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Fabrication and characterization of multilayered nanoporous platinum films deposited by electroplating and nonionic surfactant molds

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ABSTRACT

Multilayered nanoporous Pt (NPt) thin film on silicon substrate was newly fabricated and characterized for highly sensitive electrochemical sensor applications. The multi-layered NPt films were fabricated by using nonionic surfactant and electroplating technique. The surface morphologies of the fabricated multilayered NPt films (single, double, and triple layer) were then characterized using field emission scanning electron microscopy (FESEM). The fabricated NPts films exhibited highly dense nanopores with irregularly arranged grain boundaries. Their thicknesses were 0.7, 0.77, and 1 μm, which were highly affected by the structural geometries of the bottom layer. The electrochemical properties of the as-synthesized multilayered NPt films were tested in 1 M sulfuric acid and phosphate buffered saline (PBS, pH 7.4) with different concentrations of hydrogen peroxide (H_2O_2). The fabricated NPt films on silicon substrate exhibited highly improved electrochemical roughness factors (RF) of 151.45, 901.35, and 1277.7 (mean values), respectively. As expected, they exhibited high sensitivities of 279.6, 337.5, and 517.8 $\mu A\,mM^{-1}\,cm^{-2}$ in H_2O_2 concentrations up to 7 mM, respectively, due to extremely enlarged specific surface activation area.

1. Introduction

Over the past few years, extensive research has been performed to develop micro/nano structured materials with high real surface area, because of their many applications in electrochemical sensors and catalysis. 2D or 3D porous metal films for optical applications have also recently been of interest, since they permit easy fabrication of devices or electrodes [1–3].

For improving their operating performances, the porous structure should be well distributed and miniaturized. In the most practical applications, the electrodes with macropore or nanopore were strongly demanded and used according to their particular pore sizes. When these electrodes are used for the electrochemical sensors, there are some advantages of the fast, easy, and effective transfer of reactants by the macropores, while the electrode with nanopores will increase its real surface activation area resulting in high catalytic properties. The nanoporous gold or platinum with high surface area by prepared alloying/dealloying or electroplating method is particularly used as electrochemical catalyst, electrode of battery or fuel cells [4–6]. Since their unique chemical and physical properties are different from those of bulk metals [7–9], the controlling of multilayer films and porous nanostructures has received intense interest in recent years for their uses in analytical and material chemistries. Development of new techniques for 2D or 3D nanostructures of the metal nanoparticles is a critical process and an important goal in the chemistries for practical application in nanotechnology and biotechnology [10–12].

Most metallic multilayers have been produced by molecular beam epitaxy (MBE) growth [13], sputtering [14] or vacuum deposition methods [15]. Electroplating method is widely used as a surface finishing process for avoiding corrosion of metal surface, because this method is very simple and cost effective for production in comparison with the other methods. Furthermore, it is easy to fabricate the multilayered macro-nano porous metal, alloy, and composite materials with large surface activation area by controlling of the electroplating conditions [6,16,17].

In this study, highly rough and catalytic multilayered nanoporous Pt (NPt) films on silicon substrate were newly fabricated and characterized for electrochemical sensor applications. The multilayer NPt films on Si substrate were fabricated via nonionic surfactant and multi-electroplating technique. Subsequently, the morphologies and electrochemical properties of the respective NPt films (single, double, and triple layer) were characterized using field-emission SEM (FESEM), cyclic voltammetry, and amperometric method. The electrochemical roughness factors (RF) and electro-catalytic properties of the as-synthesized NPt films were

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tested in 1 M sulfuric acid and phosphate buffered saline (PBS, pH 7.4) with different concentrations of hydrogen peroxide (H_2O_2), since it is a very important intermediate or product in biochemical reactions.

2. Experimental method

2.1. Chemicals and apparatus

All the chemicals used were of analytical reagent grade. All the solutions were prepared with deionized water (resistivity ≥18 MΩ-cm). The prepared electroplating mixture for the NPt was comprised of 42% (w/w) $C_{16}EO_8$ (octaethylene glycol monohexadecyl ether, 98% purity, Fluka), 29% (w/w) deionized water (18 MΩ-cm) and 29% (w/w) HCPA (hexachloroplatinic acid hydrate, 99.9% purity, Aldrich) [18,19].

The detailed surface morphologies of the fabricated multilayered NPt films were characterized using field emission scanning electron microscopy (Hitachi S-4300, Japan) at an acceleration voltage of 15 kV. The NPt films were also measured to check their surface RF in 1 M sulfuric acid (H_2SO_4, 95–98%, ACS, Sigma–Aldrich) solution using cyclic voltammetry. 0.5 M H_2O_2 (30–32%, Dong-Woo Fine Chem., Korea) solution was prepared to test their electrochemical behaviors by diluting them in 0.1 M PBS (pH 7.4) solution.

All electrochemical experiments were carried out using an electrochemical analyzer (Model 660D series, CH Instruments Inc., USA) at room temperature. A traditional three-electrode system, which comprised a flat platinum bar as a counter electrode, respective NPt films (single, double, and triple layer) as a working electrode, and an Ag/AgCl reference electrode with 3 M NaCl, was used for the electroplating of these NPt films and for their electrochemical characterization.

Amperometric measurements of H_2O_2 were carried out in 0.1 M PBS (pH 7.4) under the desired potentials. The responsive currents corresponding to each H_2O_2 concentration were recorded after the transient being reached the steady state [19]. Before each measurement, the NPt films were electrochemically cleaned in the potential regions of the onset of oxygen and hydrogen evolution in a solution of 1 M H_2SO_4 at a scan rate of 200 mV s^{-1}. The amperometric curves, which were treated as the specific response to the H_2O_2 concentrations in PBS, were obtained after the consecutive addition of 1 mM H_2O_2.

2.2. Fabrication of the multilayered NPt films

Fig. 1 shows the fabrication sequences of the multilayered NPt thin films made by using nonionic surfactants ($C_{16}EO_8$) and HCPA-based electroplating technique. As shown in Fig. 1(a), the NPt film was electroplated on top of sputtered Pt formed on silicon oxide substrate. Liquid crystal templates of $C_{16}EO_8$ were formed on top of the Pt layer by lowering the temperature down from 85 °C to room temperature after dipping the sample into the prepared electroplating mixture. The temperature was controlled by water-jacketed vial. At this step, a liquid crystalline hexagonal structure was formed on top of the sputtered Pt surface. After that, Pt ions were electroplated into the formed nano-mold by applying a constant potential of −0.12 V vs. Ag/AgCl (35 mC charge condition) [18]. The NPt film was finally formed by removing the surfactant mold with distilled water for several hours. Although the color of the fabricated NPt film was black at first, it became shiny after several segments of cyclic voltammetry in 1 M H_2SO_4.

As shown in Fig. 1(b), the double and triple layered NPt films were fabricated on the top of single and double layered NPts films by repeating the electroplating sequences shown in Fig. 1(a). The thickness and surface roughness of each layer is different due to the change of plating current caused by the resistance change and surface morphologies of each bottom layer at the fixed potential and charge conditions. Unlike the formation of single layered NPt film, the surface structures of the double and triple layered NPt films can be more complex due to the irregular formation of the surfactant mold on the electroplated NPt film.

3. Experimental results and discussions

3.1. Morphological study of multilayered NPt films

Fig. 2 shows the top views of FESEM images of the fabricated single layered NPt film (a-b), the double layered NPt film (c-d), and the triple layered NPt film (e-f). As shown in Fig. 2(a–b), the single layered NPt film shows very dense grains which have high porosity.

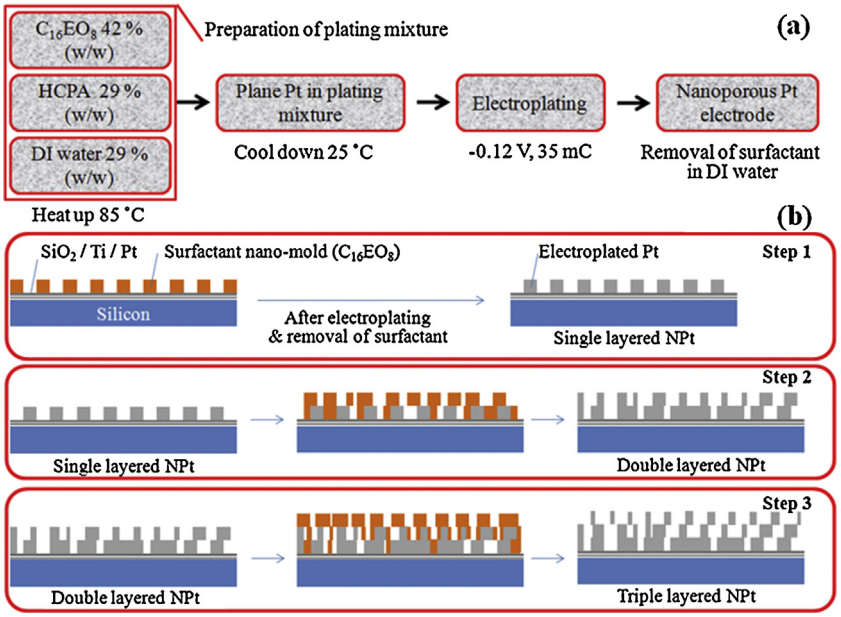

Fig. 1. (a) Electroplating method for NPt film and (b) fabrication sequence of the multilayered NPt thin film by using $C_{16}EO_8$ surfactants and HCPA-based electroplating technique.