

## Microwave-Assisted Rapid Synthesis of Magnetite Fe<sub>3</sub>O<sub>4</sub> Nanoparticles†

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Using FeSO<sub>4</sub>(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>·6H<sub>2</sub>O and triethanolamine as iron and alkali sources, magnetite Fe<sub>3</sub>O<sub>4</sub> 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 Fe<sub>3</sub>O<sub>4</sub> nanoparticles ranging from 5 to 20 nm are obtained. The magnetic property of the obtained Fe<sub>3</sub>O<sub>4</sub> nanoparticles is studied by vibrating sample magnetometer. Magnetic analysis reveals that the Fe<sub>3</sub>O<sub>4</sub> nanoparticles are ferromagnetic with a saturation magnetization of 25.5 emu·g<sup>-1</sup>. The growth mechanism of Fe<sub>3</sub>O<sub>4</sub> nanoparticles is also simply discussed.

**Key Words:** Fe<sub>3</sub>O<sub>4</sub> nanoparticles, Microwave, Magnetic property.

### INTRODUCTION

As an important member of spinel-type ferrite, magnetite (Fe<sub>3</sub>O<sub>4</sub>) has received much attention for its potential applications in lithium ion batteries<sup>1</sup>, magnetic resonance imaging<sup>2</sup>, biomolecular nanopatterning<sup>3</sup>, high-density data storage<sup>4</sup>, *etc.* Up to date, various methods were applied to prepare Fe<sub>3</sub>O<sub>4</sub> nanomaterials, such as hydrothermal<sup>5</sup>, solvothermal<sup>6</sup>, ultrasonic chemical co-precipitation<sup>7</sup>, microwave-assisted<sup>8</sup>, external magnetic field-assisted reverse co-precipitation<sup>9</sup>, thermal decomposition of the iron alkoxide precursor<sup>10</sup>. To our best of knowledge, a convenient and operable method for synthesizing Fe<sub>3</sub>O<sub>4</sub> nanoparticles is still a great challenge. In this work, Fe<sub>3</sub>O<sub>4</sub> 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 Fe<sub>3</sub>O<sub>4</sub> nanoparticles are ferromagnetic.

### EXPERIMENTAL

In a typical experimental procedure, 1 mmol ferrous ammonium sulfate [FeSO<sub>4</sub>(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>·6H<sub>2</sub>O] was dissolved in 50 mL deionized water in a 100 mL conical flask to obtain solution A. Meanwhile, 0.75 mmol triethanolamine (C<sub>6</sub>H<sub>15</sub>NO<sub>3</sub>) 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<sub>α</sub> 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 Fe<sub>3</sub>O<sub>4</sub> 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 Fe<sub>3</sub>O<sub>4</sub> data (JCPDS card No. 19-0629). The sharp diffraction peaks indicate that the synthesized Fe<sub>3</sub>O<sub>4</sub> products are highly crystalline.

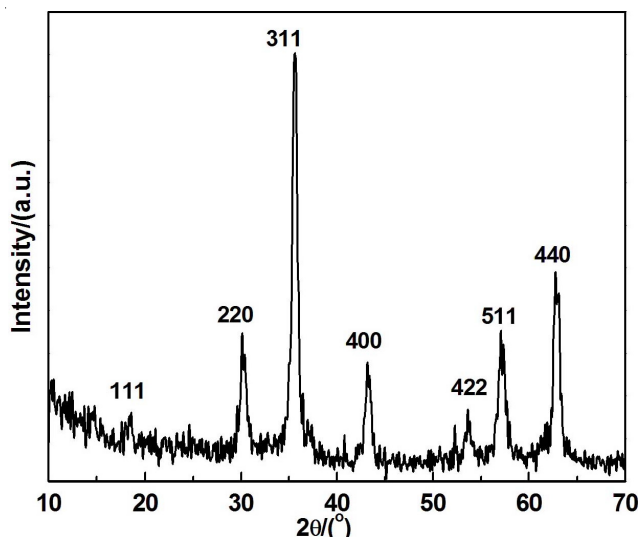


Fig. 1. Typical XRD pattern of as-prepared products

The morphology and microstructure of the prepared Fe<sub>3</sub>O<sub>4</sub> 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 Fe<sub>3</sub>O<sub>4</sub> products prepared by a microwave-assisted refluxing route using FeSO<sub>4</sub>(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>·6H<sub>2</sub>O 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 Fe<sub>3</sub>O<sub>4</sub> 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<sup>-</sup>)

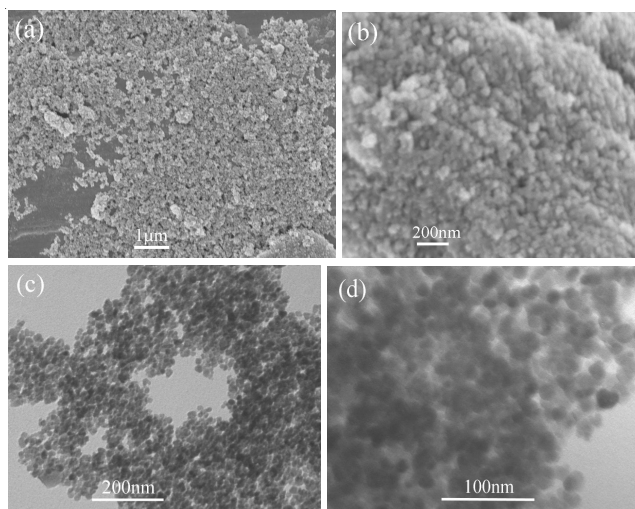
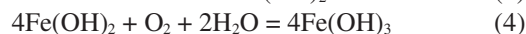
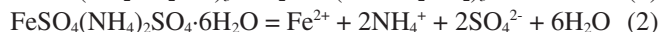


Fig. 2. Morphologies of the Fe<sub>3</sub>O<sub>4</sub> products: (a, b) field-emission scanning electron microscope image, (c, d) TEM image

[eqn. (1)]. Simultaneously, a good deal of free ferrous ions (Fe<sup>2+</sup>) were created through the dissociation of ferrous ammonium sulfate [FeSO<sub>4</sub>(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>] in the solution [eqn. (2)]. Under the condition of such alkaline environment, ferrous ion (Fe<sup>2+</sup>) would quickly react with hydroxyl ion (OH<sup>-</sup>) to generate Fe(OH)<sub>2</sub> [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)<sub>2</sub> are unstable and has strong reducibility. By means of controlling oxidation time, Fe(OH)<sub>2</sub> can be partly oxidized into Fe(OH)<sub>3</sub> by O<sub>2</sub> from the air dissolved in water [eqn. (4)]. Finally, new-produced ferric hydroxide Fe(OH)<sub>3</sub> combines with pre-formed unreacted ferrous hydroxide Fe(OH)<sub>2</sub> to produce magnetite Fe<sub>3</sub>O<sub>4</sub> through dehydration<sup>5</sup> [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 Fe<sub>3</sub>O<sub>4</sub> crystallites. Due to its strong complexing ability with metal ions, triethanolamine may selectively adsorb on the particular crystallographic facets of Fe<sub>3</sub>O<sub>4</sub> crystals, prevent the aggregation between particles and lead to the formation of smaller nanoparticles. The possible chemical reaction to synthesize Fe<sub>3</sub>O<sub>4</sub> nanoparticles are summarized as follows:



The magnetic property of the as-obtained Fe<sub>3</sub>O<sub>4</sub> nanoparticles has been investigated on a vibrating sample magnetometer at room temperature. Fig. 3 shows magnetic hysteresis loop of as-obtained Fe<sub>3</sub>O<sub>4</sub> nanoparticles measured at room temperature. Magnetic property study shows that the Fe<sub>3</sub>O<sub>4</sub> nanoparticles are ferromagnetic. The coercivity ( $H_c$ ) is 186 Oe and the remnant magnetization ( $M_r$ ) is 5.86 emu·g<sup>-1</sup>. The saturation magnetization ( $M_s$ ) is 25.5 emu·g<sup>-1</sup>, which is smaller than that of the corresponding bulk value of Fe<sub>3</sub>O<sub>4</sub> (92 emu·g<sup>-1</sup>)<sup>11</sup>. 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 Fe<sub>3</sub>O<sub>4</sub> nanoparticles<sup>12,13</sup>. The result agrees with the fact that the magnetization of small particles decreases as the particle size decreases.

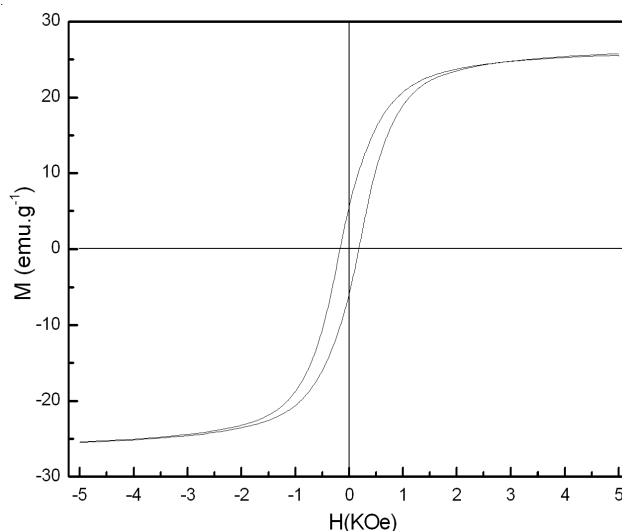


Fig. 3. Magnetic hysteresis loop of the as-obtained Fe<sub>3</sub>O<sub>4</sub> nanoparticles measured at room temperature

## Conclusion

In conclusion, Fe<sub>3</sub>O<sub>4</sub> nanoparticles with sizes of 5-20 nm were successfully prepared by employing a rapid microwave-assisted refluxing method using FeSO<sub>4</sub>(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>·6H<sub>2</sub>O as iron source in the triethanolamine solution. Magnetic hysteresis loop shows that the as-obtained Fe<sub>3</sub>O<sub>4</sub> nanoparticles are ferromagnetic. The coercivity (H<sub>c</sub>) is 186 Oe and the remnant magnetization (M<sub>r</sub>) is 5.86 emu·g<sup>-1</sup>. The saturation magnetization (M<sub>s</sub>) is 25.5 emu·g<sup>-1</sup>. The method for synthesizing Fe<sub>3</sub>O<sub>4</sub> nanoparticles is feasible, quick, nontoxic and eco-friendly.

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## REFERENCES

1. Z.M. Cui, L.Y. Jiang, W.G. Song and Y.G. Guo, *Chem. Mater.*, **21**, 1162 (2009).
2. H. Tan, J.M. Xue, B. Shuter, X. Li and J. Wang, *Adv. Funct. Mater.*, **20**, 722 (2010).
3. Z. Gu, S.X. Huang and Y. Chen, *Angew. Chem. Int. Ed.*, **48**, 952 (2009).
4. T. Hyeon, *Chem. Commun.*, **8**, 927 (2003).
5. Z.P. Cheng, X.Z. Chu, J.Z. Yin, H. Zhong and J.M. Xu, *Mater. Lett.*, **75**, 172 (2012).
6. X.Z. Wang, Z.B. Zhao, J.Y. Qu, Z.Y. Wang and J.S. Qiu, *Cryst. Growth Des.*, **10**, 2863 (2010).
7. S. Wu, A.Z. Sun, F.Q. Zhai, J. Wang, W.H. Xu, Q. Zhang and A.A. Volinsky, *Mater. Lett.*, **65**, 1882 (2011).
8. F. Miao, W. Hua, L. Hu and K.M. Huang, *Mater. Lett.*, **65**, 1031 (2011).
9. W. Zhang, S.Y. Jia, Q. Wu, J.Y. Ran, S.H. Wu and Y. Liu, *Mater. Lett.*, **65**, 1973 (2011).
10. X.A. Li, B. Zhang, C.H. Ju, X.J. Han, Y.C. Du and P. Xu, *J. Phys. Chem. C*, **115**, 12350 (2011).
11. D.H. Han, J.P. Wang and H.L. Luo, *J. Magn. Magn. Mater.*, **136**, 176 (1994).
12. R. Ramesh, M. Rajalakshmi, C. Muthamizhchelvan and S. Ponnusamy, *Mater. Lett.*, **70**, 73 (2012).
13. G.H. Gao, X.H. Liu, R.R. Shi, K.C. Zhou, Y.G. Shi, R.Z. Ma, E.J. Takayama-Muromachi and G.Z. Qiu, *Cryst. Growth Des.*, **10**, 2888 (2010).