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A novel glucose biosensor based on the immobilization of glucose oxidase onto gold nanoparticles-modified Pb nanowires

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ABSTRACT

A novel glucose biosensor was developed, based on the immobilization of glucose oxidase (GOD) with cross-linking in the matrix of bovine serum albumin (BSA) on a Pt electrode, which was modified with gold nanoparticles decorated Pb nanowires (GNPs-Pb NWs). Pb nanowires (Pb NWs) were synthesized by an L-cysteine-assisted self-assembly route, and then gold nanoparticles (GNPs) were attached onto the nanowire surface through –SH–Au specific interaction. The morphological characterization of GNPs-Pb NWs was examined by transmission electron microscopy (TEM). Cyclic voltammetry and chronoamperometry were used to study and to optimize the electrochemical performance of the resulting biosensor. The synergistic effect of Pb NWs and GNPs made the biosensor exhibit excellent electrocatalytic activity and good response performance to glucose. The effects of pH and applied potential on the amperometric response of the biosensor have been systemically studied. In pH 7.0, the biosensor showed the sensitivity of 135.5 $\mu A\,mM^{-1}\,cm^{-2}$, the detection limit of 2 μM (S/N = 3), and the response time <5 s with a linear range of 5–2200 μM. Furthermore, the biosensor exhibits good reproducibility, long-term stability and relative good anti-interference.

1. Introduction

In recent years, there is still a great demand for the development of glucose biosensor because determination of glucose concentration is very important in clinical applications (Mizutani and Yabuki, 1997; Wang, 1999; Yoshimura and Hozumi, 1996). Considerable attention has been devoted to immobilization of glucose oxidase on electrode surface, which is one of the main factors that affect the performance of a biosensor (Zhang et al., 2005). An interesting question is how to improve the performances of enzyme-based glucose biosensor with novel immobilizing materials.

Among various immobilizing materials, nanostructured materials have received increasing interest due to their novel optical, electrical, catalytic, magnetic properties, excellent biocompatibility, strong adsorption ability and potential applications in nanoelectronic devices, nanosensors, and catalysts (Choi et al., 2008; Huang et al., 2003; Shi et al., 2008; Zhang and Manohar, 2005; Zhuang et al., 2008). Noble metal nanoparticles have been extensively utilized in the past several years, owing to their extraordinary catalytic activities for both oxidation and reduction reactions. Among them, gold nanoparticles (GNPs) were one of the mostly used for immobilization of enzymes for the construction of biosensors due to their unique properties such as good conductivity, useful electrocatalytic ability and biocompatibility (Agui et al., 2006; Crespilho et al., 2006; Li and Li, 2003; Liu et al., 2006, 2005; Xiao et al., 2003; Zhou et al., 2006). GNPs can act as tiny conduction centers and can facilitate the transfer of electrons. Furthermore, it has been reported that enzymes maintained their enzymatic and electrochemical activity when immobilized on GNPs (Zhou et al., 2006). In comparison with spherical nanoparticles, one-dimensional (1-D) nanomaterials, especially nanowires, possess a number of unique physical and electronic properties that endow them with new and important activities. The excellent properties of nanowires are due to several beneficial features arising from their shape anisotropy on the electrochemical reaction at electrodes (Choi et al., 2008; Qu et al., 2007): (i) facile pathways for the electron transfer by reducing the number of interfaces between the nanoparticle catalysts and (ii) effective surface exposure to work as active catalytic sites in the electrode–electrolyte interface. It has been reported that enzymes can be adsorbed onto these nanostructures, because these materials provide large surface area for enzyme loading and friendly microenvironment to stabilize the immobilized enzymes (Birenhaum et al., 2003; Wang et al., 2005). Recent results suggest the possibility of incorporating large numbers of nanowires into large-scale arrays and complex hierarchical structures for high-density biosensors, electronics, and optoelectronics (Charles and Zhong, 2007). Biosen-

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sors based on nanowires showed improved signal-to-noise ratios, high faradaic current density, fast electron-transfer rate, enhanced sensitivities, better detection limit (Menon and Martin, 1995; Yang et al., 2006).

Recently, increasing research interest in biosensor filed has been focused on composite materials based on 1-D materials and noble metal nanoparticles with a synergistic effect (Zhang and Gorski, 2005). Materials for such purposes include carbon nanotubes, carbon nanofibers, redox mediators and metal nanoparticles. For example, coupling carbon nanofibers with palladium nanoparticles resulted in a remarkable improvement of the electroactivity of the composite materials towards reduction of H_2O_2 and oxidation of β-nicotinamide adenine dinucleotide in reduced form (NADH) (Huang et al., 2008). Zou et al. (2008) reported a glucose biosensor based on electrodeposition of platinum nanoparticles onto multi-walled carbon nanotubes. Wu et al. (2007) constructed a glucose biosensor based on multi-walled carbon nanotubes and GNPs by layer-by-layer self-assembly technique.

In this paper, taking advantage of the nanowires and GNPs, a novel nanomaterial was designed for glucose biosensor construction. The GNPs-Pb NWs nanocomposite was prepared in a simple and effective way. Pb NWs can be fabricated by an L-cysteine-assisted self-assembly route with average diameter of 60–80 nm, the method was selected because –SH group can be introduced in the nanowire during the self-assembling procedure. With the aid of –SH, GNPs can be easily adsorbed onto the Pb NWs, the obtained GNPs-Pb NWs material shows new capabilities for electrochemical biosensors because of the synergistic effect of GNPs and Pb NWs. The immobilization of glucose oxidase on Pt electrode was carried out by covalent attachment with glutaraldehyde and bovine serum albumin (BSA). The electrochemical performances of the modified electrode were investigated by cyclic voltammetry and chronoamperometry. The effects of pH value and applied potential on the biosensor behavior were also evaluated. The biosensor exhibited excellent performances, such as relative high sensitivity, low detection limit, short response time, and good storage stability.

2. Experimental

2.1. Reagents

Glucose oxidase from *Aspergillus niger* (GOD, EC 1.1.3.4, p*I* 4.2, 235 Units mg^{-1} protein), gold nanoparticles (GNps, mean particle size 5 nm) and bovine serum albumin were purchased from Sigma Co. L-cysteine and ascorbic acid were purchased from Fluka Co., acetaminophen purchased from Shanghai Chemical Reagents Co. (Shanghai, China) were of HPLC grade. $Pb(NO_3)_2$, ethanolamine and glucose was obtained from Tianjin damao Chemical Reagent Co. (China). Aluminum oxide nanopowder was purchased from Aldrich Co. All other reagents were of analytical grade and used without further purification. 3 mg mL^{-1} of GOD and 10 mg mL^{-1} BSA were prepared in 0.1 M phosphate buffer solution (PBS, pH 7.0). All aqueous solutions were prepared with doubly distilled water. All experiments were performed at room temperature, approximately 25 °C.

2.2. Preparation of gold nanoparticles modified Pb nanowires (GNPs-Pb NWs)

Pb NWs were prepared using the previous reported method, in a typical synthetic procedure, a source solution was prepared by dissolving $Pb(NO_3)_2$ (0.033 g) and L-cysteine (0.012 g) in doubly distilled water (30 mL) under magnetic stirring at room temperature. The reaction started when ethanolamine (0.2 mL) was quickly injected into the source solution. A white product formed immediately, and the solution was stirred for 20 min at room temperature. The product was separated by centrifugation and washed three times with doubly distilled water and absolute ethanol. The nanowires were dispersed in doubly distilled water (30 mL), then 1 mL of the prepared nanowires were transferred into a centrifugal tube, 100 μL GNPs were added under stirring, the solution was stirred for another 2 h. The final product was centrifuged and washed with doubly distilled water for five times to dissociate the weak adsorption of GNPs.

2.3. Fabrication of modified electrodes

5 μL of GNPs-Pb NWs was dropped onto the Pt electrode surface, after drying GNPs-Pb NWs/Pt electrode was obtained. The GOD was immobilized on the modified Pt electrode by cross-linking the enzyme through glutaraldehyde with BSA. The glucose biosensor was constructed by mixing 125 μL GOD (3 mg mL^{-1}), 25 μL BSA (10 mg mL^{-1}), and 20 μL glutaraldehyde (2%) solution, and then 5 μL of the composite solution was dropped on the GNPs-Pb NWs/Pt electrode surface, denoted as GOD/BSA/GNPs-Pb NWs/Pt, the glucose biosensor was dried and stored at 4 °C in a refrigerator. In control experiment, glucose biosensors based on Pb NWs and GNPs were also prepared with the similar procedure, denoted as GOD/BSA/Pb NWs/Pt and GOD/BSA/GNPs/Pt.

2.4. Apparatus and measurements

Electrochemical measurements were performed on a Potentiostat–Galvanostat (EG&G PARC Model 283 with a software M270). All electrochemical experiments were carried out with a conventional three-electrode system with a working electrode, Pt wire (1 mm diameter) as a counter electrode and an Ag/AgCl (saturated with KCl) as a reference electrode. All electrochemical experiments were carried out in 30 mL 0.1 M PBS. Prior to each experiment, Pt electrodes (3 mm diameter) were polished with aluminum oxide nanopowder, and then washed ultrasonically in ethanol and doubly distilled water. Cyclic voltammetric (CV) measurements were performed in the presence of 20 mM $K_3[Fe(CN)_6]$ and 0.1 M KCl. In steady-state amperometric experiment, the potential was set at +600 mV under gently magnetic stirring. Before all chronoamperometric experiments, the potential of each electrode was held at +600 mV, allowing the background current to decay to a steady-state value.

Transmission electron microscopy (TEM) images were obtained by using Tecnai G2 F20 instrument (Philips Holland).

3. Results and discussion

3.1. Characterization of the modified Pt electrodes

CV of the ferricyanide system is a convenient and valuable tool to monitor the characteristics of the surface of modified electrode. The CVs of bare, Pb NWs, GNPs, and GNPs-Pb NWs modified Pt electrodes conducted in 20 mM $[Fe(CN)_6]^{3-}$ with 0.1 M KCl are shown in Fig. 1. At the bare Pt electrode, well-defined oxidation and reduction peaks of $[Fe(CN)_6]^{3-/4-}$ were observed at +290 mV and 174 mV (Fig. 1a). After the electrode was modified with Pb NWs, a little increase in peak current was observed (Fig. 1b). Pb NWs have a large surface area which can increase the active surface area of the modified electrode, but the "block effect" induced by nonconductive Pb NWs made the peak current only increase a little. At the same time, the peak-to-peak separation (ΔEp) was almost the same as that of bare Pt electrode (Fig. 1b), which indicates that nonconductive Pb NWs have little effect on promoting electron transfer. Fig. 2c illustrates the voltammetric effect of ferricyanide on the GNPs modified electrode. Because GNPs have a catalytically active

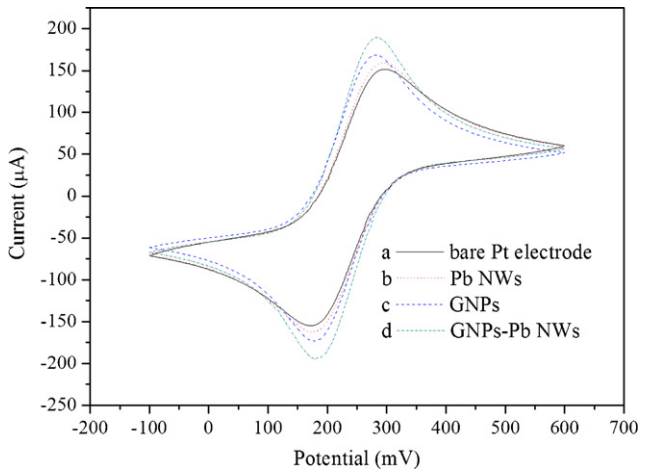

Fig. 1. Cyclic voltammograms of 20 mM $[Fe(CN)_6]^{3-}$ in aqueous 0.1 M KCl at (a) bare, (b) Pb NWs, (c) GNPs, and (d) GNPs-Pb NWs modified Pt electrodes at a scan rate of 50 mV s^{-1}.

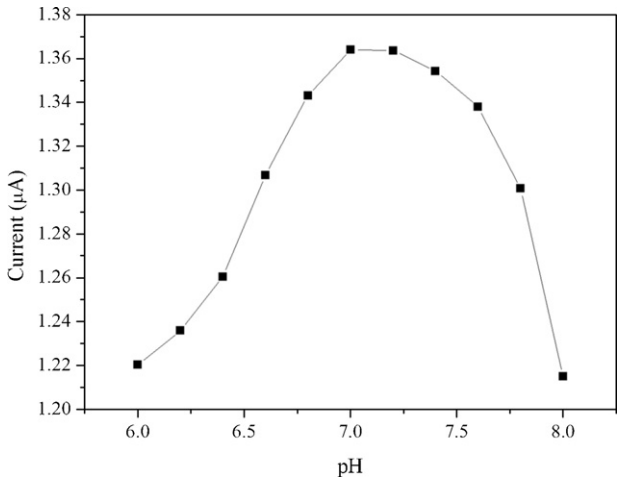

Fig. 3. Effect of pH value on the response current in 0.1 M PBS with 0.1 mM glucose at +600 mV *vs.* Ag/AgCl.

surface and excellent conductivity, the peak current increased and ΔEp decreased. For the GNPs-Pb NWs modified Pt electrode, the peak current increased more (Fig. 1d) compared with the Pb NWs and GNPs modified electrode, implying the synergistic action of the electrocatalytic activity of GNPs and Pb NWs. The ΔEp become smaller than that of Pb NWs modified and bare electrode, indicating the faster electron-transfer kinetics. The results shown that GNPs play a main role in promoting electron transfer, which can act as "electron antennae" to effectively promote electron transfer between $[Fe(CN)_6]^{3-/4-}$ and the electrode (Zhao et al., 2008).

In order to further confirm the adsorption of GNPs onto the surface of Pb NWs, which induces the synergistic effect, the transmission electron microscopy of GNPs, and GNPs-Pb NWs was performed. The results are shown in Fig. 2. It has been reported that the method used in this paper would result in Pb NWs with a chemical structure of $HSCH_2CH(NH_2)COO–Pb–OH$ (Tong et al., 2006). The presence of –SH provides active sites for the adsorption of GNPs, because GNPs can strongly bound to the functional groups, such as –CN, $–NH_2$, or –SH (Freeman et al., 1995; Grabar et al., 1995). Compared with the TEM image obtained for GNPs (Fig. 2a), the TEM image of GNPs-Pb NWs (Fig. 2b) clearly showed the presence of numerous GNPs, indicating GNPs can be easily adsorbed onto the Pb NWs to give a nanohybrid material.

3.2. CV characteristics of glucose biosensor

The CVs of GOD/BSA/GNPs-Pb NWs/Pt electrode measured in PBS (pH 7.0) at different scan rates were shown in Fig. S1. The peak currents were linearly progressing with the scan rates of less than 50 mV s^{-1} with correlation coefficient 0.9997 and 0.9999 (inset A in Fig. S1), indicating a surface-controlled electrode process. The result further confirmed that GOD has been immobilized on the electrode. When the scan rate was larger than 50 mV s^{-1}, the peak currents were proportional to the square root of the scan rate with correlation coefficient 0.9998 and 0.9916 (inset B in Fig. S1) suggesting a diffusion-controlled process. It is well known that hydrogen ion is involved in the electrode reaction of GOD. At higher scan rate, there was a hydrogen ion concentration gradient which made the electrode reaction was not a surface-controlled process. Ju et al. has also reached the same results in their research (Qin and Ju, 2003).

3.3. Effect of pH value and applied potential on the response current of the biosensor

The effect of pH value on the performance of the biosensor is very important, because the activity of the immobilized GOD is pH dependent. As shown in Fig. 3, the response current of the enzyme

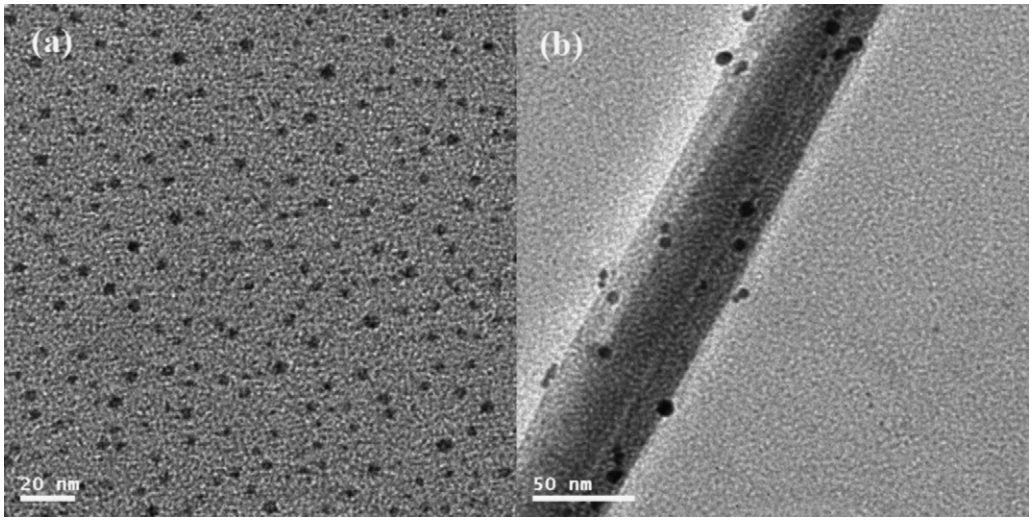

Fig. 2. TEM images of (a) GNPs, (b) GNPs-Pb NWs.

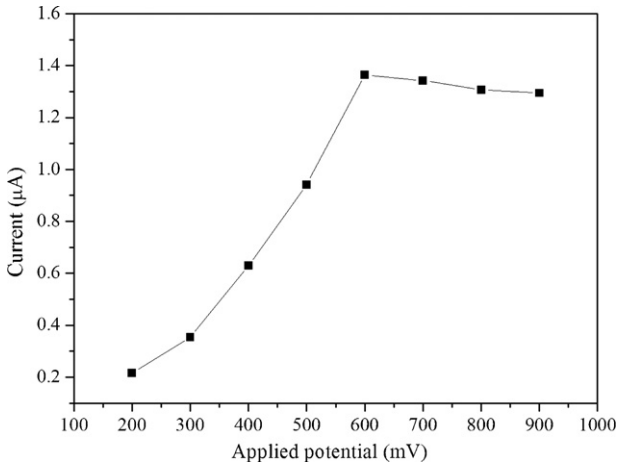

Fig. 4. Effect of applied potential on the response current in pH 7.0, 0.1 M PBS with 0.1 mM glucose.

electrode increased in the range of 6.0–7.0, and decreased at higher pH value. The current showed the maximum value at pH 7.0.

The influence of applied potential on the response of the biosensor was performed in pH 7.0, 0.1 M PBS with 0.1 mM glucose in the range of +200 mV to +900 mV. In Fig. 4, the response current increased rapidly with the increase of applied potential when the potential was lower than +600 mV, meaning that the current response is an electrochemical oxidation of H_2O_2 controlled process. When the potential was higher than +600 mV, a current plateau with small decrease appeared. The appearance of such a current plateau is attributed to the rate-limiting process of enzymatical kinetics. The similar results have been reported in pervious researches (Chu et al., 2007; Zou et al., 2008). In this work, the applied potential of +600 mV was chosen.

3.4. Chronoamperometric response

With the synergistic action of GNPs and Pb NWs, GNPs-Pb NWs modified electrode showed excellent electrocatalytic activity, larger active surface area and fast electron-transfer kinetics, which made it an ideal biosensing platform for the fabrication of glucose biosensor. The amperometric responses of GOD/BSA/Pb NWs/Pt, GOD/BSA/GNPs/Pt, and GOD/BSA/GNPs-Pb NWs/Pt electrodes at +600 mV were compared in Fig. 5. The current response of the GOD/BSA/GNPs-Pb NWs/Pt was much higher than that of GOD/BSA/Pb NWs/Pt and GOD/BSA/GNPs/Pt, the response was faster and the linear range is much wider too. It has been reported the increase the amount of enzyme loaded could improve the sensitivity and linear range (Yang et al., 2006). GNPs-Pb NWs could firmly immobilize more GOD in the sensitive films than that of Pb NWs and GNPs due to their large specific surface areas, and GNPs and BSA could also provide a biocompatible microenvironment to maintain the activity of the enzyme, which increased the sensitivity and expanded the upper detection limit. The larger surface area facilitated substrate–enzyme contact also contributed to the wider linear range. Because GNPs could provide conduction pathway between glucose and immobilized GOD which promote electron transfer due to their excellent conductivity, the response time decreased.

As for the GOD/BSA/GNPs-Pb NWs/Pt electrode, it exhibited a linear response to glucose in the range from 5 μM to 2200 μM with a correlation coefficient of 0.998. The dynamic curve showed a sensitivity of 135.5 $\mu A\,mM^{-1}\,cm^{-2}$ with a detection limit of 2 μM at the signal-to-noise ratio of 3. The sensitivity of the resulting biosensor is much higher than the previous reported 58.8 $\mu A\,mM^{-1}\,cm^{-2}$ (Zou et al., 2008), 30.64 $\mu A\,mM^{-1}\,cm^{-2}$ (Xu et al., 2007) and 29.9 $\mu A\,mM^{-1}\,cm^{-2}$ (Harpovic et al., 2004). In addition, the biosensor shows fast response achieving 95% of the steady-state current within 5 s.

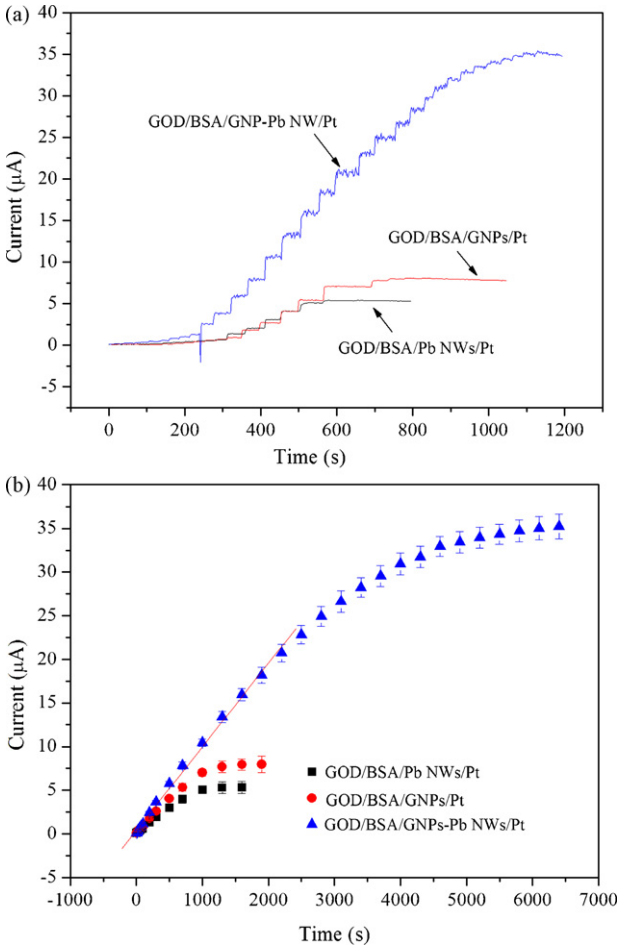

Fig. 5. (a) Amperometric responses of the enzyme electrodes upon successive addition of glucose in pH 7.0, 0.1 M PBS at +600 mV *vs.* Ag/AgCl. (b) Steady-state calibration curve of the enzyme electrodes in pH 7.0, 0.1 M PBS at +600 mV *vs.* Ag/AgCl. Error bars = ±standard deviation and $n = 5$.

When the glucose concentration is high, a plateau current was observed, showing the characteristics of the Michaelis–Menten kinetics. The apparent Michaelis–Menten constant (K_m^{app}) can be calculated from the Lineweaver–Burk equation:

$$\frac{1}{i_{ss}} = \left(\frac{K_m^{app}}{i_{max}}\right)\left(\frac{1}{C}\right) + \left(\frac{1}{i_{max}}\right)$$

where i_{ss} is the steady-state current after the addition of substrate, i_{max} is the maximum current measured under saturated substrate condition and C is the bulk concentration of the substrate. The K_m^{app}, which gives an indication of the enzyme substrate kinetics for the biosensor, was estimated based on the data obtained from the $1/i_{ss}$ *vs.* $1/C$ curve as shown in Fig. S2. The K_m^{app} in the present work was calculated to be 4.58 mM, which is much lower than the reported 14.4 mM (Zou et al., 2008) and 10.73 mM (Chu et al., 2007). This result reveals that the biosensor possesses higher enzymatic activity and the proposed immobilized GOD shows higher biological affinity to glucose.

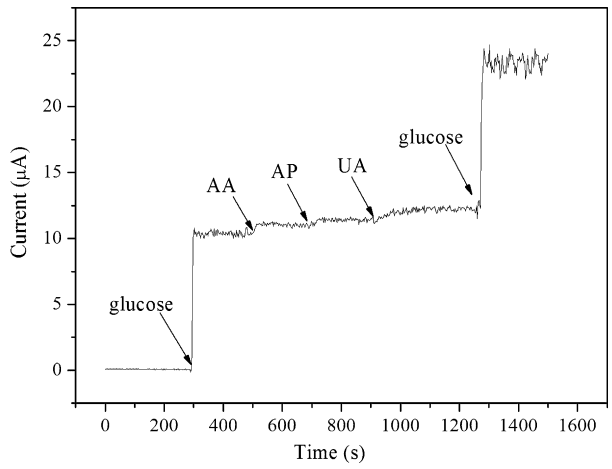

Fig. 6. Amperometric responses of the glucose biosensor upon subsequent additions of 1 mM glucose, 0.15 mM ascorbic acid (AA), 0.5 mM acetaminophen (AP), 0.15 mM uric acid (UA) and 1 mM glucose at +600 mV *vs.* Ag/AgCl, pH 7.0, 0.1 M PBS.

3.5. Selectivity reproducibility and stability of the enzyme electrode

The interferences from electroactive compounds commonly present in physiological samples of glucose such as ascorbic acid (AA), urea acid (UA) and acetaminophen (AP) used to cause problems in accurate determination of glucose. Because the level of endogenous AA, UA and AP is about 0.125 mM, 0.33 mM and 0.13 mM, respectively, the selectivity of the biosensor was examined in the presence of 0.15 mM AA, 0.5 mM UA and 0.15 mM AP. The effect was tested by adding these interferences to the glucose solution. The enzyme electrode was first kept in a stirred pH 7.0, 0.1 M PBS at +600 mV and a 1 mM glucose solution was added. Then, 0.15 mM AA, 0.5 mM UA and 0.15 mM AP were added sequentially, after that 1 mM glucose was added again, which were indicated by arrows in Fig. 6. The interference caused by the three interfering substances to 1 mM glucose was about 7.85%, 3.46% and 9.46%, respectively. Since the physiological normal level of glucose is 5.7, considering the linear range of the glucose biosensor, the real sample should be diluted and the interference caused by interfering species may be negligible, our biosensor presents an acceptable anti-interferent ability to be applied for analysis of glucose in blood.

The reproducibility was evaluated from the response to 0.1 mM glucose at five electrodes fabricated at the same condition. The results reveal that the biosensor has good reproducibility with a relative standard deviation (RSD) of 4.9%. The measurement stability of the biosensor was estimated in 0.1 mM glucose at +600 mV. The RSD is 4.2% indicating a good repeatability of the measurements. The long-term stability is an important parameter for evaluation of the performance of the biosensor, which was tested in 0.1 mM glucose solution intermittently, and the electrode was kept at 4 °C in 0.1 M PBS (pH 7.0) when not in use. The results showed in that the catalytic current response maintained more than 80.7% of its initial value after 70 days. Good reproducibility and long-term stability is attributed to the following aspects. The GNPs-Pb NWs and BSA provide a biocompatible microenvironment to maintain the activity of the enzyme, the construction process is mild, and no damage is inflicted on the enzyme molecules. On the other hand, the covalent interaction between BSA and GOD with glutaraldehyde is strong and little amount enzyme leaked out from the electrode surface.

4. Conclusion

In this work, we have demonstrated a promising glucose biosensor based on immobilizing glucose oxidase with GNPs decorated Pb NWs. The Pb NWs was synthesized by a self-assembly route aid with L-cysteine, GNPs were incorporated into the nanowire surface through –SH–Au bond. The result nanocomposite processes large active surface area, providing an excellent substrate for the immobilization of glucose oxidase. The synergistic action of GNPs and Pb NWs greatly increases the electrocatalytic activity. Under optimal conditions, the developed biosensor exhibits linear range from 5 μM to 2200 μM with a sensitivity as high as 135.5 $\mu A\,mM^{-1}\,cm^{-2}$. The enzyme electrode also displays fast response, good reproducibility, long-term stability and relative good selectivity. In summary, the novel GNPs-Pb NWs nanomaterials proposed in this study provide a very promising platform for designing biosensors with high sensitivity, low detection limit and good stability.

Acknowledgments

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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.2009.06.022.

References

Agui, L., Manso, J., Yanez-Sedeno, P., Pingarron, J.M., 2006. Sens. Actuators, B 113 (1), 272–280.
Birenhaum, N.S., Lai, B.T., Chen, C.S., Reich, D.H., Meyer, G.J., 2003. Langmuir 19 (23), 9580–9582.
Charles, M.L., Zhong, L.W., 2007. MRS Bull. 32 (2), 99–108.
Choi, S.M., Kim, J.H., Jung, J.Y., Yoon, E.Y., Kim, W.B., 2008. Electrochim. Acta 53, 5804–5811.
Chu, X., Duan, D.X., Shen, G.L., Yu, R.Q., 2007. Talanta 71 (5), 2040–2047.
Crespilho, F.N., Ghica, M.E., Florescu, M., Nart, F.C., Oliveira, O.N., Brett, C.M.A., 2006. Electrochem. Commun. 8 (10), 1665–1670.
Freeman, R.G., Grabar, K.C., Allison, K.J., Bright, R.M., Davis, J.A., Guthrie, A.P., Hommer, M.B., Jackson, M.A., Smith, P.C., Walter, D.G., Natan, M.J., 1995. Science 267 (5204), 1629–1632.
Grabar, K.C., Freeman, R.G., Hommer, M.B., Natan, M.J., 1995. Anal. Chem. 67, 735–743.
Harpovic, S., Liu, Y., Male, K.B., John, H., Luong, T., 2004. Anal. Chem. 76 (4), 1083–1088.
Huang, J.S., Wang, D.W., Hou, H.Q., You, T.Y., 2008. Adv. Funct. Mater. 18 (3), 441–448.
Huang, J.X., Virji, S., Weiller, B.H., Kaner, R.B., 2003. J. Am. Chem. Soc. 125 (2), 314.
Li, D., Li, J.H., 2003. Surf. Sci. 522 (1–3), 105–111.
Liu, Y.C., Yu, C.C., Yang, K.H., 2006. Electrochem. Commun. 8 (7), 1163–1167.
Liu, Z.M., Yang, Y., Wang, H., Liu, Y.L., Shen, G.L., Yu, R.Q., 2005. Sens. Actuators, B 106 (1), 394–400.
Menon, V.P., Martin, C.R., 1995. Anal. Chem. 67 (13), 1920–1928.
Mizutani, F., Yabuki, S., 1997. Biosens. Bioelectron. 12 (9–10), 1013–1020.
Qin, S., Ju, H.X., 2003. Analyst 128, 1420–1424.
Qu, F.L., Yang, M.H., Shen, G.L., Yu, R.Q., 2007. Biosens. Bioelectron. 22 (8), 1749–1755.
Shi, A.W., Qu, F.L., Yang, K.H., Shen, G.L., Yu, R.Q., 2008. Sens. Actuators, B 2 (129), 779–783.
Tong, H., Zhu, Y.J., Yang, L.X., Li, L., Zhang, L., 2006. Angew. Chem. Int. Ed. 45 (46), 7739–7742.
Wang, J., 1999. J. Pharm. Biomed. 19 (1–2), 47–53.
Wang, W.U., Chen, C., Lin, K.H., Fang, Y., Lieber, C.M., 2005. PNAS 102 (9), 3208–3212.
Wu, B.Y., Hou, S.H., Yin, F., Zhao, Z.X., Wang, Y.Y., Wang, X.S., Chen, Q., 2007. Biosens. Bioelectron. 22 (12), 2854–2860.
Xiao, Y., Patolsky, F., Katz, E., Hainfeld, J.F., Willner, I., 2003. Science 299 (5614), 1877–1881.
Xu, L.H., Zhu, Y.H., Tang, L.H., Yang, X.L., Li, C.H., 2007. Electroanalysis 19 (6), 717–722.
Yang, M.H., Qu, F.L., Lu, Y.S., He, Y., Shen, G.L., Yu, R.Q., 2006. Biomaterials 27 (35), 5944–5950.
Yoshimura, K., Hozumi, K., 1996. Microchem. J. 53 (4), 404–412.
Zhang, M., Gorski, W., 2005. J. Am. Chem. Soc. 127 (7), 2058–2059.
Zhang, S.X., Wang, N., Yu, H.J., Niu, Y.M., Sun, C.Q., 2005. Bioelectrochemistry 67 (1), 15–22.
Zhang, X.Y., Manohar, S.K., 2005. J. Am. Chem. Soc. 127 (41), 14156.
Zhao, W., Sun, S.X., Xu, J.J., Chen, H.Y., Cao, X.J., Guan, X.H., 2008. Anal. Chem. 80 (10), 3769–3776.
Zhou, N., Wang, J., Chen, T., Yu, Z.G., Li, G.X., 2006. Anal. Chem. 78 (14), 5227–5230.
Zhuang, Z.J., Su, X.D., Yuan, H.Y., Sun, Q., Xiao, D., Choi, M.M.F., 2008. Analyst 133 (1), 126–132.
Zou, Y.J., Xiang, C.L., Sun, L.X., Xu, F., 2008. Biosens. Bioelectron. 23 (7), 1010–1016.