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Carbon Nanotube-Ionic Liquid Composite gel based high-performance bioanode for glucose/O₂ biofuel cells

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An easy-operation and high-performance bioanode based on the composite gel of carbon nanotubes (CNTs) and ionic liquid (IL) was developed for glucose/O₂ biofuel cell (BFC). Ferrocenecarboxaldehyde (Fc) was used as the mediator and covalently immobilized on the ethylenediamine (EDA)-functionalized CNTs (CNTs-EDA). Glucose oxidase (GOD) was conveniently incorporated into the composite gel by simply grinding GOD with the CNTs-Fc/IL gel. The resulted electrode (GOD@CNTs-Fc/IL gel modified glassy carbon (GC) electrode) exhibited good catalytic activity and stability towards glucose oxidation. For the assembled glucose/O₂ BFC with the GOD@CNTs-Fc/IL gel modified GC electrode as the bioanode and a commercial E-TEK Pt/C modified GC electrode as the cathode, the open circuit potential is 0.66 V and the maximum power density of 60 $\mu\text{W cm}^{-2}$ can be achieved at 0.23 V. The ease preparation, high activity and stability of the enzyme electrode based on the CNTs/IL gel can bring about a relatively general approach for fabricating biofuel cells and biosensors.

Introduction

The gradual depletion of fossil fuels, the increasing energy need and the impressing problem of environment pollution have stimulated a wide range of R&D efforts for renewable and environment friendly energy.¹ Enzymatic biofuel cells (EBFCs), which can directly covert chemical energy to electrical energy using enzyme as catalyst,² have attracted much attention in recent decades, due to widely available biomass fuels, good biocompatibility and operability under ambient temperature.^{3,4} However, effective immobilization of enzyme at the electrode and efficient electrical communication between the redox active centers of the enzyme and the electrode are essential for the practical applications of EBFCs in portable power sources and medical implantable devices,^{5,6} as the electron-transferring unit of the enzyme is deeply embedded inside its complex protein structure.^{7,8} So far, various approaches have been considered to facilitate the electron transfer between the redox center of the enzyme and the electrode surface. These methodologies involve enzyme immobilization by physical adsorption,^{9,10} entrapment and encapsulation in sol-gels or polymers by chemical covalent binding on the surface of different support materials,¹¹⁻¹³ and use of electron mediators^{14,15} or combination of some of these.^{16,17} Even though, each of

the method reveals some advantages, the different means also introduce certain drawbacks and limitation. For example, it is difficult to maintain the stability by physically immobilization due to the continuous leakage of the enzyme into the electrolyte during operation.¹⁸ In turn, the covalent immobilization of enzyme enhances the enzyme stability, but usually leads to a loss of enzyme activity during the immobilization process.¹⁹ In addition, the co-immobilization of enzymes and mediator mainly based on the entrapment or encapsulation in polymeric matrices, also easily diffuse away from the electrode matrix into the bulk solution under the continuous operation of biofuel cells, which deteriorates the performance and lifetime of the cell.²⁰

In this regard, the effective electrical contacting of redox enzymes with electrode supports and the cell continuously operating for long periods of the enzyme electrode are still the key engineering problems for the development of high quality BFC.

On the other hand, electrochemical usage of ionic liquid (IL) and carbon nanotubes (CNTs) have been reported in a number of research and application fields, due to their unique properties.^{21,22} CNTs have been utilized as an ideal conducting materials and supports to facilitate electron transfer owing to their high electrical conductivity, electrochemical stability, great specific surface area and unique structure.^{23,24} IL has also attracted extensive electrochemical studies because of the wide electrochemical window, high ionic conductivity and good

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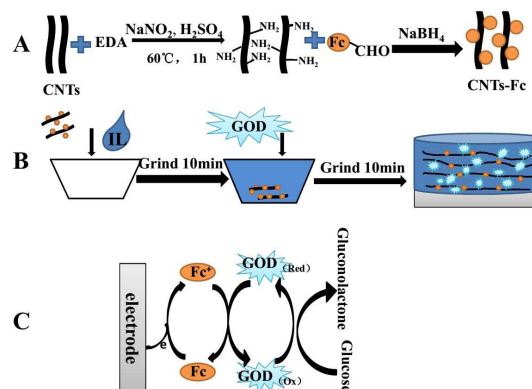
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thermal stability.²⁵ It is reasonably speculated that a combination of IL and CNTs could provide promising composite materials for preparing high performance enzyme electrodes. Firstly, the composite of IL and CNTs could benefit from IL and CNTs, and possesses good electronic and ionic conductivity, high thermal stability.²⁶ Moreover, IL is suggested to suppress CNTs tangling²⁷ and well known as good solvents for enzymes with their good biocompatibility, which makes them be a good media for biocatalysis.²⁸ In addition, the combination of CNTs and IL tends to form a homogeneous CNTs/IL bucky gel due to the inherent interaction between IL and CNTs, which makes such a protocol practically realizable.^{29,30}

Up to date, one type of gel formed by grinding CNTs and IL together have been reported useful in electrocatalysis, electrochemical sensor and biosensors due to the very attractive electrochemical performances. For example, Yu et al²⁶ prepared a novel kind of multifunctional material active for the 4 e-reduction of O₂ through rational functionalization of the MWCNT/IL bucky gel with dual tailor-made electrocatalysis of cobalt porphyrin (Cop) and prussian blue nanoparticles (PB-NPs), and the resulted multifunctional material exhibited a high electrocatalytic activity toward the apparent 4e-reduction of O₂ due to the good electronic and ionic conductivity originated from CNTs and IL. This work demonstrated that the bucky gel can serve as a "reservoir" to homogeneously accommodate electrocatalysts with enhanced electrocatalytic activity. Sun et. al³¹ also reported that Fc-filled single-walled carbon nanotubes (Fc@SWNTs)-gel, formed by grinding Fc@SWNTs and 1-butyl-3-methylimidazolium hexafluorophosphate [(BMI)PF₆] in an agate mortar, showed good electrochemical reversibility and excellent electron-transfer mediation for oxidation of H₂O₂ to O₂ and reduction to H₂O, due to the formation of the gel leading to an untangling of the heavily entangled SWNT bundles and great enhancement of the conductivity from the combination of ionic conductivity of (BMI)PF₆ IL and electrical conductivity of the SWNTs. In addition, a highly sensitive, stable and robust electrode has been fabricated by mixing MWCNT with IL and used for sensing different targets such as ascorbic acid, ferricyanide, NADH, and H₂O₂.

These researches imply that the CNTs/IL gel combines the unique and attractive electrocatalytic behavior of carbon nanotubes and IL and shows good electrochemical performance and could be promising in constructing novel chemical and biosensors and BFCs.

As far as we know, there are almost no reports focusing on the application of CNTs/IL gel in BFCs. In this work, we expect to develop an enzyme anode with high performance as the bioanode for a glucose/O₂ BFC based on the good features of CNTs/IL gel. As shown in scheme 1, Fc was firstly covalently bound on the CNT surface, and the obtained Fc-modified CNTs (CNTs-Fc) were ground with IL to form CNTs-Fc/IL gel. Then, GOD was solved in the homogeneous media of the CNTs-Fc/IL gel by further grind to prepare an enzyme electrode (GOD@CNTs-Fc/IL gel modified GC electrode), and the electrochemical properties of the enzyme electrode were characterized by typical electrochemical methods. In addition, we also constructed a BFC with the GOD@CNTs-Fc/IL gel modified GC electrode as the anode, a commercial E-TEK Pt/C modified GC electrode as the cathode, and Nafion 117 film as the membrane, and the performance of the resulting BFC was then further evaluated.



Scheme 1. Schematic illustration for the preparation of CNTs-Fc (A), CNTs-Fc/IL gel and GOD@CNTs-Fc/IL gel modified GC electrode (B), Pathway for GOD catalytical oxidation of glucose with Fc as electron mediator (C).

Results and discussion

FTIR characterization of CNTs-Fc

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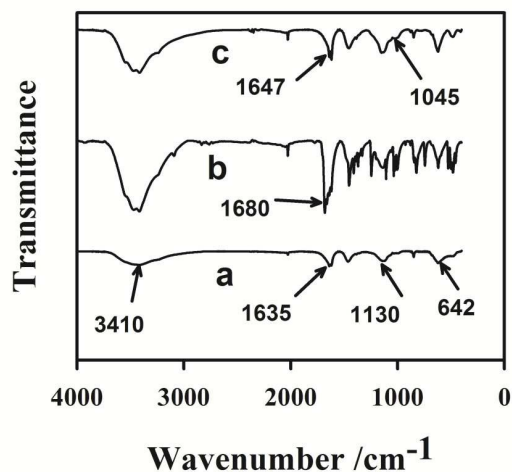


Fig. 1 FTIR spectra of CNTs-EDA (a), pure Fc (b) and CNTs-Fc (c).

The FTIR spectra of CNTs-EDA (curve a), pure Fc (curve b) and CNTs-Fc (curve c) are shown in Fig. 1. The FTIR results are basically in agreement with previous work.³⁴ In Fig. 1a, the characteristic peaks of N–H stretching vibration at 3410 cm⁻¹, and in-plane scissoring vibration at 1635 cm⁻¹ and C–N stretching vibration at 1130 cm⁻¹ from primary amine are observed, confirming the covalent modification of EDA on the CNTs. From Fig. 1b, the peak at 1680 cm⁻¹ assigned to the stretching vibration of carbonyl from the aldehyde group of Fc can be observed, indicating that the aldehyde group has already reacted with the –NH₂ group on CNTs-EDA through the Schiff-based reaction. After reduced by NaBH₄, the obtained CNTs-Fc shows the characteristic peaks of the C=O stretching of –CON at 1647 cm⁻¹ and the asymmetric stretching vibrational of –CON at 1045 cm⁻¹ (Fig. 1c), implying the successful immobilization of Fc on the CNTs.

Electrochemical characterization of the GOD@CNTs-Fc/IL gel modified GC electrode

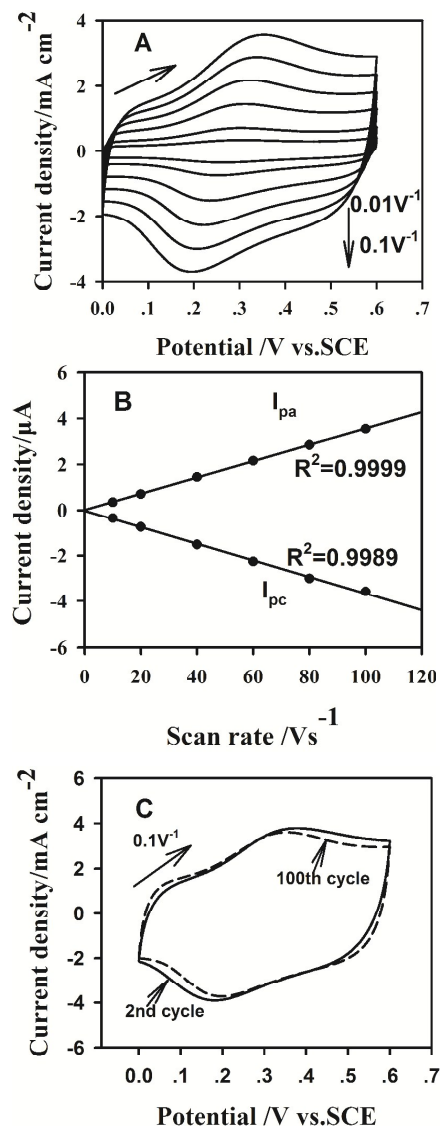


Fig. 2 Electrochemical characterization of the GOD@CNTs-Fc/IL gel modified GC electrode. (A) CV curves obtained in 0.1 M PBS (pH 7) at different scan rates, (B) the plot of anodic and cathodic peak current vs. scan rate based on (A) and (C) the repetitive potential sweep test at a scan rate of 100 mV s⁻¹.

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To confirm the enzymatic activity, the electrocatalysis of the GOD@CNTs-Fc/IL gel modified GC electrode toward glucose was also measured by cyclic voltammetry. Fig. 3A shows CVs of the GOD@CNTs-Fc/IL gel modified electrode in 0.1 M PBS (pH 7.0) solution with (curve a) and without (curve b) 80 mM glucose. As comparison, CVs of the GOD@CNTs-Fc modified GC electrode measured at the same condition are also shown in Fig. 3B. In 0.1 M PBS solution without glucose (curve b, in Fig. 3A), a pair of redox peaks with a formal potential of 0.27 V appeared, corresponding to the redox of Fc. After adding glucose into the buffer solution (curve a, in Fig. 3A), the anodic peak current increases distinctly, indicating that a typical electrocatalytic oxidation of glucose by GOD with Fc as mediator occurs at the GOD@CNTs-Fc/IL gel modified electrode. Here, the increment of the oxidation peak current density (with glucose vs. without glucose) is defined as the catalytic current density (ΔI_p). By comparing Fig. 3A with Fig. 3B, it is noted that the catalytic current density at the GOD@CNTs-Fc/IL gel modified electrode (0.75 mA cm^{-2}) is 15 times higher than that at the GOD@CNTs-Fc modified electrode (Fig. 3B). This might be attributed to the effective electron transfer among GOD, Fc and the electrode, and the excellent biocompatibility of the IL.

In addition, the stability of the GOD@CNTs-Fc/IL gel modified electrode was also evaluated by adopting the long-term cycle voltammetry test and the corresponding results are shown in the Fig. 3C. It is noted that the value of $I_p(n)/I_p(1)$ (the ratio between the current densities of the forward oxidation peak at the corresponding cycles and the first cycle) for the GOD@CNTs-Fc/IL gel modified electrode shows an obvious slower decrease (19%, Fig. 3C a) during the 500 cycles compared with that for GOD@CNTs-Fc (67%, Fig. 3C b), implying the satisfactory electrochemical stability of the GOD@CNTs-Fc/IL gel modified electrode.

The excellent electrocatalytic activity and good long-term stability of the GOD@CNTs-Fc/IL gel modified electrode toward glucose oxidation might be useful for the development of GOD-based bioanode of BFC.

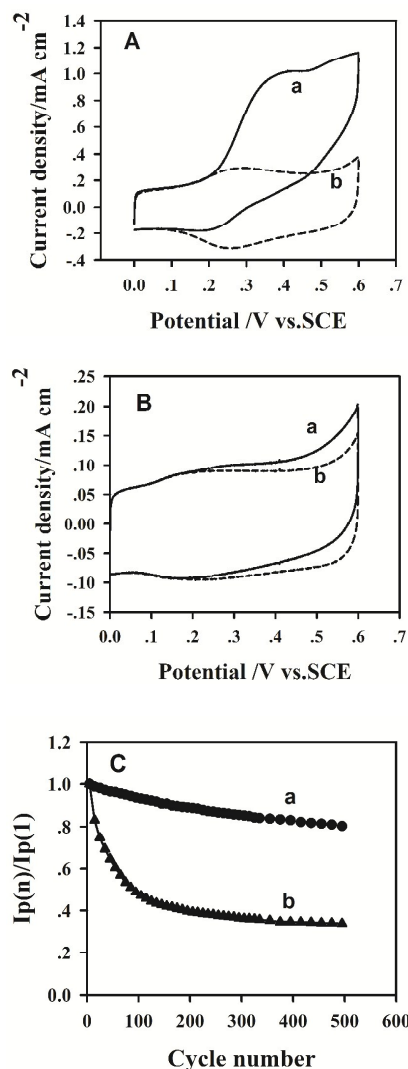


Fig. 3 Cyclic voltammograms of the GOD@CNTs-Fc/IL gel modified GC electrode (A) and the GOD@CNTs-Fc modified electrode (B) in the presence of 0.08 M glucose (curve a) and absence of glucose (curve b) in 0.1 M PBS (pH 7) at 0.01 V s^{-1} . Long-term cycle stability (C) of the GOD@CNTs-Fc/IL gel electrode (curve a) and the GOD@CNTs-Fc modified electrode (curve b) in 0.1 M PBS (pH 7) with 0.08 M glucose at 0.1 V s^{-1} (curve a).

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Parameters optimization for the preparation of the bioanode

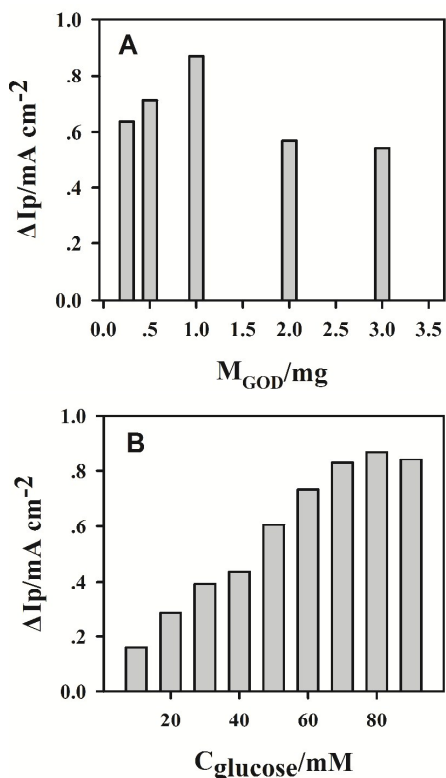


Fig. 4 The dependence of the (A) the amount of GOD (M_{GOD}) in the CNTs-Fc/IL gel for the preparation of the GOD@CNTs-Fc/IL gel (pH 7.0, $C_{glucose} = 80$ mM), (B) Glucose concentration (pH 7.0, $M_{GOD} = 1.0$ mg) on the ΔI_p value of the GOD@CNTs-Fc/IL gel electrode. Electrolyte solution, 0.1 M PBS; scan rate, 10 mV s⁻¹.

The content of GOD in the CNTs-Fc/IL gel should affect the electrochemical performance of the GOD@CNTs-Fc/IL gel modified electrode for glucose oxidation, therefore, it is necessary to optimize the GOD content during the preparation of the GOD@CNTs-Fc/IL gel. Fig. 4A shows the histogram of the dependence of ΔI_p on the amount of GOD (M_{GOD}) in the CNTs-Fc/IL gel (including 0.1 mL of IL and 100 mg of CNTs-Fc) for the preparation of the GOD@CNTs-Fc/IL gel. From Fig. 4A, it can be observed that

the value of ΔI_p increases with the increase of M_{GOD} , and then reaches the maximum value at $M_{GOD} = 1.0$ mg. Therefore, GOD@CNTs-Fc/IL gel prepared by grinding 1.0 mg of GOD with the CNTs-Fc/IL gel was adopted as the optimum proportion for the preparation of the bioanode.

The effect of the glucose concentration on the value of ΔI_p at the GOD@CNTs-Fc/IL gel modified electrode is also measured, and the plot of ΔI_p versus glucose concentration is shown in Fig. 4B. As shown in Fig. 4B, the ΔI_p value increases with the increase of glucose concentration and then approximately reaches a plateau of 0.87 mA cm⁻² at glucose concentration higher than 80 mM. Based on the above results, the performance of the bioanode and the assembled glucose/O₂ BFC would be further evaluated in the PBS containing 80 mM glucose.

Performance of the biofuel cell

Taking the GOD@CNTs-Fc/IL gel modified GC electrode as a bioanode and the commercial E-TEK Pt/C modified GC electrode as the cathode, the performance of the corresponding BFC (BFC1) was investigated in a PBS (pH 7.0) containing 80 mM glucose at room temperature. For comparison, the BFC (BFC2) with the GOD@CNTs-Fc modified electrode as the bioanode and the commercial E-TEK Pt/C modified electrode as the cathode was also evaluated. Fig. 5 presents the current and the power density of BFC1 and BFC2 as a function of the operating cell voltage (I-V and I-P curves). As shown in Fig. 5A, the open-circuit voltage (V_{oc}), the short-circuit current and the maximum power density (P_{max}) of BFC1 are 0.66 V, 0.45 mA cm⁻² and 60 μ W cm⁻² (at 0.23V), respectively. However, V_{oc} , the short-circuit current and P_{max} of BFC2 (Fig. 5B) are 0.64 V, 0.043 mA cm⁻² and 5.3 μ W cm⁻² (at 0.27V), respectively. Inspiring, the P_{max} value of the GOD@CNTs-Fc/IL gel based BFC is almost 12 times larger than that of the GOD@CNTs-Fc based BFC. Furthermore, the value of the power density of the GOD@CNTs-Fc/IL gel based BFC is about 1.2 times higher than that (50.7 μ W cm⁻²) in the case of co-immobilizing GOD and Fc on the electrodes³⁴ and much higher than that (24.50 μ W cm⁻²) in the case that graphene nanosheets were used as the electrode material to immobilize the enzyme and mediator.³⁷

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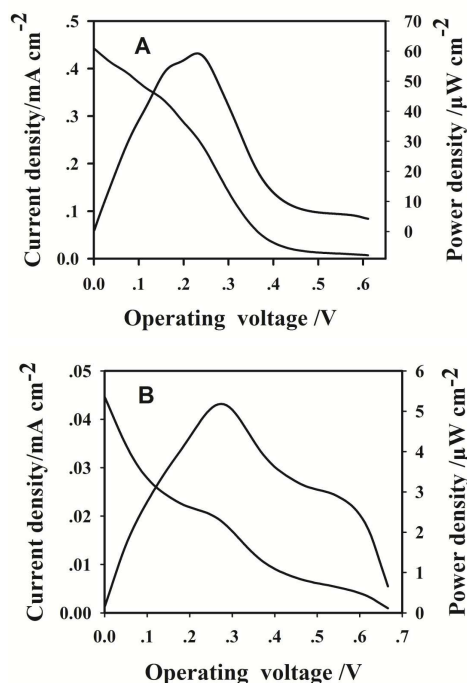


Fig. 5 The power output characteristics of the prepared glucose biofuel cell obtained by LSV at 0.001 V s^{-1} at $25 \text{ }^\circ\text{C}$. Bioanode, the GOD@CNTs-Fc/IL gel modified GC electrode (A) and the GOD@CNTs-Fc modified GC electrode (B) in 0.1 M PBS (pH 7) with 80 mM glucose; biocathode, E-TEK Pt/C modified GC electrode in 1 M H_2SO_4 solution (pH 1.0).

These considerable performances of the glucose/ O_2 BFC based on the GOD@CNTs-Fc/IL gel modified bioanode could be ascribed as follows: the uniform dispersion of CNTs in the medium of ionic liquid and the good electronic and ionic conductivity originated from CNTs and IL benefit to the fast electron transfer between enzyme and electrode; the embedding of enzyme in the CNTs / IL gel and the excellent biocompatibility of the CNTs / IL gel contribute to enhance the activity and stability of enzyme.

Conclusions

In this work, a high performance bioanode based on the composite gel of Fc modified CNTs and ionic liquid (IL) has been developed successfully. Combined the unique and attractive electrocatalytic behavior of carbon nanotubes and IL, the obtained GOD@CNTs-Fc/IL gel modified bioanode shows not only excellent catalytic activity for glucose oxidation, but also good stability. The assembled glucose/ O_2 BFC with the GOD@CNTs-Fc/IL gel modified electrode as the bioanode and a commercial E-TEK Pt/C modified GC electrode as the cathode exhibits an open circuit potential of 0.66 V and the maximum power density of $60 \mu\text{W cm}^{-2}$ at 0.23 V . It is expected that the CNTs-Fc/IL composite gel will be helpful to promote the practical application of BFCs and also useful for the development of bioreactors and biosensors.

Experimental

Reagents and materials

Glucose oxidase (GOD, from *Aspergillus niger*, 150,000 units g⁻¹, EC 1.1.3.4), and ferrocenecarboxaldehyde (Fc) was purchased from Sigma-Aldrich and used as received. E-TEK Pt/C (20%) catalyst was purchased from De Nora Elettrodi. Nafion 117 membrane was purchased from Alfa-Aesar and also used as received. Multi-walled CNTs (diameter, 20-40 nm) were purchased from Shenzhen Nanotech Port Co. 1-Butyl-3-Methylimidazolium Hexafluorophosphate ((BMI)FP₆, from Damas-beta), ethanol, N, N-dimethyl formamide (DMF) and other reagents were of analytical grade. Phosphate buffer solutions (PBS) and other aqueous solutions were prepared with doubly distilled water.

Preparation of Fc modified CNTs

Fc modified CNTs were prepared according to the literatures.^{13,32-34} In brief, the pristine CNTs (70 mg) were firstly mixed with NaNO_2 (93 mg) and EDA (85 mg). After that, concentrated H_2SO_4 (0.061 mL) was added into the above suspension with continuous stirring and the mixture was heated for 1 h at $60 \text{ }^\circ\text{C}$. After cooling, the obtained mixture was centrifuged and washed with DMF and water for several times to remove the unreacted EDA and finally dried at room temperature to obtain CNTs-EDA. Secondly, the resulted CNTs-EDA (30 mg) was dispersed in 10 mL of water under ultrasonication for half an hour, and then Fc

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aqueous solution (20 mL, 7 mg mL⁻¹) was added with stirring for 2 h at room temperature. Then, NaBH₄ (20 mg) was added into the above mixture. After stirring for another 24 h, the final product, denoted as CNTs-Fc, was centrifuged, washed with methanol and water to remove the dissociative Fc, and dried at room temperature. Fourier transform infrared (FTIR) spectroscopy (Nicolet 6700) was used to examine the prepared CNTs-Fc.

Preparation and characterization of the GOD@CNTs-Fc/IL gel modified GC electrode

Preparation of the GOD@CNTs-Fc/IL gel modified electrode was briefly illustrated as follows: IL (0.1 mL) was ground with CNTs-Fc (100 mg) for 10 min to obtain a composite gel (CNTs-Fc/IL gel) using pestle and mortar. Then, a certain amount of GOD (M_{GOD}) was ground with the above CNTs-Fc/IL gel using pestle and mortar for another 10 min to form GOD@CNTs-Fc/IL gel. Finally, to prepare the GOD@CNTs-Fc/IL gel modified electrode, a definite weight (4 mg) of the resulted black gel (GOD@CNTs-Fc/IL gel) was coated onto the surface of GC electrode (3 mm in diameter) which was well-polished with 300 and 500 nm alumina slurry in advance and stored at 4 °C for 48 hours before use. The electrochemical properties of the electrode were investigated on a CHI660D electrochemical workstation (Shanghai Chenhua Instruments Company, China). A conventional three-electrode cell was used with the GOD@CNTs-Fc/IL gel modified electrode as the working electrode, platinum wire as the counter electrode and saturated calomel electrode (SCE) as the reference electrode. All electrochemical experiments were carried out at 25 °C, and the working electrode surface was rinsed carefully with double distilled water prior to each electrochemical measurement.

To compare the differences between the developed enzyme electrode based on the CNTs-Fc/IL gel and the traditional enzyme electrode, the GOD@CNTs-Fc modified electrode was also prepared as follows: CNTs-Fc (10 mg) and GOD (1 mg) were dispersed into 1 mL of ultrapure water under ultrasonicating condition. Then, A definite volume (20 μL) of the resulted solution was transferred with a micro-syringe to the surface of the well-polished GC electrode (3 mm in diameter) and dried at 4 °C.

The performance of the BFC

To assemble a glucose/O₂ BFC, the GOD@CNTs-Fc/IL gel modified GC electrode immersed in 0.1 M PBS (pH 7.0) containing 80 mM glucose was used as the bioanode and an E-TEK Pt/C modified GC electrode immersed in 1 M sulfuric acid solution (pH 1.0) with continuously bumping oxygen was used as the cathode. For comparison, the GOD@CNTs-Fc modified GC electrode was also used as the bioanode to assemble a glucose/O₂ BFC in the same way. The E-TEK Pt/C electrode was prepared by casting 10 μL of 4 mg mL⁻¹ commercial E-TEK Pt/C (20%) on the well-polished GC electrode. Nafion 117 film was used as a separator (membrane) between two electrodes. Linear sweep voltammetry (LSV) was used to evaluate the performance of the BFC.

Acknowledgements

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