



An ultrasensitive non-enzymatic amperometric glucose sensor based on a Cu-coated nanoporous gold film involving co-mediating



Man-man Guo, Peng-shu Wang, Chao-hui Zhou, Yue Xia, Wei Huang, Zelin Li*

Key Laboratory of Chemical Biology and Traditional Chinese Medicine Research (Ministry of Education of China), National & Local Joint Engineering Laboratory for New Petro-chemical Materials and Fine Utilization of Resources, College of Chemistry and Chemical Engineering, Hunan Normal University, Lushan Road, Changsha, Hunan 410081, PR China

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ABSTRACT

In this work, we constructed an ultrasensitive non-enzymatic amperometric glucose sensor based on a Cu-coated nanoporous gold film (Cu/NPGF) for the first time, which comprised two pairs of electron mediators, Cu(II)/Cu(III) and Au/Au(I). The nanoporous gold film with high roughness ($R = 136$) was prepared by anodic potential step and the very thin Cu coating into/on the nanoporous Au was electrodeposited at constant current. In comparison with electrodeposited Cu on a smooth gold surface and with the nanoporous Au, the prepared Cu/NPGF showed significantly enhanced electrocatalytic activity for the oxidation of glucose around 0.1 V due to its nanoporous structure and the pronounced co-mediating of Cu(II)/Cu(III) and Au/Au(I), as well as their coupling $\text{Cu(III)} + \text{Au} = \text{Cu(II)} + \text{Au(I)}$. The Cu functionalized NPGF electrode also exhibited an extraordinary performance in sensing glucose with a wide linear range (2 μM –8.11 mM), short response time (3 s), ultrasensitivity (3643 $\mu\text{A mM}^{-1} \text{cm}^{-2}$), low detection limit (0.59 μM), good anti-interference and anti-toxicity, long-term stability (over 3 weeks), and satisfactory quantification of glucose concentration in human serum. We expect that functionalization of nanoporous gold films will provide a new platform for electrochemical sensors.

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1. Introduction

Rapid, sensitive and reliable sensing of glucose is of significance for clinical diagnosis [1], glucose-air biofuel cell [2], fermentation control [3], and food industry [4]. In addition to spectroscopy [5], chromatography [6], colorimetry [7], iodometry [8] and photo-electrochemical method [9], electrochemical sensors are attractive due to low-cost, simplicity, and reliability [10]. Although glucose oxidase (GOx) has been widely used to construct various kinds of amperometric biosensors for detection of glucose due to its specificity [11,12], the GOx modified electrodes have several drawbacks such as lack of stability, high price, limited conditions of use (easily affected by temperature, pH, humidity, and toxic chemicals) and complex immobilization procedures [10]. Therefore non-enzymatic glucose sensors are in progress with development of new nanomaterials [10,13,14].

Non-enzymatic glucose sensors based on different gold nanomaterials have been extensively investigated. For example, Zhou et al. [15] prepared gold nanoparticle-constituted nanotube array

electrode with prominent catalytic activity toward the electrooxidation of glucose, which displayed a linear relationship between current and glucose concentration in a range of 1–42.5 mM with a detection limit of 10 μM . Cherevko and Chung [16] fabricated a gold nanowire array with an anodic alumina oxide (AAO) template for non-enzymatic amperometric glucose detection, which responded to glucose concentration linearly up to 10 mM with a sensitivity of 309.0 $\mu\text{A mM}^{-1} \text{cm}^{-2}$ and a detection limit of 50 μM . Bai et al. [17] obtained a three-dimensional inverse-opal gold film electrode by electrodeposition of gold in the interspaces of polystyrene templates, which served as an enzyme-free glucose sensor with a linear range up to 10 mM, a sensitivity of 46.6 $\mu\text{A mM}^{-1} \text{cm}^{-2}$ and a detection limit of 3.2 μM . Chen et al. [18] made a free-standing nanoporous gold film by dealloying of Au₃₅Ag₆₅ (at.%) alloy and it demonstrated good performance in sensing glucose concentration with a linear range of 1–18 mM, a sensitivity of 20.1 $\mu\text{A mM}^{-1} \text{cm}^{-2}$ and a detection limit of 3 μM . Chen et al. [19] also prepared a gold shell decorated three-dimensional nanoporous copper film by displacement reaction, which exhibited significant electrocatalytic activity for the oxidation of methanol and high non-enzymatic sensitivity in detecting glucose. Our group previously proposed a facile method to fabricate a nanoporous gold film (NPGF) on a gold electrode with a high roughness within 5 min by anodic potential

* Corresponding author. Tel.: +86 731 88871533; fax: +86 731 88872531.
E-mail address: lizelin@hunnu.edu.cn (Z. Li).

step, which showed a linear detection range of glucose from 10 μM to 11 mM with a sensitivity of 66.0 $\mu\text{A mM}^{-1} \text{cm}^{-2}$ and a low detection limit of 8.7 μM [20]. In these nano-gold electrodes the redox pair of Au/Au(OH) was an effective electron mediator for the electrocatalytic oxidation of glucose. However, nano-gold based glucose non-enzymatic sensors need further improvement in sensitivity, stability, and applicability in real samples such as human blood glucose.

Other single and binary noble metal nanomaterials have also been extensively investigated to construct non-enzymatic glucose sensors, such as Pt nanofibers [21], Ag nanoparticle modified carbon black composites [22], Pt–Au nanocorals [21], Pt–Pd nanoflakes [23] and nanoporous PtAg [24]. However, very few [23] of these nanomaterials were applied to detect glucose in real samples such as human blood glucose.

Besides noble metals, it has already aroused a growing interest to fabricate glucose sensors with cheaper metals such as Cu, Co, Ni, Fe and Mn [14]. Especially, Cu nanomaterials with different morphologies have been prepared for electrocatalytic oxidation and sensing of glucose such as copper nanowires [25], Cu(OH)₂ nanoflowers [26], Cu(OH)₂ nanotubes [27] and Cu₂O nanospheres on reduced graphene oxide [28]. In these copper nanomaterials, the redox pair of Cu(II)/Cu(III) served as effective electron mediator in the electrocatalytic oxidation of glucose.

Compared with other classes of nanomaterials such as nanowires [29], nanorods [30], nanotubes [26], nanosheets [31], nanoflowers [25], nanodendrites [32], and so on, nanoporous structure provided a new opportunity to innovative electrocatalysts and electroanalysis [33–35]. Nanoporous materials not only enlarged specific surface area for reactant molecules but also possessed other intriguing properties related to the nanoporous structures such as discriminative electrokinetics, nano-confinement effect, electrical double layer overlapping, ion-selective impedance, etc. [34,35]. Many nanoporous films of single and binary metals have been fabricated for sensors such as Au [17–20], Pt [36,37], Ag [38], Cu [38,39], Au–Ag [40], Au–Pt [41], Ag–Pt [24], Pt–Pb [42] and Pt–Cu [24]. Functionalization of nanoporous materials with coatings of metals [19,43,44] or oxides [45,46] could also enhance electrocatalysis and electroanalysis and needs further development.

Through literature review on nano-gold, nano-copper and nanoporous materials, we consider that incorporation of the two pairs of effective electron mediators of Au/Au(OH) and Cu(II)/Cu(III) into a nanoporous structure would be a promising approach to enhance the electrocatalytic activity of electrodes for oxidation of glucose and to improve the performance of electrodes for non-enzymatic sensing of glucose. In this work, an ultrasensitive amperometric glucose sensor was successfully established indeed along this line by coating a thin layer of Cu into/on a nanoporous gold film for the first time, which was totally fabricated by electrochemical methods within 20 min at room temperature. Compared with electrodeposited Cu on a smooth gold and with the nanoporous Au, the Cu functionalized nanoporous gold film demonstrated enhanced electrocatalytic activity for oxidation of glucose due to co-mediation of the two pairs of electron mediators including their coupling $\text{Cu(III)} + \text{Au} = \text{Cu(II)} + \text{Au(I)}$. The Cu/NPGF sensor was also successfully applied to detect glucose content in human blood. We expect that functionalization of nanoporous gold films will provide a new platform for electrochemical sensors.

2. Experimental

2.1. Reagents and instruments

D-(+)-glucose (Glu) (C₆H₁₂O₆·H₂O), L-ascorbic acid (AA) (C₆H₈O₆, 99%) and uric acid (UA) were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China), Guangdong Xilong

Chemical Co. Ltd. (Guangzhou, China) and Sigma, respectively. Others reagents were also of analytical grade and used as received, and all aqueous solutions were made with Millipore ultrapure water.

Electrochemical experiments were performed on a CHI 660C electrochemical workstation (Chenhua, Shanghai, China) using a three-electrode system, where a polycrystalline gold disk (2 mm diameter), a circle platinum wire or a Pt plate, and a saturated mercurous sulfate electrode (SMSE) served as the working, counter and reference electrode, respectively. All the potentials in this work were versus SMSE.

Surface morphology images of the prepared electrode were obtained by scanning electron microscopy (SEM) on a Quanta FEG 250 microscope operated at 10 kV, and an attached energy dispersive X-ray (EDX) spectrometer (TSL EDAX, Ametek) was used to analyze the elemental composition of the electrode. The surface chemical composition of the electrode was analyzed by X-ray photoelectron spectroscopy (XPS) on a K-Alpha 1063 spectroscope operated at 12 kV with Al K α monochromatic radiation.

2.2. Preparation method of Cu/NPGF electrode

Before fabrication, the gold electrode was polished successively with metallographic sandpaper (1200 mesh) and α -alumina powders (50 nm) to a mirror-like surface, which was then sonicated three times each for 3 min in Millipore water and followed by electrochemical cleaning using cyclic voltammetry from –0.7 to 1.1 V at 100 mV s^{-1} in 1 M H₂SO₄ for 20 cycles. We denoted such treated electrode as smooth gold (SG) electrode.

The Cu/NPGF was electrochemically fabricated on the cleaned gold disk electrode by electrodeposition of Cu on the nanoporous Au that was obtained through a rapid one-step anodic potential step method as described in our previous report [20] with a slight modification in post treatment. Briefly, a potential step from the open circuit potential to 0.91 V was applied on the smooth gold electrode immersed in a 1 M KCl solution for 300 s to produce the nanoporous structure and then the electrode was transferred into a 2 M HCl solution for 10 min to remove the surface oxide layer. Sequentially, Cu coating was electrodeposited into/on the NPGF electrode in 0.1 M CuSO₄ solution under a constant cathodic current of 200 μA for 100 s. After rinsed in Milli-Q water and dried under an infrared lamp, the Cu/NPGF electrode was stored at 4 °C when not in use. For comparison, Cu was also electrodeposited on the smooth gold electrode under the same conditions, which was denoted as Cu/SG.

2.3. Electrochemical measurements

Cyclic voltammograms (CVs) were measured to compare the electrocatalytic oxidation behavior of glucose on electrodes of SG, NPGF, Cu/SG, and Cu/NPGF. The Cu/NPGF electrode was evaluated as a glucose sensor in 0.1 M NaOH solution and amperometric curves were obtained at designed potentials while the solution was kept stirring. All electrochemical experiments were operated at room temperature.

3. Results and discussion

3.1. Preparation and characterization of Cu/NPGF electrode

As shown in Fig. S1A (in Supplementary Data), the NPGF was fabricated on the smooth gold electrode by potential step to 0.91 V which located in the transition region between active electrodis-solution and passivation, and a steady dissolution current appeared under this potential which was limited by diffusion control of Cl[–] (Fig. S1B) [20]. The electrode surface became brownish black within

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