

Fabrication of Platinum Nanowires via Electrodeposition of Platinum-Phenothiazine Complex in freshly prepared Anodic Aluminium Oxide Template

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Porous anodic aluminum oxide film with self-ordered character, has been widely used as the template for fabricating nano-structural materials. In this study, highly ordered anodic aluminum oxide template was fabricated in phosphoric acid by the two-step anodic oxidation process. The anodizing voltage was maintained at 60 V. The results showed that 20 % phosphoric acid and 5 °C are suitable to prepare anodic aluminum oxide templates with a pore diameters of 130 nm. The fabricated anodic aluminum oxide films then subjected to post electrodeposition of Pt nanowires from freshly prepared Pt-phenothiazine complex, a forest of nanowires with a diameter nearly closed to the started anodic aluminum oxide pores sizes achieved. The morphology and surface structure of the anodic aluminum oxide films were examined before and after electrodeposition by; scanning electron microscopy, atomic force microscope and X-ray diffraction spectroscopy.

Key Words: Anodic aluminum oxide template, Platinum nanowires, Phenothiazine complexes, Pt-electrodeposition.

INTRODUCTION

Anodization of aluminum has become one of the most popular processing ways used for formation of porous structures with a pore diameter ranging from about 10 to over 300 nm¹. In recent years, PAA has generated interest as a candidate material for nanotechnology applications. The pore diameter, pore spacing and film thickness are all controllable through the anodization conditions, such as the choice of electrolyte, temperature and anodization time. The pore spacing may also be controlled through post anodization techniques such as chemical etching². Anodic aluminum oxide nanotubes have been extensively used as a template for the fabrication of nanowires and nanotubes as it possesses many desirable characteristics, including tunable pore dimensions, good mechanical strength and thermal stability. It is used to prepare self assembled arrays of a variety materials, metals, alloys and multilayers that can be incorporated into chemical sensors, solar cells and magneto-optic recording media³. While a range of well-developed deposition techniques have already been used to fabricate nano structures (*e.g.* electrochemical deposition⁴, electroless deposition⁵, chemical vapour deposition⁶). Electrochemical method extensively used to deposit metallic materials into nanopores of the templates in order to fabricate one dimensional nanostructures of wires and tubes⁷⁻⁹. We have

fabricated and tuned properties of platinum nanowires by electrodepositing in the pores of anodic aluminum oxide templates.

EXPERIMENTAL

Experimental methodology includes two parts:

Synthesis of anodic aluminium oxide: High-purity aluminum foil (99.98 %) with a thickness of 0.2 mm was cut into 32 mm in diameter circle were employed in present experiment to fabricate the anodic aluminum oxide template. The aluminium foil was first annealed at 500 °C for 2 h, degreased using acetone and ethanol, then rinsed in distilled water. Aluminium foil was electropolished in a mixed solution of HClO₄:C₂H₅OH = 1:4 (v/v) for 5 min to provide a smooth surface, then promptly rinsed with distilled water. The foils were then anodized in a homemade Teflon cell, where the aluminum was configured as anode and Pt foil as the cathode using a two-step oxidation process. In this work were fabricated using a 60 V DC potential with phosphoric acid (20 %) as the electrolyte at 5 for 30 min. The anodized alumina was subsequently dissolved in an etchant solution consisting of 6 wt % phosphoric acid and 1.8 wt % chromic acid, followed by a second oxidation step under the same conditions for another 2 h. Channels were finally cleared by dipping the templates into a 5 wt. % phosphoric acid solution at 20 °C for 10 min.

Fabrication of platinum nanowire arrays: Platinum-phenothiazine complex under investigated was synthesized as follows: The ligand dissolved in (15 mL) of dimethyl formamide (DMF) followed by addition drop by drop (5 mL) of metal salt (H_2PtCl_6). The resulting formation complex having dark brown colour. Electrodeposition of Pt nanowires was carried out at room temperature on the anodic aluminum oxide without removing its back (cathode) the Pt foil served as an anode and freshly prepared Pt-phenothiazine complex as electrolytic solutions. The pore size of the anodic aluminum oxide membrane and the platinum nanowires were examined using a scanning electron microscope (SEM, 54700, Hitachi) and atomic force microscope (AFM, AA 3000, angstrom). The crystallographic structures of the samples were identified using an X-ray diffractometer (XRD- 6000 with CuK_α -radiation, wave 1.5Å, 40 kV, 30 mA) at a scanning step size of $2\theta = 0.05^\circ$ in the 2θ range from 20° to 60° . Identification and study of this complex was carried out by percentage of metal analysis using AA-680 Shimadzu atomic absorption spectrophotometer. The electronic spectra of the prepared complex was recorded on a Shimadzu UV-160 spectrophotometer. FTIR spectra of the sample was recorded using IR prestige-21 spectrophotometer as CsI discs.

RESULTS AND DISCUSSION

Formation and characterization of anodic aluminium oxide templates

Current/voltage characteristics: The electrical current passing through the apparatus was measured throughout the second anodization of the aluminium sample. A typical current-time plot for this case is shown in Fig. 1. The current pattern, with a rapidly decreasing and pronounced minimum current, followed by a larger steady-state current. In this case, the minimum current was found to be about 38.1 mA/cm^2 , while the steady-state current was about 60 mA/cm^2 . It is believed the initially high current followed by its rapid descent is the result of the barrier layer formation, followed by pore nucleation and growth at the minimum current. The steady state current is caused by the oxide growth rate at the metal/oxide interface and the oxide etch rate at the solution/oxide interface at the pore bottoms being equal.

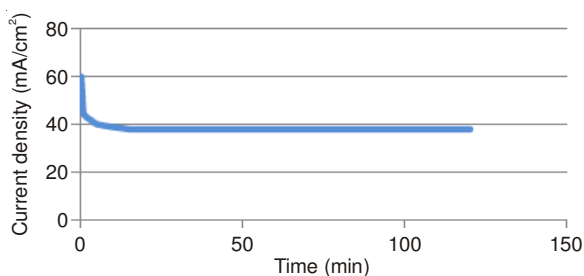


Fig. 1. The current time characteristic of anodic aluminum oxide film anodized in 20 % H_3PO_4 , 5 °C, 60 V

Atomic force microscope images: Anodic aluminium oxide template were characterized using atomic force microscope, with particular attention to the morphology of their top

surfaces. (Fig. 2) shows a micrograph of the top surface of a anodic aluminum oxide template produced from aluminum foil under an anodization voltage of 60 V. The resulting pores are fairly uniform in shape and diameter, narrow pore size distribution recorded by the same atomic force microscope test and the average diameter is 130 nm.

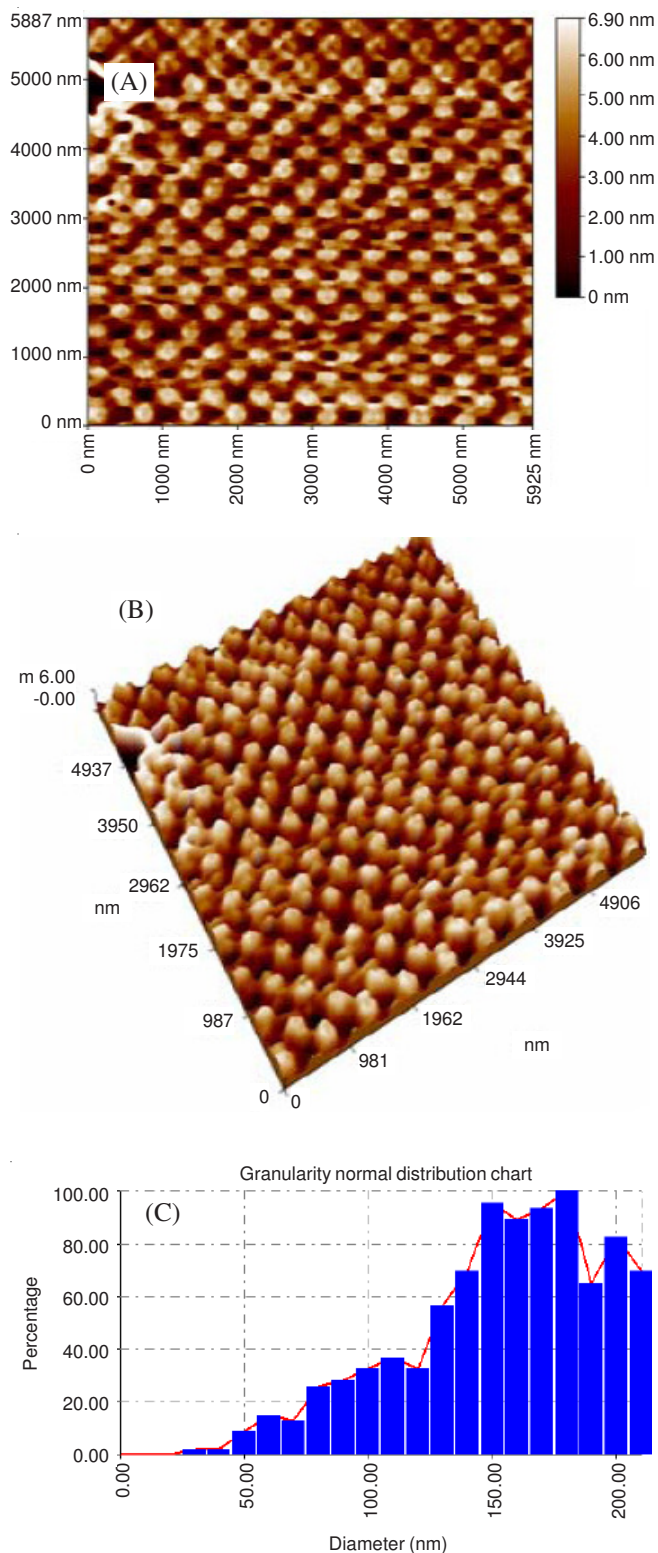


Fig. 2. Atomic force microscope topographic views (A) 2D and (B) 3D, (C) normal pore size distribution chart of AAO fabricated in 20 % Phosphoric acid at 5 °C for 2 h

Structural characterization: Fig. 3 shows the XRD spectra of anodic aluminium oxide which was obtained in phosphoric acid at 60 V; the change in the FCC to Monoclinic structure is noticeable at 111 and 200 plane, which correspond to 38.9 and 45.1 on the 2θ . The low broad peak at 38.9 and 45.1 might be indicative of amorphous aluminum oxide compound formed¹⁰. Where a peak of a maximum intensity corresponding to aluminium base metal appeared at this due to large pore diameter 200 nm.

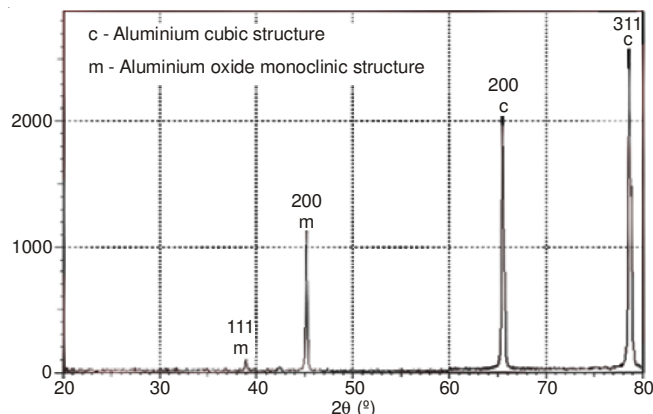


Fig. 3. XRD patterns of aluminum after anodizing for 2 h at 60 V in 5 % phosphoric acid electrolyte at 5 °C

Platinum nanowires fabrication

FTIR, UV-visible and atomic absorption spectroscopy: Platinum-phenothiazine complexes was freshly prepared to be used as a fuel to fabricate the Pt nanowire *via* electrodeposition procedure, FTIR, UV-visible and atomic absorption spectroscopy were conducted to examine the electronic structures of this complex. The results revealed the following suggested structures:



As expected, FT-IR gave good information about the complex behaviour of the ligand with various metal ion. The IR spectra of the free ligands (phenothiazine) have also been registered; characteristic frequencies of the C-N (at 1469 cm^{-1}), C-S (at 655 cm^{-1}). The IR spectra of the ligand also exhibited band at 3340 cm^{-1} and assigned to symmetrical stretching vibration for (N-H) group, while the bending vibration appeared at 1597 cm^{-1} . The C-H group asymmetrical stretching vibration appeared at 2924 cm^{-1} , while the symmetrical stretching vibration appeared at 2854 cm^{-1} . The C=C group appeared at 1570 cm^{-1} . The most important conclusions from the IR spectra of the isolated complex was: N-H band disappeared in IR spectra of the of the platinum-phenothiazine complex and accured the shift in another groups weak band stretching vibration of coordinate of metal-nitrogen appeared at 455 cm^{-1} , this result is very probable a consequence of L coordination as a monodentate ligand through nitrogen atom. A band observed around $(3468-3444) \text{ cm}^{-1}$ in the spectra of the complex, assigned to the $\nu(\text{OH})$, which refer to presence of H_2O uncoordination or out of sphere.

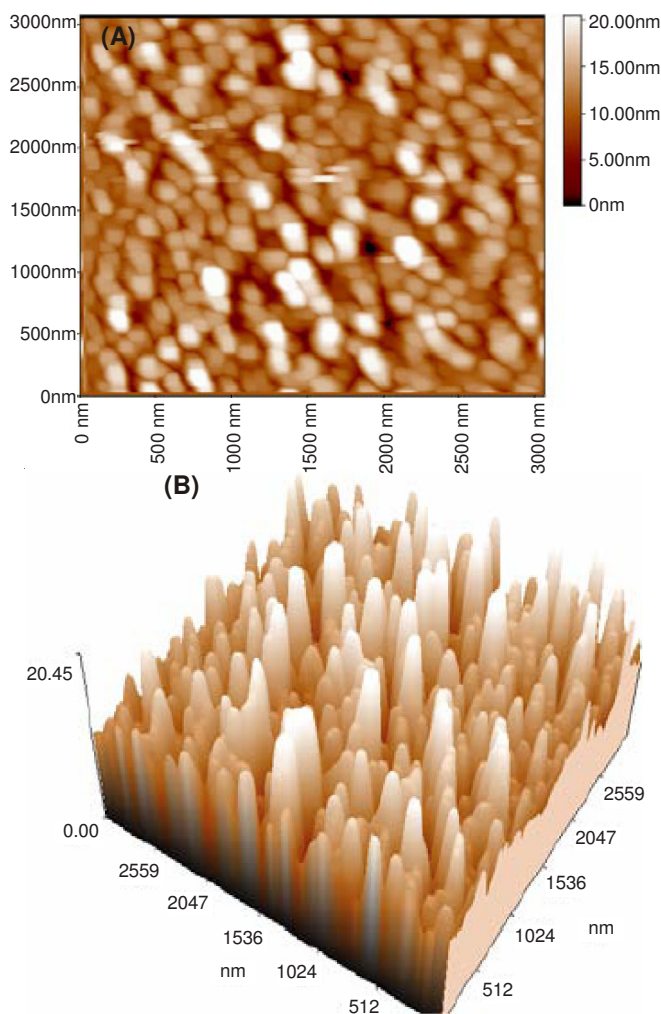
The electronic spectra of metal complex was recorded in their solution in DMF in the range 250-1100 nm at room temperature. The electronic spectrum of free ligand (L) exhibited

one main band. The absorption band appeared at 319 nm (31348 cm^{-1}) due to interligand ($\pi \rightarrow \pi^*$) transition. PtL: The platinum complex is diamagnetic as expected¹¹, the ground state suggested spin-paired octahedral stereochemistry geometry. The atomic ground state is ^5D . Two principle spin-allowed absorption bands are to be expected corresponding to the transition from the $^1\text{A}_{1g}$ and $^1\text{T}_{2g}$ excited states in addition, two bands assigned to the spin-forbidden singlet-triplet transition may be observed at lower energies than the spin allowed transition¹¹. The spectrum of the prepared brown platinum complex shows three bands in the visible region assigned to the $^1\text{A}_{1g} \rightarrow ^1\text{T}_{1g}$, $^1\text{A}_{1g} \rightarrow ^1\text{T}_{2g}$, $\text{L} \rightarrow \text{PtCT}$ transitions. The transition observed at $(10928.96) \text{ cm}^{-1}$ is assigned to the spin-forbidden transition $^1\text{A}_{1g} \rightarrow ^3\text{T}_{1g}$ ^{12,13}.

Atomic force microscope analysis of Pt nanowire:

Atomic force microscope micrograph of Pt nanowire is shown in Fig. 4. We can find out that the abundant and free defect nanowires have been prepared. The diameter of the nanowires is about 136 nm and approximately equal to those of the nanopores of anodic aluminum oxide template used in our experiments. The particle size distribution shown in (Fig. 4c).

SEM analysis of Pt nanowire array electrode: Fig. 5 a and b are the top views of the Pt nanowires at lower and higher magnifications respectively. The electrochemical plating was carried out for (10 min). According to the SEM images, the average diameter of the wire is (38 nm) and the distance from the



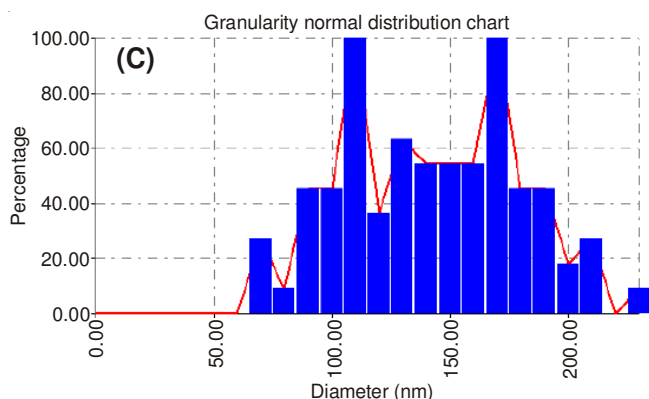


Fig. 4. Atomic force microscope top image of platinum nanowires array grown on the surface of an anodic aluminum oxide membrane by using electrodeposition methods: (A) 2D, (B) 3D, (C) particle size distribution of grown Pt nanowires

center of the wire to the center of the neighboring wire is (3 nm). They are consistent with the pore size and the inter-pore distance of the template. It is noticed that the Pt nanowires have about the same height and nearly flat top surfaces.

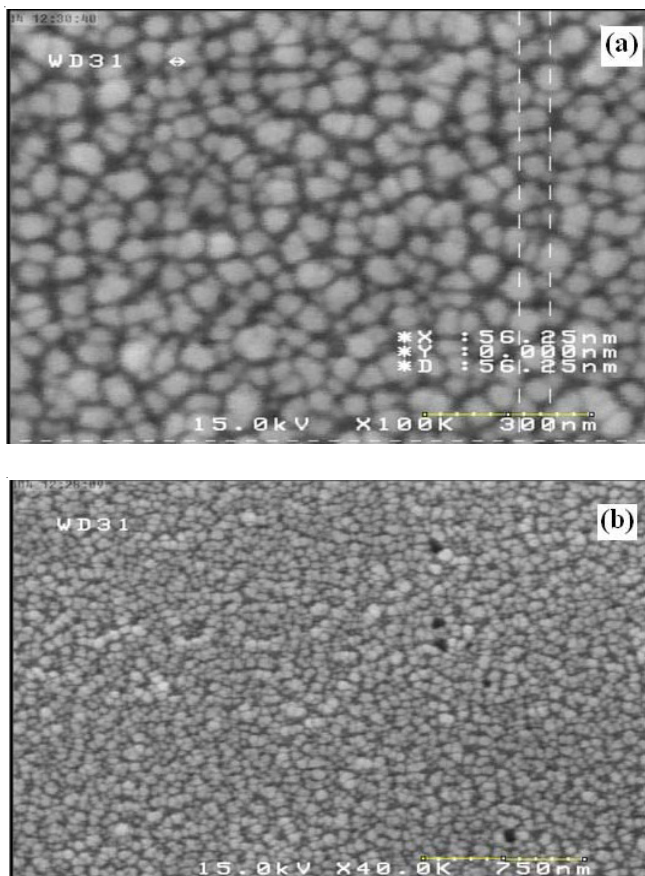


Fig. 5. SEM images of Pt nanowires synthesized with the anodic aluminum oxide template

XRD analysis of Pt nanowire arrays: The crystalline nature of the Pt nanowire was studied by powder X-ray diffraction. Fig. 6 shows the XRD diffractograms of Pt depo-

sition in anodic aluminum oxide membrane. This sample is all highly Pt(111) oriented. The Pt has a face-centered cubic structure. Here, the metal element Pt is deposited on Al_2O_3 substrates. Because metal elements possess higher surface free energy (e.g., Pt(111) is 3290 erg/cm^2 than the Al_2O_3 substrates.

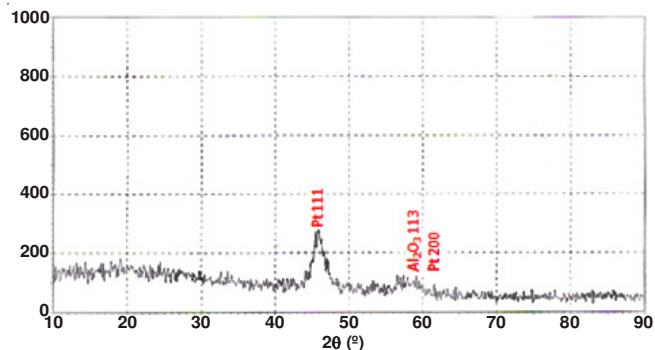


Fig. 6. XRD spectra of platinum nanowires prepared in anodic aluminum oxide membrane. The measurement was performed without removing the anodic aluminum oxide membranes

Conclusion

It has been demonstrated that the electrodeposition of platinum metal from phenathazine complex within a porous anodic aluminum oxide template yields highly ordered Pt-nanowires. This electrodeposition approach offers the obvious advantage that the deposition of particles starts at the aluminum cathode on the bottom of the nanopores and the length of Pt-wires can be easily controlled by the deposition time. We believe that this approach offers a new and convenient route to fabricate metal Pt-wires arrays and may find potential application in fuel cell and sensing devices and so on.

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