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Biosensor based on polyaniline–Prussian Blue/multi-walled carbon nanotubes hybrid composites

Yongjin Zou [a,b], Li-Xian Sun [a,*], Fen Xu [a,**]

[a] *Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China*
[b] *Graduate School of the Chinese Academy of Sciences, Beijing 100049, China*

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Abstract

In this work, a novel route for fabrication polyaniline (PANI)–Prussian Blue (PB) hybrid composites is proposed by the spontaneous redox reaction in the $FeCl_3$–$K_3[Fe(CN)_6]$ and the aniline solution. With the introduction of multi-walled carbon nanotubes (MWNTs), the PANI–PB/MWNTs system shows synergy between the PANI–PB and MWNTs which amplified the H_2O_2 sensitivity greatly. A linear range from 8×10^{-8} to 1×10^{-5} M and a high sensitivity 508.18 μA μM cm^2 for H_2O_2 detection are obtained. The composites also show good stability in neutral solution. A glucose biosensor was further constructed by immobilizing glucose oxidase (GOD) with Nafion and glutaraldehyde on the electrode surface. The performance factors influencing the resulted biosensor were studied in detail. The biosensor exhibits excellent response performance to glucose with the linear range from 1 to 11 mM and a detection limit of 0.01 mM. Furthermore, the biosensor shows rapid response, high sensitivity, good reproducibility, long-term stability and freedom of interference from other co-existing electroactive species.

Keywords: Glucose biosensor; Carbon nanotubes; Polyaniline; Prussian Blue; Hybrid composites

1. Introduction

During recent years, enzymatic biosensors have received much attention by many researchers due to their rapid response, high sensitivity and intrinsic selectivity (Yokoyama et al., 1992; Luo and Do, 2004; Zhao et al., 2005). Among the biosensors, glucose sensors have been greatly studied owing to their usefulness in the diagnostic analysis of diabetes (Sun et al., 1998; Newman and Turner, 2005; Yang et al., 2006). Most glucose biosensors are based on the oxidation or reduction of enzymatically produced H_2O_2, so the matrix for immobilization of GOD and the catalytic materials for electro-oxidation or reduction of H_2O_2 are necessary to construct a glucose biosensor. The direct detection of H_2O_2 is usually done at platinum or platinised electrode through its oxidation at anodic potential (>+0.6 V versus Ag/AgCl) (Liu et al., 1999). However, in clinical application the high positive working electrode potential required leads to interference from reducing species such as ascorbic acid and uric acid. Prussian Blue has proved be an excellent catalyst for H_2O_2 reduction at low potentials. Moreover, Prussian Blue is a relatively cheap and stable electrocatalyst compared to enzyme such as peroxidase. As a result, it is an attractive material for possible mass production of biosensors (Karyakin et al., 1995, 1996).

On the other hand, carbon nanotubes (CNTs) have emerged as new class nanomaterials that are receiving considerable interest because of their unique structure, high chemical stability and high surface-to-volume ratio. These properties make them extremely attractive for fabricating chemical sensors (Lim et al., 2005; Wang et al., 2003). Recently, composite materials based on integration of CNTs and some other materials to possess properties of the individual components with a synergistic effect have gained growing interest. Materials for such purposes include conducting polymers, redox mediators and metal nanoparticles. For example, coupling CNTs with toluidine blue resulted in remarkable improvement of the electroactivity of the composite

* Corresponding author at: Materials & Thermochemistry Laboratory, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China. Tel.: +86 411 84379213; fax: +86 411 84379213.
** Corresponding author at: Materials & Thermochemistry Laboratory, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China. Fax: +86 411 84379213.
E-mail addresses: lxsun@dicp.ac.cn (L.-X. Sun), fenxu@dicp.ac.cn (F. Xu).

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materials toward β-nicotinamide adenine dinucleotide (NADH) through synergistic effect (Zhang and Gorski, 2005). Yang et al. have also showed the synergy effect between CNTs and cobalt hexacyanoferate nanoparticles (CoNP) with the significant improvement of redox activity of CoNP (Yang et al., 2006).

PB and PANI composites film have been used for fabricating biosensor by step-by-step electrodeposition on Pt electrode (Garjonyte and Malinauskas, 2000). Though the layer of PANI was permeable to hydrogen peroxide, the response time would increased. In the present paper, a new methods for "in situ" chemically synthesized PB was proposed. PB was easily synthesized from the $FeCl_3$–$K_3[Fe(CN)_6]$ solution by using aniline as reducer and chemical oxidation polymerization of aniline simultaneously. With the introduction of MWNTs, the PANI–PB/MWNTs hybrid composites show synergistic augmentation of the response current for H_2O_2 detection. A glucose biosensor was further constructed by immobilization glucose oxidase on the PANI–PB/MWNTs hybrid composites. The effects of enzyme loading, pH dependence, applied potential and rotating rate on the current response of the composite modified electrode toward glucose were optimized to obtain the maximal sensitivity. The resulted biosensor exhibits high sensitivity, rapid response, good reproducibility, long-term stability and freedom of interference from other co-existing electroactive species.

2. Experimental

2.1. Reagents

Aniline (≥99.5%, Shenyang Lianbang reagent Factory, Shengyang, China) was distilled before experiments. The MWNTs (95% 20–60 nm) were purchased from Shenzhen Nanotech. Port. Co., Ltd. (Shenzhen, China) were treated with nitric acid during purification process and then filtered, rinsed with double-distilled water and dried. A fresh H_2O_2 aqueous solution was prepared prior to use. GOD (from *Aspergillus niger*; 300,000 unit g^{-1}) was purchased from Sanland (America). D-Glucose was used without further purification and glucose solutions were stored overnight at room temperature before use. All other chemicals from commercial source were of analytical grade and used as received. The 0.1 M phosphate buffer solution (PBS), which was made from Na_2HPO_4 and NaH_2PO_4, was always employed as supporting electrolyte. Double-distilled water was used throughout the experiments.

2.2. Apparatus and measurements

The infrared (IR) spectra of the samples in KBr pellets were recorded on Bruker Equinox 55 Fourier transform infrared spectrometer (FTIR). The morphology was determined on a JEM-2000EX transmission electron microscope (TEM) with an accelerating voltage of 20 kV.

Cyclic voltammetric and amperometric measurements were performed using an IM6e electrochemical workstation (Zahner-Elektrik, Kronach, Germany). All electrochemical experiments were carried out with a conventional three-electrode system. The working electrode was the Bioanalytical Systems (BAS) cavity glassy carbon electrode (3 mm in diameter) (GCE). Prior to each experiment, the GCE was polished successively with 1, 0.3 and 0.05 μm α-alumina powder, rinsed thoroughly with double-distilled water between each polishing step, utrasonicated successively in 1:1 nitric acid, acetone and double-distilled water and, then allowed to dry at room temperature. The rotating disk electrode (RDE) experiments were performed by BAS rotator system in conjunction with an IM6e. The rotating rate is 3000 rpm when detect H_2O_2 and glucose unless stated otherwise. An Ag/AgCl (saturated with NaCl) reference electrode was used for all measurements, and all the potentials were reported in this paper versus this reference electrode. A platinum wire was used as a counter electrode. Before all batch amperometric experiments, the potential of each electrode was held at the operating value, allowing the background current to decay to a steady-state value. All experiments were performed at room temperature.

2.3. Preparation of the PANI–PB hybrid composites

PANI–PB organic/inorganic composites were prepared as follows: to an aqueous of 0.1 M aniline + 0.1 M HCl solution 50 mL, an aqueous 0.002 M $FeCl_3$ + 0.002 M $K_3Fe(CN)_6$ + 0.1 M HCl solution 20 mL was slowly added at room temperature with a vigorous stirring. After the addition, the reaction mixture turned blue immediately, indicating the formation of PB and PANI. The precipitated PANI–PB powder was filtered and washed with 1 M HCl and finally with water several times. The hybrid material was vacuum dried for 12 h before further characterization. As compare, the PANI was prepared according the literature (Karim et al., 2005).

2.4. Modifications of the electrodes

The PANI–PB/MWNTs modified electrode was prepared as follows: 2 mg of purified MWNTs was dispersed in 5 mL dimethylformamide (DMF) with the aid of ultrasonic agitation to give a 0.4 mg mL^{-1} black suspension. Then, 5 mg of PANI–PB particles were dispersed in the MWNTs suspension by using 60 min sonication. A suspension (10 μL) of the PANI–PB/MWNTs in DMF were dropped onto the GCE surface by the spinning method and then dried under an infrared lamp. After modification, the modified electrode was rinsed with water (pH 5.3) and immersed into a solution containing 0.1 M KCl + 0.01 M HCl, where the electrode potential was cycled between −0.10 and 0.50 V at a scan rate of 0.05 V s^{-1}, until a stable voltammetric response was obtained.

GOD solution was obtained by dissolving 10 mg of GOD in 2 mL of 0.1 M PBS (pH 6.5). For the immobilization of enzyme, 3 μL of GOD solution was dropped onto the PANI–PB/MWNTs modified electrode surface carefully. After drying for 60 min at 4 °C in refrigerator, a mixture (3 μL) of glutaraldehyde and Nafion was placed on the enzyme surface as protective film (Ricci et al., 2003). The mixture was prepared as follows: 2 mL of glutaraldehyde (2.5%, v/v diluted in water) and 3 mL of Nafion

(5%, v/v in ethanol) were mixed and adjusted its pH to 5.5 using concentrated NaOH. The construction of the sandwiched enzyme biosensor was accomplished. The enzyme electrode was then left under damp conditions at 4 °C for 24 h before used.

3. Results and discussion

3.1. PANI–PB hybrid composite synthesis

PB has been synthesized through electrochemical method conventionally (Mattos et al., 2003). In this work, PB was "in situ" chemically synthesized by the spontaneous redox reaction in the $FeCl_3$–$K_3[Fe(CN)_6]$ and the aniline solution. Itaya et al. (1982) pointed out that a solution of $FeCl_3$–$K_3[Fe(CN)_6]$ in acidic media is a very strong oxidant, showing an open circuit potential highly positive (0.98 V versus SCE for a Pt disk electrode). This potential cannot be obtained in solutions of either $FeCl_3$ or $K_3[Fe(CN)_6]$, respectively. On the other hand, polyaniline can be polymerized by a wide range of chemical oxidants, such as $(NH_4)_2S_2O_8$, H_2O_2, $Ce(SO_4)_2$, $K_2Cr_2O_7$, KIO_3 and $FeCl_3$. Although the standard reduction potential for $FeCl_3$ is low (0.77 V versus the standard hydrogen electrode (SHE)), it has been proven to be a particularly useful oxidant (Yasuda and Shimidzu, 1993). It is proven that aniline can also be oxidized to anilinium radical cation by $FeCl_3$–$K_3[Fe(CN)_6]$ in acidic media then polymerized to form polyaniline.

There are several reports on the preparation of bilayer films composed of PB and conducting polymers from the point of view of preparing double-redox system (Sawant et al., 2004; Garjonyte and Malinauskas, 2000). But to the best of our knowledge, there are no reports which synthesized PB and PANI simultaneously. In the present paper, it is first time to synthesize the PANI–PB composite based on the spontaneous redox reaction of in the $FeCl_3 + K_3[Fe(CN)_6]$ solution and the aniline solution.

Fig. 1 shows the IR transmission spectra recorded for PANI and the PANI–PB composites. It can be seen that IR spectra shows a strong absorption band around 2086 cm^{-1} which is characteristic of the CN stretching in the Fe^{2+}–CN–Fe^{3+} of

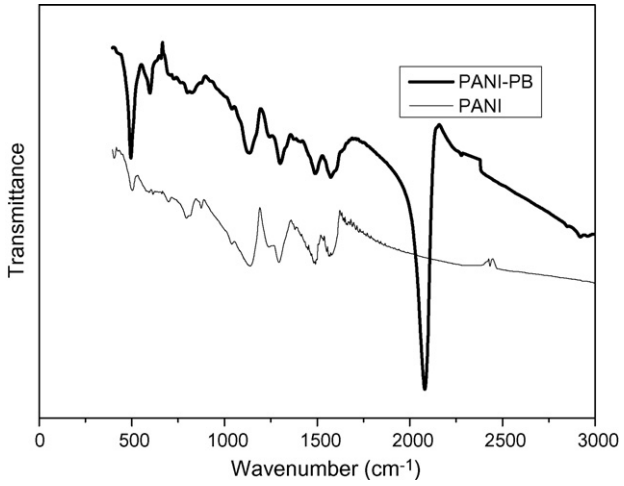

Fig. 1. IR spectra of PANI–PB and PANI alone.

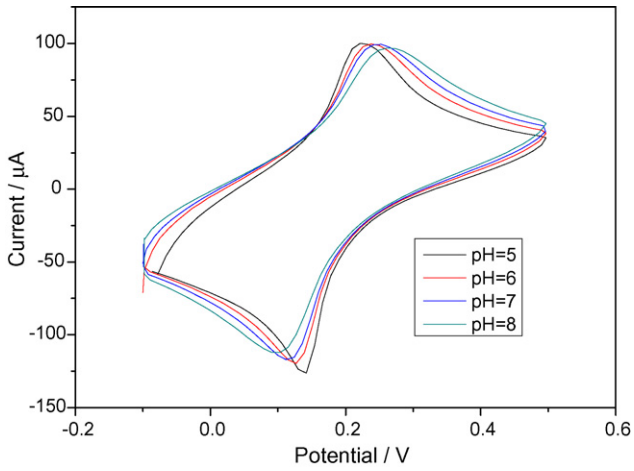

Fig. 2. Effect of pH value on the PANI–PB/WMNTs modified electrodes in pH 6.5 0.1 M PBS + 0.1 M KCl.

PB (Uemura and Kitagawa, 2003). The IR spectra also indicate that the PABI–PB are mixture because no bridging mode C–N absorption band was observed (Sawant et al., 2004). The absorption bands characteristics of emeraldine salt at 1511, 1295 and 1112 cm^{-1} assigned to ring str., C–N str., and C–H bend, respectively, which are present in the samples of PANI synthesized by other ways (Nakayama et al., 1997). The TEM image of PANI–PB hybrid composites shows the diameter of the particles is around 100 nm, with some large ones reaching about 200 nm.

3.2. Characterizations of PANI–PB/MWNTs

The PANI–PB/WMNTs modified electrodes were studied using cyclic voltammetry in a range between −0.2 and 0.5 V at different scan rates (in a range between 10 and 200 mV s^{-1}). Peak currents (both anodic and cathodic) vary linearly with the scan rates in a range between 10 and 150 mV s^{-1}. When the scan rate is higher than 200 mV s^{-1}, the wave shape is distorted severely ($\Delta E_p > 200$ mV). This indicates that the electrode reaction becomes electrochemically irreversible at higher scan rates.

The stability of the hybrid composites to pH changes was also studied by cyclic voltammetry. The ΔE_p increases with increasing the pH value (shown in Fig. 2). This may be attributed to the conductivity of PANI drops with an increase of solution pH value (Focke et al., 1987). However, the peak current did not change too much. It showed that the PB is stable in PANI–PB/MWNTs composites while the pH value changes.

The PANI–PB/WMNTs modified electrodes show a good stability after scanned in 0.1 M PBS + 0.1 M KCl (pH 6.5) for 50 cycles with no peak current decrease. After 200 cycles, the decrease of the signal was only 8% of the initial value. The good stability of the hybrid composites may be due to prepared method of the composites. The PANI has good environmental stability. It can protect the PB film. On the other hand, the MWNTs have high surface area, similar to these observed on graphite (Ricci et al., 2003), which can minimize the leakage due to the hydrolysis of ferric ions and increase the operational stability of the PB.

3.3. Electrochemical performance of PANI–PB/MWNTs modified electrodes for H_2O_2 detection

The PANI–PB/MWNTs modified electrodes can detect H_2O_2 at low potential (0.0 V). The effect of the content of MWNTs and PANI–PB in DMF solution on the performance of electrode towards H_2O_2 was investigated by varying the amount of MWNTs from 0.1 to 2 mg mL^{-1} and PANI–PB from 1 to 10 mg mL^{-1}, respectively. The current response for H_2O_2 detection was found to increase with increasing the amount of MWNTs. Further increases of the MWNTs content would cause the instability. So the magnitude of MWNTs 0.4 mg mL^{-1} was chosen. While increase in the amount of PANI–PB hybrid composites, the ΔE_p obtained from the CV increases. To keep a good reversibility of the redox reaction of the catalytic PB, 5 mg mL^{-1} of PANI–PB was selected to prepare the PANI–PB/MWNTs modified electrodes.

At the optimal conditions, the response time, detection limit, linearity range, sensitivity and electrode reproducibility for H_2O_2 detection were studied. All the measurements were performed in a 0.1 M PBS + 0.1 M KCl (pH 6.5) and at an applied potential of 0.0 V.

The H_2O_2 calibration curves obtained from the PANI–PB/MWNTs modified GCE show a good linearity in a range between 1×10^{-8} and 1×10^{-5} M with a correlation coefficient of 0.997. The detection limit is 1×10^{-8} M on signal-to-noise ratio of 3. The response time needed to reach 90% of the steady-state response was 15 s. In particular, the sensitivity is 508.18 μA μM^{-1} cm^{-2} which is much higher than 1.56 μA μM^{-1} cm^{-2} obtained from ruthenium purple anchored cinder modified RDE (Zen et al., 2003). The fabrication reproducibility, investigated at 1×10^{-7} M H_2O_2, was the relative standard deviation (R.S.D.) of 5.0% for five different modified electrodes. For five replicate measurements at 1×10^{-7} M H_2O_2 using a typical modified electrode, the R.S.D. was 2.6%. The synergistic effect between the PANI–PB and MWNTs improved the stability of composites film and amplified the sensitivity of H_2O_2.

The excellent electrocatalytic activity of the electrode toward H_2O_2 means that the electrode can represent a new electrochemical platform that provides operational access to a large number of oxidase-based enzymes for fabricating biosensors.

3.4. Effect of the GOD concentration on the response current

Enzyme loading on the electrode has a large effect on the current response. The response current increased with the increasing of the amount of enzyme loading. While the concentration of the enzyme is beyond 5 mg mL^{-1}, the response current does not increase. Moreover, the linear range diminished when the concentration of the enzyme is beyond 5 mg mL^{-1}, which is in agreement with literature reported by Razola et al. (2002). Since the oxidase-based sensor requires oxygen as the co-substrate to carry out oxidation, the oxygen tension may affect sensor response. While increasing the glucose concentration, lack of oxygen becomes the rate limiting substrate. This is the reason that the linearity is limited. With increasing of the amount of enzyme loading the reaction rate accelerated on the enzyme electrode. The saturated substrate concentration which reached the maximum reaction rate decreased due to the lack of oxygen and the linear range diminished (Li et al., 2004). Furthermore, too high an enzyme concentration will result in the leakage of the enzyme from the sensor surface and affect the stability of the sensor. Considering simultaneously the sensitivity and the linear range, 5 mg mL^{-1} of enzyme concentration was selected.

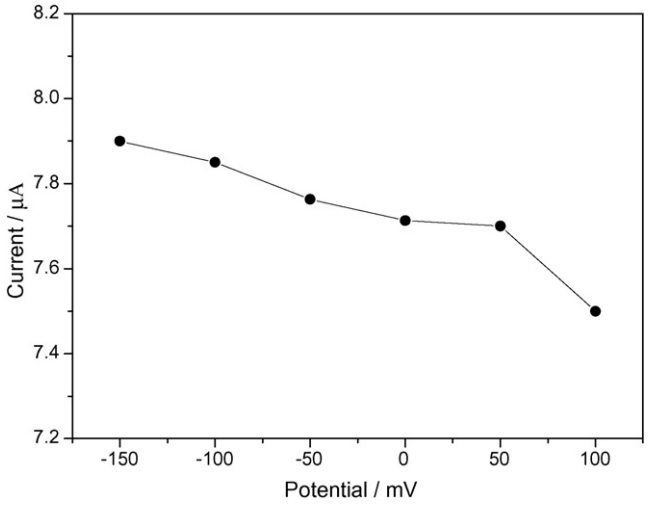

Fig. 3. Effect of applied potential on the response current in pH 6.5 0.1 M PBS + 0.1 M KCl; rotating rate, 3000 rpm.

3.5. Effect of applied potential

The choice of the applied potential at the working electrode is fundamental to achieve the lowest detection limit and to avoid the electrochemical interfering species. The effect of applied potential on the enzyme electrode response showed that the sensitivity of the enzyme electrode increased slightly with diminishing the applied potential from +100 to −150 mV (see Fig. 3). Taking into account sensitive response, effective avoiding interference and operational stability, 0.0 V was selected as the applied potential in subsequent experiments.

3.6. Effect of the value of pH on the response current

Investigation of the effect of the pH value on the performance of the biosensor is of great importance, because the activity of the immobilized GOD is pH dependent (Luo et al., 2004). The response current of the enzyme electrode increases in the pH range 5.0–6.5, the current response decreases and the background current increased at higher pH values. The current shows the maximum value at pH 6.5.

3.7. Effect of rotating rate

In the present work, the rotating disk electrode was used for glucose detection. The effect of rotating rate for glucose detection was also investigated. From Fig. 4, it can be seen that the

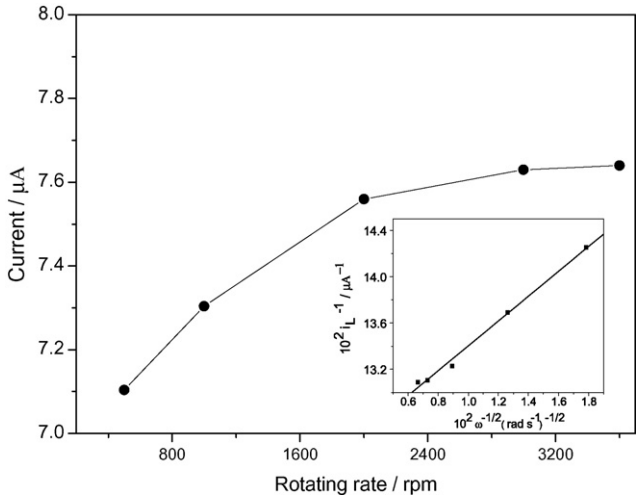

Fig. 4. Effect of rotating rate on the current response of the biosensor in pH 6.5, 0.1 M PBS + 0.1 M KCl at 0.0 V (the inset is $\omega^{-1/2}$ vs. i_L^{-1}).

response current is increased with the rotating rate increasing. The Levich plot (i_L^{-1} versus $\omega^{-1/2}$) is linear up to 3000 rpm, and after that it reaches the kinetic limitation. The response current does not increase and keep steady. Therefore, the rotating rate 3000 rpm was chose for glucose detection.

3.8. Amperometric determination of glucose at the enzyme electrode

Fig. 5 illustrates a typical current–time plot for the enzyme electrode upon the successive addition of 1 mM glucose at 0.0 V. The PANI–PB/MWNTs modified electrode reached 95% of the steady-state current within 15 s. The current response of the enzyme electrode increased along with glucose concentration. Fig. 5 (inset) shows the calibration curve of glucose at the enzyme electrode. The enzyme electrode gave a linear response to glucose in the range from 1 to 11 mM with a correlation coefficient of 0.999. The electrode has a low detection limit 0.01 mM at the signal-to-noise ratio of 3. When glucose concentration is high, a plateau current was observed, showing the characteristics of Michaelis–Menten kinetics. The apparent Michaelis–Menten constant (k_m) and the maximum current density (i_{max}) can be obtained by an amperometric method as suggested by Shu and Wilson (1976):

$$\frac{1}{i_s} = \frac{k_m}{i_{max}}\left(\frac{1}{C_g}\right) + \frac{1}{i_{max}}$$

where i_s is the steady-state current, C_g the concentration of glucose, k_m the apparent Michaelis–Menten constant and i_{max} is the maximum current. From the curve of the i_s^{-1} versus C_g^{-1}, based on the experimental data from Fig. 5, the k_m was estimated to be 5.1 mM and the i_{max} is 249.5 μA mM^{-1} cm^{-2}. The value of k_m is much lower than the reported 22 ± 2 mM (Wang et al., 1998; Sampath and Lev, 1996) and 33 mM in solution phase (Swoboda and Massey, 1965). The sensitivity of 15.36 μA mM^{-1} cm^{-2} is higher than the reported 2.59 μA mM^{-1} cm^{-2} (Cui et al., 2000) and 5.73 μA mM^{-1} cm^{-2} (Chen and Dong, 2003). These results show that the biosensor possesses higher biological affinity to glucose. The immobilized process might give rise to the microenvironment to change enzyme and affect the intrinsic properties of enzyme which could improve the affinity to glucose. The synergistic effect between MWNTs and PANI–PB may be preferable for the biosensor and improves the performances of the biosensor.

3.9. Interference tests

The number of the interfering species depends on the working potential and the nature of the sample. The most common electrochemical interfering species such as ascorbic acid and L-cysteine were evaluated. Addition of 0.2 mM ascorbic acid, 0.2 mM acetaminophen and 0.2 mM L-cysteine to 1.0 mM glucose did not produce observable interference in the biosensor response (shown in Fig. 6). That may due the low potential was

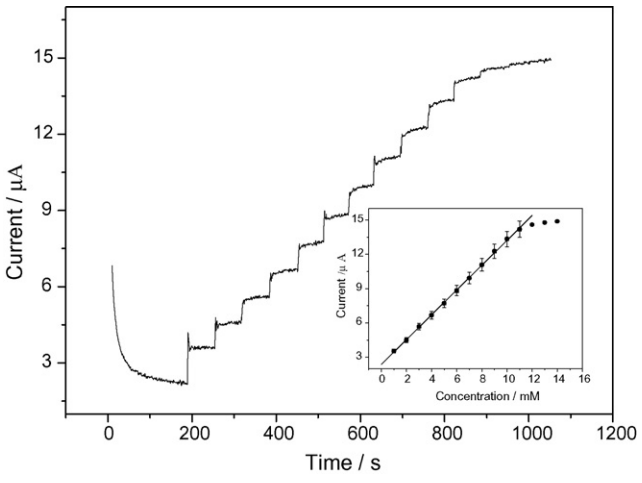

Fig. 5. Current–time curves obtained at the glucose biosensor for successive addition of 1 mM glucose. Condition:0.1 M pH 6.5 PBS + 0.1 M KCl at 0.0 V; rotating rate, 3000 rpm. Inset: calibration curve of the biosensor as a function of glucose concentrations.

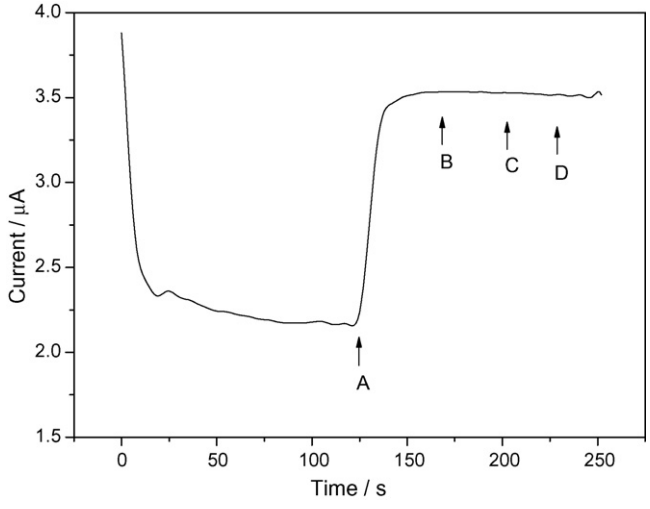

Fig. 6. Current–time recording at the biosensor for an addition of (A) 1.0 mM glucose, followed by addition of (B) 0.2 mM ascorbic acid, (C) 0.2 mM L-cysteine and (D) 0.2 mM acetaminophen, respectively. Other conditions are same as in Fig. 5.

applied. On the other hand, Nafion polymer is as an effectively perselective barrier (Wilson and Hu, 2000) which can circumvent the entry of anionic biological interferences.

3.10. Reproducibility and stability of the enzyme electrode

The reproducibility of enzyme electrode construction was estimated from the response to 5 mM glucose at five enzyme electrodes prepared under the same conditions. The results revealed that the biosensor has a satisfied reproducibility with a R.S.D. of 5.2%. The operational stability of the enzyme electrode was measured at 0.0 V in 0.10 M PBS + 0.1 M KCl containing 5 mM glucose. There is less than 2.0% relative deviation for five times continuous determinations of the same sample, which indicates that the biosensor has a good operational stability.

The storage stability of the biosensor was also studied. The steady-state response current of 5 mM glucose was determined every 2 days. When not in use, the biosensor was stored dry at 4 °C. The results show that the steady-state response current only decreases by 10% after 30 days (15 times) measurements, which indicates that the enzyme electrode was considerably stable.

There are two main factors which affect the stability of the PB-based biosensors. One is the stability of PB in neutral solution and the other is the leakage of the enzymes. In the present paper, the method prepared the PANI–PB/MWNTs made the PB have good stability. The hybrid composites provide a good microenvironment for GOD immobilization. The porous MWNTs matrix provides a high surface area for loading PANI–PB particles while the PANI thin film further stabilizes the PB film. The mixture of glutaraldehyde and Nafion, which is a good protective film and has been shown in the literature (Ricci et al., 2003), can prevent the leakage of the GOD effectively. These measures made the biosensor have long-term stability.

4. Conclusions

A novel route for fabrication PANI–PB organic/inorganic hybrid material is proposed by the spontaneous redox reaction of in the $FeCl_3$–$K_3[Fe(CN)_6]$ and the aniline solution. With the incorporation of MWNTs, a glucose biosensor based on PANI–PB/MWNTs hybrid composite was constructed. The biosensor exhibited high sensitivity, fast response and excellent stability and non-interferences. The good results can be attributed the synergistic effect between MWNTs and PANI–PB and the process for fabricating the biosensor. The PANI–PB/MWNTs hybrid material has a potential to provide operational access to a large group of oxidase enzymes for designing a variety of bioelectrochemical devices.

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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.2006.10.035.

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