Cobalt ferrite nanorings: Ostwald ripening dictated synthesis and magnetic properties†

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$CoFe_2O_4$ nanorings were synthesized by a simple solvothermal process, in which Ostwald ripening was definitely responsible for the formation of hollow structures, and their ferromagnetic behavior at room temperature was observed.

In recent years, the synthesis and functionalization of nanostructured magnetic materials have attracted great interest due to their essential significance in science and their potential applications in catalysis, information storage media, biosensing, ferrofluidics and medical diagnostics.[1] As an important spinel ferrite, cobalt ferrite ($CoFe_2O_4$) is considered to be a good candidate for high-density magnetic storage media and high-performance electromagnetic and spintronic devices because of its large magnetocrystalline anisotropy, moderate saturation magnetization, and remarkable chemical and mechanical stability.[2] Up to now, various chemistry-based approaches such as coprecipitation, thermal decomposition, polyol processes, alkaline reduction, microemulsion, and hydrothermal processes, have been developed to synthesize $CoFe_2O_4$ nanostructures.[3] However, most of the previous reports have focused on the synthesis and application of $CoFe_2O_4$ nanoparticles, and few works about other $CoFe_2O_4$ nanostructures have been reported.[4] For example, Dai *et al.* presented a microemulsion route in combination with subsequent calcination for the synthesis of $CoFe_2O_4$ nanorods, which exhibited a light inflection at low temperature.[5] Moreover, Pham-Huu *et al.* reported the fabrication of $CoFe_2O_4$ nanorods using carbon nanotubes as templates.[6] Overall, further efforts should be devoted to the controllable synthesis of $CoFe_2O_4$ nanostructures with size and shape dependent performances.

In wet chemistry synthesis, organic molecules such as surfactants, polymers, and capping ligands are usually used to manipulate the size and shape of nanomaterials.[7] Very recently, the Ostwald ripening mechanism, in which the growth of bigger particles is at the expense of smaller ones, has been exploited to synthesize hollow nanostructures.[8] For example, Li and Zeng fabricated hollow Sn doped TiO_2 nanospheres *via* Ostwald ripening under hydrothermal conditions.[9] Archer *et al.* reported a simple one-pot template-free synthesis of SnO_2 hollow nanostructures based on an unusual inside-out Ostwald ripening mechanism.[10]

Herein, we develop a poly(vinylpyrrolidone) (PVP) assisted solvothermal route to synthesize $CoFe_2O_4$ nanorings, in which the Ostwald ripening mechanism is definitely responsible for the formation of the hollow structures. The synthesis of the $CoFe_2O_4$ nanorings was carried out by reacting $CoCl_2$, $FeCl_3$, and N_2H_4 in an *N*,*N*-dimethylformamide (DMF) environment while using poly(vinylpyrrolidone) (PVP) as the surfactant during a solvothermal process. Moreover, the magnetic properties of the resultant $CoFe_2O_4$ nanorings were studied by a physical property measurement system (PPMS-9, Quantum Design). The details of the synthetic procedures are given in the ESI.†

Fig. 1 shows the morphological and structural characterization of the sample prepared by the above-mentioned PVP assisted solvothermal process proceeding at 200 °C for 20 h. From Fig. 1a, quite a few ring-like nanostructures with a wall thickness of 10–50 nm, width of 100–300 nm and length of several micrometres can be observed. The magnified TEM image (Fig. 1b) clearly indicates that the as-received sample is not of nanotubes but of nanorings, which is definitely derived from the shape contrast. Moreover, the FESEM (Fig. 1c) image reveals the co-existence of incomplete nanorings and nanoflakes (more FESEM images can be seen Fig. S1 of the ESI†). It seems that the nanorings are evolved from the nanoflakes, which will be discussed later. All the diffraction

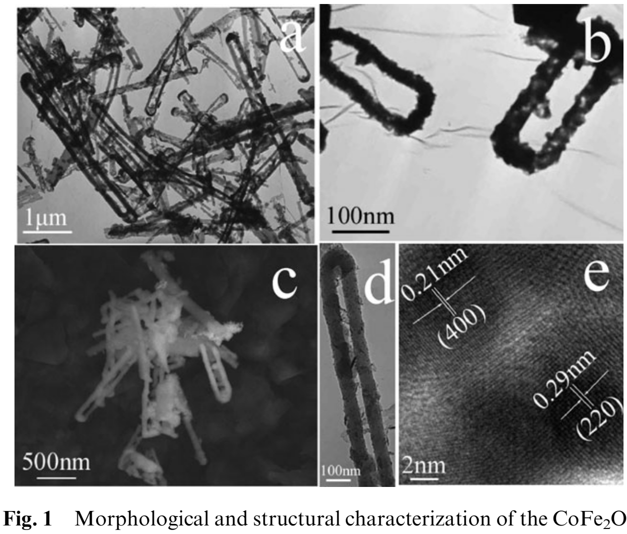

Fig. 1 Morphological and structural characterization of the $CoFe_2O_4$ nanorings: (a), (b) TEM images; (c) FESEM image; (d) TEM image; (e) HRTEM image.

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peaks in the XRD pattern of the nanorings (see ESI Fig. S2†) can be well indexed as cubic $CoFe_2O_4$ with the lattice constant a = 8.391 Å, which is consistent with JCPDS No. 22-1086. No diffraction peaks relating to Fe_2O_3 or Co_3O_4 are observed, indicative of single phase as-synthesized samples. Fig. 1e shows a typical HRTEM image taken on the wall of an individual $CoFe_2O_4$ nanoring as shown in Fig. 1d. As observed, the $CoFe_2O_4$ nanorings are composed of discrete nanoparticles with sizes of 5–10 nm, indicating that the $CoFe_2O_4$ nanorings are polycrystalline in nature. Moreover, the lattice fringes with spacings of 0.21 and 0.29 nm correspond to the {400} and {220} planes of $CoFe_2O_4$, respectively.

In order to clarify the formation process of the $CoFe_2O_4$ nanorings during the solvothermal process, the products resulting from the solvothermal processes with different reaction times were taken out for XRD and TEM characterization. The results of which are shown in Fig. 2. As can be seen from the XRD patterns (Fig. 2a), the precursor $Fe_{6-y}Co_yCl_{2-x}(OH)_{12+x}$ was first formed, and then was transformed into $CoFe_2O_4$ with extension of the reaction time. In terms of morphology, the nanoflakes, which were of $Fe_{6-y}Co_yCl_{2-x}(OH)_{12+x}$ were formed during the first 2 h solvothermal process, as revealed in Fig. 2b. It is believed that in the initial stage of the solvothermal process, the iron cobalt hydroxide with a layered structure was first formed by the reaction of Co^{2+}, Fe^{3+} and OH^-. Then, the Cl^- anions intercalated into the Fe or Co–OH layers to form $Fe_{6-y}Co_yCl_{2-x}(OH)_{12+x}$ due to the large inter-layer spacing and charge balance.[11] Due to the features of the layered structure, the $Fe_{6-y}Co_yCl_{2-x}(OH)_{12+x}$ nanoflakes could be achieved under the solvothermal conditions.[12] In the subsequent solvothermal process, the metastable $Fe_{6-y}Co_yCl_{2-x}(OH)_{12+x}$ was gradually transformed into $CoFe_2O_4$ *via* a dissolution and recrystallization process accompanied by release of Cl^- and OH^-. As a result, entities somewhat like porous nanoflakes, as shown in Fig. 2c, which were actually assemblies of $CoFe_2O_4$ nanoparticles, appeared after 6 h reaction. With extension of reaction time, an interior space at the centre of the nanoflakes was formed, in which Ostwald ripening dictated the growth by consuming the small $CoFe_2O_4$ nanoparticles existing in the inner region. With prolonged reaction for up to 12 h, the $CoFe_2O_4$ nanorings, as shown in Fig. 2d, were ultimately formed due to the complete dissolution of the inner crystallites *via* the Ostwald ripening process. Based on the morphology evolution as described above, the growth mechanism of the $CoFe_2O_4$ nanorings can be schematically illustrated, as shown in Fig. 2e. It should be mentioned that a similar Ostwald ripening mechanism was also proposed by Zeng *et al.* and Archer *et al.* for the hydrothermal preparation of TiO_2 or SnO_2 hollow nanospheres.[9,10]

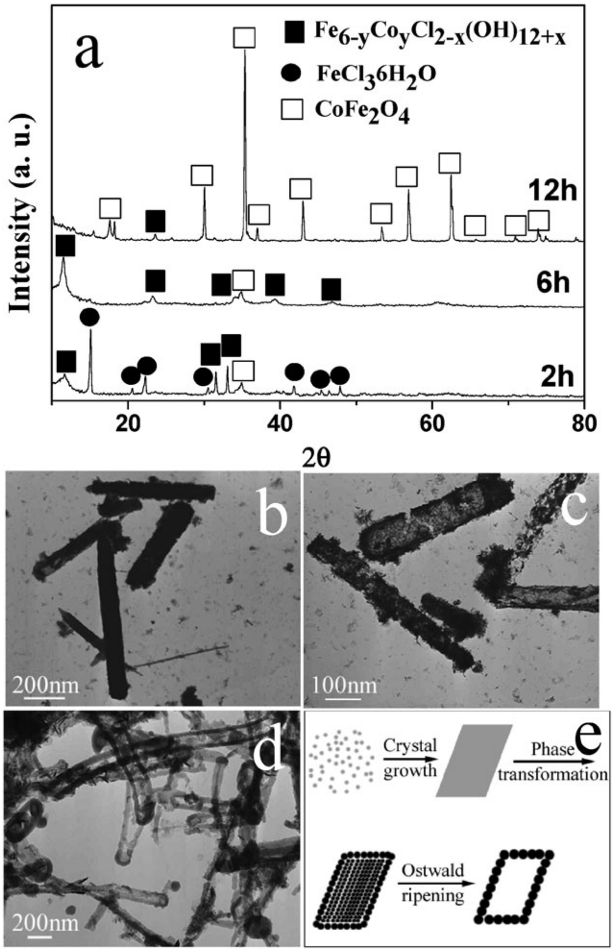

Fig. 2 (a) XRD pattern and (b), (c), (d) TEM images of the products prepared by the PVP assisted solvothermal process at 200 °C for different times; (e) schematic illustration for the growth mechanism of the $CoFe_2O_4$ nanorings.

Although the exact mechanism for the growth of $CoFe_2O_4$ nanorings is not clear, it is found that reactants such as PVP, N_2H_4 and DMF play critical roles in the formation of $CoFe_2O_4$ nanorings. Previously, PVP and DMF were usually employed to synthesize hollow nanostructures.[13] PVP acted as the soft template to tune the morphology of nanostructures, while DMF acted as not only the solvent but also the weak reducing agent. Herein, only nanoparticles were obtained in the case of the absence of PVP and DMF, which further confirms their important functions in the formation of the nanorings. Moreover, the addition of N_2H_4 ensured the formation of $CoFe_2O_4$ under hydrothermal conditions due to the reducing and mineralizing abilities of N_2H_4.

The magnetic measurements on the $CoFe_2O_4$ nanorings were performed on a quantum design PPMS magnetometer. Fig. 3a shows the curves of magnetization *versus* applied magnetic field at 10 and 300 K. As can be seen, both the M–H curves at 10 and 300 K exhibit a typical hysteresis loop with direct-temperature-proportional saturation magnetization, remnant magnetization and coercivity values indicative of the ferromagnetic behavior of $CoFe_2O_4$ nanorings in this temperature range. The temperature dependence of the magnetization of the sample in the temperature range 10–300 K was further characterized by the zero-field cooling (ZFC) and field cooling (FC) procedures in an applied magnetic field of 100 Oe, as shown in Fig. 3b. It is found that the ZFC curve gradually deviates from the FC curve at temperatures below 300 K. Moreover, the ZFC magnetization dramatically decreases with temperature, while the FC magnetization slightly changes. Therefore, the ZFC and FC analyses further confirm that the $CoFe_2O_4$ nanorings exhibit ferromagnetic behavior at room temperature, which is consistent with the previous report.[5]

$CoFe_2O_4$ nanorings have been fabricated by a PVP assisted solvothermal process in DMF, in which the Ostwald ripening

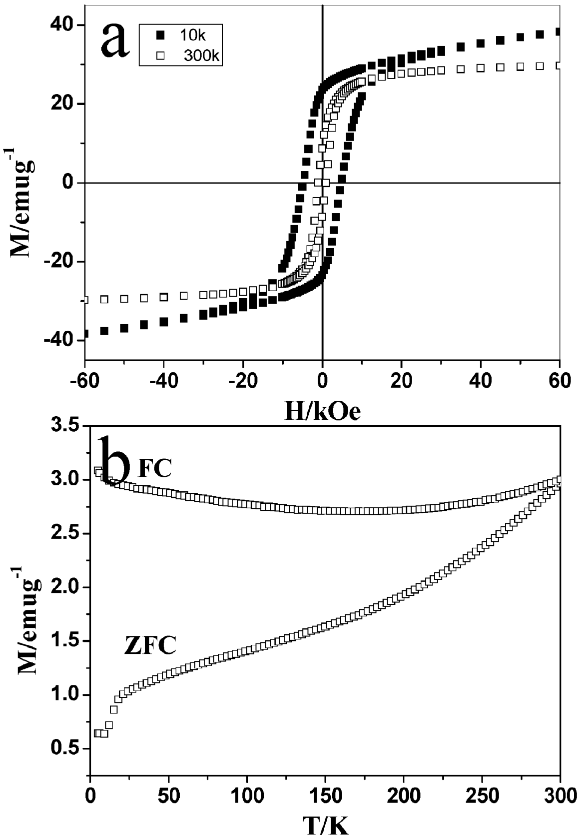

Fig. 3 (a) The *M–H* curves at 10 and 300 K, and (b) ZFC and FC curves with an applied field of 100 Oe of the $CoFe_2O_4$ nanorings.

mechanism is definitely involved. Reactants such as PVP, DMF and N_2H_4 play critical roles in the formation of the $CoFe_2O_4$ nanorings. Moreover, the $CoFe_2O_4$ nanorings exhibit ferromagnetic behavior at room temperature, which could find potential applications in high-density magnetic storage media, and high-performance electromagnetic and spintronic devices.

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