Hydrothermal synthesis of Fe_3O_4 particles with various shapes

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Magnetite (Fe_3O_4) particles with various shapes have been synthesized through a simple hydrothermal reaction. The experimental results reveal that the control of the morphology and size of magnetite particles could be realized by adjusting reaction parameters. The diamond-like and prism-shuttle-like magnetite particles with micro-size are obtained by using $\text{Fe}_3\text{O}(\text{OCOCH}_3)_6\text{NO}_3$ and $\text{FeCl}_2\cdot 4\text{H}_2\text{O}$ as iron sources. The rod-like and spherical magnetite particles with nano-size are obtained by using $\text{Fe}_3\text{O}(\text{OCOCH}_3)_6\text{NO}_3$ and $\text{FeSO}_4\cdot 7\text{H}_2\text{O}$ as iron sources. Ethylenediamine and hydrazine are used as organic bases. The particle size changed from micro-size to nano-size when $\text{FeSO}_4\cdot 7\text{H}_2\text{O}$ was used as the starting material instead of $\text{FeCl}_2\cdot 4\text{H}_2\text{O}$. The growth mechanism of magnetite particles also is discussed. The magnetic properties of all magnetite particles exhibit ferromagnetic behavior according to the magnetic hysteresis curve measured at 5 K.

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1. Introduction

In recent years, morphology and size control of magnetic materials such as magnetite (Fe_3O_4), an important spinel-type ferrite, have been attracting intensive interest because of their outstanding properties and potential applications in various fields, such as ferrofluids, catalysts, colored pigments, high-density magnetic recording media, and medical diagnostics,^{1)–8)} especially, due to the strong dependence of physical and chemical properties of magnetic particles on their morphologies and sizes.^{9)–12)} Therefore, keen interests have been expanded into controlling morphology of particles. So far, the synthesis of various morphologies of Fe_3O_4 particles has been reported by different research groups.^{13),14)} For example, Zhang and co-workers¹⁵⁾ synthesized star-like magnetite nanoparticles by the pyrolysis method using 1-adamantanecarboxylic acid (ACA) and oleylamine (OLA) as the combined surfactants. Wang et al.¹⁶⁾ have prepared Fe_3O_4 with different morphologies, such as rod-like, cross-like and spherical, by an arc-electrodeposition method. Multi-step synthetic processes or the use of multi-reagents was typically required in above processes. Moreover, these methods may complicate the synthetic procedure and limit the scale at which a material could be processed in each synthesis.

To the best of our knowledge, there are few reports on the synthesis of magnetite particles with different morphologies by a facile hydrothermal method without adding surfactants or templates. Herein, we report a simple method for the synthesis of Fe_3O_4 particles with various shapes. The synthesis is based on the deposition from the solution of ferrous/ferric mixed salt solution. Ethylenediamine and hydrazine, easily accessible substances and bidentate complex agents,^{17),18)} were selected as organic bases to control the pH of the starting solution. We investigated the relationship between morphology of magnetite particles and the starting materials under hydrothermal condition.

2. Experimental section

2.1 Synthesis of Fe_3O_4 particles

0.667 mmol of $\text{Fe}_3\text{O}(\text{OCOCH}_3)_6\text{NO}_3$ and 1 mmol of $\text{FeCl}_2\cdot 4\text{H}_2\text{O}$ (or $\text{FeSO}_4\cdot 7\text{H}_2\text{O}$) were dissolved in 20 ml deoxygenated distilled water. Organic base ethylenediamine (or hydrazine monohydrate) (2–10 ml) was added to the above solution for adjusting the pH and the mixture was stirred vigorously for 10 min at room temperature. Then, the suspension was put into a 50 ml Teflon-lined autoclave. The autoclave was sealed, and maintained at 180°C for 20 h, and then cooled to room temperature naturally. After centrifugation, black products were obtained and washed with distilled water and absolute ethanol two times, respectively, and dried in air at 60°C for 6 h.

In order to compare the role of different bases, organic base was replaced by inorganic base; sodium hydroxide (NaOH) solution (2.5 mol dm^{−3}) used as one of starting materials. The following experiment steps were the same as described above.

2.2 Characterization

X-ray powder diffraction (XRD) was performed on a Rigaku X-ray diffractometer (RINT2000V Japan) with graphite-monochromatized Cu K α radiation ($\lambda = 1.54056 \text{ \AA}$) using 30 mA and 40 kV. The diffraction pattern over the range of 10–70° in 2θ was recorded with a scanning speed of 3°/min. Scanning electron microscopy (SEM) images were taken with a JEOL Ltd., JEM–6500F field emission scanning electron microscope. Transmission electron microscopy (TEM) images were taken with a JEOL Ltd., JEM–2000FXII transmission electron microscope using an accelerating voltage of 200 kV. The samples used for TEM observations were prepared by dispersing products in ethanol under ultrasonic agitation for 10 min, then placing a drop of the dispersion onto a copper grid coated with a layer of amorphous carbon. The Brunauer–Emmett–Teller (BET) specific surface area measurement was investigated by a BELSORP-mini II adsorption measurement instrument (BEL Japan) with N₂ gas after evacuating the samples at 110°C for 8 h. Fourier transform infrared (FT–IR) spectra were recorded in the range of 4000–

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400 cm⁻¹ on a JASCO Co. FT/IR-4100 spectrometer, using transparent KBr pellets. Thermo gravimetric analysis (TGA) was carried out in a Rigaku Thermo Plus TG 8120 thermal analysis system with a heating rate of 10°C min⁻¹ from room temperature to 800°C. Magnetic properties of magnetite particles were measured by utilizing a superconducting quantum interference device (SQUID) magnetometer in the magnetic property measurement system (MPMS) of Quantum Design (USA) with fields up to 6 kOe and temperature at 5 K.

3. Results and discussion

3.1 Synthesis of magnetite particles with various shapes

3.1.1 Diamond-like Fe₃O₄

Figure 1(a) shows the XRD pattern of the product obtained by using Fe₃O(OCOCH₃)₆NO₃, FeCl₂·4H₂O and ethylenediamine as starting materials at 180°C for 20 h at the initial pH of 12.6. This XRD pattern is identified with that of magnetite (JCPDS 19-629). No diffraction peaks of any other phases were detected, indicating the high purity of the product. The strong and sharp diffraction peaks suggested that the prepared magnetite were well crystallized. **Figure 2** shows SEM images of the products prepared by using Fe₃O(OCOCH₃)₆NO₃, FeCl₂·4H₂O and ethylenediamine as starting materials at 180°C for 20 h at the different initial pH values. As shown in Fig. 2, almost all crystals have diamond-like octahedral shape. At an initial pH value of 8.6 (Fig. 2(a)), diamond-like magnetite with the size about 0.5 μm was obtained. When the initial pH value increased to 10.7, the size of diamond-like magnetite increased to about 2.5 μm (Fig. 2(b)). When the initial pH value increased to 12.6, diamond-like magnetite had the average size about 12 μm (Fig. 2(c)).

3.1.2 Prism-shuttle-like Fe₃O₄

Figure 3 shows SEM images of the products prepared by using Fe₃O(OCOCH₃)₆NO₃, FeCl₂·4H₂O and hydrazine as starting materials at 180°C for 20 h at the different initial pH values. From the SEM (Fig. 3(a)) image, it could be seen that the product at the initial pH value of 8.6 is mainly composed of uniform

prism-shuttle-like Fe₃O₄ particles with an average width of 0.5 μm and length of 1.5 μm. When initial pH value was increased, the morphology of magnetite particles maintained, but the size increased dramatically. The average length of the product increased from 1.5 μm to 3 and 5 μm as the initial pH value increased from 8.6 to 10.7 and 12.6, and the width increased from 0.5 μm to 1 and 1.5 μm, respectively, as shown in Fig. 3(a)–(c). The specific surface areas of prism-shuttle-like Fe₃O₄ obtained at various pH values are presented in **Fig. 4**. The specific surface area of the pH = 8.6 sample is 19.7 m²/g, and the surface area decreases with the increase of the initial pH value, being 3.98 and 1.16 m²/g when the initial pH value increased to 10.7 and 12.6, respectively, as shown in Fig. 4(a)–(c).

Fig. 1. XRD patterns of the products obtained by (a) using Fe₃O(OCOCH₃)₆NO₃, FeCl₂·4H₂O and ethylenediamine as starting materials at 180°C for 20 h at the initial pH of 12.6 and (b) using Fe₃O(OCOCH₃)₆NO₃, FeSO₄·7H₂O and ethylenediamine as starting materials at 180°C for 20 h at the initial pH of 8.6.

Fig. 2. SEM images of the products prepared by using Fe₃O(OCOCH₃)₆NO₃, FeCl₂·4H₂O and ethylenediamine as starting materials at 180°C for 20 h at the different initial pH values. (a) pH = 8.6, (b) pH = 10.7, (c) pH = 12.6.

Fig. 3. SEM images of the products prepared by using Fe₃O(OCOCH₃)₆NO₃, FeCl₂·4H₂O and hydrazine as starting materials at 180°C for 20 h at the different initial pH values. (a) pH = 8.6, (b) pH = 10.7, (c) pH = 12.6.

3.1.3 Rod-like Fe_3O_4

Figure 1(b) shows the XRD pattern of the product obtained by using $\text{Fe}_3\text{O}(\text{OCOCH}_3)_6\text{NO}_3$, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and ethylenediamine as starting materials at 180°C for 20 h at the initial pH of 8.6. This XRD pattern shows that the diffraction peaks are broad when compared with those of diamond-like magnetite, however, no diffraction peaks of any other phases are observed. The broadened peaks suggested that the prepared magnetite had small crystallite size.

Figure 5 shows TEM images of the products prepared by

Fig. 4. Specific surface areas of prism-shuttle-like Fe_3O_4 obtained at 180°C for 20 h at the various pH values. (a) pH = 8.6, (b) pH = 10.7, (c) pH = 12.6.

using $\text{Fe}_3\text{O}(\text{OCOCH}_3)_6\text{NO}_3$, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and ethylenediamine as starting materials at 180°C for 20 h at the different initial pH values. At the initial pH value of 8.6 rod-like Fe_3O_4 nanoparticles were obtained and their average diameter and length were 20 and 150 nm, as shown in Fig. 5(a). Nanorods were defined as materials that have a width of ~ 1 –100 nm and aspect ratios greater than 1 but less than 20, and nanowires were defined as materials that have aspect ratios greater than 20.¹⁹⁾ The aspect ratio of magnetite particles is calculated to be 7.5 from the images of Fig. 5(a), and therefore these magnetite particles are nanorods. When the initial pH value was increased to 10.7 (Fig. 5(b)), rod-like particles grew into bigger rod-like nanoparticles that have an average width of about 25 nm and a length of about 200 nm. When the initial pH value was increased to 12.7, the rod-like Fe_3O_4 nanoparticles grew up to 350 nm long and their diameters generally about 30 nm (Fig. 5(c)). With the increase of initial pH value, the length of rod-like Fe_3O_4 nanoparticles increased from 150 nm to 350 nm (Figs. 5(a)–(c)), simultaneously, the diameter increased from 20 nm to 30 nm, the aspect ratio increased from 7.5 to 11.7, correspondingly.

3.1.4 Spherical Fe_3O_4

TEM images of the products prepared by using $\text{Fe}_3\text{O}(\text{OCOCH}_3)_6\text{NO}_3$, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and hydrazine as starting materials at 180°C for 20 h at the different initial pH values are presented in Fig. 6. At the different initial pH values, particle morphology of the magnetite nanoparticles was spherical. It was also found that the spherical particle size was sensitive to the initial pH value of starting solutions. At low initial pH value small particles could be obtained, however, high initial pH value gave large particles. As shown in Figs. 6(a)–(c), the average diameter

Fig. 5. TEM images of the products prepared by using $\text{Fe}_3\text{O}(\text{OCOCH}_3)_6\text{NO}_3$, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and ethylenediamine as starting materials at 180°C for 20 h at the different initial pH values. (a) pH = 8.6, (b) pH = 10.7, (c) pH = 12.6.

Fig. 6. TEM images of the products prepared by using $\text{Fe}_3\text{O}(\text{OCOCH}_3)_6\text{NO}_3$, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and hydrazine as starting materials at 180°C for 20 h at the different initial pH values. (a) pH = 8.6, (b) pH = 10.7, (c) pH = 12.6.

of the product synthesized at pH 8.6 was about 10 nm, which gradually increased to 25 and 40 nm as initial pH value increased to 10.7 and 12.6, respectively. The specific surface areas of the spherical Fe₃O₄ particles prepared at 180°C for 20 h at different initial pH values are shown in Fig. 7. The specific surface area of the sample obtained at the initial pH of 8.6 is 66.2 m²/g, and the surface area decreased with the increase of the initial pH value, being 36.1 and 23.3 m²/g when the initial pH value increased to 10.7 and 12.6, respectively.

3.2 FT-IR Spectroscopy analysis

The FT-IR spectra of the magnetite particles prepared by using Fe₃O(OCOCH₃)₆NO₃, FeSO₄·7H₂O at 180°C for 20 h with different organic bases at the initial pH value of 12.6 are shown in Fig. 8. Three strong (3428, 1626, 568 cm⁻¹) absorption bands were observed for the two FT-IR spectra. The adsorbed water is featured by the bands at 3428 and 1626 cm⁻¹ which are assigned to O-H stretching and H-O-H bending modes of vibration, which could be ascribed to H₂O adsorbed on the products. For the band around 568 cm⁻¹ is assigned to the characteristic absorption band of the Fe-O of Fe₃O₄.²⁰⁾ Spectrum of magnetite

Fig. 7. Specific surface areas of the spherical Fe₃O₄ particles prepared at 180°C for 20 h at the different initial pH values. (a) pH = 8.6, (b) pH = 10.7, (c) pH = 12.6.

Fig. 8. FT-IR spectra of the magnetite particles prepared by using Fe₃O(OCOCH₃)₆NO₃, FeSO₄·7H₂O at 180°C for 20 h at the initial pH value of 12.6 with different organic bases. (a) ethylenediamine, (b) hydrazine.

prepared with ethylenediamine is shown in Fig. 8(a). The bands at 1071 and 1346 cm⁻¹ are attributed to bending vibration of -CH₂- group²¹⁾ and those at 2849 and 2930 cm⁻¹ are to stretching vibration of -CH₂- group.²¹⁾ For the sample prepared with hydrazine, the bands observed at 1049 and 3112 cm⁻¹ are due to the -NH₂ bending and stretching vibration, respectively²²⁾ (Fig. 8(b)). Therefore, the FT-IR results indicated the evidence for the presence of ethylenediamine and hydrazine on the particle surface.

3.3 Thermo gravimetric analysis

Figure 9 shows TG-DTA curves of magnetite particles with various shapes prepared at 180°C for 20 h at the initial pH value of 12.6. From the thermogram, there are two weight loss stages in the temperature range 50–600°C. The first weight loss at around 100°C may be due to water adsorbed on the magnetic particles surface. Around 300°C there is the second weight loss that could be attributed to release and decomposition of adsorbed organic bases (ethylenediamine or hydrazine) from the magnetic particles surface. The corresponding exothermic peaks in DTA curves are observed at 250–350°C. The weight losses are 7.5%, 6.8%, 3.0% and 2.5%, respectively, corresponding to the shapes of spherical, rod-like, prism-shuttle-like and diamond-like. The results further confirmed the adsorption of organic bases on the magnetite particle surface. Moreover, with increasing in magnetite particles size, the weight loss decreases, indicating less adsorption of organic molecules.

3.4 Magnetic properties

Figure 10 shows the magnetite hysteresis (MH) curves measured at 5 K for the magnetite particles with various shapes prepared at 180°C for 20 h at the initial pH value of 12.6. The hysteresis loops of the Fe₃O₄ particles exhibit ferromagnetic behavior with saturation magnetization (*M_s*) values of 61, 64, 80 and 83 emu/g, for spherical, rod-like, prism-shuttle-like and diamond-like magnetite particles. The saturation magnetization of all magnetite particles is lower than the bulk value of magnetite

Fig. 9. TG-DTA curves of magnetite particles with various shapes prepared at 180°C for 20 h at the initial pH value of 12.6. (a) spherical, (b) rod-like, (c) prism-shuttle-like, (d) diamond-like.

Fig. 10. Magnetite hysteresis (MH) curves measured at 5 K for the magnetite particles with various shapes prepared at 180°C for 20 h at the initial pH value of 12.6. (a) spherical, (b) rod-like, (c) prism-shuttle-like, (d) diamond-like.

92 emu/g.^{23)–25)} It may be caused by the organic bases and water adsorbed on the magnetite particles surface, which have been confirmed by FT-IR and TGA, could decrease the saturation magnetization. The magnetization of nano-size magnetite (rod-like or spherical) is lower than that of micro-size magnetite (diamond-like or prism-shuttle-like). It could be attributed to the disfigurement and disorder of surface of nano-size magnetite particles.^{26),27)} Moreover, this is also due to the presence of increasing amounts of non-magnetic materials with the increasing organic bases adsorbed on the particle surface. The change in weight loss indicated the amount of organic bases on the particle surface increased with the decrease of magnetite particles size, as shown in Fig. 9.

3.5 Growth mechanism of magnetite particles

The overall results on the products obtained at 180°C for 20 h by using different starting materials are briefly summarized in **Table 1**. Magnetite particles with different shapes including diamond-like, prism-shuttle-like, rod-like, and spherical shapes were obtained by using different organic bases and ferrous salts. It is very interesting that anisotropic crystal growth such as prism-shuttle- and rod-like shapes occurs in spite of the cubic structure of the magnetite. Also the size of magnetite particles was strongly dependent on the Fe(II) source; micro-size magnetite particles were obtained by using $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ as Fe(II) source and nano-size ones by $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$. Here we discuss size control and crystal growth of magnetite particles under this hydrothermal reaction. Magnetite particles are considered to be formed by nucleation-growth mechanism, and crystal growth occurs under hydrothermal condition because precipitation was observed at the time of adjusting the pH. By taking into account the almost same yield of the product for every condition, the number of nuclei is different from each other for Fe(II) sources. A large number of nuclei are formed when $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ was used as Fe(II) source, which result in the formation of small size particles. On the other hand, a small number of nuclei formed when $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ was used as Fe(II) source, and the nuclei could grow up to form large size particles.

Irregular shape magnetite particles were obtained by using inorganic base; sodium hydroxide solution, instead of ethylenediamine or hydrazine to control the initial pH value as shown in **Fig. 11**. It is well known that organic base plays an important

Table 1. Summary of the Results on the Products Obtained at 180°C for 20 h by Using Different Ferrous Irons and Organic Bases. Ferric Iron Source: $\text{Fe}_3\text{O}(\text{OCOCH}_3)_6\text{NO}_3$

Ferrous iron	Organic base	Morphology	Size (μm)	Yield (%)
FeCl_2	ethylenediamine	diamond-like	0.5–12	78.2
FeCl_2	hydrazine	prism-shuttle-like	1.5–5	79.3
FeSO_4	ethylenediamine	rod-like	0.15–0.35	81.3
FeSO_4	hydrazine	spherical	0.01–0.04	80.3

Fig. 11. SEM image of the products prepared by using $\text{Fe}_3\text{O}(\text{OCOCH}_3)_6\text{NO}_3$, $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ and NaOH as starting materials at 180°C for 20 h at the initial pH value of 12.6.

role in determining the crystal morphology. Organic bases with different physical and chemical properties could influence the solubility, reactivity, and diffusion behavior of the reactants; in particular, coordinating ability of the organic bases could influence the crystal morphology of the final product.^{28),29)} Ethylenediamine and hydrazine were selected as the organic base due to the difference of coordination ability; ethylenediamine can form a chelate with iron ions, and hydrazine can not form a chelate but act as a bidentate ligand to form a complex with metal ions. It was reported that nanorod formation of FeS_2 with the cubic structure under solvothermal condition added ethylenediamine.³⁰⁾ In this case a chelate of ethylenediamine played a role of a template for inorganic ion self-assembling to form nanorod of FeS_2 . When the solution contained a large number of nuclei, a chelate of ethylenediamine may be effective for anisotropic crystal growth to form nano-size magnetite particles with rod-like shape. While in solution containing a small number of nuclei a chelate of ethylenediamine can not play a role of a template but uniformly provide iron ions during crystal growth to form micro-size magnetite particles with diamond-like shape. Self-assembling of a chelate of ethylenediamine is considered to be correlated with the number of nuclei in the solution.

On the other hand it was reported that hydrazine was effective for formation of one-dimensional metal selenides, MSe ($\text{M}^{2+} = \text{Cd}, \text{Ni}, \text{Pb}$) under hydrothermal condition¹⁸⁾ and this one-dimensional crystal growth was explained by a chained tetradentate complex with hydrazine as shown in **Fig. 12**. In solution containing a small number of nuclei a similar chained complex with hydrazine may contribute the anisotropic crystal growth to form micro-size magnetite particles with prism-shuttle-like shape. In a large number of nuclei a chained complex with hydrazine uniformly provides iron ion to nucleus to form nano-size magnetite particles with spherical shape. Consequently the crystal growth under these hydrothermal conditions depended on the number of

M: metal ion

Fig. 12. Structure model of a tetradentate complex.

nucleus and form of a complex; in the case of a small number of nuclei a chained complex with hydrazine was effective to form prism-shuttle-like shape particles and in a large number of nuclei a chelate of ethylenediamine acted as a template to form rod-like shape ones.

4. Conclusions

Magnetite particles with controlled morphology and size were prepared through a facile and effective hydrothermal route. The magnetic properties of all magnetite particles exhibited ferromagnetic behavior. This work showed that morphology of magnetite particles prepared by hydrothermal reaction depended on pH adjuster and Fe(II) source. This hydrothermal route was a suitable method for the synthesis of magnetic particles with various shapes.

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