Fabrication of Au decorated CuO nanosheets electrode and its application in nonenzymatic glucose sensor

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Glucose detection is important in biological, environmental, and clinical analyses. In this study, Au modified CuO nanosheets (Au/CuO NSs) electrode was prepared and applied to construct nonenzymatic glucose sensor. The CuO NSs were characterized by scanning electron microscopy (SEM) and X-ray diffraction (XRD). Electrocatalytic oxidation of the Au/CuO NSs electrode towards glucose was studied by cyclic voltammetry (CV) and chronoamperometry. For the amperometric glucose detection, the low detection limit of 1 µM (S/N=3) with linear range from 1 µM to 1700 µM can be obtained using the Au/CuO NSs electrode. Under the applied potential of 0.6 V, the Au/CuO NSs electrode exhibited a high sensitivity of 3370.1 $\mu A\ mM^{-1}cm^{-2}$.

1. Introduction

Detection of glucose is of great importance for human health, food safety and biotechnology. Electrochemical sensors are always used to detect glucose because of the low cost, high sensitivity and quick response [1-4]. Although glucose oxidase (GOx) has attracted lots of attentions to build glucose sensors due to its high selectivity [5-9], the enzymatic biosensors still suffer from the insufficient stability originated from the nature of the enzymes [10, 11]. It is known that noble-metals display outstanding electroactivity towards glucose and various noble-metal electrodes have been studied [12-15]. Although high stability of the glucose sensors was achieved by the application of noble-metals, the noble-metals electrodes are high cost on account of the overuse of noble metals. The development of nonenzymatic glucose sensor with low cost, high sensitivity and selectivity is imperative.

CuO, a p-type semiconductor with a narrow band gap of 1.2 eV, has been widely used in semiconductors, catalysis and biosensors [16, 17]. Some efforts have been made on amperometric glucose sensors using nanostructured CuO. CuO nanofibers (NFs) electrode prepared by electrospinning was also used for glucose nonenzymatic determination and the electrode revealed a high sensitivity of 431.3 $\mu A\ mM^{-1}cm^{-2}$ and fast response (1 s) in the glucose determination [18]. CuO/MWCNTs array electrode synthesized by magnetron sputtering was applied to detect glucose and the electrode presented high sensitivity of 2596 $\mu A\ mM^{-1}cm^{-2}$ [19]. In our previous work, CuO NSs electrode was synthesized by a simple one step method and the CuO NSs electrode displayed excellent electroactivity towards glucose [20]. As we know, noble-metal modification is an effective method to save noble metals and improve the performance of biosensor. Thus, it is meaningful to study the electrocatalytic property of noble-metals modified CuO NSs electrode.

In this paper, Au modified CuO NSs electrode was prepared and the composite electrode was used to build nonenzymatic glucose sensor. The Au/CuO NSs electrode presented large surface area and numerous interspaces, which benefits the electrooxidation of glucose. It was found that the Au/CuO NSs electrode exhibited excellent electrocatalytic performance towards glucose.

2. Experiment

2.1 Materials

D(+)-Glucose and L-ascorbic acid (AA) were purchased from Sigma (USA). All other reagents were of analytical grade and used as received without further purification (Chengdu Kelong). Cu electrode (purity 99.999%) was purchased from Tianjin Aidahengsheng Technology CO., Ltd.

2.2. Preparation of Au/CuO NSs electrode

CuO NSs electrode was first prepared according to the previous report with some modifications [21]. Cu

electrode (Φ=3 mm) was first carefully polished with 0.05 μm alumina powders. Then, the polished Cu electrode was cleaned by HCl (25%), alcohol and water under ultrasound, respectively. In a typical procedure, Cu electrode was immersed into 20 mL of 0.25 M NaOH aqueous solution containing 10 mM $K_2S_2O_8$ at room temperature for 30 min to obtain CuO NSs electrode. After reaction, the CuO NSs electrode was rinsed with deionized water and transferred into a bath containing 1 mM $HAuCl_4$. Cathodic electrodeposition of Au nanoparticles onto the CuO NSs electrode was performed from the above bath at constant potential -0.2 V for 80 s.

2.3 Characterization

Morphology of the CuO NSs was analyzed on a Hitachi S-4800 field emission scanning electron microscope (FESEM). X-ray diffraction (XRD) measurements were performed on a Rigaku D/Max-2400 X-ray diffractometer using Cu Kα radiation (40 kV, 60 mA).

2.4 Electrochemical experiments

All electrochemical measurements were performed on a Potentiostat/Galvanostat Model 263 electrochemical workstation (Ametek, USA). A conventional three-electrode system was used with Ag/AgCl as the reference electrode, a platinum electrode (Φ=2 mm) as the counter electrode. CuO NSs electrode was evaluated as a glucose sensor in 0.1 M NaOH solution.

3. Results and discussions

3.1 Characterization

Fig. 1a and 1b is the XRD pattern and SEM image of the prepared CuO NSs electrode, respectively. The XRD pattern reveals that the prepared CuO NSs consist of mainly CuO phase (JCPDS 05-0661) with monoclinic structure. As can be seen from Fig. 1b, the Cu electrode is completely covered by CuO NSs after the reaction. The CuO NSs are almost perpendicular to the Cu substrate. The thickness of individual nanosheet is measured about 20 nm. The CuO NSs electrode may exhibit excellent electrocatalytic performance towards glucose due to the large surface area and numerous interspaces between nanosheets.
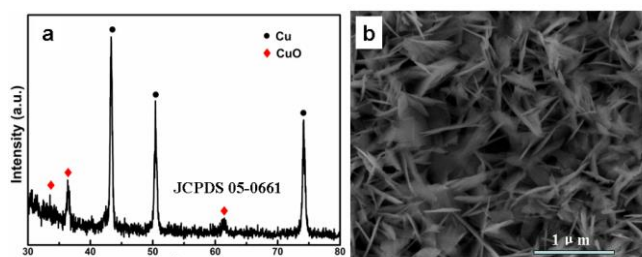

Fig .1. XRD pattern (a) and SEM image (b) of the CuO NSs electrode.

3.2 Glucose-sensor measurement

In order to obtain the optimal response to glucose, the effect of applied potential on the response current towards 0.1 mM glucose was investigated and showed in Fig. 2. As can be seen from Fig. 2a, the response current increases with the increase of the applied potential from 0.3 V to 0.6 V. Larger response current can be obtained at potential 0.6 V. However, with the further increase of the applied potential to 0.7 V, the response current is hard to stable. In addition, AA shows only little interference towards electrooxidation of glucose at 0.6 V (Fig. 2b). Therefore, 0.6 V was chosen as the optimal potential.
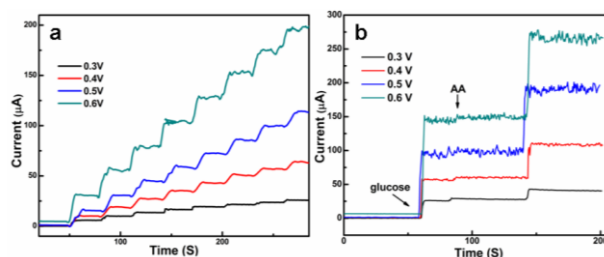

Fig. 2. (a) Dependence of the response current on the applied potential towards 0.1 mM glucose. (b) The interference of AA at different potentials (glucose:AA=0.5 mM:0.05 mM).

The electrocatalytic activity of the Cu, CuO NSs and Au/CuO NSs electrodes towards the oxidation of glucose was demonstrated first of all. Fig. 3a displays the CVs of bare Cu, CuO NSs and Au/CuO NSs electrodes in 0.1 M NaOH. It is clear that a well-defined CV curve can be obtained after reaction for 30 min, indicating the formation of CuO NSs. After Au nanoparticles were deposited, the current further increased due to the excellent conductivity of Au. Upon the addition of 1 mM glucose (Fig. 3b), evident response current was observed.
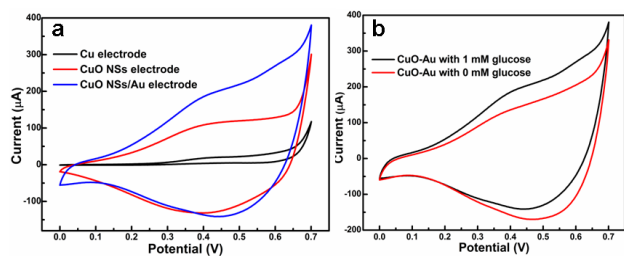
Fig. 3. (a) CVs of bare Cu, CuO NSs and Au/CuO NSs electrodes in 0.1 M NaOH. (b) CVs of Au/CuO NSs electrode with and without 1 mM glucose in 0.1 M NaOH.

Fig. 5. (a) Typical current-time response curve of Au/CuO NSs electrode towards certain concentration of glucose (40 μM, 100 μM, 200 μM) at 0.6 V in 0.1 M NaOH solution. (b) The relationship between catalytic current and the concentration of glucose.

In order to estimate the kinetics of the Au/CuO NSs electrode, the CVs of Au/CuO NSs electrode were measured in 0.1 M NaOH at different scan rates (Fig. 4a). As can be seen from Fig. 4b, the response currents at 0.6 V are proportional to the square root of the scan rates, indicating that the electrocatalytic process is diffusion controlled at the Au/CuO NSs electrode.
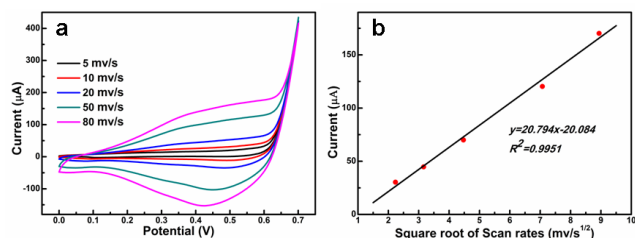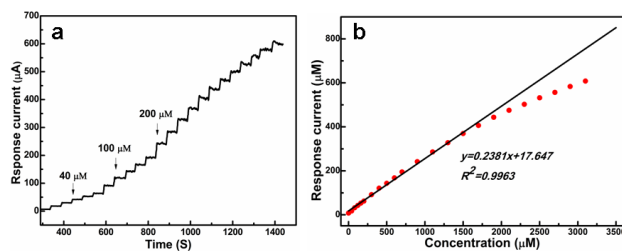

Fig. 4. (a) CVs of the Au/CuO NSs electrode in 0.1 M NaOH solution at different scan rates. (b) Response current at 0.6 V as a function of scan rate at the Au/CuO NSs electrode.

Fig. 5a displays the current-time curve of the Au/CuO NSs electrode at a constant potential of 0.6 V to successive addition of glucose into 0.1 M NaOH under stirring. A well-defined and fast response was observed with successive addition of glucose. As can be seen from Fig. 5b, the linear relationship between the response current and the glucose concentration of Au/CuO NSs electrode was obtained for concentration ranging from 1 μM to 1700 μM. The linear regression equation was given by $y = 0.2381x + 17.647$ [y (μA); x (μM);], with a correlation coefficient of $R^2 = 0.9963$. The detection limit of glucose using Au/CuO NSs electrode was found to be 1 μM (S/N=3) with a sensitivity of 3370.1 μA mM^{-1}cm^{-2}. The Au/CuO NSs electrode shows high sensitivity to glucose, indicating that the Au/CuO NSs composite can increase the electrocatalytic performance of the electrode due to the large surface area and high rate of electron transfer from glucose to the Au/CuO NSs electrode [9].

4. Conclusions

Au/CuO NSs electrode was successfully prepared by solution immersing method and followed by electrodeposition. The Au/CuO NSs electrode shows excellent electroactivity toward electrooxidation of glucose. The observed detection limit for this Au/CuO NSs electrode is 1 μM with the linear range from 1 μM to 1700 μM as well as the sensitivity of 3370.1 μA mM^{-1}cm^{-2}. On the basis of our research, the Au/CuO NSs electrode has potential applications for design of glucose sensor.

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