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Direct electrochemistry of glucose oxidase and biosensing for glucose based on boron-doped carbon nanotubes modified electrode

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Abstract

Due to their unique physicochemical properties, doped carbon nanotubes are now extremely attractive and important nanomaterials in bioanalytical applications. In this work, selecting glucose oxidase (GOD) as a model enzyme, we investigated the direct electrochemistry of GOD based on the B-doped carbon nanotubes/glassy carbon (BCNTs/GC) electrode with cyclic voltammetry. A pair of well-defined, quasi-reversible redox peaks of the immobilized GOD was observed at the BCNTs based enzyme electrode in 0.1 M phosphate buffer solution (pH 6.98) by direct electron transfer between the protein and the electrode. As a new platform in glucose analysis, the new glucose biosensor based on the BCNTs/GC electrode has a sensitivity of 111.57 μA mM^{-1} cm^{-2}, a linear range from 0.05 to 0.3 mM and a detection limit of 0.01 mM (S/N = 3). Furthermore, the BCNTs modified electrode exhibits good stability and excellent anti-interferent ability to the commonly co-existed uric acid and ascorbic acid. These indicate that boron-doped carbon nanotubes are the good candidate material for the direct electrochemistry of the redox-active enzyme and the construction of the related enzyme biosensors.

Keywords: Boron-doped carbon nanotubes (BCNTs); Glucose oxidase; Glucose; Direct electrochemistry

1. Introduction

Modifying electrode surface on the molecular scale to allow efficient electron transfer between the redox protein and the electrode is considered to be the foundation for understanding the redox properties of protein and developing the third generation biosensor (Gooding et al., 2003; Zhang et al., 2007a,b,c). Nevertheless, the redox sites of the protein are deeply seated in the protein shell, the establishment of a fast electron transfer between enzyme (such as GOD) and the electrode is a significant challenge in designing enzyme-based sensors. Nanomaterials, especially carbon nanotubes (CNTs), become an attractive material in bioelectrochemistry for the direct electrochemistry of enzymes because the direct electron communication between the redox sites of protein/enzyme and the electrode could be promoted by CNTs (Cai and Chen, 2004; Davis et al., 1997; Sun et al., 2006; Salimi et al., 2007; Viticoli et al., 2006; Wang et al., 2002a,b,c; Yamamoto et al., 2003; Zhao et al., 2002). However, the direct electrochemistry of the immobilized protein/enzyme on the CNTs modified electrodes and the performance of the related biosensors still need to be improved.

Recently, many attempts have been made in order to improve the direct electron transfer between the redox-active sites of enzymes and the electrode and to obtain the biosensor with good performance. In most cases, the direct electrochemistry of protein/enzyme was carried out based on the synergic effect of CNTs and other biocompatible materials. For example, Liu et al. reported the direct electrochemistry of glucose oxidase and electrochemical biosensing of glucose with CNTs and chitosan modified electrode (Liu et al., 2005). Based on the immobilization of GOD on the quantum dots/carbon nanotubes electrode, the direct electrochemistry of GOD was carried out and a glucose biosensor with improved performance was constructed (Liu et al., 2007). In addition, the stable films of biopolymer chitosan and carbon nanotubes were prepared by a layer-by-layer self-assembly technique and the property of the self-assembled multiplayer film in promoting the electron transfer of protein was demonstrated by incorporating microperoxidase-11 in the

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film (Xu et al., 2005). In all of these studies, the direct electrochemistry of protein was improved, but it cannot be neglected that the fabrication of the electrodes is more complex and the introduction of the biocompatible materials (such as chitosan) will increase the electrical resistance of the electrode.

On the other hand, it has been reported that the physicochemical properties of CNTs could be tailored by doping CNTs with foreign atoms (B or N atom) and the electronic, mechanic, conductive properties of CNTs could be improved obviously (Rubio et al., 1994; Wang et al., 2007; Yang et al., 2005; Zhang et al., 2006a). Doping CNTs with foreign atoms has also been reported to yield a large number of defective sites on to the nanotube surface (Jia et al., 2005a; Katz and Williner, 2004; Wang et al., 2004). Boron- or nitrogen-doped carbon nanotubes have its potential applications in many fields, such as nanosized photonic (Wang et al., 2002d) and electronic devices (Hamada et al., 1992; Mickelson et al., 2003; Satio et al., 1992; Zhang et al., 2002; Zhao and Xie, 2003), superhard materials (Liu and Cohen, 1989), electron field emitters (Teter and Hemley, 1996), and even sensitive chemical sensors (Shu and Kyeongiaem, 2003; Wang et al., 2006; Zhang et al., 2006b). Besides, nitrogen-doped carbon nanotubes have been successfully used to study the direct electrochemistry of protein (e.g. hemoglobin and glucose oxidase) and good results were obtained (Jia et al., 2005a,b).

In this work, taking glucose oxdiase as a model enzyme, we investigated the direct electrochemistry of glucose oxidase and biosensing for glucose based on the boron-doped CNTs (BCNTs) modified electrode. The biosensor based on the boron-doped CNTs modified electrode responded even more sensitively to glucose than the un-doped CNTs modified electrode.

2. Experimental

2.1. Apparatus and reagents

Electrochemical measurements were performed on a CHI660A electrochemical workstation (Chenhua Instrument Company of Shanghai, China) with conventional three-electrode cell. A glassy carbon (GC) electrode was used as the working electrode. A saturated calomel electrode (SCE) and a platinum wire were used as the reference and counter electrodes, respectively. All the potentials in this paper were in respect to SCE. Except the specific statement, the electrochemical measurements were carried out in a phosphate buffer solution (PBS, 0.1 M, pH 6.98) at room temperature ($25 \pm 2\,^{\circ}C$).

The un-doped CNTs with multi-walls and diameter of about 20–30 nm were obtained from Shenzhen Nanotech Port Company. Further purification was accomplished by sonicating CNTs in a mixture of concentrated sulfuric acid-nitric acid (3:1, v/v) for about 3 h. The treated CNTs were filtered and washed with double-distilled water, and then dried in a vacuum at 60 °C. The resulting black powders were sonicated in double-distilled water for about 1 h with a concentration of 0.5 mg mL^{-1}. Glucose oxidase (E.C. 1.1.3.4, 300 U mg^{-1}) was purchased from Amresco (USA), and used without further purification. All other chemicals were of analytical grade. Double distilled water was used throughout.

2.2. Synthesis of boron-doped carbon nanotubes

Boron-doped carbon nanotubes were synthesized through a substitution reaction. The detailed preparation procedure was referred to the reference (Han et al., 1999). In brief, the reaction was carried out in the induction-heating system with a susceptor made of graphite. B_2O_3 powder was placed in an open sintered graphite crucible and then covered with CNTs. Pure argon gas was introduced to maintain the inert atmosphere during the overall reaction. The temperature was held at 1400 K for 4 h and the following reaction occurred:

$$xB_2O_3 + (2 + 3x)C(\text{nanotubes}) \rightarrow 2B_xC(\text{nanotubes}) + 3xCO$$

The products were refluxed in 2 M NaOH aqueous solution for 2 h, filtered and washed with double-distilled water, and then dried in a vacuum at 60 °C. The content of boron in the boron-doped carbon nanotubes was determined by inductively coupled plasma-atom emission spectroscopy (ICP-AES) and equal to ca. 2 wt.%.

2.3. Preparation of the GOD/BCNTs modified electrode

The glassy carbon electrode (3 mm in diameter, ca. 0.07-cm^2) was polished to a mirror-like surface with 1.0 and 0.3 μm alumina slurry and washed with double-distilled water. The electrode was then pretreated electrochemically in 0.5 M H_2SO_4 aqueous solution by potential cycling in the potential range of −0.15 to 1.0 V at a scan rate of 50 mV s^{-1} until the stable cyclic voltammogram was obtained.

Prior to use, BCNTs were pretreated by sonicating in a mixture of concentrated sulfuric acid–nitric acid (3:1, v/v) for about 3 h, filtered and washed with double-distilled water, and then dried in a vacuum at 60 °C. Under ultrasonic stirring, 1.5 mg acid-treated BCNTs were added to 3 mL double-stilled water to form a stable black suspension (the concentration of BCNTs, 0.5 mg mL^{-1}). A 5 μL of BCNTs suspension was dropped on the surface of the pretreated GC electrode and dried under an infrared lamp to form the BCNTs modified electrode. Then the BCNTs modified electrode was immersed into 0.1 M phosphate buffer solution containing 10 mg mL^{-1} GOD for about 20 h at 4 °C in refrigerator. Finally, the GOD/BCNTs modified electrode was rinsed throughout with double distilled water to wash away the loosely adsorbed enzyme molecules. For comparison, the GOD/CNTs/GC and GOD/GC electrodes were also prepared under the same procedure. Those enzyme-modified electrodes were stored at 4 °C in refrigerator when not in use.

3. Results and discussion

3.1. Direct electrochemistry of GOD immobilized on the BCNTs/GC electrode

Fig. 1A presents the cyclic voltammograms of the bare GC, CNTs/GC, BCNTs/GC electrodes in 0.1 M deoxygenated phos-

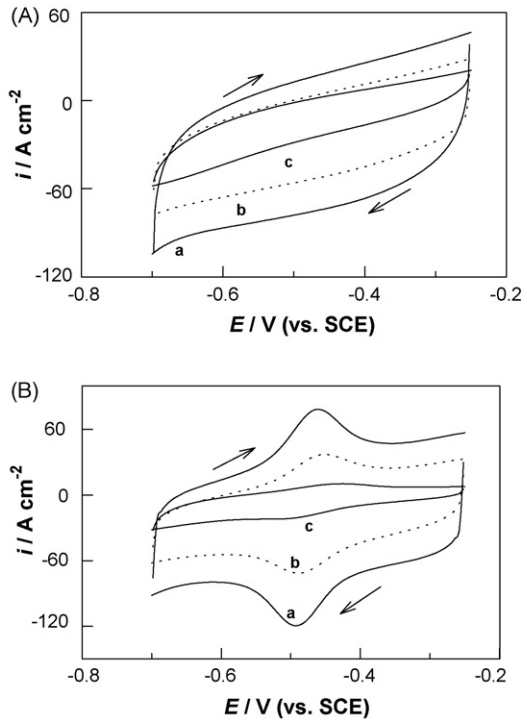

Fig. 1. Cyclic voltammograms of different electrodes in 0.1 M deoxygenated phosphate buffer solution (pH 6.98) at the scan rate of 30 mV s^{-1}. (A) (a) BCNTs/GC, (b) CNTs/GC, and (c) bare GC; and (B) (a) GOD/BCNTs/GC, (b) GOD/CNTs/GC, (c) GOD/GC.

phate buffer solution (pH 6.98) at the scan rate of 30 mV s^{-1}. It can be seen that the background current of BCNTs/GC electrode is higher than that of the CNTs/GC and bare GC electrodes. This is ascribed to the more defective sites of BCNTs introduced by B-doping (Wang et al., 2007), which would be favorable for the immobilization of enzyme and the direct electron transfer between the modified electrode and GOD. The direct electrochemistry of GOD immobilized on the BCNTs/GC, CNTs/GC and GC electrodes were also investigated and the corresponding results are shown in Fig. 1B. In Fig. 1B, except at the bare GC electrode (curve c), a pair of well-defined, quasi-reversible redox peaks can be observed at both GOD/CNTs/GC and GOD/BCNTs/GC electrodes, indicating a good electron transfer between the redox center of GOD molecules and the glassy carbon electrode without the help of the electron transfer mediators. On the other hand, the peak currents of curve (a) are much higher than those of curve (b). These demonstrate that the GOD/BCNTs/GC electrode is more beneficial to the direct electrochemistry of GOD than the GOD/CNTs/GC electrode.

On the other hand, the surface average concentration of electroactive GOD (Γ, mol cm^{-2}) can be estimated from the charge integration of the cathodic peak in the cyclic voltammogram, according to the formula of $Q = nFA\Gamma$, where Q is the charge, F is the Faraday constant, n is the number of electrons transferred and A is the area of the GC electrode (cm^2). Therefore, the amounts of the electroactive glucose oxidase at the GOD/BCNTs/GC electrodes are estimated to be 1.94×10^{-9} mol cm^{-2} ($n = 2$), which is about two times higher than that at the GOD/CNTs/GC electrode (9.8×10^{-10} mol cm^{-2}). The surface average concentrations of GOD at the BCNTs/GC and CNTs/GC electrodes are much higher than that (2.86×10^{-12} mol cm^{-2}) at the bare GC electrode (Xu et al., 2003; Zhang et al., 2007a). This indicates that the BCNTs modified electrode is much favorable for the immobilization of GOD because of its rough surface (Wang et al., 2007). Furthermore, just as N-doped CNTs (Banks et al., 2004, 2005; Jia et al., 2005a; Katz and Willner, 2004; Wang et al., 2004), BCNTs provide a large number of edge-plane-like defective sites at the surface and a better electron-conductive network, which will improve greatly the direct electron transfer between the adsorbed GOD and the electrode. All those imply that the boron-doped carbon nanotubes not only facilitate the immobilization of enzymes onto the electrode, but also improve electron shuttle between the redox active sites of enzyme and the electrode. The BCNTs will be the good candidate materials for the direct electrochemistry of the redox-active enzyme and the construction of the related enzyme biosensors.

The anodic peak potential ($E_{p,a}$) and cathodic peak potential ($E_{p,c}$) of curve a in Fig. 1B are respectively −0.464 and −0.49 V with a small peak potential separation ($\Delta E_p = 26$ mV), proving a fast electron transfer process. Additionally, the formal potential ($E^0 = 1/2(E_{p,a} + E_{p,c})$) can be calculated and equals to −0.477 V, which is close to the values reported previously (Tinoco et al., 1978; Ju et al., 2002; Liu and Ju, 2002, 2003).

The effect of the scan rate on the cyclic voltammetric performance of the GOD/BCNTs/GC electrode has also been investigated. Fig. 2 shows the plot of the peak currents versus scan rates. From Fig. 2, it can be seen that the anodic and cathodic peak currents increase with the increase of the scan rate and a linear relationship can be observed from 20 to 500 mV s^{-1} (linear regression equation: anodic peak, $y = 2.014x - 0.038$, $r = 0.999$; cathodic peak, $y = -2.109x - 0.059$, $r = 0.999$). This demonstrates that the redox reaction of GOD at the BCNTs/GC electrode is a surface-controlled process, not a diffusion-controlled process (Liu et al., 2007; Shi et al., 2007). The electron transfer rate constant (k_s) has been estimated from the peak potential separation value using the model of Laviron (Laviron, 1979). Taking a charge transfer coefficient α of 0.5, with a scan rate of 30 mV s^{-1} and $\Delta E_P = 26$ mV, the electron transfer rate constant of GOD at the BCNTs modified electrode was

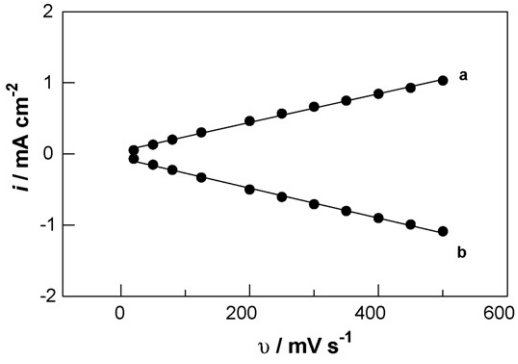

Fig. 2. The dependence of the anodic (a) and cathodic (b) peak currents of the GOD/BCNTs/GC electrode on the scan rates in 0.1 M deoxygenated phosphate buffer solution (pH 6.98).

1.56 s^{-1}, which is lager than that at the CNTs modified electrode (1.16 s^{-1}). This implies further that the BCNTs modified electrode facilitates the electron transfer between the redox-active sites of enzyme and the electrode.

It is well known that the direct electrochemistry of GOD is a two-electron coupled with two-proton reaction, which undergoes a redox reaction as follows (Huang et al., 2005; Liu and Ju, 2003; Liu et al., 2007):

$$\text{GOD-FAD} + 2e^- + 2H^+ \leftrightarrow \text{GOD-FADH}_2 \quad (1)$$

Therefore, the pH value of the solution has influence on the electrochemical behavior of GOD at the BCNTs/GC electrode. Fig. 3(A) shows cyclic voltammograms of the GOD/BCNTs/GC electrode in the solutions with different pH values. The pH values of the solutions were adjusted by adding 0.1 M HCl or 0.1 M KOH into 0.1 M PBS (pH 6.98). Stable and well-defined cyclic voltammograms can be observed in the pH range of 4.0–8.0. An increase in solution pH causes a negative shift of both cathodic and anodic peak potentials. Fig. 3(B) shows the effect of solution pH on the formal potential ($E^{0\prime}$) of the GOD/BCNTs/GC electrode, and it can be seen that the formal potential of the GOD/BCNTs/GC electrode depends linearly on the pH value in the range of 4.0–8.0 with a slop of −61.5 mV/pH ($r = 0.999$), which is close to the theoretical value of −58.6 mV/pH according to the reaction shown in Eq. (1) (Huang et al., 2005; Liu and Ju, 2003; Liu et al., 2007).

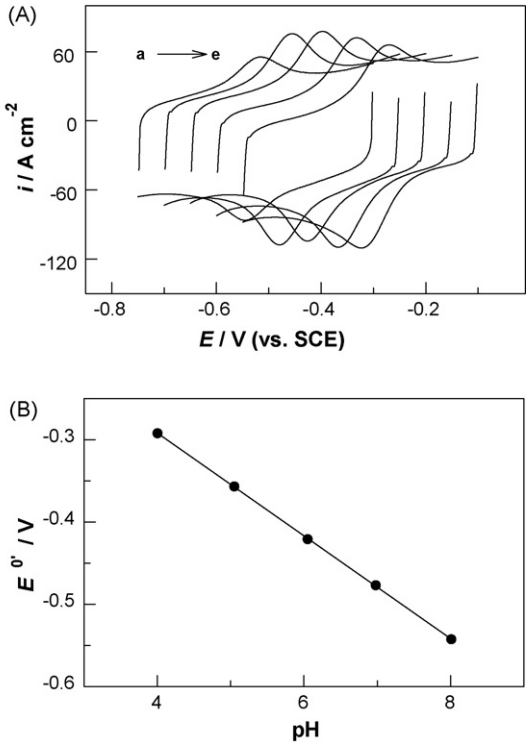

Fig. 3. (A) Cyclic voltammograms of the GOD/BCNTs/GC electrode in the deoxygenated solutions with different pH values of (a–e): 8.0, 6.98, 6.05, 5.0, 4.08. Scan rate: 30 mV s^{-1}. (B) Plot of the formal potential of the GOD/BCNTs/GC electrode as a function of pH value.

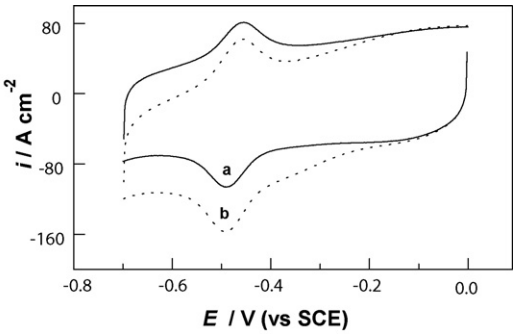

Fig. 4. Cyclic voltammograms of the GOD/BCNTs modified electrode in 0.1 M (a) deoxygenated and (b) air-saturated phosphate buffer solution (pH 6.98) at a scan rate of 30 mV s^{-1}.

3.2. Electrocatalytical behavior of the GOD/BCNTs/GC electrode

The effect of the dissolved oxygen on the electrochemical behavior of the GOD/BCNTs/GC electrode was investigated and the corresponding results are shown in Fig. 4. From Fig. 4, a pair of well-defined, quasi-reversible redox peaks was observed in both deoxygenated and air-saturated PBS (pH 6.98). However, the reduction peak current of the GOD/BCNTs/GC electrode in air-saturated PBS is larger than that in deoxygenated PBS and the oxidation peak current is in reverse. It confirms that dioxygen dissolved in the solution is catalytically reduced at the GOD/BCNTs modified electrode:

$$\text{GOD-FAD} + 2e^- + 2H^+ \leftrightarrow \text{GOD-FADH}_2$$

$$\text{GOD(FADH}_2) + O_2 \rightarrow \text{GOD(FAD)} + H_2O_2$$

Similar results have been reported on the other GOD-immobilized electrodes (Liu and Ju 2003; Liu et al., 2007; Zhang et al., 2007a).

More importantly, when glucose was added into air-saturated PBS, the reduction peak currents at the GOD/BCNTs/GC electrode decreased gradually with the increase of the concentration of glucose, as shown in Fig. 5A. According to the following enzyme-catalyzed reaction,

$$\text{Glucose} + \text{GOD(FAD)} \rightarrow \text{gluconolactone} + \text{GOD(FADH}_2) \quad (3)$$

It can be explained that glucose is the substrate of GOD, whose presence will result in an enzyme-catalyzed reaction and decrease the concentration of the oxidized form of GOD. Thus, the addition of glucose restrains the electrocatalytic reaction and leads to the decrease of the reduction current (Liu and Ju 2003; Liu et al., 2007). Based on the decrease of the reduction current, the concentration of glucose can be detected without the interference of coexistied electroactive-substance, which is different from the common glucose amperometric sensors based on the detection of the consumption of oxygen (Shinohara et al., 1988) or the production of hydrogen peroxide (Pan et al., 2005; Wu et al., 2007).

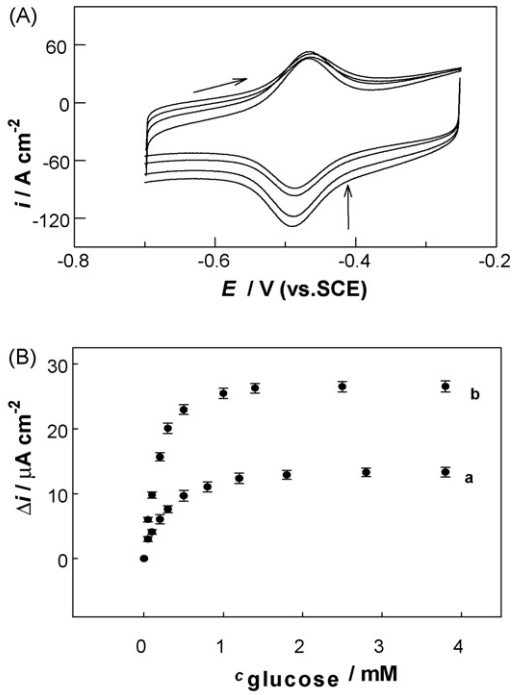

Fig. 5. (A) Cyclic voltammograms of the GOD/BCNTs/GC electrode in 0.1 M air-saturated phosphate buffer solution (pH 6.98) containing 0, 0.05, 1.2, and 3.8 mM of glucose (from bottom to top) at the scan rate of 30 mV s^{-1}. (B) Dependence of the decreased reduction peak current of (a) the GOD/CNTs/GC and (b) the GOD/BCNTs/GC electrodes on the concentration of glucose in 0.1 M air-saturated phosphate buffer solution (pH 6.98).

Fig. 5B shows the relationship between the decrease of the reduction peak current and the glucose concentration at the GOD/CNTs/GC (a) and GOD/BCNTs/GC (b) electrodes. The current values of the GOD/BCNTs/GC electrode change linearly with the concentration of glucose up to 0.3 mM with a correlation coefficient (r) of 0.994, and deviates from the linear relationship in the higher concentration region. The similar result can also be observed at the GOD/CNTs/GC electrode. However, the detection limit of the GOD/BCNTs/GC electrode (0.01 mM, S/N = 3) is lower than that of the CNTs/GC electrode (0.03 mM, S/N = 3). Furthermore, the sensitivity of the GOD/BCNTs/GC electrode is calculated to be 111.57 μA mM^{-1} cm^{-2}, much higher than that of the GOD/CNTs/GOD electrode (40.14 μA mM^{-1} cm^{-2}) and other glucose biosensors reported in literatures (Liu et al., 2007; Mamedov et al., 2002; Zhao and Ju, 2006).

On the other hand, the apparent Michalis–Menten constant (K_m^{app}), an indicator of enzyme-substrate reaction kinetics, is used to evaluate the biological activity of the immobilized enzyme. K_m^{app} can be calculated using the Lineweaver–Burk equation:

$$\frac{1}{I_{ss}} = \frac{1}{I_{max}} + \frac{K_m^{app}}{I_{max}} C_{glucose} \quad (4)$$

where I_{ss} is the steady-state response current after the addition of substrate, I_{max} is the maximum current under saturated substrate conditions, and $C_{glucose}$ is the bulk concentration of glucose. In this work, K_m^{app} of the GOD/BCNTs/GC electrode is estimated to be ~0.2 mM, which is smaller than that reported the literatures

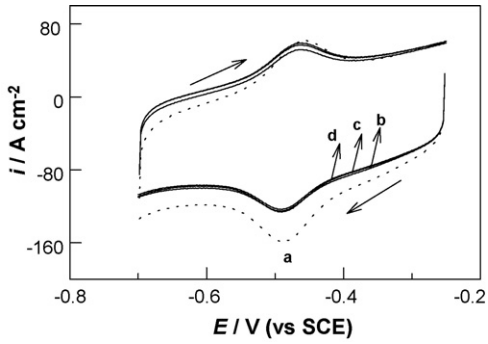

Fig. 6. Cyclic voltammograms of the GOD/BCNTs/GC electrode in 0.1 M air-saturated phosphate buffer solution (pH 6.98) containing 0 mM glucose (a), 0.5 mM glucose (b), 0.5 mM glucose + 0.01 mM AA (c) and 0.5 mM glucose + 0.01 mM UA (d). Scan rate: 30 mV s^{-1}.

(Liu and Ju 2003; Liu et al., 2007). The smaller K_m^{app} value indicates that the immobilized GOD possesses higher enzymatic activity and the GOD/BCNTs/GC electrode exhibits a higher affinity for glucose than that reported (Liu and Ju, 2003; Liu et al., 2007).

The effect of the possible interfering species, such as uric acid and ascorbic acid, on glucose detection was also investigated and the corresponding results are shown in Fig. 6. From Fig. 6, no obvious interference of 0.01 mM uric acid and 0.01 mM ascorbic acid can be observed for the cyclic voltammetric response of 0.5 mM glucose. This indicates that the GOD/BCNTs/GC electrode has a good selectivity.

The reproducibility of the glucose biosensor was also investigated by detecting 0.05 mM glucose successively for ten times, the relative standard deviation (R.S.D.) is 3.5%, demonstrating the biosensor has a good reproducibility. For the operational stability of the GOD/BCNTs/GC electrode, we did two control experiments: (1) the electrode was investigated by examining the cyclic voltammetric peak currents of GOD after continuously scanning for 40 cycles. There was nearly no decrease of the voltammetric response, indicating the enzyme electrode is stable in buffer solution. (2) The enzyme electrode was stored in buffer solution at 4 °C in refrigerator for 10 days and then cycled in PBS, the redox peak currents retain 90% of their initial response values. In comparison, the operational stability of the GOD/CNT/GC electrode was also investigated. It was found that the cyclic voltammetric peak currents of GOD retain 91% of their initial response values after continuously scanning for 40 cycles. Besides, the redox peak currents retain 80% of their initial response values after stored in buffer solution at 4 °C in refrigerator for 10 days. This implies that the GOD/BCNTs/GC electrode has better operational stability than GOD/CNT/GC electrode. The good operational stability of the GOD/BCNTs/GC electrode is attributed to the good biocompatibility of the BCNTs, which provides a perfect microenvironment for GOD to retain its bioactivity.

4. Conclusion

In this paper, B-doped carbon nanotubes (BCNTs) were used to construct a GOD electrode. The direct electrochemistry of

GOD was performed successfully and the immobilized GOD retained its bioactivity. The GOD/BCNTs/GC electrode displayed a high sensitivity (111.57 $\mu A\,mM^{-1}\,cm^{-2}$) and a wide linear range up to 0.3 mM for glucose response. Additionally, the biosensor based on the BCNTs modified electrode exhibited good stability and selectivity. Due to the simple construction and good sensing properties, the BCNTs modified electrode will provide a new electrochemical platform for the direct electrochemistry of the redox-active enzymes.

Acknowledgments

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