



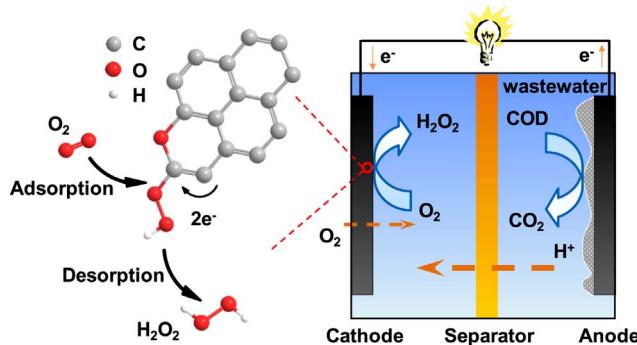
Hydrogen peroxide generation in microbial fuel cells using graphene-based air-cathodes

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GRAPHICAL ABSTRACT



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ABSTRACT

Utilization of two-electron oxygen reduction reaction (ORR) in bioelectrochemical systems (BES) is a novel way to generate H₂O₂ from wastewater, and cathode catalyst is a key factor affecting ORR performance. Here, the catalytic performance of plain graphene, oxidized graphene and graphene oxide (GO) in microbial fuel cells (MFCs) and the influence of oxygen-containing functional groups are reported. Oxidized graphene air-cathode had 78% and 131% higher H₂O₂ productions than plain graphene cathode respectively in an abiotic reactor and an MFC. GO showed nearly no H₂O₂ production in the tests. XPS revealed that oxygen atomic fraction of oxidized graphene reached 5.7%, mostly in the form of C—O—C. These results show that oxidized graphene had good catalytic performance for H₂O₂ production, and oxygen-containing functional groups, especially C—O—C could significantly enhance its performance, but overoxidation worked adversely. Meanwhile, using oxidized graphene air-cathode could realize simultaneous wastewater treatment, power output and H₂O₂ generation in MFCs.

1. Introduction

Microbial fuel cells (MFCs) are a typical form of bioelectrochemical systems (BES), which combine wastewater treatment with resources recovery and electricity production (Logan and Rabaey, 2012; Wang

and Ren, 2013). Organic pollutants in the wastewater are oxidized by electrochemically active microorganisms on the anode, and electrons are transferred to cathode via an external circuit. Then electron acceptors receive the electrons at the cathode. So far the cathode performance has been a limiting factor for MFCs (Wang et al., 2016; Yuan

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et al., 2016; Zhang et al., 2014). Among all the electron acceptors, oxygen proves as an ideal electron acceptor due to its high oxidation potential and easy availability. Oxygen reduction reaction (ORR) usually proceeds following 4-electron transfer pathway into water or 2-electron transfer pathway into H_2O_2 . H_2O_2 , featuring its strong oxidation ability and clean reaction product (H_2O), is widely used in textile industry, health care industry, chemical synthesis, etc.. In wastewater treatment, H_2O_2 is a potent source of hydroxyl radicals in the process of advanced oxidation process (AOP), which plays a significant role in the decomposition of recalcitrant pollutants (Zhuang et al., 2010). Typically, H_2O_2 is produced in large scale by anthraquinone process. However, this process suffers high cost and potentially hazardous transportation (Wang et al., 2012; Zazou et al., 2016). Using MFCs to generate H_2O_2 *in situ* is a sustainable way for advanced wastewater treatment.

Several reports have shown that it is possible to generate H_2O_2 from BES with carbon-based catalysts. Three-dimensional graphite electrode was used to achieve a H_2O_2 concentration of 196.5 mg L^{-1} in a MFC (Chen et al., 2014), and pure graphite rod electrodes produced H_2O_2 with a rate of $6.5 \text{ mg L}^{-1} \text{ h}^{-1}$ in a MFC (Fu et al., 2010). Carbon-based catalysts could also be applied in microbial electrolysis cells (MECs) for H_2O_2 production, operated by applying an external voltage to MFCs. Carbon cloth/CB cathode achieved a H_2O_2 concentration of 3.1 g L^{-1} in 4 h with an energy input of $1.1 \text{ Wh g}^{-1} \text{ H}_2\text{O}_2$ (Young et al., 2017; Young et al., 2016), and it was used to generate up to $230 \text{ mg L}^{-1} \text{ H}_2\text{O}_2$ in 6 h coupled with primary sludge treatment at the anode (Ki et al., 2017). Carbon cloth cathode (Rozendal et al., 2009) and graphite particle electrode (Chen et al., 2015) achieved improved H_2O_2 production with an applied voltage of 0.5 V and 0.4 V respectively. Others also reported the application of carbon-based catalysts in electro-Fenton process, which achieved an over 70% removal of contaminants within the wastewater (Ling et al., 2016; Zhu and Logan, 2013).

Graphene, as an important two-dimensional nanomaterial, with its excellent electron transfer properties, has attracted attentions from all over the world these years (Novoselov et al., 2012). Graphene and graphene oxide have proved to be effective in adsorption of contaminants (Sun et al., 2017). In terms of catalytic activity, graphene-modified bioanodes facilitated high maximum power density and lower transfer resistance of MFCs (Chen et al., 2017,b). Further studies revealed that, because of its high biocompatibility, graphene modification increased the power density and energy conversion efficiency of carbon cloth electrode by 2.7–3 times (Liu et al., 2012). Reduced graphene oxide (rGO) has proved to enhance the electrochemical activity and ORR activity of CoFe_2O_4 (Li et al., 2017). Moreover, researches show that the doping of N and O atoms could further enhance the electrochemical properties of graphene. It is revealed that N-doped graphene obtained by co-pyrolysis of lignosulfonate and graphene oxide showed super capacitance up to 170 F g^{-1} (Zhao et al., 2015), and that N-doped graphene exhibited excellent catalytic degradation of organic pollutants such as phenol, 2,4,6-trichlorophenol and sulfachloropyridazine by activating peroxymonosulfate (Liang et al., 2017). N-doped graphene has also attracted attentions in the field of MFCs due to its high conductivity and good electrocatalytic activity for ORR (Feng et al., 2013; Luo et al., 2011). It has been tested as cathode catalyst for ORR and a power density of 1350 mW m^{-2} was achieved (Feng et al., 2011), indicating its potential in BES. The oxygen-rich nitrogen-doped graphene synthesized with $\text{NH}_4\text{H}_2\text{PO}_4$ and $(\text{NH}_4)_2\text{HPO}_4$ also showed excellent electrochemical storage performance (Chen et al., 2016). It has been reported that graphene oxide (GO) can be synthesized through BES (Lu et al., 2015), and GO was also found catalytic for biaryl construction and oxygen-containing functional groups played an essential role (Gao et al., 2016). However, to the best of our knowledge there are few reports on applications of graphene-based materials for 2-electron ORR in BES, or on the effect of oxygen-containing functional groups on the catalytic performance for ORR in BES.

In this study, the catalytic performance of graphene-based materials

for 2-electron ORR and the influence of oxygen-containing functional groups were explored by comparing the catalytic performance of plain graphene, oxidized graphene and GO for 2-electron ORR, while Pt/C and activated carbon (AC) were used as control. The MFC with an oxidized graphene cathode could achieve simultaneous wastewater treatment, power output and H_2O_2 generation, and oxygen-containing functional groups, especially epoxide groups, were found to enhance the 2-electron ORR catalytic performance of graphene.

2. Materials and methods

2.1. Catalysts and characterization

Plain graphene (Mozhicui 2, Changzhou MoZhiCui Technology Co., LTD), graphene oxide (GO) (Institute of Coal Chemistry, Chinese Academy of Sciences) and oxidized graphene were selected as cathode catalysts, while Pt/C and activated carbon (AC) were used as control. The oxidized graphene flakes were prepared following a modified Hummers method (Zhu et al., 2015). Scanning electron microscope (SEM) was used to characterize the surface morphology of the catalysts. X-ray photoelectron spectroscopy (XPS) was used to detect the elemental composition and functional groups of the catalysts. To compare the electrical conductivity of plain graphene and GO, flakes of the two catalysts were pressed into chips of $3 \text{ mm} \times 3 \text{ mm}$ and their sheet resistances were measured by a multifunction four-probe tester (ST-2258C, Jiangsu Jingge Electronic Co., Ltd).

2.2. Air-cathode fabrication

An air-cathode consists of a diffusion layer and a catalyst layer. 705.5 mg polytetrafluoroethylene (PTFE, 60% wt.), 212 mg carbon black (Cabot, XC-72R) and 1.4 mL ethanol were mixed and stirred to form a paste. The paste was rolled onto a stainless steel mesh with a loading of $13.25 \text{ mg CB cm}^{-2}$ under 4.5 MPa for 10 min, and then it was sintered at 340°C for 20 min to fabricate the diffusion layer. After that, 200 mg catalyst, $50 \mu\text{L}$ 60 wt% PTFE, $450 \mu\text{L}$ deionized water and $300 \mu\text{L}$ ethanol were mixed and stirred into a paste, then it was coated onto the diffusion layer together with another stainless steel mesh of the same size under 4.5 MPa for 20 min to form the catalyst layer, with a catalyst loading of 17.63 mg cm^{-2} . Finally the cathode was heated at 80°C for 30 min.

2.3. Electrochemical analysis

The abiotic electrochemical reactor consisted of a 4-cm cubic-shaped anode chamber (28 mL net volume) and a 1-cm cubic-shaped cathode chamber (7 mL net volume), separated by a cation exchange membrane. A platinum mesh (Tianjin Hengshengaida Corporation) was used as a counter electrode, and a saturated calomel electrode (SCE, 0.241 V versus a standard hydrogen electrode) was used as a reference electrode placed close to an air-cathode in the other chamber. A 50 mM phosphate buffer solution (PBS), consisting of 4.57 g L^{-1} of Na_2HPO_4 , 2.45 g L^{-1} of $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$, 0.31 g L^{-1} of NH_4Cl , 0.13 g L^{-1} of KCl , was used as the anolyte and 50 mM Na_2SO_4 solution was used as the catholyte. Cyclic voltammetry (CV), linear sweep voltammetry (LSV) and chronoamperometry (CA) were employed to assess the electrochemically catalytic performance of the air cathodes. The CV and LSV tests were conducted from 0.4 V to -0.4 V vs SCE at a scan rate of 10 mV s^{-1} . The CA test was conducted at -0.4 V , -0.3 V , -0.2 V , -0.1 V , 0 V , 0.1 V , 0.2 V , 0.3 V , 0.4 V with 30 min per potential. H_2O_2 concentration in the cathode chamber was measured with titanium oxalate by spectrophotometrical analysis after 15, 30, 60 min in the CA test respectively to evaluate the abiotic electrochemical H_2O_2 production.

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