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Enhanced performance of microbial fuel cell with *in situ* preparing dual graphene modified bioelectrode

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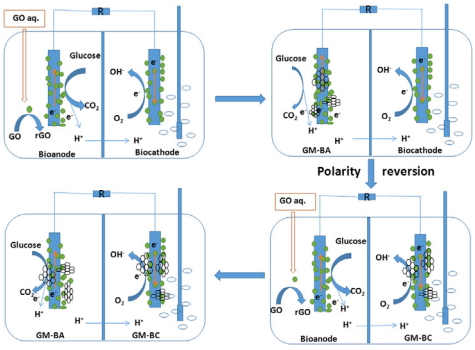
HIGHLIGHTS

- A three-step method was built to prepare dual graphene modified bioelectrode.
- 3D graphene/biofilm architectures were formed in graphene modified bioelectrode.
- The viability/thickness of microbial biofilm decreased in graphene bioelectrode.
- Electrochemical performance of graphene modified MFC was significantly enhanced.
- Mechanisms of EET process and implication of graphene modified MFC were proposed.

GRAPHICAL ABSTRACT



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ABSTRACT

This study proposed a three-step method to prepare dual graphene modified bioelectrode (D-GM-BE) by *in situ* microbial-induced reduction of GO and polarity reversion in microbial fuel cell (MFC). Both graphene modified bioanode (GM-BA) and biocathode (GM-BC) were of 3D graphene/biofilm architectures; the viability and thickness of microbial biofilm decreased compared with control bioelectrode (C-BE). The coulombic efficiency (CE) of GM-BA was 2.1 times of the control bioanode (C-BA), which demonstrated higher rate of substrates oxidation; the relationship between peak current and scan rates data meant that GM-BC was of higher efficiency of catalyzing oxygen reduction than the control biocathode (C-BC). The maximum power density obtained in D-GM-BE MFC was 122.4 ± 6.9 mW m^{-2}, the interfacial charge transfer resistance of GM-BA and GM-BC were decreased by 79% and 75.7%. The excellent electrochemical performance of D-GM-BE MFC was attributed to the enhanced extracellular electron transfer (EET) process and catalyzing oxygen reduction.

1. Introduction

Improving power production has been committed to acting out in microbial fuel cell (MFC) (Logan et al., 2015). Bioelectrode is characterized by low cost and operational sustainability, which generates immense potential; microorganism in bioanode plays

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the role of motivating organics to generate electrons; microorganism in biocathode performs to assist cathodic reactions; these electrochemically active microorganism possesses the function of extracellular electron transfer (EET) (He and Angenent, 2006).

Graphene, featuring by excellent electrical conductivity and large specific surface area, is in line with the requirements of the electrode, therefore it has been widely studied in MFCs (Cai et al., 2016; Chen et al., 2017a). The most straightforward mode was coating graphene on anode electrode, graphene coated anode (by Nafion solution) obtained the maximum power density of 2142 mW m^{-2}, which greatly improved MFC performance and EET efficiency (Hou et al., 2014). Zhao et al. (2013) manufactured anode by electro-depositing polyaniline to graphene nanoribbons on carbon paper, demonstrating a 3D microporous structure and maximum power output of 856 mW m^{-2}, which took full advantage of large specific surface area for graphene and improved MFC performance. In respect of cathode, Xiao et al. (2012) added r-GO (reduced graphene oxide) particles on carbon cloth with Nafion solution, which improved power density and decreased polarization resistance significantly. Other graphene modified cathode was generally realized by doping nitrogen or non-precious metals (Fe, Mn etc.) (Li et al., 2012). Nitrogen-doped graphene was utilized in cathode by vacuum filtration method, acquiring the maximum power density of 408 mW m^{-2}, which proved that graphene was beneficial to improve MFC performance and enhance oxygen reduction reaction (ORR) (Wang et al., 2016). All these studies achieved the improvement of MFC performance by physical/chemical process or electro-deposition method, which was troublesome operation or needed large amount of chemicals.

An interesting phenomenon is that graphene oxide (GO) could be reduced by *Shewanella* (Wang et al., 2011), *Escherichia coli* (Gurunathan et al., 2013), etc. Yong et al. (2014) constructed a MFC with 3D macroporous rGO/bacteria hybrid biofilm by self-assembly of GO via *Shewanella oneidensis* MR-1, which reached the maximum power density of 843 ± 31 mW m^{-2}. Yuan et al. (2012) built graphene scaffolds anode MFC by *in situ* microbially reduced GO via activated anaerobic sludge, and achieved the maximum power density of 1905 ± 80 mW m^{-2} and the coulombic efficiency (CE) of 54%, which enhanced MFC performance and EET efficiency. Zhuang et al. (2012) implanted the microbially reduced graphene (from anode) to cathode chamber to form 3D graphene/biofilm biocathode, and got the maximum power density of 323.2 ± 21 mW m^{-2}, which improved MFC performance and enhanced catalytic activity towards cathodic ORR. Though these studies demonstrated that *in situ* microbial-induced reduction of GO was a simple and efficient approach to prepare graphene modified bioelectrode (GM-BE) and improve MFC performance, graphene modified bioanode (GM-BA) and biocathode (GM-BC) were prepared via different methods, respectively, which operated complicatedly.

Recent studies proved that polarity reversion could provide a new approach to prepare GM-BC. Polarity reversion could alternately catalyze cathodic reaction and anodic reaction via electroactive microorganism (Cheng et al., 2010; Strik et al., 2010). In our previous studies, we also developed biocathode to realize simultaneous electricity generation and mineralization of azo dye or pH self-neutralization through polarity reversion (Li et al., 2014; Sun et al., 2015). Polarity reversion was that the polarity of the bioelectrode was reversed without refreshing the anodic and cathodic liquid during the operation of MFC. The previous anode was supplemented with inorganic carbon source ($NaHCO_3$) and given a aeration, changing to biocathode, while the previous cathode was supplemented with organic carbon source (glucose) and sealed to maintain anaerobic condition, changing to bioanode (Chen et al., 2017a). The facts testified that polarity reversion was a simple and reliable method to prepare *in situ* GM-BC. Therefore, we proposed a three-step method to prepare *in situ* dual graphene modified bioelectrode (D-GM-BE) MFC: GM-BA was firstly prepared by *in situ* microbial-induced reduction of GO in anode; then GM-BC was formed based on the polarity reversion of GM-BA; finally GO solution was added into the new anode to prepare GM-BA once again.

In this study, a three-step method was proposed to prepare D-GM-BE by *in situ* microbial-induced reduction of GO and polarity reversion in MFC. X-ray diffraction (XRD) and Raman spectra were used to evaluate the structure changes of GO reduced by microorganism, and field emission scanning electron microscopy (FESEM) and transmission electron microscopic (TEM) were conducted to observe the morphology of rGO; cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were performed to illuminate the electrochemical activity of GM-BE, and the power density and polarization curves were carried out to expound the electrochemical performance of D-GM-BE MFC; FESEM of microbial film was used to observe the apparent morphology of GM-BE, and confocal scanning laser microscopy (CSLM) was employed to interpret the viability of microbial biofilm in D-GM-BE. The experimental data could help to confirm whether D-GM-BE could improve MFC performance, and clarify the mechanisms of enhanced EET process and catalyzing ORR.

2. Materials and methods

2.1. Startup of MFC and preparation of D-GM-BE

A two chamber MFC with carbon felt (5 cm × 6 cm) as anode and cathode, and separated by cation exchange membrane (CEM) as our previous reports (Chen et al., 2017b). The anode chamber was slowly mixed using a diminutive magnetic stirrer to minimize mass transfer limitations and dissolved oxygen (DO) in cathode was controlled at 6 ~ 7 mg L^{-1} with an aeration equipment. The electrodes were placed in parallel at about 1 cm distance to the CEM and jointed up by a resistor of 500 Ω. Activate sludge was attained from a sewage treatment plant in Guangzhou City, and inoculated into anode and cathode chamber. Graphite powder was used to synthesize GO solution according to improved Hummers methods (Chen et al., 2015). Glucose and sodium bicarbonate ($NaHCO_3$) were treated as carbon source in anode and cathode chamber respectively. Phosphate buffer solution (PBS, pH 7.0), vitamin solution, and trace mineral stock solution were added into both anode and cathode chamber at the same concentration. GO solution was added into anode along with PBS etc. in the first three cycles, and the concentration of GO solution in anode was 1 mg L^{-1} (Chen et al., 2017c). GM-BA was firstly prepared by adding GO solution in anode for three cycles. Polarity reversion was conducted after the completion of GM-BA, the original GM-BA became GM-BC and the original biocathode became bioanode. The following was the repetitive preparation of GM-BA, and GO was continuously added to the new anode chamber for another three cycles. After adding GO twice and polarity reversion once, D-GM-BE was prepared. Maintained in a constant-temperature room (30 ± 1 °C), all experiments were operated at least in duplicate and the average value was reported for all data. The schematic operation of D-GM-BE MFC was shown in Fig. 1 and Table S1.

2.2. Characterization of rGO

The rGO reduced by *in situ* microbial-induced reduction of GO was characterized by morphology and structure. The characterized rGO was taken from the particles on the electrode surface. FESEM (Merlin, Germany) and TEM (Hitachi TEM system, Japan) were used to observe morphology of rGO. XRD (Empyrea, Netherlands)