Fabrication of Au/Ni Multilayered Nanowires by Electrochemical Deposition

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Abstract. Electrochemical deposition of Au/Ni multilayered nanowires using template-assisted growth technique from electrolyte containing nickel chloride and gold solution was studied in details. 60 µm-thick anodized aluminum oxide (AAO) with pore diameter of 200 nm was used as the template. Chronopotentiometry experiments were first carried out to determine the deposition conditions and the growth rate of individual Au and Ni layers. Scanning electron microscopy results revealed that the pore channels of AAO were completely filled with Au/Ni multisegmented nanowires. By selectively removing the Ni segments in the multilayered nanowires, high-yield of pure gold nanorods were obtained. Detailed studies on the nanostructures obtained were carried out using various microscopy and probe-based techniques for structural, morphological and chemical characterizations.

1. Introduction
One-dimensional nanostructures such as nanorods, nanowires, nanotubes and nanoshells, have been intensively studied because of their ability to exhibit many novel effects which are not observed in the bulk materials [1]. Among the various metals from which the nanostructures are made, gold is technologically important due to its low resistivity (2.21 µΩ cm) [2]. Apart from this, gold also has good electrical and thermal conductivity as well as high ductility and chemical inertness [3]. Therefore, gold is often utilized in medical applications especially for tumor treatment [4].

A variety of techniques have been developed for the fabrication of gold nanostructures such as lithography, chemical vapor deposition, and electrodeposition. Electrochemical deposition is a method which allows us to deposit materials in many different forms from the solutions. Different from other deposition techniques, electrochemically deposited nanowires are grown continuously from the pore bottom [5]. In this study, electrochemical deposited Au/Ni multilayered nanowires is used as the base material configuration for the fabrication of Au nanostructures. The nanowires were fabricated by sequential electrochemical deposition of two materials inside the nanochannels of an anodized aluminum oxide (AAO) template. AAO is an ideal template for the fabrication of nanostructured materials because of the many advantages it possesses, including tunable pore dimensions, good mechanical property and good thermal property. Moreover, it is cheap and capable of producing oriented arrays of metals nanostructures.

The objective of this study is to study the use of AAO to fabricate Au/Ni multilayered nanowires by electrochemical deposition.
2. Materials and Methods

Electrochemical deposition was carried out in a typical two-electrode cell with a bath volume of 100 ml. A commercial AAO template (Whatman Anodisc-13, average pore diameter 200 nm, 60 µm thick) was used as the working electrode. The back-side of the template was first sputtered with Au as a seed layer. Multi-segmented Au/Ni nanowires were obtained by electrodepositing Au and Ni sequentially via alternate switching of the electrolyte solutions for Ni and Au until the required number of segments was achieved. The gold segments were deposited from a ready-to-use cyanide-free gold bath (Technic RTU-25) at constant current of -0.34 mA at 40°C, while the Ni segments were deposited from a nickel electrolyte comprising of 1 M NiSO$_4$ + 0.5 M H$_3$BO$_3$ using a current of -3.4 mA at ambient condition.

Figure 1 shows a section of the typical current-time curves for the electrodeposition of Au/Ni multilayered nanowires. After deposition, the Au seed layer was removed and the nanowires were released by immersing the template into NaOH solution followed by repeated centrifugation and rinsing until a nanowire suspension was obtained. To yield only gold segments from the nanowires, the Ni segments were removed by selective etching using nitric acid. The Au/Ni multilayered nanowires and Au nanostructures obtained were studied by Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) while composition characterization of the materials was carried out using energy dispersive X-ray spectroscopy (EDX).

![Current-time curve for the deposition of Au/Ni multilayer nanowires.](image)

3. Results and Discussion

Figure 2 shows the typical scanning electron micrograph image of the Au/Ni multilayered nanowires embedded in AAO template. The nanowires filled the AAO nanopores channels continuously and uniformly in an oriented array and exhibit homogenous contours. After removal of the Ni segments, fragmented Au segments were obtained as seen in Figure 2 (b) and (c). As the Au segments were confined in the template, the diameters of the Au segments were determined by the pore size of the template while the lengths were determined by the deposition time. Deposition rate for Au was found to be 88 nm min$^{-1}$ while deposition rate for Ni was found to be 150 nm min$^{-1}$.
Figure 2. SEM images of (a) Au/Ni multi-segmented nanowires embedded in PAA template (b) after removal of Ni by selective etching of Au/Ni multisegmented nanowires (c) dispersion of the fragmented gold nanorod segments after removal of template. Scale bars are 5 µm.

Figure 3 shows that, instead of nanorods, Au nanodiscs can be obtained from Au/Ni multisegmented nanowires electrodeposited with much shorter segments of Au. Figure 4 provides a closer examination for the Au/Ni interface using TEM. As evident from the Selected Area Diffraction Pattern (SADP) shown in the inset and the EDX spectrum recorded, the Au segment was highly crystalline and consisted only of Au.

Figure 3. SEM images of (a) Au/Ni multi-segmented nanowires in template and (b) the corresponding dispersed Au nanodiscs after removal of Ni segments and template. Scale bars are 2 µm.
Figure 4. (a) TEM image of the Au/Ni interface from the multisegmented nanowires showing good adhesion between the two materials. The SADP for the Au segment shown in the inset is typical of a single crystalline structure. (b) EDX spectrum indicating high purity of the Au segment (the Cu peak is from TEM sample grid).

Template-assisted deposition also offers additional advantage where various morphologies of the gold nanorods can be obtained by tailoring the corresponding pore geometry of the templates used. Apart from solid gold nanostructures, the technique can be modified to produce nanoporous gold (NPG) structures. This is done by fabricating periodic multisegmented nanowires with Au-Ni composite layers alternating with Ni, followed by selective etching of Ni. Nanoporous gold is a good candidate material for high-performance catalyst and sensor due to the large specific surface area it possesses.

4. Conclusion
Au/Ni multilayered nanowire has been successfully fabricated using template assisted electrochemical deposition technique. By using AAO as template, the dimensions of the Au/Ni multilayer can be controlled precisely. Nearly 100% of the pores are filled with Au/Ni multilayer nanowires. We have also successfully demonstrated a novel, high throughput, cost and time effective technique for the synthesis of size-tailored nanomaterials such as gold nanorods. Besides Au/Ni multilayer nanowires, this technique can also be used to fabricate other metals nanostructures and has great potential for commercial exploitation as it involves only simple set up and easily scalable for industrial production.
Acknowledgement
This work was supported by the following funding sources: 03-03-01-SF0083 & NM-R&D-11-28.

5. References

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