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# Oxygen Reduction Reaction Mechanism of Nitrogen-Doped Graphene Derived from Ionic Liquid

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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 cell and metal-air batteries. Herein N-doped graphene is prepared by annealing a homogeneous mixture of graphene oxide and ionic liquid of 1-butyl-3-methylimidazolium tetrafluoroborate ([Bmim]BF<sub>4</sub>) in nitrogen atmosphere. By entrapping effect, the ionic liquid serves as both nitrogen source and restacking protectant in formation of high quality N-doped graphene sheets. Electrochemical characterizations reveal that the obtained N-doped graphene possesses excellent electro-catalytic properties for ORR in alkaline condition. The microstructure and ORR catalytic activities are highly sensitive to calcination temperature and the optimal temperature is 900 °C. Density functional theory analysis indicates from the atomic point of view that N atoms with different configurations have different effects on the ORR performance enhancement. Pyridinic N exhibits the highest ORR catalytic activity followed by graphitic N depending on the number of active sites. Based on the experimental and simulation results, the beneficial properties of the as-prepared N-doped graphene for ORR are ascribed to the superior conductivity of graphene, high nitrogen doping content and high proportion of the active graphitic and pyridinic N species.

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Keywords: Metal-free catalysts; carbon materials; heteroatom doping; oxygen reduction reaction; density functional theory.

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#### 1. Introduction

The sluggish reaction kinetic of ORR cathode is one of the major obstacles for wide applications of fuel cells and lithium-air batteries due to the difficulties in O<sub>2</sub> adsorption, O-O bond cleavage and oxides removal, which inevitable increases the use of noble catalysts (usually Pt) and raises the overall cost. To address this concern, extensive efforts have been devoted to explore non-precious metallic catalysts in the past decades [1]. Heteroatom (such as B, N, S and P) doped carbon materials, especially heteroatom doped graphene, have attracted greater search attention among all potential candidates due to remarkable ORR catalytic activity, excellent durability, high selectivity and low fabrication cost [2, 3]. They have been reported exhibiting catalytic property comparable to Pt, but better selectivity and higher durability, thus regarded as promising substitutes for conventional Pt-based catalysts [4-7]. The mechanisms concerning heteroatom doped carbon materials for enhancing the ORR catalytic activity have been widely discussed and evaluated by density functional theory (DFT) [8-10]. It is commonly found that the reallocation of the electronic charge, induced by the electro negativity difference between carbon atoms and doped heteroatoms, creates positive-charged active sites and, thus, facilitates the O<sub>2</sub> adsorption in the ORR process [11]. Further DFT investigations have shown that the change of spin density, doping cluster size and dopant-defect interactions also play significant roles in ORR performance boost in addition to the change of charge density [12, 13]. The effect of engineering the edge structure of graphene was also discussed [14]. However, these calculations are based on one or two configurations of doped N atoms separately. It is well known that N-doped carbon materials consist of three different N configurations in the carbon skeleton which might be beneficial to ORR process including graphitic N, pyridinic N and pyrrolic N. Graphitic N is generally considered as the most effective doped moiety because the positive-charged C atoms adjacent to the doped N are preferred to be adsorbed by O2 molecules [15]. On the other hand, N-doped carbon materials containing pyridinic and pyrrolic N also exhibit remarkable ORR catalytic effect [16, 17]. Therefore, better understanding of ORR mechanisms on different N configurations from the atomic point of view is highly desirable for catalyst design and fabrication.

Various heteroatom sources, such as NH<sub>3</sub>, ethylenediamine, melamine, benzyl disulfide, polymer etc., have been applied to fabricate heteroatom-doped carbon materials [18-23]. However, they are either toxic organic molecules or flammable gases, which cause not only hazards but also environmental problems. Ionic liquids (ILs) were initially developed as molten electrolyte for electrochemical applications due to its excellent ion conductivity [24]. In recent years, there are more research interests in using ILs as precursors for fabricating heteroatom doped carbon materials by carbonization method [25-27]. ILs with cross-linkable anions, such as nitrile groups, are favorable precursors of this application owing to the polymerization of cross-linkable groups at elevated temperature, giving higher carbon yield compared with conventional ILs [28, 29]. By an entrapping effect, ILs without cross-linkable groups have also been applied as precursor for the synthesis of heteroatom doped carbon materials with the assistance of foreign frameworks [30, 31]. This strategy not only enables morphology designing, but also reduces the fabrication cost compared with carbonizing pure IL. Particularly, when graphitic carbon framework is applied, the CH- $\pi$  interaction between ILs and graphitic support facilitates the directing of ILs [32, 33]. Moreover, there is no need to remove hard templates afterwards which always involves strong acid.

Herein we report a simple strategy to synthesize high-quality N-doped graphene in large scale by annealing a homogeneous mixture of graphene oxide (GO) and conventional hydrophilic ionic liquid, 1-Butyl-3-methylimidazolium Tetrafluorobotate ([Bmim]BF<sub>4</sub>). Being intrinsically charged, the [Bmim]BF<sub>4</sub> is uniformly adsorbed on the surface of GO, functioning as both N dopant and restacking protectant in the subsequent calcination process. The influence of calcination temperature on the microstructure and electro-catalytic activity towards ORR in alkaline condition is intensively investigated. Particularly, the effects of different N configurations, located both edge and inside, on ORR are systematically compared by DFT calculations in terms of the change in charges and spins as well as the HOMO-LUMO gap.

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## 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. An amount of 20 mg of as-prepared GO was dispersed homogeneously in 20 mL deionized water by ultrasonication. Then 2 mL of [Bmim]BF<sub>4</sub> 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 N<sub>2</sub> atmosphere at elevated temperature for 1 hour in a tube furnace (Carbolite HZS 12/600) with a heating rate of 5 °C min<sup>-1</sup>. 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 the samples was analyzed by X-ray photoelectron spectroscopy (XPS, PHI-5600) with Mg K $\alpha$  radiation (hv=1253.6 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 an 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  $\mu$ m alumina powder on a polishing cloth and rinsed with deionized water. An amount of 10  $\mu$ L suspension of the as-prepared catalyst (or commercial 20 wt% Pt/C (Fuel Cell Earth LLC) as reference) in anhydrous ethanol (1 mg sample mL-1) was subsequently dropped onto the polished surface of the GCE with a pipette and dried in air. This procedure was repeated for three times. Finally, 10  $\mu$ L of Nafion solution (0.5 wt%) was coated onto the surface of modified GCE and dried in air before use. All electrolytes were purged with high purity N<sub>2</sub> or O<sub>2</sub> for 40 minutes prior to measurements. In the ORR experiments, the O<sub>2</sub> (or N<sub>2</sub>) saturated condition was guaranteed by introducing constant O<sub>2</sub> (or N<sub>2</sub>) gas flow above the surface of the electrolyte. All the experiments were conducted at room temperature.

Koutecky-Levich (K-L) equation (equation 1) was applied to calculate the electron transfer number in the ORR process:

$$1/j = 1/j_k + 1/j_d = -1/j_k - 1/[0.62nF(D_{O2})^{2/3}v^{-1/6}C_{O2}\omega^{1/2}]$$
(1)

where j is the measured current density;  $j_k$  and  $j_d$  are the kinetic and diffusion limited current density, respectively; n is overall electron number transferred per oxygen molecule during ORR; F represents Faraday constant (96485 C mol-1);  $D_{02}$  is the diffusion coefficient of  $O_2$  in the electrolyte ( $1.9 \times 10^{-5}$  cm<sup>2</sup> s<sup>-1</sup> in 0.1 M KOH); v is kinematic viscosity of the electrolyte (0.01 cm<sup>2</sup> s<sup>-1</sup>);  $C_{02}$  is the bulk concentration of  $O_2$  in the electrolyte ( $1.2 \times 10^{-6}$  mol cm<sup>-3</sup> in 0.1 M KOH);  $\omega$  is the electrode rotating rate (rad s<sup>-1</sup>).

#### 3. Results and discussion

In this synthesis, GO serves as the flake template. [Bmim]BF<sub>4</sub> is absorbed on the surface of GO spontaneously by electrostatic force. It protects the restacking of GO and decomposes to supply N in the calcination, in which doping and reducing are accomplished simultaneously. Four calcination temperatures of 700, 800, 900 and 1000  $^{\circ}$ C were chosen to synthesize NG700, NG800, NG900 and NG1000, respectively. For comparison, an undoped control sample (designated as UG) was also fabricated by the same procedure at 900  $^{\circ}$ C without adding [Bmim]BF<sub>4</sub>.



Fig. 1. SEM images of UG (a) and NG900 (b). TEM (c) and HRTEM (d) images of NG900. Inset of (d): SAED pattern of the area in image d. Dark field TEM image of NG900 (e) and the corresponding elemental mapping images of the selected area in the square.



Fig. 2. Full (a) and high resolution N1s (b) XPS spectra of NG900.

Figures 1a and 1b are typical SEM images of UG and NG900, respectively. The UG is severely restacked and shows thick plate morphology after calcination at 900 °C, while NG900 displays more dispersed thin flake due to

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the protecting function of [Bmim]BF<sub>4</sub> adsorbed on the surface of GO. This structure is further confirmed by TEM characterization.

Transparent thin flake is clearly observed in Fig. 1c. The morphology similarity of NG900 to graphene obtained in wet chemical ways also confirms the template function of GO. Fig. 1d is the HRTEM image of the edge area of NG900, which reveals that the as-prepared N-doped graphene is composed of quite thin multiple layers particularly at the edge. The corresponding selected area electron diffraction (SAED) pattern indicates the polycrystalline nature of NG900. Compared with the stacked UG, the much looser and thinner nanostructure of NG900 is believed to facilitate the O<sub>2</sub> penetration, thus lower the energy barrier of ORR. For samples prepared under other temperatures, NG700 (Fig. S1) possesses poor electronic conductivity due to incomplete reduction of GO under this temperature. On the other hand, NG1000 shows more microfoldings and closer coupling among the graphene sheets for better thermodynamic stability owing to the interaction of van der waals at high temperature [34]. The elemental mapping images (Fig. 1e) not only preliminary confirm the presence of doped N element, but also reveal its homogeneous distribution throughout the graphene sheets in NG900.

XPS was conducted to reveal the surface chemical composition and the corresponding distribution of various doped N configurations. A peak of N which locates at around 400 eV is clearly seen in the full XPS spectrum of NG900 (Fig. 2a), further indicating the successful doping of N. No peak of F and B is observed probably because negative-charged GO is prone to be absorbed by positive-charged [Bmim]+.High-resolution XPS spectra of N 1s in the samples prepared under different temperature are presented in Fig. 2b and Fig. S2. All the spectra can be deconvoluted into four peaks, which correspond to pyridinic N ( $\sim$ 398.4eV), pyrrolic N ( $\sim$ 399.6eV), graphitic N ( $\sim$ 401.1eV) and oxidic N ( $\sim$ 403.1eV) [15]. The N doping content and the distribution of various N configurations derived from the deconvoluted peaks are summarized in Table 1. It is noteworthy that the N doping content decreases from 7.2% to 4.9% as temperature increases from 700 °C to 1000 °C, suggesting that the N dopant is unstable and has a chance to be removed at elevated temperature. Moreover, the percentage of each N configuration in the overall N content varies according to different calcination temperatures. As the temperature increases, the percentage of graphitic N and pyridinic N tend to increase while oxidic N and pyrrolic N decrease due to the instability of N-oxide and the five-membered heterocyclic rings. This is well consistent with the fact that pyridinic N is more stable than pyrrolic N but both transform to graphitic N at high temperature [35].

The ORR electro-catalytic activity of the as-prepared samples was investigated in 0.1 M KOH using a traditional three-electrode system. As can be seen in the cyclic voltammograms (CVs) (Fig. 3a), an obvious oxygen reduction peak appears at -0.18 V (vs. Hg/HgO) in the negative sweep of NG900, which is 0.17 V positive-shifted compared with UG. Moreover, the peak current density of NG900 is twice as large as that of UG, suggesting its superior ORR catalytic activity. Similar results were observed in linear sweep voltammograms (LSVs) (Fig. 3b), which were recorded by a rotating disk electrode. Although not as distinguished as Pt catalyst, the onset potential and the maximum current density are greatly improved after N doping. The influence of calcination temperature on ORR catalytic activity was also studied (Fig. S4). By contrast, NG700 exhibits the lowest current density and the most negative onset potential due to the unsatisfactory electronic conductivity. Moreover, as indicated in Table 1, although the N doping content of NG700 is as high as 7.2 at%, 14.2 at% of them is in the form of oxidic N, which is regarded as an ineffective N doping moiety for ORR. For the other three catalysts, NG800 and NG1000 show similar catalytic performances with more positive onset potential for NG800 and slightly larger current density for NG1000. NG900 yields the largest current density and the most positive onset potential among all the catalysts.

LSVs at different rotational speed were also recorded to reveal the ORR kinetics on various catalysts (Fig. 3c and Fig. S5). For both NG900 and UG, the current density increases with increasing rotation rate due to higher oxygen flux to the surface of the electrode. The corresponding Koutecky-Levich (K-L) plots (Fig. 3d and Fig. S6a) reflect good linear relationship between the reciprocal of current density and the reciprocal of the square root of the rotation rate in the voltage range from -0.5 to -0.9V, indicating the first-order reaction kinetics towards the concentration of dissolved oxygen on both UG and NG900 [41]. However, based on the K-L equation, the electron transfer number of NG900 is calculated as 3.19 while the value of UG is only 1.69 at -0.9V (vs. Hg/HgO) (Fig. 3d and Fig. S6b). It clearly shows that the ORR goes through a mixture of four-electron and two-electron process on NG900 while only two-electron pathway occurs on UG.

Since fuel crossover from anode to cathode is unavoidable in direct liquid fuel cell, the catalytic selectivity is vitally important for efficient ORR catalysts on cathode. A small quantity of 3 M methanol was introduced at time =

120s in chronoamperometric measurements (Fig. 4a). An obvious reversion in current density is observed on commercial Pt catalyst upon the addition of methanol, which indicates the occurrence of methanol oxidation. In contrast, the current density of NG900 remains unchanged during the whole test, suggesting its excellent ORR catalytic selectivity.

Samples	N content (at %)	Pyridinic N (at %) 398.4±0.1	Pyrrolic N (at %) 399.6±0.1	Graphitic N (at %) 401.1±0.1	Oxidic N (at %) 403.1±0.1
NG800	7.0	26.2	20.7	43.8	8.3
NG900	6.6	29.0	15.5	48.4	7.1
NG1000	4.9	33.5	8.6	51.6	6.3



Fig. 3.(a) CVs of UG and NG900. (b) LSVs of different samples at rotation rate of 2500 rpm. (c) LSVs of NG900 at different rotation rates. (d) K-L plots of NG900 from -0.5 to -0.9 V; Inset:Electron transfer number determined by the K-L plots at corresponding voltages. Electrolyte: O<sub>2</sub>-saturated 0.1 M KOH; Scan rate: 10 mV s<sup>-1</sup>.



Fig. 4. Chronoamperometric (a) and I-t curves (b) of NG900 compared to commercial 20 wt% Pt at -0.2 V (vs. Hg/HgO) in O<sub>2</sub>-saturated 0.1 M KOH.

The durability of NG900 and Pt catalysts was also investigated by I-t measurement (Fig. 4b) and repeating CV cycling in the voltage range of ORR (Fig. S7). Continuous O<sub>2</sub> reduction for 5 hrs on NG900 causes negligible loss of current density, implying its remarkable durability and potential application in alkaline fuel cell. Besides, DFT calculations proves the experimental results that the pyridinic N, followed by graphitic N, possesses the highest catalytic activity for ORR enhancement.

## 4. Conclusions

A facile method has been developed for large-scale synthesis of N-doped graphene by calcination of uniform mixture of graphene oxide and traditional hydrophilic ionic liquid [Bmim]BF<sub>4</sub> which serves as both N source and restacking protectant. The calcination temperature has profound effects on the chemical coordinating and microstructure of the electro-catalysts. The catalyst prepared at 900  $^{\circ}$ C with N doping content 6.6 at% was found to exhibit the optimal ORR catalytic performance in alkaline conditions due to a combination of superior electronic conductivity of graphene, high nitrogen doping content and high proportion of pyridinic and graphitic N configurations. Calculation based on DFT indicates that pyridinic N, followed by graphitic N, possesses the highest catalytic activity for ORR owing to the most number of active sites, which is proved directly by the experimental results. Such consistency between theoretical calculation and experiment provides us a fundamental understanding of active sites in heteroatom doped carbon materials towards ORR. This paper not only presents a facile and green way to synthesize N-doped graphene which is highly cost-effective catalysts for ORR, but also gives valuable insights into the ORR mechanisms on N-doped graphene.

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