Letter to the Editor

Fabrication and magnetic properties of Fe₃O₄ nanowire arrays in different diameters

Liying Zhang a,b, Yafei Zhang a,*

a National Key Laboratory of Nano/Micro Fabrication Technology, Key Laboratory for Thin Film and Microfabrication of MOE, Research Institute of Micro and Nano Science and Technology, Shanghai Jiaotong University, Shanghai 200240, PR China
b Key Laboratory for Magnetism and Magnetic Materials of MOE, Lanzhou University, Lanzhou 730000, PR China

A R T I C L E   I N F O

Article history:
Received 16 March 2008
Received in revised form
27 August 2008
Available online 10 October 2008

PACS:
75.50.Ss
75.75.+a
76.80.+y

Keywords:
Fe₃O₄
Nanowire
AAO template
Magnetic property

A B S T R A C T

Fe₃O₄ nanowire arrays with different diameters of \( D = 50, 100, 150 \) and 200 nm were prepared in anodic aluminum oxide (AAO) templates by an electrodeposition method followed by heat-treating processes. A vibrating sample magnetometer (VSM) and a Quantum Design SQUID MPMS magnetometer were used to investigate the magnetic properties. At room temperature the nanowire arrays change from superparamagnetism to ferromagnetism as the diameter increases from 50 to 200 nm. The zero-field-cooled (ZFC) and field-cooled (FC) magnetization measurements show that the blocking temperature \( T_B \) increases with the diameter of nanowire. The ZFC curves of \( D = 50 \) nm nanowire arrays under different applied fields \( H \) were measured and a power relationship between \( T_B \) and \( H \) were found. The temperature dependence of coercivity below \( T_B \) was also investigated. Mössbauer spectra and micromagnetic simulation were used to study the micro-magnetic structure of nanowire arrays and the static distribution of magnetic moments of \( D = 200 \) nm nanowire arrays was investigated. The unique magnetic behaviors were interpreted by the competition of the demagnetization energy of quasi-one-dimensional nanostructures and the magnetocrystalline anisotropy energy of particles in nanowires.

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1. Introduction

Quasi-one-dimensional (quasi-1D) magnetic nanowires have drawn a lot of research interest due to their unique physical properties and potential applications in magnetic recording, spin electronics, optics, sensors and thermoelectronics devices [1–4]. Recently, it was reported that Ni nanowires can be used in bioseparation and have higher yields compared with magnetic polymer microspheres [5–7]. This provides a new chance for magnetic nanowires applied in biomedical fields. Among lots of preparation methods, porous anodic aluminum oxide (AAO) template is the most common one due to the low-cost and convenient preparation process. So far, a lot of metal, alloy and multilayer magnetic nanowires based on AAO templates have been successfully fabricated. Some unique magnetic properties, such as anisotropic magnetization, GMR effect and magnetooptical property have been widely investigated [8–11]. It was found that these properties strongly depend on the diameter and the aspect ratio of nanowires.

Fe₃O₄ is an oldest magnetic recording material and has also been widely used in biomedicine as magnetic carriers due to its low-toxicity and biocompatibility [12–14]. Diverse applications require magnetic material having different magnetic properties. For example, perpendicular magnetic anisotropy is essential when nanowires are used as magnetic recording media, whereas, superparamagnetism is important for biomedical applications in order to avoid aggregations. Fe₃O₄ nanowires with different magnetic properties may have potential applications not only in magnetic devices but also in biomedicine. Up to now, a few literatures about Fe₃O₄ nanowires and nanotubes can be found [15–17]. However, there is no report on superparamagnetic Fe₃O₄ nanowires.

In our previous work, we have prepared ferromagnetic Fe₃O₄ nanowire arrays with obvious perpendicular magnetic anisotropy [17,18]. In this paper, we successfully fabricated Fe₃O₄ nanowire arrays with different diameters by tuning the oxidation acid and the voltage. The size effect of magnetic property and the static distribution of magnetic moments were investigated.

2. Experimental

A two-step anodization procedure was used to fabricate high-ordered porous AAO templates [19]. Prior to anodizing, a...
high-purity aluminum foil (99.999%) was annealed at 500 °C for 5 h in order to homogenize the microstructures and reduce the density of defects. The first anodization process was conducted under a dc constant voltage in an acid solution at 10 °C for 30 min. The foil was then dipped into a mixture solution of 0.5 M phosphoric acid and 0.2 M chromic acid for 15 min to remove the oxide layer. The foil was secondly anodized for another 3 h under the identical anodization condition and then AAO templates were obtained.

The electrodeposition was performed in a mixture solution containing FeCl₃ • 6H₂O and (NH₄)₂C₂O₄ • H₂O at an ac voltage of 15 V and frequency of 70 Hz. The deposition time is 15 min. The obtained yellowish precursor has been characterized as β-FeOOH nanowires and the possible electrochemical process has been discussed in our previous work [20]. After removing the remained aluminum substrate in a saturated HgCl₂ solution, the template containing β-FeOOH nanowires was heat-treated at 500 °C in ambient air for 2 h, and then reduced at 325 °C for 2 h in H₂ flow. The chemical process can be described as follows:

\[
2(\beta\text{-FeOOH}) = \alpha - \text{Fe}_2\text{O}_3 + H_2O \\
3(\alpha\text{-Fe}_2\text{O}_3) + H_2 = 2\text{Fe}_3\text{O}_4 + H_2O
\]

The diameter of Fe₃O₄ nanowire arrays was tuned by changing the anodization acid or voltage. The diameter of 50 nm (D = 50 nm) nanowires were prepared under the anodization voltage of 40 V in 0.3 M oxalic acid solution, and the nanowires of D = 100, 150 and 200 nm were obtained as the anodization voltages were, respectively, 60, 90 and 120 V in 0.5 M phosphoric acid solution.

A JEM-2000 EX transmission electron microscopy (TEM) was used to investigate the morphology of the nanowires. The crystal structure was characterized by selected area electron diffraction (SAED) and X-ray diffractometer (XRD, Philips XPert with Cu Kα₁ radiation). A constant-acceleration Mössbauer spectrometer with a ⁵⁷Co(Pd) source was used to investigate the micromagnetic structure of nanowires. Room-temperature magnetic properties were performed on a Lake Shore 7304 vibrating sample magnetometer (VSM). Low-temperature magnetic properties were carried out on a Quantum Design SQUID MPMS magnetometer. The nanowires were released from AAO templates in 0.1 M NaOH solution for TEM investigations. Other property characterizations were performed on the nanowire arrays containing the AAO templates.

3. Results and discussion

3.1. Morphology and structure

The typical TEM images of Fe₃O₄ nanowires with different diameters released from the AAO templates are shown in Fig. 1 a–d. The inset in Fig. 1a shows the reduced-size image. It can be seen that the lengths of the nanowires are more than 20 μm. The diameter was, respectively, 50, 100, 150 and 200 nm, which was evaluated by averaging more than 10 wires in several images. The short nanowires are due to the ultrasonic treatment before TEM investigations. Most of the nanowires are compact and uniform with large aspect ratios. The SAED pattern obtained on several nanowire arrays also demonstrated a polycrystalline spinel structure with cell constant of a₀ = 8.317 Å, which is in good agreement with the standard card of Fe₃O₄ (JCPDS card no. 85–1436). The representative XRD result of D = 200 nm nanowire arrays is shown in Fig. 1f. The crystallite sizes calculated according to the modified Scherrer relation [21]
are 4.6, 7.8, 11.4 and 15.2 nm for nanowire arrays of $D = 50$, 100, 150 and 200 nm, respectively.

3.2. Room-temperature magnetic property

The room-temperature hysteresis properties of Fe$_3$O$_4$ nanowire arrays with different diameters are shown in Fig. 2a–d, where the magnetic field is applied parallel ($H(∥)$) and perpendicular ($H(⊥)$) to the wire axis, respectively. It can be seen that the nanowire arrays of $D = 50$ nm are superparamagnetic, whereas, the three others have remanence magnetization and the coercivity increases with the diameter of nanowire arrays (see Fig. 2e). The obvious perpendicular magnetic anisotropy was observed in $D = 200$ nm nanowire arrays, for which the coercivity is 360 Oe in parallel direction, and 150 Oe in the perpendicular one. The squareness of the parallel direction is much larger than that of the perpendicular one. This diameter dependence of magnetic properties is much different from metal or alloy nanowire arrays, for which the coercivity decreases with the diameter [22,23]. The possible reason will be discussed later.

A curling model and a chain-of-sphere model with symmetric fanning mechanism have been usually used to interpret the hysteresis behavior of magnetic nanowire arrays [8,24]. In terms of these two models, the coercivity will decrease with the diameter of nanowire. This behavior has been observed on lots of metal and alloy nanowire arrays such as Fe [22] and Fe$_{0.68}$Ni$_{0.32}$ [23]. However, in case of Fe$_3$O$_4$ nanowire arrays the coercivity increases with the diameter. In metal or alloy nanowire arrays ordered crystalline and magnetic textures were found to form when they were directly electrodeposited into AAO templates [22,23]. Since the degree of alignment and demagnetization energy decrease with the diameter of nanowire, the coercivity dominated by the demagnetization energy also decreases with the

Fig. 2. Hysteresis loops of Fe$_3$O$_4$ nanowire arrays measured at room temperature: (a) 50 nm; (b) 100 nm; (c) 150 nm and (d) 200 nm. (e) Coercivity as a function of nanowire diameter: the dots are experimental data and the line is the fitted curve.
where the first term results from the contribution of shape anisotropy energy of nanowires and the second term is due to the contribution of magnetic crystalline anisotropy energy of particles. $q$ is the geometrical factor ($q = 1.8412$ for a cylinder and 2.0816 for a sphere [25]), $M_s$ the saturation magnetization ($M_s = 1.74 \times 10^4$ A/m for Fe$_3$O$_4$), $D$ the average diameter of the nanowires, $d$ the particle diameter, $K_1$ the first-order magnetic anisotropy constant ($K_1 = 1.35 \times 10^4$ J/m$^3$ for Fe$_3$O$_4$), $A$ the exchange stiffness constant ($A = 10^{-11}$ J/m), $P_c$ a coefficient ($P_c = 0.5$), and $l_m$ the exchange length ($l_m = \sqrt{A/K_s} = 27$ nm) [11]. According to Eq. (1), the coercivity decreases with a square of the nanowire diameter and increases with sixth-power of the particle size. The experimental data can be fitted well with Eq. (1) when $D/d = 20$ (see the line in Fig. 2f). This result indicates that the particle size in Fe$_3$O$_4$ nanowires increases with the diameter of nanowire, and the diameter of nanowire $D$ is 20 times the particle size $d$. The particle size can be evaluated as 2.5, 5.0, 7.5 and 10 nm for $D = 50$, 100, 150 and 200 nm nanowires, respectively. These values are less than those calculated according to the XRD results. The possible reason is that the magnetic dipole interactions between particles and nanowires were ignored in Eq. (1). The disordered spins due to the surface effect can also influence the magnitude of the coercivity.

### 3.3. Low-temperature magnetic property

Fig. 3 shows the zero-field-cooled (ZFC) and field-cooled (FC) magnetization curves of Fe$_3$O$_4$ nanowire arrays with different diameters, where the magnetic fields were all applied parallel to the wire axis. In the ZFC measurements, the samples were cooled from 325 to 5 K without applying an external field. After reaching 5 K, a field of 500 Oe was applied and the magnetic moments were recorded as the temperature increased. For FC measurements, the samples were cooled from 325 K under an applied field of 500 Oe; then the magnetic moments were recorded as the temperature increased. As seen in Fig. 3, upon increasing the temperature, all the ZFC magnetic moments increase and reach a maximum, where the temperature is referred to as the blocking temperature ($T_b$). $T_b$ is defined as the temperature at which the nanoparticles’ moments do not relax (known as blocked) during the time scale of the measurement. In our cases, the relaxation property is due to superparamagnetism of the particles. It can be seen that the blocking temperature increases with the diameter of nanowire, which also demonstrates that the particle size increases with the nanowire diameter. Using the bulk magnetic anisotropy constant $K = 1.35 \times 10^4$ J/m$^3$, the average particle size can be roughly estimated by $K = 25k_B T_b$, here $V$ is the particle volume, $k_B$ the Boltzmann constant and $T_b$ the blocking temperature. The estimated particle size is 18, 20, 21 and 25 nm for nanowire arrays of $D = 50$, 100, 150 and 200 nm, respectively. These values are larger than those estimated from $D/d = 20$ but also larger than those calculated according to the XRD results. The possible reason caused the difference on estimated sizes may be attributed to the wide size distributions, the magnetic dipole interactions between wires and particles, the magnetic texture formed in nanowires due to strong shape anisotropy, as well as the disordered surface spins. These factors may have strong influences on magnetic properties and therefore on calculated sizes. Actually, the broad peaks of ZFC curves also reveal the wide size distributions and strong magnetic interactions in nanowires. Moreover, the effective magnetic anisotropy constant of Fe$_3$O$_4$ nanoparticles is normally less than its bulky value and varies with the particle size [26]. All these factors will lead to difference of the particle size estimated according to the magnetic results and XRD results, respectively.

It is well known that the coercivity $H_c$ is normally zero above $T_b$. In Fig. 3, one can notice that $T_b$ for most of the wires is below 300 K. However, $H_c$ at 300 K for wires with $D = 100$, 150 and 200 nm is non-zero (see Fig. 2). This kind of remanent magnetization and coercivity above $T_b$ have also been observed on $\gamma$-Fe$_2$O$_3$ nanowires [27] and $\gamma$-Fe$_2$O$_3$ nanochains [28]. This property is interesting and has not been understood well till now. Maybe it ascribes to the effect of the applied field because $T_b$ normally increases with the particle size and decreases with the applied field [29].

Fig. 4a shows the temperature dependence of ZFC and FC magnetic moments of $D = 50$ nm nanowire arrays which were measured at different applied fields. The blocking temperature increases from 132 to 186 Oe when the applied field decreases from 500 to 50 Oe (see Fig. 4b). The filed dependence of blocking temperature has also been observed by other groups [30,31]. The reason is that high field can lower the energy barriers between the two easy axis orientations, and therefore lower the blocking temperature. It was reported that if the applied field reaches a critical value the blocking temperature will disappear [32]. We also found that, when the applied field is below 50 Oe the blocking temperature began to decrease with the field and reduced to 183 K at 10 Oe. This phenomenon was also observed by other researchers [33]. At a high field, the relationship between the blocking temperature and the applied field can be described by power dependence of $H_b^{1/2}$, where $H_b$ is the blocking temperature at zero field [30]. Our experimental results above 200 Oe can well be fitted by this relation (see Fig. 4b). In addition, the particle size $d$ estimated by blocking results strongly depends on the applied magnetic field as $d \propto (1-(H/15K_b))^{1/2}$.

Below $T_b$, superparamagnetic nanoparticles generally exhibit ferromagnetic features including coercivity and remanence. A
coercivities have non-linear relationship with $T$ randomly oriented particles [34,35]. Our experimental result. $H_T$ where $k = 0.5$ for an assembly of aligned particles and $k = 0.77$ for randomly oriented particles [34,35]. Our experimental results cannot be fitted well by these two models, that is, the coercivities have non-linear relationship with $T^{0.5}$ or $T^{0.77}$. The inset in Fig. 5b displays the non-linear relationship of $H_C$ versus $T^{0.5}$. This result can be easily understood by the difference of magnetization reversal mechanism between nanoparticles and nanowire arrays. The above expression (Eq. (3)) is deduced from non-interaction particles which have magnetization reversal of coherent rotation. Apparently, this reversal mechanism is unsuitable to interpret the hysteresis behaviors of Fe$_3$O$_4$ nanowire arrays. To investigate the distribution of magnetic moments of nanowires may be helpful to understand the unique magnetic properties.

$$H_C = H_C(0)(1 - CT^k),$$

where $H_C(0)$ is the coercivity at $T = 0$ K and $C$ is a parameter given by the following relation:

$$C = [k \beta / \mu_0 V]^{1/k},$$

where $\beta = \ln(\tau_{ml}/\tau_0)$ depends on the typical measurement time $\tau_m$ and the characteristic time $\tau_0$. The exponent $k$ has a value of $k = 0.5$ for an assembly of aligned particles and $k = 0.77$ for randomly orientation particles [34,35]. Our experimental results cannot be fitted well by these two models, that is, the coercivities have non-linear relationship with $T^{0.5}$ or $T^{0.77}$. The inset in Fig. 5b displays the non-linear relationship of $H_C$ versus $T^{0.5}$. This result can be easily understood by the difference of magnetization reversal mechanism between nanoparticles and nanowire arrays. The above expression (Eq. (3)) is deduced from non-interaction particles which have magnetization reversal of coherent rotation. Apparently, this reversal mechanism is unsuitable to interpret the hysteresis behaviors of Fe$_3$O$_4$ nanowire arrays. To investigate the distribution of magnetic moments of nanowires may be helpful to understand the unique magnetic properties.

$$I_{2.5}/I_{1.6} = \frac{4 \sin^2 \theta}{3(1 + \cos \theta)} = \frac{4(1 - \cos^2 \theta)}{3(1 + \cos \theta)}$$

where $\theta$ is the angle between $\gamma$ ray and magnetic moment. When $\theta = 0$, the ratio $I_{2.5}/I_{1.6} = 0$, and the moment has the same orientation with $\gamma$ beam. When $\theta = 90^\circ$, the ratio $I_{2.5}/I_{1.6} = 4/3$. If the distribution of magnetic moment is spatially isotropic, $I_{2.5}/I_{1.6} = 2/3$. It was found that the ratio of $I_{2.5}/I_{1.6}$ for all nanowire arrays almost has the same value of $2/3$ after fitting the Mössbauer spectra. The angle $\theta$ is calculated to be $48^\circ$, indicating a $48^\circ$ orientation of the mean particle moments along the wire axis.

In order to verify the orientation of magnetic moments further, an Object Oriented Micromagnetic Framework (OOMF) [36] was used to simulate the static distribution of magnetic moments. The final state originates from the minimization of the total energy density function

$$E_{total} = E_{exchange} + E_K + E_{demag},$$

3.4. Mössbauer spectrum

Fig. 6 shows the Mössbauer spectra of Fe$_3$O$_4$ nanowire arrays with different diameters collected at room temperature, where the $\gamma$ ray was applied parallel to the wire axis. It can be seen the spectrum of $D = 50$ nm nanowire arrays is a doublet, indicating superparamagnetism of nanowire arrays and in agreement well with the VSM result. With increasing diameter of the nanowire, the component of doublet reduces, whereas, the sextet part increases. This can be understood by the increased particle size with diameter of nanowires. The coexistence of doublet and sextet indicates a wide size distribution of particles in nanowires. Usually, the orientation of the magnetic moments can be calculated from the intensity ratios of 2.5 and 1.6 peaks ($I_{2.5}/I_{1.6}$) by the following relation:

$$I_{2.5}/I_{1.6} = \frac{4 \sin^2 \theta}{3(1 + \cos \theta)} = \frac{4(1 - \cos^2 \theta)}{3(1 + \cos \theta)}$$

where $\theta$ is the angle between $\gamma$ ray and magnetic moment. When $\theta = 0$, the ratio $I_{2.5}/I_{1.6} = 0$, and the moment has the same orientation with $\gamma$ beam. When $\theta = 90^\circ$, the ratio $I_{2.5}/I_{1.6} = 4/3$. If the distribution of magnetic moment is spatially isotropic, $I_{2.5}/I_{1.6} = 2/3$. It was found that the ratio of $I_{2.5}/I_{1.6}$ for all nanowire arrays almost has the same value of $2/3$ after fitting the Mössbauer spectra. The angle $\theta$ is calculated to be $48^\circ$, indicating a $48^\circ$ orientation of the mean particle moments along the wire axis.

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where $E_{\text{exchange}}$, $E_K$, and $E_{\text{demag}}$ are exchange, magnetocrystalline anisotropy, and demagnetization energy, respectively. Demagnetization energy tends to align the magnetic moments along the wire axis, whereas, magnetocrystalline anisotropy energy tends to stabilize the magnetic moments in the easy axis of the particles. The simulated orientation energy tends to align the magnetic moments along the wire axis, whereas, magnetocrystalline anisotropy energy tends to stabilize the moments along the easy axis of the particles. The simulation result (not shown) also demonstrates most of the moments have an angle of 45° along wire axis, which is in well agreement with Mössbauer results.

On basis of the distribution of the magnetic moments, the magnetic behaviors and the size-dependence of coercivity of Fe$_3$O$_4$ nanowires can be easily understood. The demagnetization energy due to quasi-1D structure is responsible for the magnetic anisotropy of the nanowire arrays, and the coercivity induced from this energy decreases with the diameter of nanowire. However, the magnetocrystalline anisotropy energy increases with the particle size and is responsible for the increased coercivity with the diameter of nanowire. The magnetic behaviors are determined by the competition of these two kinds of energies.

4. Conclusions

Fe$_3$O$_4$ nanowires with different diameters of $D = 50$, 100, 150 and 200 nm were fabricated in AAO templates. The magnetic properties vary with the diameter of nanowire, which can be understood by the increase of particle size with the nanowire diameter, and therefore the competition of the demagnetization energy and the magnetocrystalline anisotropy energy. The static magnetic moments show a 48° orientation along the wire axis. The diverse magnetic properties may have different applications, for example, the superparamagnetic nanowires of $D = 50$ nm may have potential applications in biomedicine, whereas the ferromagnetic nanowires with obvious perpendicular magnetic anisotropy may be a good candidate for high-density magnetic recording media.

Acknowledgment

This work is supported by the NSFC (Grant no. 10774062, 50671046, 10374038 and 50171032). The authors thank the Instrumental Analysis Center of Shanghai Jiao Tong University for the Materials Characterization.

References


Fig. 6. Mössbauer spectra of Fe$_3$O$_4$ nanowire arrays with different diameters. The γ beam is parallel to the nanowire axis.