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Graphene/AuNPs/chitosan nanocomposites film for glucose biosensing

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ABSTRACT

A novel glucose biosensor based on immobilization of glucose oxidase in thin films of chitosan containing nanocomposites of graphene and gold nanoparticles (AuNPs) at a gold electrode was developed. The resulting graphene/AuNPs/chitosan composites film exhibited good electrocatalytical activity toward H_2O_2 and O_2. The wide linear response to H_2O_2 ranging from 0.2 to 4.2 mM (R = 0.998) at −0.2 V, high sensitivity of 99.5 μA mM^{-1} cm^{-2} and good reproducibility were obtained. The good electrocatalytical activity might be attributed to the synergistic effect of graphene and AuNPs. With glucose oxidase (GOD) as a model, the graphene/AuNPs/GOD/chitosan composite-modified electrode was constructed through a simple casting method. The resulting biosensor exhibited good amperometric response to glucose with linear range from 2 to 10 mM (R = 0.999) at −0.2 V and from 2 to 14 mM (R = 0.999) at 0.5 V, good reproducibility and detection limit of 180 μM. Glucose concentration in human blood was studied preliminarily. From 2.5 to 7.5 mM, the cathodic peak currents of the biosensor decrease linearly with increasing the glucose concentrations. The graphene/AuNPs/GOD/chitosan composites film shows prominent electrochemical response to glucose, which makes a promising application for electrochemical detection of glucose.

1. Introduction

Electrochemical biosensors based upon nanomaterials have recently attracted considerable attention (Pandey et al., 2008; Valentini and Palleschi, 2008; Willner et al., 2007). The electrochemical method has many advantages, such as high sensitivity, good selectivity, fast detection and low cost, so a lot of electrochemical sensors with high sensitivity and selectivity toward many analytes have been prepared (Ahmed et al., 2008; Drummond et al., 2003). Due to their unique chemical and physical properties, many kinds of nanomaterials, such as gold nanoparticles (AuNPs) (Pingarron et al., 2008; Yanez-Sedeno and Pingarron, 2005), carbon nanotubes (Azamian et al., 2002; Lin et al., 2005; Rivas et al., 2007), metallic oxides (Hsing et al., 2007; Yang et al., 2004) and semiconductors (Vastarella and Nicastri, 2005) have been used widely in fabrication of biosensors for medical analysis, environmental monitoring, food quality control, etc. Especially, the unique properties of gold nanoparticles to provide a suitable microenvironment for biomolecules immobilization retaining their biological activity, and to facilitate electron transfer between the immobilized proteins and electrode substrates, have led to an intensive use of those nanomaterials for the construction of electrochemical biosensors with enhanced analytical performance with respect to other biosensor designs (Jia et al., 2008; Li et al., 2007b; Pingarron et al., 2008; Raj et al., 2005; Shen et al., 2005; Yang et al., 2007; Zhang et al., 2004b).

Graphene, a single layer of carbon atoms in a closely packed honeycomb two-dimensional lattice, has attracted considerable attention from both experimental and theoretical scientific communities in recent years (Geim and Novoselov, 2007; Li et al., 2008a). Due to their novel properties (Li et al., 2008b; Zhang et al., 2005) such as exceptional thermal and mechanical properties, high electrical conductivity, the graphene sheets have exhibited potential applications in synthesizing nanocomposites (Muszynski et al., 2008; Stankovich et al., 2006; Williarris et al., 2008; Xu et al., 2008) and fabricating various electrical devices, such as battery (Cassagneau and Fendler, 1998), field-effect transistors (Gilje et al., 2007), ultrasensitive sensors (Schedin et al., 2007) and electromechanical resonators (Bunch et al., 2007). Recently, biological and electrocatalytic applications of graphene have also started to be concerned. Dai et al. synthesized nanoscale graphene oxide sheets by branched polyethylene glycol (PEG) and they exhibited unique ability of graphene in the attachment and delivery of aromatic, water insoluble drugs (Liu et al., 2008). Berry et al. fabricated

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a novel graphene-based live-bacterial-hybrid device and a DNA-hybridization device with excellent sensitivity (Mohanty and Berry, 2008). Li and Wallace et al. have presented the growth of mouse fibroblast cell (L-929) on graphene paper, which indicated that the graphene paper was biocompatible and suitable for biomedical applications (Chen et al., 2008). Our group also constructed a graphene-based electrochemical glucose biosensor, which exhibited potential application of graphene in biosensors (Shan et al., 2009). However, studies to use the nanocomposites of graphene and AuNPs for electrochemical biosensor have not been reported as far as we know.

Chitosan with abundant amino groups exhibits good biocompatibility (Liu et al., 2005) and excellent film-forming ability originating from its protonation and solubility in slightly acidic solution and stability from insolubility in solution with pH over pK_a (6.3) (Sorlier et al., 2001). So it is a very suitable matrix for immobilizing bioactive molecules and constructing biosensors. Here, we constructed a novel enzyme immobilization matrix intended to combine the above-mentioned benefits of AuNPs, graphene and chitosan for biosensing applications. The resulting graphene–AuNPs–chitosan composites showed obvious electrocatalysis toward H_2O_2 and O_2. Further, when glucose oxidase (GOD) was immobilized into graphene–AuNPs–chitosan composites film, the resulting electrodes demonstrated favorable linear response to glucose.

2. Experimental

2.1. Materials

Graphite, hydrazine solution (50 wt%), ammonia solution (28 wt%) and chitosan were purchased from Sinopharm Chemical Reagent Co., Ltd. Polyvinylpyrrolidone (M_w = 360,000; PVP), $HAuCl_4{\cdot}3H_2O$ and $NaBH_4$ were obtained from Aldrich. Glucose oxidase (GOD, EC 1.1.3.4, Type X-S, lyophilized powder, 100–250 units/mg, from *Aspergillus niger*) and D-(+)-glucose (≥99.5%) were obtained from Sigma. Glucose stock solutions were stored overnight at room temperature before use. Hydrogen peroxide solution (30 wt% aqueous) was purchased from Beijing Chemicals. Unless otherwise stated, reagents were of analytical grade and used as received. Aqueous solutions were prepared with double-distilled water from a Millipore system (>18 MΩ cm).

2.2. Instruments

The UV–vis absorption spectra of graphene–AuNPs dispersion were collected using a CARY 500 Scan UV/Vis/NIR spectrophotometer. Fourier transform infrared spectroscopy (FTIR) was performed on a Bruker Vertex 70 spectrometer (2 cm^{-1} spectral resolution). Transmission electron microscopy (TEM) micrographs were obtained using a JEOL 2000 transmission electron microscopy operating at 200 kV. X-ray photoelectron spectroscopy (XPS) analysis was carried out on an ESCALAB MK II X-ray photoelectron spectrometer. Cyclic voltammetry (CV) was performed using a conventional three-electrode cell with a platinum wire as auxiliary electrode and an Ag|AgCl (saturated KCl) as reference in a CHI 660 Electrochemical Workstation (CHI, USA). Working electrodes were bare or modified gold electrodes (d = 2 mm). Before use, gold electrodes were carefully polished to a mirror finish with 1.0-, 0.3-, and 0.05-μm alumina slurries, successively. The electrolyte solution used for CV experiment was 0.05 M, pH 7.4 phosphate buffer solution (PBS). In blood sample test, mixing solution containing the same volume of normal human blood and PBS was used as electrolyte solution.

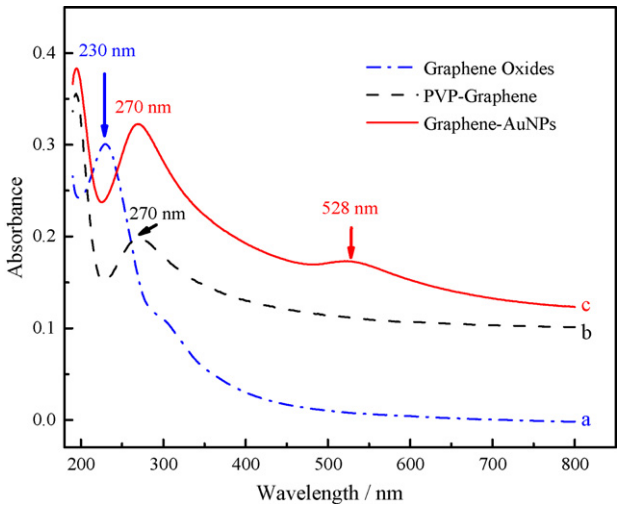

Fig. 1. UV–vis absorption spectra of (a) graphene oxides, (b) PVP-protected graphene and (c) graphene–AuNPs in water.

2.3. Synthesis of gold nanoparticles (AuNPs) and graphene nanocomposites

Graphite oxides were synthesized directly from graphite by the modified Hummers method (Hummers and Offeman, 1958; Kovtyukhova et al., 1999). The PVP-protected graphene was prepared as our previous report (Shan et al., 2009). The AuNPs-modified graphene was synthesized through the $NaBH_4$ reduction method. 2.5 mg PVP-protected graphene and 140 μL of 30 mM $HAuCl_4$ solution were dispersed into 10 mL water, and then 0.25 mL of 0.2 M $NaBH_4$ solution was added dropwise to the mixing solution under stirring. After continuously stirred for 30 min, the resulting graphene–AuNPs composites were collected by centrifugation and washed with water for three times. As a control experiment, the chitosan-protected AuNPs were also synthesized by the $NaBH_4$ reduction method. Chitosan solution (pH 5) was prepared according to previous report (Zhang et al., 2004a). 0.5 mL of 0.2 M $NaBH_4$ aqueous solution was added dropwise to 5 mL of 1.5 mM $HAuCl_4$ and 2 mg/mL chitosan solution under stirring. After stirred for 30 min, the resulting chitosan-protected AuNPs were centrifugated and washed with water for three times.

2.4. Preparation of graphene/AuNPs/GOD/chitosan electrode

1 mg graphene–AuNPs composites were added to 1 mL of 1 mg/mL chitosan aqueous solution to form homogenous dispersion with ultrasonication. 1.8 μL of the graphene–AuNPs–chitosan solution was dropped onto a gold electrode and allowed to dry in ambient air for 12 h to obtain graphene/AuNPs/chitosan-modified electrode. The graphene/AuNPs/GOD/chitosan-modified electrode was prepared by the same procedure except for dropping 1.8 μL of 1 mg/mL chitosan solution containing 5 mg/mL glucose oxidase (GOD) and 1 mg/mL graphene–AuNPs. The AuNPs/chitosan and graphene/chitosan-modified electrodes were prepared by dropping 1.8 μL of 1 mg/mL chitosan solution containing 1 mg/mL AuNPs and 1.8 μL of 1 mg/mL chitosan solution containing 1 mg/mL graphene, respectively.

3. Results and discussion

3.1. Characterizations of AuNPs-decorated graphene

The PVP-protected graphene was synthesized as our previous report (Shan et al., 2009). The successful synthesis of AuNPs-

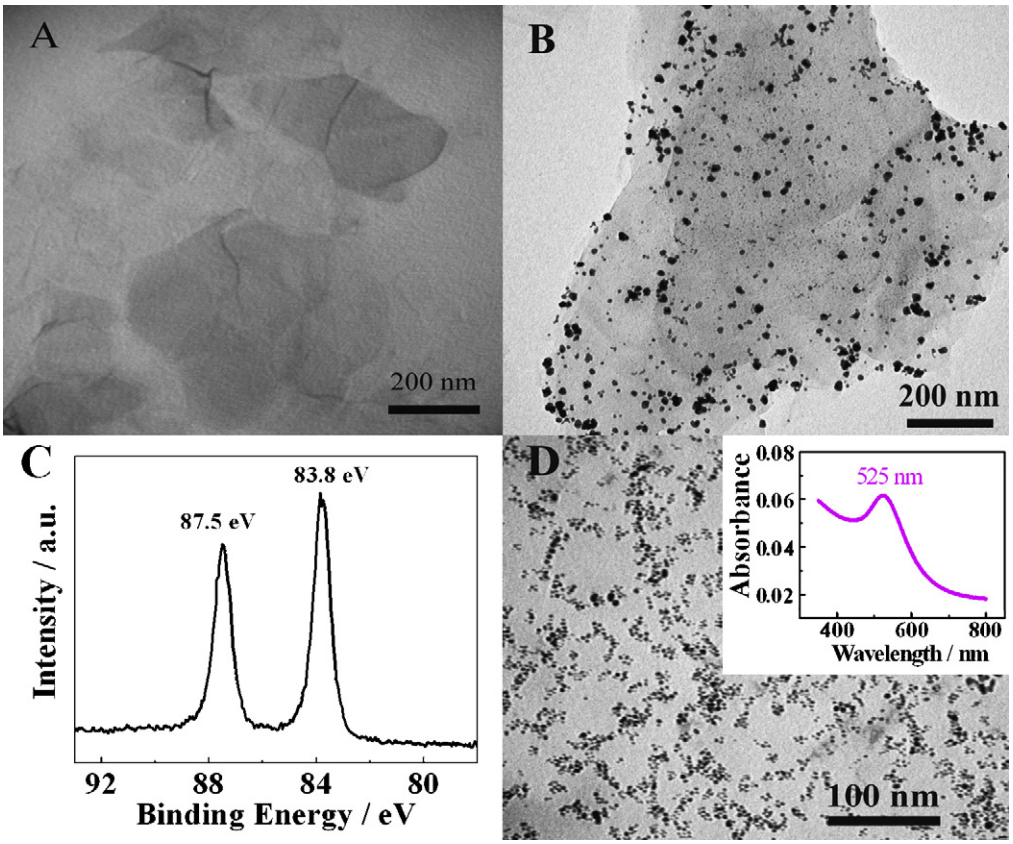

Fig. 2. TEM images of (A) PVP-protected graphene, (B) AuNPs-decorated graphene, (C) XPS spectrum of Au element in AuNPs-decorated graphene, and (D) TEM image of chitosan-protected AuNPs (corresponding UV–vis spectrum shown as inset).

decorated graphene was confirmed by UV–vis spectroscopy (Fig. 1). The UV–vis spectrum of graphene oxides (curve *a* in Fig. 1) in water shows an absorption peak at 230 nm. After formation of PVP-graphene through the hydrazine reduction, the peak of PVP-protected graphene (curve *b*) is observed at 270 nm. The absorption of PVP-protected graphene redshifts from 230 to 270 nm, suggesting that the electronic conjugation within graphene sheets is restored after the reaction (Li et al., 2008a). When AuNPs were decorated onto the graphene, the absorption peaks of graphene–AuNPs composites were observed at 270 and 528 nm (curve *c*), which was corresponding to the absorption of graphene and AuNPs.

The morphology of graphene–AuNPs was characterized further by TEM. Fig. 2A shows the TEM image of graphene nanosheets, illustrating the flake-like shapes of graphene. When the graphene was decorated with AuNPs, the TEM image shows the graphene sheets covered with AuNPs (size from 7 to 16 nm, as shown in Fig. 2B). And valence state of AuNPs was identified by XPS. The XPS spectrum of Au element in graphene–AuNPs is shown in Fig. 2C. The Au $4f_{7/2}$ peak appeared at a binding energy of 83.8 eV and the Au $4f_{5/2}$ peak appeared at 87.5 eV, confirming the formation of metallic gold (Jaramillo et al., 2003). As a control experiment, the chitosan-protected AuNPs was synthesized and characterized by the UV–vis spectroscopy and TEM. The chitosan-protected AuNPs have relatively uniform size from 3 to 7 nm from TEM image, as shown in Fig. 2D. As shown in inset of Fig. 2D, the UV–vis spectrum of AuNPs solution shows an evident absorption peak at 525 nm, which is corresponding to the absorption of AuNPs and indicates the formation of AuNPs.

3.2. Electrocatalysis of H_2O_2 at graphene/AuNPs/chitosan electrode

Graphene/AuNPs/chitosan-modified electrode exhibited high electrocatalytic activity toward H_2O_2. Fig. 3A compares the electrocatalysis toward H_2O_2 at different modified electrodes. The more obvious catalytic current and earlier onset potentials in the process of both oxidation and reduction at graphene/AuNPs/chitosan-modified electrode were observed, which indicated that graphene/AuNPs/chitosan composites had much better electrocatalysis toward H_2O_2 than other cases. This result might be attributed to the synergistic effect of graphene and AuNPs (Li et al., 2007a). Fig. 3B shows amperometric response of graphene/AuNPs/chitosan-modified electrode at −0.2 V upon successive additions of H_2O_2. As shown in the inset of Fig. 3B, a wide linear response to H_2O_2 ranging from 0.2 to 4.2 mM ($R = 0.998$) and high sensitivity of 99.5 $\mu A\,mM^{-1}\,cm^{-2}$ could be observed. In addition, the graphene/AuNPs/chitosan-modified electrode also has good reproducibility. The relative standard deviation (RSD) of the amperometric response to 1 mM H_2O_2 was 2.4% for 10 successive measurements.

In addition, the graphene/AuNPs/chitosan-modified electrode also showed an excellent reduction toward O_2. An obvious reduction wave of O_2 was observed at ca. −0.2 V (solid, red) in the presence of O_2 in phosphate buffer solution, as shown in the inset of Fig. 3A. Compared to the electrochemical reduction to O_2 (−0.3 V, dashed, blue) at graphene/chitosan-modified electrode, the graphene/AuNPs/chitosan-modified electrode had more positively reductive peak potential toward O_2.

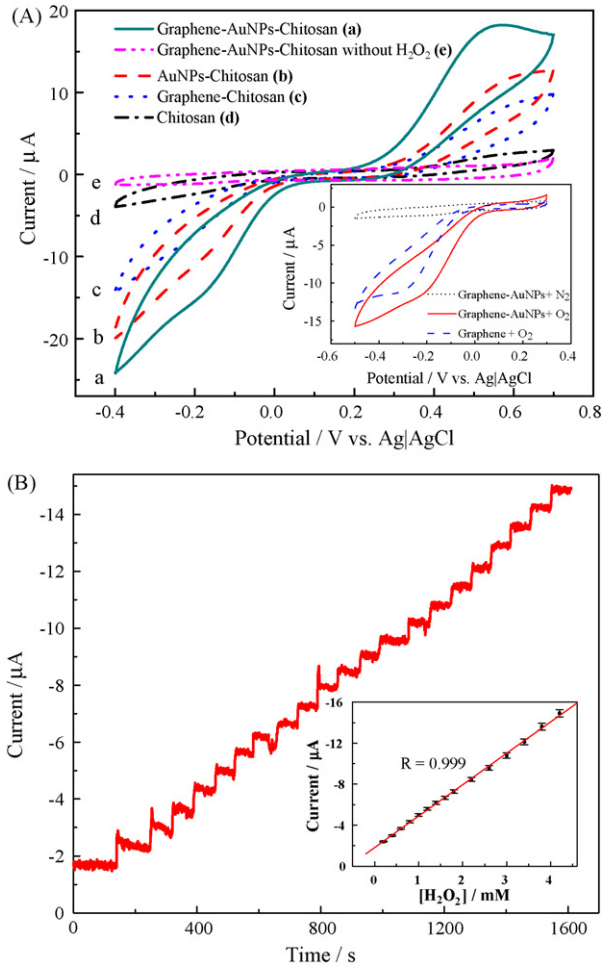

Fig. 3. (A) Cyclic voltammograms of (a) graphene/AuNPs/chitosan, (b) AuNPs/chitosan, (c) graphene/chitosan and (d) chitosan-modified electrodes in N_2-saturated phosphate buffer (0.05 M, pH 7.4) containing 2.5 mM H_2O_2, and graphene/AuNPs/chitosan-modified electrode (e) in N_2-saturated phosphate buffer. Scan rate: 0.05 V s^{-1}. The inset is cyclic voltammograms of graphene/chitosan (dashed, blue) and graphene/AuNPs/chitosan-modified electrodes (solid, red) in phosphate buffer saturated with O_2 and graphene/AuNPs/chitosan-modified electrodes in phosphate buffer saturated with N_2 (dotted, black). (B) Chronoamperometric response of graphene/AuNPs/chitosan-modified electrode in N_2-saturated phosphate buffer on injecting the concentration of H_2O_2 in 0.2 mM steps at working potential of −0.2 V. The inset is amperometric response to H_2O_2 concentration. Error bars = ±standard deviation.

3.3. Detection of glucose at graphene/AuNPs/GOD/chitosan-modified electrode

Due to its good electrocatalytical activity of graphene/AuNPs/chitosan nanocomposites to H_2O_2 and O_2, a GOD-based biosensor was further developed. The GOD was physically immobilized into the graphene/AuNPs/chitosan nanocomposite matrix prepared through casting the mixed solution containing graphene–AuNPs, GOD and chitosan directly on the electrode substrate. Fig. 4 shows the cyclic voltammograms of the resulting graphene/AuNPs/GOD/chitosan-modified electrode in various concentrations of glucose. With increase of glucose concentration, the oxidation current at positive potential also increased, while the reduction currents at negative potential decreased. It is well known that the GOD-catalysed oxidation of glucose will consume O_2 and produce H_2O_2. And the graphene/AuNPs/chitosan-modified electrode can catalyse the reactions of both H_2O_2 and O_2 (Fig. 3A), as imagined for a glucose amperometric biosensor-based GOD-modified electrode. The response increase in current at positive

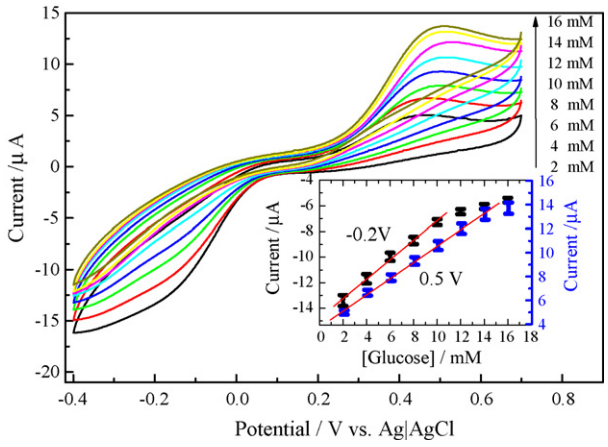

Fig. 4. Cyclic voltammetric measurements at graphene/AuNPs/chitosan-modified electrode in O_2-saturated phosphate buffer containing various concentrations of glucose: 2, 4, 6, 8, 10, 12, 14 and 16 mM from down to up. The inset is the calibration curves corresponding to amperometric responses at −0.2 and 0.5 V. Scan rate: 0.05 V s^{-1}. Error bars = ±standard deviation.

potential should come from the oxidation of produced H_2O_2, and the decrease at negative potential originated from the consumption of O_2. Although the reduction of produced H_2O_2 will result the increase in current at negatively applied potentials, it would be entirely counteracted due to the consumption of O_2.

Moreover, calibration curve corresponding to amperometric response (Fig. 4 inset) is linear against the concentrations of glucose ranging from 2 to 10 mM (R = 0.999) at −0.2 V and from 2 to 14 mM (R = 0.999) at 0.5 V. The detection limit of glucose at −0.2 V was 180 μM. The novel biosensor had good reproducibility. The relative standard deviation (RSD) of the current response to 6 mM glucose at −0.2 and 0.5 V were 3.2% and 3.5% for 10 successive measurements, respectively. The stability of the resulting biosensor was also investigated. The response currents increased by 3.2% of its initial response after 1 week and by 4.6% after half a month. Compared with those glucose biosensors based on enzyme immobilized on PtNPs–CNT matrixes (10% decrease of its initial value in 3 days) (Yang et al., 2006) or CNT–Titania–Nafion film (14% decrease after 2 weeks) (Choi et al., 2007), the graphene/AuNPs/GOD/chitosan-modified electrode (4.6% after half a month) has better storage stability. In addition, compared to the relative standard deviation (RSD) of PtNPs-based glucose biosensor (5.2% and 4.2%), (Kang et al., 2008; Yu et al., 2008) this biosensor has better reproducibility. Compared to GOD/chitosan-based biosensor (stability: 4% after 1 week; linear range: 0.6–2.8 mM), the graphene/AuNPs/GOD/chitosan-based biosensor had broader linear range and similar stability (Zhao et al., 2008).

As known, the blood glucose level of normal person ranges from 4 to 6 mM. So the linear glucose response from 2 to 10 mM based on graphene/AuNPs/GOD/chitosan nanocomposite-modified electrode is suitable for its practical application in determining blood sugar concentration. The original glucose concentration of the blood sample was hypothesized as 5 mM, and the electrolyte solution used for CV experiment was a mixing solution containing the same volume of blood and PBS. As shown in Fig. 5, the cathodic current decreases with successive addition of 1 mM glucose into the blood sample. From 2.5 to 7.5 mM, the cathodic peak currents decrease linearly with increasing the glucose concentrations (R = 0.991, the inset of Fig. 5). And the relative standard deviation (RSD) of the current response to 4.5 mM glucose was 4.7% for 6 successive measurements. Therefore, our reduction method can eliminate the interference of other molecules in blood, which makes it a promising candidate to determine blood sugar concentration in the practical clinical analysis. The

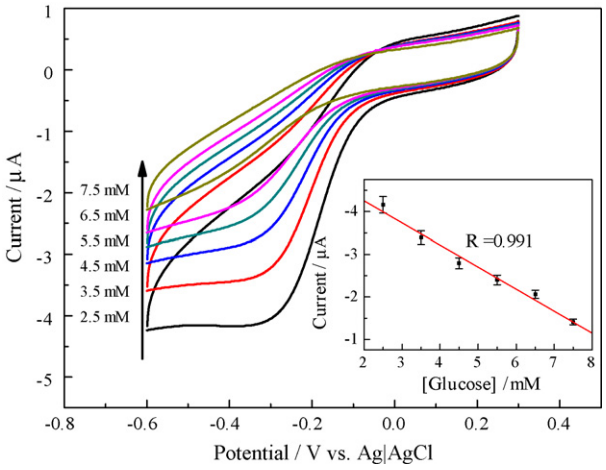

Fig. 5. CV grams at graphene/AuNPs/GOD/chitosan-modified electrode in real blood sample and PBS mixing solutions containing 2.5, 3.5, 4.5, 5.5, 6.5 and 7.5 mM glucose from down to up. Inset is the calibration curve corresponding to amperometric responses. Scan rate: 0.05 V s^{-1}. Error bar = ±standard deviation.

reproducibility of graphene/AuNPs/GOD/chitosan film-modified electrode (RSD = 4.7%) has similar results compared to some commercially marketed glucose sensors (RSD = 3–6%) (Chen et al., 1998; Dai et al., 2004; Rivers et al., 2006). The linearity and sensitivity (0.55 μA mM^{-1}) of the proposed biosensor appear to be enough for glucose measurements in blood samples.

4. Conclusion

In sum, we have successfully constructed a novel and biocompatible graphene/AuNPs/chitosan nanocomposites at the electrode. The resulting graphene/AuNPs/chitosan electrode showed high electrocatalytic activity toward H_2O_2 and O_2. The synergistic effect of graphene and AuNPs may promote the electrocalalysis toward H_2O_2. The high sensitivity and good stability at such a modified electrode led us to construct a practical glucose biosensor successfully, which could also be extended to the immobilization of some other biomolecules.

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