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

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ABSTRACT

A novel biosensor for detecting glucose had been constructed by the immobilization of glucose oxidase (GOD) on chitosan-boron-doped carbon-coated nickel (BCNi) nanoparticle modified electrode. The GOD-chitosan-BCNi bionanocomposite film was characterized with scanning electron microscope (SEM). The film was propitious to the immobilization of GOD and to the retention of its bioactivity. The direct electrochemistry and electrocatalysis of GOD on modified electrode had been investigated by cyclic voltammogram (CV) and amperometric measurements. The GOD displayed a pair of stable, well-defined and quasi-reversible redox peaks in pH 7.0 phosphate buffer solution (PBS). Furthermore, the biosensor was applied to detect glucose with a broad linear range from 2.50×10^{-5} to 1.19×10^{-3} M, the detection limit was brought down to 8.33×10^{-6} M at a signal to noise ratio of 3 and with an applied potential of −0.2 V. The proposed biosensor showed rapid response (within 3 s), low detection limit, high affinity to glucose and accepted storage stability over one-month period, which demonstrated that the chitosan-BCNi film has potential applications in the immobilization of other third-generation enzyme biosensors.

1. Introduction

Recently, direct electrochemistry of redox enzymes has attracted increasing interest both for the mechanism study of electron exchange among enzymes in biological system and for developing biosensors, biofuel cells and biomedical devices without the necessity for a mediator (Zuo et al., 2008; Fu et al., 2009). However, the direct electron transfer (ET) between redox enzymes and electrode surfaces is still extremely difficult due to several factors, such as deeply immersed redox center of enzyme, passivation of enzyme due to adsorption on electrode surface and improper orientation of the adsorbed enzyme on electrode surface (Li et al., 2007a; Salimi et al., 2006). Taking glucose oxidase (GOD) as an example, it contains two tightly bound flavine adenine dinucleotide (FAD) redox centers insulated by a protective protein shell and usually cannot show electroactivity on bare electrodes. The key issue in the development of GOD biosensor is the effective immobilization of GOD on the electrode surface. Many strategies have been developed in order to improve the direct ET between GOD and the electrode surfaces to obtain the biosensor with good performance. Those approaches, including gold nanoparticle-functionalized multiwalled carbon nanotube nanocomposites (Li et al., 2009), carbon ionic liquid (Shangguan et al., 2008), layer-by-layer self-assembling carbon nanotube and cationic polymer (Deng et al., 2010) as well as ordered mesoporous silica-SBA-15 (Wang et al., 2009a), have been widely used to construct GOD biosensors. However, some of these methods are relatively complex, requiring the use of solvents that are unattractive to the environment and result in relatively poor stability and bioactivity of GOD. Therefore, searching for a simple and reliable scheme to immobilize GOD is of considerable interest.Over the last decade, with the rapid development of nanostructured materials and nanotechnology in the fields of biotechnology, nanosized particles have received considerable attention for their novel properties (Huang et al., 2003; Josephson et al., 2001; Katz et al., 2002). Due to the special properties and protective coatings against environmental degradation, the application of nanomaterials ranges from immobilization of proteins (Rossi et al., 2004), detection of DNA hybridization (Pumera et al., 2005), drug delivery (Huang et al., 2003), immunology (Ao et al., 2006) to cell separation processes (Sonti and Bose, 1995). Wang and co-workers synthesized magnetic Fe_3O_4 nanoparticles and constructed Fe_3O_4 modified tyrosinase biosensor to monitor phenolic compounds (Wang et al., 2008). Among the magnetic nanoparticles, one recent development is carbon-coated metal nanoparticles. Carbon-coated metal crystals, was first synthesized in 1993 (Ruoff

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et al., 1993), which was nanocrystallite of transitional metal or metal carbide wrapped in graphitic-like carbon (Ling et al., 2003). Carbon-coated nickel nanoparticle (CNi) has some special features due to the effect of Ni when compared with carbon anions consisting only of carbon layers (He et al., 2009). It could potentially absorb a micromolecular pharmaceutical and be used as a magnetism-targeted drug carrier in cancer treatments (Wang et al., 2007a). In our previous work, it was found that the CNi modified electrode could accelerate the ET rate and showed excellent electrocatalytic activity of some micromolecules (Wang et al., 2007a,b). On the other hand, it has been reported that the nanomaterials could be doped with foreign (B or N atom) and the electronic, mechanic, and conductive properties of nanomaterials could be improved obviously (Deng et al., 2008; Wang et al., 2007c; Zhang et al., 2006). Doping nanomaterials with foreign atoms has also been reported to yield a large number of defective sites on to the materials surface (Jia et al., 2005). However, to the best of our knowledge, the application of boron-doped carbon-coated nickel (BCNi) nanoparticles in electrochemistry has not been reported until now.

In this paper, a novel GOD modified glassy carbon electrode (GCE) was prepared based on BCNi magnetic nanoparticles. The direct electrochemistry of GOD and biosensing for glucose has been investigated. The new biosensor exhibited rapid response (within 3 s), low detection limit, high affinity to glucose and accepted storage stability over one-month period. The proposed strategy can be extended for the development of other enzyme-based biosensors.

2. Experimental

2.1. Chemicals and reagents

Glucose oxidase (GOD, Type X-S, EC 1.1.3.4, from *Aspergillus niger*) and chitosan were purchased from Sigma–Aldrich (St. Louis, Missouri). BCNi was synthesized by an alternative current (AC) arc discharge method (Ling et al., 2003), in which two modified rods filled with a mixture of boron powder (pure about 95%, 5 μm in size) and nickel powder (pure about 99%, 5–15 μm in size) were adopted. D-(+)-Glucose was purchased from Goodtime Bio-Technology Co., Ltd (Wuhan, China). 0.1 M phosphate buffer solution (PBS) was comprised with Na_2HPO_4 and KH_2PO_4, which were from Tian-Jin Bodi Chemical Holding Co., Ltd (TianJin, China). The pH values were adjusted with NaOH (saturation concentration) and H_3PO_4 (85%). All other reagents were of analytical grade and were used as received without further purification.

2.2. Apparatus

All electrochemical measurements were carried out by a model CHI 660A electrochemical workstation (Chenhua Instrument Company of Shanghai, China), which was PC controlled. A conventional three-electrode cell (25 mm × 25 mm) was used in the measurements, with film modified GCE (3 mm diameter) as the working electrode, a saturated calomel electrode (SCE, Shanghai Ruosull Technology Co., Ltd, China) as the reference electrode and a platinum wire as the auxiliary electrode.

Ultrasonic cleaner (Branson2000, USA) was used for cleaning the electrodes. The pH values of solutions were determined by 320-S acidometer (Mettler-Toledo, Switzerland). The morphologies of the biosensors were observed by scanning electron microscopy (SEM, Philips XL30 TMP), transmission electron microscope (TEM, JEM-2000FXII) and X-ray photoelectron spectroscopy (XPS, XSAM 800). All the data were obtained at room temperature.

2.3. Fabrication of GOD-chitosan-BCNi biosensor

Before each experiment, the GCE was first polished on chamois leather with 0.05 μm alumina powders and then washed ultrasonically in doubly distilled water, anhydrous ethanol, and water, respectively. After these pretreatments, the cleaned GCE was dried in air. GOD solution with a concentration of 5 mg mL^{-1} was prepared in 0.1 M PBS (pH 7.0). Chitosan solution with a concentration of 2.5 mg mL^{-1} was prepared by dissolving 5 mg chitosan in 2.0 mL of 0.1 M acetic acid. The BCNi nanoparticles were dispersed by ultrasonic agitation in 3 M HCl for 5 h. Then the purified BCNi nanoparticles were separated by centrifugal machine and washed by doubly distilled water. Here, 1 mg mL^{-1} BCNi suspension was prepared by dispersing BCNi in 2.5 mg mL^{-1} chitosan solution with ultrasonication for about 2 h to achieve a well-dispersed suspension. In order to get the best amperometric responses of the biosensor, the composition of the GOD-chitosan-BCNi were optimized. Typically, BCNi and GOD with a volume ratio of 1:1 were mixed thoroughly, and 20 μL of this mixture was dropped on the surface of the cleaned GCE. Then the electrode was dried at room temperature. Before the experiment, the biosensor was immersed in 0.1 M PBS (pH 7.0) to wash out the nonimmobilized components from the electrode surface. When not in use, the biosensor was preserved at 4 °C in a dry state. For comparison, the GOD-chitosan-CNi/GCE and GOD-chitosan/GCE were also prepared under the same procedure.

2.4. Electrochemical measurements

Cyclic voltammetric measurements were performed in an unstirred pH 7.0 PBS at a scan rate of 0.1 V s^{-1}. Amperometric measurements were carried out in the electrochemical cell with an air-saturated 4 mL PBS in it. A magnetic stirrer (rotation speed 300 rpm) provided the convective transport during the amperometric measurement. The desired working potential −0.2 V was applied, and transient currents were allowed to decay to a steady-state value.

3. Results and discussion

3.1. Characterization of the GOD-chitosan-BCNi film

The microstructure of BCNi and the morphology of GOD films were characterized by SEM (Fig. 1). In the presence of chitosan, the globe-like BCNi were distributed evenly (Fig. 1A), which suggested that the chitosan would help the BCNi disperse in the solution. BCNi, which is protected by the carbon layer, is considerably stable and can overcome the agglomeration of nanoparticles. The uniform and stable film helped to increase the effective surface area of the electrode to load a large amount of proteins. As can be seen, the enzyme distributed regularly throughout BCNi-chitosan after entrapped in this film (Fig. 1B). The GOD-chitosan-BCNi film was compact and uniform, which indicated GOD and BCNi have been successfully incorporated in the chitosan film (Sheng et al., 2009).

The typical TEM image of the BCNi nanoparticles was present in Fig. 1C. TEM micrograph showed clearly globe-like of BCNi, which was symmetrical and simplex. Fig. 1D shows the XPS spectrum of the B1s energy level of BCNi. The B1s binding energy was at 188.2 eV, which was attributed to the binding energy for the sp^2-hybridized boron atoms substituting carbon atoms in graphite plane. It was in good agreement with the literatures (Shirasaki et al., 2000). A strong abroad shoulder peak in B1s XPS spectrum at around 192 eV can be assigned to the oxidation of boron (Cermignani et al., 1995).

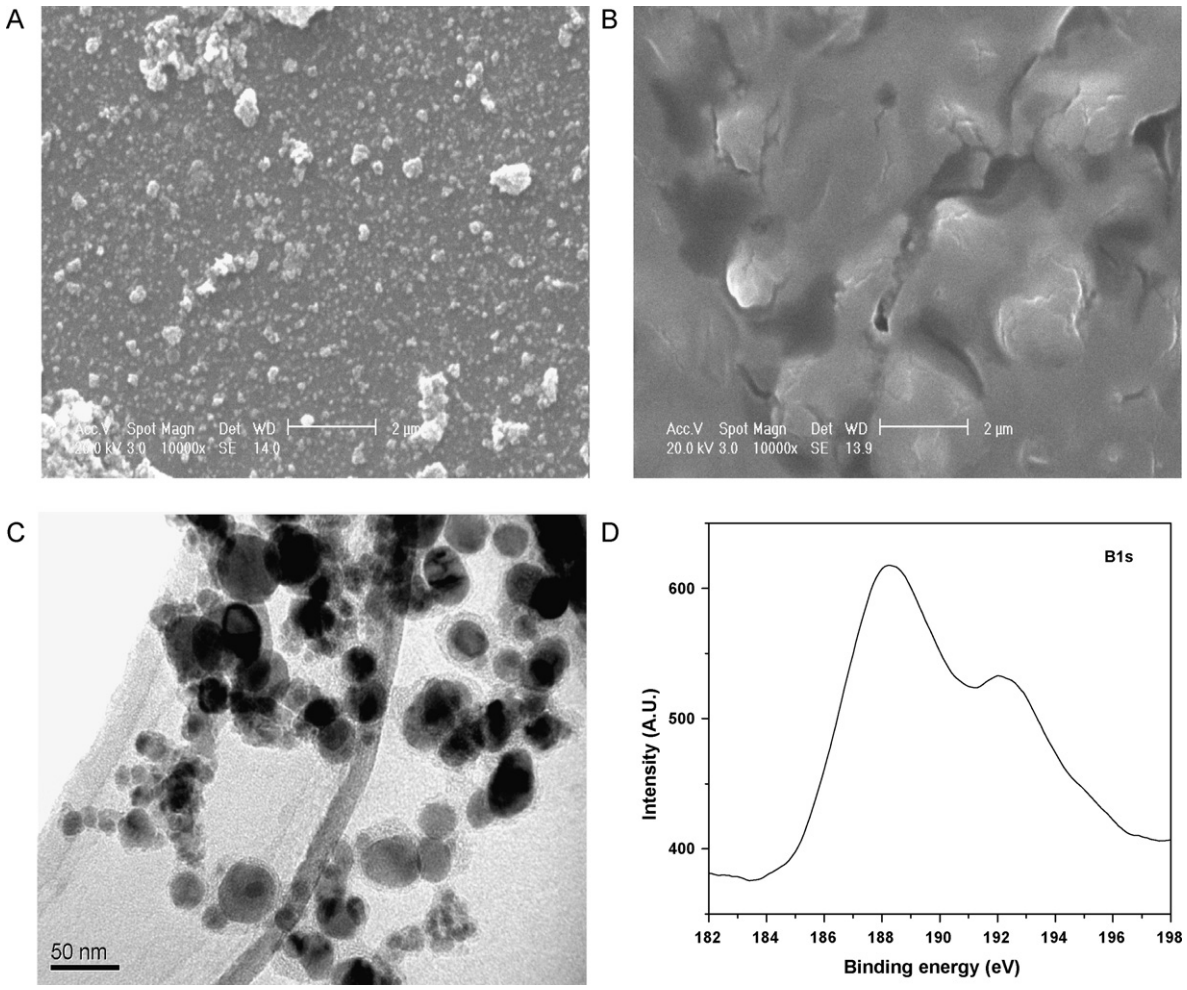

Fig. 1. SEM images of chitosan-BCNi (A) and GOD-chitosan-BCNi (B) films; TEM images of BCNi nanoparticles (C) and XPS of BCNi nanoparticles (D).

3.2. Direct electrochemistry of GOD-chitosan-BCNi modified GCE

Fig. 2 shows the typical cyclic voltammograms (CVs) at GOD-chitosan/GCE (a); GOD-chitosan-CNi/GCE (b); chitosan-BCNi/GCE (c) and GOD-chitosan-BCNi/GCE (d) in deoxygenated 7.0 PBS at 0.1 V s^{-1}. As demonstrated, there was no redox peak in the potential range of −0.1 to −0.8 V on chitosan-BCNi/GCE (Fig. 2c). After using GOD-chitosan-BCNi/GCE, a pair of stable, well-defined and quasi-reversible redox peaks was obtained (Fig. 2d). It can be concluded that the peaks were due to the reversible ET process of the redox-active site of GOD (the cofactor FAD). Comparing with the no redox peak of GOD-chitosan/GCE (Fig. 2a), it suggested that BCNi might provide a favorable microenvironment to facilitate its electron communication without the help of any other ET mediators. Additionally, GOD immobilized in GOD-chitosan-CNi film was also investigated as a control experiment (Fig. 2b). No obvious voltammetric peak was observed on GOD-chitosan-CNi/GCE in the selected potential range, which implied that the boron doping accelerated the ET from electrode substrate to the immobilized GOD, leading to the direct electrochemistry of GOD.

The amount of electroactive GOD on the electrode surface can be estimated from the charge integration of the cathodic peak in curve d. According to Faraday's laws, $\Gamma = Q/(nFA)$ (Bard and Faulkner, 2001), where Q is the charge involved in the reaction, n is the number of electrons transferred, F is Faraday's constant, and A is the electrode area, the amount of electroactive GOD was estimated to be 2.98×10^{-10} mol cm^{-2}. The value was much

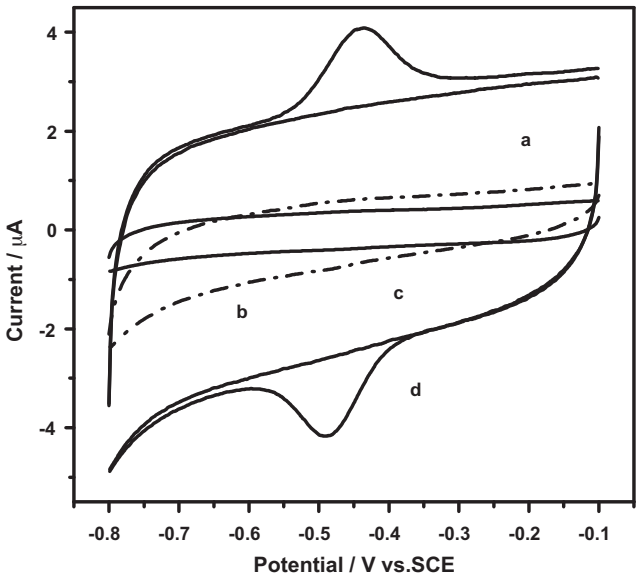

Fig. 2. Cyclic voltammograms of GOD-chitosan/GCE (a); GOD-chitosan-CNi/GCE (b); chitosan-BCNi/GCE (c) and GOD-chitosan-BCNi/GCE (d) in deoxygenated 7.0 PBS at the scan rate of 0.1 V s^{-1}.

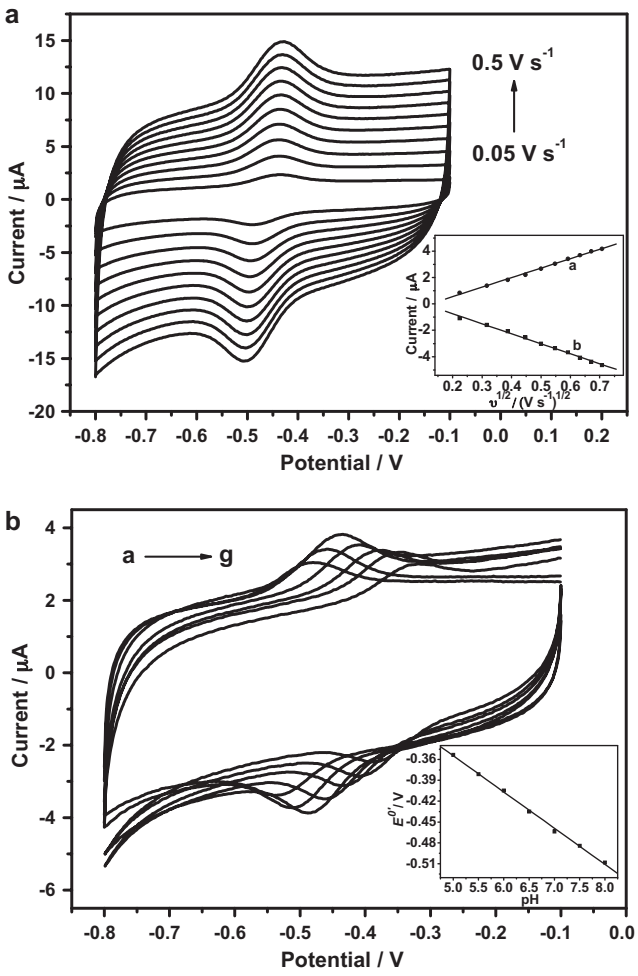

Fig. 3. (A) CVs of GOD-chitosan-BCNi/GCE in the deoxygenated 7.0 PBS at various scan rate from 0.05, 0.1, 0.15, 0.2, 0.25, 0.3, 0.35, 0.4, 0.45 to 0.5 V s^{-1} (from inner to outer). Inset: plots of the anodic (a) and cathodic (b) peak currents versus the scan rates. (B) CVs of GOD-chitosan-BCNi/GCE in the deoxygenated PBS at different pH values: 8.0, 7.5, 7.0, 6.5, 6.0, 5.5, 5.0 (a→g). Scan rate: 0.1 V s^{-1}. Inset: plots of $E^{0\prime}$ versus pH values.

larger than those of 2.86×10^{-12} mol cm^{-2} at bare GCE (Zhang et al., 2007), 1.54×10^{-11} mol cm^{-2} at GOD/CdS modified electrode (Huang et al., 2005) and 9.8×10^{-12} mol cm^{-2} at GOD/colloidal gold modified electrode (Liu and Ju, 2003). These indicated that the nanostructured BCNi provided a large active area for enzyme immobilization.

Fig. 3A presents the CVs of GOD-chitosan-BCNi/GCE at various scan rates. With the increase of scan rate the peak-to-peak separation for GOD increased. Both the cathodic and anodic peak currents were linearly proportional to the square root of scan rate ranging from 0.05 to 0.5 V s^{-1} (linear regression equation: i (a) $= -8.73 \times 10^{-7} + 7.16 \times 10^{-6} \upsilon^{1/2}$, $r = 0.998$; i (b) $= 7.71 \times 10^{-7} - 7.58 \times 10^{-6} \upsilon^{1/2}$, $r = 0.998$). This demonstrated that the electrochemistry process of GOD in chitosan-BCNi composite film belonged to diffusion-controlled (Li et al., 2007a). This was in accordance with the fact that the electron transfer of the redox-active site of GOD showed broadening separation of the redox peaks at faster scan rates, which illuminated the inability of the clusters to relax from its more active state during shorter excursions to high potentials (Compton and Laszlo, 2002). According to Laviron's equation (Laviron, 1979), the apparent ET rate constant (k_s) was estimated to be 2.5 s^{-1} from the peak potential separation value. It is higher than those of 1.56 s^{-1} at GOD-boron-doped carbon

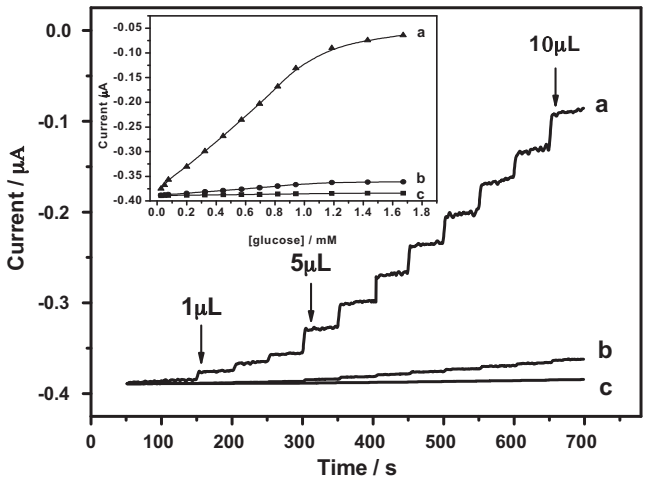

Fig. 4. Typical current–time response curves for the successive addition of 0.1 M glucose into the stirred pH 7.0 PBS with the working potential of −0.2 V at GOD-chitosan-BCNi/GCE (a), GOD-chitosan-CNi/GCE (b) and GOD-chitosan/GCE (c). Inset: Calibration curves for glucose obtained at GOD-chitosan-BCNi/GCE (a), GOD-chitosan-CNi/GCE (b) and GOD-chitosan/GCE (c).

nanotubes/GCE (Deng et al., 2008), 1.53 s^{-1} at GOD-Nafion-carbon nanotubes/GCE (Cai and Chen, 2004) and 0.3 s^{-1} at GOD-aligned single walled carbon nanotube/gold electrode (Liu et al., 2005). This further proved that the BCNi modified electrode facilitated the ET between the redox-active sites of enzyme and the electrode surface.

Fig. 3B shows the CVs of GOD-chitosan-BCNi/GCE in deoxygenated PBS over the pH range variant from 8.0 to 5.0. In general, the redox peaks shifted negatively with increasing pH, suggesting that hydrogen ion participates in the reaction of GOD (FAD). At low pH, the peak currents increased with an increasing pH, which was attributed to the enzyme activity. While the pH was higher than 7.0, the sharp decrease of the peak currents was due to the involvement of protons in the electrochemical redox reaction of GOD (FAD). The maximum peak current was found at about 7.0, which agreed with other reports of GOD-based biosensors (Wang et al., 2009a,b). Therefore, pH 7.0 was regarded as the optimum pH of electrolyte in subsequent experiments. Fig. 3B (lower inset) displays the effect of pH on the formal potential ($E^{0\prime}$), which calculated by averaging the cathodic and anodic peak potentials of the GOD-chitosan-BCNi/GCE. As can be seen, there was a linear relationship between $E^{0\prime}$ and pH with a slope of 52.1 mV pH^{-1} ($r = 0.999$), which was close to the theoretical value of 58.6 mV pH^{-1} (Deng et al., 2008; Liu et al., 2007; Li et al., 2007b). This indicated that the total number of electrons and protons taking part in the charge transfer was the same.

3.3. Electrocatalytical behaviors of GOD-chitosan-BCNi/GCE

Fig. 4 illustrates typical steady-state current–time curves for detecting glucose obtained at GOD-chitosan-BCNi/GCE (a), GOD-chitosan-CNi/GCE (b) and GOD-chitosan/GCE (c) under the optimum conditions. When the modified electrodes reached a steady baseline in blank PBS, adding glucose into the solution caused obvious current response. The cathodic current reached 95% of steady-state current within 3 s. The inset of Fig. 4 exhibits the typical calibration curves of the biosensors to glucose. The linear range of GOD-chitosan-BCNi/GCE spanned from 2.50×10^{-5} to 1.19×10^{-3} M ($r = 0.999$), with a detection limit down to 8.33×10^{-6} M at a signal to noise ratio of 3. The detection limit was obviously lower than those of GOD biosensors based on nitrogen-doped carbon nanotubes (1×10^{-5} M) (Deng et al., 2009), boron-doped carbon nanotubes (1×10^{-5} M)

(Deng et al., 2008), graphite nanosheet-Nafion composite film (6.67×10^{-5} M) (Fu et al., 2009) and graphene (6.67×10^{-4} M) (Shan et al., 2009). In addition, the sensitivity of GOD-chitosan-BCNi/GCE was 0.25 $\mu A\,mM^{-1}$, which was much higher than that of GOD-chitosan-CNi/GCE (0.023 $\mu A\,mM^{-1}$) and GOD-chitosan/GCE (0.0036 $\mu A\,mM^{-1}$). The higher sensitivity was due to the excellent conductivity and electrocatalytic activity of BCNi nanoparticles. The better performance of GOD-chitosan-CNi/GCE than GOD-chitosan/GCE maybe due to the carbon-coated nickel nanoparticles showing excellent electrocatalytic activity for the redox molecules.

The apparent Michaelis–Menten constant (K_M^{app}), an indicator of enzyme–substrate reaction kinetics, can be used to evaluate the biological activity of the immobilized enzyme. According to Lineweaver–Burk equation (Kamin and Wilson, 1980), K_M^{app} of the GOD-chitosan-BCNi/GCE, GOD-chitosan-CNi/GCE and GOD-chitosan/GCE were calculated to be 0.32, 0.48 and 0.60 mM for glucose, respectively. The results were lower than that of GOD-nitrogen-doped carbon nanotubes/GCE (2.2 mM) (Deng et al., 2009), GOD-highly ordered polyaniline nanotubes (2.37 mM) (Wang et al., 2009c), GOD-graphene-chitosan/GCE (4.4 mM) (Kang et al., 2009) and chitosan-GOD-CdS/aligned carbon nanotube–Pt nanoparticle electrode (11.86 mM) (Yang et al., 2008). The low K_M^{app} values indicated that the GOD immobilized on proposed modified electrodes exhibited high affinity to glucose.

The effect of the coexisting electroactive species, such as uric acid and ascorbic acid on the detection of glucose was investigated. There was no obvious interference of 0.1 mM uric acid injected into the 0.1 mM glucose solution. However, ascorbic acid exerted a severe influence on glucose detection. After putting a Nafion coating on the modified electrode surface (result not shown), ascorbic acid as an anion at physiological pH, its amperometric response could be efficiently eliminated (Bindra and Wilson, 1989).

The repeatability of the GOD-chitosan-BCNi/GCE was examined by detecting 0.5 mM glucose for ten successive determinations. A relative standard deviation (RSD) of 1.7% was obtained, which demonstrated that the modified electrode had good repeatability. The fabrication repeatability was investigated with five different modified electrodes, which were constructed independently with the same treatment. RSD value of 2.6% was obtained. Then the stability of the glucose biosensor was evaluated by monitoring the CV peak currents of GOD after continuously scanning for 50 cycles. The response was retained 86% value of the initial response. The long-term stability of the proposed biosensor was also estimated by measuring its response in 0.5 mM glucose after the electrode stored in dry state at 4 °C for 1 month. The biosensor retained 80.7% of its original response after 1 month, which proved that BCNi efficiently maintained the activity of GOD.

4. Conclusions

An excellent glucose biosensor based on GOD-chitosan-BCNi nanobiocomposite film had been successfully prepared. The direct electrochemistry and electrocatalysis of GOD were investigated by the effective immobilization of GOD into the nanobiocomposite film. The nanobiocomposite film was suitable for the immobilization of GOD and to the retention of its bioactivity to a large extent. The proposed biosensor showed remarkable properties including fast response, low detection limit, high affinity, satisfactory reproducibility and accepted stability. With simple fabrication process and many benefiting characteristics, the chitosan-BCNi nanobiocomposite film has great potential for the development of other enzyme-based biosensors.

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