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Glucose Electrocatalysis of Multi-walled Carbon Nanotubes/Polyvinyl Alcohol Conducting Hydrogel Composite Platinum Electrode

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Abstract: A porous conductive hydrogel electrode film of multi-walled carbon nanotubes (MWCNTs)/polyvinyl alcohol (PVA) was prepared by electrophoretic deposition technology, and the selective catalytic ability of MWCNTs/PVA on glucose was verified by cyclic voltammetry and open-circuit voltage. The electrochemical and physicochemical properties of MWCNTs/PVA porous conductive hydrogel electrode films were also characterized. The synergistic catalytic effects of MWCNTs/PVA porous conductive hydrogel electrode films and platinum electrode on the electrochemical oxidation of glucose in different PH solutions were studied.

Keywords: Conductive Hydrogels; Implantable Fuel Cells; Platinum Electrode.

1. Introduction

With the development of low power MEMS implantable devices, providing long-term stable power supply for implantable micro-power devices has become a research hotspot. It is a feasible way to solve the problem of power supply in vivo to study the non-biological catalytic implantation of glucose fuel cells with simple structure, high energy density, long-term stable performance and high biological safety. Implant surface glucose fuel cell is a promising type of non-biocatalytic glucose fuel cell. The main advantage is that the surface of the implanted device is used as the electrode film of the battery, without the need to implant additional battery housing. However, this kind of fuel cell has some problems, such as low electroactive area, electrochemical short circuit, implantable immune rejection, and complex preparation process [1-3]. These problems can only be improved by modifying the material design of the electrode film of glucose fuel cell on the surface of the implant. Porous conducting hydrogels have the dual characteristics of ionic and electronic conduction and good biocompatibility. It is the great exploration value to develop hydrogel electrode films that can selectively oxidize glucose in complex reaction systems with various components and apply them to glucose fuel cells on the surface of implants [4-6].

In this chapter, a porous conductive hydrogel electrode film of MWCNTs/PVA was prepared by electrophoretic deposition technology, and the selective catalytic ability of MWCNTs/PVA on glucose was verified by cyclic voltammetry and open-circuit voltage. The electrochemical and physicochemical properties of MWCNTs/PVA porous conductive hydrogel electrode films were also characterized. The synergistic catalytic effects of MWCNTs/PVA porous conductive hydrogel electrode films and platinum electrode on the electrochemical oxidation of glucose in different PH solutions were studied.

2. Experimental Materials and Instruments

2.1. Experimental Materials

Multi-walled MWCNTs (MWCNTs), Shenzhen Nanoport Co., LTD ;Cetyltrimethyl ammonium bromide (CTAB), Sinopharm Chemical Reagent Co. LTD ;Polyvinyl alcohol (PVA) 17-99 ,Beijing Xisi Chemical Raw Materials Co., LTD; Ethanol ,Sinopharm Chemical Reagent Co. LTD; Acetone, Sinopharm Group Chemical Reagent Co. LTD; Hydrogen peroxide ,Group Chemical Reagent Co. LTD; Sodium hydroxide, Pharmaceutical Group Chemical Reagent Co. LTD; Potassium ferricyanide, Chemical Reagent Co. LTD; Perchlorate ,Sinopharm Group Chemical Reagent Co. LTD; Potassium chloride ,Chinese Medicine Group Chemical Reagent Co. LTD; Phosphate ,Chinese Pharmaceutical Group Chemical Reagent Co. LTD; Dextrose ,Chinese Medicine Group Chemical Reagent Co. LTD; Sinopharm Sulfate, Group Chemical Reagent Co. LTD; Polyvinylidene fluoride film, Shanghai Shuo Optoelectronic Technology Co. LTD;.

2.2. Experimental Equipment

Glassy carbon electrode, glassy carbon diameter 4mm, Tianjin Aida Hengsheng; Saturated calomel electrode, Type 232, Shanghai Rez; Platinum electrode, 10mm× 10mm× 0.1mm, Beijing Cuiplatin; Auxiliary platinum electrode, 20mm×20mm×0.1mm, Beijing Cuiplatin; Dc electrophoresis instrument,DYY-6C, Beijing Liuyi Instrument Factory; Electrochemical Workstation,CHI618d, Chenhua, Shanghai; Centrifuge,HC-3018, Anhui Zhongke Zhongjia Instrument; Electronic Balance,BS210S sartorius; Water bath ultrasound,KQ-200M, Keqiao ultrasonic equipment; Pressure Sterilization Pot,LX-L, Hefei Huatai Medical Equipment; Constant temperature Heating Magnetic Agitator,CL-4, Yuhua Instrument Co., LTD. Low Temperature Refrigerator, BCD-285WNMVS, Samsung Electronics, Suzhou; Freeze-drying machine,LGJ-10, Matsuyuan Huaxing Technology; Constant Temperature hot Table Optical microscope,TK-C1031EC,JVC Kenwood Co., LTD.; Scanning electron

Microscope, Apollo 300, CamScan UK; Four probe tester, RTS-9, Guangzhou Probe Technology; Digital micrometer, 76720532-7, Shanghai constant; High precision video Contact Angle Measuring Instrument,OCA15+, DatapHysics, Germany; Flowmeter,MF5712-N-200, Nanning, Guangxi.

3. Electrode Film Preparation and Testing

3.1. The Preparation of Electrode Film

MWCNTs/PVA conductive hydrogel electrode film was prepared on the surface of glassy carbon electrode by electrophoretic deposition and freeze-thawing process. The preparation process is as follows:

(1) PVA dissolution: 10wt% PVA aqueous solution is configured under the preparation process of 90℃ water bath stirring.

(2) Washing of MWCNTs: An appropriate amount of MWCNTs was ultrasounded in 30% H2O2 for 30min and reflow for 2h at 80℃. The resulting suspension was filtered with a 0.2 micron polyvinyl fluoride membrane, and then washed with deionized water until neutral and dried.

(3) Configuration of electrophoretic sedimentation fluid: Appropriate amount of CTAB (2mg/ml) and MWCNT (2mg/ml) were placed in deionized water and ultrasonic bath for 2h. Then according to different PVA mass ratio (0%, 0.05%, 0.1%; 0.2%; 0.3%; 0.4%; 0.5%; 1%; 2%) were prepared with CTAB-MWCNTs-PVA suspension and heated in stirred water bath for 1h.

(4) Glass carbon electrode pretreatment: (a) Grinding: The surface of GCE was roughed with 0.5μm Al2O3 particles, and then finely ground with 50nm Al2O3 particles until the surface of GCE was smooth and clean; (b) Cleaning: Soak the polished GCE in ethanol solution and clean it with ultrasonic cleaner for 10 minutes to remove the surface oil; (c) Polishing: polishing the GCE until smooth on a polishing machine; (d) electrochemical activation: GCE was inserted into a three-electrode system as a working electrode, and cyclic voltammetry was carried out with dilute sulfuric acid solution with a concentration of 0.5 mmolL-1 for multiple scanning. The electrochemical activity of the surface of GCE could be improved while the electrode was cleaned.

(5) Platinum electrode pretreatment: (a) Cut the platinum electrode into 10mm10mm0.15mm electrodes. (b) Put the electrode in acetone and wash it in ultrasonic shock cleaner for 10 minutes to remove the surface oil. (c) A dilute sulfuric acid solution was prepared, the platinum electrode was removed and placed in dilute sulfuric acid. The electrode was again placed in an ultrasonic shock cleaner and cleaned for 3 minutes to remove the surface oxide layer. (d) Take out the platinum electrode, wash it with anhydrous ethanol, and dry it with nitrogen.

(6) Electrophoretic deposition process: The above CTAB-MWCNTs-PVA suspensions were added as electrophoretic deposition droplets in the deposition tank, and then the platinum electrode were immersed in the electrophoretic solution (the immersed area was 1cm2). Then the negative extremes of the electrophoresis apparatus were connected to the glass carbon electrode, and the positive electrode was connected to the platinum electrode (the distance between electrodes was 1cm). Adjust the parameters of the electrophoresis apparatus (the voltage is 30V, the deposition time is 2min). The electrophoretic deposition process is shown in Figure 3-2. After the deposition is completed, the electrophoresis instrument power is turned off.

(7) Freezing and thawing process: The electrode was removed from the solution, and when the deposited film was stable and non-flowing, it was frozen in the refrigerator at -26℃ for 10h, and then thawed at room temperature for 4h. After 4 cycles of cyclic freezing/thawing, MWCNTs/PVA conductive hydrogel electrode film was finally formed, and the prepared electrode film was placed in neutral PBS solution for reserve.

3.2. Testing

Synergistic effect of MWCNTs/PVA conductive hydrogel electrode film and platinum electrode: 0.10mol /L $HClO_4$, 0.10mol /LNaOH and 0.1mol /L PBS solutions were configured respectively. In the solution system under different PH, Cyclic voltammetry was used to test the electrocatalytic activity of MWCNTs/PVA hydrogel film modified platinum electrode, MWCNTs modified platinum electrode and bright platinum electrode on glucose, scanning speed: 50 mV/s, through nitrogen deoxygenation.

4. Results and Discussion

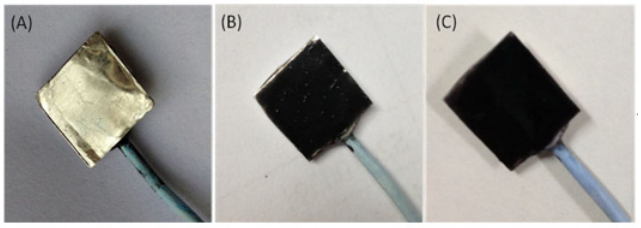

Figure 1. MWCNTs/PVA conductive hydrogel modified platinum electrode (A) platinum electrode (B)MWCNTs (C)MWCNTs/PVA

Figure 1. (A) shows a physical picture of a MWCNTs/PVA conductive hydrogel modified platinum electrode. For comparison, a carbon tube modified platinum electrode and a platinum electrode are also displayed. The platinum electrode appears silver white, and the MWCNTs modified platinum electrode has white spots on the surface, which is caused by the removal of MWCNTs during the preparation of electrode film. The platinum electrode modified with MWCNTs/PVA electrode film showed uniform and permeable black without shedding phenomenon, which indicated that PVA was conducive to the fixation of MWCNTs and would not cause the agglomeration of MWCNTs on the electrode surface.

Figure 2 shows the electrocatalytic activity of MWCNTs/ PVA-modified platinum electrode against glucose under acidic conditions. Cyclic voltammetry tests were also performed on the MWCNTs/ PVa-modified platinum electrode and platinum electrode as a control. As shown in FIG. 3-11 (A), in an acidic environment, platinum sheet has no obvious electrochemical oxidation peak for glucose, but glucose increases the electrochemical active area of platinum sheet. At the same time, a reduction peak is observed near the potential of -0.25V, but this is not reflected by the electrochemical oxidation of glucose. This should be caused by the adsorption and desorption of a small number of hydrogen ions [114]. As shown in Figure 3-11 (B), the platinum electrode modified by MWCNTs did not have an obvious oxidation peak for glucose. As shown in Figure 3-11 (C), the platinum electrode modified by MWCNTs/PVA did not have an obvious oxidation peak for glucose. By comparing Figures 3-11 (A) and 3-11 (B), it was found that

MWCNTs enhanced the adsorption capacity of platinum plates for hydrogen ions [115]. By comparing Figure 3-11 (A) and Figure 3-11 (C), MWCNTs/PVA composite hydrogel electrode film also increased the electroactive area of platinum sheet.

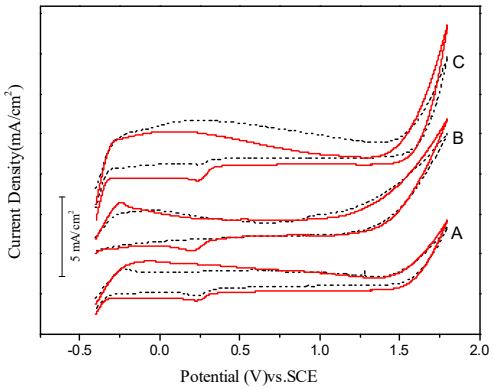

Figure 2. CV curves of different electrodes in 0.1 mol/L HClO4 solution (A is platinum electrode, B is MWCNTs modified platinum electrode, C is MWCNTs/PVA composite hydrogel platinum electrode, dotted line is blank HClO4 solution, solid line is HClO4 solution mixed with 5mM glucose solution, scanning rate: 50mV/S)

On the whole, MWCNTs/PVA composite hydrogel electrode films showed no significant electrocatalytic activity against glucose in acidic solution. Due to the obvious swelling property of PVA hydrogel in an acidic environment , the electrode film may fall off from the surface of the platinum electrode. Therefore, PVA/MWCNTs gel membranes are not suitable for catalyzing glucose in acidic environments[7-9].

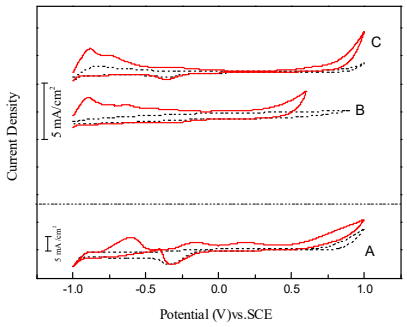

Figure 3. CV curves of different electrodes in 0.1 mol/L NaOH solution (A is platinum electrode, B is MWCNTs modified platinum electrode, C is MWCNTs/PVA composite hydrogel platinum electrode, dotted line is blank NaOH solution, solid line is NaOH solution mixed with 5mM glucose solution, scanning rate: 50mV/S)

Figure 3 shows the electrocatalytic activity of MWCNTs/ PVA-modified platinum electrode against glucose under alkaline conditions. As a control, cyclic voltammetry was also performed on the MWCNTs modified platinum electrode and platinum electrode. As shown in Figure 3-12 (A), the cyclic voltammetry curve of platinum electrode in alkaline environment shows three obvious glucose oxidation peaks near -0.55V, -0.1V and 0.25V during the scanning process from negative potential to positive potential of the electrode. As shown in Figure 3-12 (B), the cyclic voltammetry curve of the MWCNTs modified platinum electrode in the alkaline environment. In the scanning process of the electrode from negative potential to positive potential, there was an obvious oxidation peak to glucose at the potential of -0.7V, and the intensity of the current peak was relatively high, indicating that MWCNTs also had an obvious electrocatalytic activity to glucose. As shown in Figure 3-12 (C), the cyclic voltammetry curve of MWCNTs/ PVA-modified platinum electrode in an alkaline environment. In the scanning process of the electrode from negative potential to positive potential, an obvious glucose oxidation peak appeared at the potential of -0.7V, and the intensity of the current peak was relatively high. This indicates that MWCNTs/PVA electrode film has electrocatalytic activity for glucose.

By comparing FIG. 3-12 (A) and FIG. 3-12 (B), it was found that MWCNTs greatly increased the electroactive area of platinum sheet in the alkaline environment, and MWCNTs significantly shifted the oxidation peak of platinum sheet electrode to glucose, which should be caused by the synergistic effect of MWCNTs and platinum electrode on the electrochemical catalysis of glucose. By comparing Figure 3-12 (A) and Figure 3-12 (C), MWCNTs/PVA electrode film can also increase the electroactive area of platinum plate in alkaline environment, making the oxidation peak of platinum plate electrode to glucose obviously negative shift, which indicates that MWCNTs/PVA electrode film and platinum electrode also have synergistic effect on the electrocatalysis of glucose. By comparing Figure 3-12 (A) and Figure 3-12 (C), we found that the addition of MWCNTs and glucose reduced the oxygen evolution potential of platinum tablets. This issue is not the focus of this paper, but the reduction of oxygen evolution potential of platinum tablets is also a significant research direction.

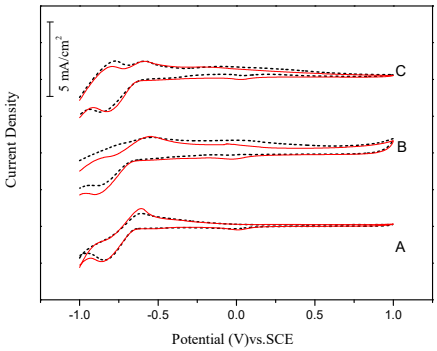

Figure 4. CV curves of different electrodes in 0.1 mol/L PBS solution (A is platinum electrode, B is MWCNTs modified platinum electrode, C is MWCNTs/PVA composite hydrogel platinum electrode, dotted line is blank PBS solution, solid line is PBS solution mixed with 5mmol/L glucose solution, scanning rate: 50mV/S, pH=7.5)

On the whole, MWCNTs/PVA composite hydrogel electrode film has an obvious promotion effect on platinum electrode electrocatalysis of glucose in alkaline environment. However, an alkaline environment with a pH greater than 9 can only be provided in the human gut environment, while the humoral environment has a neutral pH. Therefore, it is necessary to study the synergistic effect of MWCNTs/PVA composite hydrogel electrode film and platinum plate on electrocatalytic glucose under neutral environment.

Figure 4 shows the electrocatalytic activity of MWCNTs/ PVA-modified platinum electrode against glucose under alkaline conditions. As a control, cyclic voltammetry was also performed on the MWCNTs modified platinum electrode and

platinum electrode. As shown in Figure 3-13 (A), platinum electrode has no significant electrocatalytic activity on glucose in neutral solution environment, and very small oxidation peaks are observed in the process of scanning from negative potential to positive potential, which may be related to the formation of hemiacetals on glucose molecules [117, 118]. As shown in Figure 3-13 (B), the glucose oxidation peak was still not obvious, indicating that MWCNTs had limited electrocatalytic activity for glucose in a neutral environment. As shown in Figure 3-13 (C), the conductive hydrogel electrode film of MWCNTs/PVA did not weaken the electroactive area of MWCNTs, but it inhibited the diffusion of oxygen, thereby reducing the overall current. On the whole, MWCNTs/PVA composite hydrogel electrode film has a significant promoting effect on platinum electrode electrocatalysis of glucose in alkaline environment.[10-11]

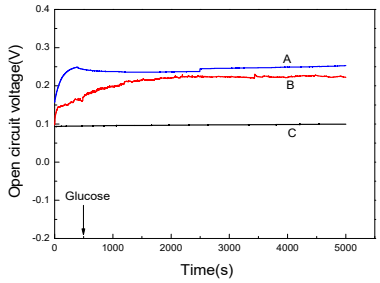

Figure 5. Open circuit voltage of different electrodes in PBS and glucose mixtures with nitrogen and oxygen mixture at 7% oxygen partial pressure (A) platinum electrode (B) MWCNTs/PVA conductive hydrogel electrode film modified platinum electrode (C) MWCNTs/PVA conductive hydrogel electrode film modified glassy carbon electrode

It was shown that the open circuit voltage of MWCNTs/PVA electrode film was continuously tested for 5000s in the mixture solution of PBS and glucose with oxygen saturation concentration of 7%. In order to exclude the influence of electrode substrate, the open circuit voltage of glassy carbon electrode modified by MWCNTs/PVA electrode film and platinum electrode were respectively tested. The open circuit voltage of a pure platinum sheet in PBS solution is also listed. The open circuit voltage of the MWCNTs/PVA modified glassy carbon electrode is about 0.09V, and the open circuit voltage remains unchanged during the experiment. The open circuit voltage of MWCNTs/ PVA-modified platinum plate finally stabilized at about 0.2V. During the experiment, the open circuit voltage gradually increased from 0.1V to 0.2V, because the platinum electrode gradually affected the open circuit voltage of the electrode film during the permeation of the solution in the electrode film. The open circuit voltage of the bright platinum electrode was about 0.25V. After adding glucose, the open circuit voltage of the platinum electrode decreased slightly, by about 15mV. None of the three electrodes caused a significant decrease in the open-circuit voltage after the addition of glucose, which was caused by the fact that none of the three electrodes showed significant catalytic activity against glucose in PBS solution. This indicates that neither platinum plate nor MWCNTs/PVA electrode film can be used as anodes for glucose cells on the surface of implants.

5. Conclusion

All manuscripts must be in English, also the table and figure texts, otherwise we cannot publish your paper. Please keep a second copy of your manuscript in your office.The co-catalytic experiments of MWCNTs/PVA conducting hydrogel electrode film and platinum electrode showed that: The synergistic effect of platinum electrode and MWCNTs/PVA hydrogel could not catalyse glucose in neutral PBS and acidic solution, but platinum electrode and MWCNTs/PVA hydrogel composite electrode had strong catalytic activity on glucose in alkaline solution with pH > 9. This suggests that MWCNTs/PVA conducting hydrogel electrode membranes may be used to implant glucose fuel cells in the human gut.

Acknowledgments

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