

HIGH THROUGHPUT SYNTHESIS OF GOLD NANORODS FROM MULTISEGMENTED NANOWIRES

K. Y. Kok*, I. K. Ng and N. U. Saidin

Malaysian Nuclear Agency, Bangi, 43000 Kajang, Selangor, Malaysia.

Multisegmented nanowire is a useful configuration for high throughput and cost effective production of nanostructures with various functionalities. Gold nanorods, for example, are useful in field emission, display, biomedical, energy and sensor applications. This work aims to produce gold nanorods via the synthesis of multisegmented Au/Ni nanowires by electrochemical deposition. Multisegmented Au/Ni nanowires were first produced by direct sequential deposition of Au and Ni, with different predetermined lengths, into the pores of porous anodized alumina (PAA) templates. High-yield of pure gold nanorods of predetermined dimensions was subsequently obtained by selectively removing the sacrificial Ni segments in the nanowires. The advantages of this method are that it is easily scalable besides time and cost saving. Detailed studies on the nanostructures obtained were carried out using various microscopy and probe-based techniques for structural, morphological and chemical characterizations.

Keywords: Multisegmented nanowires, gold nanorods, electrochemical deposition

INTRODUCTION

Multisegmented nanowires are versatile materials architectures for achieving the intended functionalities of a specific materials system. Each segment of the nanowires can be tailored with a specific property via the control of its dimension, microstructures and composition. An example is the giant magnetoresistive (GMR) multilayered nanowires where the layering structure consists of ferromagnetic material alternating with non-magnetic material of optimized lengths and compositions. This produces a large change in resistance in an external magnetic field [1]. Ni-based multisegmented nanowires have the added advantage that they can be assembled and aligned using magnetic field during the fabrication process due to the magnetic properties of Ni [2]. In addition, Ni-based multisegmented nanowire can be used for high throughput and cost effective production of various functional nanostructures, as shown in this study for the production of gold nanorods. Depending on their shape, gold can absorb different frequencies of light. Rod-shaped gold is able to absorb energy from visible to near infrared wavelengths as compared to particle-shaped gold and have very high absorption cross sections that make them ideal for cancer detection and photothermal therapy [3]. With this characteristic, near-infrared light can be used with gold nanorods to destroy tumors with minimal side effects to human tissues. Apart from this, they also

have applications in electronics, sensing, photonic, catalyst and cosmetic products [4 – 5].

Electrochemical deposition, on the other hand, has emerged as a promising route for nanostructure fabrication in recent years due to the many inherent advantages it possesses. Besides being a low-energy operation process and relatively cheaper method compared to vacuum-based techniques like chemical vapor deposition [6], it can be easily scaled up to meet commercial demands. More importantly, it is an ideal method for filling high aspect ratio templates. Electrodeposited nanowires also tend to be denser, continuous and highly crystalline. Furthermore, they are not only limited to nanowires constituted of pure elements but also of metal alloys with good control of stoichiometry. Studies have shown that nanowires with multiple segments of different metals in a controlled sequence can be fabricated by selectively varying the deposition potentials in a solution containing different metal ions [7 – 8].

Our present study focuses on the production of gold nanorods via the synthesis of multisegmented Au/Ni nanowires by template-assisted electrochemical deposition, using porous anodized alumina (PAA) membranes as scaffolds. This provides a high-throughput as well as a cost and time effective way for the fabrication of metal nanostructures. The advantage of using Ni segments is that it can be easily removed using nitric acid. The multisegmented Au/Ni nanowires are synthesized by electrochemically depositing, in between the alternate segments of a metal (which resists chemical etching),

short segments of a non-desirable and less noble metal (which is susceptible to chemical etching, e.g. Ni). This is followed by selective dissolution of the undesirable (sacrificial) metal segments to produce the gold nanorods. Using this method, high-yield of pure gold nanorods of predetermined lengths can be produced from the Au/Ni multisegmented nanowires.

MATERIALS AND METHODS

Anodised alumina membranes (Whatman Scientific) with a nominal pore diameter and thickness of 200 nm and 60 μm respectively were used as templates for the nanowire fabrication. Electrochemical deposition was carried out using a two-electrode configuration with platinum as the counter electrode and porous anodized alumina (PAA) template (pre-sputtered with a Ag seed layer at the back side) as the working electrode. Multi-segmented Au/Ni nanowires were prepared 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 template was rinsed with nanopure water between switching of the electrolyte solutions to prevent cross-contamination. Gold segments were deposited galvanostatically from a ready-to-use cyanide-free gold bath (Technic RTU-25) at a constant current of -0.34 mA at 50°C . Nickel segments were deposited from the nickel electrolyte composed of $1.5\text{ M Ni}(\text{NH}_2\text{SO}_4)_2 + 0.2\text{ M NiCl}_2 + 0.4\text{ M H}_3\text{BO}_3$ using a current of -3.4 mA at ambient condition. The length of each segment was determined by the deposition time.

After deposition, the Ag seed layer was removed using HNO_3 . The nanowires were released by immersing the template into NaOH solution followed by repeated centrifugation and rinsing using nanopure water (high purity deionised water that has ionic purity $> 17\text{ M}\Omega$) until a nanowire suspension

was obtained. The nanowires were then transferred and stored in IPA at room temperature. To yield only gold segments from the nanowires, Ni segments were removed by selective etching using nitric acid. Structural characterizations of the nanowires were carried out using high resolution optical microscope, scanning electron microscope (SEM) and transmission electron microscope (TEM). Composition characterization of the nanowires was carried out using energy dispersive X-ray spectroscopy (EDX).

RESULTS AND DISCUSSION

Fig. 1 shows the typical current and potential time traces of the Au segments during electrochemical deposition. 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} . After deposition, a section of the template was cut to inspect the embedded nanowires under high resolution digital microscope and scanning electron microscope. Fig. 2 shows the optical and SEM images recorded from the Ni/Au nanowires embedded in PAA template. The nanowires were arranged in an oriented array by the template. After removal of the Ni segments, fragmented Au segments were obtained as seen in Fig. 3 (a) and (b). The multisegmented Au/Ni nanowires exhibit, on a gross scale, uniform length and regular interfaces. 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. The morphology of the gold nanorods was determined by the pore geometry of the templates used. Fig. 4 shows that, instead of nanorods, Au nanodiscs can be obtained from Au/Ni multisegmented nanowires electrodeposited with short segments of Au.

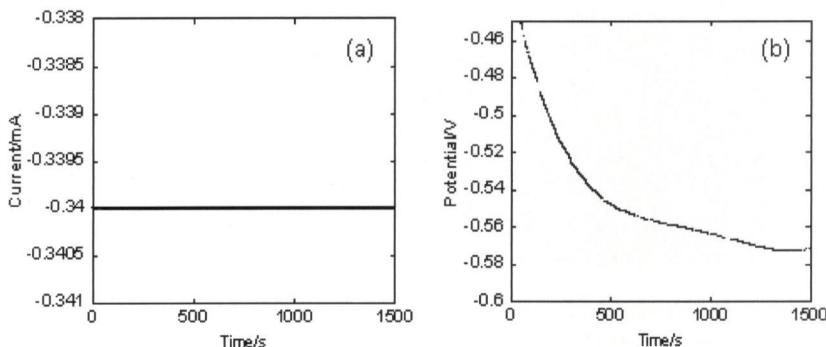


Fig. 1. (a) Current and (b) potential time traces for Au deposition.

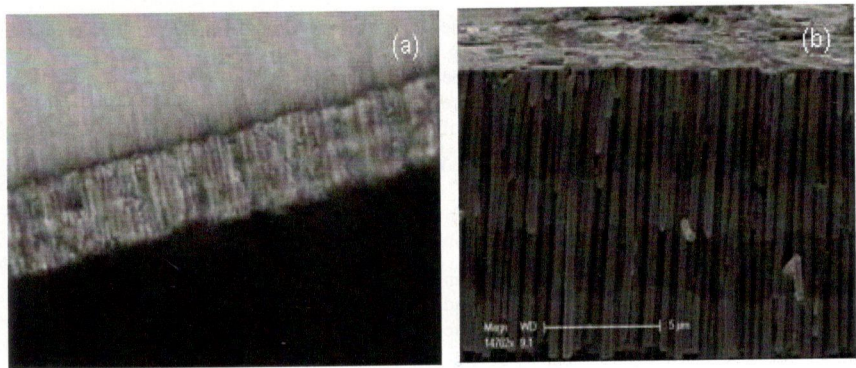


Fig. 2. (a) Optical and (b) SEM cross-sectional images of the Au/Ni multisegmented nanowires embedded in PAA templates. Individual segments of Au and Ni are clearly discernible in the figures.

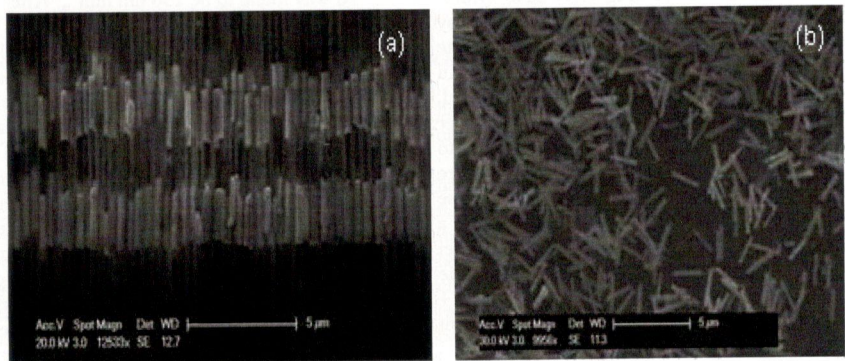


Fig. 3. SEM images of (a) Au segments remained in the PAA template after removal of Ni by selective etching of Au/Ni multisegmented nanowires. (b) Dispersion of the fragmented gold segments after removal of template.

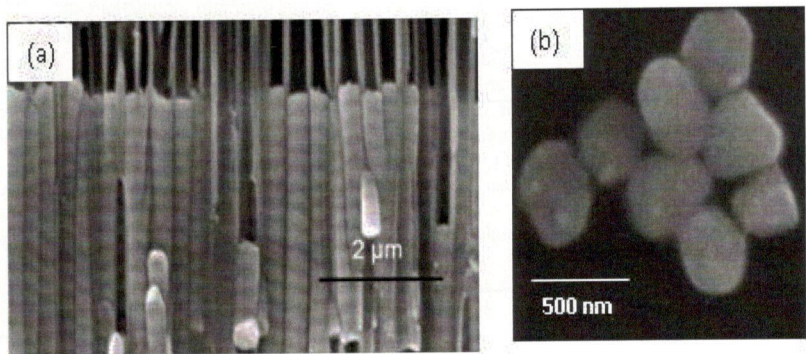


Fig. 4. SEM images of (a) multisegmented Au/Ni nanowires (embedded in the PAA template) with short segments of Au and Ni. (b) Au nanodiscs obtained from the nanowires.

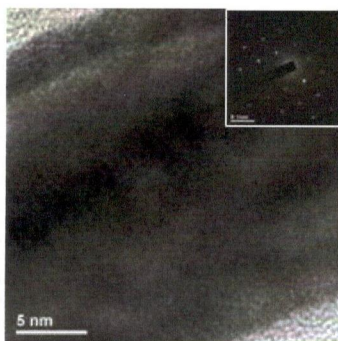


Fig. 5. HRTEM image of a gold segment. The SADP shown in the inset is typical of a single crystalline structure.

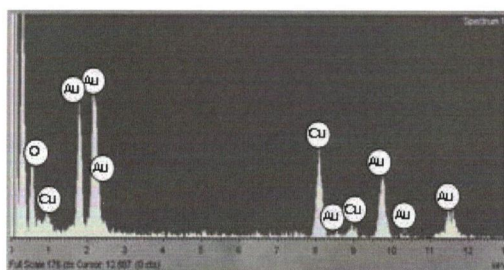


Fig. 6. Energy Dispersive X-ray spectrum indicating high purity of the Au segment (the Cu peak is from TEM sample grid).

Close examinations on the multisegmented Au/Ni nanowires performed using a transmission electron microscope (TEM) operating at 200 kV revealed that the Au segments were highly crystalline and consisted only of Au. This is clearly evident from the Selected Area Diffraction Pattern (SADP) shown in the inset of Fig. 5 and the Energy

Dispersive X-ray (EDX) trace recorded from the sample as shown in Fig. 6. Microstructures of Ni are not critical as Ni served as the sacrificial segment which will be dissolved away. The multisegmented Au/Ni nanowires also exhibit uniform lengths and regular interfaces. Fig. 7 is the high resolution TEM (HRTEM) image of the interface region between Au and Ni.

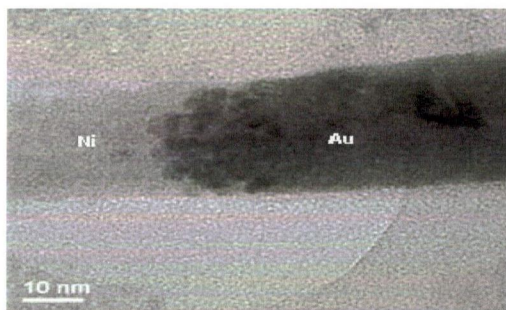


Fig. 7. HRTEM image of the Au/Ni interface from the multisegmented nanowires showing good adhesion between the two materials.

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 good candidate material for high-performance catalyst and sensor due to the large specific surface area it possesses.

CONCLUSION

We have successfully demonstrated an attractive and a versatile template-assisted electrochemical deposition technique, using multisegmented nanowires as the base structure, for the synthesis of size-tailored nanomaterials such as gold nanorods. This technique has great potential for commercial exploitation as it involves only simple set up and easily scalable for industrial production. In addition, the process is high throughput, cost and time effective.

ACKNOWLEDGEMENT

The author would like to acknowledge the support from MOSTI (03-03-01-SF0083) and Malaysian Nuclear Agency (NM-R&D-11-28) for funding this work.

REFERENCES

- [1] Kok, K. Y. and Ng, I. K. (2009). Growth and Characterisation on Giant Magnetoresistance Property of Metallic Multilayers, *Materials Research Innovations*, 13 (3) pp. 396 – 399.
- [2] Hangarter, C. M. and Myung, N. V. (2005). Magnetic Alignment of Nanowires, *Chem. Mater.* 17, pp.1320 – 1324.
- [3] Anne Trafton (2009). Tumors Targeted using Tiny Gold Particles. *MIT TechTalk*, (2009), 53 (24), pp.4.
- [4] Asefa, T., Duncan, C. T. and Sharma, K. K. (1980). Recent Advances in Nanostructured Chemosensors and Biosensors, *Analyst*, 134: pp 1980 – 1990.
- [5] Alizadeh, A., Khodaei, M. M., Karami, Ch., Workentin, M. S., Shamsipur, M. and Sadeghi, M. (2010). Rapid and selective lead (II) Colorimetric Sensor based on Azacrown Ether-functionalized Gold Nanoparticles, *Nanotechnology*, 21, 315503.
- [6] Ng, I. K. and Suzuki, H (2009). Low temperature growth of Si nanowires via vapour-liquid-solid mechanism, *Materials Research Innovations*, 13 (3) pp. 192 – 195.
- [7] Matei, E., Ion, L., Antohe, S., Neumann, R. and Enculescu, I. (2010). Multisegment CdTe Nanowire Homojunction Photodiode, *Nanotechnology*, 21, 105202.
- [8] Kok, K. Y., Hangarter, C. M., Goldsmith, B., Ng, I. K., Saidin, N. U. and Myung, N.V. (2010). Synthesis and Characterisation of Electrodeposited Permalloy (Ni₈₀Fe₂₀)/Cu Multilayered Nanowires, *J. of Mag. and Mag. Materials*, 322 (24) pp. 3876 – 3881.