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# The role of holes in improving the performance of nitrogen-doped holey graphene as an active electrode material for supercapacitor and oxygen reduction reaction

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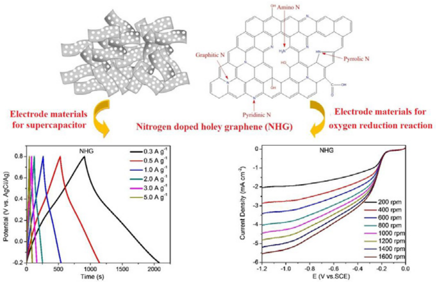
## HIGHLIGHTS

- A simple KOH etching and ball milling method is been used to synthesize NHG.
- NHG exhibits high electrochemical performance for supercapacitors.
- NHG exhibits high electrochemical performance for oxygen reduction reaction.
- The holes facilitate the formation of the NHG solid with a porous structure.
- The holes play an important role in improving the electrochemical performance of NHG.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Nitrogen doped holey graphene (NHG), with in-plane holes in its sheet plate, has been synthesized in this work through the potassium hydroxide (KOH) etching and ball milling of nitrogen doped graphene (NG). It shows that the KOH etching and ball milling does not distinctly alter the elemental composition and the relative percentages of functional groups in NG, but produce holes in its in-plane sheet plate. The obtained NHG can then be used as an active electrode material for supercapacitors and as an active electrocatalyst for oxygen reduction reaction, and exhibits significantly higher electrochemical performance than the corresponding NG. Its improved electrochemical performance could be attributed to its specific holey structure in the sheet plate and porous structure in its randomly stacked solid, which provide it with more active edge atoms, better accessibility to electrolyte, larger accommodation space for ions, faster electrolyte diffusion and movement and so on.

## 1. Introduction

The ever-increasing demand for powering portable devices has triggered a burst of research towards the development of miniaturizable alternative energy sources, such as lithium ion batteries, supercapacitors, fuel cells and etc [1–6]. The practical uses of these energy sources are required to have both high energy and power densities, which depend mainly upon the chemical and physical

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properties of the electrode materials used [7–11]. Significant efforts have therefore been devoted to exploiting new materials or improving the properties of the traditional electrode materials to boost both the energy and power densities of these energy source devices [8,12–17]. From the perspective of applications, it is generally desirable to exploit active materials that can be employed as the constituents of electrodes for uses in all the types of the energy source devices. However, the development of such materials is considerably difficult since the requirements that are proposed to improve the performance of the energy source devices of different types are not same. For instance, materials for lithium ion batteries are required to have high rate capacity of $Li^+$ intercalation/deintercalation [1,5,18], while materials for fuel cells are required to have high electrocatalytic activities towards oxygen reduction or fuel oxidation reactions [19–22].

Recently, a new material, which is generally referred to as graphene, has attracted tremendous attentions [23–25]. Because of its excellent electrical conductivity, high surface area, good flexibility, and good chemical and environmental stability, graphene has widely been used as an electrode material for LIBs, supercapacitors, fuel cells and etc., and shows great promises to improve the performance of these energy source devices [2,10,15,26]. However, due to its unique structure which consists of a single planar sheet of $sp^2$-bonded carbon atoms densely packed in a honeycomb crystal lattice, the pristine graphene is prone to aggregation to form a stack with a flake-like structure due to the $\pi-\pi$ and strong van der Waals intersheet interactions [27,28]. As a result, the diffusion of electrolytes predominantly takes place at the edge of the stack, while its diffusion across the graphene plane and into its interlayers is limited, when it is used as the electrode materials [5,29,30]. In this case, graphene might not be well utilized and the performance of the corresponding energy source devices is not well improved [27,31,32]. Great efforts have therefore been paid to the development of porous 3-dimensional graphene solids through fabricating sandwich type structures by introduction of "spacer" phases, such as, carbon nanotubes, nanoparticles and etc., or through forming 3-dimensional macroporous structures and networks by the template-directed deposition or controlled assembly of graphene [14,16,33–36]. The porous structure can promote the electrolyte solutions in/out of the electrode materials, facilitating faster electrolyte diffusion and a better utilization of active materials [14,34–37]. And additionally, the presence of holes can produce more edge atoms that are active for applications in the energy source devices [38–40]. Studies have demonstrated that the energy source devices with the electrodes containing graphene solids with a 3-dimensional porous structure usually exhibit significantly higher electrochemical performance [14,37,41–43]. An alternative way to construct the 3-dimensional porous graphene structure is to introduce in-plane holes into the graphitic nanosheets of graphene. Since the presence of the in-plane holes can increase the flexibility of the graphitic nanosheets and simultaneously decrease its van der Waals intersheet interactions, the randomly stacking of the holey graphene could lead to the formation of solids with a 3-dimensional porous structure [5,29].

Another strategy that is frequently used to improve the performance of graphene as the electrochemical materials for the energy source devices is the doping of heteroatoms into its graphitic structure [8,16,44–46]. Due to the difference in the properties between carbon and heteroatoms, the incorporation of heteroatoms can endow graphene with new properties and thus increases the usability of the graphene based materials as the electrode materials for applications in various energy source devices [36,46–50]. For example, the incorporation of N or/and B atoms into the lattice gives graphene with greatly improved electrocatalytic activity toward oxygen reduction reactions (ORR) [3,45,51]. Additionally, the presence of nitrogen on the carbon framework can also improve the wettability of graphene toward the electrolyte solutions, thus enhancing the mass transfer efficiency, and simultaneously provide pseudocapacitance, thus increasing the energy density of supercapacitors [52,53].

The introduction of in-plane holes into the graphitic nanosheets of nitrogen-doped graphene would produce nitrogen-doped holey graphene (NHG). We would expect that NHG can be used as a promising electrode material for the energy source devices, since its holey structure can facilitate the formation of the solid with a 3-dimensional porous structure, while the doped nitrogen could improve its performance as the promising electrode material. To demonstrate this, we synthesize NHG through a procedure involving the fabrication of NG and the subsequent KOH etching and ball milling. The obtained NHG is then used as the electrode material for the supercapacitors and as the electrocatalyst for the ORR. The experimental results show that NHG can greatly improve the performance of the supercapacitors and exhibits the significantly enhanced electrocatalytic activity. The improvements in the performance of the supercapacitors and the enhancement in its electrocatalytic activity could be attributed to its holey structure and porous morphology in its randomly stacked solid, since the presence of in-plane holes in the graphene sheet plate can produce more edge atoms that are active for the charge storage and the ORR, while the presence of pores in its randomly stacked solid facilitates the fast diffusion and movement of electrolytes, allowing for the better utilization of active materials.

## 2. Experimental

### 2.1. Chemicals and reagents

TIMREX® PG25 natural graphite is obtained from TIMCAL Ltd. Concentrated sulfuric acid ($H_2SO_4$, 95%), methanol ($CH_3OH$, ≥99.7%), potassium permanganate ($KMnO_4$, ≥99.0%), sodium nitrate ($NaNO_3$, ≥99.0%), hydrochloric acid (HCl, 37%), hydrogen peroxide aqueous solution ($H_2O_2$, 35%), melamine (99%), and isopropanol ($CH_3CH(OH)CH_3$, ≥99.5%) are purchased from Sigma–Aldrich. The commercially available Johnson Matthey (JM) Pt/C 40 wt.% (Pt loading: 40 wt.% Pt on the carbon black) is purchased from the Johnson Matthey Corp. These chemicals are used as received without further purification. Deionized water (DI $H_2O$) through Millipore system (Milli-Q®) is used in all experiments.

### 2.2. Materials preparation

#### 2.2.1. Preparation of GO

The synthesis of GO is done using a procedure developed by Hummers et al. [54]. Typically, 2 g of graphite and 2.5 g of $NaNO_3$ are first mixed with 150 mL of $H_2SO_4$ (95%) in a 500 mL flask. The mixture is then stirred for 30 min with an ice bath, which is followed by the addition of 15 g of $KMnO_4$ under vigorous stirring. The rate of the $KMnO_4$ addition is well controlled to maintain the reaction temperature below 20 °C. The reaction mixture is then stirred overnight at room temperature, followed by addition of 180 mL of $H_2O$ also under vigorous stirring. After that, the reaction temperature is rapidly increased to 98 °C and keeps for 24 h, which leads to a color change from black to yellow. Followed by the addition of 80 mL of 35% $H_2O_2$ aqueous solution, the reaction mixture is cooled down to room temperature. The obtained graphene oxide is washed by rinsing and centrifugation with 5% HCl and $H_2O$ for several times, and then filtrated and dried under vacuum.

#### 2.2.2. Preparation of nitrogen-doped graphene (NG)

For the synthesis of NG, 40 mg of GO is first dispersed in 40 mL of $H_2O$ by sonication. 0.2 g of melamine is then added. The obtained