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ORIGINAL CONTRIBUTION

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Hematite nanoparticles as polystyrene microsphere coatings and hollow spheres: preparation and characterization

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Abstract A novel method of fabricating composite particles with core–shell structures is demonstrated. The particles comprised monodisperse submicrometer-sized copolymer latex spheres as cores and Fe_2O_3 crystallites as shells. The shell was formed by controlled hydrolysis of aqueous iron solutions, and the growth of hematite on the surface of the copolymer spheres was controlled by slow injection. Hollow spheres were obtained by calcinations of the so-coated copolymer lattices at 500°C in air. The void size of these hollow spheres was determined by the diameter of the copolymer template, and the wall thickness could be easily controlled in the range of 20–60 nm by using this coating process. The structure and the composition of the spheres were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), and thermogravimetric analysis (TGA). It can be seen that a crystallite change and a crystal phase transformation occurred during coating and calcination of the composite spheres. The formation of the composite particles is simply explained by the nucleation of iron oxide on the surface of the latex followed by growth of the iron compound shell.

Introduction

Hybrid microspheres usually consist of core microspheres coated with shell microspheres of substantially smaller diameter (nanoparticles) and of similar or different chemical composition. Previous studies have described the methods for the synthesis of hybrid microspheres composed of polystyrene (PS) microspheres coated with metal or metal oxide nanoparticles, and for the coating of different core substrates with a variety of shell materials (e.g. iron oxide colloids with uniform layers of silica, and cationic polystyrene latex with metal particles) [1, 2, 3]. Several studies have been conducted on the preparation of polymer cores covered with inorganic shells, such as silica [4], CdTe [5], and iron compounds [6, 7, 8, 9], which makes it possible to extend the use of the such particles in different areas of high technology. By using the layer-by-layer (LbL) method based on colloidal templates, Caruso et al. demonstrated that nanocomposite multilayers could be assembled on particle surfaces [10, 11, 12, 13, 14, 15]. Submicrometer-sized composite particles with multilayer arrays of silica [10, 11], Fe_3O_4 [12, 13], and TiO_2 nanoparticles were prepared with nanometer-scale control of the thickness.

In addition, hollow spheres produced by colloidal template are of interest in diverse applications, such as fillers, coatings, catalysts, capsule agents, pigments, and drug delivery [14, 15], owing to their low densities, large specific surface areas, and optical properties. Caruso and coworkers recently reported a modified template approach, based on the LbL method and a colloidal template, for the synthesis of novel composite core–shell materials and hollow spheres, and submicrometer-sized

hollow spheres were obtained after the removal of the template from the solid-core multilayered-shell particles either by calcination or by chemical extraction [16, 17]. However, control of the desired thickness of the layer in this process was time consuming. Hiroshi Shiho also reported a method of producing hollow iron oxide spheres by controlled hydrolysis of an aqueous solution of $FeCl_3$ in the presence of PS particles [18]. However, the wall thickness of the composite microspheres was uncontrollable in this approach, and the procedure took more than 48 h for coating at a high temperature of 100°C as a result of the one-off addition of $FeCl_3$. In this paper, we report a new, rapid technique for the preparation of core–shell-structured hollow spheres at a lower temperature. The wall thickness of the structured spheres could be easily controlled in the range of 20–60 nm by using a slow-injection coating process. The void size of these hollow spheres was determined by the diameter of the copolymer template.

Experimental

Styrene (St) and methacrylic acid (MAA) were purified by distillation. Ferric chloride hexahydrate, ethylene glycol, hydrochloric acid (all AR), potassium persulfate (KPS, Beijing) were used without further purification. Negatively changed, sulfate- and carboxyl-stabilized St/MAA copolymer spheres were prepared as described elsewhere [19]. Iron solution (0.8 M) was prepared by dissolving ferric chloride in deionized water.

The first step in the preparation of the hollow hematite spheres is to fabricate the composite particles. To prevent aggregation of core particles, the copolymer latex was dispersed by sonication after being diluted with water. The dispersions containing 30 mg dm^{-3} copolymer latex, 20 mmol dm^{-3} hydrochloric acid, 24 mmol dm^{-3} hexamethylenetetramine (HMTA), and 14.5 mol dm^{-3} ethylene glycol (EG) were heated to 80°C under gentle stirring. Then 0.8 M iron solution was slowly injected into the system at a rate of 0.1–0.6 mL min^{-1} over 1.5–5 h. After the systems were deposited for 40 min, the supernatant solution was discarded, and the particles were resuspended in distilled water under mild stirring. The composite particles obtained were filtered and dried at 60°C for 24 h. To produce hollow hematite particles, the composite spheres were calcined for 4 h in a furnace at 500°C with a heating rate of 10°C min^{-1}. The hollow spheres were dispersed in water by gentle sonication for 1–2 min.

Electrophoresis measurements were performed using a Malvern Zetasizer 3000 HS on particles dispersed in air-equilibrated deionized water [15]. The average size and morphology of the copolymer spheres, the composite particles, and the hollow spheres were determined by transmission electron microscopy using a JEM-100CXII (JEOL) microscope and scanning electron microscopy (SEM) using a JSM-6301F instrument operated at an accelerating voltage of 5 kV. The crystals of coated and hollow particles were examined by X-ray diffraction (XRD) using a Japan D/MAX-RB diffractometer, operated at 40 kV, 120 mA, using Cu Kα; light-absorption of the particles in aqueous solutions of hollow particles was analyzed using UV spectra collected with a Cary 4G, and thermogravimetric analysis (TGA) using a TG/DSC analyzer (NETZSCH STA 449C) at a heating rate of 10°C min^{-1}.

Results

TEM and SEM analyses

The St/MAA copolymer latex was prepared by emulsifier-free emulsion polymerization of St with MAA monomer. A typical TEM image obtained is given in Fig. 1a. The microspheres were spherical in shape and mono-disperse in size, with a diameter of about 240 nm. The IR spectra of the copolymer spheres revealed well-defined characteristic bands of the St unit, and a characteristic peak at 1,698 cm^{-1} is attributed to carbonyl stretching of carboxyl groups, indicating the copolymerization of MAA and St. The TEM image in Fig. 1b illustrate particles coated with coarse shells consisting of separate akaganeite nanoparticles. Thus, hydrolysis of the aqueous solution of $FeCl_3$ in the acid produced the crystals of akaganeite (β-FeOOH) nanoparticles [20]. Coarse coated particles comprising separated particles of akaganeite formed at pH 1–2 after 5 h.

In order to form a relatively smooth and thick shell of hematite, slow injection of the $FeCl_3$ aqueous solution was used to keep the concentration of ferric ion low (1.2×10^{-3} mol dm^{-3}) and in the neutral pH range throughout the whole coating process. The iron solution (20–60 mL) was injected into the system at 0.1 mL min^{-1}. TEM images shown in Fig. 2 were employed to follow the composite shell thickness at different times and to examine the morphology of the coated particles. The thickness of the outer layer could also be altered from 20 to 60 nm while the latex cores were coated with hematite particles by using different injection times. By extending the injection time, the average diameter increment is 20 ± 10 nm. These results clearly show that the thickness of the nanoparticle's hematite multilayer shell surrounding the colloidal particles could be tailored by using a slow-injection coating process (i.e., as a function of the injection time). At a constant temperature (e.g., 80°C), the injection rate of the $FeCl_3$ solution had a pronounced effect on the nature of the surface layer. At a slower rate of injection (0.05 mL min^{-1}), tiny, isolated particles of the coating material became discernible on the surface of the latex

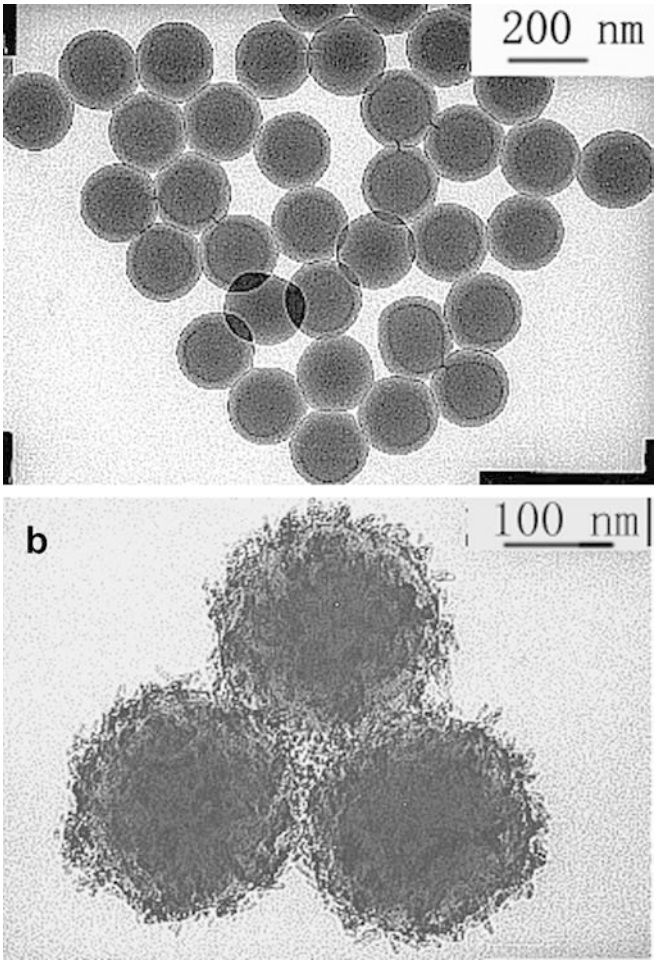


Fig. 1a,b TEM of carboxyl-modified copolymer microspheres (**a**) and nanchematite-coated particles of copolymer spheres (**b**)

cores. These primary particles provide the nuclei for subsequent growth of iron oxide particles. By altering the injection rate (0.1–0.3 mL min^{-1}), a smooth coverage developed as illustrated in Figures 3b and c. Finally, at an even higher injection rate of 0.6 mL min^{-1}, only mixed dispersions were found (Fig. 3d). Obviously, the injection rate of the iron solution is a key factor in controlling the morphological structures of the coated spheres.

Figure 4 shows the hollow spheres obtained under the experimental conditions. The hollow spheres were complete and structurally intact after calcinations, as confirmed by SEM (Fig. 4a). TEM images of the calcined samples (Figs. 4b and c) revealed a reduced electron density of the spheres after calcining, indicating that hollow spheres were obtained. The voids of these hollow, hematite spheres were about 220-nm spheres, depending on the diameter of copolymer spheres. The wall thicknesses of the hollows in Figs. 4b and c are approximately 30 and 55 nm, respectively, and the

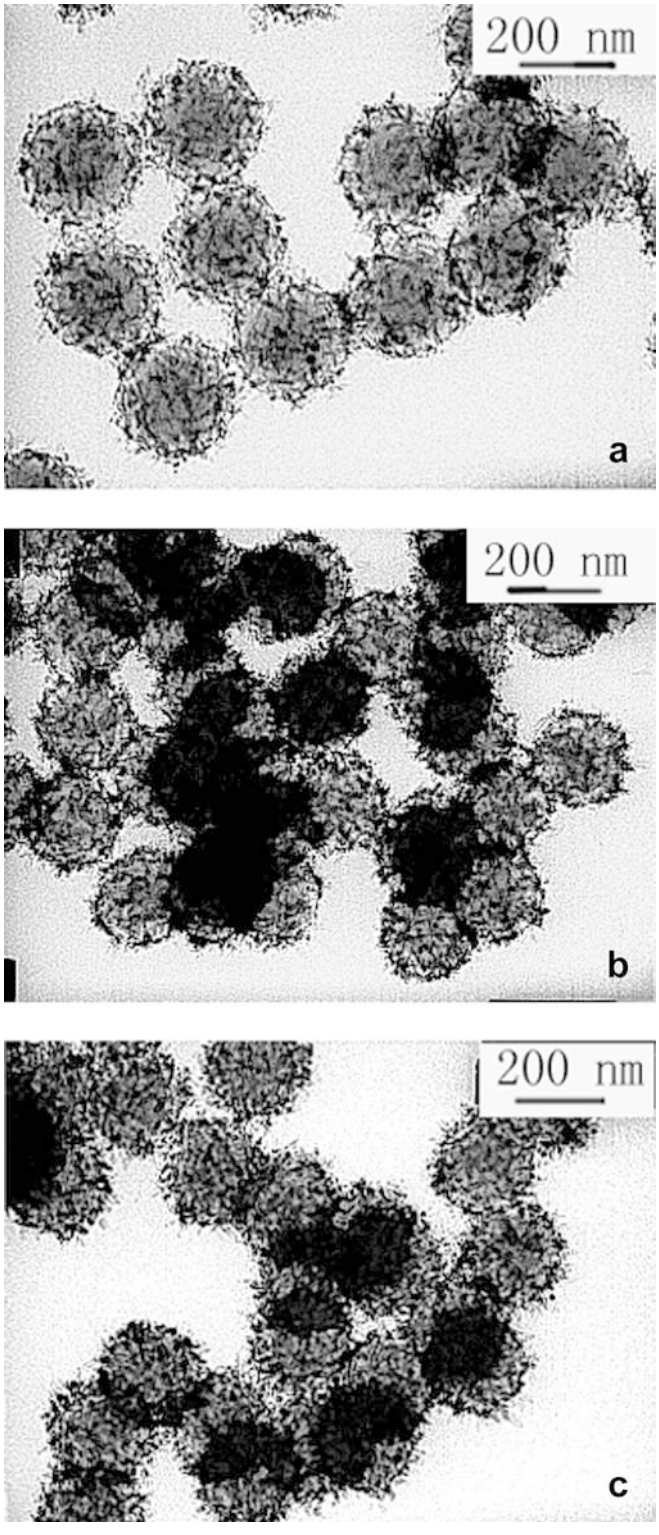


Fig. 2a–c TEM images of coated copolymer microspheres by slow injection with different injection times (t) **a** 1.5 h, **b** 3.5 h, **c** 5.0 h. The average diameters of the composite particles are 255, 280, and 310 nm (the error is approximately ± 10 nm)

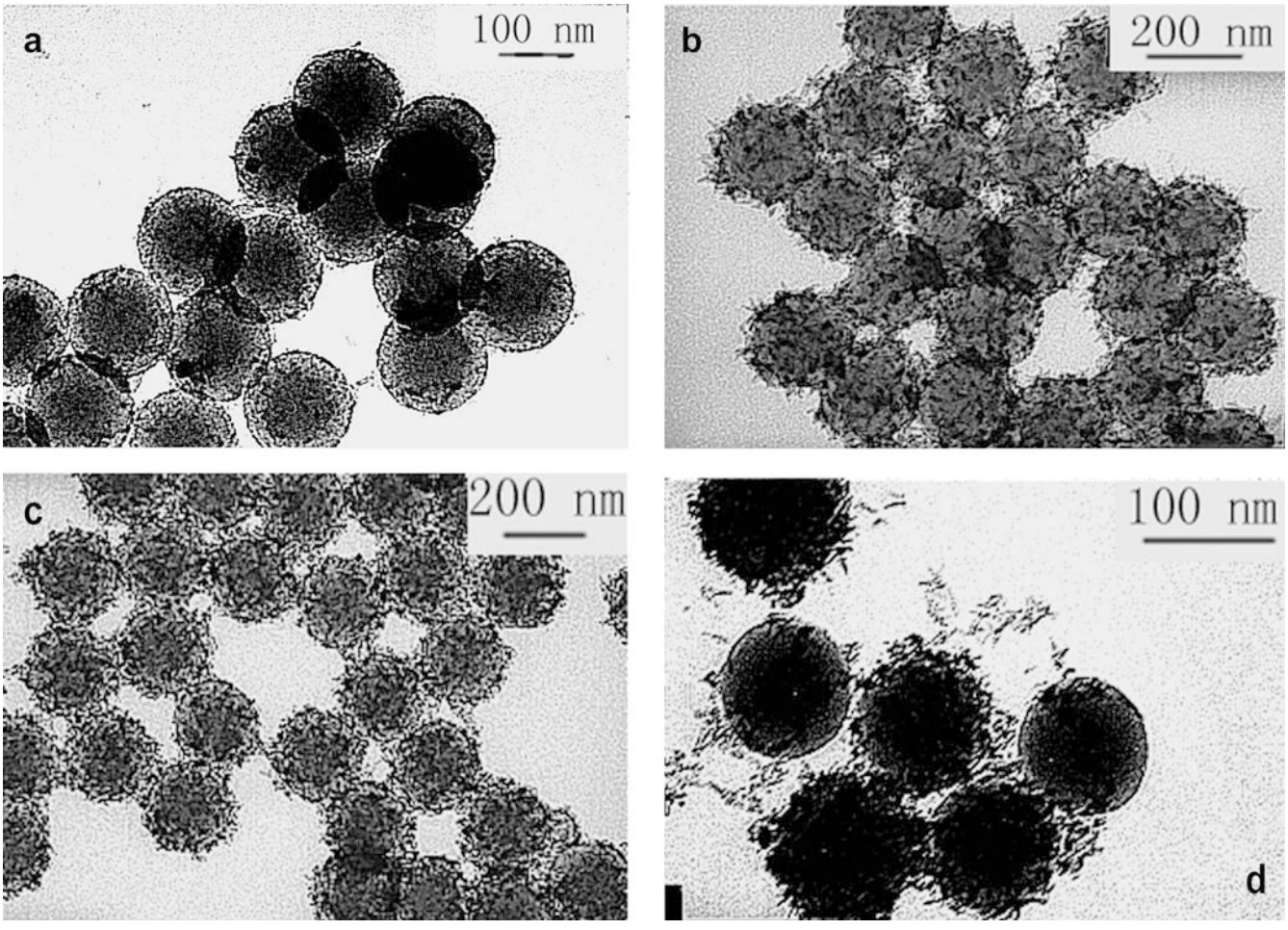


Fig. 3a–d TEM of particles obtained by coating a dispersion containing 30 mg dm^{-3} copolymer latex, 20 mmol dm^{-3} hydrochloric acid, 24 mmol dm^{-3} HMTA, and 14.5 mol dm^{-3} EG, injecting $FeCl_3$ solution for 1.5 h at **a** 0.05 mL min^{-1}, **b** 0.1 mL min^{-1}, **c** 0.3 mL min^{-1}, **d** 0.6 mL min^{-1}

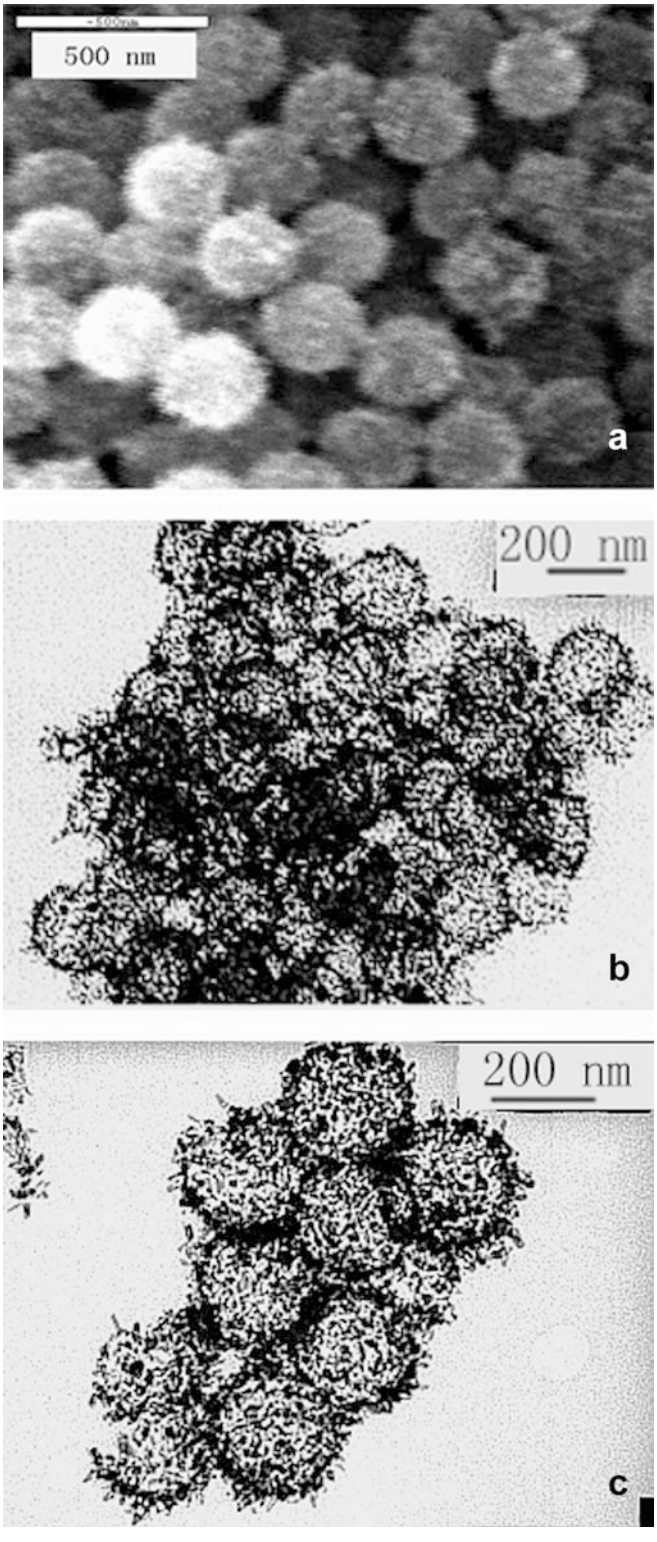
diameters of the hollow spheres produced were about 10% smaller than those of the corresponding composite spheres. Figure 4b shows the TEM images of a random aggregate of hollow, hematite spheres after they have been separated by gentle sonication in water.

XRD analyses

The different phases of the iron oxide coated copolymer particles and hollow spheres heated in air were characterized by XRD (Fig. 5). Curve 4a implies that the tiny particles on the surface of copolymer latex are β-FeOOH crystallites. Curves 4b and c, which refer to the composite particles, show the shell crystallites comprise the α-Fe_2O_3 phase with traces of the Fe_3O_4 phase, indicating a phase transformation from β-FeOOH to α-Fe_2O_3 after 3.0 h injection. XRD patterns for the series of nanoparticles collected after 3.0-h and 5.0-h coatings on copolymer spheres were also obtained. Peak positions did not shift with injection time and shell thickness, but half peak widths decreased, indicating the increase of α-Fe_2O_3 crystallite throughout the coating experiment. Curves 5d and e show that after calcinations the crystallites of hollow particles comprise only α-Fe_2O_3, indicating the transformation of crystallite phase from Fe_3O_4 to α-Fe_2O_3 and the increase of the size of crystallites.

UV analyses

Growth of the iron-based nanoparticles was monitored using a spectrophotometer, and a UV/visible spectrum was recorded from 200 to 350 nm every 10 min. A sequence of UV/vis absorption spectra obtained during a typical reaction are shown Fig. 6. The observed peak was due to iron oxide coated copolymer microspheres. During the reaction process, this typical peak shifted from 209 to 225 nm because the iron oxide nanoparticles on the surface of the copolymer latex grew with injection



◀

Fig. 4 a SEM image of hematite hollow spheres prepared by slow-injection coating of copolymer particles, followed by calcining at 500°C; **b** TEM image of the corresponding sample showing the hollow nature of the particles, prepared with an injection time of 3.5 h; **c** TEM image of the hollow particles of the coated latex, prepared with an injection time of 5.0 h

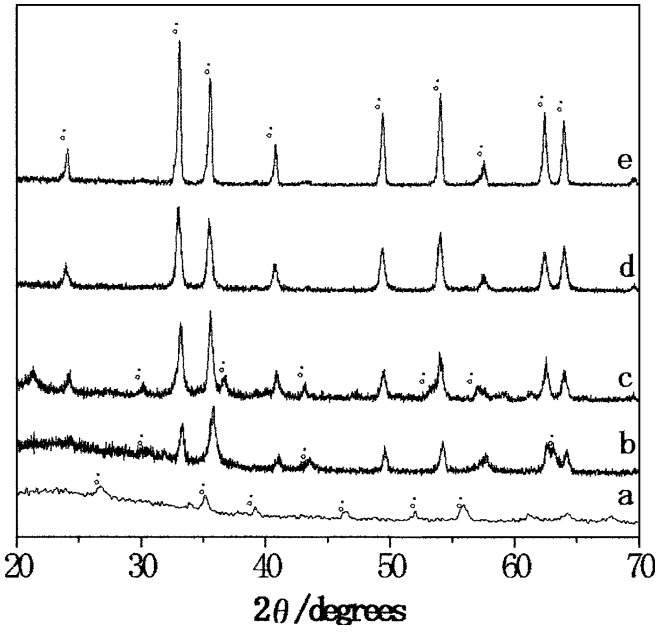


Fig. 5a–e XRD patterns of the changing iron oxide of coated copolymer particles with the injection time: **a** 1.0, **b** 3.0, **c** 5.0 h; and of the hollow hematite particles obtained of **d** sample b, **e** sample c after being calcined at 500°C for 3 h: ◇ β-FeOOH, □ Fe_3O_4, ◆ α-Fe_2O_3

time, thus indicating that hematite-coated latex could be fabricated after 89 min. In another UV spectrum (Fig. 7), a very broad absorption peak near 400 nm was observed for hollow, hematite spheres. The spectra of the corresponding wall nanoparticles of hollow spheres from a range of coating layers were superimposed with a periodic oscillation. The red shift in Fig. 7 corresponds to the increasing thickness of the hollow wall. Moreover, after calcinations, the enhancement of the corresponding size of particles of the hollow wall can also cause the peak position to change from 365 nm at 1.5 h to 409 nm at 5.0 h, as shown in Figs. 7c and a, respectively.

TG analyses

Figure 8 shows the weight loss of coated particles when they were heated to 600°C. Up to 230°C, a small weight loss (3.2%) was observed during TGA probably due to the evaporation of residual moisture in the sample. As a result of decomposition of the core-polymer particles, a weight of loss of 36.7% was measured between 350 and 440°C. A partial change of the shell composition from Fe_3O_4 to hematite occurred. The weight loss of 4.1% at 230–267°C shows the desorption of H_2O molecules adsorbed on the particle surface and the elimination of

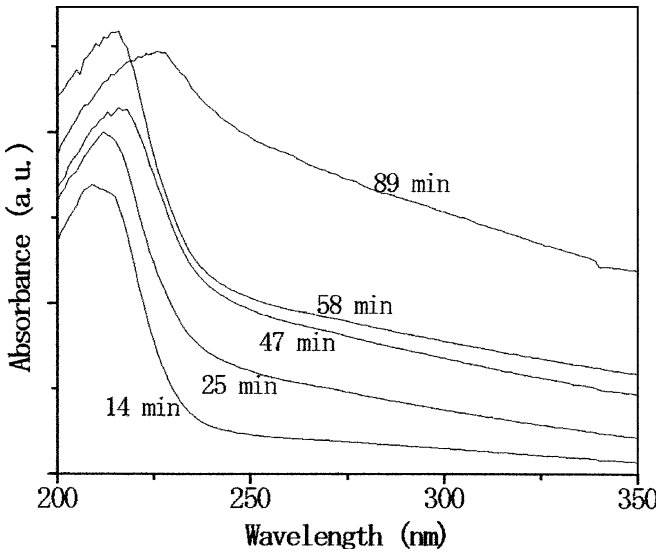


Fig. 6 Evolution of the UV/vis absorption spectra of the hematite-coated particles growth proceeds. The peak is due to the resonance of iron oxide coated copolymer spheres. Each spectrum is labeled with the corresponding injecting time

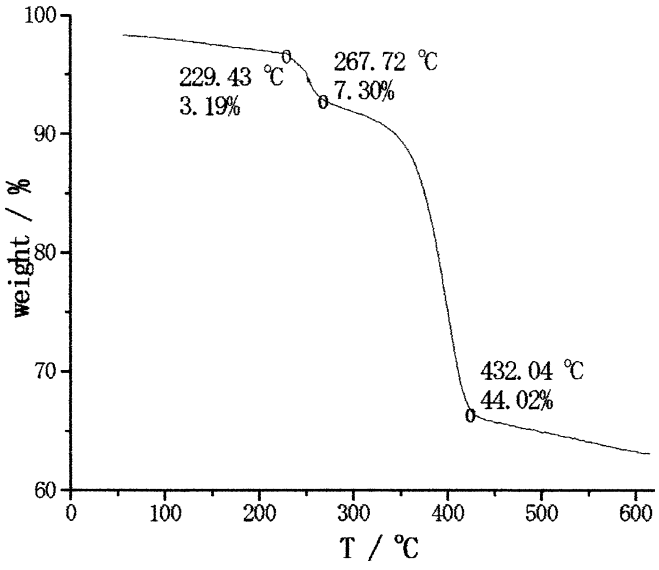


Fig. 8 Thermal gravimetric analysis of polymer/hematite (core–shell) particles. The weight percent lost approximately equals the mass of the core at 400°C

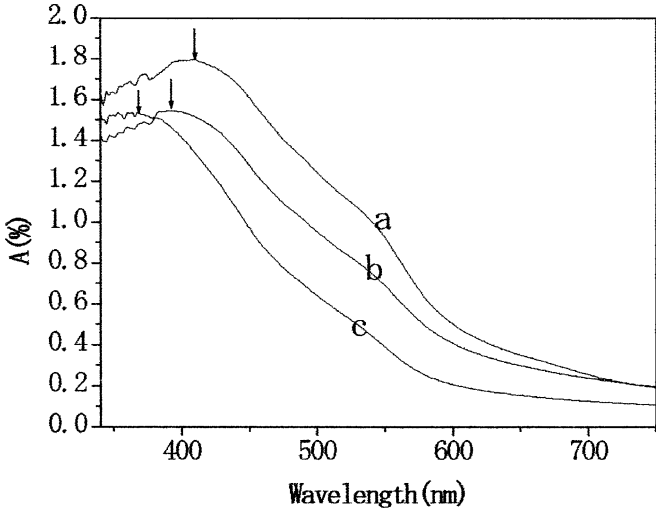


Fig. 7a–c UV absorption of hollow particles after calcining of the composite particles coated with the injection time **a** 5.0 h, **b** 3.5 h, **c** 1.5 h by Fe_2O_3 nanoparticles

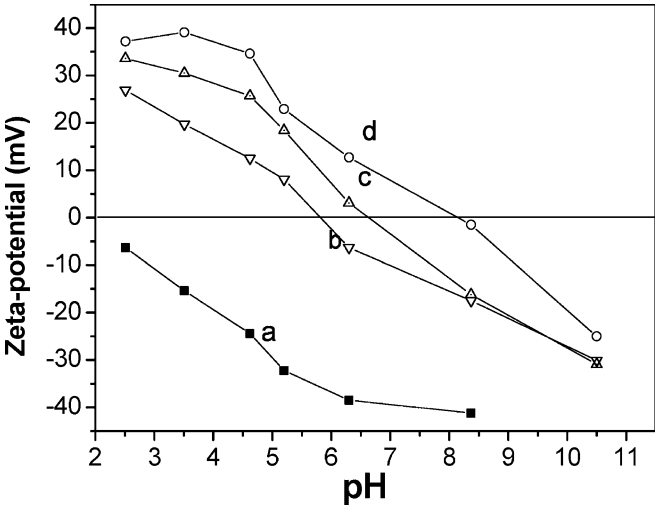


Fig. 9a–d Variation of zeta potential for the polymer latex (**a**) and the composite spheres at different injection times with pH values, **b** 1.5 h, **c** 3.0 h, **d** 5.0 h

surface OH^- groups coordinated to the particle surface Fe^{3+} ion by the dissociation of H_2O.

Zeta potential

Electrophoresis measurements revealed that the ζpotential of the latex particles owing to sulfate and carboxyl ions on the surface of the copolymer colloids did not exceed −40 mV. Figure 9 shows the variations of zeta potentials with pH values for the polymer latex and the composite spheres for different injection times. The isoelectric point (iep) of PS spheres is less than 2.0; the ieps of composite spheres at different injection times are pH 5.8 (1.5 h), 6.6 (3.0 h), and 8.1 (5.0 h).

Discussion

It has been demonstrated that polystyrene particles could be covered with a smooth inorganic layer by hydrolysis of metal ions in the presence of the polymer

latex [7, 21]. It was of interest to apply this method to iron compounds because of the easy modification of polymer colloids with magnets. This paper has demonstrated that negatively charged copolymer microspheres could be quickly coated with crystalline hematite, and that the thickness of the shell layers could be controlled by the injection time of the iron solution. The process of coating may be explained by the nucleation on the surface of the latex, and the heterocoagulation between the inorganic nanoparticles precipitated in situ and the core latex, followed by the growth of the iron compound shell.

It was suggested that the hematite nanoparticles were actually formed at pH 1–2 through a distinct two-stage phase transformation from $Fe(OH)_3$ to β-FeOOH and β-FeOOH to α-Fe_2O_3 [20, 22]. However, this gel–sol method for obtaining hematite shell on PS spheres requires more than 48 h at 100°C in pH 1.4–2.0. According to the report of Sapieszko et al., as the concentration of ferric ions is reduced, a hydroxy ferric complex, $Fe(OH)_2^{+}$, becomes the precursor responsible for the formation of α-Fe_2O_3 with increase in pH up to the neutral range only at 80°C [23]. On the other hand, the adsorption of the negatively charged SO_4^{2-} ions on the surface of copolymer latex to the positively charged ferric complexes [24] makes it possible that the copolymer latex is quickly coated by hematite at lower temperatures. The method of slow injection at 80°C for controlled hydrolysis of aqueous solutions of $FeCl_3$ can keep high basic concentrations and a low excess concentration of ferric ions during the whole coating process.

The coating hematite on the copolymer latex could be achieved by controlling the pH in the system by the addition of HCl acid and HTMA, which resulted in the optimum pH for heterocoagulation of hematite on the copolymer latex. The pH of the reaction system was 5.4 before coating and 6.0 after coating. The variations of zeta potentials with pH values for the composite spheres (Fig. 9) signify that it is easy to cause heterocoagulation between the copolymer latex and hematite at pH 2.5–6.5. The iep values of the composite spheres for different injection times show that the surface of composite particles was transformed from acidic to alkaline. When good coatings were obtained in this system, the pH before and after coating was 5.0–6.5.

At the beginning of the injection, the Fe^{3+} is adsorbed to the surface of copolymer spheres as the hydrated $Fe(OH_2)_6^{3+}$ species and forms the $Fe(OH)_2^{+}$ in the presence of base [24], which may form a localized nucleation site for the formation of α-Fe_2O_3 or β-FeOOH in lower concentrations. The XRD pattern in Figure 5a clearly shows that tiny β-FeOOH particles are adsorbed to the latex, and there was not a coating shell of iron compound in Fig. 3a. After 90-min injection, the nucleation of α-Fe_2O_3 occurred, then hematite particles grow, and β-FeOOH particles totally disappeared after coating for 3.0 h, as shown in Fig. 4b. Since the formation of hematite particles occur exclusively on the surfaces of the composite particles, the hematite particles on the surfaces of the polymer particles may act as seeds which prevent the nucleation of hematite in the solution phase. Sugimoto et al. reported that the rate of transformation from β-FeOOH to α-Fe_2O_3 is greatly increased by a decrease in $[Fe^{3+}]$ or an increase in pH [23]. In view of no formation of akaganeite as the intermediate to hematite after the dissolution of the former in Fig. 4c, direct formation of hematite (and magnetite) may follow, because of the sufficiently low steady supersaturation below the solubility product of akaganeite.

This explanation applies to the change of injection rate of iron solution. After injecting at 0.05 mL min^{-1} for 1.5 h, only tiny particles occurred on the copolymer surface and shell was not obtained. These tiny particles are regarded as akaganeite and crystal nuclei of Fe_2O_3 and coating in the nucleation stage. At 0.3 mL min^{-1} for 1.5 h, the hematite nuclei grow by the deposition of ferric ion, and the composite particles are formed as a result of some hematite obtained (Figs. 3b and c). The surface of the composite spheres is smoothed out only after extended coating when enough hematite is produced, a case similar to systems with prolonged injection times. At 0.6 mL min^{-1}, mixed dispersions are generated because larger amounts of hematite are formed, a lot of which fall off the coating shell (Fig. 3d), essentially resembling the system at the lowest HTMA content. Obviously, the injection rate of the iron solution and the loaded amount of hematite are the key factors in controlling the morphological structures of the coated microspheres.

The formation of cracks in hollow particles is influenced by the heating rate of calcinations. When the original coated particles were heated quickly, polystyrene cores rapidly decomposed to CO_2 and H_2O (vapor), causing the break-up of the shell walls by the pressure of the gases. At a relatively low heating rate (10°C min^{-1}), complete shells were obtained as shown in Fig. 3, whereas cracked hollow particles resulted from calcinations at a heating rate of 50°C min^{-1}. A high cooling rate could also cause crack formation as a result of thermal shrinkage of hematite.

Conclusion

Core–shell particles with Fe_2O_3 crystallite have been prepared as described in this paper. Hollow spheres are obtained by calcination. These have a well-defined void size determined by the diameter of the copolymer template. The thickness of the resulting homogeneous wall is moderated by controlling the concentration of iron ion

by the method of slow injection. The injection time and the injection rate of iron solution can influence the coating. The results of XRD and TGA indicated that lattices dimensions and crystallite size for the particles were increased with injection time, and a crystal phase transformation occurred during the process. Moreover, the heating rate can also influence the integrated hollow spheres. An explanation of the coating process of slow injection has been given. This method should be extendible to prepare hollow spheres of other materials.

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