

Preparation of Hyperbranched Structures of α -Fe₂O₃

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Hierarchical structures of metal oxides comprised of nanoparticles, nanorods, and nanobelts as building blocks have attracted great interest due to their novel structures, properties, and applications.¹⁻³ However, the preparation of high-quality crystals with hyperbranched structures is a challenging issue. The majority of these structures are formed by hierarchical self-assembly mechanisms, and the snowflake-like morphology is a typical example of a hyperbranched structure. Considerable effort has been devoted to the synthesis of metal oxides and metal sulfides with snowflake-like morphologies.⁴⁻⁷

α -Fe₂O₃ is an n-type semiconductor with a band gap of 2.1 eV, and is used today in catalysis, sensors, magnetic recording media, rechargeable lithium batteries, and as a pigment.⁸⁻¹² Various techniques have been used to synthesize α -Fe₂O₃ with rod, wire, spindle, flower, and dendritic morphologies.¹³⁻¹⁶ However, relatively little is known of fabricating α -Fe₂O₃ with a snowflake-like morphology, and all successful attempts to date have involved the hydrothermal decomposition of K₃[Fe(CN)₆], which makes it difficult to examine the evolution of hyperbranched structures due to the difficulty of controlling the decomposition rate of K₃[Fe(CN)₆].¹⁷⁻¹⁹ Here we report a simple method for producing hyperbranched structures of α -Fe₂O₃ based on a hydrothermal reaction in aqueous solutions containing KCN and FeCl₃.

Experimental Section

FeCl₃·6H₂O (Aldrich) and KCN (Aldrich) were used as received. In a typical procedure, a mixed solution containing 40 mL of 0.05 M FeCl₃·6H₂O and 40 mL of 2.00 M KCN was placed in a Teflon-sealed autoclave at 140 °C for 16 h. In order to investigate the evolution of the morphologies of the α -Fe₂O₃ crystals produced, different KCN concentrations (0.25 M, 0.50 M, 1.00 M, and 2.00 M) were used at fixed 0.05 M FeCl₃. To investigate the effects of concentration of FeCl₃, different FeCl₃ concentrations (0.001 M, 0.005 M, 0.01 M, and 0.05 M) were also used at fixed 1.50 M KCN. The products were filtered and washed with ethanol several times, and then dried at 60 °C for 12 h in an oven.

α -Fe₂O₃ crystal structures were analyzed by powder X-ray diffraction (XRD, Rigaku DMAX-III A) using Cu K α radiation, and crystal morphologies were characterized by scanning electron microscopy (SEM, Hitachi S-4300). The Raman spectra of the products were obtained with a Raman spectrometer (HORIABA Jobin Yvon T64000) using radiation of 514.5 nm from an argon ion laser.

Results and Discussion

Figure 1 shows the XRD patterns and Miller indices of the α -Fe₂O₃ crystals obtained from an aqueous mixture containing 40 mL of 0.05 M FeCl₃·6H₂O and 40 mL of 2.00 M KCN reacted at 140 °C for 16 h. Most of peaks were assigned to the rhombohedral phase of α -Fe₂O₃ and concurred with literature data (JCPDS 33-0664, $a = 5.035$ Å, $c = 13.740$ Å). The peaks asterisked around at 14° and 22° are unidentified. There are many iron oxides and iron oxyhydroxides such as hematite (α -Fe₂O₃), magnetite (Fe₃O₄), wüstite (FeO), goethite (α -FeOOH), lepidocrocite (γ -FeOOH). Since iron oxides and iron oxyhydroxides have their unique Raman spectra, Raman spectroscopy is a good method to examine iron oxides and iron oxyhydroxides. Figure 2 shows the Raman spectrum of the as-prepared product obtained from an aqueous mixture containing 40 mL of 0.05 M FeCl₃·6H₂O and 40 mL of 2.00 M KCN. All of Raman peaks correspond to those of α -Fe₂O₃. In the Raman spectrum of α -Fe₂O₃, the peak at 225 and 498 cm⁻¹ were assigned to A_{1g} modes. The peaks at 247, 293, 412, and 613 cm⁻¹ were also assigned to E_g modes. The intense peak at 1320 cm⁻¹ is assigned to a two-magnon scattering which arise from the interaction of two magnons created on antiparallel close spin sites.²⁰ No other peaks were detected, indicating that this simple method yields only α -Fe₂O₃ free from other iron oxides and iron oxyhydroxides.

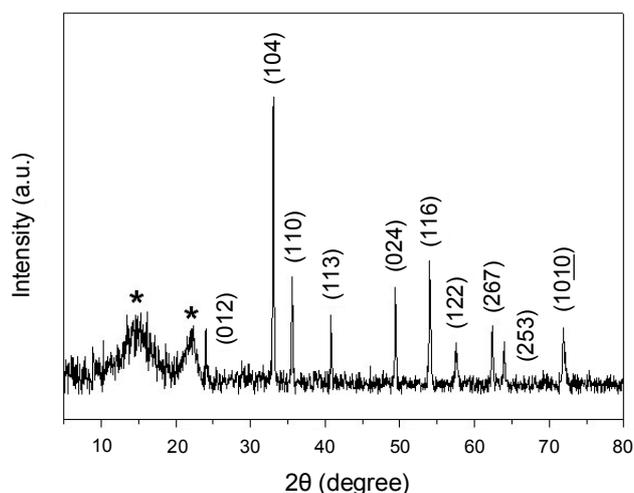


Figure 1. XRD pattern of snowflake-like α -Fe₂O₃ synthesized at [FeCl₃] = 0.05 M and [KCN] = 2.00 M under hydrothermal conditions for 16 h at 140 °C.

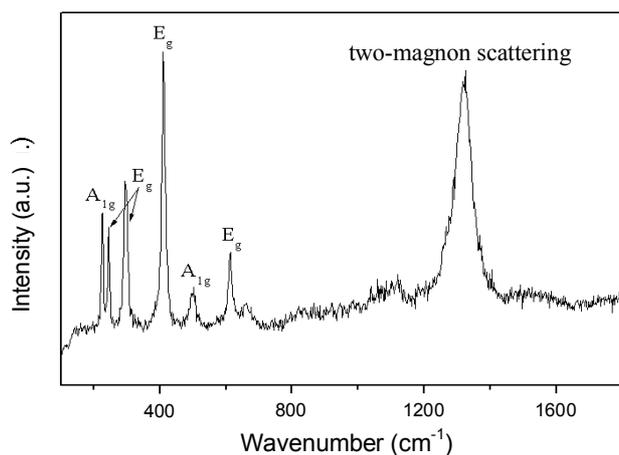


Figure 2. Raman spectrum of snowflake-like α - Fe_2O_3 synthesized at $[\text{FeCl}_3] = 0.05 \text{ M}$ and $[\text{KCN}] = 2.00 \text{ M}$ under hydrothermal conditions for 16 h at 140°C .

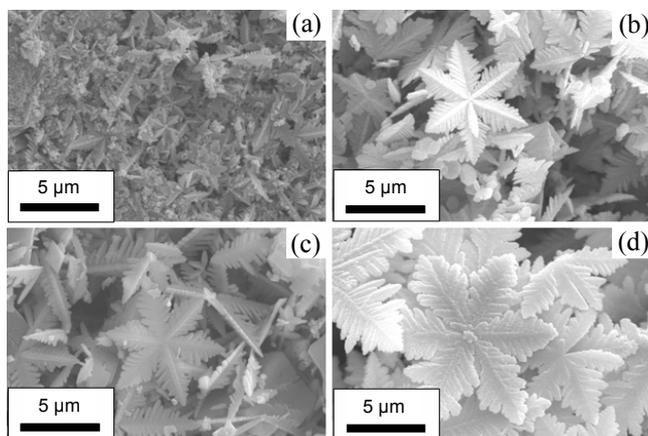


Figure 3. SEM images of α - Fe_2O_3 products obtained at $[\text{FeCl}_3] = 0.05 \text{ M}$ using different concentrations of KCN: (a) 0.25 M, (b) 0.50 M, (c) 1.00 M, and (d) 2.00 M.

Figure 3 shows SEM images of the α - Fe_2O_3 crystals obtained by reacting aqueous solutions of different concentrations of KCN and 0.05 M FeCl_3 . When the concentration of KCN is 0.25 M, pine tree-like α - Fe_2O_3 crystals of average length 2 μm were formed (Figure 3a). This pine tree morphology exhibits symmetrically disposed branches and side-branches about a single central axis. The crystals began to resemble snowflakes with a six-fold center of symmetry and an average arm length of 3.5 μm at 0.50 M KCN (Figure 3b). When the concentration of KCN is increased to 1.00 M, these crystals increased in size to an average arm length of 4 μm . As might be expected, the main arms of the crystals were at almost 60° to each other, and similarly, side-branches also formed an angle of 60° with the main crystal arms (Figure 3c). At 2.00 M KCN, the side-branches grew more so and became interconnected and adopted a snowflake-like appearance with an average arm length of 5.5 μm (Figure 3d). Therefore, as the concentration of KCN was increased from 0.05 M to 2.00 M, while keeping the concentration of FeCl_3 constant at 0.05 M, the morphology of the α - Fe_2O_3 changes from the pine tree-like crystals of 2 μm length to sharp snowflake-like crystals of 3.5 μm length, and

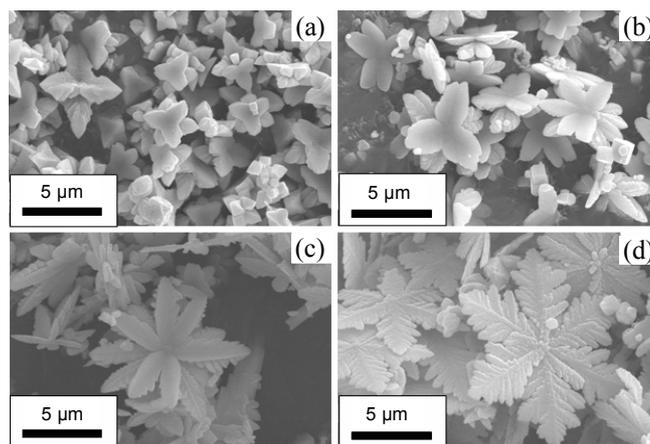


Figure 4. SEM images of α - Fe_2O_3 products obtained at $[\text{KCN}] = 1.50 \text{ M}$ using different concentrations of FeCl_3 : (a) 0.001 M, (b) 0.005 M, (c) 0.01 M, and (d) 2.00 M.

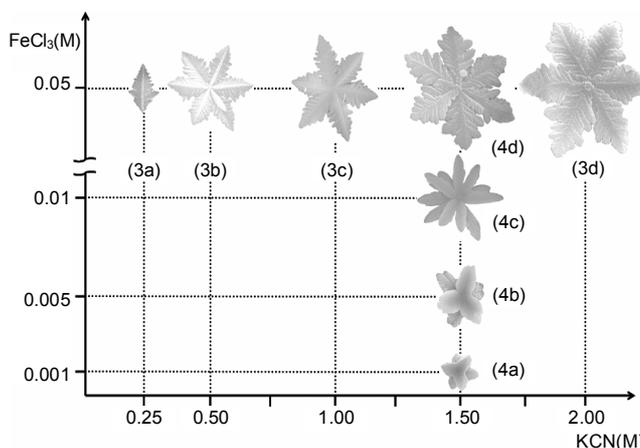


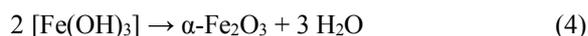
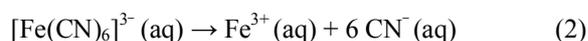
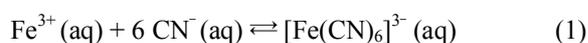
Figure 5. (a) Schematic illustration of the shape evolution of α - Fe_2O_3 crystals.

finally to smooth snowflake-like crystals of 5.5 μm length.

To investigate the effect of concentration of FeCl_3 , the α - Fe_2O_3 crystals were prepared by reacting aqueous solutions of different concentrations of FeCl_3 with fixed 1.50 M KCN as shown in Figure 4. When the concentration of FeCl_3 was 0.001 M, star-like α - Fe_2O_3 crystals were formed (Figure 4a). The three dimensional star-like α - Fe_2O_3 crystals have six arms with 1.5 μm lengths extending outside from a center. When the concentration of FeCl_3 was increased to 0.005 M, the product was a mixture of paired three-leaf crystals and paired six-leaf crystals (Figure 4b). The length of each leaf is about 2.5 μm . As we can see from Figure 4b that one side of the leaf is smooth, whereas the other is striped. These paired crystals have face-to-face crystal growth pattern. The stripped face tends to pair with another stripped face. Therefore, the paired three-leaf and six-leaf crystals have two-dimensional structures such as paired plates. When the concentration of FeCl_3 was further increased to 0.01 M, the paired six-leaf crystals were formed with each leaf of 4 μm length (Figure 4c). Finally, the snowflake-like crystals of 5.3 μm length without any paired three-leaf and six-leaf crystals were obtained at

0.05 M FeCl₃ (Figure 4d). Therefore, as the concentration of FeCl₃ was increased from 0.001 M to 0.05 M at fixed 1.50 M KCN, the morphology of the α -Fe₂O₃ changes from the small size of three dimensional paired star-like crystals to the middle size of two dimensional paired three-leaf and six-leaf shaped crystals, and finally to the large size of snowflake-like crystals. Fig. 5 shows schematically the shape evolution of α -Fe₂O₃ from the pine tree-like to the snowflake-like and from the star-like to the snowflake-like with increasing the concentrations of KCN and FeCl₃, respectively.

Since CN⁻ ion is a very strong ligand, it was expected to chelate Fe³⁺ to form [Fe(CN)₆]³⁻. The formation constant of [Fe(CN)₆]³⁻ at 25 °C is about 1×10^{42} .¹⁷ However, [Fe(CN)₆]³⁻ dissociates slowly into Fe³⁺ ions under hydrothermal conditions, and these ions react with OH⁻ under basic conditions to form Fe(OH)₃, which on dehydration forms α -Fe₂O₃. The set of chemical reactions involved in the formation of α -Fe₂O₃ are as follows:



The concentrations of KCN and FeCl₃ play important roles in the formation of various morphologies such as a star, paired three-leaf, paired six-leaf, pine tree, and snowflake. The unique shaped crystals of α -Fe₂O₃ could form because of the slow release of Fe³⁺ ions due to the stability of the [Fe(CN)₆]³⁻ complex, which allows sufficient time for self-assembly to produce the crystals having morphologies of star, paired three-leaf, paired six-leaf, pine tree, and snowflake.

As the concentration of FeCl₃ is increased, the morphology of the α -Fe₂O₃ crystals varies from star-like to snowflake-like via paired three-leaf and six-leaf shapes. In general, the shape of crystals can be explained in terms of the growth rates along <001> and <111>. For star-like crystals having six arms to form, the growth rate along <100> is almost equal to those along <010> and <001>. This means that the crystal growth along x, y and z axes are preferred for the star-like crystals. However, paired three-leaf, paired six-leaf, and snowflake-like shapes α -Fe₂O₃ crystals have two-dimensional structures. For these two dimensional shapes of α -Fe₂O₃ crystals to form, the growth rate along <001> is must be slower than those along <100> and <010>. The crystal growth along z axis is hindered at higher concentration of FeCl₃ to form two dimensional crystals. When the concentration of FeCl₃ was increased to 0.005 M from 0.001 M, the crystals tend to be grown along the plane compared to the axis. The star-like crystals changed to three-leaf shaped which have three leaves on the top plate and other three leaves on the bottom plate. As the crystals are grown further by increasing the concentration of FeCl₃, the paired six-leaf shaped crystals are formed by splitting three leaves to six leaves. Finally, the snowflake-like crystals are formed by taking apart the pairing of the paired six-leaf shaped crystals. Therefore, FeCl₃ plays important role in change of crystal morphology from three dimensional star-like crystals

to two dimensional snowflake-like crystals.

The evolution of α -Fe₂O₃ crystal morphologies with the concentration of KCN from pine tree to snowflake can be also explained by a simple crystal growth mechanism. As the concentration of KCN increases, crystal morphology changed from a pine tree-like to a snowflake-like morphology. On increasing the concentration of CN⁻ ions, the self-assembly reaction rate of α -Fe₂O₃ increases and progressive branching steps are initiated. The first crystal growth started at the main arm at an angle of 60° to form a pine tree-like shape, and when branching crystal growth was started at arms with a six-fold symmetry, the snowflake morphology was formed by secondary growth. Finally they form snowflakes with wide branches by the third phase of crystal growth. Furthermore, these morphologies have two-dimensional structures, and thus, crystal growth perpendicular to the crystal plane is appreciably slower than that in the crystal plane. Therefore, KCN does not affect the crystal growth along z axis but the crystal planes. The formation of two-dimensional hyperbranched structures appears to depend on reaction rate in the crystal plane. When the concentration of KCN was increased, the rate of formation of α -Fe₂O₃ also increased and higher-order hyperbranched crystals with wide branches were formed.

In conclusion, we have synthesized various shapes of α -Fe₂O₃ crystals by hydrothermal reaction between KCN and FeCl₃ in aqueous solution. The concentrations of KCN and FeCl₃ were found to substantially affect the shape of the hyperbranched crystal structures produced. The shape evolution of α -Fe₂O₃ from pine tree-like to snowflake-like and from star-like to snowflake-like can be explained by simple crystal growth mechanism.

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References

1. Antonietti, M.; Ozin, G. A. *Chem. Eur. J.* **2004**, *10*, 28.
2. Mann, S. *Angew. Chem. Int. Ed.* **2000**, 2839, 3392.
3. Song, H. C.; Park, S. H.; Huh, Y. D. *Bull. Kor. Chem. Soc.* **2007**, *28*, 477.
4. He, K.; Xu, C. Y.; Zhen, L.; Shao, W. Z. *Mater. Lett.* **2008**, *62*, 739.
5. Chen, X.; Wang, X.; Wang, Z.; Yang, X.; Qian, Y. *Cryst. Growth Des.* **2005**, *5*, 347.
6. Wu, Z.; Pan, C.; Yao, Z.; Zhao, Q.; Xie, Y. *Cryst. Growth Des.* **2006**, *6*, 1717.
7. Ma, Y.; Qi, L.; Ma, J.; Cheng, H. *Cryst. Growth Des.* **2004**, *4*, 351.
8. Bandara, J.; Mielczarski, J. A.; Kiwi, J. *Langmuir* **1999**, *15*, 7680.
9. Hayashi, K.; Iwasaki, K.; Morii, H.; Xia, B.; Okuyama, K. *J. Nanopart. Res.* **2001**, *3*, 149.
10. Jiang, J. Z.; Lin, R.; Lin, W.; Nielsen, K.; Morup, S.; Dam-Johansen, K.; Clasen, R. *J. Phys. D Appl. Phys.* **1997**, *30*, 1459.
11. NuLi, Y.; Zhang, P.; Guo, Z.; Munroe, P.; Liu, H. *Electrochim. Acta* **2008**, *53*, 4213.
12. Matijevic, E. *Chem. Mater.* **1993**, *5*, 412.
13. Pu, Z.; Cao, M.; Yang, J.; Huang, K.; Hu, C. *Nanotech.* **2006**, *17*, 799.
14. Han, Q.; Xu, Y. Y.; Fu, Y. Y.; Zhang, H.; Wang, R. M.; Wang, T. M.; Chen, Z. Y. *Chem. Phys. Lett.* **2006**, *431*, 100.
15. Mitra, S.; Das, S.; Mandal, K.; Chaudhuri, S. *Nanotech.* **2007**, *18*, 275608.
16. Jia, C.; Cheng, Y.; Bao, F.; Chen, D.; Wang, Y. *J. Cryst. Growth* **2006**, *294*, 353.
17. Cao, M.; Liu, T.; Gao, S.; Sun, G.; Wu, X.; Hu, C.; Wang, Z. L. *Angew. Chem. Int. Ed.* **2005**, *44*, 4197.
18. Zhang, X.; Sui, C.; Gong, J.; Su, Z.; Qu, L. *J. Phys. Chem. C* **2007**, *111*, 9049.
19. Hu, X.; Yu, J. C.; Gong, J. *J. Phys. Chem. C* **2007**, *111*, 11180.
20. de Faria, D. L. A.; Silva, S. V.; de Oliveira, M. T. *J. Raman Spectr.* **1997**, *28*, 873.