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Nitrogen-doped MoS_2/carbon as highly oxygen-permeable and stable catalysts for oxygen reduction reaction in microbial fuel cells

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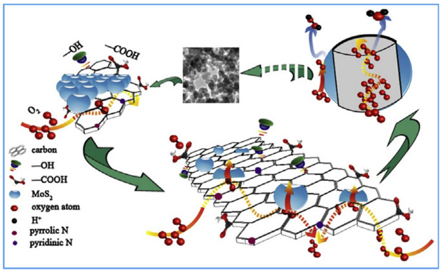
HIGHLIGHTS

- Dissolved oxygen concentration on cathode interface is an influential factor for ORR.
- N-doped MoS_2/carbon (N-MoS_2/C) with porous structure can be obtained by adding F127.
- Regular honeycomb structure of N-MoS_2/C is favorable for O_2 permeation and diffusion.
- Abundant active sites of N-MoS_2/C derived from rich defects can enhance ORR activity.
- MFCs with N-MoS_2/C (900 °C) cathode has higher power output than that of Pt/C.

GRAPHICAL ABSTRACT



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ABSTRACT

Developing non-noble metal catalysts with high oxygen-permeability and activity for oxygen reduction reaction (ORR) is crucial for microbial fuel cells (MFCs). In this study, nitrogen-doped molybdenum disulfide/carbon (N-MoS_2/C) is prepared using melamine as nitrogen and carbon sources. Ammonium molybdate, thiourea and Pluronic F127 are used as Mo source, S source and surfactant, respectively. Mo-S-melamine complex precursor is obtained through the evaporation-induced self-assembly route, which is then carbonized at 800, 900 and 1000 °C to fabricate N-MoS_2/C. Defect-rich N-MoS_2/C has a large number of exposed active sites and a high oxygen permeability. N-MoS_2/C (900 °C) with regular honeycomb structure shows the maximum power density of 0.815 W m^{-2}, which is far higher than that of Pt/C (0.520 W m^{-2}) and only has a decline of 1.23% after 1800 h operation in MFCs. Four-electron ($4e^-$) reduction of O_2 is the main ORR pathway for N-MoS_2/C (900 °C), attributing to the efficient permeation, adsorption, activation and reduction of O_2 on the active sites. The synergy among abundant defects, N-species (pyridinic N, graphitic N and Mo—N_x) and high conductivity contributes to the promising ORR activity. This simple synthetic route of N-doped metal sulfides/carbon composites displays a new prospect for preparation of ORR catalyst.

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1. Introduction

Compared with other energy generation systems, the greatest advantages of microbial fuel cells (MFCs) are that MFCs can purify wastewater by converting organics into energy [1–4]. As the new source of biological energy, especially, the single-chamber MFCs with air-cathode have attracted more and more attentions [5,6]. So far, one of the chief obstacles of this air-type MFCs is the sluggish permeation (supply) and reduction (consumption) of oxygen on the cathode, which results in the low current density and power output, and high over-potential in MFCs [7,8]. Platinum (Pt)-based materials are commonly considered as the efficient cathode catalysts for oxygen reduction reaction (ORR) [9], but the high cost and poor tolerance limit their development and application in MFCs [10,11]. In addition, since the corrosion of the interface between the carbon support and the Pt nanoparticles, the activity and durability (stability) of Pt/C for ORR are inevitably degraded after a long-time operation [12]. Therefore, to find the high-performance and low-cost electrocatalysts for ORR are the key issues to be solved for MFCs development [13].

Carbon-based catalysts are usually used to replace the Pt/carbon (Pt/C) because of their high electrical conductivity and low cost [14–16]. Many studies report that nitrogen (N)-doped carbon without metals has been used to improve the ORR performance [12,17–19]. Noto et al. report that carbon nitride-based electrocatalyst display a high ORR activity and a remarkable tolerance towards the undesirable conditions [12,19]. The N atoms are embedded in carbon-based matrix to enhance the ORR stability for the long-term operation [19]. Li et al. prepare N-doped reduced graphene oxide (NGs) using melamine or urea as nitrogen source. The NGs exhibits higher ORR catalytic activity than that of reduced graphene oxide. In addition, the NGs (melamine as nitrogen source) show the thin-flakes of graphene-like structure, and N-doped level and quaternary N content are higher than those of NGs samples with urea as nitrogen source [20]. He et al. prepare N-doped carbon nanotubes (N-CNTs) as the MFCs cathode catalysts by vertically growing on carbon cloth (CC). The power density of N-CNTs-CC (542 mW m^{-2}) is greater than that of Pt/C-CC cathode [21]. The defects of two adjacent C atoms can be caused by doping N atoms, leading to the enhanced combination/adsorption capacity for oxygen atoms and the improvement of ORR activity [22,23]. Additionally, pyridinic and pyrrole types of N in carbon are considered as the key constituents for improving the electrocatalytic performance of ORR [24]. Pyrrolic-N plays an important role in the initial step of ORR, which can be served as the active sites to catalyze O_2 reduction to H_2O_2. The next step is that pyridinic-N can help the fast H_2O_2 reduction to water. Furthermore, it is also reported that N-coordinated metal ($M-N_x$) can energetically catalyze a direct $4e^-$ reduction of oxygen to water [25–27].

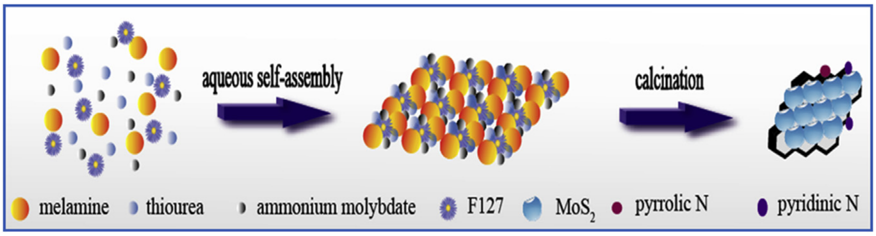
Furthermore, transition metals sulfides (sphere-like Co_3S_4NC, Co-sulfides/graphene, molybdenum disulfide and etc.) with modest activity and stability have been used as the lithium battery cathode catalysts [28]. Among them, molybdenum disulfide (MoS_2) is a kind of graphene-like layered material and has been used in hydrogen evolution reaction and ORR [29]. It has been confirmed that the catalytic activity of MoS_2 is closely related to its active edge sites [31]. The edges of Mo in MoS_2 can be served as a preferred location for the chemisorption and reduction of oxygen [29–31]. Moreover, the covalent sulfide can contribute to the fast transfer of electrons through the exposed S edges [32]. We can suppose that MoS_2 with abundant active edge sites may be suitable for enhancing the cathodic ORR performance in MFCs because of its fast adsorption of oxygen. However, MoS_2 with lamellar structure is easily stacked together because of the van der Waals force along the (002) plane, which may seriously reduce the number of active sites for ORR [33–35]. Therefore, it may be feasible to combine the MoS_2 with N-doped carbon (N-MoS_2/C) to enhance the structural stability and ORR activity of MoS_2, which can exploit the synergistic effects among MoS_2, N-species and carbon structure of carbon [36]. Furthermore, the stack (aggregation) of MoS_2 nanoparticles (nanosheet) may also be relieved by embedding in carbon structure, which can correspondingly maintain the smooth pathways for the permeation, transfer (diffusion) and reduction of oxygen.

In this study, the N-MoS_2/C is prepared using the aqueous evaporation-induced self-assembly process and carbonization (800–1000 °C) method. Melamine (as carbon and nitrogen sources), thiourea, ammonium molybdate and amphiphilic triblock copolymers (Pluronic F127, (EO)106-(PO)70-(EO)106, as the soft template) are used to prepare the defects-rich N-MoS_2/C with high oxygen permeability (highly porous structure). The aims of this study are (1) to explore the crystalline phase and structure of N-MoS_2/C at different carbonization temperatures (800–1000 °C); (2) to illustrate the relationship between oxygen permeability and ORR activity of N-MoS_2/C; (3) to evaluate the long-time performance of N-MoS_2/C as the cathode catalysts for MFCs; (4) to clarify relationship between the cathodic oxygen transport (permeation/supply) and ORR (consumption). These catalysts are expected to have the promising ORR activity together with high stability and low internal resistance than those of the Pt-based catalysts.

2. Experimental section

2.1. Synthesis of N-MoS_2/C composites

The simple synthesis procedure was shown in Scheme 1. 0.25 g of thiourea (A.R, Tianli Chemical Reagent Co., Ltd., Tianjin, China) was firstly dissolved in 40 mL of deionized water (Milli-Q, Millipore Corp., Bedford, MA) and stirred continuously at 40 °C. After several minutes, the solution was changed from turbid to a clear-water state and then 1.26 g of melamine (A.R, Guangfu Chemical Research Institute, Tianjin, China) was added into the clear solution for stirring 2 h (at 90 °C). Subsequently, the aqueous solution of F127 (Pluronic F127, (EO)106-(PO)70-(EO)106, Sigma-Aldrich, St. Louis, USA) (1 g of F127 was dissolved in 10 mL of deionized water for stirring 2 h at 40 °C) and 0.12 g of ammonium molybdate (A.R, Tianjin Kemiou Chemical Reagent, Tianjin, China) were added to



Scheme 1. Synthesis route for N-MoS_2/C composite.