Super-rapid Hydrothermal Synthesis of Highly Crystalline and Water-soluble Magnetite Nanoparticles Using a Microreactor

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Highly crystalline and water-soluble magnetite nanoparticles having an average diameter of 6.5 nm were synthesized from aqueous $FeCl_3 + KOH$ solution by a flow-through hydrothermal method with a microreactor at 673 K and 30 MPa during residence time of 2×10^{-3} s. L-Ascorbic acid was used as a modifier and a reductant.

Magnetite (Fe_3O_4) nanoparticles have been attracting much attention in biomedical fields such as magnetic separation, drug delivery, and magnetic resonance imaging because of their stability and biocompatibility.[1] For these applications, desirable characteristics of the nanoparticles are narrow size distribution, high crystallinity, high value of saturation magnetization, good biocompatibility, and water-soluble nature. Recently, some methods have been proposed such as high-temperature organic phase decomposition and solvothermal synthesis for preparing Fe_3O_4 nanoparticles having the above-mentioned characteristics.[2,3] However, these methods are complicated or require complex preparation of starting solutions in addition to use of some organic solvents with low biocompatibility during the preparations.

A flow-through supercritical hydrothermal (FTSH) method has been widely known as an environmentally benign process and used for producing highly crystalline metal oxide nanoparticles. The method promises rapid heating of starting solutions to supercritical water (SCW) conditions of low metal oxide solubility and high hydrothermal reaction rate.[4] Moreover, SCW supplies interesting reaction fields for preparing surface-modified metal oxide nanoparticles through dehydration reaction between hydroxy groups of hydrated metal oxide surface and modifiers such as carboxylic acids and alcohols.[5] However, there are no reports for producing Fe_3O_4 nanoparticles under 10 nm with high crystallinity and water-soluble nature.

In this work, we tried to synthesize highly crystalline and water-soluble magnetite nanoparticles under 10 nm by the FTSH method. L-Ascorbic acid (AA) was selected as a modifier and a reductant because of high biocompatibility. In order to prevent the decomposition of AA at high temperatures >ca. 413 K,[6] the synthesis was carried out with a short residence time by introducing a microreactor.[7]

Starting solution was prepared by dissolving precise amounts of $FeCl_3 \cdot 6H_2O$ (purity >99%, Kanto Chemicals) and AA (purity >99.9%, Wako Pure Chemicals) in distilled and deionized water (resistivity >0.18 MΩ m). Concentrations of $FeCl_3$ (C) and AA were 0.1 and 0.14 mol kg^{-1}, respectively. Aqueous KOH solution (0.3 mol kg^{-1}) was also prepared. The KOH concentration was determined on the basis of calculated Fe_3O_4 solubility (S) at 673 K and 30 MPa to establish high degree of supersaturation ($\sigma = \ln(C/S) > 11$) for obtaining nanoparticles under 10 nm.[7] AA was used as a reductant of Fe^{3+} and a modifier of the nanoparticles surface.

Synthesis was performed by the FTSH method with a microreactor, which was composed of three micromixiers and two microtubes. The method was used for superrapid heating of the starting solution and exact definition of a residence time. Details are shown in our previous work.[7] In this work, reaction temperature and pressure were 673 K and 30 MPa, respectively. The residence time was set to 2×10^{-3} s. Produced particles were recovered as a slurry solution, removed using a membrane filter, washed with pure water, and dried at 333 K in an electric oven for 24 h. For comparison, synthesis without AA was also carried out with starting solutions of 0.1 mol kg^{-1} $FeCl_2$ and 0.2 mol kg^{-1} KOH.

The crystal structures of the products were analyzed by powder X-ray diffractometry (XRD, D8 ADVANCE, BRUKER), using Cu Kα_1 radiation. The crystallite sizes of the products were calculated from FWHM of the (311) diffraction line by the Scherrer equation. Observation of these products was performed by transmission electron microscopy (TEM, JEM-2010, JEOL). The particle size distribution of the powder product and the average particle size with the coefficient of variation (C.V.) were determined on the basis of the diameter of about 200 particles measured from the TEM image. The particle size distribution in the recovered solution was measured with a submicron particle size analyzer (PSA, N5, Beckman Coulter). The surface of Fe_3O_4 nanoparticles was analyzed by Fourier transform infrared spectrometry (FT-IR, 8400S, Shimadzu). The weight loss of the products at temperatures ranging from 298 to 723 K was measured by thermogravimetric analysis (TGA, TG-DTA2020SA, BRUKER AXS). The magnetic property of the Fe_3O_4 particles at room temperature was measured with a vibrating sample magnetometer (VSM, VSM-5, Toei Kogyo). Concentration of remaining Fe ion in the recovered aqueous solution were measured by atomic absorption spectrophotometry (AA, AA-6300, SHIMADZU) to evaluate conversion of Fe ion into solid product.

The conversion was more than 99%. This implies that the reaction is finished within the short residence time of 2×10^{-3} s. Figure 1a shows the XRD patterns of the products with and without AA. Major peaks in both products were assigned to Fe_3O_4 (JCPDS 19-0629). The crystallite sizes of the products with and without AA were 6.7 and 20.4 nm, respectively, depending on the starting materials. Figure 1b shows the FT-IR spectra of

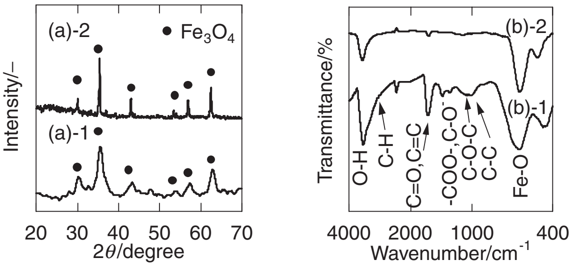

Figure 1. (a) XRD patterns of the products (1) with AA and (2) without AA. (b) FT-IR spectra of the products (1) with AA and (2) without AA.

the products with and without AA. The band at 593 cm^{-1} in both products was assigned to the Fe–O vibration.[8] In the case of the product with AA, the broad band around 3500 cm^{-1} was assigned to the OH stretching motion of the hydrated Fe_3O_4 surface and AA.[9] Then the bands at 2924, 1650, 1100, and 1010 cm^{-1} were assigned to the C–H, C=O and C=C, C–O–C, and C–C stretching motions of AA, respectively.[10,11] In addition, the band around 1400 cm^{-1} was assumed to be the symmetrical C=O stretching motion of the hydroxylate (–COO–) binding to the Fe_3O_4 surface[12] or the C–O stretching motion of the binding between $C–O^-$ and $Fe^{\delta+}$ of the Fe_3O_4 surface.[11] The FT-IR result means that the Fe_3O_4 surface is mainly covered with AA. The weight loss of the product gradually decreased with increasing temperature to around 573 K, and further decrease was not observed at higher temperature. This is probably due to the decomposition of AA on the Fe_3O_4 surface in addition to crystallization of hydrated Fe_3O_4. Figure 2a shows the particle size distribution of the product with AA from the TEM image. An average particle diameter was 6.5 nm (C.V. = 0.4). This value was in good agreement with 6.7 nm of the crystallite size from the XRD analysis. The result shows that each nanoparticle in TEM is a single crystal under 10 nm. Figures 2b and 3a show the particle size distribution of the product with AA from the PSA measurement and the pictures of the recovered solutions, respectively. The average diameter from PSA was around 40 nm, which was larger than that from TEM and XRD results owing to the weak aggregation. The obtained Fe_3O_4 particles were stably dispersed in the recovered solution (Figure 3a-1) in contrast to the particles prepared without AA (Figure 3a-2). Figure 3b shows the VSM result of the product with AA. Saturation magnetization was ca. 23 emu g^{-1}. The value was similar to that of poly(acrylic acid)-capped Fe_3O_4 nanoparticles with an average particle size of 6.6 nm and high crystallinity, ca. 19 emu g^{-1}.[2] In the VSM measurement, the mass of the nanoparticles includes modifiers on the Fe_3O_4 surface. Therefore, saturation magnetization of pure magnetite nanoparticles is assumed to be much higher.

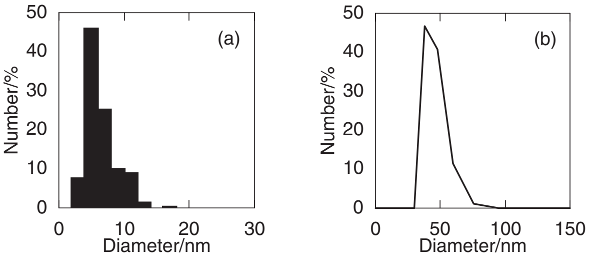

Figure 2. Particle size distributions of the product with AA from (a) TEM and (b) PSA.

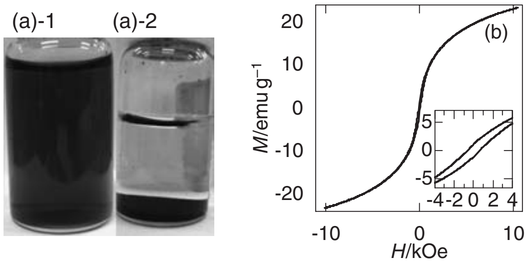

Figure 3. (a) Pictures of the recovered solutions (1) with AA and (2) without AA. (b) VSM result of the products with AA. Inset is expanded curve.

In conclusion, we demonstrated super-rapid hydrothermal synthesis of highly crystalline and water-soluble magnetite nanoparticles under 10 nm using a microreactor. The microreactor successfully worked for both production of nanoparticles by rapid heating of starting solution and prevention of decomposition of L-ascorbic acid used as a modifier and a reductant.

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