

Research Article

Preparation and Characterization of Magnetic Chitosan Microcapsules

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By dispersing aqueous precipitant in liquid paraffin to prepare a W/O emulsion then adding chitosan (CS) solution, CS microcapsules have been successfully prepared. It is a facile way to prepare polymer microcapsules by using aqueous precipitant or nonsolvent as template, which avoids the removal of template and would free from the necessity to cross-link the microcapsule as usual methods to directly form dense shell. The hollow feature of the obtained materials is revealed. The diameter of the microcapsules ranges from several μm to over 100 μm . Magnetic CS microcapsules have been prepared in this way when Fe^{3+} and Fe^{2+} were mixed with CS to prepare a mixture starting solution. The appearance and microstructure of the composite microcapsules were studied. The results indicate that the formed Fe_3O_4 nanoparticles are embedded in the CS matrix evenly due to strong interaction between the Fe_3O_4 nanoparticles and the CS molecules. The Fe_3O_4 content and the magnetic properties of the composite microcapsule were measured. The composite microcapsules were calcined in air at 700°C to prepare pure inorganic hollow microspheres. It is general to prepare hollow polymeric or composite particles by using this method.

1. Introduction

Hollow polymeric microcapsules have characteristics such as low density, high specific surface area, surface permeability, and economical, which make them promising applications in chemistry, biotechnology, and materials science [1–3]. The preparation of polymeric microcapsules has often involved self-assembly of amphiphilic block copolymers [4, 5], sacrificial core-template method [2, 6–10], and emulsion polymerization [11, 12]. At the same time, some of the above-mentioned, technologies could be combined to produce novel hollow polymeric microcapsules [13, 14]. Moreover, hollow polymer microcapsules have also been prepared by microencapsulation method [15–17].

Chitosan (CS), a kind of natural hydrophilic polysaccharide, is nontoxic and biocompatible. Some approaches, especially sacrificial template method, have been developed to prepare the chitosan hollow microspheres or microcapsules.

For example, cross-linked *N*-methylated chitosan hollow microspheres have been prepared by using templates of cyclohexane droplets [18]. The obtained hollow microspheres show pH sensitivity and may be applied as drug carrier. Li et al. [19] prepared uniform-sized hollow chitosan microspheres by sacrificial template method. In that case, chitosan molecules were adsorbed onto the surface of sulfonated polystyrene templates through electrostatic interaction between the sulfonic acid groups on the templates and the amino groups of chitosan. Subsequently, the adsorbed chitosan layer was cross-linked with glutaraldehyde. After removal of the sulfonated polystyrene core, chitosan hollow microspheres were obtained to have an average diameter of about 842 ± 41 nm. Stimuli-responsive multilayer chitosan hollow microspheres were fabricated by sacrificial template method combined with a sequential layer-by-layer electrostatic assembly technique [20]. Therein, polystyrene sulfonate templates were used to absorb polycations of CS molecules,

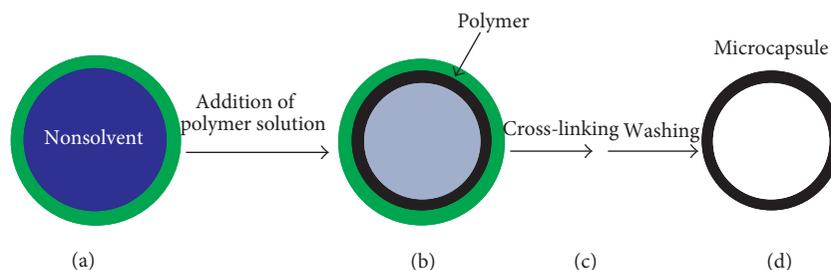


FIGURE 1: Schematic process of preparing the polymer microcapsules.

which then absorb polyanions of carboxymethyl chitosan. The size of the final hollow microspheres is claimed to mainly depend on the template size. However, the preparation of hollow chitosan microsphere by the sacrificial template method is tedious and the process of removal of templates may ruin the shells.

In this paper, it is aimed to fabricate hollow chitosan microcapsules by a facile template-free way, which is similar as the microencapsulation method. The microencapsulation method usually requires a double emulsion ($W_1/O/W_2$); namely, a water in oil emulsion (W_1/O) should be dispersed in a second water phase (W_2). The middle oil layer containing polymer will form the shell of the final polymer microcapsule after evaporation of the oil (water immiscible organic solvent), while the internal water produces the hollow feature of the final microcapsules. This method has the advantage of avoiding the removal of template, because the template is water. For example, Yu et al. [17] have successfully prepared biocompatible polyester microcapsules in this manner, which is claimed to be a template-free approach. Therefore, aqueous precipitant or nonsolvent other than just a normal aqueous phase was firstly dispersed in oil in this work, and then a polymer solution was added to be precipitated at the surface of the nonsolvent droplets to form the hollow microcapsules. The aqueous template avoids the removal of template as usual methods for preparation microcapsules, and the aqueous precipitant or nonsolvent would free from the necessity of cross-linking of the microcapsule to directly form dense shell. Moreover, magnetic composite microcapsules have also been *in situ* prepared simultaneously from the mixture solution of chitosan and ferriions by this method. The composite microcapsules were further calcined in air to produce pure inorganic hollow microspheres. In addition, alginate hollow microcapsules were prepared by this method too. The preparations of the microcapsules have been described, and the obtained microcapsules were characterized. It is expected to develop a new method of fabrication of polymer microcapsules by using aqueous nonsolvent as template.

2. Experimental

2.1. Materials. Chitosan (CS), with a degree of deacetylation of 90%, was purchased from Jinan Haidebei Marine Bioengineering Co., Ltd (Shandong, China). The viscosity-average molecular weight (M_η) of CS was determined in a 0.1 mol/L $\text{CH}_3\text{COONa}/0.2$ mol/L CH_3COOH buffer at 30°C

to be 1.44×10^5 g/mol according to $[\eta] = 6.589 \times 10^{-3} \cdot M^{0.88}$ [21]. Sodium alginate (SA) with a weight-average molecular weight (M_w) of 7×10^4 g/mol was supplied by Xiamen Renchi Chemical Industry Co. Ltd (Xiamen, China). Calcium chloride (CaCl_2), glutaraldehyde (GA), hexahydrate ferric chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), tetrahydrate ferrous chloride ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$), ammonia, acetone, and acetic acid are analytical reagents, while ethanol petroleum ether, liquid paraffin, and Span-80 are industrial grades, respectively. The reagents were purchased from commercial resources in China and were used as received.

2.2. Preparation of Microcapsules. The preparation of the polymer microcapsules is schematically shown in Figure 1. Namely, 20 mL 25% ammonia aqueous solution was dropped into an 80 mL 5% (volume fraction) span-80/liquid paraffin solution under stirring in a flask. A reverse emulsion was obtained after stirring at a speed of 400 rpm for over 0.5 h (step a). Then, 15 mL CS/ $\text{Fe}^{3+}/\text{Fe}^{2+}$ mixture solution was added dropwise into the reverse emulsion with stirring (step b). The mixture solution with CS weight concentration of 5 wt% was prepared by mixing CS 2 wt% acetic acid solution with ferri ions aqueous solution according to the solution weight ratio of 1:1, where the ferri ion aqueous solution before mixing had Fe^{3+} and Fe^{2+} concentrations of 1.0 and 0.5 mol/L, respectively. A continuous 1 h stirring was carried out after the total addition of mixture solution. Then the flask was placed in a 40°C bath, and 5 mL GA was added with stirring for another 1 h (step c). After that, the slurry was filtrated then washed in turn with petroleum ether, ethanol, acetone, and distilled water to obtain the final magnetic CS microcapsules (step d). Pure CS microcapsules were also prepared in the same procedure as above, except that pure CS solution was used.

Moreover, SA microcapsules were prepared in the same way. By using the same amounts of reagents as the preparation of the CS microcapsules, 1 wt% CaCl_2 aqueous solution was dispersed in span-80/liquid paraffin solution to prepare the reverse emulsion, and then a 2 wt% SA aqueous solution was added under stirring. After cross-linking and washing, SA microcapsules were prepared.

2.3. Characterizations of Microcapsules. The microcapsules in wet state and after ambient dried were observed with a ME600 optical microscope (OM, Nikon, Japan). The wet

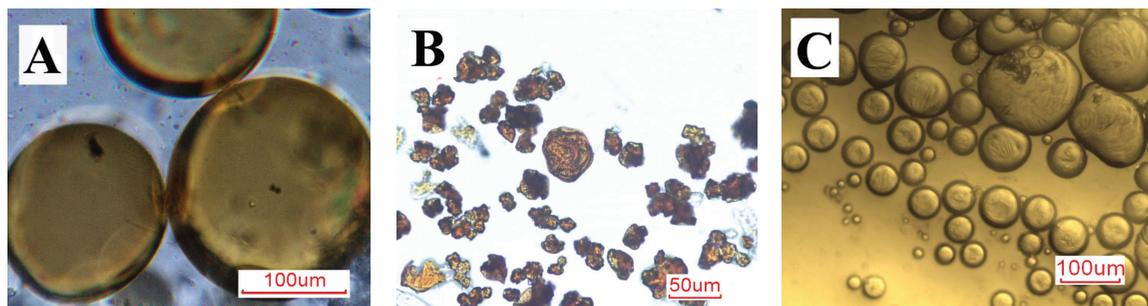


FIGURE 2: OM images of the wet magnetic CS microcapsules (A), the microcapsules after drying in air (B), and the wet SA microcapsules (C).

microcapsules were vacuum dried and then were coated with a thin layer of gold (approximately 2 nm) to observe their microstructures by using a scanning electron microscope (SEM, LEO 1530, LEO, Germany), or the wet microcapsules were directly observed by using an XL30 SEM apparatus equipped with a cold stage (FEI, Holland). Moreover, the magnetic CS microcapsules were calcined in air at 700°C for 2 h, and the obtained product was also coated with gold to be observed by the SEM apparatus.

Transmission electron microscopy (TEM) was performed with a JEM-2100 electron microscope (JEOL, Tokyo, Japan) at 200 kV. The wet magnetic CS microcapsules were embedded in epoxy resin, and then the ultrathin sections were obtained via sectioning on an LKB-8800 ultratome.

Fourier transform infrared (FTIR) characterizations of the CS-based microcapsules were performed on a Nicolet Avatar 360 instrument (Nicolet, Madison, WI, USA) at 25°C. The microcapsules were firstly vacuum dried at 40°C for over 48 h and then grounded to mix with KBr to produce disks for the measurements.

X-ray diffraction (XRD) patterns of the CS-based microcapsules were recorded by using a PANalytical diffractometer (PANalytical, The Netherlands) with Cu-K α radiation. The vacuum-dried microcapsules were continuously scanned from 10° to 80° (2 θ) at a speed of 0.0167°/s.

Thermogravimetric analysis (TGA) measurements of the microcapsules were performed with a NETZSCH 409EP thermal analyzer (Netzsch, Germany) under air atmosphere at a heating speed of 10°C/min from 25 to 700°C.

A vibrating sample magnetometer VSM-5-15, (TOEI Industry Co., Ltd, Japan) was used to assess the magnetic properties of the magnetic microcapsules. Certain amount of the microcapsules was positioned in the magnetometer and was balanced before measurements. The hysteresis of the magnetization was determined by increasing magnetic field intensity (H) from -20000 Oe to +20000 Oe at 27°C, and the magnetic properties for the spheres were evaluated in terms of saturation magnetization (M_s) and coercivity.

3. Results and Discussion

3.1. Preparation of the Microcapsules. Figure 2 shows the OM images of the obtained microcapsules. It can be seen that spherical microparticles have been successfully prepared

(Figures 2(A) and 2(C)). As illustrated in Figure 1, reverse microemulsion of W/O can be prepared upon mixing ammonia aqueous solution or CaCl₂ aqueous solution with span-80/liquid paraffin solution. When dropping the polymer solutions into the microemulsions, the CS will be precipitated due to the neutralization reaction between the solvent of acetic acid and the ammonia, while the SA will be precipitated by Ca²⁺ crosslinking, respectively. When the CS/Fe³⁺/Fe²⁺ mixture solution was added, the ferri ions would be precipitated along with the CS at the same time. The precipitated polymers were further cross-linked by GA in order to strengthen the obtained microparticles, otherwise the particles would be easily broken. The obtained particles reveal several μm to over 100 μm in diameter, but shrink apparently after drying in air (Figure 2(B)), indicating hollow structure of the particles.

The particles were viewed by SEM, with the images shown in Figure 3. The SEM images of particles prepared from pure CS (Figure 3(A)) and from CS/Fe³⁺/Fe²⁺ mixture (Figure 3(B)) show empty pocket structure, which should be resulted from shrinkage of the particles by removal of the inside water during drying. The empty pocket structure clearly evidences the hollow feature of the obtained materials. Moreover, the wet particles were directly observed by using an environmental SEM apparatus equipped with a cold stage sampler. The SEM image shown in Figure 3(C) indicates spherical particle of the composite material, although wrinkled surface is observed due to the shrinkage of the particle during observation. A broken particle was magnified to show hollow feature of the inner part (Figure 3(D)). These results clearly indicate that polymer would be precipitated to form the shell of microcapsules, as schematically shown in Figure 1. According to microemulsion, the size of dispersed precipitant or nonsolvent droplets can be tuned by adjusting the concentration of emulsification agents or the stirring rate [16, 22], so the scale of the microcapsules is expected to be tunable.

3.2. Microstructures of the Microcapsules. When the acidic mixture solution of ferri ions and CS was added to the emulsion containing alkali ammonia solution, the CS and the iron ions could be precipitated at the same time due to the fast neutralization reaction. It has been suggested [23] that the ferri ions were transformed into Fe₃O₄. However,

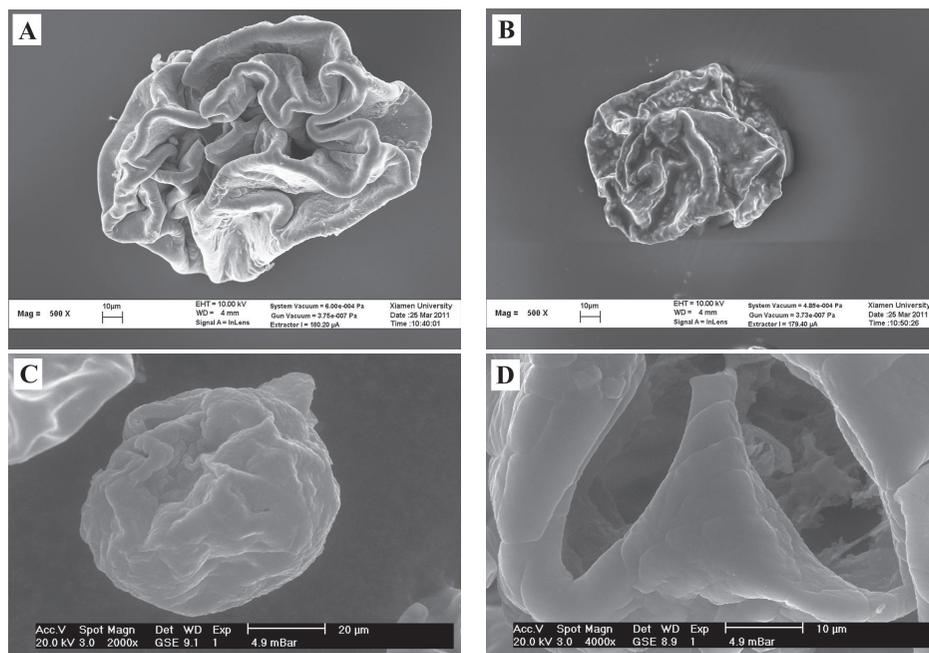


FIGURE 3: SEM images of a pure CS (A) and a magnetic (B) CS microcapsules. The SEM images of the magnetic CS microcapsules shown in (C) and (D) were obtained by using an environmental SEM apparatus equipped with a cold stage sampler.

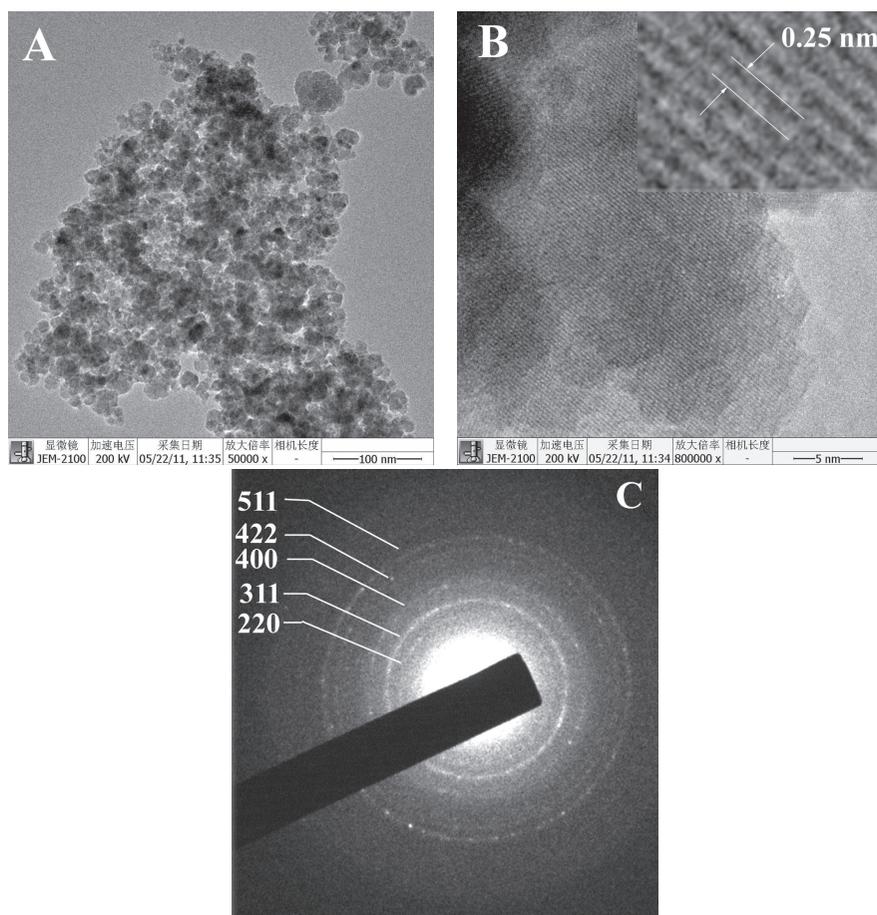


FIGURE 4: TEM image (A), high-resolution TEM image (B), and electron diffraction pattern of the composite microcapsules (C). The insert is an enlarged part of (B) to show the lattice spacing of (311) planes of cubic magnetite.

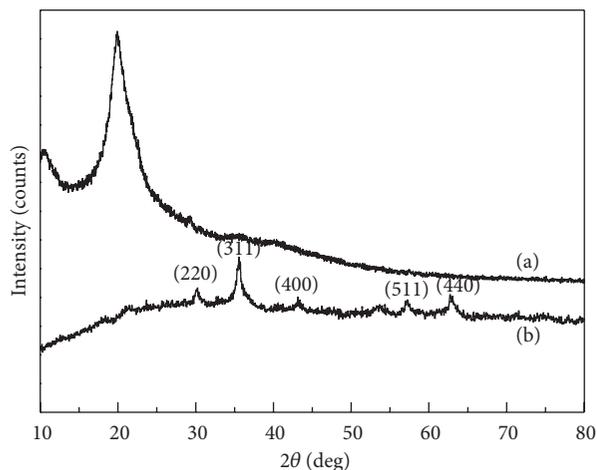


FIGURE 5: XRD patterns of the pure CS (a) and the composite (b) microcapsules.

the composite microcapsules exhibit smooth and dense structure, and no obvious phase separation has been found, as shown in Figure 3. The TEM image of the obtained composite microcapsules is shown in Figure 4(A). It can be observed that the formed Fe_3O_4 nanoparticles are almost evenly embedded in the CS matrix, and no obvious agglomerate of the Fe_3O_4 nanoparticles can be found. The scale of the Fe_3O_4 nanoparticles is in the range from 10 to 20 nm. High-resolution TEM image of the Fe_3O_4 shown in Figure 4(B) indicates each particle is a well-ordered crystal. The distance between two adjacent lattice fringes is measured to be about 0.25 nm, which corresponds to the lattice spacing of (311) planes of cubic magnetite [24]. Moreover, the well-crystallized structure of the Fe_3O_4 nanoparticles can also be evidenced by the characteristic electron diffraction rings shown in Figure 4(C), whose positions correspond to the crystallographic parameters of the fcc structure of magnetite [25, 26].

The XRD patterns of the pure CS and the composite microcapsules are shown in Figure 5. The pattern of pure CS reveals only broad diffraction at 2θ around 19.8° . The pattern of the composite microsphere exhibits six characteristic peaks at $2\theta = 30.1^\circ, 35.5^\circ, 43.1^\circ, 53.4^\circ, 57.0^\circ$, and 62.6° , which can be indexed to the diffraction planes of (220), (311), (400), (422), (511), and (440) for the crystallized structure of the Fe_3O_4 , respectively. The result is consistent with the TEM observation described above. At the same time, it is interesting to note the disappearance of the diffraction peak of CS in the XRD pattern of the composite microcapsules, which might be caused by the presence of Fe_3O_4 nanoparticles in the CS matrix.

The FTIR spectra of the pure CS microcapsules and the Fe_3O_4 nanoparticle contained composite microcapsules are shown in Figure 6. The pure CS microcapsules show a typical FTIR spectrum of CS. The peaks at around 897 and 1160 cm^{-1} in the FTIR spectrum are assigned to saccharide structure of CS, and its C–O–C functional groups are found to locate at 1051 and 1089 cm^{-1} . The characteristic bands of

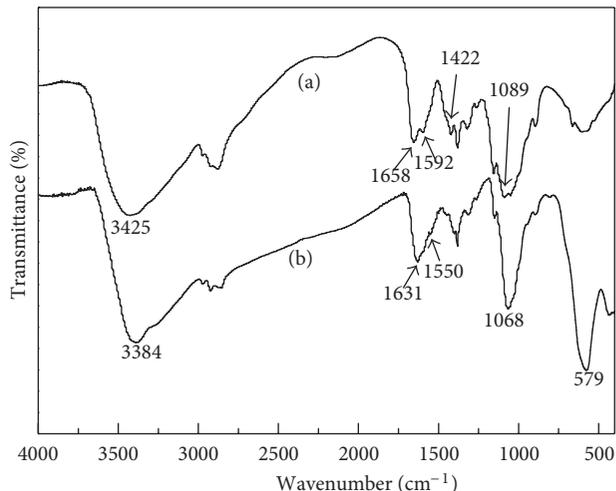


FIGURE 6: FTIR spectra of the pure CS (a) and the magnetic composite (b) microcapsules.

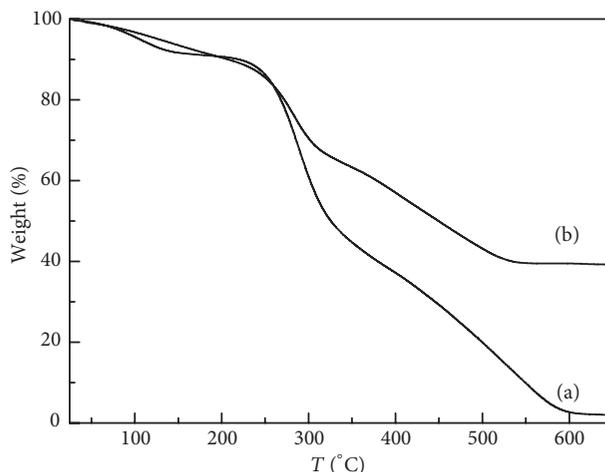


FIGURE 7: TGA curves of the pure CS (a) and the magnetic composite (b) microcapsules.

amide-I, amide-II, and amide-III for CS are found at 1658, 1592, and 1380 cm^{-1} , respectively. The peak at 1422 cm^{-1} is attributed to the –NH deformation vibration of the amine groups belonging to CS. For the composite microcapsules, the spectrum is similar to that of pure CS, except that some peaks shift to lower or to higher frequencies. It is noted that the FTIR spectrum of the composite microcapsules exhibits a strong band at 579 cm^{-1} , which is assigned to magnetite Fe_3O_4 [23]. Therefore, the shifts of the characteristic bands of CS in the spectrum of the composite microcapsules could be attributed to the presence of Fe_3O_4 nanoparticles in the CS matrix. Moreover, the shifts indicate strong interaction between CS and the Fe_3O_4 nanoparticles [20, 27–29], so that, the interaction benefits the stabilization of the formed Fe_3O_4 nanoparticles by the neighboring CS molecules and prevents them from agglomerating, which is consistent with the SEM and TEM observations. The interaction between

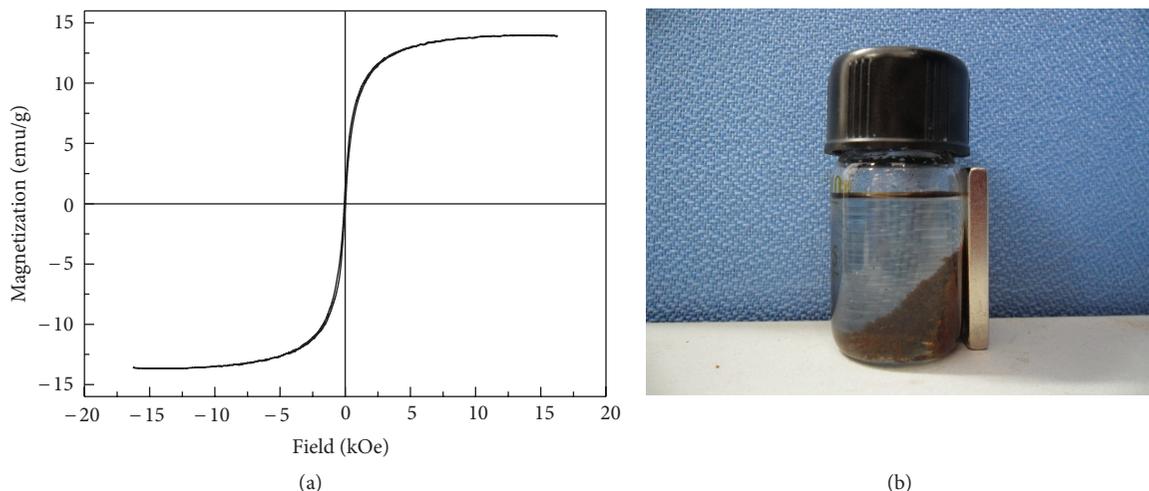


FIGURE 8: Hysteresis loop of the magnetic composite microcapsules at room temperature (a) and a photo picture to show the magnetic property of the magnetic composite microcapsules (b).

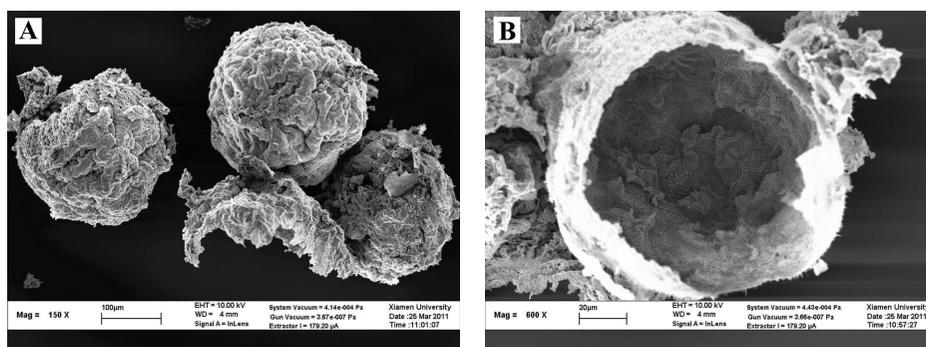


FIGURE 9: SEM images of hollow magnetic CS microcapsules after calcination.

CS and the Fe_3O_4 nanoparticles may also interfere with the crystallization of CS, as shown in Figure 5.

3.3. Properties of the Composite Microcapsules. The Fe_3O_4 content in the composite microcapsules was determined by TGA [23]. Figure 7 shows the thermograms of the pure CS and the composite microcapsules. The thermogram of the pure CS microcapsules exhibits three obvious stages of weight losses, corresponding to the removal of absorbed water, the thermal decomposition of CS, and the oxidation of charred CS. The ash content of CS is thus determined to be 1.9%. The composite microcapsules display similar thermal behavior as the pure CS microcapsules. However, almost constant weight residue is found for the composite microcapsules when the temperature is higher than 640°C , suggesting the presence of only iron oxide and ash. Therefore, the weight content of Fe_3O_4 in the composite microcapsules is calculated to be 39.1%. According to our previous work [23], the Fe_3O_4 content could be tuned easily by changing the starting amount of ferri ions.

The magnetic properties of the composite microcapsules were measured with a vibrating sample magnetometer, with the results shown in Figure 8(a). The invisible hysteresis

suggests superparamagnetic property of the material. It is known that the character of the ideal superparamagnetic materials with size less than 20 nm is zero coercivity and zero remanence. The present result indicates that the Fe_3O_4 nanoparticles in the composite microspheres are less than 20 nm, which is consistent with the TEM observation. The M_s of the composite microspheres determined from the hysteresis loop is 13.9 emu/g, indicating reasonable magnetic property (Figure 8(b)). The magnetic microcapsules might have remarkably advantageous biomedical applications [30, 31] like holding drug for target drug delivery, as heating agent for anti-cancer magnetic hyperthermia treatment, and so forth.

The composite microcapsules were calcined in a muffle furnace at 700°C . The SEM images of the obtained products are shown in Figure 9. It is found that the calcined material retains spherical shape (Figure 9(A)), and a broken microsphere indicates the hollow feature of the particles (Figure 9(B)). It is known from the TGA results that the CS in the composite microsphere could be thermally decomposed at this temperature totally, so the residue would be only iron oxide. Therefore, the hollow particle of pure iron oxide has been prepared.

4. Conclusions

In this work, CS and CS composite microcapsules were prepared by the method of reverse emulsification, in which aqueous precipitant or nonsolvent other than normal aqueous phase was used to directly result in the hollow feature of the materials. The diameter of the microcapsules ranges from several μm to over $100\ \mu\text{m}$, which is believed to be tunable by adjusting the concentrations of emulsification reagents and the stirring rate. When Fe^{3+} and Fe^{2+} are mixed with CS to prepare a mixture solution, magnetic composite microcapsules can be prepared. The experimental results indicate that the formed Fe_3O_4 nanoparticles are embedded in the CS matrix evenly. It is found that strong interaction exists between the Fe_3O_4 nanoparticles and the CS molecules, which stabilize the Fe_3O_4 nanoparticles and prevent them from agglomerating. The Fe_3O_4 nanoparticles are in the range from 10 to 20 nm, which endues the composite microcapsules with superparamagnetic properties. Based on the hollow feature of the composite microcapsules, hollow inorganic particles of pure iron oxide can be prepared after calcining the obtained composite microcapsules. The microcapsules might have potential applications in fields such as waste water treatment, drug delivery, and catalyst carrier.

Acknowledgments

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