Electronic Supplementary Information

From Covalent Triazine-based Framework to N-doped Porous Carbon/Reduced Graphene Oxide Nanosheets: Efficient Electrocatalysts for Oxygen Reduction

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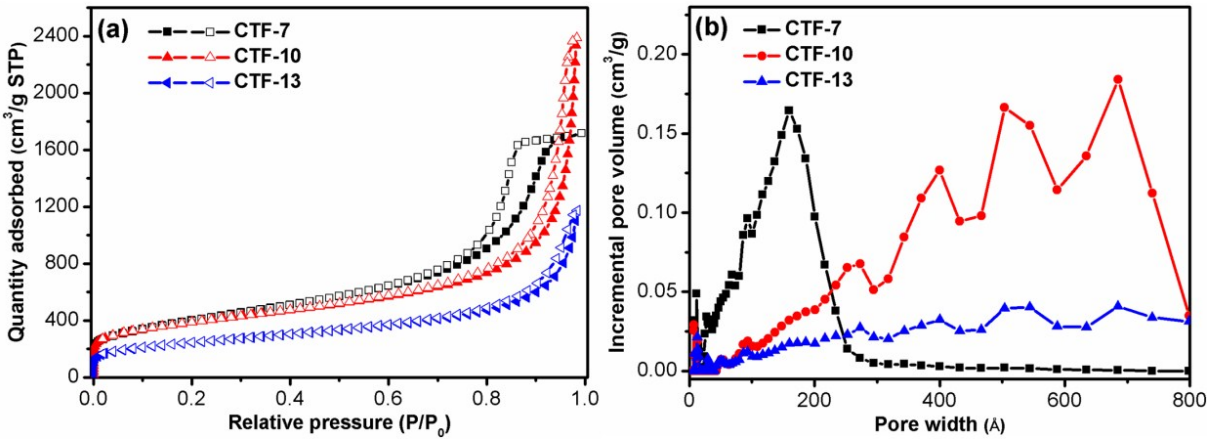

Fig. S1. (a) N_2 sorption isotherms at 77 K for CTFs obtained on the basis of different mass ratios of DCBP and $ZnCl_2$ and (b) the corresponding pore size distributions calculated by the DFT model.

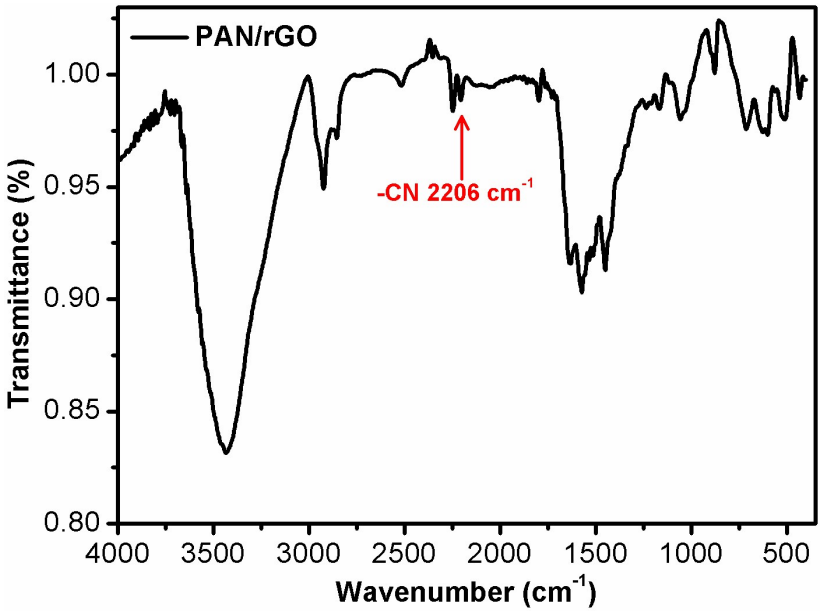

Fig. S2. FT-IR spectrum of PAN/rGO. A vibration at *ca.* 2206 cm^{-1} is detected that can be assigned to the -CN stretching vibration, illustrating the successful fabrication of PAN on rGO.

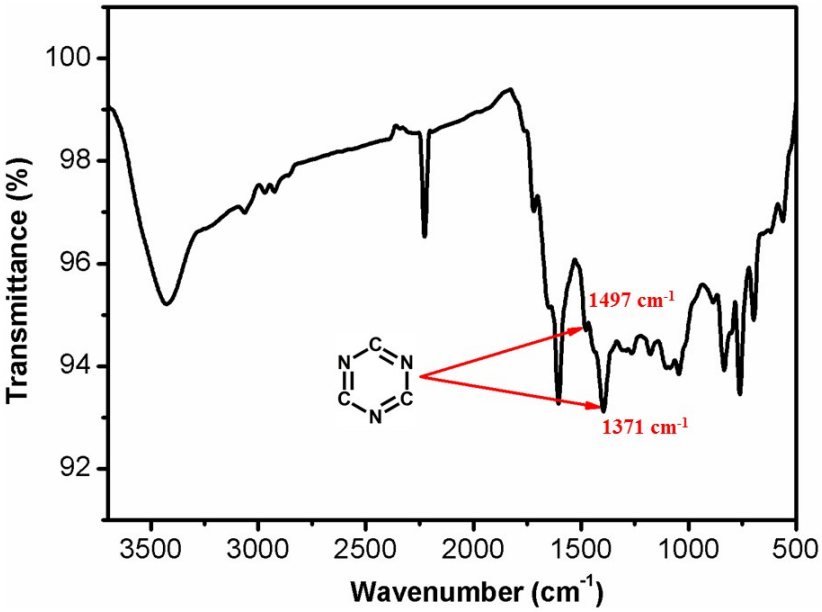

Fig. S3. FT-IR spectrum indicating the formation of CTF during polymerization process. The formation of triazine rings is supported by the the two strong absorption bands at 1497 and 1371 cm^{-1}, revealing the aromatic C−N stretching and "breathing" modes in the triazine unit, respectively.

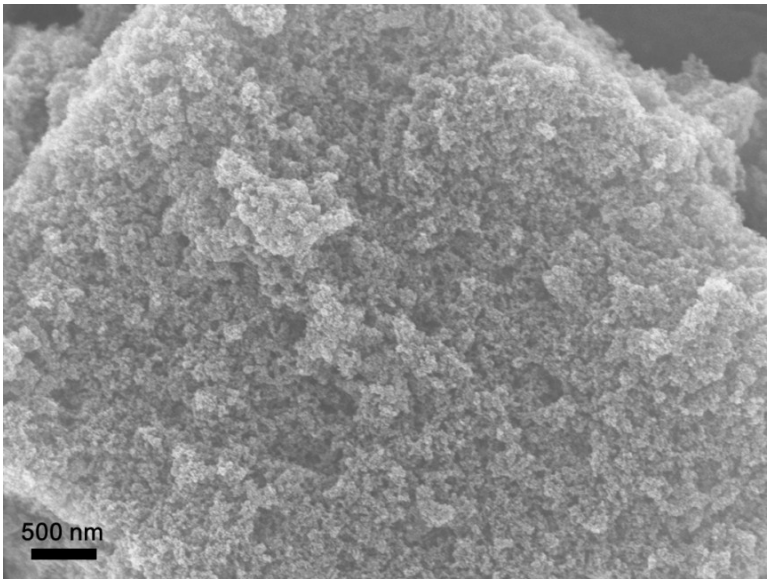

Fig. S4. SEM image of NHC-950.

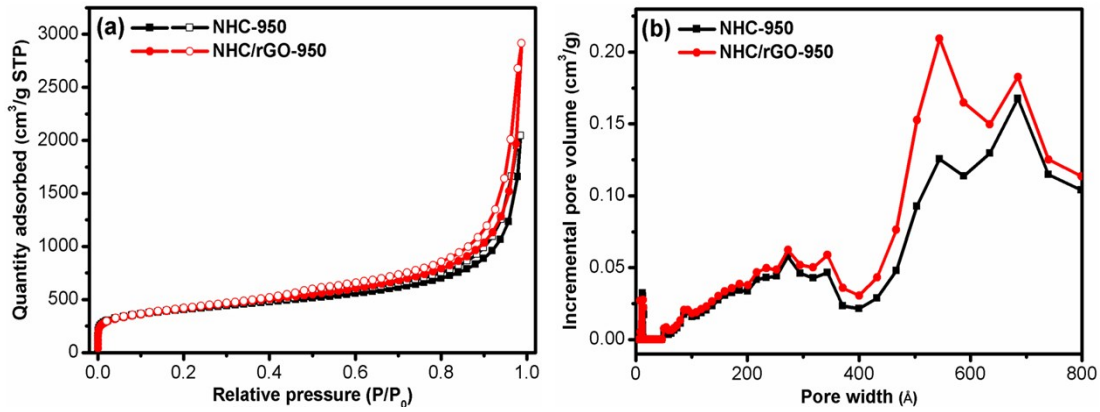

Fig. S5. (a) N_2 sorption isotherms for NHC-950 and NHC/rGO-950 at 77 K and (b) the corresponding pore size distributions calculated by the DFT model.

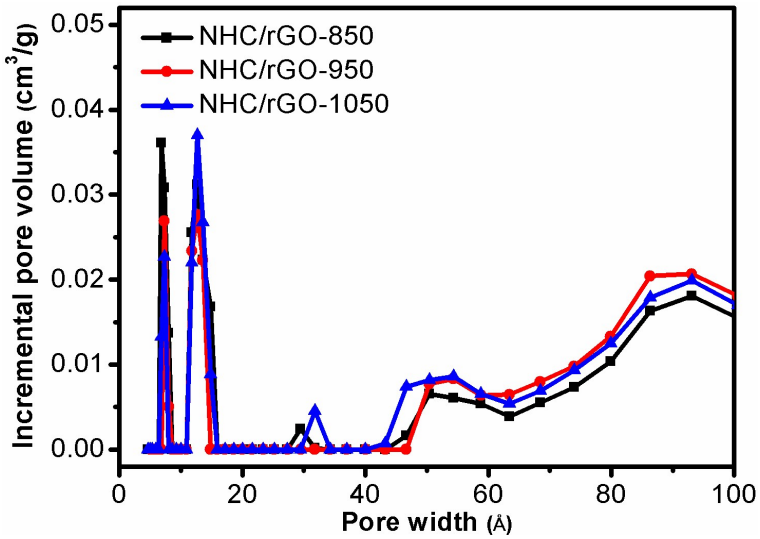

Fig. S6. The pore size distributions below 10 nm for NHC/rGO-T at 77 K calculated by the DFT model.

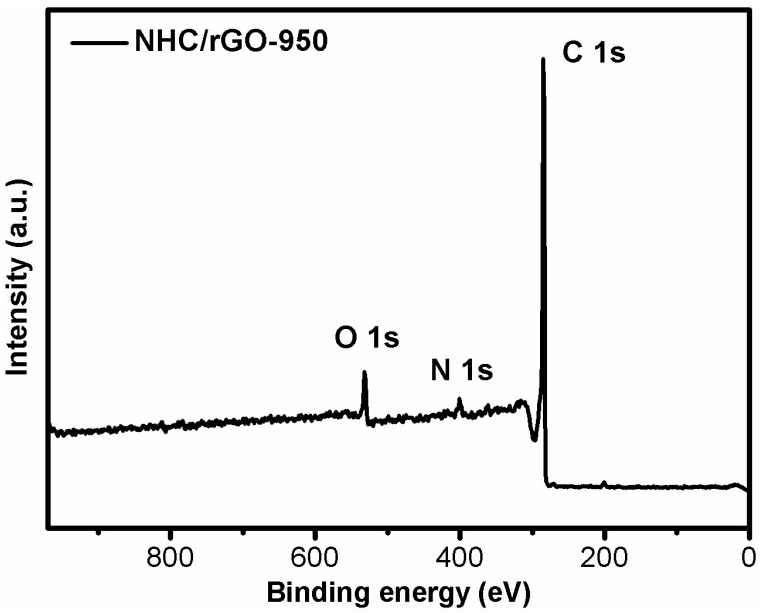

Fig. S7. XPS survey spectrum of NHC/rGO-950.

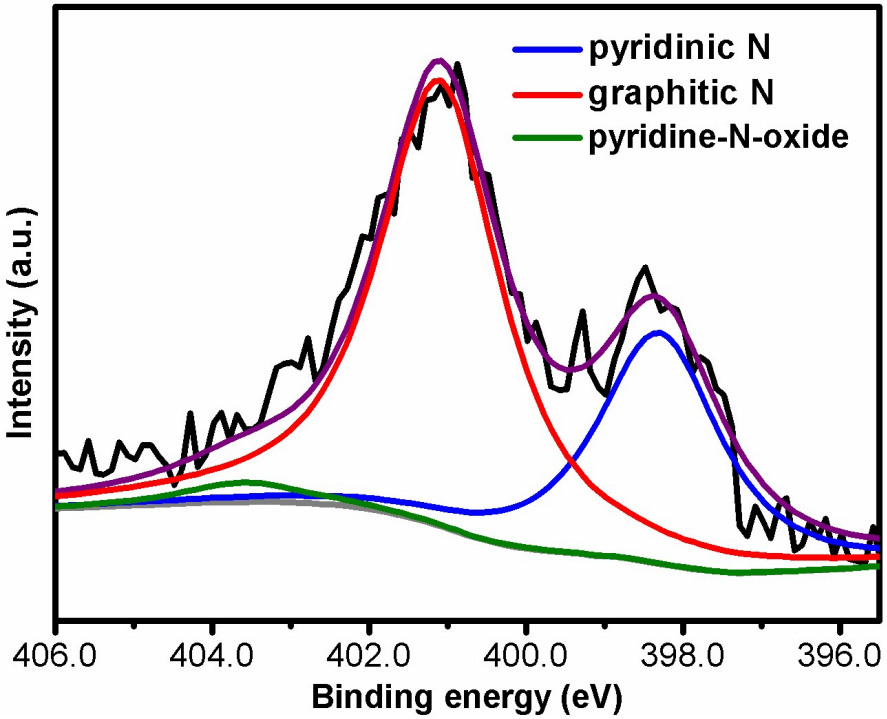

Fig. S8. The high-resolution N1s XPS spectrum of NHC/rGO-850.

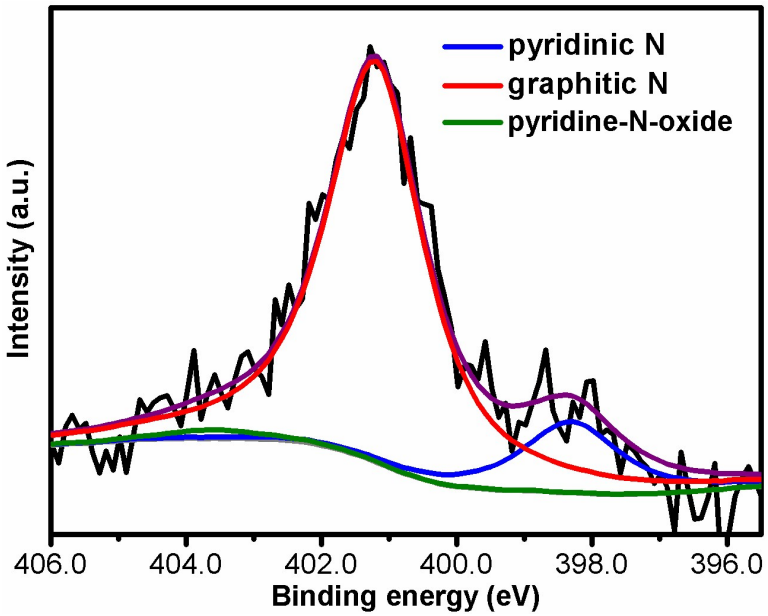

Fig. S9. The high-resolution N1s XPS spectrum of NHC/rGO-1050.

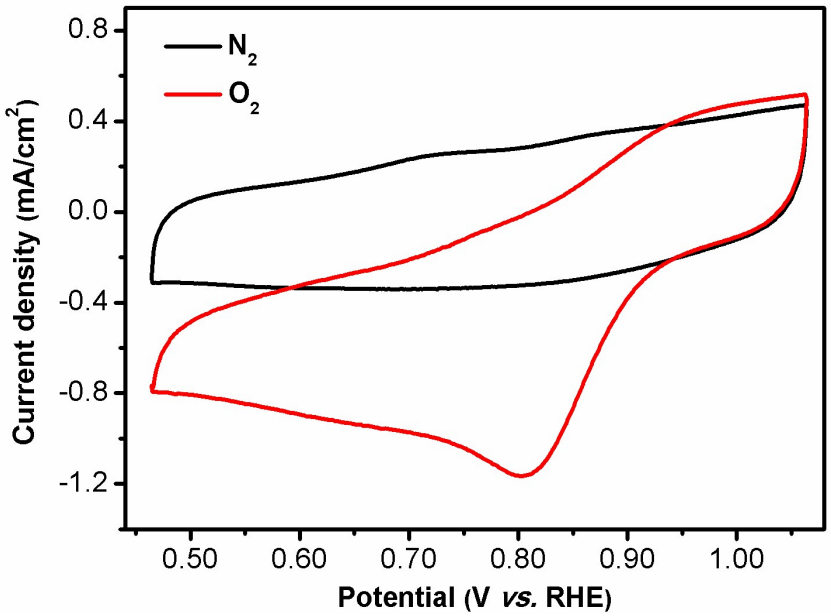

Fig. S10. CV curves of Pt/C in N_2 and O_2-saturated 0.1 M KOH solution.

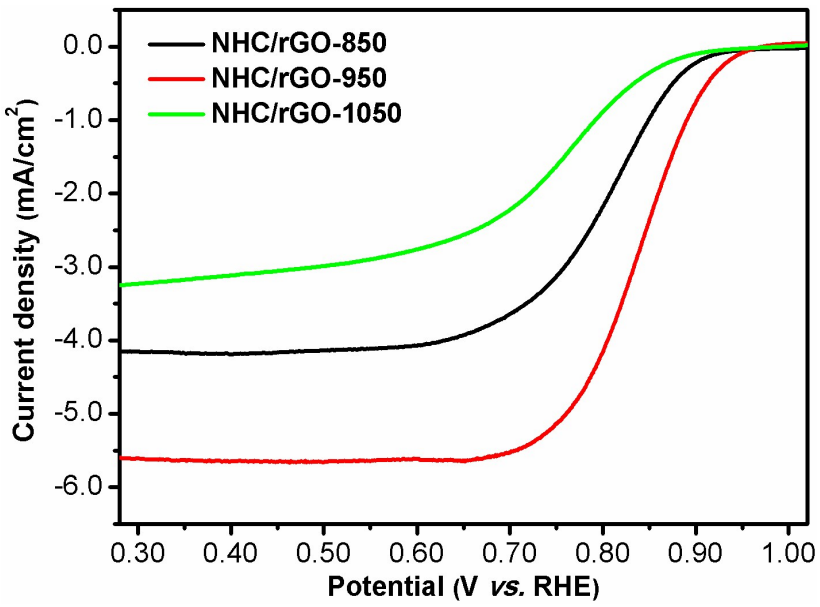

Fig. S11. Electrochemical ORR activity evaluation for NHC/rGO-T (T = 850, 950 and 1050) obtained at different pyrolysis temperatures in 0.1 M KOH solution.

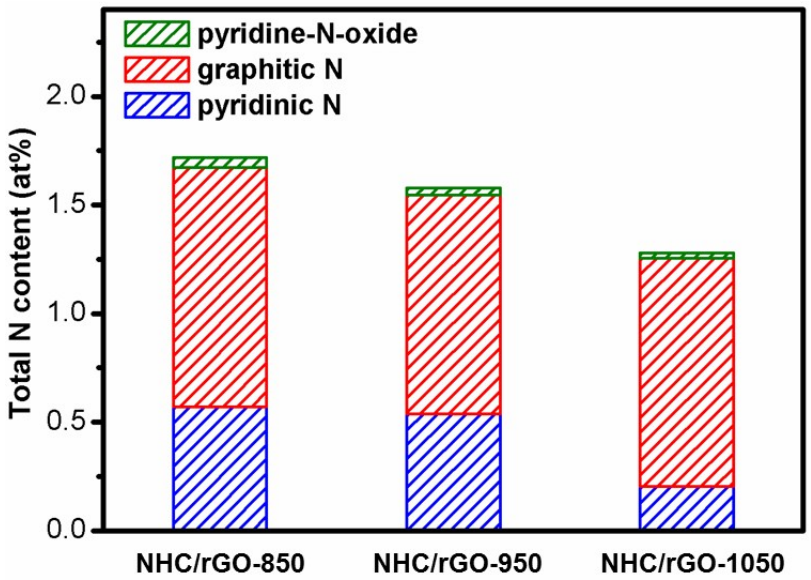

Fig. S12. Summary of the different nitrogen levels in NHC/rGO-T.

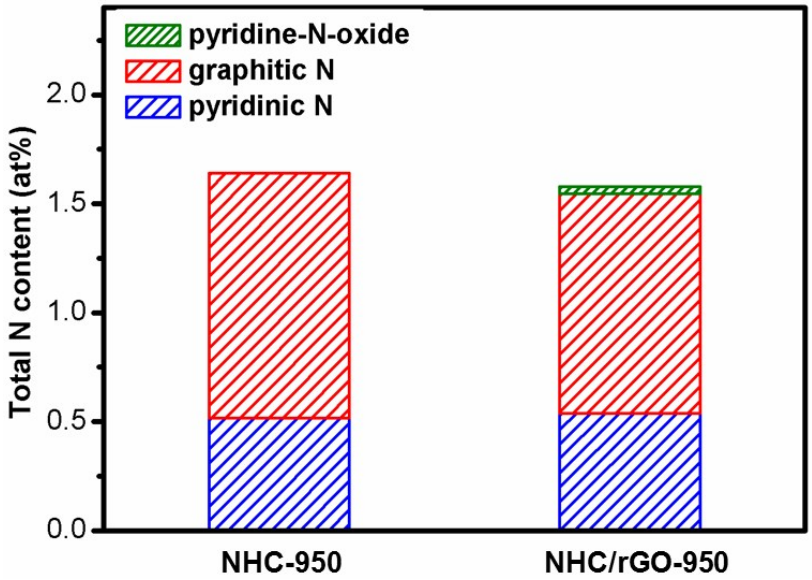

Fig. S13. Summary of the different nitrogen levels in NHC/rGO-950 and NHC-950.

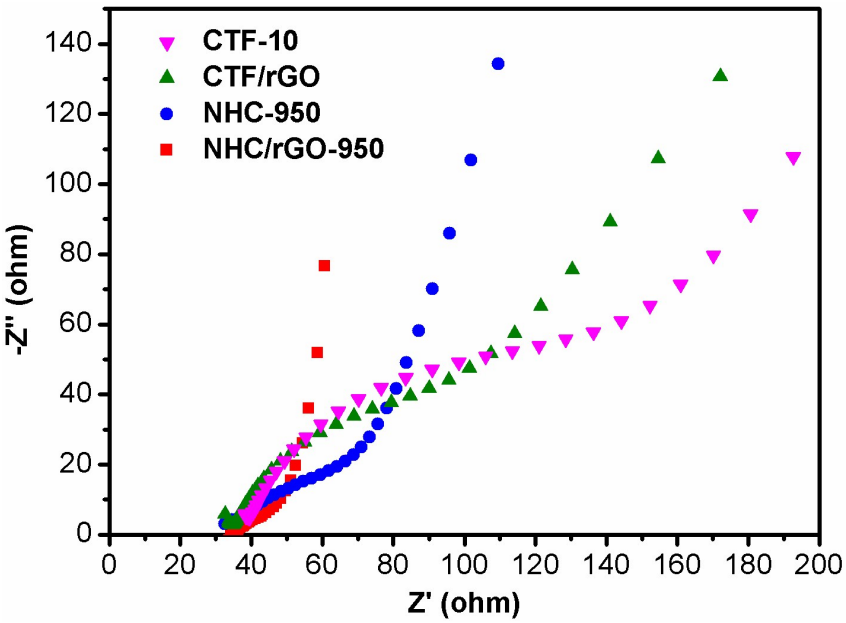

Fig. S14. Nyquist plots of electrochemical impedance spectra for different samples in 0.1 M KOH.

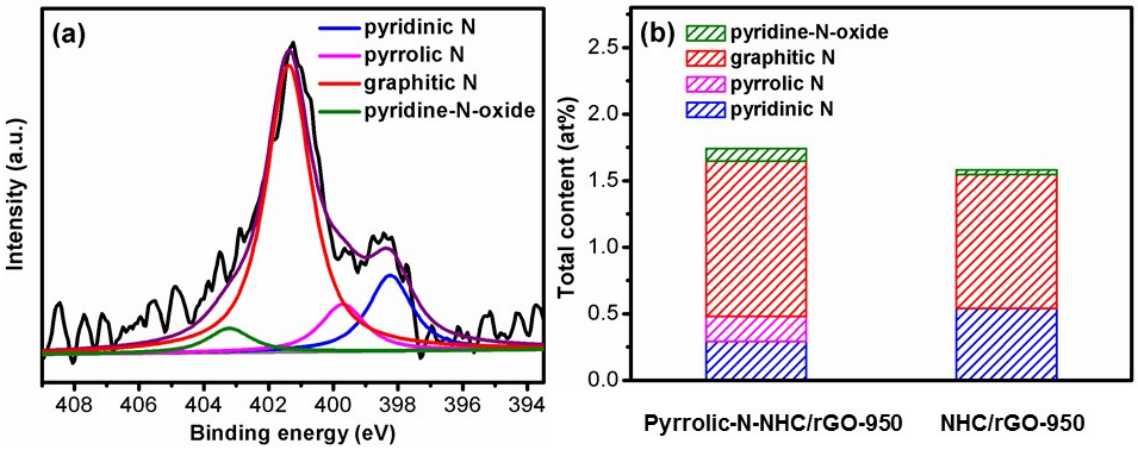

Fig. S15. (a)The high-resolution N1s XPS spectrum and (b) summary of the different nitrogen levels of pyrrolic-N-NHC/rGO-950.

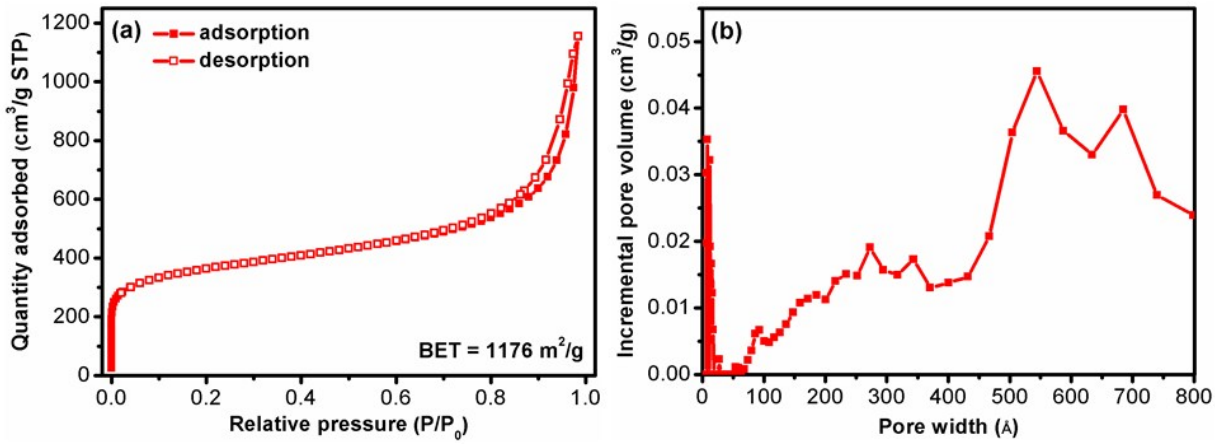

Fig. S16. (a) N_2 sorption isotherms for pyrrolic-N-NHC/rGO-950 at 77 K and (b) the corresponding pore size distributions calculated by the DFT model.

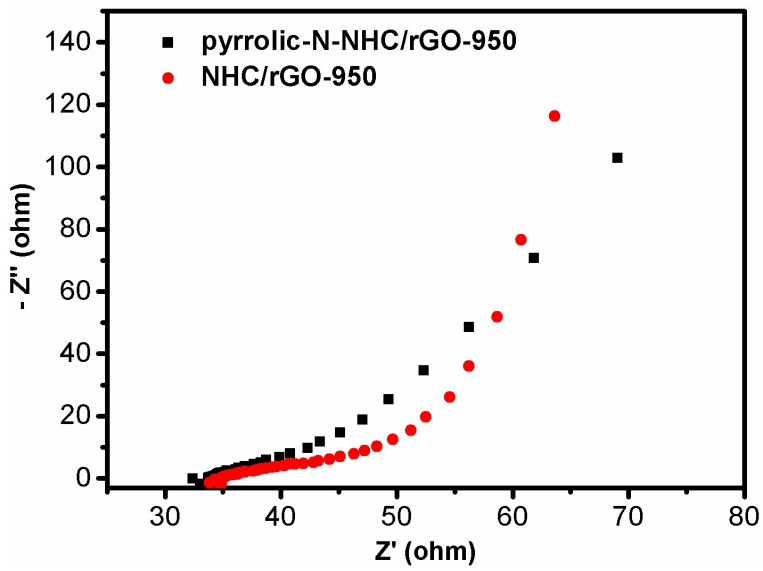

Fig. S17. Nyquist plots of electrochemical impedance spectra for pyrrolic-N-NHC/rGO-950 in 0.1 M KOH.

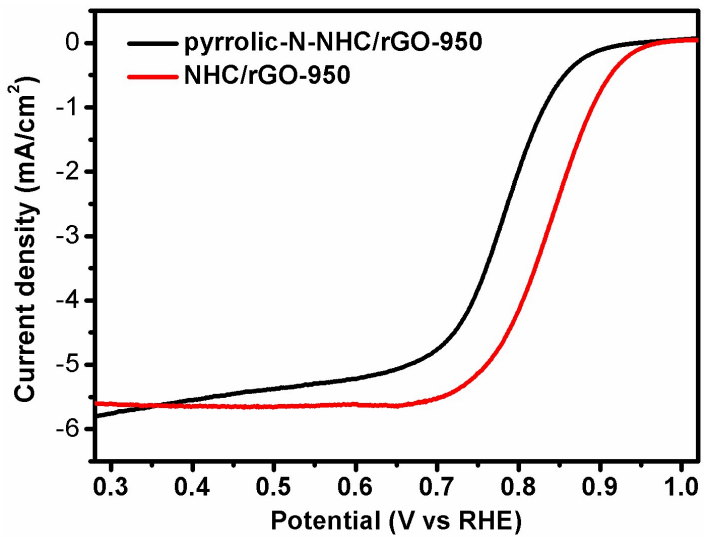

Fig. S18. LSV curves of pyrrolic-N-NHC/rGO-950 in O_2-saturated 0.1 M KOH solution at a rotation speed of 1600 rpm.

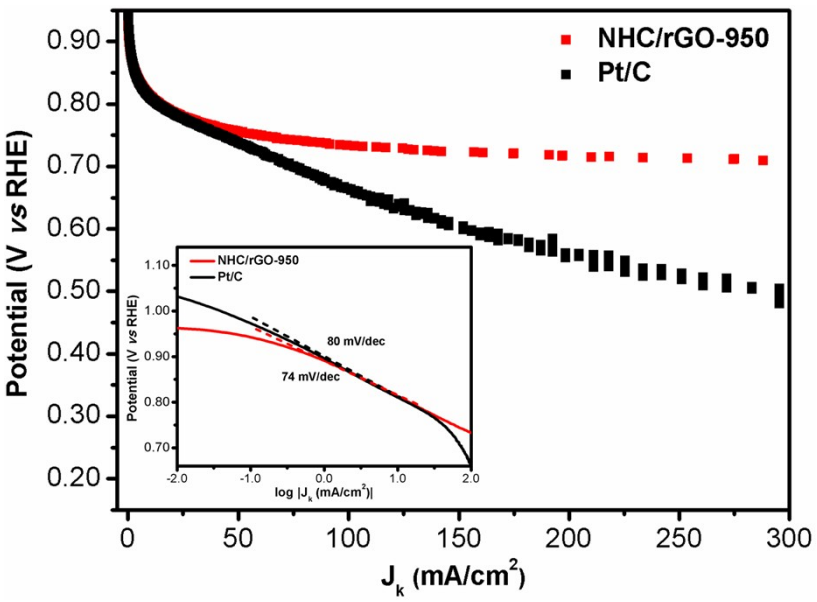

Fig. S19. Kinetic behavior of NHC/rGO-950 and Pt/C (inset: Tafel plots of NHC/rGO-950 and Pt/C).

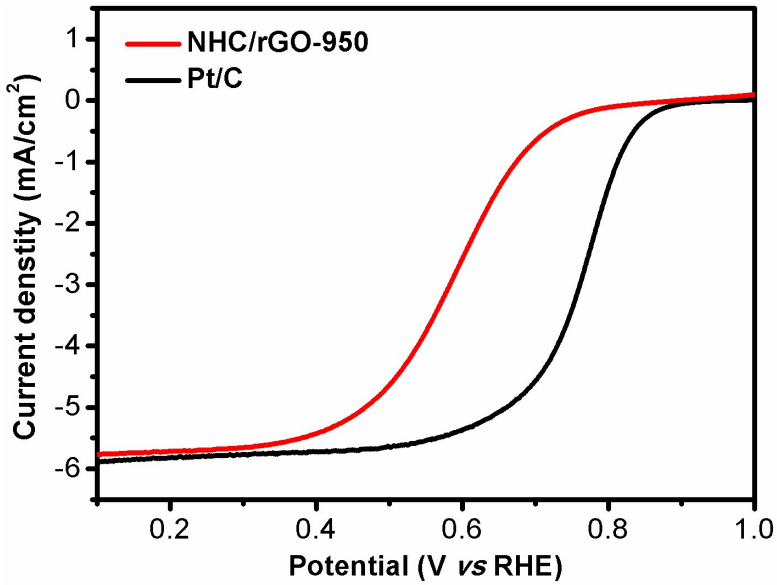

Fig. S20. LSV curves of NHC/rGO-950 in O_2-saturated 0.1 M $HClO_4$ solution at a rotation speed of 1600 rpm.

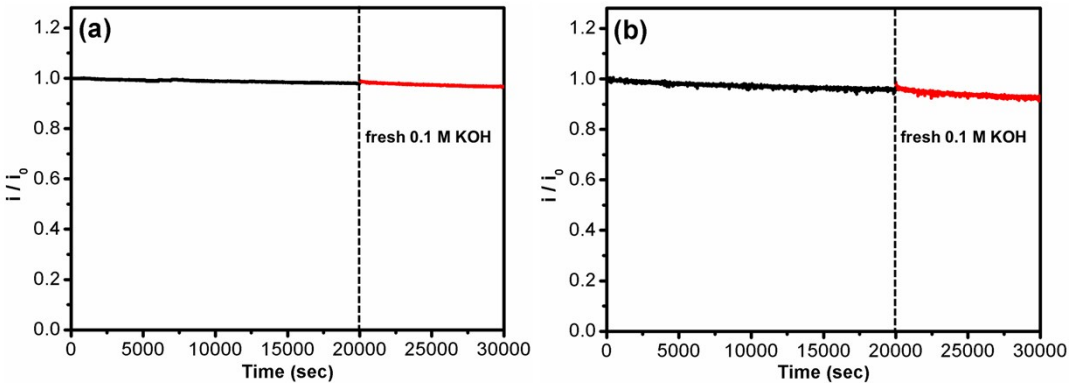

Fig. S21. Time-dependent current density curves for (a) NHC/rGO-950 and (b) Pt/C in 20000s and restarting the electrocatalytic test in a fresh portion of the 0.1 M KOH for another 10000s.

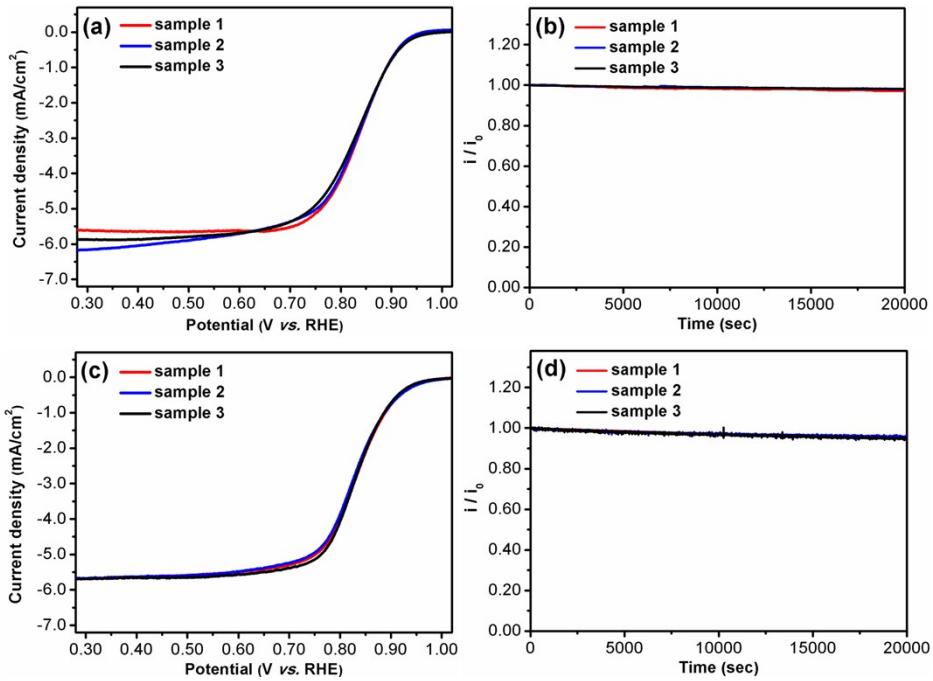

Fig. S22. The reproducibility of (a) LSV curves and (b) time-dependent current density curves for NHC/rGO-950. The reproducibility of (c) LSV curves and (d) time-dependent current density curves for Pt/C. The slightly larger curve deviation in (a) should be caused by three batches of the NHC/rGO-950 catalyst.

Table S1. Elemental analysis of N for different samples.

Sample	NHC-950	NHC/rGO-950	NHC/rGO-850	NHC/rGO-1050	pyrrolic-N-NHC/rGO-950
N [%]	1.64	1.58	1.72	1.28	1.74

Table S2. Comparison of ORR performance for NHC/rGO-950 with other metal-free electrocatalysts or Pt-based reference catalysts in 0.1 M KOH solution.

Catalyst	Half-wave potential (V vs RHE)	Tafel slope (mV/dec)	Kinetic current at 0.8 V (mA/cm^2)	Mass activity at 0.8 V (mA/mg)	Reference
NHC/rGO-950	0.83	74	14.45	51.6[a]	This work
g-C_3N_4@ CMK-3	0.76	113	1.52	17.9[a]	*J. Am. Chem. Soc.* 2011, **133**, 20116
G-CN800	0.76	--	3.08	44[a]	*Angew. Chem. Int. Ed.* 2011, **50**, 5339
NGS-H	0.75	--	1.70	56.7[a]	*J. Power Sources* 2011, **196**, 9970
Mesoporous N-Carbon	0.79	--	5.4	8.2[a]	*J. Am. Chem. Soc.* 2011, **133**, 206
POMC-3	0.76	--	6.5	8.2[a]	*J. Am. Chem. Soc.* 2012, **134**, 16127
P, N-CNT	0.75	--	3.0	37.5[a]	*J. Phys. Chem. Lett.* 2012, **3**, 2863
PDMC800°C	0.73	--	0.70	7[a]	*J. Am. Chem. Soc.* 2013, **135**, 7823
NG-1000	0.82	--	12.77	45.1[a]	*ACS Appl. Mater. Interfaces* 2013, **5**, 11108
GNPCSs-800	0.81	--	13.43	67.2[a]	*Angew. Chem. Int. Ed.* 2014, **53**, 14235
Carbon-L	0.69	--	0.55	5.5[a]	*Energy Environ. Sci.* 2014, **7**, 442
GFMC3	0.8	--	1.93	7.6[a]	*Phys. Chem. Chem. Phys.* 2014, **16**, 4251
HCH-dca-900 (r = 1.0)	0.71	--	1.21	2.6[a]	*J. Mater. Chem. A* 2014, **2**, 605
meso/micro-PoPD	0.85		17.9	179[a]	*Nat. commun.* 2014, **5**, 4973
CNT/ HDC-1000	0.82	68	8.3	13.8[a]	*Angew. Chem. Int. Ed.* 2014, **53**,4102
ING	0.79	83	2.50	5[a]	*Carbon* 2015, **95**, 930
P-CHS-2	0.77	--	4.59	9.1[a]	*Carbon* 2015, **82**, 562
TTF-F	0.77	--	3.22	10.7[a]	*Adv. Mater.* 2015, **27**, 3190
NMCS-3	0.76	--	2.10	3[a]	*Angew. Chem. Int. Ed.* 2015, **54**, 588
N-MCNs	0.78	--	3.12	7.8[a]	*Angew. Chem. Int. Ed.* 2015, **54**, 15191
MPSA/GO-1000	0.82	--	12.43	41.4[a]	*Angew. Chem. Int. Ed.* 2016, **55**, 2230
N-CNS-120	0.76	--	6.34	31.1[a]	*Adv. Mater.* 2016, **28**, 5080
NGM	0.77	--	3	12[a]	*Adv. Mater.* DOI:10.1002/adma.201601406
N,P-CGHNs	0.82	--	6.34	21.1[a]	*Adv. Mater.* 2016, **28**, 4606

N/S-2DPC-60	0.75	--	1.70	6.8[a]	*Adv. Funct. Mater.* DOI:10.1002/adfm.201602158
NPC-F	0.84	--	13.43	56.0[a]	*Adv. Mater.* 2016, **28**, 1981
PtCu	0.84	47	13.43	839.6[b]	*J. Electrochem. Soc.* 2012, **159**, B444.
PtCu NFs	0.89	--	15.11	1056[b]	*Adv. Mater.* 2016, **28**, 8712
Pt/C	0.83	80	13.49	134.9[a]	This work

[a] mass activity is calculated by the mass of total catalyst
[b] mass activity is calculated by the mass of Pt.

Table S3. ICP analysis for NHC/rGO-950 before and after reation.

Sample	Fe	Co	Pt	Zn
Before reaction	20 ppm	18 ppm	N.D.	N.D.
After reaction	10 ppm	16 ppm	N.D.	N.D.