vibration
	C=C	1596, 1492 and 1448	Stretching vibration ^d

^a From the phenyl ring of PS.

^b From the alkyl substituent of PS.

^c From the monoreplacement in the phenyl ring group of PS.

^d Formation vibration of the framework of PS.

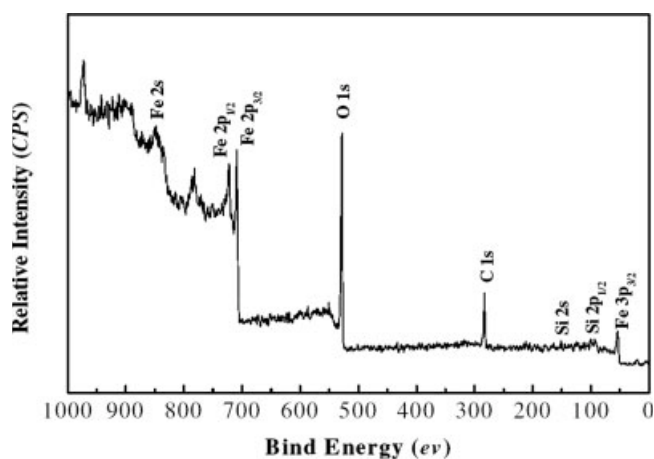


Figure 2 The XPS spectra of magnetic particles modified by 3-MPS.

inating from a big bulk of polystyrene chains. The peak at 1627 cm^{-1} , in Figure 1, is from the absorbed CO_2 and $3200\text{--}3500\text{ cm}^{-1}$ are from absorbed H_2O . On comparing the three spectra in Figure 1, we can see strong resonance signals at about 2927 and 2858 cm^{-1} for spectrum b with the magnetic particle capped with 3-MPS, and for spectrum c, the magnetic particle coated with polystyrene. This signal corresponds to the stretching vibration of C—H bond. For spectrum b, the strong and broad peak at about 1300 cm^{-1} originates from Si—O bond and C—O—C bond of the silane coupler. The weak band around 1700 cm^{-1} is from the vibration of C=O bond of ester group on 3-MPS that shifts to lower wave

number possibly because of a conjugation between bonds of C=O and C=C at the end group. It is suggested that the silane coupler (3-MPS) be bonded to the surface of the magnetic particles by the reaction of silanol of 3-MPS with —OH groups of the surface of magnetic particles. For spectrum c in Figure 1, the peaks at around 3028 cm^{-1} is assigned to the stretching vibration of C—H in the phenyl ring of PS, three peaks at 1596 , 1492 , and 1448 cm^{-1} to the formation of vibration of the framework of PS, and two peaks at 700 and 756 cm^{-1} to the out-of-plane bending vibrations of C—H from the monoreplacement in the phenyl ring group of PS (Table I). The spectra in Figure 1 demonstrate good adhesion of polystyrene coated onto the surface of magnetic particles. To further determine whether 3-MPS molecules were anchored onto the surface of magnetic particles or not, we also carried out the XPS measurement. Figure 2 shows the XPS spectrum of magnetic particles modified by 3-MPS. The XPS scans are used primarily to provide an elemental composition of the surface and to detect contaminations. In Figure 2, eight major peaks are observed, which are at 151 eV due to Si 2s electrons, at 100 eV due to Si 2p electrons, at 528 eV due to O 1s electrons, at 283 eV due to C 1s electrons, at 848 eV due to Fe 2s electrons, at 722 eV due to Fe 2p $_{1/2}$ electrons, at 709 eV due to Fe 2p $_{3/2}$ electrons, and at 54 eV due to Fe 3p $_{3/2}$ electrons. By comparing the integrated area of core-level photoemission peaks for these atoms in narrow scan spectrum, the atomic concentration can be obtained. Therefore, the atomic content of carbon is 22%, oxygen 48%, silicon 8%, and

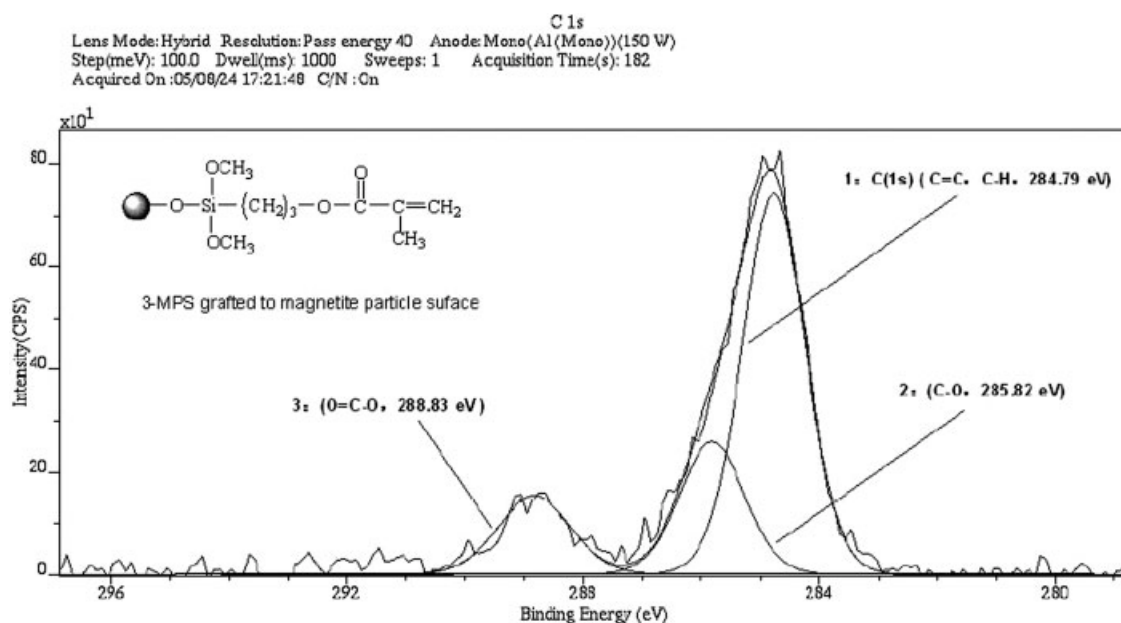


Figure 3 The narrow scans of the individual core level peaks C (1s) and the curve fitting.

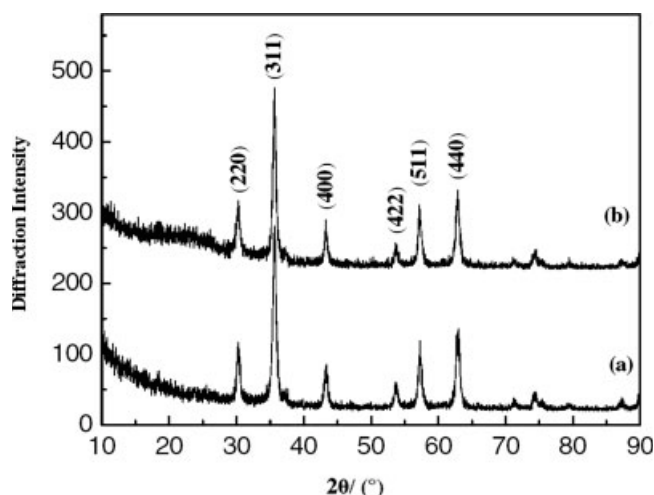


Figure 4 The X-ray powder diffraction patterns of (a) magnetic particles and (b) 3-MPS-magnetic particles.

iron 22%. To investigate the subtle changes on the surface chemistry after silanization with 3-MPS for 6 h, narrow scans of the individual core level peaks are necessary. Narrow scan of C 1s spectrum is shown in Figure 3. The C 1s core-level photoemission peak is highly asymmetric, and we are therefore obliged to do curve fitting to explain the chemical structure of 3-MPS layer. According to the chemical structure of the 3-MPS layer shown in Scheme 1, there should be four chemically distinct carbon environments in the 3-MPS layer, but in practice it is difficult to distinguish CH_3 and CH_2 from $\text{C}=\text{C}$. We then fit the C 1s core-level photoemission peak with three peaks, so that the peak at 284.79 eV assigned to carbons including the CH_2 , CH_3 , and $\text{C}=\text{C}$, the peak at 285.82 eV due to the carbon bond

to oxygen (CH_2-O), and the peak at 288.83 eV due to the carbon in ester linkage ($\text{O}=\text{C}-\text{O}$). The ratio for the integrated area of the peak at 285.82 eV to that of the peak at 288.83 eV is found to be nearly 2. These results show that the chemical structure of the silanized layer is consistent with the structure suggested in Scheme 1. The XPS results further suggest that the organosilane 3-MPS is covalently coupled to the surface of magnetic nanoparticles.

Characterization of magnetic particles

Morphology

The crystal structure was investigated by means of XRD. Figure 4 displays the XRD pattern of untreated magnetic particles and treated magnetic particles with 3-MPS. According to the XRD data, the standard Fe_3O_4 crystal with spinel structure has six diffraction peaks: {2 2 0}, {3 1 1}, {4 0 0}, {4 2 2}, {5 1 1}, and {4 4 0}.²³ Comparing the pattern in Figure 4 with the standard magnetite (JCPDS: 87-2334), it can be concluded that magnetite nanoparticles coated by silane coupler are also of spinel structure. In addition, from the data of XRD, the size of magnetic particles can be calculated according to the Scherrer equation,²² the crystalline size of the prepared magnetic particle was about 19 nm. Figure 5 shows the micrographs of the uncoated magnetic particles [Fig. 5(a)] from TEM and PS-coated magnetic microspheres [(Fig. 5(b)] from AFM. From Figure 5(a), it can be seen that the uncoated magnetic particles are rather polydispersed with diameters in the range from 6 to 30 nm. Comparatively, the PS-coated magnetic spheres [Fig. 5(b)] are uniform with diameters in range from 1 to 2 μm .

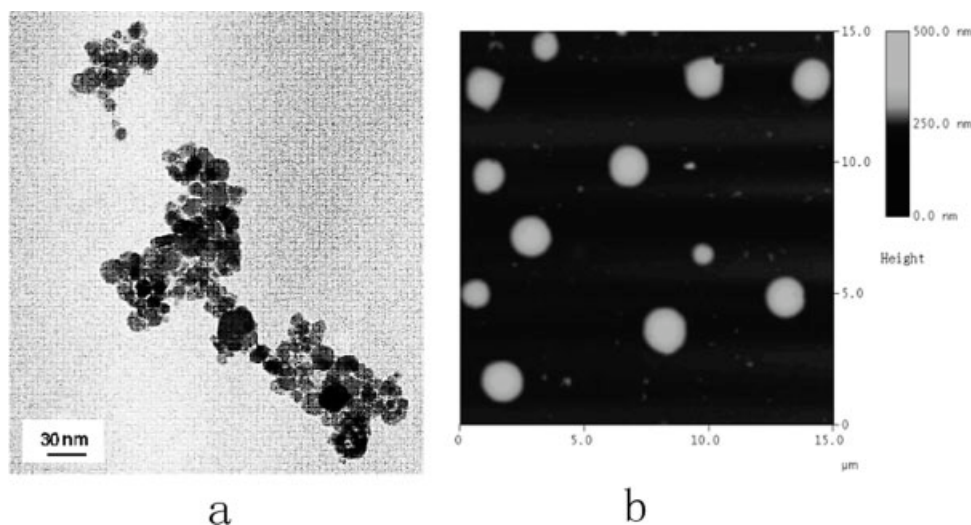


Figure 5 The micrographs of (a) Fe_3O_4 particles from TEM and (b) PS-coated Fe_3O_4 microspheres from AFM.

Magnetic property

The magnetic properties of the magnetic particles were analyzed at room temperature by VSM. The magnetization curve can be obtained by plotting the magnetization of the sample with the applied magnetic field. Figure 6 shows the magnetization curves of the prepared samples: (a) Fe_3O_4 particles, (b) 3-MPS treated magnetic nanoparticles, and (c) PS-coated Fe_3O_4 . The corresponding results from VSM, such as the values of saturation magnetization, remnant magnetization, and coercive field for all samples are listed in Table II. From Figure 6, the magnetization curves of various samples display a ferrimagnetism behavior, with slender hysteresis. As shown in Table II, the coercivity field and remnant magnetization are found to be less than 60 Oe and 7 emu/g, respectively. Comparing the three curves, from a to c, the ferromagnetic behavior becomes weaker and weaker. The saturation magnetization (M_s) changes in the following order: $a > b > c$. The M_s of untreated magnetic particles is 74.71 emu/g, which is lower than that of the bulk phase (92 emu/g).²⁴ The hysteresis loop, which is the unique characteristic of the weak ferromagnetic behavior, is clearly observed ($M_r = 0.17$ emu/g) in Figure 6(c). It can be inferred from the hysteresis loops that the composite magnetic spheres are magnetically soft at room temperature. The coercive force changes in the following order: $c < a < b$. This trend can be well correlated to the sizes of the magnetic particles. The coercive force is known to follow a peak with the increase in particle size and at a critical size it attains the maximum value.²⁵ Thus, Sample 3, having the largest size of magnetic particles, belongs to the right side

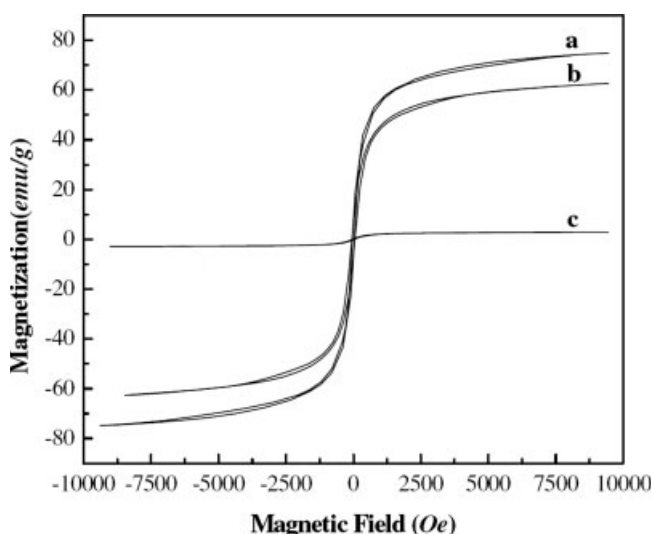


Figure 6 The magnetization curves of (a) Fe_3O_4 particles (Sample 1), (b) 3-MPS-magnetic nanoparticles (Sample 2), and (c) PS-coated Fe_3O_4 composite microspheres (Sample 3).

TABLE II
Magnetization Data for Various Samples Measured at Room Temperature

Sample	M_s (emu/g)	H_c (Oe)	M_r (emu/g)
1	74.71	36.86	6.93
2	62.60	55.25	6.32
3	2.85	35.13	0.17

of the peak, where the particles are of multidomain systems. In the case of Sample 2 and Sample 1, as they have comparatively smaller particle size, their behavior can be related to that of a single domain system placed on the left side of the peak with Sample 2 near the maximum and Sample 1 with a smaller coercivity.

CONCLUSIONS

In conclusion, we describe an efficient means of preparing magnetic polystyrene microspheres. Powder XRD measurements indicated the spinel structure for the magnetic nanoparticles and the average grain size of 19 nm in diameter. Transmission electron micrographs showed that the magnetic nanoparticles had a size distribution of 6–30 nm. The maximum particle size of the magnetic PS microspheres is in the range of 1–2 μm according to transmission electronic microscopy. The results of Fourier transform infrared spectroscopy and X-ray photoelectron spectroscopy showed that 3-methacryloxypropyltrimethoxy silane was covalently coupled to the surface of magnetic nanoparticles. The microspheres were characterized with slender hysteresis by magnetization curves.

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