Journal of Magnetism and Magnetic Materials 389 (2015) 144–147

Contents lists available at ScienceDirect

Journal of Magnetism and Magnetic Materials

journal homepage: www.elsevier.com/locate/jmmm

Letter to the Editor

Electrochemical synthesis of core–shell magnetic nanowires

ARTICLE INFO

Keywords:
Fe@Au
Core–shell
Magnetic
Nanowires
Electrodeposition
Biofunctional

ABSTRACT

(Fe, Ni, CoFe) @ Au core–shell magnetic nanowires have been synthesized by optimized two-step potentiostatic electrodeposition inside self-assembled nanopores of anodic aluminium templates. The optimal electrochemical parameters (e.g., potential) have been firstly determined for the growth of continuous Au nanotubes at the inner wall of pores. Then, a magnetic core was synthesized inside the Au shells under suitable electrochemical conditions for a wide spectrum of single elements and alloy compositions (e.g., Fe, Ni and CoFe alloy). Novel opportunities offered by such nanowires are discussed particularly, the magnetic behavior of (Fe, Ni, CoFe) @ Au core–shell nanowires was tested and compared with that of bare nanowires. These core–shell nanowires can be released from the template thereby opening novel opportunities for biofunctionalization of individual nanowires.

1. Introduction

Magnetic nanostripes/nanowires (NS/NW) are attracting much interest in connection with their striking magnetic behavior and their application in advanced technologies. Specific functionalization offers novel opportunities in energy and environmental developments (e.g., electrochemical capacitors or magnetocaloric systems) [1,2] as well as biomedical treatments [3,4]. Currently, template-assisted electrochemical growth has been demonstrated to be a very successful method for the production of nanoscaled systems with nearly ideal cylindrical characteristics [5–7]. Most typically, anodic aluminum oxide (AAO) membranes are employed as templates to grow arrays of columnar nano-objects with an adjustable geometry, thanks to its versatility and low cost [8].

Recent advances have allowed the synthesis of multisegment NW with modulated diameter and composition along their length [9]. Next step is likely related to the challenging growth of NW with radially distributed composition (i.e., bilayer or core–shell cylindrical nanowires). Besides, the use of transition metals compounds, especially Fe oxides, as well as Au allows the use of NW in biological applications, thanks to their low toxicity [10]. In transition metals–Au core–shell nanowires (TM@Au NW), Au protects the metallic core against oxidation while offering a platform for biological functionalization [11]. Electroless is the most extended approach to the synthesis of this kind of core–shell NW. Nevertheless, it creates impurities in the synthetized NW due to the template charging or the action of mediator molecules used during the process [12,13]. Electrodeposition alternatives avoid this problem, but demands multiple steps [14,15]. Thus, the main objective of this study is to introduce a less expensive, relatively simple and reliable, two-step electrodeposition method for the scalable synthesis of TM@Au NW [16]. After a controlled electroplating of Au nanotubes along the lateral wall of the pores in AAO membranes, a wide variety of TM (i.e., Fe, Ni, Co and their alloys) core magnetic systems have been grown in the second electrodeposition. A second objective has been the testing of the particular magnetic behavior of such TM@Au NW, together with their release to confirm their possible use in subsequent biofunctionalization.

2. Experimental

Anodic aluminum oxide, AAO, templates were prepared by two-step anodization under oxalic bath to form an hexagonal lattice of parallel self-assembled cylindrical pores [17]. The alumina barrier layer was removed using H_3PO_4 (5 wt%) and the pores widened to 80 ± 5 nm diameter while the interpore distance remained at 105 ± 5 nm. A thin film of Au (~35 nm thickness) was then sputtered at the membrane bottom avoiding the complete covering of the pores.

Controlled two-step potentiostatic electrodeposition was employed to fill the nanopores using a three-electrode system. In the first step the Au shell is grown inside the nanopores, with an electrolyte composed by 0.93 g l^{-1} $HAuCl_4 \cdot 3H_2O$ and 30 g l^{-1} H_3BO_3. Different potentials were considered (−0.35 V, −0.8 V, −1 V and −1.25 V) to determine the optimal conditions for the shell growth. The second electrodeposition was performed to fill the shells with a range of different magnetic cores. The electrolytes used were: (i) for Fe core: Fe (60 g l^{-1} $FeSO_4 \cdot 7H_2O$ + 10 g l^{-1} H_3BO_3 + 10 g l^{-1} $C_6H_8O_6$); (ii) for Ni core: Ni (30 g l^{-1} $NiSO_4 \cdot 7H_2O$ + 46 g l^{-1} $NiCl_2$ + 40 g l^{-1} H_3BO_3); and (iii) for CoFe core: $Co_{90}Fe_{10}$ alloy (35 g l^{-1} $CoSO_4 \cdot 7H_2O$ + 5 g l^{-1} $FeSO_4 \cdot 7H_2O$ + 10 g l^{-1} H_3BO + 10 g l^{-1} $C_6H_8O_6$). Electrodeposition voltage was fixed at −1.5 V, −1.0 V and −1.8 V respectively. Fe and CoFe electroplating was kept under N_2 flux to avoid the reactants oxidation.

Shape and dimensions of NW were analyzed using a FEI NOVA NANO 230 High Resolution Scanning Electron Microscope (HR-SEM).

http://dx.doi.org/10.1016/j.jmmm.2015.04.059
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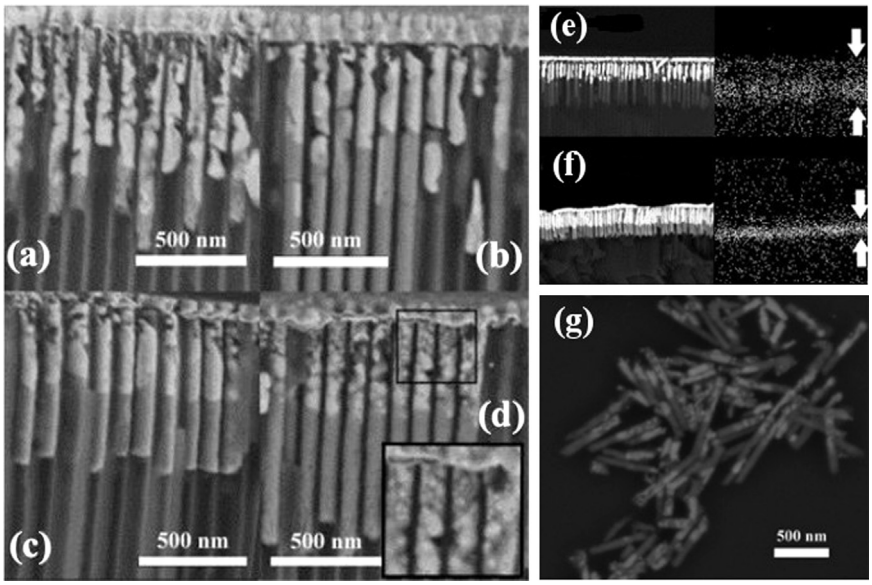

Fig. 1. SEM cross section image of AAO templates with Au nanotubes grown under different applied potentials: −0.35 (a), −0.80 (b), −1.00 (c) and −1.25 V (d) electrodeposited for 30 min and filled with Fe. Fe distribution measured by EDX for samples deposited at −1.00 V after 30 min (e) and 60 min (f). SEM image of released Fe@Au NW over a silicon substrate (g).

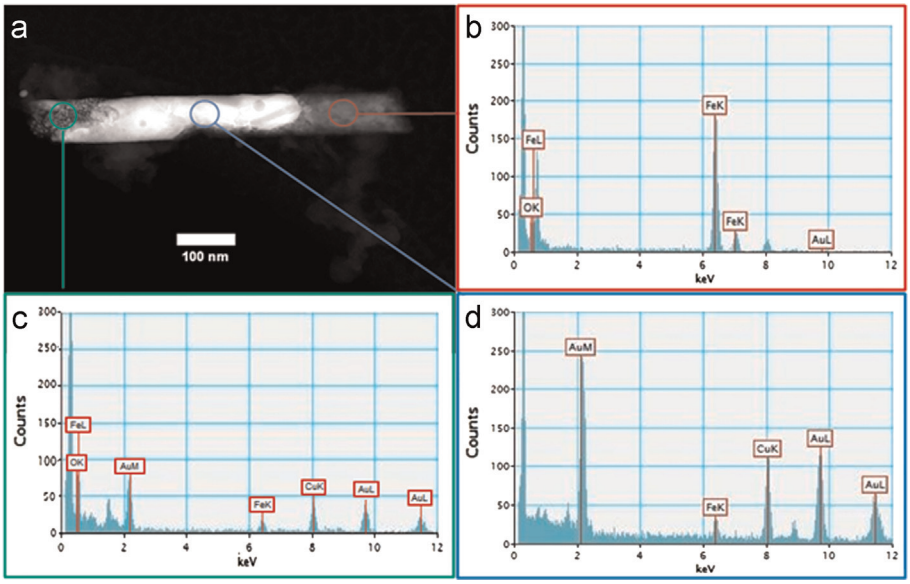

Fig. 2. STEM image of a single Fe@Au NW (a). EDX patterns of indicated regions, uncover core in red (b), partially covered core (c) and Fe@Au core shell region in blue (d). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Compositional distribution of the components in the NW was studied using a secondary electrons vCD detector, as well as an Energy Dispersive X-ray Spectrometer (EDX). Local compositional spectra were acquired by a TITAN CT Scanning Transmission Electron Microscope (STEM) using a HAADF detector. The crystal structure was characterized using PANalytical X'pert Pro X-ray diffractometer in Bragg-Bretano geometry. The sample was scanned at 20–100° (2θ) each 0.02° with a Cu-Kα ($\lambda = 1.5405$ Å) source. For magnetic response analysis, a Vibrating Sample Magnetometer (VSM), ADE system EV7 KLA-Tencor was employed with a maximum magnetic field of 1.5 T. As control, uncovered magnetic NW were grown in a single step electrodeposition using the electrolytes described.

3. Result and discussion

We have paid particular attention to the continuity of the Au nanotubes obtained and to the adjustment of electrodeposition conditions before their occlusion when growing inside the pores, a less studied aspect in previous reports. Continuity of Au nanotubes is better contrasted when a different transition metal (TM) is also present so that, Fig. 1(a)–(d) shows the secondary electrons Scanning Electron Microscopy, SEM, images of Fe filled Au nanotubes obtained using different potentials during Au growth. Usually, the electrochemical conditions for the growth of Au nanotubes include low concentration of Au in the electrolyte and low voltage or current, depending on the method [18,19]. In our case, the concentration of Au in the electrolyte was kept constant at a low value (2.75 mM) while the voltage was varied from −0.35 V to −1.25 V. The potential was applied for 30 min for all the cases. The images show that −1.0 V was the most suitable potential to achieve continuous Au walls. Note that the different contrast of Au (brighter) and Fe (darker) elements allows us to identify each element in the images. Darker imaged Fe can be visualized inside