



Gold nanowire array electrode for non-enzymatic voltammetric and amperometric glucose detection

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ABSTRACT

The non-enzymatic voltammetric and amperometric detection of glucose using a gold nanowire array electrode is described. The voltammetric detection of glucose was performed by cyclic and differential-pulse voltammetry. The detection of glucose by partial and direct oxidation of glucose during the anodic and cathodic potential sweeps was shown in cyclic voltammetry. An unusual decrease in overpotential for partial oxidation of glucose on a Au NW array electrode was observed. A linear differential-pulse voltammetric response for partial oxidation of glucose was observed up to a glucose concentration of at least 20 mM with a sensitivity of $41.9 \mu\text{A mM}^{-1} \text{cm}^{-2}$ and detection limit below $30 \mu\text{M}$ (signal-to-noise ratio of 3) for glucose oxidation at low potentials, where the influence of possible intermediates can be avoided. The amperometric response was also linear up to a glucose concentration of 10 mM with a sensitivity of $309.0 \mu\text{A mM}^{-1} \text{cm}^{-2}$. The wide dynamic range and high sensitivity, selectivity and stability, as well as good biocompatibility of the Au NW electrode make it promising for the fabrication of non-enzymatic glucose sensors.

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1. Introduction

The development and improvement of glucose sensors based on voltammetry and especially amperometry has been the subject of experimental studies for almost fifty years going back to the work of Clark and Lyons in 1962, where they reported on the preparation of an enzyme sensor for the first time [1]. The majority of known glucose sensors are based on the immobilization of glucose oxidase (GOx) which was proposed by Updike and Hicks in 1967 [2]. Such sensors show high selectivity and good sensitivity and are fast and reversible. However, the lack of stability due to the intrinsic nature of enzymes remains the main problem in the practical application of such sensors [3–6]. Also, in some applications, it is necessary to have sensors which are stable when exposed to high temperatures and an aggressive environment [7]. Therefore, numerous studies have been devoted to the investigation and preparation of glucose sensors without using enzymes [4,8–11]. In some studies, the use of bare platinum or gold electrodes was proposed [3,4,12–15]. However, these electrodes suffer from low sensitivity, poor selectivity and poisoning by intermediates and chloride [6], which has led to the search for other active materials for glucose oxidation. Some of these drawbacks were overcome by modifying the surface of noble metals with different metal ad-layers [10,16–23]. However,

the low sensitivity and toxicity of ad-metals such as Tl, Pb and Bi have hindered the development in this field [7].

A tremendous breakthrough in the area of sensors, particularly glucose sensors, was made by applying nanomaterials, including Au [7,24,25], Pt [26–28], Pt–Pb [29,30] and Cu [31] nanoparticles (synergetic effect of metal nanoparticles and carbon nanotubes is usually utilized in such sensors), Pt nanotubes [32], Au [33,34] and Pt [35–38] porous films, and Pt–Pb [39] and Au [40,41] nanowires, nanostructured boron-doped diamond (BDD) electrodes [42] instead of bulk electrodes. The research conducted in this area has been concentrated on nanoparticles and porous materials and only a few groups have reported on the applications of nanowires. For our best knowledge, all sensors prepared using gold nanowires are based on the application of enzymes [40,41,43–46]. It was shown that by immobilizing of enzymes on Au NW electrode, the analytical properties, mainly sensitivity, were drastically improved. As an example, the sensitivity of Au NW electrode to hydrogen was 37 times higher than that of the conventional electrode [45]. On the other hand, a Pt–Pb nanowire array electrode was applied for preparation of an enzyme-free glucose sensor. The good sensitivity and a linear range of up to 11 mM were achieved by using such non-enzymatic sensor. However, toxicity of lead reduces the applicability of such a sensor. On the other hand, gold can be used as a biocompatible and stable material for glucose sensor [41,47–49].

Herein, we present an enzyme-free glucose sensor prepared by the electrodeposition of gold nanowires within an anodic alumina oxide (AAO) template and subsequent transfer of the obtained array onto a glass substrate. The electrochemical oxidation of glucose in

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0.1 M NaOH solution was investigated using cyclic voltammetry. Further, the voltammetric and amperometric detection of glucose was explored.

2. Experimental details

2.1. Reagents

Gold electrolyte IM-Gold series was purchased from Japan Pure Chemical. Sulfuric acid (95.0%) was provided by Samchun Chemicals (Korea). Sodium hydroxide was obtained from Yakuri Pure Chemical (Japan). Polydimethylsiloxane (PDMS Sylgard 184A and 184B) was obtained from Dow Corning (USA). L-Ascorbic acid (AA) and D-(+)-glucose were purchased from Sigma–Aldrich. All of the solutions were prepared from deionized (DI) water and deaerated by N₂ gas for 20 min before use.

2.2. Instruments

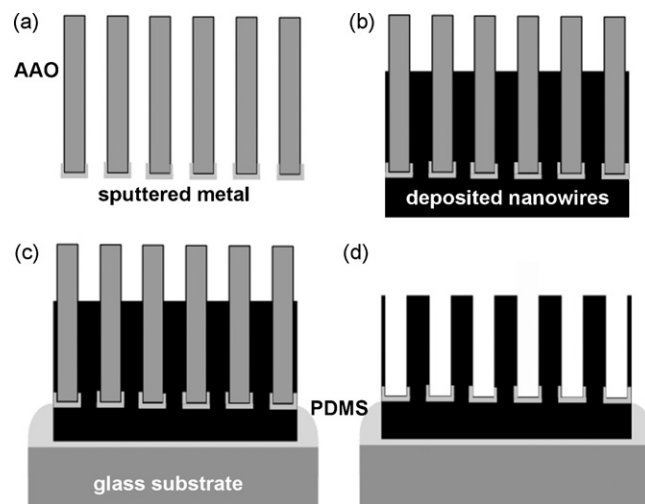
The electrochemical experiments were performed using an electrochemical workstation (Zahner® Elektrik IM6ex, Germany). Hg/HgO (0.098 V vs. NHE) and Pt plate were used as the reference and counter electrodes, respectively. The chemical composition of the prepared nanowires was measured by energy dispersive X-ray analysis (EDX) performed in a field emission scanning electron microscope (FESEM) (JEOL JSM-7000F). Scanning electron microscopy was utilized for the investigation of the morphology of the deposited nanowires. The structural properties were examined by X-ray diffractometry (XRD) (Bruker AXS with Cu K α radiation at 40 kV and 40 mA).

2.3. Electrode preparation

The porous anodic aluminium oxide (AAO) template with pores about 70 nm in diameter was prepared through a two-step anodization process, as described in our previous work [50]. To form a conducting layer, a thin film of gold was sputtered on the back side of the AAO template using conventional ion sputtering. The electrodeposition of the gold nanowires was carried out at a constant potential (−0.9 V vs. Hg/HgO). Then, the Au nanowire (NW) array electrode was prepared by transferring the nanowire array from the AAO template onto a glass substrate. To do so, the glass substrate was covered by a thin layer of PDMS. The PDMS precursor was prepared by mixing the liquid pre-polymer (Sylgard 184A) and the curing agent (Sylgard 184B) at a ratio of 10:1 by weight. The mixture was degassed for 30 min in air to remove any bubbles. A thin layer of the PDMS precursor was put on a glass substrate and, immediately, a piece of AAO containing the deposited nanowires was attached to the glass/PDMS substrate. The curing of PDMS was carried out at 80 °C for 2 h. Then the AAO was removed using 2 M NaOH solution. The obtained electrode was cleaned by DI water and dried in N₂ gas. The experimental procedure used for the preparation of the Au NW array electrode is presented in Scheme 1.

2.4. Electrochemical experiments

All of the electrochemical experiments were carried out at room temperature in a standard three-electrode system. Before each experiment, the solution was purged by N₂ gas for 20 min. The real surface area of the Au NW array electrode was determined by measuring the peak of the reduction of gold oxide monolayer of the cyclic voltammogram (CV) in 1 M H₂SO₄ solution. The Au NW array electrode was evaluated as a glucose sensor in 0.1 M NaOH solution. CV measurements were carried out in the potential range of −0.7 to 0.7 V vs. Hg/HgO. A differential-pulse voltammetric (DPV) investigation was carried out in the potential range of −0.7 to −0.2 V at



Scheme 1. Schematic representation for the fabrication of the Au NW array electrode. (a) Anodic alumina oxide (AAO) template with Au conductive layer deposited on the back side. (b) AAO template after the deposition of the metal nanowires. (c) AAO/nanowire template sealed to a glass substrate by cured PDMS. (d) Au NW array electrode formed by the removal of the AAO.

a rate of 20 mV s^{−1}, step height of 5 mV, step width of 1 s, pulse width of 200 ms, pulse height of 50 mV and sampling period of 50 ms. The amperometric curves were obtained after adding the desired amount of glucose with the solution being stirred constantly. The current density in this paper was reported as the ratio of the recorded current to the geometrical area of the electrode.

3. Results and discussion

3.1. Preparation and characterization of the Au NW array electrode

There are several methods of using nanowires and nanotubes for analytical applications. The most common of them is the modification of a bulk electrode such as a gold or glassy carbon electrode (GCE) with nanowires. In this method, the nanowires are firstly dispersed in a solvent and then, by the dropping of the dispersion on the electrode surface and subsequent drying, the modified electrode is obtained. However, the poor adhesion of the nanowire or nanotube layer to the surface of the bulk electrode makes it difficult to utilize such electrodes. To overcome this problem, a second layer consisting of a transparent material, such as Nafion®, is usually used as an analyte membrane [51,52]. More recently, the growth of a nanowire array directly on the GCE bulk electrode was proposed, by attaching AAO to the electrode [53].

In our approach, we firstly deposited metal nanowires within an AAO membrane and then transferred the modified AAO membrane to a glass substrate using PDMS as a supporting layer. By the electrodeposition of metal nanowires within the AAO template, a thin layer of metal is also deposited on the back side of the AAO template. However, the small thickness of this film makes it difficult to handle the nanowire array electrode without additional support. On the other hand, the advantage of this method is the possibility of using a broad variety of metals or alloys that can be deposited within the AAO template. Unlike modified electrodes, the electrode produced herein does not require any additional adhesive layer. Moreover, the nanowires are ordered in the 3D array.

A top view SEM image of the electrodeposited Au NW array, which consists of 0.7 μm long Au nanowires, is presented in Fig. 1(a). The diameter of the nanowires is approximately 70 nm, which is defined by the diameter of the holes in the AAO template.

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