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A simple method for forming amorphous rare earth-transition metal alloy nanotube arrays

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ABSTRACT

Arrays of rare earth-transition metal alloy $Co_{68}Nd_{32}$ and $Co_{96}Sm_4$ nanotubes, with amorphous structures and outer diameters of ca. 270–330 nm and with lengths of over 30 μm, have been fabricated for the first time by direct current electrodeposition with a mercury cathode via anodic aluminum oxide (AAO) template. The using of mercury cathode is a crucial condition for the growth of nanotubes and the co-reduction of Co^{2+}, Nd^{3+} and Sm^{3+} in aqueous solution without any chemical modification of the pores of AAO, since the liquid mercury has characters of excellent conductivity and fluidity, high surface tension, high photoelectric work function, and high over-potential. A possible growth mechanism for the nanotubes is proposed. The as-prepared nanotube arrays display low coercivity and uniaxial magnetic anisotropy, and the easy magnetization direction is perpendicular to the nanotubes axes.

1. Introduction

Ordered nanostructure arrays have received wide attentions in the field of nanotechnology because of their intriguing electronic, optical, and magnetic properties for fabricating various functional nanodevices [1–12]. Template-based synthesis, pioneered by Martin [2], has gained increasing interest in preparing one dimensional nanostructures because of its ability to control the dimensions of the nanostructures. Among the template-based synthesis approaches, electrodeposition is a simple, low-cost, and ingenious technique. A wide range of magnetic materials such as metal [3–10] and alloy [11,12] nanowire arrays have been prepared by electrodeposition in anodic aluminum oxide (AAO) membrane. In addition, tubular nanostructures such as Au [13], Pt [14], Pd [15], Bi [16], Fe [17,18], Co [19–21], Ni [22–24], Co–Cu [25], Bi–Sb [26] and Bi–Te [27] nanotubes have also been fabricated by electrodeposition with some extra strategies such as chemical modification of AAO channels, multistep template replication, using high current or precursors etc. But these methods are tedious or result in impurities in the nanotubes, and among previous published literatures, the electrode layers assembled with AAO membrane are mostly gained by vacuum sputtering of noble metal Au or painting of Ag, which are uneconomical and hardly reduces the metal ions with low potentials. Therefore, it is still a challenge to develop simple and versatile electrodes and to fabricate systematically alloy nanotubes arrays. In our previous work [28], a strategy for using a mercury cathode during the template electrodeposition was first presented to fabricate $Co_{81}Ni_{19}$ and $Co_{37}Fe_{63}$ alloy nanotubes.

Compared with crystalline materials, amorphous alloys also have excellent properties such as soft magnetism, high intensity and hardness, good toughness and corrosion resistance [29]. Particularly, amorphous rare earth-transition metal (RE-TM) alloys have the unique properties such as high magnetism, photoemission, superconductivity, magnetooptics recording, etc. due to the 4f electrons. Since the first synthesis of $Au_{75}Si_{25}$ amorphous slice [30], amorphous materials such as ferromagnetic alloy films [31–33], cobalt-based alloys [34,35], Fe–P [36], Co–P [37] alloy nanowires were fabricated with different strategies. However, there are only a few reports on one dimensional rare earth alloys synthesized by electrodeposition because the rare earth ions have low redox potentials and are difficult to be reduced in aqueous solution.

Herein, we further extend the system of template electrodeposition with mercury cathode and report a simple method to synthesize high-density, large-area, and uniform amorphous magnetic

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nanotube arrays of $Co_{68}Nd_{32}$ and $Co_{96}Sm_4$ with mercury cathode during direct current (DC) electrodeposition from aqueous solution. Compared with Au or Ag electrode, the advantages of mercury electrode are obvious: (1) Better conductivity and fluidity. Mercury has a good electric ability and is dynamic under the electric current, which cause the formation of amorphous products; (2) High surface tension. The surface of mercury is convex due to its surface tension, which induced the deposition preferentially grow along the side walls of the nanochannels, and resulted in the forming of nanotubes; (3) High photoelectric work function (4.52 eV) and over-potential. It can prevent the formation of hydrogen gas, and may reduce the metal ions, especially rare earth metal ions with lower potentials; (4) As a liquid electrode, mercury can contact firmly with the pores of AAO membrane and easy to be cleared away. In addition, mercury electrode with AAO membrane can also further extend the scopes of the electrodeposition system.

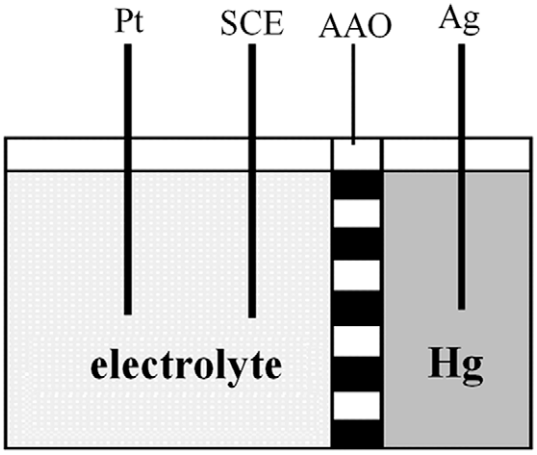

Fig. 1. The schematic illustration of the self-made cell.

2. Experimental procedure

The AAO membranes (Anodise®), made by Whatman Inc. (SEM images revealed the pore diameters in the range 200–300 nm), were dipped into 5 wt.% phosphoric acid solution at 35 °C for 10 min to remove the residual obstacle film and to widen the pores. These were then washed with distilled water and absolute ethanol for several times, respectively, dried at 85 °C for 30 min and then in vacuum oven for 8 h subsequently. After these treatments, the AAO membrane was placed in the middle of a reaction cell (Fig. 1). A small amount of mercury and the electrolyte (75 g L^{-1} $NdCl_3$, 29 g L^{-1} $CoCl_2{\cdot}6H_2O$, 105 g L^{-1}citric acid, 30 g L^{-1} boric acid and some saccharin with pH 3) were injected in each cell at room temperature. Electrochemical deposition was performed in a standard three-electrode system consisting of a AAO template clung mercury working electrode, a platinum plate counter-electrode and a standard saturated calomel electrode (SCE) reference electrode. DC electrodeposition was conducted at −1.135 V vs SCE at room temperature without stirring. After electrodeposition, the mercury clinging to AAO membrane was swept out with a brush, and the as-synthesized AAO membrane filled with the deposits was polished by sand paper, and then washed with distilled water and absolute ethanol for further analysis. When the electrolyte was replaced by 77 g L^{-1} $SmCl_3$, 28 g L^{-1} $CoCl_2{\cdot}6H_2O$, 105 g L^{-1} citric acid, 30 g L^{-1} boric acid and some saccharin with pH 3.5, the $Co_{96}Sm_4$ nanotube arrays were also obtained at −1.300 V vs SCE. All the reagents used in the experiments are AR purity.

X-ray powder diffraction (XRD) was carried out on a SHIMADZU XRD-6000 X-ray diffractometer with Cu Kα radiation (λ = 0.154060 nm) in the 2θ range from 20° to 80°. Transmission electron microscopy micrographs (TEM) and selected-area electron diffraction (SAED) were taken using a Hitachi H-800 transmission electron microscope, with an accelerating voltage of 200 kV. Scanning electron microscopy (SEM) and energy-dispersive X-ray spectrometry (EDX) were performed using LEO-1530VP field emission microscope. Magnetization was measured at room temperature

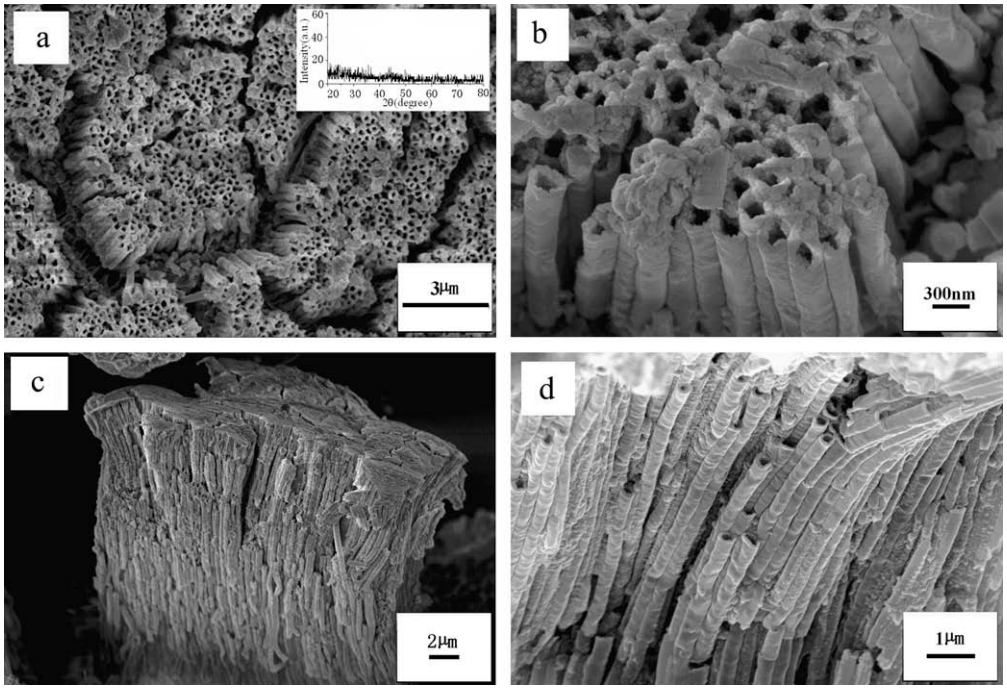

Fig. 2. SEM images of Co–Nd nanotube arrays partly etched in 2 M NaOH. (a) and (b) top views; (c) and (d) cross-section views. Insert of (a) is the XRD pattern of Co–Nd nanotubes.