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Fabrication of magnetic hollow silica nanospheres for bioapplications

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Different kinds of nanospheres are used in magnetic nanosphere fabrication for bioapplications. In this paper, we report a successful synthesis of magnetic hollow silica nanospheres (MHSNS). The MHSNS were fabricated with a one step coating of Fe_3O_4 magnetic nanoparticles (NPs) (~ 10 nm) and silica on nanosized (20–100 nm) spherical calcium carbonate (CaCO_3) surface under alkaline conditions, in which the nanosized CaCO_3 were used as nanotemplates and tetraethoxysilane and magnetic NPs were used as precursors. The as-synthesized nanospheres were immersed in an acidic solution to remove nanosized CaCO_3 , forming MHSNS. The MHSNS were characterized by SEM, TEM, and SQUID. SEM and TEM results showed that a smooth surface of MHSNS and a thin layer of silica (~ 10 nm) embedded with the magnetic NPs was successfully formed. No nanosized CaCO_3 nanotemplates were observed. SQUID measurement demonstrated that magnetization of MHSNS was dependent on temperature, exhibiting superparamagnetism. The MHSNS have potential applications in biomedicine and bioseparation. © 2005 American Institute of Physics. [DOI: 10.1063/1.1851885]

Magnetic nanoparticles with properties of superparamagnetism, high saturation magnetization, high magnetic susceptibility and low toxicity, have been studied broadly for applications in biology and medicine, including magnetic bioseparation, drug delivery, magnetic resonance imaging contrast enhancement, and hyperthermia treatment of cancer.^{1,2}

Magnetic nanoparticles are usually prepared in diamagnetic carriers to enhance biocompatibility and prevent their natural tendency of aggregation.³ Inorganic and organic matrices were employed to integrate with magnetic nanoparticles to form composite microspheres,⁴ natural macromolecules,⁵ and synthetic polymers.⁶ In addition, biodegradable polysaccharide, dextran, albumin, cellulose, polylactic acid, and poly(alkyl cyanoacrylate) have also been used as magnetic carriers.^{7,8}

Among the different carriers, silica seems to be one of the ideal supporting materials since silica matrices embedded with nanomagnets can be easily used to provide functionalities, prevent anisotropic magnetic dipolar attraction in absence of an external magnetic field, and enhance the wear and corrosion resistance of the magnetic nanoparticles.^{9,10} Submicron-sized silica spheres encapsulating Fe, $\gamma\text{-Fe}_2\text{O}_3$, and Fe_3O_4 have been synthesized.^{9–15} Magnetic silica micro-

spheres can also be fabricated by coating silica microsphere surfaces with magnetite using ferrite plating,¹⁶ sonochemical deposition,¹⁷ self-organization,¹⁸ and layer-by-layer alternate assembly.¹⁹

Magnetic hollow nanospheres, however, are of special interests since they have unique properties, such as large surface area, hollow cores, and magnetism. They may lead to potential applications in biomedicine. The magnetic nanopar-

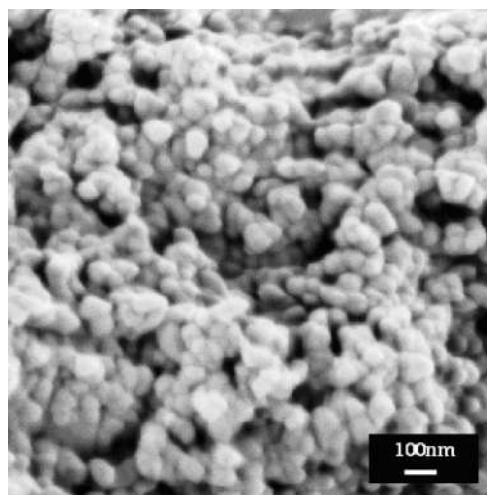


FIG. 1. FESEM image of MHSNS. The surfaces of MHSNS are smooth and few magnetic nanoparticles are seen on the surfaces.

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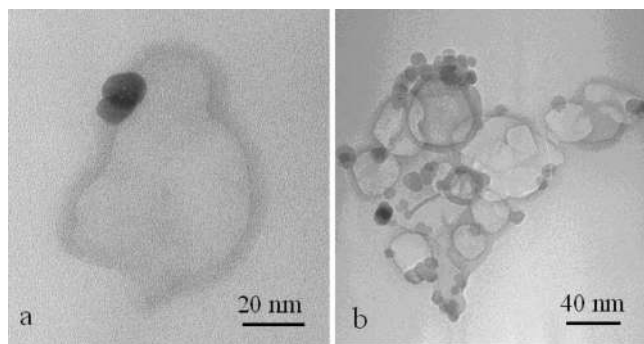


FIG. 2. TEM images of (a) single MHSNS and (b) aggregated MHSNS.

ticles embedded in the shells of hollow silica nanospheres may decrease the interaction of magnetic nanoparticles with biosystems and maintain their properties during biocycling. Submicron-sized magnetic hollow spheres with magnetite nanoparticles sandwiched between silica layers were synthesized by using SiO_2 and Fe_3O_4 nanoparticles as precursors and anionic polystyrene as templates.²⁰ Silica-coated γ - Fe_2O_3 hollow spherical particles with an average size of 150 ± 100 nm were fabricated by an aerosol pyrolysis method.²¹ In this paper, we report a novel synthetic route for magnetic hollow silica nanospheres (MHSNS) via a sol-gel method by using nanosized calcium carbonate as a sacrificial template, and Fe_3O_4 nanoparticle and tetraethoxysilane (TEOS) as precursors.

One gram of spherical calcium carbonate nanoparticles synthesized by a high gravity technique²² with a diameter of 25–60 nm, was dispersed in a mixture of ethanol and distilled water by sonication. Then 4 ml of magnetic fluid (Fe_3O_4 nanoparticles dispersed in methanol, ~ 14 mg/ml) (Ref. 23) and 1.04 g of TEOS and 50 ml of ammonium hydroxide were added into the suspension to reach a pH of 11.²⁴ The suspension was stirred by a mixer for 2 h, aged for 4 h at room temperature, and subsequently filtered and rinsed with distilled water and ethanol. The filter cake was dried at 60 °C for 6 h and then immersed in an acetic acid solution ($\text{HAc}:\text{H}_2\text{O}=1:10$, $\text{pH}=2.5$) for 12 h. The product was afterwards filtered, rinsed with distilled water, and dried at 60 °C for 7 h to yield MHSNS.

The surface morphology of MHSNS was examined using a LEO 1530 VP field emission scanning electron microscope (FESEM). Transmission electron microscopy (TEM) was performed on a JEOL 2010 electron microscope with an acceleration voltage of 200 kV equipped with EDAX energy dispersive spectroscopy (EDS). X-ray powder diffraction (XRD) data was obtained on a Philips X'Pert-MPD diffractometer equipped with a graphite monochromator and $\text{Cu } K\alpha$ (1.5418 Å) radiation. Magnetic properties were measured with a Quantum Design MPMS-5S SQUID magnetometer.

Figure 1 shows a FESEM image of MHSNS. It can be seen that MHSNS have well-defined spherical or elliptical shapes. Due to the nature of the attractive force of nanospheres, the MHSNS aggregated when dried and loaded on FESEM specimen holders. Few magnetic nanoparticles were found on surface area during observation. Both single and aggregated MHSNS can be found in the yielded product as

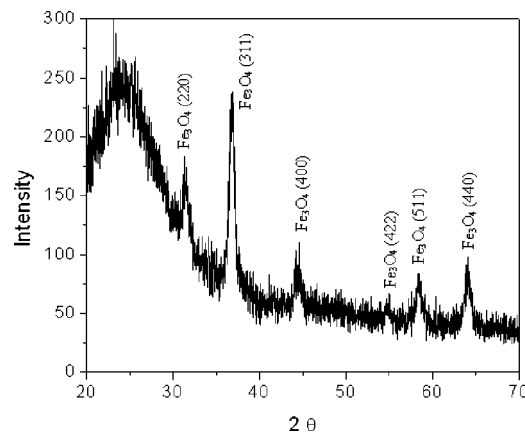


FIG. 3. XRD pattern of MHSNS, showing spinel structures of magnetite nanoparticles. The broad peak is from amorphous silica.

shown in TEM micrographs of Figs. 2(a) and 2(b), respectively. The silica hollow nanospheres have a diameter of 25–60 nm with a shell thickness of about 10 nm. Fe_3O_4 nanoparticles with a diameter of 10 nm are mostly embedded in the silica shells, which gives hollow silica nanospheres magnetic properties. TEM observations show a few magnetic particles, sticking on the surface of hollow silica nanospheres, which has less influence on the properties. It is noted that no residual CaCO_3 nanoparticles were detected by EDS analysis, which implied the weak acetic acid penetrated the shell of silica effectively etched away the CaCO_3 nanoparticle cores, and generated the hollow structures. Yin *et al.*²⁵ also etched away Ag nanowires and achieved silica nanotubes using similar method for fabrication of nanotubes. Even though the silica had a condensation process, the nanopores still existed apparently, when the shell was about 10 nm thin. Therefore, the silica synthesized using TEOS has nanopores on the surface connecting the inner and outside of hollow structures. This unique feature has potential applications for biomedicines.

Figure 3 exhibits XRD pattern of MHSNS. XRD data analysis indicates that standard magnetite crystal with spinel structure have diffraction peaks of {220}, {311}, {400}, {422}, {511}, and {440}. The XRD pattern of MHSNS is in good

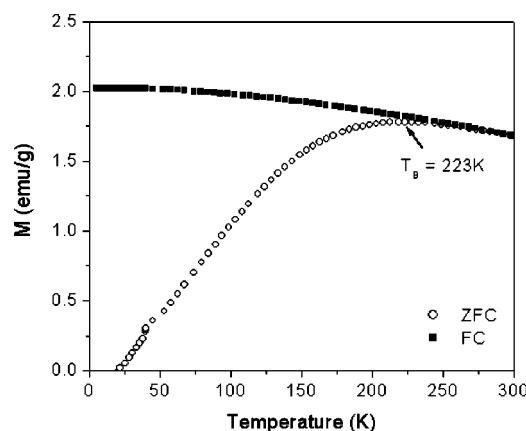


FIG. 4. Temperature dependence of magnetization of MHSNS at ZFC and FC conditions. The MHSNS shows superparamagnetic behavior above the blocking temperature at ZFC condition.

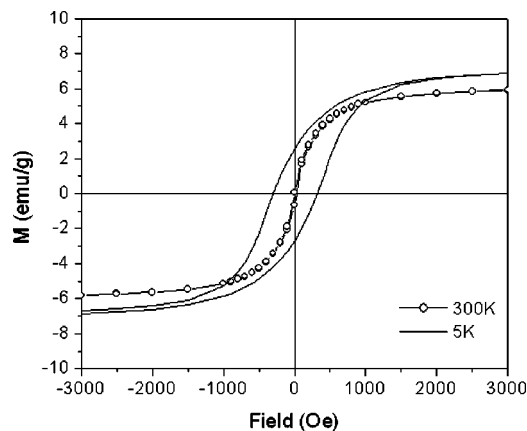


FIG. 5. Hysteresis loops of MHSNS at 5 and 300 K. The absence of coercive hysteresis at 300 K is characteristic of superparamagnetic nanoparticles.

agreement with that of standard Fe_3O_4 spinel structure. It can be thus concluded that magnetite nanoparticles dispersed in the silica shell have a spinel structure of Fe_3O_4 , which shows they were not damaged during the acid etching and low temperature heating. The broad peak from 20° to 28° demonstrates the existence of amorphous SiO_2 structures as a supporting matrix.

Zero-field-cooled (ZFC) and field-cooled (FC) magnetization data in the temperature range of 5–300 K were shown in Fig. 4. In ZFC experiment, the initial field was set to zero as the sample was cooled to the lowest temperature. A field of 100 Oe was then applied and the magnetization was measured as the sample was heated from 5 to 300 K. In FC experiment, a field of 100 Oe was applied as the sample was cooled to the lowest temperature and the magnetization was measured as the sample was heated from 5 to 300 K in the field of 100 Oe. The ZFC curve shows a maximum at 223 K, which is the blocking temperature (T_B). Such a behavior is characteristic of superparamagnetism and is due to the progressive blocking of the magnetic moment of nanoparticles when decreasing the temperature.²⁶

MHSNS exhibit superparamagnetism and ferromagnetism above and below the blocking temperature, respectively. To ensure these features, the field-dependent hysteresis loops of MHSNS were measured at temperatures both below and above the blocking temperature, as shown in Fig. 5. The magnetization vs field data at 5 K displays hysteresis with saturation magnetization of 7.8 emu/g (at the field of 50 000 Oe) and coercivity of 316 Oe, which confirms that MHSNS are ferromagnetic below the blocking temperature. The absence of coercive hysteresis at 300 K is characteristic of superparamagnetic nanoparticles.

In summary, magnetic hollow silica nanospheres were successfully synthesized using calcium carbonate cores as sacrificial templates and TEOS and magnetite as precursors. The TEM results showed that MHSNS were consisted of a

thin layer of silica embedded with Fe_3O_4 nanoparticles. No calcium carbonate nanotemplates were observed after the acid etching. Even though the magnetite nanocomposites were subjected to weak acetic acid etching and low temperature heating process, the magnetic properties of Fe_3O_4 nanoparticles embedded inside the silica shells still remained. Our previous study indicated that hollow silica synthesized using calcium carbonate as template has a large surface area and is favorable for drug adsorption and delivery.²² It is therefore expected that MHSNS can be exploited as delivery vehicles and supports in bioscience applications.

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