GRAPHENE LAMINATION FOR HIGH GLUCOSE OXIDASE LOADING AND SENSITIVE GLUCOSE DETECTION

Yabin. Hao, Minghe. Fang, Zhe. Ying, You. Zeng*

* Shenyang National Laboratory for Materials Science, Institute of Metal Research, Chinese Academy of Science, 72 Wenhua Rd., Shenyang 110016, China, E-mail: yzeng@imr.ac.cn

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ABSTRACT

Graphene oxide (GO) has received considerable attention in real-time glucose detection due to its high surface area, excellent electrical conductivity and good biocompatibility. However, the reactive sites of GO increases background current of biosensors, which makes a current offset and limits the sensitivity. In this work, functional graphene (FG) and electrochemically reduced graphene oxide (RGO) was laminated on the surface of glass carbon electrodes, then the glucose oxidase (GOD) was absorbed on the graphene lamination layers, and thereafter chitosan (CS) was casted onto the obtained electrodes. This FG-RGO-GOD-CS electrode shows faster heterogeneous electron transfer rate (3.557 s^{-1}) and much higher enzyme loading (3.80 × 10^{-9} mol/cm^2) as compared with other graphene oxide-based biosensors. As shows in figure 1, the cathodic current decreases linearly with the increase of glucose concentration, and the sensitivity is calculated to be 72.29 μA mM^{-1} cm^{-2}. With the advantage of facile fabrication, high conductivity and high enzyme loading, the FG-RGO lamination structure may be a good candidate in the production of cost-effective biosensors and biofuel cells.

1 INTRODUCTION

Diabetes mellitus is one of the most prevalent chronic diseases in the world[1]. It is diagnosed as blood glucose concentration is higher than normal range. Therefore, it is of great significance to determine and monitor blood glucose concentration in a sensitive, fast and accurate way. With the demand of diagnostic analysis of diabetes, a lot of works have focused on the detection of glucose, such like skin test, blood electrochemistry measurement and saliva diagnose. Electrochemical biosensors, with the advantages of low cost, simplicity, portability and fast exhibition, are widely used in glucose detection. A wide variety of nanomaterials, such like conducting polymer[2], metal oxide[3], and mesoporous silica[4], have been reported as electrode materials for the fabrication of glucose biosensor.

Recently, carbon materials such as carbon nanotubes (CNTs) and graphene are proved as promising electrode materials and received considerable attention in real-time glucose detection. Graphene, a well-defined monolayer of carbon atoms in a two-dimensional honeycomb lattice, is specially adapted for the use of glucose detection due to its exceptional physicochemical properties[5]. Its high surface area (theoretically, 2630 m^2/g for single-layer graphene) and biocompatibility are favorable for increase the loading of the target enzyme, glucose oxidase (GOD), which catalyzes glucose to Glucono-δ-lactone and produces electric signal; the excellent electrical conductivity and small band gap of graphene are beneficial to directly conduct electrons from GOD to the electrode surface[6]. Furthermore, compared

with CNTs, graphene can be obtained easily by chemical exfoliation of the graphite.

A lot of glucose biosensor works have employed graphene and graphene composites as electrode materials to immobilize GOD[6,7]. However, few of them give their attention to the problem that the reactive sites of graphene oxide (GO) increases background current of biosensors, which makes a current offset and limits the sensitivity. Notably, in order to increase the loading of GOD, functional groups of GO should be increased, but inevitably sacrificing eletrical conductivity. To solve this conflicting problem, functional graphene was used in this work.

2 EXPERIMENTS

Graphene prepared by thermal expansion exfoliation from graphite was slightly oxidized to be functional graphene (FG). FG and GO was laminated on the surface of glass carbon electrodes, then GOD was absorbed on the graphene lamination layers, and thereafter chitosan (CS) was casted onto the obtained electrodes. The FG-GO-GOD-CS electrode was electrochemically reduced to RFG-RGO-GOD-CS, making FG and GO more conductive.

3 RESULTS & DISCUSSION

As is shown in fig.1, the semicircle of the RFG plot was dismissed and only a linear line was seen, while the semicircle of the RGO still remained. The EIS curve in figure 1 indicates that the conductivity of RFG film is better than RGO film, so the RFG film greatly improves the conductivity and the electron transfer process. The redox peak potentials of GOD shifted slightly with the increase of scan rate.

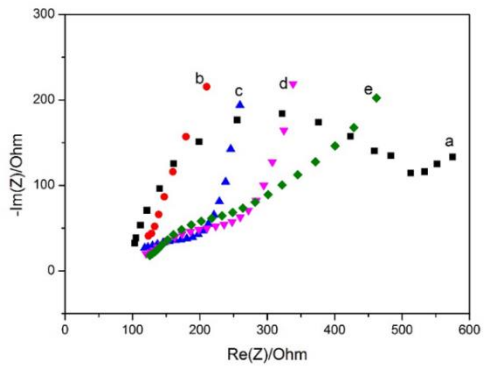

Figure 1. Nyquist plot of EIS for (a) GCE; (b) GCE-RFG; (c) GCE-RFG-RGO; (d) GCE-RFG-RGO-GOD; (e) GCE-RFG-RGO-GOD-CS.

The influence of the scan rate on the cyclic voltammetric performance of the RFG-RGO–GOD–CS/GCE was investigated in Figure 2. The anodic peak current and cathodic peak current increase linearly with the increase of scan rate ranging from 25 to 300 mV s^{-1}. The redox processes of the GOD–RFG-RGO–CS nanocomposite gave roughly symmetric anodic and cathodic peaks at relatively slow scan rates. When the scan rate increases, the redox potentials of GOD shift slightly. This RFG-RGO-GOD-CS electrode shows faster heterogeneous electron transfer rate (3.557 s^{-1}) and much higher enzyme loading (3.80×10^{-9} mol/cm^2) as compared with other graphene oxide-based biosensors.

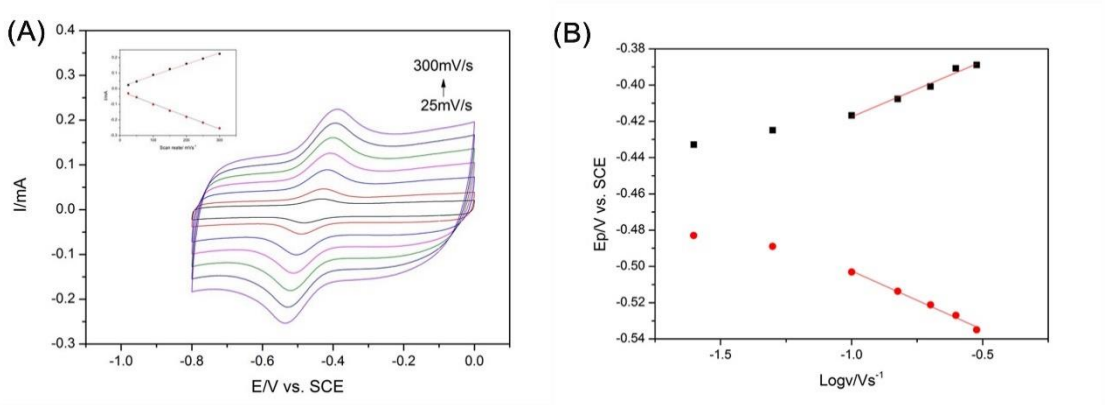

Figure 2. (A) Cyclic voltammograms of the modified GCE with GOD–RFG-RGO–CS film in PBS with 0.1 M KCl at different scan rates (from inner to outside): 25, 50, 100, 150, 200, 250 and 300 mV s^{-1}, inset is the plot of the peak current vs. scan rates. The redox peak potentials of GOD shifted slightly with the increase of scan rate. (B) The relationship of the peak potential (Ep) vs. the logarithm of scan rate (log v), the linear fitting at scan rates from 100 mVs^{-1} to 300 mVs^{-1}.

As is shown in figure 3, the cathodic current decreases linearly with the increase of glucose concentration, and the sensitivity is calculated to be 72.29 μA mM^{-1} cm^{-2}, which is higher than other GO-based biosensors. With the advantage of facile fabrication, high conductivity and high enzyme loading, the FG-RGO lamination structure may be a good candidate in the production of cost-effective biosensors and biofuel cells.

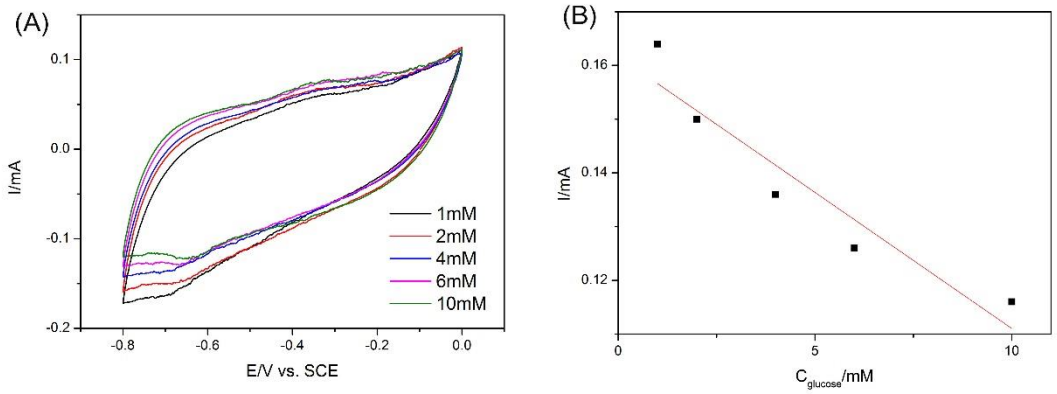

Figure 3. (A) Cyclic voltammograms of RFG-RGO–GOD–CS/GCE in PBS with 0.1 M KCl at a scan rate of 100 mVs^{-1} in the presence of different concentrations of glucose: 1, 2, 4, 6, 10mM, respectively; (B) plot of cathodic current at −0.60 V of FG-RGO–GOD–CS/GCE versus glucose concentrations.

4 CONCLUSIONS

Lamination of functional graphene and graphene oxidase achieves direct electron transfer of GOD and is efficient for glucose sensing. Lamination of double layers graphene apparently increases the peak current of the biosensor. The peak current of the biosensor changes linearly with scan rate, pH and glucose concentration. The sensitivity of the prepared biosensor is 72 μA mM^{-1} cm^{-1}. With the advantage

of facile fabrication, high conductivity and high enzyme loading, the FG-RGO lamination structure may be a good candidate in the production of cost-effective biosensors and biofuel cells.

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