



Direct Electrodeposition of Gold Nanostructures onto Glassy Carbon Electrodes for Non-enzymatic Detection of Glucose



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ABSTRACT

Dendrite-like gold nanostructures (DGNs) were directly electrodeposited onto the surface of a glassy carbon electrode (GCE) via the potentiostatic method without any templates, surfactants, or stabilizers. The effects of the deposition time, potential and the concentration of precursor solution on the evolution of the nanostructure and on the electrocatalytic activity of the DGNs were systematically investigated using scanning electron microscopy (SEM), transmission electron microscopy (TEM) and electrochemical methods including cyclic voltammetry, linear voltammetry and chronoamperometry. The results confirmed that DGNs have good electrocatalytic activity towards the electro-oxidation of glucose in a neutral phosphate buffer solution (PBS, pH 7.4). A non-enzymatic glucose sensor fabricated with the DGNs as an electrocatalyst showed a quick response (less than 2 s), a low detection limit (0.05 mM), a wide and valuable linear range (0.1–25 mM), a high sensitivity ($190.7 \mu\text{A cm}^{-2} \text{ mM}^{-1}$) and good repeatability and stability. In addition, the commonly interfering species, such as ascorbic acid (AA), uric acid (UA), and 4-acetaminophen (AP), did not cause obvious interference because of the use of a low detection potential (0.15 V vs. Ag/AgCl). This work demonstrates a simple and an effective sensing platform for the non-enzymatic detection of glucose.

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1. Introduction

Glucose sensors have been extensively studied over the past twenty years because of their applications in the prevention and treatment of diabetes mellitus, from which millions of people suffer [1]. Therefore, there has been an increasing demand for the development of inexpensive glucose sensors that have high selectivity, sensitivity, and good stability [2,3]. Most studies are based on glucose oxidase (GOx) bound to electrode transducers, in which hydrogen peroxide is produced from the oxidation of glucose and can be amperometrically detected to be stoichiometrically related to glucose levels. Although enzymatic detection shows a high sensitivity and a great selectivity, the sensitivity to the environment and the instability are the primary difficulties to overcome. In addition, the oxidation of H_2O_2 usually requires a relatively high positive potential (usually over +0.6 V vs. SCE) [4,5]. Many other electroactive species that commonly coexist in biological fluids, such as

ascorbic acid (AA), uric acid (UA), and 4-acetamidophenol (AP), can also be oxidized at such high potentials, and their electrochemical signals thus severely affect the selectivity of the biosensors [6].

To overcome these problems, many attempts have been devoted to develop non-enzymatic glucose biosensor using noble metal nanomaterials to substitute the enzyme as electrocatalyst. The majority of these sensors rely on the current response of glucose oxidation directly at the surface of the nanomaterials modified electrode. Thus the non-enzymatic biosensor exhibited much higher stability for a long period and resistance ability to the environmental factors than the glucose biosensor using enzyme [7,8]. To date, a large amount of metals and oxide nanoparticles, such as Pd [1,6], Pt [9–13], Au [2,14–19], Cu_2O [3,20] and CeO_2 [21], have been implemented in electrochemical catalytic reactions. Among these materials, non-enzymatic biosensors using Cu nanomaterials as electrocatalyst for glucose sensing, an alkaline solution environment is usually required. Although Pt nanomaterials show high catalytic properties in neutral buffers to glucose molecules, their intrinsic activities are normally suppressed because they are easily poisoned by intermediates and products generated during the experimental processes [22]. Au as a potential candidate has attracted much attention for the unique properties of its

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nanostructures, such as good conductivity, useful electrocatalytic activity, and biocompatibility [23,24]. Moreover, nanosized gold structures exhibit superior poison resistivity toward the electro-oxidation of glucose due to their large surface-to-volume ratio and the presence of highly active binding sites on the surface of the particles [25]. Therefore, using Au nanostructure material as a catalyst would be expected to meet the need of non-enzymatic detection of glucose.

Many methods have been used to obtain gold nanostructures, such as self-assembly with polymers [26–28], seed-mediated growth [29–32] and thermal-driven attachment [33]. However, the application of surfactants, bridging agents and organic solutions in the reactions might reduce the electrocatalytic activity of Au nanoparticles due to blocking of the active sites. So challenges still exist in the preparation of Au nanostructures with a clean surface and a high catalytic ability. On the other hand, dendrite-like gold nanostructures (DGNs) have received considerable interests for their larger specific surface area and the extensive applications in super hydrophobic property, diverse catalytic fields, such as electro-oxidation of ethanol and glucose [19,24]. It is well known that electrodes with increased specific surface areas can provide improved performance for kinetically controlled reactions, such as glucose oxidation. However, the influence of the specific surface area on diffusion-controlled reactions is tiny, for example, most interference (AA and UA) oxidation on the electrodes. Thus, fabricating electrodes with high surface areas is a promising method to increase the electrochemical response of glucose while limit the impact of interferences reactions [12,22]. This means that dendrite-like gold nanostructures with larger surface area will lead to a higher sensitivity for glucose detection, as well as a better selectivity. However, to our knowledge, a systematic study on the non-enzymatic detection of glucose using DGNs has not been reported.

In this work, the dendrite-like gold nanostructures was fabricated by a potentiostatic method which is very simple and clean. The obtained DGNs with extremely increased specific surface area displayed a high catalytic activity in the oxidation of glucose. Moreover, the normal interferences that coexist in physiological conditions, such as AA, UA, and AP, can be effectively avoided due to the high specific surface area and the lower detection potential. The influence of the electrodeposition conditions, such as the deposition time, deposition potential and the concentration of precursor solution, was also investigated to find out the impact factors on the morphology of the gold nanostructures and the catalytic performance in the oxidation of glucose. It is interestingly found that the catalyst material of DGNs generated under the optimized electrodeposition conditions shows a rapid response and high sensitivity towards the catalytic oxidation of glucose.

2. Experimental Section

2.1. Materials

$\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ was purchased from Aldrich Co., Ltd. Ascorbic acid (AA), uric acid (UA), 4-acetaminophen (AP), glucose, absolute alcohol, $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$, $\text{NaH}_2\text{PO}_4 \cdot 3\text{H}_2\text{O}$, concentrated sulfuric acid (H_2SO_4) and KCl were obtained from the Sinopharm Chemical Reagent Co. Ltd. All the chemicals were of analytical grade. A phosphate buffer solution (PBS, 0.1 M, pH 7.4) was prepared from $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ and $\text{NaH}_2\text{PO}_4 \cdot 3\text{H}_2\text{O}$. Solutions of glucose, AA, UA and AP were prepared using PBS. Rod-shaped glassy carbon electrodes (GCE, 3 mm in diameter) were obtained from the Gaoss Union Instrument Company, Wuhan, China, and bulk gold electrode (2.0 mm in diameter) was ordered from BAS. Co. Ltd. Both of the electrodes were polished sequentially with slurries of

0.3 and 0.05 μm alumina to create a mirror finish, and then they washed sequentially in pure water, ethanol and pure water while sonicating for 1 min in each. After washing, the electrodes were thoroughly rinsed with pure water and dried with nitrogen gas. In all the procedures, the pure water we used was prepared with a Kertone Ultrapure Water System P60-CY (Kertone Water Treatment Co.Ltd, resistivity > 18 $\text{M}\Omega \cdot \text{cm}$). Additionally, all the experimental measurements were carried out at room temperature.

2.2. Apparatuses

The size and morphology of the Au nanostructures deposited on the glassy carbon electrode surfaces were characterized with scanning electron microscopy (SEM) and transmission electron microscopy (TEM; FEI TECNAI20, USA). All the electrochemical measurements were carried out with a 550 electrochemical workstation (Gaoss Union Instrument Company, Wuhan, China) in a conventional three-electrode cell. For SEM characterization, we used a removable glassy carbon electrode that could be directly examined under the scanning electron microscope. For TEM characterization, the dendrite-like gold nanostructures were first scraped from the GC electrode and then dispersed in pure water with sonication for 1 hour. Subsequently, 10 μL of the suspension was casted on a copper mesh, and dried under ambient conditions, and finally transferred into the microscope for observation.

2.3. Procedures for preparing the DGN-modified GC electrode

Direct electrodeposition of the DGNs onto the GC electrode surface was carried out via a potentiostatic method [19,34,35]. First, the precursor solution was prepared by dissolving a predetermined amount of $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ into a 0.1 M KCl solution. Then, the treated GC electrode was immersed into the electrolyte solution and used as the working electrode. A clean platinum wire and a Ag/AgCl electrode were used as the counter and reference electrodes, respectively. Finally, the electrodeposition was performed under potentiostatic mode. The resulting electrodes were thoroughly rinsed several times with pure water. In this work, we systematically investigated the effects of the electrodeposition conditions, such as the deposition time, deposition potential and the concentration of precursor solution, on the morphology of gold nanoclusters and their catalytic performance in the oxidation of glucose. The obtained GCEs were characterization using SEM, TEM and electrochemical tests, and the GCE fabricated under the optimal electro-deposition conditions (3600 s, -0.3 V, 10 mM HAuCl_4) was selected to investigate the catalytic properties. CV and LSV experiments were performed in 0.5 M H_2SO_4 and 0.1 M PBS with and without 10 mM glucose.

3. Results and Discussion

3.1. Characterization of the morphology and structure of the DGNs

3.1.1. The impact of the electrodeposition potential on morphology

For the electrodeposition technique, the applied potential is an important factor for controlling the morphologies of gold nanostructures [22,35]. SEM characterization was used to investigate the effect of the electrodeposition potential on the morphology of the dendrite-like gold nanostructures. Fig. 1 shows typical SEM images of DGNs obtained under different potentials for 3600 s in a 10 mM HAuCl_4 solution. Under a potential of +0.3 V, the as-prepared product consisted of a large number of well dispersed and uniform microstructures with a diameter of approximately 3 μm (Fig. 1 A). The image reveals that these microstructures are flowerlike and

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