Fabrication of superparamagnetic magnetite/poly(styrene-co-12-acryloxy-9-octadecenoic acid) nanocomposite microspheres with controllable structure

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Abstract
We herein report a novel and facile approach to the fabrication of the superparamagnetic magnetite/poly(styrene-co-12-acryloxy-9-octadecenoic acid) nanocomposite microspheres with controllable structure via γ-ray radiation induced inverse emulsion polymerization under room temperature and at ambient pressure. 12-Acryloxy-9-octadecenoic acid (AOA, containing part of sodium salts Na-AOA) as a surfactant can also copolymerize with the styrene. It is interesting that just by changing the added amount of styrene, the magnetic hollow spheres with different wall thickness and various sizes of core, up to the magnetic solid spheres, can be obtained. The final products were thoroughly characterized by X-ray powder diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), transmission electron diffraction (TEM), field-emission scanning electron microscopy (FESEM), thermogravimetric analysis (TGA) which showed the formation of magnetite/poly(styrene-co-AOA) nanocomposite microspheres. Magnetic hysteresis loop measurements showed that the magnetic nanocomposite microspheres exhibited superparamagnetism, which should make them have potential applications in biotechnology and biomedicine. Furthermore, we also proposed a possible formation mechanism of these magnetic microspheres with different morphologies.

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1. Introduction
Magnetic materials for extensive potential applications in materials science have attracted intense attention because of their unique physical properties such as superparamagnetism. For example, they have been used in biomedical applications as carriers for magnetic drug targeting [1,2], as matrices for the separation and purification of DNA or RNA [3,4], as tags for magnetic biosensors [5–7], as agents for magnetothermo therapy [8,9], and as contrast agents for magnetic-resonance imaging (MRI) [10–12]. The applications, such as magnetically controllable photonic crystals [13–16], nanoelectromechanical systems [17], and so on, are also very sought-after subjects for scientists.

In recent years many groups have synthesized hollow or solid magnetic nanocomposite microspheres with many methods. Generally, LBL (layer-by-layer) method is a very important method to prepare the hollow magnetic microspheres whose wall thickness can be precisely controlled [18]. Unfortunately, the method is complicated because it is necessary to etch out the templated core for the formation of hollow structure. Recently, Li and co-workers [19] prepared amphiphilic superparamagnetic ferrite/block copolymer hollow submicromospheres through the solvothermal method at high temperature and under high pressure. However, the preparation conditions are rigorous and the wall thickness cannot be controlled. Koo et al. [20] used a simple method, namely the emulsification of a multiphase mixture, for the preparation of polymeric microcapsules with iron oxide (γ-Fe₂O₃) magnetic particles embedded in the polymer shell. At the same time, it remains problematic that the wall thickness cannot be tunable. Furthermore, there are some methods to the preparation of solid magnetic nanocomposite microspheres including conventional [21,22] or surfactant-free emulsion polymerization [23], dispersion polymerization [24], microemulsion [25] and miniemulsion polymerization [26,27]. Therefore, for chemists, the development of simple and effective synthetic methods to obtain uniform superparamagnetic nanocomposite microspheres with controllable structure is still a very impending task.

Inverse emulsion (including miniemulsion and microemulsion) was usually applied to the polymerization of hydrophilic monomers, such as acrylamide, acrylic acid, salt of acrylic acid and n-isopropylacrylamide. The polymerization can be initiated by water-soluble initiators (KPS, APS), oil-soluble initiator (BPO) or radiation sources (γ-ray or UV). Recently, a facile approach to hollow microspheres through inverse emulsion polymerization induced by γ-ray radiation has been reported [28,29]. In this approach, water droplets acted as a template for the formation of hollow structure, so etching the templated core can be avoided. For example, Wu et al. [28] prepared CdS/polystyrene composite hollow spheres through the
polymerization of styrene and the formation of CdS nanoparticles at the interface of microemulsion droplets initiated by γ-ray radiation.

In our recent study, we used amphiphilic magnetic nanoparticles (MPSs) with active hydrophilic hydroxyl groups and hydrophobic oleic ester groups existed at the surface to prepare (multi)hollow superparamagnetic magnetite/polystyrene nanocomposite microspheres via interfacial polymerization technique [30], inverse miniemulsion polymerization [31], and double emulsions polymerization [32]. However, the drawback of those works is that the as-synthesized microspheres are not monodisperse, limiting the downstream applications.

In this paper, we report on a facile approach to fabricate the superparamagnetic nanocomposite microspheres with controllable structure via γ-ray radiation induced inverse emulsion polymerization under room temperature and at ambient pressure. AOA (containing part of sodium salts Na2-AOA) as a surfactant can also copolymerize with the styrene. It is interesting that just by changing the added amount of styrene, the magnetic hollow spheres with different wall thickness and various sizes of core, up to the magnetic solid spheres, can be obtained. The overall synthetic procedure is shown in Scheme 1. The formation mechanism of the magnetic microspheres with different morphologies in this paper will be discussed later. The γ-ray is chosen to induce the polymerization of monomer due to the reactions at low temperature, which is useful to keep the stability of inverse emulsion during polymerization. Especially, the products synthesized by γ-ray are beneficial to their bio-applications because the contamination of chemical initiators is avoided and the final products are sterilized.

2. Materials and methods

2.1. Materials

Styrene and kerosene were generally of reagent grade from Shanghai Chemical Regents. AOA (the structure shown in Fig. 1) was used as received from USTC Chuangxin Co., Ltd. (China) [33,34]. Styrene was distilled under a reduced pressure to remove the inhibitor prior to use. All other materials from Shanghai Chemical Regents were of analytical grade and used without any further purification, including ferric chloride (FeCl3), benzoyl peroxide (BPO), ferrous sulfate heptahydrate (FeSO4·7H2O), oleic acid, aqueous ammonia [25%/w/w], and ethanol.

2.2. Synthesis of magnetite nanoparticles surface-modified with oleic acid (MPSs)

MPSs were synthesized by the conventional coprecipitation method with some modification as our previous work [30], which used in this work is the same as Mag-2 listed in Table 1 mentioned in that paper. TEM images of MPSs are shown in that paper. In a typical experiment, FeCl3 (7.31 g, 0.045 mol) and FeSO4·7H2O (8.35 g, 0.03 mol) were first dissolved in 30 ml of distilled water, and the resulting solution was poured into 70 ml of distilled water under vigorous stirring at 85 °C. Then 30 ml of NH3·H2O (25 wt.%) and 2 g of oleic acid were successively added at once. The reaction continued for another 3 h. At last the black precipitates were isolated with the help of a magnet and further washed with distilled water and ethanol for several times.

2.3. Preparation of magnetic nanocomposite microspheres with controllable morphology

In a typical experiment, MPSs (0.1 g), AOA (1 g) and BPO (0.05 g) were dispersed in the mixture of styrene (1 g) and kerosene (6.98 g), and then 10 ml water was added dropwise into the above solution under vigorous stirring. The mixture was continued to stir for 1 h and the formed inverse emulsion was continuously bubbled with nitrogen for 20 min to remove oxygen, then sealed to be irradiated in the field of a 1.30 × 1015 Bq 60Co γ-ray source at the dose rate of 68.3 Gy/min for 23 h. At last, the inverse emulsion was destabilized by adding ethanol. The brown precipitates were separated with the help of a magnet and washed repeatedly with ethanol, then dried in air at ambient temperature. The detailed experimental conditions and main results in this paper are listed in Table 1.

2.4. Characterization of magnetic nanocomposite microspheres with controllable morphology

Powder XRD patterns of as-synthesized samples were recorded with a Japan Rigaku D/max γ SAXS diffractometer equipped with graphite monochromatized Cu Kα radiation (λ = 0.154178 nm), employing a scanning rate of 0.02°/s in the 2θ range from 20 to 80°. FTIR spectrum was carried out on a Bruker Vector-22 FTIR spectrometer using KBr method. TEM images were observed on a Hitachi model H-800 transmission electron microscope with an accelerating voltage of 200 kV. For microtoming samples, the sample powder was embedded into epoxy resin, which was then ultra-microtomed to a thickness of ca. 70 nm. FESEM images were obtained on a JEOL JSM-6700 field-emission scanning electron microanalyzer. TGA analysis was performed with a Shimadzu TGA-50H instrument under an atmosphere of nitrogen with a gas flow of 25 cm3 min−1. The sample was heated from 50 to 600 °C at 10 °C min−1. The magnetic properties (M–H curves) of powder samples at room temperature were evaluated on a MPMS XL magnetometer (Quantum Design Corporation). During measurement, the applied magnetic field successively varied in the sequence 0 – 1 – 0 – −1 – 0 T. And magnetic susceptibilities were not corrected for the background signal of the sample holder and for diamagnetic susceptibilities of all atoms, because they were very small (<10−4 emu/g) and could be neglected.

3. Results and discussion

3.1. Characterization of superparamagnetic nanocomposite microspheres with different structure

The XRD patterns of the MPSs and the as-synthesized sample 2 are shown in Fig. 2. It can be seen that their peaks are identical although the baseline in the range of low 2θ is raised due to the existence of polymer in Fig. 2a, indicating that the structure of MPSs is kept essentially unchanged during the emulsion polymerization. All the diffraction peaks can be indexed as the face-centered cubic structure of magnetite (JCPDS card. File no. 74-0748).

FTIR spectrum of the sample 2 demonstrates the formation of poly(styrene-co-AOA) [see Fig. 3]. The bands at 698 and 755 cm−1 can be assigned to flexural vibrations (ν(C-H)) of benzene ring, 1451, 1492 and 1601 cm−1 can be checked to benzene ring vibrations (ν(C-C)) of polystyrene, and 2852 and 2922 cm−1 can be attributed to νC-H of saturated –C–H groups, while the band at 3026 cm−1 can be assigned to νC-H of benzene ring. Moreover, the band at 1730 cm−1 is observed and corresponds to the stretching vibration of C=O group (νC=O) of poly(styrene-co-AOA). The band at 1379 cm−1 and 1269 cm−1 corresponds to the flexural vibrations (ν(C-O)) and the stretching vibration (ν(C-O)) of carboxyl groups, respectively. The bands at 1028 cm−1 and 1176 cm−1 can be assigned to the stretching vibration (ν(C-O)) of ester groups.

The morphology and structure of magnetic nanocomposite microspheres were investigated by TEM and FESEM. Figs. 4 and 5 presents the TEM and SEM images of four samples prepared with...
different amounts of styrene, respectively. The average wall, average core size and the average spheres size were listed in Table 1. As shown in Fig. 4a, it is observed that sample 1, polymerized with 0.5 g of styrene, is mainly composed of hollow spheres with a very small core, which is proved by the obvious contrast between the pale center and the dark edge as reported for other hollow spheres and the broken spheres as shown in the inset picture of Fig. 5a. The mean diameter, shell thickness and core size are estimated from Scheme 1.

**Scheme 1.** Schematic illustration of the procedure for preparing magnetite/polystyrene microspheres with different morphologies.
Figs. 4a and 5a and b to be around 530 nm, 50 nm and 110 nm, respectively. When the added amount of styrene is increased to 1 g (sample 2), TEM image (Fig. 4b) illustrate that the shell of hollow spheres becomes thicker (100 nm) while the size of these hollow sphere and the core is the same as that of sample 1 (see Fig. 5c and d). Therefore, the different wall thickness of the magnetic nanocomposite microspheres could easily be obtained by simply altering the added amount of styrene in the present study. As the added amount of styrene is increased to 1.5 g for sample 3, the core in the hollow spheres become bigger, which can be verified by the TEM image (Fig. 4c) and SEM images (Fig. 5e and f). However, the shell thickness of hollow spheres doesn’t increase. The sphere size, the shell thickness and the diameter of core for sample 3 are about 650 nm, 100 nm and 250 nm, respectively. If the added amount of styrene is increased to 2.5 g (sample 4), it is worth noting that monodisperse solid spheres are obtained as shown in Figs. 4d and 5g and h. The diameter of the spheres decreases to around 200 nm, much smaller than those of the other three samples.

To further demonstrate the location of MPs in the magnetic nanocomposite spheres, cut-section TEM images (Fig. 6) were obtained by microtoming sample 2 embedded in epoxy resin. From Fig. 6, the hollow structure of sample 2 can be further verified and the location of MPs is in the shell of magnetic nanocomposite spheres and in the inner core.

For study the change of morphology along with the irradiation time, samples 5 and 6 had been done contrast to sample 2. TEM images of them are shown in Fig. 7, which illustrate the morphology of them is also hollow with a core as similar as sample 2. When irradiation time is 8 h (sample 5, absorbed dose with 33 kGy), the average wall thickness, average core size and average sphere size are 60, 52 and 475 nm, respectively, which are all smaller than that of sample 2. When the reaction time is 16 h (sample 6, absorbed dose with 66 kGy), the average wall thickness, average core size and average sphere size are 92, 94 and 510 nm, respectively, which are all bigger than those of sample 5, but still smaller than those of sample 2. The results show that the average wall thickness, average core size and average sphere size of the products become more and more bigger along with the irradiation time prolongs.

Fig. 8 shows the TGA curve of as-synthesized sample 2. For sample 2, the initial weight loss of 0.33% (up to 160 °C) is due to the evaporation of physically adsorbed water, and the subsequent loss of 12.4% (160–300 °C) is due to the decomposition of oligomer. Between 300 and 600 °C, a weight loss of 29.58% is attributed to removal of the poly(styrene-co-AOA). The residual weight of 13.26% should be that of the pure magnetite nanoparticles. So we

Table 1
The experimental conditions and different morphologies of the samples.a

<table>
<thead>
<tr>
<th>Samples</th>
<th>Mass of styrene added (g)</th>
<th>Absorbed dose (×10³ Gy)</th>
<th>Morphology of microspheres</th>
<th>Average wall thicknessb (nm)</th>
<th>Average core sizeb (nm)</th>
<th>Average sphere sizec (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.5</td>
<td>94</td>
<td>Hollow with a core</td>
<td>50</td>
<td>110</td>
<td>530</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>94</td>
<td>Hollow with a core</td>
<td>100</td>
<td>110</td>
<td>530</td>
</tr>
<tr>
<td>3</td>
<td>1.5</td>
<td>94</td>
<td>Solid</td>
<td>100</td>
<td>250</td>
<td>650</td>
</tr>
<tr>
<td>4</td>
<td>2.5</td>
<td>94</td>
<td>Solid</td>
<td>92</td>
<td>52</td>
<td>475</td>
</tr>
<tr>
<td>5</td>
<td>1</td>
<td>33</td>
<td>Hollow with a core</td>
<td>72</td>
<td>94</td>
<td>510</td>
</tr>
<tr>
<td>6</td>
<td>1</td>
<td>66</td>
<td>Hollow with a core</td>
<td>60</td>
<td>94</td>
<td>475</td>
</tr>
</tbody>
</table>

a Other conditions: H₂O 10 ml, MPs 0.1 g, BPO 0.05 g, kerosene 6.98 g.
b Obtained from TEM images.
c Obtained from FESEM images.
can estimate that the magnetite content is 13.30% (13.26/99.67/C2 100%) for sample 2.

3.2. Formation mechanism of superparamagnetic nanocomposite microspheres with different structure

According to the above experimental results, we propose a possible formation mechanism of magnetic nanocomposite microspheres with different structures (see Scheme 1). When water is added to the mixture of MPs, kerosene, AOA and styrene to form the inverse emulsion, the MPs tend to assemble at the interface of water and oil phase due to their amphipathic property [30]. Meanwhile, some styrene is dissolved in the micelles of Na–AOA and some amphiphilic MPs in the aqueous phase. If added amount of styrene is relatively low as samples 1, 2 and 3, the reactive route is showed as route 1 in Scheme 1. When the inverse emulsion is irradiated by γ-ray, many active intermediates such as e\textsubscript{aq}\textsuperscript{0}, H\textsuperscript{\textbullet} and OH\textsuperscript{\textbullet} are then generated owing to the radiolysis of water (see Reaction (1) in Scheme 1). Meanwhile, the redox reaction occurs between the oxidant (BPO) and the strong reducing agent (e\textsubscript{aq}\textsuperscript{0}) at the interface of water and oil and the oil-soluble benzoyloxy radical is generated (see Reaction (2)) [29]. These radicals (H\textsuperscript{\textbullet}, OH\textsuperscript{\textbullet} and benzoyloxy radical) may abstract hydrogens from the active hydroxyl groups at the surface of MPs located at water/oil interface (see Reaction (3)), leading to the formation of free radicals at the surface of MPs (shown in Reaction (3)). Therefore, the polymerization of monomer (including styrene and AOA) would be induced by those free radicals including H\textsuperscript{\textbullet}, OH\textsuperscript{\textbullet} and benzoyloxy radical and free radicals at the surface of MPs (shown in Reaction (3)). Therefore, the polymerization of monomer (including styrene and AOA) would be induced by those free radicals including H\textsuperscript{\textbullet}, OH\textsuperscript{\textbullet} and benzoyloxy radical and free radicals at the surface of MPs (see Reaction (4)) at the interface of water and oil phase and completed quickly due to less styrene, which is helpful to the formation of the shell of hollow magnetic nanocomposite microspheres. Of course, the monomer is mainly induced to polymerize by H\textsuperscript{\textbullet} and OH\textsuperscript{\textbullet} due to their stronger activities. On the other hand, the monomer dissolved in the micelles of Na–AOA can be initiated by H\textsuperscript{\textbullet} and OH\textsuperscript{\textbullet} in water phase. Once the polymer chain is formed in the micelle (called latex particle), the monomer dissolved in other micelles will enter the latex particle and make it propagate, resulting in the formation of a core. Finally, the hollow spheres with a core are obtained. When the more styrene was added, it is stand to reason that the more polystyrene produced, leading to the formation of thicker shell and bigger core (comparing sample 1 with samples 2 and 3). Moreover, the morphology of samples 5 and 6 further validates the rationality of the mechanism. Along with the irradiation time prolongs, their morphologies (samples 2, 5 and 6) are all hollow with a core, but the average wall thickness, average core size and average sphere size of the products just become more and more bigger. Meanwhile, cut-section TEM images also further verify the location of MPs in the shell of nanocomposite spheres and in the inner core, which is consistent with the mechanism. Whereas, when the added styrene increases further to 2.5 g (sample 4), the styrene concentration becomes bigger in the oil phase, which increases the compatibility of polystyrene chains with the oil phase. Once the polystyrene chains are formed in the initial stage of polymerization, they would continue propagating and go deep into the oil phase. Along with the polymerization processes, the polystyrene chains with critical length would precipitate from the oil phase, namely nucleation, on which MPs and AOA are gradually absorbed.
to stabilize it. Then these latex particles continue to propagate, resulting in the formation of solid spheres (see the second route).

The above results are consistent with our previous work [31] except the formation of hollow spheres with a core. The reason may be that in the previous work the used surfactant is non-ion surfactant (sorbitan monooleate) which hardly forms the micelles in the aqueous phase.

3.3. Magnetic properties of superparamagnetic nanocomposite microspheres

Magnetic characterization of the sample 2 measured at 300 K is shown in Fig. 9. It can be seen that its coercivities approach to 0 Oe, indicating that it is superparamagnetic, which is believed to be derived from the well-dispersed MPs in polymer matrix. The saturation magnetization (Ms) for the superparamagnetic nanocomposite microspheres is close to 8.2 emu/g which will make it be promising for the bio-applications. The magnetic separability of such magnetic nanocomposite was tested in ethanol by placing a magnet near the glass bottle. The brown particles were attracted toward the magnet within 20 s (see Fig. 9b), demonstrating directly that the nanocomposite microspheres possessed magnetic properties. This will provide an easy and efficient way to separate magnetic nanocomposite microspheres from a sol or a suspension system and to carry drugs to targeted locations under an external magnetic field.

4. Conclusions

In summary, a novel and facile approach has been developed to fabricate the magnetic nanocomposite microspheres with controllable structure via γ-ray radiation induced inverse emulsion polymerization. The different morphologies such as magnetic hollow spheres with different wall thickness and various sizes of core, or magnetic solid spheres can be tuned by simply changing the initiated amount of styrene. The possible formation mechanism of the different morphologies has been investigated. Magnetic measurement shows that the magnetic nanocomposite microspheres exhibit superparamagnetism, which will make them have potential applications in biotechnology and biomedicine.

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