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Bacterial cellulose membrane supported three-dimensionally dispersed silver nanoparticles used as membrane electrode for oxygen reduction reaction in phosphate buffered saline

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ABSTRACT

A novel bacterial cellulose (BC) membrane supported silver nanoparticles (AgNPs) was synthesized with a facile *in situ* growth method. The physicochemical properties of AgNP/BC were characterized by scanning electron microscope (SEM), transmission electron microscopy (TEM) and X-ray diffraction (XRD). The results demonstrate that AgNPs with diameters of 10–20 nm were anchored throughout the three-dimensional network of BC membrane. The as-prepared AgNP/BC membrane was used as cathodic electrode to investigate its catalytic activity to oxygen reduction reaction (ORR) in phosphate buffered saline (PBS) for the first time. As a result, the maximum current density obtained with AgNP/BC was -3.94 mA cm^{-2}, which was higher than Ag electrode and AgNP. Besides, the maximum current density of AgNP/BC only decreased 4.3% in electrolyte with 10 mmol L^{-1} glucose. Such AgNP/BC membrane with advantages including biocompatibility, facile synthesis, high catalytic activity and good glucose tolerance could be valuable to ORR in implanted glucose fuel cells.

1. Introduction

Glucose fuel cells (GFCs) have been employed as power suppliers for implanted medical devices by oxidizing glucose and reducing oxygen to generate electric energy [1]. Comparing with conventional batteries, GFCs possess higher theoretical specific energy, lower cost and better environmental friendliness [2]. Because glucose and oxygen are both present and continuously replenished in physiological fluids by the metabolism, this revolutionary approach is theoretically able to provide enough energy along the patient lifetime without any need of battery replacements [3]. Furthermore, fuel cells can theoretically provide hundreds of mW of power if glucose and oxygen are efficiently and selectively oxidized and reduced. However, the oxygen reduction often constitutes a limitation for the power of GFCs due to the interference of human body fluid [4]. Therefore, further improvements in catalytic materials for oxygen reduction reaction (ORR) are urgently demanded. Considering body fluids as electrolyte, ORR catalysts should be highly catalytic efficient, tolerant to glucose and biocompatible [5].

Generally, Pt and Pt-based electrocatalytic materials are the most common and efficient catalyst for ORR, but their high cost is a critical issue limiting its widespread application in various electrochemical technologies [6–9]. Besides, the catalytic efficiency of Pt for ORR would be significantly decreased in physiological fluids due to its high catalytic efficiency for glucose oxidation [10–12].

Among all the non-Pt catalysts, Ag is supposed to be a competitive material owing to its relative low cost and high activity toward ORR [13–16]. Significantly, Ag could selectively reduce oxygen in body fluids since Ag as an element does not cause glucose oxidation. In current studies, Ag nanoparticles (AgNPs) used as catalysts to ORR are dispersed on various base materials, for instance, carbon nanotubes (CNT) and graphene oxides (GO). However, CNTs and GOs are found to be homininoxious when they infiltrate into human body fluids [17,18]. Therefore, novel biocompatible materials in which silver nanoparticles (AgNPs) are highly dispersed need to be developed.

Bacterial cellulose (BC) is a burgeoning biomedical material with good biocompatibility [19]. It has been applied in a variety of biomedical fields as artificial blood vessels, vascular grafts and scaffolds for tissue engineering [20–24]. In microscopic view, BC membrane is a three-dimensional network composed of plenty of nanoscale fibers. Noticeably, AgNPs could be *in situ* reduced and three-dimensionally dispersed in the BC network through a facile hydrothermal method by oxidizing 3 hydroxyls into carboxyls in each BC monomer [25]. At present, AgNP/BC hybrids have been

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mostly applied in wound dressing for its compatibility, good mechanical and antimicrobial properties [26–28]. Besides, it is a remarkable fact that such AgNP/BC membrane possesses high activity toward ORR in theory due to the three-dimensionally dispersion and nanoscale diameter of AgNPs, enabling it to be directly used as cathode membrane electrode of GFCs without any film-forming process. However, such AgNP/BC hybrids have not been reported to be applied as catalyst for ORR.

In this study, a bacterial cellulose (BC) membrane supported silver nanoparticles (AgNPs) was synthesized with a facile hydrothermal method. Three-dimensionally dispersed silver nanoparticles were grown *in situ* in the network of BC membrane, which was confirmed by X-ray diffraction (XRD), scanning electron microscope (SEM) and transmission electron microscope (TEM). Such AgNP/BC synthesis was directly used as membrane electrode for oxygen reduction reaction (ORR) for the first time. The evaluation on the ORR activity of BC, Ag electrode, AgNP and AgNP/BC were investigated through cyclic voltammetry (CV) and linear sweep voltammetry (LSV) in phosphate buffered saline. In addition, glucose tolerance of AgNP/BC was investigated in electrolyte with and without 10 mmol L^{-1} glucose. And a CV test before and after 500 cycles was employed to characterize the stability of AgNP/BC.

2. Materials and methods

2.1. Chemicals and materials

Bacterial cellulose was offered by Hainan Yida Food Co., Ltd. (China). $AgNO_3$, NaOH, NaCl, KCl, KH_2PO, $Na_2HPO_4{\cdot}12H_2O$ and $AgNO_3$ were purchased from Sinopharm Chemical Reagent Beijing Co., Ltd. Dulbecco's modified eagle medium (DMEM) was purchased from Gibcobrl. All chemicals were of analytical grade. Commercial Ag nanoparticles solution (1000 PPM, mean diameter of 20 nm) was purchased from Shanghai Huzheng nano technology Co., Ltd. Other reagents and solvents were purchased from the domestic suppliers and used as received.

2.2. Synthesis of AgNP/BC

The AgNP/BC membrane was synthesized with an *in situ* hydrothermal method according to our recent report [25]. The bacterial cellulose membranes were washed with deionized water and then immersed in 0.1 M NaOH solution at 95 °C for 1 h to remove the impurities such as medium, endotoxin et al. on the membranes. Finally, samples were rinsed with deionized water to pH = 7 and stored in deionized water at room temperature prior to further experimentation. Then silver ammonia solution (Tollens reagent, 0.1 mol L^{-1}) was prepared. The purified BC membranes were soaked in silver ammonia solution for 24 h and then thoroughly washed to remove residual chemicals on surface. Subsequently, BC membranes were kept in a warm water bath at 95 °C for 30 min, and after then the resulting membranes were washed with running deionized water to remove the residual chemicals. AgNP/BC hybrid gel-membranes were obtained.

2.3. Physical characterization

Phase identification was performed using a Rigaku D/max-RB X-ray diffraction (XRD, Rigaku Corporation, Japan). The samples were scanned from 10° to 90° at the speed of 10°/min. The surface and internal morphologies were examined by using an Apollo 300 scanning electron microscope (SEM, UK) and a transmission electron microscope (TEM; JEOL JEM-2100F). The actual silver amount in BC was quantified with atomic absorption spectrophotometer (AA300, Perkin Elmer; USA), in which the measured silver content was 0.56 mg, 24.2% of AgNP/BC. The conductivity of AgNP/BC was 1.1 ± 0.05°S/cm, measured with four probe method (RG-200PV, Napson Corp., Japan).

2.4. Electrochemical preparations and measurements

The AgNP/BC membrane was directly used for electrochemical measurements by tacking to the glassy carbon electrode (GCE) with copper conductive adhesive. As comparison, 1.1 mg commercial AgNPs with diameter of 20 nm were deposited onto a 0.196 cm^2 GCE with electrophoretic deposition. This control sample was marked as AgNP.

The electrocatalytic activities of the catalysts were studied in a three-electrode cell, which is composed of a Pt sheet counter electrode, a saturated calomel electrode (SCE, 0.245 V vs. NHE) reference electrode and a modified GCE working electrode, was utilized to perform the electrochemical measurement on a CHI 618D electrochemical Analyzer (Chenhua, China). Cyclic voltammetry (CV) tests were measured in the nitrogen saturated and oxygen saturated 0.1 M phosphate buffered saline (PBS, pH 7.4) at a sweep rate of 20 mV s^{-1} from 1.3 V to −0.7 V, respectively. The rotating disk electrode (RDE) voltammetry was also carried out in the 0.1 M PBS saturated with oxygen at a scan rate of 10 mV s^{-1} from 0.5 V to −0.7 V at various rotating speeds from 400 rpm to 2500 rpm by a Pine RDE setup (Pine Instrument Company, USA) combined with the CHI 618D electrochemical Analyzer.

3. Results and discussion

3.1. Characterization of AgNP/BC

The SEM images in Fig. 1A–C shows the morphologies of the surface of pure BC, the surface and across section morphologies of as-prepared AgNP/BC, respectively. Fig. 1A clearly depicts an interconnective network composed of BC nanofibers with pore size in 100 s nanometers. After the hydrothermal treatment, stable, uniform silver nanoparticles were evenly dispersed and anchored throughout the BC membrane, as shown in Fig. 1B and C. Besides, the silver nanoparticles in Fig. 1C were connected to each other, providing pathway for the transmitting of electron. The mean diameters of surface and internal silver nanoparticles were found to be 25.5 (Fig. 1B) and 18.5 (Fig. 1C) nm, respectively. The TEM image shows the morphology of silver nanoparticles of AgNP/BC in Fig. 1D, in which spherical particles with diameter of 10–20 nm were observed.

The XRD patterns of pure BC, the surface and interior of AgNP/BC are shown in Fig. 2. The peaks at $2\theta = 14.7°$, 16.8° and 23.2° of all materials could be attributed to the characteristic diffraction peaks of (110), (1 $\bar{1}$ 0) and (200) lattice plane of BC structure, respectively [29,30]. In the pattern of AgNP/BC, besides the BC lattice plane diffraction peak, the newly presented peaks located at $2\theta = 38.1°$, 44.3°, 64.4°, 77.5°and 81.5°corresponded to the (111), (200), (220), (311) and (222) planes of Ag crystals, respectively [31,32]. No characteristic diffraction peak of Ag_2O, AgO or other silver oxides appears in the pattern. On the basis of the results of XRD characterization, it also indicates that AgNP/BC membrane was successfully prepared by this *in situ* growth method. The mean size of Ag particles is 26.24 and 19.76 nm, respectively, calculated from the (111) plane diffraction peak of Ag crystal by the Scherrer equation [33], identifying with the SEM results.