

Growth of Carbon Nanotubes on Graphene as Efficient Air-cathode for Highly H₂O₂-producing Microbial Fuel Cell

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ABSTRACT

An efficient highly conductive three-dimensional (3D) air-cathode manufactured by growth of carbon nanotubes (CNTs) on graphene sheets (GNS) for the improvement of H₂O₂-producing microbial fuel cell (MFC) is reported. 3D architured GNS-CNTs hybrid as air-cathode allows for an enhanced production rates of H₂O₂ within its hierarchical porous structure. Correspondingly, the resulted GNS-CNTs hybrid showed adjustable electrochemical performance as an MFC air-cathode. Importantly, different electron transfer efficiencies on GNS-CNTs hybrid air-cathode result in different electric charge distributions, which affects its molecular spatial arrangement and three-dimensional conformation. The nanostructure enhances the air-cathode interaction and electron transfer rate. This work paves a feasible pathway to prepare carbon nanomaterials with favorable 3D architecture and high performance, for use in MFC and energy conversion.

Keywords: microbial fuel cell; hydrogen peroxide; degradation; GNS-CNTs

1 INTRODUCTION

Hydrogen peroxide is an environmental friendly strong oxidant, Chemical bleaching agent. At the same time, it is a series precursor of important peroxide products [1]. With the request of environmental protection, Hydrogen peroxide has been widely used in chemical, medicine, food, electronic and environmental protection, which has become a new clean oxidant to replace the traditional methods of K₂Cr₂O₇ and KMnO₄, attracting more and more attention. However, the traditional method of synthesis of hydrogen peroxide is the anthraquinone process. This process, in general, requires multi-step separation and increases capital and operational costs. It also brings much pollution on our environment [2]. Microbial fuel cells (MFCs) are a newly developed bioelectro-chemical system that employs microorganisms as catalysts to oxidize organic and inorganic matters for electricity generation [3]. Recently, several studies [4, 5] has demonstrated this concept of using an MFC to achieve cathodic production of H₂O₂ on the surfaces of carbon materials. Maybe synthesis of H₂O₂ in

microbial fuel cell(MFC) is an effective method to realize the cleaner production [6].

Wastewaters created by printing and dyeing processes contain a large number of organic pollutants. The pollutants consuming dissolved oxygen, consequently damage the ecological balance of the water and endangering aquatic life. It is very difficult to economically treat these wastewaters using traditional biochemical, physical, and chemical approaches.

If H₂O₂ produced from MFC can be mixed with Fe²⁺ solution, which called Fenton reagent (H₂O₂ and Fe²⁺), a new system (MFC-Fenton system) will be established. One report [2] has shown that using MFC-Fenton to degrade non-biodegradable chemicals such as dyes in wastewater with energy produced from wastewater will be expected. Fenton reagent (H₂O₂ and Fe²⁺) for the production of hydroxyl radicals, are strong oxidants of organic pollutants in wastewaters.

Fenton system, an advanced oxidation process, works rapidly, produces no secondary pollution, and has a high pollutant removal rate [1]. This system involves deep oxidation, which is easy to achieve, and has prospects for a broad range of applications. However, one limitation is its production of H₂O₂, which may hamper a conventional Fenton system's commercial applications [2]. The MFC-Fenton system schema diagram was shown in Fig.1.

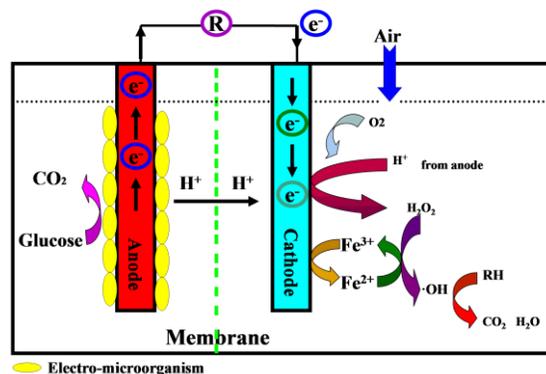


Fig.1. The MFC-Fenton system schema diagram

Cathodic reduction of oxygen to H₂O₂ (O₂ + 2H⁺ + 2e⁻ → 2H₂O₂) has been well described in the literature [3, 4, 5]. There is also growing interest in microbial fuel cells

(MFCs), which can couple anodic oxidation of organics to the cathodic production of H_2O_2 [6]. Bacteria oxidize organic substrates in the anode, generating protons and electrons. The electrons flow through an external circuit to the cathode, where the MFC uses oxygen or air [7] to accept the protons and electrons.

Methylene blue (MB), the represent of azo dyes materials, which often constitute an important portion of wastewater effluent, are non-biodegradable and show a relatively high persistence in soils and aquatic systems [8]. The molecular structure of MB will be oxidized by a hydroxyl radical ($\cdot OH$), which is generated from aqueous mixtures of ferrous iron (Fe^{2+}) and hydrogen peroxide (H_2O_2) [Eq.(1)] [7].



Based on the above considerations, we chose MB as the target pollutant in this study.

The materials of the electrode constitute an important part of an MFC and play a significant role in electricity generation, thereby affecting H_2O_2 production. Carbon nanotubes (CNTs) exhibit very promising properties as a catalyst support [9, 10, 11]. In addition, electrodes modified with carbon nanotubes (CNTs) have been shown to enhance the performance of biosensing systems [12–15] and MFCs due to their high aspect ratio of high conductivity [16–18]. Carbon nanotubes (CNTs) represent classic one-dimensional (1D) structured carbon materials, possessing distinct mechanical properties, large theoretical surface area, good electronic conductivity, and high electrochemical stability. Meanwhile, graphene nanosheets (GNS), consisting of a single layer or a few layers of graphitic carbon, is a typical two-dimensional (2D) structural material, which has been demonstrated as an ideal scaffold for doping elements or functionalizing components. CNTs and GNS were also described as being highly biocompatible allowing for bacteria immobilization and proliferation. So far, most studies were carried out in electrochemical configuration; electrodes were coated with nanostructure modification and produced promising current densities. In recent years, a series of studies on combining 1D CNTs with 2D graphene nanosheets (GNS) have been reported for a variety of applications.

Here we report on the performance of this new 3D GNS-CNTs material microbial electrode, as a air-cathode for MFC. This study examines the air-cathode architecture by coating carbon cloth with GNS-CNTs, forming a highly conductive air-cathode with a high specific surface area in an MFC.

2 MATERIALS AND METHODS

A double-chamber MFC consisting of two identical plexiglass chambers separated by a proton exchange membrane (Nafion 117, Dupont Co., USA) was constructed. Each chamber had an effective volume of 75 mL. Carbon felt (Q-CARBON Co., Ltd., Shanghai, China) with dimensions of 5.0 cm \times 5.0cm was suspended in anode

chambers without a catalyst coating. An air-cathode was similarly prepared following a previously described procedure [19] using carbon black (CB) and GNS-CNTs as catalysts. Air-cathode is constructed as Fig.2. To synthesize GNS-CNTs, 200 mg of graphite oxide was dispersed in 200 mL of water. Then, 0.29 g $Co(NO_3)_2 \cdot 6H_2O$ was added into the solution, followed by stirring for 4 h at room temperature. After that, 6.0 g urea was introduced into the above suspension and the mixed solution was stirred continuously at 80 $^{\circ}C$ until a gray powder was obtained. The gray powder was then transferred to a tube furnace and annealed at 900 $^{\circ}C$ for 1 h under an argon atmosphere to obtain GNS-CNTs. The distance between the anode and cathode was 4.0 cm. Insulated copper wires were used to connect the circuit with an external resistance of 1k Ω unless otherwise specified. The MFCs were operated in duplicate in each experimental condition.

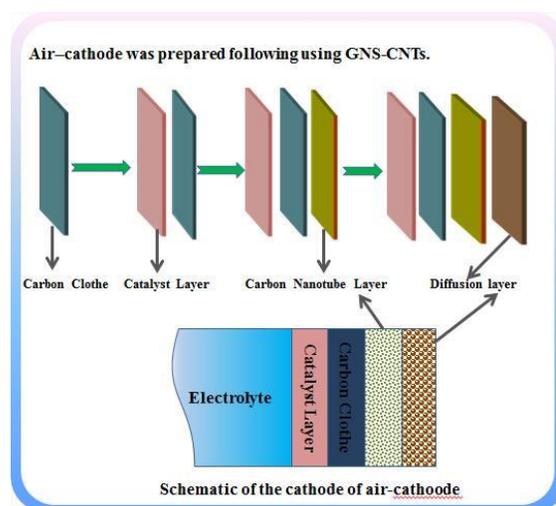


Fig.2. Preparation of the GNS-CNT Hybrids air-cathode

2.1 Microbial inoculum and MFC operation

MFCs were inoculated with anaerobic sludge. Glucose, with an initial concentration of 1 g L^{-1} chemical oxygen demand (COD), was used as the carbon source and poured into the anode chambers of the MFC, along with a medium containing the following (per liter of deionized water): NH_4Cl , 0.31 g; KCl , 0.13 g; $Na_2HPO_4 \cdot 12H_2O$, 4.756 g; $NaH_2PO_4 \cdot 2H_2O$, 2.452 g; and trace mineral element solution, 12.5 mL [20]. The final pH of this medium was adjusted to 7.0 using 0.1M $NaOH$ or HCl . After stable voltage outputs were achieved, a glucose medium without anaerobic sludge was used to replace the solutions in the MFCs. The catholyte used was Na_2SO_4 (0.1 mol L^{-1}).

To determine the rate of H_2O_2 production, experiments under different reaction conditions (external resistance, Na_2SO_4 concentration, and catholyte pH) were conducted. In the experiment on MB degradation, catholytes containing

MB and in-situ generated H_2O_2 were used. The Fenton reaction with Fe^{2+} as a catalyst occurred in the cathode chamber during the process of H_2O_2 generation.

2.2 Analyses

The voltages produced by the MFCs were recorded at 30-minute intervals using a precision multimeter and a data acquisition system (Keithley Instruments 2700, USA). The H_2O_2 concentrations were determined using the spectrophotometry of a titanium (IV) oxysulfate–sulfuric acid complex ($TiOSO_4 \cdot xH_2SO_4 \cdot xH_2O$) [21]. The MB concentrations were determined using a UV-vis spectrophotometer (UV-1100, China) at 410 nm with 1-hour intervals [4]. At each scheduled sampling interval, 1.5 mL of the sample was withdrawn from the cathode chamber for H_2O_2 and MB analyses. The COD was measured using the standard closed reflux method [7]. The morphologies of the electrode surfaces were studied by using a scanning electron microscope (SEM) (JEOL, JSM-5900; Japan).

3 RESULTS AND DISCUSSION

Considerable efforts have been exerted to develop operating conditions that can enhance the H_2O_2 production rate [4, 23]. As can be seen from Fig.3 to Fig.5, the H_2O_2 -producing MFC with GNS-CNTs as air cathode is more effective. The higher production rates were achieved on the GNS-CNTs air cathode with different operating conditions. To understand the difference of H_2O_2 generation between different cathode materials, a comparison among the production rates were observed with different external resistance, electrolyte concentration, pH of electrolyte.

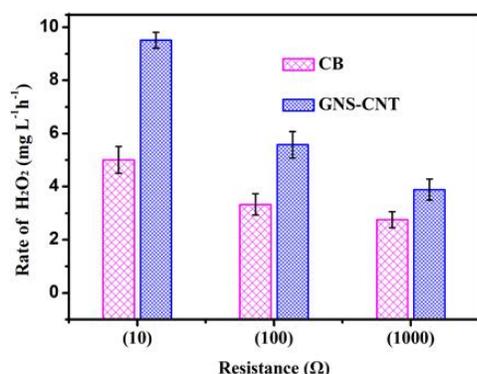


Fig.3. Effect of external resistances on the H_2O_2 production rate

In the experiments carried out with different external resistances, the H_2O_2 production rate increased with decreased external resistance (Fig.3). Six hours later, the highest H_2O_2 production rate of 9.5 ± 0.3 mg L⁻¹h⁻¹ was achieved with the GNS-CNTs air-cathode at a resistance of 10 Ω, which was 47.3% higher than that with the CB air-cathode. As previously demonstrated [4], activation loss occurred at high resistance in the H_2O_2 -producing MFC,

current densities increased with decreased external resistance. Therefore, in order to obtain more H_2O_2 , operation of the H_2O_2 -producing MFC at low resistance is feasible.

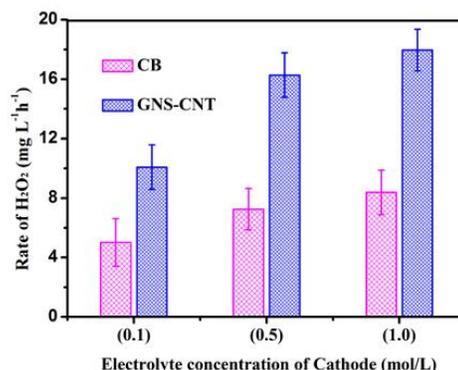


Fig.4. Effect of catholyte concentration on the H_2O_2 production rate

Fig.4 shows that production rates of H_2O_2 can be significantly increased by applying a high concentration of catholyte (Na_2SO_4). The production rates of H_2O_2 increased significantly when a high catholyte (Na_2SO_4) concentration was used. The optimal condition in which to maximize H_2O_2 production was 1.0 mol L⁻¹ Na_2SO_4 , which yielded the highest H_2O_2 production rate of 18.0 ± 1.4 mg L⁻¹h⁻¹. This increase in catholyte concentration can be explained by the transport of cations other than protons through the cation exchange membrane and by the consumption of protons in the cathode reaction [22]. Compared with the CB air-cathode, the H_2O_2 production rates at the GNS-CNTs air-cathode doubled under the same conditions.

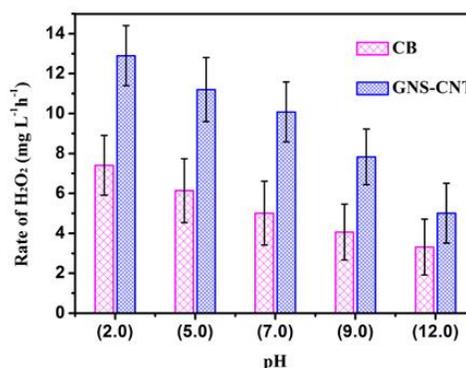


Fig.5. Effect of catholyte pH on the H_2O_2 production rate

It provides similar results to the different pH of catholyte, that the production rates of H_2O_2 on GNS-CNTs air-cathode is higher. The effect of pH on the H_2O_2 production rate at the cathode is shown in Fig.5. The pH has a strong influence on the H_2O_2 production rate in the range of pH 2.0–12.0. At low pH the production rate of H_2O_2 was obviously favored. As the pH increased, the production rate of H_2O_2 continuously decreased. At pH 2.0, the maximum H_2O_2 production rate reached 12.9 ± 1.5 mg L⁻¹h⁻¹ at the GNS-CNTs air-cathode, whereas at pH 12.0, a

rate of only $5.01 \pm 1.6 \text{ mg L}^{-1} \text{ h}^{-1}$ H_2O_2 was obtained under the same conditions. As such, the H_2O_2 production rate continuously decreased with increasing pH. Similar results were observed in the CB air-cathode. Maybe this reaction was thus strongly pH dependent. Lower pH might make the reaction more favorable. Moreover, under the same conditions, the H_2O_2 production rates at the GNS-CNTs air-cathode were higher than those at the CB air-cathode.

Fu et al. [6] investigated a H_2O_2 production rate of $6.75 \text{ mg L}^{-1} \text{ h}^{-1}$ at the cathode using spectrographically pure graphite rods as the cathode, whereas Liu et al [24] investigated a H_2O_2 production rate of $0.28 \text{ mg L}^{-1} \text{ h}^{-1}$ using a carbon felt air-cathode. In our study, the H_2O_2 was produced at a rate of $18.0 \pm 1.4 \text{ mg L}^{-1} \text{ h}^{-1}$ (Fig.4), which was more compared with those in previous reports [6, 24]. In research by Rozendal et al [23], the maximum rate of H_2O_2 production was $79.2 \text{ mg L}^{-1} \text{ h}^{-1}$, but the 0.5 V applied voltages (energy) were added.

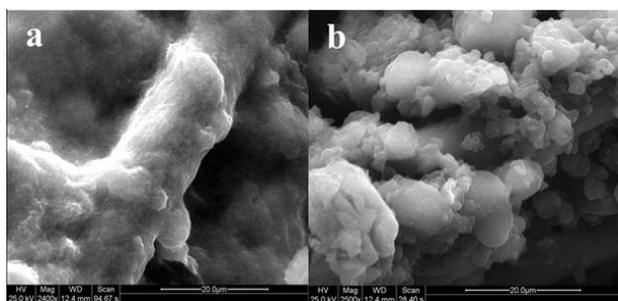


Fig.6. (a) Scanning electron microscopy of GNS-CNTs air-cathode. (b) Scanning electron microscopy of CB air-cathode.

Studies on cathode materials such as GNS-CNTs are aimed at understanding its role and effect on reaction pathways. H_2O_2 was produced at the cathode of the MFC by accepting the electrons that were transferred from the anode. In this study, GNS-CNTs were used as the air-cathode (Fig.6); they are highly crystalline compared with CB, and are distributed more evenly on the surface. Their unique electrical and structural properties allow them to act as catalyst supports and enhance catalyst activity [9-11]. The GNS-CNTs modified air-cathode H_2O_2 -MFC systems thus resulted in reduced internal resistance [18] and consumed fewer electrons, which increased the production rates of H_2O_2 .

4 CONCLUSIONS

In this study, a significant acceleration of H_2O_2 production and MB reduction was observed with GNS-CNTs air-cathode in MFC. The efficiency of H_2O_2 production was strongly related to the catholyte pH, the external resistance, and the catholyte concentration. The optimal condition for maximizing H_2O_2 generation was able to reach $99.6\text{-}116.4 \text{ mg L}^{-1}$. This study demonstrated that the commercialized

MFC technology with GNS-CNTs air-cathode is promising for H_2O_2 production and wastewater treatment.

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