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Macroscale porous carbonized polydopamine-modified cotton textile for application as electrode in microbial fuel cells

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HIGHLIGHTS

- A novel porous and biocompatible NC@CCT electrode is fabricated for MFCs.
- NC@CCT is coated by N-doped carbon nanoparticles.
- The power density of MFC with NC@CCT is 80.5% higher than that of carbon felt.
- The synthesis method is facile, cost-effective and environment-friendly.

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ABSTRACT

The anode material is a crucial factor that significantly affects the cost and performance of microbial fuel cells (MFCs). In this study, a novel macroscale porous, biocompatible, highly conductive and low cost electrode, carbonized polydopamine-modified cotton textile (NC@CCT), is fabricated by using normal cheap waste cotton textiles as raw material via a simple in situ polymerization and carbonization treatment as anode of MFCs. The physical and chemical characterizations show that the macroscale porous and biocompatible NC@CCT electrode is coated by nitrogen-doped carbon nanoparticles and offers a large specific surface area (888.67 $m^2 g^{-1}$) for bacterial cells growth, accordingly greatly increases the loading amount of bacterial cells and facilitates extracellular electron transfer (EET). As a result, the MFC equipped with the NC@CCT anode achieves a maximum power density of 931 ± 61 mW m^{-2}, which is 80.5% higher than that of commercial carbon felt (516 ± 27 mW m^{-2}) anode. Moreover, making full use of the normal cheap waste cotton textiles can greatly reduce the cost of MFCs and the environmental pollution problem.

1. Introduction

Microbial fuel cells (MFCs), as a green bioenergy technology, can utilize the microbial bacteria to oxidize and decompose organic wastes, achieving two goals of wastewater treatment and electricity generation, and providing an ideal solution for the environment and energy issues we are facing [1–3]. Therefore, in recent years, this ideal technology has attracted great attention of researchers all over the world. However, wastewater treatment and electricity generation are two long-term goals of developing the MFCs technology, because large scale practical applications of MFCs are yet hindered owing to their low performance and high cost of construction [4,5].

In MFCs, the anode provides a carrier for bacterial cells growth, and can transmit electrons produced by decomposition of organic waste, has a vital impact on the performance of MFCs. The main reason for the low performance of MFCs may be inadequate bacterial cells loading on anode [6]. Consequently, the ideal anode material should possess good conductivity, biocompatibility, high specific surface area, non-corrosive and low-cost characteristics [7]. Nowadays, carbon-based electrodes, which are widely used commercial anodes, suffer from poor bacterial loading and low EET efficiency [8–12]. To enhance the performance of MFCs, various modifications of these carbon-based electrodes have been extensively studied including conductive materials, carbon nanotubes (CNTs), noble metals and surface treatments [13–20]. Although these modifications have greatly promoted the performance, they are too expensive for practical applications of MFCs. Hence, developing high-performance and low-cost anode is crucial to improving the performance of MFCs.

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Cotton textile is a low-cost, flexible and porous material made by weaving or pressing natural cellulose fibers [21]. Cotton directly converts into carbonized cotton via a facile carbonization treatment, which remains its structural properties and compatibility in textiles as well as produces highly conductive fibers [22–24]. Accordingly, owing to their excellent properties, cotton-based materials as electrode materials have drawn widespread attention [25]. Xie et al. reported a three-dimensional (3D) CNT-textile anode for MFCs, which offered an open 3D space for internal microbial colonization and affinitive CNT surface for improved EET [4]. Unfortunately, CNT coatings are not only expensive but also might be inhibitory or even toxic to microorganisms [26,27]. Therefore, these have inspired us to develop environmentally friendly, biocompatible and inexpensive cotton textile materials that can greatly promote performance and reduce cost of MFCs.

Herein, for the first time, using cheap normal waste cotton textiles as raw material via a simple in situ polymerization and carbonization treatment, we successfully fabricate a novel porous, biocompatible, high conductivity, and low-cost flexible electrode, carbonized polydopamine-modified cotton textile, as anode electrode material in MFCs. Because waste cotton textiles are always treated as garbage and the recovery rate is very low, resulting in waste of resources and environmental pollution problem. If these waste cotton textiles can be recycled, which not only saves resource, but also reduces the environmental pollution problem. Furthermore, polydopamine (PDA), which is a well-known biological macromolecule and widely distributed in animals, has been used as an environment-friendly nitrogen source and carbon source in our study. The physical and chemical characterizations of novel NC@CCT material were investigated, and the performance of NC@CCT used as the MFC anode was also evaluated. The results showed that the MFC equipped with NC@CCT anode performed better than that of commercial carbon felt anode and carbonized polydopamine-modified cotton textile could be a valid approach to fabricate high-performance anode of MFCs.

2. Experimental section

2.1. Preparation of CCT electrode

Using normal waste cotton textile as raw material, highly conductive and porous carbonized cotton textile (CCT) electrode was fabricated via a simple ultrasonic cleaning, drying and carbonization treatment, involving ultrasonic cleaning cotton textile with 1 M NaOH and 1 M HCl solution successively, then drying the as-prepared cotton textile at 60 °C for 24 h, finally carbonizing the dry cotton textile at 1000 °C for 1 h in Ar gas condition.

2.2. Preparation of nitrogen-doped CCT electrode

The polydopamine-modified cotton textile was prepared via the in situ polymerization of dopamine. Firstly, the as-prepared cotton textile was immersed in 200 mg mL^{-1} dopamine hydrochloride solution (pH = 8.5). Secondly, the polymerization was carried out for 24 h under stirring. Then, the sample was collected, washed with deionized water and dried at 60 °C for 24 h in vacuum. Finally, the polydopamine-modified cotton textile was carbonized at 1000 °C for 1 h in Ar gas and vacuum condition to prepare nitrogen-doped CCT (NC@CCT) electrode.

2.3. Materials characterization

The morphologies of electrode and biofilm were observed by using FESEM (ZESISS ULTRA 55, Germany). The elemental analysis was carried out on energy-dispersive X-ray spectroscopy (EDS, Oxford INCA Energy TEM 250, England). The XPS measurements were carried out on ESCALAB 250 (Thermo Fisher Scientific, USA). The XRD pattern was obtained on X-ray diffractometer (XRD, Bruker D8 Advance, Germany) with Cu Kα radiation (λ = 1.5405 nm) from 10° to 80°. The Raman spectra were recorded by using Laser confocal Raman spectroscopy (Lab RAM Aramis, HORIBA, Japan). The specific surface area of electrode was calculated by Brunauer-Emmett-Teller (BET) method. Pore size distribution was characterized with a porosimetry analyzer (Micrometrics, ASAP 2020, USA) and analyzed according to the Barrett-Joyner-Halenda (BJH) adsorption model. The electrical resistivity analysis was recorded on a four-probe conductivity measurement device (RST-8, Guangzhou). The biomass attachment onto the anode was determined by the Modified Bradford Protein Assay Kit (Sangon Biotech, Shanghai, China).

2.4. MFC construction and operation

An air-cathode cylindrical MFC, consisting of a polymethyl methacrylate chamber with a volume of 28 mL, was constructed as previously reported [28]. The CCT and NC@CCT anodes (2.0 cm × 2.0 cm × 0.1 cm) were connected with a titanium wire. For comparison, carbon felt (CF) electrode with the same size was also used as anode. The cathode was prepared as previously reported [7] and the cathodic catalyst was Pt/C (0.5 mg cm^{-2}).

To start up the MFCs experiments, the reactors were inoculated with 5.0 mL effluent of matured single chamber MFC anolyte and 23 mL of sodium acetate (1 g L^{-1}) medium solution as previous report [7]. The medium solution was consists of 50 mM phosphate buffer solution (pH 7.0), 12.5 mL L^{-1} vitamin solution, and 12.5 mL L^{-1} mineral solution. The polarization curve was operated by varying the external resistance in the MFCs from 8000 Ω to 100 Ω. The power density was normalized by the projected surface area of the anode (4.0 cm^2). All experiments were operated in fed-batch mode and performed in triplicate.

2.5. Electrochemical measurements

Electrochemical measurements were performed on Solartron 1480 (Solartron Analytic, England) in a three electrode half cell: the NC@CCT, CCT and carbon felt anodes were used as the working electrode, the titanium wire and saturated calomel electrode (SCE) were used as the counter electrode and the reference electrode. For the chronoamperometric (CA) measurement, the working electrode was poised at 0.2 V (*vs.* SCE) and the current was obtained. The chronopotentiometry (CP) was carried out at 0.1 μA after formation of a stable biofilm. The cyclic voltammograms (CV) was performed from −0.6 V to 0.3 V (*vs.* SCE) with a scan rate of 10 mV s^{-1}. Electrochemical impedance spectroscopy (EIS) was performed on the electrochemical station (Autolab PGSTAT-302 N, Metrohm Co., Switzerland) in the MFC at open circuit potential in a frequency range of 10^5–10^{-2} Hz with a sinusoidal perturbation signal of 5 mV.

3. Results and discussion

3.1. Preparation and characterization of NC@CCT electrode

The porous carbonized polydopamine-modified cotton textile (NC@CCT) electrode was fabricated via a simple in situ polymerization and carbonization treatment. The schematic synthesis route of NC@CCT is displayed in Fig. 1a. Using cheap waste cotton textiles as raw material, and cutting a waste cotton textile (CT) (Fig. 1b) with thickness of 0.1 cm into small pieces, after cleaning and drying, then in suit polymerization of dopamine, finally carbonizing at 1000 °C for 1 h in Ar gas condition, the CT directly converted into the black NC@CCT with a similar thickness (0.1 cm) and slight shrinkage in size (Fig. 1c), due to the shrinkage of cellulose fibers in the cotton textile during carbonization treatment process. After carbonization treatment, the NC@CCT was flexible under folding condition (Fig. 1d). The raw material is low-cost and biocompatible, moreover, the synthesis route is facile and environment-friendly.

The morphologies of CT, CCT and NC@CCT were characterized by