

Hydrothermal Synthesis of Leaf-Shaped Ferric Oxide Particles

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Abstract: For the first time, leaf-shaped ferric oxide particles were prepared from an aqueous solution of potassium ferricyanide $[K_3Fe(CN)_6]$ by hydrothermal process. Images obtained from SEM (scanning electron microscope) revealed that leaf-shaped ferric oxides (around 1.5 μm in length) were clearly exhibited when the hydrothermal temperature was 150 $^{\circ}C$, while as the temperature was increased to 200 $^{\circ}C$ leaf-shaped ferric oxide particles with larger size were observed. XRD (X-ray diffraction) patterns testified that the obtained ferric oxides were $\alpha-Fe_2O_3$ with well-structured crystal faces. Interestingly, histograms describing the distribution of samples indicated that the distribution of obtained ferric oxide particles did not accord with gaussian distribution

Keywords: Microstructure, Leaf-shaped particles, Crystal structure, Hydrothermal synthesis.

Introduction

Iron oxides, as the main super paramagnetic material, can offer a great potential applications in different areas such as ferrofluids, color imaging, magnetic refrigeration, detoxification of biological fluids, magnetically controlled transport of anti-cancer drugs, magnetic resonance imaging and magnetic cell separation¹. Many methods were developed to generate ferric oxides, including gel-sol processing^{2,3}, forced hydrolysis processing^{4,5}, hydrothermal processing treatments^{6,7}, electrochemical deposition⁸. Among these developed ways, thermal decomposition route is the commonly selected method due to its several advantages (a) effective control of size and shape of the particles; (b) easy manipulation and shorter preparation time; (c) fewer impurities in the final products. Hydrothermal treatment of iron salt could prepare iron oxides as the preparation conditions were appropriate, for example, Wang group reported the synthesis and magnetic properties of Fe_3O_4 in which

$\text{Fe}(\text{CN})_3 \cdot 9\text{H}_2\text{O}$ was utilized as the iron-contained precursor⁹. Professor Musić discussed the effects of urotropin on the chemical and micro structural properties of Fe-oxide powders that were prepared by the hydrolysis of aqueous FeCl_3 solution¹⁰. Meanwhile, $\alpha\text{-Fe}_2\text{O}_3$ were also widely investigated, *e.g.*, Professor Yan reported¹¹ the hierarchical assembly of SnO_2 nanorod arrays on $\alpha\text{-Fe}_2\text{O}_3$. Research group led by Professor Ulman demonstrated that doped Mn(III) could suppress the transition from $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles to the $\alpha\text{-Fe}_2\text{O}_3$ structure¹². Ferric oxide particles of many shapes, including spheres, cubes, rods, platelets and spindles, were all prepared¹³. To the best of our knowledge, till now, there is no paper reporting the preparation of leaf-shaped iron oxide particles.

In this hydrothermal process, potassium ferricyanide aqueous solution were kept in a Teflon-lined autoclave at the required temperatures for 3 h, in which except for water and potassium ferricyanide, no other reductive reagents were introduced. Subsequently, after 48 h sedimentation at room temperature, leaf-shaped ferric oxides with well-structured crystals were formed, which are novel phenomena that have never been reported so far.

Experimental

Preparation of ferric oxide particles

All the chemicals were analytical grade and used without further purification. In this experiment, 20 mL aqueous solution containing 5×10^{-3} M potassium ferricyanide was placed in a Teflon-lined autoclave first, and then this sealed autoclave was placed in an oven at room temperature, subsequently, the temperature of oven was increased to 150 °C or 200 °C within 20 min and then the temperature was kept for 3 h. After 48 h sedimentation at room temperature, the resultant products were washed by redistilled water carefully and dried by ambient air successively. Lastly, the obtained particles were directly used for characterization.

Characterization

The morphology of obtained ferric oxide particles were characterized by a Hitachi model S-570 scanning electron microscope (SEM). X-ray diffraction (XRD) patterns were recorded on a Bruker D8 Advance diffractometer (Germany) with Cu K α as the radiation source ($\lambda=0.154$ nm), the 2θ range used in this measurement was from 5° to 85°. Particle size distribution was measured on a JL-1155 laser particle analyser (Chengdu Jinxin Instrument Co., Ltd (China)). FT-IR spectrum was recorded on a Fourier transform infrared spectrometry (1730, P-E, USA).

Results and Discussion

The typical digital photos for the samples are presented in Figure 1, where the yellow solution, *i.e.*, A1, is potassium ferricyanide solution of 5×10^{-3} M, and the beaker containing red particles obtained at 150 °C is denoted as A2, samples obtained at 200 °C is denoted as A3. One can see that after hydrothermal process, some red particles were formed at the bottom of the beaker, and as the temperature was 200 °C the solution became transparent, as shown by A3 in Figure 1, suggesting that iron element in potassium ferricyanide was totally converted into the resultant particles by this hydrothermal process.

To our surprise, the leaf-shaped particles are clearly observed by SEM images as shown in Figure 2. Figure 2A is the resultant products obtained at 150 °C where well-structured leaf-shaped particles are exhibited, as shown by the circled leaf. While as the hydrothermal

temperature is 200 °C as shown by Figure 2B, more larger leaf-shaped particles are observed at the same magnification, indicating that when the temperature is 200 °C more iron elements were transferred into the products and thus in the same sedimentation time, more larger particles of ferric oxide were formed. To our knowledge, this is the first time to report the leaf-shaped ferric oxide particles

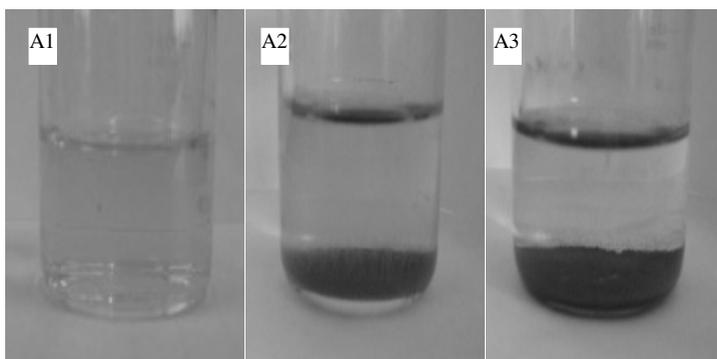


Figure 1. Digital photos for the as-prepared samples. A1: 5×10^{-3} M $\text{K}_3\text{Fe}(\text{CN})_6$ aqueous solution, A2: samples obtained at 150 °C; A3: obtained at 200 °C.

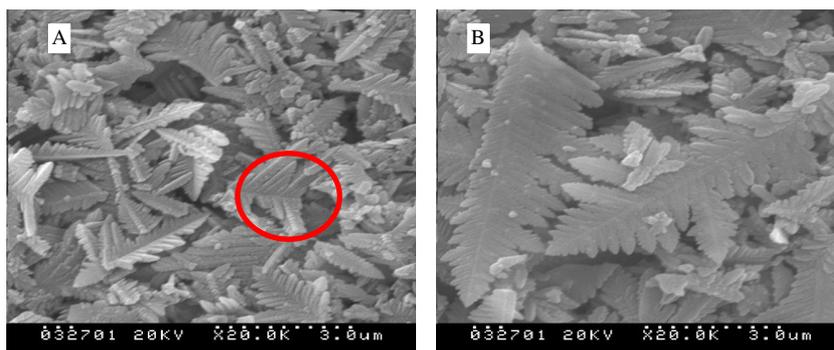


Figure 2. SEM images of the resultant leaf-shaped particles prepared at various temperature: (A) 150 °C (B) 200 °C.

Figure 3 shows the XRD patterns of the resultant particles. All diffraction peaks can be perfectly indexed to $\alpha\text{-Fe}_2\text{O}_3$ (JCPDS 33-664), according with the former report very well¹³. Two patterns that obtained at different temperature are very similar, and the intensities of diffraction peaks become stronger for the samples obtained at 200 °C (as shown by Figure 3A) when compared to the samples obtained at 150 °C (as shown by Figure 3B), suggesting that 200 °C is beneficial to the formation of ferric oxides with well-structured crystal faces.

Particle size distribution of the resultant particles was also measured, as illustrated by the histogram in Figure 4, where the white rods represent the distribution of samples prepared at 150 °C, and the red rods correspond to the samples obtained at 200 °C. Generally, particle size distribution should tally with the gaussian distribution, for instance, the research group led by Abd-Shukor¹⁴ reported the histogram of Fe_3O_4 particles prepared by the pyrolysis reaction of organometallic compound, in which particle size distribution accorded

with the gaussian distribution very well. While, in our work, it can be seen from Figure 4 that the particle size distribution does not accord with gaussian distribution, *i.e.*, particles with the larger diameter are the main part of the resultant particles, indicating that there should be a crystal growth process during the sedimentation process after hydrothermal treatment.

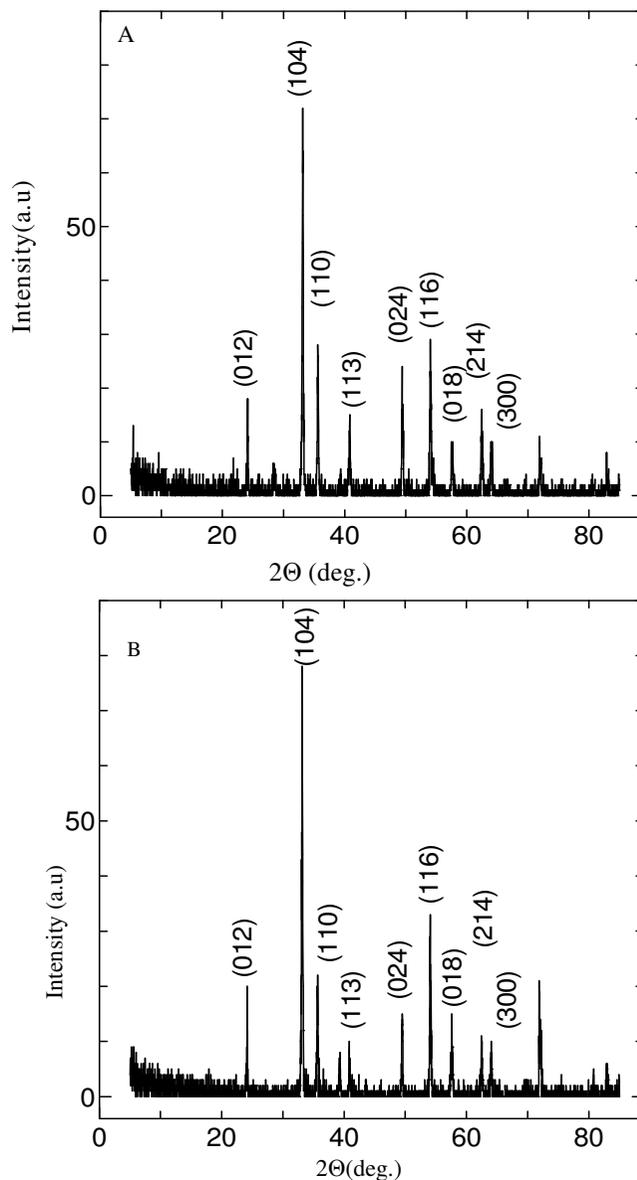


Figure 3. XRD patterns of α -Fe₂O₃ particles prepared at different temperatures, (A) 150 °C (B) 200 °C.

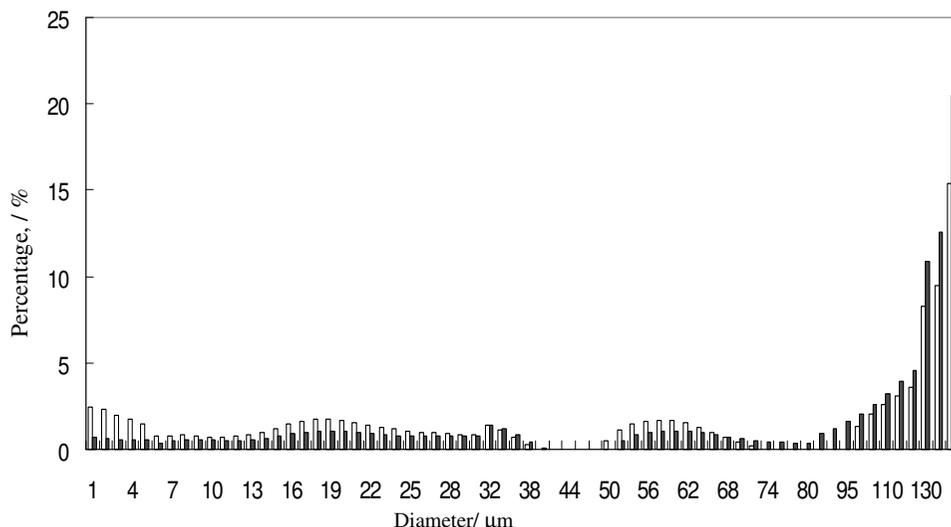


Figure 4. Curve of particle size versus frequency distribution, white bar: obtained at 150 °C; red bar: obtained at 200 °C

FT-IR spectroscopy is another powerful technique to feature iron oxides. Figure 5A & 5B correspond to the FT-IR spectra of particles prepared at 150 °C and 200 °C, respectively. Two similar spectra were exhibited, consistent with the XRD plots presented in Figure 3 very well. Zheng *et al*⁹ has pointed that the spectroscopic bands located at 580 cm^{-1} were related to the vibration of Fe-O functional group. Moreover, since the shape of our obtained IR spectra is similar to the IR spectra presented Zheng *et al*⁹, thus the spectroscopic peak located at 530.4 (or 528.5) cm^{-1} and 451.3 (or 447.5) cm^{-1} are the characteristic absorption bands of ferric oxides. For the absorption peaks at 1616 and 1400 cm^{-1} , generally, they are assigned to the asymmetrical and symmetrical stretching vibration of carboxylate(O-C=O)¹⁵.

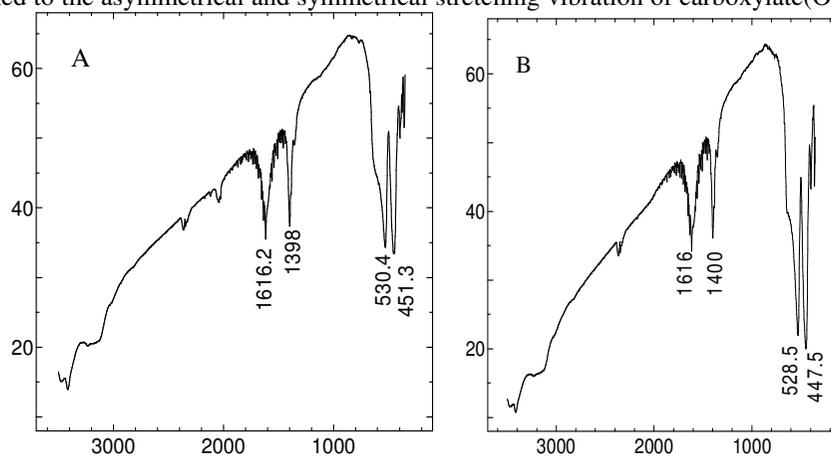


Figure 5. FT-IR spectra for the obtained Fe_2O_3 , (A) Obtained at 150 °C (B) obtained at 200 °C

Till present, the formation mechanism of ferric oxides is unclear. For example, for the $\alpha\text{-Fe}_2\text{O}_3$ cubes, Bailey¹⁶ proposed the dissolution re-crystallization mechanism, *i.e.*, at the

beginning, rod-like particles of β -FeOOH were formed, and then β -FeOOH dissolved and re-crystallized to form α -Fe₂O₃ cubes. While, Sugimoto et al. suggested that the formation of hematite pseudo cubic particles was ascribed to the specific adsorption of chloride ions or ferric complexes to {012}, and the adsorption restrained the growth in the directions normal to {012} face. Kandori *et al.*³ proposed the aggregation mechanism of α -Fe₂O₃ particles based on the porous structure of the spherical hematite¹⁷.

In this work, due to the existing of absorption peaks at 1616 and 1400 cm⁻¹, the carbon element, from Fe(CN)₆³⁻, should participate in the hydrothermal process, probably similar to the reported work¹⁵ in which except for Fe(NO₃)₃·9H₂O and Mg(NO₃)₂·6H₂O, C₆H₈O₇·H₂O were used as raw materials to prepare MgFe₂O₄. Unfortunately, with present technique, we can not present a satisfied interpretation to our observed phenomena.

Conclusions

Leaf-shaped ferric oxide particles were prepared directly from the hydrothermal process of potassium ferricyanide [K₃Fe(CN)₆] as has never been reported so far. Results obtained from SEM and XRD all strongly demonstrated that α -Fe₂O₃ was formed by this mild hydrothermal process. FT-IR spectra also indicated the formation of Fe-O and C-C=O bands, and suggested that carbon element existing in Fe(CN)₆³⁻ participated in the hydrothermal process though the exact interpretation could not be achieved by the present technique. Presenting the leaf-shaped ferric oxides, and its preparation method as well, is the main contribution of this preliminary work.

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