

Hydrothermal synthesis of magnetite particles with uncommon crystal facets



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ABSTRACT

Hydrothermal synthesis of Fe₃O₄ (magnetite) particles was carried out using organic compounds as morphology control agents to obtain magnetite crystals with uncommon facets. It was established that the morphology of Fe₃O₄ crystals obtained by hydrothermal treatment of an aqueous solution containing Fe²⁺ and organic compounds depended on the organic compound used. The shape of the Fe₃O₄ particles obtained when no additives were used was quasi-octahedral. In contrast, the addition of picolinic acid, citric acid or pyridine resulted in the formation of polyhedral crystals, indicating the presence of not only {1 1 1}, {1 0 0} and {1 1 0} facets but also high-index facets including at least {3 1 1} and {3 3 1}. When citric acid was used as an additive, octahedral crystals with {1 1 1} facets also appeared, and their size decreased as the amount of citric acid was increased. Thus, control of Fe₃O₄ particle morphology was achieved by a simple hydrothermal treatment using additives.

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1. Introduction

Fe₃O₄ (magnetite) is an extremely important compound that is employed in a variety of applications such as MRI contrast agents [1], high-density magnetic energy storage [2], catalysts [3], and pigments [4]. It is well known that different crystal facets of Fe₃O₄ exhibit different functionalities. Therefore, control of which crystal facets are present is crucial for further improvement of Fe₃O₄ properties. Typically, {1 1 1} faceted octahedral Fe₃O₄ particles with sizes of 5–170 nm are obtained by wet chemical processes in the laboratory [5]. The Fe₃O₄ particles generally assume an octahedral shape, since the compound has a face-centered cubic (fcc) structure and the order of stability of the facets is {1 1 1} > {1 0 0} > {1 1 0} ≫ other facets [6]. However, recent reports have demonstrated the synthesis of Fe₃O₄ with facets other than

the most stable {1 1 1} facets exposed. Amemiya et al. succeeded in synthesizing {1 1 1} faceted Fe₃O₄ nanocrystals using wild magnetotactic bacteria [7]. However, the same group found that mutant forms of the same bacteria synthesized Fe₃O₄ nanocrystals with high-index facets such as {2 1 0} and {3 1 1}, and that these crystals exhibited exceptional performance in radical polymerization [8]. These results indicate that Fe₃O₄ particles with facets other than {1 1 1} can exhibit enhanced functionality.

For mass production, chemical synthesis is typically preferred to “biological” and “bioinspired” processes. Yu et al. and Zhao et al. reported that synthesis of Fe₃O₄ particles with low-index facets, including {1 0 0} and {1 1 1}, could be achieved by a solvothermal method, employing a chelating agent and an organic solvent such as hydrazine or ethylene glycol [9,10]. However, chemical synthesis of Fe₃O₄ crystals with high-index facets has not yet been achieved. Nevertheless, there have been several reports on hydrothermal synthesis of metal and other oxide crystals with different facets using organic additives that act as morphology control molecules [11,12]. In these studies, the morphology could be controlled by adsorption of additives onto specific surfaces, which led to changes in the surface energy. To date, there have been no reports on the synthesis of Fe₃O₄ with various crystal facets using only water, which is an environmentally benign solvent. Therefore, the hydrothermal method employing additives may also offer a simple, promising route to synthesize Fe₃O₄ crystals with diverse facets.

In the present study, an attempt was made to synthesize Fe₃O₄ particles with high-index facets by a hydrothermal method employing organic compounds as morphology control molecules.

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2. Experimental

2.1. Synthesis

Ferrous chloride tetrahydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, >99.0%), picolinic acid ($\text{C}_6\text{H}_5\text{O}_2\text{N}$, >98.0%), nicotinic acid ($\text{C}_6\text{H}_5\text{O}_2\text{N}$, >98.0%), glycolic acid ($\text{C}_2\text{H}_4\text{O}_3$, >98.0%), and hydrochloric acid (HCl , 35.0–37.0%) were purchased from Kanto Chemical Co., Inc. Pyridine ($\text{C}_5\text{H}_5\text{N}$, >99.5%), citric acid ($\text{C}_6\text{H}_8\text{O}_7$, >98.0%), and sodium hydroxide (NaOH , >97.0%) were purchased from Wako Pure Chemical Industries, Ltd. All the reagents were used as supplied without further purification.

Magnetite crystals were prepared using the following hydrothermal reaction: 5 mmol of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ and 0–15 mmol of an organic additive (citric acid, glycolic acid, picolinic acid, nicotinic acid or pyridine) were dissolved in 20 ml of distilled water with stirring. The ratio of organic compound to Fe^{2+} is denoted by X ($[\text{organic compound}]/[\text{Fe}^{2+}] = X$). Upon addition of picolinic acid, the solution turned red, while colorless solutions were obtained with all other additives. After the formation of a transparent solution, 10 ml of NaOH aq. (4 mol L^{-1}) was immediately added to the solution and a suspension was formed. The prepared suspension (30 ml) was stirred vigorously, and then sealed in a Teflon-lined stainless steel autoclave. The autoclave was heated at 473 K for 6 h, and subsequently cooled to room temperature. Black precipitates were collected from the mixture by magnetic separation and sequentially rinsed three times, each time first with distilled water and then with ethanol. The final product was obtained after air drying at room temperature.

2.2. Characterization

The crystal phases present in the samples were characterized using powder X-ray diffraction (XRD; Bruker D2 Phaser, 40 kV and 30 mA) with $\text{CuK}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). Data were collected in the 2θ - θ scanning mode with a scan speed of $12^\circ \text{ min}^{-1}$ and a step size of 0.02° . The phase composition was confirmed by Raman spectroscopy (Jasco NRS-3300) in the backscattering geometry using an excitation laser with a wavelength of 732.2 nm and a power of 90 W. The incident beam was focused on the sample through a $100\times$ microscopic objective lens to form a spot with a size of $2 \mu\text{m}$. The surface morphology of the particles was observed using scanning electron microscopy (SEM, Hitachi SU1510) at an accelerating voltage of 5 kV. To identify the facets present, another SEM system equipped with an electron backscatter diffraction detector (SEM-EBSD, JEOL JSM-7100F) was used at an accelerating voltage of 20 kV. Samples for SEM-EBSD observation were prepared by dispersing the particles in ethanol and placing a drop of the suspension on a copper grid. Absorption spectra were measured using Fourier transform infrared (FT-IR) spectroscopy (Jasco, FT/IR-4200) in the wavenumber range $400\text{--}4000 \text{ cm}^{-1}$. For the FT-IR measurements, all samples were diluted in KBr matrix pellets. Thermogravimetric-differential thermal analysis (TG-DTA, Shimadzu DTG-60H) was also performed. For this purpose, the sample was heated at a rate of 20 K min^{-1} under a 50 ml min^{-1} air flow up to a maximum temperature of 1273 K, with Al_2O_3 powder used as a reference.

3. Results and discussion

Fig. 1 shows XRD patterns for samples synthesized by hydrothermal treatment of aqueous iron solutions in the absence or presence of 5 mmol of organic compounds ($X = 1.0$). The sample obtained in the absence of additives consisted of Fe_3O_4 with a trace amount of metallic iron (Fig. 1(a)). Splitting of the $\text{K}\alpha_1$ and $\text{K}\alpha_2$ peaks was clearly observed. This indicates that the Fe_3O_4 particles may have been larger than those previously reported using

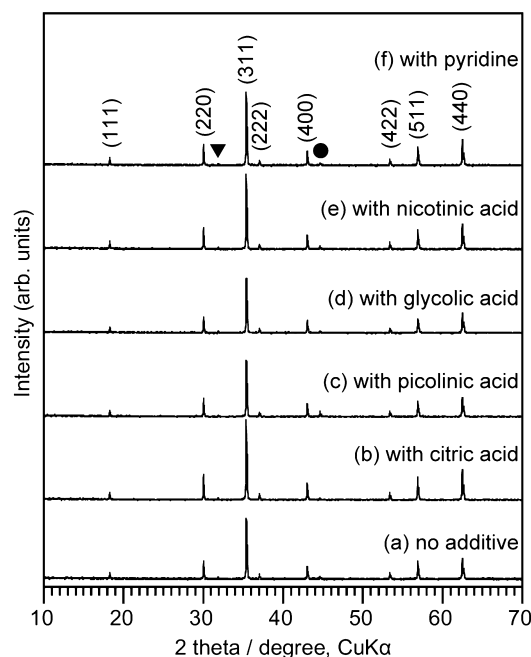


Fig. 1. XRD patterns for samples prepared by hydrothermal treatment of aqueous iron solutions in the absence and presence of additives ($X = 1.0$). Circles and triangles indicate, respectively, peaks due to metallic iron and $\text{K}\beta$ peaks associated with $\{3\ 1\ 1\}$ planes in Fe_3O_4 .

the hydrothermal method [13,14]. The XRD patterns for the samples synthesized using different organic compounds indicated that they were also composed of Fe_3O_4 and a trace amount of metallic iron (Fig. 1(b)–(f)). It is well known that Fe_3O_4 exhibits an XRD pattern similar to that for $\gamma\text{-Fe}_2\text{O}_3$ (maghemite). However, Raman spectroscopy (see Supporting Information Fig. S1) did not reveal the characteristic Raman shifts at 700 and 1160 cm^{-1} associated with $\gamma\text{-Fe}_2\text{O}_3$ [15] for any of the samples. It was therefore concluded that single-phase Fe_3O_4 samples were obtained using the present technique, despite the presence of organic compounds capable of acting as morphology control molecules.

Fig. 2 shows SEM images of samples obtained by hydrothermal treatment of aqueous iron solutions in the absence or presence of organic compounds ($X = 1.0$). As shown in Fig. 2(a), Fe_3O_4 particles synthesized in the absence of organic compounds had a quasi-octahedral structure, indicating the presence of $\{1\ 1\ 1\}$ and $\{1\ 1\ 0\}$ facets, which is consistent with the results of previous studies [9,10]. Fig. 2(b) shows that for the sample produced in the presence of citric acid, octahedral crystals with $\{1\ 1\ 1\}$ facets were formed. In contrast, when picolinic acid or pyridine was used as the additive, polyhedral particles with triangular, hexagonal, and pentagonal shapes were obtained, along with a small fraction of quasi-octahedral crystals (Fig. 2(c) and (f)). These particles may have high-index facets, because the facet shapes could not be formed by only $\{1\ 1\ 1\}$, $\{1\ 0\ 0\}$ and $\{1\ 1\ 0\}$ planes. Fig. 3 shows an SEM image and the results of an SEM-EBSD analysis of a sample obtained using equimolar amounts of picolinic acid and Fe. At first, a crystal orientation was determined for a multi-faceted particle by analysis of the Kikuchi lines observed by EBSD. Then, the angles formed by the facets were carefully measured, and the ideal angles were calculated. Finally, on the basis of the energy of each facet, it was concluded that the particle had at least $\{1\ 1\ 1\}$, $\{1\ 1\ 0\}$, $\{3\ 1\ 1\}$ and $\{3\ 3\ 1\}$ facets. Other high-index facets might also be present, because many crystal facets could be observed on other crystals (Fig. 2(c)). Further analysis is underway to determine the structure more precisely. Samples prepared using glycolic acid mainly contained octahedral particles with a small proportion of polyhedral

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