The fabrication and magnetic properties of nanowire-like iron oxide

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Abstract

Nanowire-like iron oxides (α-Fe$_2$O$_3$, Fe$_3$O$_4$ and γ-Fe$_2$O$_3$) of diameter about 200 nm and length up to 8 μm were assembled into anodic aluminium oxide templates through electrodeposition followed by a heat-treating process. These wires have polycrystalline structures and consist of fine particles whose magnetic moments have preferred orientations in the templates. Some unique magnetic properties, such as perpendicular magnetic anisotropy in Fe$_3$O$_4$ wires, reduced transition temperature in α-Fe$_2$O$_3$ and Fe$_3$O$_4$ wires, and superparamagnetism in γ-Fe$_2$O$_3$ wires, were observed. The properties can be understood by their unique structures induced by reduced dimension and the competition of the shape and crystalline anisotropy.

1. Introduction

Ordered quasi-one-dimensional (1D) magnetic nanostructures have been of great interest both for theoretical study and for potential nanodevice applications due to their peculiar structural characteristics, size effects and some novel physical properties that are different from the bulk materials [1, 2]. A large variety of quasi-1D nanostructures, such as nanotubes, nanorods, nanowires, and nanobelts, have been synthesized by various techniques. One of the commonly used methods for generating quasi-1D nanostructures is based on the electrodeposition of various materials in porous anodic aluminium oxide (AAO) templates [3, 4]. This technique has been applied to fabricate metal and alloy nanowires as parallel arrays that displayed unique magnetic properties (e.g. anisotropy magnetization) [5, 6]. It is, however, limited for use with oxide-based magnetic materials (e.g. ferrite), mainly due to technical difficulties involved in the formation of oxides through electrochemical deposition. Developing a new and, in particular, cost-effective technique for fabricating quasi-1D ferrite nanostructures is of great scientific

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and commercial interest. We have developed a low-cost method based on electrodepositing a precursor β-FeOOH into the AAO templates, followed by a heat-treating process. In earlier work, we reported the fabrication and some properties of α-Fe$_2$O$_3$ [7] and Fe$_3$O$_4$ [8] wires. γ-Fe$_2$O$_3$ wires were also synthesized recently. In our extensive research, we found that these wires are composed of fine particles and the magnetic moments of these particles have preferred orientations. Also their magnetic properties can be interpreted satisfactorily by these unique structures. We think that these nanostructures might more suitably be named nanowire-like systems. In this paper, we report the fabrication process and magnetic properties of γ-Fe$_2$O$_3$ wires. We also summarize and compare the properties of α-Fe$_2$O$_3$, Fe$_3$O$_4$ and γ-Fe$_2$O$_3$ wires.

2. Experiment

The detailed fabrication procedure of AAO templates is described elsewhere [9]. In this study, a two-step anodization process was employed [10] and all the templates were anodized at 120 V_{DC} for 3 h in 0.5 M phosphoric acid. After the anodization, the AAO templates were electrodeposited for 10 min in a mixed solution containing 9 g l^{-1} FeCl$_3$·6H$_2$O and 14 g l^{-1} (NH$_4$)$_2$C$_2$O$_4$·H$_2$O, where the voltage and frequency are 15 V_{AC} and 70 Hz, respectively. Then precursor β-FeOOH nanowires can be obtained [11].

After removing the remaining aluminium layers in a saturated HgCl$_2$ solution, the precursor membranes were placed in a horizontal tube furnace and calcined in air at 600 °C for 2 h. The product was characterized as α-Fe$_2$O$_3$ [7]. Then the α-Fe$_2$O$_3$ wires were reduced at 325 °C for 2 h in a hydrogen flow of 30 ml min^{-1}, and the product was verified as Fe$_3$O$_4$ [8]. γ-Fe$_2$O$_3$ wires can be obtained when Fe$_3$O$_4$ wires are heat-treated at 300 °C for 2 h in air.

3. Results and discussion

The detailed report on the preparation and characterization of the precursor β-FeOOH can be found in [11]. The following are related to the characterization and properties of three iron oxides nanostructures after heat-treating the precursor wires.

Figure 1 shows the x-ray diffraction (XRD, Philips X'Pert) patterns of the three oxides with AAO templates. All of them have polycrystalline structures with broadening peaks. α-Fe$_2$O$_3$ wires corresponding to the standard JCPDS 33-0664 can be easily identified. However, the other two samples have almost the same diffraction peaks due to the same spinel structure for Fe$_3$O$_4$ and γ-Fe$_2$O$_3$. Mössbauer spectrum (MS) analysis was used to verify the phase further. The polycrystalline structures of these samples indicate that the crystal orientations are imperfect, which is different from most metal and alloy nanowires electrodeposited in AAO templates directly [5, 12]. It can be conjectured that our samples are composed of fine particles with different crystal orientations due to dehydration of the precursor and the ac current electrodepositing process.

Figure 2(a) shows a scanning electron microscope (JEO 2000 SEM) image of the top view of the templates. The average pore diameter is about 200 nm. The morphologies of the three oxides after dissolving the templates in 0.1 M NaOH solution are shown in figures 2(b)–(d), respectively. The insets display the corresponding selected area electron diffraction (SAED) patterns. The average diameter of the wires is about 200 nm, which is in good agreement with the size of the pores of the AAO templates, and the average length is up to 8 μm. Since Fe$_3$O$_4$ and γ-Fe$_2$O$_3$ have similar SAED patterns, the inset pattern shown in figure 2(c) was taken on several wires, whereas the pattern in figure 2(d) was taken on an individual wire. The bright diffraction rings show the polycrystalline spinel structures which are in good agreement with
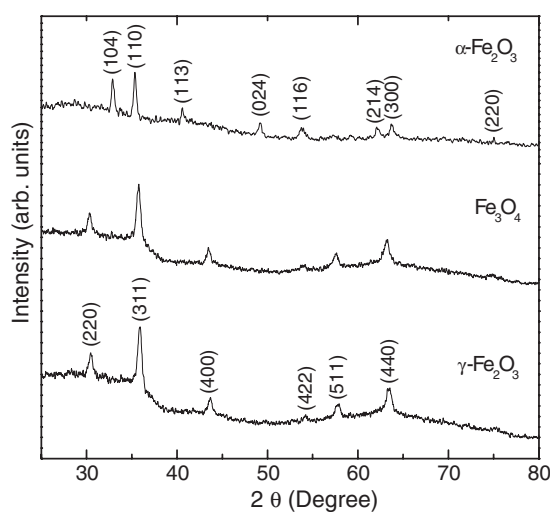
Figure 1. XRD patterns of three iron oxides (α-Fe$_2$O$_3$, Fe$_3$O$_4$ and γ-Fe$_2$O$_3$) wires.

the XRD results. The irregularly arranged spots on the individual wire indicate the existence of fine crystallized particles with different crystal orientations.

MS of the three oxides in AAO templates with the γ-ray parallel to the wire axis are shown in figure 3. Since all MS at 300 K contain a large percentage of doublets, low temperature MS were collected to test that the doublets resulted from the contribution of superparamagnetic particles. Figure 3(a) shows the MS of α-Fe$_2$O$_3$ wires at 300 and 80 K. The 300 K MS is composed of a doublet and a sextet whose hyperfine field (H_{hf}) is about 50.11 T. Figures 3(b) and (c) show the MS of Fe$_3$O$_4$ and γ-Fe$_2$O$_3$ wires at 300 and 20 K. The 300 K MS in figure 3(b) consists of one doublet and two sextets in which the H_{hf} are 47.4 and 43.9 T, respectively. However, the 300 K MS in figure 3(c) is composed of one doublet and one sextet in which the H_{hf} is 46.5 T. From the different values of the H_{hf}, two oxides can be identified because the values of the hyperfine fields of the A- and B-site for Fe$_3$O$_4$ have an obvious difference; however, for γ-Fe$_2$O$_3$ the values are almost the same [13]. The H_{hf} of these wires are less than those of the bulk materials mainly due to the existence of collective magnetic excitation caused by the size distribution of the crystallites [14]. The reduced relative area of the doublet in the 80 K MS in figure 3(a) and the vanished doublets in the 20 K MS shown in figures 3(b) and (c) indicate that the doublets result from the contributions of the superparamagnetic phase.

The relative intensity ratio of the sextet for the three oxides at low temperature is different, indicating that the direction of the magnetic moments of the particles is different. The intensity ratio for the α-Fe$_2$O$_3$ wires in the 80 K MS is nearly 3:4:1, suggesting that the spins align almost perpendicular to the wire axis. However, for Fe$_3$O$_4$ and γ-Fe$_2$O$_3$ wires they are neither parallel nor perpendicular to the wire axis. This is different from the MS of metal and alloy nanowires in which lines 2 and 5 are almost absent, suggesting that the moments are perfectly aligned [12]. Moreover, for a given oxide, the ratios at room and low temperature are also different. This can be understood by the effect of the thermal agitation. The MS of the three oxides wires are also different from the isotropic particle systems where the moments aligned randomly. All of these differences might be related to the competition of the shape and the crystalline anisotropy.

The magnetic properties of these iron oxides wires at room temperature were investigated with a Lake Shore 7304 vibrating sample magnetometer. No remanence was observed in
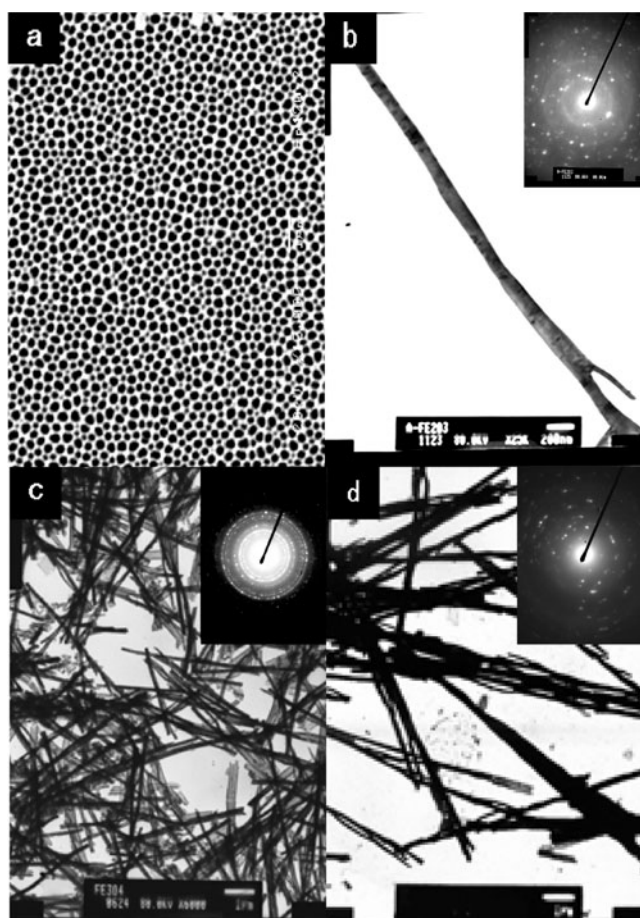
Figure 2. (a) SEM micrograph of the top view of AAO templates. (b)–(d) TEM images of α-Fe$_2$O$_3$, Fe$_3$O$_4$ and γ-Fe$_2$O$_3$ wires, respectively. The insets are the corresponding SAED patterns. The inset pattern in figure 2(c) was taken on several wires and in figure 2(d) was taken on an individual wire.

α-Fe$_2$O$_3$ wires at room temperature. However, when the temperature decreased to 80 K with an applied field of 5 T, weak ferromagnetism (WF) was observed (shown in figure 4(a) measured on a quantum design Magnetic Property Measurement System). The magnetic moments in WF state may have contributions from both the canting of the sublattice magnetization directions and from uncompensated spins as observed for α-Fe$_2$O$_3$ nanoparticles [15], because our wires are composed of fine α-Fe$_2$O$_3$ particles. Figure 4(b) shows the hysteresis loops of Fe$_3$O$_4$ wires at room temperature, in which the $H_\parallel$ and $H_\perp$ indicate that the external field was applied parallel and perpendicular to the wire axis, respectively. The expected magnetic anisotropy was found. The coercivity (H_c) and remanence ratio (M_r/M_s) are 378 Oe and 0.6 in the parallel direction, which are higher than 147 Oe and 0.1 in the perpendicular one. Furthermore, in the parallel direction, technical saturation occurs in fields of about 2 kOe, whereas in the perpendicular direction the wires are not magnetically saturated in a field of 8 kOe. This suggests that the magnetic moments of Fe$_3$O$_4$ particles in the templates have preferred orientations due to the shape anisotropy. However, from MS results they are not parallel to the wire axis. Figure 4(c) shows the hysteresis loops for the γ-Fe$_2$O$_3$ wires at room temperature which
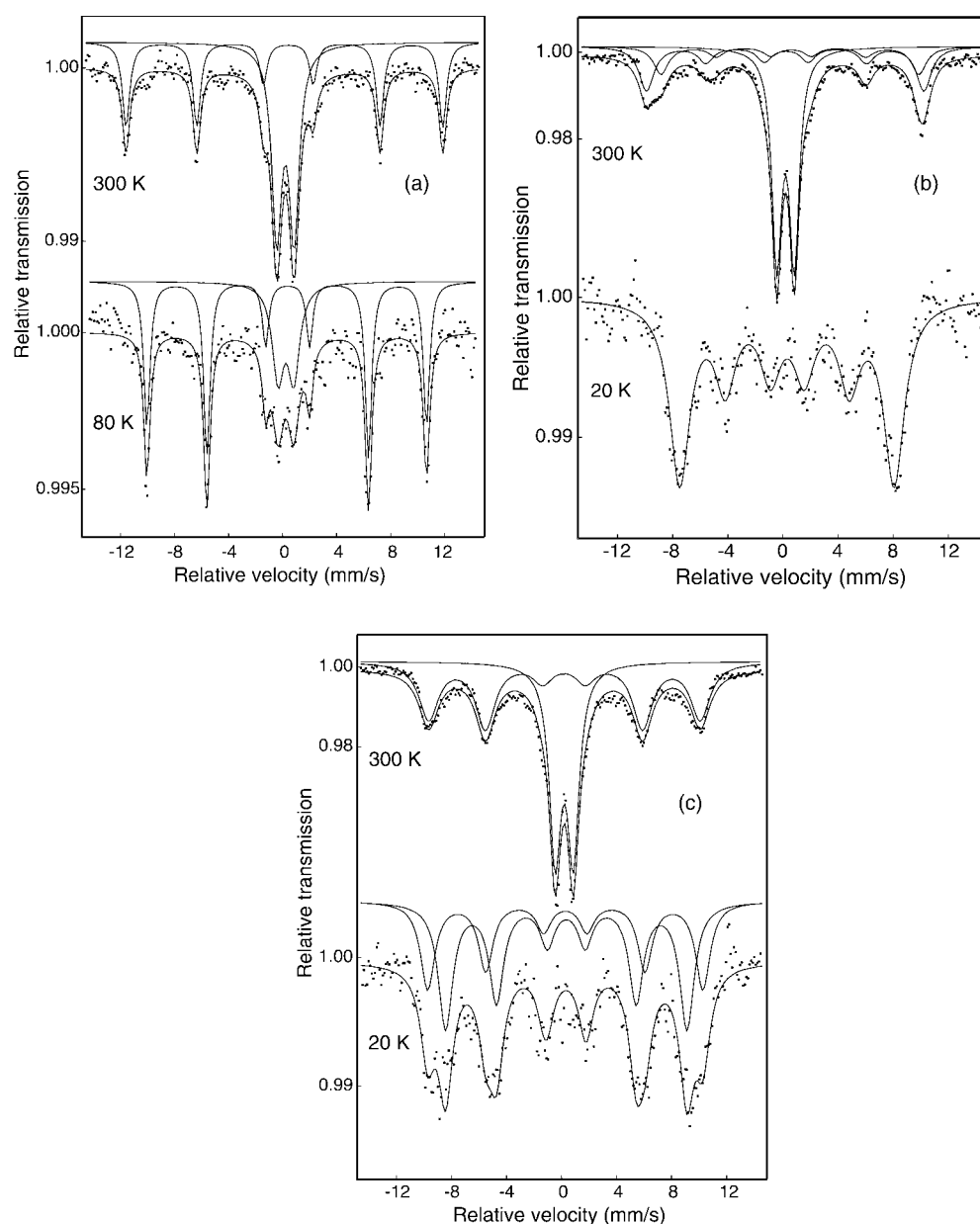
Figure 3. MS of (a) α-Fe$_2$O$_3$ wires at 300 and 80 K, (b) Fe$_3$O$_4$ wires at 300 and 20 K, and (c) γ-Fe$_2$O$_3$ wires at 300 and 20 K.

are close to superparamagnetic behaviour. This should be attributed to the size of γ-Fe$_2$O$_3$ particles that are in the superparamagnetic scale, and the magnetic moments of the particles cannot be stabilized due to thermal activation. The different saturated magnetic moments in the parallel and perpendicular directions are due to the different demagnetization fields in the two directions.

Figure 5 shows the temperature dependence of the magnetization for α-Fe$_2$O$_3$ and Fe$_3$O$_4$ wires, respectively. For α-Fe$_2$O$_3$, below 80 K the magnetization increases with increasing
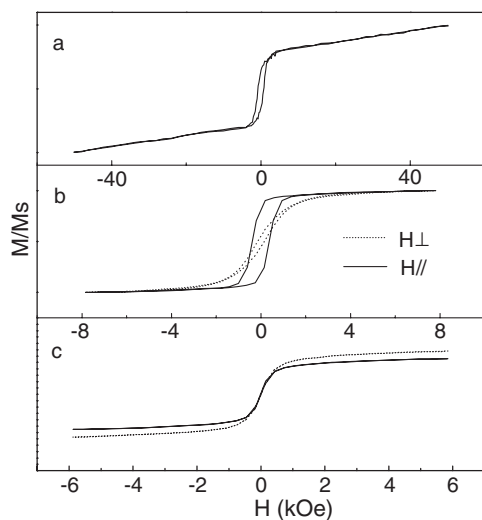
Figure 4. Hysteresis loops of (a) α-Fe$_2$O$_3$ wires at 80 K, (b) Fe$_3$O$_4$ wires at room temperature, and (c) γ-Fe$_2$O$_3$ wires at room temperature.
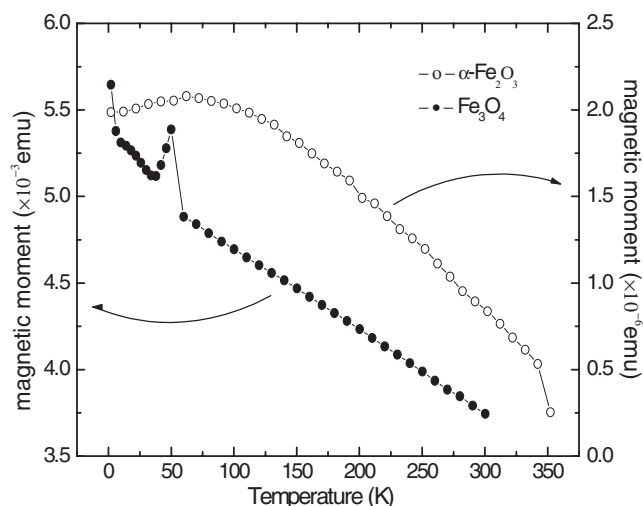

Figure 5. Temperature dependence of the magnetization for α-Fe$_2$O$_3$ and Fe$_3$O$_4$ wires, respectively.

temperature, which is characteristic of antiferromagnetism. Above 80 K it decreases with increasing temperature. This behaviour is more like that of ferromagnetism which corresponds well with the WF of α-Fe$_2$O$_3$ above the Morin transition temperature (T_M). When the temperature is at about 350 K the magnetization sharply decreases to near zero. This temperature can be explained as the Néel transition temperature (T_N). So, for α-Fe$_2$O$_3$ wires the T_M is about 80 K and the T_N is about 350 K, which are much less than those of the bulk materials. A decreased T_M value was also observed on small α-Fe$_2$O$_3$ particles [16].

For Fe$_3$O$_4$ wires measured at 2 T the magnetization increases as the temperature decreases. When the temperature decreases to 50 K the magnetization first decreases and then increases with decreasing temperature. The change of the magnetization at 50 K can be interpreted

by a Verwey transition where the crystal structure changes from cubic to monoclinic [17]. The transition temperature (T_V) is much lower than that of the bulk materials of about 120 K, which is due to the reduced dimension. A reduced T_V value was also observed on nanosized particles [18] and films [19]. The decreased magnetization at T_V was explained by Muxworthy [20] as the formation of an e-sublattice in which the e-sublattice electrons align antiparallel to the net magnetization of the A- and B-sublattice when cooling through T_V. He attributed the increased magnetization below T_V to the paraprocess in which the e-sublattice was destroyed or aligned in the direction of the field when the applied field is large enough to cause technical saturation. Our experimental results seem to be interpreted by this model. However, the jump of the saturation magnetization at T_V is not much sharper than that observed by Muxworthy. This can be attributed to the particle size distribution in the wires. The variations in stoichiometry can also strongly affect T_V [21]. In addition, it must be mentioned that the sharply increased magnetization at very low temperature might have a contribution from the superparamagnetism.

4. Conclusion

Nanowire-like iron oxide (α-Fe$_2$O$_3$, Fe$_3$O$_4$ and γ-Fe$_2$O$_3$) wires of diameter about 200 nm and length up to 8 μm were successfully synthesized in AAO templates. The wires have polycrystalline structures and consist of fine particles. The magnetic moments of these particles have preferred orientations. The moments of the α-Fe$_2$O$_3$ particles in the templates are almost perpendicular to the wire axis, whereas they are neither parallel nor perpendicular to the axis for Fe$_3$O$_4$ and γ-Fe$_2$O$_3$ particles. At room temperature, perpendicular magnetic anisotropy is observed clearly only in Fe$_3$O$_4$ wires, and no remanence was found in α-Fe$_2$O$_3$ and γ-Fe$_2$O$_3$ wires. The transition temperatures T_M and T_N for α-Fe$_2$O$_3$ wires and T_V for Fe$_3$O$_4$ wires are reduced to about 80, 350 and 50 K, respectively, which are much less than the values for bulk materials. These unique magnetic properties result from the reduced dimensions as well as the induced preferred orientations of the magnetic moments of the oxide particles in the wires.

Acknowledgments

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