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Fabrication of gold nanowires (GNW) using aluminum anodic oxide (AAO) as a metal-ion sensor

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Abstract−Anodic aluminum oxide (AAO) is a self-organized nanostructured material that contains high-density, uniform cylindrical pores that are aligned perpendicularly to the surface of the materials. Therefore, AAO nanostructures are very useful templates for applications such as electrochemical detection of metal ions and fabrication of nanowires or nanotubes. We fabricated an AAO template thorough two-step anodizing as an electrochemical sensing electrode. Gold nanowire (GNW) was prepared via in-situ electrochemical deposition on the AAO template. Then, the GNW/AAO electrode was functionalized with 1,6-hexadecanethiol. In the electrochemical analysis, the electron signals of the GNW/AAO changed by combining mercury ion and the thiol group on the electrode. The amperometric response was determined in the presence of the mercury ions. Consequently, a proof-of-concept test showed that the GNW/AAO electrode is a possible tool that can act as a heavy metal ion sensor.

Keywords: Nanostructures, Microstructure, Electrochemical Measurements, Electron Microscopy

INTRODUCTION

Nanomaterials have been found to have unique physicochemical properties that allow them to be used in many fields, including for sensors, catalysts, and biological labeling [1]. Considerable efforts have focused on the fabrication of novel nanostructures and devices, and many research groups have been intensively working to such ends. There are several methods that can be used to fabricate nanomaterials including the sol-gel process, chemical vapor deposition, and seed-mediated methods [2,3]. In particular, templating methods seem to be the most popular for fabricating nanomaterials, including nanowires, nanodots, and nanotubes. Commonly used templates are polycarbonate membranes, carbon nanotubes, and anodic aluminum oxides (AAO). Of these, the most used template is that of anodic aluminum oxide. Masuda et al. [4] reported that AAOs have received a great deal of attention in the last few decades, and that these are widely used as templates to prepare various nanostructures. AAOs have distinctive properties that include good reproducibility, cost-effectiveness, and easy control of pore diameter and length via control of the anodizing condition [5,6]. Due AAO having nano-scale pores, many researchers have pursued further studies using AAO templates.

We prepared the AAO by the two-step anodizing method, and then fabricated a gold nanowire (GNW) on the AAO template. A GNW has a large surface area and more electroactive sites when compared to bare gold particles, and thus it has the ability for fast transfer of the electrons and high electrocatalytic activity. Even though several studies have fabricated nanowires using an AAO template [8-11], few studies have done so for metal ion detection using GNW/AAO electrodes. Therefore, we fabricated a GNW/AAO substrate to be used as a sensor to detect mercury ions. For electrochemical sensing, the GNW/AAO electrode was modified with 1,6-hexadecanethiol (HDT), which has a high affinity with mercury ion [12] and is characterized by measuring the current change according to the concentration of mercury ion. Consequently, we tested the possibility of using HDT/GNW/AAO electrodes as metal ion sensors via electrochemical analysis.

EXPERIMENTAL

1. Fabrication of Anodic Aluminum Oxide Template

All chemical reagents were purchased from Sigma-Aldrich. The AAO templates were fabricated via two-step anodizing [4]. The high-purity aluminum foil was cut into $1\times5\times0.0025\ \text{cm}^3$. Prior to the electrochemical process, the aluminum foil was degreased with acetone and was rinsed in deionized water. Then, aluminum foil was annealed in 500 °C for 5 hr. Subsequently, the foils were degreased in 0.1 M NaOH and 0.1 M HNO_3 at 40 °C for 5 min, rinsed with deionized water, and then electropolished in a 1 : 4 mixture by volume of $HClO_4$ and C_2H_5OH at 20 V for 2 min. The first anodizing process was under constant voltage at 40 V in 0.3 M oxalic acid at 1 °C for 12 hr. Then chemical removal of the anodic oxide layer was performed in a mixture of 6 wt% phosphoric acid and 1.8 wt% chromic acid. The second anodizing process was performed in the same conditions as the first anodizing. Then the AAO was dipped in 0.1 M phosphoric acid at 30 °C for 1 hr for the pore widening process

2. Fabrication of Gold Nanowire/AAO Electrode

Fig. 1 shows a simple procedure for fabrication of HDT/GNW/AAO electrodes to detect mercury ion. For electro-deposition of

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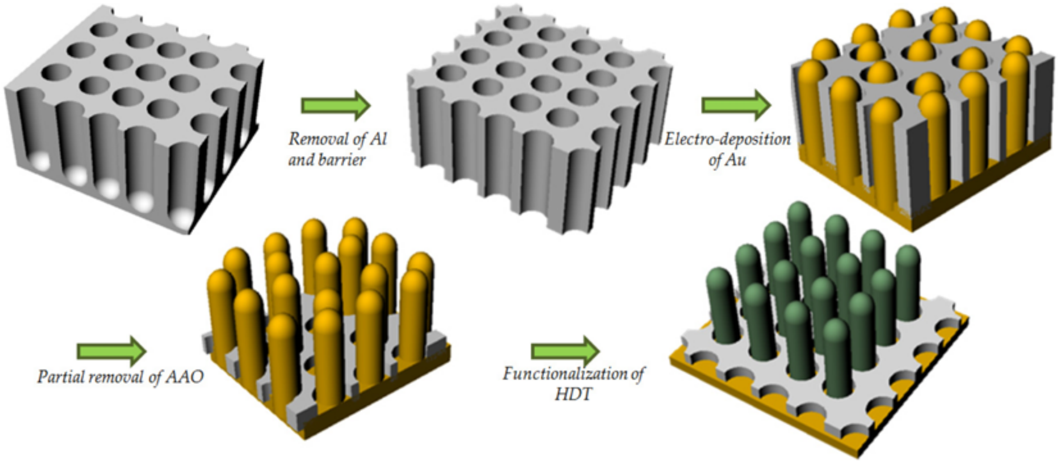

Fig. 1. Fabrication schematics of HDT/GNW/AAO electrodes for detection of metal ions in the aqueous phase.

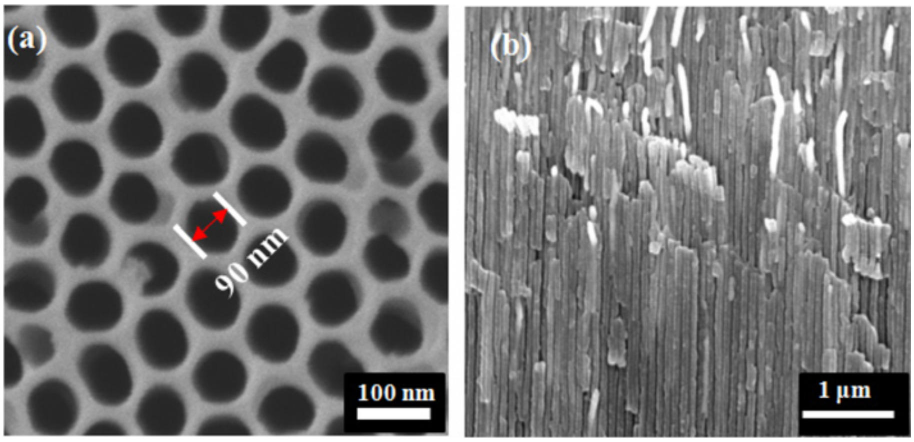

Fig. 2. SEM images of (a) top-view of AAO and (b) side-view of GNW/AAO.

GNW within AAO, a gold thin film was deposited on a side of the AAO template (as the electrode) by vacuum evaporation. Prior to electro-deposition, the remaining aluminum was removed by dipping the template in a saturated $CuCl_2$ solution [13]. Subsequently, the H_2PO_4 solution was used to remove the barrier layer [14]. To prepare GNW in AAO, the electro-deposition was performed using 1 wt% $HAuCl_4$ containing 0.5 M $HClO_4$ electrolyte. The electro-deposition potential was of about −0.18 V for 20 min [10]. For the electrochemical sensing electrode, the GNW/AAO electrode was dipped into 10 mM HDT for 12 hr.

3. Characterization

The morphology and size of the resulting materials were observed by using a field emission scanning electron microscope (FE-SEM, JEOL JSM-6700F) equipped for energy dispersive analysis (EDS). All electrochemical analyses were performed using a potentiostat (Won-A Tech, WEIS-500).

RESULTS AND DISCUSSION

The AAO template was prepared by using the typical two-step anodizing method. The AAO properties, such as shape, size, and length, are easily controlled by manipulating the experimental conditions [5,6]. After AAO was fabricated within the oxalic acid electrolyte, the AAO template was obtained, as shown in Fig. 2(a). The AAO template is arranged hexagonally and the uniform pores are aligned vertically in the aluminum foil through the two-step anodizing. The pore diameter of AAO is of about 90 nm and the length is of about 8 μm. The AAO template was fabricated by two-step anodization, namely, field-enhanced oxide dissolution mechanism. In the first anodization step, an irregular pitch was produced on Al foil, and oxide layer was removed by etching solution (mixture of 5 wt% phosphoric acid and 1.8 wt% chromic acid). And then, the second anodization was conducted under the same anodizing condition as the first step. The regular hexagonal structures then form on the aluminum surface, and the second anodizing step generates regular and dense pores with a hexagonal structure [14].

To use AAO as the conducting electrode, the remaining aluminum substrate was partially removed in the $CuCl_2$ solution. Compared to the commonly used $HgCl_2$, the $CuCl_2$ solution is more environmental friendly since no hazardous products (Hg^0) are produced [13]. Fig. 2(b) shows the vertically aligned GNW in the AAO template. $[AuCl_4]^-$ ions are then impregnated at the bottom edges of the AAO pores, and the Au ions receive electrons to become Au atoms. The nanowires begin to grow out of the AAO pores. The

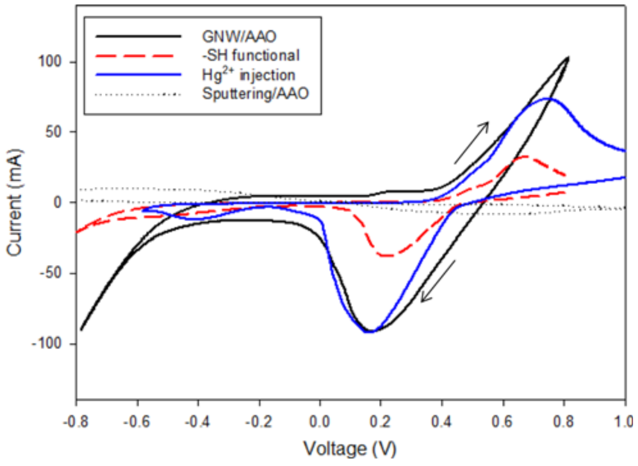

Fig. 3. Cyclic voltammogram of HDT/GNW/AAO electrodes immobilized with HDT in 0.5 M H_2SO_4 (scan rate: 100 mV/s).

diameter and length of the GNW is of about 90 nm and 3 μm, respectively. Note that the pore size and length are determined according to the AAO dimensions.

The electrochemical behavior of the GNW/AAO electrodes was characterized in 0.5 M H_2SO_4 using cyclic voltammetry (CV) (Fig. 3). Even in conditions of a low pH, the GNW/AAO electrode is not affected due to its corrosion resistance. All the electrochemical analyses were carried out in a standard three-electrode system. To compare the CV features, the Au sputtered on the AAO and Au/AAO electrodes was obtained. The Au/AAO electrode showed a small background current (dotted line in Fig. 3). It was found that the GNW/AAO electrode had a large surface area compared to that of the Au/AAO electrode. This indicates that the GNW/AAO electrode has higher electron conductivity than the Au/AAO electrode.

The anodic peak of the GNW/AAO appears at 0.15 V in the range of potential from −0.8 to 0.8 V (black line in Fig. 3). The redox peak takes place between the Au^0 and $[AuCl_4]^-$ ion complex. The redox peak of the HDT/GNW/AAO electrode shifted toward the positive potential, and the morphology was converted irreversibly during the combined functional group (red line in Fig. 3). The peak change of the cathodic current indicated that mercury ions combine with the electrodes on the mercapto group (SH) in HDT. The anodic peak of the HDT/GNW/AAO appears at 0.21 V, and the cathodic peak at 0.67 V. As shown by the blue line in Fig. 3, the electrical signals suggest that mercury ions combined with the thiol group on the GNR with oxo-bridge bonding [Au-$(CH_2)_6$-S-O-Hg-O-S-$(CH_2)_6$-Au].

The as-made GNW/AAO electrode was modified with HDT. The mercapto group can be used to detect many heavy metal cations, such as Ni^{2+}, Pb^{2+}, Mn^{2+}, Cd^{2+}, Zn^{2+}, Fe^{2+} and Hg^{2+} [15,16]. Of these, the mercapto group has a strong affinity to mercury ions [17]. To detect mercury ions, we measured the current changes induced by the bonding between the mercury ions and the adsorption sites using chronoamperometry, which is a method to measure the current generated through the electronic exchange. The current change occurred spontaneously when it was bound to the mercury ion charge and the functional group charge. Therefore, measuring the electrochemical response shows that it is possible to immediately check for the presence of mercury ions.

10 μM of mercury ions were added into a working vessel. The amperometric response of the HDT/GNW/AAO electrode showed a stair-shaped current change, as in Fig. 4(a). In our previous research [18,19], porous gold electrodes with a large surface area were effectively working as metal ion sensors. Powder type of porous gold could be used as electrode after plating on the ITO glass through calcination at 150 °C. This durability of electrode is weak because cracks easily occur in small external factors. Whereas, AAO template acts as support for GNR, and thus GNR/AAO electrode has the advantage of maintaining the structure which is enhanced durability of the electrode. In this work, GNW/AAO with a geometrically large surface compared to Au/AAO showed a higher performance for electrochemical detection of metal ions in an aqueous phase. When compared to HDT/GNW/AAO electrodes, HDT/Au/AAO electrode did not show an amperometric response [Fig. 4(b)]. In Fig. 5, the current density is plotted against the corresponding mercury ion concentration, showing a linear response. The linear range of the HDT/GNW/AAO electrode is from 10 to 70 μM with R^2 of 0.9741. Therefore, this experiment confirmed that the as-made HDT/GNW/AAO electrodes were adequate for use as mercury ion sensors due to the real-time change in the electrical signals.

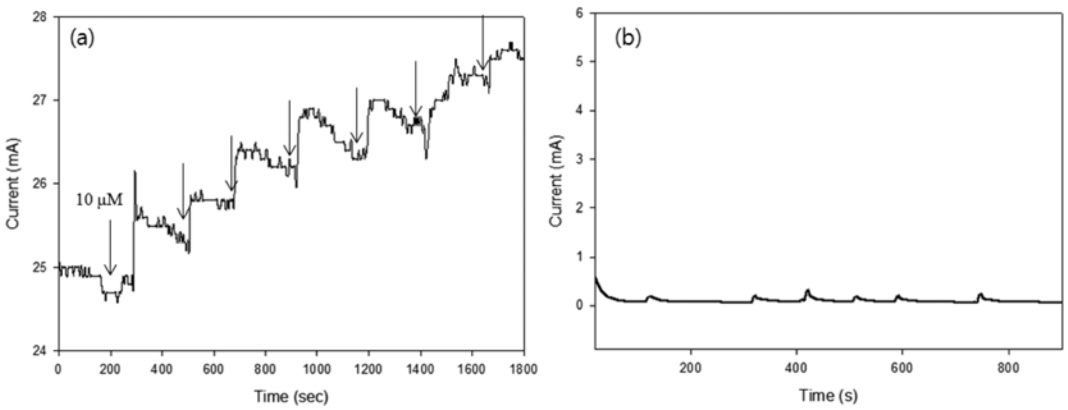

Fig. 4. Current change with mercury ion addition using (a) HDT/GNW/AAO electrode and (b) HDT/Au/AAO electrode.

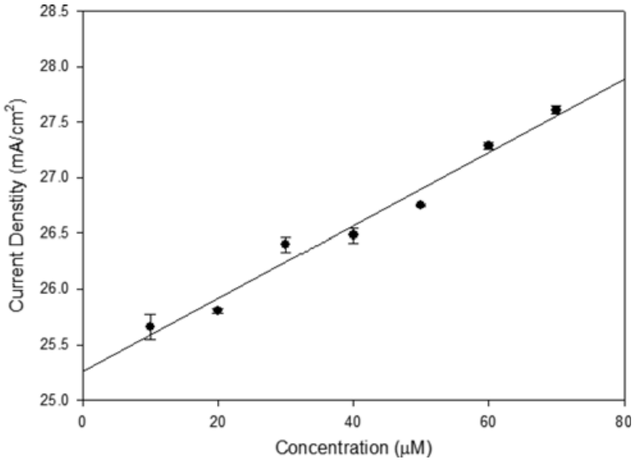

Fig. 5. Current density with concentration of mercury ion for HDT/GNW/AAO electrode.

CONCLUSIONS

Well-ordered AAOs were produced by a two-step anodizing process, for a sensing application, the GNW was electro-deposited on the AAO followed by functionalization with HDT. GNW/AAO electrodes showed better detection performance than Au/AAO electrodes in cyclic voltammetry analysis. Through analysis of the real-time response, the stair-shaped change in the electrical signals showed that mercury ions combined with the functional group. HDT/GNW/AAO electrodes were used to detect mercury ions with ppb levels, and these revealed a high linearity from 10 to 70 μM. Since a vertically aligned GNW/AAO has a large surface with a high conductance when compared to Au/AAO, it might have great utility as a sensing electrode for applications in biochemistry and electrochemistry.

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