Nanopillar Arrays with Superior Mechanical Strength and Optimal Spacing For High Sensitivity Biosensors

Venkataramani Anandan,[1] Yeswanth L Rao[1] and Guigen Zhang[1,2,3] *

[1]Micro/Nano Bioengineering Lab, Department of Biological and Agricultural Engineering
[2]Nanoscale Science and Engineering Center, [3]Faculty of Engineering
University of Georgia, Athens, GA 30602
*Correspondence addressed to: gzhang@engr.uga.edu

ABSTRACT

The fabrication of metallic nanopillar structures and their application as electrodes in electrochemical processes are discussed in this report. Structures of arrays of vertically standing nanopillars were fabricated by electrodeposition technique with the use of porous anodic alumina as masking templates. To explore the possibility of using these nanostructures for biosensing applications, they were evaluated mechanically and electrochemically. Mechanically, these standing nanopillars should have sufficient strength to sustain the capillary forces caused by the nanopillar-liquid interactions. Electrochemically, these standing nanopillars should provide increased sensitivity in an electrochemical process. Our results showed that the nanopillars were mechanically stable during the electrochemical process and the electrodes with nanopillars exhibited increased electrochemical response as compared with flat electrodes.

Keywords: nanopillars, electrodes, mechanical strength, electrochemical sensitivity, biosensors, porous anodic alumina.

1. INTRODUCTION

Recently, many types of vertically aligned nanostructures, such as carbon nanotubes [1, 2] and nanorods have been fabricated for potential use in biosensors development. In general, electrochemical biosensors utilize electrodes made of gold, silver, graphite or carbon based materials. When nanostructures are incorporated in these electrodes, there will be tremendous increase in their surface area without affecting too much their overall dimensions, thus making it possible to enhance the sensing capabilities for those biosensors. The ability of carbon nanotubes to improve the electrochemical sensing capability has been reported [3].

To date, many nanostructures have been fabricated using chemical vapor deposition (CVD) [4], physical vapor deposition (PVD) [5] and template based electrodeposition technique [6-8]. Lately, evidence has emerged to reveal that the nanotubes and nanorods developed by CVD and PVD could not sustain the capillary forces caused by the nanostructure-liquid interactions [4, 5]. Upon water contact, these nanotubes and nanorods deformed severely and exhibited nano-carpet effect [5], thus posing a serious problem for their application in functional biosensors devices. The majority of the biosensors will have to be exposed to an aqueous environment. Therefore, to be useful as a component in a biosensor, these nanostructures need to have sufficient mechanical strength to overcome the capillary forces.

To address this issue, instead of using a vapor based deposition technique we have developed an aqueous based deposition technique (i.e., electrodeposition) to fabricate nanostructures. We believe that the nanopillar structures fabricated in an aqueous environment by electrodeposition technique will possess sufficient mechanical strength to withstand the capillary interaction in an aqueous environment. To do so, we will use porous anodized alumina (PAA) sheets as templates and electrodeposit metallic materials through the pores of the PAA templates to form structures of vertically aligned nanopillars.

2. MATERIALS AND METHOD

2.1 Reagents

For fabricating gold and silver nanopillar structures, gold potassium cyanide (OROTEMP24) and silver potassium cyanide (ACR1025) solutions (Tehnic Inc.) were used. For the PAA templates, porous anodic alumina discs (Whatman Inc.) were used. For electrochemical analysis, Na_2SO_4 and $K_4Fe(CN)_6$ (J.T.Baker) were used. All solutions were prepared using distilled water.

2.2 Fabrication of Films of Nanopillars

Prior to electrodeposition, a thin layer of gold (about 150nm thick) was sputter-coated on one side of PAA

discs to provide the conductive contact as well as the supporting base for the nanopillars. To start the deposition, a gold coated PAA disc was connected to the anode (working electrode) of a three-electrode system and immersed in OROTEMP24 solution for gold deposition. Pt wire gauze was used as the counter electrode and Ag/AgCl as the reference electrode. During deposition, gold was deposited into the pores of the PAA disc from the uncoated side under a constant current density of 5mA/cm^2 for 5 minutes at 65°C. The height of the nanopillars was controlled by the deposition duration. After deposition, the PAA template was removed by dissolving it in a 2.0M NaOH solution. After the template removal, structures with arrays of standing gold nanopillars were obtained. The morphology of the nanopillar structures was characterized using scanning electron microscope (SEM).

2.3 Mechanical Durability

To evaluate the mechanical strength of these nanopillars, a water droplet test was performed. The details of the test is described elsewhere [5]. In brief, a water droplet was placed on the top surface of a nanopillar structure and allowed it to dry for several hours. After that, the morphology of the nanopillars was examined under SEM and a comparison was made with SEM images of the same nanopillar structure obtained prior to the water droplet test.

2.4 Electrochemical Measurements

The electrochemical responses of the nanopillar structures were investigated in electrolytes of either Na_2SO_4, or Na_2SO_4 supplemented with $K_4Fe(CN)_6$. As a control, a flat gold electrode with equal exposed area was also tested. Cyclic voltammetric tests were performed at a sweep rate of 100mV/s at a potential range between -0.4V and 0.1V, and chronoamperometric tests were conducted at a constant applied potential of 0.25V. All the tests were performed in a conventional three-electrode cell using Solartron 1480 multistat with Pt wire as the counter electrode and Ag/AgCl as the reference electrode.

3 RESULTS AND DISCUSSION

3.1 SEM Analysis

Figure 1A shows an SEM image of a gold nanopillar structure. These individual nanopillars have dimensions of 150 nm in diameter and 4.5 μm in height with an aspect ratio of 30. Clearly, these nanopillars exhibited slight bunching at the top. We believe this bunching phenomenon can be attributed to the combined effects of the high aspect ratio in these nanopillars and the capillary force exerted on the nanopillars by the electrolyte solution during the removal of PAA templates. A higher aspect ratio will

reduce the flexural rigidity of these nanopillars. When the aspect ratio is low, such a bunching deformation was not present. As shown in Figures 1B and 1C, when the aspect ratio is at 10, both the silver nanopillars (Fig.1B) and copper nanopillars (Fig.1C) did not show any deformation, unlike the gold nanopillars with an aspect ratio of 30 (Fig.1A).

After being subjected to the water droplet test, these nanopillars with high aspect ratio (30) did not show any further deformations, unlike the nanorods fabricated using PVD technique [5]. Figure 1D shows the SEM image of the gold nanopillar arrays after going through electrochemical tests several times. Clearly, no visible change in the morphology of the nanopillars can be seen. This result indicates that the nanopillar arrays fabricated using electrodeposition have sufficient mechanical strength to withstand the capillary interaction forces in aqueous conditions.
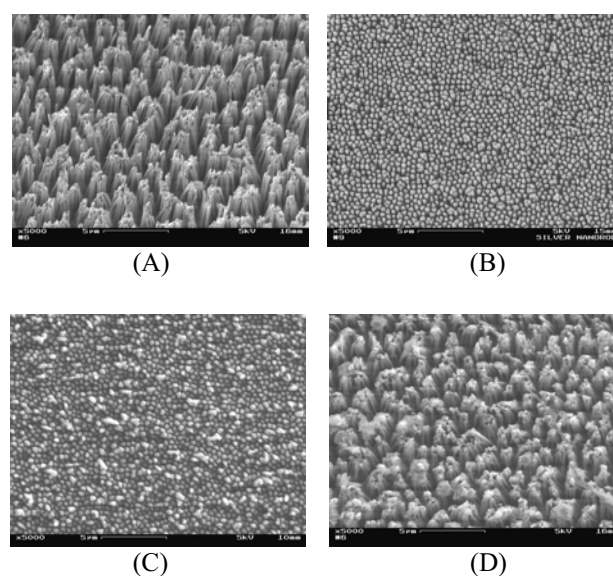

Figure-1. (A) Gold nanopillar arrays (aspect ratio =30) immediately after deposition; (B) Silver nanopillar arrays (aspect ratio = 10) as deposited; (C) Copper nanopillar arrays (aspect ratio = 10) as deposited; (D) Gold nanopillar arrays (aspect ratio = 30) after the water droplet test and several electrochemical tests.

3.2 Cyclic Voltammetry Response

Cyclic voltammetry was performed on gold nanopillar electrodes and gold flat electrodes in 1M Na_2SO_4 for evaluating the electrolytically active surface area. Both the electrodes have the same exposed surface area of 16mm^2. Figures 2A and 2B show the voltammograms of gold nanopillar and flat electrodes, respectively. It is clear from the voltammograms that the nanopillar electrode exhibits a larger charging current compared with the flat surface electrode. The charging current obtained at gold nanopillar electrode is approximately 100 times higher than that of the flat electrode. This indicates that the electrolytically exposed

surface area of the nanopillar arrays is about 100 times larger than that of the flat electrode surface because the charging current is directly related to the actual exposed surface area of the electrode. Based on the SEM image in Fig.1A, with the consideration of the fact these gold nanopillars have a high aspect ratio of 30, the actual surface area increase due to these nanopillar structures is estimated to be at the same magnitude (about 80-100 times).
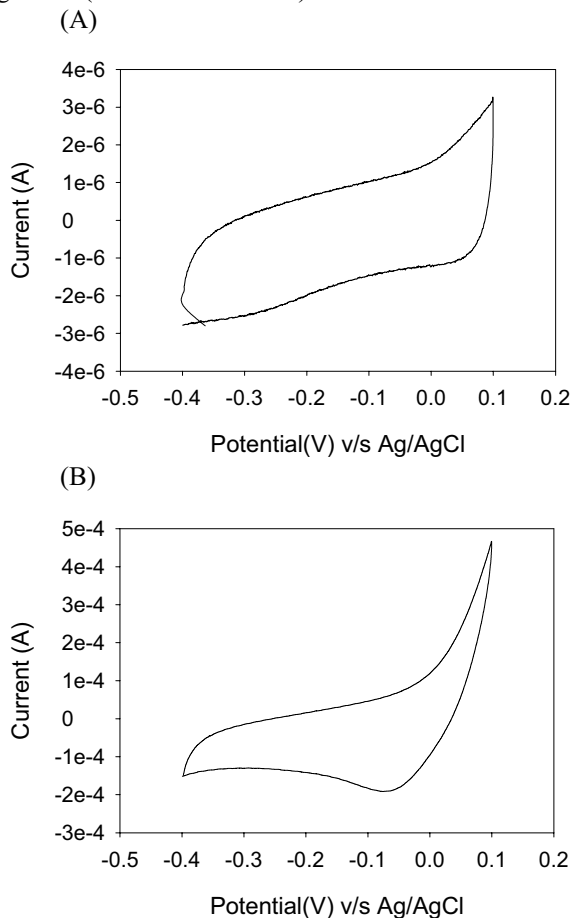
(A)

(B)

Figure-2. (A) Cyclic voltammetry response of gold flat electrode; (B) Cyclic voltammetry response of gold nanopillar array electrodes. Both in 1M Na_2SO_4 electrolyte.

3.3 Chronoamperometric Response

To explore the sensitivity of nanopillar structures in electrochemical processes, we performed chronoamperometry tests. These chronoamperometric tests were performed at the onset potential of oxidation of $K_4Fe(CN)_6$. To determine the onset potential of oxidation of $K_4Fe(CN)_6$, we first performed a cyclic voltammetry test with a flat gold electrode in 1mM $MK_4Fe(CN)_6$ and $0.5MNa_2SO_4$ solution. Figure 3 shows the cyclic voltammogram. From this result, the onset potential of oxidation of $K_4Fe(CN)_6$ was determined to be 0.25V vs. Ag/AgCl. We then used this as the step potential for the chronoamperometric tests.
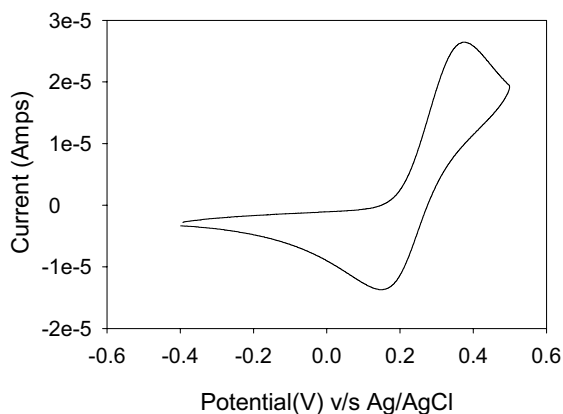

Figure-3. Cyclic voltammetry response of gold flat electrode in 1mM M $K_4Fe[CN]$ and 0.5M Na_2SO_4.
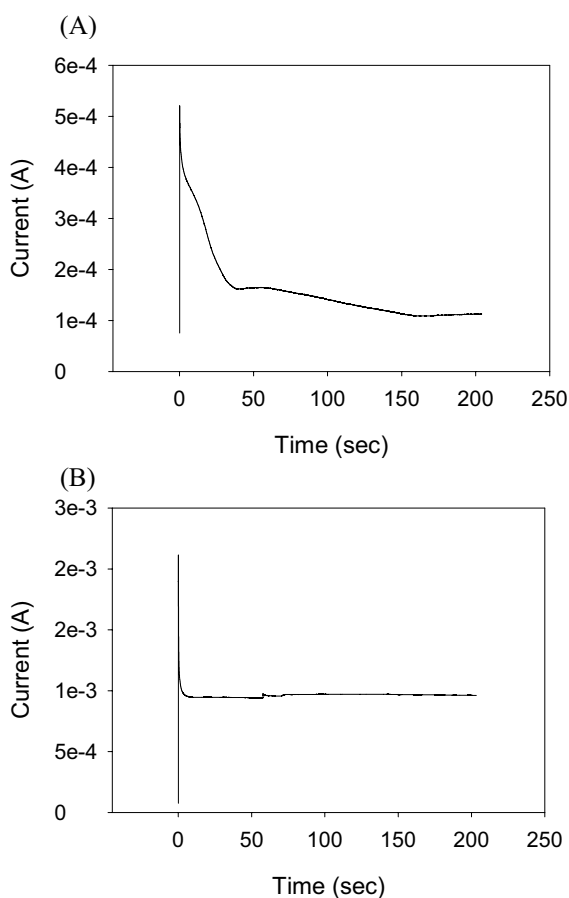
(A)

(B)

Figure-4. (A) Chronoamperometric response of gold flat electrode; (B) Chronoamperometric response of gold nanopillar electrode. Both in 0.5M Na_2SO_4 and 1mM $K_4Fe[CN]_6$.

Figures 4A and 4B show the chronoamperometric responses of the gold flat electrode and nanopillar array electrode, respectively, in 1mM $K_4Fe[CN]_6$. It is seen that the steady state current with nanopillar electrode is about 8 times higher than that with flat electrode. This increase in steady state current will determine the enhanced sensitivity

in biosensing applications due to the incorporation of nanopillar array structures into the electrodes.

4. CONCLUSION

In this report, we have fabricated metallic nanopillar array structures which could withstand aqueous interaction forces. We also demonstrated that the nanopillar arrays do not exhibit any deformation after the electrochemical processes. We observed about 8 times increase in steady state current output in gold nanopillar arrays with respect to the flat surface gold electrode. These results show that these nanopillar array structures are viable for use in high sensitivity sensors.

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