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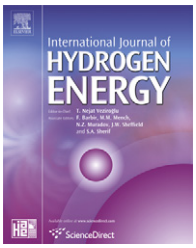

# A mediatorless microbial fuel cell using polypyrrole coated carbon nanotubes composite as anode material

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ABSTRACT

A microbial fuel cell (MFC) was constructed using polypyrrole (PPy) coated carbon nanotubes (CNTs) composite as an anode material and *Escherichia coli* as the biocatalyst. The composite PPy-CNTs were synthesized by the in situ chemical polymerization of pyrrole on the CNTs using ammonium persulfate as an oxidant. The electrocatalytic behaviors of the composite modified anode were investigated by means of cyclic voltammetry, electrochemical impedance spectroscopy and discharge experiments. The PPy-CNTs modified anode showed better electrochemical performance than that of plain carbon paper. The amount of the loading of the composite on the anode was also investigated. The power output of the MFC increased along with the increase of the composite loading. In the absence of exogenous electron mediators, the MFC with the composite modified anode contained 5 mg $cm^{-2}$ PPy-CNTs exhibited a maximum power density 228 mW $m^{-2}$, which is much higher than those reported in the literature so far for *E. coli* using efficient electron mediators. These results show that the PPy-CNTs composite anode is promising for MFC application.



## 1. Introduction

A microbial fuel cell (MFC) is an electrochemical device that can directly convert the chemical energy contained in organic matter into electricity by means of the catalytic activity of living microorganisms. Generally, the MFC consists of an anode and a cathode, separated by a membrane. At the anode, microorganisms convert organic material under anoxic conditions. These microorganisms use the electrode as the electron acceptor. The electrons flow through an external circuit to the cathode, where oxygen is reduced to water. At present, the microbial fuel cell is considered to be a very popular and promising bio-electrochemical power source for directly recovering electrical energy from carbohydrates as well as organics in wastewater [1–3]. However, the power output of the MFC is too low for practical applications, which is mainly due to the difficult electron transfer between bacterial cells and extracellular electrode [4,5]. Therefore, a high-performance electrode material is most essential. Especially, the anode material and its structure, can directly affect the bacteria attachment, electron transfer and substrate oxidation.

To date, carbon materials such as carbon cloth and carbon paper are applied in most MFC electrode due to their good stability in the microbial inoculum mixture, high conductivity and high specific surface area. Nevertheless, they have little

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electrocatalytic activity for the electrode microbial reactions. Modification of the carbon materials is the main approach for improving their performance. Many attempts have been made to improve anode performance of the MFC. Schröder et al. proposed a novel MFC concept using polyaniline-modified platinum as an anode, which boosted the power output of the MFC to reach current density far above those described before [6]. Although the power density is high, this MFC system requires improvements to overcome the inherent drawbacks such as the need for a potential-pulse operation to maintain the catalytic activity of the anode [6]. Recently, they investigated the properties of tungsten carbide as anodic electrocatalyst for MFC application [7,8]. Qiao et al. reported the feasibility by using carbon nanotube/polyaniline composite as anode material for MFC [9]. Chen et al. reported the improved performances of *Escherichia coli*-catalyzed microbial fuel cells with composite graphite/PTFE anodes [10].

Carbon nanotubes (CNTs) have emerged as new class nanomaterials that are receiving considerable interest because of their unique structure, high conductivity and high surface-to-volume ratio. These properties make them extremely attractive for fabricating electrodes [11–13]. However, it has been reported that CNTs have a cellular toxicity that could lead to proliferation inhibition and cell death [14,15]. Thus, they are not suitable for MFC unless modified to reduce the cellular toxicity. Recently, conducting polymer/CNTs composites have received significant interest because the incorporation of CNTs in conducting polymers can lead to new composite materials possessing the properties of each component with a synergistic effect. Sahoo et al. reported that the PPy-coated carbon nanotubes have significantly higher electrical conductivity than that of neat carbon nanotubes [16]. These performance made polymer/CNTs would be useful in MFC. Among all the conducting polymers studied up to date, PPy can be considered as one of the most attractive materials due to its excellent conductivity, stability and biocompatibility even in neutral pH solution. Yuan and Kim modified the anode of the MFC with electropolymerized PPy and improved the power density of the MFC greatly [17]. In this paper, we investigate the performances of the composite PPy-CNTs modified carbon paper for MFC and discuss the influence of the anodic composition on the discharge behaviors on glucose oxidation via electrochemical catalysis of bacteria *E. coli*.

## 2. Material and methods

### 2.1. Chemicals and materials

Pyrrole (≥99.5%, Shenyang Lianbang Reagent Factory, Shengyang, China) was distilled under reduced pressure prior to use. Ammonium persulfate (APS) was purchased from Tianjin Jizhun Reagent Factory (China). The multi-walled carbon nanotubes (MWNTs) (95%, 20–60 nm) were purchased from Shenzhen Nanotech Port Co., Ltd. (Shenzhen, China) and treated with nitric acid during purification process and then filtered, rinsed with double-distilled water and dried. All other chemicals were of analytical grade and used as-received, unless stated otherwise. As binder, a 5% Nafion 117 (DuPont Co.) solution was used. A perflourinated membrane (Nafion 112, DuPont Co.) was pretreated by boiling in $H_2O_2$ (30%), deionized water, 0.5 M $H_2SO_4$, and deionized water (each time for1 h), respectively. In order to prevent membrane swelling by water when it was placed in the MFC compartment, membranes were stored in deionized water prior to use. Phosphate buffer solution (PBS; 0.1 M, pH 7) was made from $Na_2HPO_4$ and $NaH_2PO_4$. Deionized (DI) water was used in all experiments.

### 2.2. Synthesis of PPy-coated CNTs

PPy-coated CNTs were synthesized by in situ polymerization of pyrrole on CNTs. In a typical process, 0.1 g treated CNTs were first dispersed in the mixed solvent of 0.01 M HCl and 0.01 mM sodium dodecylsulfonate (SDS) solutions at room temperature for 2 h using an ultrasonic homogenizer. Thereafter, pyrrole was added into this solution and stirred for 0.5 h, an APS solution (2 g/ml) was added dropwise (1 ml/min) to the above solution with constant sonication at ambient temperature. The reaction mixture was stirred for 24 h. The black suspension was collected by filtration and rinsed with deionized water and ethanol. Finally the powder was dried under vacuum at 60 °C for 24 h. As compared with PPy-CNTs, PPy was synthesized in the same way in the absence of CNTs.

### 2.3. Characterization of PPy and PPy-CNTs composite

The infrared (IR) spectra of the samples in KBr pellets were recorded on Bruker Equinox 55 Fourier transform infrared spectrometer (FT-IR). The morphology was determined on a JEM-2000EX transmission electron microscope (TEM) with an accelerating voltage of 20 kV.

### 2.4. Cell culture conditions

*E. coli* (DH5$\alpha$) was grown for 20 h to the stationary phase in LB medium (10 g/L peptone, 5 g/L yeast extract, and 10 g/L NaCl). The resting cells were harvested by centrifugation at 4000*g*. The produced bacteria were washed for three times with PBS and then suspended in a 0.1 M anaerobic PBS containing 10 mM glucose. Bacterial growth was measured by optical density (OD) at 660 nm. The concentration of *E. coli* cells was about $10^9$ cells $mL^{-1}$. Before every test, nitrogen was purged into the suspension for 20 min to remove oxygen from the cell.

### 2.5. Electrochemical measurements

Cyclic voltammetric (CV) and electrochemical impedance spectroscopy (EIS) measurements were performed using an IM6e electrochemical workstation (Zahner-Elektrik, Kronach, Germany). All electrochemical experiments were carried out with a conventional three-electrode system. An Ag/AgCl (saturated with NaCl) reference electrode was used for all measurements. A platinum wire was used as a counter electrode. For EIS tests, a frequency range of 100 K–0.1 Hz was utilized with a potential amplitude of 10 mV. The electrolyte solution was purged with high-purity nitrogen for at least 15 min prior to CV and EIS experiments and a nitrogen