

Electronic Supplementary Information:

Graphene-Wrapped Nitrogen-Doped Hollow Carbon Spheres for High-Activity Oxygen Electroreduction

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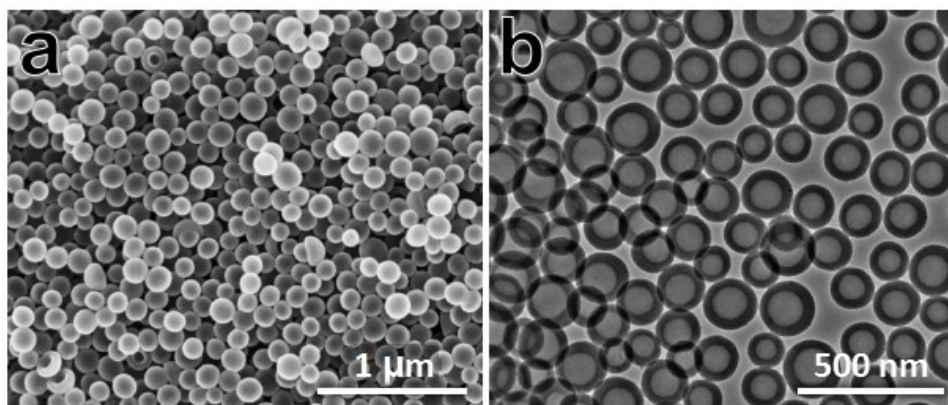


Figure S1. (a) SEM and (b) TEM images of HPSs.

Table S1. Textural properties of NGC-800, NGC-950, NGC-1100, NHCSs and NG.

Sample	$S_{\text{BJH}}^{\text{a}}$ ($\text{m}^2 \cdot \text{g}^{-1}$)	$V_{\text{tot}}^{\text{b}}$ ($\text{cm}^3 \cdot \text{g}^{-1}$)	Pore size ^c (nm)
NGC-800	819	0.99	2.4/ 42.9
NGC-950	722	0.85	2.8/ 8.1/ 42.9
NGC-1100	618	0.68	6.7/ 42.9
NHCSs	939	1.27	8.1/ 40.9
NG	119	0.35	< 10

a Determined by the BET method at P/P_0 of 0.05-0.15.

b Total pore volume for pores at P/P_0 of 0.99.

c determined by the BJH method from the desorption.

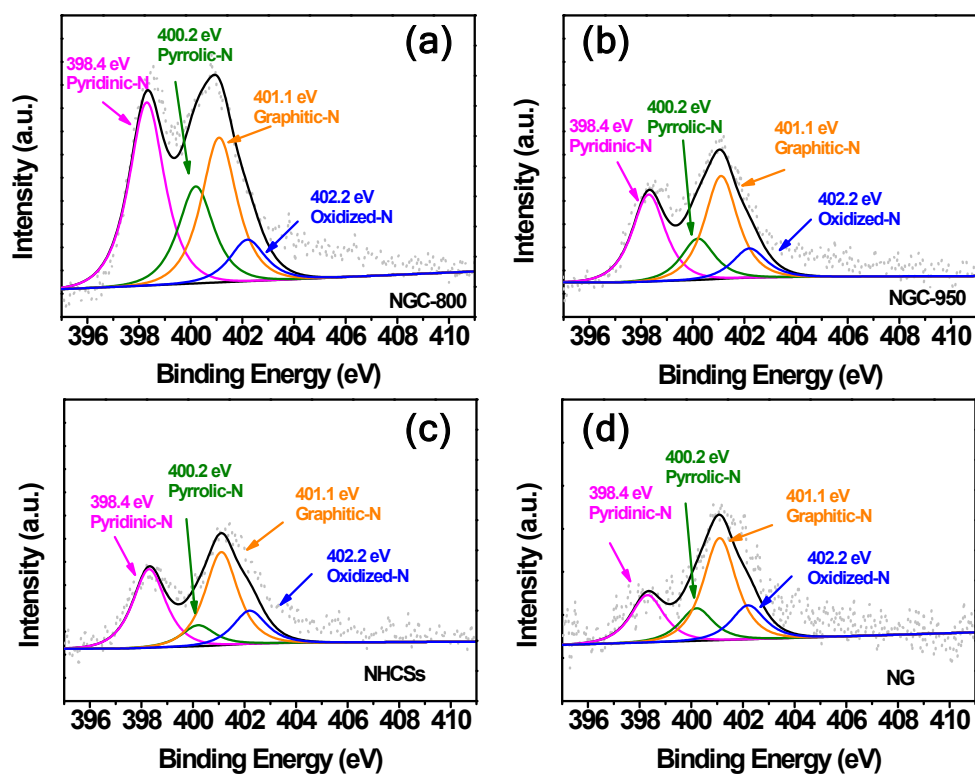


Figure S2. High-resolution N1s XPS spectra of (a) NGC-800, (b) NGC-950, (c) NHCSs and (d) NG.

Table S2. Elemental composition of NHCSs and NGCs determined by XPS analysis.

Samples	Carbon (at.%)	Nitrogen (at.%)	Oxygen (at.%)	N/O molar ratio
NGC-800	88.74	7.96	3.30	2.41
NGC-950	91.67	4.92	3.41	1.44
NGC-1100	92.90	3.44	3.66	0.94
NHCSs	94.35	3.88	1.77	2.19
NG	93.05	2.65	4.30	0.59

Table S3. The peak position and relative composition of different nitrogen groups obtained from the N 1s signal.

Sample	Pyridine-N		Pyrrolic-N		Quaternary-N		Pyridine-N-O	
	Peak position (eV)	at. %	Peak position (eV)	at. %	Peak position (eV)	at. %	Peak position (eV)	at. %
NGC-800	398.3	36.3	400.2	19.7	401.1	35.8	402.2	7.9
NGC-950	398.3	33.7	400.2	15.8	401.1	39.2	402.2	11.4
NGC-1100	398.3	26.3	400.2	12.0	401.1	46.8	402.2	14.9
NHCSs	398.3	38.7	400.2	11.0	401.1	35.2	402.2	16.1
NG	398.3	21.9	400.2	15.1	401.1	47.3	402.2	15.7

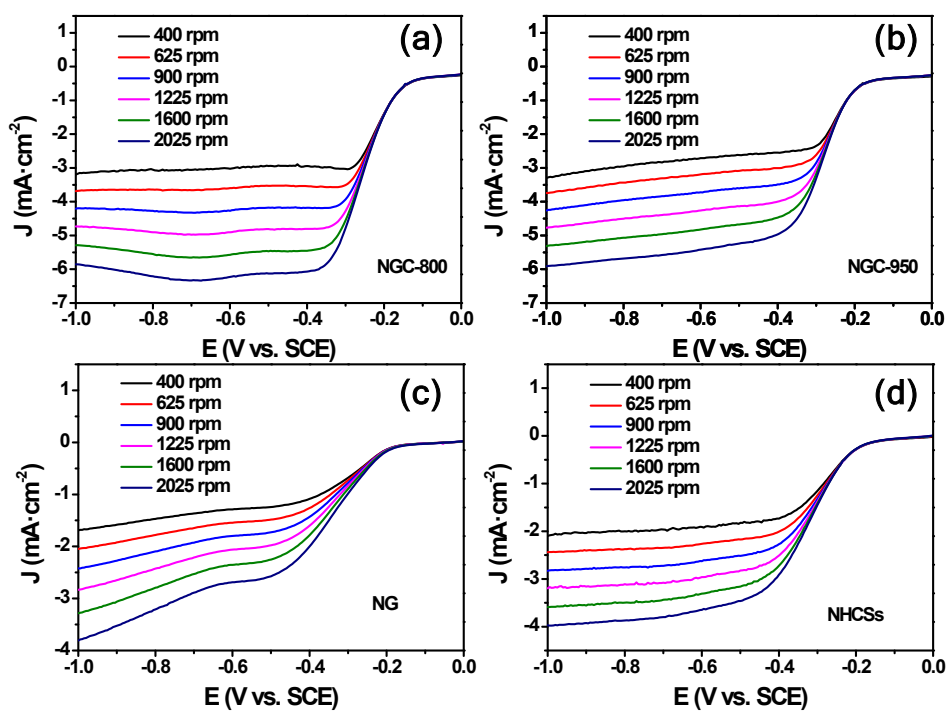


Figure S3. LSV curves of (a) NGC-800, (b) NGC-950, (c) NG-1100 and (d) NHCS-1100 at different rotation speeds obtained in O_2 -saturated 0.1 M KOH solution.

Table S4. Comparison of the ORR performance of NGC-1100 and other metal-free nitrogen-doped electrocatalysts.

Catalysts	Mass loading (mg cm ⁻²)	E _{1/2} -E _{1/2} (Pt/C) (mV)	Current density (mA cm ⁻²)	n	Ref.
NGC-1100	0.51	72	5.7	3.91	This work
NP-PG	0.15	90	4.4	3.7-4.0	¹
PM-CNP	0.29	100	6.0	3.5	²
B,N-G	0.28	80	5.01	3.8	³
HCH900	0.46	81	4.2	3.82	⁴
NCHCs	0.4	61	6.5	3.6-3.8	⁵
NHCS-1000	0.5	49	5.2	3.87-3.98	⁶
N-CNF	0.4	50	5.2	3.97	⁷
HAZ-800	/	48	3.55	3.60	⁸

References for Electronic Supplementary Information:

1. X. Wang, Y. Liu and P. Wu, *Chem. Eng. J.*, 2017, **328**, 417.
2. G. Zhu, T. Chen, Y. Hu, L. Ma, R. Chen, H. Lv, Y. Wang, J. Liang, X. Li, C. Yan, H. Zhu, H. Liu, Z. Tie, Z. Jin and J. Liu, *Nano Energy*, 2017, **33**, 229.
3. Y. Zheng, Y. Jiao, L. Ge, M. Jaroniec and S. Z. Qiao, *Angew. Chem.*, 2013, **125**, 3192.
4. C. Han, J. Wang, Y. Gong, X. Xu, H. Li and Y. Wang, *J. Mater. Chem. A*, 2014, **2**, 605.
5. X. Zheng, X. Cao, X. Li, J. Tian, C. Jin and R. Yang, *Nanoscale*, 2017, **9**, 1059.
6. T. Zhou, Y. Zhou, R. Ma, Z. Zhou, G. Liu, Q. Liu, Y. Zhu and J. Wang, *Carbon*, 2017, **114**, 177.
7. H.-W. Liang, Z.-Y. Wu, L.-F. Chen, C. Li and S.-H. Yu, *Nano Energy*, 2015, **11**, 366.
8. S. Gao, H. Fan and S. Zhang, *J. Mater. Chem. A*, 2014, **2**, 18263.