Characterization of $\gamma$-Fe$_2$O$_3$ nanoparticles prepared by transformation of $\alpha$-FeOOH

MIAO Hua, LI Jian*, LIN YueQiang, LIU XiaoDong, ZHANG QingMei & FU Jun

School of Physics Science and Technology & MOE Key Laboratory on Luminescence and Real-Time Analysis, Southwest University, Chongqing 400715, China

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$\gamma$-Fe$_2$O$_3$ nanoparticles were successfully synthesized by a chemically induced transformation of $\alpha$-FeOOH. In this method, the precursor ($\alpha$-FeOOH) was prepared by chemical precipitation, and then treated with a mixed FeCl$_2$/NaOH solution to produce the nanoparticles. X-ray diffraction indicated that when the precursor was treated with FeCl$_2$ (0.22 mol/L) and NaOH (0.19 mol/L), pure $\gamma$-Fe$_2$O$_3$ nanoparticles were obtained. However, when the concentration of FeCl$_2$ was <0.22 mol/L or the concentration of NaOH was <0.19 mol/L, $\alpha$-FeOOH and $\gamma$-Fe$_2$O$_3$ phases co-existed in the nanoparticles. Transmission electron microscopy observations showed that in the samples with co-existing phases, the nanoparticles did not have identical morphologies. The pure $\gamma$-Fe$_2$O$_3$ nanoparticles were polygonal rather than spherical. The volume ratio of $\alpha$-FeOOH and $\gamma$-Fe$_2$O$_3$ was estimated for the two-phase samples from magnetization data obtained from a vibrating sample magnetometer. This chemically induced transformation is novel, and could provide an effective route for the synthesis of other metal oxide nanocrystallites.

$\alpha$-FeOOH, $\gamma$-Fe$_2$O$_3$, FeCl$_2$/NaOH solution, transition, nanoparticles

Nanomaterials attract a great deal of interest because of their distinct optical, magnetic, electronic, mechanical and chemical properties compared with those of the bulk material. The unique properties of nanomaterials are caused by changes in the band structure with the decrease in particle radius, and are a result of the quantum confinement effect [1–7]. Magnetic nanoparticles have been studied extensively because of their technological and fundamental scientific importance. Among the many known magnetic nanoparticles, ferrimagnetic Maghemite ($\gamma$-Fe$_2$O$_3$) has attracted considerable attention. Its structural characteristics permit a wide range of potential applications including in ferrofluids, magneto-optical and magnetic recording media, catalysis, and biology [8–12]. Methods for the production of $\gamma$-Fe$_2$O$_3$ nanoparticles include the co-precipitation [8], the mechanochemical method [11], thermal decomposition [13,14], sol-gel preparation [1,15], micro-emulsion techniques [16] and hydro-thermal synthesis [17,18]. During the synthesis of nanoparticles, anti-aggregation agents (e.g. surfactants) and toxic organic solvents are often added to the solution to control the size of the $\gamma$-Fe$_2$O$_3$ nanoparticles [19]. In addition, heat treatment, such as annealing and hydrothermal processes, is often employed to improve the crystallinity and enhance the ferromagnetism [8,19]. However, these treatments complicate the process.

Currently, the development of simple and reliable synthetic methods for the synthesis of magnetic nanoparticles with designed chemical components, which strongly affect the properties of magnetic materials, is a significant challenge. Generally, the preparation of $\gamma$-Fe$_2$O$_3$ particles by FeOOH transformation is a complex process [20,21] that can be summarized as follows:

$$\begin{align*}
\alpha(\gamma)\text{-FeOOH} & \xrightarrow{\text{dehydration}} \alpha(\gamma)\text{-Fe}_2\text{O}_3 \xrightarrow{\text{reduction}} \gamma\text{-Fe}_2\text{O}_3, \\
\text{Fe}_3\text{O}_4 & \xrightarrow{\text{oxidation}} \gamma\text{-Fe}_2\text{O}_3.
\end{align*}$$
In this paper, a single-step method is proposed for preparation of pure and highly crystalline γ-Fe₂O₃ nanoparticles by the thermal chemical treatment of α-FeOOH at 100°C.

1 Experimental

(i) Materials. All the reagents were of analytical grade, and distilled water was used as the solvent.

(ii) Preparation of the precursor. In a typical synthetic procedure for the precursor, hydrochloric acid (HCl, 4.17 mL) was added to hydrated iron chloride solution (FeCl₃ solution, 1 mol/L, 80 mL). Sodium hydroxide solution (NaOH solution, 0.6 mol/L, 500 mL) was then quickly added to the solution at room temperature. The solution was heated to boiling point for 5 min with vigorous stirring, and it changed color from brown to orange. The solution was then allowed to cool, and the orange precursor slowly precipitated. The precipitate was washed with HNO₃ solution (0.01 mol/L) until it reached pH 7–8.

(iii) Preparation of nanoparticles. To investigate the effect of the concentration of the mixed FeCl₂/NaOH solution on the phase transition, the following solutions were used: (1) a fixed concentration of NaOH (0.19 mol/L), and either 0.02 mol/L (sample B1) or 0.07 mol/L (sample B2) FeCl₂; and (2) a fixed concentration of FeCl₂ (0.22 mol/L), and either 0.10 mol/L (sample C1) or 0.19 mol/L (sample C2) NaOH (Table 1).

The precursor was added to 540 mL of the FeCl₂/NaOH solution, and then the solution was heated to boiling point for 30 min. During this time, the solution gradually changed color from orange to black. The solution was then allowed to cool, and the nanoparticles slowly precipitated. The precipitate was washed with HNO₃ solution (0.01 mol/L) until it reached pH 7–8, and then dehydrated with acetone to obtain a powder.

(iv) Characterization. The crystalline phases of the synthesized particles were identified using a XD-2 X-ray diffractometer (XRD) (Beijing Purkinje General inst., China) using Cu Kα (λ=0.1541 nm) radiation. The morphologies of the precursor and nanoparticles were observed by a Tecnai 10 transmission electron microscope (TEM) (Philips, Netherlands). A EV11 vibrating sample magnetometer (VSM) (ADE, USA) was used to measure the magnetic properties of the product at room temperature.

2 Results and discussion

XRD patterns showing the crystalline structure of the samples are given in Figure 1. For the precursor (sample A), the positions of the major diffraction peaks and their relative intensities corresponded to those of α-FeOOH (Goethite, PDF#29-0713). For sample C2, the positions and relative intensities of the major diffraction peaks corresponded to γ-Fe₂O₃ (Maghemite, PDF#24-0081). In XRD, it is difficult to distinguish γ-Fe₂O₃ and Fe₂O₃ (FeO·Fe₂O₃) because they produce similar diffraction peaks. However, in alkaline solution, Fe²⁺ is unstable and Fe³⁺ cannot reduce to Fe²⁺. Consequently, the Fe₂O₄ phase was ignored in the analysis, although some FeO and/or Fe₂O₃ may be adsorbed on the particles. Samples B1, B2 and C1 were all two-phase materials of α-FeOOOH and γ-Fe₂O₃. This indicates that, depending on the concentration of FeCl₂ or NaOH, α-FeOOOH is partially transformed into γ-Fe₂O₃. With samples B1 and B2, lower concentrations of FeCl₂ were used and the products were two-phase materials. However, as the concentration of FeCl₂ increased for sample C1, the proportion of the α-FeOOH phase reduced. With sample C2, the concentration of NaOH was 0.19 mol/L, and α-FeOOH was completely transformed into γ-Fe₂O₃. The XRD results show that the concentrations of FeCl₂ and NaOH have an important influence on the phase composition of the products.

TEM observations showed that there were agglomerated and well dispersed regions of nanoparticles in the precursor (sample A). For the two-phase α-FeOOH/γ-Fe₂O₃ materials (samples B1, B2 and C1), the morphologies of the nanoparticles were not identical. The pure γ-Fe₂O₃ nanoparticles (sample C2) were almost all polygonal structures. Typical TEM images are shown in Figure 2. High-resolution TEM results confirmed that sample C2 was crystalline (inset in Figure 2, C2).

The magnetization curves of the samples are shown in Figure 3. The precursor (sample A) exhibited paramagnetic properties and all the other samples showed hysteresis (inset, Figure 3). The magnetization (at 9×10⁵ kA/4 m) and coercivity of all the samples are listed in Table 2. For the

| Sample | FeCl₂ (mol/L) | NaOH (mol/L) | Phase composition | Remarks                  |
|--------|--------------|--------------|-------------------|--------------------------|
| A      | 0            | 0            | α-FeOOH           | Spherical particles, agglomerate |
| B1     | 0.02         | 0.19         | α-FeOOH+γ-Fe₂O₃   | Floccule form, rod type   |
| B2     | 0.07         | 0.19         | γ-Fe₂O₃+α-FeOOH   | Polygonal particles, flake type |
| C1     | 0.22         | 0.10         | γ-Fe₂O₃+α-FeOOH   | Polygonal particles, rod type |
| C2     | 0.22         | 0.19         | γ-Fe₂O₃           | Polygonal particles       |
nanoparticles containing both $\alpha$-FeOOH and $\gamma$-Fe$_2$O$_3$ (samples B1, B2 and C1), the differences in the magnetization correspond to the phase ratio.

The above results indicate that there are both single nanoparticles and pre-existing bulk aggregates in the precursor. During treatment, the $\alpha$-FeOOH nanoparticles could form more bulk aggregates. These $\alpha$-FeOOH aggregates were transformed into $\gamma$-Fe$_2$O$_3$ nanoparticles by heat treatment with a mixed solution of FeCl$_2$ (0.22 mol/L) and NaOH (0.19 mol/L) as follows:

$$\alpha$$-FeOOH(aggregate) $\rightarrow$ $\gamma$-Fe$_2$O$_3$(nanoparticle)+H$_2$O.

When the concentration of FeCl$_2$ was <0.22 mol/L or that of NaOH was <0.19 mol/L, only some of the $\alpha$-FeOOH was transformed into $\gamma$-Fe$_2$O$_3$. $\alpha$-FeOOH and $\gamma$-Fe$_2$O$_3$ have significantly different magnetic properties. Using the magnetization of single-phase $\alpha$-FeOOH and $\gamma$-Fe$_2$O$_3$ nanoparticles, the volume fraction of each phase in the two-phase nanoparticles could be estimated. For these nanoparticles, the magnetization can be described as follows:

$$M = (1 - y)M_a + yM_f,$$

where $M$ is the magnetization of the two phase system; $M_a$ and $M_f$ are the magnetizations of pure $\alpha$-FeOOH nanoparticles (sample A) and pure $\gamma$-Fe$_2$O$_3$ nanoparticles (sample C2), respectively; and $y$ is the volume fraction of the $\gamma$-Fe$_2$O$_3$ phase. In this experiment, the specific magnetization was measured directly. Since $M=\rho\sigma$, where $\rho$ is the density, magnetization can be expressed as follows:

$$\left[(1 - y)\rho_a + y\rho_f\right]\sigma = (1 - y)\rho_a\sigma_a + y\rho_f\sigma_f,$$

where $\rho_a$ (4.00 g/cm$^3$) and $\rho_f$ (4.899 g/cm$^3$) are the densities of $\alpha$-FeOOH and $\gamma$-Fe$_2$O$_3$, respectively; and $\sigma$, $\sigma_a$ and $\sigma_f$ are the specific magnetizations of the $\alpha$-FeOOH/$\gamma$-Fe$_2$O$_3$ nano-composite and the single-phase $\alpha$-FeOOH and $\gamma$-Fe$_2$O$_3$ nanoparticles, respectively. When $\sigma$, $\sigma_a$ and $\sigma_f$ in the same magnetic field are known, the value of $y$ can be obtained. To reduce the error, the values of $\sigma$, $\sigma_a$ and $\sigma_f$ in a high magnetic field (at 9×10$^3$ kA/4 m), which are written as $\sigma'$, $\sigma_a'$ and $\sigma_f'$, should be used, that is,

$$y = \frac{\rho_a(1-\sigma_a'/\sigma')}{(\rho_a\sigma_f' - \rho_f\sigma_a')/\sigma' - (\rho_f - \rho_a)}.$$

Based on the experimental results for the two-phase samples, $y$ or $(1-y)$ was calculated (Table 2). From the experimental magnetization curves of samples A and C2, $\sigma_a$, $\sigma_f$, the calculated $y$, and the first magnetization curves of samples B1, B2 and C1 can be fitted by

$$\sigma = \frac{(1 - y)\rho_a\sigma_a + y\rho_f\sigma_f}{(1 - y)\rho_a + y\rho_f}.$$

The fitted curves (Figure 4) were in agreement with the experiment results. This confirms the estimated $y$ are accurate.
Figure 3  Magnetization curves of samples A, B1, B2, C1 and C2.

Table 2  VSM data and volume fractions of α-FeOOH and γ-Fe$_2$O$_3$ nanoparticles for samples A, B1, B2, C1 and C2

| Sample | Magnetization (A m$^2$/kg) at 9x10$^3$ kA/4πm | Coercivity (kA/4πm) | α-FeOOH (1−y) | γ-Fe$_2$O$_3$ (y) |
|--------|---------------------------------------------|----------------------|---------------|------------------|
| A      | 2.57                                        | 0                    | 100%          | 0                |
| B1     | 13.41                                       | 57.17                | 85%           | 15%              |
| B2     | 63.65                                       | 73.46                | 2%            | 98%              |
| C1     | 38.80                                       | 43.13                | 46%           | 54%              |
| C2     | 64.88                                       | 117.58               | 0             | 100%             |
3 Conclusion

In contrast to other preparation methods, the method developed in this paper is simple, inexpensive, and reliable for the production of pure and highly crystalline $\gamma$-Fe$_2$O$_3$ nanoparticles. The $\alpha$-FeOOH precursor was directly transformed into $\gamma$-Fe$_2$O$_3$ nanoparticles in FeCl$_2$/NaOH solution, and the concentrations of FeCl$_2$ and NaOH played an important role in the phase transformation. When the $\alpha$-FeOOH precursor was heat treated with a mixed solution of FeCl$_2$ (0.22 mol/L) and NaOH (0.19 mol/L), it was completely transformed into $\gamma$-Fe$_2$O$_3$ nanoparticles. Different volume fractions of each phase in the $\alpha$-FeOOH/$\gamma$-Fe$_2$O$_3$ system were obtained by changing the concentration of FeCl$_2$ or NaOH. The $\alpha$-FeOOH aggregates may act as seeds to form the $\gamma$-Fe$_2$O$_3$ nanoparticles, and the sizes of these aggregates determine the size of the $\gamma$-Fe$_2$O$_3$ nanoparticles. Calculated magnetization curves agreed with the experimental data. This is a novel chemically induced transformation process and preparation route for $\gamma$-Fe$_2$O$_3$ nanoparticles, and could be used for the synthesis of other metal oxide nanocrystallites, which will be the subject of further investigations.

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