

**Supporting information**

**Single-crystal  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> hexagonal nanorings: stepwise influence of different anionic ligands (F<sup>-</sup> and SCN<sup>-</sup> anions)**

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### Experimental Details:

*Materials:* All the reagents were A.R. grade and were used in preparation without further purification: ferric chloride ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ , China Medicament Co.), sodium fluoride (NaF, Tianjin Chemical Reagent Co.), sodium sulfocyanide (NaSCN, Tianjin Chemical Reagent Co.). Double-distilled water was used throughout the experiment.

*Synthesis:* The hexagonal  $\alpha\text{-Fe}_2\text{O}_3$  nanorings were synthesized by a hydrothermal approach. In brief, at room temperature, 80 mL transparent and yellow aqueous solution of  $\text{FeCl}_3$  (23.1 mM), NaF (15.0 mM) and NaSCN (1.0 mM) was transferred into a 100 mL Teflon-lined stainless steel autoclave. The autoclave was sealed and maintained at 220 °C for 48 h as a typical synthesis procedure. After reaction, the autoclave was cooled to room temperature naturally. The precipitate was separated by centrifugation, subsequently washed with distilled water for several times, and then dried at 60 °C in air. To investigate the effect of reaction time, the reaction time was adjusted to 8, 16, 24 and 48 h under the same NaF and NaSCN concentration. To study the effect of the  $\text{SCN}^-$  anions, its concentration was changed to 0.5 mM and 2.0 mM at the same reaction time (48 h) and NaF concentration (15.0 mM). To make the influence of  $\text{H}^+$  ions clear, the pH value of the initial solution was changed to 1.0 and 3.0 under the typical experimental condition.

*Characterization:* X-ray powder diffraction (XRD) measurements were performed on a D8 Advance Bruker AXS diffractometer, using a  $\text{Cu-K}\alpha$  radiation ( $\lambda=1.5406 \text{ \AA}$ ) at 40 kV, 40 mA, employing a scanning rate of  $0.02^\circ \text{ s}^{-1}$  in the  $2\theta$  range from  $10^\circ$  to  $80^\circ$ . The morphologies of the samples were observed on a scanning electron microscope (SEM, LEO 1530VP). The fine crystal structures of the particles were investigated by a transmission electron microscope (TEM, JEM-2010FEF at 200 keV).

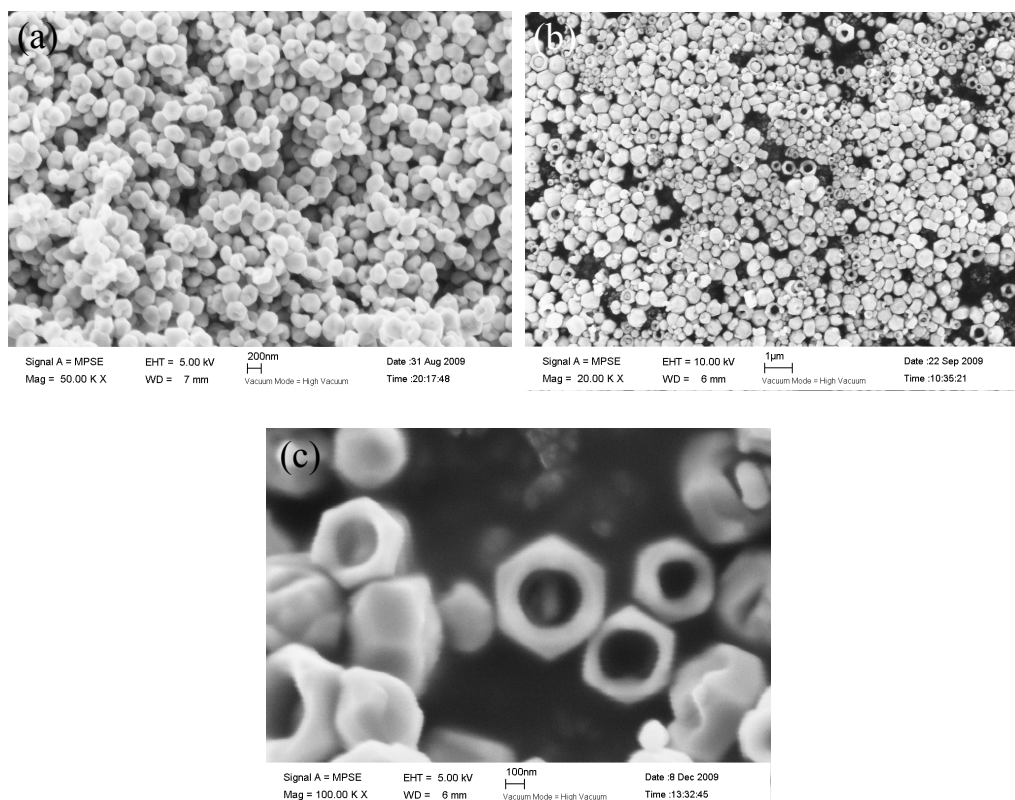


Fig. S1 SEM images of the products at different  $\text{SCN}^-$  concentrations: (a) 0.5 mM and (b) 2.0 mM, (c) is the high magnification image of (b).

On the basis of analysis in the communication, it is easy to understand the morphologies evolution of the particles at different  $\text{SCN}^-$  concentrations. When the  $\text{SCN}^-$  concentration is 0.5 mM, the amount of  $\text{SCN}^-$  anions is not enough to pierce the particles in the reaction process. With  $\text{SCN}^-$  anions concentration of 2.0 mM, the amount of  $\text{SCN}^-$  anions is not enough to pierce the big particles, but is overmuch for small particles. The formation of the circular inner ring is because the high  $\text{SCN}^-$  anions concentration depressed the selective dissolution to some extent. As to the nonuniform size distribution of the  $\alpha\text{-Fe}_2\text{O}_3$  particles, we think it should be attributed to the increase of the  $\text{SCN}^-$  anions. The increased  $\text{SCN}^-$  anions would decrease the concentration of the free  $\text{Fe}^{3+}$  ions in the initial reaction solution, which directly affect the nuclei formation and the last size of the  $\alpha\text{-Fe}_2\text{O}_3$  particles.

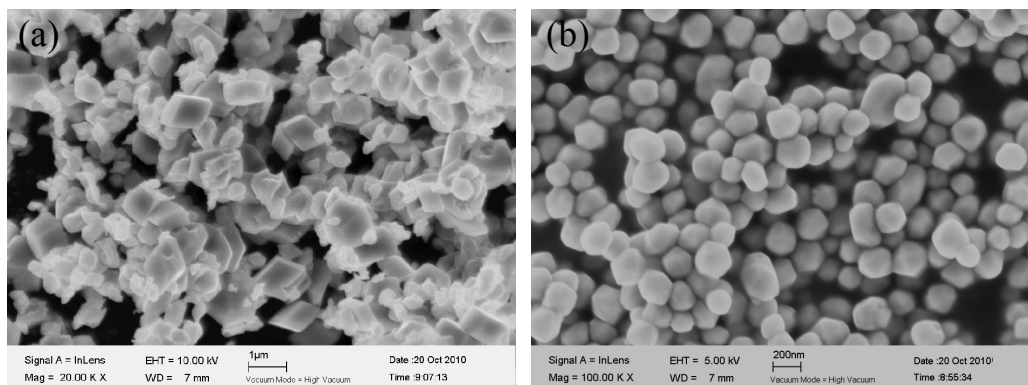
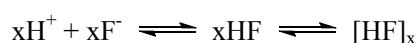


Fig.S2 SEM images of the products at different initial pH value: (a) 1.0 and (b) 3.0.

When the initial pH of the reaction solution is 1.0, the size of the particles (Fig. S2a) is much larger than that under pH=2.18 (Fig. 1b), and no nanoring structures can be found. At pH of 1.0, the concentration of  $H^+$  ions is 0.1 M. As a weak acid, HF possesses a dissociation constant of  $6.6 \times 10^{-4}$ , indicating that HF will be formed in the solution (*N. A. Lange, J. A. Dean, Lange's Handbook of Chemistry (13th edited), McGraw-Hill, New York, American, 1985*). In fact, more stable  $[HF]_x$  molecules can be formed under the effect of hydrogen bond in the solution, as shown by following equation (*C. Chambers, A. K. Holliday, Modern Inorganic Chemistry, Butterworths, London, UK, 1975*).



The initial low pH would make this equilibrium move toward the right hand so that the effect of the  $F^-$  anions would be depressed. This is the reason why no hexagonal-bipyramid particles can be found. The low pH also facilitate the reaction of equation (1) in the manuscript, and the reaction might happen before the formation of  $\alpha\text{-Fe}_2\text{O}_3$  particles. Consequently, there is no dissolution structures (such as rings, tubes, holes, and so on) were found in Fig. S2a. When pH=3.0, most of the particles remain polyhedral morphology (Fig. S2b). This is because the high pH not facilitates the reaction of equation (1) in the manuscript.

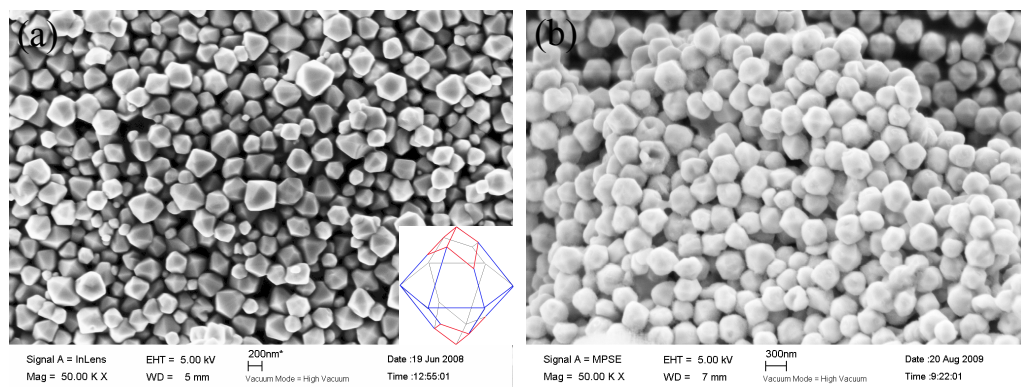


Fig.S3 SEM images of (a) the product obtained when only  $F^-$  anions presented, and (b) the particles in (a) were hydrothermally treated with  $SCN^-$  anions (1.0 mM) presented.