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Controlled modification of carbon nanotubes and polyaniline on macroporous graphite felt for high-performance microbial fuel cell anode

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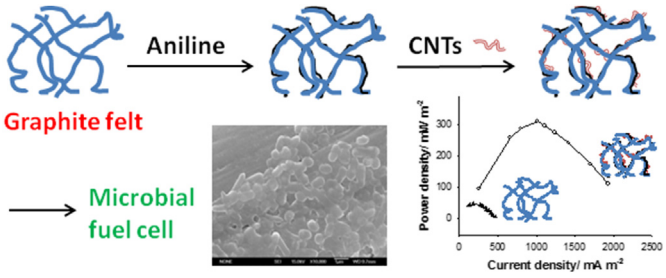
HIGHLIGHTS

- Polyaniline (PANI) was electropolymerized on the surface of graphite felt (GF).
- Carbon nanotubes (CNTs) were electropheritically immobilized on the PANI/GF.
- CNT modification increased the effective surface area and electrical conductivity.
- A mediator-free dual-chamber microbial fuel cell was constructed from the anode.
- The MFC power output increased drastically with the CNT modification.

GRAPHICAL ABSTRACT



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ABSTRACT

Polyaniline (PANI) was electropolymerized on the surface of macroporous graphite felt (GF) followed by the electrophoretic deposition of carbon nanotubes (CNTs). The as-prepared macroporous material was characterized by scanning electron microscopy, water contact angle goniometry and electrochemical techniques. Upon the modification of PANI, a rough and nano-cilia containing film is coated on the surface of the graphite fibers, transforming the surface from hydrophobic to hydrophilic. The subsequent modification by CNTs increases the effective surface area and electrical conductivity of the resulting material. The power output of a mediator-free dual-chamber microbial fuel cell (MFC) constructed from the GF anode and an exoelectrogen *Shewanella putrefaciens* increases drastically with the CNT modification. The CNT/PANI/GF MFC attains an output voltage of 342 mV across an external resistor of 1.96 kΩ constant load, and a maximum power density of 257 mW m^{-2}, increased by 343% and 186%, compared to that of the pristine GF MFC and the PANI/GF MFC, respectively. More bacteria are attached on the CNT/PANI/GF anode than on the PANI/GF anode during the working of the MFC. This strategy provides an easy scale-up, simple and controllable method for the preparation of high-performance and low-cost MFC anodes.

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1. Introduction

Microbial fuel cells (MFCs) directly convert chemical energy to electrical energy by harnessing the metabolism of exoelectrogens, microorganisms that can mediate extracellular electron transfer (EET) [1–4]. Ideally, the final electron acceptor of an exoelectrogen should be a solid conductor, i.e., the anode. Owing to the enzymatic diversity and various strain availability of exoelectrogens, MFCs are able to recover the energy of various organic molecules in human excrement [5], marine sediment [6–9], wastewater [10,11], etc. Apparently, MFCs have a great potential for a broad range of applications, such as wastewater treatment and bioremediation with concomitant energy production [10,11], electronic power sources for space shuttles, and biosensors [12–15]. However, low power output remains one of the main obstacles for their widespread practical applications.

Reduced oxidoreductases of exoelectrogens at the extracellular membrane rely on three principal, but not mutually exclusive EET mechanisms in transferring their electrons to the exogenous final acceptor: direct electron transfer; indirect electron transfer via shuttling of excreted mediators; and through electrically conductive pili [16–18]. Therefore, development of anode materials, which can directly affect the bacterial attachment, electron transfer and substrate oxidation, is a key factor for the MFC performance and cost-effectiveness [19].

Among different electrode materials used as the anode of MFCs, carbon-based materials such as carbon cloth, carbon paper, especially graphite/carbon felt have been the mostly adopted because of their very low costs, excellent electrical conductivity, chemical stability, non-corrosiveness, and good biocompatibility [19–22]. In brief, graphite felt (GF), a three-dimensional (3D) porous carbon material, possesses a high specific surface area to interface with bacteria, resulting in high power density. However, the hydrophobic surface property of graphite compromises its ability for the bacterial attachment and electron transfer via shuttling of bacterial excreted mediators. Modification of the surface morphology and property might enhance the attachment and the viability of the bacteria, facilitating the EET mechanism, therefore enhancing the MFC performance.

Carbon nanotubes (CNTs), a carbon based nanomaterial consisting of cylindrical graphene sheets [23], with unique electrical and structural properties, have been incorporated into MFC anodes [24–26]. The incorporation of 20 wt.% CNT into a conductive polymer anode increases the power density of MFCs [24]. The MFC anode of vertically aligned, forest type multiwalled carbon nanotubes (MWCNTs) increases the anode surface-to-volume ratio, therefore improves the microbial ability to couple and transfer electrons to the anode [26].

As a conductive polymer, polyaniline (PANI) has been used for the MFC anode preparation due to its facile processibility, high hydrophilicity, electrical conductivity, biocompatibility and stability [21,24,27–30]. The positively charged PANI in neutral solutions electrostatically interacts with the negatively charged bacterial membrane [31]. Thus, a high bacterial density with high biodiversity has been observed on the surface of a carbon felt anode modified by PANI, corresponding to a 35% increase in the power output [28]. Of notice is also the decoration of PANI on graphene to promote bacterial adhesion and biofilm formation [21,30].

This paper unravels a new strategy for the electrophoretic adsorption of CNTs on PANI modified macroporous GF, serving as an anode in a mediator-free microbial fuel cell using exoelectrogen *Shewanella putrefaciens*. The surface morphology, surface hydrophilicity, and the electrochemical properties of the modified GF were characterized. The CNT modification was controllable with high reproducibility and the anode conductivity was not compromised by any nonconductive polymer binder. The effect of PANI and CNT modification on the MFC power output was investigated, and the CNT adsorption conditions were optimized.

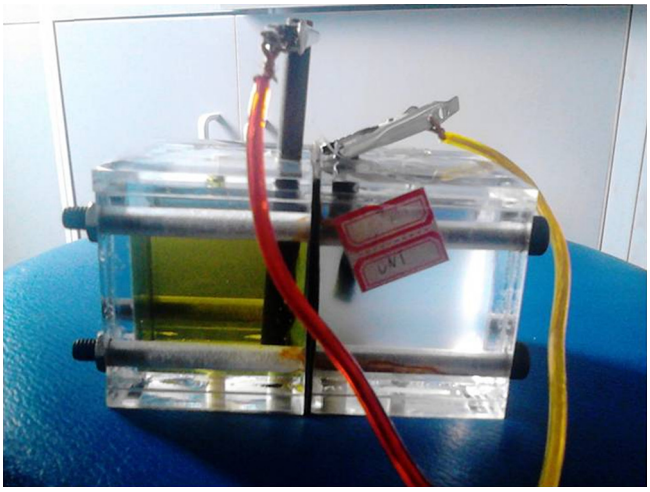

Fig. 1. The picture of the dual-chamber MFC with two equal rectangular cells with a Nafion PEM sandwiched between the two chambers (left: cathodic chamber, right: anodic chamber).

2. Experimental

2.1. Materials and reagents

Multiwalled carbon nanotubes (MWCNTs) (outer diameter < 8 nm, bundle length 10–30 μm, purity > 95%) were purchased from Chengdu Organic Chemicals (Chengdu, P.R. China). Macroporous graphite felt (GF) (pore size 200–300 μm, thickness: 4 mm, carbon content: 98%) was purchased from Beijing Sanye Carbon (China). Nafion 117 (thickness: 183 μm, density: 360 g m^{-2}, conductivity: 0.083 s cm^{-1}, exchange capacity: 0.89 meq g^{-1}) (DuPont, USA) was used as a proton exchange membrane (PEM) in the microbial fuel cells. MWCNTs were treated by refluxing in a mixture of sulfuric and nitric acids (3:1 v/v) at 25 mg mL^{-1} for 4 h to enhance their hydrophilicity and thus aqueous dispersivity. Ultracentrifugation of the MWCNT slurry at 20,000 rpm followed by the pellet washing to neutral pH by deionized water was repeated several times. The resulting neutral MWCNT-water suspension of ~3.3 mg mL^{-1} was centrifuged at 7000 rpm. The collected supernatant was used for modification of GF. All other chemicals were obtained from a local chemical agent and used without further purification. Deionized water (>18.2 MΩ cm^{-1}) obtained from a Millipore water system was used in all the experiments.

2.2. Instrumentations and analysis

Pristine or modified GF before and after MFC running, was probed by scanning electron microscopy (SEM, JEOL JSM 6700F, operated at 5 kV or 15 kV). Based on static water contact angle measurement, the surface property of the pristine or PANI modified GF was probed by an optical goniometer (JC2000C1, Shanghai Zhongchen Digital Technique Apparatus, China) using the sessile drop method in air atmosphere. The CNT loading amount at the modified GF was determined by measuring the absorbance at 249 nm of the CNT suspension before and after the CNT loading, by using a UV–Vis spectrophotometer (UV-2450, Shimadzu Scientific Instrument, Japan). All electrochemical measurements were performed at room temperature (25 °C) using a CHI-660C