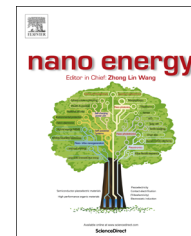


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# Constructing holey graphene monoliths via supramolecular assembly: Enriching nitrogen heteroatoms up to the theoretical limit for hydrogen evolution reaction

Jie-Min Ge<sup>1</sup>, Bing Zhang<sup>1</sup>, Li-Bing Lv, Hong-Hui Wang, Tian-Nan Ye, Xiao Wei, Juan Su, Kai-Xue Wang, Xin-Hao Li\*, Jie-Sheng Chen

School of Chemistry and Chemical Engineering, Shanghai Jiao Tong University, Shanghai 200240, PR China

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## Abstract

Carbocatalysts with low cost and high stability are highly desirable to substitute expensive Pt-based materials for electrocatalysis. High conductivity, highly porous structure and high concentration of dopants are essential for efficient metal-free carbon-based electrocatalysts. Herein, a facile method was utilized to fabricate nitrogen-rich holey graphene monoliths (NR-HGM) from cheap molecules and ammonium sulfate with the nitrogen content close to the upper limit of nitrogen-doped carbons. Our sample showed relatively high electrochemical catalytic activity and stability for hydrogen evolution reaction (HER) in both acid and base electrolytes, surpassing state-of-the-art metal-free HER catalysts in the literature.

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## Introduction

The development of sustainable electrocatalysts with low cost, high stability and excellent electrocatalytic activity remains at the heart of modern material science and green

chemistry [1]. Metal-free carbon materials show great potential as sustainable catalysts or electrocatalysts, due to their relatively low cost and excellent activity comparable to commercial platinum catalysts [1a,2]. Among the carbon allotropes, nitrogen-doped graphenes (NG) with high surface areas, high conductivity and acceptable stability have been considered as “noble” candidates for electrocatalysis applications, including fuel cells, electrochemical water splitting reactions, chlor-alkali electrolysis process, and Li/Zn-air batteries [3]. The concentration of nitrogen dopants was

\*Corresponding author.

E-mail address: [xinhaoli@sjtu.edu.cn](mailto:xinhaoli@sjtu.edu.cn) (X.-H. Li).

<sup>1</sup>These authors contributed equally to this work.

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usually very low for the samples obtained via chemical modification of layered graphite oxides, especially for those obtained at high temperature (e.g. 1000 °C)[4]. High temperature was essentially required to ensure the degree of graphitization in these carbon-based materials and thus high conductivity for better electrocatalytic performance. On the other hand, high temperature could however significantly depress the N content with an upper limit of 14.32 wt% at 1000 °C according to theoretical studies [4]. Increasing the concentration of electron-rich nitrogen atoms in the graphene lattice to a high level without disturbing their degree of graphitization still remained a great challenge for mass production of nitrogen-doped graphenes at the moment [4h,5].

Two dimensional (2D) structure of NG with very large aspect ratio makes the aggregation of graphene layers easy to happen when the NG were packaged into dry powder or dispersed into solution for practical electrocatalytic applications [6]. Molecules cannot transfer through graphene sheets, even though the thickness of graphene was only 0.34 nm. Consequently, the number of exposed active sites of aggregated NG significantly decreases, resulting in unwanted loss in electrocatalytic activity. As a result, much effort has been devoted to construct porous graphene assemblies to facilitate the mass transfer [4b,7]. Crumpled NG sheets with rich amount of interlayer nanopores have well exhibited the advantage of porous structure for electronic applications against assemblies of graphene flakes, although ions could still not pass through crumpled sheets. Further generating nanoholes by activating graphene layers could obviously elevate the catalytic performance of these materials to a great extent [7b]. With regards to possible application in electrocatalysis, current methods, including base-etching method and boric acid-etching methods, could introduce a great amount of heteroatom (O or B)-defects to the  $sp^2$  frameworks and obviously block the electron transfer for electrocatalysis by slightly opening the band gap of graphene [8]. Developing powerful method for mass production of highly porous NG, bearing opened nanopores, without sacrificing their conductivity would obviously benefit for their electrocatalytic applications in large-scale [7a,9].

Herein, we proposed an effective approach for the facile synthesis of connected three-dimensional monoliths of nitrogen-rich holey graphene monoliths (Nr-HGM) from molecules in the presence of cheap ammonium sulfate. Our method could simultaneously introduce high concentration of nitrogen dopants (even at 1000 °C) and opened nanopores into graphene layers. The as-obtained metal-free Nr-HGM could function as carbo-electrocatalysts with superb electrocatalytic activity and stability for HER and ORR in both acid and base electrolytes.

## Experimental

### Materials

Dicyandiamide (DCDA) (Acros Organics, 99.5%), glucose (AR, Sinopharm Chemical Reagent Co. Ltd.) and Ammonium sulfate (99.999% Aldrich).

### Preparation of nr-HGM and control samples

Homogeneous mixtures of ammonium sulfate, glucose and dicyandiamide (DCDA) with a mass ratio  $M_{s/c}$  (sulfate in ammonium sulfate: carbon in glucose) from 5% via 10%, 20% and 30% to 40% were heated to 800, 900, or 1000 °C ( $3.3\text{ °C min}^{-1}$ ), kept at the same temperature for 1 h under the protection of  $N_2$  flow ( $20\text{ mL min}^{-1}$ ), and naturally cooled to room temperature. Note that the mass ratio of glucose to DCDA was fixed to 1:40 for all samples. The as-obtained Nr-HGM was directly used for characterizations and electrochemical tests. Intermediate sample named as graphitic- $C_3N_4$  and carbon complex (g- $C_3N_4$ -C-550) was obtained at 550 °C with a mass ratio  $M_{s/c}$  of 30%. NG was obtained at 900 °C with the same condition of Nr-HGM-900 without the existence of ammonium sulfate.

### Electrochemical measurements

The electrochemical activities of Nr-HGM samples and Pt/C (20 wt%) were carried out by using the rotating disc electrode (RDE) technique. The catalysts inks were prepared by dispersing 5 mg samples or Pt/C in the solution containing 80  $\mu\text{L}$  of a 5 wt% of Nafion solution in alcohol, 350  $\mu\text{L}$  of water and 750  $\mu\text{L}$  of ethanol. The working electrode was prepared by transferring 10  $\mu\text{L}$  ink onto a glassy carbon rotating disk electrode (5 mm in diameter, from PINE Instruments, USA), yielding an catalyst loading of 42.4  $\mu\text{g}$ . The electrochemical tests were performed on a CHI 660 C electrochemical workstation.

#### HER test

The electrolytes were 0.1 M KOH solution and 0.5 M  $H_2SO_4$  solution, respectively. Cyclic voltammetry (CV) was obtained at  $50\text{ mV s}^{-1}$  after purging the electrolytes with  $N_2$  gas for 1 h. Linear scanning voltammetry (LSV) measurements were performed by using the RDE at a rotating speeds of 1600 rpm in  $N_2$ -saturated electrolytes at a sweep rate of  $10\text{ mV s}^{-1}$ . Different scan rates of  $5\text{ mV s}^{-1}$ ,  $10\text{ mV s}^{-1}$ ,  $20\text{ mV s}^{-1}$  and  $50\text{ mV s}^{-1}$  were also used to further study the mass transfer process.

#### EIS test

The electrochemical impedance spectroscopy (EIS) measurements for the Nr-HGM were performed in  $N_2$ -saturated 1 M KOH solution at a bias voltage of  $-1.8\text{ V}$  using platinum wire as the counter electrode with the frequency range from 100 kHz to 0.01 Hz. All measurements were conducted at room temperature.

### Characterizations

The SEM measurements were performed on a FEI Nova NanoSEM 2300. The TEM and HRTEM measurements were taken with a JEM-2100 F microscope operated at an acceleration voltage of 200 kV. Raman spectra were acquired using an inVia-reflex micro-Raman spectrometer (Renishaw, UK) with a 532 nm wavelength incident laser. The Powder X-ray diffraction (XRD) patterns were recorded on a Bruker D8 Advance X-ray diffractometer with  $Cu-K\alpha$  radiation ( $\lambda=1.5418\text{ \AA}$ ) with a scan rate of  $6^\circ\text{ min}^{-1}$ . The XPS measurements were conducted on a Kratos Axis Ultra DLD spectrometer using a monochromated Al  $K\alpha$

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