

Magnetic properties of amorphous β -FeOOH nanowire arrays

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Abstract

β -FeOOH nanowire arrays with diameters of 50–200 nm have been fabricated by electrochemical deposition using two-step anodic porous alumina templates. The as-prepared nanowires are homogeneous and have large aspect ratios. The selected area electron diffraction photo performed on a single wire was used to confirm the amorphous crystal structure further. The magnetic properties of these nanowire arrays were firstly investigated by using a SQUID magnetometry. The ZFC and FC studies show that these nanowire arrays exhibit spin-freezing phenomena at low temperature. The temperature-dependent magnetization curves show that the Neel transition temperatures are much lower than that of bulk material. Moreover, hysteresis was found at 5 K and the coercivities up to about 1500 Oe. The size-dependent magnetic properties were also investigated. These abnormal magnetic behaviours can be interpreted in terms of the amorphous crystal structure and the low dimensionality of the nanowire arrays.

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1. Introduction

In recent years, quasi-one-dimensional (quasi-1D) nanowires have received much attention due to their fundamental importance in basic research, e.g., nanowires have great potential for testing and understanding fundamental concepts about the roles of dimensionality and size on physical properties, and they also have potential applications in electronics, optoelectronics, and memory devices [1–3]. One of the commonly used methods for generating nanowires is based on the electrodeposition of various materials in porous anodic alumina templates (AAT). A lot of metal, alloy and multilayer nanowire arrays based on AAT have been fabricated, and some unique properties, such as anisotropy magnetization, GMR effect and magneto-optical property have also been studied [4–6].

Iron oxyhydroxides (FeOOH), such as α -, β - and γ -type, have distinctive properties and are widely used in electrode materials, lithium batteries and preparation of magnetic recording media materials [7–9]. β -FeOOH is an antiferromagnetic material with Neel transition temperature $T_N \approx 270$ –296 K. As an intermedial precursor, it has been usually used to prepare magnetic recording materials, for example, Fe_3O_4 and $\gamma\text{-Fe}_2\text{O}_3$ [10]. Moreover, this material, which exhibits a large tunnel-type structure where the iron atoms are strongly bonded to the framework that constitutes the tunnels, has been reported to be a promising candidate for an active iron-based material for lithium batteries [9]. β -FeOOH is also a semiconductor with the band gap of 2.12 eV [11] and can be used in the pigment industry, in oxidation/reduction reactions and hydroprocessing of coal as catalysts [12,13]. Therefore, well-defined 1D β -FeOOH nanostructures might be a promising precursor for preparation of high-order quasi-1D Fe_3O_4 and/or $\gamma\text{-Fe}_2\text{O}_3$ nanowire arrays, which might have potential applications in high-density perpendicular magnetic recording media and nanosensors. Moreover, well-defined 1D β -FeOOH nanostructures also have potential

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applications in lithium batteries and semiconductor electronic devices [14].

In our previous work, the initial results of β -FeOOH nanowire arrays based on AAT were reported, which were fabricated by using one-step anodization method [15]. In that paper, the nanowires were characterized by X-ray diffractometer (XRD), transmission electron microscopy (TEM), infrared spectroscopy (IR), and Mössbauer spectroscopy (MS). It was found that those nanowires have an amorphous crystal structure according to the XRD result. From the TEM image it can be seen that the nanowires are not only inhomogeneous, but also have branches along the wires. Furthermore, the aspect ratios of the wires are not large enough to be regarded as 1D nanostructures.

Since β -FeOOH possesses an interesting magnetic structure, some reports on magnetic properties of bulk materials can be easily found [16,17]. However, the investigations on nanosized materials are sparse, especially to our knowledge, there is no report on 1D nanomaterials. In this paper, we fabricated quasi-1D β -FeOOH nanowire arrays with tunable diameters by using a two-step anodization procedure [18,19]. The as-prepared nanowires are homogeneous and have large aspect ratios, and are close to quasi-1D nanostructures. The magnetic properties, such as hysteresis, zero-field-cooling (ZFC) blocking and magnetic order transition were firstly investigated.

2. Experimental

A two-step anodization procedure was used to fabricate the high-order porous AAT, which was described in detail elsewhere [18,19]. In this study, high-purity aluminum foil (99.999%) was anodized twice in 0.3 M oxalic acid or 0.5 M phosphoric acid solutions at 10 °C. Prior to anodizing, the aluminum foils were annealed at 500 °C for 5 h in order to homogenize the microstructures and reduce the density of defects in the foils. This was essential for the formation of high-quality nanochannels over large areas in the alumina substrates. Subsequently, the foils were electropolished in the solution of C_2H_5OH mixed with $HClO_4$ (4:1 in volume) in order to obtain a high quality of flat surfaces. Then, anodization was carried out under a condition of constant cell voltage in 0.3 M oxalic acid or 0.5 M phosphoric acid solutions. The temperature was kept constant at 10 °C. The preformed alumina layer was removed by phosphoric acid mixed with chromic acid, and then the aluminum foil with a fresh and clean surface was anodized again under the same anodizing condition. After anodization, β -FeOOH nanowires were prepared by AC (15 V, 70 Hz) electrodeposition in the solution of $FeCl_3 \cdot 6H_2O$ (9 g/L) mixed with $(NH_4)_2C_2O_4 \cdot H_2O$ (14 g/L) with a pH value of 7. The temperature for the electrodeposition was 25 °C. After removing the remained aluminum foils in a saturated $HgCl_2$ solution the films of β -FeOOH nanowire arrays based on AAT were obtained.

Different-diameter nanowires can be obtained by changing the anodization acid or/and voltage. The nanowires

with diameter of 50 nm were obtained when the alumina foil was anodized at 40 V in 0.3 M oxalic acid solution, whereas, the 120, 160, and 200 nm nanowires were obtained when the foils were anodized in 0.5 M phosphoric acid solution at 60, 90 and 120 V, respectively. In order to investigate the morphology of the nanowires by TEM, the wires were released from the AAT in 0.1 M NaOH solution.

The structure and the morphology of the nanowires were characterized using a Philip X'Pert diffractometer with $Cu K\alpha$ radiation and a JEO 2000 TEM. The morphology of porous alumina templates was investigated on a JSM-5600 scanning electron microscopy (SEM). Magnetic property measurements were performed on a quantum design MPMS SQUID magnetometer. The applied external magnetic field is parallel to the wire axis. All measurements were carried out on the nanowires with AAT except for the investigation of TEM.

3. Results and discussion

Figs. 1(a) and (b) show the representative SEM images of ordered porous AAT which was anodized in oxalic acid at 40 V_{DC} and in phosphoric acid solution at 120 V_{DC}, respectively. The nanopores are homogeneous and the average diameter is about 50 and 200 nm, respectively. Fig. 1(c) and (d) show the corresponding TEM images of β -FeOOH nanowires which were electrodeposited into the above AAT. It can be seen that the wires are homogenous and no branches was found. The average diameters are 50 and 200 nm and lengths up to about 15 μ m. The aspect ratios are about 75:1 and 300:1, indicating the as-prepared nanowires can be regarded as quasi-1D nanostructures.

In our previous work, it was found that the nanowires have an amorphous structure according to the XRD result and the selected area electron diffraction (SAED) pattern performed on several wires. In order to confirm the amorphous structure, SAED pattern was taken on a single wire. Fig. 1(e) and (f) show the TEM image and its SAED pattern. From the broadening blurred rings it can be concluded that the as-prepared β -FeOOH nanowires indeed have amorphous crystal structure.

The ZFC and field-cooling (FC) magnetization curves of β -FeOOH nanowire arrays with diameter of 50 nm are shown in Fig. 2. The applied field is 1000 Oe. The detailed change near the transition temperature is shown in the inset of Fig. 2. It can be noticed that at low temperature the two curves are separated and the spins are frozen on the ZFC curve. The blocking temperature can be estimated about 13 K from the maximum of the ZFC curve. In addition, a kink can be observed at about 15 K on FC curve. Considering the magnetic phase transition behavior in antiferromagnetic materials, the kink might be corresponding to the antiferromagnetic ordering temperature T_N . This temperature is much lower than 270–299 K which observed on bulk materials [20].

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