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Rapid communication

Synthesis and magnetic properties of nickel ferrite nano-octahedra

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Abstract

High yield of nickel ferrite nano-octahedra with size distribution from 40 to 90 nm were synthesized through a simple hydrothermal method. The formation of faceted octahedra enclosed by {111} planes implies the much faster growth rate along ⟨100⟩ over ⟨111⟩ for face-centered cubic phase during hydrothermal process. Magnetic measurements indicated that the sample is soft-magnetic materials with much lower coercivity and much higher saturation magnetization compared to the nickel ferrite nanocrystals with similar size distribution but irregular shapes reported earlier.

Keywords: Nickel ferrite; Nano-octahedron; Magnetic property; Hydrothermal

1. Introduction

AFe_2O_4 ferrospinels are a very important group of magnetic materials since they cover a wide range of applications from low wave number to microwave and from low to high permeability [1]. The unit cell contains 32 O-atoms in cubic closest packing with eight tetrahedral and 16 octahedral occupied sites. Among the ferrospinels, the inverse type is particularly interesting due to its high magnetocrystalline anisotropy, high saturation magnetization, and unique magnetic structure. Nickel ferrite ($NiFe_2O_4$) with an inverse spinel structure shows ferrimagnetism that originates from magnetic moment of anti-parrallel spins between Fe^{3+} ions at tetrahedral sites and Ni^{2+} ions at octahedral sites [2]. As more and more attentions have been devoted to the nano-sized magnetic materials for their unique properties compared to their bulk counterparts, the scientific interest on nano-sized nickel ferrite is on the rising. Various methods, such as sol–gel [3], co-precipitation [4], sonochemical preparation [5], citrate precursor techniques [6] and mechanical alloying [7], have been developed to fabricate nickel ferrite nanoparticles. However, the irregularity of particle morphology and the agglomeration of particles still remain the main problems. Hydrothermal methods have been extensively used to prepare diversiform nano-particles due to the good controllability of particle morphology. In this paper, we report the hydrothermal synthesis and magnetic property of nickel ferrite nano-octahedra.

2. Experiment

For hydrothermal reactions, all the reagents were of analytical grade and used as received. In a typical synthesis process, 0.5 mmol $NiCl_2 \cdot 6H_2O$ and 1 mmol $Fe(NO_3)_3 \cdot 9H_2O$ were dissolved in 6 ml distilled water, followed by addition of 6 ml 2 M KOH solution. The mixture was then transferred into a Teflon-lined stainless-steel autoclave of 20 mL capacity. The sealed tank was heated to and maintained at 160 °C for 10 h in an oven and then air-cooled to room temperature (RT). The resulting black–brown precipitates were collected by filtration and washed with de-ionized water and pure

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ethanol for several times, and finally dried in a vacuum oven at 60 °C for 5 h.

To identify the product structure, powder X-ray diffraction (XRD) patterns of the samples were recorded by RIGAKU-DMAX2500 X-ray diffractometer with Cu $K\alpha$ radiation ($\lambda = 1.54056$ Å) at a scanning rate of 5°/min for 2θ ranging from 5° to 85°. The morphologies and microstructures of the as-synthesized samples were observed by FEI Sirion scanning electron microscope (SEM) at 5 KV and JEOL-2010 transmission electron microscope (TEM) at 200 KV, respectively. Magnetic properties of the as-synthesized sample were measured using a physical property measurement system (PPMS).

3. Results and discussion

The XRD pattern of the as-synthesized sample shown in Fig. 1 presents many strong and sharp crystalline peaks attributed to the face-centered cubic $NiFe_2O_4$ phase with lattice constant $a = 0.833$ nm (PDF #100325). Besides, the two weak peaks between (220) and (311), (311) and (222) came from the existence of a tiny amount of α-Fe_2O_3 phase (PDF # 840309). The SEM image in Fig. 2 shows the general morphology and high yield of the $NiFe_2O_4$ octahedrons. The facets of the octahedrons are apparently distinguishable, as is further revealed by the single one in the inset. The size distribution of the octahedrons ranges from 40 to 90 nm. Further observation on the facet structure of the octahedrons was conducted by TEM and high-resolution TEM (HRTEM). Fig. 3a–d shows the various projection morphologies of octahedrons when along different projection directions, from which the high geometric symmetry of the octahedron can be obtained. The consistent lattice orientation of the octahedral particles reveals their single crystalline nature, while the evolutions of brightness contrast from right-top to left-bottom of the particle in Fig. 3a, and that from center to edges of the particles in Fig. 3b and c, respectively, reflect the corresponding variations in sample thickness along the direction of incident electron beam, which could be ascribed to the octahedral shape of the nano-crystals. The Fast Fourier Transform (FFT) pattern (inset in Fig. 3a) from the whole lattice region of Fig. 3a can be indexed to the face-centered cubic $NiFe_2O_4$ phase along the $\langle 110 \rangle$ zone axis, indicating that the facets are {111} planes. Similar analysis of the FFT patterns in Fig. 3b and c reveals that the corresponding octahedrons are oriented with [001] and [111] parallel to the incident electron beam, respectively. As a summary of the above observation, a structure model of the nano-crystalline octahedron enclosed by {111} planes is presented in Fig. 3d. The shape of crystals is mostly determined by the relative growth rate between different directions during their formation. In terms of the shape evolution of polyhedral nano-crystals with cubic structure, Wang pointed out that the ratio R, the growth rate along $\langle 100 \rangle$ to that along $\langle 111 \rangle$, plays a key role in determining the final morphology of nano-particles [8]. With the increasing of R, the shape of particles undergoes an evolution from cube ($R = 0.53$) to cubooctahedron ($R = 0.87$), and finally to octahedron ($R = 1.73$). It is known that nano-particles usually have specific shape because a single-crystal nano-particle has to be enclosed by crystallographic facets that have lower energy [9]. Therefore, it is believed that the formation of nickel ferrite nano-crystalline octahedrons during the hydrothermal process proceeds in a way with much faster growth rate along $\langle 100 \rangle$ over that along $\langle 111 \rangle$ due to the lowest energy of the {111} surfaces.

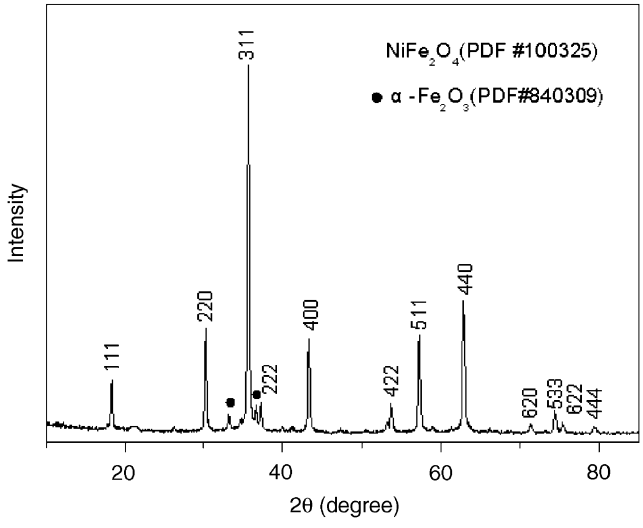

Fig. 1. XRD pattern of the as-synthesized nickel ferrite octahedrons.

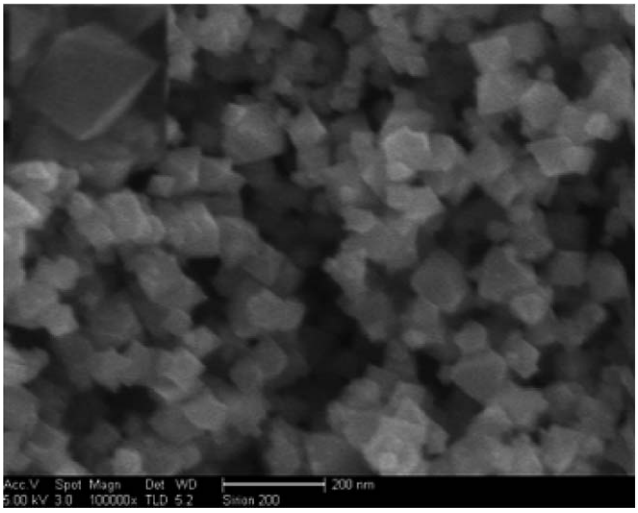

Fig. 2. SEM image of the as-synthesized nickel ferrite octahedrons (the inset shows an enlarged single octahedron).

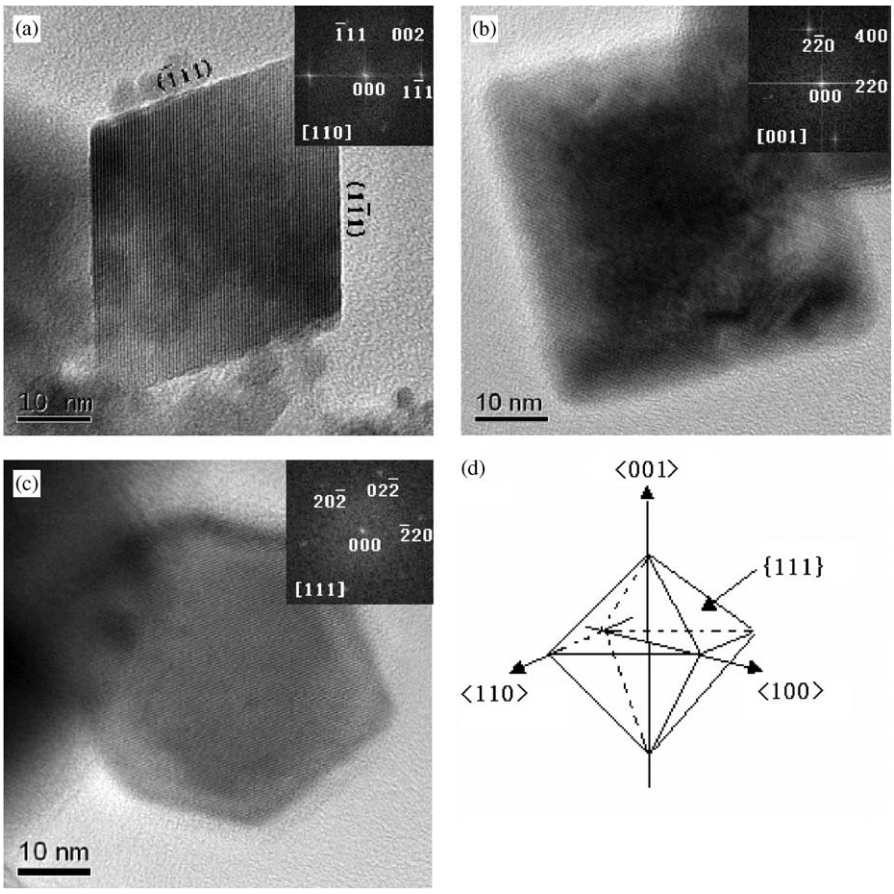

Fig. 3. HRTEM images of the nickel ferrite octahedrons observed along different directions: (a) along [110]; (b) along [001]; (c) along [111]. The insets are corresponding FFT patterns; (d) structure model of an octahedral crystal.

The magnetization curves of the nickel ferrite nano-octahedrons measured at RT and 10 K are shown in Fig. 4. At RT, the sample presented excellent soft-magnetic property with coercivity less than 30 Oe, while at 10 K the coercivity increased to 268 Oe. The saturation magnetization of the sample at RT and 10 K was 49.6 and 57.6 emu/g, respectively, close to the bulk value of nickel ferrite. It is well known that for magnetic particles the size has significant influence on their magnetic properties. For relatively larger particles, magnetic domains are formed to reduce the static magnetic energy. The number of domains diminishes with decreasing particle size. The particles turn into single domain ones with their size under a critical radius (for nickel ferrite, this parameter is about 100 nm [10]), resulting in the increasing coercive force due to vanishing of the magnetization caused by the movement of domain walls. It was earlier reported by Morrish et al. [11] that at RT the nickel ferrite nanoparticles, with irregular shapes and sizes from 60 to 100 nm, exhibited less saturation magnetization (37.6 emu/g) and much larger coercivity (500 Oe) compared to the values of their bulk counterpart. Although the size distribution of particles in our experiment is in the similar region to that of literature [11], the coercive force is much lower while the saturation magnetization is much large, which should be related to the unique faceted structure of the nano-octahedrons. Further investigation on the relationship between the magnetic properties and the faceted structure of nickel ferrite is underway.

4. Conclusions

High yield of soft-magnetic nickel ferrite nano-octahedra with size distribution from 40 to 90 nm have been synthesized through a simple hydrothermal method. The morphology of octahedron enclosed by {111} planes implies much faster growth rate along $\langle 100 \rangle$ over $\langle 111 \rangle$ directions during the formation of nickel ferrite nano-phase. For this sample, the coercivity was less than 30 Oe at RT and increased to 268 Oe at 10 K, and the saturation magnetization was 57.6 and 49.6 emu/g at 10 k and RT, respectively. Compared to the nickel ferrite nano-crystals with similar size

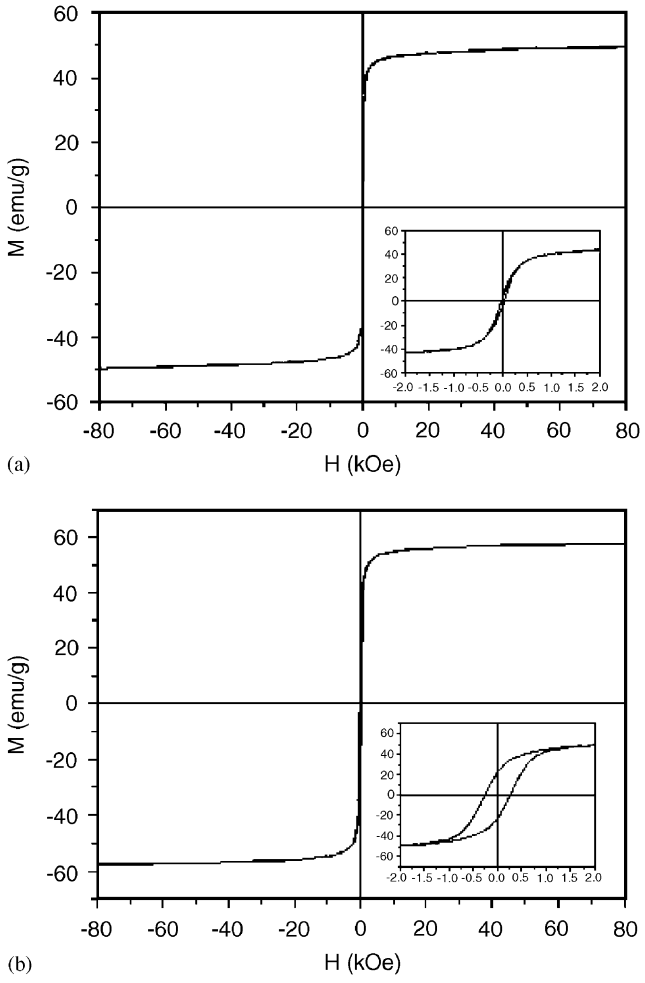

Fig. 4. Magnetization curves of nickel ferrite nano-octahedrons at (a) 300 K and (b) 10 K. The insets are the enlargements of the center part of the curves.

distribution but irregular shapes reported earlier, our sample exhibited much lower coercivity and much higher saturation magnetization, which is probably due to their unique faceted octahedral morphology.

Acknowledgments

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