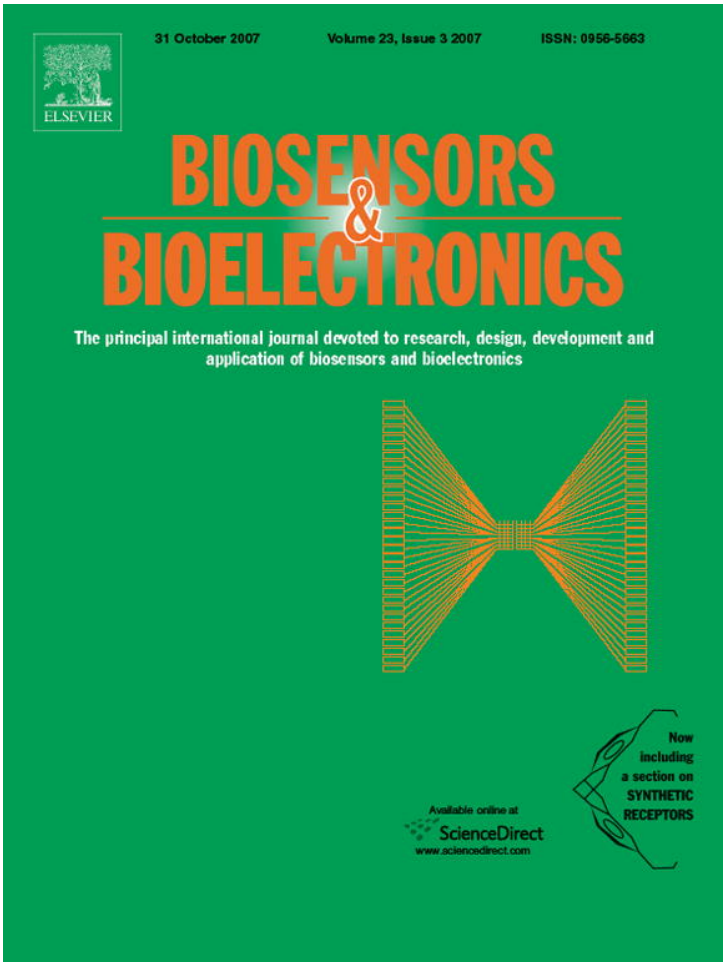

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BIOSENSORS & BIOELECTRONICS
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Short communication

Carbon nanotubes and glucose oxidase bionanocomposite bridged by ionic liquid-like unit: Preparation and electrochemical properties

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Received 25 March 2007; received in revised form 20 June 2007; accepted 26 June 2007
Available online 21 July 2007

Abstract

For their biocompatibility and potential bionanoelectronic applications, integration of carbon nanotubes (CNTs) with biomolecules such as redox enzyme is highly anticipated. Therein, CNTs are expected to act not only as an electron transfer promoter, but also as immobilizing substrate for biomolecules. In this report, a novel method for immobilization of biomolecules on CNTs was proposed based on ionic interaction, which is of universality and widespread use in biological system. As illustrated, glucose oxidase (GOD) and single-walled carbon nanotubes (SWNTs) were integrated into a unitary bionanocomposite by means of ionic liquid-like unit on functionalized SWNTs. The resulted bionanocomposite illustrated better redox response of immobilized GOD in comparison of that prepared by weak physical absorption without ionic interaction. As a potential application of concept, the electrochemical detection of glucose was exemplified based on this novel bionanocomposite.

Keywords: Carbon nanotubes; Glucose oxidase; Ionic liquids; Bionanocomposite; Electrochemistry

1. Introduction

Carbon nanotubes (CNTs) are leading the development of new nanotechnology because of their outstanding electronic, mechanical, and thermal properties, such as for strong materials and fast electronic circuits (Ajayan, 1999; Guldi et al., 2005). In addition, due to satisfied biocompatibility, another promising development of CNTs involves integration with biological systems, such as nucleic acids (Yim et al., 2005), protein (Chen et al., 2001; Patolsky et al., 2004), lipid (Qiao and Ke, 2006), carbohydrate (Wang et al., 2006), peptide (Li et al., 2006; Pantarotto et al., 2004), to form functional hybrid assemblies, which shows great potential in bionanoelectronic applications (Bianco and Prato, 2003; Katz and Willner, 2004). It has been reported that functionalized CNTs are able to cross cell membranes and accumulate in the cytoplasm, and even reach the nucleus, without being cytotoxic (in concentrations up to 10 mM) (Pantarotto et al., 2004; Wu et al., 2005).

In the field of electroanalysis, CNTs-modified electrodes have exhibited strong and stable electrocatalytical response towards many important biomolecules related to human health, such as β-nicotinamide adenine dinucleotide (NADH) (Musameh et al., 2002), ascorbic acid (AA), dopamine (DA) (Wang et al., 2002) and cytochrome C (cyt c) (Zhao et al., 2005). Moreover, the integration of biomolecules with CNTs would enable the prepared bionanocomposites as potential biosensors and bioelectronic devices (Gong et al., 2005; Wang, 2005; Wildgoose et al., 2006). For instance, many researches have been focused on CNTs–glucose oxidase (GOD)-based biosensor to monitor the blood glucose levels *in vitro* or *in vivo* for the treatment of diabetics (Gao et al., 2003; Lin et al., 2004; Liu and Lin, 2006; Liu et al., 2005; Patolsky et al., 2004; Wang and Musameh, 2005; Wang et al., 2003; Zhang et al., 2005). In these bioelectroanalytical applications, CNTs acted as not only an electron transfer accelerator between biospecies and electrode substrates, but also as an enzyme immobilizer. Therefore, the

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doi:10.1016/j.bios.2007.06.010

effective immobilization of GOD on the CNTs surface must be carefully addressed. Several approaches have been extensively developed to immobilize enzymes on CNT, such as covalent binding (Lin et al., 2004; Patolsky et al., 2004; Zhang et al., 2005), direct physical adsorption (Gao et al., 2003; Guan et al., 2005; Guiseppi-Elie et al., 2002; Wang et al., 2003), layer-by-layer (LbL) assembly (Liu and Lin, 2006) and entrapment (Liu et al., 2005; Salimi et al., 2004; Wang and Musameh, 2005). Each method shows individual advantages and drawbacks (Liu and Lin, 2006). For instance, the physical absorption or entrapment method is very simple, but the distribution of enzyme is not uniform and is sometimes unstable due to leaking with time. In contrast, covalent method provides stronger binding, but it is not so facile and often needs long reaction time.

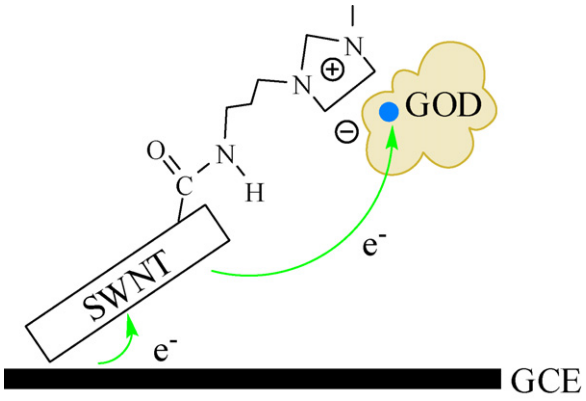
Based on its universality and widespread use in biological systems, ionic interaction emerges as a simple, but also powerful approach to guarantee efficient bindings (Guldi and Prato, 2004). In addition, it offers control over the molecularly organized integration of functional building blocks and the performance of the required function. It is well known that most biomolecules are charged in biological environments. Therefore, ionic functionalization of CNTs would provide an alternative method to easily immobilize biomolecules so as to prepare CNTs-based bionanocomposites. However, the related studies were few (Hamon et al., 1999). Recently, we have developed one methodology to prepare multifunctional compounds based on an ionic liquid (IL) backbone (Zhang et al., 2006). As illustrated, it also provided a novel method for ionic functionalization of CNTs. Different from previous report based on acid–base reaction (Hamon et al., 1999), here the ionic property of IL unit on CNTs was no longer depended on the pH. Such a feature would allow a more general electrostatic interaction between functionalized CNTs and biological molecules, and could serve as the basis for developing biocompatible CNTs compounds.

Therefore, in this report, as a part of our ongoing development of CNTs integrated biological assemblies (Zhang et al., 2005), the ionic integration of CNTs and GOD into the bionanocomposite was further investigated by means of ionic liquid-like unit, and the electrochemical properties of this novel bionanocomposite including direct electron transfer of GOD and electrochemical detection of glucose were preliminarily investigated (Scheme 1) too.

2. Experimental

2.1. Reagents

Pristine single-walled carbon nanotubes (SWNTs, >90%, length 5–15 μm, diameter <2 nm) were produced by CVD process and were obtained from Shenzhen Nanotech Port Co. Ltd., China in purified form. GOD (EC 1.1.3.4, Type X-S, lyophilized powder, 100–250 units/mg, from *Aspergillus niger*) and D-(+)-glucose (≥99.5%) was obtained from Sigma. 3-Bromopropylamine and 1-methylimidazole were obtained from Acros. And before use, 1-methylimidazole was distilled. Hydrogen peroxide solution (30 wt.%) was purchased from Beijing Chemical Reagent (Beijing, China), and a fresh solution of H_2O_2 was prepared daily. Glucose stock solutions were stored overnight at room temperature before use. Unless otherwise stated, other reagents were of analytical grade and were used as received.



Scheme 1. SWNT–IL–GOD bionanocomposite-modified glassy carbon electrode.

2.2. Instruments

Cyclic voltammetric (CV) measurements were performed in a conventional three-electrode cell with a platinum wire as the auxiliary electrode and an Ag|AgCl (saturated KCl) as the reference electrode with a CHI 660 Electrochemical Workstation (CHI, USA). The working electrode was bare or modified glassy carbon electrode (GCE, $d = 3$ mm). Before using, GCE was polished carefully with 1.0-, 0.3-, and 0.05-μm alumina slurry to a mirror finish, respectively.

2.3. Preparation of SWNT–IL–GOD-modified GCE (GCE/SWNT–IL–GOD)

IL-like unit functionalized SWNT (SWNT–IL–Br) was prepared by previously reported method (Zhang et al., 2006). In general, it was based on an amidation between carboxylic acid functionalized SWNT (SWNT–COOH) and the amine-terminated IL (1-propylamine-3-methylimidazolium bromide, IL–NH_2). The IL–NH_2 was prepared by reaction of 1-methylimidazole (0.02 mol) with 3-bromopropylamine (0.02 mol) in 50 mL ethanol under reflux in N_2 atmosphere for 24 h, and then purified by recrystallization (Bates et al., 2002). ESI–MS (H_2O): positive ion, 140; ^{1}H NMR (D_2O): $\delta = 8.74$ (s, 1H), 7.48 (s, 1H), 7.42 (s, 1H), 4.29 (t, 2H), 3.84(s, 3H), 3.02 (t, 2H), 2.23 (m, 2H). SWNT–COOH was prepared by reflux the as-received SWNT in 3 M HNO_3. SWNT–IL– was prepared by ultrasonicating a solution of 5 mg of the SWNT–COOH, 10 mg of IL–NH_2, and 10 mg of dicyclohexylcarbodiimide (DCC) in 10 mL of dimethylformamide (DMF) for 15 min, and then vigorously stirring at 50 °C for 24 h. Then, un-reacted SWNT were removed by centrifuging. After that SWNT–IL–Br was filtered by nylon membrane with 0.22 μm pores, thoroughly washed with DMF, ethanol and water, respectively. Then 16 μL of SWNT–IL–Br aqueous solution (0.05 mg/mL) was dropped on the surface of a GCE. After dried in air for 24 h,

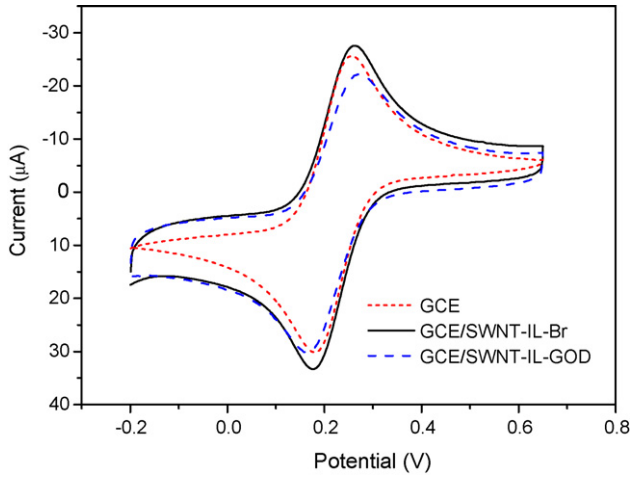


Fig. 1. Cyclic voltammograms of 2 mM $K_3Fe(CN)_6$ with 0.1 M KCl at bare GCE (dotted), GCE/SWNT–IL–Br (solid) and GCE/SWNT–IL–GOD (dashed).

SWNT–IL–Br-modified GCE (GCE/SWNT–IL–Br) was thus obtained. Because the isoelectric point, I_p of GOD is 4.5, it is net negatively charged at pH > I_p, and would exchange Br^- anion on SWNT–IL– to GOD (−). Hence, GCE/SWNT–IL–GOD was obtained by soaking GCE/SWNT–IL–Br in phosphate-buffer saline (PBS, 0.05 M, pH 7.4) containing GOD (2.5 mg/mL) at 4 °C for 24 h. And before performing the CV experiment, GCE/SWNT–IL–GOD was thoroughly rinsed with PBS to remove unwanted GOD by weak physical absorption. In control experiments, pristine SWNT and SWNT–COOH were also used to immobilize GOD, and the samples were prepared *via* same method, except that pristine SWNT was dispersed in DMF for better solubility.

3. Results and discussion

3.1. Monitoring the preparation of SWNT–IL–GOD bionanocomposite on GCE by $Fe(CN)_6^{3-}$ electroactive probe

The assembly of SWNT–IL–Br on the GCE and the anionic exchange from SWNT–IL–Br to SWNT–IL–GOD could be monitored by potential cycling in $Fe(CN)_6^{3-}$ solution. It was relied on that the electron transfer between the electroactive species and the electrode was strongly influenced by the properties of the interface (Jia et al., 2002; Zhang et al., 2004). For bare GCE, one pair of well-defined redox wave of $Fe(CN)_6^{3-}$ was observed (dotted curve in Fig. 1). When SWNT–IL–Br was assembled on the GCE, apart from change in charging current, the cyclic voltammogram was almost identical (solid curve in Fig. 1). It was because SWNT has good electronic conductivity and a large surface area.

After GOD was further exchanged on the electrode, the peak current decreased and the peak-to-peak potential difference increased (dashed curve in Fig. 1). It indicated that the GOD played a critical role in altering the electrode and aqueous interface. The reduction in peak current probably originated from the blocking effect of GOD on the electrode surface. And the increase of peak-to-peak separation was likely due to some blocking of the effective electrode area by GOD, but also the presence of GOD on the surface of SWNT might further inhibit the rate of electron transfer. Therefore, it was concluded that GOD and SWNT were successfully integrated by means of ionic interaction. The further evidence of ionic interaction between GOD and SWNT–IL– was given by the measurements of direct electron transfer of GOD in SWNT–IL–GOD bionanocomposite, and the control experiments were also performed as follows.

3.2. Cyclic voltammetry of SWNT–IL–GOD bionanocomposite

Fig. 2a (solid curve) shows a CV at GCE/SWNT–IL–GOD in N_2-saturated PBS (0.05 M, pH 7.4). A pair of well-defined and nearly symmetric redox peaks was observed. The formal potential ($E^{0'}$) calculated by averaging the cathodic and anodic peak potentials was found to be ca. −0.45 V (versus Ag|AgCl). The

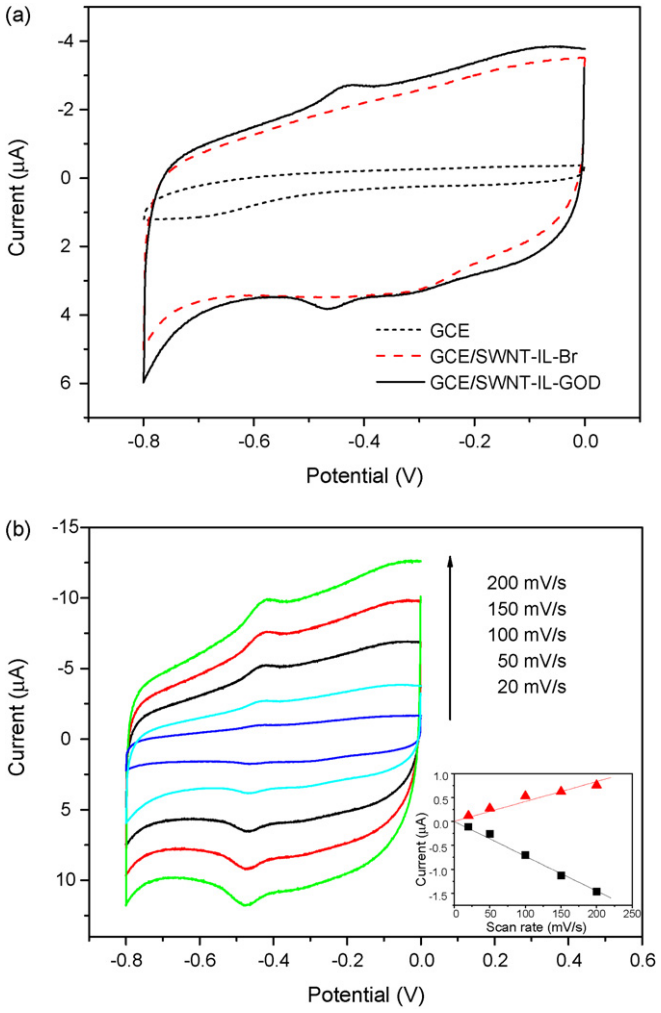


Fig. 2. (a) Cyclic voltammetric measurements at bare GCE (dotted), GCE/SWNT–IL–Br (dashed) and GCE/SWNT–IL–GOD (solid) in 0.05 M N_2 saturated PBS solution (pH 7.4). Scan rate: 0.05 V s^{-1}. (b) Cyclic voltammetric measurements at GCE/SWNT–IL–GOD electrode in 0.05 M N_2 saturated PBS solution at different scan rates. Scan rate: 0.02, 0.05, 0.1, 0.15 and 0.2 V s^{-1} from inner to outer. Inserted is the calibrated plot of peak currents vs. scan rates.

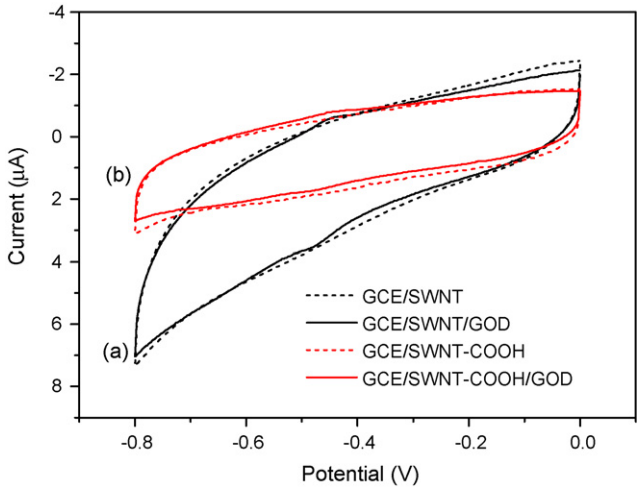


Fig. 3. Cyclic voltammetric measurements at (a) GCE/SWNT (dotted), GCE/SWNT/GOD (solid), (b) GCE/SWNT–COOH (dotted) and GCE/SWNT–COOH/GOD (solid) in 0.05 M N_2 saturated PBS solution (pH 7.4). Scan rate: 0.05 V s^{-1}.

peak-to-peak separation (ΔE_p) was calculated as ca. 0.033 V and the ratio of the cathodic current over the anodic one was close to 1. For comparison, the control experiments without GOD and the bare GCE did not show such redox waves (dashed and dotted curves in Fig. 2a). It indicated that the redox waves were ascribed only to GOD. These features were the characteristic of the reversible electron transfer process of the redox active centre (flavin adenine dinucleotide, FAD) in GOD biomolecules (Cai and Chen, 2004; Guiseppi-Elie et al., 2002; Liu et al., 2005). It suggested that the direct electron transfer of GOD on SWNT–IL– could be achieved. Fig. 2b shows CVs of the GCE/SWNT–IL–GOD at various scan rates. The small peak-to-peak separation and the linear relationship between the peak currents and scan rates (up to 0.2 V s^{-1}) indicated that the redox process of the prepared bionanocomposite was a reversible and surface-confined process. It is well known that the active redox centre of GOD, flavin adenine dinucleotide (FAD) is deeply embedded in a protective protein shell, which makes the direct electron communication with electrodes extremely difficult. Therefore, SWNT might facilitate a reversible electron transfer process between the GOD and the electrode substrate.

The observed redox response coincided with previously reported direct electron transfer of GOD on CNT immobilized with other methods (Cai and Chen, 2004; Guiseppi-Elie et al., 2002; Liu et al., 2005). To verify the advantage of IL-like unit functionalized SWNT nanocomposites for GOD conjugation, two more control experiments were undertaken. For this purpose, pristine SWNT and SWNT–COOH was instead used to immobilize GOD and modified onto GCEs by the same method. Results indicated that at the pristine SWNT-modified GCE, the direct electron transfer of GOD could be observed (Fig. 3a), but the redox waves were not as obvious as that at SWNT–IL-modified electrode. And at the SWNT–COOH-modified GCE, almost no obvious direct electron transfer of GOD was observed (Fig. 3b). The GCE/SWNT/GOD, GCE/SWNT–COOH/GOD and GCE/SWNT–IL–GOD were prepared almost under identical conditions. For instance, the same loading of SWNT onto GCEs, the same concentration of GOD in PBS solution, and also the same time for the adsorption of GOD were used. Also each experiment was repeated three times, and no distinct differences were found. The distinguished difference among these experiments should be ascribed to the different functionalized SWNT.

Indeed, previous reports have pointed out that GOD could physically absorb on the surface of SWNT weakly (Cai and Chen, 2004; Guiseppi-Elie et al., 2002; Wang et al., 2003). Here IL-like unit on the surface of SWNT might play an additionally delicate role in the effective immobilization of GOD on SWNT through ionic interaction, which contributed to subsequent direct electron transfer. As known, GOD is net negatively charged in the pH 7.4 solution, and SWNT–COOH was also negatively charged, hence the electrostatic repulsion between them was against the physical absorption of GOD. In contrast, here the IL-like unit (imidazolium cation) was positively charged. Moreover, like many other ILs, here the charge state of IL-like unit was not depended on pH. It was in favor of conjugation of negatively charged GOD. Moreover, Br^- anion in SWNT–IL– was ready to be exchanged (Zhang et al., 2006). Therefore, the ionic interaction provided an extra ionic affinity between SWNT and GOD, which is helpful for the immobilization of GOD on SWNT. Results indicated that this immobilization has achieved better redox response of immobilized GOD on the electrode surface.

3.3. Detecting glucose at GCE/SWNT–IL–GOD

As discussed aforementioned, GOD on SWNT–IL– could undergo a reversible direct electron transfer on the modified electrode. It suggested that SWNT–IL– was positioned within the tunneling distance of FAD moiety, but the fact that whether or not GOD was denatured still was unknown. Achieving the direct electron transfer of redox enzyme and maintain its substrate-specific enzyme activity are both important for the potential biological applications. If the bioactivity of immobilized GOD was retained, the integrated bionanocomposite could be used to build glucose sensor. In general, the principle of the glucose electrochemical biosensor is based on the amperometric detection of H_2O_2 or O_2, which is generated or consumed during the course of the GOD-catalyzed oxidation of glucose in the presence of dissolved oxygen. The biocatalytical process for the oxidation of glucose in the presence of GOD can be summarized as following two processes:

$$GOD_{(ox)} + \text{glucose} \rightarrow GOD_{(red)} + \text{gluconolactone} + 2H^+ \quad (1)$$

$$GOD_{(red)} + 2H^+ + O_2 \rightarrow GOD_{(ox)} + H_2O_2 \quad (2)$$

Generally, the amperometric detection of H_2O_2 could be undertaken either by reduction or oxidation. But considering the serious interference of other related biomolecules such as AA and DA by oxidation in the practical clinical analysis (Wang et al., 2002), hence the reduction method was carried out.

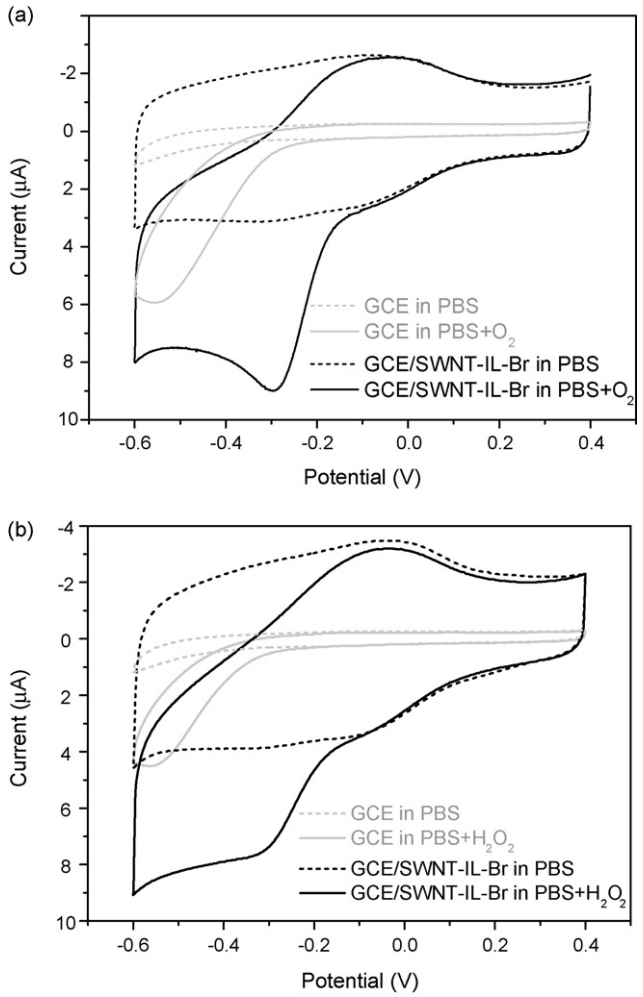


Fig. 4. (a) Cyclic voltammetric curves at bare GCE (gray) and GCE/SWNT–IL–Br (black) in 0.05 M air saturated (solid) PBS solution and after degassed with pure N_2 (dotted). (b) Cyclic voltammetric curves at bare GCE (gray) and GCE/SWNT–IL–Br (black) in 0.05 M N_2 saturated PBS solution in the absence (dotted) and in the presence (solid) of 2.5 mM H_2O_2. Scan rate: 0.05 V s^{-1}.

Some reports had pointed out that "CNTs" (on which metal impurities were the active sites (Sljukic et al., 2006)) possess a remarkable electrocatalytical activity towards O_2 and H_2O_2 reduction (Gong et al., 2005; Lin et al., 2004; Liu and Lin, 2006; Wang et al., 2003), which are practiced in a wide range of biosensor applications. Therefore, whether the electrocatalytical property was also reserved in the IL-like unit functionalized "SWNT" was rather important and should be investigated firstly. Fig. 4a shows CVs at GCE/SWNT–IL–Br in the absence and in the presence of O_2 in PBS solution. An obvious reduction wave of O_2 at GCE/SWNT–IL–Br was observed at ca. −0.3 V (solid black curve). In contrast, the reduction potential of O_2 at bare GCE was at ca. −0.55 V (solid gray curve). It indicated that "SWNT–IL–Br" retained the high electrocatalytical activity towards the reduction of O_2. The electrocatalytical effect was also observed at the same electrodes for the electrochemical reduction of H_2O_2 (Fig. 4b). Particularly, the reduction peak of H_2O_2 was also around −0.3 V. Therefore, the above results indicated that ionic functionalization of "SWNT" with IL-like

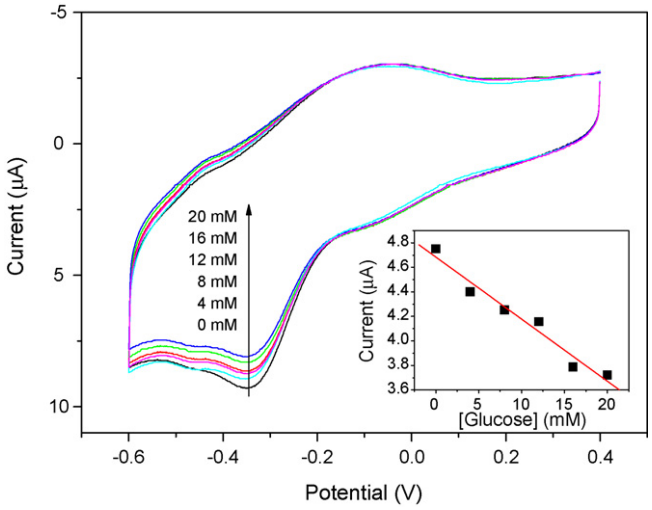


Fig. 5. Cyclic voltammetric measurements at GCE/SWNT–IL–GOD in various concentrations of glucose PBS solution saturated with air: 0, 4, 8, 12, 16, and 20 mM from outer to inner. The inset is the calibration curve corresponding to amperometric responses. Scan rate: 0.05 V s^{-1}.

unit did not affect its electrocatalytical activity towards reduction of O_2 and H_2O_2 to H_2O, which was in favor of further utilization of detecting glucose.

It also should be noted that, because SWNT–IL– could electrochemically reduce both O_2 and H_2O_2 at the similar reduction potential, both the generation of H_2O_2 and the consumed O_2 should be taken into account (Eqs. (3) and (4)). Compared with the reduction of one O_2 molecule to H_2O, the reduction of one H_2O_2 molecule at SWNT-modified electrode were two electrons less. Thus if the reaction of Eq. (2) occurred, the total reduction current (O_2 and H_2O_2) would be decreased:

$$O_2 + 4H^+ + 4e \rightarrow 2H_2O \quad (3)$$

$$H_2O_2 + 2H^+ + 2e \rightarrow 2H_2O \quad (4)$$

Fig. 5 shows the CVs at GCE/SWNT–IL–GOD in different concentrations of glucose PBS solution (saturated with air). The peak current originating from reduction of O_2 and H_2O_2 became smaller as the concentration of glucose increased. Therefore, it indicated that the specific enzyme–substrate activity of GOD was reserved in the SWNT–IL–GOD bionanocomposite. Moreover, the calibration curve corresponding to amperometric responses (Fig. 5, inset) is linear versus the concentrations of glucose ranging from 0 to 20 mM. It provided us a potential application of such a bionanocomposites in biosensor towards electrochemical detection of glucose.

4. Conclusion

In summary, a novel method for immobilization of biomolecules on CNTs was developed based on ionic interaction, which is of universality and widespread use in biological systems. As an example, glucose oxidase (GOD) and SWNT were integrated into a unitary bionanocomposite through an ionic liquid-like unit. Results indicated that the ionic liquid-like unit on SWNT provided an extra ionic affinity between

SWNT and GOD, which facilitated the preparation of bionanocomposite with better redox response of immobilized GOD. Additionally, the bioactivity of immobilized GOD was retained and the electrochemical detection of glucose could be achieved by this novel bionanocomposite. The optimization for the sensitivity, the limit of detection and the long-term stability of the bionanocomposite is important for practical applications, and the comparison with other methods still requires further studies.

Acknowledgements

The authors are most grateful to the National Science Foundation of China (Nos. 20475053 and 20673109), Department of Science and Technology of Jilin Province (No. 20050102) and Ministry of Science and Technology of China (No. 2006BAKB05).

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