Short communication

Iron tetrasulfophthalocyanine functionalized graphene as a platinum-free cathodic catalyst for efficient oxygen reduction in microbial fuel cells

Yezhen Zhang, Guangquan Mo, Xuwen Li, Jianshan Ye*

School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510641, PR China

A B S T R A C T

Noncovalent functionalization of graphene with iron tetrasulfophthalocyanine (FeTsPc) is achieved not only to prevent the aggregation of graphene but also form an efficient electrocatalyst for the oxygen reduction reaction (ORR) in a dual-chamber microbial fuel cell (MFC). The electrochemical activity of the FeTsPc-functionalized graphene (FeTsPc-graphene) is evaluated towards the ORR using cyclic voltammogram (CV) and linear sweep voltammogram (LSV) methods. More positive peak potential and larger peak current of ORR are found using FeTsPc-graphene electrode as compared to FeTsPc electrode, suggesting enhanced activity of FeTsPc after adsorbing on graphene surface. The maximum power density of 817 mW m^{-2} obtained from the MFC with a FeTsPc-graphene cathode is higher than that of 523 mW m^{-2} with a FeTsPc cathode and is close to that of 856 mW m^{-2} with a Pt/C cathode. Thus, FeTsPc-graphene nanocomposites can be a good alternative to Pt catalyst in MFCs.

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1. Introduction

Microbial fuel cells (MFCs) are renewable energy devices that convert organic substrates into electricity via the catalyzation of microorganisms. Since their ability of treating wastewater and simultaneously generating electricity, MFCs have attracted increasing interests recently [1–12]. Oxygen is an ideal electron acceptor for MFC cathodes due to its high oxidation potential, accessibility in environment and clean product [13]. However, the poor kinetics of oxygen reduction reaction (ORR) in the MFC cathodic medium limits the efficient utilization of oxygen as final electron acceptor for most cathode materials [14]. To solve this problem, platinum (Pt) is widely used as catalyst of ORR in MFC cathodes [15]. Nevertheless, in virtue of its high cost, limited supply and possible poisoning by the substrate or by-products, alternative catalyst material with high catalytic activity and low cost is of high priority.

Due to its fascinating physical and chemical properties, graphene has been attracting extensive interest in the fields of lithium ion batteries, supercapacitor, liquid crystal, nanoelectronic devices, field emitters and electrochemical catalyst [16–23]. Graphene has been reported as electrochemical catalyst for ORR in alkaline and acid media [24,25], while the electrochemical properties of graphene used in neutral medium have not been thoroughly studied. Moreover, monolayeric graphene sheet tends to

irreversibly agglomerates or form multilayeric graphite through strong π–π stacking and van der Waals interaction [26]. Since most of its unique properties are only associated with individual sheets, it is highly important to prevent graphene sheets from aggregation. Recently, some methods containing covalent and noncovalent functionalization of graphene have been used to obtain dispersed graphene [27,28], of which noncovalent way is more favorable for it can maintain the electronic structure of graphene. Tetrasulfophthalocyanine (FeTsPc) is a negatively charged and water-soluble aromatic macromolecule that can prevent agglomerates of graphene sheets through the coulomb repulsion.

In this study, FeTsPc functionalized graphene (FeTsPc-graphene) was prepared with the purpose not only of preventing the aggregation of graphene but also simultaneously forming an efficient catalyst for ORR, which might be a potential alternative to Pt in MFCs.

2. Experimental

2.1. Chemicals and materials

Nafion (5%), FeTsPc and 2-hydroxy-1, 4-naphthoquinone (HNQ, 97%) were purchased from Sigma–Aldrich. Pt/C (40%) was obtained from Johnson Matthey. Nafion 112 (Dupont, USA) was used as a cation exchange membrane. All other chemicals were from local chemical agents, and deionized water (>18.4 MΩ cm^{-1}) was used throughout.

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* Corresponding author. Tel.: +86 20 87113241; fax: +86 20 87112901.
E-mail address: jsye@scut.edu.cn (J. Ye).

Graphene was obtained by the chemical oxidation–reduction treatment of graphite [29,30]. In a typical procedure, graphite (5 g) was first added into the stirred mixture of concentrated sulfuric (87.5 mL) and nitric acid (45 mL) in ice-water bath. $KClO_3$ (55 g) was then added into the mixture. This mixture was kept stirring for 4 days at room temperature, after which, water (4 L) was added into the slurry and the mixture was then filtered to obtain graphite oxide. After drying at 80 °C, graphene oxide was exfoliated in deionized water by ultrasonic treatment for 2 h to form a colloidal graphene oxide suspension. Finally, the graphene oxide suspension was reacted with hydrazine monohydrate (1 μL: 3 mg graphene oxide) for 24 h at 80 °C to obtain the graphene sheets.

FeTsPc-graphene was prepared as follows: graphene (20 mg) was dispersed in 10 mL water containing 4 mg of FeTsPc. The mixture was ultrasonicated for 6 h at room temperature. The resulting suspension was filtered and thoroughly rinsed with water to remove the non-adsorbed FeTsPc and then dried at 80 °C for 12 h to obtain FeTsPc-graphene.

2.2. Electrode preparations

The prepared FeTsPc-graphene was dispersed in Nafion (0.1%) to give a homogeneous suspension (1.6 mg mL^{-1}) under ultrasonication. Graphene (1.6 mg L^{-1}), FeTsPc (0.27 mg mL^{-1}) and Pt/C (1.6 mg mL^{-1}) were also prepared with the similar method. The prepared mixture (2 μL) was dropped onto glass carbon electrode (GCE, diameter 3 mm), denoted as FeTsPc-graphene/GCE. Similar procedures were applied for preparation of graphene/GCE, FeTsPc/GCE and Pt/C/GCE.

Carbon fiber sheet (Hesen, China) was cut into 2 cm × 2 cm and 3 cm × 3 cm pieces and then were sequentially soaked for 1 h in 1.0 M HCl, deionized water, 1.0 M NaOH and deionized water. Carbon papers of 3 cm × 3 cm were used as MFC anodes. FeTsPc-graphene (1.6 mg) was dissolved in 1 mL Nafion (0.1%) and drop casted onto carbon paper of 2 cm × 2 cm to fabricate FeTsPc-graphene cathode with the loading of 0.2 mg cm^{-2}. Similar procedures were used to fabricate graphene, FeTsPc and Pt/C (40%) cathodes with the loading of 0.2, 0.033 and 0.2 mg cm^{-2}, respectively.

2.3. MFC construction and system set-up

The MFC reactor was constructed using two round polymethylmethacrylate (PMMA) templates (Φ = 15 cm, 3 cm in thickness). The anodic or cathodic compartment was an inner cylinder (Φ = 9 cm, 2 cm in depth) in each template. The two compartments were screwed together and separated by two PMMA disc gaskets (Φ = 15 cm, 3 cm × 3 cm square window in center) with Nafion 112 membrane (effective area of 9 cm^2).

Phosphate buffer solution (PBS) consisted of 10.0 g of $NaHCO_3$ and 8.5 g of NaH_2PO_4 L^{-1}. Culture medium, a mixture of 10.0 g of peptone, 5.0 g of NaCl and 3.0 g of beef powder L^{-1}, was sterilized in an autoclave (Sanshen Shanghai, China) at 120 °C for 20 min, and then placed in the incubator (Shenxian Shanghai, China) at 37 °C for 24 h before using. Original *Escherichia coli* (ATCC 25922, Guangdong Institute of Microbiology) biocatalyst was grown anaerobically in the culture medium at 37 °C for 18–24 h. *E. coli* culture (5 mL) was inoculated to anode (saturated with nitrogen for 20 min before inoculation). PBS was employed as catholyte while PBS containing 5 mM of HNQ, 10.0 g of glucose and 5.0 g of yeast extract L^{-1} was employed as anolyte. Both the volumes of anolyte and catholyte were 115 mL. For comparing the performance of cathodes fabricated by different materials, graphene based MFC (MFC-graphene), FeTsPc-graphene based MFC (MFC-FeTsPc-graphene) and Pt/C based MFC (MFC-Pt/C) were set up respectively.
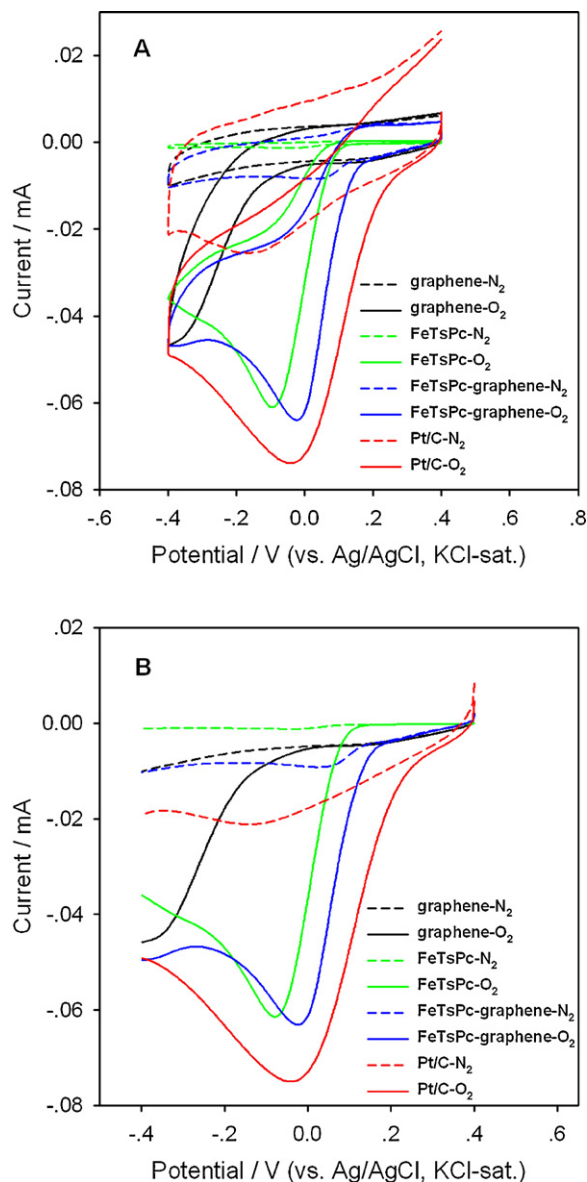

Fig. 1. CV (A) and LSV (B) of graphene/GCE (black line), FeTsPc/GCE (green line), FeTsPc-graphene/GCE (blue line) and Pt/C/GCE (red line) in N_2-saturated (dotted line) or O_2-saturated (solid) PBS. Scan rate: 50 mV s^{-1}. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Except *E. coli*, all equipments used in the experiment were sterilized in the ultraviolet for 30 min in order to prevent contamination from other bacteria.

2.4. Electrochemical measurements

CV and LSV were performed in PBS medium on a CHI660C (Chenhua, China) for characterization of the ORR on different catalysts. A three-electrode system of a working electrode, a platinum counter electrode and an Ag/AgCl (saturated KCl) reference electrode was employed.

Cell testing was carried out with a MFC characterization system (Ingsens Instrument, China). Varied resistance (0–10 kΩ) was used as the external load for the determination of power output. Cell voltages (V) were recorded across the external resistance (R) every 30 s at 35 °C. Current (I) was calculated as $I = V/R$. Power (P) was calculated as $P = V \times I$. Both I and P were normalized to the geometric surface area of cathodes.
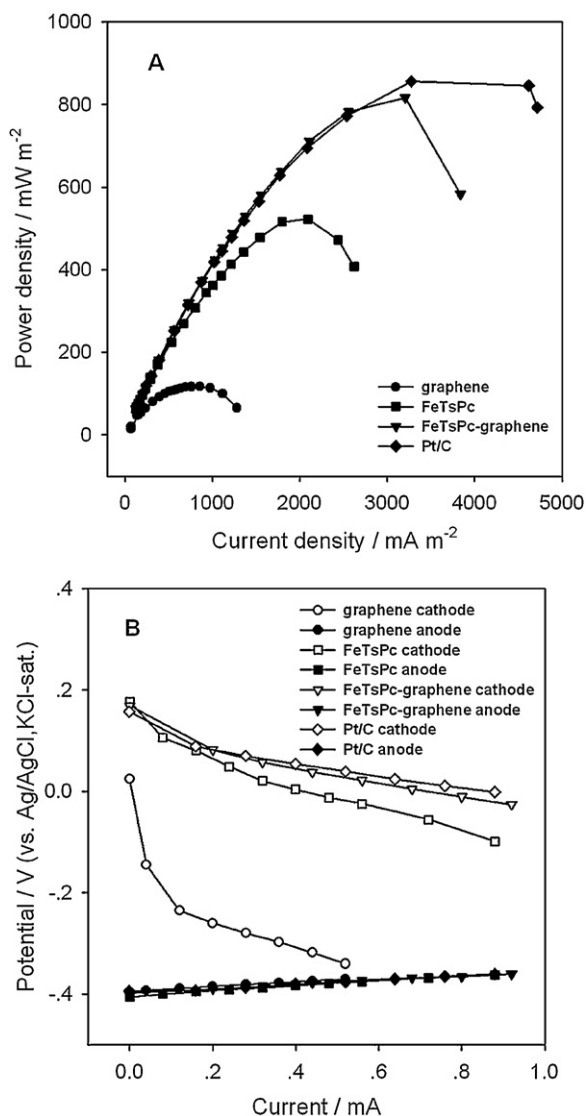
Fig. 2. Power generation properties of MFCs operated with the graphene (circle), FeTsPc (square), FeTsPc-graphene (triangle) and Pt/C (diamond): (A) power density curves of four MFCs and (B) anode (filled symbol) and cathode (open symbol) polarization curves.

3. Results and discussion

3.1. Characterization of graphene and FeTsPc-graphene

Our previous studies indicated that FeTsPc could be adsorbed onto graphene sheets [30]. The interaction between graphene and FeTsPc via π–π stacking interaction was further approved by UV–vis spectrophotometry (data not shown). The spectrum of graphene solution did not show obvious absorption peak from 800 to 500 nm, while the spectrum of FeTsPc solution exhibits an absorption peak at about 632 nm which corresponds to the π–π transition of the tetrasulfophthalocyanine ligand, characteristic of FeTsPc monomeric species. The absorption peak of FeTsPc-graphene solution shifted from 632 to 646 nm, demonstrating the formation of conjugated system.

3.2. Electrochemical performance

Due to the N_4-chelate structure, FeTsPc bears uniform electron density and abundant π-conjugation system. Therefore, it can be adsorbed on graphene surface via π–π stacking interaction. The amount of FeTsPc adsorbing on graphene was estimated to be 2.49×10^{-9} mol cm^{-2} [30], indicating multilayer conformation of FeTsPc on graphene. Therefore, the high coverage of FeTsPc can provide enhanced active sites for ORR.

CV and LSV were used to evaluate the electrocatalytic behavior of various cathode materials for ORR in the presence and absence of oxygen. As shown in Fig. 1A, the oxygen reduction peak could be clearly observed on FeTsPc-graphene at approximately −0.02 V. It was close to that obtained at Pt/C (−0.04 V) and more positive than those at graphene (−0.39 V) and FeTsPc electrode (−0.06 V). The peak current was also close to that of Pt/C and higher than those of graphene and FeTsPc electrodes. It indicated the high catalytic activity of FeTsPc-graphene composite to ORR. Similar phenomenon was also observed on LSV curves (Fig. 1B).

Compared to the traditional pyrolysis treatment, functionalization of graphene with FeTsPc is more convenient and efficient to prepare high-performance ORR catalyst.

3.3. The performance of MFCs with different cathodic catalysts

The electricity generated by FeTsPc-graphene, graphene, FeTsPc and Pt/C were examined in a dual-chamber MFC inoculated with *E. coli* (ATCC 25922). The power density curves are shown in Fig. 2A. The maximum power density achieved from MFC-FeTsPc-graphene was 817 mW m^{-2}, which was higher than those from MFC-graphene (118 mW m^{-2}) and MFC-FeTsPc (523 mW m^{-2}). It indicated that the FeTsPc-graphene composite had higher electrocatalytic activity. The high surface area of graphene is beneficial to adsorb the FeTsPc. Furthermore, the energy output of MFC-FeTsPc-graphene was close to MFC-Pt/C (856 mW m^{-2}). This result suggested that FeTsPc-graphene could be a competitive alternative to Pt for MFC catalyst. Anode and cathode polarization curves are shown in Fig. 2B. All the MFCs employed 3 cm × 3 cm carbon papers as anodes and the anolyte contained 5 mM HNQ [31] to avoid the anode limiting, so the anode potentials of all reactors were the same. But cathode potentials of these MFCs varied from each other. The diversity of MFC performances may be caused by the diversified catalytic activity of the catalysts.

4. Conclusions

FeTsPc has been directly modified onto graphene through non-covalent method. The resulting FeTsPc-graphene exhibits significantly high oxygen reduction activity. With the FeTsPc-graphene modified cathode, the maximum power density of 817 mW m^{-2} has been obtained, which is close to that of a Pt/C cathode of 856 mW m^{-2}. Therefore, FeTsPc-graphene offers a good alternative to Pt in MFC practical applications.

Acknowledgements

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