

Fabrication of nanoporous copper oxide film biosensor with a polymer sphere template and its application to glucose sensing

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Abstract: A nanoporous CuO film biosensor was fabricated on a Cu substrate electrode by the colloidal-crystal polystyrene template technique with the help of potentiostatic plating and potential cyclic scanning. The direct electrocatalytic oxidation of glucose in alkaline medium on nanoparticle CuO film modified electrode has been investigated in detail. When applied to detect glucose, the sensor exhibited a linear response of up to 3.2 mmol/L of glucose, and a high sensitivity of $3\,799\ \mu\text{A} \cdot \text{mM}^{-1} \cdot \text{cm}^{-2}$, higher than that of most nonenzymatic glucose sensors reported in the literature. The sensor response time was less than 3 s and the detection limit was $0.37\ \mu\text{mol/L}$ (at signal/noise=3). This improvement is due to the nanoporous structure and the greatly enhanced effective surface area. In addition, the sensor also performed well for measuring glucose concentrations in human blood serum samples. The results indicate that the nanoporous CuO film modified electrode allows highly sensitive and selective, stable, and fast amperometric sensing of glucose and is thus promising for the further application in nonenzymatic glucose sensors development.

Key words: polystyrene sphere template; electrodeposition; glucose; nonenzymatic biosensor

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多孔纳米氧化铜修饰电极的制备及分析应用

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摘要: 利用胶体晶体模板法和循环伏安电镀法成功地在铜电极表面合成了多孔纳米氧化铜薄膜, 并应用于碱性溶液中葡萄糖的直接电催化氧化。制备的修饰电极在 $5\ \mu\text{mol/L} \sim 3.2\ \text{mmol/L}$ 的浓度范围内对葡萄糖具

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有线性响应关系,灵敏度为 $37.99 \text{ A} \cdot \text{m} \cdot \text{mol}^{-1}$,达到稳定电流值所需要的时间小于 3 s. 在 3 倍信噪比条件下,该传感器的检测限为 $0.37 \mu\text{mol/L}$,明显优于其他非酶传感器,这要归功于多孔氧化铜的结构,该结构能够增加电极表面的活性位点,提高葡萄糖氧化过程中的电子转移速率. 同时,该传感器对实际血样的测定具有很高的准确度,结果表明,该多孔氧化铜材料具有较高的灵敏度和选择性,在非酶葡萄糖传感器领域具有广阔的应用前景.

关键词: 聚苯乙烯模板;电沉积;葡萄糖;非酶生物传感器

0 Introduction

Diabetes has become one of the most common health problems nowadays, and the research on the detection technique of the human body glucose is thus of great significance. Most of the known amperometric biosensors for glucose monitoring are based on glucose oxidase (GOx), due to their high sensitivity, specificity and low detection limit^[1-2]. But the greatest weakness of the enzymatic glucose sensors is the lack of stability. Their GOx can easily be affected by temperature, pH value, humidity and toxic chemicals^[3]. To resolve this problem, numerous studies have been performed to determine glucose concentration without using enzymes^[4-10]. The direct electro-oxidation of glucose on different substrates such as gold^[11], copper^[12], and electrode modified with platinum^[7], bismuth^[6], nickel^[13], and copper^[14-15] has been explored in the hope of developing effective enzyme-free biosensors. However, poisoned by adsorbed intermediates and chloride^[11-12], low sensitivity and poor selectivity are main drawbacks of these sensors. Hence, it is important to explore a nonenzymatic sensor with high sensitivity, stability, and fast response for the detection of glucose by amperometry.

Recently, nanomaterials with special physical and chemical properties, especially metallic nanoparticles, have been widely applied in biosensors and shown good performance through increasing the active surface area and enhancing the mass transport and catalysis. Among them, there was a great amount of interest on the application of copper and copper oxide nanoparticles for the nonenzymatic detection of glucose^[16-18]. It is well-

known that Cu nanomaterials are unstable for electroanalysis, for they are easily oxidized in air and solution^[19-21]. In comparison, CuO nanomaterials are relatively stable and are promising in the development of nonenzymatic glucose sensors, because of their good electrochemical activity, highly specific surface area, and the possibility of promoting electron transfer reactions at a lower overpotential^[22-23]. On the other hand, the electrodeposition of CuO nanoparticles is simple and time-saving.

Also, porous materials are commonly used for surface modification. An important method for preparation of the nanoporous structure is to electrodeposit it on metal surfaces with physical templates. The templates are used as a mould, defining where the nucleation and growth can occur and altering the diffusion layer for the electrodeposition process. The size of the pores and the periodicity of the porous structures can be controlled and tuned by changing the size of the colloid and thickness of the template^[24]. Furthermore, the open, interconnected, periodic large porous structure ensures accessibility of reactants to the surface active sites of the electrode. Until now, there have been few reports on the application of nanoporous CuO materials in nonenzymatic glucose detection.

Herein, the nanoporous CuO film biosensor was fabricated and characterized, and applied to detect serum glucose successfully. Normally, noble metal and glass carbon surfaces are employed as the substrate electrodes. For comparison, copper was chosen as the work electrode material because of its low cost and high conductivity and especially its compatibility with the nanoporous

copper oxide film. The structured nanoporous film was prepared by electrochemical reduction of CuSO_4 in the voids of polystyrene (PS) latex spheres template, and then oxidized in situ into CuO nanoparticles by cyclic potential scanning^[25], followed by chemical removal of the template using toluene, thus producing a good nonenzymatic sensor for the electrocatalytic oxidation of glucose in alkaline solution.

1 Experimental

1.1 Reagents

Analytical grade $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, KCl, NaOH, toluene, glucose and so on were all purchased from Shanghai Chemical Reagent Company (Shanghai, China) and used without further purification. All solutions in this study were prepared with double-distilled water.

1.2 Instrumentation

All electrochemical experiments were carried out on a LK2005 Electrochemical Work Station (LANLIKE, Tianjing, China). The three-electrode system consisted of a glucose biosensor as working electrode, a reference electrode (a saturated calomel electrode) and a counter electrode (platinum wire). Scanning electron microscope (SEM) images were obtained on a JEOL JSM-6700F SEM system. XRD patterns were recorded via a Philips X'Pert PRO S X-ray diffractometer with Cu K_α radiation ($\lambda = 1.5406 \text{ \AA}$). X-ray photoelectron spectroscopy (XPS) measurements were performed on an ESCALAB MK2 spectrometer (VG Co., UK) with Mg K_α radiation as the source for excitation.

1.3 Assembly of the colloidal templates

Polystyrene spheres (PS) were synthesized by an emulsifier-free emulsion polymerization technique, according to Ref. [26]. Before modification, the Cu electrode surface (2.0 mm diameter) was polished on wet fine emery SiC abrasive paper and 0.3 μm alumina slurries, respectively, and then sonicated successively in ethanol, acetone and doubly distilled water for 10

min, respectively. Finally, the electrode was dried with high purity N_2 . Approximately 10 μL of aqueous suspension of the monodisperse polystyrene spheres diluted with water to 0.5% (mass fraction) was spread over the Cu electrode surface. The electrode was kept in a saturated humidity chamber and then allowed to dry slowly over 24 h. After water was evaporated, the electrode surface appeared opalescent, as expected, with colours from green to red, depending on the angle of observation. The template is robust and adheres well to the Cu electrode. There is no evidence for the re-suspension of the latex particles when the modified electrode is placed in contact with the plating solution^[27].

1.4 Synthesis of nanoporous CuO film

The nanostructured copper was first electrodeposited in the gaps of the template modified Cu electrode at a constant potential of -0.40 V for 120 s in 100 mmol/L KCl solution containing 10 mmol/L CuSO_4 (pre-purged with N_2 for 10 min and keeping N_2 flowing over the solution throughout the deposition process), and then the electrode was rinsed with distilled water and dried with N_2 . After that, the electrode was repeatedly scanned in 100 mmol/L NaOH solution with cyclic voltammetry under the potential range of -0.50 to 0.30 V at $50 \text{ mV} \cdot \text{s}^{-1}$ for 20 cycles, allowing the nanostructured Cu to be oxidized into nanostructured CuO. After the deposition, the electrode was soaked in toluene for 1 h to dissolve away the polystyrene template. Lastly, the electrode was washed with doubly distilled water and dried with N_2 for subsequent use. All experiments were performed at ambient temperature ($25 \text{ }^\circ\text{C} \pm 1 \text{ }^\circ\text{C}$).

2 Results and discussion

2.1 Formation of nano-copper oxide film

Fig. 1 shows the repetitive cyclic voltammograms of the redox process of copper oxide on the surface of Cu electrode in 100 mmol/L

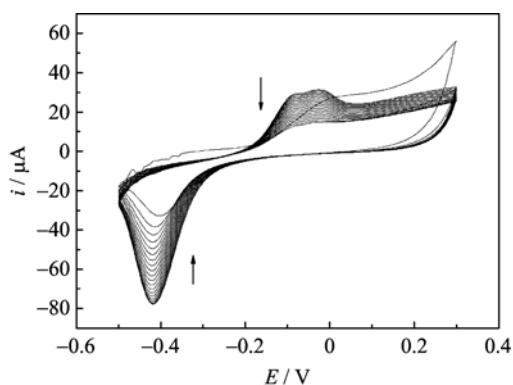
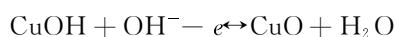
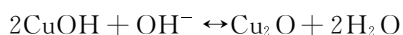
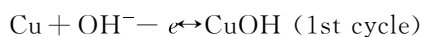


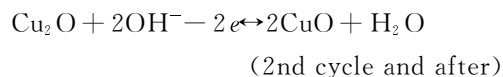
Fig. 1 Cyclic voltammograms of the deposition process of CuO on the surface of Cu electrode in 100 mmol/L NaOH solution at $50 \text{ mV} \cdot \text{s}^{-1}$

NaOH solution. There are two anodic peaks and one cathodic peak, which can be attributed to the redox process between copper and copper oxide. The anodic peaks represented the oxidation of Cu_2O and CuOH to CuO , respectively, and the cathodic peak was attributed to the reduction of CuO to Cu_2O (CuOH)^[25]. With the procedure of the potential scan, the redox peak currents all decreased due to the increase of surface resistance of the electrode, indicating that copper oxide has been successfully deposited on the surface of the Cu substrate electrode. The mechanism of the electrodeposition is as follows:

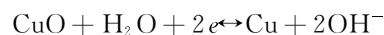
Anodic process:



(2nd cycle and after)



Cathodic process:



2.2 Characterization of the nanoporous CuO structure

The XRD pattern of the as-prepared sample is attributed to the orthorhombic phase, as shown in Fig. 2(a)B, where the peaks marked with arrows can be indexed to this phase. Compared with the standard diffraction patterns (JCPDS Card No. 45-0937), no characteristic peaks from impurities were detected. The result indicates that the CuO nanostructure is pure and well crystallized. The compact CuO film is also shown as a reference in Fig. 2(a)A, where the peaks can also be seen in the same positions for a compact sample. However, their relative intensities of the peaks are different from those of the nanoporous sample, indicating the negative effect of the nanoporous structure on crystallization^[26]. XPS is a powerful technique for the study of transition metal compounds having localized valence-orbitals. The nanoporous CuO was further characterized by XPS as shown in Fig. 2(b). In the Cu ($2p$) region, the Cu ($2p_{3/2}$) and Cu ($2p_{1/2}$) band showed a single peak at 931.7 eV and 951.5 eV, respectively. The peak-to-peak difference is about 20 eV, which reveals that the copper atoms deposited on the electrode surface were of bivalence. The two shake-up satellites located at 943.2 eV and 961.7 eV, indicate the presence of CuO at the sample

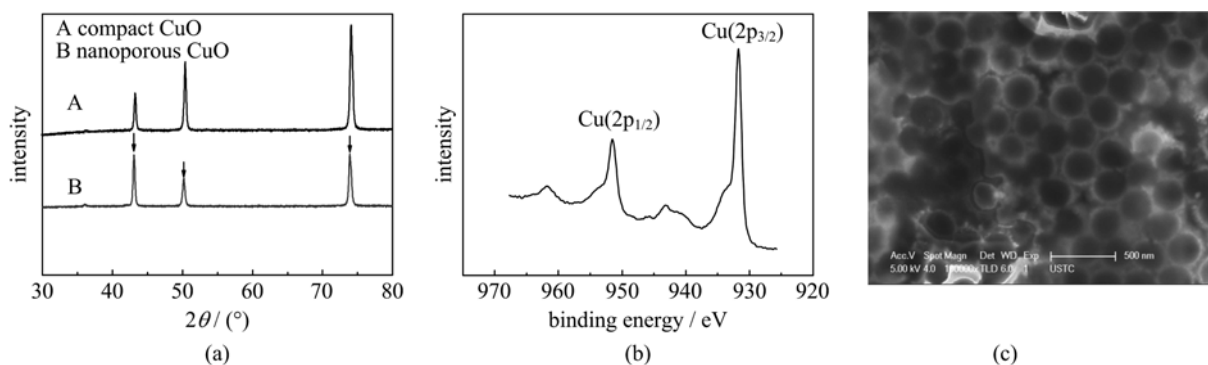


Fig. 2 XRD patterns of the different CuO films deposited on Cu surface (a), XPS spectrum of the nanoporous CuO film (b), and SEM image of the nanoporous CuO film (c)

surface. The as-prepared sample was also studied by SEM. As shown in Fig. 2(c), the honeycomb-like nanoporous structure surface morphology was formed, and the spherical voids left in the CuO nanocrystals are attributed to the removal of the polystyrene spheres. It should be noted that the void diameter depends on the size of polystyrene spheres being used.

2.3 Glucose sensing at the nanoporous CuO modified electrode

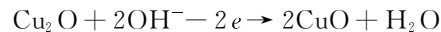
The electrocatalytic activity of the unmodified Cu electrode and the nanoporous CuO modified Cu electrode towards the oxidation of glucose in an alkaline solution were investigated. Fig. 3 (a) shows cyclic voltammograms of 1 mmol/L glucose in 50 mmol/L NaOH solution at the bare Cu electrode and the nanoporous CuO modified electrode.

In the absence of glucose, no oxidation peaks could be observed at either electrode. After addition of 1.0 mmol/L glucose, an oxidative wave, corresponding to the irreversible glucose oxidation, was observed for both electrodes. However, at the nanoporous CuO modified electrode, a rapid increase in current appeared, starting at about 0.3 V, with the appearance of an obvious oxidation peak at around 0.6 V, indicating that nanoporous CuO played a significant role in the oxidation of glucose. The substantially higher

current from the nanoporous CuO modified electrode than that from the bare Cu electrode in response to the glucose oxidation, is considered to be the result of larger surface area and more electrocatalytic active sites provided by the nanoporous CuO film. Furthermore, the cyclic voltammograms in glucose solution at different scan rates are shown in Fig. 3(b), where the peak current for the anodic oxidation of glucose is proportional to the square root of the scan rate. A linear relationship between i_p and $v^{1/2}$ was observed in the scan range of 20 ~ 500 $\text{mV} \cdot \text{s}^{-1}$ ($i_p = 19.37 + 7.05v^{1/2}$, $R = 0.9981$), which illustrates that electrocatalytic reaction is diffusion controlled.

Furthermore, a kinetic limitation has been found in the reaction and we speculate that the reaction is a typical EC' catalytic process. The following reactions could be used to explain the participation of Cu(II) in the anodic oxidation of glucose in alkaline medium:

Anodic polarization process:



Coupled homogeneous chemical reaction:



Detailed experiments on the influence of the NaOH concentration and the applied potential of the modified electrode were also carried out. As shown in Fig. 4(a), a series of NaOH solutions of

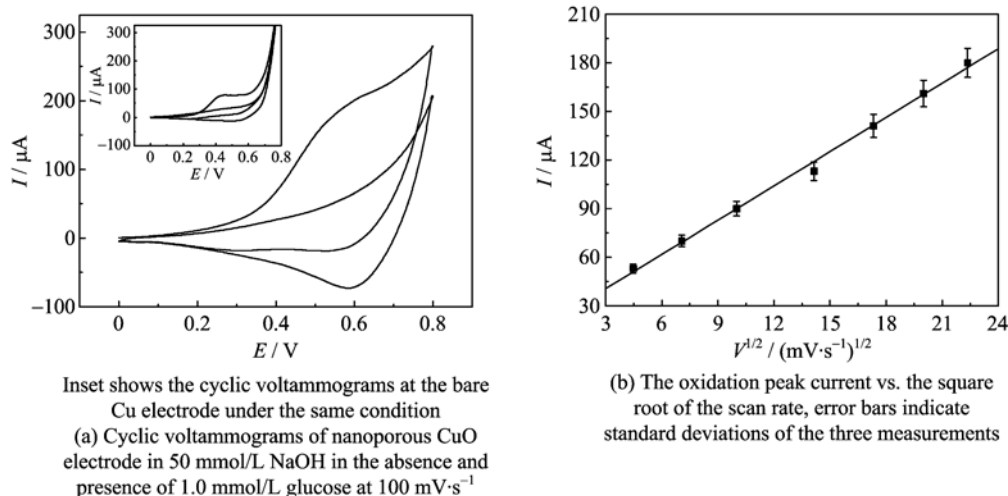


Fig. 3 Glucose sensing at the nanoporous CuO modified electrode

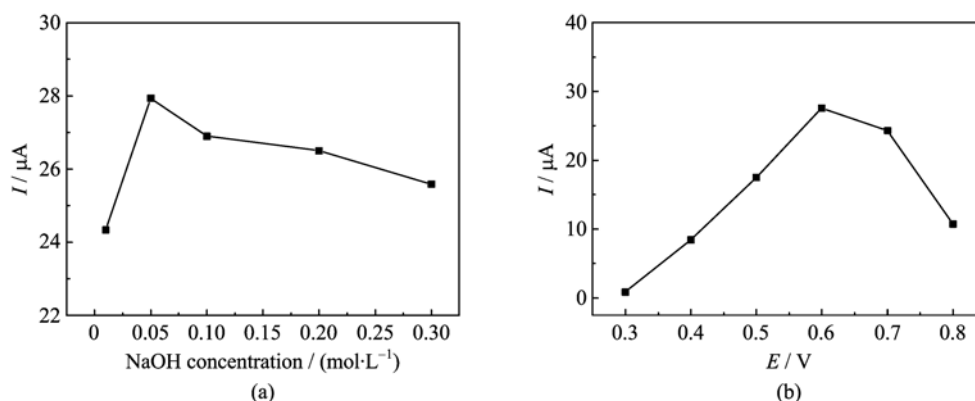
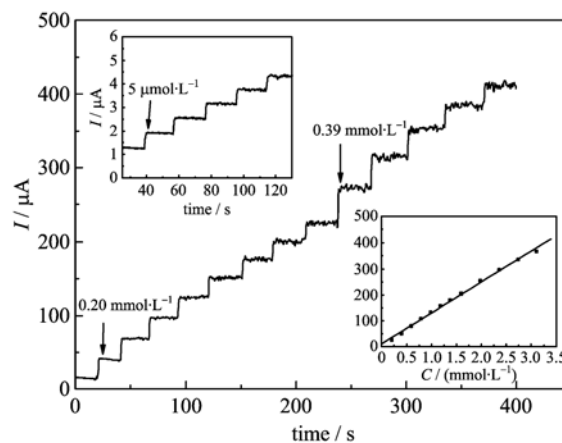


Fig. 4 Effect of NaOH concentrations (a) and applied potentials (b) on peak current in 0.2 mmol/L glucose for the nanoporous CuO electrode

different concentrations were used to study the alkaline effect on the oxidation of glucose. The peak current first increased with the concentration of NaOH until it reached 50 mmol/L, and then decreased with the further increase in NaOH concentration. The optimal value of the applied potential was obtained by amperometric measurement of glucose in 50 mmol/L NaOH solution at applied potentials of 0.3, 0.4, 0.5, 0.6, 0.7 and 0.8 V. The result shown in Fig. 4(b) demonstrates that the maximum current response was obtained at 0.6 V. Thus, 50 mmol/L NaOH and an applied potential of 0.6 V were chosen for subsequent experiments.

2.4 Amperometric detection of glucose on nanoporous CuO modified electrode

Since chronoamperometry under stirred condition is much more sensitive than cyclic voltammetry, it was employed to estimate the low detection limit. Fig. 5 shows the steady-state catalytic current time response of the nanoporous CuO modified electrode with successive additions of 40 mmol/L glucose solution into 10 mL of 50 mmol/L NaOH solution at the applied potential of 0.6 V. The current response of the sensor exhibited a linear dependence on glucose concentration, and the calibration curve for glucose measurement is $I/\mu\text{A}=11.38+119.28C/(\text{mmol}\cdot\text{L}^{-1})$ with the correlation coefficient of 0.998 8. The sensitivity is estimated to be $37.99\text{ A}\cdot\text{m}\cdot$



Top inset displays the response to low concentration of glucose; bottom inset shows the calibration curve of the biosensor as a function of glucose concentration

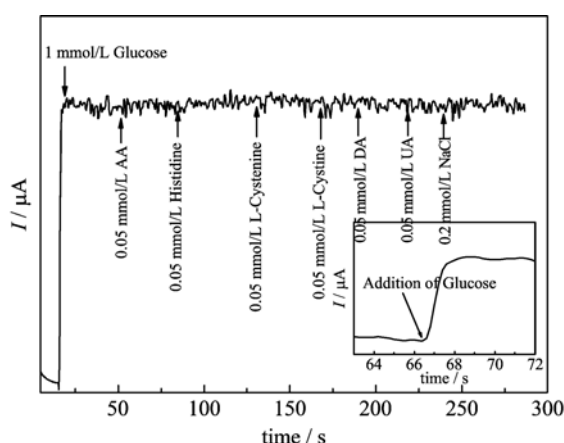
Fig. 5 Amperometric response of the nanoporous CuO modified electrode at potential 0.6 V in 50 mmol/L NaOH solution for successive addition of glucose

mol^{-1} , and the sensor displays a linear range of 5 $\mu\text{mol}/\text{L}$ to 3.2 mmol/L glucose concentration with a detection limit of 0.37 $\mu\text{mol}/\text{L}$ (at signal/noise=3). The performance of the biosensor is compared with those of other reported CuO-based nonenzymatic glucose sensors^[28-31]. The sensitivity of our sensor is substantially higher than that of other glucose sensors, and our sensor also displays an excellent detection limit and linear range. All the data from our sensor reveal the properties of high sensitivity, low detection limit and excellent linear range, which are attributed to the fact that nanoporous CuO film can greatly increase the electrocatalytic active areas and promote electron

transfer in the oxidation of glucose.

2.5 Stability and selectivity of the biosensor

The stability of our electrode was determined by storing the sensor under ambient condition for 30 d. After 7 d and 30 d, the current response remained at 98.3% and 91.8%, respectively. The current responses to 1 mmol/L glucose were measured 6 times using the same electrode with a relative standard deviation (RSD) of 2.1%. For the three electrodes which are different and freshly made independently under the same conditions, the RSD was 4.6%. These results confirm that our sensor has high stability as well as good reproducibility that makes it applicable for practical use. The current response becomes stable in less than 2 s, which indicates a rapid enough response of the sensor towards glucose. We also investigated the interference effect of ascorbic acid (AA), uric acid (UA) and NaCl, which normally co-exist with glucose in real samples. The physiological glucose level is 3 to 8 mmol/L and the other oxidizable interferents are present at levels as low as 0.1 mmol/L. Therefore, interference tests were carried out by adding 1 mmol/L glucose, followed by interferents listed. The results demonstrate an almost negligible effect of the interferents (Fig. 6). Furthermore, the



Inset shows the response time of the nanoporous CuO modified electrode to achieve steady-state currents

Fig. 6 Interference test of the sensor in 50 mmol/L NaOH solution at 0.6 V with 1 mmol/L glucose and other interferents as indicated

chloride poisoning, which has been a major problem for most metal or metal oxide electrochemical glucose sensors, was not found in our study.

Finally, in order to illustrate the practical utility of the resulting glucose biosensor, human serum samples were assayed. Fresh serum samples were supplied by a local hospital, which were first analyzed with a standard clinical assay based on glucose dehydrogenase electrode method. Then every 100 μ L serum sample was added to 10.0 mL of 50 mmol/L NaOH solution under the operation potential of 0.6 V. Tab. 1 displays the results of these blood glucose determinations. The data from the proposed glucose sensor are in good agreement with the results provided by the local hospital.

Tab. 1 Amperometric determination of glucose in human blood serum samples

blood sample	given by	proposed	RSD/% ^a
	hospital	nonezymatic sensor	
	/(mmol · L ⁻¹) / (mmol · L ⁻¹)		
1	4.1	4.3 ± 0.30	4.3
2	5.2	5.0 ± 0.19	2.2
3	6.0	6.2 ± 0.32	3.2
4	7.3	7.0 ± 0.44	3.6
5	10.0	9.8 ± 0.29	1.7

【Note】 ^a RSD/% calculated from three separate experiments

3 Conclusion

In summary, we have successfully synthesised a nanoporous CuO film on the Cu substrate electrode by the colloidal-crystal template technique and film plating/cyclic voltammetry method for the first time. This facile and effective process increased the porosity of the surface, resulting in a material with an increased surface area, which makes the exposure of the surface to the reactants more effective. The modified electrode was mechanically and chemically stable and exploited to fabricate a nonenzymatic glucose sensor. Because of its large effective surface area, interconnected microenvironments, the fabricated nanoporous copper oxide film showed higher

electrocatalytic activity towards glucose oxidation in alkaline solutions. Meanwhile, the interference from the oxidation of common interfering species such as AA, UA and DA were effectively avoided. Thus, this nanoporous CuO material with enhanced sensitivity and selectivity is promising for fabrication of nonenzymatic glucose biosensor. On the other hand, the preparation method of our sensor can be readily extended to make a screen-printed electrode with a large surface area. The successful preparation of nanoporous CuO material is relatively simple and very effective, thus providing a promising platform for further development of other biosensors.

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