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Solvothermal synthesis of $CoFe_2O_4$ hollow spheres

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Abstract Hollow $CoFe_2O_4$ spheres consisted of $CoFe_2O_4$ nanoparticles were synthesized by a facile solvothermal treatment of an ethylene glycol solution of $FeCl_3 \cdot 6H_2O$, $CoCl_2 \cdot 6H_2O$, and NaAc at 200 °C in the presence of polyethylene glycol and oleic acid. The products were characterized by powder X-ray diffraction, transmission electron microscopy, selected area electron diffraction, high-resolution transmission microscopy, scanning electron microscopy. The magnetic properties were evaluated using a vibrating sample magnetometer. The probable mechanism of the formation of Hollow $CoFe_2O_4$ spheres was discussed.

Introduction

In recent years considerable attention has been focused on hollow nanostructures owing to their higher specific surface area, lower density and better permeation, and potential applications in catalysts, chemical sensors, drug delivery, photonic crystal, low-density structural materials and in biotechnology [1]. Generally, there are two approaches for preparing such materials. One is based on the use of various removable templates including polymer latex spheres [2], silica sol–gel [3, 4], microemulsion droplets [5], liquid crystals [6], liquid droplets [7], surfactant vesicles [8], polymer micelles [9], polymer-surfactant complex micelles [10, 11], functional surfactant micelles [12], and metal nanoparticles [13]. For example, we have prepared hollow Ni nano/microstructures via hydrothermal treatment of alkaline solution of $Ni(DS)_2$ and NaH_2PO_2 [12]. Another is based on the utilization of some physical phenomena, such as the Kirkendall effect or Ostwald ripening [14–17], For example, Alivisatos and co-workers synthesized hollow nanocrystals of cobalt oxide and chalcogenides through a Kirkendall effect [14]. Hollow structures also can be achieved by mild hydrothermal process [18, 19], γ-irradiation [20], ultrasonication [21]. Spinel ferrites (MFe_2O_4; M = Fe, Co, Ni, Mn, Zn) are among the most important magnetic materials and have been widely used in electronic devices, information storage, magnetic resonance imaging (MRI), and drug-delivery technology [22–27]. Because of the practical reasons mentioned above, the synthesis of nanostructured $CoFe_2O_4$ has also attracted considerable attention. Some methods for preparation of $CoFe_2O_4$ nanomaterials have been reported [28–38]. However, there are very few reports on the preparation of hollow $CoFe_2O_4$ spheres [39]. Chen et al. described a facile route for preparation of submicrometer ferrite/block copolymer hollow spheres. Herein, we report a method for the synthesis of $CoFe_2O_4$ hollow spheres via solvothermal treatment of an ethylene glycol solution of $FeCl_3 \cdot 6H_2O$, $CoCl_2 \cdot 6H_2O$ and NaAc (sodium acetate) at 200 °C in the presence of oleic acid and polyethylene glycol (PEG). This method is simple and requires no expensive reagents.

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Experimental section

All the regents were of analytical purity, and were used without further purification. Polyethylene glycol (average molecular weights (M_w) of 400) oleic acid (OA), ethylene glycol (EG), and poly(vinyl pyrrolidone) (PVP) (average molecular weights (M_w) of 40,000) were obtained from Shanghai Chemical Reagent Company.

The X-ray powder diffraction (XRD) pattern of the as-prepared products was collected on a Shimadzu XD-3A X-ray diffractometer with CuK_α radiation (λ = 0.15147 nm). Transmission electron microscopy (TEM) images and selected area electron diffraction patterns (SAED) were obtained by employing JEOL JEM-200CX transmission electron microscope, using an accelerating voltage of 200 kV. Scanning electron microscopy (SEM) images were taken on a JEOL-JSM6360LA scanning electron microscope. Using a Lake Shore 7303–9309 vibrating sample magnetometer performed room-temperature magnetic characterization of the $CoFe_2O_4$ nanocrystals.

In a typical synthesis, $FeCl_3 \cdot 6H_2O$ (0.676 g, 2.5 mmol) and $CoCl_2 \cdot 6H_2O$ (0.278 g, 1.25 mmol) were dissolved in ethylene glycol (20 mL) to form a clear solution, followed by the addition of NaAc (1.8 g, 21.95 mmol), polyethylene glycol (1.0 mL) and oleic acid (2.0 mL). The mixture was stirred vigorously for 30 min and then sealed in a Teflon-lined stainless-steel autoclave (30 mL capacity). The autoclave was heated to and maintained at 200 °C for 8 h, and allowed to cool to room temperature. The black products were washed several times with water and absolute ethanol and dried at 60 °C for 3 h.

Results and discussion

Figure 1 shows the power XRD pattern from the as-prepared product. The diffraction characteristic peaks are quite similar to those bulk $CoFe_2O_4$, which can be indexed as the cubic structure $CoFe_2O_4$ with lattice constants of a = 0.839 nm. This is in good agreement with the reported data (JCPDS File No 22-1086). No impurity peaks were observed, indicating that the nanomaterials obtained via our current synthetic methods consist of pure phases. However, the peaks were relatively broad compared with those of the bulk materials. Based on the calculation of Scherrer's formula, the average particle diameter is about 15.5 nm.

The morphology and microstructure of the $CoFe_2O_4$ products were further examined with TEM, SAED, high-resolution transmission microscopy (HRTEM) and SEM. Figure 2a shows a typical TEM image of the $CoFe_2O_4$ products. The TEM image in Fig. 2a reveals that the products consist of many sphere particles and

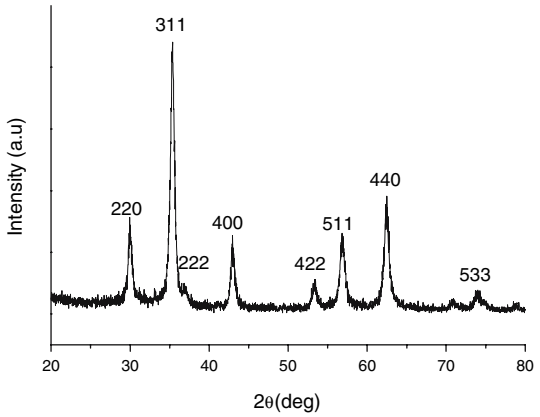

Fig. 1 XRD pattern of the $CoFe_2O_4$ nanocrystals obtained in the typical synthesis

nanoparticles. The sphere particles have pale color regions in the central parts in contrast to dark edges, indicating that they are hollow spherical structure. The diameter of $CoFe_2O_4$ hollow spheres is in the range of 220–360 nm. The TEM image of a $CoFe_2O_4$ hollow sphere in Fig. 2b clearly reveals that the spherical shell is built up of numerous $CoFe_2O_4$ nanoparticles. The size of $CoFe_2O_4$ nanoparticles is in the range of 7–18 nm, and the average particle diameter is about 15 nm, which verifies the calculating result based on the XRD data. Figure 2c is a SAED of $CoFe_2O_4$ hollow spheres, suggesting that the $CoFe_2O_4$ spheres are polycrystalline. HRTEM image (Fig. 2d) also shows that the $CoFe_2O_4$ hollow sphere is multicrystalline and the fringe space is about 0.21 nm, close to the interplanar (400) distance of cubic structure $CoFe_2O_4$ (0.209 nm). The SEM image of $CoFe_2O_4$ products (Fig. 2e, f) further verifies that they have hollow spherical structure.

In a typical synthesis, the usage of polyethylene glycol and oleic acid is 1.0 and 2.0 mL respectively. To learn more about the formation of $CoFe_2O_4$ hollow spheres, we also characterized the size and morphology of $CoFe_2O_4$ nanomaterials obtained from their synthesis using different amounts of polyethylene glycol and oleic acid. When the amount of oleic acid was kept at 2.0 mL, and the amount of polyethylene glycol was in the range of 2–3 mL, $CoFe_2O_4$ hollow spheres and nanoparticles were too obtained. Figure 3a shows the typical TEM images of $CoFe_2O_4$ hollow spheres and nanoparticles prepared in the presence of polyethylene glycol (2.0 mL) and oleic acid (2.0 mL), the diameter of $CoFe_2O_4$ hollow spheres are in the range of 150–420 nm and the nanoparticles in the range of 5–15 nm. When the usage of polyethylene glycol was kept at 1.0 or 2.0 mL, and the usage of oleic acid was decreased to 1.0 mL, we found that the products were $CoFe_2O_4$ hollow spheres and nanoparticles yet. Figure 3b shows the typical TEM images of $CoFe_2O_4$ hollow spheres and

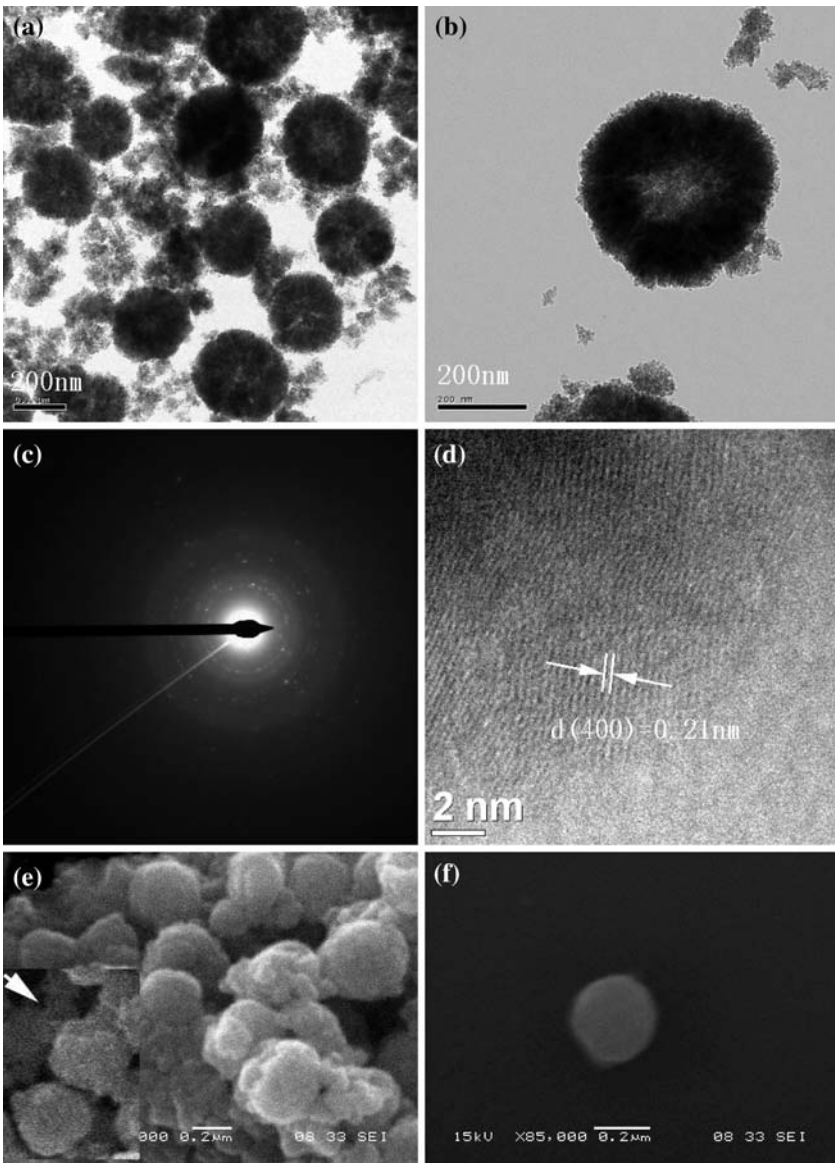

Fig. 2 (**a**) TEM image of the $CoFe_2O_4$ hollow spheres and nanocrystals, (**b**) TEM image of a $CoFe_2O_4$ hollow sphere, (**c**) SAED image of the $CoFe_2O_4$ nanocrystals obtained in the typical synthesis, and (**d**) HRTEM image of a $CoFe_2O_4$ hollow sphere. (**e**) SEM image of the $CoFe_2O_4$ hollow spheres and nanocrystals. The inset is the SEM image of the broken $CoFe_2O_4$ hollow sphere (**f**) SEM image of a $CoFe_2O_4$ hollow sphere

nanoparticles prepared in the presence of polyethylene glycol (2.0 mL) and oleic acid (1.0 mL), the diameter of $CoFe_2O_4$ hollow spheres and nanoparticles are in the range of 150–470 nm. When PVP (300 mg) was used instead of polyethylene glycol, the hollow spheres were also obtained (Fig. 3c). When the usage of oleic acid was kept at 2.0 mL and polyethylene glycol was not used, or only polyethylene glycol was used and no oleic acid, we found that the products were all $CoFe_2O_4$ nanoparticles and no $CoFe_2O_4$ hollow spheres. Figure 3d shows the typical TEM images of $CoFe_2O_4$ nanoparticles prepared in the presence of oleic acid (2.0 mL), the diameter of $CoFe_2O_4$ nanoparticles are in the range of 13–20 nm. The $CoFe_2O_4$ nanomaterials show excellent dispersibility in ethanol and poor dispersibility in water, which indicates that the surface of the products was covered by hydrophobic surfactants. Infrared spectroscopy analysis further verifies this conclusion (Fig. 4). The strong peak at 1,710 cm^{-1} belonging to v_s (OCO) stretching vibration mode of free oleic acid molecule is not found, and absorption peak at 1,550 cm^{-1} is appeared in infrared spectroscopy, which indicates that oleic acid molecules are bonded with $CoFe_2O_4$ nanoparticles (chemisorbed), and resulting in the changing of absorption peak location [40]. Weak peak at 1,100 cm^{-1} should belong to v_s (COC) stretching vibration mode of polyethylene glycol molecule. Strong peak at 2,921 cm^{-1} should be belonged to v_s (CH) stretching vibration mode of polyethylene glycol or oleic acid molecules. Thermogravimetric analysis (TG-DSC) also reveals the presence of polyethylene glycol and oleic acid molecules in the products. The TG-DSC for the product showed an initial weight loss of 15.09% from 190 to 430 °C mainly corresponding to the pyrolysis of PEG molecules, followed by another weight loss of 11.25% from 430 to 800 °C mainly for the

decomposition of oleic acid molecules from the product, the remaining residue was $CoFe_2O_4$.

Based on the above facts, we speculate that the formation of $CoFe_2O_4$ nanoparticles and hollow spheres may be relevant to the little water/oil drops and spherical vesicles as soft structural templates as shown in Fig. 5. When the reaction temperature is raised, the crystalline water is released and polyethylene glycol, oleic acid molecules extend toward the water phase with their hydrophilic group, resulting in the formation of many little water/oil drops. $FeCl_3$, $CoCl_2$ react with NaAc in the water phase of little liquid drops, and form $CoFe_2O_4$ nanoparticles. Then, $CoFe_2O_4$ nanoparticles are assembled into hollow spheres via the spherical vesicles formed by oleic acid and polyethylene glycol/PVP molecules. The detailed formation mechanism of $CoFe_2O_4$ hollow spheres needs to be investigated further.

The magnetic properties of $CoFe_2O_4$ nanomaterials consisted of nanoparticles and hollow spheres obtained in the typical synthesis were investigated with a vibrating sample magnetometer. Figure 6 shows the magnetization curve measured at 300 K for the $CoFe_2O_4$ nanomaterials obtained in the typical synthesis. The saturation magnetization (M_s), remanent magnetization (M_r), and coercivity (H_c) are ca. 58.94 emu g^{-1}, 11.05 emu g^{-1}, and 226 Oe for the $CoFe_2O_4$ nanomaterials at 300 K, respectively. The M_s

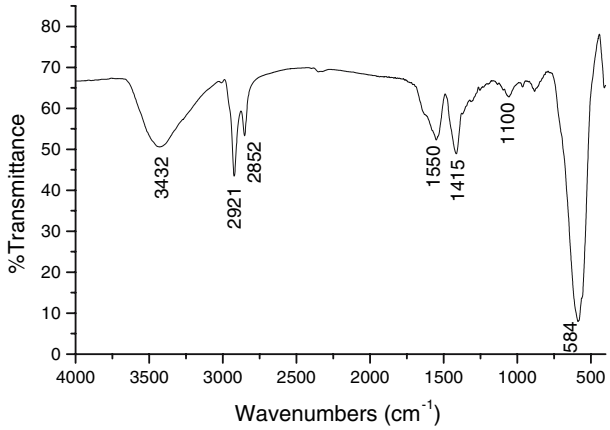

Fig. 4 IR pattern of the $CoFe_2O_4$ hollow spheres and nanocrystals obtained in the typical synthesis

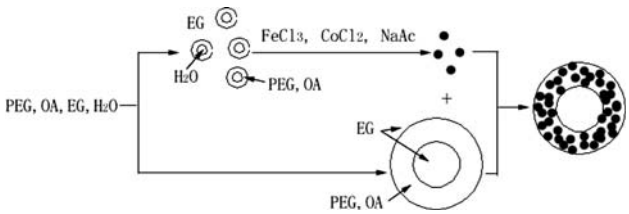

Fig. 5 An illustration of the possible formation process of the $CoFe_2O_4$ hollow spheres and nanocrystals. (PEG, OA, and EG denote polyethylene glycol, oleic acid, and ethylene glycol respectively)

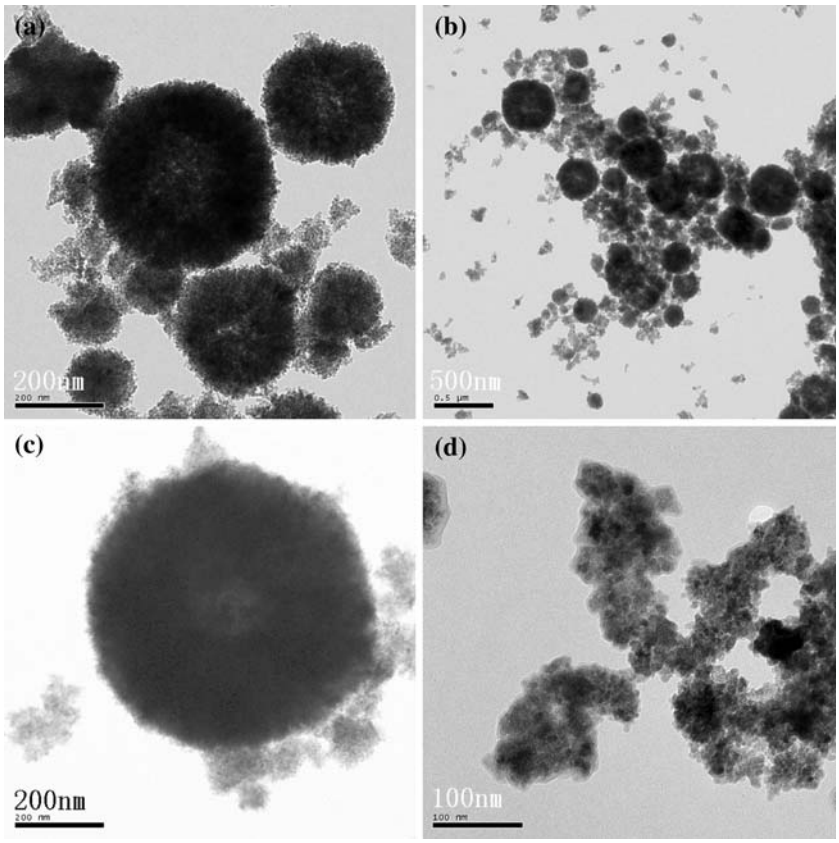

Fig. 3 TEM image of the $CoFe_2O_4$ hollow spheres and nanocrystals, (**a**) oleic acid = 2 mL, polyethylene glycol = 2 mL (**b**) oleic acid = 1 mL, polyethylene glycol = 2 mL (**c**) oleic acid = 2 mL, PVP = 300 mg (**d**) oleic acid = 2 mL

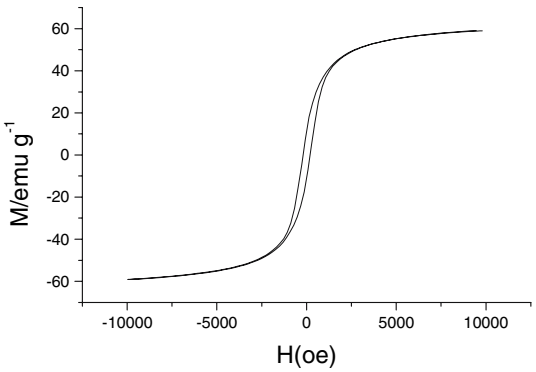

Fig. 6 Hysteresis loop of the $CoFe_2O_4$ nanomaterials obtained in the typical synthesis at 300 K

of the $CoFe_2O_4$ nanomaterials is lower than that of the corresponding bulk material (about 80 emu g^{-1}). Compared with the H_c value of bulk $CoFe_2O_4$ reported in literature (5,400 Oe) [41], the $CoFe_2O_4$ nanomaterials also exhibit smaller coercivity, which should be attributed to their nanostructure [42–43].

Conclusion

In summary, we have succeeded in synthesizing $CoFe_2O_4$ hollow spheres and nanoparticles by a facile solvothermal treatment of an ethylene glycol solution of $FeCl_3 \cdot 6H_2O$, $CoCl_2 \cdot 6H_2O$ and NaAc at 200 °C in the presence of polyethylene glycol and oleic acid. Since it is a simple process, we believe that it can be applied to synthesize other metal oxides. Further research is under progress in our laboratory.

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