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Synthesis and characterization of magnetite nanoparticles by a simple solvothermal method

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Magnetite (Fe_3O_4) nanoparticles were successfully synthesized via a simple solvothermal process and characterized by X-ray diffraction, field emission scanning electron microscopy, and physical property measurement system (PPMS). It was found that the diameters of as-synthesized Fe_3O_4 nanoparticles became larger as the reaction temperature increased, and the magnetic properties of these nanoparticles could change from ferrimagnetic to superparamagnetic with the decrease in particle size. A possible mechanism for the formation of Fe_3O_4 nanoparticles has also been proposed.

Keywords: *Fe_3O_4 nanoparticles; ethylene glycol; solvothermal process; magnetic properties*

1. Introduction

On the nanometer scale, properties of materials are dramatically different from their bulk counterparts [1]. Unique properties of nanomaterials arise from a large fraction of atoms residing on the surface of these particles and the finite number of atoms in each crystalline core [2]. Magnetite (Fe_3O_4), as a common ferrite with a cubic inverse spinel structure, exhibits unique electric and magnetic properties, based on the transfer of electrons between Fe^{2+} and Fe^{3+} ions at the octahedral sites [3]. In recent years, the synthesis of nanostructured magnetic materials, especially Fe_3O_4 nanoparticles, has become a particularly important research field and is attracting growing interest [4–6]. Besides practical applications in industry such as in catalysis, ceramics, energy storage, magnetic data storage, and ferrofluids [7, 8], magnetite nanoparticles have already been applied in clinical diagnosis and medicine transporters [9].

Conventionally, Fe_3O_4 nanoparticles are produced via aqueous or organic solution synthesis. A hydrothermal reaction of $(NH_4)_2SO_4{\cdot}FeSO_4{\cdot}6H_2O$ in the presence of hydrazine produces Fe_3O_4 particles of about 70 nm [10]. Other aqueous solution syntheses such as coprecipitation of ferrous (Fe^{2+}) and ferric (Fe^{3+}) ions or by thermal de-

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composition of alkaline solution of Fe^{3+} chelate in the presence of hydrazine and by sonochemical decomposition of hydrolyzed Fe(II) salt have also been developed in recent years. But none of these synthesis methods could be used for the fabrication of nanoparticles smaller than 20 nm and with a satisfactory size distribution [11–13]. An organic solution phase decomposition route has been widely used in iron oxide nanoparticle synthesis, and decomposition of $Fe(cup)_3$, $Fe(acac)_3$, or $Fe(CO)_5$ followed by oxidation can lead to high quality monodisperse γ-Fe_2O_3 nanoparticles [14–16], which usually requires relatively higher temperatures and a complicated operation. The solvothermal process is one of the successful methods for growing crystals in which the grains formed have a better crystallinity than those obtained with other methods, and it has been used to obtain Fe_3O_4 fine particles with highly uniform sizes. Gao et al. used $Fe(acac)_3$ as a precursor to fabricate magnetite nanoparticles with the diameter below 20 nm which can be controlled easily through tailoring surfactants under solvothermal conditions [17]. Yan et al. prepared size controlled Fe_3O_4 nanoparticles via the solvothermal method by using mixed surfactants of SDS and PEG as protective reagents. The sizes of the nanoparticles can be varied from 15 nm to 190 nm by adjusting some experimental parameters such as the reaction time, initial concentration of reactants, and the molar ratio of reactant to protective reagents, etc. [18]. However, even though they produce highly crystalline and uniformly sized magnetic nanoparticles, these synthesis routes cannot be applied to large scale economic production because they usually require complicated operations and sometimes expensive/toxic reagents. Herein, we present a simple surfactant-free solvothermal process to synthesize Fe_3O_4 nanoparticles employing $Fe(NO_3)_3{\cdot}9H_2O$ and KOH as the starting materials, ethylene glycol as the solvent. Reduction of the Fe^{3+} by ethylene glycol is expected. The size of the as-synthesized magnetite nanoparticles can be controlled easily through adjusting reaction temperature in the ethylene glycol system. Magnetic properties of the Fe_3O_4 nanoparticles synthesized at various temperatures were also investigated.

2. Experimental

Chemical regents used in the present work were: iron nitrate ($Fe(NO_3)_3{\cdot}9H_2O$), potassium hydroxide (KOH) and ethylene glycol ($C_2H_6O_2$). All the chemicals were of analytical grade.

A typical synthesis procedure was as follows: 4.85 g $Fe(NO_3)_3{\cdot}9H_2O$ and 2.46 g KOH were separately dissolved in 10 cm^3 of ethylene glycol. Then the mixed solution was stirred vigorously for 10 min. The resulting mixture was loaded into a 50 cm^3 Telfon lined autoclave, which was then filled with ethylene glycol up to 80% of the total volume. The autoclave was sealed and maintained at a certain temperature which was controlled from 200 °C to 250 °C for 24 h. Finally, it was cooled down to room temperature naturally. The products were washed several times with deionized water

and absolute ethanol to remove any impurities, and then dried at 60 °C for 6 h for characterization.

The as-prepared powder samples were characterized by X-ray powder diffraction (XRD) using a Rigaku D/max-RA X-ray diffractometer (Rigaku, Tokyo, Japan) with CuK_α radiation (λ = 1.5406 Å). Field emission scanning electron microscopy (FESEM) images were obtained from a SIRION FESEM (FEI, Eindhoven, the Netherlands). Magnetization was measured by using a physical property measurement system (PPMS-9T, Quantum Design, San Diego, CA).

3. Results and discussion

Figure 1 shows the XRD patterns of the samples formed by the solvothermal process and held at various temperatures for 24 h. Curve 1a displays the XRD pattern of the sample prepared by the solvothermal reaction at 200 °C. Obviously, all the peaks can be indexed to a pure phase Fe_3O_4 with a cubic inverse spinel structure belonging to the *Fd*3*m* space group, fully consistent with the reported data (JCPDS: 85-1436). The XRD pattern of the sample synthesized at 250 °C is shown in Fig. 1, curve b. All the diffraction peaks could also be indexed to pure phase Fe_3O_4, and no impurities were detected. In correspondence with the increase in the reaction temperature, from 200 °C to 250 °C, the peaks became stronger and sharper. This indicates that an increase in temperature would promote evolution and crystallization of magnetite.

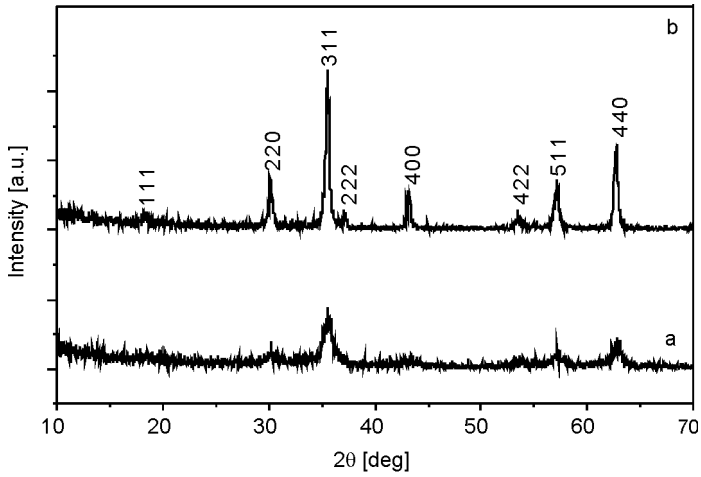

Fig. 1. X-ray diffraction patterns of the solvothermally synthesized samples at: a) 200 °C, b) 250 °C for 24 h

Figures 2a and 2b show the SEM images of samples solvothermally treated at 200 °C and 250 °C for 24 h, respectively. As shown in Fig. 2a, the powder consists of

uniform spherical nanoparticles with an average diameter of about 12 nm. However, when the solvothermal temperature was promoted to 250 °C, considerable changes in the diameter of Fe_3O_4 crystallites could be found. As shown in Fig. 2b, the increased temperature resulted in uniform spherical Fe_3O_4 particles, having an average size of about 53 nm, implying that a relatively higher temperature would promote crystallization of the magnetite phase. These observations are highly consistent with the above XRD results. The larger particle sizes of crystals prepared at higher temperature can be attributed to the (natural) dynamics of crystal nucleation.

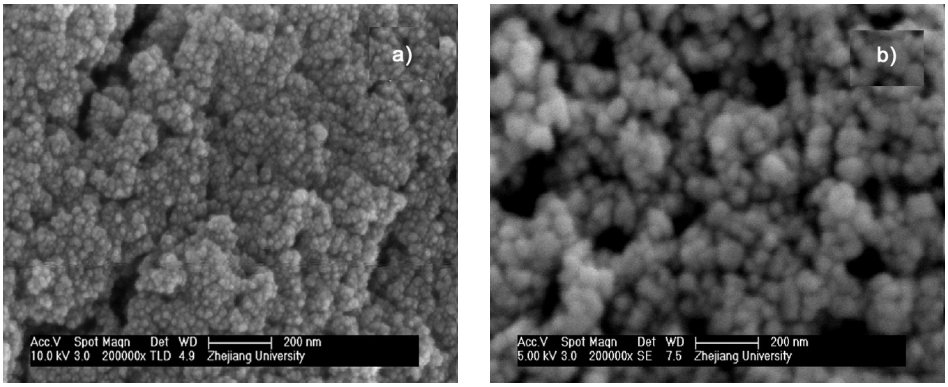

Fig. 2. Scanning electron microscopy images of the solvothermally synthesized Fe_3O_4 powders at: a) 200 °C, b) 250 °C for 24 h

In our experiment, $Fe(NO_3)_3 \cdot 9H_2O$ and KOH were dissolved in ethylene glycol, and then $Fe(OH)_3$ fast precipitated. Ethylene glycol, a strong reducing agent with a relatively high boiling point [19–24], served as both a solvent and reducing agent. $Fe(OH)_2$ was obtained through reduction of $Fe(OH)_3$ with ethylene glycol in the solvothermal process. Due to this treatment at 200 °C or 250 °C, $Fe(OH)_3$ and newly produced $Fe(OH)_2$ formed more stable Fe_3O_4 phase in high alkaline solutions (pH higher than 12). From the above analysis, the corresponding possible reaction describing the formation of the Fe_3O_4 nanoparticles can be expressed by the following equations:

$$Fe^{3+} + 3OH^- \rightarrow Fe(OH)_3 \quad (1)$$

$$10Fe(OH)_3 + C_2H_6O_2 \rightarrow 2H_2CO_3 + 10Fe(OH)_2 + 6H_2O \quad (2)$$

$$2Fe(OH)_3 + Fe(OH)_2 \rightarrow Fe_3O_4 + 4H_2O \quad (3)$$

The magnetization of the as-prepared samples under magnetic field at room temperature was also investigated. The magnetization curves (Fig. 3a) do not display hysteresis, the coercivity field and remnant magnetization cannot be detected from the curves, indicating that Fe_3O_4 nanoparticles synthesized by the solvothermal process at 200 °C have superparamagnetic properties. The magnetization curve (Fig. 3b) showed

ferrimagnetic-like properties and the bulk-like behaviour was observed. The coercive field is 109.7 Oe and the remnant magnetization is 13.6 emu/g. This result is in agreement with the data reported by Sun et al. [25].

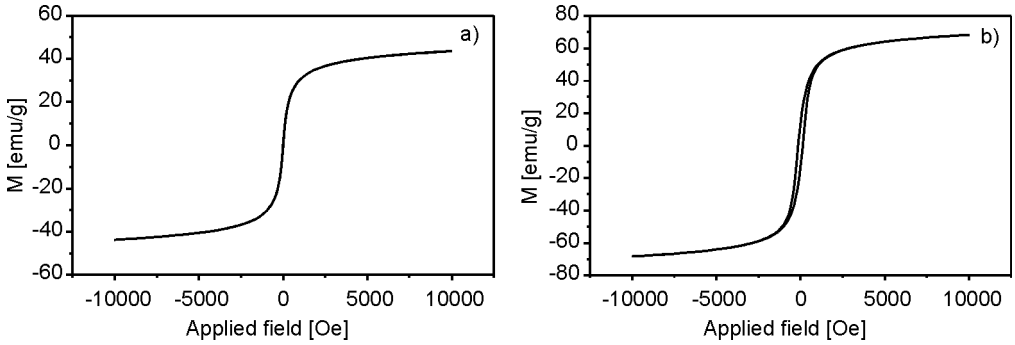

Fig. 3. The magnetization curves recorded at room temperature for the solvothermally synthesized Fe_3O_4 nanoparticles at: a) 200 °C, b) 250 °C for 24 h

From the magnetization curves (Figs. 3a, b), we can also see that the saturation magnetization (M_s) of the Fe_3O_4 nanoparticles increases from 43.60 to 68.82 emu/g when the sizes of magnetite increase in accordance with the rise in solvothermal temperature, from 200 °C to 250 °C. The magnetic properties of the as-synthesized Fe_3O_4 nanoparticles change when the particle size is decreased. This can be attributed to the significant size effect [26]: for particles of very small size, anisotropy energy is lower than the heat disturbance energy of ions, thus magnetization has no strong orientation in a particular direction, and the movement of the ions is random. Consequently, the sample should exhibit superparamagnetic properties, like a paramagnetic body. As the nanoparticle size increases, the anisotropy energy barriers increase accordingly, and superparamagnetic behaviour is replaced by ferrimagnetism.

4. Conclusions

A simple solvothermal method for synthesizing Fe_3O_4 nanoparticles has been presented. XRD and SEM data for the Fe_3O_4 nanoparticles synthesized by the solvothermal process showed that increasing the reaction temperature would improve the evolution and crystallization of Fe_3O_4 nanoparticles. A one step, low-cost, surfactant free method described in the paper is suitable for large-scale production. It may also be employed for the preparation of other kinds of inorganic nanoparticles.

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References

[1] YANG T.Z., SHEN C.M., YANG H.T., XIAO C.W., XU Z.C., CHEN S.T., SHI D.X., GAO H.J., Surf. Interface Anal., 38 (2006), 1063.
[2] PUNTES V.F., KRISHNAN K.M., Appl. Phys. Lett., 78 (2001), 2187.
[3] CORNELL R.M., SCHWERTMANN U., *The Iron Oxides: Structure, Properties, Reactions, Occurrence and Uses*, VCH Publisher, NewYork, 1996.
[4] YANG T., SHEN C., LI Z., ZHANG H., XIAO C., CHEN S., XU Z., SHI D., LI J., GAO H., J. Phys. Chem. B, 109 (2005), 23233.
[5] MA D., GUAN J., NORMANDIA F., DENOMMEE S., ENRIGHT G., VERES T., SIMARD B., Chem. Mater., 18 (2006), 1920.
[6] ARRUEBO M., GALAN M., NAVASCUES N., TELLEZ C., MARQUINA C., IBARRA M.R., SANTAMARIA J., Chem. Mater., 18 (2006), 1911.
[7] BEYDOUN D., AMAL R., LOW G.K.-C., MCEVOY S., J. Phys. Chem. B, 104 (2000), 4387.
[8] RAJ K., MOSKOWITZ R., J. Magn. Magn. Mater., 85 (1900), 233.
[9] FU L., DRAVID V.P., JOHNSON D.L., Appl. Surf. Sci., 181 (2001), 173.
[10] LI Y.D., LIAO H.W., QIAN Y.T., Mater. Res. Bull., 33 (1998), 841.
[11] SAPIESZKO R.S., MATIJEVIC E., J. Colloid Interface Sci., 74 (1980), 405.
[12] VIJAYAKUMAR R., KOLTYPIN Y., FELNER I., GEDANKEN A., Mater. Sci. Eng., A286 (2000), 101.
[13] FRIED T., SHEMER G., MARKOVICH G., Adv. Mater., 13 (2001), 1158.
[14] ROCKENBERGER J., SCHER E.C., ALIVISATOS P.A., J. Am.Chem. Soc., 121 (1999), 11595.
[15] HYEON T., LEE S.S., PARK J., CHUNG Y., NA H.B., J. Am. Chem. Soc., 123 (2001), 12798.
[16] SUN S.H., ZENG H., J. Am. Chem. Soc., 124 (2002), 8204.
[17] HOU Y.L., YU J.F., GAO S., J. Mat. Chem., 13 (2003), 1983.
[18] YAN A.G., LIU X.H., QIU G.Z., WU H.Y., YI R., ZHANG N., XU J., J. Alloys Compd., 458 (2008), 487.
[19] PENG Q., DONG Y.J., LI Y.D., Angew. Chem. Int. Ed., 42 (2003), 3027.
[20] PENG Q., XU S., ZHUANG Z.B., WANG X., LI Y.D., Small., 1 (2005), 216.
[21] SUN X.M., LI Y.D., Angew. Chem. Int. Ed., 43 (2004), 3827.
[22] SUN X.M., LI Y.D., Angew. Chem. Int. Ed., 43 (2004), 597.
[23] WANG J.W., WANG X., PENG Q., LI Y.D., Inorg. Chem., 43 (2004), 7552.
[24] ZHANG Y., LI Y.D., J. Phys. Chem. B, 108 (2004), 17805.
[25] SUN S.H., ZENG H., ROBINSON D.B., RAOUX S., RICE P.M., WANG S.X., LI G.X., J. Am. Chem. Soc., 126 (2004), 273.
[26] ZHANG L.D., *Nanometer materials and nanometer structure*, Science Press, Beijing, 2001.

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