



Dual-functional cubic cuprous oxide for non-enzymatic and oxygen-sensitive photoelectrochemical sensing of glucose



Hongbo Li^{a,*}, Jing Li^a, Daye Chen^b, Yanxia Qiu^a, Wei Wang^{a,*}

^a School of Chemistry and Chemical Engineering, Yancheng Institute of Technology, Yancheng 224051, PR China

^b Maternal and Child Health Hospital of Yancheng, Yancheng 224002, PR China

ARTICLE INFO

Article history:

Received 3 March 2015

Received in revised form 21 May 2015

Accepted 26 May 2015

Available online 11 June 2015

Keywords:

Non-enzymatic
Photoelectrochemical
Sensor
Glucose
Cuprous oxide

ABSTRACT

A novel non-enzymatic and oxygen-sensitive photoelectrochemical (PEC) sensor for glucose was first constructed based on dual-functional cubic cuprous oxide. Herein, cuprous oxide acts both as an excellent catalyst for the preoxidation of glucose and as a photocathode for the PEC non-enzymatic glucose sensing. The fabricated cuprous oxide was characterized by scanning electron microscopy, X-ray diffractometry, X-ray photoelectron spectrometry, and UV–vis spectrophotometry. Under the optimized conditions, the PEC sensing was linear in its response to the logarithm of concentration of glucose in the range of 0.0005 to 6 mmol L⁻¹ with a detection limit of 0.3 μmol L⁻¹. The same concentration of other common species did not interfere with the detection of glucose, and the results of the PEC sensor corresponded well with those obtained by the commercially available enzymatic glucose sensor. This novel non-enzymatic and oxygen-sensitive PEC sensor exhibited good performance with its high sensitivity, good selectivity, wide linear range, low cost, and portable features. Also it provides an alternative way for improving non-enzymatic PEC sensor of glucose.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

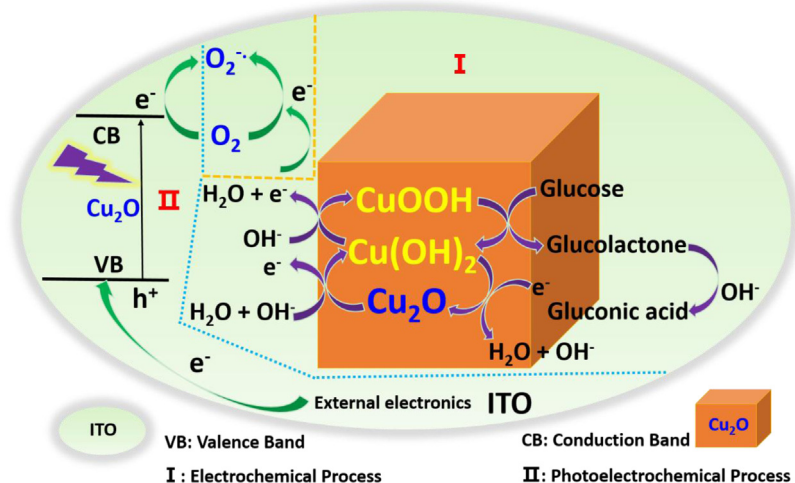
Glucose is an important analyte in clinical diagnostics, because high concentration of glucose is the cause of diabetes [1]. In the last decades, enzyme-based electrochemical biosensors have been widely developed for glucose determination due to their good selectivity and high sensitivity [2,3]. However, they suffer from poor stability because the glucose oxidase can be easily affected by pH, humidity, temperature, ionic detergents and other types of interference [4–6]. To address these problems, non-enzymatic electrochemical sensors based on the direct oxidation of glucose have been explored (e.g. Pt [7], Au [8], Cu [9], Pt–Pb [10], Pt–Te [11], NiO [12], Co₃O₄ [13], MnO₂ [14], RuO₂ [15], Fe₂O₃ [16], CuO [17] and Cu₂O [18]). Recently, Dong group developed Au/Pt nanoparticles–TiO₂ hybrid nanostructure for non-enzymatic photoelectrochemical (PEC) sensing of glucose [19]. Moreover, Ju group proposed a glucose oxidase modified CdTe-based PEC sensor for glucose based on the decreased photocurrent caused by the consumption of dissolved oxygen as an electron acceptor [20]. However, each of these methods suffers from at least one undesirable limitation such as limited selectivity, low sensitivity,

operational complexity, and lack of economy or speed. Therefore, there is still a challenge to develop an alternative approach for a facile, portable, selective, sensitive, and environment-friendly detection method of glucose.

PEC detection has been a newly emerging but dynamically developing analytical technique due to its inexpensive and simple photoelectric devices [21–29]. It possesses potentially higher sensitivity than conventional electrochemical methods due to the reduced background signals and the separated excitation source (light) and detection signal (electricity) [30–37]. The detection principle is that the photocurrent/photopotential change could be brought about by the interactions between various recognition elements and their corresponding target analytes [23,38–42]. Cuprous oxide, an important p-type semiconductor with a band gap of ~2.1 eV, can not only act as the catalyst for non-enzymatic glucose sensors but also as an excellent photoelectric beacon [43]. During the process of electrode reaction, the Cu(III)/Cu(II) redox couple can catalyze the oxidation of glucose to gluconolactone in alkaline solution [44,45]. With the increase of copper valence, part of the free electrons reduce adsorbed molecular oxygen to a superoxide radical anion (O₂^{-•}) [46]. Based on the consumption of dissolved oxygen, the photocurrent is suppressed since dissolved oxygen is employed as an electron acceptor during the PEC process [47].

Inspired by the above works, dual-functional cuprous oxide both can directly catalyze glucose by Cu(III)/Cu(II) redox couple and

* Corresponding authors. Tel.: +86 515 88298735; fax: +86 515 88298735.
E-mail addresses: hbli@ycit.edu.cn (H. Li), wangw@ycit.edu.cn (W. Wang).



Scheme 1. Schematic illustration of the preoxidation and then PEC detection of glucose using cubic Cu_2O -based photocathode.

act as an excellent photocathode material for PEC sensing. Then the non-enzymatic and oxygen-sensitive PEC sensing of glucose was first developed based on single dual-functional cubic cuprous oxide. In this work, the environment-friendly Cu_2O -based photocathode was successfully prepared by one step electrodeposition. Compared with conventional techniques for the preparation of nano semiconductor thin films, such as molecular beam epitaxy, radio-frequency magnetron sputtering, sol-gel process and pulsed laser deposition, electrodeposition presents many advantages: (i) the deposition is realized at low temperature and at atmospheric pressure; (ii) it requires a simple low cost apparatus; and (iii) the film thickness can be controlled by the charge consumed during the deposition process. Herein, the robust Cu_2O -based photocathode exhibited excellent performance for the non-enzymatic and oxygen-sensitive PEC sensing of glucose. In addition, the possible mechanism was also investigated in detail (Scheme 1).

2. Experimental

2.1. Materials and reagents

All chemicals were obtained from commercial sources and used without further purification. $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (99.999%) and sodium citrate tribasic dihydrate ($\geq 99.5\%$), were purchased from Sigma-Aldrich (St. Louis, MO). Glucose ($\geq 99.5\%$) was from Aladdin Chemistry Co. Ltd. The whole blood samples for real sample determination were from the volunteers of Maternal and Child Health Hospital of Yancheng. All other chemicals were of analytical grade. In this work, 0.1 mol L^{-1} NaOH was always employed as the supporting electrolyte. Aqueous solutions were prepared with ultrapure water (Milli-Q, Millipore).

2.2. Apparatus

Scanning electron microscopy (SEM) was performed using a Hitachi S-4800 scanning electron microscope (Hitachi, Tokyo, Japan). X-ray diffraction (XRD) pattern of Cu_2O was measured in the range of $2\theta = 10\text{--}80^\circ$ by step scanning on the Bruker D8 Advance (super speed) diffractometer (Bruker-AEX, German) with $\text{Cu K}\alpha$ radiation ($k = 0.15406 \text{ nm}$) operated at 40 kV and 100 mA. UV-vis spectrum was recorded at room temperature with a Cary 5000 ultraviolet and visible spectrophotometer (Varian, USA). X-ray photoelectron spectroscopy (XPS) analysis was carried on an ESCALAB250Xi X-ray photoelectron spectrometer. PEC measurements were performed with a home-built PEC system.

The photocurrent-time curve was obtained by the technique of current-time on a CHI660D electrochemical workstation (CH Instruments, Shanghai, China) with chopped light every 10 s. In this work, a 250 W tungsten halogen lamp light was used for the emission of continuous spectrum (simulated sunlight irradiation, 585,000 lx). The distance between the light source and the electrode was fixed at 10 cm. All experiments were carried out at room temperature using a conventional three electrode system with the modified ITO substrates ($\Phi 5 \text{ mm}$, resistivity $10 \Omega \text{ sq.}^{-1}$, Zhuhai Kaivo Electronic Components Co. Ltd., China) as the working electrode, a platinum wire as the auxiliary electrode, and a saturated calomel electrode as the reference electrode.

2.3. Preparation of photocathode and detection procedure

The electrodeposition of cuprous oxide was performed in an electrochemical workstation using a standard three-electrode system according to the previous work [48]. Before electrodeposition, an ITO electrode ($1 \text{ cm} \times 4 \text{ cm}$) was cleaned with NaOH (1 mol L^{-1}) and H_2O_2 (30%), washed with acetone and ultrapure water, and dried at room temperature. By means of a circle-shaped mask centered at one end of ITO, then the electrodeposited Cu_2O film of 5 mm in diameter on ITO substrate was obtained from an alkaline solution containing 0.05 mol L^{-1} CuSO_4 and 0.1 mol L^{-1} sodium citrate tribasic dihydrate with three-electrode system. The solution was adjusted to pH 11 with 4 mol L^{-1} NaOH before electrodeposition, and then it was performed by controlling the electrodeposition temperature at 60°C , the stable potential of -0.4 V and the electrodeposition time of 20 min. Finally, the as-prepared Cu_2O film was rinsed with ultrapure water three times and dried at 100°C for 1 h. Afterwards, the fabricated Cu_2O -based photocathode was used to detect glucose in 0.1 mol L^{-1} NaOH by the preoxidation on the conditions of 0.6 V and 8 s and then the current-time curve experimental technique at a bias voltage of -0.2 V with simulated sunlight irradiation. Controlled experiments were operated according to the same procedure, except the glucose consisted of either dopamine, ascorbic acid, uric acid, or NaCl.

3. Results and discussion

3.1. Characterization of Cu_2O

The morphology of the as-synthesized Cu_2O was imaged by Field Emission Scanning Electron Microscopy (FESEM). Fig. 1(A) shows the low-magnification SEM image of uniform Cu_2O microcrystal

Download English Version:

<https://daneshyari.com/en/article/7145666>

Download Persian Version:

<https://daneshyari.com/article/7145666>

[Daneshyari.com](https://daneshyari.com)