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Synthesis of Ni/Au multilayer nanowire arrays for ultrasensitive non-enzymatic sensing of glucose

Lirong Qin[1], Lizhong He[1], Jianwei Zhao*, Binglin Zhao, Yingying Yin, Yu Yang

School of Physical Science and Technology, Southwest University, Chongqing 400715, PR China

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ABSTRACT

Ni/Au multilayer nanowire arrays were fabricated by an electrochemical method using anodic aluminum oxide as template. Each nanowire has a length of 2.5 μm and diameter of 70 nm with alternating Ni and Au layers along its axis. A novel glucose sensor was then developed using a Ni/Au multilayer nanowire array immobilized on an ITO electrode. The resulting sensor exhibited two specific linear ranges at 0.25 μM–2 mM and 2–5.5 mM, with very high sensitivities (3372 and 1906 μA mM^{-1} cm^{-2}, respectively). The detection limit was as low as 0.1 μM with a signal-to-noise ratio of 3. An excellent selectivity and acceptable stability were also achieved. These results indicate that Ni/Au multilayer nanowire arrays are promising new platforms for the construction of non-enzymatic glucose sensors.

1. Introduction

In recent years, the development of rapid and reliable glucose determination sensors has been very important because they can be used not only as a diabetes marker in clinical diagnostics, but also as a label in environmental monitoring [1–3]. Compared to conventional spectrophotometric sensors, electrochemical sensors have several remarkable advantages, such as high sensitivity, simple instrumentation, low production cost, promising speed, and so on [4–6]. Because the activity of glucose oxidase can be affected by temperature, pH, humidity, detergents, and toxic chemicals, the development of non-enzymatic glucose sensors with a low detection limit and wide response range is highly desired [6–9].

The nanostructure-based non-enzymatic detection of glucose has been reported due to superior catalytic properties of nanomaterials [10–13]. Among them, noble metal (such as Au and Pt) nanostructures have shown fascinating properties for the oxidation of glucose, but the high cost and poor stability have limited their practical applications [14–16]. Therefore, the development of a more active and cheaper catalyst for non-enzymatic glucose detection is crucial. Ni based nanostructures have been attracting increasing attention because they exhibited remarkably catalytic performance for glucose by means of the redox couple of Ni(II)/Ni(III) in alkaline solution [17–19]. However, it has been reported that both bimetallic and alloy nanostructures have higher electrocatalytic activities and enhanced stabilities due to the synergistic effect between the metals [20–23]. For example, Sheng et al. [24] reported that PtNi alloy nanoparticles had higher electrocatalytic activity toward the oxidation of glucose due to the introduction of Ni. Miao et al. [25] studied the electrocatalytic oxidation of glucose with Ni/Ag bimetallic alloys and observed that the presence of both Ag and Ni in the alloys facilitated the electrocatalytic glucose oxidation, exhibiting an interesting synergistic effect.

Compared with other types of nanostructures, multilayer nanowires are a novel kind of bimetallic materials [26–28]. Considering their unique electronic properties, high specific surface area, and high electrocatalytic activity [29], multilayer nanowires can provide a new basis for electrochemical sensors. However, to the best of our knowledge, no studies concerning this application have been reported yet. In this study, a Ni/Au multilayer nanowire array is successfully synthesized by a simple template-assisted pulse electrodeposition method. After dissolving the template, the prepared nanowire array could be transferred and immobilized on ITO glass. This system can be used as an effective electrochemical sensor for the detection of glucose. The electrochemical experiments show that this sensor possesses several excellent properties.

* Corresponding author.
E-mail address: zhaojw@swu.edu.cn (J. Zhao).
[1] These authors contributed equally to this work.

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2. Material and methods

2.1. Reagents and measurements

Glucose, ascorbic acid, uric acid, L-tyrosine, and Nafion solution were obtained from Sigma-Aldrich. Chloroauric acid was purchased from Sinopharm. Nickel hexahydrate, nickel sulfate hexahydrate, boric acid, and ethanol were obtained from Chongqing Chuandong. All other chemicals were of analytical grade, and deionized water was used throughout the experiments. The electrochemical measurements were carried out on a CHI 660E electrochemical analyzer with a three-electrode system: a modified electrode as the working electrode, an Ag/AgCl electrode as the reference electrode, and a Pt electrode as the counter electrode. All experiments were performed at ambient temperature ($20 \pm 1\,^{\circ}C$). The composition of the prepared products was determined by X-ray Diffraction (XRD, D8 Advance). The morphology and structure were characterized using field-emission scanning electron microscopy (SEM, JSM 7100F) and transmission electron microscopy (TEM, JEM 2010) equipped with an energy dispersive X-ray spectroscope (EDS).

2.2. Fabrication of the Ni/Au multilayer nanowires

The anodic aluminum oxide (AAO) templates were homemade using a previously reported two-step anodization process [29,30]. The electrodeposition process of the Ni/Au multilayer nanowires was performed in a three-electrode system similar with previous reports [31–33]. A thin Au layer was sputtered on the rear side of the AAO templates to serve as the working electrode for the subsequent electrodeposition. A graphite electrode was used as the counter electrode and an Ag/AgCl electrode was used as the reference electrode. A single electrolyte was used for the electrodeposition of both Au and Ni segments, and was composed of $5\,g{\cdot}L^{-1}$ $HAuCl_4{\cdot}4H_2O$, $10\,g{\cdot}L^{-1}$ $NiCl_2$, $5\,g{\cdot}L^{-1}$ $NiSO_4$, and $3\,g{\cdot}L^{-1}$ H_3BO_3. The multilayer Ni/Au nanowires were deposited alternately using pulse signals (deposition potentials and time) specific to the target materials: (1) −0.35 V for 25 s to deposit the Au layer, and (2) −1.3 V for 10 s to deposit the Ni layer. The total time of the electrochemical deposition was 20 min. During the electrodeposition, the electrodeposition electrolyte was continuously agitated by a magnetic stirrer. After electroplating, the multilayer Ni/Au nanowires were annealed at 650 °C in a tubular furnace for 6 h. For comparison, Ni nanowires electrodeposited only at −1.3 V in the same electrolyte are obtained and characterized (see the Supporting information).

2.3. Preparation of the nanowire array electrode

After deposition, the AAO template containing the nanowires was immersed in a $2\,mol\,L^{-1}$ NaOH solution to dissolve the AAO template. Subsequently, the nanowire array connected to the Au layer was cleaned with deionized water. Then, the nanowire array was transferred to a conductive ITO, which was cleaned ultrasonically with a $0.5\,mol\,L^{-1}$ H_2SO_4 solution for 1 h, then absolute ethanol, and finally deionized water for 30 min. Finally, when the nanowire array dried, an epoxy resin was used to cover the edge between the ITO and the nanowire array. Fig. 1 shows the schematic for the fabrication of the electrode. Based on the image, the area of the electrode is about $0.07\,cm^{-2}$.

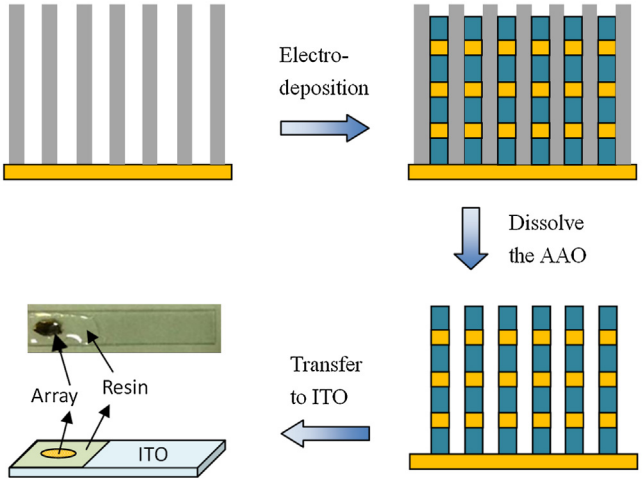

Fig. 1. Schematic illustration for the fabrication of a Ni/Au multilayer nanowire array and electrode assembly.

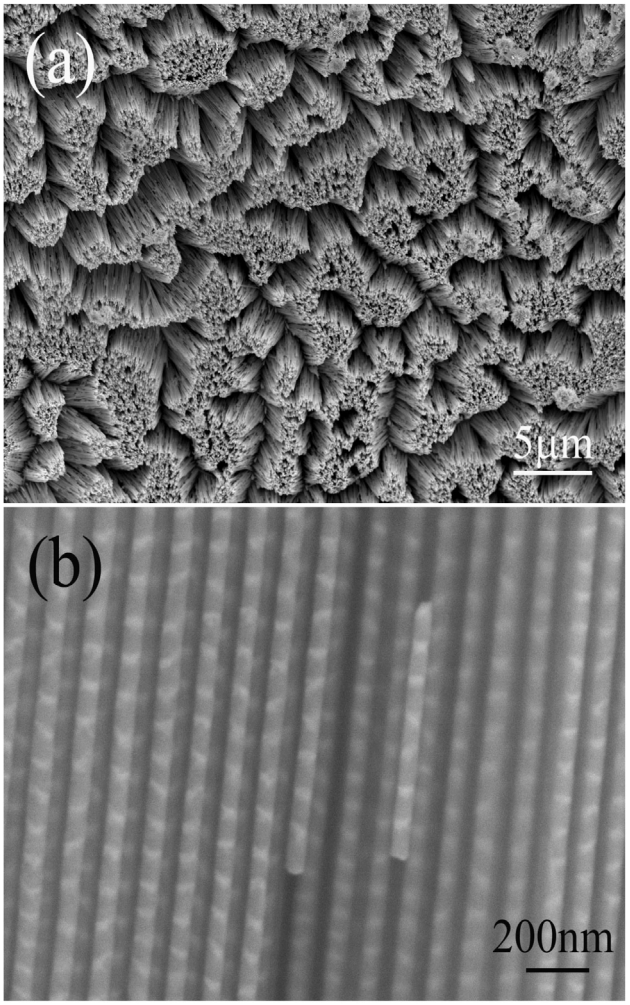

Fig. 2. (a) Typical low-magnification SEM image of a Ni/Au multilayer nanowire array after dissolving the AAO template; (b) High-magnification SEM image.

3. Results and discussion

After the removal of the AAO template, the morphology of the product was investigated using SEM. As shown in Fig. 2(a), the low-magnification overhead SEM image reveals that large quantities of well-aligned nanowires were obtained. The average length of the nanowires is about 2.5 μm. Fig. 2(b) shows a side view of the multilayer nanowires. It shows that every nanowire has a smooth surface with an average diameter of about 70 nm, corresponding to the diameter of the channels in the AAO template. The alternating Au and Ni layers along the axis of the nanowires can be clearly observed as well.