



Porous nitrogen-doped carbon nanosheet on graphene as metal-free catalyst for oxygen reduction reaction in air-cathode microbial fuel cells



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ABSTRACT

Porous nitrogen-doped carbon nanosheet on graphene (PNCN) was used as an alternative cathode catalyst for oxygen reduction reaction (ORR) in air-cathode microbial fuel cells (MFCs). Here we report a novel, low-cost, scalable, synthetic method for preparation of PNCN via the carbonization of graphite oxide–polyaniline hybrid (GO–PANI), subsequently followed by KOH activation treatment. Due to its high concentration of nitrogen and high specific surface area, PNCN exhibited an excellent catalytic activity for ORR. As a result, the maximum power density of 1159.34 mW m⁻² obtained with PNCN catalyst was higher than that of Pt/C catalyst (858.49 mW m⁻²) in a MFC. Therefore, porous nitrogen-doped carbon nanosheet could be a good alternative to Pt catalyst in MFCs.

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1. Introduction

Microbial fuel cell (MFC) is one of the most promising methods to generate electrical energy from organic and inorganic matter [1]. Oxygen has been considered as the most favorable cathodic electron acceptor among various oxidants due to its easy availability in the environment with the capacity to give a high power output [2]. However, without catalysts the kinetic reaction rate of the oxygen reduction is very low and the performance of an air-cathode MFC is quite poor [3]. As a commonly used catalyst for oxygen reduction reaction (ORR) in MFCs, platinum has greatly hindered the practical application of large scale MFCs due to its relatively high cost and sensitivity to poisoning [4,5]. Therefore, developing effective and low-cost catalysts for ORR, such as iron phthalocyanine, Co-naphthalocyanine (CoNpc), manganese dioxide, lead dioxide and nickel powder, has aroused extensive research interest [6–11].

Recently, nitrogen-doped carbon materials have attracted considerable attention in practical and fundamental research of ORR in alkaline medium due to their high catalytic activity, excellent reliability and environmental friendliness [12–18]. Maldonado and Stevenson reported that nitrogen-induced defects on carbon structure can increase the edge plain exposure which supports additionally the catalytic activity [19]. The synthesis of N-doped carbon materials often uses chemical vapor deposition (CVD) process under the exposure of reactive gases (NH₃) [20,21], however, it usually increases production cost due to its complicated procedure. Newly, the carbonization of N-containing polymers such as polypyrrole, poly(p-phenylene), poshanlypyrrolidone, polyacrylonitrile, polyaniline (PANI) and melamine, is an easy way to obtain various types of nitrogen-rich carbon materials retaining the

morphology of the precursors [22–25]. Among them, polyaniline (PANI) has been used as an attractive precursor for synthesis of nitrogen-doped carbon material. For instance, G. Wu et al. reported the nitrogen-doped graphene sheets as a new catalyst for ORR, which was prepared by the carbonization of polyaniline and Co precursors using MWNTs as a template [26].

Lately, particular care was paid to the practical and fundamental research of porous nitrogen-doped carbon materials for supercapacitors and fuel cells due to their desirable characteristics including a high surface area and a high catalytic activity. R. Silva et al. reported a new catalyst polyaniline (PANI)-derived N- and O-doped mesoporous carbon (PDMC) which was synthesized by polymerizing PANI in situ within the pores of SBA-15 mesoporous silica, followed by subjecting PANI/SBA-15 to carbonization under an inert atmosphere [27]. This method using SBA-15 mesoporous silica which can etch away the silica framework when carbonization under an inert atmosphere to make the catalyst a porous structure. However, the high cost of SBA-15 mesoporous silica may limit the large-scale application of PDMCs. Chemical activation has been shown as a very efficient and low-cost method to obtain carbons with high surface area and narrow micropore distribution [28,29]. In this study, porous nitrogen-doped carbon nanosheet on graphene (PNCN) was prepared by the carbonization of graphite oxide–polyaniline hybrid (GO–PANI) and the chemical activation with KOH to effectively develop the microporosity of nitrogen-doped carbon material. PNCN was prepared via four processes: (1) Graphite oxide (GO) was synthesized from natural graphite by a modified Hummer's method. (2) GO–PANI was synthesized via an in-situ polymerization of aniline in a GO solution. (3) GO–PANI nanocomposite was converted into nitrogen-doped carbon material by heat treatment at 850 °C, and (4) nitrogen-doped carbon material was activated by KOH. In addition, previously published studies about N-doped carbon catalysts were

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mostly used in metal-air batteries or fundamental research of ORR. However, in this study we also focused on the application of PNCN in MFCs. Due to its high surface area and high nitrogen content, the prepared porous nitrogen-doped carbon material in this study exhibited a high catalytic activity with the maximum power density of $1159.34 \text{ mW m}^{-2}$ compared to Pt/C (858.49 mW m^{-2}) in MFCs.

In the present study, the catalyst characterization was investigated through Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), BET and X-ray photoelectron spectroscopy (XPS). The evaluation on the ORR activity of NCN and PNCN were investigated through linear sweep voltammetry (LSV). Further performance examination was evaluated in MFCs with NCN and PNCN catalyst air cathodes.

2. Experimental

2.1. Catalyst preparation

Graphite oxide (GO) was synthesized from natural graphite (300 μm , Qingdao Graphite Company) by a modified Hummer's method [30]. Exfoliation of GO (20 mg) in 40 mL of H_2O were achieved by ultrasonication in an ultrasonic bath (KQ-600KDE, 600 W). After that, 86 mL of 0.25 M aniline monomers (solvent: 1 M HCl) were added into the above suspension and sonicated for 1 h. Afterwards, 86 mL of 0.25 M ammonium persulfate (APS, solvent: 1 M HCl) were rapidly added into the above mixture and stirred for 8 h at $0\text{--}2^\circ\text{C}$, the yellow-brown suspension gradually changed to deep green color. Finally, the prepared GO-PANI nanocomposite was washed repeatedly and dried in a vacuum oven at 80°C for 24 h.

Porous nitrogen-doped carbon nanosheet (PNCN) was prepared as follows: the as-prepared precursor was heated to 850°C and pyrolyzed for 2 h under nitrogen flow. Then the carbonized sample (NCN) and KOH were mixed with a weight ratio of 1:4, and were heated up to 850°C for 1 h. Subsequently, the activated sample was washed with 0.5 M HCl solution and distilled water for several times until the pH value remained constant, followed by drying at 100°C for 12 h.

2.2. Electrode preparation

The air-cathode was manufactured by pressing wet-proof gas diffusion layers (50 wt.% Na_2SO_4 and 50 wt.% polytetrafluoroethylene (PTFE)), catalyst layer (86 wt.% activated carbon, 12 wt.% Nafion (5%, HESN, China), and 2 wt.% acetylene black powder, containing 5 mg cm^{-2} PNCN catalyst) and stainless steel net. As controls, the Pt/C (20%, HESN, China), NCN and active carbon air cathodes were fabricated using the same procedure. The Pt/C and NCN catalyst were also loaded onto the air cathode at 5 mg cm^{-2} . In order to investigate the ORR performance, the linear sweep voltammetry (LSV) was performed in a three-electrode configuration. The working electrodes were prepared as follows: 10 mg of catalyst and 4.3 mg of acetylene black was added into 20 mL of alcohol and then subjected to ultrasonic vibration for 1 h. Subsequently, 60 μL of Nafion was added into the resulting suspension, and then heated by electric furnace until it became a paste. Finally, each catalyst paste was pasted onto carbon paper (2 cm^2) by brush and then dried at a room temperature for 48 h.

2.3. MFC construction and operation

MFC was constructed as previously described [31]. The air-cathode single chamber MFC was built with a cylindrical plastic tube, which had an inner diameter of 6 cm and total height of 8 cm. The air-cathode ($5 \times 2 \text{ cm}^2$) was placed on one side of the outer surface of the MFC, whereas the anode was cylindrical carbon brush with a diameter of 4 cm. Two electrodes were separated by 1 cm. For comparing the performance of MFCs with different cathode catalysts, four air-cathode single chamber MFC reactors with PNCN, NCN, Pt/C and non-catalyst air cathodes, were set up for the experiments. MFC reactors were inoculated using anaerobic

sludge collected from another MFC which had been operated continuously in our lab. MFC reactors were operated using nutrient buffer solution (NBS) containing the following: acetate, 1 g/L; KCl, 130 mg L^{-1} ; $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$, 4.97 g L^{-1} ; $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$, 2.75 g L^{-1} ; and other trace elements required for microorganism growth as reported by Liu and Logan [32]. The nutrient buffer solution (200 mL) was refreshed when the voltage decreased to below 50 mV, forming a fed-batch. All experiments were conducted at a room temperature ($24 \pm 1^\circ\text{C}$).

2.4. Analysis and calculation

The output voltage was measured across an external resistor (1500 Ω resistor except where indicated otherwise) using a data acquisition system connected to a computer. Polarization curve of MFCs and the performance of the electrode potential were measured as previously described [33]. Power density was according to $P (\text{mW m}^{-2}) = 1000U \times J$, where J is the current density (A m^{-2}), which is calculated by $J = U / (R \times A)$ based on external resistance $R (\Omega)$ and projected surface area of cathode $A (\text{m}^2)$; 1000 is based on the unit change. To measure electrode potentials, a digital voltmeter was used against a saturated Ag/AgCl reference electrode. Polarization curves were obtained by plotting potential and power density against current density. Electrode potential was measured at variable resistance points (9000–50 Ω) during stabilized fuel cell operation.

To electrochemically characterize the catalyst, linear sweep voltammetry (LSV) was performed using an electrochemical workstation (SP-240, Bio-Logic), with a three-electrode configuration consisting of a Ag/AgCl reference electrode, a working electrode (the catalyst-modified carbon papers), and a platinum foil counter electrode placed in 50 mmol L^{-1} phosphate buffered solution (PBS) aerated by oxygen (O_2) or nitrogen (N_2) for 1.5 h.

3. Results and discussion

3.1. Characterization of PNCN

In this experiment, polyaniline (PANI) nanosheets grown on the surface of GO are fabricated through the chemical polymerization process under the aid of ammonium persulfate (Fig. 1A, B). After the carbonization of PANI-GO hybrid material, carbon nanosheets from the pyrolysis of PANI still maintain their sheet morphology with the width/length less than 15 nm homogeneously covered on graphene sheet (Fig. 1C). Subsequent activation with KOH results in the formation of PNCN with large surface area (Fig. 1D). N_2 adsorption-desorption isotherms of PNCN exhibits type IV isotherms with a distinct hysteresis loop at a relative pressure p/p_0 ranging from 0.4 to 1, as well as higher Brunauer-Emmett-Teller surface area of $1398 \text{ m}^2 \text{ g}^{-1}$ compared with the carbonized sample NCN ($183 \text{ m}^2 \text{ g}^{-1}$) (Fig. 2). The increased BET surface area can be attributed to the chemical activation treatment, which is a very efficient method to obtain carbons with high surface area and micro-pore distribution [28]. The first step in the chemical activation with KOH is a redox reaction between NCN and KOH. In this step, the produced metallic potassium can be inserted/intercalated in NCN. Thus K intercalation compounds are formed during the activation reaction. As it is well known that these derivatives are unstable in air, especially due to moisture [29]. When the K intercalation compounds are exposed to air, metallic potassium produced during the redox reaction will lead to the separation and degradation of the graphitic layers which gives rise to a high portion of micro-pore.

The XPS spectrum has a predominant narrow graphitic C 1s peak at 284.6 eV, along with an obvious N 1s peak at 400.1 eV and an obvious O 1s peak at 536.8 eV (Fig. 3). The N 1s spectra of PNCN consist of pyridinic-N (398.7 eV), pyrrolic-N (400.1 eV), and graphitic-N (401.7 eV). Pyridinic-N is a nitrogen atom that bonds to two carbon atoms on the edge of a carbon plane and a carbon vacancy. Many electrocatalytic reactions show increased kinetics on carbon edge planes

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