Microwave-Assisted Rapid Synthesis of Magnetite Fe₃O₄ Nanoparticles†

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Using FeSO₄(NH₄)₂SO₄·6H₂O and triethanolamine as iron and alkali sources, magnetite Fe₃O₄ nanoparticles are synthesized through a microwave-assisted chemical route. The as-prepared products are characterized by X-ray diffraction, field-emission scanning electron microscopy and transmission electron microscopy. The sizes of Fe₃O₄ nanoparticles ranging from 5 to 20 nm are obtained. The magnetic property of the obtained Fe₃O₄ nanoparticles is studied by vibrating sample magnetometer. Magnetic analysis reveals that the Fe₃O₄ nanoparticles are ferromagnetic with a saturation magnetization of 25.5 emu·g⁻¹. The growth mechanism of Fe₃O₄ nanoparticles is also simply discussed.

Key Words: Fe₃O₄ nanoparticles, Microwave, Magnetic property.

INTRODUCTION

As an important member of spinel-type ferrite, magnetite (Fe₃O₄) has received much attention for its potential applications in lithium ion batteries¹, magnetic resonance imaging², biomolecular nanopatterning³, high-density data storage⁴, etc. Up to date, various methods were applied to prepare Fe₃O₄ nanomaterials, such as hydrothermal⁵, solvothermal⁶, ultrasonic chemical co-precipitation⁷, microwave-assisted⁸, external magnetic field-assisted reverse co-precipitation⁹, thermal decomposition of the iron alkoxide precursor¹⁰. To our best of knowledge, a convenient and operable method for synthesizing Fe₃O₄ nanoparticles is still a great challenge. In this work, Fe₃O₄ nanoparticles with diameters of 5-20 nm are fabricated through a simple, rapid microwave-assisted refluxing route. The crystal structure and morphology are studied by XRD, field-emission scanning electron microscope and TEM measurements. Magnetic property study shows that the as-prepared Fe₃O₄ nanoparticles are ferromagnetic.

EXPERIMENTAL

In a typical experimental procedure, 1 mmol ferrous ammonium sulfate [FeSO₄(NH₄)₂SO₄·6H₂O] was dissolved in 50 mL deionized water in a 100 mL conical flask to obtain solution A. Meanwhile, 0.75 mmol triethanolamine (C₆H₁₅NO₃) was dissolved in 10 mL deionized water to obtain solution B. Then, The solution B was added into the solution A under

stirring. Keep stirring until the solution colour changing from dark green to grass green. The obtained grass green reaction solution was transferred into a MAS-II apparatus, then irradiated with microwave irradiation (power 300 w) under stirring with 500 r/min at the refluxing temperature of 90 °C for 8 min. After cooling down to room temperature and standing overnight, the black precipitate has strong magnetism and can be separated by a magnet, washed with anhydrous ethanol and deionized water for several times and then finally dried in a vacuum at 60 °C for 6 h.

Microwave-heating was performed on a MAS-II microwave synthesis/extraction reaction workstation (work frequency 2.45GHz, power adjustable range 0-1000W, Shanghai Sineo Microwave Chemistry Technology Co., Shanghai, China). The phase purity of the as-synthesized products was examined by X-ray diffraction using a Philips X'Pert PRO SUPER X-ray diffractometer equipped with graphite monochromatized CuK_α radiation ($\lambda = 1.541874\text{\AA}$). Field-emission scanning electron microscope images of the sample were taken on a field-emission microscope (JEOL JSM-6700F). The transmission electron microscope images of the samples were performed on a H-7650 transmission electron microscope.

RESULTS AND DISCUSSION

The crystal structure of as-prepared products was investigated by XRD analysis. Fig. 1 shows a typical XRD pattern of

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the products. Seven prominent XRD peaks can be indexed to the Fe₃O₄ crystal planes of (111), (220), (311), (400), (422), (511) and (440), which present a face-centered cubic (fcc) spinel structure with the measured lattice constants $a = 8.394 \text{ \AA}$, agreeing with the standard values of the reported Fe₃O₄ data (JCPDS card No. 19-0629). The sharp diffraction peaks indicate that the synthesized Fe₃O₄ products are highly crystalline.

Fig. 1. Typical XRD pattern of as-prepared products

The morphology and microstructure of the prepared Fe₃O₄ products were characterized by field emission scanning electron microscopy and transmission electron microscopy. Fig. 2(a) and 2(b) present the field-emission scanning electron microscope images of Fe₃O₄ products prepared by a microwave-assisted refluxing route using FeSO₄(NH₄)₂SO₄·6H₂O as iron source in the triethanolamine solution, which indicate that nanoparticles are main products. Corresponding TEM images are shown in Fig. 2(c) and (d). We can see that the obtained Fe₃O₄ nanoparticles are homogeneously dispersed. The diameters of particles range from 5 to 20 nm.

In the reaction solution, as an alkaline organic amine, triethanolamine can hydrolyze to produce hydroxyl ion (OH⁻)

[eqn. (1)]. Simultaneously, a good deal of free ferrous ions (Fe²⁺) were created through the dissociation of ferrous ammonium sulfate [FeSO₄(NH₄)₂SO₄] in the solution [eqn. (2)]. Under the condition of such alkaline environment, ferrous ion (Fe²⁺) would quickly react with hydroxyl ion (OH⁻) to generate Fe(OH)₂ [eqn. (3)]. According to the different cell potentials in alkaline solution: $E^0\text{Fe}(\text{OH})_3/\text{Fe}(\text{OH})_2 = -0.56 \text{ eV}$; $E^0\text{O}_2/\text{OH}^- = 0.401 \text{ eV}$, Fe(OH)₂ are unstable and has strong reducibility. By means of controlling oxidation time, Fe(OH)₂ can be partly oxidized into Fe(OH)₃ by O₂ from the air dissolved in water [eqn. (4)]. Finally, new-produced ferric hydroxide Fe(OH)₃ combines with pre-formed unreacted ferrous hydroxide Fe(OH)₂ to produce magnetite Fe₃O₄ through dehydration⁵ [eqn. (5)]. Besides as an alkaline reagent, it is presumed that triethanolamine can also acts as a modification agent influencing the morphology and size of Fe₃O₄ crystallites. Due to its strong complexing ability with metal ions, triethanolamine may selectively adsorb on the particular crystallographic facets of Fe₃O₄ crystals, prevent the aggregation between particles and lead to the formation of smaller nanoparticles. The possible chemical reaction to synthesize Fe₃O₄ nanoparticles are summarized as follows:

The magnetic property of the as-obtained Fe₃O₄ nanoparticles has been investigated on a vibrating sample magnetometer at room temperature. Fig. 3 shows magnetic hysteresis loop of as-obtained Fe₃O₄ nanoparticles measured at room temperature. Magnetic property study shows that the Fe₃O₄ nanoparticles are ferromagnetic. The coercivity (H_c) is 186 Oe and the remnant magnetization (M_r) is 5.86 emu·g⁻¹. The saturation magnetization (M_s) is 25.5 emu·g⁻¹, which is smaller than that of the corresponding bulk value of Fe₃O₄ (92 emu·g⁻¹)¹¹. The decrease of saturation magnetization may due to the smaller particle size and existence of a few non-magnetic triethanolamine molecules on the surface of Fe₃O₄ nanoparticles^{12,13}. The result agrees with the fact that the magnetization of small particles decreases as the particle size decreases.

Fig. 2. Morphologies of the Fe₃O₄ products: (a, b) field-emission scanning electron microscope image, (c, d) TEM image

Fig. 3. Magnetic hysteresis loop of the as-obtained Fe₃O₄ nanoparticles measured at room temperature

Conclusion

In conclusion, Fe₃O₄ nanoparticles with sizes of 5-20 nm were successfully prepared by employing a rapid microwave-assisted refluxing method using FeSO₄(NH₄)₂SO₄·6H₂O as iron source in the triethanolamine solution. Magnetic hysteresis loop shows that the as-obtained Fe₃O₄ nanoparticles are ferromagnetic. The coercivity (H_c) is 186 Oe and the remnant magnetization (M_r) is 5.86 emu·g⁻¹. The saturation magnetization (M_s) is 25.5 emu·g⁻¹. The method for synthesizing Fe₃O₄ nanoparticles is feasible, quick, nontoxic and eco-friendly.

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