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Letter to the Editor

Fabrication and magnetic properties of Fe_3O_4 nanowire arrays in different diameters

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ABSTRACT

Fe_3O_4 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.

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 bio-separation 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 magneto-optical property have been widely investigated [8–11]. It was found that these properties strongly depend on the diameter and the aspect ratio of nanowires.

Fe_3O_4 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. Fe_3O_4 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 Fe_3O_4 nanowires and nanotubes can be found [15–17]. However, there is no report on superparamagnetic Fe_3O_4 nanowires.

In our previous work, we have prepared ferromagnetic Fe_3O_4 nanowire arrays with obvious perpendicular magnetic anisotropy [17,18]. In this paper, we successfully fabricated Fe_3O_4 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

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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 $FeCl_3 \cdot 6H_2O$ and $(NH_4)_2C_2O_4 \cdot H_2O$ 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 nanowire arrays and the possible electrochemical process has been discussed in our previous work [20]. After removing the remained aluminum substrate in a saturated $HgCl_2$ 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 H_2 flow. The chemical process can be described as follows:

$$2(\beta\text{-FeOOH}) = \alpha - Fe_2O_3 + H_2O$$
$$3(\alpha\text{-}Fe_2O_3) + H_2 = 2Fe_3O_4 + H_2O$$

The diameter of Fe_3O_4 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 X'Pert with Cu $K\alpha_1$ radiation). A constant-acceleration Mössbauer spectrometer with a ^{57}Co(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 Fe_3O_4 nanowires with different diameters released from the AAO templates are shown in Fig. 1a–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 nanowires of $D = 200$ nm (see Fig. 1e) is composed of bright diffraction rings, indicating a polycrystalline spinel structure. The inset in Fig. 1e is a SAED pattern taken on an individual wire. The dissymmetrical dots indicate a polycrystalline structure and non-crystallization texture was formed. The reason is the dehydration of β-FeOOH during heat-treating processes and therefore fine crystallites were formed in the nanowire. The XRD results performed on different-diameter nanowire arrays also demonstrated a polycrystalline spinel structure with cell constant of $a_0 = 8.317$ Å, which is in good agreement with the standard card of Fe_3O_4 (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]

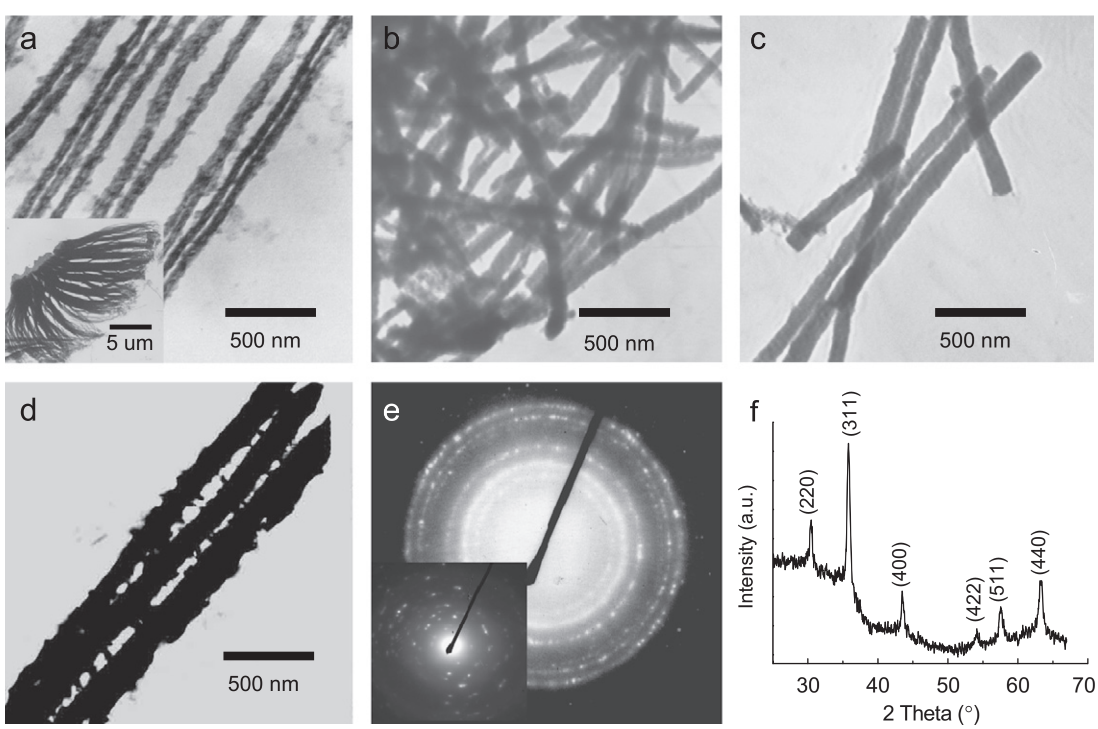

Fig. 1. The typical TEM images of Fe_3O_4 nanowires with different diameters: (a) 50 nm; (b) 100 nm; (c) 150 nm and (d) 200 nm. (e) The SAED pattern taken on several nanowires of $D = 200$ nm. (f) XRD results carried on $D = 200$ nm nanowires. The inset in (a) is reduced size nanowires of $D = 50$ nm. The inset in (e) is a SAED pattern taken on an individual nanowire of $D = 200$ nm.