A Novel Method to Synthesize Monodispersed Magnetite Nanoparticles

Feng Dang,*[1] Naoya Enomoto,[1] Junichi Hojo,[1] and Keiji Enpuku[2]
[1]*Department of Applied Chemistry, Faculty of Engineering, Kyushu University, Fukuoka 819-0395*
[2]*Research Institute of Superconductor Science and Systems, Kyushu University, Fukuoka 819-0395*

(Received January 29, 2008; CL-080097; E-mail: dangfeng@cstf.kyushu-u.ac.jp)

Monodispersed ca. 30 nm magnetite nanoparticles were synthesized in a 20/80 ethanol–water solution under ultrasonic irradiation. Both the ethanol–water solution and ultrasonic irradiation were important for the synthesis of the monodispersed magnetite nanoparticles. The ethanol–water solvent improved the monodispersibility of the magnetite particles, on the other hand, limited the formation of magnetite under mechanical stirring. The 100% cubic magnetite particles were successfully synthesized in ethanol–water solution under ultrasonic irradiation.

Magnetite nanoparticles, because of low toxicity, are being used in biomedical areas such as magnetic cell separation, magnetically embolizing blood vessels, carrying chemical drugs, and so on.[1–4]

Magnetite nanoparticles with narrow size distribution can be synthesized easily by coprecipitation of a stoichiometric mixture of Fe^{2+}:$Fe^{3+} = 1/2$ or $2/3$ in alkaline solution.[5,6] The decomposition of $FeCup_3$ or $Fe(CO)_5$ followed by oxidation can also lead to monodispersed magnetite particles.[7,8] However, the magnetite particles synthesized in these methods are too small (ca. 10 nm) to obtain high magnetic properties. Magnetite particles can also be synthesized through a process including dissolution of $Fe(OH)_2$ and precipitation of an oxidized phase in aqueous solution.[9,10] In this method, the magnetite particles need a long time to be synthesized, and to obtain large particle size and broad size distribution. The magnetic properties of large particles can meet the demands of practical use in biomedical areas, but broad size distribution can not obtain precise results.

Sonochemical technique is an effective method to synthesize magnetic nanoparticles. Sonochemistry arises from acoustic cavitation phenomenon, that is, the formation, growth, and collapse of bubbles in a liquid medium.[11] The extremely high temperature of about 5000 K, pressure (ca. 20 MPa), and very high cooling rates (ca. 10^{10} K/s) which come from the collapse of the bubbles, can obtain extreme reaction conditions which lead to many unique properties of the synthesized particles; the microjet effect resulting from the collapse of the bubbles can lead to microscopic mixing in the procedure which creates a relatively uniform reaction condition. Gedanken et al.,[12–14] Enomoto et al.,[15] and Mizukoshi et al.[16] have synthesized Fe_3O_4 nanoparticles by using the sonochemical method. The formation of magnetite under ultrasonic irradiation is accelerated significantly.

Solvent is an important parameter to control the nucleation and crystal growth in the formation of ceramic particles.[17,18] Solubility of dissolved oxygen and iron ions can be changed by using different solvent, furthermore, solvent influences the oxidation rate and dissolution of iron ions when magnetite is synthesized through oxidizing $Fe(OH)_2$ precipitate. Ethanol has a lower solubility of oxygen and iron ions than water because of the low permittivity. Ethanol–water solution can reduce the solubility of oxygen and the dissolution of Fe^{2+} and Fe^{3+} ions. Nucleation and crystal growth can be controlled by using ethanol–water solution in the synthesis of magnetite to improve the monodispersibility of particles.

In this study, monodispersed ca. 30 nm magnetite nanoparticles were synthesized in a 20/80 ethanol–water solution under ultrasonic irradiation.

A mixed solvent of anhydrous ethanol and distilled water was obtained at 20/80 by volume and bubbled for 30 min with Ar gas. $Fe(OH)_2$ precipitate was obtained by mixing a 0.01 mol/L $FeCl_2$ ethanol–water solution and a 2 M NaOH aqueous solution. The $Fe(OH)_2$ precipitate was irradiated by an ultrasonic horn in open air at 50 °C to synthesize magnetite nanoparticles. The power of ultrasonication was determined to be 16 W/cm^2. The initial pH value of the $Fe(OH)_2$ suspension was controlled at 12.6 by adding 2 M NaOH solution.

Figure 1 shows transmission electron microscopic (TEM) photographs of samples synthesized in 20/80 ethanol–water solution and aqueous solution under mechanical stirring (MS) and ultrasonic irradiation (US). Needle-like crystals were observed for the sample synthesized in 20/80 ethanol–water solution for 24 h under mechanical stirring. The needle-like crystals were confirmed as α-FeOOH from fourier transform infrared spectroscopic spectra (FT-IR) although only magnetite was confirmed from X-ray diffractometric patterns (XRD). The 100% cubic magnetite particles could not be obtained in ethanol–water solution under mechanical stirring, on the other hand, 100% cubic magnetite particles were successfully synthesized in 20/80 ethanol–water solution under ultrasonic irradiation. It only took 1 h to form 100% magnetite particles in ethanol–water solution, whereas it took 24 h to form 100%

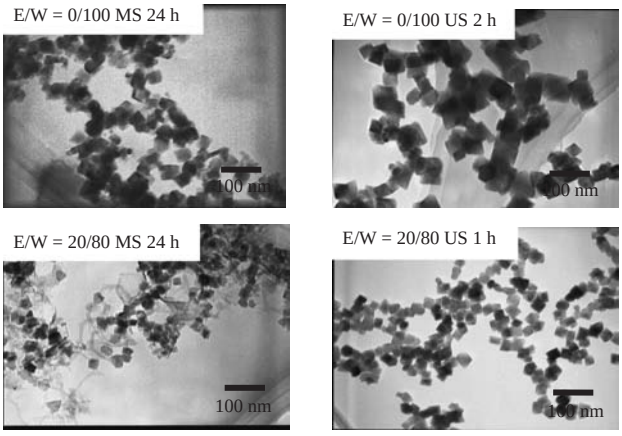

Figure 1. TEM micrographs of the samples synthesized in 20/80 ethanol–water solution and aqueous solution under ultrasonic irradiation and under mechanical stirring at 50 °C.

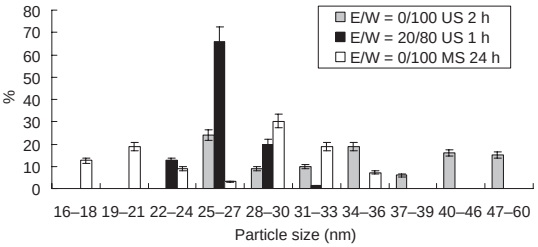

Figure 2. Size distributions of the samples synthesized in 20/80 ethanol–water solution and aqueous solution at 50 °C.

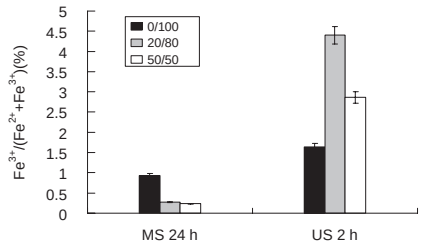

Figure 3. Oxidation of Fe^{2+} in ethanol–water solutions under ultrasonic irradiation for 2 h and mechanical stirring for 24 h at 50 °C using air as dissolved gas.

magnetite particles in aqueous solution under mechanical stirring through oxidizing $Fe(OH)_2$ precipitate.[19] Figure 2 illustrates the size distributions of the samples synthesized in 20/80 ethanol–water solution and aqueous solution. Narrow size distribution was obtained for the sample synthesized in 20/80 ethanol–water solution under ultrasonic irradiation which almost 70% particles were about 27 nm in size through counting more than 200 particles from TEM photographs.

The oxidation of Fe^{2+} and dissolution of iron ions are important parameters in the synthesis of magnetite particles from $Fe(OH)_2$ precipitate.[9] Ethanol–water solvent has lower solubility of oxygen and iron ions than water because of the low permittivity. The low solubility of oxygen limited the oxidation of Fe^{2+}, furthermore, limited the supply of iron ions in the formation of magnetite. The oxidation of Fe^{2+} at 50 °C for 24 h in air in ethanol–water solutions and aqueous solution was measured by the absorption spectrum of Fe^{3+} in solution.[19] The oxidation of Fe^{2+} was limited in ethanol–water solution under mechanical stirring as shown in Figure 3. On the other hand, the lower solubility of iron ions in ethanol–water solution also limited the dissolution of iron ions from $Fe(OH)_2$ precipitate. The supply of iron ions in the nucleation and crystal growth of magnetite particles was limited and the formation of magnetite was limited.

In the sonochemical synthesis of magnetite in ethanol–water solution, ultrasonic irradiation was thought to accelerate the oxidation of Fe^{2+}. Fe^{2+} was oxidized by dissolved oxygen when magnetite was synthesized under mechanical stirring, on the other hand, Fe^{2+} was mainly oxidized by the radical species ($OH^{\bullet}$) and H_2O_2 created from water molecules at the extremely high temperature and pressure through the collapse of bubbles when the magnetite was synthesized under ultrasonic irradiation.[9–14] The dissolution of iron ions from green rust ($Fe(OH)_2$ precipitate) was also accelerated in the formation of magnetite. Microscopic stirring can be obtained from the microjet effect (400 km/h) under ultrasonic irradiation.[11] It dispersed the green rust effectively in the formation of magnetite and accelerated the dissolution of iron ions from green rust. Furthermore, the extremely high temperature and pressure created by the collapse of the bubbles also accelerated the dissolution of iron ions from green rust. The oxidation of Fe^{2+} was even accelerated in ethanol–water solution under ultrasonic irradiation as shown in Figure 3. The oxidation of Fe^{2+} in ethanol–water solution under ultrasonic irradiation and mechanical stirring shown in Figure 3 was correspondent with the formation rate of magnetite particles in ethanol–water solution.

In conclusion, the ethanol–water solvent and ultrasonic irradiation influenced the formation of magnetite significantly. Monodispersed ca. 30 nm magnetite nanoparticles were synthesized rapidly in the ethanol–water solution under ultrasonic irradiation.

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