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A Novel Biosensor for Determination of Glucose Based on MWCNTs/ZrO_2-Pt Nanocomposite

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Abstarct: Multiwalled carbon nanotubes/ZrO_2-Pt(MWCNTs/ZrO_2-Pt) composite was synthesized by a chemical route. The structure and composition of the MWCNTs/ZrO_2-Pt composite were confirmed by means of transmission electron microscopy, and Raman spectroscopy. Due to the good electrochemical activity property of MWCNTs/ZrO_2-Pt composite, a glucose biosensor was constructed by absorbing glucose oxidase (GOD) on the hybrid material. A direct electron transfer process is observed at the MWCNTs/ZrO_2-Pt/GOD-modified glassy carbon electrode. The glucose biosensor has a linear range from 4.0 to 24.0 mM, which is suitable for glucose determination by real samples. It should be worthwhile noting that, from 4.0 to 12.0mM, the cathodic peak currents of the biosensor decrease linearly with increasing the glucose concentrations in human blood. Meanwhile, the resulting biosensor can also prevent the effects of interfering species. Moreover, the biosensor exhibits satisfying reproducibility, good operational stability and storage stability. Therefore, the MWCNTs/ZrO_2-Pt /GOD biocomposite could be promisingly applied to determine blood sugar concentration in the practical clinical analysis.

Keywords: Multiwalled Carbon Nanotubes, Electrochemical Biosensors, Platinum Nanoparticles

1. Introduction

In medicine and animal physiology, ‘‘blood sugar’’ refers to glucose in the blood. Glucose is the primary source of energy for the bodices. Blood-sugar concentration, or glucose level, is tightly regulated in the human body. Normally, the blood-glucose level is maintained within the range 4–6 millimolar (m M). Failure to control blood-glucose level within the normal range leads to high (hyperglycemia) or low (hypoglycemia) blood sugar. Diabetes, characterized by persistent hyperglycemia in clinical medicine, is one of the leading causes of death and disability in the world, affecting over 100 million people worldwide. Maintenance of blood-glucose concentration within the normal physiological range has been recognized as an important way to prevent development of diabetes-related complications. Large numbers of methods have therefore been proposed to monitor blood-glucose concentration, and the amperometric biosensor based on enzyme electrodes is a primary choice because of its high sensitivity, short response time, and low cost of instrumentation [1].

For the electrochemical biosensor applications, the electrode modifying material is expected to possess several characteristics such as good electron transduction capability, physical or chemical environment for the stable immobilization of enzyme, bioactivity, easy accessibility towards the analyte and large surface area. Literature reveals that all these important characteristics cannot be inbuilt in a single material. Hence, there is always a demand for the development of composite materials, comprising two or more components, to achieve adequate sensitivity and stability for the biosensors [2-4].

Nowadays the pursuit of non-enzymatic glucose sensing with rapid response and precise measurement is a vigorous and competitive area of research. The direct oxidation of glucose by different electrodes in the absence of enzyme has been studied [5–10]. Various metal electrodes such as Pt, Au, and Ag have been proved to be highly electro-active in the anodic oxidation of glucose requiring a high overpotential. However, these can be problematic due to poisoning/fouling of the electrode surface, especially at gold and platinum

electrodes. Additionally the cost of these precious metals needs to be considered. As a consequence, there are increasing interests on the fabrication of modified electrodes with low operating potential by enhancing electron transfer kinetics. In comparison, a few transition metal complexes, including the various transition metal hexacyanoferrate modified electrodes, have been shown to be efficient electro-catalysts for anodic oxidation of glucose, giving enhanced stability towards the target analyte, with low detection limits and wide analytical ranges achievable [11–16]. In this area problems from the instability of modified electrodes are evident and limit widespread implementation. Consequently in this paper, we describe a simple route to the production of uniform functional nickel hexacyanoferrate nanoparticles using electrochemical deposition. The preparation method is simple and nickel hexacyanoferrate nanoparticles may be readily formed on a glassy carbon electrode surface constructing a simple, economical and accurate amperometric sensor for glucose. The non-enzymatic glucose biosensor based on nickel hexacyanoferrate (NiHCF) modified electrodes provides a prominent augmentation of response current toward glucose with a good stability and reproducibility.

In this paper, ZrO_2 was wrapped on MWCNTs at 60 °C by $ZrCl_2$ hydrolysis in acidic solution. PtNPs were in situ dispersed over the amorphous ZrO_2-wrapped MWCNTs to form MWCNTs/ZrO_2-Pt nanocables. Transmission electron microscopy (TEM) image shows that the MWCNTs/ZrO_2 surface is covered with PtNPs at high density. The MWCNTs/ZrO_2-Pt nanocomposite was deposited on a glassy carbon electrode (GCE), and then a glucose biosensor was constructed by absorbing GOD on the hybrid material. The DET of GOD is observed at the MWCNTs/ZrO_2-Pt/GOD-modified GCE. A linear range from 4.0 to 24.0 mM was mainly studied in phosphate buffer solution (PBS), which is suitable for glucose determination by real samples. Moreover, the glucose concentration in human blood was preliminarily studied by the resulting biosensor.

2. Experimental

2.1. Preparation of MWCNTs/ZrO_2-Pt Nanocomposite

The MWCNTs (Sigma- Aldrich) were treated with HNO_3 (Merck) at 60 °C for 12 h by continuous stirring. The product was centrifuged and washed with ultrapure water until its pH value approaches to 7. The MWCNTs/ZrO_2 nanocables were prepared according to the method reported by Chen et al. [17]. Briefly, 30mg of MWCNTs were dissolved in 18mL of water at room temperature. Subsequently, 0.15mLof HCl (Fluka), 0.66 g of $Zr(NO_3)_2$ (Merck), and 0.3 g of urea (S. D. Fine) were added. The mixture was then continually stirred at 60 °C for 6 h. The product was rinsed with distilled water and then dried at 60 ◦C under vacuum. For the preparation of MWCNTs/ZrO_2-Pt composite, 1.0mg of MWCNTs/ZrO_2 and 0.10 g of hydrazine were dissolved in 5.2mL of water, and then 0.74mL of 13.5mM hexachloroplatinic (Merck) acid aqueous solution was added dropwise over several minutes. After stirring for 12 h, the product was centrifuged, washed with ultrapure water and then dried at room temperature under vacuum.

2.2. Preparation of MWCNTs/ZrO_2-Pt and MWCNTs/ZrO_2-Pt/GOD Composite Films

The GCE (5mm in diameter) was polished subsequently with alumina slurry, and sonicated in water for several times to get mirror image. To prepare the MWCNTs/ZrO_2-Pt-modified GCE, 3μL of 2mg/mL MWCNTs/ZrO_2-Pt aqueous solution were coated on the polished GCE with a microsyringe and dried in air. In order to prepare MWCNTs/ZrO_2-Pt/GOD composite film, 5μL of 3mg/mL GOD PBS were dropped on the MWCNTs/ZrO_2-Pt modified GCE, and then dried for ca. 24 h at 4 °C. After polishing, the MWCNTs/ZrO_2-Pt/GOD-modified assembly electrode was prepared in the same way as the MWCNTs/ZrO_2-Pt/GOD-modified GCE. Finally, 2μL of 0.5% Nafion aqueous solution was dropped on the MWCNTs/ZrO_2-Pt/GOD composite film to prevent the loss of biocomposite. Those enzyme-modified electrodes were stored at 4°C in refrigerator when they were not in use.

2.3. Instruments and Measurements

TEM image was taken with JEOL 2000 transmission electron microscope operating at 200 kV. Raman spectra were collected using a Renishaw Raman system model 1000 spectrometer. The 514.5- nm radiation from a 20mW air-cooled argon ion laser was used as exciting source. Cyclic voltammetry (CV) scans were performed using a Wenking PGS 95 with full computerized system. All electrochemical measurements (besides blood sample test) were performed in a three-electrode electrochemical cell. A Au wire and a KCl-saturated Ag/AgCl electrode were used as the counter and reference electrode, respectively. The assembly electrode consists of a GCE (as working electrode, 5 mm in diameter), an Ag sheet (as reference electrode) and a Pt sheet (as counter electrode) (Figure 7).

3. Results and Discussion

3.1. Structure Characterization

Figure 1 and 2 display the TEM images of MWCNTs/ZrO_2 and MWCNTs/ZrO_2-Pt nanocables, respectively. From the TEM image of MWCNTs/ZrO_2,we can see that there is a uniform layer coating the MWCNTs. The diameter of these nanocables is about 20–35 nm, and the thickness of the coating layer is about 5–12 nm. After immobilization of PtNPs, the resulting TEM image reveals that spherical Pt particles are present as dark dots with non-ordered distribution (Figure 2). The diameter of Pt nanoparticles ranges from 3.4 to 6.0 nm, and their mean diameter is 4.5nm (inset of Figure 2).

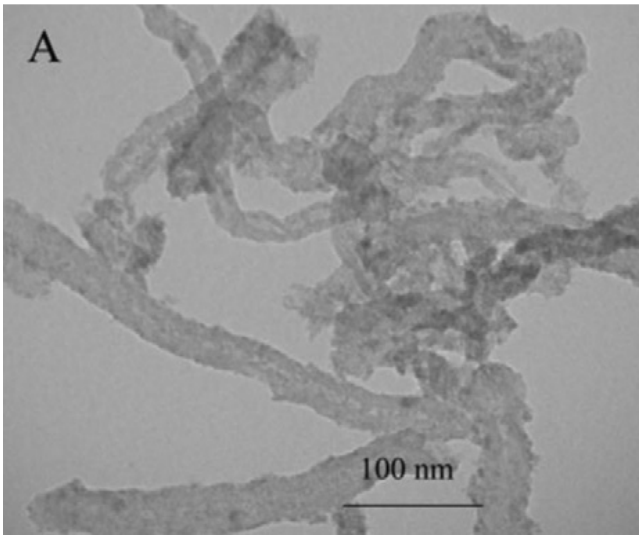

Figure 1. *TEM images of the MWCNTs/ZrO_2, particle size distribution as inset.*

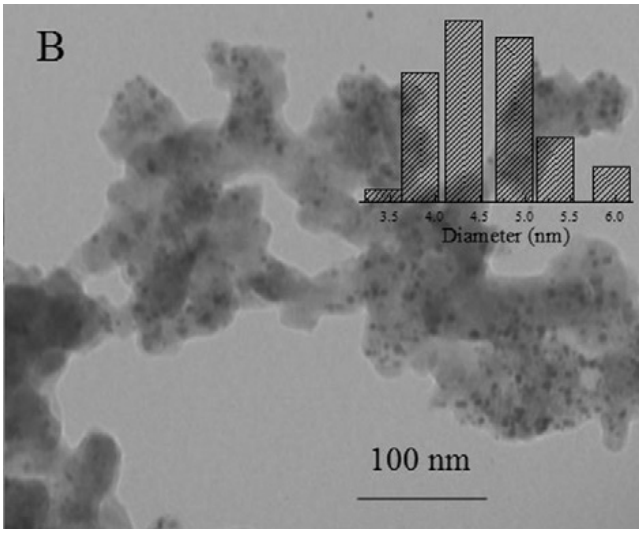

Figure 2. *TEM images of the MWCNTs/ZrO_2-Pt nanocables, particle size distribution as inset.*

Figure 3 shows the Raman spectra of the MWCNT-COOH, MWCNTs/ZrO_2 and MWCNTs/ZrO_2-Pt nanocomposite. The characteristic peaks of MWCNTs are observed at 1352cm^{-1} (D band) and 1584cm^{-1} (G band), respectively. The ratio of the D band to the G band (R value) is from 1.05 to 1.22, associated with the change from MWCNT-COOH to MWCNTs/ZrO_2. It is suggested that ZrO_2 particles have improved the roughness of MWCNTs [14]. The R value of MWCNTs/ZrO_2-Pt nanocomposite is reduced to 1.11, which indicates that PtNPs grew in the pores of ZrO_2 and some defects disappeared. From the MWCNTs/ZrO_2 to the MWCNTs/ZrO_2-Pt composite, the reduction of the R value and the little upshift in the two bands might be related to the interactions between MWCNTs/ZrO_2 and deposited Pt atoms [18].

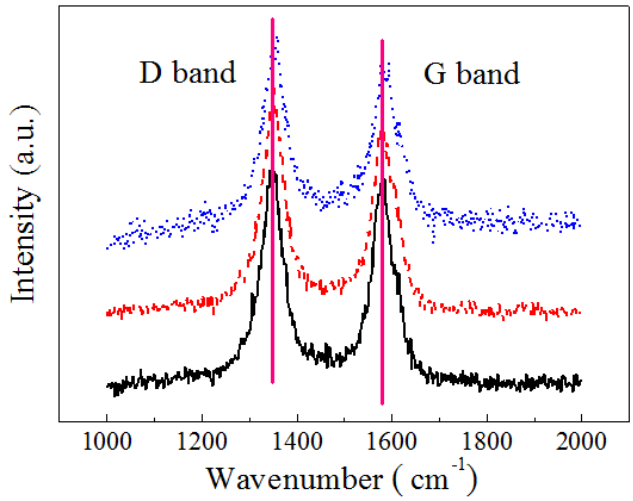

Figure 3. *Raman spectra of the MWCNT-COOH (solid), MWCNTs/ZrO_2 (dashed), and MWCNTs/ZrO_2-Pt (dotted) composites.*

3.2. Electrochemical Properties

Figure 4 displays the CVs at MWCNTs/ZrO_2-Pt in N_2-saturated and O_2-saturated 0.05 M PBS (pH 7.0) solution. An obvious reduction wave of O_2 at MWCNTs/ZrO_2-Pt -modified GCE is observed at ca. −0.25V (solid black curve). In contrast, the reduction potential of O_2 at a bare GCE is at ca. −0.55V (solid gray curve). However, no peaks are seen in the N_2-saturated solution at the above two electrodes. Therefore, we conclude that MWCNTs/ZrO_2-Pt retains a high electrocatalytical activity toward the reduction of O_2. The electrocatalytical effect of H_2O_2 is also observed at the same electrode.

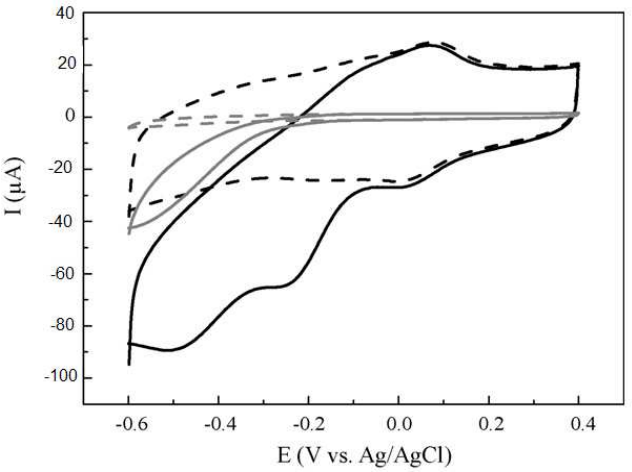

Figure 4. *(A) CV curves at the bare GCE (gray) and the MWCNTs/ZrO_2-Pt –modified GCE (black) in 0.05M O_2- saturated (solid) and N_2-saturated (dashed) PBS (pH 7.0) solution.*

(Figure 5). The initial potential of H_2O_2 reduction is about −0.03V at the MWCNTs/ZrO_2-Pt -modified GCE (solid black curve). Therefore, these results clearly suggest that the MWCNTs/ZrO_2-Pt composite can electrocatalytically reduce O_2 and H_2O_2, which is in favor of further utilization of glucose sensing.

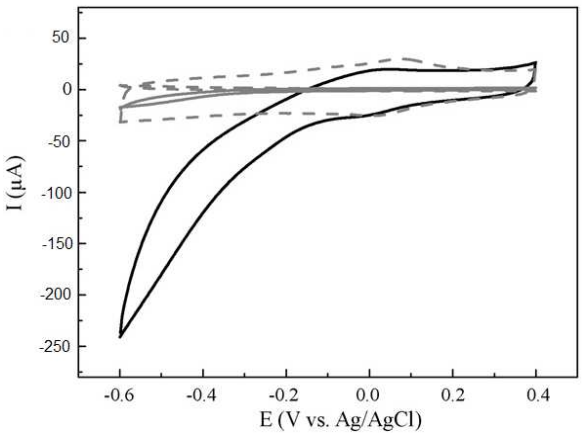

Figure 5. *CV curves at the bare GCE (gray) and the MWCNTs/ZrO_2-Pt – modified GCE (black) in 0.05 M N_2-saturated PBS (pH 7.0) solution in the absence (dashed) and in the presence (solid) of 6.0m M H_2O_2. Scan rate: 0.1 Vs^{-1}.*

3.3. Glucose Biosensor

Figure 6 shows the CV curve at the MWCNTs/ZrO_2-Pt /GOD modified GCE in 0.05 M N_2-saturated PBS (solid curve). A pair of well-defined and nearly symmetric redox peaks is observed. The peak-to-peak separation (ΔEp) is calculated to be ca. 0.035V and the ratio of the cathodic current over the anodic one is close to 1. For comparison, the CV curve without GOD at MWCNTs/ZrO_2-Pt -modified GCE does not show such redox waves (dashed curve). It indicates that the redox waves are ascribed to the redox active center in GOD biomolecules [19] and the DET of GOD can be achieved on the MWCNTs/ZrO_2-Pt-modified GCE.

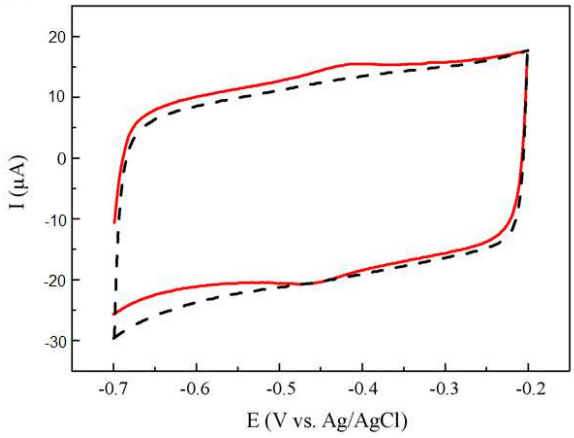

Figure 6. *CV grams at the MWCNTs/ZrO_2-Pt-modified (dashed), MWCNTs/ZrO_2-Pt /GOD-modified GCE (solid) in 0.05 M N_2-saturated PBS (pH 7.0) at a scan rate of 0.1 Vs^{-1}.*

Figure 7 shows CVs of the MWCNTs/ZrO_2-Pt /GOD-modified GCE at various scan rates. The small ΔEp value and the linear relationship (R = 0.999) between the peak currents and scan rates indicate that the redox process of the prepared biocomposite is a reversible and surface-confined process. Therefore, the MWCNTs/ZrO_2-Pt composite might facilitate a reversible electron transfer process between GOD and electrode substrate. MWCNTs were pointed out to play an important role in the DET of GOD [20]. Meanwhile, ZrO_2 as linking material can provide a well conductive and porous substrate to facilitate the reversible electron transfer and immobilize GOD molecules in the pores [21-23]. Finally, Pt NPs have good electrocatalysis toward H_2O_2 reduction, which is generated during the course of the GOD-catalyzed oxidation of glucose in the presence of dissolved oxygen. A glucose sensor was fabricated to verify the bioactivity of Immobilized GOD deposited on the MWCNTs/ZrO_2-Pt composite.

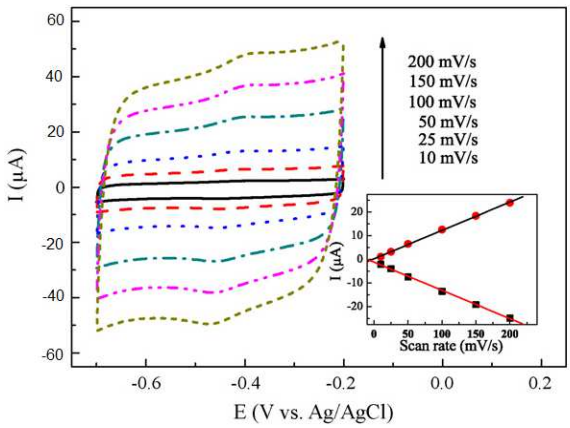

Figure 7. *CV grams at the MWCNTs/ZrO_2-Pt /GOD-modified GCE in 0.05 M N_2-saturated PBS solution at various scan rates. Scan rate: 10, 25, 50, 150 and 200mVs^{-1} from inner to outer. Inset is the calibrated plot of peak currents vs. scan rates.*

Figure 8 shows the CV grams at the MWCNTs/ZrO_2-Pt /GOD modified GCE in different concentrations of glucose in air-saturated PBS. The peak current decreases with the increase of the glucose concentrations [24]. It suggests that the specific enzyme-substrate activity of GOD has been reserved in the MWCNTs/ZrO_2-Pt composite. As shown in the inset of Figure 8, a linear relationship between the amperometric responses and the concentrations of glucose is observed ranging from 4.0 to 24.0mM.

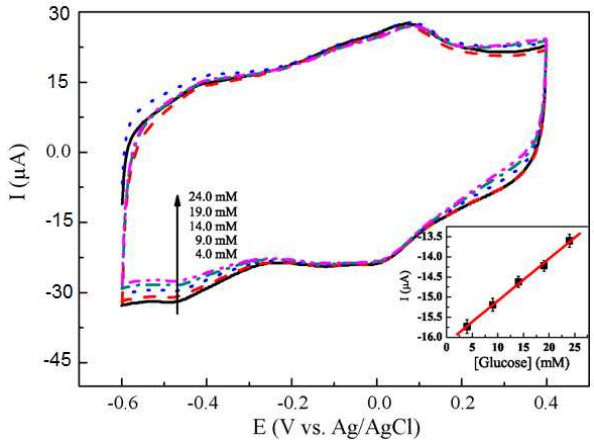

Figure 8. *CV grams at the MWCNTs/ZrO_2-Pt /GOD-modified GCE in various concentrations of glucose PBS (pH 7.0): 4.0, 9.0, 14.0, 19.0 and 24.0 mM from outer to inner. Inset is the calibration curve corresponding to amperometric responses. Scan rate: 0.1 Vs^{-1}.*

The detection limit of the MWCNTs/ZrO_2-Pt /GOD-modified GCE biosensor is 5 μM by amperometric current-time method Figure 9. Therefore, the MWCNTs/ZrO_2-Pt composite has a great potential for the application in electrochemical detection of glucose. As known, fasting blood glucose ≥7.0mM (126 mg/dL) and/or postprandial blood glucose ≥11.1mM (200 mg/dL) is the base of diagnosis of diabetes. So the linear glucose response from 4.0 to 24.0mM based on our MWCNTs/ZrO_2-Pt /GOD biocomposite is suitable for determining blood glucose concentration.

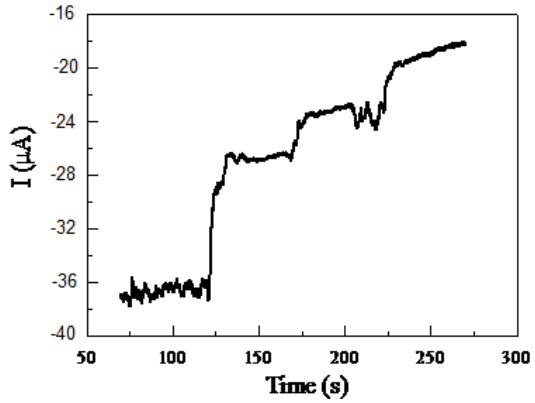

Figure 9. *Steady-state response of the MWCNTs/ZrO_2-Pt/GOD-modified GCE with successive addition of 5.0 μM glucose into 0.05 M air-saturated PBS (pH 7.0) solution (applied potential: -0.45 V vs. Ag\|AgCl in saturated KCl solution).*

Figure 8 show CV grams at the MWCNTs/ZrO_2-Pt /GOD-modified GCE in various concentrations of glucose PBS (pH 7.0): 4.0, 9.0, 14.0, 19.0 and 24.0mMfrom outer to inner. Inset is the calibration curve corresponding to amperometric responses. Scan rate: 0.1 Vs^{-1}. blood sample test, 30 μL of human blood (4.0 mM sugar concentration) were coated on the MWCNTs/ZrO_2-Pt /GOD-modified assembly electrode with a microsyringe. The drop of blood must cover all the three electrodes of the assembly electrode, and is used as electrolyte. The cathodic current decreases with successive addition of 0.4 μL 0.17 M glucose solution (Figure 10**)**. From 4.0 to 12.0mM, the amperometric responses linearly change with the glucose concentration (inset of Figure 10).

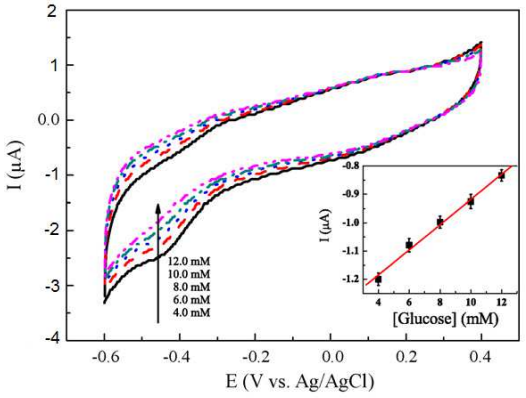

Figure 10. *CV grams at the MWCNTs/ZrO_2-Pt/GOD-modified assembly electrode in blood sample containing 4.0, 6.0, 8.0, 10.0, 12.0mM glucose from outer to inner. Inset is the calibration curve corresponding to amperometric responses. Scan rate: 0.1 Vs^{-1}.*

3.4. Interference Study and Performance Evaluation

The glucose amperometric enzyme sensors are based on the electro-reduction of hydrogen peroxide produced by the enzymatic oxidation of glucose. In general, the amperometric detection of H_2O_2 could be undertaken either by reduction or oxidation.

However, within the living body, there is concomitant electrooxidation of many interfering species, such as AA, DA, UA, alcohol and so on [25-26]. Therefore, the electro-reduction method was carried out in this paper in order to remove the serious interference in the practical sample analysis. The biosensor was immersed into a cell containing 10mL of 0.05M air-saturated PBS (pH 7.0) with stirring and then each substrate solution was added to the cell. For the glucose solution (0.2 mM), the sensor output increases, and a maximum current is obtained within 25 s. When AA (0.2 mM), DA (0.2 mM), UA (0.2 mM), alcohol (17 mM), and morphine (1.0 mM) solution were added to the cell, the current does not change (Figure 11).

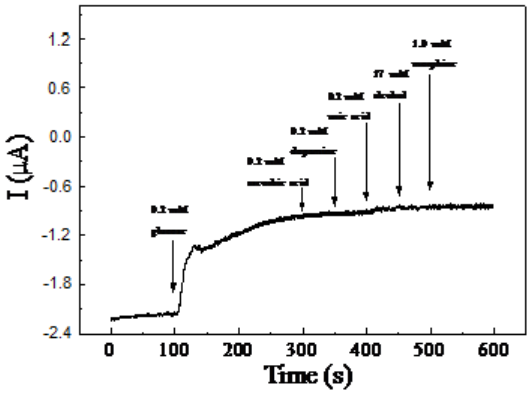

Figure 11. *Typical response curves of the MWCNTs/ZrO_2-Pt/GOD-modified assembly electrode. Sample solution was added in pH 7.0 PBS under a -0.45 V potential (vs. Ag/AgCl).*

Therefore, the biosensor can eliminate the interference of other molecules in blood by electro-reduction method. The MWCNTs/ZrO_2-Pt /GOD biocomposite as a promising candidate could be used to determine blood glucose concentration in the practical clinical analysis. In addition, the influence on the specificity of substrate-enzymatic reaction is very complicated due to the existence of interfering species. We hope we will give a reasonable answer in the nearest future. The glucose detection performances of the proposed biosensor are compared with other sensors. As shown in results, the MWCNTs/ZrO_2-Pt/GOD-modified electrode offers reasonable linear range for glucose detection of real sample and the precision of detection is much better than the previous report of glucose detection of human blood [27]. However, in comparison with the charge transfer glucose sensor previously described by Lee et al. [28, 29], it shows little bad performance. The relative standard derivation (RSD) of our method is 2.5% for 15 detections in 6.0 mM glucose blood sample at a same modified electrode. However, the method and mechanism are

totally different from the previous report which was performed on measurements of small (D-gluconate + H^+) ion fluctuation to determine the glucose concentration. In this work, the measurements of glucose are achieved via electrochemical detection of the liberated H_2O_2 during the oxidation of glucose. It is worthwhile noting that the cost of the biosensor is even lower than that of the currently used methods. Moreover, the amount of blood in one test is only 30 μL, which is acceptable for patients. Furthermore, this biosensor can be used even over 15 times. Therefore, the biosensor could be promisingly applied to determine blood glucose concentration in the practical clinical analysis. The storage stability of the biosensor was also investigated. After two week storage at 4°C, the redox peak currents retain 89% of their initial response values. It is hopefully that the performance of our biosensor can be improved further by combining screen-printing technique. About 3 dollars are charged for a blood glucose test at hospital. Recently, the popular method used at home is blood glucose strip. The price of blood glucose strip is about 1 dollar but the strip cannot be used repeatedly. Moreover, the reproducibility of the strip method is not satisfied. The detailed calculation of the cost of MWCNTs/ZrO_2-Pt biocomposite is as follows. Firstly, the cost of the assembly electrode was about 20 dollars and it can be used for several thousands times. On the assumption that one assembly electrode can be used for 1000 times, only 0.03 dollars are needed in one test at the electrode part. Secondly, the cost of the MWCNTs/ZrO_2-Pt composite is ca. 100 dollars/g. However, the amount of biocomposite using for one chip is 6×10^{-6} g. So the cost of the MWCNTs/ZrO_2-Pt composite for one chip is only ca. 6×10^{-4} dollars; Thirdly, the price of GOD is 6400 dollars/g. 1.5×10^{-5} g of GOD is needed for one chip. Thus the cost of GOD is ca. 0.1 dollars for one chip. Finally, the price of Nafion for one chip is ca. 0.002 dollars. In a word, the cost of biosensor is much less than 0.02 dollars in one test if one chip is used for 10 times. Therefore, the cost of the biosensor is less than that of the currently used methods. Combining with screen-printing technology, the cost of biosensor will be further decreased.

3.5. Stability

The DET of GOD in the biosensor exhibits high stability, and its voltammetric response remains stable even after continuous scanning for 50 cycles. The reproducibility of enzyme electrode construction was estimated from the response to 10.0 mM glucose at five-enzyme electrodes prepared under the same conditions. The results reveal that the biosensor has satisfying reproducibility with a RSD of 5.3%. The operational stability of the enzyme electrode was measured by a same enzyme electrode's continuous response to 0.05M PBS containing 10mM glucose. The RSD is 3.4% for continuous five-time determinations. After one-week storage at 4°C, the response current of the biosensor decreases 2.6% in 0.05 M PBS containing 10.0 mM glucose. The redox peak currents retain 93% of their initial response values after two weeks. After one month, the redox peak currents retain 90% of their initial response. This implies that the MWCNTs/ZrO_2-Pt /GOD-modified electrode has good reproducibility and stability. The good representation of the biosensor can be attributed to following reasons. First, the conductive and mesoporous structure of ZrO_2 facilitate to immobilize the enzyme and keep the configuration of GOD. Moreover, the strong interaction between the negatively charged enzyme and the positively charged composite avoids the enzyme loss. Second, Pt NPs offer a hospitable environment for GOD and possess satisfying electrocatalysis toward reduction of oxygen and hydrogen peroxide. Therefore, the MWCNTs/ZrO_2-Pt composite could be used to immobilize GOD efficiently and further retain the bioactivity of adsorbed GOD.

4. Conclusion

The MWCNTs/ZrO_2-Pt composite is a good biosensor for blood glucose determination because of their unique properties at nanoscale, MWCNTs nanostructure or incorporation of nanomaterials into MWCNTs has contributed to improving the MWCNTs functions, including large surface-to-volume ratio, enhanced conductivity, high chemical stability, excellent electrochemical catalysis of biomolecules.

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