

Microstructure and Mechanical Properties Analysis of Multi-walled Carbon Nanotubes/Polyvinyl Alcohol Conducting Hydrogel Electrode Film

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Abstract: According to the good conductivity and electrocatalytic activity of nano platinum and multi-walled carbon nanotubes (MWCNTs) and the hydrogel properties of polyvinyl alcohol (PVA), MWCNTs and PVA double-network porous hydrogels were designed and prepared. The surface of the conductive hydrogel electrode film formed a three-dimensional porous structure, and the stacking of the PVA-coated MWCNTs formed a nanoscale micropore structure. However, the micropore network structure inside the electrode film was not obvious, which was the reason why the electrode film did not selectively catalyzed glucose. The elastic modulus of PtNPs/MWCNTs/PVA electrode film is consistent with that of PVA. Its modulus of elasticity is close to that of human tissue.

Keywords: Conductive Hydrogels; Implantable Fuel Cells; Glucose; Modulus of Elasticity.

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 [1-2]. 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 [3].

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 and prepared. The surface of the conductive hydrogel electrode film formed a three-dimensional porous structure, and the stacking of the PVA-coated MWCNTs formed a nanoscale micropore structure. However, the micropore network structure inside the electrode film was not obvious, which was the reason why the electrode film did not selectively catalyzed glucose. The elastic modulus of PtNPs/MWCNTs/PVA electrode film is consistent with that of PVA. Its modulus of elasticity is close to that of human tissue [4-5].

2. Materials and Instruments

2.1. Materials

2.1.1. Sub-section Headings

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. 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, Guangx.

3. Preparation and Testing

3.1. Preparation

References 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°C water bath stirring.

(2) Washing of MWCNTs: An appropriate amount of MWCNTs was ultra sounded in 30% H₂O₂ for 30min and reflow for 2h at 80°C. 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) 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°C 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) Microstructure analysis of PtNPs/MWCNTs/PVA conducting hydrogel electrode films: The composite conductive hydrogel samples were freeze-dried in a freeze-drying machine. After the samples were treated with gold spray, the porous structure and PtNPs distribution were observed by Apollo300 field emission scanning electron microscope with a scanning voltage of 5kV.

(2) Mechanical properties analysis of PtNPs/ MWCNTs/ PVA conductive hydrogel electrode films: Tensile test on the texture analyzer, the sample in accordance with the national standard, the electrode film deposited on the stainless-steel mold of 4mm wide and 50mm long, using vernier caliper to test the thickness of the electrode film, input into the texture analyzer, tensile experiment, tensile speed: 5mm/s.

4. Results and Discussion

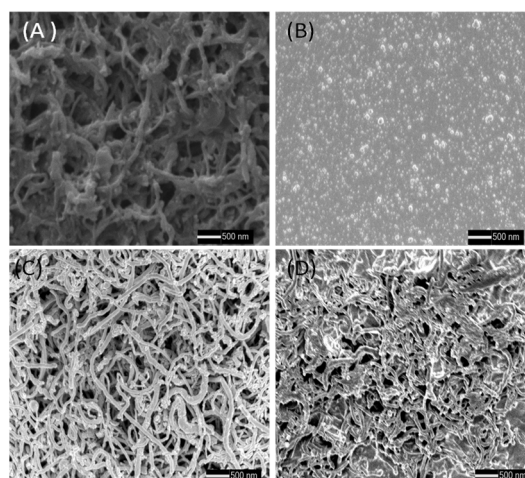


Figure 1. (A) SEM of MWCNTs/PVA (B) SEM of PtNPs (C) SEM of the surface of PtNPs/MWCNTs/PVA conducting hydrogel electrode film (D) SEM of the interior of PtNPs/MWCNTs/PVA conducting hydrogel electrode film

Figure 1 (A) shows the three-dimensional porous structure of MWCNTs/PVA conducting hydrogel electrode films. The stacking of MWCNTs coated with PVA forms nanoscale micropore structures with a diameter of about 200nm. The reasons for the formation of micropores have been explained in Chapter 3. Figure 1 (B) shows the form of PtNPs on the surface of the glassy carbon electrode, which is spherical. Figure 1(C) shows the distribution of PtNPs on the surface of MWCNTs/PVA conducting hydrogel electrode film. A large number of silvery PtNPs are formed on the surface of MWCNTs. Figure 1(D) shows the internal structure of PtNPs/ MWCNTs/ PVA conducting hydrogel electrode film. No morphologically identifiable PtNPs were found in the electrode film, and the pores between MWCNTs were also blocked by PVA. This explains why PtNPs/ MWCNTs/PVA electrode films cannot selectively catalyze glucose: The porous hydrogel layer rich in PtNPs only exists in the outer region of the electrode film. The pore characteristics inside the electrode film are reduced, and there is no long enough oxygen consumption path formed in the electrode film. Therefore, the overall electrode potential of the electrode film is still determined by the reduction potential of dissolved oxygen.

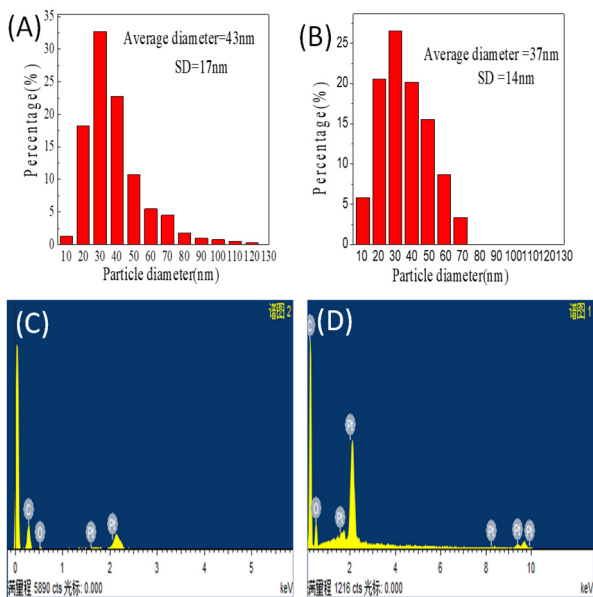


Figure 2. (A) Particle size distribution of PtNPs on the glassy carbon electrode (B) Particle size distribution of PtNPs on the surface of the MWCNTs/PVA conducting hydrogel electrode film (C) the outer surface of the PtNPs/ MWCNTs/ PVA conducting hydrogel electrode film (D) the interior of the PtNPs/MWCNTs/PVA conducting hydrogel electrode film EDS

In Figure 2 (A), the particle size distribution is 10-120nm, with an average particle size of 43 ± 19 nm. According to literature review, the particle size of PtNPs is mainly controlled by the in-situ reaction time of VC. As shown in Figure 2 (B), the particle size distribution of PtNPs on the surface of MWCNTs/PVA conductive hydrogel electrode film was 10-70nm, with an average particle size of 37 ± 14 nm. By comparing Figure 2 (A) and Figure 2 (B), MWCNTs/PVA conducting hydrogel electrode film can narrow the size distribution of PtNPs. In situ reduction of PtNPs using MWCNTs/PVA conducting hydrogel electrode film as template is conducive to the enrichment of PtNPs on the electrode surface, but at the same time, smaller particle size can be obtained. Figure 2 (C) shows Pt,C and O elements outside the PtNPs/MWCNTs/PVA conducting hydrogel electrode film, in which Pt element reaches 8.53wt%. Figure 4-14 (D) shows Pt, C and O elements in the PtNPs/ MWCNTs/ PVA conducting hydrogel electrode film, and the mass ratio of platinum reaches 11.45wt%. EDS can only be used for qualitative analysis, but not quantitative analysis [6].

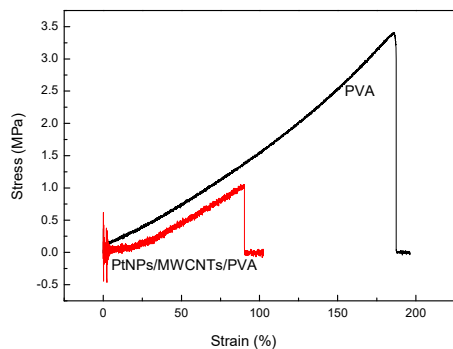


Figure 3. Stress-strain curves of PtNPs/MWCNTs/ PVA conducting hydrogel electrode films

Figure 3 shows the stress-strain curve of PtNPs/ MWCNTs/ PVA conducting hydrogel electrode film, which was also tested as a comparison of the stress-strain curve of PVA hydrogel. The fracture strength of PVA hydrogel was 3.38 Mpa, and that of PtNPs/MWCNTs/PVA conductive hydrogel electrode film was 1.04 Mpa. The strength of electrode film was more than 3 times lower than that of PVA hydrogel, which was caused by MWCNTs weakening the continuous hydrogel network of PVA. From the figure, we can also observe that the elongation of PtNPs/MWCNTs/PVA conductive hydrogel electrode film is reduced by half. However, it was also found that MWCNTs and PtNPs did not change the elastic modulus of PVA, which indicated that PtNPs/MWCNTs/PVA electrode film and human tissue still maintained similar elastic modulus [7].

5. Conclusion

The surface of PtNPs/MWCNTs/PVA electrode film conductive hydrogel electrode film formed a three-dimensional porous structure, the stacking of MWCNTs coated by PVA formed a nanoscale micropore structure, the diameter of the micropore is about 200nm, and the load of platinum is about 10wt%, but the micropore network structure inside the electrode film was not obvious. This is why the electrode film does not selectively catalyze glucose. The fracture strength of PtNPs/MWCNTs/PVA electrode film is about 1Mpa, which is 1/3 of that of PVA gel, but the elastic modulus of PtNPs/MWCNTs/PVA electrode film is consistent with that of PVA.

Acknowledgments

This paper was supported by Hebei Natural Science Foundation (E2019409072).

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