



Carbon nanotube/gold nanoparticles/polyethylenimine-functionalized ionic liquid thin film composites for glucose biosensing

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ABSTRACT

A novel glucose biosensor based on immobilization of glucose oxidase (GOD) in thin films of polyethylenimine-functionalized ionic liquid (PFIL), containing a mixture of carbon nanotubes (CNT) and gold nanoparticles (AuNPs) and deposited on glassy carbon electrodes, was developed. Direct electrochemistry of glucose oxidase in the film was observed, with linear glucose response up to 12 mM. The PFIL-stabilized gold nanoparticles had a diameter of 2.4 ± 0.8 nm and exhibited favorable stability (stored even over one month with invisible change in UV–vis spectroscopic measurements). In addition, CNT were also well dispersed in the PFIL matrix, then, the resulting CNT/AuNPs/PFIL composites film showed high electrocatalytic activity toward reduction of hydrogen peroxide and oxygen. Here, PFIL, due to its high ionic conductivity, good solubility to CNT, and stability to nanoparticles, played an important role in constructing stable CNT/AuNPs/PFIL/GOD composites. And good biocompatibility of PFIL also offered a friendly environment for the immobilization of biomolecules.

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1. Introduction

Over the last decade, gold nanoparticles (AuNPs) have attracted increasing research attention for applications in catalysis and sensors (Daniel and Astruc, 2004; Raguse et al., 2007). AuNPs generally possess excellent catalytic activity and offer a hospitable environment for biomolecules. AuNPs catalyze oxygen reduction (Raj et al., 2005) and enable direct electrochemistry of glucose oxidase (Li et al., 2007a,b), hemoglobin (Yang et al., 2007b) and cytochrome c (Wang and Wang, 2004). Zhang et al. (2005a,b) fabricated glucose biosensors by covalently attaching glucose oxidase to gold-nanoparticle-monolayer-modified Au electrodes.

Since carbon nanotubes (CNTs) were discovered in 1991 (Iijima, 1991), they have attracted much attention due to their unique properties, such as high electrical conductivity, mechanical strength and chemical stability. In electrochemistry, carbon-nanotube (CNT)-based electrochemical and biosensors have been developed to detect hydrogen peroxide (Wang et al., 2003), ascorbic acid (Wang

et al., 2002), NADH (Musameh et al., 2002), nucleic acids (Dastagir et al., 2007) and neurotransmitters (Chen et al., 2003). However CNTs also display poor solubility in a wide range of solvents, especially water which hinders their use in chemical sensing applications. Non-covalent functionalization – e.g., co-dispersion with polymers such as Nafion (Wang et al., 2003) or chitosan (Liu et al., 2005b; Zhang et al., 2004) – has proven successful in solubilizing CNTs without negative impact to desired physicochemical properties, and the resulting composites have demonstrated potential for sensor applications. In addition, good solubility of CNTs in certain ionic liquids (ILs) has also been demonstrated recently (Fukushima et al., 2003; Zhang et al., 2005b).

Ionic liquids have been extensively used as modifiers recently at electrode surfaces for fabrication of gas sensors (Jin et al., 2006; Yu et al., 2005) and biosensors (Liu et al., 2005a; Yang et al., 2007a) due to their unique electrochemical properties, such as high ionic conductivity and relatively wide electrochemical window. The general method is to immobilize ionic liquid units on the electrode by physically mixing into polymer matrix. But ionic liquid components are easily diffused due to their wide solubility in the solutions, especially during electrochemical measurements.

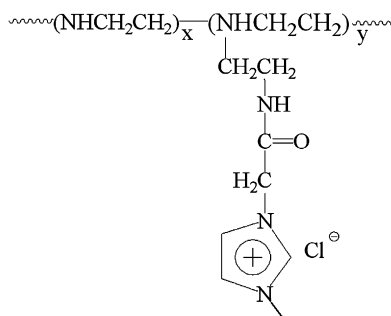
In our group, a polyethylenimine-functionalized ionic liquid (PFIL, as illustrated in Scheme 1) has been reported by covalent attachment of a carboxyl terminated ionic liquid on polyethylenimine (Shen et al., 2005). Since IL units are covalently modified on polyethylenimine, ILs can be steadily and easily immobilized on the electrode surface. Moreover, the results have also indicated that the

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Scheme 1. Structure of polyethylenimine-functionalized ionic liquid (PFIL).

PFIL combines the individual advantages of each functional part in the material: high ionic conductivity and solvation properties originating from the ionic liquid moieties; and good immobilization and film stability from the polyethylenimine (Shen et al., 2005, 2007).

Here we report results of investigation of a novel enzyme immobilization matrix intended to combine the above-mentioned benefits of gold nanoparticles, CNTs and ionic liquids for sensor applications. The resulting CNT-AuNP-PFIL composites showed obvious electrocatalysis toward reduction of H_2O_2 and O_2 . Further, when glucose oxidase was immobilized into CNT-AuNPs-PFIL thin films, the resulting electrodes demonstrated favorable linear catalytic response to glucose.

2. Experiment

2.1. Reagents

Polyethylenimine (PEI; $M_w = 25\,000$), $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ and NaBH_4 were obtained from Aldrich. PFIL was prepared as described previously (Shen et al., 2005). Multi-walled carbon nanotubes (MWCNT) prepared by chemical vapor deposition (CVD) were purchased from Shenzhen Nanotech Port Ltd. Co. (China). Glucose oxidase (EC 1.1.3.4, Type X-S, lyophilized powder, 100–250 units/mg, from *Aspergillus niger*) and D-(+)-glucose ($\geq 99.5\%$) were obtained from Sigma. Glucose stock solutions were stored overnight at room temperature before use. Hydrogen peroxide solution (30 wt.% aqueous) was purchased from Beijing Chemical Reagent Co. Dialysis membranes (MWCO 10,000 Da) were from Sino-American Biotechnology Co. Aqueous solutions were prepared with double-distilled water from a Millipore system ($>18\text{ M}\Omega\text{ cm}$).

2.2. Instruments

UV–vis absorption spectra were collected using a CARY 500 Scan UV/Vis/NIR spectrophotometer. Micrographs of transmission electron microscopy (TEM) were obtained using a JEOL 2000 transmission electron microscope operating at 200 kV. Cyclic voltammetry (CV) measurements were performed using a conventional three-electrode cell with a platinum wire as auxiliary electrode and an Ag/AgCl (saturated KCl) as reference in a CHI 660 Electrochemical Workstation (CHI, USA). Working electrodes were bare or modified glassy carbon (GC, $d = 3\text{ mm}$). Before use, GC electrodes were carefully polished to a mirror finish with 1.0-, 0.3-, and 0.05- μm alumina slurries, successively.

2.3. Synthesis of PFIL-stabilized AuNPs

0.4 mL of 30 mM HAuCl_4 was added to 2 mL of 1.5 mg/mL PFIL aqueous solution, followed by rapid addition of 0.72 mL of 0.2 M NaBH_4 solution under vigorous agitation. After stirring for 20 min,

the resulting solution was dialyzed for two days against double-distilled water to remove borides.

2.4. Preparation of MWCNT-AuNPs-PFIL film

Before used, MWCNT were purified by suspending the MWCNT with aid of ultrasonic agitation for 2 h in a 3:1 (v/v) mixture of concentrated sulfuric and nitric acid. 2 mg dry MWCNT were added to 1 mL of 1.5 mg/mL PFIL aqueous solution. Sonication for 1 h at ambient temperature yielded uniformly dispersed MWCNT-PFIL solution, which was then mixed with an equal volume of as-prepared PFIL-AuNP solution. Subsequently, 2 μL of the resulting MWCNT-AuNP-PFIL solution was dropped onto a glassy carbon electrode and allowed dried in ambient air for 24 h. The resulting modified electrode is denoted as GC/MWCNT-AuNP-PFIL. For control experiments, GC/PFIL, GC/AuNP-PFIL and GC/MWCNT-PFIL electrodes were also prepared by this simple drop-casting technique.

2.5. Immobilization of GOD in MWCNT-AuNPs-PFIL film

GC/MWCNT-AuNP-PFIL electrodes were soaked in 2 mg/mL GOD solution (0.05 M phosphate-buffered saline, pH 7.4) for 24 h at 4°C . At this pH, GOD ($pI \sim 4.5$) bears a net negative charge, allowing counter-anions in the PFIL film to exchange with GOD ($-$). The resulting GC/MWCNT-AuNP-PFIL-GOD electrodes were thoroughly rinsed with PBS to remove excess GOD.

3. Results and discussion

3.1. Characterization of MWCNT-AuNPs-PFIL nanocomposites

Fig. 1A shows a representative TEM image of PFIL-stabilized AuNPs, with corresponding size-distribution histogram centered around mean diameter $2.4 \pm 0.8\text{ nm}$. Fig. 1B shows UV–visible absorption spectra of HAuCl_4 -PFIL aqueous solution before and after addition of borohydride. The broad absorption peak at 500–550 nm corresponds to the plasmon resonance band of AuNPs formed after addition of the reducing agent. The UV–vis spectrum of PFIL-AuNPs solution did not change when stored over one month at room temperature (Fig. S1), confirming that the resulting PFIL-stabilized AuNPs were extremely stable.

MWCNT dispersed by sonication in aqueous PFIL solution (Fig. 1C) remained suspended for two weeks without change. As reported earlier (Kong et al., 2000; Munoz et al., 2005; Shim et al., 2001; Sun and Gao, 2003), amine groups possessed high affinity for physisorption along the CNTs' sidewalls and carboxylic groups on the MWCNT. The imidazolium cation in PFIL could be attracted onto MWCNT due to electrostatic interaction (Munoz et al., 2005; Zhou et al., 2004). So, driving force involved into the functionalization of PFIL on MWCNT' sidewalls was a combination of PFIL physisorption on MWCNT sidewalls and electrostatic interaction between the oppositely charged MWCNT and PFIL components. Fig. 1D displayed a TEM image of mixed MWCNT, AuNPs and PFIL solution. The AuNPs (as shown in Fig. 1C) were well dispersed and the size of AuNPs had no change in comparison with that in Fig. 1A.

3.2. Electrochemical characteristics of MWCNT-AuNPs-PFIL film

Cyclic voltammetric measurements of 2 mM $[\text{Fe}(\text{CN})_6]^{3-}$ at different electrodes were performed and results were shown in Fig. S2. Potential differences of peak-to-peak (ΔE_p) at bare, PFIL, AuNPs-PFIL, and MWCNT-AuNPs-PFIL modified GC electrodes were 79, 71, 82 and 78 mV, respectively. Peak current at GC/MWCNT-AuNPs-PFIL was much larger than those at bare and other modified GC

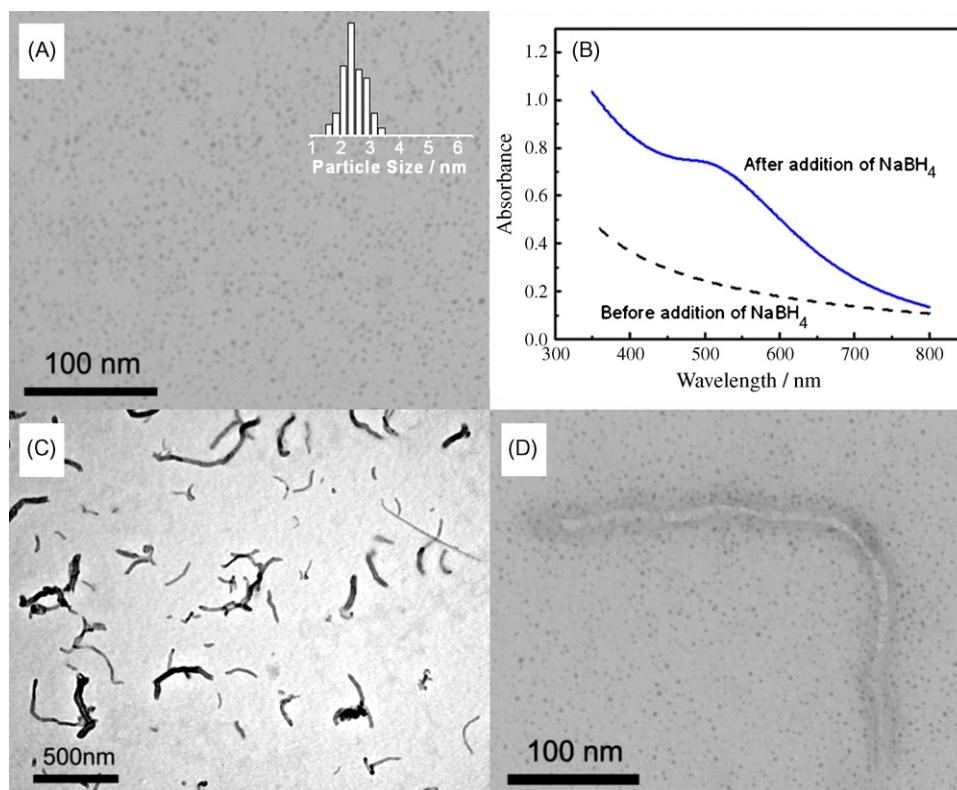


Fig. 1. (A) TEM image and corresponding nanoparticle size analysis histogram of PFIL-stabilized AuNPs. (B) UV-vis absorption spectra of HAuCl₄-PFIL solution before (dashed) and after (solid) addition of NaBH₄. (C) TEM images of PFIL solution dispersing 2 mg/mL of MWCNT and (D) the resulting MWCNT-AuNPs-PFIL solution.

electrodes due to increase of surface area after addition of MWCNT and AuNPs. These results also indicated that PFIL, AuNPs-PFIL and MWCNT-AuNPs-PFIL films all had good electronic conductivity and resulted in a more accessible surface to GC. Here, such redox activity at modified electrodes should be ascribed to high ionic conductivity from ionic liquid moieties in PFIL and electronic conductivity from CNTs and AuNPs components.

3.3. Electrocatalysis of MWCNT-AuNPs-PFIL film

GC/MWCNT-AuNPs-PFIL exhibited high electrocatalytic activity toward reduction of H₂O₂. Fig. 2 compares the electrocatalytic reduction to H₂O₂ at PFIL, AuNPs-PFIL, MWCNT-PFIL, and MWCNT-AuNPs-PFIL modified GC electrodes, respectively. An obvious reduction current at GC/MWCNT-AuNPs-PFIL clearly indicated that

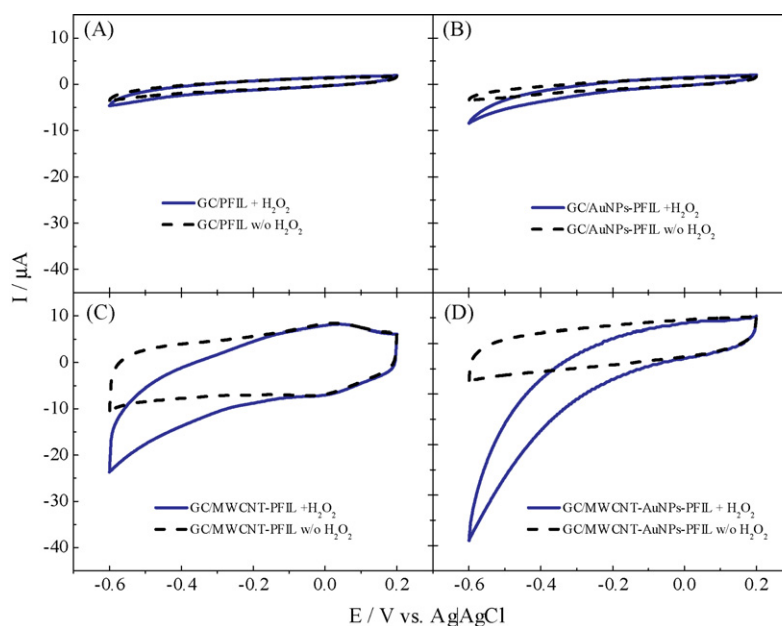


Fig. 2. Cyclic voltammograms of (A) PFIL, (B) AuNPs-PFIL, (C) MWCNT-PFIL and (D) MWCNT-AuNPs-PFIL film modified GC in 0.05 M N₂-saturated PBS solution (pH 7.4) in the absence (dashed) and presence of 5 mM H₂O₂ (solid) at scan rate of 0.05 V s⁻¹.

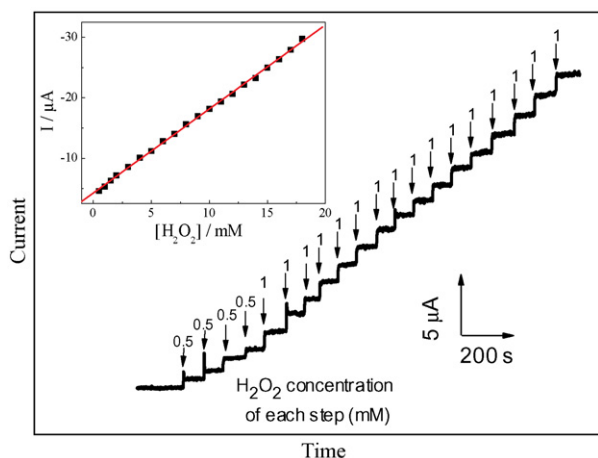


Fig. 3. Chronoamperometric response of GC/MWCNT-AuNPs-PFIL film electrode in N_2 -saturated PBS solution (0.05 M, pH 7.4) upon continuous addition of different concentration H_2O_2 for each step. Working potential: -0.35 V. Inset: amperometric response to H_2O_2 concentration ($R = 0.9995$).

MWCNT-AuNPs-PFIL film had much better electrocatalytic activity toward reduction of H_2O_2 than other cases. Fig. 3 showed amperometric response of GC/MWCNT-AuNPs-PFIL at -0.35 V upon successive additions of different concentration H_2O_2 . As shown in the inset of Fig. 3, a wide linear response to H_2O_2 ranging from 0.5 to 18 mM ($R = 0.9995$) could be observed with a quite fast response (<5 s). The sensitivity of this MWCNT/AuNPs/PFIL toward H_2O_2 reduction was ca. $15.6 \mu A mM^{-1} cm^{-2}$, which were quite similar to early reported CNT dispersed in Nafion film ($15.5 \mu A mM^{-1} cm^{-2}$) (Wang et al., 2003) and a little bit higher than that in CNT/chitosan modification ($14 \mu A mM^{-1} cm^{-2}$) (Luo et al., 2005). Our results in sensitivity are quite comparative to other films, which have been previously used to disperse the CNTs. Here, ionic liquid polymer (PFIL) not only is helpful for this dispersion of CNTs (Zhang et al., 2005a,b) due to its wide solubility, but also shows merits in electrochemical measurements (decrease of overpotential, high time response and enhanced electrochemical signal) due to its high ionic conductivity and promoted mass diffusion (Shen et al., 2005, 2007).

Similarly, GC/MWCNT-AuNPs-PFIL also showed an excellent reduction toward O_2 . An obvious reduction peak of O_2 was observed at ca. -0.35 V (solid) in the presence of O_2 in PBS solution, as shown in Fig. S3.

3.4. Direct electrochemistry of GOD in MWCNT-AuNPs-PFIL film

Fig. 4A (dashed) showed a CV curve of GC/MWCNT-AuNPs-PFIL in N_2 -saturated PBS (0.05 M, pH 7.4). No any redox characteristic can be observed. After the immobilization of GOD into the MWCNT-AuNPs-PFIL film matrix, a pair of well-defined and nearly symmetric redox peaks was obtained (solid). The formal potential (E^0) calculated by averaging cathodic and anodic peak potentials was estimated as ca. -0.42 V (vs. Ag/AgCl) with ca. 75 mV peak-to-peak separation and ca. 1 ratio of cathodic to anodic current intensity. In comparison, it can be concluded that the redox waves should be ascribed only to GOD, which is characteristic of reversible electron transfer process of redox active center (flavin adenine dinucleotide, FAD) in the GOD (Cai and Chen, 2004; Guiseppi-Elie et al., 2002; Liu et al., 2005b). Thus, a direct electron transfer of GOD in such a MWCNT-AuNPs-PFIL film has been achieved successfully. Fig. 4B showed CV grams of the GC/MWCNT-AuNPs-PFIL at various scan rates. The peak-to-peak separation and its linear relationship between peak current and scan rate (up to $0.2 V s^{-1}$) indicated that the redox process of GOD in this composite film was a reversible

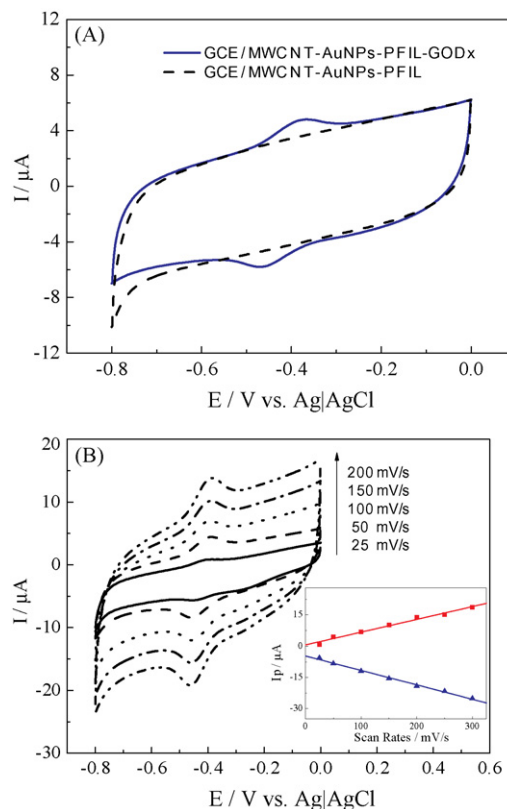
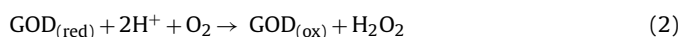
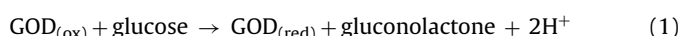


Fig. 4. (A) Cyclic voltammograms of GC/MWCNT-AuNPs-PFIL (dashed) and GC/MWCNT-AuNPs-PFIL-GOD (solid) in 0.05 M N_2 -saturated PBS solution (pH 7.4) at scan rate of $0.05 V s^{-1}$. (B) Cyclic voltammograms at various scan rates from 0.025, 0.05, 0.1, 0.15, to $0.2 V s^{-1}$, respectively. Inset: plot of peak currents vs. scan rates.

and surface-confined process. It is well known that the active redox center 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, here MWCNT and AuNPs might facilitate a direct electron transfer process between the GOD and electrode substrate. In addition, high ionic conductivity and biocompatibility originated from ionic liquid units should be helpful for this direct electron transfer of GOD on the electrode surface (Li et al., 2007a; Liu et al., 2007; Zhang et al., 2007).

3.5. Detection of glucose at GC/MWCNT-AuNPs-PFIL-GOD

As described above, GOD in MWCNT-AuNPs-PFIL film could undergo a reversible direct electron transfer. But, in fact, it was still unknown whether or not GOD was denaturalized. Achieving the direct electron transfer of redox enzyme and maintaining its substrate-specific enzyme activity are both important for its potential biological applications. When bioactivity of immobilized GOD was retained, the integrated bionanocomposite should catalytically oxidize the glucose, which is commonly used in fabrication of glucose biosensor. In general, principle of glucose electrochemical biosensor is realized based on amperometric detection of H_2O_2 or O_2 , which is generated or consumed during the course of 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:



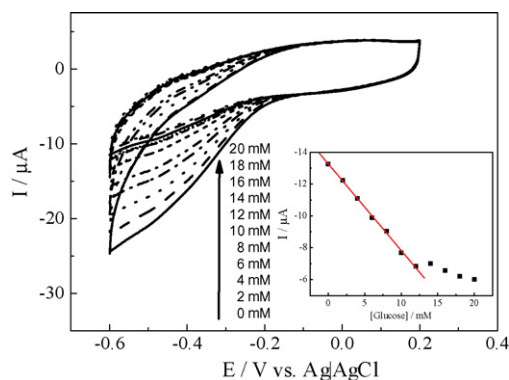


Fig. 5. Cyclic voltammetric measurements at GC/MWCNT-AuNPs-PFIL-GOD in various concentrations of glucose PBS solution saturated with O_2 : 0, 2, 4, 6, 8, 10, 12, 14, 16, 18 and 20 mM from outer to inner. The inset is the calibration curve ($R = 0.9991$) corresponding to amperometric responses at -0.35 V. Scan rate: 0.05 V s^{-1} .

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 ascorbic acid (AA) and dopamine (DA) by oxidation in the practical clinical analysis (Wang et al., 2002), hence reduction method was often carried out.

It also should be noted that, because MWCNT-AuNPs-PFIL could electrochemically reduce both O_2 and H_2O_2 , both generation of H_2O_2 and consumed O_2 should be taken into account (as shown as follows in Eqs. (3) and (4)). Compared with reduction of one O_2 molecule to H_2O , the reduction of one H_2O_2 molecule at MWCNT-AuNPs-PFIL modified electrode are two electrons less. Thus if the reaction of Eq. (2) occurred, the total reduction current (O_2 and H_2O_2) would be decreased.



Fig. 5 shows CV curves of GC/MWCNT-AuNPs-PFIL-GOD in different concentrations of glucose/PBS solution (saturated with O_2). The reduction current originating from reduction of O_2 and H_2O_2 became smaller and smaller with increases of the concentration of glucose, confirming that the specific enzyme–substrate activity of GOD was reserved in such MWCNT-AuNPs-GOD-PFIL bionanocomposites. The good biocompatibility and high electrocatalytic property might result from the presence of MWCNT, Au nanoparticles and PFIL. Compared with other electrolytes, PFIL has its own good advantages. Firstly, PFIL has good biocompatibility and kept the bioactivity of GOD. Secondly, the improved ionic conductivity of PFIL (Shen et al., 2005) from ionic liquid moieties, promoted mass transfer with high diffusion coefficient for targeted substrates (Shen et al., 2007), and increased electrocatalytic activity are also much favorable for its potential applications in biosensors. Moreover, in this method, GOD could be stabilized at the surface of GC/MWCNT-AuNPs-PFIL through electrostatic interactions between positively charged ionic liquid group and negatively charged glucose oxidase in a neutral solution after a simpler coating, as demonstrated early (Zhang et al., 2007). Such GOD immobilization does not leak easily and is much simpler than other methods.

Moreover, calibration curve corresponding to amperometric response (Fig. 5 inset) is linear against the concentrations of glucose ranging from 2 to 12 mM ($R = 0.9991$). Normally, the blood glucose level is maintained between about 4 and 6 mM. So the linear glucose response from 2 to 12 mM in this work is enough and suitable for its practical application in determining blood sugar concentra-

tion. In addition, GOD sensors made by other methods have also shown similar results. For example, Zhu et al. (2007) fabricated a bi-enzymatic glucose biosensor based on co-immobilization of peroxidase and glucose oxidase on a carbon nanotubes electrode whose linear response range was from 0.030 to 2.43 mM. Wu et al. (2007) constructed amperometric glucose biosensor based on multilayer films via layer-by-layer self-assembly of multi-wall carbon nanotubes, gold nanoparticles and glucose oxidase, which exhibited linear response range toward glucose from 0.1 to 10 mM.

4. Conclusion

In sum, we have successfully constructed a novel glucose biosensor based on MWCNT-AuNPs-PFIL-GOD thin film at the glassy carbon electrode. The PFIL, an ionic liquids polymer, was used for dissolving MWCNT, protecting AuNPs and forming a stable thin film to achieve uniformly MWCNT, AuNPs and GOD composites. The resulting bionanocomposites retained the bioactivity of GOD and also exhibited a good electrochemical response to glucose, which offered an excellent possibility for glucose biosensing. Similarly, such bionanocomposites can also be extended to some other immobilizations of biomolecules, which is still under our investigation.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.bios.2008.07.057.

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