Full Paper

Amperometric Glucose Biosensor Based on Platinum Nanoparticles Combined Aligned Carbon Nanotubes Electrode

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Abstract
A sensitive amperometric glucose biosensor based on platinum nanoparticles (PtNPs) combined aligned carbon nanotubes (ACNTs) electrode was investigated. PtNPs which can enhance the electrocatalytic activity of the electrode for electrooxidating hydrogen peroxide by enzymatic reaction were electrocrystallized on 4-aminobenzene monolayer-grafted ACNTs electrode by potential-step method. These PtNPs combined ACNTs' (PtNPs/ACNTs) surfaces were characterized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The highly dispersed PtNPs on ACNTs can be obtained. The enzyme electrode exhibits excellent response performance to glucose with linear range from $1 \times 10^{-5} - 7 \times 10^{-3}$ mol L^{-1} and fast response time within 5 s. Furthermore, this glucose biosensor also has good reproducibility. It is demonstrated that the PtNPs/ACNTs electrode with high electrocatalytic activity is a suitable basic electrode for preparing enzyme electrodes.

Keywords: Glucose, Biosensor, Aligned carbon nanotubes electrode, Pt nanoparticles, Electrocatalytic

1. Introduction

The area of amperometric glucose biosensor based on the use of glucose oxidase (GOD) has received great attention in the past few years [1–5]. The basis of the analyses is either by the amperometric detection of glucose with the GOD immobilized on the substrate, or by the oxidation of the side product hydrogen peroxide (H_2O_2) generated in the reaction. But for the active site of GOD being deeply embedded within a protective protein shell, the realizing of the direct electron transfer for glucose is extremely difficult. So the glucose biosensor based on the direct determination of H_2O_2, for selective, fast and sensitive glucose determination, without using membranes or redox mediator, has been proposed. Metal nanoparticles have been used to construct the interface for direct electron transfer between modified electrode and glucose solution and retaining their bioactivity at the same time. Much glucose biosensors that consisting of the metallic micro- or nanoparticles dispersed on electrode surface for catalyzing H_2O_2, such as gold [6], palladium [7], rhodium [8], ruthenium [9], copper [10], and platinum [11] have been put forward. Pt as a kind of noble metal has high electrocatalytic activity and there is extensive recognition and deeply research on it [12–16]. The reports have demonstrated that Pt nanoparticles can facilitate the electron transfer and increase the surface areas with enhanced mass transport characteristics [17–21]. Along with the development of the nanotechnology, many methods have been put forward on

glucose biosensor with Pt nanoparticles (PtNPs). Yang and coworkers reported PtNPs doped sol–gel/carbon nanotubes composite electrochemical biosensors for the detection of glucose [22]. Birkin et al. demonstrated that PtNPs could be used in combination with singlewall carbon nanotubes for constructing electrochemical sensors with remarkably improved sensitivity toward H_2O_2 [23]. Chu et al. reported a new amperometric glucose biosensor based on electrodepositing of platinum nanoparticles onto covalently immobilized carbon nanotube electrode [24]. These results show that remarkable electrocatalytic activity can be observed when PtNPs combined with the electrode.

Owing to their nanodimensions, rich electronic states, large surface area, high mechanical strength, and excellent chemical and thermal stability, carbon nanotubes (CNTs) have attracted a great deal of interests [25]. But there is much defects in curved randomly oriented CNTs [26, 27]. Studies of individual carbon nanotubes demonstrated that the structurally most perfect nanotubes have resistivities an order of magnitude lower than those found previously and that defects in the carbon nanotubes structure caused substantial increases in the resistivity [27–29]. So, the randomly carbon nanotubes often need assembly or integration. Aligned carbon nanotubes (ACNTs) is one kind of vertically aligned and mechanically isolated carbon nanotubes. Compared with tangled carbon nanotubes, aligned carbon nanotube arrays have less disfigurement and the resistivity is lower. Thereby, ACNTs have higher electrical

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conductivity and higher surface area than CNTs do, which can be considered as the surface area-enhancing component in the electrode. ACNTs electrode has attracted much attention [30]. Our group has reported determination of nitrite with the electrocatalytic property to the oxidation of nitrite on thionine modified aligned carbon nanotubes [31]. Tang and coworker used electrochemical oxidation method to detected glutathione at well-aligned carbon nanotube arrays electrode and depositing platinum on well-aligned carbon nanotubes arrays for methanol oxidation [32–33]. Gao et al. reported a new glucose sensors based on glucose-oxidase-containing polypyrrole/aligned carbon nanotubes coaxial nanowire electrode [34]. Making aligned carbon nanotubes ideal electrodes for constructing favorable electrochemical reaction platform is anticipated.

In this paper, we combined the advantageous features of PtNPs and ACNTs to develop a glucose sensor with high sensitivity. The high dispersion of PtNPs catalysts on the wall side of the ACNTs arrays were electrocrystallized on 4-aminobenzene monolayer-grafted ACNTs electrode by potential-step electrodeposition method according to other work [35, 36]. As shown in Scheme 1, first, an ordered 4-aminobenzene monolayer was grafted onto the wall of ACNTs. Then, $PtCl_6^{2-}$ monolayer was adsorbed onto the grafted ACNTs surface by electrostatic interaction. Finally, PtNPs adhered onto the side wall of ACNTs through pulsed potentiostatic reduction. The catalysis of PtNPs on glucose was investigated and the detection sensitivity increased greatly. After several experimental conditions, such as effects of applied potential and pH value etc. have been optimized. The proposed method has a detection limit of 8.89×10^{-6} mol L^{-1}, a linear range of 1×10^{-5}–7×10^{-3} mol L^{-1}, and good reproducibility.

2. Experimental

2.1. Chemicals and Instruments

Glucose oxidase (GOD, E.C.1.1.3.4, Type VII, 190 U/mg, from *Aspergillus niger solid*), l-ascorbic acid, uric acid, and β-D (+)-glucose were purchased from Sigma. The glucose solution was prepared with double distilled water and stored over 24 h before use in order to allow the equilibrium of the isomers. Nafion ethanol solution (1 wt%) was obtained from Aldrich and used as received without further purification. Bovinoid Serum Albumin (BSA) was purchased from Ding Guo Bioengineering Co. Ltd (Beijing,China). H_2PtCl_6 (spectroscopically pure) was purchased from Shanghai reagent Co. Ltd. All other reagents are commercially available and of analytical grade. All solutions were prepared with double distilled water. Phosphate buffer solutions (PBS) (0.1 M) with various pH values was prepared by mixing stock standard solutions of Na_2HPO_4 and KH_2PO_4 and adjusting the pH with 0.1 M H_3PO_4 or 0.5 M NaOH.

Amperometric experiments were performed with CHI 660A electrochemical workstation (CH Instruments Co. USA). The modified ACNTs working electrode, the platinum wire counter electrode and the Ag/AgCl reference electrode were inserted into the 10 mL cell through holes in its Teflon cover. A magnetic stirrer provided the convective transport during the amperometric measurement. SEM images were obtained by the JEOL-JSM-5610LV (JEOL Co. Japan). TEM images were obtained by the JEOL-JEM-2100F (JEOL Co. Japan).

2.2. Fabrication of PtNPs/ACNTs Electrode

The ACNTs were prepared by chemical vapor deposition (CVD) method [37] and was sputtered with an around 200 nm of gold layer [38]. The ACNTs would not spread around with the gold layer on it after been peeled off from the Si floor in 10% HF solution. Further purification was accomplished by immerse the ACNTs in 30 wt% nitric acid at 25 °C for 2 h to remove the metallic iron particles (the catalyst for the growth of ACNTs) [39]. For electrochemical study, the well-aligned carbon nanotubes were cut into 1 mm^2 which was used as the working electrode. The Cu wire was fixed onto the back of the ACNTs slice use the carbon
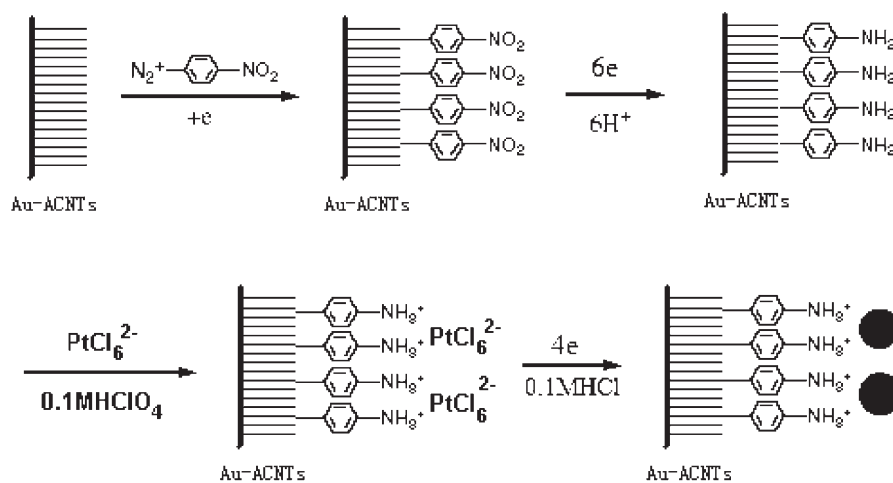
Scheme 1. Schematic procedure for the preparation of PtNPs combined ACNTs surface.

electric glue. The exposed part of the Cu wire was covered with epoxy resin. The electrochemical pretreatment of the ACNTs electrode was performed in 0.1 M H_2SO_4 solution in the presence of 2.5 mM 4-nitrobenzenediazonium tetrafluoroborate by scanning between −0.5 V and 0.1 V (vs. Ag/AgCl). After the electrochemical pretreatment, the electrode was successively rinsed with 0.1 M H_2SO_4 and ultrapure water to remove the physically adsorbed materials. Then the ACNTs electrode was immersed into 0.1 M $HClO_4$ solution containing 1.5 mM $PtCl_6^{2-}$ solution for several minutes and transferred to a 0.1 M HCl blank solution. At last, with a pulsed potential stepped from 0.7 to −0.2 V (vs. Ag/AgCl), the $PtCl_6^{2-}$ adsorbed on the 4-aminobenzene monolayer-graft ACNTs was changed into PtNPs to fabricate a PtNPs/ACNTs electrode [35, 36].

2.3. Procedure of Glucose Detection

2 μL of GOD (950 U/mL) was cast onto the PtNPs/ACNTs electrode surface and airing at room temperature. And then, 2 μL of Nafion aqueous solutions (1 wt%) was cast on the surface of the resulting GOD/PtNPs/ACNTs electrode. After the Nafion film was dried, the Nafion/GOD/PtNPs/ACNTs electrode was washed thoroughly with double-distilled water and stored in PBS (PH 7.4) at 4 °C for future use. For comparison, the enzyme electrode without PtNPs (Nafion/GOD/ACNTs) was prepared by the same procedure described above. Amperometric measurements were performed in PBS (pH 7.4) buffer solution under quiescent conditions after mixing equably at room temperature. The desired working potential (+0.3 V) was applied and transient background currents were allowed to decay to a steady-state value.

3. Results and Discussion

3.1. Preparation and the Morphologies of PtNPs/ACNTs Electrode

Considering that many metals including Pt would not adhere with carbon nanotubes directly because the carbon nanotubes have very hydrophobic surface. The surface modification or activation have been attempted to improve metal deposition onto them. Cyclic voltammograms of 2.5 mM 4-nitrobenzenediazonium tetrafluoroborate in 0.1 M H_2SO_4 at ACNTs electrode is shown in Figure 1. The first sweep give a broad irreversible reduction wave (a) at 0.03 V (vs. Ag/AgCl), which is attributed to the formation of the 4-nitrobenzene radical form the diazonium derivative [36, 40]. This first one-electron wave is immediately followed by a second irreversible six-electron wave (b) at −0.37 V (vs. Ag/AgCl) which corresponds to the reduction of the nitro group into an amino group. On the second cycle, the waves trailed off, this indicates that the monolayers formed on the ACNTs surface and may hinder the further reduction of 4-nitrobenzenediazonium tetrafluoroborate,

the nitro groups are reduced to amines, the reduction mechanisms in acidic medium have been investigated in detail in other work [36]. Compared with the above literature, we can also observe that the ACNTs electrode exhibits a dramatic improvement in the response for the reduction of 4-nitrobenzenediazonium tetrafluoroborate. The cathodic peak potential values at the glassy carbon electrode in above literature were −0.14 and −0.49 V, respectively. There are about 100 mV higher of the potential for the reduction of 4-nitrobenzenediazonium tetrafluoroborate on ACNTs electrode than that on glassy carbon electrode. The shift of the peaks is a strong predication of the catalysis on ACNTs electrode, which indicates a more facile reaction occurring at ACNTs compared to other carbon substrates. After modification, the electrode was successively rinsed with 0.1 M H_2SO_4 and distilled water to remove the physically adsorbed materials, and then immersed into 0.1 M $HClO_4$ solution containing 1.5 mM $PtCl_6^{2-}$ solution for several minutes. $PtCl_6^{2-}$ adsorbed ACNTs electrode was then transferred into 0.1 M HCl blank solution and PtNPs were grown on the 4-aminobenzene monolayer grafted ACNTs electrode by a pulsed potentiostatic method. The potential was stepped from 700 to −200 mV (vs. Ag/AgCl). A typical current–time transient seen for $PtCl_6^{2-}$ anions on a 4-aminobenzene monolayer grafted ACNTs electrode in the 0.1 M HCl dilute solution is shown in Figure.2. Curve a represents the transients of 4-aminobenzene monolayer grafted ACNTs without $PtCl_6^{2-}$ anions. Comparing with these two transients, curve b exhibits a much larger current, which clearly shows that $PtCl_6^{2-}$ has been coordinated and reduced on the 4-aminobenzene monolayer grafted ACNTs surfaces.

The micrographs of PtNPs/ACNTs composite have been investigated by SEM and TEM images. Figure 3 shows the SEM and TEM images (the inset) of (A) ACNTs and (B) PtNPs/ACNTs electrode. It can be observed that the
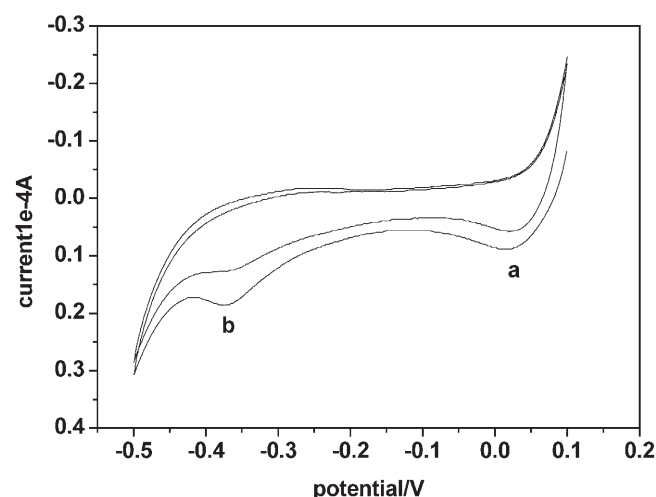

Fig. 1. Cyclic voltammetry of 2.5 mM 4-nitrobenzenediazonium tetrafluoroborate in 0.1 M H_2SO_4 at a ACNTs electrode; a) the first reduction wave; b) the second reduction wave; scan rate, 5 mV/s
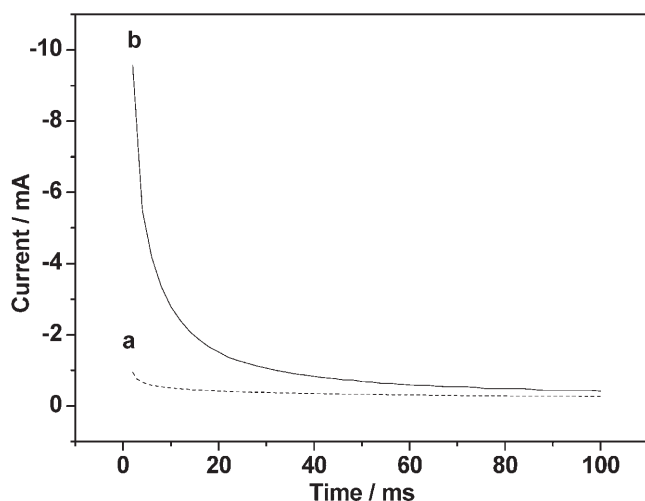
Fig. 2. Typical current–time transient on a) the 4-aminobenzene monolayer grafted ACNTs electrode without $PtCl_6^{2-}$ anions; b) the 4-aminobenzene monolayer grafted ACNTs electrode with $PtCl_6^{2-}$ anions; in 0.1 M HCl.

Fig. 4. Cyclic voltammograms of 5×10^{-2} mol L^{-1} H_2O_2 in 0.1 mol L^{-1} PBS (pH 7.4) on a) glassy carbon electrode, b) ACNTs electrode, c) PtNPs/ACNTs electrode. Scan rate: 100 mV s^{-1}

morphologies of the ACNTs are vertically and orderly aligned together and have slick outer wall before modified by PtNPs (Fig. 3A and the inset). SEM studies (Fig. 3B) confirmed that the attachment of PtNPs to ACNTs didn't change the vertical morphologies of the ACNTs. Compared with ACNTs, the PtNPs/ACNTs become thick and the outer walls of the ACNTs are covered with a lot of PtNPs with the size of 10–20 nm (Fig. 3B, the inset). The well-defined dispersed Pt on the wall of the ACNTs indicated that NH_2 group could be equably distributing on the wall of the ACNTs through the electrochemical progress.

3.2. Electrocatalytic Properties of PtNPs/ACNTs Electrode

To evaluate catalytic activity for H_2O_2 electrooxidation of the PtNPs/ACNTs electrode, Figure 4 compares the electrochemical behaviors of the glassy carbon electrode, ACNTs electrode and PtNPs/ACNTs electrode modified at glassy
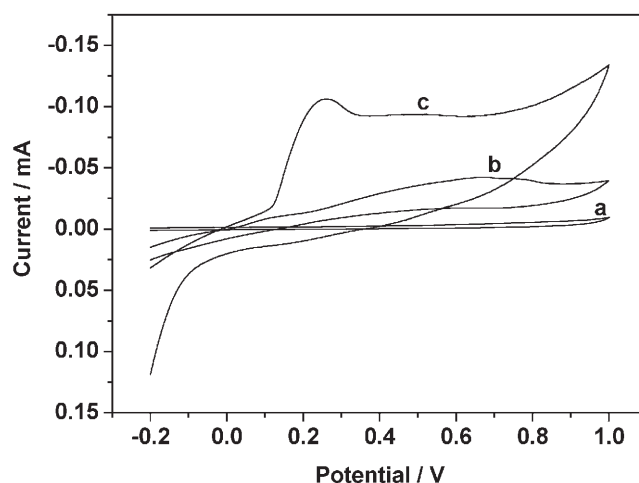
carbon electrode in 5×10^{-2} mol L^{-1} H_2O_2 in 0.1 mol L^{-1} PBS (pH 7.4) solution at the scan rate of 100 mV s^{-1}. As shown in Figure 4a, there is no obvious electrocatalytic activity for H_2O_2 oxidation on glassy carbon electrode in such potential range from -0.2 V to 1.0 V. There is a small oxidation peak of H_2O_2 at 0.68 V in Figure 4 (line b), which indicates that ACNTs have electrocatalytic activity for H_2O_2 oxidation in such potential range. The background current of ACNTs electrode is larger than that of glassy carbon electrode. This may be attributed to the high specific surface area of the ACNTs. On the other hand, there is obvious oxidation peak of H_2O_2 at the potential of 0.25 V on PtNPs/ACNTs electrode (Fig. 4c), which implies that the PtNPs/ACNTs electrode has higher electrocatalytic activity for H_2O_2 oxidation than that on ACNTs electrode. The above phenomenon indicates that the PtNPs grafted on the ACNTs as catalyst can accelerate the transfer of the electron between the surface of the modified electrode and the solution.
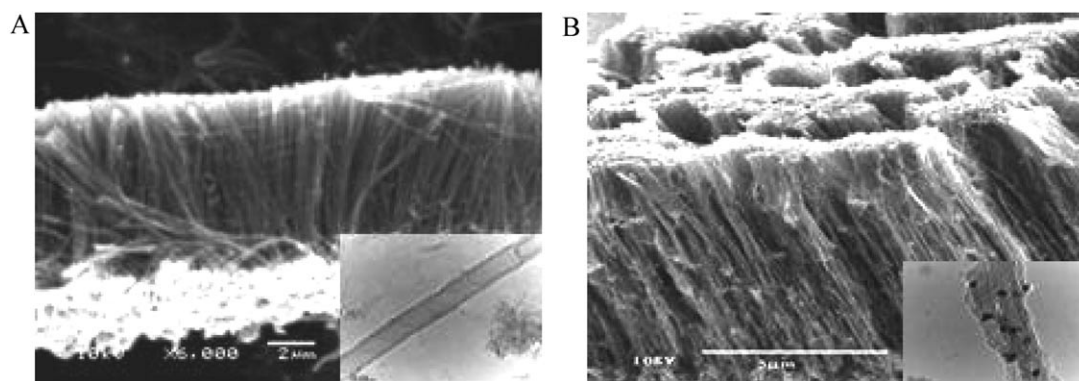

Fig. 3. SEM images of A) ACNTs, B) PtNPs/ACNTs. Inset: the TEM images.

3.4. Optimization of the Glucose Determination Conditions

The pH value of the solution and the working potential are important conditions in glucose detection. The effect of the pH value of the detected solution on the response behavior of the Nafion/GOD/PtNPs/ACNTs electrode has been tested. In the range of 5.0 to 8.0, the maximum response current density can be observed at pH 7.4. When the pH value is greater or less than 7.4, the response current dropped off. So pH 7.4 was chosen for the detecting pH value. The applied potential was changed from 0.1 V to 0.8 V and the corresponding response current to 1×10^{-5} mol L^{-1} glucose is presented in Figure 5. It can be seen in Figure 6 that the response current increased rapidly with the increase of applied potential when the potential was under 0.3 V. There is a platform when the potential was higher than 0.3 V and the potential on 0.3 V attended to the peak. This indicates that the response of the Nafion/GOD/PtNPs/ACNTs electrode is controlled by the electrochemical oxidation of hydrogen peroxide. The appearance of such a current plateau is attributed to the rate-limiting process of enzymatical kinetics, and the potential at which the current plateau appears is dependent upon the electrode nature. Therefore, 0.3 V was used for the detecting potential.

3.5. Amperometric Response of Glucose on Nafion/GOD/PtNPs/ACNTs Electrode

The Nafion/GOD/PtNPs/ACNTs electrode has excellent and strong electrocatalytic properties and facilitates the low potential amperometric measurement of glucose. Figure 6 shows the calibration curve between response current of Nafion/GOD/PtNPs/ACNTs electrode and glucose concentra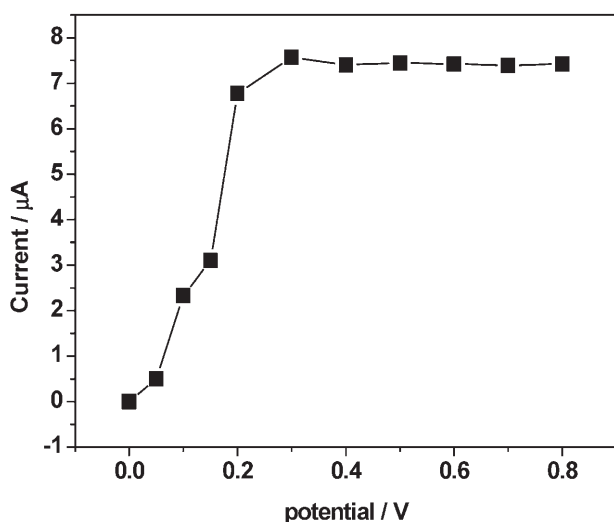tion in PBS (pH 7.4) at applied potential of 0.3 V. The calibration plot was linear over a wide concentration range of $1 \times 10^{-5} - 7 \times 10^{-3}$ mol L^{-1} and only a slight curvature on large concentration with fast response time within 5 s. This response range for glucose is larger than that reported in other work [24]. As shown during the successive additions of low concentration glucose, a well defined current – time response is observed (the inset). A correlation of coefficient is 0.994 and a detection limit of 8.89×10^{-6} mol L^{-1} is observed when signal to noise is 3. Since the electrode response is kinetic, the apparent Michaelis – Menten constant (k_m) can be obtained by an amperometric method as suggest by Shu and Wilson (1976).

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

where i_s is the steady-state current, C_g is the concentration of glucose, k_m is the apparent Michaelis – Menten constant and i_{max} is the maximum current. The apparent Michaelis – Menten constant k_m was estimated to be 9.28 mM. A similar study at Pt/ppy/GOD electrode is also performed and its apparent Michaelis – Menten constant is equal to 10.73 mM [24]. These results reveal that there is no substantial loss of GOD activity, indicating the immobilization procedures in the present study are biocompatible and can retain the GOD's activity.

The influence of ascorbic acid and uric acid on the glucose response is minimized not only due to low potential but also due to the presence of Nafion which behaves as a barrier to ascorbic and uric acid due to its negative charge. As shown in Figure 7, there is weak response when adding ascorbic acid and uric acid of 1×10^{-4} mol L^{-1} into the same concentration of glucose solution. The reproducibility of five Nafion/GOD/PtNPs/ACNTs electrode was calculated by the response to 1×10^{-4} mol L^{-1} glucose at the potential of 0.3 V.

Fig. 5. Effect of applied potential on steady-state response current of glucose on Nafion/GOD/PtNPs/ACNTs electrode in PBS (pH 7.4) containing 1×10^{-5} mol L^{-1} glucose.
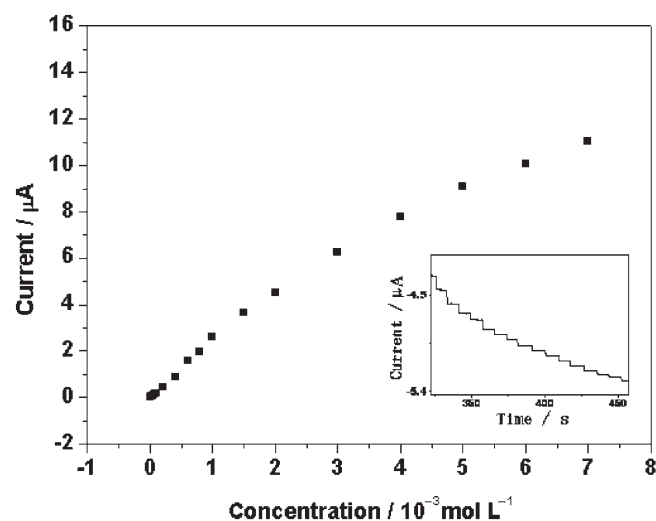

Fig. 6. Calibration curve between the response current of Nafion/GOD/PtNPs/ACNTs electrode and glucose concentration in PBS (pH 7.4) at applied potential of 0.3 V.
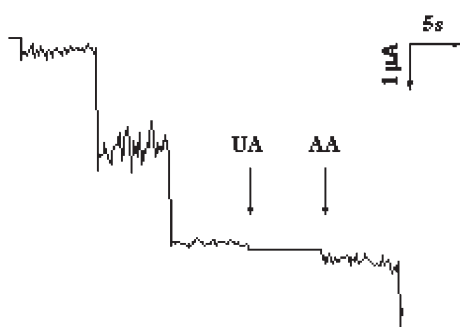
Fig. 7. Influence of electroactive interferents on Nafion/GOD/PtNPs/ACNTs electrode in glucose solution (1×10^{-4} mol L^{-1}, PBS pH 7.4). UA: uric acid (1×10^{-4} mol L^{-1}); AA: ascorbic acid (1×10^{-4} mol L^{-1}).

The relative standard deviation is 4.6%. The stability of the Nafion/GOD/PtNPs/ACNTs electrode under storage conditions (PBS, pH 7.4, 4 °C) was investigated using the same PBS containing 1×10^{-4} mol L^{-1} glucose, and the corresponding result shown only 7% loss of the response current can be observed within 5 days. After 20 days, the response current is still retained 80% which implied the Nafion/GOD/PtNPs/ACNTs electrode is compatible with the immobilized enzyme and is helpful to maintain the bioactivity of GOD.

4. Conclusions

In summary, we have demonstrated a new approach for the fabrication of glucose biosensors based on Nafion/GOD/PtNPs/ACNTs electrode for the selective and sensitive detection of glucose. The PtNPs can be combined with ACNTs by electrochemical method and the nanosized Pt particle is uniformly distributed. Owing to ACNTs' nanodimensions, rich electronic states, large surface area and excellent chemical stability, the electron transfer between the electrode and the glucose solution has been promoted. PtNPs dispersed on the ACNTs can enhanced the electrocatalytic activity for the oxidation of hydrogen peroxide. The experimental results have demonstrated that this glucose biosensor possesses an excellent response performance on glucose

5. Acknowledgements

6. References

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