

Preparation of ellipsoidal hematite/polymer hybrid materials and the corresponding hollow polymer ellipsoids

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ABSTRACT

Ellipsoidal hematite/poly(ethyleneglycol dimethacrylate) core-shell hybrid materials were prepared by distillation precipitation polymerization of ethyleneglycol dimethacrylate (EGDMA) in the presence of 3-(methacryloxy)propyl trimethoxysilane (MPS)-modified hematite (α -Fe₂O₃) particles as the seeds. The polymerization of EGDMA was performed in neat acetonitrile with 2,2'-azobisisobutyronitrile (AIBN) as initiator to coat MPS-modified hematite seeds through the capture of EGDMA oligomer radicals with the aid of vinyl groups on the surface of the MPS-modified hematite particles in absence of any stabilizer or surfactant. The shell-thickness of the core-shell hybrid particles was controlled by the feed of EGDMA monomer during the polymerization. Other hematite/polymer core-shell hybrid particles, such as hematite/polydivinylbenzene (α -Fe₂O₃/PDVB) and hematite/poly(divinylbenzene-co-methacrylic acid) (α -Fe₂O₃/P(DVB-co-MAA)) were also prepared by this procedure. Hematite/poly(*N,N'*-methylenebisacrylamide-co-methacrylic acid) (α -Fe₂O₃/P(MBAAm-co-MAA)) were synthesized with unmodified hematite particles as the seeds. Hollow polymer ellipsoids were subsequently developed after the selective removal of the hematite core with hydrochloric acid (HCl) from hematite/polymer core-shell hybrids. The resultant core-shell hybrid particles and hollow polymer ellipsoids were characterized by transmission electron microscopy (TEM), Fourier transform infrared spectra (FT-IR) and vibrating sample magnetometer (VSM).

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1. Introduction

During the last decade, the organic-inorganic hybrid materials, which combine the properties of inorganic and organic components within a single material, have attracted expanding interest for material scientists due to their advantages of the organic polymer matrix having facile process-abilities, flexibilities, and various functional groups, together with characteristics of the inorganic particles in terms of mechanical strength, modulus, and thermal stability [1,2]. The organic-inorganic hybrid materials can exhibit novel and excellent properties, such as mechanical, chemical, electrical, rheological, magnetic, optical, and catalytic, by varying the compositions, dimensions, and structures, which have proven diverse applications as drug-delivery system, diagnostic, coating and catalyst [3–8].

Hematite (α -Fe₂O₃), which is the most stable iron oxide under ambient conditions with *n*-type semiconducting properties, low cost and high resistance to corrosion, has been extensively utilized as the products for gas sensors, catalysts, pigments, magnetic

recording media, anti-corrosive agents, and lithium-ion batteries with great scientific and technical importance [9–15]. Many efforts have been devoted towards the incorporation of magnetic particles into core-shell structures in order to control the particle shape, size, and magnetic properties [16–18]. For instance, the solvent-free atom transfer radical polymerization (ATRP) has been used for the synthesis of α -Fe₂O₃/polystyrene (PSt) core-shell nano particles with well-defined shape [19]. Zeolite capsule encapsulated with α -Fe₂O₃ have been afforded by a wet impregnation technique [20]. The colloidal polypyrrole-magnetite-silica nano particles have been synthesized by the aqueous deposition of silica onto ultrafine (15–20 nm) magnetite particles via controlled hydrolysis of sodium silicate with the subsequently oxidative polymerization of pyrrole using various oxidants in the presence of silica-coated magnetite particles [21]. The uniform coating of silica onto the ultrafine hematite particles has altered most properties of the iron oxide particles, such as the dispersibility in either aqueous or non-aqueous media [22], in which the anisometric shape of hematite cores was preserved with benefits via introduction of other functional materials on the particles. Hematite/silica/polypyrrole (α -Fe₂O₃/SiO₂/PPy) ellipsoidal sandwich composite spheres as well as SiO₂, SiO₂/PPy, PPy hollow capsules and PPy ellipsoidal hollow capsules with movable hematite cores have been successfully

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afforded from hematite olivary particles through the oxidative polymerization of pyrrole in the presence of FeCl_3 as oxidant with subsequently selective removal of the inner cores, respectively [23].

In these years, polymer hollow microspheres have attracted much attention for their wide applications, such as encapsulation for controlled-release of drug and enzymes, fillers, pigments, catalysts, and adsorption materials for sound, which have been prepared by a variety of physical and chemical techniques [24–27]. However, non-spherical core-shell particles and the corresponding hollow particles have scarcely reported in the literature with the difficulty to get the suitable non-spherical template [23,28], which would be more attractive for their applications as ordered arrays due to the lower symmetries compared to the spherical particles. Most of the non-spherical particles and their ordered assembly structures have been forcibly obtained from original spherical ones under ion-irradiation or mechanical pressure [29]. It is still a challenge to get non-spherical polymer particles with well-defined shape and controllable size via the facile polymerization.

In our previous work, distillation precipitation polymerization has been successfully developed as a facile and powerful technique for the preparation of SiO_2 /PMBAAm composite [30], SiO_2 /PDVB and SiO_2 /PEGDMA hybrid [31] core-shell microspheres. More recently, ellipsoidal tri-layer hematite/ SiO_2 /PDVB hybrid particles were prepared by distillation precipitation polymerization of divinylbenzene (DVB) in the presence of hematite/3-(methacryloxy) propyl trimethoxysilane (MPS)-modified silica (SiO_2) core-shell particles as the seeds [32]. Here, we introduce the distillation precipitation polymerization as a facile method for the synthesis of ellipsoidal hematite/polymer core-shell hybrid materials in absence of any stabilizer or additive, and the further development of the corresponding polymer hollow ellipsoidal particles by the removal of hematite cores in hydrochloric acid (HCl) aqueous solution.

2. Experimental

2.1. Chemicals

Ferric chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) was purchased from Tianjin Guangfu Fine Chemical Engineering Institute. 3-(Methacryloxy)-propyl trimethoxysilane (MPS) was purchased from Aldrich and distilled under vacuum. Ethyleneglycol dimethacrylate (EGDMA) was purchased from Alfa Aesar and used without any purification. Divinylbenzene (DVB, 80% DVB isomers) was supplied as technical grade by Shengli Chemical Factory, Shandong, China, which was washed with 5% aqueous sodium hydroxide and water, then dried over anhydrous magnesium sulfate prior to utilization. Methacrylic acid (Tianjin Reagent Factory I, China) was purified by vacuum distillation before use. *N,N'*-Methylenebisacrylamide (MBAAm, chemical grade, Tianjin Bodi Chemical Engineering Co.) was recrystallized from acetone. 2,2'-Azobisisobutyronitrile (AIBN) was provided by Chemical Factory of Nankai University and recrystallized from methanol. Hydrochloric acid (HCl) was supplied by Tianjin Chemical Reagents II Co. as analytical grade. Acetonitrile (analytical grade, Tianjin Chemical Reagents II Co.) was dried over calcium hydride and purified by distillation before use. All the other reagents were of analytical grade and used without any further treatment.

2.1.1. Synthesis of shuttle-like MPS-modified hematite particles

Shuttle-like monodisperse hematite ($\alpha\text{-Fe}_2\text{O}_3$) particles were synthesized according to the method in the literature [23]. Hematite particles were obtained via aging the aqueous solution of 2×10^{-2} M FeCl_3 and 4×10^{-4} M NaH_2PO_4 at 95 °C for three days. The formation of hematite particles was reflected by the appearance of a brick-red color in the hydrolysis system. The resultant

hematite particles were centrifugated, decanted, and redispersed in acetone for three times, then dried at 50 °C under vacuum, till constant weight.

MPS (1.0 g, 4.0 mmol) was introduced into 20 mL of the ethanol suspension of hematite particles (0.5 g) under stirring in a 50-mL round-bottom flask. Coating of hematite particles with MPS was achieved by stirring the mixture of hematite particles and MPS for 8 h at 50 °C. The resultant MPS-modified hematite particles were purified by centrifugation, decantation, and resuspension in ethanol to remove the excessive MPS. The final MPS-modified hematite particles were dried in a vacuum oven at 50 °C till constant weight.

2.2. Preparation of ellipsoidal hematite/PEGDMA core-shell hybrids by distillation precipitation polymerization

A typical procedure for the distillation precipitation polymerization: In a dried 50-mL two-necked flask, 0.1 g of MPS-modified hematite particles were suspended in 40 mL of acetonitrile as a brick-red suspension. Then EGDMA (0.3 mL, total as 0.75 vol% of the reactive system) and AIBN (0.006 g, 2 wt% relative to the monomer) were dissolved in the suspension. The two-necked flask attached with a fractionating column, Liebig condenser and receiver was submerged in a heating mantle. The reaction mixture was heated from ambient temperature till the boiling state within 7 min and the reaction system was kept under refluxing state for further 5 min. Then the polymerization was carried out with distilling the solvent out of the reaction system and the reaction was ended after 20 mL of acetonitrile was distilled off the reaction mixture within 40 min. After the polymerization, the resultant hematite/PEGDMA core-shell hybrid materials were purified by repeating centrifugation, decantation, and resuspension in acetone with ultrasonication for three cycles. The hybrid particles were then dried in a vacuum oven at 50 °C till constant weight.

The other distillation precipitation polymerizations to prepare hematite/PEGDMA with different polymer thickness and hematite/PDVB, hematite/P(DVB-co-MAA) were much similar to that of the typical procedure by varying the mass ratio of EGDMA monomer to MPS-modified hematite particles, or comonomers, while the amount of AIBN initiator was maintained at 2 wt% relative to the monomer. The treatment of these core-shell hybrid particles was the same as that for the typical procedure. The reproducibility of the polymerizations was confirmed through several duplicate and triplicate experiments.

2.3. Preparation of ellipsoidal hematite/P(MBAAm-co-MAA) core-shell composites by distillation precipitation polymerization

The distillation precipitation polymerization to prepare hematite/P(MBAAm-co-MAA) core-shell composites was much similar to that of the typical procedure to prepare hematite/PEGDMA hybrids by varying the monomers from EGDMA to MBAAm (0.02 g) and MAA (0.08 mL) in the presence of unmodified hematite (0.1 g) as seeds, while the amount of AIBN initiator was maintained at 2 wt% relative to the comonomers and the amount of acetonitrile was maintained as 40 mL. The treatment of the core-shell composite particles was the same as that for the typical procedure to prepare hematite/PEGDMA hybrids. The reproducibility of the polymerizations was confirmed through several duplicate and triplicate experiments.

2.3.1. Synthesis of hollow polymer ellipsoids

The resultant hematite/polymer core-shell ellipsoidal particles were immersed in hydrochloric acid (HCl, 5 wt%) aqueous solution for 2 h. The hollow polymer ellipsoids were purified by several centrifugation/washing cycles in water till pH of 7. The resultant

hollow polymer ellipsoids were dried in a vacuum oven at 50 °C till constant weight.

2.3.2. Characterization

The size and morphology of hematite, hematite/polymer core-shell particles, and the corresponding hollow polymer ellipsoids were determined by transmission electron microscopy (TEM, Tecnai G2 20-S-TWIN).

The magnetic properties of MPS-modified hematite particles and hematite/PEGDMA core-shell hybrids were studied with a vibrating sample magnetometer (9600 VSM, BDJ Electronic Inc, Troy MI, US) at room temperature.

Fourier transform infrared spectra (FT-IR) were scanned over the range of 400–4000 cm^{-1} with potassium bromide slice on a Bio-Rad FTS 135 FT-IR spectrometer.

3. Results and discussion

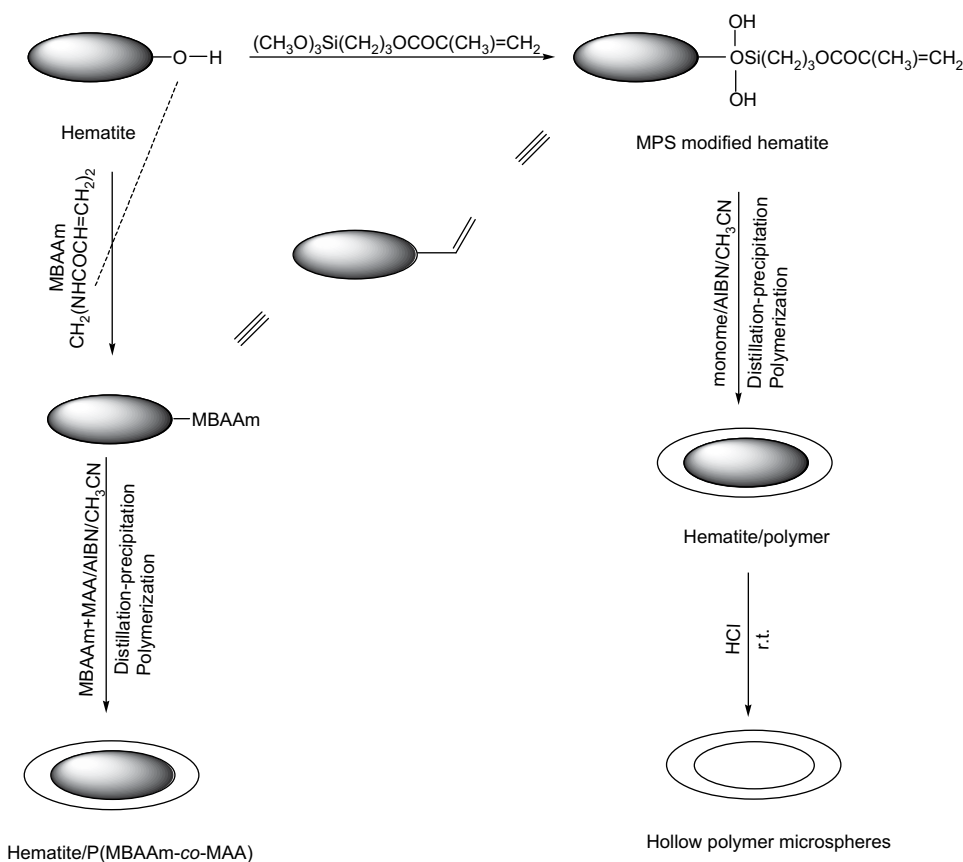
Scheme 1 illustrates the synthesis of hematite/polymer core-shell hybrids by distillation precipitation polymerization of various monomers in the presence of hematite particles as the seeds and the further development of the corresponding hollow polymer ellipsoids.

3.1. Preparation of ellipsoidal hematite/PEGDMA core-shell hybrids

It is difficult to directly coat PEGDMA onto the hematite nanoparticles without modification for the preparation of hybrids containing hematite and polymer due to the hydrophobic nature of EGDMA component lacking the efficient interaction with the hydrophilic hematite particles. To overcome such problem, it is necessary to incorporate the reactive vinyl groups on the surface of

hematite particles. Coating of hematite nanoparticles with MPS to introduce the reactive vinyl groups on the surface is capable of accomplishing such requirement. The reactive vinyl groups on the surface of hematite particles would permit the encapsulation of PEGDMA component onto inorganic hematite cores by radical capture of the newly formed oligomers and monomers during the second-stage distillation precipitation polymerization to result in hematite/polymer core-shell hybrid ellipsoids. MPS-modified hematite particles were synthesized by the possible condensation of MPS with the reactive hydroxyl groups of shuttle-like hematite particles during the hydrolysis in absence of any surfactant to incorporate the reactive vinyl groups on the surface of ellipsoidal inorganic cores. This was much different from that of our previous work [32], in which MPS-modified hematite particles were afforded by the condensation of hydroxyl groups between the siliceous components during the modification via hydrolysis and the hematite/silica core-shell ellipsoids was prepared with the aid of poly(*N*-vinylpyrrolidone) surfactant. As shown in **Fig. 1A** with a typical TEM micrograph, uniform MPS-modified hematite nanoparticles were prepared by homogeneous hydrolysis from solution of iron salt (FeCl_3) in the presence of phosphate anion (NaH_2PO_4) and subsequently grafted by MPS, which indicated that MPS-modified hematite nanoparticles had a shuttle-like ellipsoidal shape and the thickness was very close to that of unmodified hematite ellipsoids (TEM micrograph shown in **Supplementary data**). This result implied that only a very thin siliceous layer was formed during the modification of MPS just to incorporate the reactive vinyl groups onto the surface of inorganic ellipsoids. The mean lengths of major and minor axes were 352 and 83 nm, respectively.

The successful modification of hematite particles was confirmed further by FT-IR spectrum as shown in **Fig. 2a** with the presence of



Scheme 1. Preparation and mechanism for the formation of ellipsoidal hematite/polymer hybrid materials and the corresponding ellipsoidal hollow polymer microspheres.

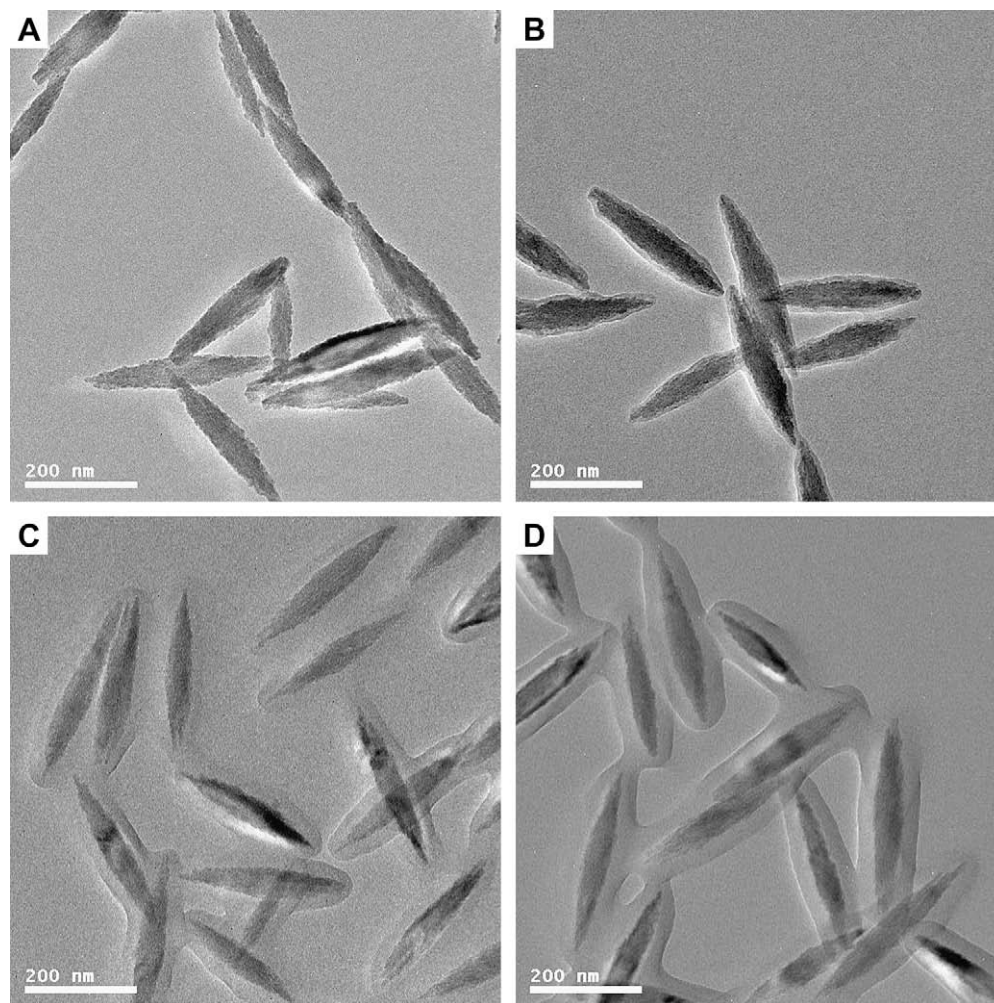


Fig. 1. TEM micrographs of microspheres: A) shuttle-like hematite particles; B–D) hematite/PEGDMA core-shell particles with different EGDMA feed during polymerization: B) 0.3 mL; C) 0.4 mL; D) 0.5 mL. 1) Reaction conditions: in 40 mL of acetonitrile and AIBN as initiator of 2 wt% relative to the monomer.

the bands at 1636 and 1669 cm^{-1} corresponding to the stretching vibrations of the vinyl groups and carbonyl groups of hydrolyzed MPS component, respectively. The residual reactive vinyl groups on the surface of PDVB cores were essential to further grow the

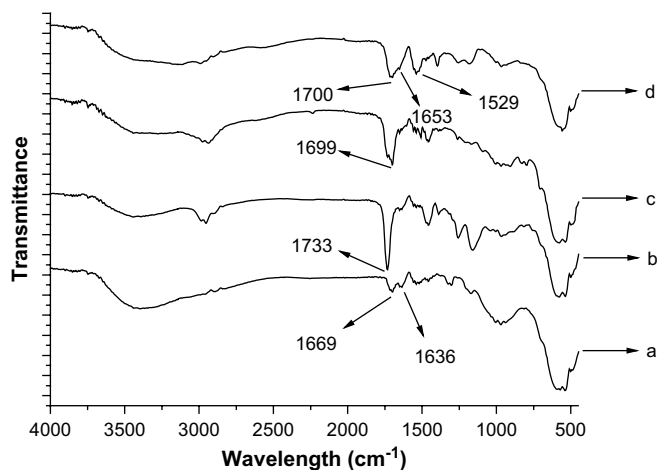


Fig. 2. FT-IR spectra: a) MPS-modified hematite; b) hematite/PEGDMA; c) hematite/P(DVB-co-MAA); d) hematite/P(MBAAm-co-MAA).

polymer microspheres [33] and to afford monodisperse core-shell functional polymer microspheres [34] by distillation precipitation polymerization in our previous work, in which the newly formed oligomers and monomers in the reaction system were efficiently captured by the reactive vinyl groups without formation of any secondary-initiated particles during the further-stage polymerization. In the present work, the MPS-modified hematite shuttle-like particles were used as the seeds for the distillation precipitation polymerization to fully coat polymer shell-layer onto the inorganic hematite cores for the construction of hematite/polymer core-shell hybrids as illustrated in Scheme 1.

An important concern for the present work is to synthesize hematite/polymer hybrid ellipsoids and to retain the particles with well-defined shape and adjustable thickness. A series of experiments were initially conducted to investigate the effect of the EGDMA feed on the morphology of the resultant hematite/PEGDMA core-shell hybrid particles during the distillation precipitation polymerization. TEM micrographs of the resultant hematite/PEGDMA core-shell hybrid particles with different EGDMA loadings are shown in Fig. 1B–D. The results indicated that the final hematite/PEGDMA core-shell hybrid particles had ellipsoidal shape with smooth surface in the absence of any secondary-initiated particles with EGDMA ranging from 0.30 to 0.50 mL, which demonstrated that the reactive vinyl groups on the surface of MPS-modified hematite seeds efficiently captured the newly

Table 1
Reaction conditions, sizes, polymer shell-thicknesses, yields and magnetic parameters of the hematite cores, hybrid hematite/polymer particles with different thicknesses of shell-layer

| Entry | Hematite [g] | Monomer [mL] | Particle size (major/minor axis) [nm] | Polymer shell-thickness (major/minor axis) [nm] | Yield (%) ^c | Coercivity (H_c) [Oe] | Saturation magnetization (M_s) [emu/g] | Remanent magnetization (M_r) [emu/g] |
|----------------|--------------|-----------------------------|---------------------------------------|---|------------------------|---------------------------|--|--|
| A ^a | 0 | 0 | 352/83 | 0/0 | 0 | 243.9 | 0.323 | 0.0761 |
| B ^a | 0.1 | EGDMA 0.3 mL | 380/107 | 14/12 | 18 | 209.5 | 0.215 | 0.0575 |
| C ^a | 0.1 | EGDMA 0.4 mL | 428/158 | 38/37 | 23 | 200.7 | 0.186 | 0.0525 |
| D ^a | 0.1 | EGDMA 0.5 mL | 442/176 | 45/47 | 27 | 251.5 | 0.104 | 0.0299 |
| E ^a | 0.1 | DVB 0.3 mL | 368/98 | 8/8 | 11 | – | – | – |
| F ^a | 0.1 | DVB 0.1 mL MAA 0.1 mL | 390/124 | 19/20 | 26 | – | – | – |
| G ^b | 0.1 | MBAAm 0.02 g MAA 0.08 mL | 384/113 | 16/15 | 48 | – | – | – |

^a MPS-modified hematite particles as the seeds.

^b Hematite particles as the seeds.

^c Yield = $(M_{\text{hematite/polymer}} - M_{\text{hematite}}) / M_{\text{monomer}} \times 100\%$.

formed EGDMA oligomers during the encapsulation of the inorganic seeds by distillation precipitation polymerization. The TEM micrographs in Fig. 1B–D proves the core-shell structures of the hematite/PEGDMA ellipsoids having polymeric PEGDMA shell-layer (light in contrast) and inorganic hematite core (dark in contrast).

The surface modification of the polymer component leading to hematite/PEGDMA core-shell hybrid structure is studied further by FT-IR spectrum as shown in Fig. 2b, which had a strong peak at 1733 cm^{-1} corresponding to the vibration of the carbonyl group unit in ester group of PEGDMA component.

The experimental conditions for distillation precipitation polymerizations of EGDMA with different loadings with MPS-modified hematite particles as the seeds, sizes and yields of the resultant hematite/PEGDMA core-shell hybrids are summarized in Table 1. The polymer shell-thickness was measured by TEM characterization, which was calculated as the half of the difference between the average lengths in major/minor axis direction of the final core-shell hybrids and those of the corresponding MPS-modified or unmodified hematite seed particles. The major/minor axis of the ellipsoidal hematite/PEGDMA hybrids increased significantly from 380/107 to 442/176 nm with increasing EGDMA feed from 0.30 to 0.50 mL for the distillation precipitation polymerization. These results meant that the thickness of PEGDMA shell-layer was significantly increased from 14/12 to 45/47 nm in the major/minor axis direction with the EGDMA feed enhancing from 0.30 to 0.50 mL for the polymerization. The yields of the final hematite/PEGDMA core-shell hybrid ellipsoids (the mass ratio as the amount of PEGDMA coated onto the inorganic seeds to total EGDMA monomer for the polymerization) were considerably increased from 18 to 27% with increasing EGDMA feed from 0.30 to 0.50 mL. The higher yields led to the significant increase of size for the resultant hematite/PEGDMA core-shell ellipsoids with higher EGDMA loadings, as there were not any newly secondary-initiated particles formed during the polymerization. In other words, the thickness of the PEGDMA shell-layer can be well and facilely controlled in the range of 14–47 nm via altering the EGDMA feed from 0.30 to 0.50 mL during the polymerization.

3.2. Preparation of ellipsoidal hematite/polymer core-shell hybrids with various polarity and functional groups on the polymer shell-layer

The polarity of the polymer microspheres is an important factor for many applications. Further, microspheres with various functional

groups have wide utilization in many fields, such as solid carriers for the immobilization of biological substances including enzymes, antibodies, etc. [35]. To confirm the present synthetic route as a general strategy, the other core-shell hematite/polymer hybrids with different polarities and functional groups on the outer polymer shell-layer were prepared by distillation polymerization in presence of either MPS-modified $\alpha\text{-Fe}_2\text{O}_3$ or unmodified $\alpha\text{-Fe}_2\text{O}_3$ as the seeds as illustrated in Scheme 1. In our previous work, polydivinylbenzene (PDVB) [33] and poly(divinylbenzene-co-methacrylic acid) (P(DVB-co-MAA)) [36] were facilely synthesized by distillation precipitation polymerization. To investigate the present route as a general strategy, hematite/PDVB with non-polar shell-layer and hematite/P(DVB-co-MAA) with carboxylic acid group on the shell-layer were prepared by distillation precipitation polymerization, which were shown in Fig. 3A and B, respectively. The results indicated that the hematite/polymer hybrid ellipsoids had a typical core-shell structure with polymeric PDVB shell-layer (light in contrast) and inorganic hematite core (dark in contrast). The characteristic weak peak at 709 cm^{-1} was covered by the peak of hematite core, which was attributed to the typical adsorption of the phenyl group of DVB component in FT-IR spectrum (data not shown here) of hematite/PDVB particles. The FT-IR spectrum (the curve in Fig. 2c) of hematite/P(DVB-co-MAA) ellipsoids has a strong peak at 1699 cm^{-1} corresponding to the vibration of the carbonyl unit in carboxylic acid group of PMAA component, which confirmed the successful incorporation of the active carboxylic acid group onto the polymer shell-layer.

In our previous work, hematite/silica/PMBAAm tri-layer hybrids were prepared by distillation precipitation polymerization [32], in which PMBAAm was coated onto hematite/silica core with the aid of the synergetic hydrogen-bonding interaction between the hydroxyl group of silica layer and the amide group of MBAAm component. To get hydrophilic hematite/polymer core-shell hybrid ellipsoids with carboxylic acid group on the shell-layer, hematite/P(MBAAm-co-MAA) ellipsoidal particles were prepared by distillation precipitation polymerization in the presence of unmodified hematite particles as the seeds. The typical TEM micrograph of hematite/P(MBAAm-co-MAA) ellipsoids is shown in Fig. 3C, in which a typical core-shell structure with polymeric PMBAAm shell-layer (light in contrast) and inorganic hematite core (dark in contrast) was clearly observed. Here, the hydrogen-bonding interaction between the hydroxyl groups of hematite particles and the amide group of MBAAm as well as the carboxylic acid group of MAA may play a key role during the distillation precipitation polymerization and act as a driving force for encapsulation of PMBAAm on

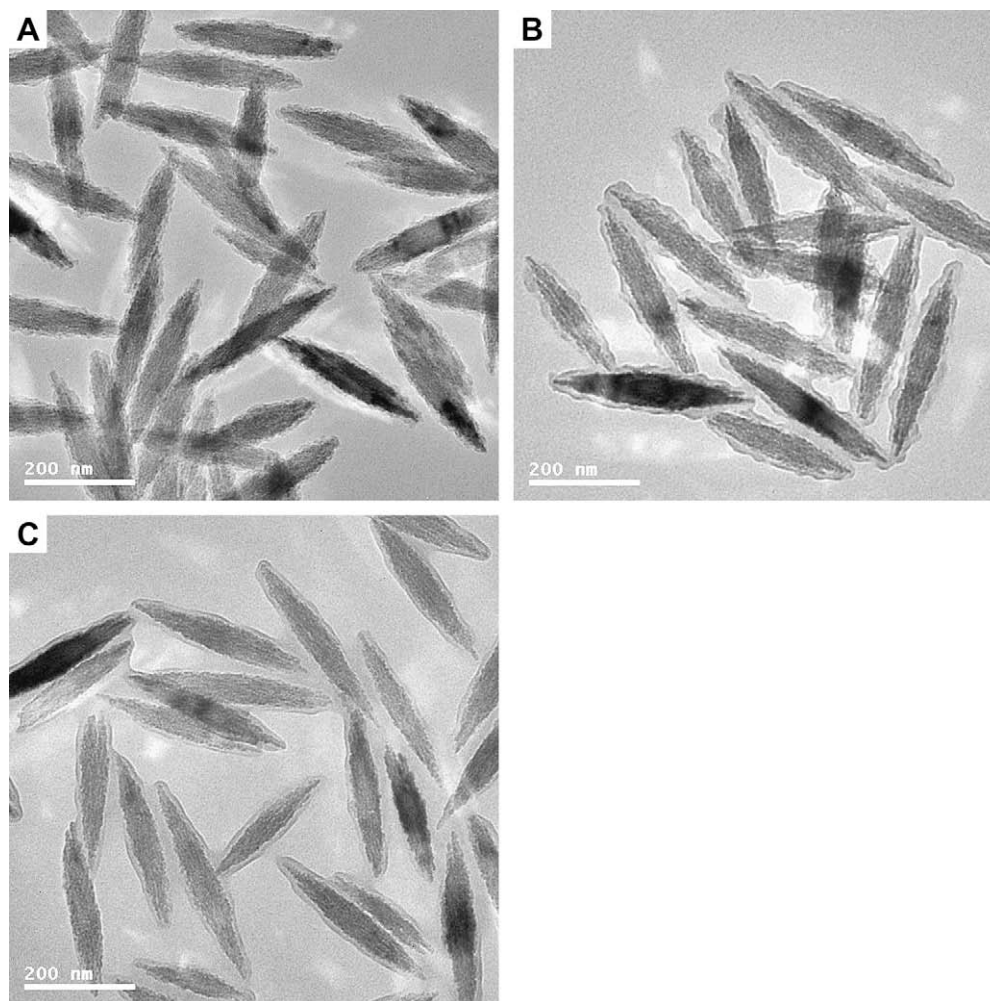


Fig. 3. TEM micrographs of hematite/polymer ellipsoids: A) PDVB; B) P(DVB-co-MAA); C) P(MBAAm-co-MAA).

hematite cores. This was much different from those reported in our previous work [30–32,37], in which the inorganic/polymer hybrid/composite structures were formed with the aid of the reactive surface of the silica component. In the present reaction system, MBAAm was firstly adsorbed onto the surface of hematite particles via hydrogen-bonding interaction and the reactive vinyl groups were incorporated. Then the adsorbed vinyl groups on the surface of hematite particles captured the newly formed MBAAm-co-MAA oligomers for the growth of hematite/P(MBAAm-co-MAA) core-shell composite ellipsoids. The successful incorporation of P(MBAAm-co-MAA) component into the shell-layer was confirmed further by FT-IR spectrum in Fig. 2d with the strong peaks at 1653 and 1529 cm^{-1} attributing to the stretching vibration of carbonyl units of P(MBAAm-co-MAA) and the bending vibration of N–H bond for PMBAAm component. Here, P(MBAAm-co-MAA) shell-layer was directly coated onto hematite core to result in a uniform core-shell hematite/P(MBAAm-co-MAA) in absence of any additive, which may prove the present synthetic route as a general method for the other inorganic/polymer systems, including titanium oxide, tin oxide, zirconium oxide as the cores. The mechanism of the growth for polymer microspheres [38] and construction of silica/PMBAAm core-shell composites [30] driven by hydrogen-bonding interaction were investigated in detail in our previous work.

The experimental conditions for distillation precipitation polymerization of hematite/polymer tri-layer hybrid microspheres with various polarity and carboxylic acid groups are summarized in Table 1. The sizes of $\alpha\text{-Fe}_2\text{O}_3$ /PDVB, $\alpha\text{-Fe}_2\text{O}_3$ /P(DVB-co-MAA), and

$\alpha\text{-Fe}_2\text{O}_3$ /P(MBAAm-co-MAA) were considerably increased from $352/83\text{ nm}$ (major/minor axis) of $\alpha\text{-Fe}_2\text{O}_3$ core to $368/98$, $390/124$, and $384/113\text{ nm}$, respectively. In other words, the polymer shell-layers with thicknesses of $8/8$, $19/20$, and $16/15\text{ nm}$ were successfully coated onto inorganic cores via distillation precipitation polymerization. The yields of $\alpha\text{-Fe}_2\text{O}_3$ /PDVB, $\alpha\text{-Fe}_2\text{O}_3$ /P(DVB-co-MAA), and $\alpha\text{-Fe}_2\text{O}_3$ /P(MBAAm-co-MAA) were 11%, 26% and 48%, respectively. The yield of $\alpha\text{-Fe}_2\text{O}_3$ /PDVB (11%) was a little lower than those of $\alpha\text{-Fe}_2\text{O}_3$ /PEGDMA (18%) and $\alpha\text{-Fe}_2\text{O}_3$ /P(MBAAm-co-MAA) (48%) under similar conditions. This was originated from the nature that divinyl groups of EGDMA and MBAAm were connected with flexible structure with higher reactivity, while the divinyl groups of DVB were connected by the rigid phenyl groups resulting in higher steric hindrance and lower reactivity. These results were consistent with the results reported in our previous work for the distillation precipitation polymerization of DVB [33], EGDMA [39] and MBAAm [40]. All these results indicated that the thickness of polymer shell-layer having different polarities and functional groups was conveniently controlled by the feed of comonomer ratio for the distillation precipitation polymerization.

3.2.1. Magnetization property of hematite/PEGDMA core-shell hybrids

Bulk hematite is an anti-ferromagnetic material below Morin temperature (T_M) of 263 K and exhibits a weak ferromagnetic property between 263 K and Neel temperature (T_N) of 955 K . The magnetic properties of hematite and hematite/PEGDMA hybrid

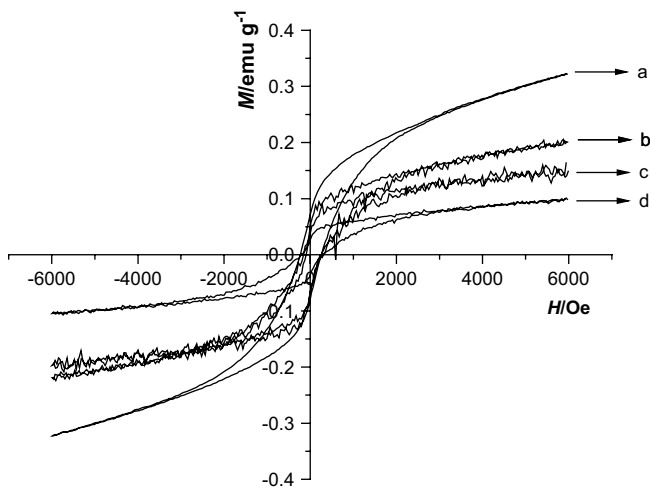


Fig. 4. Hysteresis loops for samples at room temperature: a) MPS-modified hematite; b–d) hematite/PEGDMA with different PEGDMA shell-thicknesses (minor axis): b) 12 nm; c) 37 nm; d) 47 nm.

materials were studied by using a vibrating sample magnetometer (VSM) at room temperature. Fig. 4 shows the magnetization curves of hematite shuttle-like particles and hematite/PEGDMA core-shell hybrids with various PEGDMA shell-thickness ranging from 12 to 47 nm (minor axis). The obvious magnetic hysteresis loops are observed for the hematite/PEGDMA core-shell hybrid from the field-dependent magnetization plots in Fig. 4. In other words, the remanence existed when the magnetic field was removed, indicating that all the resultant hematite/PEGDMA core-shell hybrid ellipsoids showed hysteresis feature and retained weak ferromagnetic properties originating from ellipsoidal hematite cores at room temperature. The magnetic properties of the hematite/PEGDMA core-shell hybrids with different PEGDMA shell-thickness are listed in Table 1. The coercivity (H_c), saturation magnetization (M_s), and remanent magnetization (M_r) values for MPS-modified hematite core-shell ellipsoids were 243.9 Oe, 0.323 emu/g, and 0.076 emu/g, respectively. The saturation magnetization of hematite/PEGDMA core-shell hybrids was slightly decreased from 0.215 to 0.104 emu/g with increase of PEGDMA shell-thickness from 12 to 47 nm (minor axis), while the remanent magnetization was

simultaneously decreased from 0.0575 to 0.0299 emu/g. These results indicated that the magnetization of the hematite/PEGDMA core-shell hybrid materials decreased with the increase of polymer component due to the decrease of the effective mass of the hematite core. The recent simulation and experiment work in three-dimensional systems has shown that maximal jammed packing (MRJ) of non-spherical particles depended on a non-trivial way on aspect ratio and can become denser than that of the corresponding spheres [41,42]. The hematite/polymer ellipsoidal hybrids may be potentially unique candidates for assembling the ordered structure in magnetic field due to the magnetization property originating from hematite cores.

3.2.2. Hollow polymer ellipsoids

In our previous work, hollow polymer ellipsoids [32], hollow polymer microspheres [30,31], hollow polymer microspheres with movable Au cores [37] were prepared by the selective removal of the silica layer, in which highly corrosive reagent hydrofluoric acid was necessary for etching process. Here, hematite cores were selectively removed by soaking the hematite/polymer core-shell ellipsoids in hydrochloric acid (5 wt%) to afford the corresponding hollow polymer ellipsoids. The driving force for such selective removal was due to the formation of ferric chloride (FeCl_3), which permeated through the polymer shell of the core-shell hybrids during the etching process. The removal procedure in the present work was much mild compared to the utilization of hydrofluoric acid as etching reagent.

The typical TEM micrographs of PEGDMA hollow ellipsoids with thickness of 37 nm (minor axis) and PDVB hollow ellipsoids (with thickness of only 8 nm) are shown in Fig. 5A and B, respectively, in which the convincing capsules with regular ellipsoidal shapes and uniform sizes were observed. Partially collapsed PDVB ellipsoids with deformed shape were observed in Fig. 5B, which implied that the polymer shell-layer with only 8 nm was not thick enough to support the cavities during the selective etching of hematite cores. The hollow polymer ellipsoids were shown in Fig. 5A, indicating that the shell-thickness (37 nm) of PEGDMA hollow ellipsoids were thick enough to get the convincing hollow ellipsoidal structure in the presence of ellipsoidal rings with non-segmented ellipsoids and a cavity in the interior. All these results further confirmed the successful and complete removal of hematite cores by dilute hydrochloric acid during the etching process.

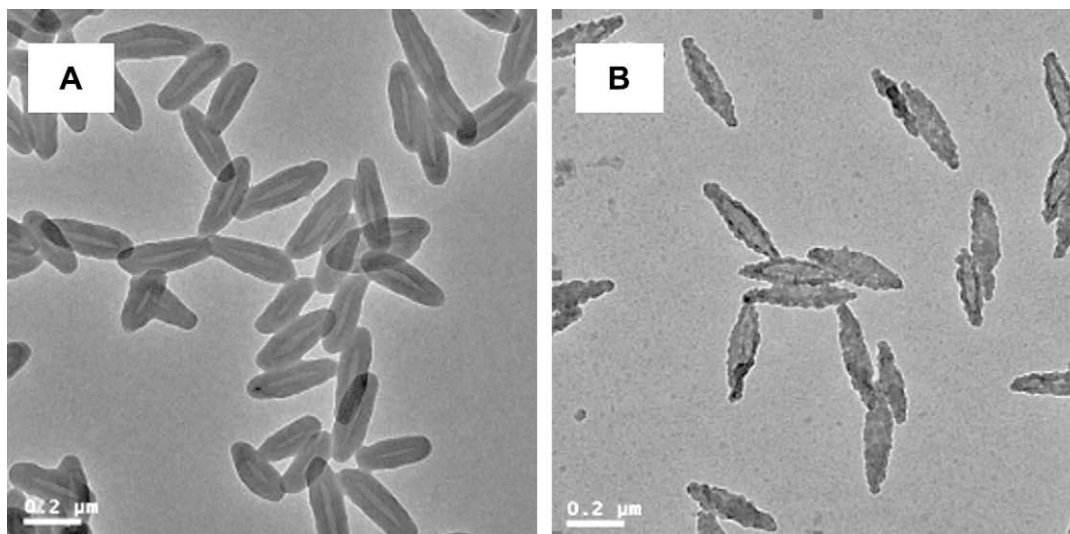


Fig. 5. TEM micrographs of hollow polymer ellipsoids: A) PEGDMA; B) PDVB.

4. Conclusion

Ellipsoidal hematite/PEGDMA core–shell hybrids were prepared by distillation precipitation polymerization of EGDMA in neat acetonitrile with AIBN as initiator in the presence of MPS-modified hematite core–shell particles as the seeds, in which the incorporated reactive vinyl groups on the surface of the seeds played a key role for the formation of the ellipsoidal hybrids with regular shape via the capture of the EGDMA oligomers and monomers during the polymerization. The thicknesses of PEGDMA shell-layer of the resultant hematite/PEGDMA hybrids were facilely controlled in the range of 12–47 nm (minor axis) and 14–45 nm (major axis) by altering the EGDMA monomer feed from 0.30 to 0.50 mL during the polymerization. The magnetization of the hematite/PEGDMA core–shell hybrid ellipsoids decreased with an increase of the polymer component due to a decrease of the effective mass of the magnetic hematite cores. The hollow polymer ellipsoids were further developed with the selective removal of hematite core in dilute hydrochloric acid. The hematite/polymer with non-polarity shell-layer such as hematite/PDVB and carboxylic acid group on the shell-layer such as hematite/P(DVB-co-MAA) were also prepared. The core–shell hematite/P(MBAAm-co-MAA) ellipsoids with hydrophilic polymer shell-layer having carboxylic acid were prepared by distillation precipitation polymerization, in which the synergetic hydrogen-bonding interaction between the hematite cores and the amide group of PMBAAm as well as the carboxylic acid group of PMAA component acted as a driving force for the construction of core–shell inorganic/polymer ellipsoids. The application of the ellipsoidal core–shell hybrids and hollow polymer ellipsoids with various polarities and functionalities is now being studied systematically in our group.

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Appendix. Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.polymer.2008.08.043.

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