Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Electronic Supplementary Information

Temperature-Direct Growth Ultra-hollow Carbon Framework of Pyridinic Nitrogen-Doped as an Efficient Electrocatalyst for Oxygen Reduction Reaction

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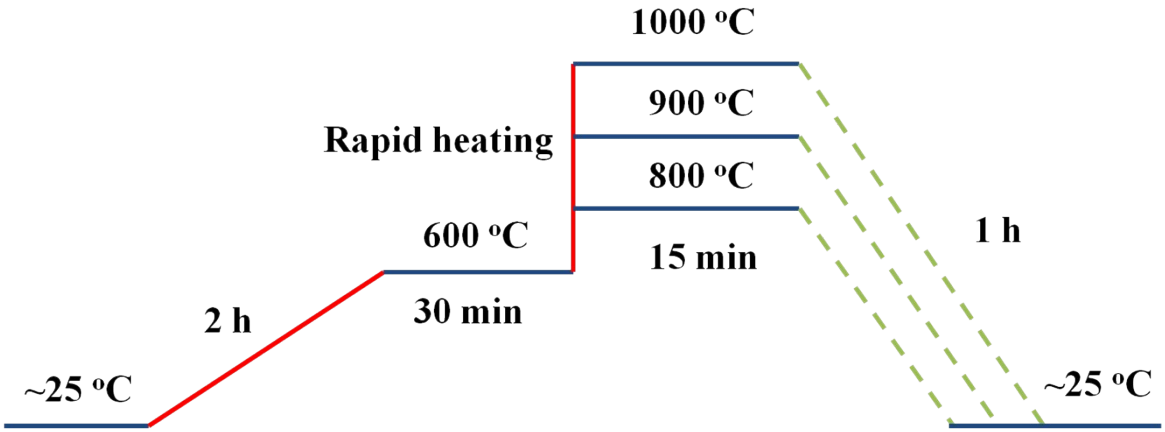

Figure S1 Temperature-program for the synthesis of N-HCF-Ts.

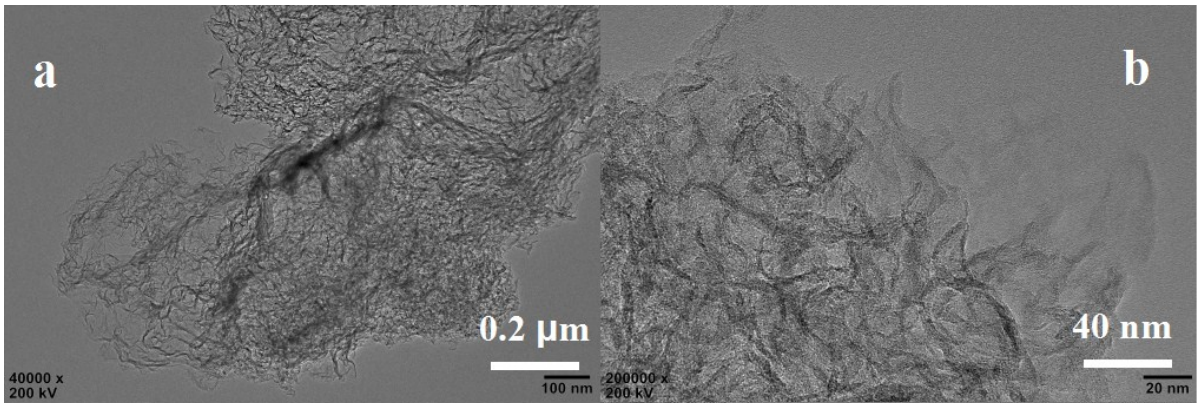

Figure S2 TEM images of (a, b) N-HCF-1000.

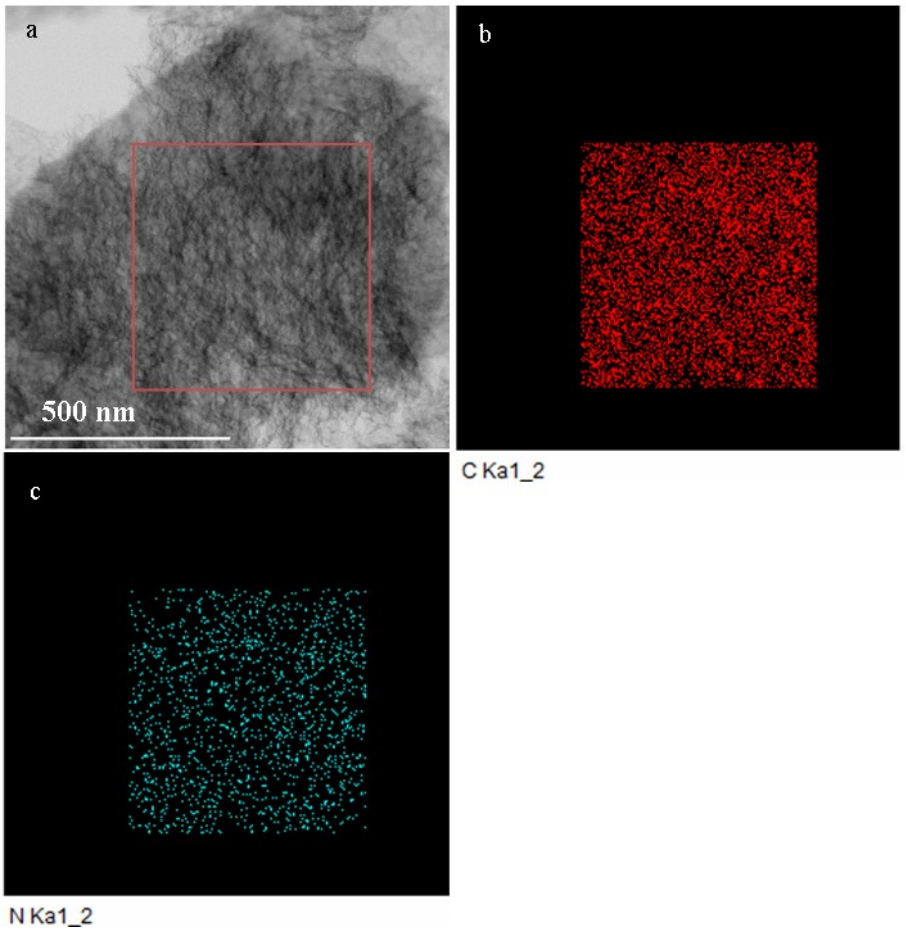

Figure S3 (a) STEM image and (b, c) C, N elemental maps of N-HCF-900.

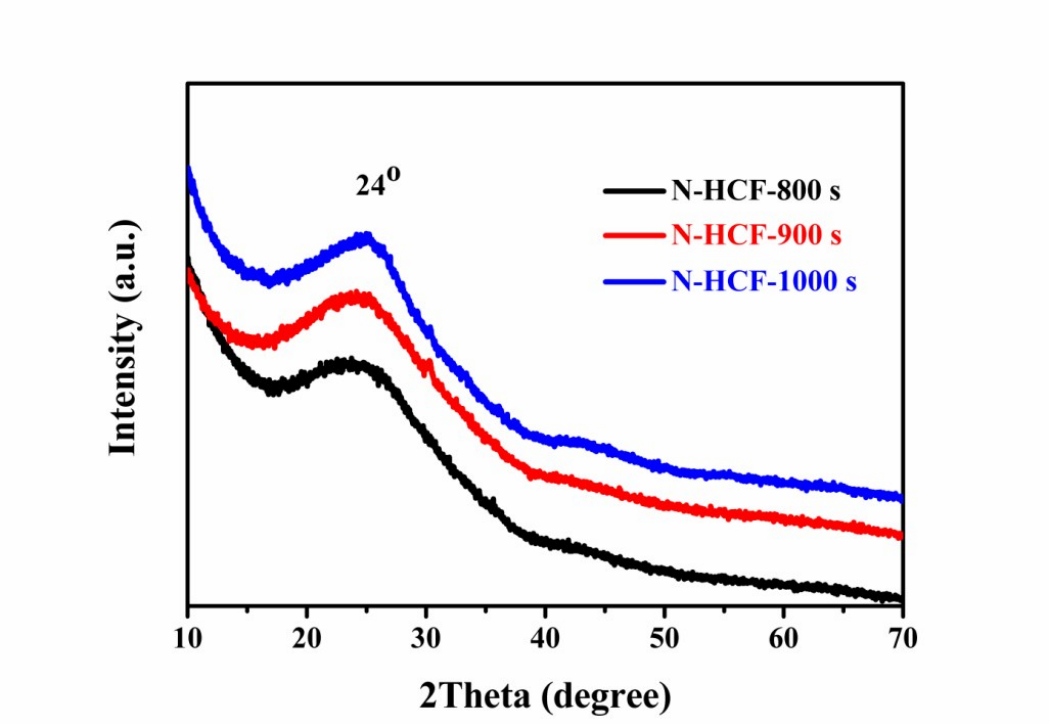

Figure S4 Wide angle XRD patterns of N-HCF-Ts synthesized by slow heating for 2h at corresponding temperature.

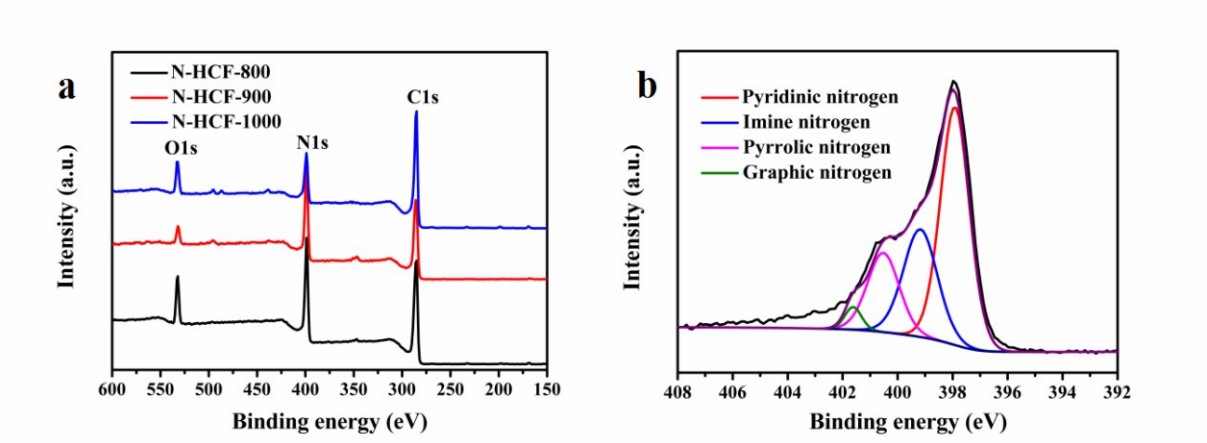

Figure S5 (a) Survey XPS spectra of various N-HCF-Ts, (b) N1s of N-HCF-900 synthesized with normal heating procedures: From room temperature to 600 °C within 4 h, then the temperature was elevated to 900 °C for 1h.

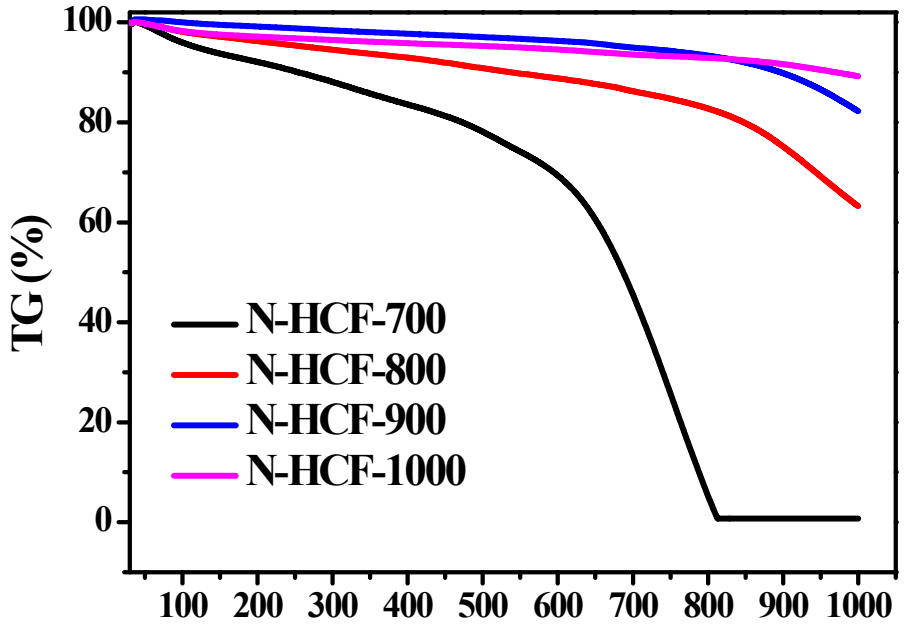

Figure S6 TG curves of various N-HCF-Ts under flowing nitrogen condition.

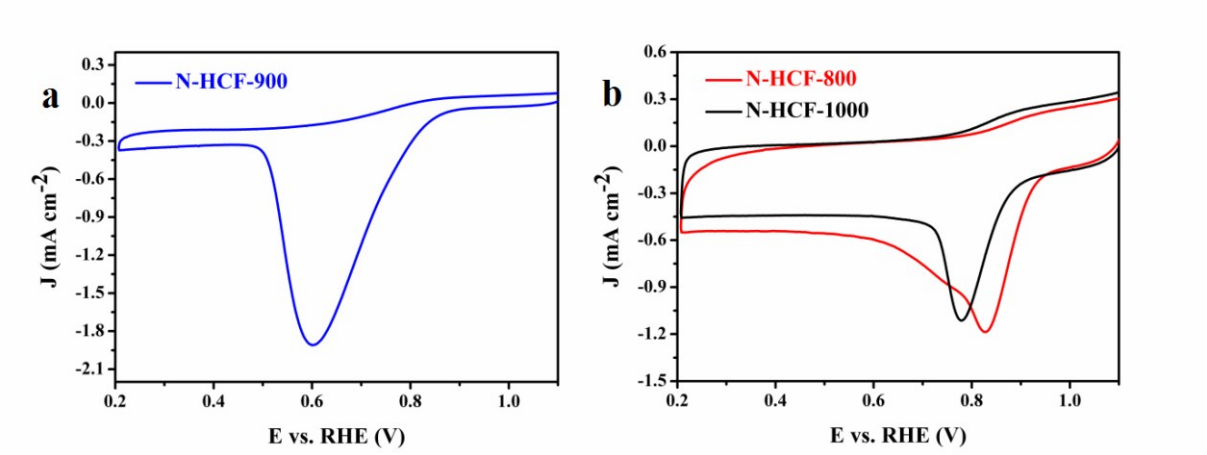

Figure S7 (a) CV curves of N-HCF-900 synthesized with normal heating procedures and (b) CV curves of N-HCF-800 and N-HCF-1000 in O_2 saturated 0.1 M KOH aqueous solution with a scan rate of 10 $mV \cdot s^{-1}$.

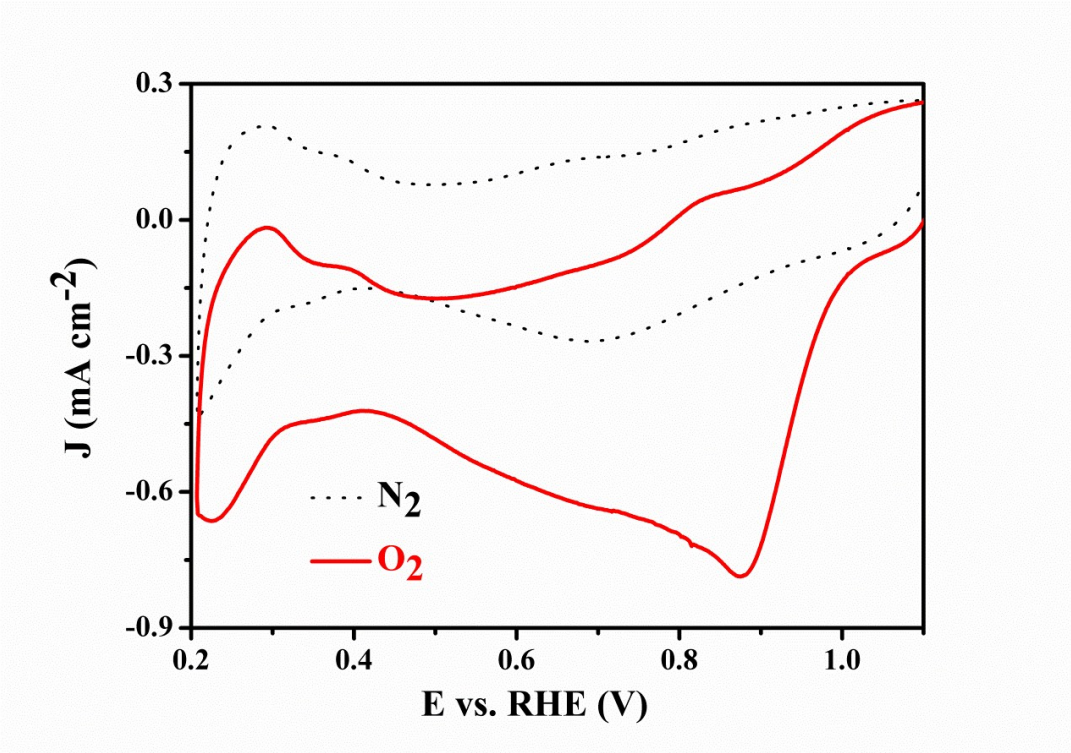

Figure S8 CV curves of Pt/C in N_2 and O_2 saturated 0.1 M KOH aqueous solution with a scan rate of 10 $mV \cdot s^{-1}$.

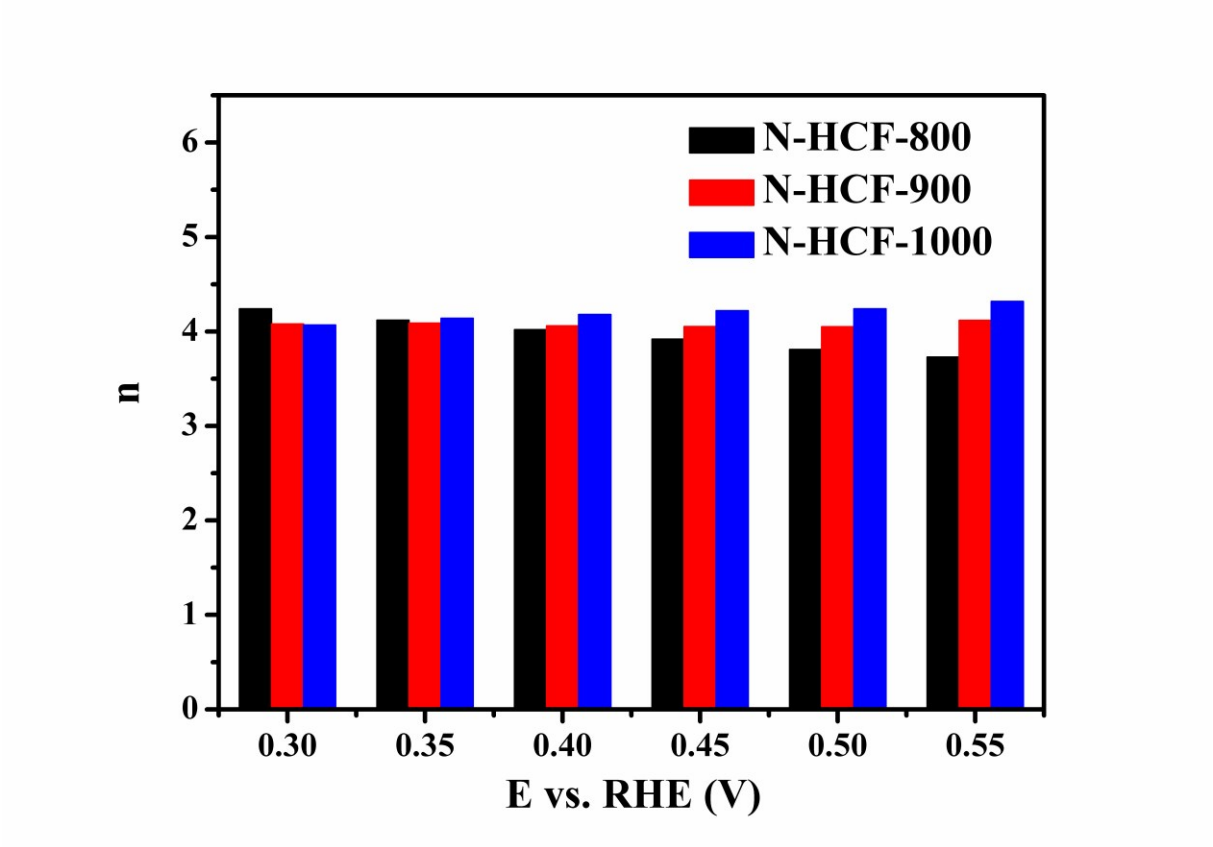

Figure S9 The electron numbers of various N-HCF-Ts calculated from their K-L plots, respectively.

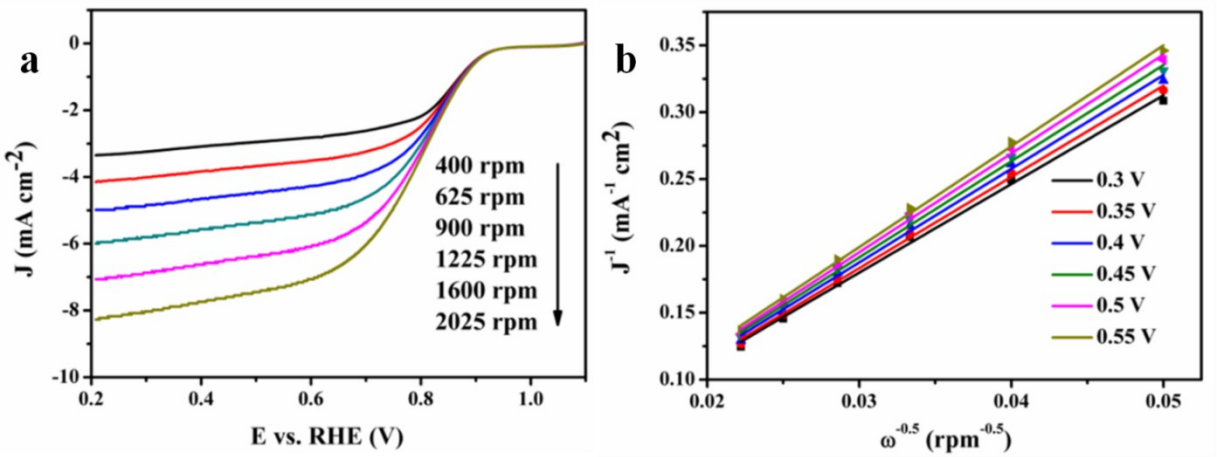

Figure S10 a) LSV curves of N-HCF-800 at different rotating rates. b) K-L plots at different potentials based on the results of (a).

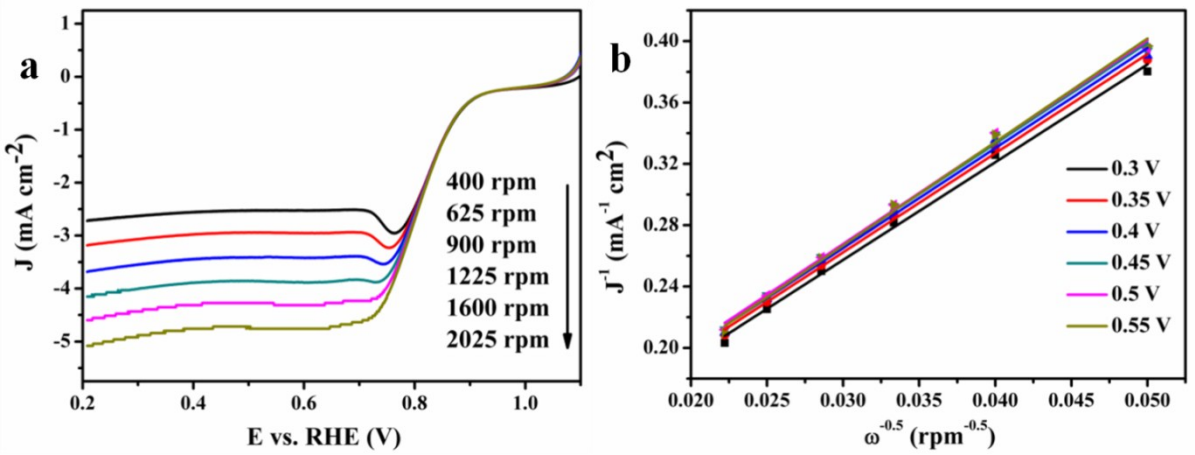

Figure S11 a) LSV curves of N-HCF-1000 at different rotating rates. b) K-L plots at different potentials based on the results of (a).

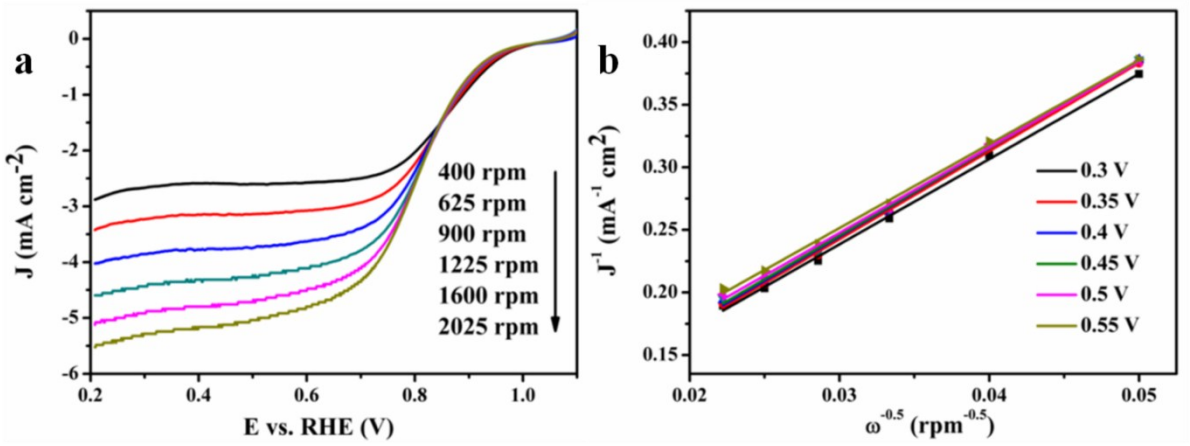

Figure S12 a) LSV curves of Pt/C at different rotating rates. b) K-L plots at different potentials based on the results of (a). The electron numbers were calculated to be about 4.

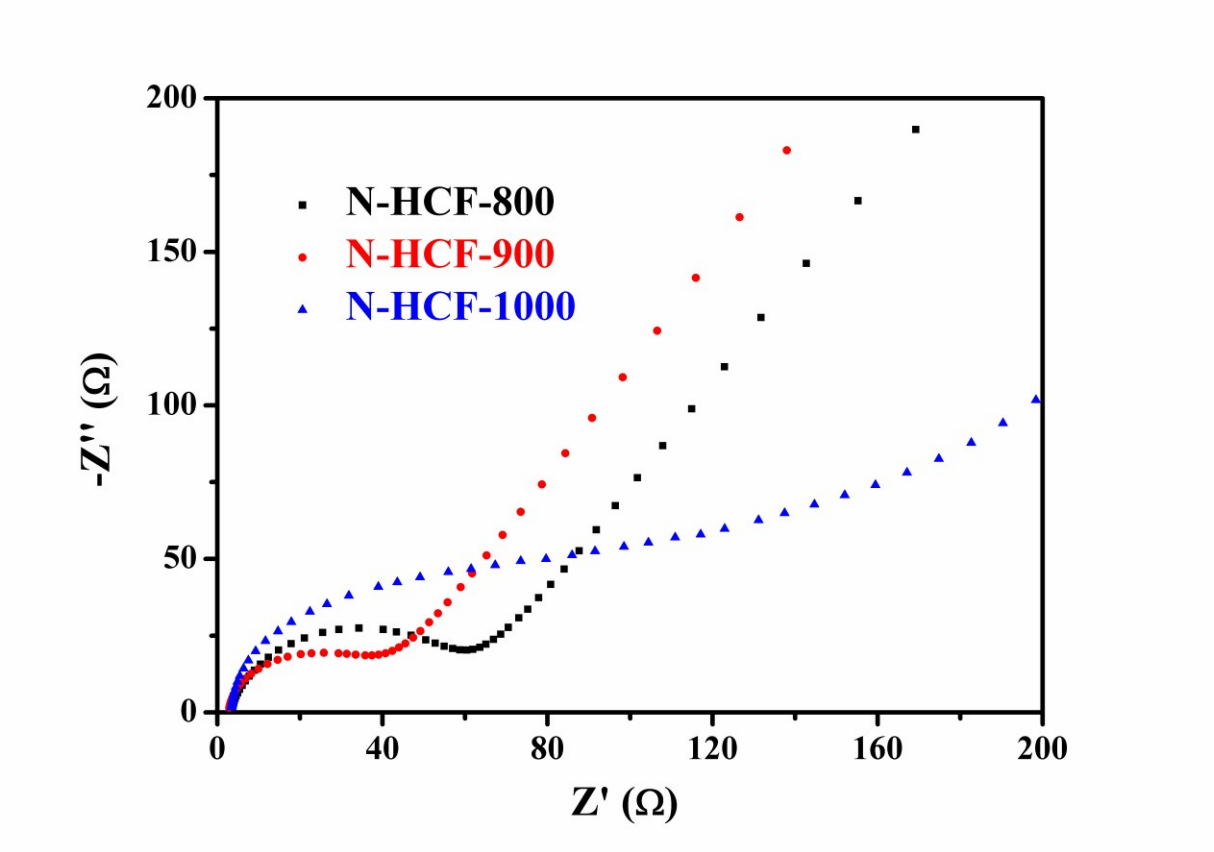

Figure S13 Electrochemical impedance spectroscopy (EIS) analyses of the N-HCF-Ts catalysts. EIS were recorded in 0.1 M KOH at 1 V vs RHE with 5 mV ac potential from 1 Hz to 2000 kHz.

Table S1 A summary of nitrogen contents, BET surface areas and pore volumes on other porous carbons reported in the literature.

Porous carbons	N Contents (wt%)	S_{BET} (m^2/g)	V_p (cm^3/g)	References
AS-4-800	-	2850	1.35	*Energy Environ. Sci.*, **2011**, *4*, 1765
SU-MAC-800	2.58	2369	0.81	*J. Am. Chem. Soc.*, **2016**, *138*, 1001
NGF-1	-	851	4.28	*Adv. Mater.*, **2012**, *24*, 4419
HCM-DAH-1	3.53	670	0.46	*J. Am. Chem. Soc.*, **2011**, *133*, 11378
SIL-6 (mesoporous carbon nitrides)	45.9	939	0.92	*Energy Environ. Sci.*, **2011**, *4*, 4668
3D HPG	-	1810	1.22	*Adv. Mater.*, **2013**, *25*, 2474
CAS40-1.75	2.93	1101	4.31	*J. Mater. Chem. A*, **2013**, *1*, 8961
MDCM	-	2700	5.35	*Adv. Mater.*, **2015**, *27*, 4903
HPC5b2-1000	-	2517	5.53	*Energy Environ. Sci.*, **2014**, *7*, 355
NMCS-1	7.65	363	0.48	*Angew. Chem. Int. Ed.*, **2015**, *54*, 588
ZnFumarate	-	4793	3.99	*Chem. Commun.*, **2013**, *49*, 2192
KCU-C 4-2	-	1327	4.1	*Energy Environ. Sci.*, **2013**, *6*, 1785
THPC	6.25	2870	2.19	*Energy Environ. Sci.*, **2013**, *6*, 2497
K900	-	2064.8	1.41	*Nanoscale*, **2014**, *6*, 12120
CPC-700	6.9	3242	1.51	*Chem. Mater.*, 2015, 27, 1349
A-NMC	10.8	1417	0.91	*Adv. Funct. Mater.*, **2013**, *23*, 2322
Meso-PoPD	9.5	685	0.71	*Nat. Comm.*, **2014**, *5*, 4973
N-CNS-120	11.6	1077	3.06	*Adv. Mater.,* **2016***, 28*, 5080
MCN/C	22.1	338	0.06	*Chem. Eng. J.,* **2012***, 203,* 63.
H-NMC-2.5	13.1	537	0.17	*Adv. Funct. Mater.,* **2013**, **23**, 2322
NPC-2	4.5	1256	0.52	*Environ. Sci. Technol.* **2015**, *49*, 7063.

a-NDC6	4.2	1360	0.57	*Chem. Commun.* **2012**, *48*, 735.
N-HCF-1000	**13.4 (60.1 % pyridinic nitrogen)**	**1073**	**6.45**	**This work**
N-HCF-900	**19.8 (60.3 % pyridinic nitrogen)**	**1434**	**8.47**	**This work**
N-HCF-800	**24.3 (61.2 % pyridinic nitrogen)**	**897**	**4.45**	**This work**
N-HCF-900[a]	**16.2 (50.3 % pyridinic nitrogen)**	**910**	**4.68**	**This work**

[a] Synthesized with normal heating procedures: From room temperature to 600 °C within 4 h, from 600 to 900 °C within 2 h and calcination at 900 °C for 1h.

Table S2. Summary of reported ORR performance of metal-free catalysts. All catalysts were tested in 0.1 M KOH.

Sample	Catalyst loading (mg cm^{-2})	Onset[a] potentials (V vs. RHE)	Reduction[b] potentials (V vs. RHE)	Limiting current density @1600rpm (mA cm^{-2})	Reference
N-HCF-800	**0.2**	**0.915**	**0.83**	**7.07**	**This work**
N-HCF-900	**0.2**	**0.921**	**0.83**	**7.74**	
N-HCF-1000	**0.2**	**0.875**	**0.69**	**4.60**	
Pt/C	**0.2**	**0.914**	**0.87**	**5.89**	
VA-NCNTs	unknown	unknown	0.75	4.1@1400rpm	*Science* **2009**, *323*, 760
PoPD	0.1	unknown	0.83	5.8	*Nat. Commun.* **2014**, *5*, 4973
N-CNS	0.2	0.89	0.76	5.8	*Adv. Mater.* **2016**, *28*, 5080
NG	0.29	unknown	0.80	7.8	*Angew. Chem. Int. Ed.* **2012**, *51*, 9689
CA-TCA	0.29	0.84	0.65	1.82	*Green Chem.* **2012**, *14*, 1515
NSG700	0.12	0.86	0.71	4.1	*Chem. Commun.* **2014**, *50*, 4839
NCNC	0.10	0.84	0.75	40@2500rpm	*Adv. Mater.* **2012**, *24*, 5593
N-graphene QDs	unknown	0.97	0.71	12.2	*J. Am. Chem. Soc.* **2012**, *134*, 18932
NG	0.14	0.87	0.65	2.85	*Adv. Energy Mater.* **2012**, *2*, 884
PDI- NOMGAs	0.026	0.84	0.71	6.1	*Angew. Chem. Int. Ed.* **2010**, *122*, 2619
VA-BCN	unknown	unknown	0.70	5.7@1000rpm	*Angew. Chem. Int. Ed.* **2011**, *50*, 11756
NDCN	0.61	0.96	0.69	5.68	*Angew. Chem. Int. Ed.* **2014**, *126*, 1596

NG	0.038	0.93	0.65	7.8	*Adv. Funct. Mater.* **2012**, *22*, 3634
POMC	unknown	0.86	0.78	5.3	*J. Am. Chem. Soc.* **2012**, *134*, 16127
S-graphene	unknown	unknown	0.68	7.2	*ACS Nano* **2012**, *6*, 205
PG	0.05	0.92	0.60	3.67	*Adv. Mater.* **2013**, *25*, 4932
NHCS	0.32	unknown	0.69	5.87	*Nanoscale* **2016**, *8*, 18134
N, S-HCS	unknown	0.93	0.78	5.5	*Nanoscale* **2016**, *8*, 19086

[a]The potential value corresponding to 5% of the diffusion-limited current density (*J*L) was defined as the onset potential.[1]

References

1 X. Zhou, J. Qiao, L. Yang, J. Zhang, *Adv. Energy Mater.* 2014, 4, 1301523.