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Non-enzymatic glucose sensors based on controllable nanoporous gold/copper oxide nano hybrids



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ABSTRACT

A kind of dealloyed nanoporous gold (NPG)/ultrathin CuO film nano hybrid for non-enzymatic glucose sensing has been prepared by a simple, in-situ, time-saving and controllable two-step electrodeposition. The three-dimensional and bicontinuous nanoporous structure of the nanocomposites have been characterized by scanning electron microscope (SEM) and transmission electron microscopy (TEM), and the electrochemical tests have been estimated by cyclic voltammetry and single potential step chronoamperometry (SPSC). The optimal NPG/CuO electrode exhibits great electrocatalytic activity towards glucose oxidation and also shows obvious linear response to glucose up to 12 mM with a high sensitivity of $374.0 \mu\text{A cm}^{-2} \text{mM}^{-1}$ and a good detection limit of $2.8 \mu\text{M}$ ($S/N=3$), as well as strong tolerance against chloride poisoning and interference of ascorbic acid and uric acid.

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1. Introduction

The development of glucose sensors is of a vital importance in diabetes control, food industry and bioprocess monitoring [1–3]. Since Clark and Lyons developed the first enzyme electrode in the 1960s [4], there have been many impressive advances in the design and use of glucose biosensors based on the superior selectivity and non-toxicity of enzyme based electrodes [1,5]. However, more critical demands, such as withstanding with harsh conditions (e.g. high operating temperature), relatively long shelf life and eventual low cost, have proposed new challenges to enzyme based glucose sensors. Accordingly, non-enzymatic glucose sensors utilizing metal and metal oxide nanomaterials have attracted numerous attentions in the recent years [6–9], due to their low cost and promising capabilities including long stability, rapid response, ultra-low detection limit and great sensitivity even as high as $\text{mA mM}^{-1} \text{cm}^{-2}$ [10,11]. Among them, CuO has been widely studied for non-enzymatic glucose sensing as a result of its ease of synthesis, low cost and high electroactivity, especially good poisoning tolerance [10,12]. Various nanostructured CuO with different morphologies, such as nanowires [13], nanoplatelets [14], nanospheres [15], nanorods [16], and nanofibres [17,18], have been proposed. A fundamental conflict for CuO based electrodes

remaining to be addressed is that, as a p-type semiconductor, large loading of CuO would generate high response signal; however, accompanied by increased charge transfer resistance. To deal with this, many efforts have been made to develop nanocomposite electrodes like CuO/multiwalled carbon nanotubes (MWCNTs) [19], CuO/graphene [20] and CuO nanoneedle/graphene/carbon nanofiber [21] in order to generate a synergistic effect. It should also be noted that the unsupported nanostructures of CuO are somewhat unstable during the long electrochemical procedure, as a result of undesirable segregation and growth, giving restriction in the capability of glucose oxidation [10]. Additionally, CuO based electrodes in previous work display the ultrahigh sensitivities, the linear range is relatively narrow within the realm of blood glucose concentration in human body (i.e. 2–10 mM), which is limited in the application of in-vivo and online monitoring. Therefore, exploring novel materials and new technology are imperative for non-enzymatic glucose sensors.

Recently, dealloyed nanoporous gold (NPG) is a truly self-supported material with three-dimensional and bicontinuous nanoporous structure [22,23]. The composites of NPG and metal oxides, such as NPG/MnO₂ [24] and NPG/RuO₂ [25], have been achieved as high-performance electrochemical supercapacitors due to their promising electron transfer capability and high stability. Most recently, Lang and his coworkers have reported NPG micro-electrodes decorated with Co₃O₄ nanoparticles by the hydrothermal method, which exhibited ultrahigh electrocatalytic activity towards glucose oxidation [26]. In this paper, a simple, time-saving and

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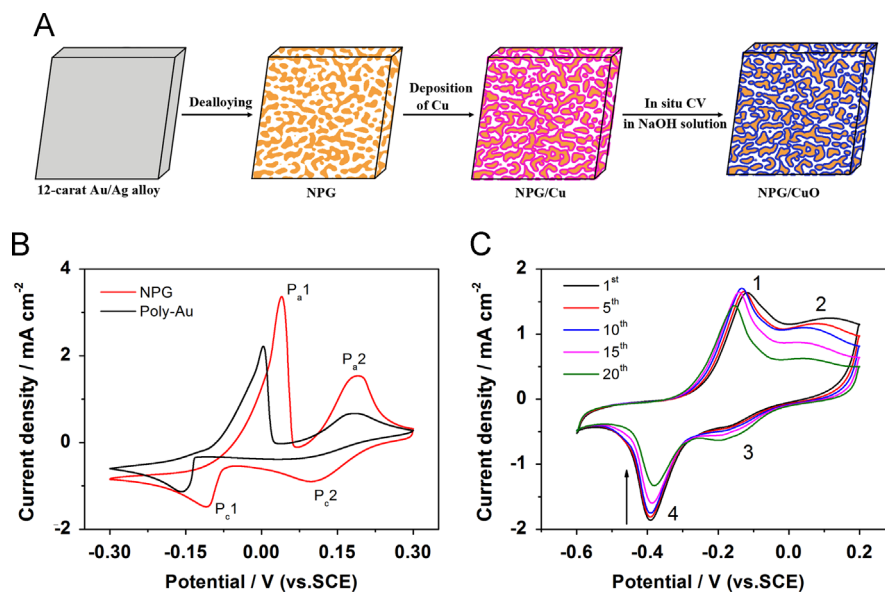


Fig. 1. (A) Schematic drawing of the synthesis of NPG/CuO electrode. (B) CVs of NPG (red) and poly-Au (black) in 0.1 M KCl solution containing 10 mM CuCl₂ at 10 mV s⁻¹. (C) CVs of NPG/Cu electrode in 0.1 M NaOH at 100 mV s⁻¹. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

controllable two-step electrodeposition has been adopted to fabricate NPG/CuO hybrid electrodes. Cu is firstly electrodeposited onto the NPG surface under a constant potential in CuCl₂ solution and electrochemically oxidized into CuO via cyclic voltammetry in alkaline solution [27] (Fig. 1A). TEM and SEM results show that the NPG preserves its original bicontinuous nanoporous structure and the CuO film is ultrathin (with a thickness of ~5 nm). It is expected that the composites of NPG and ultrathin CuO film would possess enhanced electrochemical activities, improved biocompatibility, larger accessible surface area and promoted electron transfer. The detailed electrochemical behaviors show NPG/CuO electrode that serves as an excellent sensitive non-enzymatic glucose sensor with a wider linear range compared to conventional CuO based on the electrodes reported in the previous literatures.

2. Experimental section

2.1. Chemicals and apparatus

Potassium chloride (KCl, 99.99%), cupric chloride dihydrate (CuCl₂ · 2H₂O, 99.99%), sodium hydroxide (NaOH, 99.99%), sodium chloride (NaCl, 99.99%) and β-D-glucose (99.99%) were supplied by Aladdin (China). Ascorbic acid (AA, 99%), uric acid (UA, 99%), sulfuric acid (H₂SO₄, 98%) and nitric acid (HNO₃, 65%) were ordered from Shanghai Sinopharm Chemical Co., Ltd. (Shanghai, China). All chemicals were used as received without any further purification. Ultrapure water with a resistivity > 18.25 MΩ cm⁻¹ was obtained from a UPH-IV ultrapure water purifier (Chengdu Ultrapure Technology Co., Ltd, China).

All the electrochemical experiments were performed on a LK2005A electrochemical workstation (Lanlike Company, Tianjin). A classical three-electrode cell was used, with a Pt wire counter electrode, NPG/CuO working electrode, and a saturated calomel reference electrode (SCE). All potentials were reported with respect to SCE.

Morphology characterization of NPG and NPG/CuO samples was performed by field emission scanning electron microscope (FESEM, Hitachi SU-70) and transmission electron microscopy (TEM; JEOL JEM-2100). The SEM was also equipped with an energy dispersive X-ray spectroscopy (EDX) system for elemental analysis.

2.2. Preparation of NPG

NPG sheets were fabricated by dealloying 100-nm-thick Au/Ag leaves (12-carat, Sepp Leaf Products, New York) in concentrated HNO₃ for 30 min at 30 °C as in the previous work [23]. After carefully cleaning with ultrapure water, the NPG films were placed onto pre-polished glassy carbon electrode (GCE) with a diameter of 4 mm and redundant parts were removed carefully with toothpicks. Before electrodeposition, cyclic voltammetry of NPG in 1 M H₂SO₄ were carried out to create high surface areas.

2.3. In situ electrodeposition of CuO onto NPG/CuO electrodes

NPG/CuO composite electrodes were synthesized by the electrodeposition of CuO onto the surface of NPG electrodes using a simple film plating/potential cycling procedure [27] (Fig. 1A). In brief, a constant deposition potential was applied to the NPG electrode in 0.1 M KCl solution containing 10 mM CuCl₂ (pre-bubbled with N₂ to remove O₂). The optimized deposition time here was 120 s. After rinsing with ultrapure water, the NPG/Cu was oxidized in situ into NPG/CuO in 0.1 M NaOH solution by cycling potential from -0.6 to 0.2 V at 100 mV s⁻¹ for 20 cycles. For comparison, similar strategy was used to grow CuO onto a polished polycrystalline gold electrode, denoted as Au/CuO.

3. Results and discussion

3.1. NPG/CuO preparation

Fig. 1B shows typical cyclic voltammograms (CVs) of NPG and normal polycrystalline gold (poly-Au) in 10 mM CuCl₂ solution. As for NPG, two pairs of redox peaks, P_{a1}/P_{c1} and P_{a2}/P_{c2}, indicating two different deposition/stripping processes, can be found. According to the previous work [28–30], P_{c1}/P_{a1} is associated to the redox pair of freely Cu²⁺ and deposited Cu from the overpotential deposition (OPD), as a diffusion controlled process. Meanwhile, P_{c2}/P_{a2} is due to the redox Cu underpotential deposition (UPD) and stripping of Cu on the gold electrode, being a surface-constrained electrochemical process. Compared with poly-Au electrode, enhancements of current density on the NPG electrode are much more

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