

Formation of ϵ -Fe₂O₃ Nanocrystals through Segregation in Mesoporous Silica Particles

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Nanosized ϵ -Fe₂O₃ crystals with a diameter below 20 nm were successfully prepared at 600 °C in a mesoporous silica matrix. The formation of the metastable iron oxide occurred through nanoscale segregation in an immiscible SiO₂-Fe₂O₃ system having a mesoporous structure. The nanocrystals incorporated into ca. 50 nm-size particles of the mesoporous silica exhibited a coercive field up to 8 kOe.

A family of ferromagnetic iron oxides, such as magnetite (Fe₃O₄) and maghemite (γ -Fe₂O₃), has been utilized for magnetic recording and storage. Generally, a large coercive field (H_c) is hardly obtained in nanoscale particles because of their low magnetocrystalline anisotropy constant. Recently, a nanocrystal of a particular iron oxide phase, ϵ -Fe₂O₃, was reported to exhibit a giant H_c of 20 kOe at room temperature.¹ The specific phase has been prepared by the crystallization of Fe^{III} in silica or the decomposition of Y₃Fe₅O₁₂ in silica at a high temperature above 1000 °C.¹⁻³ Size-controlled preparation of ϵ -Fe₂O₃ nanoparticles was achieved using a microemulsion system containing silica and alkaline earth ions.^{4,5} However, detailed formation mechanism of ϵ -Fe₂O₃ in silica matrix has not been clarified. Moreover, lowering the process temperature is practically advantageous for preparation of small particles and thin films of the specific iron oxide.

A wide variety of mesoporous silica produced by self-assembly of surfactant molecules and silica-precursor species has been investigated since the synthesis of M41S family.⁶⁻⁸ Because of a highly porous structure having restricted nanospaces with high specific surface area, mesoporous silica was suggested to be suitable as a medium for controlled preparation of nano-sized functional crystals including ϵ -Fe₂O₃.⁹ Mesoporous silica nanoparticles with a diameter of 30–50 nm were fabricated using a cationic surfactant as a template and a nonionic block copolymer as a suppressant of grain growth.^{10,11} Since the fine grains in a nanometer scale are transparent to visible light and exhibit a remarkable potential as an easy-to-handle form having highly accessible mesopores, the incorporation of functional nanocrystals into the mesopores could be utilized to fabricate a novel type of nanomaterials. This letter describes successful fabrication of ϵ -Fe₂O₃ nanocrystals in mesoporous silica particles at 600 °C.

Mesoporous silica particles containing iron ions were prepared by a binary surfactant system as reported in previous articles.^{10,11} A certain amount of iron(II) chloride tetrahydrate, 1.2 g of cetyltrimethylammonium chloride (CTAC), and 2.4 g of a triblock copolymer (Pluronic F127; EO₁₀₆PO₆₀EO₁₀₆) were dissolved in 40 g of a hydrochloric acid solution at pH 2. Then, 4.0 g of tetraethoxysilane (TEOS) was added to the surfactant solution. An iron(II) complexed with ethylenediaminetetraacetate (EDTA) was used as an iron source instead of its chloride. The divalent iron compounds were suitable for the metal source

because of a high solubility in water. After being stirred at room temperature for 1 h, 4.0 g of aqueous ammonia (NH₄OH, 28 mass %) was introduced into the precursor solution. Typical molar concentrations in the final solution were 376 mM TEOS, 74 mM CTAC, 3.7 mM F127, and 1.29 M NH₄OH. The molar ratio of iron to silicon (R) was varied in the range between 0.05 and 0.23. Resultant pale green solution changed into darkish blue sol, and then ochre powder was obtained after evaporation of the disperse medium followed by washing using water/ethanol. This color change is ascribed to the oxidation of Fe^{II} into Fe^{III} on the drying process. Red-brown powder was finally produced by calcination in air at 550–1000 °C.

According to micrographs obtained with an FEI Tecnai F20 field-emission transmission electron microscope (TEM) (Figure 1a), a hexagonal array of mesopores with a diameter of ca. 2 nm was obtained without iron ions after the removal of organic compounds by calcination. On the other hand, the introduction of iron ions into the silica matrix was found to deform the ordered mesostructure with a decrease in specific surface area from low-angle X-ray diffraction (XRD) patterns and nitrogen adsorption-desorption measurement (Figures S1 and S2 in Supporting Information).¹² However, the presence of mesopores with a high specific surface area above 600 m²/g was maintained even after the calcination, while the ordered array of mesopores was not clearly observed in TEM images (Figure 1b). Dark spots with a diameter of 10–20 nm were found in the iron-containing silica particles after the calcination at 600 °C. From the lattice images (Figures 1c and 1d), the spots were identified to be ϵ -Fe₂O₃. Diffraction peaks assigned to ϵ -Fe₂O₃ were also detected by XRD for the mesoporous silica/iron oxide composite (Figure S3).¹² The actual molar ratio of iron to silicon of the products was confirmed to be almost the same as that in the precursor solutions by using energy-dispersive X-ray analysis (Bruker AXS Quantax). Resultingly, we prepared a single phase of ϵ -Fe₂O₃ at a relatively low temperature 550–600 °C at $R = 0.05$ – 0.23 . Since conventional techniques using nonporous silica matrix required calcination at a high temperature around 1000 °C for the formation of the specific metastable phase, we drastically lowered the process temperature using the porous silica matrix. In consequence, we obtained ϵ -Fe₂O₃-incorporated mesoporous silica nanoparticles having a high specific surface area. Larger crystals were obtained at a higher temperature because the diffraction peaks were enhanced by calcination at 1000 °C (Figure S3).¹² However, the mesopores in the silica particles were collapsed by the high-temperature treatment.

The nanoparticles of ϵ -Fe₂O₃ at 600 °C were also obtained using the system inclusive CTAC and TEOS, but exclusive F127 (Figure S4).¹² Thus, the suppressant for the grain growth was not required for lowering the process temperature. However, the templating micelles could not promote the crystallization of ϵ -Fe₂O₃ directly, because the organic components were basically removed at a temperature below 550 °C. Since silica matrix is

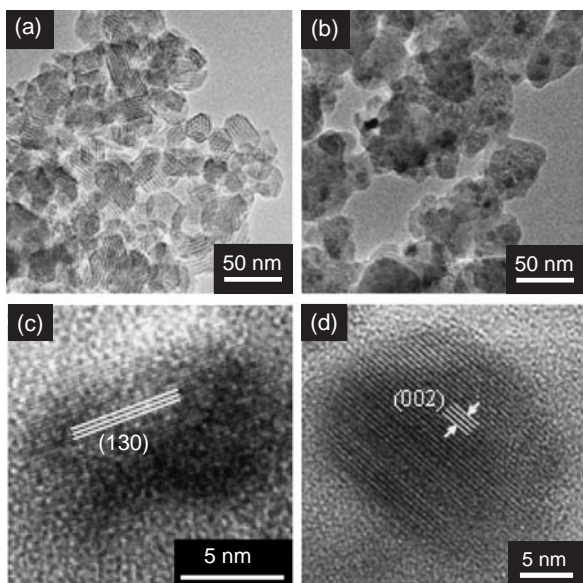


Figure 1. TEM images of mesoporous silica nanoparticles (a) and silica/iron oxide composite particles ($R = 0.23$) (b)–(d).

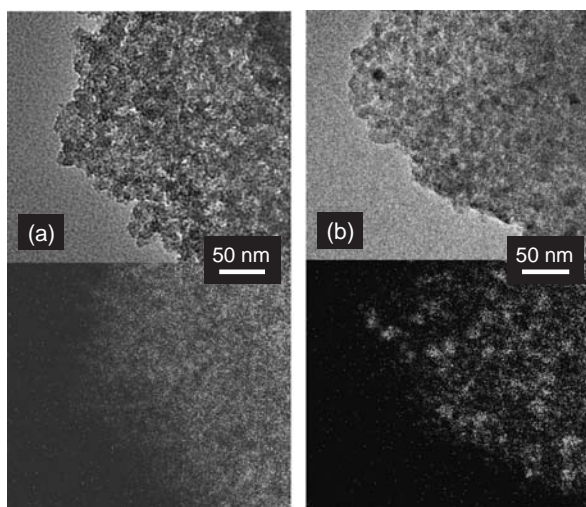


Figure 2. TEM images (upper) and mapping images of iron (lower) by electron energy-loss spectroscopy (EELS) for iron-incorporated mesostructures ($R = 0.23$) before (a) and after (b) calcination at 600 °C.

essential for the formation of the metastable iron oxide according to the previous works,^{1–5} the organic component is assumed to provide a suitable nanoscale structure of silica matrix. As shown in Figure 2a, iron ions were homogeneously dispersed in the silica matrix before calcination. Because Fe_2O_3 is immiscible in SiO_2 in thermodynamic terms, phase separation would occur spontaneously in the unstable $\text{SiO}_2\text{–Fe}_2\text{O}_3$ system at a high temperature (Figure 2b). Therefore, a metastable $\varepsilon\text{-Fe}_2\text{O}_3$ phase could be produced through nanoscale segregation. The mesoporous structure originating from the surfactant micelles exhibits a high specific surface area promoting the crystallization of $\varepsilon\text{-Fe}_2\text{O}_3$ in the immiscible system. Although $\varepsilon\text{-Fe}_2\text{O}_3$ was produced in mesoporous silica,⁹ a low-temperature synthesis of the specific phase has not been reported. When we used

EDTA– Fe^{II} complex as another iron source, $\varepsilon\text{-Fe}_2\text{O}_3$ was not obtained in mesoporous silica at 600 °C. In this case, iron ions were not dispersed in the silica matrix because the anionic complex was located in the micelle phase of the original mesostructure. This fact supports that the presence of iron ions dissolved in the silica network is essential for the formation of $\varepsilon\text{-Fe}_2\text{O}_3$. Metastable iron phases, such as $\gamma\text{-Fe}_2\text{O}_3$ and $\varepsilon\text{-Fe}_2\text{O}_3$, are composed of tetrahedron of four-coordinated Fe^{III} ion and octahedron of six-coordinated Fe^{III} ion, while stable $\alpha\text{-Fe}_2\text{O}_3$ consists of the six-coordinated ions. As mentioned above, Fe^{II} in the precursor solution was oxidized to Fe^{III} in the silica matrix during a drying process. Since Fe^{III} was reported to exist in the four-coordinated state in silicate glasses,¹³ the metastable iron oxides could be easily constructed through separation from the silica phase. Moreover, a size effect for the stabilization of $\varepsilon\text{-Fe}_2\text{O}_3$ was suggested on the basis of thermodynamical analysis.⁵ Thus, the formation of $\varepsilon\text{-Fe}_2\text{O}_3$ particles having a specific size could be achieved in mesoporous silica matrix at a relatively low temperature. According to field dependent magnetization curves (Figure S5),¹² H_c of $\varepsilon\text{-Fe}_2\text{O}_3$ nanocrystals incorporated into mesoporous silica particles ($R = 0.05$) was 8 kOe, which was larger than that of $\gamma\text{-Fe}_2\text{O}_3$, and in the same order as that reported previously.¹

In summary, mesoporous silica matrix was found to be suitable for the preparation of nanosized $\varepsilon\text{-Fe}_2\text{O}_3$ crystals exhibiting a high coercive field. This new type of nanomaterials would be utilized as magnetic and transparent sol and coating for various medical and optical applications.

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