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ORIGINAL PAPER

Poly(phenylenediamine) film for the construction of glucose biosensors based on platinized glassy carbon electrode

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Abstract Three phenylenediamine isomers (including *ortho*-, *meta*- and *para*-derivatives) were electrochemically polymerized to give polyphenylenediamine (PPD) films on platinized glassy carbon electrodes. Amperometric glucose sensors were developed by immobilizing glucose oxidase (GOx) into these polymer matrices during polymerization. Effects of the polymerization potential, polymerization charge, monomer concentration, GOx concentration and Pt deposition charge on the performance of the enzyme electrode to glucose were investigated. These resulting GC/Pt/PPD-GOx electrodes showed rapid electrochemical responses to hydrogen peroxide and glucose, and very good anti-interference ability to ascorbic acid. Correlation between the electroanalytical behaviors of the enzyme electrodes and the polymer structures was examined.

Keywords Phenylenediamine isomers · Electropolymerized poly(phenylenediamine) films · Platinum deposits · Glucose biosensor

1 Introduction

Since the first application of enzyme electrode by Clark and Lyons [1] utilizing glucose oxidase immobilized at the Clark-type polarographic oxygen electrode for the analysis of glucose, research on enzyme-based biosensors has gained a lot of attention and interest. Entrapment of enzymes to polymer membranes is one of the most popular techniques used for the immobilization of enzymes. Electro-immobilization of enzymes into conducting or non-conducting polymer matrices such as polypyrrole, polyaniline, polythiophene, polyphenol, polyphenylenediamine and other polymers has been reported [2–9]. When compared with the other methods for enzyme immobilization, this approach has the advantages of simplicity, possible control on the amount of immobilized enzymes and polymer thickness. Electropolymerized films offer wide immobilization capabilities and extremely large diversity in the development of biosensors [7].

The formation of electrochemically synthesized non-conducting film on the electrode surface is regarded as self-terminated [5]. The non-conducting film would block further access of monomers to the electrode surface, resulting in a thin and uniform film [10]. Representatively, the electrochemical polymerization of *o*-phenylenediamine (*o*PD) in neutral media is known to produce thin, hydrophobic, insulating films at the electrode surface [11, 12]. The possible structural unit of these films is suggested as a symmetrical "quinoid" structure [13, 14]. The *ortho*- or *para*-coupling of radicals generated at the electrode surface leads to the deposition of a PPD film on the electrode [15]. The electropolymerization of *o*-, *m*-, and *p*-phenylenediamine has been reported recently [16]. Three phenylenediamine isomers (including *ortho*-, *meta*- and *para*-derivatives) were electrochemically polymerized on palladium disk electrodes. The permeability and permselectivity of polyphenylenediamine films for hydrogen peroxide, ascorbic acid, uric acid, acetaminophen, and cysteine were compared. P*m*PD films usually showed good anti-interference ability to the interferences examined. Literature reports suggested that the performance of a glucose biosensor with

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electropolymerized coating varied greatly with fabricating conditions, including monomer structure, supporting electrolyte, pH, electropolymerization methods, glucose oxidase concentration, etc. [17–26] It has been reported that the interference blocking abilities and thus the permselectivities of PPD polymers were concentration dependent [25].

This paper focuses on the preparation and characterization of glucose enzyme electrodes on platinized glassy carbon electrode with electrochemically synthesized polyphenylenediamine coatings. Platinum deposits offer lower over-potential for hydrogen peroxide oxidation at enzyme electrodes [19, 27, 28], resulting in great enhancement in the sensitivity. Effects of the Pt deposition charge, polymerization potential, polymerization charge, monomer concentration, and GOx concentration on the performance of the enzyme electrode to glucose were investigated. The performance of the constructed glucose biosensors with three different polyphenylenediamine films, namely poly(*o*-phenylenediamine) (P*o*PD), poly(*m*-phenylenediamine) (P*m*PD), and poly(*p*-phenylenediamine) (P*p*PD), obtained by various experimental conditions were compared.

2 Experimental

2.1 Chemicals and apparatus

Glucose oxidase (GOx, Type VII from *Aspergillus niger*) and L-dopamine were purchased from Sigma (St. Louis, MO, USA). Hydrogen peroxide (30–32 wt%), β-D-glucose, 1,2-phenylenediamine (*o*PD), 1,3-phenylenediamine (*m*PD), 1,4-phenylenediamine (*p*PD), L-ascorbic acid (AA), and potassium hexachloroplatinate(IV) were obtained from Aldrich (Milwaukee, WI, USA). The phenylenediamine monomers, namely *o*PD, *m*PD, and *p*PD, were recrystallized twice from water before use. All other chemicals were of analytical reagent.

Glucose stock solution was allowed to mutarotate for at least 24 h before use. A 0.1 M phosphate buffer solution (pH 7.0) served as supporting electrolyte for both the electropolymerization and amperometric determination. All solutions used were prepared with doubly distilled water.

All electrochemical experiments, including electropolymerization and amperometric measurements, were carried out by a BAS-100BW electrochemical analyzer (Bioanalytical Systems, Inc., West Lafayette, IN, USA) using a conventional three-electrode system. Glassy carbon working electrodes of 3 mm in diameter were purchased from BAS. A platinum wire electrode was used as auxiliary electrode. All potentials were quoted versus the Ag|AgCl reference electrode.

2.2 Electrodeposition of platinum black

The electrochemical measurement system was similar to that described previously [29]. The glassy carbon working electrode was firstly cleaned by hand polish progressively with wet alpha alumina powder (Buehler, Lake Bluff, IL, USA). Then, the electrode was rinsed with doubly distilled water and sonicated in water for 5 min, followed by further rinsing. After that, the electrode was subject to voltammetric sweeping in 0.5 M H_2SO_4 in the range of −0.20 to +1.20 V at 50 mV s^{-1} until stable background curves were obtained. Platinum deposition on the glassy carbon electrode was carried out using potentiostatic technique in 0.1 M HCl containing 2.0 mM K_2PtCl_6. A constant potential of −0.25 V was applied to the three-electrode system for 20 min. The average charge for platinum deposition ranged from 9 to 11 mC, corresponding to about 70 μg cm^{-2} platinum deposited on the surface of electrode.

2.3 Electropolymerization of phenylenediamines

Electropolymerization of phenylenediamine was carried out by cyclic voltammetric technique. The potential ranges for polymerization of *o*PD, *m*PD, and *p*PD were −0.20 to +0.75 V, −0.20 to +0.95 V, and −0.20 to +0.65 V, respectively. The scan rate employed was 20 mV s^{-1}. Glucose enzyme electrodes were prepared by electrochemical polymerization of the phenylenediamine monomer in the presence of GOx at a concentration of 2 g L^{-1} (400 enzyme units per millilitre or 4.0×10^5 units L^{-1}). The freshly prepared enzyme electrode was rinsed carefully with phosphate buffer to remove the loosely bound GOx molecules and oligomer residues from the surface of electrode. The electrode was stored in 0.1 M phosphate buffer solution (pH 7.0) under 4 °C before use.

2.4 Amperometric measurements

The steady-state amperometric response to glucose was measured by voltammetric technique at constant potential. The newly prepared enzyme electrode was dipped into the phosphate buffer solution with gentle stirring at 300 rpm, and a constant potential of +0.65 V was applied for about 5–10 min to allow the background current to decay to a constant level.

The amperometric measurement was performed at room temperature with gentle stirring. All solutions used in the amperometric studies were aerated by bubbling air for 15 min prior use. Amperometric response of the enzyme electrode to glucose injection was measured at a constant potential of +0.65 V. When aliquots of glucose standard

solution were added to the buffer, the response current due to hydrogen peroxide formed by enzyme catalytic oxidation of glucose was recorded.

3 Results and discussion

3.1 Electrochemical deposition of platinum

The construction of biosensors utilizing platinized carbon electrodes have been reported in the literature [19, 27, 28]. The glucose biosensors prepared in this work were based on the hydrogen peroxide detection mode. The H_2O_2 content produced by the enzymatic reaction was electro-oxidized at the surface of platinum black, and then the output current was recorded. The deposited platinum layer played an important role to the performance of the enzyme electrode. The effects of the amount of Pt deposition on the electrode response were examined. When the deposition charge reached the range of 9–11 mC, corresponding to 5–6 μg of platinum deposits on the surface of glassy carbon electrode, the enzyme electrodes gave the best sensitivity. The aggregates of the electrodeposited platinum were uniform and roughly spherical, according to the SEM study reported by others [19]. When the platinum was of smaller quantity, the surface of glassy carbon was not completely covered by Pt particles, resulting in low response current. When sufficient amount of Pt particles was deposited to cover the whole electrode surface, a three-dimensional structure of Pt black layer was obtained. The 3-D structured layer possessed larger surface area that offered more active sites for enzyme immobilization and electrochemical oxidation of H_2O_2 [19].

3.2 Electropolymerization of phenylenediamines

Cyclic voltammetric technique is useful for the mechanistic investigation of electrochemical reactions. Our previous report [16] indicated that PPD films prepared by cyclic voltammetry usually offered comparable or better H_2O_2 permeability and permselectivities for H_2O_2 over ascorbic acid and uric acid. Figure 1a shows the cyclic voltammograms of 5 mM *m*PD at the platinized glassy carbon electrode in phosphate buffer. An anodic shoulder wave with a broad wave at more positive potentials was observed at around +0.53 V in the first scan cycle. Oxidation of *m*PD at platinized glassy carbon was irreversible. The peak current decreased on continuous cycling, indicating that a compact and insulating polyphenylenediamine (PPD) film was formed which blocked further access of the monomer to the electrode surface. Figure 1b shows the cyclic voltammograms of *m*PD in the presence of glucose oxidase.

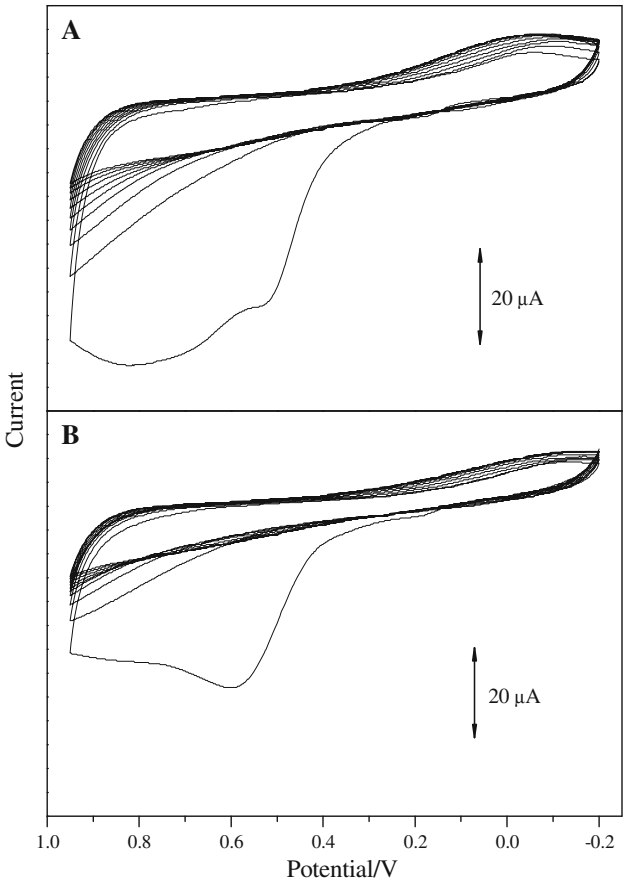

Fig. 1 Cyclic voltammograms for the electropolymerization of *m*-phenylenediamine at GC/Pt electrode. **a** 5 mM *m*PD; and **b** 5 mM *m*PD + 2 g L^{-1} GOx. Supporting electrolyte: 0.1 M phosphate buffer (pH 7.0); scan rate: 20 mV s^{-1}

No significant difference was observed in the voltammetric responses except that the broad anodic wave at more positive potentials gave a lower current.

Voltammetric responses of the other two phenylenediamine monomers were also examined. The oxidation of the three PD isomers at platinized glassy carbon was irreversible. According to the first cycle of voltammetric scan, the oxidation potential for *o*PD, *m*PD, and *p*PD were +0.33, +0.53, and +0.24 V, respectively. The order of the oxidation was the same as that for palladium electrode described previously [16]. The peak current decreased continuously, indicating that a compact and insulating PPD film was formed which blocked further access of the monomer to the electrode surface. There was no significant change in the voltammetric response when GOx was added to the PD solution, indicating that the enzyme did not have significant effects on the electropolymerization reaction. However, the current usually decayed a little bit slower when GOx was present, especially for P*o*PD and P*p*PD, indicating a slower formation rate of the insulating film.

3.3 Preparation of enzyme electrodes

3.3.1 Effects of potential range for electropolymerization

The optimum potential range for the electropolymerization of phenylenediamines by cyclic voltammetric technique was evaluated. The glucose biosensors were prepared with a monomer concentration of 20 mM and 2 g L^{-1} glucose oxidase. The response current was measured at a glucose concentration of 5.0 mM in phosphate buffer with a constant applied potential of +0.65 V. Figure 2 shows the electrode response (sensitivity) for each glucose biosensor as a function of the upper-limit potential. For the P*o*PD films, when the voltammetric scan was performed between −0.20 V and +0.75 V, the resulting enzyme electrode gave the best sensitivity to glucose. The response current decreased nearly to zero when the upper-limit potential was larger than +0.85 V. For P*p*PD, the response current decreased with increasing upper-limit potential. On the other hand, a monomer concentration of 5 mM was employed for *m*PD because of the lower solubility. The response for the P*m*PD enzyme electrode increased when higher upper-limit potential was used for electropolymerization. This might be due to the fact that a more positive oxidation potential was required for the oxidation of *m*PD. For P*o*PD and P*p*PD, the higher overpotential might cause the over-oxidation or destruction of PPD film [16, 30] that yielded low sensitivity to the analyte. The order of oxidation potential of the three PDs were reported as *m*PD > *o*PD > *p*PD, consistent with the previous investigation [16]. The electropolymerization of the three isomers of phenylenediamine were initiated by the formation of free radicals produced during the anodic scan [15, 31]. The higher the potential employed, the faster the radicals were produced. Thus the upper-limit of applied potential for cyclic electropolymerization was an important parameter for the biosensor construction and should be carefully selected. Experimental results indicated that the optimum potential scan ranges for electropolymerization were as follows: *o*PD, −0.20 to +0.75 V; *m*PD, −0.20 to +0.95 V; *p*PD, −0.20 to +0.65 V.

3.3.2 Effects of monomer concentration

The monomer concentration employed for the polymerization process played a very important role in improving the sensor performance. A wide range of monomer concentrations (from 5 to 200 mM) was employed for electropolymerization in this study. Figure 3 shows the effects of the monomer concentration employed for electropolymerization on the glucose response of the GC/Pt/PPD-GOx electrodes. Experimental results indicated that great improvement in the sensitivity of enzyme electrode was obtained with increasing monomer concentration for *p*PD, but less change was observed for *o*PD. The amperometric response of the GC/Pt/P*p*PD-GOx electrode prepared with 20 mM monomer showed a wide linear range up to 4 mM for glucose determination. At a *p*PD concentration of 200 mM, the electrode response (sensitivity) was 16 times larger than that obtained at a monomer level of 10 mM. A maximum amperometric response current of 17.8 μA was resulted for the GC/Pt/P*p*PD-GOx electrode at a glucose

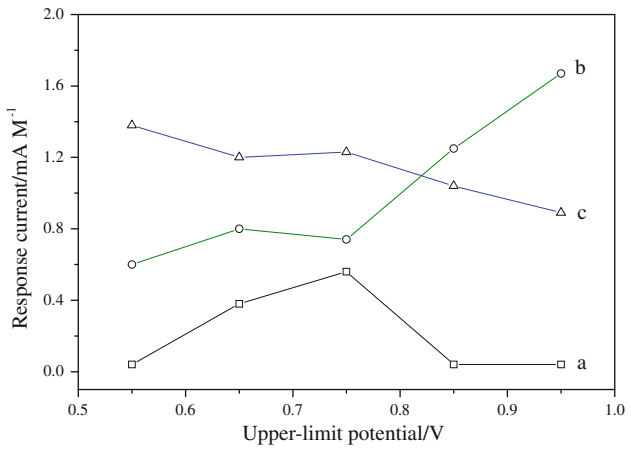

Fig. 2 Effects of the upper-limit potential for cyclic voltammetric polymerization on the response of GC/Pt/PPD-GOx electrodes to glucose. (*a*) P*o*PD 20 mM *o*PD + 2 g L^{-1} GOx; (*b*) P*m*PD: 5 mM *m*PD + 2 g L^{-1}; (*c*) P*p*PD: 20 mM *p*PD + 2 g L^{-1} GOx. Low-limit potential: −0.20 V; supporting electrolyte: 0.1 M phosphate buffer (pH 7.0); scan rate: 20 mV s^{-1}. Glucose detection potential: +0.65 V; stirring rate: 300 rpm; glucose concentration: 5.0 mM

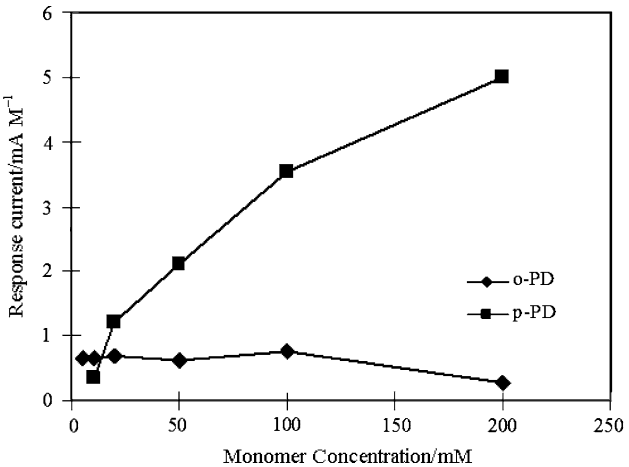

Fig. 3 Effects of monomer concentration on the amperometric response of the GC/Pt/PPD-GOx electrodes to glucose. (*a*) P*o*PD: *o*PD + 2 g L^{-1} GOx, −0.20 to +0.75 V; (*b*) P*m*PD: *m*PD + 2 g L^{-1}, −0.20 to +0.95 V; (*c*) P*p*PD: *p*PD + 2 g L^{-1} GOx, −0.20 to +0.65 V. Conditions for glucose determination were the same as Fig. 2

concentration of 3.5 mM. The effects of *m*PD content on the sensor performance were not explored further due to its poor solubility in phosphate buffer.

3.3.3 *Effects of polymerization charge*

One of the advantages of using electropolymerized films for enzyme immobilization is that the total amount of polymer can be controlled by adjusting the charge passing through, thus the amount of enzyme molecules immobilized could be controlled. Thicker films usually can hold more enzyme molecules but are more resistant to the diffusion of glucose and H_2O_2 within the film, thus lower sensitivity and slow response might be resulted. Figure 4 shows the effect of electropolymerization charge on the performance of glucose biosensors. Polymerization charges were controlled by the number of sweeping cycles. It was assumed that the polymer thickness was proportional to the total charge. However, the polymerization charge might not have direct relationship with the amount of enzyme immobilized because some of the oligomers were soluble and diffused to the bulk solution during the electropolymerization process. It showed that different polymers had different optimum polymerization charge. For the GC/Pt/P*o*PD-GOx electrode, the current response increased with the polymerization charge and reached a maximum at 12 mC. The response current decreased at higher polymerization charge. For P*m*PD films, the film formation was self-terminated after a charge of about 1.5 mC had passed, and the resulting enzyme electrode offered acceptable sensitivity. The enzyme electrode with P*p*PD coating gave maximum current response for polymerization charge from 6 to 17 mC.

3.3.4 *Effects of GOx concentration*

As reported previously [32], glucose oxidase molecules were embedded into the polymer films in the form of counter ions. The enzyme molecules, negatively-charged in pH 7.0 phosphate buffer solution [33], were incorporated via electrostatic interaction with the cationic radicals. On the other hand, the concentration of enzyme affected the biosensor response. GOx concentrations from 0.5 to 3 g L^{-1} (1.0–6.0 $\times$ 10^5 units L^{-1}) were commonly used for the preparation of glucose biosensors [17, 21, 23, 32]. The biosensor response to glucose as a function of enzyme concentration in the electropolymerization bath is shown in Fig. 5. For *o*PD and *p*PD, the electrode response increased with increasing GOx concentration and then reached constant values at 1.0 g L^{-1} (2.0×10^5 units L^{-1}) and 0.5 g L^{-1} (1.0×10^5 units L^{-1}) for *o*PD and *p*PD, respectively. It seemed that a GOx concentration of 4.0×10^5 units L^{-1} was sufficient to obtain a sensitive enzyme electrode. The GC/Pt/P*o*PD-GOx and GC/Pt/P*p*PD-GOx electrodes could accept a higher enzyme loading. On the other hand, the response of the GC/Pt/P*m*PD-GOx electrode increased with increasing GOx content continuously. A higher GOx concentration was beneficial for glucose determination.

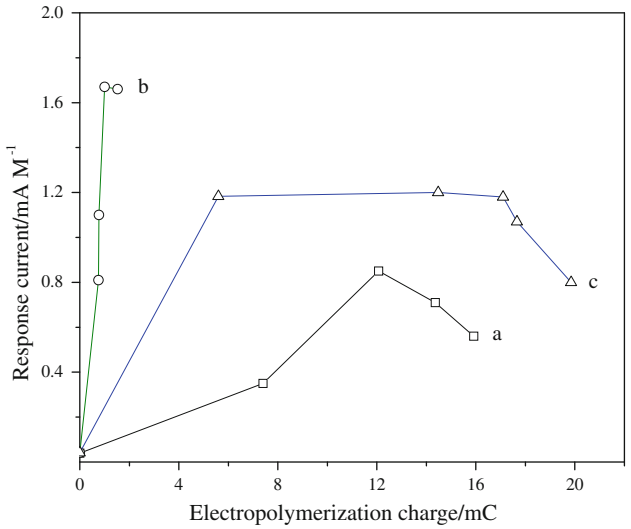

Fig. 4 Effects of polymerization charge on the response of the GC/Pt/PPD-GOx electrodes to glucose. (*a*) P*o*PD: 20 mM *o*PD + 2 g L^{-1} GOx, −0.20 to +0.75 V; (*b*) P*m*PD: 5 mM *m*PD + 2 g L^{-1}, −0.20 to +0.95 V; (*c*) P*p*PD: 20 mM *p*PD + 2 g L^{-1} GOx, −0.20 to +0.65 V. Conditions for glucose determination were the same as Fig. 2

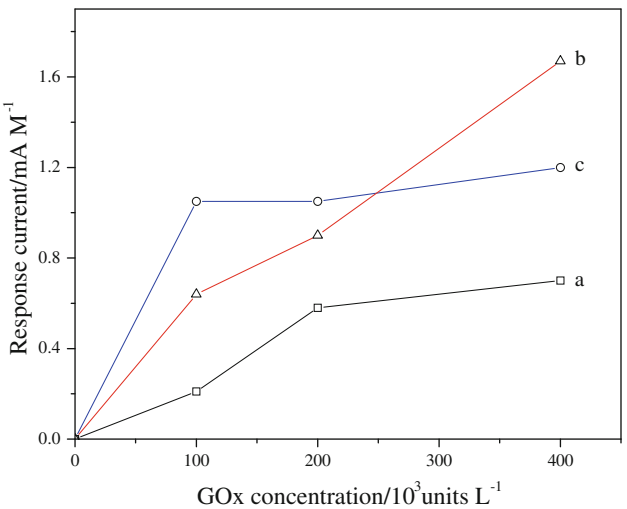

Fig. 5 Effects of enzyme concentration on the electrode response of the GC/Pt/PPD-GOx biosensors to glucose. (*a*) P*o*PD: 20 mM *o*PD + GOx, −0.20 to +0.75 V; (*b*) P*m*PD: 5 mM *m*PD + GOx, −0.20 to +0.95 V; (*c*) P*p*PD: 20 mM *p*PD + GOx, −0.20 to +0.65 V. Conditions for glucose determination were the same as Fig. 2

3.4 Glucose determination

Glucose was determined at the enzyme electrodes using amperometric method. An appropriate volume of glucose stock solution was injected into the stirring buffer and then the response current was recorded under a constant applied potential of +0.65 V. The short response time of less than 3 s was considered satisfactory.

Figure 6 shows the amperometric response of the GC/Pt/P*m*PD/GOx electrode as a function of glucose concentration. The enzyme electrode was prepared by cyclic voltammetric technique in a 0.1 M phosphate buffer solution containing 5 mM *m*PD and 2 g L^{-1} GOx. The linearity of the electrode response extended to 5 mM of glucose. The slope of the linear region can be considered as the biosensor sensitivity. For the GC/Pt/P*m*PD/GOx electrode, the detection sensitivity to glucose is 1.96 mA M^{-1}. Similarly, amperometric responses of the GC/Pt/P*o*PD-GOx and GC/Pt/P*p*PD-GOx electrodes were also examined. The response characteristics for the three enzyme electrodes employed for glucose determination are summarized in Table 1. The linear range for glucose determination was about 5 mM with a detection sensitivity of 0.99 mA M^{-1} at the GC/Pt/P*o*PD-GOx electrode. For the GC/Pt/P*p*PD-GOx electrode, the linear range extended to 10 mM of glucose with a detection sensitivity of 0.83 mA M^{-1}. The highest sensitivity was observed for GC/Pt/P*m*PD-GOx electrode, which is about two-fold larger than those for the other two types of PPD electrodes. All three types of PPD biosensors showed much better sensitivity over bare Pt electrode with a sensitivity of about 0.065 mA M^{-1} at +0.65 V vs. SCE [34]. The response characteristics for the three enzyme electrodes employed for glucose determination are summarized in Table 1. At higher glucose concentration, the response current deviated from the linearity and followed the Michaelis–Menten kinetics.

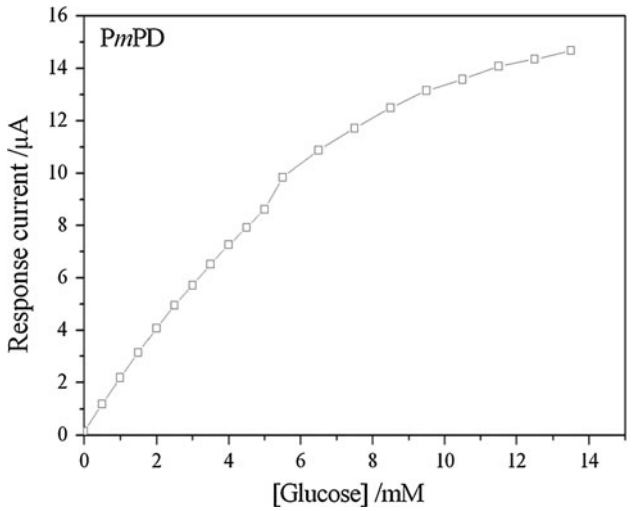

Fig. 6 Electrode response of the GC/Pt/P*m*PD-GOx electrode under optimum conditions. Conditions for preparation: 5 mM *m*PD + 2 g L^{-1} GOx, −0.20 to +0.75 V, Q = 1.0 mC. Conditions for glucose determination were the same as Fig. 2

3.5 Interference

For a non-conducting polymer film based enzyme electrode, one of the functions of the polymer is to expel interfering species such as ascorbic acid. In this work, the responses to hydrogen peroxide, ascorbic acid (AA), and L-dopamine (DA) at various electrodes were compared in order to evaluate the anti-interference performance of the PPD-based enzyme electrodes. Voltammetric responses to hydrogen peroxide (0.2 mM), ascorbic acid (0.1 mM), and L-dopamine (0.1 mM) at various electrodes in 0.1 M phosphate buffer were examined. Experimental results are plotted in Fig. 7. The working electrodes included bare GC/Pt electrode, PPD film covered GC/Pt electrodes (GC/Pt/PPD), and enzyme immobilized GC/Pt/PPD electrodes (GC/Pt/PPD-GOx). The response to hydrogen peroxide decreased slightly when the electrode surface was covered by PPD film or PPD-GOx film, indicating that the PPD film was very permeable to small H_2O_2 molecules. Generally, the permeability to H_2O_2 was of similar level at different GC/Pt/PPD and GC/Pt/PPD-GOx electrodes. The response current for ascorbic acid at PPD-covered electrodes was only 2–3% of the response current at bare electrode. It indicated that all three types of PPD films showed similar anti-interference ability to ascorbic acid. While for L-dopamine, the response current decreased by more than 98% in the presence of PPD coatings. The PPD films showed excellent anti-interference ability to ascorbic acid and L-dopamine. The permeability and permselectivity of different polyphenylenediamine films for hydrogen peroxide, ascorbic acid, uric acid, acetaminophen, and cysteine have been reported [16]. P*m*PD films showed good permselectivity for hydrogen peroxide in the presence of

Table 1 Response characteristics for polyphenylenediamine-based enzyme electrodes employed for glucose determination

	GC/Pt/P*o*PD-GOx	GC/Pt/P*m*PD-GOx	GC/Pt/P*p*PD-GOx
Sensitivity (mA M^{-1})	0.99	1.96	0.83
Linear range (mM)	0–5	0–5	0–10
Detection limit (μM)	0.1	0.1	0.1

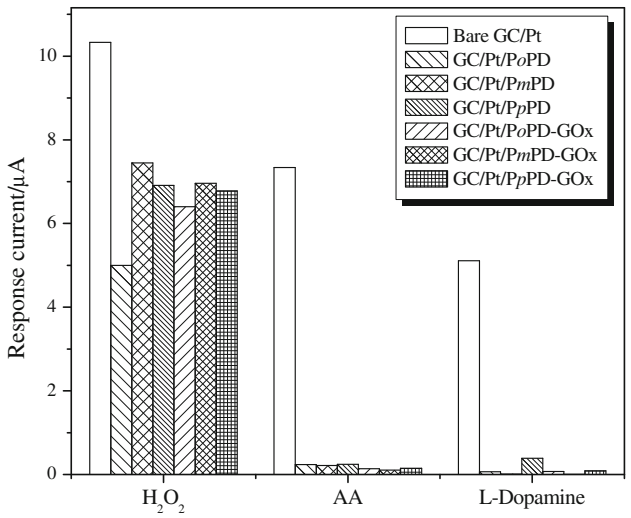

Fig. 7 Response to hydrogen peroxide (0.2 mM), ascorbic acid (0.1 mM), and L-dopamine (0.1 mM) at various electrodes in 0.1 M phosphate buffer (pH 7.0). Detection potential: +0.65 V, stirring rate: 300 rpm. GC/Pt/P*o*PD-GOx and GC/Pt/P*o*PD: 20 mM *o*PD, −0.20 to +0.75 V, 6 cycles; GC/Pt/P*m*PD-GOx and GC/Pt/P*m*PD: 5 mM *m*PD, −0.20 to +0.95 V, 10 cycles; GC/Pt/P*p*PD-GOx and GC/Pt/P*p*PD: 20 mM *p*PD, −0.20 to +0.65 V, 6 cycles. GOx concentration = 2 g L^{-1} when employed

ascorbic acid, uric acid, and acetaminophen. The permeability and permselectivity of the polymer films are important factors governing the electrode performance of glucose biosensors with polymer coatings. The permeability and permselectivity of the polyphenylenediamine films have been examined at different concentrations of hydrogen peroxide and interferences [21–25]. It has been reported that the permselectivities of PPD polymers were concentration dependent [25].

4 Conclusions

Glucose biosensors based on three different types of poly(phenylenediamine) films, obtained from electropolymerization of the *ortho*-, *meta*- and *para*-phenylenediamine monomers on Pt black modified glassy carbon electrodes, were constructed and characterized. The PPD films showed good anti-interference ability to ascorbic acid and L-dopamine. When compared with enzyme electrodes prepared on Pt disks, good response sensitivity to glucose was obtained for all three types of PPD-based glucose biosensors constructed, probably due to the large surface area of the platinum black layer. The presence of glucose oxidase gave little effect to PPD film formation during the voltammetric cycling, but caused a slight decrease in the rate of film formation. Rapid response of less than 3 s could be achieved, probably due to the presence of thin polymer film. P*o*PD and P*p*PD films offered similar performance in terms of sensitivity, permeability, and anti-interference ability. On the other hand, the enzyme electrode utilizing P*m*PD film showed higher sensitivity to glucose and lower permeability to the interfering species. The metal deposition and thin film of PPD are well-suited for enzyme electrode construction.

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