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Graphene oxide supported magnesium oxide as an efficient cathode catalyst for power generation and wastewater treatment in single chamber microbial fuel cells

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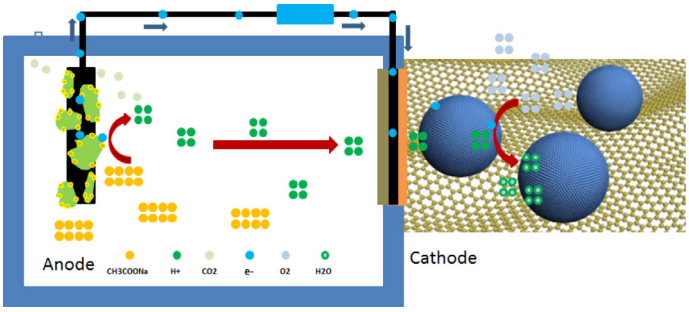
HIGHLIGHTS

- A facile and effective method to synthesize graphene oxide/magnesium oxide nanocomposite.
- Magnesium oxide catalyst is successfully attached with surface of graphene oxide.
- Microbial fuel cells with GO/MgO generate a high power density of 755.63 mW m^{-2}.
- This composite electrode exhibits excellent electrocatalytic activity.

GRAPHICAL ABSTRACT

The synthesized GO/MgO nanoflower with high electrocatalytic performance can be used as cathode catalyst in single chamber microbial fuel cell to generate bioelectricity and degrade organic matters.



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ABSTRACT

Microbial fuel cell (MFC) is a promising device which can simultaneously deal with pollutions and generate renewable electricity power. In a single-chamber MFC, the performance of cathode catalyst is one of the key factors that determine power generation. In this study, we applied the nanoflower-shaped graphene oxide hybridized MgO (GO/MgO) nanocomposite to the cathode carbon cloth, which could significantly optimize the reactors' performance at a low price. A series of characterizations on GO/MgO confirmed that the magnesium oxide was successfully decorated on the surface of graphene oxide. The oxygen reduction reaction (ORR) test of cathode indicated that the electrochemical activity of GO/MgO cathode was higher than a bare MgO cathode or pure GO cathode. Consequently, the power density of MFC catalyzed by GO/MgO was enhanced to 755.63 mW m^{-2}, which was equivalent to 86.78% of MFCs catalyzed by Pt/C (870.75 mW m^{-2}). In addition, it obtained a chemical oxygen demand removal efficiency of 79.5%, and a coulombic efficiency of 31.6%, which also saw the best result among the three cathodes. After approximately 20 cycles running, the power density of the MFC used GO/MgO cathode kept still a stable level. Especially, it saved 93.3% cost while comparing to Pt/C catalyst, but achieved a similar electrochemical result, which helps to realize a scale-up design.

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1. Introduction

Microbial fuel cells (MFCs) as a promising biological-electrochemical technology can utilize electricigens as biocatalyst to degrade organic wastewater and generate bioelectricity without any pollution [1]. Nowadays, the MFC including double chamber, single chamber, flat and up-flow designs had been widely developed [2]. In single-chamber MFCs, the electrons and protons from the oxidation of organic substrate by electricigens in the anode chamber were transferred to the cathode through an external circuit or PEM, respectively, reacting with the oxygen and generating current [3]. Moreover, the performance of MFCs was also closely related to the design of MFCs, the type of electrodes, inoculum pretreatment and activity of microorganism [4]. What really matters in addition to these general factors was catalyst used. So many studies had reported the performance of MFCs used various cathode catalysts such as MnO_2/GO cathode, CeO_2/Pt/C cathode and Cobalt oxide/nanocarbon cathode [2,5,6]. Nowadays, the noble metal such as platinum (Pt) and platinum based alloys had been still considered as cathode catalyst of MFCs due to its effective and promising electrocatalytic activity [7].

It should be noted that Pt could be not an ideal catalyst material for large scale application in MFCs due to its expensive cost and easily poisoned by sulfide in anode chamber [2]. Consequently, kinds of affordable catalysts with high electrocatalytic performance need to be developed for enhancing the output power of the MFCs. Noori et al. reported that the MFCs used V_2O_5 nanoflower decorated cathode achieved excellent power density of 6.06 W m^{-3} [8]. Ge et al. studied that the MFCs equipped with nano urchin-like $NiCo_2O_4$ modified cathode had a higher power density than the commercial Pt/C, reaching 1730 mW m^{-2} [9]. These transitional metals hybridized carbon-based materials as cathode catalyst of MFC had been reported in many literatures [5,10,11].

Although these transitional metal can exhibit superior power performance, surprisingly little attention has been devoted to the application non-transitional metal as cathode catalyst. Nanostructures magnesium oxide (MgO) had drawn widespread attention due to its strong surface reactivity and significant applications in superconductors and catalysts [12,13]. Besides, MgO was a cheap alkaline earth metal oxide and it can be prepared by a facile precipitation-aging-calcination method [14]. In addition, different structure of MgO such as nanosheets, nanoflowers, and nanoparticles exhibited distinct performances [14–16]. Fang et al. synthesized the nanoflowers-MgO by a simple chemical method, and this material exhibited much higher relative dielectric constant than MgO micropowder samples [17]. Yang et al. studied that the nanometer sized MgO with columnar defects was introduced into high temperature copper oxide to improve the critical current density of superconductors [18]. The above reports confirmed that the electrochemical activity of MgO was strongly affected by the distribution and structure of MgO phase.

Considering the drawback of MgO in terms of poor electrical conductivity, various types of conductive carbonaceous nanomaterials such as activation carbon, graphite, Vulcan XC-72, carbon nanotubes and graphene oxide (GO) had been employed as the favorable materials for non-precious metal catalyst to increase the electrochemical active areas and improve their catalytic activity in MFCs [19]. Among these carbon-based materials, GO with a two-dimensional structures exhibited high thermal conductivity, large theoretical surface area, good chemical stability and giant electron mobility [15,20,21]. Accordingly, GO was considered as a supported material for various applications in environmental pollution treatment, electrochemical biosensors and physicochemical catalyst [22–24]. Recently, graphene oxide based nanomaterials had been utilized as electrochemical catalysts to enhance the power output in MFCs. Wen et al. employed manganese dioxide hybridized graphene nanosheet as cathode catalyst of MFCs to generate a maximum power density of 2083 mW m^{-2}, which was higher than pure manganese dioxide catalyst (1470 mW m^{-2}) [25]. Garino et al. reported that reduced graphene oxide/SnO2 nanocomposite was employed as cathode catalyst in seawater based MFCs and this catalyst represented promising electrocatalytic activity comparable to Pt catalyst [26]. All studied demonstrated that the graphene oxide-based composites with effective electrochemical performance and conductivity can be considered as precursors of metal oxide to accelerate the ORR.

Since promising electrocatalytic activity of MgO and the superb conductive performance of GO, we prepared the GO/MgO nanocomposite by modified Hummers method [27]. Herein, this composite was used as the cathode catalyst of single chamber MFC to improve the output power and remove wastewater. As a comparison, pure GO and bare MgO were utilized as a benchmark material for application in MFCs. The physical performances of these catalysts were characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS), and the electrochemical properties were also evaluated using cyclic voltammetry (CV), linear sweep voltammetry (LSV), electrochemical impedance spectroscopy (EIS) and Rotating Disk Electrode (RDE). Finally, the power performance of single chamber MFCs coated different catalysts were assessed by polarization curve, power density, chemical oxygen demand (COD) and coulombic efficiency.

2. Materials and methods

2.1. Synthesis and characterization of catalysts

The natural graphite power was used to manufacture graphene oxide (GO) by a modified method of Hummers [27]. During synthetic, the graphene powder of 0.5 g, sodium nitrate of 0.5 g, concentrated sulfuric acid of 23 ml and potassium permanganate of 3 g was mixed slowly in an ice water bath. After the mixture solution was stirred about 1 h, deionized water of 140 ml was added gently into the mixture solution, and this reaction process kept approximately 1 h. Then H_2O_2 (30%) was dropped into the mixture solution until the color of the mixture solution changed obviously from deep brown to bright yellow. The mixture solution was centrifuged at 8000 rpm and washed by hydrochloric acid (4–5 times) and deionized water (5–7 times), respectively. Finally, the exfoliated GO was obtained by drying the samples in freezing drier at 60 °C overnight.

For the preparation of GO/MgO, 0.5 g of GO was added in a flask with 300 ml deionized water. After GO dispersion was sonicated for 1 h, 0.5 g of magnesium oxide nanoparticles were added to the flask. Finally, the GO/MgO composites were obtained by centrifuging and dried at 60 °C. All chemicals were of analytical grade supplied by the Aladdin (China) and utilized for this study without any further treatment.

The composites were characterized by field emission scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS) (Carl Zeiss EVO LS10, UK), X-ray diffraction (XRD), fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy. The XRD measurement were conducted by a powder X-ray diffractometer (BRUKER, Germany) with a Cu Kα radiation source (λ = 1.5418 Å) operating at 30 mA and 40 kV. The data were collected between scattering angles (2θ) of 5° to 80° in steps of 0.02°. XPS data were conducted using a Thermo Scientific K-Alpha XPS system (Thermo Fisher Scientific, UK) with an Al Kα