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Electrochemically synthesized polyethylene glycol coated ferromagnetic nanowire arrays

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ABSTRACT

Polyethylene glycol (PEG) coated Fe, Co, and Ni nanowires (NWs) were fabricated by a template assisted electrochemical deposition method. In this process, polymer and metal ions were deposited simultaneously at room temperature. The effects of different pore diameters of the anodized aluminum oxide (AAO) templates, concentration of electrolytes, and applied current on the growth of the magnetic wires were studied. The polycrystalline polymer-coated ferromagnetic-nanowire arrays were found to have high coercivity with PEG not affecting the magnetic properties. Relative to uncoated metal nanowires, the outer polymer coating strengthens high aspect ratio wires, preventing them from breaking as easily.

1. Introduction

One-dimensional materials have been intensively studied in the past few decades owing to their potential applications in various fields including sensors [1], field effective transistors [2], optical waveguides [3], resonators [4], and generators [5]. Application of these materials can be advanced by significantly controlling the distribution, aspect ratio and alignment during the fabrication. A number of studies have been carried out on the synthesis of one-dimensional (1D) nanostructured materials such as nanowires, nanotubes, and nanorods. Synthesis of such materials can be accomplished by a variety of ways [6–9]. One common method is template assisted electrodeposition where 1D materials are grown within anodized aluminum oxide (AAO) templates. Nanowires grown using this method have high aspect ratios and their radius can be tuned in the range from 20 nm to 500 nm. The length and diameter of these template-grown structures can easily be controlled by varying the time of synthesis, applied current, and pore diameters in the AAO membranes. This is important for directing net physical properties. In addition, by coating the outer layers of the nanowires with metals [10,11], oxides [12], semiconductors [13,14], or by encapsulating polymers inside nanotubes [15], the physical and chemical properties of the nanowires can be altered.

Interest in ferromagnetic nanowires arise from their unique physical properties including enhanced magnetic coercivity related to their large shape anisotropy. Therefore, these nanowires have wide applications in several different fields such as sensors [16], data storage [17], catalysis [18], drug and gene delivery [19–21], and magnetic imaging [22]. Advantages of using nanowires in biomagnetics have been studied by Hultgren et al. for cell separation, binding and physical manipulation in mammalian cells relative to magnetic beads. The result showed that wires worked better than beads possibly due to the wires large magnetic moment. The high magnetic nanowire coercivity increases their response to external magnetic fields, which is important for directing magnetically active species to target sites in the body [20]. Further, the surface of magnetic nanowires can be modified using polymers or oxide materials in order to prevent toxicity after internalization or to increase in functionalization toward analyte. In this study, polyethylene glycol (PEG) was used as a uniform coating on nanowires.

PEG is a biocompatible, biodegradable, protein resistant, nontoxic polymer that has been utilized in a variety of biomedical applications [23]. Syntheses of nanomaterials involving PEG have been studied by a number of groups. The outer polymer can

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interact with therapeutic proteins hence coated nanocomponents may have potential use in various biotechnological and biomedical applications [24,25]. Anwar et al. have used a PEG assisted co-precipitation method to grow morphologically varied nanoparticles of $Mn_{0.5}Ni_{0.5}Fe_2O_4$ [26]. Topkaya et al. used the same method for the synthesis of PEG coated $CoFe_2O_4$ nanoparticles; the magnetic nanoparticles were found to show room temperature saturation and coercive field values close to bulk $CoFe_2O_4$ [27]. Muraliganth et al. have synthesized carbon-coated single-crystalline Fe_3O_4 nanowires using a microwave hydrothermal method with PEG-400; in this case the PEG served as a soft porous template that allowed the growth of nanowires [28].

Herein we report a new approach to the synthesis of metal nanowires in the presence of PEG at room temperature in which the length of nanowires depends on the duration of synthesis. This results in a series of PEG-coated magnetic nanowires. The PEG is found to impact the growth rate of some of the wires, but magnetically, the quality of the wires is retained with improved structural stability. The presence of PEG as an outer coating on magnetic materials may be useful in different fields such as in biomedical, pharmaceutical and catalytic applications in which PEG can be used as a route for surface modifications of nanowires to allow functionalization with bioactive ligands.

2. Experimental

2.1. Synthesis of anodized aluminum oxide (AAO) templates

A two-step anodization process was used to fabricate AAO templates with pore diameters less than 100 nm and a three-step anodization was used to grow templates with diameters greater than 100 nm.

2.1.1. Two-step anodization

High purity Al foil (Sigma–Aldrich, 99.999%, 1 cm × 2.5 cm × 0.25 mm) was degreased in acetone and annealed in an argon atmosphere at 450 °C for 5 h. Subsequently, the foil was electropolished using a solution containing perchloric acid and ethanol (1:4 volume ratio) at 25 V. (*Caution:* The combination of perchloric acid and alcohols is a known explosion hazard—extreme caution should be exercised, even if the mixture is cooled.) Anodization was carried out with 0.3 M oxalic acid at 40 V at 17 °C for approximately 12 h. The oxide layer was completely etched in a mixture of chromic acid (1.8 wt.%) and phosphoric acid (5 wt.%) at 80 °C so that the remaining Al surface (with a hemispherical pattern) would help in the further growth of uniform pores. A second step of anodization was carried out for 3 h, using similar reaction conditions as the first step of anodization, to grow uniformly arranged continuous pore channels.

2.1.2. Three-step anodization

Templates with 130 nm pore diameter were fabricated where an additional third step of anodization was conducted at 100 V, 5 °C for 2 h. This higher applied voltage led to an increase in the interpore distances [29]. Finally, oxide sections were removed from the Al film by an electrochemical etching process and the required sized pores were obtained by treating these templates with phosphoric acid (5 wt.%).

2.2. Synthesis of polymer coated ferromagnetic nanowires

For template assisted electrochemical deposition, one side of the AAO template was sputtered with a silver metal layer and used as the working electrode. Ag/AgCl acted as the reference electrode and a platinum wire as the counter electrode. A VMP2 potentiostat (Princeton Applied Research Inc.) was used to grow wires at an applied current of −0.25 mA for ∼4.5 h. Various deposition solutions were prepared by changing the concentration of PEG (MW1500) and the metal salts (Table 1). Several different polymer–metal NWs such as PEG–Ni, PEG–Fe and PEG–Co nanowire arrays were grown using the above procedures. When needed, the AAO template was removed by treating the samples with 0.1 M NaOH solution overnight and then gently rinsing the NW sample with distilled water and acetone.

2.3. Characterization

The surface morphology and structure of the NWs were characterized using a LEO 130 VP field emission scanning electron microscope (FESEM) and a JEOL EM 2010 transmission electron microscope (TEM). For TEM analysis of the NWs, AAO samples containing NWs were placed in 0.1 M NaOH solution overnight to dissolve the template and then carefully rinsed with distilled water and acetone. TEM samples were prepared by evaporating a drop of an ethanol nanowire solution on a TEM grid; samples were analyzed at an accelerating voltage of 200 kV. To measure the crystallinity and phase purity of the NWs, X-ray powder diffraction (XRD) was performed using a Philips X-pert PW 3040 MPD diffractometer with a CuKα X-ray source. Finally, the magnetic behavior of the wires was studied at room temperature with a vibrating sample magnetometer (VSM, Lake Shore 7300 series).

3. Results

PEG-coated magnetic nanowires were readily synthesized using room temperature electrochemical deposition method. AAO templates with an average diameter of either 60 nm or 130 nm (Fig. 1a and b) were used to grow Fe, Co, and Ni containing wires. All the pore channels were uniformly filled with nanowires. Fig. 1 shows cross-sectional views of a series of PEG-coated magnetic nanowires grown using different pore diameter templates.

To study the wire growth rate in the presence of polymer in the electrolytic solution, polymer coated Ni nanowire arrays were fabricated using the PEG–Ni-1 composition given in Table 1 at a constant current of −0.25 mA in both 60 nm and 130 nm AAO templates. The FESEM images of these wires within the templates are given in Fig. 1c and d. The result showed smaller pore diameters (e.g., 60 nm) led to a decrease in the length of nanowires, opposite to what is typical for wire growth without the presence of polymer in such membranes.

This approach of synthesis of nanowires was not limited to just the study of nanowire growth using templates with different pore diameters. Further studies of wire growth focused on growth of nanowires at a constant pore diameter (130 nm templates) and by modifying the nanowire synthesis conditions by varying the applied current and the concentrations of metal salt and polymer. When the applied current was doubled (as given in Table 1 for PEG–Ni-2) relative to the usual conditions, the result showed that

Table 1
Deposition solutions used to grow PEG-magnetic nanowires.

Type of nanowires	H_3BO_3	Polyethylene glycol	Metal salt	Current (mA)
PEG–Ni-1[a]	0.02 M	0.02 M	0.05 M	−0.25
PEG–Ni-2[a]	0.02 M	0.02 M	0.05 M	−0.50
PEG–Ni-3[a]	0.02 M	0.02 M	0.1 M	−0.25
PEG–Ni-4[a]	0.02 M	0.04 M	0.05 M	−0.25
PEG–Fe[b]	0.02 M	0.02 M	0.05 M	−0.25
PEG–Co[c]	0.02 M	0.02 M	0.05 M	−0.25

[a] Metal salt: $NiSO_4 \cdot 6H_2O$.
[b] Metal salt: $FeSO_4 \cdot 7H_2O$.
[c] Metal salt: $CoSO_4 \cdot 7H_2O$.