Modification Effect of SCN^- Ions on the Morphology of α-Fe_2O_3 Nanoparticles

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Based on the concentration difference of exposed dangling Fe^{3+} ions on different crystal facets, an "oriented dissolution" along $[\bar{2}21]$ direction of α-Fe_2O_3 was carried out via a redox reaction between coordinative ions SCN^- and exposed Fe^{3+} ions. It is a new effective route to modify the morphology of α-Fe_2O_3 nanoparticles.

Control over crystallization is one of the most important techniques in modern materials science owing to its potential to produce well-defined particles with unique structures at the nanometer or micrometer scale.[1] In order to improve the material properties for specific technological applications, various approaches have been developed to control the microstructures of nanomaterials. As nucleation and growth are highly sensitive processes, crystallization is usually controlled by various additives. Recently, utilizing the special adsorption of anions on some determined crystal facets, a method named as "oriented dissolution" has been developed to modify the morphologies of nanoparticles. For example, using the special coordination of $H_2PO_4^-$ ions to the surface hydroxy groups on (001) planes, α-Fe_2O_3 nanotubes and nanorings were fabricated by dissolving spindle α-Fe_2O_3 nanoparticles along [001];[2,3] ZnO nanorings were made by dissolving ZnO nanodisks along [001] under the effect of sodium bis(2-ethylhexyl) sulfosuccinate (NaAOT) and $NH_3 \cdot H_2O$ in a mixture of butanol and water;[4] $Cd(OH)_2$ nanorings were fabricated by dissolving nanoplates along the direction perpendicular to plate under ultrasonic irradiation.[5]

Iron oxides represent an important class of materials used in a wide range of applications including catalysis,[6] magnetic devices,[7] environment protection,[8] sensors,[9] drug delivery,[10] clinical diagnosis,[11] and water splitting.[12] Furthermore, they combine such functionality with low cost and low toxicity.[13] α-Fe_2O_3 nanotubes and nanorings have been obtained on the basis of different surface hydroxy group configuration on different crystal facets.[2,3] Can we modify the nanostructures utilizing the self properties of α-Fe_2O_3 crystal, for example, the concentration difference of exposed dangling Fe^{3+} ions on different crystal facets? Out of this consideration, SCN^- ions, as a reducing agent and strong ligand to Fe^{3+} ions, were selected to investigate this hypothesis.

In a typical experimental procedure, 0.5 g of $FeCl_3 \cdot 6H_2O$ and 0.05 g of NaSCN were dissolved in 80 mL of distilled water. Then, the solution was transferred into a Teflon-lined stainless steel autoclave with 100-mL capacity. The autoclave was sealed and maintained at 220 °C for 48 h. After the reaction was complete, the autoclave was cooled to room temperature on standing. The produced precipitate was separated by centrifugation, subsequently washed with distilled water for several times, and then dried at 60 °C in air. All the reagents were A.R. grade and were used in preparation without further purification. X-ray powder diffraction (XRD) measurement was performed on a D8 Advance Bruker AXS diffractometer, using a Cu Kα radiation ($\lambda = 1.5406$ Å). The morphology of the samples was investigated by a scanning electron micrograph (SEM, LEO 1530VP) and a transmission electron micrograph (TEM, JEM-2010FEF).

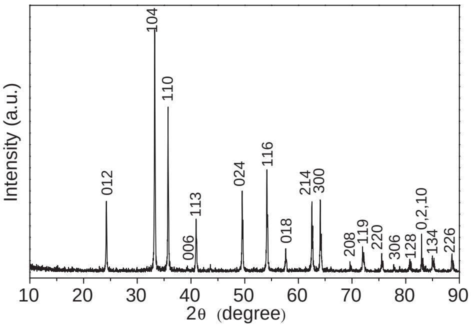

Figure 1. XRD pattern of the synthesized product.

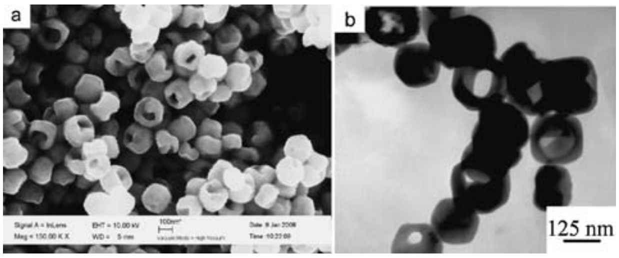

Figure 2. SEM and TEM images of the synthesized product.

Figure 1 shows the XRD pattern of the synthesized product, from which the synthesized product can be exclusively indexed to α-Fe_2O_3, according to standard data (JCPDS 33-0664). No other impurities such as Fe_3O_4, $Fe(OH)_3$, and FeOOH can be observed.

Figures 2a and 2b present the SEM and TEM images of synthesized product, respectively. Seen from Figure 2a, the particles were well dispersed and most of them possessed a hole in the middle. Seen from Figure 2b, the hole had pierced these particles completely. Actually, nanorings or nanocylinders were more appropriate to these particles. Then, are they similar to the reported α-Fe_2O_3 nanotubes and nanorings, that were obtained by "oriented dissolving" initial particles along [001] direction?

To investigate the growth process of these pierced particles, a detailed time-dependent morphology evolution study was done at 220 °C. Figure 3 presents the SEM images of samples obtained at different reaction time from 8 to 36 h. For reaction time of 8 h (Figure 3a), most of the particles are well-dispersed quasicubic nanoparticles with an average size 150 nm. Figure 3b

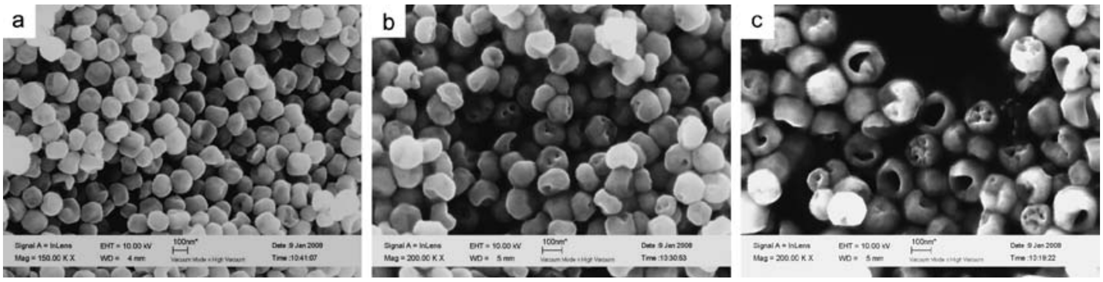

Figure 3. SEM images of the products at different reaction time: (a) 8, (b) 24, and (c) 36 h.

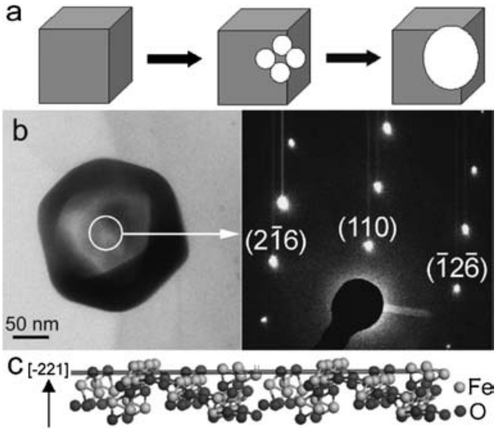

Figure 4. (a) Schematic of the morphologies evolution process, (b) SAED analysis of an intermediate particle, and (c) crystal structure of $(\bar{2}21)$ plane, in which Fe atoms are dangling.

shows the product obtained after 24 h reaction, in which small holes present on the surface of the particles. It is notable that these small holes aggregated together and arrayed along the same direction. The product obtained after 36 h is shown in Figure 3c, in which some big holes had come into being in many particles and in other particles aggregated small holes still existed.

Based on evidence from the above time-dependent morphology evolution, the formation of the nanocylinders can be proposed as "dissolving" the quasi-cubic precursors from the face toward the interior along a special direction. The dissolution process began at several points and was followed by forming several small holes along that special direction. As the reaction proceeds, coalescence occurs among these small holes and a bigger hole forms in the particles, the reaction would keep going until all of the particles possess this structure. The whole process is illustrated in Figure 4a. That is to say, like reported α-Fe_2O_3 nanotubes and nanorings, the formation of nanocylinders also obeyed an "oriented dissolution" mechanism. To identify the direction of the oriented dissolution, selected area electron diffraction (SAED) was carried out on an individual intermediate particle in Figure 4b along the dissolving direction, and the SAED patterns could be indexed to the $[\bar{2}21]$ zone axis of rhombohedral α-Fe_2O_3. Therefore, the dissolution process should occur on $(\bar{2}21)$ planes.

$$Fe_2O_3 + 2SCN^- + 6H^+ \rightarrow 2Fe^{2+} + (SCN)_2 + 3H_2O \quad (1)$$

Then, what is the driving force for the "oriented dissolution"? Unlike $H_2PO_4{}^-$ ions, SCN^- ions can not react with the surface hydroxy groups to form a monodentate or bidentate innersphere complex.[2] SCN^- ions are strong coordinative anion to Fe^{3+} ions, so the coordination effect between SCN^- ions and dangling Fe^{3+} ions would be the dominant reaction at the beginning. However, as a quasi-halogen ion, SCN^- possesses reductive ability at high pressure and high temperature. Consequently, after the coordination reaction achieves equilibrium, a redox reaction may occur between coordinative SCN^- ions and oxidant Fe^{3+} ions, as eq 1 shows. To realize the redox reaction, SCN^- ions must come close to those exposed Fe^{3+} ions and form coordinative structure. Thus the reaction should occur on $(\bar{2}21)$ planes because $(\bar{2}21)$ planes possess more dangling Fe^{3+} ions compared with other planes (see Figure 4c, Supporting Information Figure S1 and Table S1[14]). Although the (001) planes possesses the largest Fe^{3+} ion concentration, but the steric effect on (001) planes is more obvious than that on $(\bar{2}21)$ planes that possess more dangling Fe^{3+} ions. This result is consistent with its above-mentioned SAED analysis.

In summary, based on the difference of exposed dangling Fe^{3+} ions on different crystal planes, an "oriented dissolution" along $[\bar{2}21]$ direction was carried out via a redox reaction between coordinative SCN^- ions and dangling Fe^{3+} ions. It is a new effective route to modify the morphologies of α-Fe_2O_3 nanoparticles. This approach may be extended to the modification of other metal oxides, if the metal ions have coordination ability and appropriate ligands have been selected.

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14 Supporting Information is also available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.