

Magnetic-field-induced synthesis of magnetic γ -Fe₂O₃ nanotubes

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1. Introduction

Nanometer-scale magnetic materials and devices are a scientifically interesting and technologically important area of research with many present and future applications in biomedicine, magnetic recording, and spin electronics. In particular, considerable effort has been made in the area of one-dimension (1D) nanostructured materials, such as nanotubes,^[1] nanorods,^[2] and nanowires.^[3] Recently, various approaches including anodic aluminum oxide (AAO) hard template process, lecithin soft template and redox methods have been developed for the preparation of these 1D magnetic materials. One of the important classes of 1D nanostructure is magnetic nanotubes. The magnetic properties of these nanotubes can be used to control the formation of their assembled structures, producing an advantage over nonmagnetic nanotubes in some applications. However, to the best of our knowledge, there have been few reports about maghemite nanotubes by far. Maghemite (γ -Fe₂O₃), which has a cubic spinel structure, is an important material for various applications in industry and technology, for example spin electronic devices, high-density magnetic recording, and biosensors etc.

On the other hand, applications of the magnetic fields for advanced material processing and treatment have been of interest for recent years. It has been demonstrated that martensitic transformation is affected by an external magnetic field when the martensite is a ferromagnetic phase and the parent is a paramagnetic phase.^[4] Magnetic fields have also been used to create in-plane-aligned membranes of carbon nanotubes (CNTs)^[5] and highly conductive and mechanically anisotropic CNTs polymer composites.^[6] The alignment

of CNTs in magnetic fields arises from the anisotropic magnetic susceptibility of nanotubes. Stronger effects or unknown effects are expected if applying a high magnetic field during magnetic nanostructure fabrication process. In this communication, we report a novel method for synthesizing ferromagnetic γ -Fe₂O₃ nanotubes by a template process with the aid of high magnetic field. These nanotubes are characterized by structural, morphological, and magnetization measurements.

2. Experimental

Commercial AAO templates with pore diameter of 100 nm (Anodisc 47, Whatman) were employed for the synthesis of the Fe₂O₃ nanotubes. The template was immersed in a approximately saturated Fe(NO₃)₃·9H₂O solution (3M) for 20 minutes and then was dried in vacuum at 60°C for 3h. This procedure was repeated for another three times, but impregnation time was changed from 20 min to 10 min, 5min, and 5min for other times, respectively. After immersions and drying for four times, the AAO template was annealed in an electrical furnace, which was installed in the room temperature bore of cryogen-free superconducting magnet.^[7] A magnetic field of 12 T was applied during heat treatment. The annealing temperature was 500 °C; The annealing time was 2h. When the AAO template was cooled down to the room temperature, the magnetic field was decreased to zero. The direction of the magnetic field was perpendicular and parallel to the AAO membrane plane, respectively. The products were then termed as the B \perp samples and B// samples, respectively. In order to evaluate the effect of the magnetic field, the AAO templates were annealed under the same conditions but without any magnetic field. Finally, the annealed AAO template was dissolved in 5M NaOH

solution, and then collected reddish-brown solid was rinsed with deionized water and absolute ethanol several times to obtain the Fe_2O_3 nanotubes.

3. Results and discussions

Figure 1 shows the x-ray diffraction (XRD) patterns of the Fe_2O_3 samples prepared at 500 °C for 2 hours without a magnetic field and with a 12 T magnetic field. For the samples formed without an applied magnetic field, the XRD pattern matches well that of $\alpha\text{-Fe}_2\text{O}_3$ (standard cards, JCPDS No. 33-0664), clearly demonstrating that the as-synthesized samples are a single phase of $\alpha\text{-Fe}_2\text{O}_3$. However, XRD patterns of the products produced under a magnetic field are quite different from those of the 0 T samples. For the B// samples, the XRD pattern is similar to that for the B \perp samples, although the diffraction peaks for the B \perp samples seem a little bit narrower. In the case of the B \perp samples, the major peaks at 2θ values of 30.1, 35.5, 43.2, 53.8, 57.2 and 62.89 correspond to the 220, 311, 400, 422, 511, and 440 crystal planes of $\gamma\text{-Fe}_2\text{O}_3$, respectively, which can be indexed to cubic spinel phase of $\gamma\text{-Fe}_2\text{O}_3$ with lattice constants, $a=8.310(1)\text{\AA}$. These values are in good agreement with the standard values of bulk $\gamma\text{-Fe}_2\text{O}_3$ (JCPDS card No. 25-1402). In Figure 1, the peak widths for all the specimens, at full width at half-maximum, are wide, indicating the formation of ultrafine particles. This result suggests that $\gamma\text{-Fe}_2\text{O}_3$ has been formed by applying a high magnetic field during processing.

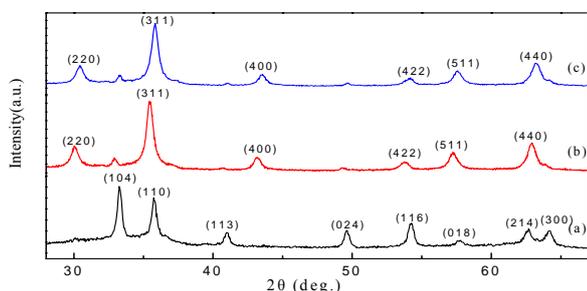


Fig. 1. XRD patterns of the Fe_2O_3 samples without a magnetic field (a), and with a 12 T magnetic field: the B (\perp) samples (b) and the B (//) samples (c).

Figure 2 presents the SEM micrographs at different magnifications of $\gamma\text{-Fe}_2\text{O}_3$ samples prepared under a 12 T magnetic field. Obviously, SEM images of the material formed inside the pores showed iron oxide tubes. In the case of the B \perp samples, a low-magnification view shows a bundle of $\gamma\text{-Fe}_2\text{O}_3$ nanotubes, and the length is about 30 μm (Figure 2a). A higher magnification image reveals that the $\gamma\text{-Fe}_2\text{O}_3$ nanotubes are arranged roughly parallel to one another (Figure 2b). This demonstrates clearly that magnetic nanotubes can be produced efficiently by the application of magnetic field. For the B// samples, the lengths of the nanotubes are shorter than that of B \perp samples relatively (Figure 2c), and it can be also found that some nanotubes split or crash into individual nanoparticles (Figure 2d), as supported by the broadening of peaks in the XRD pattern. The reason is because the direction of magnetic field is perpendicular to that of fixed action from AAO template, and when the magnitude of the magnetic force exceeds that of the fixed force from AAO template, the split of the nanotubes occurs and even some nanoparticles are formed. It is interesting to note by comparing Figure 2a and 2c, the effect of a magnetic field is different between B \perp and B// samples. It seems that the magnetic field works more effectively to produce better $\gamma\text{-Fe}_2\text{O}_3$ nanotubes when the direction of applied fields was perpendicular to the AAO membrane plane during processing.

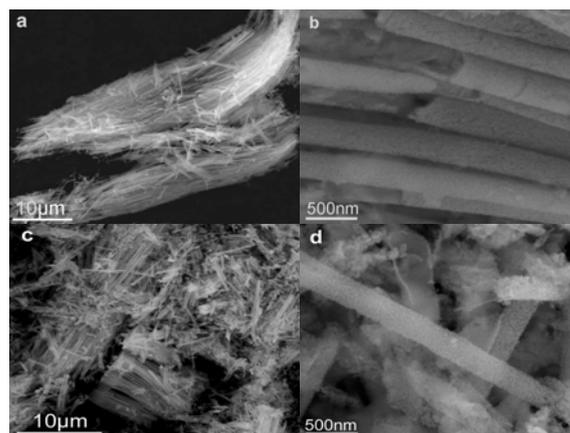


Fig. 2. SEM images of the magnetic field treating samples: (a) Low-magnification view of the B (\perp) samples. (b) Walls of the nanotube bundles. (c) Low-magnification view of the B (//) samples. (d) the B (//) samples at high magnification.

Figure 3 shows room-temperature hysteresis loops of samples prepared with and without the magnetic field after removing the AAO templates. From Fig. 3, it is immediately noticed that the samples produced without field (A) exhibit room-temperature weak ferromagnetism. However, for the samples annealed in the presence of 12 T magnetic field, a fully ferromagnetic behavior is observed. For the B (\perp) samples (C), the saturation magnetization (M_S), coercivity (H_c) and remanent magnetization (M_R) at 300K are $46.1 \text{ emu}\cdot\text{g}^{-1}$, 28.0 Oe , $2.35 \text{ emu}\cdot\text{g}^{-1}$, respectively. The M_S value is smaller than the corresponding values of the bulk sample ($M_S = 76 \text{ emu}\cdot\text{g}^{-1}$). The deviation is likely due to the nanostructured $\gamma\text{-Fe}_2\text{O}_3$ and trace of impurity. In addition, the same ferromagnetic character is found for the samples prepared with the field applied along the template plane (B). However, the corresponding values of M_S , H_c and M_R are slightly smaller than those corresponding to samples with the field imposed in the perpendicular direction (the B (\perp) samples). This difference can be attributed to the difference in morphology between both samples, as demonstrated by SEM results in Figure 2. Therefore, the above results clearly show that Fe_2O_3 samples changed their weak ferromagnetic character at zero field to ferromagnetic behavior at a field of 12T, in other words, the external magnetic field could be responsible for the formation of $\gamma\text{-Fe}_2\text{O}_3$ nanotubes.

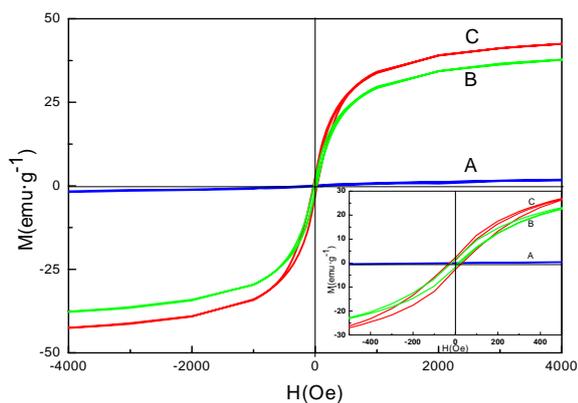


Fig. 3. Hysteresis loops measured at 300K for the samples without a magnetic field (A), and with the B (\parallel) samples (B), and the B (\perp) samples (C). The inset is the full range of the hysteresis between -500 and 500 Oe.

From XRD results, the sample synthesized in the absence of high magnetic field was indexed to $\alpha\text{-Fe}_2\text{O}_3$, whereas the sample prepared with a 12T magnetic field was verified to $\gamma\text{-Fe}_2\text{O}_3$ mostly, which indicates that the 12T magnetic field affected the phase of samples intensively, because the only difference in preparation method between the samples is the magnitude of external magnetic field. From a thermodynamic perspective, magnetic field, like temperature, is an independent variable that changes the free energy. Thus, when magnetic field is applied, the resulting free energy changes are classified into two terms: the thermal Gibbs free energy, $\Delta G_T(T)$, and the magnetic Gibbs free energy, $\Delta G_M(T, H)$. Therefore, if a 12T external magnetic field is imposed during the heating treatment, a new equilibrium will be come.

It is very common that the product of the thermal decomposition for $\text{Fe}(\text{NO}_3)_3$ is $\alpha\text{-Fe}_2\text{O}_3$ without a magnetic field.^[8] But, the exact mechanism for the formation of $\gamma\text{-Fe}_2\text{O}_3$ under the high magnetic field is not completely understood. A possible explanation is that $\alpha\text{-Fe}_2\text{O}_3$ forms at 500°C firstly for the thermal decomposition of $\text{Fe}(\text{NO}_3)_3$ and then, $\alpha\text{-Fe}_2\text{O}_3$ is transformed to $\gamma\text{-Fe}_2\text{O}_3$ in the presence of high magnetic field. The total Gibbs free energy of the transformation from $\alpha\text{-Fe}_2\text{O}_3$ to $\gamma\text{-Fe}_2\text{O}_3$ can be described as $\Delta G_T + \Delta G_M$ owing to the existence of magnetic field. Compared to $\alpha\text{-Fe}_2\text{O}_3$, $\gamma\text{-Fe}_2\text{O}_3$ is metastable. It can be easily transformed to $\alpha\text{-Fe}_2\text{O}_3$ in the absence of magnetic field at 500°C ,^[9] which indicates that ΔG_T is positive. The existence of ΔG_M is a result of the difference in magnetic susceptibility between $\gamma\text{-Fe}_2\text{O}_3$ and $\alpha\text{-Fe}_2\text{O}_3$. This energy can be expressed as

$$\Delta G_M = -\frac{1}{2}\mu_0(\chi_\gamma - \chi_\alpha)H^2$$

Where μ_0 is the permeability of free space, χ_γ is the magnetic susceptibility of $\gamma\text{-Fe}_2\text{O}_3$ at a temperature T , χ_α is the magnetic susceptibility of $\alpha\text{-Fe}_2\text{O}_3$ at a temperature T , and H is the applied magnetic field. At 500°C , $\gamma\text{-Fe}_2\text{O}_3$ is ferromagnetic while $\alpha\text{-Fe}_2\text{O}_3$ is antiferromagnetic, because the Curie temperature for $\gamma\text{-Fe}_2\text{O}_3$ is 590°C .

Therefore, χ_γ is larger than χ_α at 500°C,^[10] which suggests that ΔG_M is negative and the total free energy ($\Delta G_T + \Delta G_M$) is reduced due to the external magnetic field. As a result, there is a great tendency for the formation of γ -Fe₂O₃ with the strength of magnetic field (H^2). So, magnetic energy is thought to be the driving force for the formation of γ -Fe₂O₃. Moreover, it was reported that the magnetic field can enhance the nucleation rate of magnetic materials.^[11] Thus, we deduce that the presence of the external magnetic field might promote formation rate of γ -Fe₂O₃. As a consequence, the γ -Fe₂O₃ nanotubes can be obtained when 12T magnetic field is applied during the heat treatment.

4. Conclusions

In summary, we propose the use of high magnetic field as a viable alternative tool for magnetic γ -Fe₂O₃ nanotube processing, with the advantages of a simple, yet very efficient, and contact-free method. Phase identification, microstructure analysis and magnetic measurements clearly indicate that γ -Fe₂O₃ nanotubes have been formed under a 12 T magnetic field. Such a novel approach to preparing magnetic nanotubes may be very useful for technological applications, such as high-density magnetic recording media and electronic devices.

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