Preparation of Magnetic Hybrid Microspheres with Well-Defined Yolk-Shell Structure

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A facile and efficient route was reported to prepare a kind of yolk-shell magnetic hybrid microspheres by suspension polymerization and calcinations method. The morphology, structure, and composition of the magnetic microspheres were characterized by FTIR, XRD, TEM, SEM, and TGA analysis. The vibrating-sample magnetometry (VSM) results clearly showed that the magnetic particles were superparamagnetic with saturation magnetization of 32.82 emu/g which makes the microcomposites easily controlled by an external magnetic field. The results revealed that the magnetic hybrid microspheres might have important applications in magnetic bioseparation and drug delivery.

1. Introduction

In recent years, magnetic particles have been paid considerable attention due to their superparamagnetic properties and potential applications, for example, magnetic bioseparation [1, 2], drug delivery [3, 4], magnetorheological fluid [5], magnetic resonance imaging contrast enhancement [6, 7], targeted drug [8], gene separation from biochemical products and cells [9], microwave absorption [10], high saturation magnetization, high magnetic susceptibility, biocompatibility, and low toxicity. Therefore, more and more researchers have focused on the fascinating feature of targeting [11–13]. However, because bare magnetic particles are liable to aggregation and rapid biodegradation when they are exposed to a biological system, coupled with a limited carrying capacity, it is quite necessary to combine magnetic particles with other carriers to achieve targeted delivery efficiently [14–16].

Various inorganic and polymeric materials have been reported as carriers of magnetic materials [17–20]. Recently, polymers which could stabilize magnetic particles are receiving more and more attention. Polymers can increase repulsive forces more than surfactants. In addition, a polymer coating on the surface used for the designed purpose of a well-defined composite of materials and their dispersions offers a high potential of application in several fields [21–24]. There are mainly two methods to prepare Fe3O4@polymer composite particles: first polymer coating Fe3O4 or modified Fe3O4 is used directly [25–27]; second Fe3O4 is first prepared by the coprecipitation of ferrous and ferric ions at the ratio of 1:2 in an alkaline medium and at the same time Fe3O4@polymer is prepared, because Fe3O4 contains ferrous and ferric iron at this ratio [28, 29].

In this contribution, we report a simple and efficient route to prepare yolk-shell monodisperse superparamagnetic polymer@Fe3O4 composite microspheres, using ferric ions as the only source of iron. Unlike traditional synthesis methods, we first prepare Fe(OH)3@PMMA. Then, the magnetic hybrid microspheres were obtained by calcination. The well control of the calcination temperature contributes to getting well-defined yolk-shell magnetic hybrid microspheres. The unique advantage of the yolk-shell morphology lies in the presence of internal void space to accommodate the targeted drug.

2. Experimental Details

2.1. Materials. Methyl methacrylate (MMA, 99 wt.%, Shanghai Chemical Reagent Company, China) was distilled under
Stirring Magnetic microspheres Suspended emulsion polymerization Calcination Fe(OH\textsubscript{3})@PMMA microspheres

Figure 1: Schematic illustration of the synthesis process of magnetic microspheres.

reduced pressure before polymerization. Absolute ethanol was of reagent grade. Benzoyl peroxide (BPO) (97 wt.%, Aldrich) was used as received. Poly(vinyl pyrrolidone) (PVP, K30) was purchased from Shanghai Chemical Regent Company, China. Ferric nitrate (Fe(NO\textsubscript{3})\textsubscript{3}), sodium hydroxide (NaOH), and sodium dodecylbenzene sulfonate (SDBS) were purchased from Tianjin Guangfu Chemical Reagents Company, China. Water used throughout all experiments was distilled followed by deionization.

2.2. Preparation. The overall synthesis procedure and possible mechanisms for formation of the monodisperse magnetic hybrid microspheres were illustrated in Figure 1, and the detailed procedures are described as follows.

(1) Preparation of Fe(OH\textsubscript{3})@PMMA Composite Microspheres. In a typical preparation procedure, 0.5 g SDGS and 80 mL deionized water were added into a 250 mL four-necked flask fitted with a condenser, coupled with a mechanical overhead stirrer, and at the same time inlet for nitrogen gas. 3 mL 1M NaOH and 1 mL 1M Fe(NO\textsubscript{3})\textsubscript{3} were added in turns as the water was heated to 60°C. Then, 5 mL methyl methacrylate was injected into the mixture above under continuous vigorously stirring. The initiator BPO (0.15 g) that dissolved in 20 mL deionized water was then added into the flask, and the flask was heated to 70°C gradually in an oil bath with stirring. The polymerization was maintained for 2 h. The particles, which appear yellow in color, were centrifuged at 7000 rpm for 5 min, the supernatant was removed, and the pellet was resuspended in water. This wash process was performed three times. After the last wash, the supernatant was removed, and the pellet was dried under ambient conditions.

(2) Preparation of Magnetic Particles. The obtained Fe(OH\textsubscript{3})@PMMA composite microspheres were heated to 350°C at a ramp rate of 100°C h\textsuperscript{-1} under N\textsubscript{2} atmosphere in a pipe furnace and kept at this temperature for 2 h to remove CO\textsubscript{3}\textsuperscript{2−} and water. Then, a kind of black powder was obtained from the crucible after calcinations [30]. A possible mechanism was that by calcination of PMMA@Fe(OH\textsubscript{3}) at 350°C for 3 h under N\textsubscript{2} atmosphere, Fe\textsubscript{3}O\textsubscript{4} nanoparticles were formed, and part of PMMA coating was carbonized. Then, the inner Fe\textsubscript{3}O\textsubscript{4} NPs were reduced to Fe\textsubscript{3}O\textsubscript{4} by the resulting outer carbon layers during the calcination process [31, 32].

2.3. Characterizations. A Hitachi S3400 SEM was used to determine the morphology and composition of the products with samples previously coated with gold via vapour deposition. TEM measurements were made on a Philips CM12 TEM/STEM with an accelerating voltage of 120 kV. XRD analysis was carried out on a D/Max 2500V/PC X-ray diffractometer using Cu (40 kV, 30 mA) radiation. FTIR spectroscopy was done in solid state on a PerkinElmer Spectrum100. TGA were performed on a TGA Q50 from TA Instrument using a temperature ramp from 30 to 600°C at 10°C/min under nitrogen atmosphere. Specific surface area N\textsubscript{2} adsorption measurements were performed on a Micromeritics ASAP 2010 V4 analyzer (Nor-mass, GA) and the data were subjected to the Brunauer-Emmett-Teller ( BET) treatment. The magnetic properties were investigated with a BHV-55 vibrating-sample magnetometer (VSM) at room temperature.

3. Results and Discussion

3.1. FTIR Analysis. Figure 2 shows the infrared spectra of Fe(OH\textsubscript{3})@PMMA composite microspheres (a) and magnetic microspheres (b). The prominent bands in the FTIR spectrum (Figure 2(a)) were associated with the polymerization of the acrylic (C=O at 1728 cm\textsuperscript{-1}, -CH between 2840 and 2955 cm\textsuperscript{-1}, -CH\textsubscript{2} at 1457 cm\textsuperscript{-1}, and C-O between 1082 and 1270 cm\textsuperscript{-1}) [28, 33]. As seen from Figure 2(b), the typical adsorption peaks of PMMA were weakened, which further demonstrated that PMMA template was mostly removed.
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from the composite microspheres by means of calcination. And the adsorption centered at 580 cm\(^{-1}\) corresponding to the Fe-O vibration related to the magnetite phase [34, 35]. The IR analysis provides some insights into the composition of the core and the composite.

3.2. Nanostructure and Component. The surface morphology and components of the prepared sample Fe(OH)\(_3\)@PMMA were examined by SEM and EDS, respectively, as shown in Figures 3(a) and 3(b). The SEM image showed that the products were composed of some well monodispersed spheres with a coarse surface. As illustrated in Figure 3(b), EDS analysis indicated that, besides weak Al peaks, only C, Fe, and O were detected, which provides evidence for the presence of Fe(OH)\(_3\)@PMMA particles. Based on the above results, it has been confirmed that PMMA was hybridized with Fe(OH)\(_3\) [28]. TEM measurements could provide further insights into the morphology and structure of composite particles, and TEM images of resultant microspheres were shown in Figure 3(c). It shows that magnetic microspheres were of spherical shape with a particle size in the range of 150–300 nm, and they have two phases [31, 36]. The bright phase maybe is partly carbonized polymer and the dark phase is magnetic Fe\(_3\)O\(_4\). Most interestingly, these composite particles have a novel yolk-shell morphology. Moreover, it is observed that very thin layer was facilely coated on the surface of Fe\(_3\)O\(_4\) NPs which maybe is partly carbonized PMMA [37]. It could be noted that the calcination temperature was controlled pretty well. Figure 3(d) shows the corresponding SAED pattern taken from the single sphere. The diffraction rings suggest that the magnetite spheres were polycrystalline, confirming that the sphere was composed of many small particles. From inside to outside, the rings can be indexed to (220), (311), (400), (422), and (440) planes of spinel Fe\(_3\)O\(_4\), respectively. The magnetic hybrid microspheres are composed of the porous hollow spheres reported by Cheng et al. [36].

3.3. XRD Analysis. XRD measurement was an effective way to further investigate the presence of intercalation in composites. Figure 4 shows the X-ray diffraction pattern of Fe(OH)\(_3\)@PMMA (a) and magnetic microspheres (b). Because of the high concentration of PMMA, there were no sharp diffraction peaks in the diffractogram of Fe(OH)\(_3\)@PMMA microspheres, which could confirm their noncrystalline nature (Figure 4(a)). Based on Figure 4(b), characteristic diffraction peaks at 2\(\theta\) of 30.2\(^\circ\), 35.7\(^\circ\), 43.3\(^\circ\), 57.2\(^\circ\), and 62.6\(^\circ\) were assigned to [220], [311], [400], [333], and [440] lattice planes of Fe\(_3\)O\(_4\). On the basis of the analysis above, it was confirmed that magnetic microspheres were successfully prepared. XRD patterns of the magnetic hybrid microspheres indicate that all the characteristic peaks match well with the standard crystal phase of magnetite (JCPDS numbers 894319, 19–0629) [38, 39]. So the spinel structures of magnetite in the samples were retained. Moreover, the intensity of diffraction peaks for the magnetic composite microspheres became lower as the Fe\(_3\)O\(_4\) content decreased [4]. XRD patterns revealed that Fe\(_3\)O\(_4\) content significantly affected the characteristic peak intensities of the Fe\(_3\)O\(_4\)/PMMA composite microspheres. PMMA had little influence because of its transparency over the Fe\(_3\)O\(_4\) peak range.

3.4. Nitrogen Sorption Isotherm. The nitrogen adsorption-desorption isotherms of Fe(OH)\(_3\)@PMMA (a) and magnetic microspheres (b) were presented in Figure 5. It could be observed from Figure 5(a) that the sorption isotherm was of type III, which demonstrated that Fe(OH)\(_3\)@PMMA nearly have no porous. After being calculated, the BET surface area increased from 3.19 m\(^2\)/g to 32.98 m\(^2\)/g and the sorption isotherm was of type IV (Figure 5(b)) and displayed an obvious hysteresis loop, which demonstrated that magnetic microspheres were typical porous materials. This may be explained by the fact that after calculating part of PMMA was carbonized and the BET surface area was increased [40]. Furthermore, the relatively large pore volume was 1.33 cm\(^3\)/g by using the BET method, which could endow magnetic microspheres with large drug loading capacity.

3.5. TGA Analysis. The materials were quantified by TGA under nitrogen atmosphere. Figure 6 shows the TGA curves of Fe(OH)\(_3\)@PMMA composite microspheres and magnetic microspheres. After being calcined at 600\(^\circ\)C, the Fe(OH)\(_3\)@PMMA composite nanosphere sample lost 80.5% of its weight in two steps (Figure 6(a)). The weight loss before 270\(^\circ\)C can be assigned to the dehydration of Fe(OH)\(_3\) and components of the prepared sample Fe(OH)\(_3\)@PMMA. After being calcined at 350\(^\circ\)C for 2 h, but there still have a small amount of residue PMMA [41].
Figure 3: SEM image (a) and EDS spectrum (b) of Fe(OH)$_3$@PMMA microspheres; TEM image (c) and single sphere SAED pattern (d) of magnetic microspheres.

Figure 4: XRD patterns of (a) Fe(OH)$_3$@PMMA composite microspheres and (b) magnetic microspheres.

Figure 5: Nitrogen sorption isotherm of (a) Fe(OH)$_3$@PMMA composite microspheres and (b) magnetic microspheres.

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3.6. Magnetic Property Testing. The Fe(OH)$_3$@PMMA composite and the magnetic microspheres were dispersed in water by vigorous shaking, respectively; the Fe(OH)$_3$@PMMA composite results in a brown-colored suspension and it cannot be aggregated in the presence of an external magnetic field [42]. However, the magnetic microspheres result in a black-colored suspension and they could be separated from solution in a short period under an external magnetic field. Once the external magnetic field was evacuated, the magnetic hybrid microspheres can be redispersed into the solution with slight shaking (Figure 7). These results show that magnetic microspheres have been successfully produced; they possess excellent magnetic responsivity and redispersibility, which is of great importance in practical manipulation [30, 43].

3.7. VSM Analysis. The magnetization of samples was evaluated by VSM. Figure 8 shows the magnetization curve of Fe(OH)$_3$@PMMA composite microspheres and magnetic microspheres, respectively. It can be seen that the Fe(OH)$_3$@PMMA composite microspheres (Figure 8(a)) almost have no magnetism, but after calcining, they possessed a characteristic of paramagnetic with the saturation magnetization value of about 32.82 emu/g. They also exhibited superparamagnetism at room temperature because of no hysteresis and remanence (Figure 8(b)) [44].

4. Conclusions

In conclusion, we have successfully prepared the magnetic microspheres with diameters in the range of 150–300 nm. TEM results demonstrated that the obtained magnetic microspheres have a novel yolk-shell structure and were well mono-dispersed. The magnetic microspheres exhibited the feature of polycrystalline, increased BET surface area, and the high
Figure 8: Room temperature hysteresis curves of magnetite with (a) Fe(OH)$_3$@PMMA composite microspheres and (b) magnetic microspheres.

magnetic saturation. Taking into account the suitable size, special structure, and good hydrophilic and biocompatible properties, the magnetic microspheres will have wide applications in biomedical fields such as targeted drug delivery, biomolecular separations, cancer treatment, and magnetic resonance imaging.

Competing Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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References


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