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End-closed NiCoFe-B nanotube arrays by electroless method

A. Azizi [a,b,*], M. Mohammadi [a,c], S.K. Sadrnezhaad [a,c]

[a] Department of Nanotechnology and Advanced Materials, Materials and Energy Research Center, P.O. Box 14155-4777, Tehran, Iran
[b] Department of Chemical and Biomolecular Engineering, Tulane University, New Orleans, LA 70118, USA
[c] Department of Materials Science and Engineering, Sharif University of Technology, P.O. Box 11155-9466, Tehran, Iran

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ABSTRACT

A novel approach is obtained during the fabrication of NiCoFe-B nanotube arrays via electroless method. Porous anodic aluminum oxide (AAO) templates fabricated by anodization of aluminum foil were sensitized using $PdCl_2$ solution and immersed into electroless plating baths at room temperature to produce nanotube arrays. Compositional and morphological properties of the nanotube arrays are characterized. Results indicates the formation of end-closed nanotubes with the dimension of 100–130 nm in outside diameter, which is determined by the pore size of the AAO template, and about 15 nm in thickness of tube walls. The possible formation mechanism of end-closed metallic nanotube arrays is discussed.

1. Introduction

Self-assembling magnetic nanostructures have recently attracted much attention due to their potential applications [1,2]. Scientifically interesting properties of magnetic metal nanotubes have aggravated their use in nanomedicine, high-density magnetic recording media and sensing devices [2]. As a recent finding, nanotube arrays that are closed on one end have ability to utilize for drug delivery applications [3].

Using a porous template helps quick, inexpensive and environmentally benign preparation of nanotubes [4,5]. Various templates like track-etched membrane, diblock copolymer, polycarbonate and anodic aluminum oxide (AAO) have been used for structure formation. Among all these, the AAO has specific utilizations provoked by parallel pore channels and the holes that can be controlled by proper adjustment of the anodization conditions [6].

Both metallic nanotubes and nanowires can be assembled by chemical vapor deposition [7], electroplating [8] and supercritical fluids [9] on appropriately selected templates. Using electroless technique simplifies synthesizing method and the instrument that is required [10,11]. Electroless technique is a chemical deposition process which involves the use of chemical agents to coat an alloy onto the suitable sites of a template [4,12,13]. It does not need the electrical conductivity of the deposited substance and the deposition starts from pore walls and growth inwardly. Hollow fibrils or nanotubules have previously been produced, therefore, by this process [4].

This paper demonstrates the formation of NiCoFe nanotubes by electroless deposition method on AAO templates. What makes this work different from previous efforts is the formation of end-closed nanotubes which are announced for the first time by the specified method in this paper.

2. Material and methods

AAO templates were prepared by two-step anodization of annealed aluminum foil (99.99%-Merck). The foil was chemically treated in 1 M NaOH for 3 min at room temperature and rinsed with distilled water and acetone. The surface of the foil was electropolished in a mixture of $HClO_4$ and ethanol (1:4 in vol.) below 5 °C by applying 20 V voltage. Anodization was conducted for 20 h in 0.3 M phosphoric acid electrolyte under constant potential (120 V). A cooling system was used to keep the temperature unchanging (1.5 ± 1.5 °C). After the first anodization step, the porous film formed was stripped by immersion of the foil into a solution containing 2 wt.% phosphoric acid plus 6 wt.% chromic acid at 60 °C. Second anodization step was carried out with the same conditions were used in the first step. A rather uniform array of AAO nanowells were formed in this step.

Template pretreatment before the fabrication of NiCoFe nanotube arrays consisted of AAO immersion into an aqueous solution containing 1 g/L $PdCl_2$ and 12 g/L HCl kept under low vacuum situation for 3 min to enhance the solution into the pores. The procedure followed by polishing of the top surface with refined sandpaper. This is due to prevention of forming an unwanted alloy film on the AAO surface which seals the entrance of the pores preventing the nanotubes to

* Corresponding author. Department of Nanotechnology and Advanced Materials, Materials and Energy Research Center, P.O. Box 14155-4777, Tehran, Iran. Tel.: +98 9125322039; fax: +98 2166005717.
E-mail addresses: azizi@alum.sharif.edu, aazizi@tulane.edu (A. Azizi).

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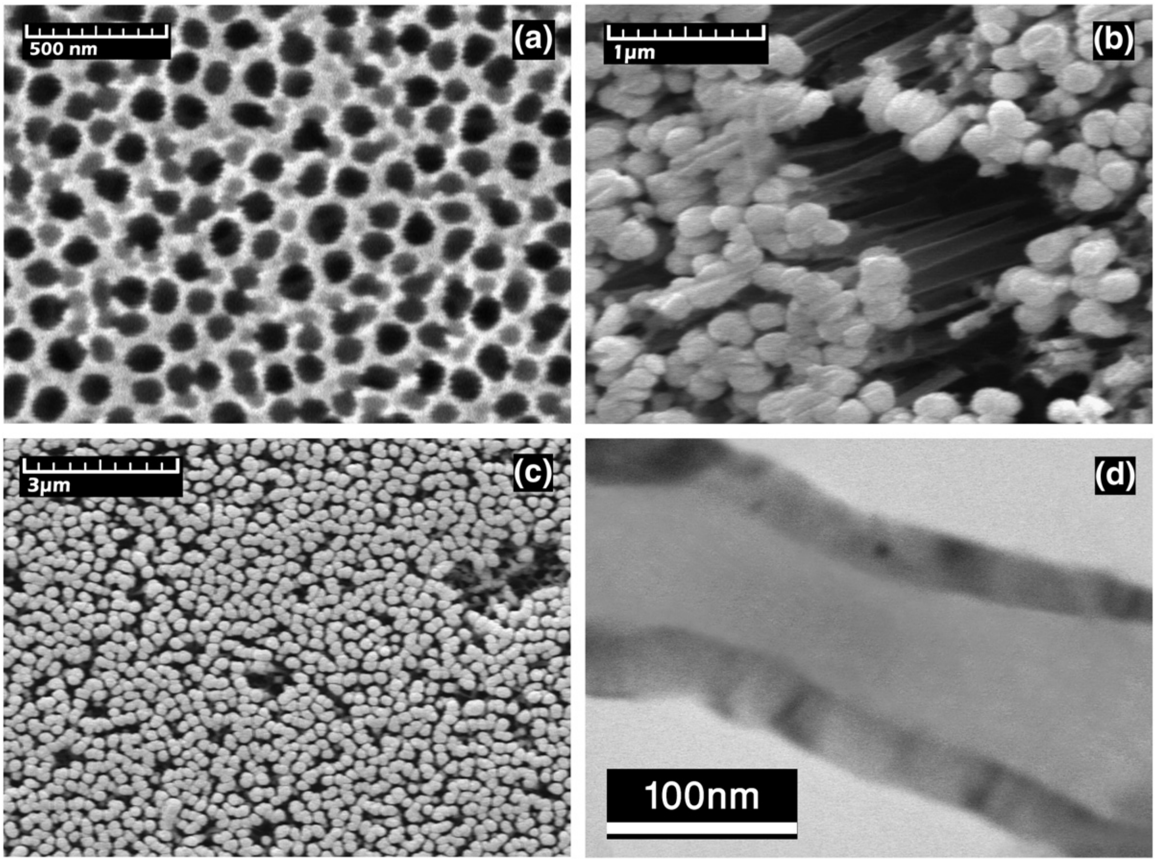

Fig. 1. (a) FE-SEM morphology of the anodized AAO and (b) side view FE-SEM, (c) top view FE-SEM and (d) TEM image of the end-closed NiCoFe-B nanotube arrays.

form [14]. The treated template was washed with deionized water and dried.

The formation of NiCoFe nanotube arrays was carried out by immersion of the treated AAO template into the electrolyte bath for 20 min at the room temperature. The bath contained 8.5×10^{-3} M $NiSO_4{\cdot}6H_2O$, 2.5×10^{-2} M $CoSO_4{\cdot}7H_2O$, 1.3×10^{-2} M $FeSO_4{\cdot}7H_2O$, 0.143 M lactic acid and 7×10^{-2} M DMAB and its pH was fixed at ~7–8. The selected pH was due to the fact that solutions with both higher and lower pH values could corrode the AAO membrane.

Morphologies of both the AAO and the metallic nanotubes were characterized and compared. Field emission scanning electron microscope (FE-SEM) and transmission electron microscope (TEM) were used for this purpose. In order to obtain a better morphology for the NiCoFe, partial dissolution of the AAO membrane into 1 M NaOH was of help. Energy dispersive X-ray spectrometer (EDS) and inductively coupled plasma-optical emission spectrometer (ICP-OES) were also employed to determine the chemical composition of the nanotubes.

3. Results and discussion

Fig. 1(a) illustrates the morphology of the AAO template. Its diameter pores is estimated about 100–120 nm.

Fig. 1(b) shows the FE-SEM image of the 20 min coated AAO template. As is seen in the figure, 20 min deposition results in nanotube NiCoFe-B array creation. An interesting phenomenon is end-closed nanotube formation. To the best of the authors' knowledge, this is the first time that the end-closed NiCoFe-B nanotube arrays are formed during electroless deposition procedure. Fig. 1(c) illustrates the top view of the synthesized nanotubes indicating good order, separation and uniformity of the produced nanotube arrays.

The TEM image of the NiCoFe-B nanotubes fabricated by explained procedure is seen in Fig. 1(d). Image analysis of the nanotubes microstructure indicated about 110 nm for their outer diameter, corresponding well to the average internal diameter of the pores on the AAO. According to the TEM image, average wall thickness of the nanotubes is about 15 nm. These figures are related to the electroless deposition conditions and can simply be controlled by template fabrication parameters [5].

The reactions ending in NiCoFe-B nanotube arrays formation are as follows [6,15]:

$$Pd^{2+}+2e=Pd \quad E^0=915\,mV \tag{1}$$

$$Ni^{2+}+2e=Ni \quad E^0=-250\,mV \tag{2}$$

$$Co^{2+}+2e=Co \quad E^0=-280\,mV \tag{3}$$

$$Fe^{2+}+2e=Fe \quad E^0=-440\,mV \tag{4}$$

The standard electrode potentials of the reduction reactions are shown by E^0. In the electroless deposition process, the electrode potential of the oxidation reactions for reduced agent is lower than the reduction potential of the metallic ions present in the bath [15]. At larger metal electrode potentials, the difference between the oxidizer and the reductant potentials will become greater. This leads to a higher possibility for the redox reaction [6].

Reduction of metal and oxidation of boron ions by DMAB can be described by the following reactions [15]:

$$3Me^{2+}+2R_2NHBH_3+6H_2O=3Me^0+2R_2NH_2^+ +2B(OH)_3+3H_2+4H^+ \tag{5}$$