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Facile in-situ fabrication of graphene/riboflavin electrode for microbial fuel cells

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ABSTRACT

A novel graphene/riboflavin (RF) composite electrode was developed and its potential application as microbial fuel cell (MFC) anode was demonstrated. Graphene layers were first grown on the surface of graphite electrode by a one-step in-situ electrochemical exfoliation approach. Then, noncovalent functionalization of the graphene layers with RF was achieved by a simple spontaneous adsorption process. The graphene/RF electrode was extensively characterized by transmission electron microscopy, Fourier transform infrared spectroscopy, Raman analysis, and cyclic voltammetry analysis. Remarkably, when applied as the anode of *Shewanella oneidensis* MR-1 inoculated MFCs, the graphene/RF electrode significantly decreased charge transfer over-potential and enhanced cell attachment, which in turn delivered about 5.3- and 2.5-fold higher power output, when compared with that produced by the bare graphite paper electrode and graphene electrode, respectively. These results demonstrated that electron shuttle immobilization on the electrode surface could be a promising and practical strategy for improving the performance of microbial electrochemical systems.

1. Introduction

Microbial fuel cell (MFC) is an emerging and promising technology for energy-saving wastewater treatment because it could convert the chemical energy of organic chemicals into electrical energy, and thus has the potential to recover energy from wastewater [1–4]. As a promising environmental biotechnology for wastewater treatment and renewable energy production, MFC has attracted much attention in the past decade [5]. It has made great progress and various potential applications such as self-powered biosensor [6,7], remote/low density power supply [8,9], and wastewater treatment have been demonstrated [10,11]. However, low power output becomes the main bottleneck of MFC and limits its practical and large-scale applications.

Therefore, great efforts have been made to improve the power output of MFC with electrode modification during the past decades. For example, electrode modification with various nanomaterials such as graphene, carbon nanotube, metal oxide nanoparticles, and conductive polymers, have been used as electrode modifiers, which significantly improved the power output of MFCs [12–16]. In particular, graphene, a single atomic layer of carbon atoms arranged in a hexagonal lattice, showed immense potential in improving the performance of MFCs owing to its extraordinary electrical and physiochemical properties [17]. For example, by electrochemical reduction of chemically synthesized graphene oxide and depositing it on carbon cloth or other electrode through different methods, the power output of MFC was significantly enhanced [18–20]. Although these findings demonstrated the potential of graphene modification in improving MFC performance, the graphene synthesis and modification procedures are quite complicated and time-consuming. Recently, a one-step in-situ approach for the growth of graphene layers on the surface of graphite paper (GP) was developed, which showed significant advantages over the above-mentioned strategies [21,22]. Besides, electron shuttle manipulation is another powerful strategy to improve the power output of MFCs by enhancing the extracellular electron transfer (EET) efficiency [23]. Electron shuttle, such as quinone, thionin, riboflavin (RF), methyl viologen, and neutral red, can effectively facilitate EET between bacteria and electrode, and thus boost power output. However, addition of these mediators directly into the electrolyte may lead to their washing out in

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continuous operation and also pose potential environmental problems. Therefore, immobilization of mediators onto the surface of anode may solve these problems. It has been reported that immobilization of anthraquinone-2,6-disulphonicdisodium salt on the electrode with covalent grafting onto the graphite surface improved the power output to about 94% [24,25]. Besides, copolymerization of electron shuttle with conductive polymers on the electrode surface is another interesting strategy [26]. However, these strategies require complicated grafting or polymerization process. As graphene presents excellent noncovalent adsorption property towards different low molecular weight compounds, it might be a promising carrier for electron shuttle immobilization with simple adsorption procedure[26].

In this study, we demonstrated a facile in-situ approach to fabricate RF immobilized graphene/RF (GO/RF) composite electrode (Fig. S1). The composite electrode was characterized in detail with scanning electronic microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), Raman analysis, and cyclic voltammetry (CV) analysis. Furthermore, the MFC performances, including voltage output, power output, and anodic biofilm with the composite electrode, were compared in detail with those of other conventional electrodes.

2. Materials and methods

2.1. Electrode fabrication

GP (Jinglong Special Carbon, Beijing, China) was first immersed in chloroform overnight, washed with absolute ethanol to remove possible impurities, and dried at room temperature. The pretreated GP (1×2 cm) was then connected to titanium wire as the GP electrode. The GP electrode was further electrochemically exfoliated in 0.1 M sulfuric acid with direct current (DC) power supply (10 V) to allow in-situ formation of graphene on its surface [24]. This electrochemically fabricated graphene electrode was denoted as the GO electrode.

RF solution was prepared by dissolving RF (analytical grade) in aqueous solution (95 μM). The GP and GO electrodes were immersed into the RF solution for 48 h (designated as GP/RF, GO/RF, respectively) to facilitate physical absorption. The prepared GP/RF and GO/RF composite electrodes were washed thrice with distilled water to remove the unadsorbed RF and dried at 30 C. The composite electrodes were characterized and used as MFC anodes.

2.2. Electrode characterization

The electrochemical properties of different electrodes were characterized by CV analysis using CHI660E electrochemical workstation (CHI, Shanghai, China). A three-electrode system, comprising saturated calomel electrode (SCE, +0.243 vs. SHE) as reference electrode and platinum wire as counter electrode, was constructed in 0.1 M PBS (pH = 6.8). After purging nitrogen into the electrolyte for 15 min to remove the dissolved oxygen, the different electrodes (before and after MFC operation) were subjected to CV analysis between −0.7 and −0.2 V with a scanning rate of 2 mV/s.

FTIR was conducted using Nexus 470 FTIR (Thermo Fisher Nicolet, USA) from 400 to 4000 cm^{-1}. Raman spectra were measured from 500 to 3500 cm^{-1} *via* DXR Raman Microscope

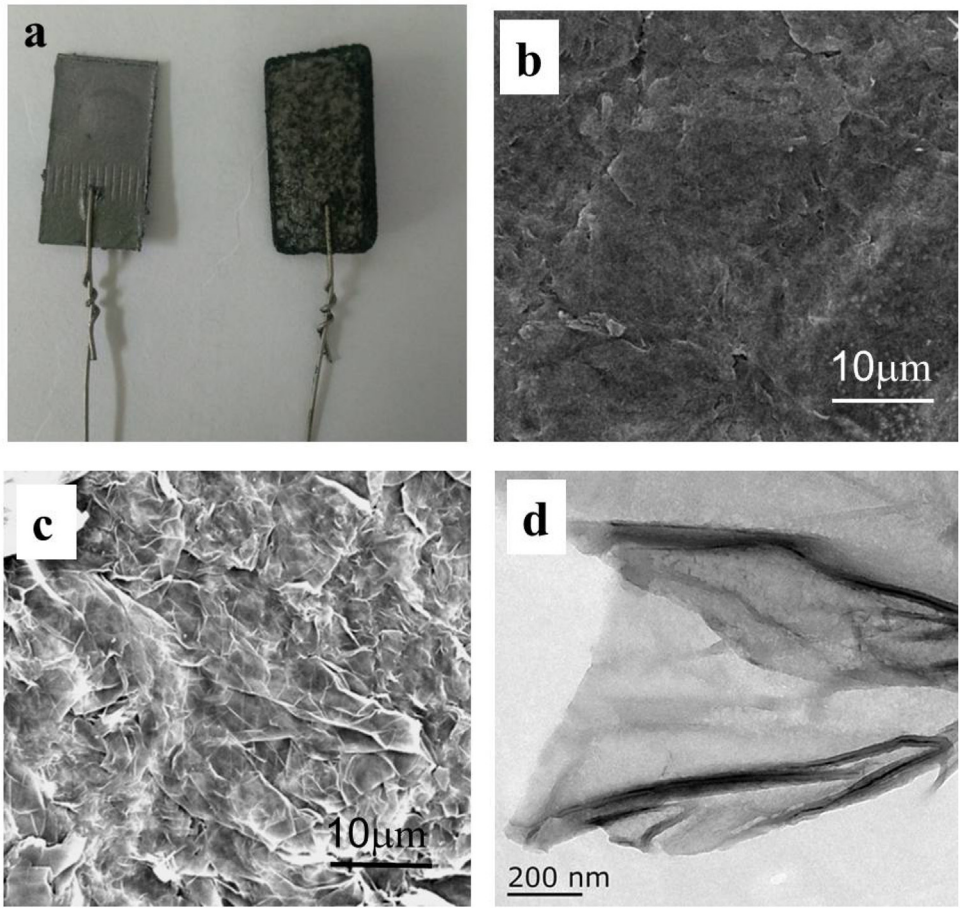

Fig. 1. Morphology of GP and GO electrodes. Photograph of the GP electrode (left) and GO electrode (right) (a). SEM image of the GP electrode (b) and GO electrode (c). TEM image of the graphene layers from the GO electrode surface (d).