Strategy to control magnetic coercivity by elucidating crystallization pathway-dependent microstructural evolution of magnetite mesocrystals

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Mesocrystals are assemblies of smaller crystallites and have attracted attention because of their nonclassical crystallization pathway and emerging collective functionalities. Understanding the mesocrystal crystallization mechanism in chemical routes is essential for precise control of size and microstructure, which influence the function of mesocrystals. However, microstructure evolution from the nucleus stage through various crystallization pathways remains unclear. We propose a unified model on the basis of the observation of two crystallization pathways, with different ferric (oxyhydr)oxide polymorphs appearing as intermediates, producing microstructures of magnetite mesocrystal via different mechanisms. An understanding of the crystallization mechanism enables independent chemical control of the mesocrystal diameter and crystallite size, as manifested by a series of magnetic coercivity measurements. We successfully implement an experimental model system that exhibits a universal crystallite size effect on the magnetic coercivity of mesocrystals. These findings provide a general approach to controlling the microstructure through crystallization pathway selection, thus providing a strategy for controlling magnetic coercivity in magnetite systems.
Magnetic coercivity behavior is essential for demonstrating magnetism in fine particles and is also a crucial performance indicator for a wide range of electrical and biomedical applications. Of many magnetic materials, magnetite (Fe₃O₄), which is biocompatible and exhibits superparamagnetic–ferrimagnetic transition depending on its size, has been extensively studied as a diagnostic and therapeutic reagent, leading to advances in the biomedical field. To date, shape, size, and composition are used to control magnetic coercivity for applications such as magnetic particle imaging (MPI), which require nonlinear magnetism or magnetic hyperthermia requiring hysteresis loss. However, remarkable advances currently appear unlikely. The microstructure provides a breakthrough in the control of coercivity because crystallite size and intercrystallite magnetic interaction are closely related to coercivity. To verify this at the nanoscale, the magnetic mesocrystal (an assembly of smaller crystallites) is a promising model system for exhibiting collective magnetic coercivity behavior influenced by individual crystallites. Magnetic mesocrystals have been reported to exhibit magnetic properties dissimilar from those of single-crystalline particles, depending on the structural arrangement and the magnetic coupling between crystallites. However, we still do not understand the correlation between the microstructure of the mesocrystal and its magnetic properties due to the complexity of the phenomenon. Controlling the crystallite size of mesocrystals at the nanoscale would experimentally reveal this correlation, but chemically controlling the microstructure of mesocrystals synthesized in a bottom-up process still remains a challenge.

The correlation between the microstructure of the Fe₃O₄ mesocrystal and its crystallization pathway is an essential underpinning of this study. Understanding the crystallization mechanism in chemical routes is crucial for precise control of the microstructure of Fe₃O₄ mesocrystals, which affects magnetic functions. In general, the crystallization mechanism of materials is described by the classical nucleation and growth theory, through which the crystals are spontaneously nucleated in solution and are grown after reaching critical size. For several systems, crystalline phases are not formed directly from solution but by stepwise phase transformations preceded by metastable intermediates. Formation of metastable intermediates advances with solubility, and are governed by the Ostwald step rule that the phases with a lower kinetic energy barrier are formed prior to the one with a higher barrier. Recently, several mechanisms besides the classical nucleation and growth model have been observed during the transformation steps of intermediate or crystalline phases. In particular, depending on the particle attachment model, mesocrystals comprising assemblies of smaller crystallites frequently exhibit a nonclassical pathway in which crystallization proceeds via attachment of nanometric building blocks (including prenucleation clusters or nanoparticles) and not atom accretion.

In these complex processes, the transient metastable intermediate state acts as a precursor to the post-nucleation stage in which the crystalline phase is formed. This intermediate state affects the type and structure of the final crystalline phase, as proposed primarily in calcium carbonate (CaCO₃), calcium phosphate (Ca₃(PO₄)₂), and calcium sulfate (CaSO₄) systems. The Fe₃O₄ phase is also commonly formed stepwise through a series of intermediates down to the lowest-energy rather than being formed directly from ionic precursors. For Fe₃O₄, various types of ferric (oxyhydr)oxide polymorphs [e.g., α-FeO(OH), β-FeO(OH), and γ-FeO(OH)] and ferrihydrite have been observed as intermediates. Because ferric (oxyhydr)oxide polymorphs represent similar solubilities, the types of intermediates appearing before the Fe₃O₄ phase can be significantly varied based on experimental conditions such as pH, additive content, and Fe³⁺ and Fe²⁺ cation concentrations. Furthermore, nonclassical crystallization mechanisms, which occur in the formation of ferric (oxyhydr)oxide intermediate or Fe₃O₄, can also affect the type of intermediate. Baumgartner et al. observed the crystallization process via particle attachment in Fe₂O₃ formation and proposed that the energetic stability of primary crystallites can influence the presence of ferrihydrite intermediates. These prior observations provide useful experimental and theoretically indications regarding the role of crystallization pathways. However, we still cannot fully explain the pathways via a universal mechanism, and the evolution of the microstructure during the reaction remains unclear.

In this study, we provide two crystallization pathways of Fe₃O₄ mesocrystals in which different ferric (oxyhydr)oxide polymorphs appear separately as intermediates on each pathway. We uncover that the microstructure of Fe₃O₄ mesocrystal is affected by which pathway governs the overall reaction and can be chemically controlled by polymorph selection of iron (oxyhydr)oxide. Based on this understanding, diameter and crystallite size of Fe₃O₄ mesocrystals are controlled independently. Finally, we report the successful experimental implementation of the crystallite size effect of Fe₃O₄ mesocrystal on the magnetic coercivity curves as a function of the diameter. Because Fe₃O₄ mesocrystals represent crystallographically ordered aggregate of spheres, we can discuss the collective coercivity behavior, which is difficult to observe in singular particle.

Results

Microstructure control via crystallization pathway selection.

We hypothesized that if the Fe₃O₄ phase was formed from different ferric (oxyhydr)oxide polymorphs as intermediates, there would be differences in the microstructure of the Fe₃O₄ mesocrystal because of the different crystallization mechanisms. If possible, we could chemically control the microstructure by selecting an intermediate among the polymorphs, and eventually, change the crystallite size of the Fe₃O₄ mesocrystal. To verify our hypothesis, we observe the crystallization pathways of Fe₃O₄ mesocrystals consisting of different crystallite sizes synthesized using the modified polyol method. We identified two crystallization pathways, shown in the schematic illustration (Fig. 1).

In pathway 1, Fe₃O₄ primary crystallites with a size of 3–4 nm are produced in the lepidocrocite matrices, and the Fe₃O₄ mesocrystals grow such that the crystals adhere to each other in the same crystallographic direction (nonclassical pathway). In pathway 2, Fe₃O₄ does not form directly in the lepidocrocite but apparently forms via stepwise transformation from lepidocrocite and goethite, conforming with the Ostwald step rule (classical pathway). Broadly, the entire reaction proceeds concurrently through these classical and nonclassical pathways. However, each pathway produces Fe₃O₄ mesocrystal at different stages. In pathway 1, the Fe₃O₄ mesocrystal forms at an early stage in the reaction, while in pathway 2, it is nucleated at a later stage in the reaction. Further, the microstructure is affected by the pathway governing the entire reaction and can be chemically controlled. We confirmed that the size of the crystallites formed in pathway 1 is smaller than that of those formed in pathway 2.

Crystallization processes of sample 1 and sample 2. We compared the formation process and microstructural evolution of Fe₃O₄ mesocrystals having the same ~60 nm diameter (D)
but different crystallite sizes (C) of 23 and 43 nm (Sample 1 (S1): $D = 62 \pm 3$ nm, $C = 23 \pm 3$ nm; Sample 2 (S2): $D = 61 \pm 4$ nm, $C = 43 \pm 3$ nm) synthesized using Fe:NaOAc:H$_2$O ratios of 2:15:150 and 1:3:200, respectively (Supplementary Figs. 1, 2). Uniform 60 nm Fe$_3$O$_4$ mesocrystals are synthesized in both cases.

Crystallization-pathway-dependent microstructural evolution. An analysis of the microstructure along each crystallization pathway is presented in Fig. 3. As shown in Fig. 3a, in the early stage of the reaction in S1, Fe$_3$O$_4$ mesocrystals, comprising spherical primary crystallites in nanocrystalline lepidocrocite intermediates, appear after 1 h of refluxing. In region 1, the fast Fourier transform (FFT) pattern of the Fe$_3$O$_4$ mesocrystal appears as a spot pattern, indicating that the primary crystallites have slightly tilted and almost identical orientations. The spots closest to the center are indexed as the (220) family of planes of Fe$_3$O$_4$. This is the characteristic phenomenon of mesocrystal formation in which the building units are crystallographically aligned.

Figure 3b shows that the FFT pattern of the primary crystallite on the Fe$_3$O$_4$ mesocrystal surface has the same crystallographic orientation as the core. The Fe$_3$O$_4$ mesocrystal and primary crystallites are attached along the direction of the (220) planes. In region 2, spherical intermediates appear and exhibit an unclear FFT pattern attributed to short-range order (Fig. 3a). The SAED pattern of the intermediates also forms a wide ring pattern, indicating that the intermediate phase exhibits poor crystallinity (Supplementary Fig. 5). After 1.5 h of refluxing, the growth of Fe$_3$O$_4$ mesocrystals through oriented attachment of the primary crystallites becomes prominent (Fig. 3c). Comparing the samples that reacted for 1 and 1.5 h, the number of primary crystallites around the mesocrystals increases more rapidly as the reaction time increases. The FFT results gradually change from a single to polycrystalline ring pattern indexed as Fe$_3$O$_4$ with increasing distance from the mesocrystal. This is because the primary crystallites are randomly oriented at the periphery of the mesocrystal, unlike those on the surface of the mesocrystal. Furthermore, we measured the number and size of primary crystallites in the TEM images and observed that the size of the primary crystallite lepidocrocite (ICDD no. 00-044-1415). With increasing reflux time, the peaks of the Fe$_3$O$_4$ phase become prominent and sharpened. For S2, we identify the tubular intermediate phase observed primarily in pathway 2 (Fig. 2c). At 3.5 h, the peak from lepidocrocite decreases, and that from goethite (ICDD no. 00-029-0713) appears, indicating that tubular ferric (oxyhydr)oxide intermediates could be assigned to goethite, a polymorph of lepidocrocite.

Crystallization-pathway-dependent microstructural evolution.
crystallites is fixed at $3.5 \pm 0.3$ nm, but their number increases 2.8 times as the Fe$_3$O$_4$ mesocrystal grows (Fig. 3d). This suggests that the growth mode can be attributed to the attachment of primary crystallites and not the accretion of ions or atoms.

We investigate crystallization pathway 2 of the Fe$_3$O$_4$ mesocrystal by analyzing the microstructure of S2 in which the mesocrystal crystallizes primarily from tubular goethite (Fig. 3e). We observed a consistent phenomenon in the later stage of the reaction in S1 (Supplementary Fig. 6). The structures of tubular goethite and the Fe$_3$O$_4$ mesocrystals are clearly distinguishable from each other in these reaction intermediates. Ferric (oxyhydr)oxide intermediates to the Fe$_3$O$_4$ phase, we can gain more insight into the crystallization of Fe$_3$O$_4$ mesocrystals in S1 and S2 using the Johnson–Mehl–Avrami–Kolmogorov (JMAK) model (Fig. 4)\textsuperscript{33}. This model has been extensively applied to phase transformation and polymorphic transformation of solid phase systems, and it can be written as

$$n = a + (b \times c),$$

where $a$ is the time-dependent nucleation rate ($a > 0$), $b$ is the dimensionality of the grown phase ($0 < b < 3$), and $c$ is the growth rate ($c = 0.5$ or 1)\textsuperscript{33–35}.

**Growth kinetics of crystallization pathways.** As discussed in the preceding sections, two coexisting pathways are competitively responsible for the crystallization process of Fe$_3$O$_4$ mesocrystals. They originate from different mechanisms and participate in different stages of the reaction to form Fe$_3$O$_4$ mesocrystals that exhibit distinct growth kinetics. Because the nucleation and growth of Fe$_3$O$_4$ mesocrystals can be explained through phase transformation under isothermal conditions, from ferric (oxyhydr)oxide intermediates to the Fe$_3$O$_4$ phase, we can gain more insight into the crystallization of Fe$_3$O$_4$ mesocrystals in S1 and S2 using the Johnson–Mehl–Avrami–Kolmogorov (JMAK) model (Fig. 4)\textsuperscript{33}. This model has been extensively applied to phase transformation and polymorphic transformation of solid phase systems, and it can be written as

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**Adjacent primary crystallites constituting the Fe$_3$O$_4$ mesocrystals in both samples are coarsened and densely packed, with the appropriate orientation (Supplementary Fig. 6). The size of the crystallite is determined by the post-coarsening process due to variations in the reactant concentrations, with S1, dominated by pathway 1, having smaller crystallites than that with S2, which is dominated by pathway 2.**
Figure 4a shows the timeline of the reaction and the JMAK model. We applied the model separately for each pathway because the kinetics of the transformation depends on the ferric (oxyhydr)oxide polymorph from which the Fe3O4 mesocrystals originate. Neither S1 nor S2 contains any phase other than Fe3O4 after the reaction is complete. Thus, we regard \( f \) as the volume fraction grown at a particular time with respect to the final volume formed at the end of each pathway (Supplementary Region 2).
Phases at each time are indicated. Solid and dotted lines represent crystallization pathways 1 and 2, respectively. Fe₃O₄ mesocrystals grown via pathway 1 of S₁ (pathway 1), S₁ (pathway 2), and S₂ (pathway 2) are similar, which implies that the mechanism of Fe₃O₄ mesocrystal growth at the interface of preexisting Fe₃O₄ mesocrystals, we can thus deduce one-dimensional growth (b = 1) and decreasing nucleation rate in pathway 2 (a = 0.4–0.6).

**Chemical control of the crystallization pathways.** We show that ferric (oxyhydr)oxide polymorphs play an essential role in determining the crystallization pathway of Fe₃O₄, which differentiates the microstructures of Fe₃O₄ mesocrystals derived via each crystallization mechanism. We propose that the crystallization pathways of Fe₃O₄ can be selected by varying the chemical content. Recent experimental and theoretical studies indicate that the solution chemistry affects the free-energy landscape that directly governs polymorph selection. The free-energy landscape is determined by the ratio of surface to bulk energy, which is a function of solution chemistry. Consequently, even minor variations in reactant type and concentration influence the phase is selected as intermediate among the ferric (oxyhydr)oxide polymorphs, which have different solubilities. The graphs in Fig. 5a–c represent the effect of the chemical content including FeCl₃·6H₂O, NaOAC, and H₂O on the diameter and crystallite size of the Fe₃O₄ mesocrystals. The modified polyol method has been widely used for a decade, but we were able to observe changes in the diameter and crystallite size over a wide range of chemical content and developed a comprehensive understanding of the synthesis process. Here, we focused on how crystallite size varies with NaOAC/FeCl₃·6H₂O ratio and H₂O content in terms of which crystallization pathway covers the entire reaction (see Supplementary Section 13). Increasing the content ratio of FeCl₃·6H₂O (the Fe precursor) to that of NaOAC and H₂O (the OH⁻ sources) can lead to a reduction in crystallite size, implying that pathway 1 gradually accounts for the entire reaction. The reason could be the effect of excess Fe³⁺ cations, which could be reduced to Fe²⁺ by the subsequent reaction with ethylene glycol. As the Fe²⁺ concentration increases, it is adsorbed onto the surface of the iron (oxyhydr)oxide phases, and it transfers electrons to the bulk iron (oxyhydr)oxide, thus promoting nucleation of Fe₃O₄. As shown in Fig. 5c, when H₂O is added in excess to the NaOAC/FeCl₃·6H₂O ratio, the Fe₃O₄ phase is no longer formed, and the reaction is blocked at the intermediate phase. This is because excess H₂O interferes with dehydration in the stepwise phase transformation of pathway 2.
A model for the magnetic coercivity behavior. Based on an understanding of the reaction, we can precisely control the diameter and crystallite size of Fe₃O₄ mesocrystals (Supplementary Figs. 9–12) and analyze the effect of crystallite size on $H_c$ (Fig. 5d). Figure 5d presents the $H_c$ variation of Fe₃O₄ mesocrystals as a function of diameter below $D_s$ for five groups representing different crystallite sizes; the crystallite size of each group of mesocrystals is kept constant. $D_s$ is the critical size at which a particle changes from single magnetic domain to multiple domains and is 105 nm for Fe₃O₄. All the groups fit the empirical equation $H_c = g + \frac{h}{D^{3/2}}$ when $D < D_s$, where $a$, $g$, and $h$ are constants, and $D$ is the mesocrystal diameter. $H_c$ shows a consistent relationship with $D^{-3/2}$ as it decreases in inverse proportion to the square root of the volume, like in Sharrock’s time-dependent $H_c$ expression. The empirical constant $g$ increases with increasing crystallite size, while $h$ decreases (Supplementary Table 1). The $H_c$ curve of the group with larger crystallites increases more steeply. The fitted $H_c$ curve from our previous study is included for reference, and it increases more rapidly than the $H_c$ curve in this study because the crystallite sizes of the samples used in the reference increased with increasing mesocrystal diameter. This implies that the $H_c$ curve fitting we obtained reflects the crystallite change accurately. Because the crystallites are magnetically coupled, in a manner reminiscent of mesocrystals, the Fe₃O₄ mesocrystals behave like a single particle. However, the Fe₃O₄ mesocrystals are simultaneously influenced by the individual size effect of the crystallite, which is a subunit of Fe₃O₄ mesocrystals. According to Jacobs and Bean’s chain-of-spheres model, the coercive force required for a magnetically coupled chain-of-spheres is lower than that of an ellipsoid with the axial ratio of the Stoner-Wohlfarth model. The Fe₃O₄ mesocrystals are an aggregate of crystallites with the same...
crystallographic orientation and can be represented as ordered aggregate of spheres (Fig. 5e). The ordered aggregate of spheres needs a lower coercive force to reverse the magnetic moment than that for a spherical particle of the same volume. Furthermore, when an aggregate is composed of smaller spheres, $H_c$ is reduced because the magnetically coupled interface increases. As the number of constituent spheres increases, $H_c$ gradually increases. This suggests that the chain-of-spheres model can also be adopted in spherical models that neglect shape anisotropy.

**Discussion**

We have discovered a new approach to chemically control the microstructure of Fe$_3$O$_4$ mesocrystals based on the crystallization pathways, which suggests that the polymorphism of iron (oxyhydr)oxide intermediates can affect the crystallization mechanism. We demonstrate that the growth mechanism of Fe$_3$O$_4$ mesocrystals from different iron (oxyhydr)oxide polymorphs leads to a variation in the microstructure of the mesocrystal characterized by the JMAK model. The former pathway, following oriented attachment, produces a small crystallite, while the latter, following the classical model by stepwise transformation, produces a large crystallite. These two parallel crystallization pathways operate competitively, and we were able to selectively control the ratio of the pathways that govern the entire reaction depending on the NaOAC/FeCl$_3$·6H$_2$O ratio and H$_2$O content. We hereby propose the $H_c$ model for Fe$_3$O$_4$ mesocrystals 100 nm or less in size, which facilitates fundamental magnetism in fine particles. To the best of our knowledge, this is the first report of $H_c$ variation in Fe$_3$O$_4$ mesocrystals synthesized using the same method as a function of both diameter and crystallite size. The Fe$_3$O$_4$ mesocrystals synthesized via chemical routes, with diameters ranging from a few nanometers to a hundred nanometers and exhibiting soft magnetism, are of emerging technological interest.

**Methods**

**Synthesis of Fe$_3$O$_4$ mesocrystals.** We use a modified polyol method that has been widely employed to synthesize metal/metal oxide mesocrystals with a controlled diameter in a wide range.$^{2,3}$ This method is effective for investigating the nucleation and growth process. The experimental procedure is as follows: we use iron chloride hydrate (FeCl$_3$·6H$_2$O), sodium acetate (NaOAC), and ethylene glycol (which are commonly used in the modified polyol method) as the Fe precursor, hydroxyl ion supplier, and solvent, respectively. We do not use any other surfactant or modifier. In a typical synthesis of Fe$_3$O$_4$ mesocrystals, FeCl$_3$·6H$_2$O, NaOAC, and distilled water are completely dissolved in 50 mL of ethylene glycol under vigorous mechanical stirring to form a yellow-brown turbid solution. FeCl$_3$·6H$_2$O (>97%, Sigma-Aldrich, Korea), NaOAC (>98.5%, Sigma-Aldrich, Korea), and ethylene glycol (>99.5%, Samchun Chemicals, Korea) are used as received. We add distilled water (Millipore Direct-Q UV 3) to the weighed FeCl$_3$·6H$_2$O powder to obtain the appropriate concentration. Next, the desired volume of FeCl$_3$·6H$_2$O aqueous solution is injected rapidly into the ethylene glycol solution NaOAC. Here, the Fe(OH)$_3$ precipitation of FeCl$_3$·6H$_2$O and distilled water should be carefully controlled because they significantly influence the diameter and crystallite size of the final Fe$_3$O$_4$ mesocrystals. The solution is then refluxed for 8 h, during which period it turns reddish-brown and then slowly becomes black. The temperature is set to 200 °C, but the size of the mesocrystals can be controlled by adjusting the duration of the reaction at temperatures between 70 and 90 °C. After cooling to room temperature, the black aggregate of spheres (Fig. 5e). The ordered aggregate of spheres needs a lower coercive force to reverse the magnetic moment than that for a spherical particle of the same volume. Furthermore, when an aggregate is composed of smaller spheres, $H_c$ is reduced because the magnetically coupled interface increases. As the number of constituent spheres increases, $H_c$ gradually increases. This suggests that the chain-of-spheres model can also be adopted in spherical models that neglect shape anisotropy.

**JMAK model of crystallization of Fe$_3$O$_4$ mesocrystals.** We tried to demonstrate two observed crystallization pathways using JMAK kinetics. Because neither S1 nor S2 contains any phase other than Fe$_3$O$_4$ after the reaction is complete, we regard $f$ as the volume fraction of Fe$_3$O$_4$ mesocrystals transformed from the appropriate intermediate. Thus, the JMAK equation yields the following:

$$\frac{df}{dt} = 1 - \exp\left(-\frac{kt}{C_0}\right),$$

where $f$ is the volume fraction of the material transformed, $t$ is the transformation time, $k$ is a constant, and $n$ is the Avrami exponent. $V_i$ is the volume of Fe$_3$O$_4$ mesocrystals grown at each transformation time, and $V_f$ is the final volume of Fe$_3$O$_4$ mesocrystals for each intermediate. The Avrami exponent $n$ can be written as follows:

$$n = a + (b + c)w,$$

where $a$ is the time-dependent nucleation rate ($a > 0$), $b$ is the dimensionality of the grown phase ($0 < b < 3$), and $c$ is the growth rate ($c = 0.5$ or 1). The value of $a$ indicates the nucleation rate as follows:

$$a = (no\text{ nucleation}, 0 < a < 1\text{ (increasing nucleation)}), a > 1\text{ (constant nucleation)}.$$
For S2, because the Fe₃O₄ mesocrystals are formed primarily from goethite, we considered the refluxing time of 3 h at which Fe₃O₄ crystals start to form, as $t_{\text{trans}} = 0$. For pathway 2 of S2 (from Gt to Fe₃O₄, $t_{\text{trans}} = 3–8$ h, $k_{\text{trans}}$, pathw2 = 0–5 h):

$$\frac{\frac{1}{2}n_r_{\text{trans}, \text{pathw2}}}{{\left(\frac{1}{2}n_r_{\text{trans, pathw2}} - \frac{1}{2}n_r_{t}\right)^{n}}} = 1 - \exp\left(-\left(k_{\text{trans, pathw2}}\right)^n\right) \tag{3}$$

Data availability

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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