

Characterization of γ -Fe₂O₃ nanoparticles prepared by transformation of α -FeOOH

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Received September 9, 2010; accepted April 19, 2011

γ -Fe₂O₃ nanoparticles were successfully synthesized by a chemically induced transformation of α -FeOOH. In this method, the precursor (α -FeOOH) was prepared by chemical precipitation, and then treated with a mixed FeCl₂/NaOH solution to produce the nanoparticles. X-ray diffraction indicated that when the precursor was treated with FeCl₂ (0.22 mol/L) and NaOH (0.19 mol/L), pure γ -Fe₂O₃ nanoparticles were obtained. However, when the concentration of FeCl₂ was <0.22 mol/L or the concentration of NaOH was <0.19 mol/L, α -FeOOH and γ -Fe₂O₃ 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 γ -Fe₂O₃ nanoparticles were polygonal rather than spherical. The volume ratio of α -FeOOH and γ -Fe₂O₃ 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.

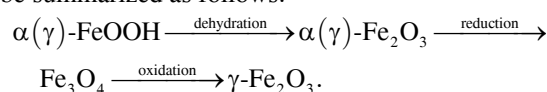
α -FeOOH, γ -Fe₂O₃, FeCl₂/NaOH solution, transition, nanoparticles

Citation: Miao H, Li J, Lin Y Q, et al. Characterization of γ -Fe₂O₃ nanoparticles prepared by transformation of α -FeOOH. Chinese Sci Bull, 2011, 56: 2383–2388, doi: 10.1007/s11434-011-4559-z

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 (γ -Fe₂O₃) 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 γ -Fe₂O₃ 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 γ -Fe₂O₃ 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 γ -Fe₂O₃ particles by FeOOH transformation is a complex process [20,21] that can be summarized as follows:



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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 K α ($\lambda=0.1541$ 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 Fe₃O₄ (FeO·Fe₂O₃) because they produce similar diffraction peaks. However, in alkaline solution, Fe²⁺ is unstable and Fe³⁺ cannot reduce to Fe²⁺. Consequently, the Fe₃O₄ 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 -FeOOH and γ -Fe₂O₃. This indicates that, depending on the concentration of FeCl₂ or NaOH, α -FeOOH 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 9×10^3 kA/4 π m) and coercivity of all the samples are listed in Table 2. For the

Table 1 XRD and TEM measurements on samples A, B1, B2, C1 and C2

Sample	FeCl ₂ (mol/L)	NaOH (mol/L)	Phase composition	Remarks
A	0	0	α -FeOOH	Spherical particles, agglomerate
B1	0.02	0.19	α -FeOOH+ γ -Fe ₂ O ₃	Floccule form, rod type
B2	0.07	0.19	γ -Fe ₂ O ₃ + α -FeOOH	Polygonal particles, flake type
C1	0.22	0.10	γ -Fe ₂ O ₃ + α -FeOOH	Polygonal particles, rod type
C2	0.22	0.19	γ -Fe ₂ O ₃	Polygonal particles

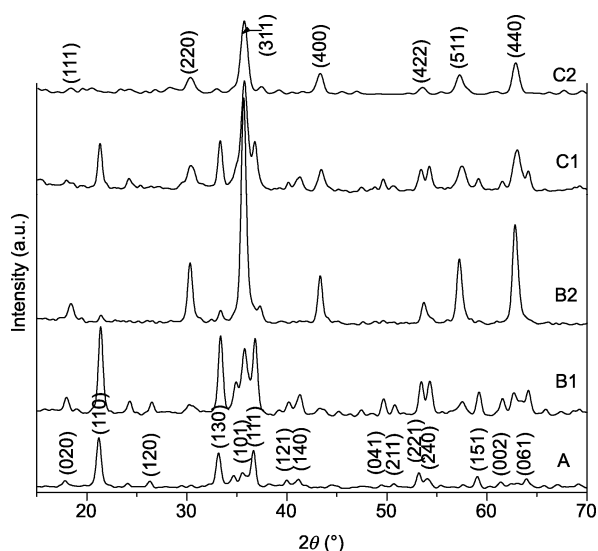


Figure 1 XRD spectra of samples A, B1, B2, C1 and C2.

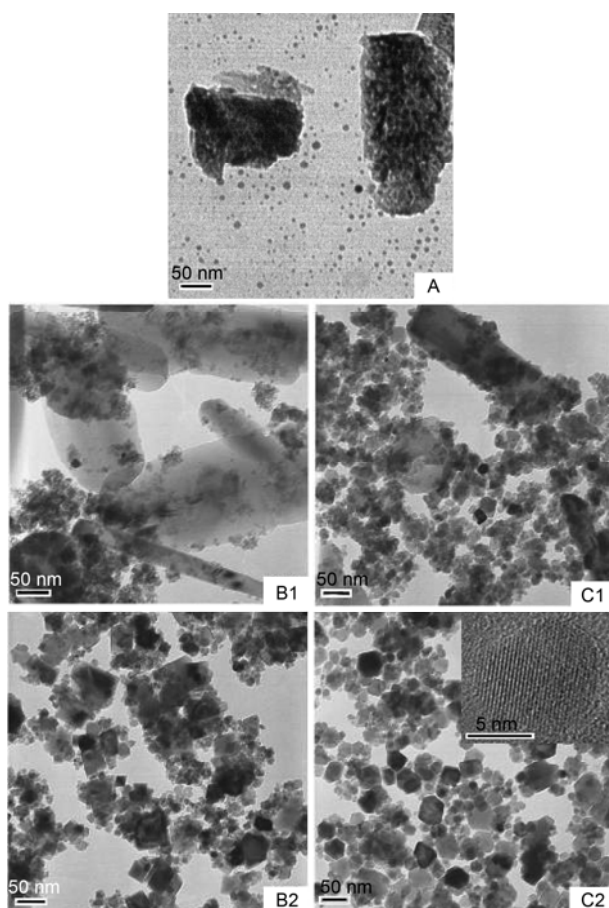
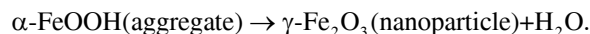


Figure 2 TEM micrographs of samples A, B1, B2, C1, C2 and high resolution TEM micrograph of sample C2.

nanoparticles containing both α -FeOOH and γ -Fe₂O₃ (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 α -FeOOH nanoparticles could form more bulk aggregates. These α -FeOOH aggregates were transformed into γ -Fe₂O₃ nanoparticles by heat treatment with a mixed solution of FeCl₂ (0.22 mol/L) and NaOH (0.19 mol/L) as follows:



When the concentration of FeCl₂ was <0.22 mol/L or that of NaOH was <0.19 mol/L, only some of the α -FeOOH was transformed into γ -Fe₂O₃. α -FeOOH and γ -Fe₂O₃ have significantly different magnetic properties. Using the magnetization of single-phase α -FeOOH and γ -Fe₂O₃ 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:

$$M = (1-y)M_\alpha + yM_\gamma,$$

where M is the magnetization of the two phase system; M_α and M_γ are the magnetizations of pure α -FeOOH nanoparticles (sample A) and pure γ -Fe₂O₃ nanoparticles (sample C2), respectively; and y is the volume fraction of the γ -Fe₂O₃ phase. In this experiment, the specific magnetization was measured directly. Since $M = \rho\sigma$, where ρ is the density, magnetization can be expressed as follows:

$$[(1-y)\rho_\alpha + y\rho_\gamma]\sigma = (1-y)\rho_\alpha\sigma_\alpha + y\rho_\gamma\sigma_\gamma,$$

where ρ_α (4.00 g/cm³) and ρ_γ (4.899 g/cm³) are the densities of α -FeOOH and γ -Fe₂O₃, respectively; and σ , σ_α and σ_γ are the specific magnetizations of the α -FeOOH/ γ -Fe₂O₃ nano-composite and the single-phase α -FeOOH and γ -Fe₂O₃ nanoparticles, respectively. When σ , σ_α and σ_γ in the same magnetic field are known, the value of y can be obtained. To reduce the error, the values of σ , σ_α and σ_γ in a high magnetic field (at 9×10^3 kA/4 π m), which are written as σ' , σ'_α and σ'_γ , should be used, that is,

$$y = \frac{\rho_\alpha(1-\sigma'_\alpha/\sigma')}{(\rho_\gamma\sigma'_\gamma - \rho_\alpha\sigma'_\alpha)/\sigma' - (\rho_\gamma - \rho_\alpha)}.$$

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, σ_α , σ_γ , the calculated y , and the first magnetization curves of samples B1, B2 and C1 can be fitted by

$$\sigma = \frac{(1-y)\rho_\alpha\sigma_\alpha + y\rho_\gamma\sigma_\gamma}{(1-y)\rho_\alpha + y\rho_\gamma}.$$

The fitted curves (Figure 4) were in agreement with the experiment results. This confirms the estimated y are accurate.

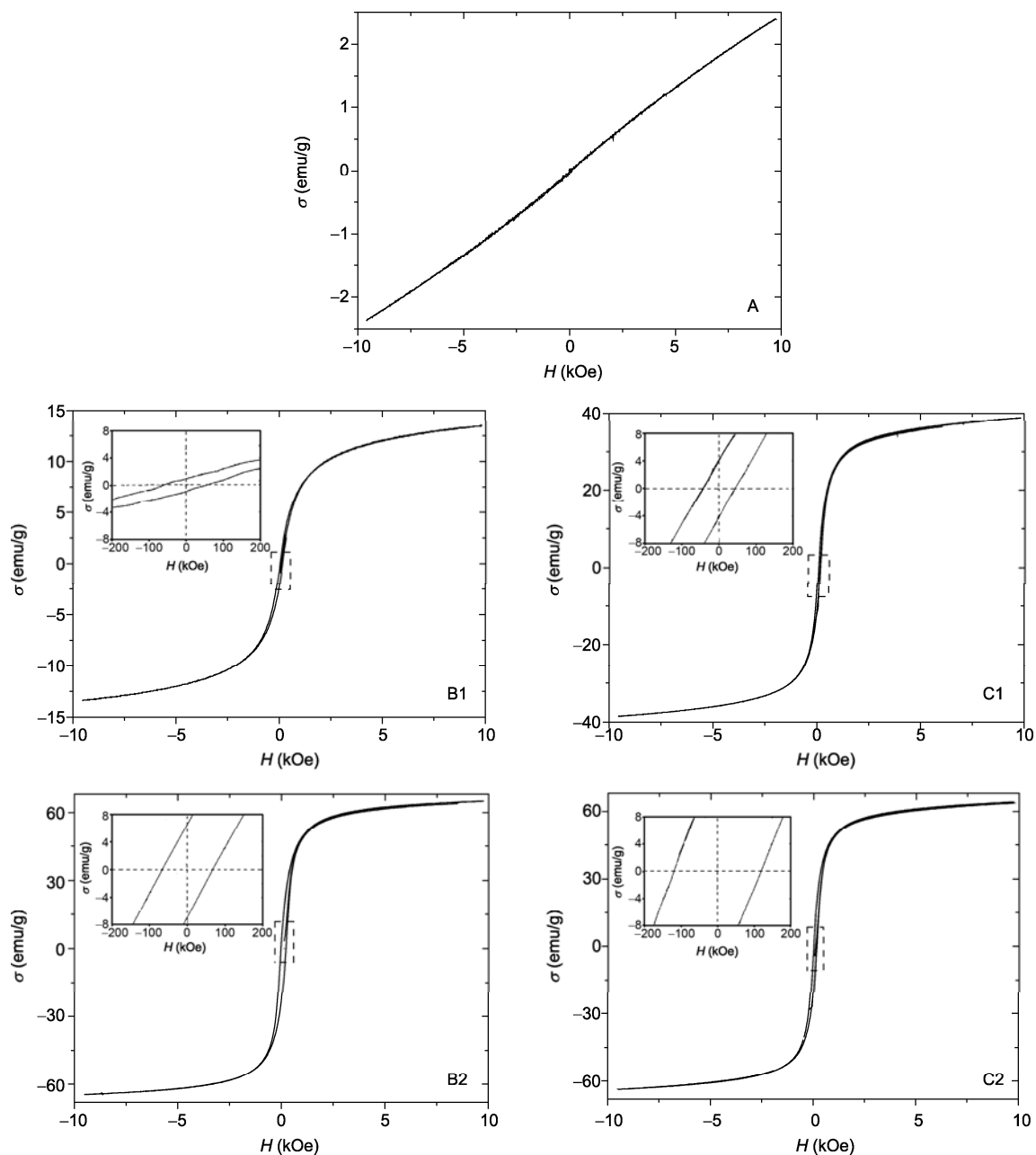


Figure 3 Magnetization curves of samples A, B1, B2, C1 and C2.

Table 2 VSM data and volume fractions of α -FeOOH and γ -Fe₂O₃ nanoparticles for samples A, B1, B2, C1 and C2

Sample	Magnetization ($A \text{ m}^2/\text{kg}$) at $9 \times 10^3 \text{ kA}/4\pi \text{ m}$	Coercivity ($\text{kA}/4\pi \text{ m}$)	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%

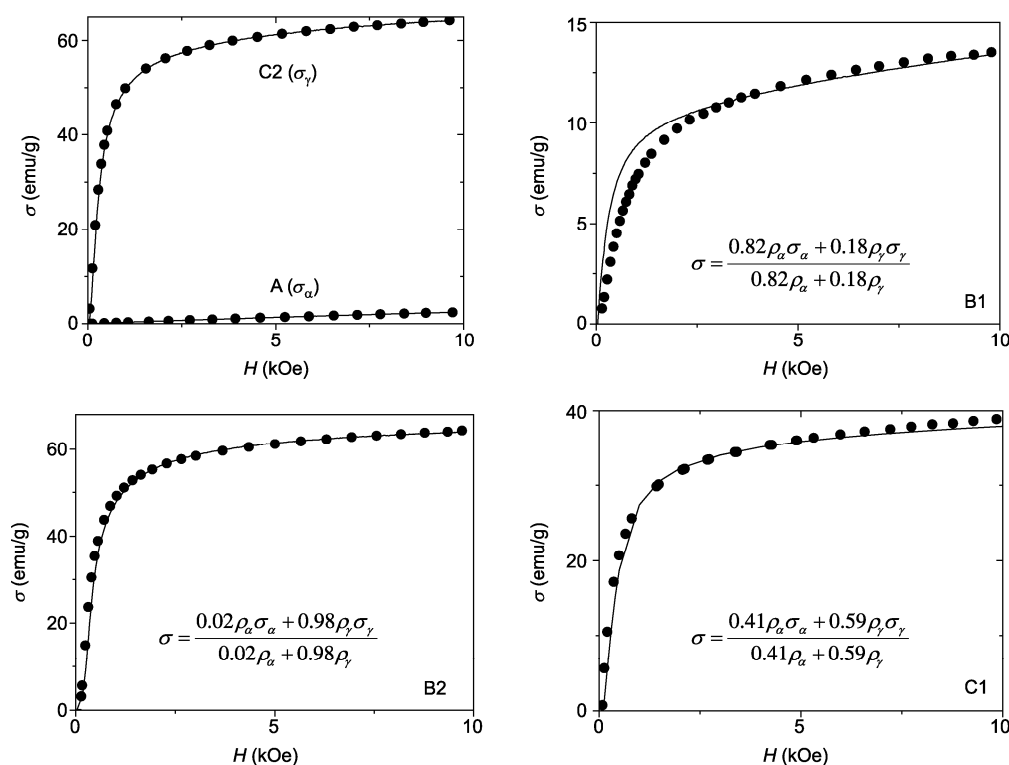


Figure 4 The measured first magnetization curves of samples A and C2, and the fitted first magnetization curve of samples B1, B2 and C1. Experimental data (•) and fitted curve (—).

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 γ - Fe_2O_3 nanoparticles. The α - FeOOH precursor was directly transformed into γ - Fe_2O_3 nanoparticles in $\text{FeCl}_2/\text{NaOH}$ solution, and the concentrations of FeCl_2 and NaOH played an important role in the phase transformation. When the α - 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 γ - Fe_2O_3 nanoparticles. Different volume fractions of each phase in the α - FeOOH/γ - Fe_2O_3 system were obtained by changing the concentration of FeCl_2 or NaOH . The α - FeOOH aggregates may act as seeds to form the γ - Fe_2O_3 nanoparticles, and the sizes of these aggregates determine the size of the γ - Fe_2O_3 nanoparticles. Calculated magnetization curves agreed with the experimental data. This is a novel chemically induced transformation process and preparation route for γ - Fe_2O_3 nanoparticles, and could be used for the synthesis of other metal oxide nanocrystallites, which will be the subject of further investigations.

This work was supported by the National Natural Science Foundation of China (11074205).

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