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# Template growth of nitrogen-doped mesoporous graphene on metal oxides and its use as a metal-free bifunctional electrocatalyst for oxygen reduction and evolution reactions

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## ABSTRACT

Metal-free electrocatalyst is an emerging energy material to replace precious metal for effective oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) in a working electrochemical energy conversion device. Developing an effective bifunctional catalyst with abundant highly active sites and full exposure to reactants is strongly considered. Herein a nitrogen-doped mesoporous graphene framework (NMGF) was proposed with intrinsic N/O heteroatoms and abundant topological defects for metal-free ORR/OER. The NMGF was fabricated by direct chemical vapor deposition on MgO template. The as-obtained NMGF exhibited high porosity with a large specific surface area of  $1440\text{ m}^2\text{ g}^{-1}$  as well as a high electrical conductivity of  $57.0\text{ S cm}^{-1}$ . This unique structure is demonstrated to possess several advantages, including plentiful active centers due to defects and heteroatoms, improved utilization efficiency by very high electrochemically active surface area and hydrophilic surface, facilitated ion diffusion through interconnected pores and smooth electron transportation in the highly conductive 3D framework, thereby leading to superior ORR and OER bifunctional activity. The ORR half-wave potential was  $0.714\text{ V}$ , and the potential to reach  $10.0\text{ mA cm}^{-2}$  OER current density was  $1.664\text{ V}$  with the potential gap of  $0.95\text{ V}$ . This bifunctional performance was better than routine precious metal-based catalysts (e.g. Pt/C and  $\text{IrO}_2$ ) for oxygen redox reaction.

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## 1. Introduction

The urgent request to solve the energy crisis and environmental problems brings great interests in clean, renewable energy sources, and emerging energy storage devices, like solar cells, hydrogen fuel cells, and metal-air batteries. One critical issue in the related sustainable chemistry is the transformation between water and oxygen, including oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) [1–4]. Both ORR and OER are 4-electron processes, suffering from their sluggish kinetics and high overpotential, which strongly limit the efficiency of relative energy devices. This calls for efficient electrocatalysts for ORR and OER [5–7]. In some particular cases like rechargeable metal-air batteries, ORR and OER are required to occur on the same electrode during the charge and discharge process, respectively [8–10]. Therefore, the bifunctional electrocatalysis of ORR and OER is of great significance [8,11].

Precious metals and their oxides are effective electrocatalysts in these reactions, including Pt and PtRu for ORR [12,13] and Ir and  $\text{IrO}_2$  for OER [14–16]. However, the high cost and limited natural abundance of the precious metals obstruct their large-scale applications, and the precious metal catalysts usually afford poor activity in bifunctional catalysis [17,18]. In recent years, the research and development of non-precious metal bifunctional catalysts for ORR and OER has been strongly considered. Catalysts based on transition metal compounds were firstly investigated, and Co- and Mn-based high-performance bifunctional catalysts were reported [19–22]. In 2014, Tian et al. [23] proposed a metal-free nanocarbon catalyst with remarkable activity on both ORR and OER. Since then, increasingly more carbon nanomaterials were reported as ORR/OER bifunctional catalysts attributed to their various, controllable structure and high electrical conductivity [11,24–28]. During the researches on carbon nanomaterials for ORR/OER electrocatalysis, two kinds of structural configurations, heteroatom and defect, have attracted much attention and been demonstrated as active sites [26,27,29–32].

To take full advantage of the active sites and facilitate the oxygen transport, the metal-free carbon based electrocatalyst is

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preferred to be highly porous, which always results in a defective structure with high electrical resistance [33–35]. In the electrocatalysis of ORR and OER, however, the gas transport in the pore and electron transport in the electrode are both important issues. More understandings are required to rationally design an effective electrocatalyst with intrinsic ORR/OER reactivity as well as full exposure of active centers to electrolyte.

In order to balance the porosity and electrical conductivity in nanocarbon electrocatalysts with intrinsic reactivity for ORR/OER, a 3D metal-free nanocarbon with interconnected pores constructed by continuous graphene layers was proposed herein. This energy material, named as N-doped mesoporous graphene framework (NMGF), presents a highly porous morphology with high conductivity, and possesses both kinds of active sites: the heteroatom (nitrogen) and the defect (five- and seven-carbon rings, C5 and C7) derived from the curves of the graphene. Besides, the unique structure of NMGF significantly contributes to the full accessibility of active sites for ORR/OER. Consequently, the as-fabricated NMGF material is demonstrated to be a superior metal-free bifunctional electrocatalyst for both ORR and OER.

## 2. Experimental

### 2.1. Material synthesis

The NMGF was synthesized using chemical vapor deposition (CVD) method with mesoporous MgO as template [36,37] and methane/ammonia as carbon/nitrogen source. 0.50 g MgO template was dispersed uniformly into a quartz boat and then placed in the center of a horizontal quartz tube reactor. The tube was then inserted into a furnace at atmospheric pressure. Under the protection of Ar at a flow rate of 200 mL min<sup>-1</sup>, the quartz reactor was heated to 950 °C, and then both CH<sub>4</sub> (50 mL min<sup>-1</sup>) and NH<sub>3</sub> (40 mL min<sup>-1</sup>) were introduced into the reactor for 10 min. After the CVD growth of NMGF, the furnace was cooled to room temperature in the atmosphere of H<sub>2</sub> (10 mL min<sup>-1</sup>) and Ar. The product was then mixed with 500 mL of 6 mol L<sup>-1</sup> HCl and heated in oil bath at 80 °C for 24 h to remove the MgO template. The acid was washed off by deionized water during a vacuum filtering process. Finally, the filter cake was dried by a freeze-drying method to obtain the NMGF sample. MGF was prepared in a similar way in which ammonia was not introduced in the CVD growth.

To verify the role of pore structure and defects in the NMGF, a control sample N-doped graphene (NG) was synthesized from chemical reduction of graphene oxide (GO). 30 mL of 2.0 mg mL<sup>-1</sup> GO aqueous solution was mixed with 1.80 g urea by 30 min ultrasonic dispersion. Then the suspension was treated by hydrothermal method at 180 °C for 18 h. After the vacuum filtering, washing, and freeze-drying, the NG sample was achieved.

### 2.2. Structural characterization

The morphology of the graphene-based electrocatalysts was characterized using a JSM 7401F scanning electron microscope (SEM) operated at 3.0 kV and a JEM 2010 high-resolution transmission electron microscope (TEM) operated at 120.0 kV. The Brunauer–Emmett–Teller (BET) specific surface area (SSA) of the samples was probed by N<sub>2</sub> adsorption/desorption at liquid-N<sub>2</sub> temperature using Autosorb-iQ2-MP-C system. The specific surface area was calculated by the multipoint Brunauer–Emmett–Teller (BET) method with the relative pressure of 0.05–0.30, and the pore-size distribution was calculated based on quenched solid density function theory model using the adsorption branch. The electrical conductivity of plate-samples with a diameter of 13.0 mm and a thickness of ca. 10 μm, which were prepared by compression

at 10.0 MPa, was measured using ST-102A four-probe technique (4Probes Tech., China) with Keithley 2636A Source Meter. The amounts of N-containing functional groups on NMGF were identified using X-ray photoelectron spectroscopy (XPS) by Escalab 250xi. Raman spectra were obtained using a Horiba Jobin Yvon LabRAM HR800 Raman spectrophotometer with He–Ne laser excitation at 633 nm. The contact angle was collected on Dataphysics OCA20. A volume of the pure water droplet employed in the measurement was 2 μL.

### 2.3. Electrochemical characterization

All electrochemical measurements were performed in a three-electrode system, using Pt sheet as a counter electrode and saturated calomel electrode (SCE) as a reference electrode. Rotating ring-disk electrode (RRDE) coated with electrocatalyst was used as the working electrode. This three-electrode system was controlled by a CHI 760D electrochemistry workstation and the measurements were carried out in O<sub>2</sub>-saturated 0.10 M KOH solution. Before other measurements were applied, the catalyst was cycled several times by cyclic voltammetry (CV) to obtain a stable CV curve. The OER and ORR activities were tested by linear sweep voltammetry (LSV) at the scan rate of 10.0 mV s<sup>-1</sup>.

The working electrode was fabricated by a drop casting method. 5.0 mg catalyst was dispersed in 0.95 mL ethanol and 0.05 mL 5.0 wt.% Nafion solution by 1.0 h sonication to form a relatively uniform suspension. Then 10.0 μL of the catalyst suspension was transferred onto the glass carbon electrode (GC, 0.196 cm<sup>2</sup>) via a controlled drop casting approach. The electrode was finally dried by natural evaporation. In addition to the three carbon materials, two commercial precious metal catalysts were also used as contrast samples: Pt/C catalyst with 20 wt.% Pt (Sigma–Aldrich), and 99.99% IrO<sub>2</sub> catalyst (Alfa Aesar).

The ORR electron transfer number  $n$  was determined as followed:

$$n = \frac{4I_d}{I_d + I_r/N}$$

where  $I_d$  is disk current,  $I_r$  is ring current and  $N$  is current collection efficiency of the Pt ring which was determined to be 0.26.

Electrochemical active surface area (ECSA) was determined by measuring the capacitive current associated with double-layer charging from the scan-rate dependence of cyclic voltammetry (CV). This measurement was performed on the same working electrodes among a potential window of 0.95–1.05 V vs. reversible hydrogen electrode (RHE) and scan rates ranging from 20 to 100 mV s<sup>-1</sup>. Then linear fitting of the charging current density differences ( $\Delta j = j_a - j_c$  at the potential of 1.00 V vs. RHE) against the scan rate was done. The slope is twice of the double-layer capacitance  $C_{dl}$ , which is used to represent ECSA.

The potential vs. RHE ( $E_{vs, RHE}$ ) was calculated by the following equation:  $E_{vs, RHE} = E_{vs, SCE} + 0.059 \text{ pH} + 0.241$  ( $E_{vs, SCE}$  stands for the potential vs. SCE) and the overpotential  $\eta = E_{vs, RHE} - 1.23$ .

## 3. Results and discussion

### 3.1. The NMGF grown on MgO templates

The morphology and synthesis method of NMGF are illustrated in Fig. 1. The MgO template is composed by closely packed nanocrystals with a size of 4–8 nm (Fig. 1a). The 3D graphene was deposited on the surface of the MgO template (Fig. 1b) during CVD growth. After the template was etched by HCl, the graphene framework with abundant mesopores and continuous graphene layers was achieved (Fig. 1c).

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