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Carbon paper electrode modified with TiO_2 nanowires enhancement bioelectricity generation in microbial fuel cell

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ABSTRACT

A novel TiO_2 nanowires (TiO_2 -NWs) successfully modified a carbon paper (CP) substrate through hydrothermal reaction was used as bioanode in microbial fuel cell (MFC). TiO_2 -NWs with solid structure and approximate diameter of 10 nm formed an interconnected open pore along CP surface through SEM and TEM images. After stable operation 3 cycles, the maximum power density output of MFC used TiO_2 -NWs/CP as anode was 392 mW m^{-2}, this value increased by 49.5% compared to that of the raw CP (198 mW m^{-2}). Cyclic voltammetry (CV) analysis indicated TiO_2 -NWs could mediate direct extracellular electron transfer (EET) between the bacterium and the electrode, a pair of redox peaks with midpoint potential $E_m = -0.27$ V showed biofilm formation on the surface of TiO_2 -NWs/CP electrode. Smaller semicircle at the high frequency region represented the lower charge-transfer resistance from electrochemical impedance spectroscopy (EIS) measurement, which was advantageous for promoting electron transfer corresponding to the higher current density output in characterization of CV. In this work, TiO_2 -NWs/CP electrode improved the MFC performance owing to the high specific surface area, good biocompatibility, and electrochemical activities. Thus, the results suggested that it would provide more choices for further developing of MFC.

1. Introduction

Shewanella loihica PV-4 is a kind of exoelectrogen which is commonly inoculated in the anodic chamber of microbial fuel cells (MFCs). Organic compounds can be oxidized by the respiration of bacteria, and electrons stored in organic matters will be transferred to the surface of electrode via the bacterial outer membrane proteins [1,2]. In general, *Shewanella* has two distinct extracellular electron transfer (EET) pathways, one is direct electron transfer way through the outer membrane c-type cytochromes protein transfer, the other is indirect pathway through bacterial self-secreted electronic mediator (riboflavin molecules) [3–5]. MFC is a promising energy technology. But due to the high cost limits the practical application [6]. Therefore, it is very significant to obtain the anode material with low cost and high biological electrocatalytic activity.

Up to now, graphite fiber brush [7], reticulated vitreous carbon [8], carbon nanofiber [9] and carbon paper [10] are frequently used in MFC as the carbon based anode materials due to high conductivity and chemical stability. To enhance the anodic performance, exogenous electron mediator is added to the electrolyte, such as an anthraquinone-2,6-disulphonic disodium salt (AQDS), humic acid, quinone and neutral red etc. These mediators have been used to facilitate indirect electron transfer to the anode [11,12], but they are usually expensive, toxic and easily washed away [13], resulted in extra increased cost, pollution of the electrolyte, and not easy to operate. Therefore, a solid state and non-toxic mediator was modified to the surface of the electrode to efficiently and stably accelerate EET to the electrode.

In order to increase the specific surface area of electrode and promote long-distance EET, nanostructured materials is used to modify the electrode surface, many kinds of nanomaterials are electrically conductive and biocompatible with microorganisms [14] (such as Fe_2O_3, α-FeOOH and FeS). Nakamura et al. demonstrated the role of a-Fe_2O_3 colloids in promoting a long-distance EET process in the bacterial network [15]. It was previously reported that ITO anode modified by α-Fe_2O_3 nanorod and chitosan (CS) utilizing a layer-by-layer (LBL) assembly technique, the MFC produced higher current comparing with the bare ITO [16]. While fabricating an anode by rolling α-FeOOH into activated carbon on stainless steel mesh, the maximum

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power density of the MFC increased by 36% [17]. The modified anode by Fe_3O_4 also enhanced the power density [18]. Thus, through the construction of nanostructured anodes could enlarge the surface area of the electrodes to facilitate long distance electron transfer.

TiO_2 is well known as an *n*-type semiconductor and it has attracted many research groups' interest in the world. TiO_2 has been wildly used in many fields. For example, supercapacitor [19], dyesensitized solar cells [20], electrochemical biosensors [21], etc. This is reason it has good biocompatibility, physical and chemical stability, and environmentally friendly [22], which have attracted the abroad application of TiO_2 in the MFC fields. It was previously reported that nanostructured polyaniline/titanium dioxide composite as the anode (PANI-TiO_2) can significantly improve the power density of MFCs than using polyaniline alone [23]. Wen et al. reported that anatase TiO_2 nanoparticles modified carbon cloth anode is a slightly smaller output current I_{max} than that of CNTs modified electrode (3.25 vs 3.64 A cm^{-2}) [24]. One of the reason may be the smaller specific surface area, and TiO_2 particles have a larger impedance. However, to the best of our knowledge, the reports about the application of nanostructured TiO_2 without compositing other conductive material in MFC are only a few. We expect that the surface of the carbon electrode modified with TiO_2 nanowires can form a porous and cross-linked structure, which can greatly increase the specific surface area of the electrode and help to form a larger biofilm for improving bioelectricity generation.

In view of this, we reported the preparation of TiO_2 nanowires (NWs) on the surface of carbon paper (CP). The modified electrode was used as the anode of MFC and inoculated with *S. loihica* PV-4. EET was investigated from the c-type cytochromes on the outer membrane of *S. loihica* PV-4 in the presence of TiO_2 -NWs, and demonstrated the role of semiconductive nano-TiO_2 in promoting a long-distance EET process in the bacterial network. CP was modified by TiO_2 -NWs greatly outperforms carbon electrode owing to its abilities to open porous interface and electrochemical activity surface area. TiO_2 -NWs/CP electrode with more bacteria formed biofilm facilitated direct electron transfer, and provided the higher power density output.

2. Experimental

2.1. Reagents and apparatus

Carbon paper was purchased from ShangHai HESEN Electrical Appliance Co. Ltd. Proton exchange membrane (PEM, Nafion 117) was purchased from DuPont (Wilmington, DE). Tetrabutyl titanate, anhydrous ethanol and other chemical reagents were purchased from Sinopharm Chemical Reagent Co., Ltd. All the reagents were of analytical grade without further purification and distilled water was used throughout the experiment. Before use, CP was ultrasonically cleaned for an hour with acetone, ethanol and ultrapure water respectively, then dried in an oven at 80 °C. TiO_2 sol was synthesized in laboratory.

The surface morphology of TiO_2 -NWs and CP were characterized by a field emission scanning electron microscopy (FESEM, Zeiss, Germany). The internal structure of TiO_2 -NWs was observed by transmission electron microscopy (TEM, JEM-200CX, JEOL, Japan). Raman spectra were measured using an inVia Raman Microscope (Renishaw Corporation, United Kingdom) with 785 nm laser excitation. The crystalline structure of TiO_2 -NWs was determined by X-ray diffraction (XD-3A, Shimadzu Corporation, Japan). All electrochemical experimental data were recorded with CHI760D electrochemical workstation (CH Instruments Inc., China).

2.2. Preparation of TiO_2 -NWs/CP electrode

At room temperature (25 °C), we synthetized the titania sol. 30 ml of ethanol into the beaker, following slowly instilled 5 ml of tetrabutyl titanate into the ethanol using disposable plastic dropper with the rapid stirring, then added 0.8 ml of acetic acid to the mixed solution of ethanol and tetrabutyl titanate. At the beginning, the solution was clear and transparent. After stirring the solution approximate 2 days, we found it gradually become milky. It can be used to be loaded on the surface of CP when its color turned milky completely. Put the clean CP into TiO_2 sol, soaking it for 15 min, then dried it at 80 °C. After that, calcined it for 30 min in a tubular fumace at 350 °C, forming TiO_2 nanoparticles on the CP surface (TiO_2 nanoparticle seeded substrate). When the CP with TiO_2 nanoparticle cooled down to room temperature, hydrothermal reaction would be conducted in the Teflon-lined stainless steel autoclave (100 ml in volume), which was filled with 70 ml of aqueous solution of 10 M NaOH, then placed it in an oven at 180 °C for 28 h. After the hydrothermal reaction, the sample immersed in 0.1 M hydrochloric acid for 2 h, then repeatedly washed using ultrapure water until its surface was of neutral and dried at 80 °C. Finally, put the dried simple to the tubular fumace and calcined it at 550 °C for 1 h in the nitrogen atmosphere.

2.3. MFC construction and operation

A double chamber microbial fuel cell (MFC) was constructed with "H" type. The volume of both anode and cathode were 350 ml and separated by proton exchange membrane (PEM). Every chamber was sealed with rubber stoppers and the 1000 Ω resistor was connected at the start-up stage. TiO_2 -NWs/CP (2 × 2.5 cm) and raw CP (4 × 4 cm) were used as anode and cathode electrode respectively, with the spacing of 6 cm. The electrode was connected with a copper conductor, and the resistance at the junction was no more than 2 Ω, then sealed using a silicone rubber in order to prevent the corrosion of the metal from the solution.

Initially, three hundred milliliters of defined media (DM) was added into the anode chamber and bubbled with nitrogen until oxygen was completely removed. Then inoculated with *S. loihica* PV-4 for culturing 2 days in DM. The catholyte contained 50 mM potassium ferricyanide ($K_3[Fe(CN)_6]$) and 100 mM PBS (phosphate buffer solution). The polarization curve can be tested after more than two consecutive cycles and stable voltage output of MFC. The measurement was done by varying the external resistance and the variation range was 40 kΩ to 80 Ω. When the different external resistance was connected between the anode and the cathode, the voltage change was closely monitored until the output voltage achieved stability. All MFCs were operated at 30 ± 0.5 °C in anaerobic conditions. The control experiment was performed under the same conditions only using bare CP as the anode.

2.4. Bacterial culture

Bacterial culture followed a previous report [15]. *S. loihica* PV-4 was grown aerobically in Marine Broth (100 ml; 20 g l^{-1}), and incubated with shaking at 30 °C until the optical density at 600 nm (OD600) reached about 1.0. Subsequently, the supernatant was removed by centrifugation (7570 g, 5 min). Marine Broth was replaced with 100 ml of defined media [DM; $NaHCO_3$ (2.5 g l^{-1}), $CaCl_2{\cdot}2H_2O$ (0.08 g l^{-1}), NH_4Cl (1.0 gnL^{-1}), $MgCl_2{\cdot}6H_2O$ (0.2 g l^{-1}), NaCl (10 g l^{-1}), and HEPES (7.2 g l^{-1})]. The concentrated cells were washed three times with DM, after that, the cells were further cultivated aerobically in DM at 30 °C for 2 days using lactate as a carbon source.