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Preparation of Multi-walled Carbon Nanotubes/Polyvinyl Alcohol Conducting Hydrogel Electrode Films and Electrocatalysis of Biological Small Molecules

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Abstract: According to the good conductivity and electrocatalytic activity of multi-walled carbon nanotubes (MWCNTs) and the hydrogel properties of polyvinyl alcohol (PVA), MWCNTs and PVA double-network porous hydrogels were designed. MWCNTs/ PVA conductive hydrogels were prepared by electrophoretic deposition (EPD) and freeze-thaw cyclic crosslinking process. The electrochemical performance and microstructure of MWCNTs/PVA electrode film showed that MWCNTs/PVA hydrogel electrode film has a highly hydrophilic porous conducting hydrogel network structure. Although MWCNTs/PVA hydrogel electrode film has no obvious catalytic activity on glucose in PBS solution. However, it has obvious catalytic activity on dopamine and ascorbic acid.

Keywords: Conductive Hydrogels; Implantable Fuel Cells; Glucose; PVA.

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].

Through the previous literature research, MWCNTs have good electrical conductivity and electrochemical activity, and PVA hydrogels have good hydrophilicity and biocompatibility. MWCNTs were added into the cross-linked PVA hydrogel network, and the direct contact between MWCNTs and biological tissues was avoided by embedding MWCNTs using the hydrogel network. However, the electrochemical performance and conductivity of MWCNTs were inhibited by the highly cross-linked hydrogel network. Exploring the selective catalytic effect of MWCNTs/PVA conducting hydrogel electrode film on glucose in PBS solution is the key problem of whether MWCNTs/PVA conducting hydrogel electrode film can be used in glucose fuel cells [7].

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 Al_2O_3 particles, and then finely ground with 50nm Al_2O_3 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) Electrophoretic deposition process: The above CTAB-MWCNTs-PVA suspensions were added as electrophoretic deposition droplets in the deposition tank, and then the platinum electrode and the glass carbon 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). After the deposition is completed, the electrophoresis instrument power is turned off.

(6) Freezing and thawing process: The glassy carbon 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

(1) Electrochemical probe characterization of MWCNTs/PVA conducting hydrogel electrode films:

A mixture of K_3 [Fe $(CN)_6$]/PBS solution: 1 mmol L^{-1} K_3 [Fe $(CN)_6$] and 0.1 mol L^{-1}PBS was prepared. The MWCNTs/PVA conducting hydrogel electrode film was tested for cyclic voltammetry and AC impedance using a three-electrode system. The cyclic voltammetry scanning speed was as follows: 100 mV/s; Ac impedance scanning frequency: 1-106 Hz, initial level is open circuit potential, through nitrogen deoxygenation.

(2) Electrocatalytic performance characterization of MWCNTs/PVA conducting hydrogel electrode films:

The PBS-glucose mixed solution was 5.0 mmol L^{-1} glucose and 0.1 mol L^{-1}PBS (PH=7.5). Cyclic voltammetry was used to evaluate the electrocatalytic activity of MWCNTs/PVA conducting hydrogel electrode film on glucose in a three-electrode system. The scanning speed was as follows: 100mV/s, through nitrogen deoxygenation. The PBS-dopamine mixed solution was: 1 mmol L^{-1} dopamine and 0.1 mol L^{-1}PBS mixed solution (PH=7.5); Mixed solution of 2 mmol L^{-1} ascorbic acid and 0.1 mol L^{-1}PBS (PH=7.5); The cyclic voltammetry curve of MWCNTs/PVA conducting hydrogel electrode film in mixed solution of 1 mmol L^{-1} dopamine, 2 mmol L^{-1} ascorbic acid and 0.1 mol L^{-1}PBS (PH=7.5) was tested in a three-electrode system. The scanning speed was 30 mV/s.

(3) Selective Catalysis of MWCNTs/PVA conducting hydrogel electrode films

Configuration of PBS-glucose solution: A mixture of 5.0 mmol L^{-1} glucose and 0.1 mol L^{-1}PBS (PH=7.5) and a mixture of oxygen and nitrogen with a partial pressure of 7% oxygen were injected into the solution. The effect of glucose on the open-circuit voltage of glassy carbon electrode modified with MWCNTs/PVA hydrogel electrode film and platinum electrode modified with MWCNTs/PVA hydrogel electrode film was investigated in a three-electrode system. Test conditions: the mixture of oxygen and nitrogen at 7% oxygen partial pressure was continuously injected into the solution, and 5mmol/L glucose was added after 500s

3.3. Results and Discussion

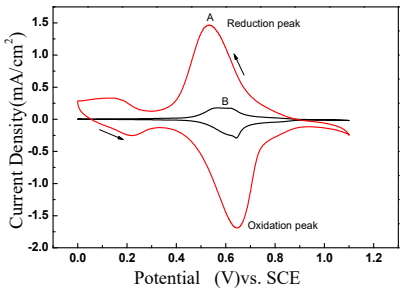


Figure 1. Cyclic voltammetry of electrode films(A) MWCNTs/PVA, (B) GCE

Figure 1 shows the cyclic voltammetry curves of MWCNTs/ PVA film modified glassy carbon electrode (A) and glassy carbon electrode (B) for $K_3Fe(CN)_6$ in PBS solution. A has two pairs of REDOX peaks at a potential of around 0.2V and 0.6V. The REDOX peak around 0.2V May be formed by the adsorption and desorption of hydrogen ions in the solution, or it may be the micro-response of some carbon tubes with high functional group activity to potassium ferriccyanide. This paper does not take this peak as the main research object. The REDOX peak of about 0.6V corresponds to the electrochemical reaction of the electron probe $K_3Fe(CN)_6$. It can be seen from the figure that the electrochemical reaction activity of $K_3Fe(CN)_6$ on the MWCNTs/ PVA modified electrode is significantly higher than that on the glassy carbon electrode

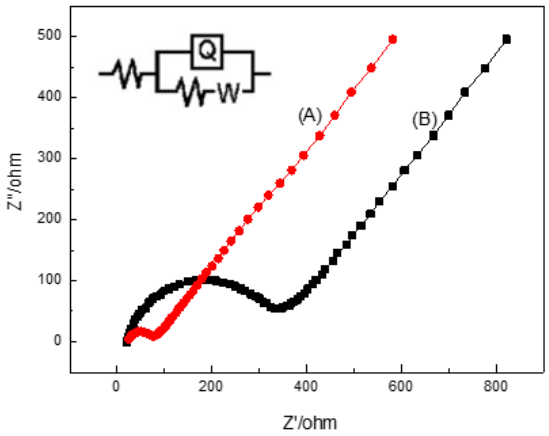


Figure 2. AC impedance measurement of electrode films (A) MWCNTs/PVA, (B) GCE

Figure 2. shows the electrochemical AC impedance spectra of PVA/MWCNTs hydrogel modified electrode (A) and unmodified bare glass carbon electrode (B) in PBS solution containing 1 mM $K_3Fe(CN)_6$ obtained by electrophoretic deposition. We use the simulation software Zview to select R(Q(RW)) equivalent circuit to analyze the specific values of the four equivalent circuit components. For bare copper electrode, R1=18.57, Q=3.7610-5, W=0.005706, R2=313, n=0.73. Where, R1 is the solution resistance, R2 is the surface charge transfer resistance, Q is the constant phase element, and W is the diffusion resistance. n is a constant characterizing constant phase. At 0.5n1, Q is capacitive and can replace the double electric layer capacitor as the equivalent component of the interface double electric layer. For the modified electrode, R1=22.36, Q=6.6510-5, W= 0.01279, R2= 54.32, n=0.68. The R2 on the glassy carbon electrode is much larger than that on the modified electrode, so it precisely indicates that the modified electrode film increases the rate of charge on the electrode surface. Meanwhile, we also note that the diffusion resistance of the modified electrode film is only twice that of the glassy carbon electrode surface, which indicates that the material diffusion inside the electrode film is less inhibited[8].

The cyclic voltammetry curves of glucose on a glassy carbon electrode modified with MWCNTs/PVA conducting hydrogel electrode film in PBS solution were shown. By comparing the cyclic voltammetry curves with and without glucose, it was found that MWCNTs/PVA conducting hydrogel electrode films did not show new oxidation peaks to glucose in PBS solution, and glucose only reduced the current intensity of the electrode films at high potential oxygen evolution. These results indicate that MWCNTs/PVA conducting hydrogel electrode films have no electrocatalytic activity for glucose in PBS solution. It was shown in the literature that MWCNTs had catalytic activity on glucose at pH greater than 9. The test was conducted in PBS solution with neutral pH, so the experimental results in this paper were consistent with those in the literature. This indicates that although MWCNTs can improve the conductivity of the electrode, the electroactive area and the invertibility of the electrode reaction, they have no catalytic activity for glucose in the neutral simulated body fluid, and the electrode film must introduce noble metal catalyst to catalyze glucose. Dopamine and ascorbic acid are active substances in vivo, and MWCNTs/PVA conductive hydrogel electrode films may catalyse these substances [9].

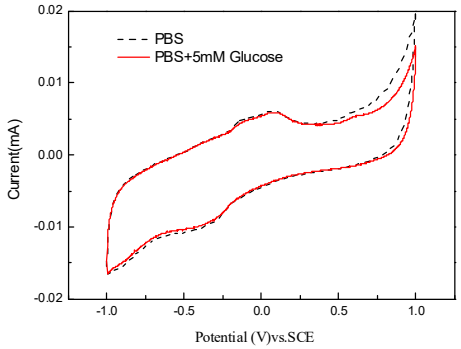
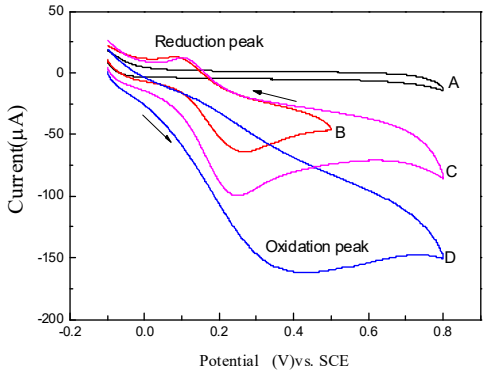


Figure 3. CV curve of glucose induced by MWCNTs/PVA conducting hydrogel electrode film (dashed line is 0.1mol/ L PBS solution, solid line is 5.0 mmol/L glucose mixed with 0.1mol/L PBS solution)



(A) blank PBS (B) 1mmol/L DA (C) 2mmol/L VC (D) 1mmol/L DA and 2mmol/L VC

Figure 4. Electrocatalysis of dopamine and ascorbic acid by MWCNTs/PVA electrode films

As shown in Figure 3-7 (A), the cyclic voltammetry curve was obtained by potential scanning (scanning speed: 30 mVs−1) of the PVA/MWCNTs hydrogel modified electrode in PBS solution. It can be seen that the cyclic voltammetry curve obtained by potential scanning on the modified electrode in the blank PBS buffer solution is a smooth curve with no current peak generated. When DA is added, there is an obvious REDOX peak on the cyclic voltammetry curve (FIG. 3-7 (B)), so it can be determined that DA is electrooxidized and electro reduced on the electrode surface. When AA was added, there was an obvious oxidation peak on the cyclic voltammetry curve (FIG. 3-7 (C)), so it could be determined that AA was electrooxidized on the electrode surface, but no reduction peak was observed. When AA and

DA were added, the cyclic voltammetry curve showed an obvious REDOX peak (Figure 3-7 (D)). The curve shape of the oxidation peak is closer to that of DA alone, but the intensity of the current peak is increased, which indicates that in the electrooxidation process of the mixture, the electrooxidation of DA is promoted, while the electrooxidation of AA is inhibited. The reason is that there is a reversible reaction between dopamine and dopaminoquinone in solution, and dopaminoquinone can react with ascorbic acid to form dopamine, but the reaction is non-reversible, which leads to a decrease in the peak current of AA. The presence of AA plays a certain catalytic role in the oxidation of DA, thus enhancing the electrochemical oxidation degree of dopamine [10]. The curve contour of the reduction peak of DA in Figure 3-7 (D) is very close to that in Figure 3-7 (B) and almost coincides, indicating that the reduction peak of DA is basically not affected by AA, which may be because there is a reversible reaction between dopamine and dopaminoquinone, and ascorbic acid only changes the equilibrium point of the reversible reaction between dopamine and dopaminoquinone, but does not inhibit the electrochemical reduction of dopamine. Although the hydrogel-modified glassy carbon electrode with PVA/MWCNTs could not catalyze glucose in PBS solution, it showed obvious electrocatalytic activity against dopamine and ascorbic acid.

4. Conclusion

According to the good conductivity and electrocatalytic activity of MWCNTs and the characteristics of PVA, a double-network porous hydrogel electrode film of MWCNTs and PVA was designed. The porous hydrogel electrode film with high hydrophilic nanopore structure was prepared by electrophoretic deposition and freeze-thawing cyclic crosslinking process.

(1) By adjusting the content of PVA, the threshold of 0.4wt %PVA was determined as the conductivity of MWCNTs/PVA conductive hydrogel electrode film, and the conductivity of MWCNTs/PVA conductive hydrogel was 0.1s/cm.

(2) The electrochemical reaction of MWCNTs/PVA conductive hydrogel electrode film on potassium ferricyanide is quasi-reversible. The electroactive area of MWCNTs/PVA electrode film is 5.9 times that of the glass carbon electrode, and the transmission rate of electric charge on the electrode surface is also improved.

(3) MWCNTs/PVA conductive hydrogel electrode film had no catalytic activity on glucose in neutral simulated body fluid, but had catalytic effect on dopamine, citric acid and other active substances. MWCNTs/PVA conductive hydrogel could not selectively catalyze glucose in oxygen-rich PBS solution on either glassy carbon substrate or platinum substrate.

Acknowledgments

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