

## Supplementary Materials

### **Secondary–Heteroatom–Doping–Derived Synthesis of N, S Co–Doped Graphene**

#### **Nanoribbons for Enhanced Oxygen Reduction Activity**

*Bing Li<sup>†</sup>, Tingting Xiang<sup>†</sup>, Yuqi Shao, Fei Lv, Chao Cheng, Jiali Zhang, Qingchao*

*Zhu, Yifan Zhang and Juan Yang\**

School of Materials Science and Engineering, Jiangsu University, Zhenjiang 212013, China

\*Correspondence: [yangjuan6347@ujs.edu.cn](mailto:yangjuan6347@ujs.edu.cn)

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

### *Materials and reagents*

Multi-walled CNTs were purchased from Suzhou Tanfeng Graphene Technology Co., Ltd.  $\text{H}_2\text{SO}_4$  (AR, 98%),  $\text{HCl}$  (AR, 38%),  $\text{H}_2\text{O}_2$  (AR, 30%),  $\text{KOH}$  (AR, 99%),  $\text{KMnO}_4$  (AR, 99.5%), urea (AR, 98.5%) and sulfoarea (AR, 99%) were obtained from Sinopharm Chemical Reagent (SCR, Shanghai, China). All reagents were used as received without further purification.

### *Synthesis of GNRs*

300 mg of commercial multi-walled CNTs were the raw materials and mixed with 72 mL of 98%  $\text{H}_2\text{SO}_4$  in a small beaker. The mixture was stirred for 30 min and dispersed in the ultrasonic machine for 10 min. 1.5 g of  $\text{KMnO}_4$  was slowly added into the mixture, and the beaker was placed in a larger beaker with ice water. The mixture was put in an oil-bath pan and the temperature was kept at 65 °C for 1 h. The solution was then poured into 500 mL of ice, followed by the addition of 18 mL of  $\text{H}_2\text{O}_2$ . The reaction lasted for 10 min, and GNRs were obtained after filtration, rinsing and freeze drying.

### *Structural characterization*

The microstructure of samples was observed by scanning electron microscopy (SEM, JEOL JSM-7800F; Tokyo, Japan), with an acceleration voltage of 5 kV, and by high-resolution transmission electron microscopy (TEM, JEOL JEM-2100; Tokyo, Japan) working at 120 kV. Element mapping analyses were detected using a JEOL JSM-2100F microscope at an accelerating voltage of 15 kV. X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi; Thermo Fisher, Waltham, MA, USA), with the

excitation source of Mg K $\alpha$ , was used to analyze the chemical composition and bond configuration, and the detection sensitivity of XPS was at 0.1%. Raman spectra were collected using a Raman spectrometer (Thermo Fisher, Waltham, MA, USA) with a 532 nm wavelength of laser light at 5 mW).

#### *Electrochemical characterization*

Electrochemical characterization of the catalysts was performed in a standard three-electrode cell using an electrochemical workstation (CHI760E; Shanghai Chen Hua Medical Instruments Co., Ltd., Shanghai, China). A Pt wire counter electrode and an Ag/AgCl reference electrode in saturated KCl solution were used. A rotating disk electrode (RDE; PIN USA, Glendale, CA) with a glassy carbon disk (5 mm in diameter) was used as the working electrode for cyclic voltammetry (CV) and RDE measurement. A rotating ring-disk electrode (RRDE; PIN USA, Glendale, CA) with a glassy carbon disk (area of 0.2475 cm<sup>2</sup>) and a Pt ring (area of 0.1866cm<sup>2</sup>) was used as the working electrode for RRDE measurement. All potentials measured against an Ag/AgCl electrode in this study were converted to potentials vs. reversible hydrogen electrode (RHE) according to  $E_{\text{vs. RHE}} = E_{\text{vs. Ag/AgCl}} + (0.059 \text{ pH} + 0.197) \text{ V}$ .

Catalysts (2 mg) were dispersed in a 1 mL mixed solvent of isopropanol and nafion (19.88:0.12) for at least 2 h of sonication to form a homogeneous ink. Then, the catalyst ink (20  $\mu\text{L}$ ) was loaded onto an RDE or RRDE and dried overnight at room temperature. An electrolyte of 0.1 M KOH was saturated with oxygen or nitrogen by bubbling O<sub>2</sub> or N<sub>2</sub> for 30 min before each experiment. Prior to all the measurements, the deposited

catalyst was electrochemically cleaned in N<sub>2</sub>-saturated 0.1 M KOH for 20 CV cycles at a scan rate of 50 mV s<sup>-1</sup>.

For CV measurement, the working electrode was cycled between 1.17 ~ -0.06 V in O<sub>2</sub>- or N<sub>2</sub>-saturated KOH solution at 50 mV s<sup>-1</sup>. RDE measurement was conducted from 0.96 ~ -0.06 V at rotation speeds from 625 to 2500 rpm in O<sub>2</sub>-saturated 0.1 M KOH at 10 mV s<sup>-1</sup>. A flow of O<sub>2</sub> was maintained over the electrolyte during the recording of the RDE in order to ensure its continuous gas saturation. Koutecky–Levich (K–L) plots (J<sup>-1</sup> vs.  $\omega^{-1/2}$ ) were analyzed at various electrode potentials. The slopes of their linear fit lines were used to calculate the number of electrons transferred (n) on the basis of the K–L equation [43]:

$$\frac{1}{J} = \frac{1}{J_K} + \frac{1}{J_L} = \frac{1}{J_K} + \frac{1}{0.62nFC_0D_0^{2/3}\nu^{-1/6}\omega^{1/2}}$$

where J is the measured current density, J<sub>K</sub> and J<sub>L</sub> are the kinetic and diffusion-limiting current densities,  $\omega$  is the angular velocity, n is the electron transfer number, F is the Faraday constant (96485 C mol<sup>-1</sup>), C<sub>0</sub> is the concentration of dissolved O<sub>2</sub> (1.2×10<sup>-6</sup> mol cm<sup>-3</sup>), D<sub>0</sub> is the diffusion coefficient of O<sub>2</sub> (1.9×10<sup>-5</sup> cm<sup>2</sup> s<sup>-1</sup>) and  $\nu$  is the kinematic viscosity of the electrolyte (0.01 cm<sup>2</sup> s<sup>-1</sup>). For the Tafel plots, the kinetic current was calculated from the mass-transport correction of the RDE by:

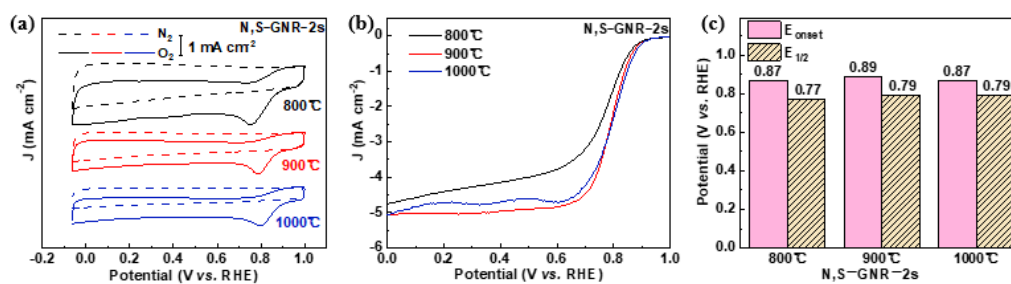
$$J_K = \frac{J_L \times J}{J_L - J}$$

RRDE measurement was conducted at a rotation speed of 1600 rpm in O<sub>2</sub>-saturated 0.1 M KOH at 10 mV s<sup>-1</sup>. The potential of the Pt ring was fixed at 0.5 V. The HO<sub>2</sub><sup>-</sup> (%) and the electron transfer number (n) were determined by the following equations:

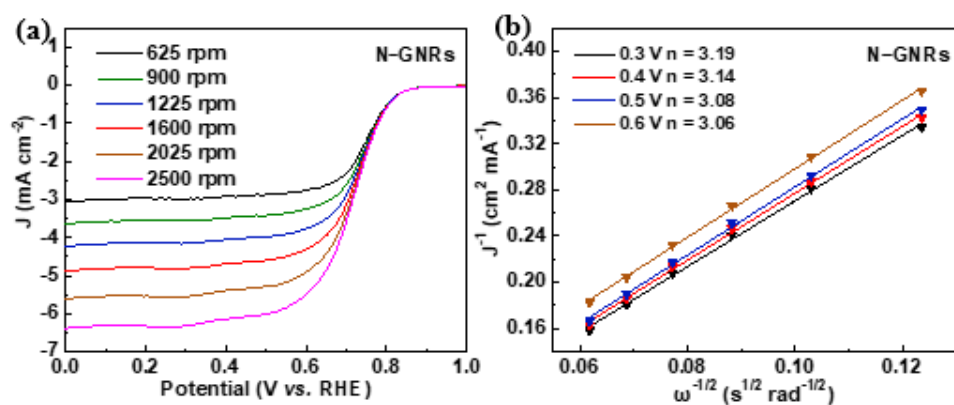
$$HO_2^- (\%) = 200 \times \frac{I_r/N}{I_d + I_r/N}$$

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

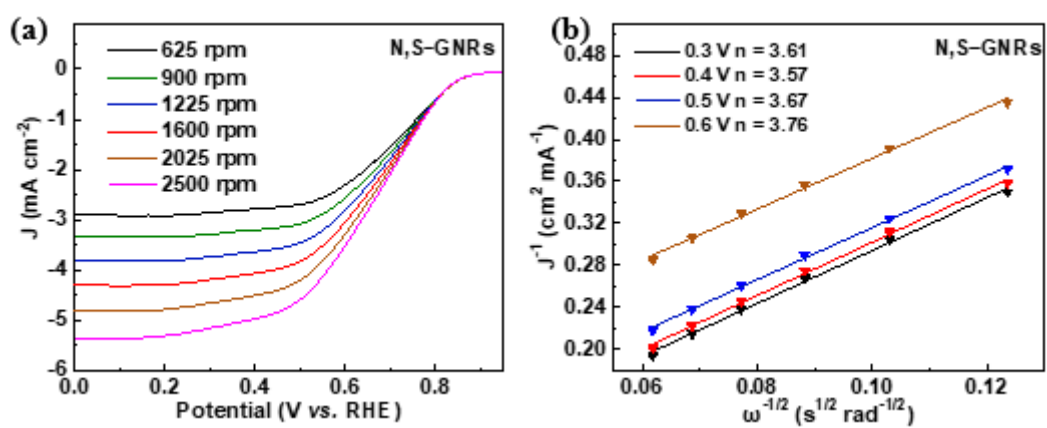
where  $I_d$  is the disk current,  $I_r$  is the ring current and  $N$  is the current collection efficiency of the Pt ring.  $N$  was determined to be 0.37 from the reduction of  $K_3[Fe(CN)_6]$ .



**Figure S1.** Electrochemical characterizations of N, S-GNR-2s synthesized at different temperatures in 0.1 M KOH. (a) CV curves in  $\text{O}_2$ -saturated and  $\text{N}_2$ -saturated solution. (b) RDE polarization curves at 1600 rpm. (c) Onset potentials and half-wave potentials.

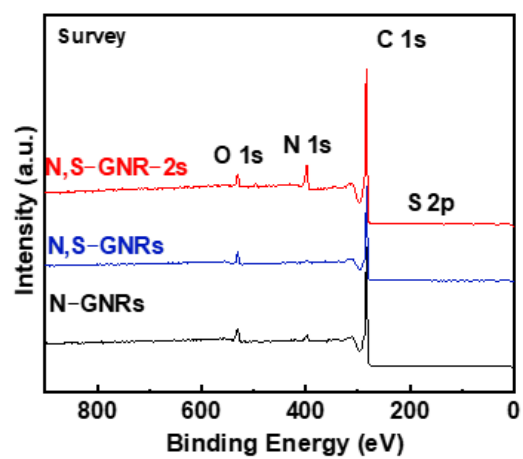


**Figure S2.** Electrochemical characterizations of N-GNRs. (a) RDE polarization curves at different rotating speeds in 0.1 M KOH and (b) the corresponding K-L plots at different potentials.



**Figure S3.** Electrochemical characterizations of N, S-GNRs. (a) RDE polarization curves at different rotating speeds in 0.1 M KOH and (b) the corresponding K-L plots at different potentials.





**Figure S4.** An XPS survey of N-GNRs, N, S-GNRs and N, S-GNR-2s.

**Table S1.** An electrocatalytic property comparison between our work and some relevant studies.

Materials	$E_{\text{onset}}$	$E_{1/2}$	n	References
N, S-GNR-2s	0.89 V vs. RHE	0.79 V vs. RHE	3.66 – 3.67	This work
N, S co-doped hierarchically porous carbon	0.84 V vs. RHE	0.74 V vs. RHE	–	[47]
N, S co-doped mesoporous dominated carbons	0.796 V vs. RHE	0.613 V vs. RHE	3.76 – 4.02	[48]
N/S co-doped multi-walled carbon nanotubes	0.87 V vs. RHE	0.71 V vs. RHE	3.8 – 3.9	[49]
N, S co-doped porous carbons	0.913 V vs. RHE	0.829 V vs. RHE	3.91 – 3.98	[50]
N, S co-doped graphene	0.002 V vs. Hg/HgO	–	2.98 – 3.36	[51]
N, S co-doped CNT-graphene hybrids	0.94 V vs. RHE	0.76 V vs. RHE	–	[52]
N, S co-doped oxygen functionalized carbons	0.92 V vs. RHE	0.81 V vs. RHE	3.9	[53]
N, S co-doped hierarchical porous carbon nanospheres	1.01 V vs. RHE	0.85 V vs. RHE	–	[54]
N, S-doped carbon framework	–	0.86 V vs. RHE	3.86 – 3.96	[55]

**Table S2.** The elemental contents of N-GNRs, N, S-GNRs and N, S-GNR-2s based on XPS analysis in Figure S4.

Materials	C %	N %	O %	S %
N-GNRs	88.81	5.43	5.76	–
N, S-GNRs	89.80	5.67	3.33	1.20
N, S-GNR-2s	84.66	10.93	3.40	1.01

### Supplementary References

43. Li, W.; Min, C.G.; Tan, F.; Li, Z.P.; Zhang, B.S.; Si, R.; Xu, M.; Kiu, W.; Zhou, L.; Yang, X.K., Bottom-Up Construction of Active Sites in a Cu-N<sub>4</sub>-C Catalyst for Highly Efficient Oxygen Reduction Reaction. *ACS Nano* **2019**, *13*, 3177–3187.
47. Li, R.R.; Liu, F.; Zhang, Y.H.; Guo, M.M.; Liu, D. Nitrogen, Sulfur Co-Doped Hierarchically Porous Carbon as a Metal-Free Electrocatalyst for Oxygen Reduction and Carbon Dioxide Reduction Reaction. *ACS Appl. Mater. Inter.* **2020**, *12*, 44578–44587.
48. Liu, J.T.; Wei, L.L.; Wang, H.Q.; Lan, G.J.; Yang, H.J.; Shen, J.Q. In-situ synthesis of heteroatom co-doped mesoporous dominated carbons as efficient electrocatalysts for oxygen reduction reaction. *Electrochim. Acta* **2020**, *364*, 11137335.
49. Patil, I.M.; Reddy, V.; Lokanathan, M.; Kakade, B. Nitrogen and Sulphur co-doped multiwalled carbon nanotubes as an efficient electrocatalyst for improved oxygen electroreduction. *Appl. Surf. Sci.* **2018**, *449*, 697–704.
50. Li, Y.Q.; Xu, H.B.; Huang, H.Y.; Gao, L.G.; Zhao, Y.Y.; Ma, T.L. Facile synthesis of N, S co-doped porous carbons from a dual-ligand metal organic framework for high performance oxygen reduction reaction catalysts. *Electrochim. Acta* **2017**, *254*, 148–154.
51. Zhang, H.H.; Liu, X.Q.; He, G.L.; Zhang, X.X.; Bao, S.J.; Hu, W.H. Bioinspired synthesis of nitrogen/sulfur co-doped graphene as an efficient electrocatalyst for oxygen reduction reaction. *J. Power Sources* **2015**, *279*, 252–258.
52. Huang, B.B.; Hu, X.; Liu, Y.C.; Qi, W.; Xie, Z.L. Biomolecule-derived N/S co-doped CNT-graphene hybrids exhibiting excellent electrochemical activities. *J. Power Sources* **2019**, *413*, 408–417.
53. Wang, S.T.; Liu, Y.; Liu, X.P.; Chen, Y.; Zhao, Y.L.; Gao, S.Y., Fabricating N, S Co-Doped Hierarchical Macro-Meso-Micro Carbon Materials as pH-Universal ORR Electrocatalysts. *ChemistrySelect* **2022**, *7*, e202200044.
54. Zhang, X.R.; Wang, Y.Q.; Du, Y.H.; Qing, M.; Yu, F.; Tian, Z.Q.; Shen, P.K. Highly active N,S co-doped hierarchical porous carbon nanospheres from green and template-free method for super capacitors and oxygen reduction reaction. *Electrochim. Acta* **2019**, *318*, 272–280.
55. Nong, J.; Zhu, M.; He, K.; Zhu, A.S.; Xie, P.; Rong, M.Z.; Zhang, M.Q. N/S co-doped 3D carbon framework prepared by a facile morphology-controlled solid-state pyrolysis method for oxygen reduction reaction in both acidic and alkaline media. *J. Energy Chem.* **2019**, *34*, 220–226.