

Nanosculpting of Electrodeposited Multilayered Nanowires and Nanotubes

Maoshi Guan¹ and Elizabeth J. Podlaha-Murphy²

¹Department of Chemical Engineering, Louisiana State University, Baton Rouge, Louisiana

²Department of Chemical Engineering, Northeastern University, Boston, Massachusetts

The electrochemical fabrication of compositionally modulated, multilayered nanowires, and to a lesser extent nanotubes, has been widely studied, but not the selective etching of them. We will present results on the electrochemical etching of one of the nanolayers that comprise the nanowires/tubes. In contrast to etching multilayered nanowires/tubes by a chemical route, an electrochemical method can result in novel intermediate structures ranging from bamboo-like wires and tubes to complete etching to form disks and rings. As a model system, nanolayers of Au and Co-rich CoAu were electrodeposited in a sandwich fashion into nanoporous alumina and polycarbonate membranes. The Co-rich layers were selectively etched potentiostatically and the current transients inspected. The current response indicated when the surface area of the nanowires/tubes is enhanced due to shape change under diffusion controlled dissolution and signaled when the layers were completely etched. Cyclic voltammetry was also employed to characterize and track the etching process. SEM confirmed the partially etched and completely etched nanostructures.

Introduction

Nanoporous, metallic nanowires can provide unique properties and new applications with enhanced surface area and well-defined pore morphology. One, conventional fabrication method is to deposit an alloy and chemically dissolve a sacrificial element. For example, Ji and Searson [1,2] electrodeposited a gold-silver binary alloy nanowire using a nano-templating method. The nanowire was chemically etched to remove the silver and to create the nanoporous structure. Qin *et al.* [3] electrodeposited a layered alloy of Au/Ag and Au/Ni as a nanowire; the less noble element (i.e., Ag and Ni) were subsequently chemically etched. In this paper, we electrochemically etch a layered alloy nanowire in order to create intermediate structures and expand the technique to include nanotubes.

Electrochemical etching is applied to a collection of nanowires/tubes by means of an external circuit under potentiostatic conditions. The dissolution can be controlled by monitoring the applied current and hence charge, and it is carried out in more benign solutions compared to chemical etchants. In this study, the fabrication of Au/CoAu nanoscale bamboo-like structures is developed by etching nanowires and nanotubes in KCl electrolytes. The evolution of the shape change is monitored with time by examining the current during anodization and cyclic voltammetry at intermittent stages of etching.

Experimental

The AuCo alloy and multilayered nanostructures were electrodeposited from a single, sulfite electrolyte containing 0.29 M $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$, 0.47 M $\text{C}_6\text{H}_8\text{O}_4 \cdot \text{H}_2\text{O}$, 1.78 M KOH, 1.25 mM Au (Techni[®] Gold 25 E - a sulfite containing electrolyte), pH of 6.15. This non-cyanide-containing electrolyte was developed in our prior study [4]. To electrodeposit Au/CoAu

multilayered nanowires into anodic alumina oxide (AAO) membranes a gold sputtering step was used to create a conductive layer on one end of the membrane followed by a two step galvanostatic, square-wave pulsed plating [5]. A gold layer was deposited at a current density of -2 mA/cm^2 and a cobalt rich Co-Au (96 wt % Co) alloy at -6 mA/cm^2 . The deposition time was varied depending on the desired layer size. In order to release the nanowires from the template, the alumina template was dissolved in 2 M KOH with ultrasonication. Membranes with large pore diameters were used to create nanotubes by minimizing the amount of gold sputtering on the backside of the membrane.

The nanowires were then cleaned by sequential centrifugation and rinsed with deionized distilled water and ethanol. The electrode for etching the nanowires/tubes is shown in Figure 1. The nanowires/tubes were fixed on the electrode surface by a double sided adhesive conductive carbon tab (Electron Microscopy Sciences) typically used for SEM. The Co-rich layer of the Au/CoAu nanowires and nanotubes were electrochemically anodized in 2 M KCl under potentiostatic control at an overpotential of 0.04 V vs SCE.

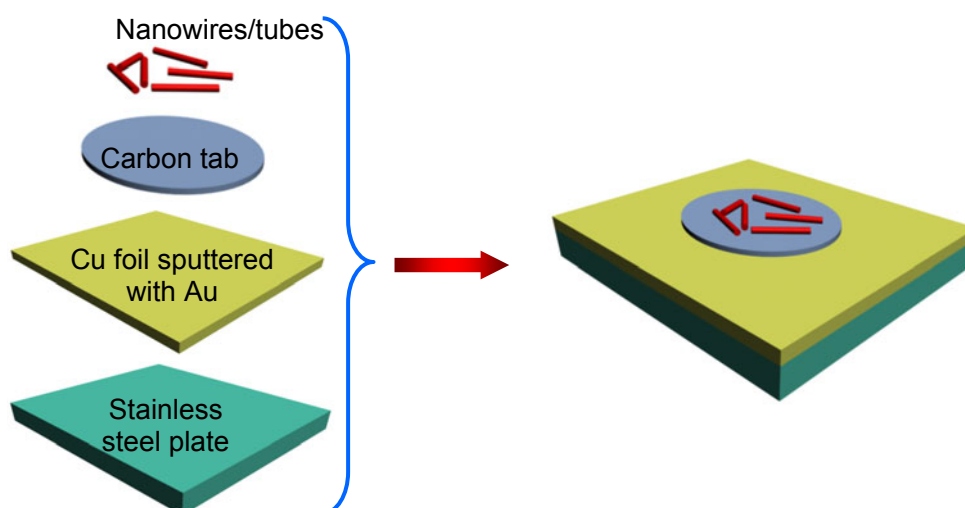


Figure 1. Schematic illustration of the working electrode used for electrochemical etching

A Hitachi S-3600N SEM was used to characterize the nanowires before and after electrochemical etching.

Results and Discussion

Figure 2 (a-c) is a plane-view SEM image of a Au 25 nm / CoAu 50 nm multilayered nanowire during the process of electrochemically etching. Figure 2 (a) shows an array of nanowires and a single nanowire at higher magnification (inset) prior to etching. The gold layer was deposited for 180 s and the Co-rich layer for 33 s. The multilayer structure is observable. After partially etching the nanowire, Figure 2 (b), nano-bamboo like structures emerge from the preferential etching of the Co-rich layer. Images in different magnification scales are shown. After completely etching of the Co-rich CoAu alloy layers, Figure 4, uniform and parallel Au nanodisks are formed. The end stage of etching is the same result

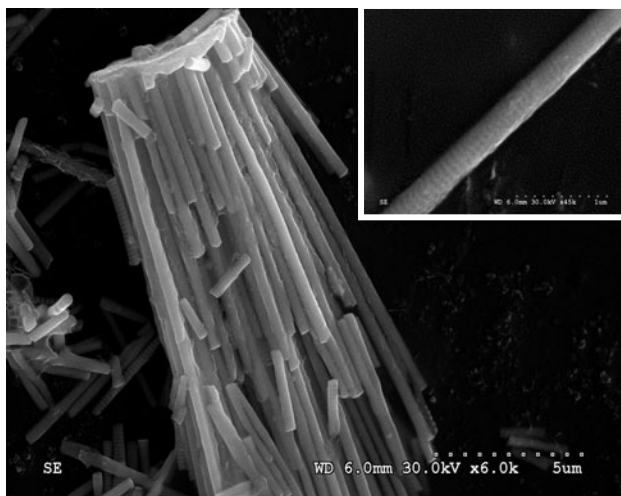


Figure 2 (a). SEM images of Au 25 nm / CoAu 50 nm nanowire electrodeposited in 0.2 μm AAO membrane (as deposited)

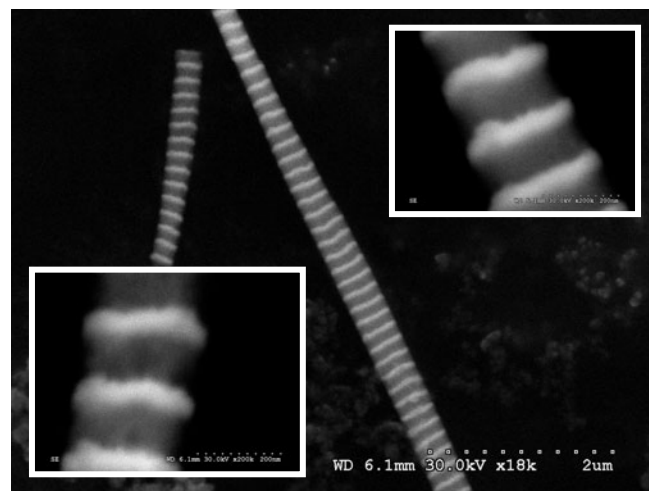


Figure 2 (b). SEM images of Au 25 nm / CoAu 50 nm nanowire partially etched electrochemically for 900 s (nanobamboo).

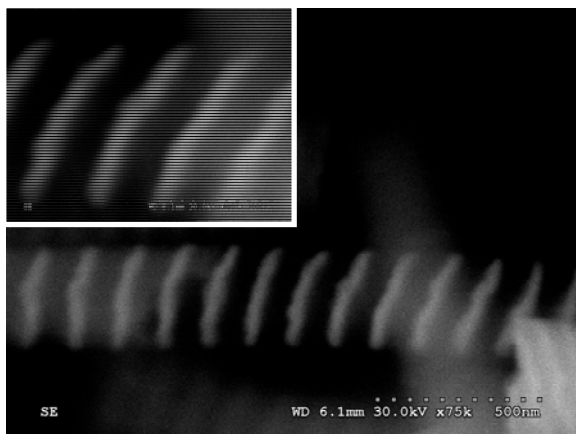


Figure 2 (c). SEM images of Au 25 nm / CoAu 50 nm nanowire completely etched

as chemical etching, but the intermediate structures are unique to the electrochemical etching method.

As etching progresses, there is a response in current and this current can be used to track the etching process. Also the total current response, or charge, $\int Idt$, should reflect the amount of mass etched. Nanowires with four different AuCo layer sizes were electrodeposited in AAO membranes with a pore size of 0.1 μm . Each set had the same total length of 12 μm and the same Au layer thickness of 25 nm, but different CoAu layer sizes: 20, 50,

100, 150 nm. The layer sizes were controlled by changing the deposition time. A constant volume of 60 μL of nanowire suspension was carefully transferred to the surface of the substrate. After the samples were fully dried, electrochemical etching experiments were tested. The current response as a function of time during electrochemical etching of four Au/CoAu nanowire electrodes is plotted in Figure 3. Each sample of a collection of nanowires with a fixed layer size exhibits a typical peak shape with a maximum. The current increases due to the larger surface area of the partially etched nanowires. As more and more material is removed the area decreases and hence the current decreases. The thicker the CoAu layer size, the higher value of the peak is achieved. The larger CoAu alloy layer size reflects more mass etched, consequently larger surface area is created during the etching process and a larger current arises. Finally, when the Co-rich CoAu alloy layers are completely etched away, there is no further material left for etching. The anodic current approaches zero. It is not always equal to zero because there is a distribution of current across the electrode and not every nanowire is etched exactly at the same time.

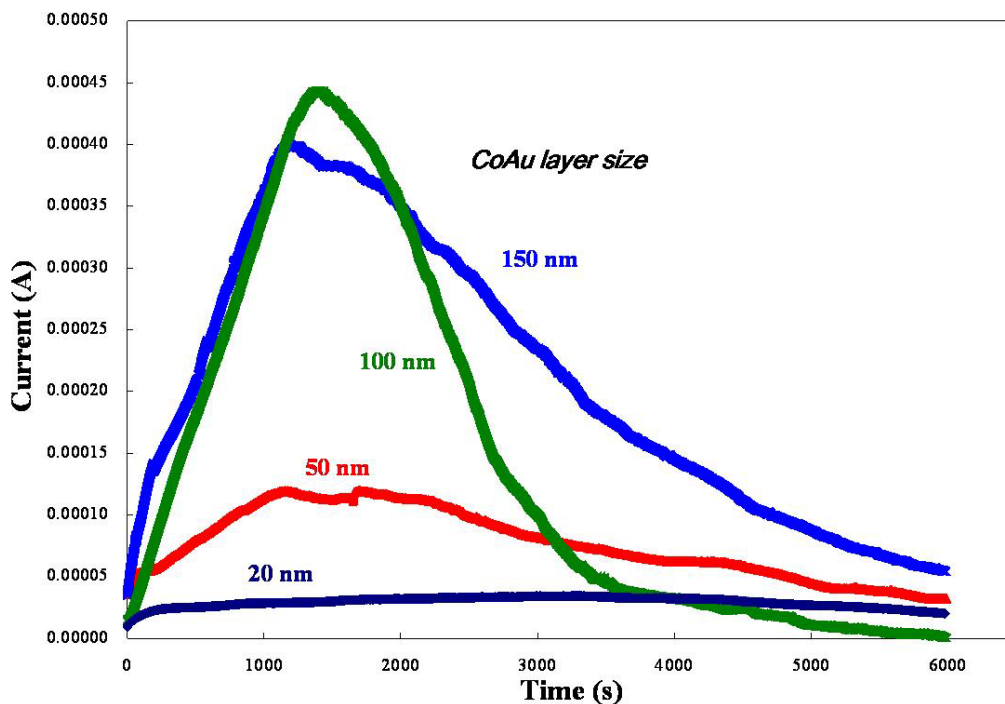


Figure 3. Anodic charges as the function of time during the process of the selective electrochemical etching of Au/CoAu nanowires on carbon electrodes with four different CoAu layer sizes including 20, 50, 100, and 150 nm

Table 1 is a summary of the charge measured (integrated current over time) during the evolution of etching the nanowires having different layer sizes. The maximum charge was found to be proportional to the etched layer size.

Table I. Ratio of CoAu layer sizes and ratio of charges @ 6000 s

CoAu layer size (nm)	Ratio of CoAu layer size	Anodic charge (C)	Ratio of charge
150	7.5	1.2509	7.2
100	5.0	0.8737	5.0
50	2.5	0.4597	2.6
20	1.0	0.1746	1.0 (reference)

In a similar approach, nanotubes can also be electrochemically etched to create nanotube bamboos and nanorings. Figure 4 shows an SEM image of a nanotube partially etched. The Au layers were electrodeposited with the same conditions as in Figure 3 (25 nm) and the Co-rich CoAu layers were electrodeposited for 99 s to create layers of 150 nm. In order to readily deposit a tubular form, a large diameter membrane template was chosen, available commercially in polycarbonate filters. After deposition, the polycarbonate was removed by dichloromethane.

Figure 5 is a plot of the charge, determined from the measured current response, with time for three electrodes having different Co-rich CoAu nanolayers in the form of nanotubes. The

gold layer was 50 nm and similar to the nanowire response in Table 1, the charge was proportional to the etched layer size.

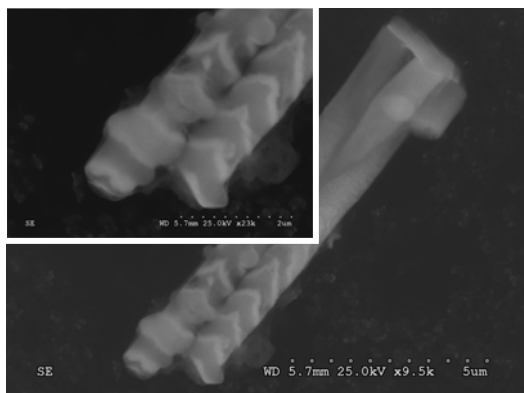


Figure 4. SEM images of Au 25 nm / CoAu 150 nm nanotubes with diameter of 1.0 µm after partial electrochemical etching of Co-rich CoAu layer

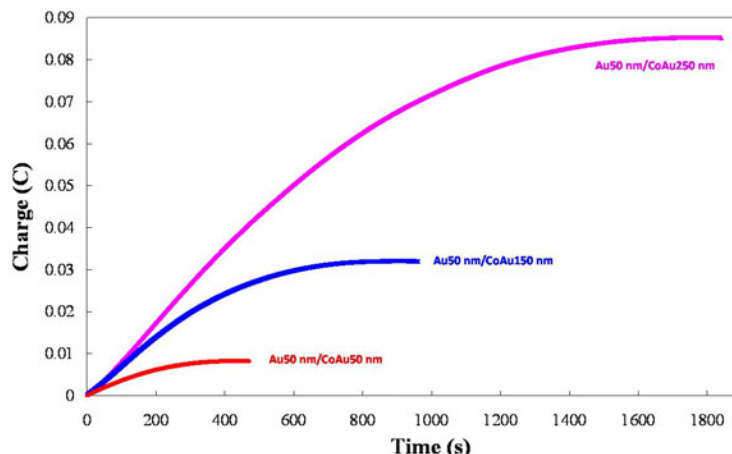


Figure 5. Anodic charges as the function of time during the process of selective electrochemical etching of Au/CoAu nanotubes on carbon electrodes with three different CoAu layer sizes: 50, 100, and 250 nm.

Cyclic voltammetry (cv) was used as a way to further distinguish changes in the etching process. The ferric/ferrocyanide redox couple is a reaction to characterize electrode surfaces since the reaction involves no deposit and thus no change in the electrode area. An electrolyte containing 0.001 M potassium ferricyanide, 0.003 M potassium ferrocyanide in 0.5 M NaOH where used to characterize a nanowire electrode. Figure 6 shows the reponse of the ferri/ferrocyanide reactions at different sweep rates (50, 100 and 150 mV/s) of the potential on an unetched nanowire electrode with layer sizes of Au 25 nm / CoAu 100 nm. For each sweep rate, in the forward scan, the main reaction at the working electrode was the reduction of the ferricyanide ion (near -0.6 V vs SCE).



When the potential becomes more negative than the potential of the main reaction, the current increases due to the side reaction of water reduction on the Au/CoAu nanowires and carbon substrate.



The applied potential was reversed and the potential was scanned in a positive direction. The large anodic peak (near 0 V vs SCE) is the oxidation of the ferrocyanide ion, which reflects the larger concentration of the ferrocyanide ion in solution.



The ending point of the scan does not return to its original value due to the capacitance effect of the double layer.

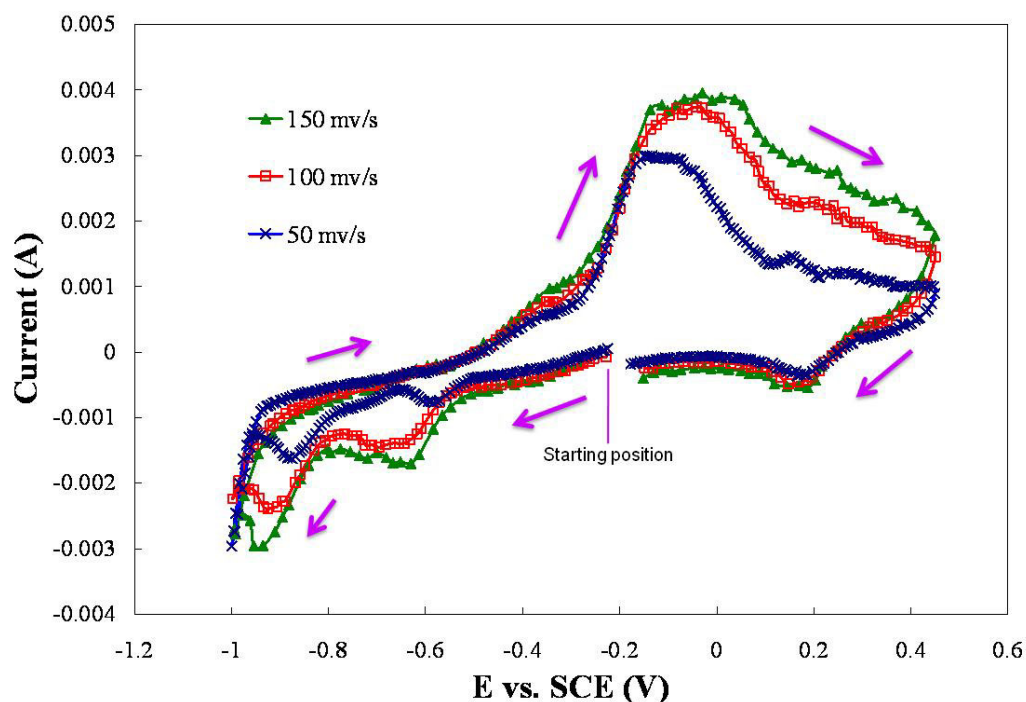


Figure 6. Cyclic voltammograms measured at three different sweep rates: 50, 100 and 150 mV/s in the ferricyanide/ferrocyanide solution on a carbon electrode with unetched nanowires Au 25 nm / CoAu 100 nm

Changes in the electrode nanolayers due to etching changed the current response and also changed the capacitance. Figure 7 is a set of cyclic voltammograms of a single size nanowire electrode (Au 25 nm / CoAu 50 nm) etched at different times in the region where ferricyanide reduction occurs. The etched nanowire response was more ohmic in nature reflective of an increase in the resistivity of the surface. During the forward scan (toward more negative potentials), the current increased in the region where ferricyanide is reduced (-0.6 V vs. SCE) only with large etching times and did not increase in a systematic way with etching time. However, the electrode capacitance increased with an increase of the etching time and could be a better measure to monitor the etching process. At the five different etching times: 600, 1300, 3500, and 6000 s, the capacitances were 0.6, 1.3, 2.2 and 2.5 mF, respectively. The increasing of capacitance as a function of etching time is largest in the beginning as the surface area is enhanced, but then changes less as the loss of mass of the electrode reduces the increase in surface area.

Conclusions

Au/CoAu multilayers were electrodeposited into nanoporous templates to form either nanowires or tubes. The CoAu layer was subsequently etched potentiostatically and the current was monitored over time. The electrochemical etching technique was used to show that controlled, partial etching of nanowires/tubes can be achieved and bamboo nanostructures formed. The nanowires/tubes can be characterized by the charge measured during etching and the response of the electrode capacitance determined from cyclic voltammetry

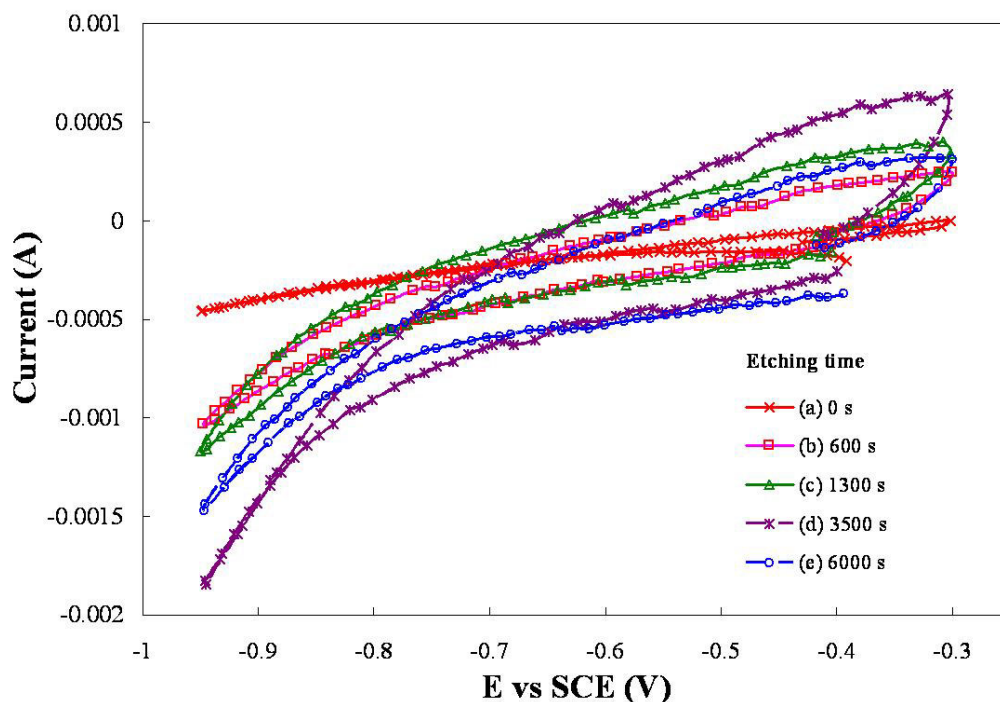


Figure 7. Cyclic voltammograms of Au 25 nm / CoAu 50 nm nanowires which were electrochemically etched with different etching time: (a) 0 s, (b) 600 s, (c) 1300 s, (d) 3500 s and (e) 6000 s

Acknowledgments

The authors gratefully acknowledge NSF (CBET-0746467) and the Center for Biomolecular Multi-scale Systems at LSU for partial support of this work.

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