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Facile synthesis of graphene-phthalocyanine composites as oxygen reduction electrocatalysts in microbial fuel cells

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ABSTRACT

In the path of direct energy conversion and wastewater disposal through microbial fuel cells (MFCs), the oxygen reduction reaction (ORR) plays a pivotal role. However, kinetic limitations hinders the spread of such technology requiring the use of a catalyst to develop efficient and cost effective devices. Herein we report a facile method for the preparation of iron-based catalyst supported on graphene oxide (GO) obtained by electrochemical exfoliation of graphite in aqueous solution of ammonium sulfate. Two different strategies to include nitrogen functionalities on/in GO matrix have been used, such as one-step nitrogen-doping in solution and post treatments based on annealing with ammonia gas. Iron (II) phthalocyanine (FePc) was used as iron source and deposited on GO by pyrolysis-free impregnation. Tuning the adjustable parameters governing the materials preparation allowed producing GO nanosheets with unique morphology and surface properties for enhancing the interaction with FePc. By combining the use of microscopy, electrochemical and spectroscopic techniques, a correlation between structure and surface chemistry of the prepared materials with catalytic activity towards ORR was established. The applicability of iron-based materials as ORR cathodes was evaluated by assembling single chamber air-cathodes MFCs, which power and voltage generation over time were acquired. The obtained results demonstrated that FePc/GO-based electrocatalysts can be used for electricity generation and waste treatment at the cathode side of MFCs.

1. Introduction

Anthropic impact on ecosystem is one of the most important topic of this century. With the aim of air and water pollution reduction, it is paramount to develop efficient energy conversion and waste disposal systems to support a greener way of life. On that purpose, microbial fuel cell (MFC) is an attractive technology suited for degrading organic pollutants while harvesting electrical energy at the same time [1–3]. In a typical MFC, the organics are oxidized into carbon dioxide, protons, and electrons by many different bacteria in anodic biofilms. Previous studies have demonstrated that exoelectrogenic bacteria, including Shewanella and Geobacter [4], are able to release electrons from the oxidation reaction outside the cell directly to the anode, where they move through the external circuit generating useful electricity. Due to high potential and natural abundance, oxygen is the most used oxidant at the cathode side. However, the operating conditions of MFCs, such as ambient temperature and neutral pH, severely limit the oxygen reduction reaction (ORR), resulting in high overpotential and slow kinetics. Hence, the use of catalysts is needed to accelerate ORR, but Platinum is not suitable for MFCs applications, being a rare and expensive metal, which can be deactivated in a polluted environment [5]. Many materials have been investigated as ORR catalysts in MFCs, such as bacterial catalysts [6], enzymes [7], and abiotic cathodes. Among abiotic cathodes, carbon nanostructures have been widely explored, due to high mechanical strength and electrical conductivities, high surface area, and tunable morphology and surface properties. Activated carbons, carbon nanotubes, nanofibers, and graphene have been frequently used as cathode catalysts in different types of MFCs. However, they allow achieving low power generation due to an intrinsic low ORR activities at neutral pH [8–11].

Platinum group metal-free (PGM-free) catalysts have proved to be a promising alternative to Pt due to their high activity in a neutral environment and good stability towards MFC fuels. Those catalysts, based on the coordination of a transition metal (M) with nitrogen in a carbon

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matrix, can be obtained by either pyrolysis of a metal salt (Co, Mn, Fe) and a nitrogen- and carbon-rich organic precursor [12–17] or integration of metal macromolecules having M–N bonds with carbon nanostructures [18–23]. Materials performance has been related to the content and type of nitrogen, to the coordination between metal and nitrogen, and surface properties and morphology of the conductive carbon support. Among carbon nanostructures, graphene oxide (GO) appears ideally suited as catalyst support: in fact, the presence of oxygen-containing surface groups and hydrophilicity increase availability of anchoring sites for catalyst particles and prevent the restack of graphene sheets [24,25]. Following the first report for the preparation of single-layer graphene [26], several approaches to fabricating graphene and GO have been developed: micromechanical cleavage [26], chemical vapor deposition [27], epitaxial growth [28] allow achieving high quality graphene, but the high cost and low production rate make such methods unsuitable for commercial applications. Chemical exfoliation allows reducing costs, but is still a time-consuming method, which involves the use of environmentally harmful chemicals and guarantees a lack of control on morphology [29]. By contrast, electrochemical exfoliation of graphite has been demonstrated to be an effective approach for preparing high quality graphene, at low cost and high production rate [30–32]. We report here a facile and efficient approach for large-scale preparation of ORR catalysts based on iron phthalocyanine (FePc) supported on nitrogen-doped GO. Insights on the effect of surface chemistry and morphology on catalytic activity have been achieved, and finally the catalyst has been applied at the cathode side of MFCs to evaluate application for power generation.

2. Experimental

2.1. Materials

2.1.1. Preparation of graphene oxide (GO)

GO was obtained by electrochemical exfoliation of graphite in a two-electrode cell. The working electrode was a graphite rod (GoodFellow, ϕ = 3 mm; L = 5 cm, particle size 20–100 μm, and purity 99%) and a counter electrode was a platinum wire (Amel Electrochemistry). The electrodes were immersed in an aqueous solution which composition is indicated in Table 1, applying a voltage in the 7–16 V range to promote graphite exfoliation. The obtained suspension was filtered under vacuum with a nylon membrane (pore size: 0.2 μm) and washed with DI. The powder was then dried in an oven at 70 °C for 12 h. When specified, the powder was also post-treated at 400 °C for 4 h under NH_3 flow.

2.1.2. Preparation of FePc/GO catalysts

0.5 g of GO were added to 30 mL of a methanol solution containing 17 mg mL^{-1} of FePc. The resulting mixture was stirred for 45 min. The mixture was heated in a water bath at 70 °C to evaporate methanol and the resulting powder was completely dried in an oven at 70 °C for 3 h, obtaining samples labeled as indicated in Table 1.

Table 1
Composition of the electrolyte solution used for graphite exfoliation, GO post treatment, and sample labeling.

Electrolytic solution	Post-treatment	Sample labeling	
		without catalyst	with catalyst
0.1 M $(NH_4)_2SO_4$	–	GO	FePc/GO
0.1 M $(NH_4)_2SO_4$ + 0.5 M NH_4OH	–	GO(N)_L1	FePc/GO(N)_L1
1 M $(NH_4)_2SO_4$ + 5 M NH_4OH	–	GO(N)_L2	FePc/GO(N)_L2
0.1 M $(NH_4)_2SO_4$	NH_3 gas	GO(N)_g	FePc/GO(N)_g

2.2. Methods

2.2.1. Materials characterization

Atomic Force Microscopy (AFM) was carried out in air using a Veeco Multiprobe IIIa instrument. Experiments were carried out in tapping mode by using Si tips with a spring constant of about 40 N/m and a typical curvature radius on the tip of 7 nm. All samples were dispersed in DI to a 0.01 mg mL^{-1} content and deposited on freshly cleaved Mica substrates.

Raman Spectroscopy was performed with a DXR Raman Microscope (Thermo Scientific) using laser excitation wavelength of 532 nm with a 10 X objective. Laser power was maintained at 0.1 mW. Experimental data were fitted using OMNIC™ Series Software.

Fourier Transform Infrared Spectroscopy (FTIR) was carried out by means of a FTIR100 spectrometer (Perkin Elmer) in transmittance mode. Samples were pelleted in 150 mg of KBr using a Specac manual hydraulic press, by applying a pressure of 7 tons for 5 min. The diameter of pellets was 13 mm.

X-ray Photoelectron Spectroscopy (XPS) was performed using an Omicron DAR 400 A l/Mg Kα nonmonochromatized X-ray source, and a VG-CLAM2 electron spectrometer. Samples were dispersed in ethanol to a 1 mg mL^{-1} content and deposited on silicon wafer.

Cyclic Voltammetry (CV) was carried out by using a VMP3 Potentiostat (Bio Logic Science Instruments) controlled by computer through EC-Lab V10.18 software. A conventional three electrode cell was used: the reference electrode was a saturated calomel electrode-SCE, (Amel 303/SCG/12), the auxiliary electrode was a platinum wire (Amel, 805/SPG/12), and the working electrode (WE) was a glassy carbon disk (GC, 0.196 cm^2 area) modified with catalyst layer. The catalyst layer was prepared by dispersing either GO or FePc/GO (4 mg) in 270 μL of ethanol and 135 μL of DI. This dispersion was treated in an ultrasonic bath for 30 min. Then, 50 μL of Nafion solution (5 wt. % in lower aliphatic alcohols and water, Aldrich) were added to the dispersion and vortexed for 2 min. An aliquot of the resulting dispersion was deposited on the GC electrode to a catalyst loading of 0.27 mgcm^{-2} (corresponding to 0.013 mgcm^{-2} iron loading in the case Fe-based composites) and dried at 40 °C for 4 min.

CV experiments were carried out at room temperature in 100 mM neutral phosphate buffer solution (PBS), saturated with either nitrogen or oxygen. Each tests consisted in 5 cycles, CV curves shown in the manuscript refer to the 5th cycle (scan rate 5 mVs^{-1}). Linear Sweep Voltammetry was carried out in O_2-saturaeted PBS at a scan rate of 5mVs^{-1}. Electrical double-layer capacitance (CDL) of GO sheets was estimated by recording CV curves in N_2-saturated atmosphere and measuring the capacitive current at 0.95 V in the absence of faradic contribution at different scan rates (5, 10, 25, 50, and 100 mVs^{-1}). CDL was obtained from slope of linear plot of capacitive current vs scan rate [10,33]. All potential values in the manuscript were measured vs. SCE and then converted to the reversible hydrogen electrode (RHE) scale.

2.2.2. Tests in microbial fuel cells

MFC cathodes were prepared by modifying carbon cloth electrodes with the diffusion layer (exposed to air) and the catalyst layer (faced to MFC solution). The diffusion layer was prepared as previously described [34,35]. The deposition of the catalyst layer was carried out on the opposite side of the diffusion layer by brushing a suspension prepared from 64 mgmL^{-1} of either GO or FePc/GO in a mixture containing DI, Nafion solution, and 2-propanol (1:8:4, as volume ratio). The electrodes were dried at room temperature for 24 h. The catalyst loading was 10 mgcm^{-2} (corresponding to 0.5 mgcm^{-2} iron loading in the case of FePc/GO cathodes).

MFC cathodes (diameter 4 cm) were assembled in a single-chamber air-cathode MFC (inner volume: 28 mL) which anode was a graphite fiber brush. MFCs were firstly acclimated as described before [36] and fed with phosphate buffer solution containing 1 g L^{-1} of sodium acetate. Polarization and power density curves were acquired by