Particuology 10 (2012) 450–455

Contents lists available at SciVerse ScienceDirect

Particuology

journal homepage: www.elsevier.com/locate/partic

Carbon nanotubes coated with platinum nanoparticles as anode of biofuel cell

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ARTICLE INFO

Article history:
Received 19 July 2011
Received in revised form 3 November 2011
Accepted 13 November 2011

Keywords:
Multiwall carbon nanotubes
Dendrimer-encapsulated platinum nanoparticles
Glucose oxidase
Biofuel cells
LbL self-assembly

ABSTRACT

A hybrid system of carbon nanotubes (CNTs) coated with poly (amidoamine) (PAMAM) dendrimer-encapsulated platinum nanoparticles (Pt-DENs) and glucose oxidase (GOx) was prepared through the layer-by-layer (LbL) self-assembly approach and then used as anode in enzyme-based biofuel cells (BFCs). The assembly process was monitored by ζ-potential measurement, and the as-resulted Pt-DENs/CNTs nanocomposites were characterized by transmission electron microscopy (TEM). The performance of electrodes modified by Pt-DENs/CNTs was also investigated by electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV). We found that the Pt-DENs/CNTs could enhance the electron transfer between the redox centers in enzyme and the electrode surfaces. Furthermore, by employing the Pt-DENs/CNTs modified electrodes as anode, the enzyme-based BFCs operated in a solution containing glucose generated an open-circuit voltage of approximately 640.0 mV and a maximum current density of about 90.0 μA/cm^2, suggesting that Pt-DENs/CNTs may serve as an alternative anode to previously used noble metals in BFC applications.

1. Introduction

Biofuel cell (BFC), as a special kind of fuel cell, uses organic compounds as fuel and enzyme, directly or indirectly, as catalyst (Kim, Jia, & Wang, 2006). Compared to conventional fuel cells, BFCs have the advantages of high efficiency, no pollution, mild reaction conditions and good biocompatibility (Zheng et al., 2010). Enzyme-based BFCs have attracted much attention because of their higher currents and power densities, leading to their use in micro-electronics, especially as implantable power (Barton, Gallaway, & Atanassov, 2004; Wen et al., 2010). However, the low electron transport rate (ETR) in bio-system has been the bottleneck in the development of BFCs (Bullen, Arnot, Lakeman, & Walsh, 2006). Previous experiments suggest that, ETR tends to decrease with increasing electron transport distance. To enhance the ETR of BFCs, an ideal approach is direct electron transfer in BFCs.

Extensive study of the electrochemistry of enzymes has provided a platform for constructing new kinds of biomedical devices, such as biofuel cells (Inamuddin, Shin, Kim, So, & Kim, 2009; Legar et al., 2003; Thévenot, Toth, Durst, & Wilson, 2001). In conventional electrodes, enzymes have a rather slow rate of heterogeneous electron transfer because of the unfavorable orientations of enzymes at electrodes (Li, Xu, Yao, Zhu, & Chen, 2006). Fortunately, such materials as carbon nanotubes (Wang & Musameh, 2005), metal nanoparticles (Carbonera et al., 2010) and biomaterials (Zhou, Zhong, Yang, Shang, & Li, 2006), have been found capable of modifying the electrodes to improve direct electron transfer between the enzymes and the electrodes.

Due to their excellent electrochemical properties, carbon nanotubes (CNTs) have been intensively studied in electrochemistry (Tasca et al., 2008; Zhu, Zhai, Yang, Tian, & Guo, 2007), especially for enzyme-based BFCs (Salimi, Hallaj, & Khayatian, 2005; Wen et al., 2010; Wu et al., 2009). Tunnel conduct is known to be capable of increasing the conductivity of enzyme membrane (Grohn, Bauer, Akpalu, Jackson, & Amis, 2000). Because of their unique quantum tunneling effect, metal nanoparticles are greatly helpful to electron transfer, and also to increase the electroconductivity of enzyme membrane effectively even at very low concentrations (Carbonera et al., 2010). Highly branched dendritic macromolecules poly(amidoamine) (PAMAM) were shown to possess good biocompatibility and adequate functional groups for chemical fixation, both beneficial to modify electrode surface

Abbreviations: BFCs, biofuel cells; CNTs, carbon nanotubes; CV, cyclic voltammetry; EDC, 1-ethyl-3-[3-(dimethylamino)propyl] carbodiimide; EIS, electrochemical impedance spectroscopy; ETR, electron transport rate; GOx, glucose oxidase; ITO, indium tin oxide; LbL, layer-by-layer; MEA, membrane electrode assembly; OCP, open circuit potentials; PAMAM, poly(amidoamine); PBS, phosphate buffer solution; Pt-DENs, dendrimer-encapsulated platinum nanoparticles; TEM, transmission electron microscopy.

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1674-2001/$ – see front matter © 2012 Published by Elsevier B.V. on behalf of Chinese Society of Particuology and Institute of Process Engineering, Chinese Academy of Sciences.
http://dx.doi.org/10.1016/j.partic.2011.11.014

(Caminade & Majoral, 2010). Furthermore, the dendrimer of PAMAM was found capable of encapsulating metal nanoparticles to improve electrode performance (Tang, Zhu, Xu, Yang, & Li, 2007; Xu, Zhu, Tang, Yang, & Li, 2007).

With these in view, the present work is undertaken to fabricate an enzyme anode for BFCs by using a hybrid system of CNTs coated with PAMAM dendrimer-encapsulated platinum nanoparticles (Pt-DENs/CNTs), and to investigate their electrochemical properties. This is the first time to employ (GOx/Pt-DENs)/CNTs as enzyme electrodes for biofuel cell anodes, and to investigate the performance of the as-designed BFCs under physiological conditions.

2. Experimental

2.1. Chemicals and methods

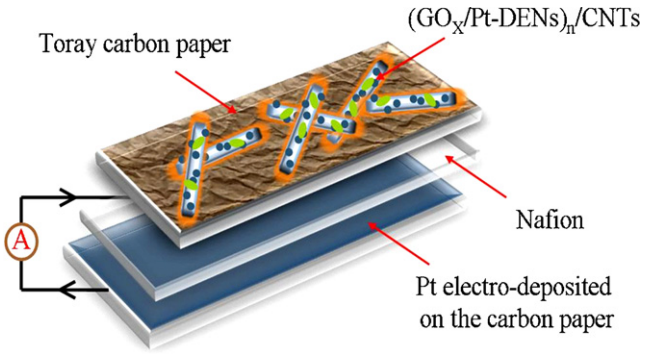
Fourth-generation PAMAM dendrimer-encapsulated platinum nanoparticles (Pt-DENs) were obtained according to the previous literature (Zhu, Zhu, Yang, Xu, & Li, 2007). Glucose oxidase (GOx, 150 U/mg) was purchased from Sigma–Aldrich. CNTs (diameter 20–50 nm, length 5–15 μm) from Shenzhen Nanotech Port Co. (China) were pretreated via sonication in 1:3 concentrated nitric–sulfuric acids for 4 h. All other chemicals in the experiment were of analytical grade. Doubly distilled and deionized water were used throughout the experiment. Phosphate buffer was used for immobilization and electrochemical measurements. The HRTEM images were obtained by using a JEOL-2100F TEM at an acceleration voltage of 200 kV. Nafion membrane purchased from DuPont was used as a proton exchange membrane in this work. Toray carbon paper was obtained from Toray Industries Inc. (Japan). Electrochemical measurements were carried out by using a CHI 660C electrochemical workstation, purchased from Shanghai Chen Hua Instrument Inc. (China). The voltage and current outputs generated by the biofuel cells were measured by using a Keithley 2400 Source Meter made by Keithley Instruments Inc. (USA).

2.2. Preparation of CNTs coated with Pt-DENs (Pt-DENs/CNTs)

First of all, CNTs were pretreated by ultrasonic dispersion in a mixture of concentrated HNO_3 and H_2SO_4 (volume ratio 1:3) for 4 h, followed by thorough washing with deionized water until the filtrate became neutral, dialyzed in doubly distilled water for 48 h, then dried under vacuum after air pump filtration, and finally dispersed in doubly distilled water at a concentration of 10 mg/mL. After the acid-treatment, the surface of CNTs was left with the carboxylic groups, which imparted a hydrophilic nature to facilitate further functionalization by Pt-DENs. The Pt-DENs/CNTs heterostructures were covalently coupled by 1-ethyl-3-[3-(dimethylamino)propyl] carbodiimide (EDC), which can link Pt-DENs and CNTs. The EDC reaction was carried out for 8 h under continuous stirring.

2.3. Preparation of enzyme anode modified by $(GOx/Pt\text{-}DENs)_n$/CNTs nano composites

The isoelectric point (I_p) of GOx is about pH 4.9. Therefore at around pH 6.8, GOx is negatively charged, which can act as a polyanionic material for preparing films layer by layer. In an aqueous solution of pH 6.8, Pt-DENs surface is positively charged. Herein, the negatively charged GOx could be anchored on the positively charged Pt-DENs/CNTs surface by alternatively assembling a GOx layer and a Pt-DENs layer. In short, GOx/Pt-DENs/CNTs hybrid was gained by mixing the Pt-DENs/CNTs nanocomposites with the GOx in a PBS (pH 6.8) for 30 min, and centrifuging at 8000 rpm for 10 min, and then washing with doubly distilled water three times to remove the supernatant. The as-prepared composite was denoted as GOx/Pt-DENs/CNTs. This operation process was repeated to form the final $(GOx/Pt\text{-}DENs)_n$/CNTs heterostructures, composed of the suitable layers (n) of Pt-DENs/CNTs and GOx. The process was characterized by ζ-potential measurement and the resultant nanocomposites were characterized by HRTEM.



Scheme 1. Schematic for enzymatic biofuel cell using $(GOx/Pt\text{-}DENs)_n$/CNT as anode.

2.4. Biofuel cell operation

Half-cell experiments were performed in a three-electrode electrochemical cell by using indium tin oxide (ITO) electrode modified with $(GOx/Pt\text{-}DENs)_n$/CNTs as the working electrode, a KCl-saturated Ag/AgCl (3 M KCl) electrode as a reference electrode and platinum wire as the counter electrode in all cases. For the three electrode experiments, unless noted otherwise, electrochemical measurements were performed in a phosphate buffer solution (PBS, 0.1 M, and pH 6.8) at room temperature (about 25 °C).

As illustrated in Scheme 1, the biofuel cell includes $(GOx/Pt\text{-}DENs)_n$/CNTs and Toray carbon paper (anode electrode) and Pt electrodeposited on the surface of the Toray carbon paper (cathode electrode), The cathode electrode was prepared by deposition of Pt on carbon paper in H_2SO_4 (0.5 M) and $H_2PtCl_6{\cdot}6H_2O$ (1 mM) bath under a deposition potential of –0.4 V, with a scanning rate of 50 mV/s. The Nafion membrane was boiled in 3% hydrogen peroxide and then in alternating baths of boiling water and 1 M H_2SO_4. The Toray carbon paper and Pt doped Toray carbon paper (cathode) were positioned on opposite sides of the Nafion membrane and hot pressed at 0.5 MPa and 140 °C for 3 min to obtain the membrane electrode assembly (MEA) (Brown, Takechi, & Kamat, 2008). Then the $(GOx/Pt\text{-}DENs)_n$/CNTs suspension was added dropwise onto the Toray carbon paper side to form the anode. The voltage and current outputs generated by the biofuel cell were measured by using a Keithley 2400 Source Meter made by Keithley Instruments, Inc.

3. Results and discussion

3.1. Morphology of the Pt-DENs/CNTs heterostructures

As previously demonstrated, the acid-treated CNTs were shortened and modified with carboxylic groups (such as carboxylic acid groups). These oxygen-containing groups imparted a hydrophilic nature to CNTs thus facilitating further functionalization by Pt-DENs by covalent interaction of Pt-DENs with EDC. The TEM image in Fig. 1 shows well-organized nanosized platinum nanoparticles. The diameter of Pt nanoparticles, finely distributed on the surface of CNTs, was about 2–4 nm. The results illustrate that dendrimer could be used as a good template for preparing mono-dispersed metal