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Electrodeposited Au/FeAu Nanowires with Controlled Porosity

S. Lucatero,a W. H. Fowl,b and E. J. Podlah,a,*,z

aChemical Engineering Department and bBiology Department, Northeastern University, Boston, Massachusetts 02115, USA

Multilayer nanowires tailored with alternating AuFe porous layers and Au nonporous segments were fabricated by galvanic square-wave pulsed electrodeposition from an AuFe cyanide-free electrolyte. Control of porosity and composition was achieved via modulation in pulsed time and applied current density. Nanowires with decreased porosity were observed upon increasing time of the AuFe alloy layer or shifting the applied current density to more negative values. This transition was consistent with an increased amount of material being deposited. The single-step approach presented is less time-consuming than conventionally fabricated nanoporous materials, requiring additional etching of prefabricated solid alloys.

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Nanostructures consisting of alternating nonmagnetic/magnetic thin films with different nobility display unique properties of interest in several technological applications, such as giant magnetoresistance sensors for detecting magnetic storage media and biofunctionalized magnetic beads. Electrodeposition is a particularly well-suited method for the fabrication of multilayers as thin films and more recently nanowires and nanotubes. Tailoring multilayers is a particularly convenient way to tune physicochemical properties, such as optical reflectivity, tensile strength, hardness, conductivity, and coercivity. In applications such as localized drug delivery, catalysis, and surface reactions in biomicroelectromechanical systems and nanoelectronics, porous substrates displaying high surface-to-volume ratio and controlled porosity are desirable. Conventionally, metal-based porous materials are generated by subsequent etching of prefabricated solid alloys; a porous structure of the more noble element arises simultaneously as dissolution of the less noble species is induced chemically or electrochemically. A single-step approach for the fabrication of multilayer nanowires consisting of alternating porous/solid layers and controlled porosity is presented here. Unlike other methods to create porous nanowires, the method is based on directly depositing a porous metal, without involving additional chemical etching or anodization of the less noble alloy component. A AuFe electrolyte was chosen as a model system because the deposition can proceed over a wide range of potential with varying composition, current efficiency, and hence porosity. To the authors’ knowledge, fabrication of porous multilayer nanowires by direct electrodeposition has not been achieved before. Gold and iron alloys are electrodeposited from cyanide electrolytes owing to the strong stabilizing ability of these species for metal ions. As an alternative, a noncyanide electrolyte is developed by replacing the complexant cyanide with a more benign ligand, i.e., citric acid, following the methodology presented by Guan and Podlaha for analogous AuCo alloys. The resulting electrolyte for Au alloy electrodeposition is similar to that of Valizadeh et al. but without the cyanide species. The parameters for the nanowire deposition were guided by the deposition of thin films onto rotating cylinder electrodes (RCEs).

Experimental

An RCE and polycarbonate (PC) nanoporous membranes were used as working electrodes. For thin-film deposition, the RCE was utilized to characterize the compositional dependence and efficiency of the deposits. The thin films were galvanostatically deposited in a cell with a copper RCE (length of 6 cm and diameter of 0.6 cm), a stationary platinum mesh as a counter electrode (CE), and a reference saturated calomel electrode. The experiments were performed at three different RCE rotation rates, i.e., 200, 400, and 650 rpm, and the current density was varied in the range of −0.3 and −20 mA/cm². Extended deposition times were needed for an accurate composition characterization of thin films obtained at the lowest current densities. The same experimental setup described was also used to generate polarization curves at a sweep rate of 5 mVs⁻¹.

The nanowire growth was done using track-etched PC membranes (6 µm thick and 100 nm pore diameter, Osmonics) as templates. The cathode consisted of the PC membrane spattered on one side with Au and placed inside a poly(ether ketone) holder, whereas a Au anode aligned horizontally to the membrane was the CE. Multilayers were deposited without agitation by current pulses. The nanowires were released from the templates using a dichromate bath for 12 h and ultrasonication; solvent removal was achieved by repeated dilution/centrifugation with a high purity ethanol.

The electrolyte solution used for electrodeposition studies and nanowire fabrication consisted of (i) citric acid, 0.49 M; (ii) FeSO₄, 0.29 M; (iii) KOH, 1.07 M; and (iv) 2.5 mM Au (Techni Gold 25 E). The pH was adjusted to 6.15 with diluted H₂SO₄ or KOH at room temperature, and deionized ultra filtered water (Fisher Scientific) was utilized for all experiments. Quantitative compositional analysis of the deposits and nanowires was conducted by X-ray fluorescence spectroscopy operating at 45 keV, 2 mA in air with a collimator of 100 µm in size. Approximately 20 µL of concentrated nanowire suspension was placed in a Cu/carbon-coated transmission electron microscopy (TEM) grid and visualized under a H9262 TEM microscope operating at an accelerating voltage of 60 kV in bright field. Scanning electron microscopy (SEM) images were taken with the aid of a Hitachi S4800 field emission SE microscope operated at 3.0 kV.

The porosity was quantitatively characterized by image analysis (Image J, NIH, Baltimore, MD). Processing of original TEM files consisted of binary image reconstruction at a predetermined grayscale threshold. Approximately 100 in-focus segments were measured to obtain a representative porosity determination, which was calculated as the ratio of void area and total area.

Results and Discussion

Thin films.—The cathodic polarization behavior of the citric acid electrolyte at 200, 400, and 650 rpm and a sweep rate of 5 mVs⁻¹ is shown in Fig. 1a using the RCE. A region where the potential is affected by the rotation rate was observed between −0.3 and −1.1 V (−0.2 to −10 mA/cm²). This behavior is indicative of the Au limiting current density; it is expected because this species is maintained at a relatively low concentration in the electrolyte solution (2.5 mM) compared to Fe (0.29 M). Conversely, Fe being present in excess in the solution exhibits a kinetic-controlled behavior in the region examined and is unaffected by the rotation rate.

The composition of the electrodeposits as a function of current...
density and rotation rate (Fig. 1b) indicated the range between −0.9 and −5 mA/cm² favorable for Au deposition, whereas FeAu alloys were obtained at higher current densities, becoming richer in Fe with current density. There is a large change in the deposit composition with the rotation rate after an applied current density of −5 mA/cm². At high current density, deposits developed a dendritic (porous) appearance. An example of the morphology is shown in SEM images (Fig. 2) at a low (Fig. 2a) and high (Fig. 2b) magnification. The thin film was deposited at −10 mA/cm² at a rotation rate of 200 rpm, and the morphology shows pores on the order of 100 nm. The current efficiency was relatively low, between 2 and 10%, in the range of rotation rate and current density studied. At low current densities that current efficiency is very low, then rises and remains steady, between 5 and 10% (Fig. 1b).

Partial current densities as a function of steady-state potential at different rotation rates are shown in Fig. 3. At potentials less negative than −0.7 V, Au deposition is under both diffusion and kinetic control at any rotation rate, whereas in the range of −0.7 and −0.9 V, the partial current density of Au, \( i_{Au} \), shows predominantly a diffusion control behavior and an influence of rotation rate on \( i_{Au} \) was observed (Fig. 3a). This diffusional behavior extends from −0.7 to −1.0 V (−0.7 to −1.1 V) at 400 (650) rpm. As the potential became more negative \( i_{Au} \) decayed, this effect was, however, less pronounced as the rotation rate increased, and may have been due to the migration of Au ions away from the electrode surface. There was an influence of rotation rate on the partial current of iron, \( i_{Fe} \), at potentials less negative than −0.8 V, whereas at more negative potentials, \( i_{Fe} \) becomes less sensitive to variations in rotation rate, which suggests a mostly kinetically controlled reaction (Fig. 3b).

The partial current of side reactions \( i_{\text{side}} \) (Fig. 3c) was comparatively high with respect to either \( i_{Au} \) or \( i_{Fe} \), which suggested a significant gas evolution in the range of potentials studied.

**Figure 1.** Alloy electrodeposition onto an RCE (a) effect of rotation rate on the polarization behavior at 200 rpm and (b) deposit composition and efficiency.

**Figure 2.** SEM images of RCE deposits at \( i = -10 \) mA/cm² and 200 rpm.
Nanowires in Fig. 5 were deposited by removing one of the layers. Figure 5a shows nanowires that were deposited without the Au layer. The current density was pulsed between $i_1 = -0.9 \text{ mA/cm}^2$ ($t_1 = 135 \text{ s}$) and $i_2 = -0.9 \text{ mA/cm}^2$ ($t_2 = 25 \text{ s}$). The resulting deposit was discontinuous and porous. The nanowire in Fig. 5b is a representative example of those fabricated at $i_1 = -0.9 \text{ mA/cm}^2$ ($t_1 = 135 \text{ s}$) and $i_2 = -0.9 \text{ mA/cm}^2$ ($t_2 = 25 \text{ s}$), eliminating the Fe-rich layer. These nanowires were dense. Thus the porous region is a result of the deposition of the Fe-rich layer, and the Au layer helps to structurally support the porous region.

Figure 4. Control of porosity in multilayer nanowires by varying the current density $i_2$. 10, 12, 15, and 20 mA/cm$^2$ in (a), (b), (c), and (d), respectively; $i_1 = -0.9 \text{ mA/cm}^2$, $t_1 = 135 \text{ s}$, and $t_2 = 25 \text{ s}$ in all cases.

Relatively low efficiencies (Fig. 1b) due to an increased $i_{al}$ (Fig. 3c) contribute to gas bubble formation and may be responsible for the dendritic deposits both in thin films (Fig. 2) and nanowires (Fig. 4 and 5). An efficiency of 14.5% was determined for the AuFe porous layer, which is approximately twice the value determined for the thin film, RCE experiment at 200 rpm (i.e., ~7%, Fig. 1b), suggesting that the deposition occurs in the nanowires in a non-steady-state regime.

A similar trend in the nanowire porosity by increasing only the pulse time of the alloy layer, $t_2$, is shown in Fig. 6. In all cases, $i_1 = -0.9 \text{ mA/cm}^2$, $t_1 = 135 \text{ s}$, and $i_2 = -10 \text{ mA/cm}^2$, and the pulse times $t_2$ were 25, 35, 50, and 75 s in Fig. 6a-d, respectively. A decreased porosity was observed by increasing $t_2$ from 25 to 75 s. At $t_2 = 75 \text{ s}$, the porous/solid interface was difficult to observe. Upon increasing either current density or deposition time, the charge increases, which suggests that the observed decreased porosity at extended $t_2$ or $t_2$ was due to an increase in the total mass deposited. Thicker porous layers did not develop by increasing either $t_2$ or $t_2$; this is consistent with a kinetic deposition control of the main reaction (rather than a transport control). According to the partial current density data (Fig. 3) at $|i_2| > 10 \text{ mA/cm}^2$, i.e., $E \approx -1.0 \text{ V}$, $i_{al}$ is...
mostly under kinetic control; hence the concentration of bulk Fe is uniform within the porous layer and the deposition occurs within the pores rather than at its surface rendering denser layers. An estimate of the predicted change in the nanowire porosity with \( t_1 \) and \( t_2 \) is presented in the Appendix and captures the qualitative observations in Fig. 4 and 6.

Conclusions

A single-step electrodeposition approach was developed for the synthesis of porous nanowires guided by thin-film experiments. This method was not only advantageous to create porous deposits with alternating solid layers but was also used to modulate porosity as well as composition by varying the conditions of the pulsed current scheme used for their fabrication. A contributing factor for porosity development was gas evolution occurring simultaneously during the electrodeposition process. A predicted decrease with either \( t_2 \) or \( t_2 \) is presented in the Appendix and agreed with qualitative features of the TEM observations.

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