Supporting Information

Enriched Graphitic N in Nitrogen-doped Graphene as A Superior Metal-free Electrocatalyst for Oxygen Reduction Reaction

Xiangyu Lu,[a] Dan Wang,[a] Liping Ge,[a] Lihui Xiao,[a] Haiyan Zhang,[b] Lilai Liu,[c] Jinqiu Zhang,[a] Jinqiu Zhang,[a] Maozhong An[a] and Peixia Yang*[a]*

a MIIT Key Laboratory of Critical Materials Technology for New Energy Conversion and Storage, School of Chemistry and Chemical Engineering, Harbin Institute of Technology, Harbin, 150001 China.

b College of Life Science, Henan University, Kaifeng, 475004 China

c College of Environmental and Chemical Engineering, Heilongjiang University of Science and Technology, Harbin, 150022 China.

[a]*E-mail: yangpeixia@hit.edu.cn
[b]*E-mail: zhanghy150@sina.com

Table S1 The content of N, C and O for N-G-800, N-G-900 and N-G-1000 (at%)

Samples	C	N	O
N-G-800	88.34	6.65	5.01
N-G-900	89.58	4.68	5.57
N-G-1000	89.1	3.46	7.44

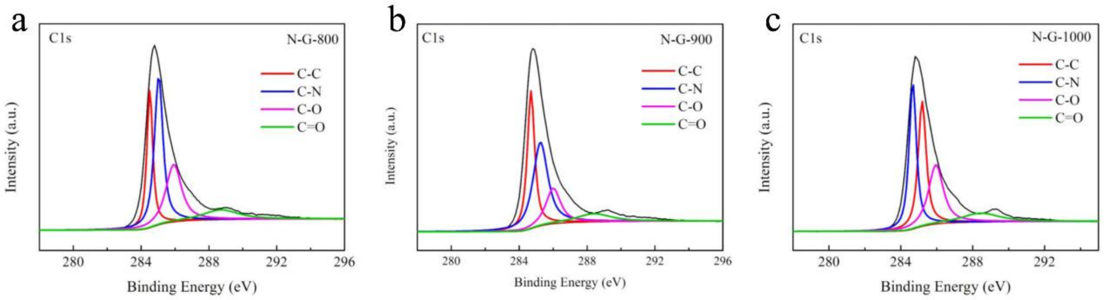

Fig. S1 High-resolution C1s spectra of (a) N-G-800, (b) N-G-900 and (c) N-G-1000.

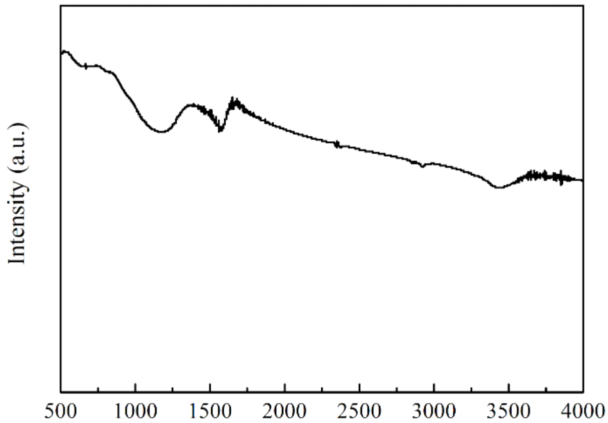

Fig. S2 FT-IR spectra of N-G-1000

Table S2. Summary of N contents N-G-800, N-G-900 and N-G-1000.

Samples	Species	contents (%)	contents (at%)
N-G-800	pyridinic N	36.98	2.46
	pyrrolic N	30.27	2.01
	graphitic N	16.93	1.13
	oxidized N	15.82	1.05
N-G-900	pyridinic N	29.97	1.40
	pyrrolic N	19.72	0.92
	graphitic N	30.15	1.41
	oxidized N	20.16	0.94
N-G-1000	pyridinic N	29.25	1.01
	pyrrolic N	15.29	0.53
	graphitic N	41.54	1.44
	oxidized N	13.92	0.48

Table S3. The electrochemical parameters of the samples

Samples	E_{onset} / V (vs.RHE)	$E_{1/2}$ / V (vs.RHE)	j@0.3 V / mA cm^{-2}
N-G-800	0.929	0.820	5.23
N-G-900	0.979	0.845	5.54
N-G-1000	0.982	0.862	5.48
20% Pt/C	0.968	0.833	5.30

Table S4. ORR activity comparison between this work and catalysts in the literature.

Materials	$E_{1/2}$ (V) in 0.1 M KOH	References
This work	0.862 (vs. RHE)	This work
NDGs-800	0.85 (vs. RHE)	1
NGS4−900	0.859 (vs. RHE)	2
NGA	-0.17 (vs. Ag/AgCl)	3
N/3D-GNS-850	0.80 (vs. RHE)	4
NMGF	0.714 (vs. RHE)	5
NGC900	0.84 (vs. RHE)	6
NGM	0.77 (vs. RHE)	7
G-CN/C-2	0.79 (vs. RHE)	8
NGCNPs-T600	-0.131 (vs. SCE)	9
NHCS-1000	-0.215 (vs. SCE)	10
CNx/CMK-3	0.83 (vs. RHE)	11
NMNC-1000	0.759 (vs. RHE)	12
FeNx-PNC	0.85 (vs.RHE)	13
C-FeZIF-900-0.84	0.86 (vs.RHE)	14
NiO/CoN PINWs	0.68 (vs.RHE)	15
cal-CoZIF-VXC72	0.84 (vs.RHE)	16

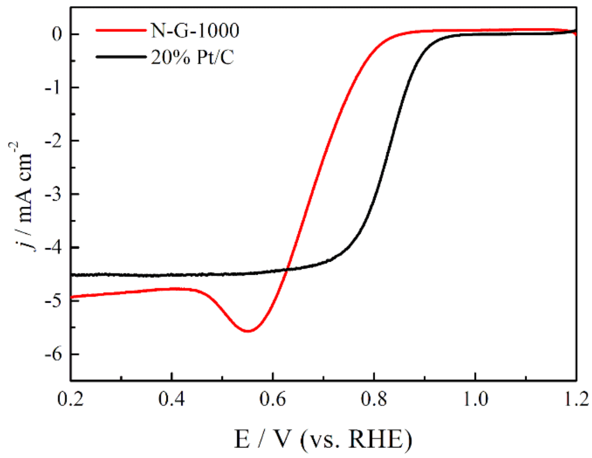

Fig. S3 N-G-1000 and commercial 20 wt % Pt/C in O_2-saturated 0.1 M $HClO_4$ at a scan rate of 10 mV s^{-1} and electrode-rotation speed of 1600 rpm

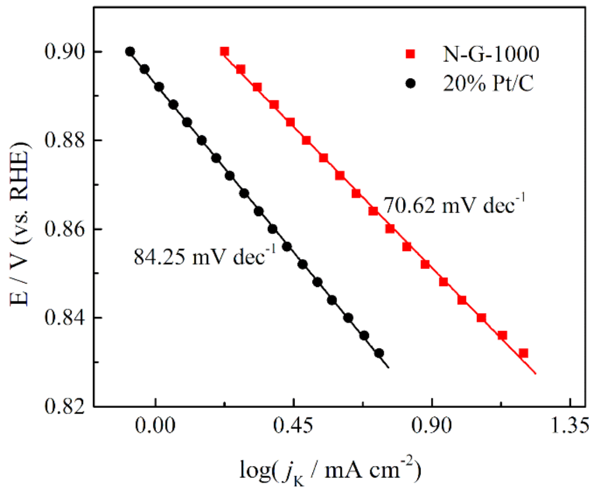

Fig. S4 Tafel plots with 1600 rpm RDE of N-G-1000 and Pt/C.

Table S5. Active centers of the N-doped graphene catalysts for ORR between this work and the recent reports in the literature.

Names of nitrogen doped graphene	Active centers
N-G-1000 (this work)	Carbon atoms neighboring Graphitic N.
N-doped zigzag graphene ribbons[17]	Graphitic N next to the edge.
Polyaniline/RG-O, polypyrrole/RG-O[18]	Graphitic N determines the limiting current density, and pyridinic N improves the onset potential.
Nitrogen doped graphene[19]	Graphitic N configuration.
Mesoporous nitrogen-doped graphene[20]	Pyrrolic nitrogen along with the mesoporous structure of graphene.
Nitrogen-doped graphene[21]	Pyridinic N.
Highly oriented pyrolitic graphite[22]	Carbon atoms next to pyridinic N.

References

1 Q. Wang, Y. Ji, Y. Lei, Y. Wang, Y. Wang, Y. Li, S. Wang, *ACS Energy Letters*, 2018, **3**, 1183-1191.

2 Q. Xiang, Y. Liu, X. Zou, B. Hu, Y. Qiang, D. Yu, W. Yin, C. Chen, *ACS Appl. Mater. Interfaces*, 2018, **10**, 10842-10850.

3 L. Zhao, X. Sui, J. Li, J. Zhang, L. Zhang, G. Huang, Z. Wang, *Applied Catalysis B: Environmental*, 2018, **231**, 224-233.

4 S. Kabir, K. Artyushkova, A. Serov, P. Atanassov, *ACS Appl. Mater. Interfaces*, 2018, **10**, 11623-11632.

5 H. Wang, C. Tang, Q, Zhang, *Catalysis Today*, 2018, **301**, 25-31.

6 R. Luo, C. Liu, J. Li, C. Wang, X. Sun, J. Shen, W. Han, L. Wang, *ACS Appl. Mater. Interfaces*, 2017, **9**, 32737-32744.

7 C. Tang, H. Wang, X. Chen, B. Li, T. Hou, B. Zhang, Q. Zhang, M. Titirici, F. Wei, *Adv. Mater.*, 2016, **28**, 6845-6851.

8 X. Fu, X. Hu, Z. Yan, K. Lei, F. Li, F. Cheng, J. Chen, *Chem. Commun.*, 2016, **52**, 1725-1728.

9 R. Ma, Y. Zhou, P. Li, Y. Chen, J. Wang, Q. Liu, *Electrochimica Acta*, 2016, **216**, 347-354.

10 T. Zhou, Y. Zhou, R. Ma, Z. Zhou, G. Liu, Q. Liu, Y. Zhu, J. Wang, *Carbon*, 2017, **114**, 177-186.

11 C. Xiao, X. Chen, Z. Fan, J. Liang, B. Zhang, S. Ding, *Nanotechnology*, 2016, **27**, 445402.

12 C. Guo, X. Tong, X. Guo, *Int. J. Hydrogen Energy*. 2016, **41**, 22941-22951.

13 L. Ma, S. Chen, Z. Pei, Y. Huang, G. Liang, F. Mo, Q. Yang, J. Su, Y. Gao, J.A. Zapien, C. Zhi, *ACS Nano*, 2018, **12**, 1949-1958.

14 Y. Deng, Y. Dong, G. Wang, K. Sun, X. Shi, L. Zheng, X. Li, S. Liao, *ACS Appl. Mater. Interfaces*, 2017, **9**, 9699-9709.

15 J. Yin, Y. Li, F. Lv, Q. Fan, Y. Zhao, Q. Zhang, W. Wang, F. Cheng, P. Xi, S. Guo, *ACS Nano*, 2017, **11**, 2275-2283.

16 B. Ni, C. Ouyang, X.B. Xu, J. Zhuang, X. Wang, *Adv. Mater.*, 2017, **29**, 1701354−1701360.

17 Wang X.; Hou Z.; Ikeda T.; Huang SF.; Terakura K.; Boero M,. *Phys. Rev. B* **2011**, 84, 245434. 1-7.

18 L. Lai, J.R. Potts, D. Zhan, L. Wang, C.K. Poh, C. Tang, H. Gong, Z. Shen, J. Lin, R.S. Ruoff, *Energy Environ. Sci.*, 2012, **5**, 7936-42.

19 Y. Liu, J. Li, W. Li, Y. Li, F. Zhan, H. Tang, Q. Chen, *Int. J. Hydrogen Energy*, 2016, **41**, 10354-10365.

20 S.M. Unni, S. Devulapally, N. Karjule, S. Kurungot, *J. Mater. Chem.*, 2012, **22**, 23506-13.

21 J. Wu, L. Ma, R.M. Yadav, Y. Yang, X. Zhang, R. Vajtai, J. Lou, P.M. Ajayan, *ACS Appl. Mater. Interfaces*, 2015, **7**, 14763-9.
22 D. Guo, R. Shibuya, C. Akiba, S. Saji, T. Kondo, J. Nakamura, *Science*, 2016, **351**, 361-5.