

Direct Electrochemical Fabrication of Metallic Nanopillar Array on Au Electrode Surface by the Template Technique

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This letter presents a novel, simple approach for direct electrochemical fabrication of metallic (Au or Pt) nanopillar array on gold electrode surface, employing cysteamine as a molecular anchor and anodic aluminum oxide as template without any sputtered metal as electrical conductor. The nanopillar arrays were grown directly on the electrode surface, and the prepared nanopillar array electrodes were used directly and easily to the electrochemical application.

Nanoelectrode ensembles (NEEs) are important in electrochemistry and electroanalysis because of interesting and unusual electrochemical phenomena that are predicted to occur.^{1,2} Owing to their favorable electrochemical properties, nanoelectrode systems have potential applications in the creation of organized nanodevices such as data storage systems, sensor arrays, and electrochemically controlled drug delivery systems.³⁻⁵ To date, several approaches have been proposed and applied to the preparation of NEEs, such as, the "polycarbonate template synthesis" approach,^{2,6} the "microphase separation" approach,⁷ the block copolymer self-assembling method,^{1,8} the "hexagonal (H_1) lyotropic liquid crystalline phase" method,⁹ the "template-directed seeding growth" approach,¹⁰ and the colloidal nanoparticle self-assembly techniques.¹¹

Use of anodic aluminum oxide (AAO) nanoporous membrane as template is an approach to fabricate nanostructured materials. Anodic alumina is a self-ordered nanoporous membrane that consists of an array of parallel straight nanopores of almost uniform diameter and length.^{12,13} Using this template, one can not only make nanometer features in the size from ≈ 10 to > 100 nm but also modify the dimensions by changing the porous geometry of AAO nanopores. In most of the studies, however, the focus has been on the preparation of nanowire and nanorods using AAO membranes as templates. The applications of these nanoporous structures in the design and manufacture of arrays of nanosized features have been explored to a less degree and have begun to attract attention in the fabrication of electronic, magnetic, and photonic devices.¹⁴⁻¹⁷ A critical issue to make arrays is to create individually separated nanopillars by overcoming the sagging of nanorods or nanowires after the removal of anodic alumina templates. Herein, we report a simple method of direct electrochemical fabrication of metallic (Au or Pt) nanopillar array on Au electrode surface using AAO as template and cysteamine as a molecular anchor. The proposed approach has some attractive features including the direct growth of the nanopillar array on the surface of conducting electrodes and the easy and direct use of the prepared nanopillar array electrodes to electrochemical application.

The whole preparation process is outlined in Figure 1. A cleaned gold electrode (AuE, 99.99%, 1-mm diameter) was first

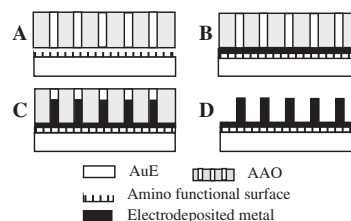


Figure 1. Schematic view of the procedure of direct electrochemical fabrication metallic nanopillar arrays electrode. (A) AAO film on amino functional AuE surface; (B) After metal deposition on amino functional AuE surface; (C) After metal deposition in the AAO; (D) After removal of AAO template.

soaked in 20 mM deoxygenated aqueous cysteamine solution for 8 h at room temperature in darkness. The resulting cysteamine monolayer-modified electrode was thoroughly rinsed with water to remove physically adsorbed cysteamine. The anodic alumina template membranes were purchased from Whatman Corp. with quoted pore diameter 100 nm. The AAO membrane without any sputtered metal as electrical conductor was placed on the wet AuE with the electrolyte. This membrane was pressed close to the electrode surface in a home-made electrochemical cell with the polytetrafluoroethylene holder (Figure 1A).

The electrochemical deposition of gold or platinum was performed in a conventional three-electrode system in 5 mM H_2AuCl_4 or $H_2PtCl_6/30$ g/L H_3BO_3 electrolyte solution with the modified AuE as working electrode, a platinum wire as counter electrode and a saturated calomel electrode (SCE) as reference electrode. Gold or platinum particles were deposited under a galvanostatic current density of $7 \mu A cm^{-2}$ for 10 h. At the initial stage, the electrolyte solution for electrochemical deposition diffused to the AuE surface through AAO membrane. Then, gold or platinum particles were directly deposited on the amino-functional surface of the AuE surface, so that a gold or platinum film was formed in the interspace between the AAO membrane and the electrode surface (Figure 1B). We found that wetting the AuE surface prior to the application of the AAO membrane can result in more even gold or platinum deposition because there was an even layer of electrolytes between the electrode surface and the AAO membrane. The gold or platinum film formed between the AAO membrane and the electrode surface acts as a basis for the subsequent deposition of gold or platinum particles, and it is necessary because AAO membranes have interconnected pores near the surface.¹⁸ Once the electrodeposited gold or platinum particles filled the interspace between the AAO membrane and the electrode surface, they began to be deposited into the pores of the AAO membrane (Figure 1C). After the deposition was complete, the AAO templates were removed in a NaOH solution to expose a freestanding array of metallic nanopillar on

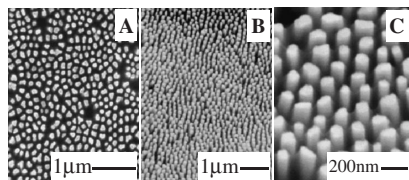


Figure 2. Field emission SEM images of the platinum nanopillar arrays electrode after AAO template removal by chemical etching: A) top view; B) side view; C) side view, high magnification.

the AuE surface (Figure 1D). The mercapto group of adsorbed cysteamine layer on the AuE surface bond with Au to form a strong Au–S bond. When gold or platinum is electrochemically deposited on the electrode surface, the strong affinity of the amino group of cysteamine for gold or platinum helps to form a gold or platinum film between the AAO membrane and the electrode surface. So, the adsorbed cysteamine layer on the AuE surface acts as a molecular anchor, which leads to individually separated metallic nanopillars by overcoming the sagging of nanorods after the removal of AAO templates.

The morphology of the platinum nanopillar array electrodes after AAO template removal by chemical etching was examined under a field emission-scanning electron microscope (SEM). Figure 2A is a top view of the platinum nanopillars. The film appears to contain uniform white dots all across the AuE surface. Figure 2B is a SEM micrograph of the arrays taken with the specimen stage tilted at $\approx 30^\circ$ with respect to imaging electronic beam. It revealed that the white dots are actually the tips of uniform nanopillars oriented perpendicularly to the AuE surface. These nanopillars are essentially separate from each other. A SEM micrograph of the arrays at a higher magnification is shown in Figure 2C. The resulting platinum nanopillars had same dimensions as the pores in the AAO template, with an average diameter of ≈ 100 nm.

The electrochemical property of the platinum nanopillar array electrodes prepared by the above controlled processes was investigated by linear-sweep voltammetry using the reversible redox couple $[\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}$. It is well known that under normal conditions, diffusion dynamics at microelectrodes is quite different from that at macroelectrodes.¹⁹ Diffusion layer to macroelectrode with a large surface area is planar and hence mass transport efficiency is low and the diffusion process is attributed to a nonsteady state. However, diffusion to a microelectrode is rapid ensuring a high mass transport coefficient, and may reach a steady state in a very short time. Figure 3 shows a comparison of the linear-sweep voltammograms obtained at the plat-

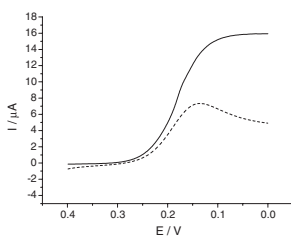


Figure 3. Linear-sweep voltammograms in 10 mM $\text{K}_3\text{Fe}(\text{CN})_6$ + 0.1 M KCl of the platinum nanopillar arrays electrode (dash line) and the polished platinum electrode (solid line) (vs SCE). Scan rate: 10 mV/s.

inum nanopillar array electrodes and a polished platinum electrode of the same diameter. The voltammogram recorded at the platinum nanopillar array electrodes differs from that recorded at the polished platinum electrode. An almost S-shaped voltammogram was observed on the platinum nanopillar array electrodes because of the radial nature of diffusion associated with nanopillar arrays. The current at platinum nanopillar array electrodes are much higher than that at the polished platinum electrode. The difference in the current reflects the effective active surface areas that are accessible to the electrolytes and the edge-effect of microelectrodes. Apparently, the platinum nanopillar array electrodes have a higher effective surface area, which is desirable for high efficiency and sensitivity of many devices.

In summary, we have developed a novel and simple method for direct electrochemical fabrication of metallic (Au or Pt) nanopillar array on Au electrode surface using cysteamine as a molecular anchor and AAO as a template without any sputtered metal as electrical conductor. The proposed approach can directly and easily prepare metallic nanopillar array electrodes, and it would have great potential applications for the fabrication of the microsensors and other microelectronic devices. The applications of these nanopillar array electrodes in biosensors are currently in progress.

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