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Transformation of ferrihydrite in the presence or absence of trace Fe(II): The effect of preparation procedures of ferrihydrite

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ABSTRACT

Two-line ferrihydrite was prepared by two different procedures. In procedure 1, which is widely used, ferrihydrite (named as ferrihydrite-1) was prepared by droping NaOH solution into Fe(III) solution. In procedure 2, which is rarely reported, ferrihydrite (named as ferrihydrite-2) was prepared by adding Fe(III) and NaOH solutions into a certain volume of water simultaneously. The results showed that mixing procedures of Fe(III) and alkaline were critical in the sub-microstructures and the conversion mechanisms of ferrihydrites in the presence or absence of trace Fe(II). The sub-microstructure of ferrihydrite-1 favored the mechanism of its dissolution re-crystallization and hematite nanoparticles with rough surface were obtained. The sub-microstructure of ferrihydrite-2 favored the solid state transformation from ferrihydrite to hematite and hematite nanoparticles with smooth surface were formed. These research results will be helpful for us to control the synthesis of hematite nanoparticles with different surface state.

1. Introduction

Ferrihydrite is a common, naturally occurring Fe(III) (hydr) oxide in the earth's crust, soils and sediments. It plays a substantial role in the sequestration of contaminants from groundwater and streams through adsorption and co-precipitation due to its high surface area and intrinsic reactivity. It is also manufactured for use as a scavenger of heavy metals and metalloids during the treatment of wastewaters and in remedial activities [1]. Moreover, ferrihydrite is a metastable species in iron oxide family. With time, it generally transforms to more thermodynamically stable ones such as hematite and/or goethite etc. As such, the study of ferrihydrite has been the subject of much scientific research in environmental, material and soil sciences [2–6].

The crystallinity of ferrihydrite synthesized or found in nature is relatively poor, which has hampered accurate structure determination by traditional methods that rely on long-range order. Ferrihydrite is generally classified according to the number of X-ray diffraction lines that the material gives: typically 2-line ferrihydrite and 6-line ferrihydrite. It was thought that the main difference between 2- and 6-line ferrihydrite is the size of their coherent scattering domains [7]. Some works concluded that probably 6-line ferrihydrite may be a metastable intermediate in the conversion of 2-line ferrihydrite into hematite [8,9] and this hypothesis was confirmed recently by the calculation of Gibbs free energy of formation for the two forms of ferrihydrite [10]. In the reference literature ferrihydrite was given different chemical formulae such as $Fe_5HO_8\cdot 4H_2O$ [11], $Fe_2O_3\cdot 2FeOOH\cdot 2.6H_2O$ [12] and $5Fe_2O_3\cdot 9H_2O$ [13] etc. and $5Fe_2O_3\cdot 9H_2O$ is the most widely reported. Michel et al. [1,14] used high-energy X-ray total scattering for pair distribution function (PDF) analysis to observe both the short- and intermediate-range ordering (exceeding ~15 Å) of synthetic ferrihydrite using different methods. Based on their results, ferrihydrite was given another formula $Fe_{10}O_{14}(OH)_2$. However, more recently, Rancourt and Meunier [15] contested the structure for ferrihydrite obtained by Michel et al. Academically, such disputation is common, especially for the determination of structure of small-sized particles with poor crystallinity like ferrihydrite. But, any proposed structure for ferrihydrite should be quantitatively consistent with the basic physicochemical properties of the material [15].

The transformation of ferrihydrite under different conditions has been the subject of material science. Proposed transformation mechanisms from ferrihydrite to hematite in solution range from dissolution of precursor followed by precipitation of product to solid state transformation within precursor aggregate or topotactic transformation accompanied by the phase transformation [16,17]. The occurrence of the solid state transformation in solution is governed by various factors, including the relationship in structure between precursor and final product as well as experimental conditions, etc. A similarity in structure between

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the precursor and the final product is the precondition for the solid state transformation to occur in solution.

Recently, we found that Fe(II) adsorbed onto ferrihydrite can catalyze the transformation from ferrihydrite to hematite at pH 5–9 and 100 °C [18]. On the one hand, Fe(II) can accelerate the dissolution of ferrihydrite, which leads to the formation of hematite particles by dissolution re-crystallization mechanism. On the other hand, it can accelerate the solid state transformation from ferrihydrite to hematite in solution. In the experimental processes, we found that there are some differences in the sub-microstructure of ferrihydrite obtained from different procedures of mixing Fe(III) and NaOH solutions. More interestingly, these differences have obvious effect on their intrinsic reactivity, including the transformation time, the size and surface state of product particles, as well as the transformation mechanism. This paper attempted to investigate the differences of ferrihydrites prepared by different procedures and their transformation mechanisms. The results obtained in the current work not only can help us to control the synthesis of hematite nanoparticles with different surface structure but also understand explicitly the dependence of the transformation mechanism on the sub-microstructure of precursor.

2. Experimental methods

Ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$), ferrous chloride ($FeCl_2 \cdot 4H_2O$) and sodium hydroxide (NaOH) of analytical purity and distilled water were used. The ferric salt solutions were filtered through a 0.22 μm Millipore filter to remove any particulate contaminants before use.

Ferrihydrite was synthesized by the following different procedures.

Procedure 1. 6.0 mol/L NaOH solution was added into 50 mL of Fe(III) solution (1.0 mol/L) until pH 7 under vigorous stirring (The gel formed in this system was named as ferrihydrite-1.), followed by the addition of trace Fe(II) solution ($n_{Fe(II)}/n_{Fe(III)} = 0.02$) to the above mixture. The pH of the system was again adjusted to 7 by a dilute NaOH solution (1.0 mol/L). At the same time, the total volume of the system was adjusted to 100 mL.

Procedure 2. NaOH solution (6.0 mol/L) and 25 mL of Fe(III) solution (2.0 mol/L) were added simultaneously into 40 mL of water at RT under vigorous stirring. The rate of adding two solutions was controlled by maintaining pH 7 with accuracy of better than 0.5 pH unit. The gel formed at RT was named as ferrihydrite-2. Then trace Fe(II) solution ($n_{Fe(II)}/n_{Fe(III)} = 0.02$) was added into the system and the pH of the system was again adjusted to the desired value by dilute NaOH solution (1.0 mol/L). At the same time the total volume of the system was adjusted to 100 mL.

The experiments were carried out under nitrogen gas and oxygen-free distilled water was used in all stages. Then the slurry formed in the above two systems was heated, with nitrogen flowing within the vessel until it boiled. The suspension was refluxed for a certain time varying from 3 min to 22 h depending on the reaction conditions. The product was centrifuged and washed thoroughly with distilled water and dried at about 70–80 °C.

X-ray diffraction (XRD) patterns of the samples were obtained with a Bruker diffractometer D8 ADVANCE using a Cu$K\alpha$ radiation. Infrared (IR) spectra were conducted over the range 200–4000 cm^{-1} with a Nicolet Magna FTIR-550 Fourier-transform infrared spectrometer. Transmission electron micrographs (TEM) were obtained with a Hitachi H-7500 and high resolution transmission electron micrographs (HRTEM) were obtained with H-9000. The samples were dispersed in ethanol using an ultrasonic treatment.

3. Results and discussion

3.1. XRD patterns and IR spectra of ferrihydrite-1 and ferrihydrite-2

Fig. 1 presents XRD patterns of ferrihydrites-1 and ferrihydrites-2. As shown in Fig. 1, there is a little difference between ferrihydrite-1 and ferrihydrite-2. Compared to ferrihydrite-2, another two weak peaks were found at $2\theta \sim 28^\circ$ and $\sim 45^\circ$ in XRD pattern of ferrrihydrite-1 besides the peaks at $2\theta \sim 35^\circ$ and $\sim 63^\circ$, which probably indicates that ferrihydrite-1 has a better ordering and crystallization. Moreover, their color has obvious difference (supporting information Fig. 1). By naked-eye observation, not only the color of ferrihydrite-2 is much lighter than that of ferrihydrite-1, but also the former looks more uniform than the latter. These results suggest that mixing method of Fe(III) and NaOH solutions markedly affected the aggregate of ferrihydrite, and this may also explain the difference in color [19].

Fig. 2 shows IR spectra of the two precursors. The prominent bands at ~1600 and ~3400 cm^{-1} can be attributed to adsorbed or lattice water, although the latter band is expected also to contain a contribution from the stretching of OH groups of ferrihydrite [20]. According to data obtained by Ristic et al. [21], the bands at ~1500 and ~1400 cm^{-1} in Fig. 2b is attributed to carbonates because ferrihydrite is very susceptible to CO_2 from air. However, those two bands did not appear in ferrihydrite-1 (Fig. 2a). At wavenumber less than 1000 cm^{-1}, ferrihydrite-1 shows three bands at ~459, ~599 and ~671 cm^{-1} and ferrihydrite-2 shows two bands at ~459, ~585 and a shoulder at ~710 cm^{-1}. All these bands can be attributed to Fe–O bond in the samples. It is known that the degree of crystallinity and the aggregation of particles and the shape of particles can influence the positions of the IR bands of sample

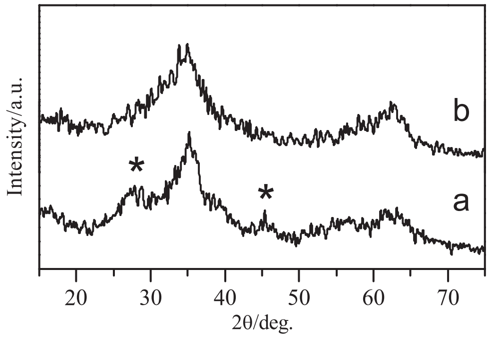

Fig. 1. XRD patterns of (a) ferrihydrite-1 and (b) ferrihydrite-2.

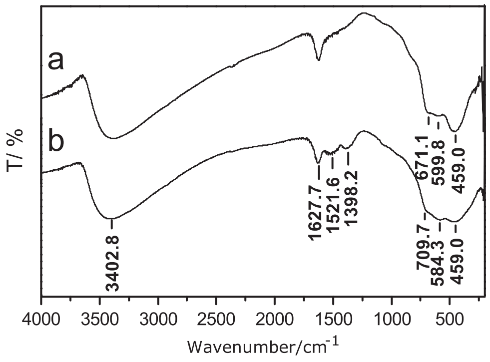

Fig. 2. IR spectra of (a) ferrihydrite-1 and (b) ferrihydrite-2.

as well as their relative intensities and broadening [22]. The differences between the two ferrihydrites in IR spectra reveal some differences in their sub-microstructure to a certain degree. Here, using the term "sub-microstructure" is due to that the testing techniques (XRD pattern and IR spectra) used in the current paper belong to traditional methods that rely on long-range order. In any case, the differences in XRD patterns, IR spectra as well as the color between the two ferrihydrites supply some information on the structure of ferrihydrite.

3.2. Transformation of ferrihydrite-1 and ferrihydrite-2

It is known that ferrihydrite can be transformed into hematite particles after refluxing for a certain time. However, the transformation times of different ferrihydrites are different. The results show that the final transformation time of ferrihydrite-2 is much shorter than that of ferrihydrite-1. Fig. 3a shows TEM images of the product obtained by heating ferrihydrite-1 for 22 h at 100 °C. As shown in Fig. 3a, there are some amorphous particles in the product besides some big hematite particles. Most of the amorphous particles in the product are confirmed to be unconverted ferrihydrite by dissolving the sample in HCl solution of pH 1 for 1 h [23]. When ferrihydrite-2 was used as precursor, not only the transformation time (only 3.5 h) is much shorter than that of ferrihydrite-1 but also the particle size of hematite is obvious smaller than that obtained by ferrihydrite-1 (Fig. 3). Moreover, the particles obtained by ferrihydrite-2 are more uniform. These results further indicate that the sub-microstructure of ferrihydrite has a significant influence on its reactivity. The previous research showed that the transformation from ferrihydrite to hematite in solution is carried out either by the solid state transformation mechanism (i.e. the structural rearrangement within ferrihydrite aggregate) or the dissolution re-crystallization [3,17]. High temperatures or a pH close to the point of zero charge (pzc) of ferrihydrite favor the structural rearrangement within ferrihydrite aggregate [24]. Schwertmann [24] thought that the amount of Fe in the ferrihydrite aggregate determines the final size of the hematite crystal which is, therefore, related to the aggregate size of the precursor. The above results lead us to the conclusion that the sub-microstructure of ferrihydrite-2 is much similar to that of hematite, thus it needs a shorter time to complete the dehydration and rearrangement processes within ferrihydrite aggregate. Small aggregate of ferrihydrite-2 results in small-sized hematite particles, and vice versa. This conclusion will be further confirmed by following experimental data.

3.3. Transformation of ferrihydrite-1 and -2 in the presence of trace Fe(II)

The presence of trace Fe(II) can accelerate the transformation from ferrihydrite to hematite. The catalytic behavior of Fe(II) is shown in two aspects—the catalytic dissolution re-crystallization and the catalytic solid state transformation [18]. The two mechanisms were triggered by the electron transfer between Fe(II) and Fe(III). Figs. 4 and 5 show TEM images of the samples taken out during the transformation process of ferrihydrite-1 and ferrihydrite-2, respectively. When ferrihydrite-1 with trace Fe(II) was heated to boiling point, a small amount of hematite particles were found (Fig. 4a). However, the amount of hematite particles is so little at this moment that the color of the suspension is still dark red–brown (supporting information Fig. 2b). Under the same conditions, a great deal of hematite particles have been formed in the ferrihydrite-2 system (Fig. 5a), and the color of the suspension has changed to red (supporting information Fig. 3b). The results indicate that the total transformation process of ferrihydrite-1 needs about 0.5 h to complete while that of ferrihydrite-2 only needs about 15 min (Fig. 5b). Moreover, the particle size of hematite obtained from ferrihydrite-2 (~50 nm) is less than that from ferrihydrite-1 (~80 nm). This result is consistent with the one in Fig. 3.

To further investigate the transformation mechanism, changes in the pH value of the system were determined as a function of the reaction time (Fig. 6). As shown in Fig. 6, the pH decreases with reaction time for both ferrihydrite-1 (Fig. 6a) and ferrihydrite-2 (Fig. 6b). However, the difference between the initial and final pH values, that is, ΔpH for ferrihydrite-2 is much smaller than that for ferrihydrite-1. When ferrihydrite-2 was prepared at 60 °C, the ΔpH becomes very small (Fig. 6c). These results can be repeatable, suggesting that those ΔpHs can reflect some relationship between the sub-microstructure of ferrihydrite and the two transformation mechanisms.

In the experimental process, it was found that the final pH in ferrihydrite-1 system is always less than 1.0 (Fig. 6a) after completing the transformation, while the final pH is about 4.0 in ferrihydrite-2 system (Fig. 6b) under the same conditions. When ferrihydrite-2 is prepared at 60 °C, the pH value decreases only one pH unit. If ΔpH is converted into the concentration of H^+ ions released in the reaction process by the formula

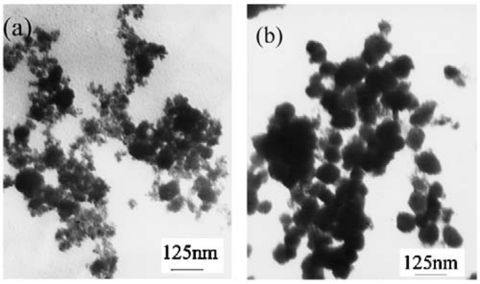

Fig. 4. TEM images of the samples using ferrihydrite-1 as a precursor (a) 5 min (boiling) and (b) 15 min.

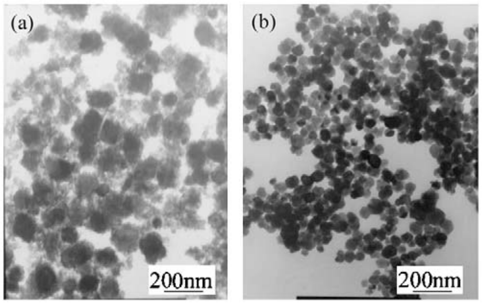

Fig. 3. TEM images of hematite particles prepared by (a) ferrihydrite-1 ($t = 22$ h) and (b) ferrihydrite-2 ($t = 3.5$ h).

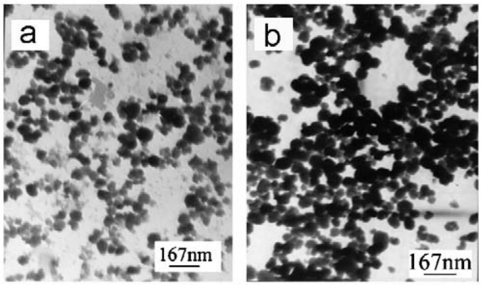

Fig. 5. TEM images of the samples using ferrihydrite-2 as a precursor (a) 5 min (boiling) and (b) 15 min.

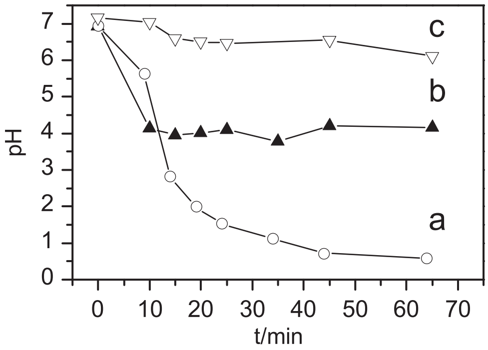

Fig. 6. pH versus time curves (a) ferrihydrite-1, (b) ferrihydrite-2 and (c) ferrihydrite-2 prepared at 60 °C.

Table 1
pH changes during the phase transformation of different ferrihydrites.

Ferrihydrites	Initial pH	Final pH	ΔpH	The concentration of H^+ ion released into solution (mol/L)
Ferrihydrite-1	6.94	0.59	−6.35	0.257
Ferrihydrite-2	6.92	4.17	−2.75	6.75×10^{-5}
Ferrihydrite-2 prepared at 60 °C	7.16	6.11	−1.05	7.07×10^{-7}

$[H^+] = (10^{-pH})_{final} - (10^{-pH})_{initial}$, the difference between the different ferrihydrites becomes more obvious. The pH changes during the phase transformation for all prepared samples are shown in Table 1.

The reasons for the decrease in pH are as follows. Firstly, some H^+ ions are probably adsorbed on the surface of ferrihydrite. As the reaction proceeds, these ions are desorbed from ferrihydrite into solution, which causes the decrease of pH. Secondly, Fe(II) can catalyze the dissolution of ferrihydrite. The species dissolved in solution may be $Fe(OH)_2^+$ and/or $Fe(OH)^{2+}$ and/or Fe^{3+}, depending on the pH of reaction system [25]. Actually, this solution is a very dilute one of Fe(III). Fe(III) ions are easily hydrolyzed at 100 °C. This hydrolysis is accompanied by deprotonation, which also leads to a decrease of pH. Thirdly, at the same time those Fe(III) ions such as $Fe(OH)_2^+$ or $Fe(OH)^{2+}$ in solution can condense to form polymer. Flynn [26] thought the formation of polymer involves condensation of monomeric.

$$[Fe(OH)_2{}^+]_n + Fe^{3+} + 2H_2O \rightarrow [Fe(OH)_2{}^+]_{n+1} + 2H^+ \tag{1}$$

$$2[Fe(OH)_2\ (H_2O)_{(4-2p)/2}(OH)_{2p/2}{}^{(1-p)+}]_n \rightarrow [Fe(H_2O)\ (OH)_{2/2}\ O_{3/3}]_{2n} + 2n(1-p)\ H^+ + 2n\ H_2O \tag{2}$$

The formation of polymer is also accompanied by deprotonation. Of the three reasons, the latter two indicate that the dissolution re-crystallization mechanism exists in the present system.

Comparing the results of ferrihydrite-1 to ferrihydrite-2 in Fig. 6 and Table 1, it is thought that the decrease of pH in ferrihydrite-2 system mainly results from the desorption of H^+ ions. That is, the proportion of the dissolution re-crystallization mechanism in ferrihydrite-2 system is smaller than that in ferrihydrite-1 system. On the contrary, the solid state transformation dominates in the former system. Because the solid state transformation occurs within ferrihydrite aggregate, it is accompanied by dehydration, which leads to a small pH decrease. When ferrihydrite-2 was prepared at 60 °C, its dissolution becomes more difficult [25], thus the formation path of hematite by the dissolution re-crystallization mechanism is limited to a large extent. Thus, the decrease of pH should be the least (Fig. 6c). At this time, the transformation of ferrihydrite is completed mostly by the solid state transformation.

Moreover, the above results indicate that the transformation rate of ferrihydrite-2 is obviously larger than that of ferrihydrite-1, which means the rate of the solid state transformation is larger than that of the dissolution re-crystallization. In fact, when ferrihydrite-2 was prepared at 60 °C, it was found that the transformation from ferrihydrite-2 to hematite was completed in 3 min (Fig. 7a). Hereafter, there are not any obvious changes in the size of hematite particles with the reaction time (Fig. 7b).

High-resolution TEM (HRTEM) and ED patterns investigations of hematite particles provide further insight into the difference in the sub-microstructure between ferrihydrite-1 and ferrihydrite-2 (Fig. 8). Fig. 8a indicates that the surface of hematite particle is uneven and it looks like 20–30 nm sized aggregate. These small particles are likely formed by dissolution re-crystallization mechanism first and then aggregate together. But the whole hematite particle is not an aggregate of 20–30 nanosized particles, because its X-ray diffraction peaks (Fig. 9) are very narrow and sharp and ED pattern (inserted in Fig. 8a) is not diffraction rings but diffraction spots. These results indicate that the two mechanisms (i.e. the dissolution re-crystallization and the solid state transformation) coexist in the transformation of ferrihydrite-1 in the presence of trace Fe(II). When ferrihydrite-2 was prepared at 60 °C, its dissolution becomes more difficult [25], thus, hematite particles are formed mostly by the solid state transformation. At this moment, not only the transformation time becomes very short (only 3 min) but also the ED pattern (inserted in Fig. 8b) of the product indicates that those hematite are single crystal particles. This result is consistent with the conclusions obtained by the pH versus time curve.

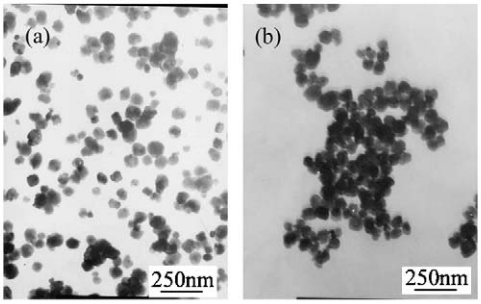

Fig. 7. TEM images of the samples using ferrihydrite-2 prepared at 60 °C as a precursor (a) 3 min (boiling) and (b) 13 min.

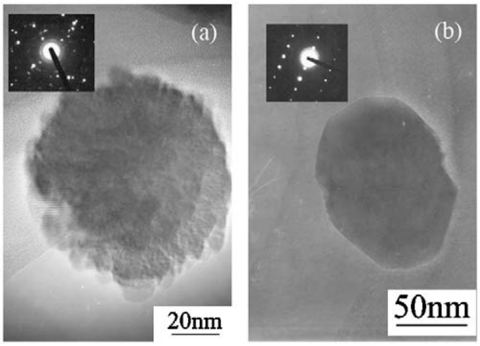

Fig. 8. HRTEM images and ED patterns (inserted in TEM images) of hematite particles obtained by (a) ferrihydrite-1 and (b) ferrihydrite-2 prepared at 60 °C.

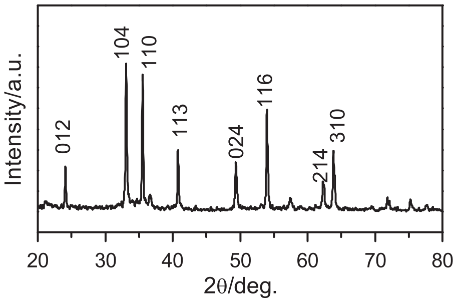

Fig. 9. XRD pattern of hematite obtained by ferrihydrite-1.

4. Conclusions

The effect of the sub-microstructure of ferrihydrites prepared by different procedures on their transformation processes was studied in the presence or absence of trace Fe(II) and the relationship between the two transformation mechanisms was illuminated. The results show that ferrihydrite-1 needs a longer time to complete its transformation to hematite than ferrihydrite-2. The two mechanisms (i.e. the dissolution re-crystallization and the solid state transformation) coexist in the transformation of ferrihydrite-1 in the presence of trace Fe(II), which leads to the formation of hematite particles with rough surface. The catalytic solid state transformation mechanism predominates in the transformation process of ferrihydrite-2, which leads to the formation of single crystal hematite particles with a smooth surface. Based on these results, the preparation of hematite nanoparticles with different surface state can be effectively controlled.

Supporting information

Digital photos of ferrihydrites prepared by two procedures and digital photos of the samples taken at different times in the transformation process of ferrihydrite-1 and ferrihydrite-2.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at 10.1016/j.jssc.2009.03.030.

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