Gel-hydrothermal Preparation of Hollow $CoFe_2O_4$ Nanospheres and Their Properties

Lingyun Chen,*[1] Chenglan Zhao,[1] and Junfeng Bai[2]
[1]*College of Chemistry and Chemical Engineering, Chongqing University, Chongqing 400030, P. R. China*
[2]*State Key Laboratory of Coordination Chemistry, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, P. R. China*

(Received December 11, 2008; CL-081154; E-mail: lychen@cqu.edu.cn)

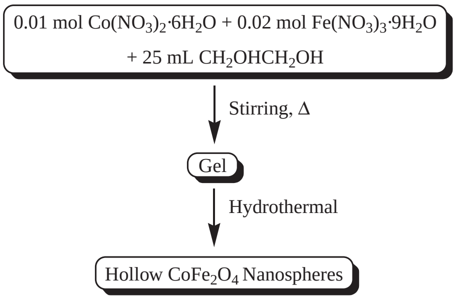
Hollow $CoFe_2O_4$ nanospheres were successfully prepared through hydrothermal decomposition of a gel of Co–Fe–glycol in solution. The products have average diameters of ca. 80 nm with a Brunauer–Emmett–Teller (BET) surface area of about $76.5\,m^2\cdot g^{-1}$, exhibiting low saturation magnetization and high coercivity.

Recent years have witnessed the rapid development of hollow spherical structure materials which may exhibit unique physical and chemical properties, such as low density, large specific surface area, and hollow structures, and have potential applications in many areas including catalysis, optics, electrics, magnetics, medicine-release, drug delivery, and selective adsorption.[1–3] Up to now, numerous efforts have been devoted to the preparation of hollow nanospheres.[4–7] However, exploring simple and facile methods for the preparation of hollow spheres is still of scientific and technical importance.

$CoFe_2O_4$, as an important magnetic material, exhibits relatively high saturation magnetization and coercivity, high thermal and chemical stability, and good mechanical hardness, and its nanostructure has potential applications in many fields including high-density magnetic recording, magnetic response imaging, and drug delivery.[8–10] Up to now, there are few reports on hollow nanospheres composed of ternary metal oxides.[11,12] Herein, we report a novel hydrothermal route for the preparation of hollow $CoFe_2O_4$ nanospheres using gel as single-source precursor. The objective of the present investigation is to prepare ternary oxide hollow spheres. In comparison to other preparations, the advantage of our route lies in its simpleness without using any template or surfactant. In addition, the adsorption and magnetic properties were also investigated, and a formation mechanism was also proposed on the basis of the results of experiments.

All chemicals were of analytical grade and used as received without further purification. The synthetic process is illustrated in Scheme 1. First, 0.01 mol of $Co(NO_3)_2\cdot 6H_2O$ and 0.02 mol of $Fe(NO_3)_3\cdot 9H_2O$ were dissolved in 25 mL of glycol under stirring at room temperature for half an hour and heated at 80 °C finally forming dry Co–Fe–glycol gel. Then 0.02 g of gel was dissolved in 8 mL of deionized water. After that, the solution was transferred into a Teflon-lined stainless steel autoclave with a capacity of 10 mL, which was hydrothermally treated at 180 °C for 12 h. After cooling to room temperature, the products were separated by centrifugation, washed with water and absolute ethanol three times, and dried at 60 °C for 3 h in vacuum.

The products were characterized by powder X-ray diffraction (XRD, Shimadzu XRD-6000 X-ray diffractometer), inductively coupled plasma atomic emission spectrometer (ICP-AES, Thermo Fisher Scientific ICP-IRIS Advantage), X-ray photoelectron spectroscopy (XPS, VG MICROLB-MKΠ XPS spectrometer), field emission scanning electron microscopy (FESEM, Carl Zeiss INC. LEO1530VP SEM), transmission electron microscopy (TEM, Philips Tecnai 12 microscope), specific surface area and pore size distribution analysis (Coulter SA-3100 analyzer), and vibrating sample magnetometry (VSM, Lake Shore 7303-9309 VSM).



Scheme 1. Schematic flow chart for the preparation of hollow $CoFe_2O_4$ nanospheres by the gel-hydrothermal route.

The crystal structures of the products were first characterized by XRD. Figure 1 shows an XRD pattern of a product. All diffraction peaks can be indexed as inverse spinel structure $CoFe_2O_4$, which is consistent with the standard value for bulk $CoFe_2O_4$ phase (JCPDS file No. 22-1086). The sharp peaks are ascribed to the nanocrystalline nature of the product prepared with the present approach. From the ICP-AES results, the atomic ratio of Co to Fe is 0.49, which is close to that of $CoFe_2O_4$. These results indicate that the products contain no impurities.

The XPS spectrum of the hollow $CoFe_2O_4$ spheres in Figure S1 shows signals for Co, Fe, and O.[15] The $Co2p_{3/2}$ signal appears at 781.4 eV with a satellite peak at 786.6 eV; the peak at 796.9 eV is ascribed to the $Co2p_{1/2}$ level. The Fe2p levels with binding energies of 711.6 and 725.0 eV are assigned to $Fe2p_{3/2}$ and $Fe2p_{1/2}$, respectively. The O1s signal is located at 530.9 eV,

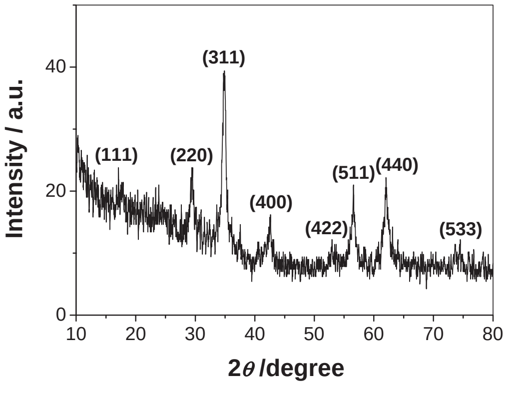


Figure 1. XRD pattern of a product at 180 °C for 12 h.

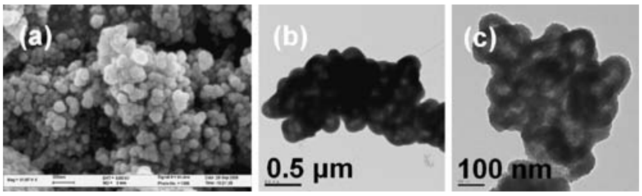


Figure 2. Typical FESEM image (a) and different resolution TEM images ((b) and (c)) of the $CoFe_2O_4$ products.

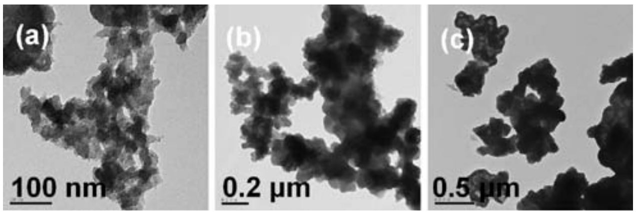


Figure 3. TEM images of as-prepared products at 180 °C for different reaction time of (a) 0.5, (b) 3, and (c) 6 h.

and no other O1s level can be detected, indicting that there is no impurity in the product.

The size and morphology of the products were examined by electronic microscopic techniques. From the FESEM image in Figure 2a, large-scale $CoFe_2O_4$ nanospheres with average size of about 90 nm were formed with surfaces composed of nanoparticles. On the basis of typical TEM images in Figures 2b and 2c, the products show spherical hollow nanostructures with a wall thickness of ca. 20 nm.

By simply altering the reaction time at 180 °C, different products were obtained with TEM images shown in Figure 3. When the reaction time was half an hour, the products consisted of plate-like structured $CoFe_2O_4$ composed of nanoparticles. With the increase of reaction time, spherical hollow structures appeared at 6 h. XRD patterns in Figure S2 show that all the products at 180 °C for different reaction time were $CoFe_2O_4$.[15]

The N_2 adsorption–desorption curve in Figure 4a shows a hysteresis loop with a BET surface area of $76.5\,m^2\cdot g^{-1}$, which indicates that mesopores with a broad pore size distribution are present in the hollow $CoFe_2O_4$ spheres.

The magnetization curve of the hollow $CoFe_2O_4$ spheres at 180 °C for 12 h examined at room temperature is shown in Figure 4b. A hysteresis loop can be observed, indicating that the hollow nanospheres are ferromagnetic. With an increase in the external magnetic field to 15000 Oe, a saturation magnetization of $63.5\,emu\cdot g^{-1}$ is achieved, which is less than that of the bulk cobalt ferrite of $72\,emu\cdot g^{-1}$. Meanwhile, the coercivity of the hollow $CoFe_2O_4$ nanospheres shows a relatively high value of 850 Oe, which is close to that of the bulk cobalt ferrite (980 Oe). A possible reason may be due to the interaction between the nanoparticles composing the hollow spheres.[13]

When hydrothermal reaction was directly carried out of Co^{2+} and Fe^{3+} in solution, only irregular $CoFe_2O_4$ nanopowder was obtained.[14] The possible formation mechanism of our preparation is illustrated in the following. First, it dissolves and forms a brown-yellow colloidal solution. Then with the increase of temperature, the dispersed gel begins to decompose into nanoparticles and finally forms hollow nanospheres by Ostwald ripening.[7] During the hydrothermal process, the Co–Fe–glycol gel plays an important role. Further research and exploration of the detailed formation mechanism is going on.

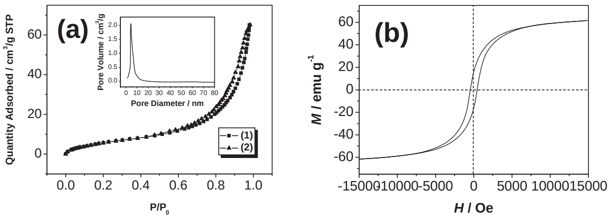


Figure 4. (a) N_2 adsorption (1)–desorption (2) isotherm and BJH pore-size distribution plot (inset) and (b) the hysteresis curve of the $CoFe_2O_4$ hollow nanospheres at 180 °C for 12 h.

In summary, without using any template or surfactant, hollow $CoFe_2O_4$ nanospheres were obtained by direct hydrothermal decompositon of Co–Fe–glycol gel. It provides a simple, facile, and environmentally friendly route for the preparation of hollow nanospheres on a large scale which have potential applications in various areas such as catalysis, drug carriers, and magnetic recording.

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