



Nitrogen-doped graphene derived from ionic liquid as metal-free catalyst for oxygen reduction reaction and its mechanisms[☆]



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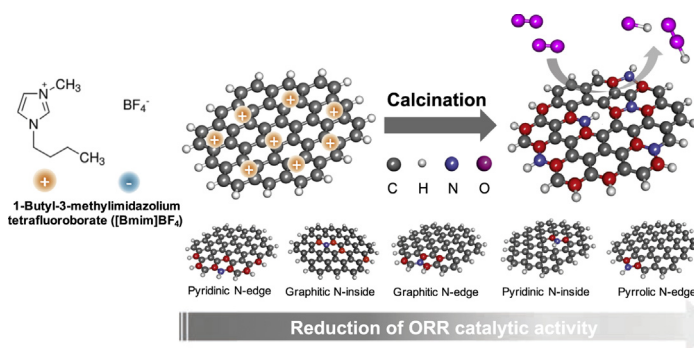
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HIGHLIGHTS

- N-doped graphene with N content of 6.6% is synthesized facilely and environmentally.
- Ionic liquid [Bmim]BF₄ acts as both N source and restacking protectant in synthesis.
- NG900 shows E_{onset} of −39 mV (vs. Hg/HgO) and current density of 5.83 mA cm^{−2} at 2500 rpm.
- Pyridinic N configuration at the edge contributes most to ORR performance boost.

GRAPHICAL ABSTRACT



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ABSTRACT

It is of great significance to develop N-doped carbon materials possessing high catalytic activity, excellent durability and low cost for oxygen reduction reaction (ORR) due to imperative for energy devices with high energy density, such as fuel cells and metal-air batteries. Herein, N-doped graphene is prepared by annealing a homogeneous mixture of graphene oxide (GO) and ionic liquid of 1-butyl-3-methylimidazolium tetrafluoroborate ([Bmim]BF₄) in N₂ atmosphere. By entrapping effect, the ionic liquid serves as both N source and restacking protectant in formation of high-quality N-doped graphene sheets. Electrochemical characterizations reveal that the obtained N-doped graphene possesses excellent electrocatalytic properties for ORR in alkaline condition with onset potential of −39 mV (vs. Hg/HgO) and current density of 5.83 mA cm^{−2} at −0.9 V (vs. Hg/HgO) at 2500 rpm. The microstructure of the prepared catalysts and their ORR catalytic activities are highly sensitive to calcination temperature and the optimal temperature is 900 °C. Density functional theory (DFT) analysis indicates from the atomic point of view that N atoms with different configurations contribute unequally to the ORR performance enhancement. Pyridinic N at the edge of graphene plays the most significant role in improving ORR performance owing to the largest number of active sites and lower band gap. Based on the experimental and simulation results, the beneficial properties of the as-prepared N-doped graphene for ORR are

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ascribed to the superior conductivity of graphene, the high N doping content and the high proportion of active pyridinic N species.

1. Introduction

The ever-growing global energy demand and the mission of environmental protection have promoted the exploration of renewable energy storage and conversion technologies [1,2], among which fuel cell and metal-air battery show great prospect owing to high energy density and environmental friendliness [3–5]. However, their wide application is severely hampered by the sluggish reaction kinetics of oxygen reduction reaction (ORR) on cathode, requiring high loading of Pt catalysts to maintain the performance of energy devices [6,7]. In the past few decades, extensive efforts have been devoted to exploring advanced noble metal-free catalysts in order to improve ORR catalytic activity and lower the cost [8]. Among all potential candidates, heteroatom-doped (such as B, N, S, and P) carbon materials, especially heteroatom-doped graphene, have attracted great research attention due to intrinsic merits of graphene, low fabrication cost and remarkable ORR catalytic activity [9–13]. The mechanism concerning heteroatom-doped carbon materials for ORR performance enhancement has been extensively discussed and evaluated by density functional theory (DFT) [14–16]. It is commonly considered that the reallocation of the electronic charge, induced by the electronegativity difference between carbon atoms and doped heteroatoms, creates positive-charged active sites and, thus, facilitates the O₂ adsorption in the ORR process [17]. Further DFT investigations have shown that the change of spin density, doping cluster size and dopant-defect interactions also play a significant role in ORR performance boost in addition to the change of charge density [18,19]. It is noteworthy that these calculations regarding N-doped graphene, which is one of the most promising substitutes for Pt catalyst, are exclusively based on substituting N atoms for C at the edge of graphene framework [20]. However, revealed by comprehensive experimental results, N-doped carbon materials consist of three effective N configurations for ORR in the carbon skeleton including pyridinic N, pyrrolic N and graphitic N, each of which could locate either inside or at the edge of graphene [21,22]. Therefore, It is highly desirable for material design and mechanism exploration to figure out how each N configuration functions in ORR from the atomic point of view and which one is the most effective configuration.

For heteroatom doping, various heteroatom sources, such as ammonium, ethylenediamine, melamine, benzyl disulfide, polymer, etc., have been applied to fabricate heteroatom-doped carbon materials [23–27]. However, they are either flammable or toxic, resulting in hazards and environmental problems. Ionic liquids (ILs), defined as semi-organic salts existing in the liquid state below 100 °C, were initially developed as molten electrolyte for electrochemical applications due to its excellent ion conductivity [28]. In recent years, there are more research interests in using ILs as precursors for fabricating heteroatom-doped carbon materials by carbonization method [10,29,30]. ILs with cross-linkable anions such as nitrile groups are regarded as favorable precursors of this application owing to the polymerization of cross-linkable groups at elevated temperature, giving higher carbon yield compared with conventional ILs [31,32]. By an entrapping effect, ILs without cross-linkable groups have also been reported as precursors for the synthesis of heteroatom-doped carbon materials with the assistance of foreign frameworks [33,34]. Compared with carbonizing pure ILs with cross-linkable groups, this strategy not only enables delicate morphology design, but also reduces fabrication cost. Particularly, when graphitic carbon framework is applied, the CH- π interaction between ILs and graphitic support facilitates the entrapping and directing of ILs into carbon skeleton [4,35].

Herein, we report a simple strategy to synthesize high-quality N-

doped graphene by annealing a homogeneous mixture of graphene oxide (GO) and conventional hydrophilic ionic liquid, 1-Butyl-3-methylimidazolium Tetrafluoroborate ([Bmim]BF₄). Being intrinsically charged, the [Bmim]BF₄ can be uniformly adsorbed on the surface of GO, serving as both N dopant and restacking protectant in the subsequent calcination process. Moreover, the use of GO as foreign carbon framework eliminates template removal process which inevitably involves strong acid or alkaline, rendering it promising for large-scale production and improved environmental performance. The as-fabricated N-doped graphene shows remarkable electrocatalytic activity towards ORR in alkaline conditions with a maximum current density of 6 mA cm⁻². The influence of calcination temperature on the microstructure and ORR catalytic activity is intensively investigated. The effect of each N configuration in graphene, inside or at the edge, on ORR performance is systematically calculated by DFT. This work not only presents a facial and scalable way to fabricate cost-effective catalysts for ORR, but also possesses high academic value in understanding its mechanisms.

2. Experimental

2.1. Synthesis of N-doped graphene

In a typical synthesis, GO was firstly prepared from graphite powder (Acros) according to a modified Hummers method [35,36]. An amount of 20 mg of as-prepared GO was dispersed homogeneously in 20 mL deionized water by ultrasonication. Then 2 mL of [Bmim]BF₄ was dropped into the GO solution by pipette under stirring followed by adjusting the pH of the suspension to around 11 with diluted NaOH solution. The suspension was placed on a hotplate and heated at 120 °C under vigorous stirring until sticky carbon ink was obtained. Finally, the pasty mixture was transferred to a covered crucible and calcined in N₂ atmosphere at elevated temperature for 1 h in a tube furnace (Carbolite HZS 12/600) with a heating rate of 5 °C min⁻¹. The samples after calcination were subjected to ORR electrochemical test without any post-treatment.

2.2. Material characterization

The morphology and microstructure of the as-synthesized catalysts were characterized by scanning electron microscopy (SEM, JEOL JSM-6490) and transition electron microscopy (TEM, JEOL JEM 2100F). The surface chemical composition of samples was analyzed by X-ray photoelectron spectroscopy (XPS, PHI-5600) with Al K α radiation ($h\nu = 1486.6$ eV). The full and high-resolution spectra were recorded in step sizes of 0.5 eV and 0.1 eV, respectively, at a pass energy of 58.7 eV. All XPS spectra were corrected with respect to C 1s peak at 284.8 eV.

2.3. Electrochemical test

A traditional three-electrode system connected to a CHI 660 electrochemical testing system was applied to all the electrochemical tests in this paper. A glassy carbon electrode (GCE, diameter of 5 mm, PINE instruments, USA), a Pt foil and a Hg/HgO (1 M KOH) electrode were selected as the working, counter and reference electrodes, respectively. For the rotating disk electrode (RDE) experiment, a PINE rotator was used. Prior to coating, the surface of GCE was polished in sequence with 1.0, 0.3 and 0.05 μ m alumina powders on a polishing cloth and rinsed with deionized water. An amount of 10 μ L suspension of the as-prepared catalyst (or commercial 20 wt% Pt/C (Fuel Cell Earth LLC) as

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