Synthesis and Charaterization of Hexagonal-like Fe_3O_4 via Glycothermal Route

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Hexagonal-like Fe_3O_4 nanoparticles were hydrothermally synthesized from iron chloride, using diethylene glycol (DEG)–water mixed solvent as the medium. The as-prepared powders were characterized in detail by conventional techniques such as X-ray diffraction, and transmission electron microscopy, and their magnetic properties were evaluated on a vibrating magnetometer.

Magnetic nanoprticles have been widely studied because of their fascinating properties and wide range of potential applications in ferrofluids, information storage and medicine. Among magnetic particles, iron oxides (Fe_2O_3 and Fe_3O_4) have been extensively investigated. Various methods have been reported in the literature for the preparation of ultrafine particles of Fe_3O_4, such as reduction of hematite by CO/CO_2[1] or H_2,[2] coprecipitation of the solution of iron/ferric mixed salt,[3] microwave plasma synthesis,[4] microemulsion methods,[5] ultrasound irradiation.[6] Among them, hydrothermal process has been widely used to prepare single crystal and ceramic powder. In the past ten years, it has been employed to generate novel oxides,[7] polyanion clusters,[8] and zeolite materials.[9] In this paper, hexagonal-like Fe_3O_4 particles have been prepared by a one-step hydrothermal procedure from iron(III) chloride ($FeCl_3$), diamine hydrate ($H_4N_2 \cdot H_2O$) and sodium hydroxide (NaOH) in diethylene glycol (DEG)–water mixed solvent.

The chemical reagents used in the work were iron(III) chloride ($FeCl_3 \cdot 6H_2O$), diethylene glycol (DEG), sodium hydroxide (NaOH), and hydazine hydrate ($H_4N_2 \cdot H_2O$, 50% water). All the chemicals were of analytical grade. An appropriate amount of iron(III) chloride (0.15g) and 30-mL DEG were put into a Teflon-lined stainless autoclave (50 mL). Sodium hydroxide (0.6 g) was dissolved into 5.0-mL of $H_4N_2 \cdot H_2O$ and then the mixture was slowly dropped into the Teflon-lined stainless autoclave. Then, the autoclave was put into an oven, kept at 160 °C for 12 h, then cooled to room temperature on standing. The products were filtered, washed several times with distilled water and absolute ethanol, and finally dried in a vacuum oven at 25 °C for 12 h.

The samples, which were recorded at a scanning rate of 0.05°/s with the 2θ range from 10 to 70°, were characterized by XRD using an X-ray diffractometer with high-intensity Cu Kα radiation ($\lambda = 1.5418$ Å). TEM images were taken with a Hitachi model H-800 transmission electron microscope, using an accelerating voltage of 200 kV. Their magnetic properties were measured on a BHV-55 vibrating sample magnetometer at room temperature.

XRD pattern (Figure 1) of the prepared product can be clearly seen and indexed to the face-centered cubic spinel structure of pure Fe_3O_4 with a lattice parameter of $a = 8.393$ Å (JCPDS card No. 85-1436), which is close to that reported in the previous literature.[10] No peaks of metal hydroxides or other impurities were detected, suggesting the complete transformation to Fe_3O_4. The strong and sharp peaks revealed that Fe_3O_4 particles were well crystallized.

Morphology and size of the product were studied by TEM. Figure 2a showed that as-prepared sample mainly consisted of hexagonal flakes with the size of 100–200 nm. Figure 2b gave a typical hexagonal nanoflake and the corresponding SAED pattern (inset in Figure 2b). The diffraction spots suggested that the flake was single crystalline. ED patterns recorded on different individual nanoflakes were essentially the same, implying the single crystalline nature of these flakes. In the glycothermal route, the nature of solvent has great influence on the final product.[11,12] DEG is a weak bidentate ligand and can react with metal ions to form metal complexes, which may serve as molecular templates in control of the crystal growth. The use of DEG also can efficiently stabilize the surface of the nanoparticles,[14] thus avoids the agglomeration of the initial formed nuclei and may favor the formation of the hexagonal-like flakes. To improve the understanding of the effect of DEG, contrast experiment was carried out in aqueous solution without DEG, keeping the concen-

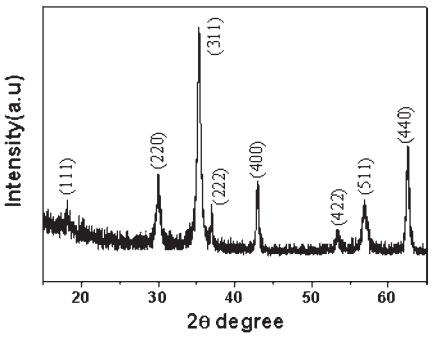

Figure 1. XRD pattern of the sample.

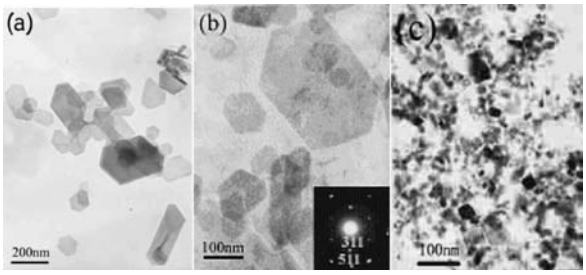

Figure 2. a) TEM image of the sample. b) A typical hexagonal Fe_3O_4 nanoflake and the corresponding ED pattern (inset in Figure 2b). C) TEM image of the sample prepared without DEG.

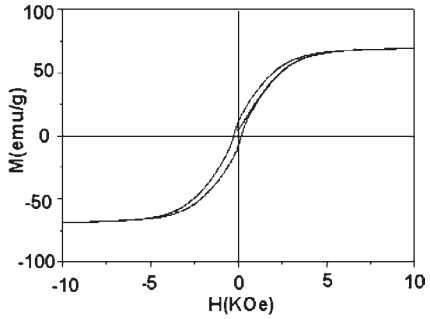

Figure 3. M–H (magnetization–hysteresis) loop of as-prepared Fe_3O_4 nanoflakes measured at room temperature.

trations of reactants and temperatures constant. TEM image indicated that a few nanoparticles were obtained (Figure 2c). This difference suggested that DEG play an important role in the formation of hexagonal-like magnetite flakes. The exact influence of the polyol solvent on the morphology undoubtedly needs further investigation.

Magnetic measurements on thus-prepared nanoflakes were conducted and M–H hysteresis loop was presented in Figure 3. The saturation magnetization (Ms) reached 68 emu/g, lower than those of similarly sized nanoparticles prepared by other methods[15] and bulk Fe_3O_4 (92 emu/g),[16] possibly for their novel morphology.[17] The coercivity reached 174 Oe, not showing superparamagnetization due to the particle size exceeded the single magnetic domain size of Fe_3O_4.[18]

We have successfully prepared nanoscale hexagonal-like Fe_3O_4 flakes using iron(III) chloride ($FeCl_3$) and hydrazine hydrate ($H_4N_2 \cdot H_2O$) as starting materials and DEG–water mixed solvent as the medium. The results obtained from TEM measurements indicate that the DEG has a significant influence on the formation of flake-like Fe_3O_4 nanocrystals. The resultant Fe_3O_4 nanoflakes may provide interesting possibilities for further applications in the ferrofluids, information storage, and medicine fields.

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