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Preparation and Properties of Nano Platinum/Carbon Nanotubes/Bacterial Cellulose Conductive Hydrogel Electrode Films

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Abstract: Using the natural nanomesh structure of bacterial cellulose (BC), the good conductivity of multi-walled carbon nanotubes (MWCNTs) and the good electrocatalytic activity of nano platinum (PtNPs), a three-way porous conductive hydrogel of PtNPs and BC was designed. The infiltrating and doping of MWCNTs on BC thin films was realized by ultrasonic assisted electrophoretic deposition process, which ensured the dual characteristics of ionic and electronic conduction of electrode films. The adsorption capacity of BC for chloroplatinic acid and the strong reductivity of sodium borohydride were also used to realize the high-load PtNPs recombination on MWCNTs/BC porous layered conductive hydrogel electrode films. By testing the electrochemical performance of PtNPs/MWCNTs/BC conductive hydrogel electrode film and characterization of microstructure, the electrode film not only has high electroactive area, low surface charge transfer resistance and good diffusion permeability and other electrochemical characteristics, but also shows high catalytic activity for glucose in PBS solution. The most important finding is that the electrode film can selectively catalyze glucose in oxygen-rich PBS solution. The porous layered structure of PtNPs/MWCNTs/BC electrode membrane and the high load dispersion of PtNPs are the reasons for the selective catalytic ability of PtNPs/MWCNTs/BC conductive hydrogel electrode membrane, which can be used for the implanted surface glucose fuel cell.

Keywords: Bacterial Cellulose; Fuel Cell; Nano Platinum.

1. Introduction

Bacterial Cellulose (BC) is a kind of cellulose mainly synthesized by Acetobacter xylinum, also known as Microbial cellulose [1-5]. As a natural biopolymer, this unique three-dimensional network structure gives BC many unique physical, chemical and mechanical properties, such as biological activity, biodegradability, biological adaptability, high crystallinity, high water holding capacity, microfine nanofiber network, high tensile strength and high elastic modulusl. Therefore, BC has received extensive attention in biomedical and electronic fields in recent years, and its application scope includes wound dressing, burn treatment, tissue regeneration, skin substitutes, catalyst sensing materials, electronic equipment etc. [5-8]. In recent studies, BC/Pt nanocomposites have shown excellent electrical conductivity and are often used as fuel cells and biosensors. BC/Pt nanocomposites are prepared by liquid phase chemical reduction method, and the resulting composites have high electrocatalytic activity.

Using the natural nanomesh structure of BC), the good conductivity of MWCNTs and the good electrocatalytic activity of PtNPs, a three-way porous super layered conductive hydrogel of PtNPs, MWCNTs and BC was designed. The porous layered structure can selectively catalyze glucose in oxygen-rich PBS solution, which can be used for the implanted surface glucose fuel cell.

2. Materials and Instruments

2.1. Materials

Cetyltrimethyl ammonium bromide (CTAB), Sinopharm Chemical Reagent Co., LTD.; Bacterial Cellulose (BC), Hainan Yide Food Co., LTD.; Glucose, Sinopsin Chemical Reagent Co., LTD.; Ethanol, Sinopharm Chemical Reagent Co., LTD.; Acetone, Sinopharm Chemical Reagent Co., LTD. Potassium ferricyanide, Sinophosphate Chemical Reagent Co., LTD.; Phosphate, Sinopharm Chemical Reagent Co., LTD.; Sodium borohydride, Sinopharm Chemical Reagent Co., LTD.; Chloroplatinic acid, Sinopharm Chemical Reagent Co., LTD.; .Figures.

2.2. Instruments

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;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, UK, CamScan; Four probe tester, RTS-9, Guangzhou Probe Technology; High precision video contact Angle measuring instrument, OCA15+, DatapHysics, Germany.

3. Preparation and Testing

3.1. Preparation

PtNPs /MWCNTs/BC conductive hydrogel electrode film was prepared by the ultrasonic-assisted electrophoretic deposition combined with chemical in-situ reduction. The specific process is as follows:

1) Pretreatment of BC: Rinse the whole sheet of BC with a thickness of about 2mm for several times with deionized water, and test the pH of the bleaching solution with pH test paper, so that the pH value is stable in the range of 5.8-6.5; The rinsed BC was placed in 0.1mol/L NaOH solution, heated at 90℃ for 1h, and then rinsed repeatedly with ionized water until neutral. Finally, the washed BC was cut into a number of small rounds with a diameter of 1.5cm using a special cutter and put into PBS solution for use.

2) Preparation of MWCNTs/BC electrode film: round sheet BC was fixed on the surface of glassy carbon electrode using a special plastic fixture, and the electrodeposition of glassy carbon electrode was carried out in the dispersion solution of CTAB-MWCNTs by ultrasonic assisted electrodeposition process. The concentration of CTAB and MWCNTs was 2mg/ml, the ultrasonic parameters were 28 kHz, 400 W, the electrophoretic deposition voltage was 36V, the opposite electrode was copper electrode, the electrode spacing was 1cm, the deposition time was 1h.

3) Preparation of PtNPs/MWCNTs/BC electrode film: The MWCNTs/BC electrode film was placed in 50mM chlorophenic acid solution for 3h, and then placed in 0.1 mol/L sodium borohydride solution, at 40℃, stirring magneto, reaction for 3h, and finally the electrode film was washed with deionized water, put in PBS solution for use.

3.2. Testing

1) Conductivity of PtNPs/MWCNTs/BC conducting hydrogel electrode film: After using digital micrometer to test the thickness of different electrode films, put the sample to be tested under the four-probe conductance meter, input the thickness, diameter, current, range and other information of the tested sample, and then test. Five locations were tested on each sample, five times at each location, and the surface conductivity of each sample was the average of all test values for each sample.

2) Electrocatalytic test of PtNPs/MWCNTs/BC conductive hydrogel electrode films: Mixed solution of 5.0 mmol L−1 glucose and 0.1 mol L−1PBS (PH=7.5); Mixed solution of 2 mmol L−1 dopamine and 0.1 mol L−1PBS (pH=7.5); A mixture of 2 mmol L−1 fructose and 0.1 mol L−1PBS (pH=7.5); A mixture of 2 mmol L−1 ascorbic acid and 0.1 mol L−1PBS (pH=7.5) was deoxygenated with nitrogen. Cyclic voltammetry was performed on the electrode film in a three-electrode system.

3) Selective catalytic test of PtNPs/MWCNTs/BC conductive 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), and nitrogen and oxygen mixed gas with 7% oxygen saturation concentration was continuously injected. In a three-electrode system, open-circuit voltage test was conducted on the electrode film.

4) Microstructure of PtNPs/MWCNTs/BC conductive hydrogel electrode films: The samples of the composite conductive hydrogel were freeze-dried in the freeze-drying machine. After the samples were treated with gold spray, the microstructure of the electrode film was observed by Apollo300 type field emission scanning electron microscope with a scanning voltage of 5KV. In this section, the surface roughness of the electrode film was characterized by laser confocal microscope.

5) Thermal stability test of PtNPs/MWCNTs/BC conductive hydrogel electrode films: Thermogravimetric analyzer was used for analysis. The heating rate was 10℃/min, the nitrogen flow rate was 50ml/min, and the temperature range was 25-550℃.

6) Grain analysis of PtNPs/MWCNTs/BC conductive hydrogel electrode films: X-ray diffractometer is used to analyze the phase of the electrode film to determine the crystalline state of the material. The experimental parameters were Cu target, the acceleration voltage was 40 kV, the current intensity was 150 mA, the sample interval of the counter was 0.02 °, the scanning speed was 10 °/min, and the scanning range was 2θ: 10-90 °.

4. Results and Discussion

4.1. Conductivity of Conductive Hydrogel Electrode Films

Table 1. The conductivity of the electrode film（s/cm）

Materials	BC	MWCNTs/BC	PtNPs/MWCNTs/BC
conductivity	$<10^{-6}$	0.1867	0.587

As shown in Table 1, the conductivity of three different electrode films is tested in this section by using a four-probe conductance instrument. The conductivity of pure BC was much less than 10^{-6}s/cm, and the conductivity of MWCNTs/BC electrode film was 0.1867 s/cm, indicating that MWCNTs greatly improved the conductivity of BC. The conductivity of PtNPs/MWCNTs/BC electrode film was close to 0.587 s/cm, indicating that PtNPs did not improve the MWCNTs/BC electrode film greatly, because PtNPs did not exist in a continuous form [9].

4.2. Electrocatalytic Activity of Conductive Hydrogel Electrode Films

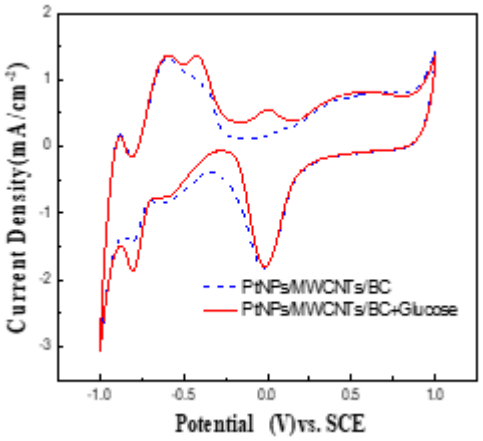

Figure 1. CV curve of glassy carbon electrode modified with PtNPs/MWCNTs/BC conducting hydrogel electrode film (dashed line is PBS solution, solid line is PBS mixed with 5mM glucose)

Figure 1. CV curves of glassy carbon electrode modified with PtNPs/MWCNTs/BC conductive hydrogel electrode film in PBS solution and PBS and glucose solution. By comparing the effect of glucose on the cyclic voltammetry curve of glassy carbon electrode modified by PtNPs/MWCNTs/BC conducting hydrogel electrode film, we found

that PtNPs/MWCNTs/BC conducting hydrogel electrode film had obvious oxidation peak on glucose. In the vicinity of -0.4V and 0.1V respectively, it indicates that the conducting hydrogel has obvious electrocatalytic activity to glucose. It is important that the oxidation peak near the -0.4V electrode potential is the one that has the greatest influence on the open-circuit voltage of the electrode film [10].

4.3. Selective Catalysis of the Conductive Hydrogel Electrode Films

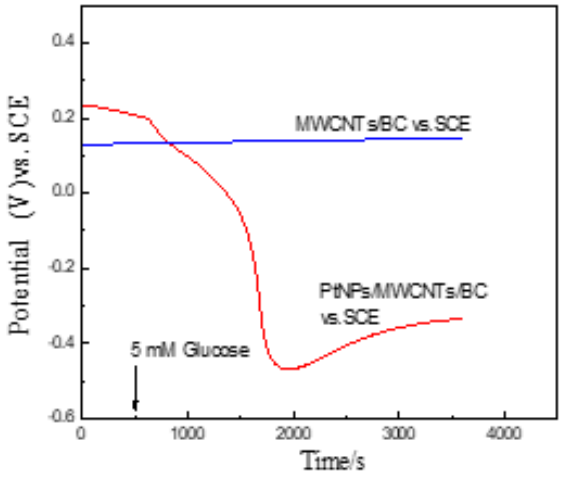

Figure 2. Open-circuit voltage of a glassy carbon electrode modified with PtNPs/MWCNTs/BC conductive hydrogel electrode film in oxygen-rich PBS solution

Figure 2 shows the open-circuit voltage of glassy carbon electrodes modified with PtNPs/MWCNTs/BC and MWCNTs/BC conductive hydrogel electrode films in oxygen-rich PBS solution. 5mmol/L glucose solution was added to the solution 500S after the test. From the above picture, we can see that: The addition of glucose made the open circuit voltage of MWCNTs/BC electrode film basically unchanged, but decreased the open circuit voltage of PtNPs/MWCNTs/BC electrode film to -340 mV vs. SCE. These data indicate that PtNPs/MWCNTs/BC conductive hydrogel electrode film overcomes the problem of mixed electromotive force formed by glucose and dissolved oxygen, that is to say, PtNPs/MWCNTs/BC conductive hydrogel electrode film selectively catalyzes glucose under oxygen-rich conditions. PtNPs/MWCNTs/BC conductive hydrogel electrode film has selective catalysis. The reason for this selective catalysis is related to the layered structure of the electrode film and the discrete distribution of PtNPs in the electrode film, which will be discussed in detail in the following paper [11-13].

4.4. Microstructure of PtNPs/MWCNTs/BC Conductive Hydrogel Electrode Films

Figure 5-14 (A) shows the internal SEM of PtNPs/ MWCNTs/ BC. PtNPs are distributed uniformly and discreetly along the dense BC network, and PtNPs in this region play a role in consuming solution oxygen. FIG. 5-14 (B) shows EDS in PtNPs/MWCNTs/BC, whose PtNPs content can reach 36.62 wt%, indicating a high nano-platinum content. FIG. 5-14 (C) SEM image of PtNPs/MWCNTs/BC cross section. The electrode film presents a layered structure containing a large number of PtNPs, and the distance between the layers constitutes a long enough solution oxygen diffusion path. In this way, there is an anoxic environment inside the electrode film, and the electrochemical oxidation of glucose dominates the electrode potential of the electrode film. Figure 5-14 (D) shows the SEM image of interlaminar fibers of PtNPs/MWCNTs/BC electrode film. A large number of PtNPs are embedded in the BC fibers, and PtNPs show discrete and homogeneous distribution. PtNPs in this region also play a role in consuming solution oxygen. FIG. 5-14 (E) shows the SEM outside the PtNPs/MWCNTs/BC electrode film. In this figure, dense MWCNTs and white PtNPs are observed. Figure 5-14 (F) shows EDS outside the PtNPs/MWCNTs/BC conductive hydrogel electrode film, whose PtNPs content can reach 21.28wt %, and the relative decline of platinum content is caused by the relative increase of MWCNTs [14].

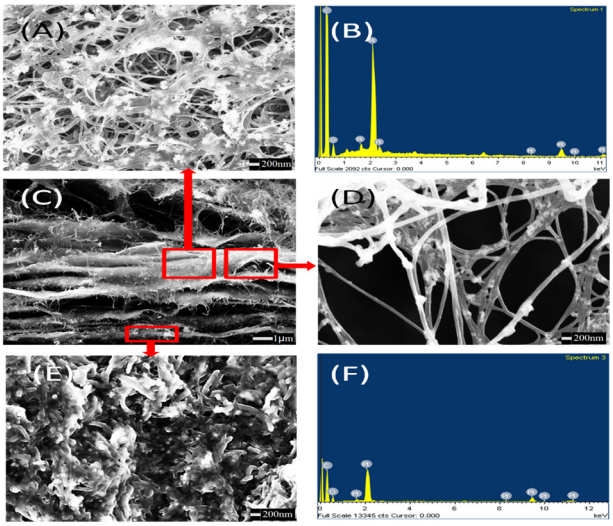

Figure 3. Microstructure and composition of conductive hydrogel electrode film: (A) Morphology inside PtNPs/MWCNTs/BC (B) EDS inside PtNPs/MWCNTs/BC (C) Cross section of PtNPs/MWCNTs/BC (D) PtNPs/MWCNTs/BC electrode Interlaminar fibers of the membrane (E) PtNPs/MWCNTs/BC outer surface (F) EDS outside PtNPs/MWCNTs/BC. All samples were freeze-dried in liquid nitrogen

4.5. XRD Analysis of PtNPs/MWCNTs/BC Conductive Hydrogel Electrode Film

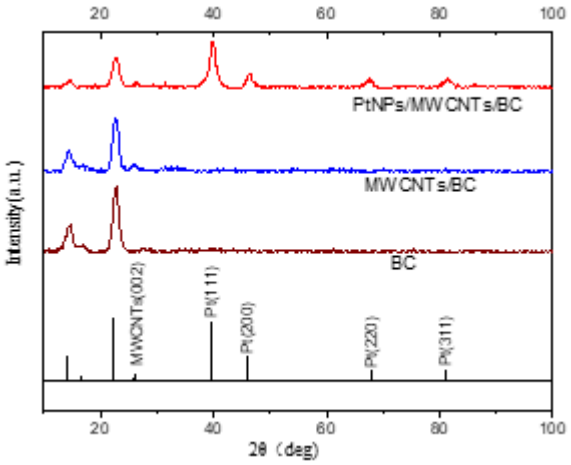

Figure 4. XRD analysis of PtNPs/MWCNTs/BC conductive hydrogel electrode film

Figure 4 shows the XRD of three different electrode materials, BC, MWCNTs/BC and PtNPs/MWCNTs/BC. BC three obvious characteristic peak at 2 θ = 14.2 °, 16.6 ° and 22.4 ° in three specimens were observed, PtNPs and MWCNTs decreases the BC the intensity of the diffraction

peak. MWCNTs characteristics appeared in the 2 θ = 26 ° diffraction peak, the characteristics of the PtNPs diffraction peak appeared in 2 θ = 39.5 °, respectively, 46.1 ° and 67.9 ° and 81.2 °, respectively corresponding to the platinum (111), (200), (220), and (311) crystal plane. Pt (111) was used to estimate the average grain size of PtNPs. According to Scherrer's formula, the average particle size of PtNPs was 7.8 nm, which indicated that although there was an aggregation phenomenon of PtNPs in the electrode film, the average particle size was still small [15-18].

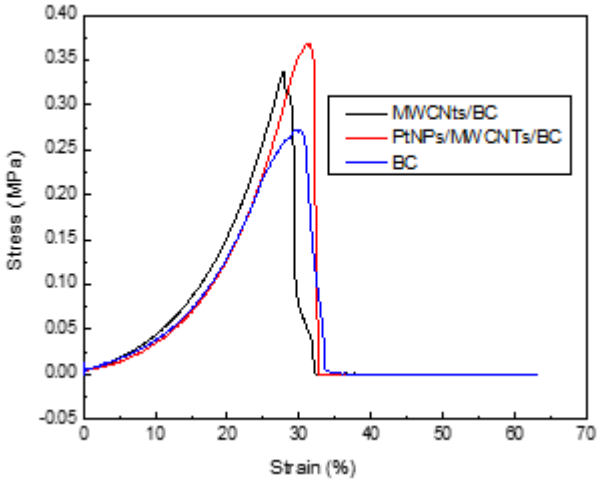

Figure 5. Stress-strain curves of PtNPs/MWCNTs/BC conducting hydrogel electrode films

Figure 5 shows the tensile stress-strain curve of PtNPs/MWCNTs/BC conducting hydrogel electrode film, which is also placed in the figure as a comparison of the stress-strain curve of BC and MWCNTs/BC conducting hydrogel electrode film. The fracture strength of BC was 0.27 Mpa, that of MWCNTs/BC conducting hydrogel electrode film was 0.32 Mpa, and that of PtNPs/MWCNTs/BC conducting hydrogel electrode film was 0.37 Mpa. MWCNTs and PtNPs increased the synergistic effect of BC fiber during tensile process, so MWCNTs and PtNPs did not change the elastic modulus and elongation of BC when the fracture strength was increased, which indicated that the mechanical similarity between PtNPs/MWCNTs/BC conductive hydrogel electrode film and implanted tissue still existed [19-21].

5. Conclusion

PtNPs/MWCNTs/BC electrode film had obvious electrocatalytic activity on glucose solution in neutral simulated body fluids. It also has catalytic activity on a variety of active substances in the body, such as dopamine, fructose and citric acid. The open circuit voltage of PtNPs/ MWCNTs/BC conductive hydrogel electrode film decreased from 0.22 v.vsce to -0.34 v. vsce after 5mM glucose was added into the solution, which fully indicated that under oxygen-rich conditions, PtNPs/ MWCNTs/BC conducting hydrogel electrode films have the ability to be selective to glucose, which can be used in the surface glucose fuel cells of implants. SEM and EDS experiments show that: PtNPs/MWCNTs/BC electrode film has a layered structure. The discrete homogeneous distribution of PtNPs in BC directly catalyzes the depletion of dissolved oxygen and glucose reactions. In the interior of the electrode, the electrochemical oxidation of glucose is the dominant reaction of the electrode. The electrode potential of the whole electrode film is close to the electrooxidation potential of glucose under the condition of hypoxia. The fracture strength of PtNPs/MWCNTs/BC electrode film was about 0.37Mpa, higher than that of pure BC, but the elastic modulus of PtNPs/MWCNTs/BC electrode film was consistent with that of BC.

Acknowledgments

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