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Preparation and Characterization of Conductive Hydrogel Electrode Films of Nano Platinum/Multi-Walled Carbon Nanotubes/Polyvinyl Alcohol

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Abstract: Nano platinum were prepared on multi-walled carbon nanotubes/polyvinyl alcohol conducting hydrogel electrode film by electrostatic adsorption principle and mild in-situ reduction. The microstructure, conductivity, electrochemical performance and electrocatalytic activity of PtNPs/MWCNTs/PVA conducting hydrogel electrode film were studied. And the selective catalytic ability of the electrode film to glucose in oxygen-rich PBS solution, and the relationship between the selective catalytic ability and the preparation technology of the electrode film was analyzed.

Keywords: Nano Platinum; Multi-walled Carbon Nanotubes; Polyvinyl Alcohol; Fuel Cell.

1. Introduction

The conducting hydrogel has the softness similar to biological tissue, and the mechanical modulus is similar to that of biological tissue. When it comes into contact with blood, body fluid and human tissue, it shows good biocompatibility. It is similar to the extracellular matrix in nature. After water absorption, it can reduce friction and mechanical effects on surrounding tissues, significantly improve the interaction between electrode materials and human tissues, and also has an ideal interface that can respond to tissues through bioelectricity. Due to its high-water content, low surface tension, low impedance and electrical activity, it can transfer charge with cells and tissues through the electromagnetic action site of biological tissues, forming the "electroactive biocompatible interface" between biological materials and cells or tissues. This ideal interface, which responds to the electric field between materials and tissues, can better avoid the adhesion and desorption of proteins and cells, promote the transmission of bioelectrical signals between implant materials and biological tissues, and avoid the formation of tissue cysts and scar tissue [1-5].

Nano platinum were prepared on multi-walled carbon nanotubes/polyvinyl alcohol conducting hydrogel electrode film by electrostatic adsorption principle and mild in-situ reduction. The microstructure, conductivity, electrochemical performance and electrocatalytic activity of PtNPs/ MWCNTs/ PVA conducting hydrogel electrode film were studied. And the selective catalytic ability of the electrode film to glucose in oxygen-rich PBS solution, and the relationship between the selective catalytic ability and the preparation technology of the electrode film was analyzed.

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 Materials Co., LTD.; Ethanol, Sinopharm Chemical Reagent Co., LTD.; Acetone, Sinopharm Chemical Reagent Co., LTD. Hydrogen peroxide, Sinophosphate Chemical Reagent Co., LTD.Chloroplatinic acid, Sinopharm Chemical Reagent Co., LTD.; Potassium ferricyanide, Sinophosphate Chemical Reagent Co., LTD.; Sodium chloride, Sinopharm Chemical Reagent Co., LTD.; Phosphate, Sinopharm Chemical Reagent Co., LTD.

2.2. Experimental Equipment

GlassyGlassy carbon electrode, glassy carbon diameter 4mm, Tianjin Aida Hengsheng; Saturated calomel electrode, Type 232, Shanghai Rez; Platinum electrode, 10mm× 10mm× 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, Suzhou Samsung Electronics; 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

3. Electrode Film Preparation and Testing

3.1. The Preparation of Electrode Film

(1) 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.

(2)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.

(3) Electrode pretreatment:

The electrodes were put into acetone, ethanol and deionized water respectively according to the second storage, and washed in ultrasonic shock cleaner for 10 minutes to remove the surface oil; The dilute sulfuric acid solution was prepared, and the electrode was put into the dilute sulfuric acid, and then placed in the ultrasonic shock cleaner for 3 minutes to remove the surface oxidation layer. Remove the electrode, wash it with anhydrous ethanol, and dry it with nitrogen.

(4) Electrophoretic deposition and freeze-thaw 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 output end of the electrophoresis apparatus was connected to the glass carbon electrode and the positive end was connected to the copper electrode (the distance between the 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 3-1. After the deposition is completed, the electrophoresis instrument power is turned off. Remove the glassy carbon electrode from the solution. When the film was stable and did not flow, it was frozen in the refrigerator at -26℃ for 10h, and then thawed at room temperature for 4h. After 4 cycles of freezing/thawing, MWCNTs/PVA conductive hydrogel electrode films were finally formed. The prepared electrode films were placed in neutral phosphate buffer solution for reserve.

(5) Preparation of PtNPs conductive gel: MWCNTs/PVA films were prepared on glassy carbon electrodes using the electrophoretic deposition method described above. The composite electrodes were immersed in 18ml chloroplatinic acid (CPA) solution (0.5ml, 10mmol/L chloroplatinic acid) for 3 hours, and then reduced in situ with ascorbic acid (1ml, 0.1mol/L) for 24h.

3.2. Testing

(1) Electrocatalytic test of PtNPs/ MWCNTs/ PVA conducting hydrogel electrode films:

PBS-glucose solution was prepared: 5.0 mmol/L glucose and 0.1 mol/L PBS solution (pH=7.5), and PtNPs/ MWCNTs/ PVA conductive hydrogel electrode film was tested by cyclic voltammetry at a speed of 100mV/s in a three-electrode system. At the same time, the influence of glucose concentration (2-40 mmol/L) on the cyclic voltammetry curve of electrode film was also studied. The effect of 0.1 mol/L NaCl on the cyclic voltammetry curves of PtNPs/ MWCNTs/ PVA conducting hydrogel electrode films was tested. All the above solutions were deoxygenated by nitrogen.

(2) Selective catalytic test of PtNPs/MWCNTs/PVA conducting hydrogel electrode films

Pbs-glucose mixed solution was configured: 5.0 mmol L−1 glucose and 0.1 mol L−1PBS mixed solution (PH=7.5), the flow rate of oxygen and nitrogen gas mixture was 0.5 Lmin-1, and the concentration of oxygen in the solution was 7% oxygen saturation. The open circuit voltage of PtNPs/ MWCNTs/ PVA hydrogel electrode film was tested in a three-electrode system.

(3) Stability of PtNPs/MWCNTs/PVA conducting hydrogel electrode films

Configuration of PBS-glucose solution: The cyclic voltammetry of PtNPs/MWCNTs/PVA hydrogel electrode films was tested in a three-electrode system with a mixture of 5.0 mmolL−1 glucose and 0.1 molL−1PBS (PH=7.5) for 500 cycles at a scanning speed of 100 mV s−1.

3.3. Results and Discussion

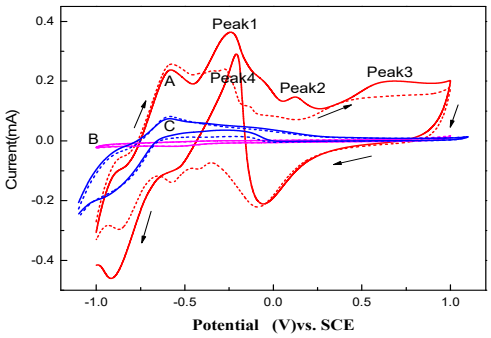

Figure 1. Electrocatalytic activity of different electrode membranes on glucose (A) PtNPs/MWCNTs/PVA (B) MWCNTs/PVA (C) PtNPs (dashed line is blank PBS solution, solid line is PBS solution mixed with 5mM glucose, arrow indicates scanning direction)

Figure 1 shows the electrocatalytic activity of three different electrode membranes for glucose in PBS solution. As shown in Figure 1 (A), during the scanning process from negative potential to positive potential, PtNPs/ MWCNTs/ PVA conducting hydrogel electrode film showed three obvious oxidation peaks on glucose, indicating that the electrode film had obvious catalytic ability on glucose. As shown in Figure 1(B), MWCNTs/PVA electrode films have no catalytic activity on glucose, which is consistent with the conclusions in the literature and Chapter 3, MWCNTs catalyze glucose only when pH is about 9. As shown in Figure 1 (C), PtNPs electrode film has a weak electrocatalytic activity on glucose. However, due to the small electroactive area of PtNPs on the glassy carbon electrode, the oxidation current presented is very weak. According to literature, the three oxidation peaks of platinum to glucose are mainly three: hydrogen adsorption and desorption in the negative potential region; The formation of glucose intermediates in the region of the double layer; Oxidation and reduction of PtO in positive potential region. The catalytic effect of PtNPs/ MWCNTs/ PVA hydrogel electrode film on glucose also follows the above rules. In the low potential region (Peak1), the so-called "hydrogen region" (−0.4V to 0V), the oxidation peak is caused by the adsorption of hydrogen atoms on the surface of the electrode and the release of electrons from the heterohead carbon atoms in the glucose molecule. In the double layer region (0V-0.3V), the oxidation peak of Peak2 is formed due to the catalytic effect of Pt (OH)ad on the glucose adsorbed on the electrode surface. In the so-called "oxidation zone" (> 0.3V), the oxidation peak peak3 is derived from the formation of PtO film, and a large amount of glucose is directly catalyzed on the electrode surface. During the process of scanning potential from 0.1V to -0.5V,

Peak 4 is formed due to partial desorption of oxygenated PtNPs [6-8].

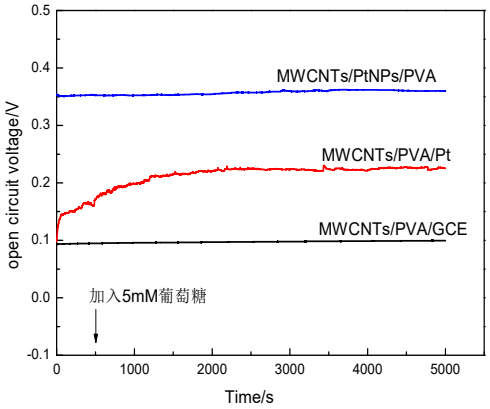

Figure 2. Open-circuit voltages of different electrode films in oxygen-rich PBS and glucose mixtures

Figure 2 shows the open circuit voltage of the PtNPs/ MWCNTs/ PVA electrode film in neutral PBS solution for a continuous test of 5000s. As a comparison, the open circuit voltage of the MWCNTs/PVA modified platinum electrode and the glassy carbon electrode are also listed in the figure. 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 PtNPs/MWCNTs/PVA electrode film is about 0.35V, and keeps the trend of flat. This is unusual, PtNPs/ MWCNTs/ PVA electrode film has obvious electrocatalytic activity on glucose, but glucose has no obvious effect on the open-circuit voltage of the electrode film. In order to solve this problem, a series of PtNPs/MWCNTs/PVA conductive hydrogel electrode films were prepared by using different electrophoretic deposition voltages, and the relationship between surface roughness and open-circuit voltage was tested.

As shown in Figure 3 (A), when the electrode potential was 0.5V, the current time curve of PtNPs/MWCNTs/PVA conducting hydrogel electrode film against glucose assessed the stability of the electrode film. Curve A1 was tested without Nacl in the solution, while 0.1mol/L of Nacl was added into the test system of curve A2. We found that sodium chloride caused a delay in the electrode film reaching steady state and the steady-state current value was lower than that without sodium chloride. As shown in Figure 3 (B), after 500 cycles of cyclic voltammetry test, the peak oxidation current of glucose (0.5V) maintained about 80% of the initial peak current (curve B1), while chloride ion accelerated the decay rate of the peak oxidation current of the electrode film (curve B2).

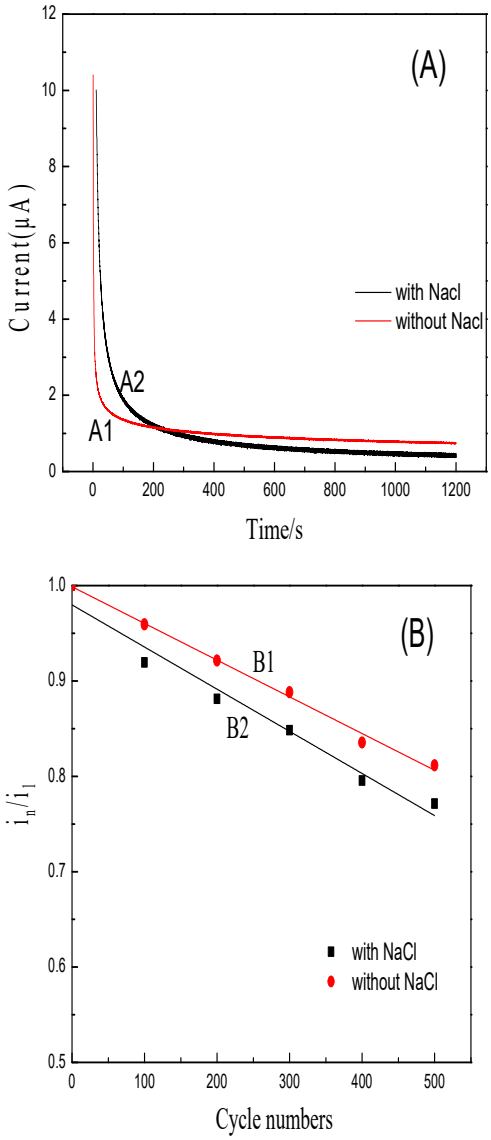

Figure 3. Stability of PtNPs/MWCNTs/PVA electrode film (A) Current time curve of PtNPs/MWCNTs/PVA conducting hydrogel electrode film (B) The relationship between the peak current of PtNPs/MWCNTs/PVA conducting hydrogel electrode film and the number of scanning cycles

4. Conclusion

The electroactive area of PtNPs/MWCNTs/PVA hydrogel electrode film is 7 times that of MWCNTs/PVA hydrogel electrode film. The electron transport rate on the surface of PtNPs/MWCNTs/PVA hydrogel electrode film was slightly lower than that on the surface of MWCNTs/PVA hydrogel electrode film. It was also found that the PtNPs/ MWCNTs/ PVA electrode film had the effect of ion enrichment, which could reduce the resistance of solution to a certain extent. PtNPs/MWCNTs/PVA electrode films had significant electrocatalytic activity on glucose solution in neutral simulated body fluids; The electrocatalytic process of glucose is neither diffusion control nor adsorption control, but a mixed control process. When the glucose concentration exceeds 5mM, the catalytic glucose behavior of the electrode film at low electrode potential will be inhibited, and chloride ion has a strong inhibitory effect on the catalytic glucose behavior of the electrode film at low electrode potential. PtNPs/ MWCNTs/ PVA electrode films did not have the ability to selectively catalyze glucose in oxygen-rich PBS solution;

Electrophoretic deposition has little effect on the surface morphology of the electrode film, and can only be used for oxygen consuming cathode lamination glucose fuel cells.

Acknowledgments

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