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The influence of hollow structure on the magnetic characteristics for Fe₃O₄ submicron spheres

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In this paper, nearly monodisperse Fe₃O₄ hollow and solid submicron spheres were synthesized using a simple solvothermal method. The TEM investigation clearly reveals the successful realization of the hollow structure of magnetite spherical particles by the method. The average diameter of the Fe₃O₄ hollow and solid submicron spheres is about 300 and 500 nm, respectively. The submicron spheres are composed of nanometer-sized grains, with grain sizes of 21 and 28 nm for the hollow and solid spheres, respectively. Magnetic hysteresis measurements indicate that the hollow structure has higher coercive force and lower saturation magnetization than the solid submicron spheres. Magnetization versus temperature curve shows a peak at 107 K in the zero-field-cooled (ZFC) runs for the hollow structure, which corresponds to the blocking temperature of the nanograins. The blocking temperature correlates well with the volume of the nanograins according to Stoner–Wohlfarth theory. The hollow structure exhibits the magnetic properties of individual nanograins because of the weak coupling among them. However, the above-described feature is absent in the solid spheres, due to stronger magnetic coupling between the grains. © 2011 American Institute of Physics. [doi:10.1063/1.3563075]

Recently, much attention has been devoted to the fabrication of nano- and microscale hollow structures because of their potential applications in catalysts, artificial cells, coating, and especially in the delivery-vehicle systems for dyes and inks.¹ Among these materials, magnetic nanospheres with the hollow structure have received much attention for their peculiar properties and potential applications in high-density magnetic data storage, spintronic devices, ferrofluids, and magnetic resonance imaging.^{2–5} Nanostructured Fe₃O₄, as one of the most important and best known magnetic materials, is promising for various kinds of applications due to its distinct properties from those of its bulk counterpart.^{6–9}

Generally, there are two routes to achieve these hollow structures. One is the template method, which needs to use colloidal particles or supramolecular assemblies as cores. However, the template preparation still remains a great challenge. First, the colloidal particle surfaces need modification to ensure the successful coating of shell substances, and supramolecular assemblies are sensitive to solution environment. Second, it is usually required to remove the templates after the synthesis by separate techniques, such as, acid washing, base etching, and calcination. Consequently, the template procedures are technically complicated, which limit their applications to some extent.¹⁰ Another is the self-assembly route, which is controlling process factors to organize the components into hollow structures. For example, CoPt superparamagnetic hollow spheres were prepared by Vasquez *et al.* with

a one-pot reaction that uses Co nanoparticles as a sacrificial template.² Hollow Fe₇Co₃ nanospheres were achieved by Huang *et al.* with a simple one-pot method in aqueous solution with KBH₄ as the reducing agent and sodium dodecyl sulfonate as the stabilizing agent.³ He *et al.* synthesized Co₃O₄ hollow spheres using a surfactant-assisted solvothermal method.⁵ Single-crystal Fe₃O₄ hollow spheres with a diameter of 200–300 nm and a shell thickness of 50 nm have been successfully synthesized in high yield by Yu *et al.* using a template-free solvothermal route.⁸ Herein, we report a facile solvothermal method for the preparation of monodisperse Fe₃O₄ hollow submicron spheres. Solid Fe₃O₄ submicron spheres were obtained by simply modifying the reaction condition. In addition, most previous investigations focused on the preparation of Fe₃O₄ hollow structure without detailed studies of the influences of the hollow structure on their magnetic properties, the magnetic properties of Fe₃O₄ hollow and solid submicron spheres were investigated in this study.

In a typical experiment for synthesizing Fe₃O₄ hollow submicron spheres, 5 mmol of FeCl₃·6H₂O was dissolved in 40 ml ethylene glycol to form a clear solution, followed by the addition of 60 mmol urea and 1.0 g polyethylene glycol-10000. The mixture was stirred vigorously for 30 min and then sealed in a Teflon-lined stainless-steel autoclave at 200 °C for 8 h. The solid submicron spheres were achieved by prolonging reaction time to 12 h and decreasing urea to 15 mmol, whereas the other procedure parameters were kept the same.

Figure 1 shows the XRD pattern of the obtained Fe₃O₄ hollow submicron spheres. All diffraction peaks can be readily indexed to the fcc Fe₃O₄ phase. Well-resolved diffraction

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FIG. 1. (Color online) XRD patterns of the Fe_3O_4 hollow structure.

peaks reveal good crystallinity of the Fe_3O_4 specimens. In addition, it is hard to distinguish the Fe_3O_4 and $\gamma\text{-Fe}_2\text{O}_3$ by either the XRD or magnetic properties. It was well known that Fe_3O_4 and $\gamma\text{-Fe}_2\text{O}_3$ have a significant difference in electricity. Fe_3O_4 has good electrical conductivity, whereas $\gamma\text{-Fe}_2\text{O}_3$ was insulating. For proving Fe_3O_4 crystalline phase, the as-prepared powders were pressed to the pellet, and its resistance was measured. The resistivity of the pressed pellet is in the range of $100\ \Omega\ \text{m}$, which is within the range of Fe_3O_4 pressed powders. So we can rule out the possibility of $\gamma\text{-Fe}_2\text{O}_3$, which is insulating. In addition, we can distinguish Fe_3O_4 and $\gamma\text{-Fe}_2\text{O}_3$ powders with a simple method. Fe_3O_4 powders have a black color, but $\gamma\text{-Fe}_2\text{O}_3$ has a different color of reddish brown. In this study, the as-prepared powders have a black color, which presents the achievement of Fe_3O_4 powders. The average grain size of the hollow and solid submicron spheres was calculated according to the following Debye–Scherrer's formula:

$$D_m = (0.89\lambda) / [\delta(2\theta) \cos \theta], \quad (1)$$

where λ is x-ray wavelength, θ is the Bragg scattering angle, and $\delta(2\theta)$ is the line broadening at half the maximum intensity in radians.^{11,12} The calculated results show the average grain diameter for the hollow and solid submicron spheres is about

FIG. 3. (Color online) Magnetic hysteresis loops of Fe_3O_4 hollow and solid submicron spheres at 5 and 300 K.

21 and 28 nm, respectively. Consequently, the obtained submicron spheres should be polycrystalline aggregates and composed of nanograins. SEM and TEM images of the hollow and solid submicron spheres are presented in Fig. 2. The nearly monodisperse Fe_3O_4 solid spheres have an average diameter of about 500 nm. An enlarged image [Fig. 2(e)] shows that Fe_3O_4 solid spheres are composed of smaller nanograins. The size of the nanograins is about 20–30 nm, which is consistent with the XRD peak broadening calculation. The hollow structure has smaller particle size and the average particle diameter is about 300 nm. The TEM image of Fe_3O_4 hollow submicron spheres shows a clearly fluffy and hollow structure.

The magnetic hysteresis loops of Fe_3O_4 hollow and solid submicron spheres were measured at 300 and 5 K and are shown in Fig. 3, all of which show a strong magnetic response to a varying magnetic field. The coercive force (H_c) is about 5.0 and 141.2 Oe at 300 and 5 K for the solid submicron spheres, respectively, and is 48.3 and 184.6 Oe for the hollow structure at the two temperatures. The solid submicron spheres have a saturation magnetization (M_s) of 72.6 and 84.1 emu/g at 300 and 5 K, whereas it is 64.9 and 71.4 emu/g for the hollow structure. It is known that the

FIG. 2. SEM and TEM images for the Fe_3O_4 hollow structure [(a)–(c)] and for the Fe_3O_4 solid spheres [(d)–(f)].

FIG. 4. (Color online) Magnetization (M) vs temperature (T) measured in both ZFC and FC runs for Fe_3O_4 solid (a) and hollow (b) submicron spheres.

discontinuities and broken bonds at the surfaces of grains that would otherwise link Fe cations through the superexchange coupling, which leads to a canted spin structure. Fe_3O_4 particles with nanometer size have a large specific surface area and a large portion of surface irons. Consequently, the magnetization of Fe_3O_4 nanomaterials is significantly lower than the bulk. Compared to the solid submicron spheres, the hollow ones have smaller particle and grain sizes, which is responsible for the smaller M_s . The hollow structure has larger H_c than the solid submicron spheres at either 300 or 5 K. According to Stoner–Wohlfarth theory, the coercive force of nanoparticles is given by the following equation:^{13,14}

$$H_c = \frac{2K}{\mu_0 M_s}, \quad (2)$$

where μ_0 is the vacuum permeability, M_s the saturation magnetization, and K the anisotropy constant, which is proportional to the volume and surface anisotropy constant K'_v and K'_s , and inversely proportional to the diameter of particle ($K = K'_v + 6K'_s/d$).^{11,15} The hollow structure has a smaller grain size than the solid submicron spheres, thus the enhancement of the coercivity for the hollow structure results from an increase in the anisotropy constant and a decrease in the saturation magnetization. In addition, the hollow submicron spheres have a void in the center and a fluffy appearance as seen from the TEM images. Therefore, relative weak magnetic coupling between magnetic grains are expected, which results in larger K and H_c .¹⁴ Figure 4 shows the ZFC and field-cooled (FC, with a cooling field of 50 Oe) magnetization as a function temperature. A significant difference in the ZFC and FC magnetization curves was observed between hollow and solid submicron spheres. There is a remarkable peak around 107 K in the ZFC curves of the hollow sample, which corresponds to the blocking temperature T_b . Stoner–Wohlfarth theory gives^{14,16}

$$T_b = \frac{K}{25k_B} V, \quad (3)$$

where K represents the anisotropy constant, k_B the Boltzmann constant, and V the particle volume. Equation (3) can be used to calculate the average size of the grains of hollow submicron spheres, which turns out to be about 19 nm, in agreement with the XRD result of 21 nm. One might expect a blocking temperature around 250 K for the solid submicron spheres

based on their grain size of 28 nm. However, data in Fig. 4 shows no sign of any blocking behavior for this sample. Difference microstructures (different spatial arrangements of the grains) in the hollow and solid submicron spheres play a key role here. In the hollow structure, the magnetic properties of individual nanograins are revealed because of the weak coupling among them. On the other hand, the nanograins are strongly coupled magnetically in a solid sphere, which results in a larger effective domain size than the grain size.¹⁷ Thus the superparamagnetic behavior is not observed as evidenced by the absence of the blocking temperature below 350 K.

In conclusion, Fe_3O_4 hollow structure was synthesized by a simple one-pot solvothermal method. For the investigation of the influence of the hollow structure on the magnetic properties, solid submicron spheres were obtained by simply adjusting the parameters during the procedure. The average diameter of the hollow and solid submicron spheres is about 300 and 500 nm, and the grain size is about 21 and 28 nm, respectively. The measurement of magnetic hysteresis loops revealed that the hollow structure has higher coercive force and lower saturation magnetization than solid submicron spheres. The hollow structure exhibits a blocking temperature of 107 K, which correlates well with the average size of the nanograins. The hollow structure presents the magnetic properties of individual nanograins because of the weak coupling among them. On the other hand, the above-described feature is absent in solid submicron spheres, due to stronger magnetic coupling between the nanograins.

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