TEMPLATE-ASSISTED GROWTH OF NANOSTRUCTURED FUNCTIONAL MATERIALS

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ABSTRACT

Template-assisted growth is an important nanoelectrochemical deposition technique for synthesizing one-dimensional (1-D) nanostructures with uniformly well-controlled shapes and sizes. A good template with well-defined dimensions is imperative for realizing this task. Porous anodic alumina (PAA) has been a favorable candidate for this purpose as it can be tailor-made with precise pore geometries, such as pore length and diameter as well as inter-pore distances, via the anodisation of pure aluminium. This paper reports the fabrication of PAA templates and electrochemical synthesis of functional nanostructures in the form of nanowires using PAA templates as scaffolds. Axial heterostructured and homogeneous nanowires formed by engineering materials configuration via composition and/or layer thickness variations were fabricated for different functionalities. X-ray diffraction and imaging techniques were used to elucidate the microstructures, morphologies and chemical compositions of the nanowires produced. Due to their large surface area-to-volume ratios, and therefore high sensitivities, these functional nanostructures have useful applications as critical components in nanosensor devices and various areas of nanotechnology. Potential applications include as hydrogen gas sensors in nuclear power plant for monitoring structural integrity of reactor components and containment building, as well as environmental monitoring of air pollution and leakages of toxic gases and chemicals.

ABSTRAK

Templat membantu pertumbuhan ialah pemendapannanoelectrochemical penting teknik kerana mensintesis ekamatra (1-D) nanostructures dengan bentuk-bentuk yang dengan seragamdikawal dengan baik dan saiz-saiz. Satu contoh baik dengan dimensijelas penting kerana menyedari tugas ini. Alumina anod berliang(PAA) telah menjadi seorang calon baik untuk tujuan ini sebagai iamungkin adalah ditempah dengan liang tepat geometri-geometri, seperti liang panjang dan garis pusat serta jarak antara liang, melalui anodisation aluminium tulen. Laporan-laporan akhbar inirekaan templat PAA dan sintesis elektrokimia nanostructuresfungsian di bentuk nanowires menggunakan templat PAA apabila aram-aram. Heterostructured paksi dan nanowires homogendibentuk oleh tatarajah bahan-bahan kejuruteraan melalui komposisidan / atau variasi-variasi ketebalan lapisan dipasang untukkefungsian-kefungsian berbeza. Belauan sinar-x dan teknik-teknikpengimejan merupakan digunakan untuk menjelaskanmicrostructures, morphologies dan mengarang kimia nanowiresmenghasilkan. Disebabkan kawasan permukaan besar mereka untuk nisbah-nisbah jumlah , dan oleh itu sensitiviti-sensitiviti tinggi, nanostructures fungsian ini mempunyai permohonan-permohonanberguna apabila komponen kritikal di alat-alat nanosensor danpelbagai bahagian nanoteknologi. Permohonan-permohonan berpotensi termasuk apabila pengesan-pengesan gas hidrogendalam logi kuasa nuklear untuk memantau keutuhan strukturkomponen-komponen reaktor dan bangunan pembendungan, sertapengawasan persekitaran pencemaran udara dan kebocoran gas-gas toksik dan bahan kimia.

Keywords: Template-assisted growth, electrodeposition, nanowires

INTRODUCTION

Gas sensor industry is growing in recent years due to increasing consumer concerns on safety and environmental pollution issues. Hydrogen gas sensors for example, are widely used in nuclear industries for monitoring structural integrity of reactor components, containment building and nuclear waste repository besides air pollution control and monitoring of leakages of toxic gases/chemicals [Gnanasekaran & Periaswami, 1996]. In addition, as hydrogen fuel cell is gaining its importance in automotive industry due to its potential for substantially cleaner emissions than internal combustion engines (ICEs), hydrogen sensors are expected to be the essential components of the fuel cycle from safety to fuel cell performance.

Solid-state sensors based on one-dimensional nanostructures, such as nanowires or nanotubes, have been the focus of sensor development lately due to the advantages they offer over conventional sensors fabricated from thin/thick films and compact powders. Among the advantages are excellent response time, detection accuracy, better signal-to-noise ratio and improved 3S (stability, sensitivity, selectivity) requirements [Cui et al., 2003]. In this work, Au and Pd one dimensional nanostructures were fabricated via template-assisted growth technique for hydrogen gas sensing. Porous anodic alumina (PAA) was used as the templates for confining the electrodeposited materials within their nanopores to produce nanowires with controllable dimensions.

A two-step anodisation process was adopted for fabricating the PAA templates. The effects of anodisation conditions on pore structures of the templates were systematically studied and optimized to improve the qualities of the nanowires produced. Multi-segmented Au/Ni nanowires were obtained by direct sequential deposition of different materials with different predetermined lengths into the pores of PAA templates. By selectively dissolving the Ni segments in the Au/Ni multisegmented nanowires, pure gold nanorods of predetermined lengths and diameters were successfully produced. This has provided a high-throughput and cost-effective way for synthesizing nanosized gold particles. Alternatively, the Ni segments were sacrificially transformed into Pd nanostructures via galvanic displacement. Nanowires doped with Au and Pd showed enhanced surface adsorption and catalytic activity upon exposure to hydrogen gas and hence exhibiting excellent gas sensing properties. [Yun et al., 2004; Penner, 2010]. They are good candidates for the fabrication of hydrogen gas sensors.

MATERIALS AND METHODS

Template fabrication

High purity aluminium foils were used for the fabrication of the PAA templates. To prepare the PAA templates of pore diameters ranging from 20 – 30 nm, the Al foils were anodized in 1.8 M sulphuric acid at anodisation potentials of less than 20 V. PAA of larger pore sizes were prepared using 0.3 M oxalic acid and higher working range of voltages. First anodisation was carried out for 1 hour under a constant voltage to produce an array of pores on the template which were then removed to create periodic intents. This was followed by a second anodisation conducted at the same potential. After second anodisation, the remaining Al was etched away and the exposed barrier layer was removed by immersing the template in 5% H_3PO_4 (v/v %) at room temperature. This pore widening process unblocked the ends of the pore channels.

Nanostructures fabrication

Electrodeposition of nanowires was carried out using a two-electrode configuration with platinum as the counter electrode and the PAA template, pre-sputtered with a Au seed layer at the back side, as the working electrode. 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 composed of 1 M $NiSO_4$ + 0.5 M H_3BO_3 using a current of -3.4 mA at ambient condition. 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 Pd segments, on the other hand, were obtained by galvanically displacing the sacrificial Ni segments in a solution consisting of 1 mM $Pd(NO_3)_2$ at room temperature. Detailed characterisations of the templates and the nanostructures produced were performed using a combination of microscopy, diffraction and probe-based techniques.

RESULTS & DISCUSSION

Fig. 1 shows the current transient curve recorded from first anodisation process of aluminium, showing different stages of pore formation of the PAA template. In the first few seconds, a thin dielectric barrier layer with high electrical resistance was formed on the surface of the Al. This resulted in a rapid drop in current (A). Further application of the electric field and exposure to the electrolyte attacked the weak points of this barrier layer and initiated the formation of the pores in the honeycomb structure of the aluminium oxide (B). This process was accompanied by an increase in the current (C) until a steady state was reached when the pores were propagated further into the lattices at constant rate (D). Second anodisation sustained the pore ordering resulted from first anodisation and further pore propagation until the required thickness was achieved. The inter-pore distance of the lattice was found to increase linearly with voltage for both the sulphuric acid and oxalic acid electrolytes used as shown in Fig. 2. Quantitative analysis on pore density and porosity were performed using image analysis software. Pore densities in the range of 10^{10} pores cm^{-2} and porosities of between 0.2 – 0.3 were obtained for the PAA templates produced.

X-ray diffractograms recorded from the pure Al foil and porous aluminium oxide formed on the PAA template before and after removal of aluminium shows that polycrystalline Al foil was transformed by the anodisation process into porous aluminium oxide which was structurally amorphous.

Pore widening was found to have significant influence on the pore morphologies of PAA templates. After anodisation, cylindrical pores were seen partially covered by near hemispherical domes, formed from the barrier oxide, as exemplified in Fig. 4. Our results show that prolonged pore widening process tend to suffer from the undesirable effects of irregular pore enlargement, merging of neighboring pores and damage of the upper surface of PAA template. A good template exhibits highly ordered honey-comb arrays of parallel pore channels with little or no tilting and without lateral branching as typically shown in Fig. 5.

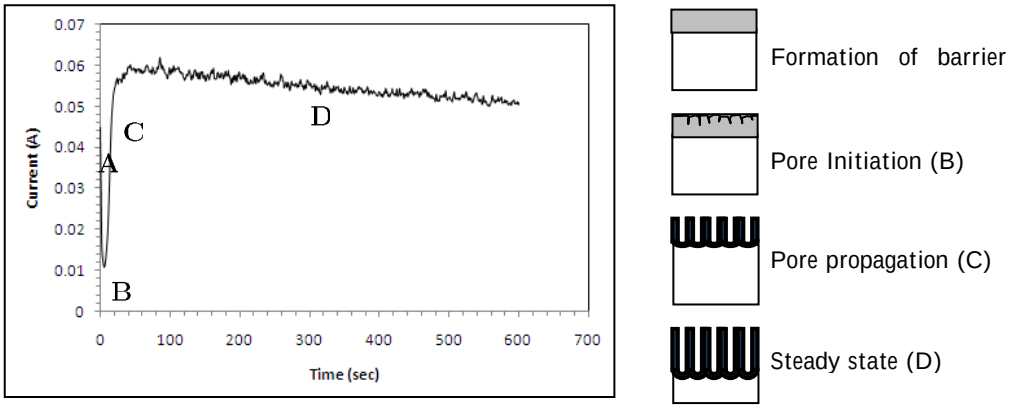

Figure 1: Current transient curve recorded from first anodisation process of aluminium.

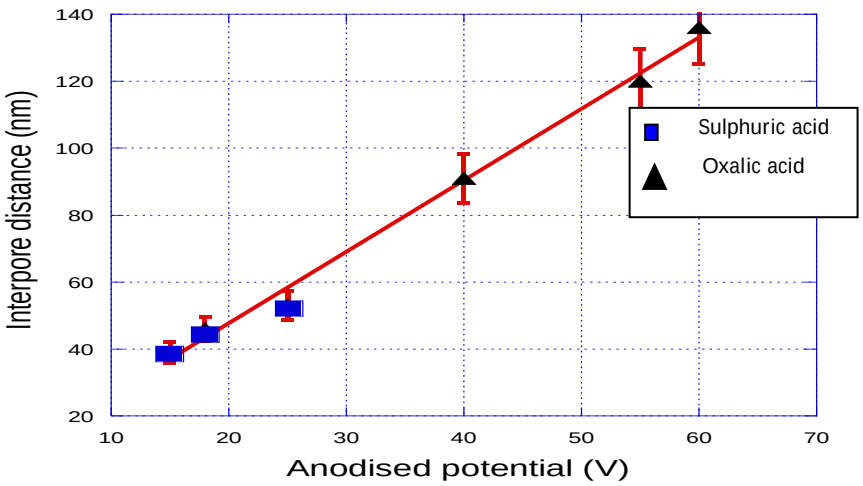

Figure 2: Graph of inter-pore distance against anodisation potential

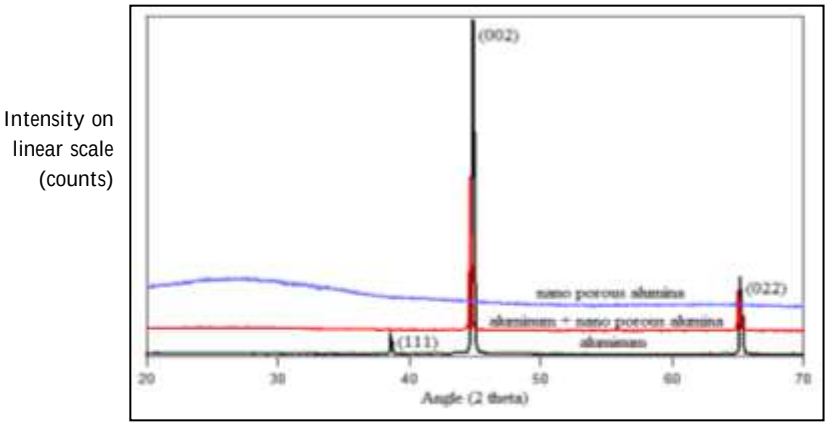

Figure 3: X-ray diffractograms of pure alumunim foil and nano porous aluminum oxide film, before and after removal of aluminium. Full removal of Al results in a broad and low background corresponding to amorphous alumina.

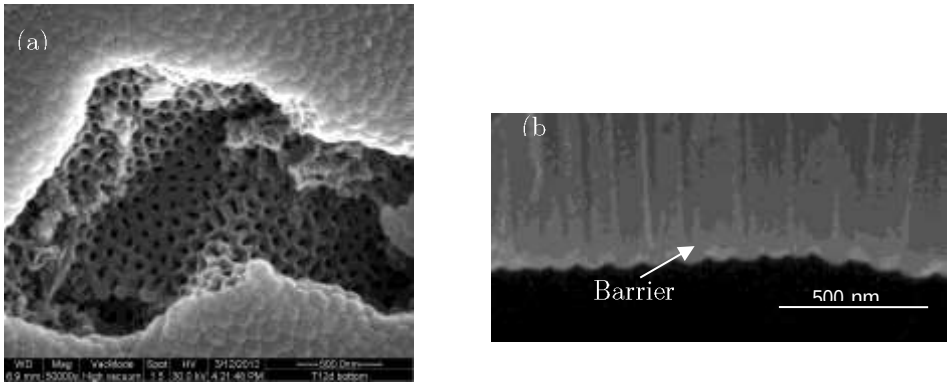

Figure 4: SEM images of a PAA template. (a) bottom-view of the template showing regular pore structure partially covered by barrier oxide layer and (b) cross-sectional view of pore channels showing near hemispherical dome-shape barrier layer at the ends of the channels.

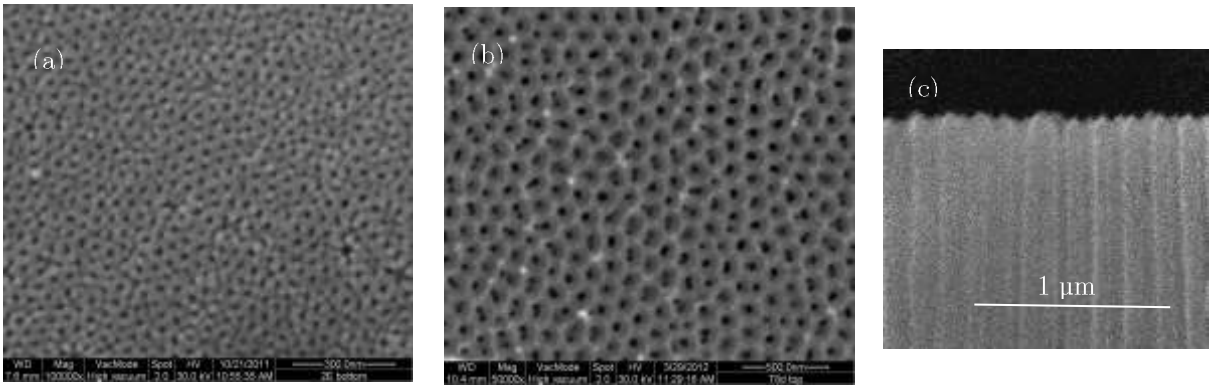

Figure 5: SEM images of PAA templates with (a) pore diameter of 30 nm fabricated at 20°C using 1.8 M sulphuric acid, (b) pore diameter of 52 nm fabricated at 10°C using 0.3 M oxalic acid and (c) cross-sectional view of the regularly-aligned pore channels in (b).

Fig. 6 is the typical SEM image of the Au nanostructures (embedded in PAA template) obtained from multi-segmented Au/Ni nanowires after removal of Ni segments. Diameters of the Au segments were determined by the pore sizes of the template used while their lengths were determined by the deposition time.

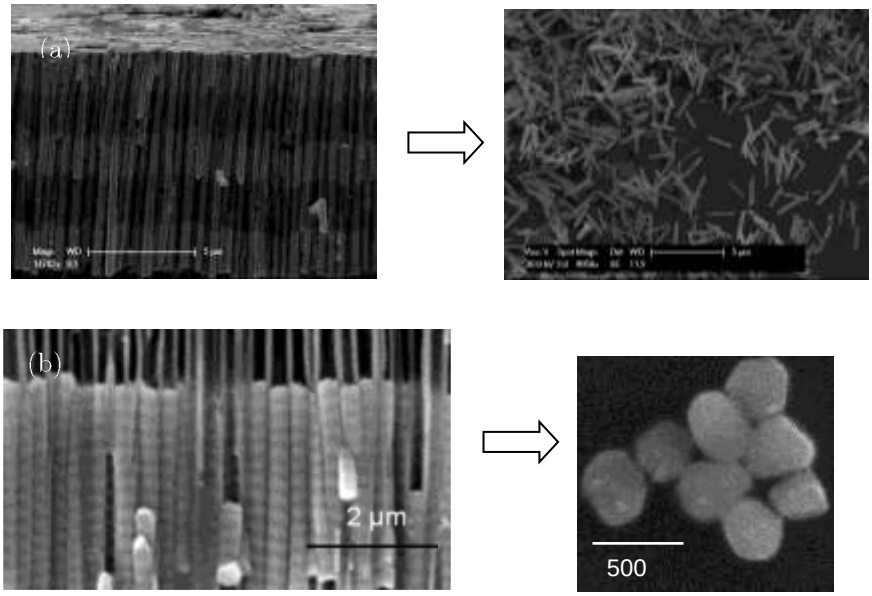

Figure 6: SEM images of (a) Au/Ni multi-segmented nanowires embedded in PAA template and the corresponding dispersed Au nanorods and (b) Au/Ni multi-segmented nanowires in template and the corresponding dispersed Au nanodiscs after removal of Ni segments and template.

Alternatively, the sacrificial Ni segments were galvanically displaced in a solution consisting of Pd to form segments of Pd nanotubes as shown in Fig. 7. EDX trace from the sample shows no presence of Ni. The Ni segments were fully displaced after 20 minutes in the solution at room temperature. Increase in electrolyte temperature enhanced the displacement rate. Longer reaction time tends to thicken the Pd surface with aggregation of Pd particles forming roughened Pd nanotubes.

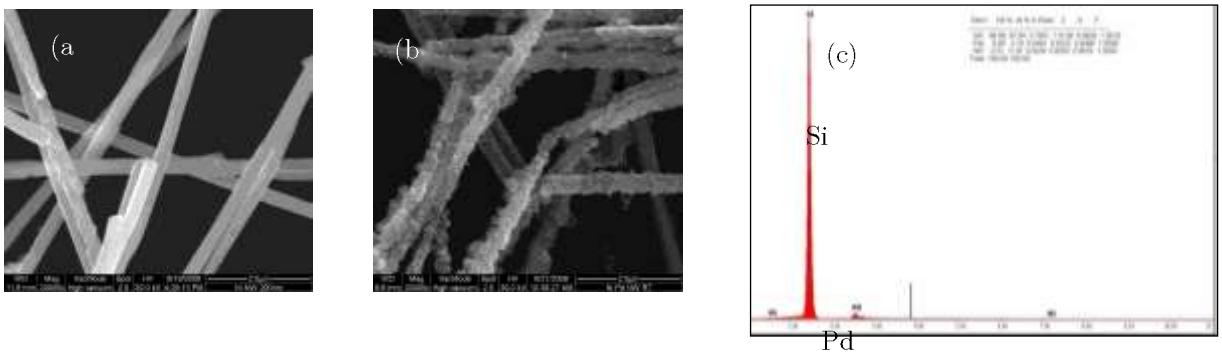

Figure 7: SEM images and EDX spectrum of the Pd/Ni nanostructures: (b) after galvanically displacing the nickel nanowires in (a) with Pd electrolyte at room temperature for 20 min. No Ni is present in the EDX spectrum indicating complete displacement of Ni. (The nanostructures were dispersed on Si substrate for SEM evaluations).

CONCLUSION

We have successfully demonstrated that various nanostructures could be synthesized using a combination of template-assisted electrodeposition and post-growth galvanic displacement techniques. The dimensions of the nanostructures can be controlled using PAA templates with well-defined pore geometries as determined by the anodisation conditions used. Using multi-segmented nanowires as the base structure, we have also demonstrated an attractive and versatile electrodeposition technique for the synthesis of size-tailored nanomaterials, such as nanosized gold particles and Pd nanostructures suitable for hydrogen gas sensing.

ACKNOWLEDGEMENT

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