

Supplementary Information

Cellulose Dissolution and Encapsulation Strategy to Prepare Carbon Nanospheres with Ultra-Small Size and High Nitrogen Content for Oxygen Reduction Reaction

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RHE calibration

The calibration was performed CV at a scan rate of 5 mV s^{-1} in the high purity H_2 -saturated 0.1 M KOH with a Pt plate ($1 \text{ cm} \times 1 \text{ cm}$) as a working electrode, Hg/HgO electrode as a reference electrode, and platinum wire as a counter electrode. The average of the two potentials at which the current density equaled zero was taken to be the thermodynamic potential for the hydrogen electrode reactions (**Fig. S1**), $E(\text{vs. RHE}) = E(\text{vs. Hg/HgO}) + 0.896 \text{ V}$.

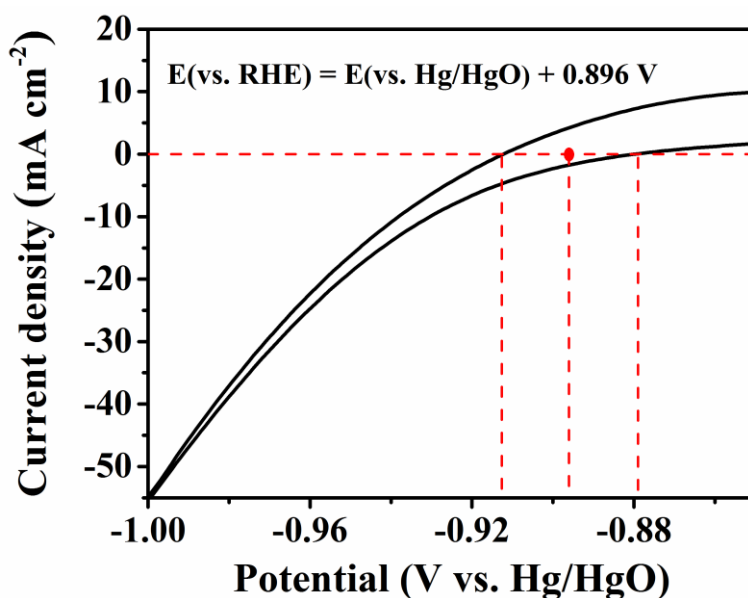


Fig. S1 Calibration of potentials of the Hg/HgO electrode in 0.1 M KOH to the reverse hydrogen electrode (RHE).

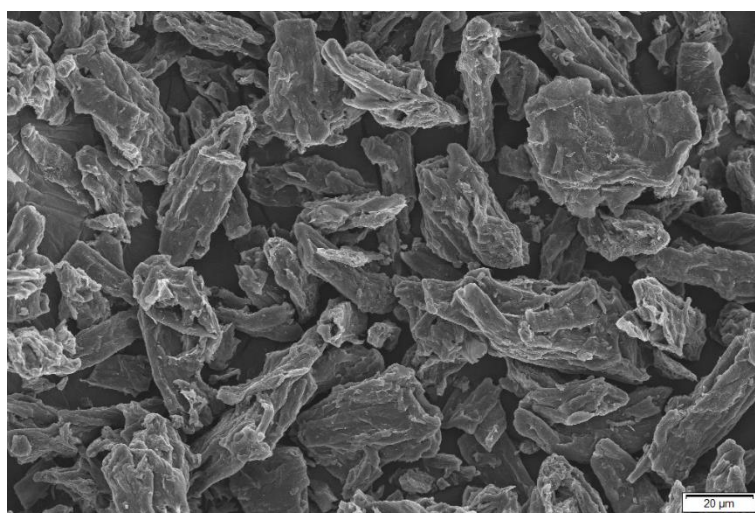


Fig. S2 SEM image of microcrystalline cellulose directly derived carbon.

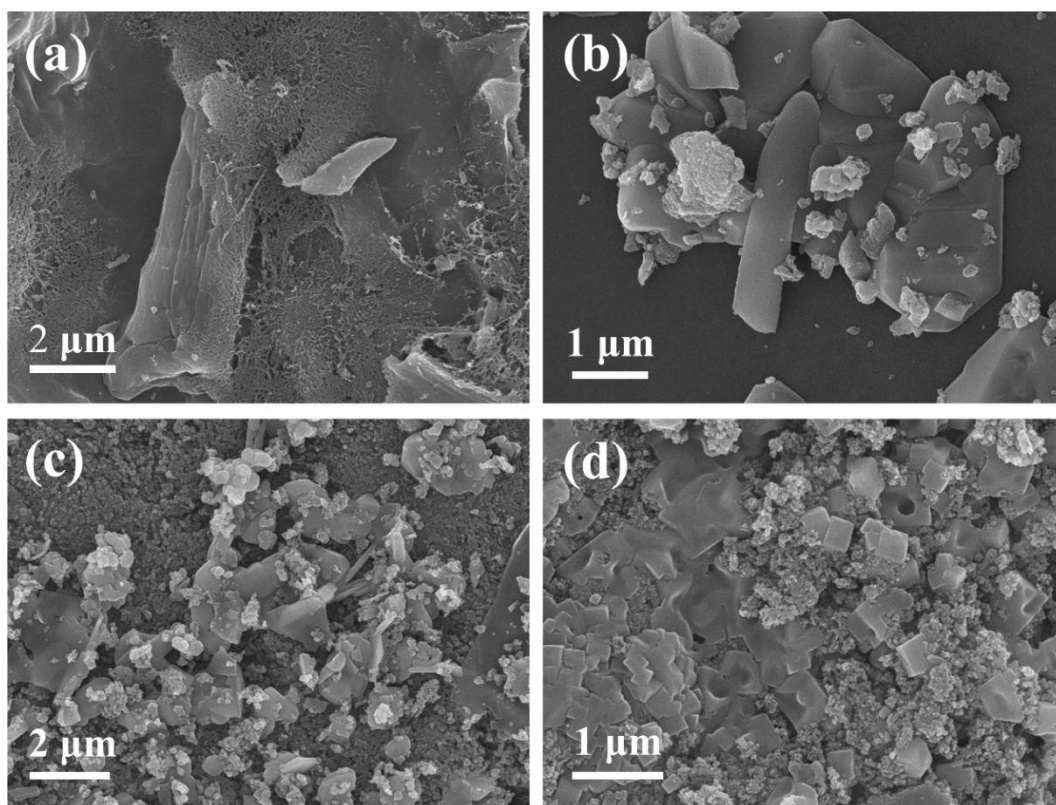


Fig. S3 SEM images of (a) NCN@ZnCl₂-0, (b) NCN@ZnCl₂-2, (c) NCN@ZnCl₂-3 and (d) NCN@ZnCl₂-7, respectively.

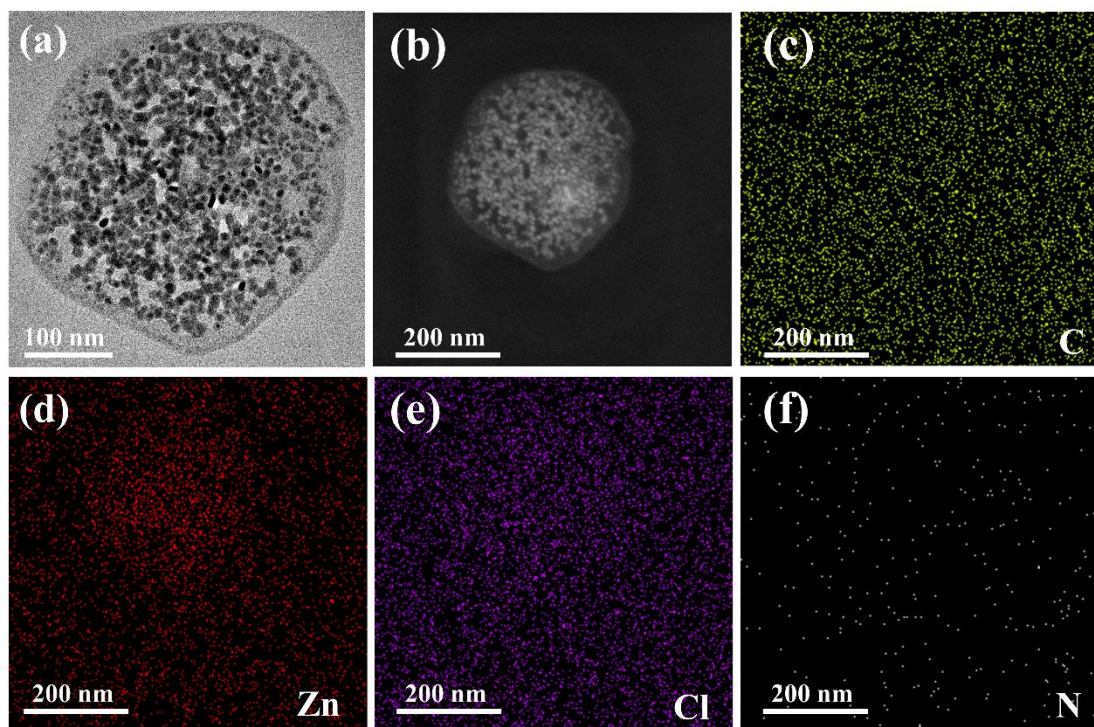


Fig. S4 TEM image (a), scanning transmission electron microscopy (STEM) image (b) and corresponding C (c), Zn (d), Cl (e), and N (f) elemental mappings of NCN@ZnCl₂-7 at 500 °C.

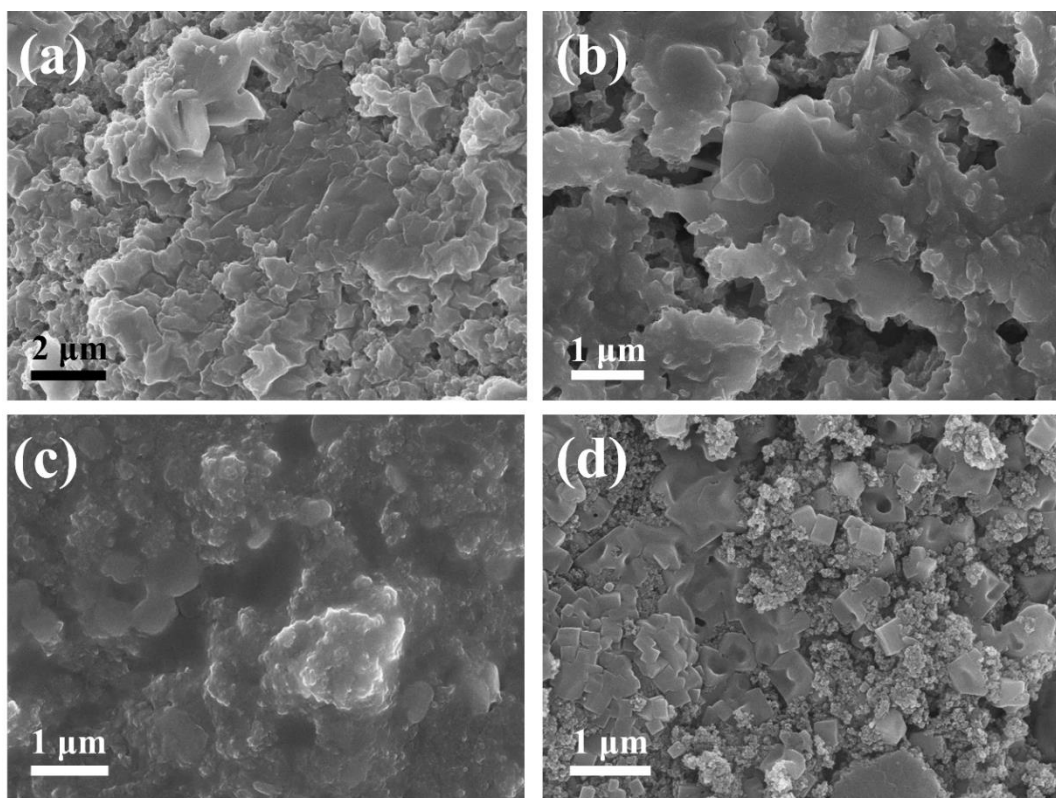


Fig. S5 SEM images of NCN@ZnCl₂-7 pyrolysis state: (a) pyrolysis at 500 °C, (b) 600 °C, (c) 700 °C and (d) 800 °C.

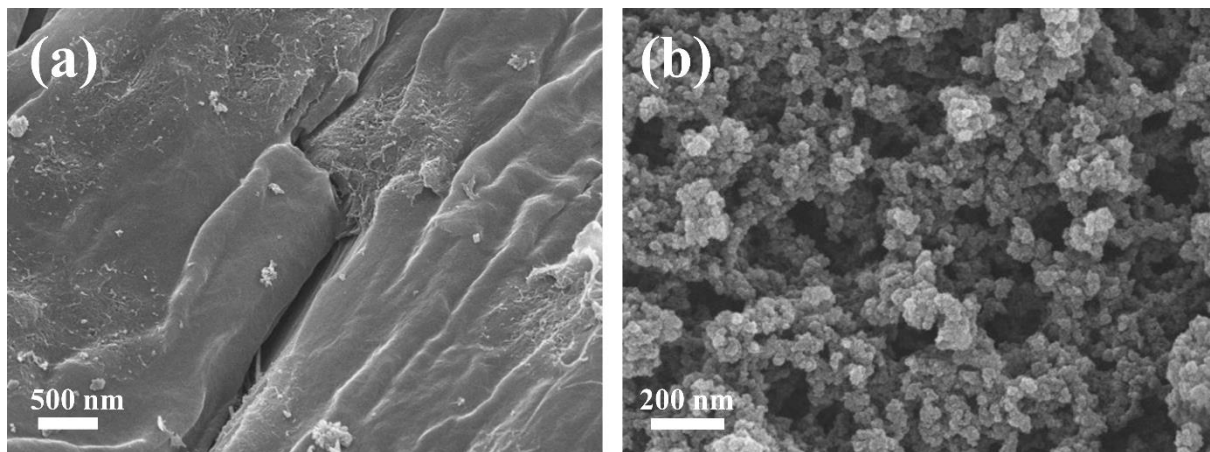


Fig. S6 SEM images of (a) NCN-0 and (b) NCN-7.

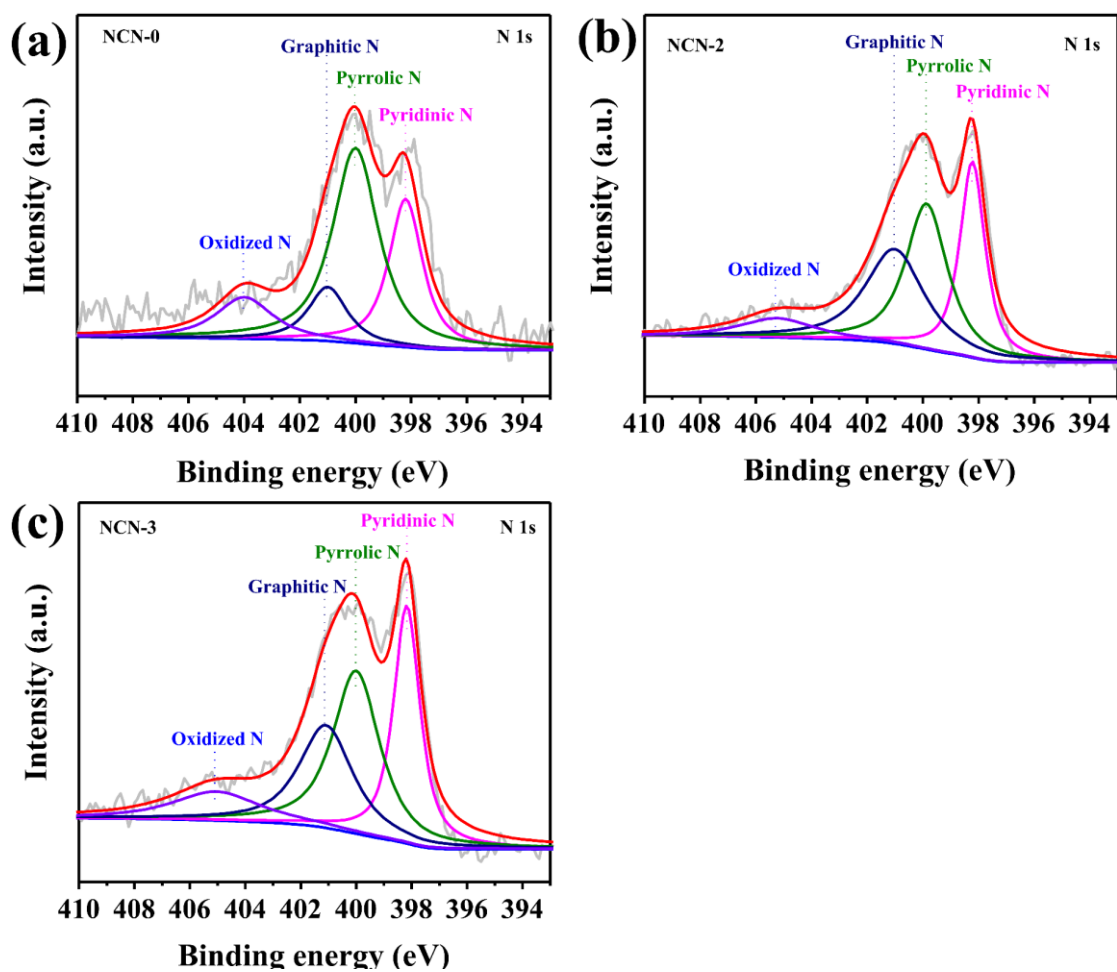


Fig. S7 High-resolution N 1s XPS spectra of (a) NCN-0, (b) NCN-2 and (c) NCN-3, respectively.

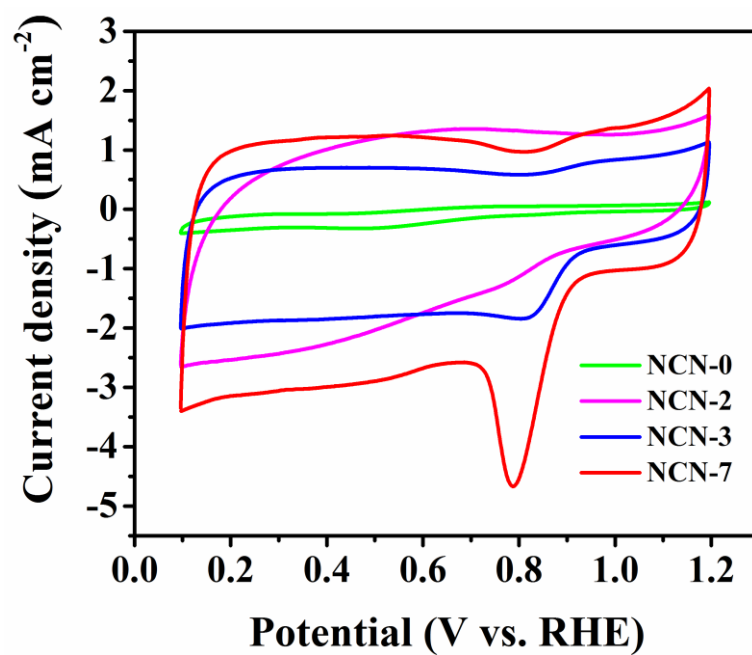


Fig. S8 Cyclic voltammetry (CV) curves of NCN-X (X=0, 2, 3 and 7) conducted in O₂-saturated KOH solution with a scan rate of 50 mV s⁻¹.

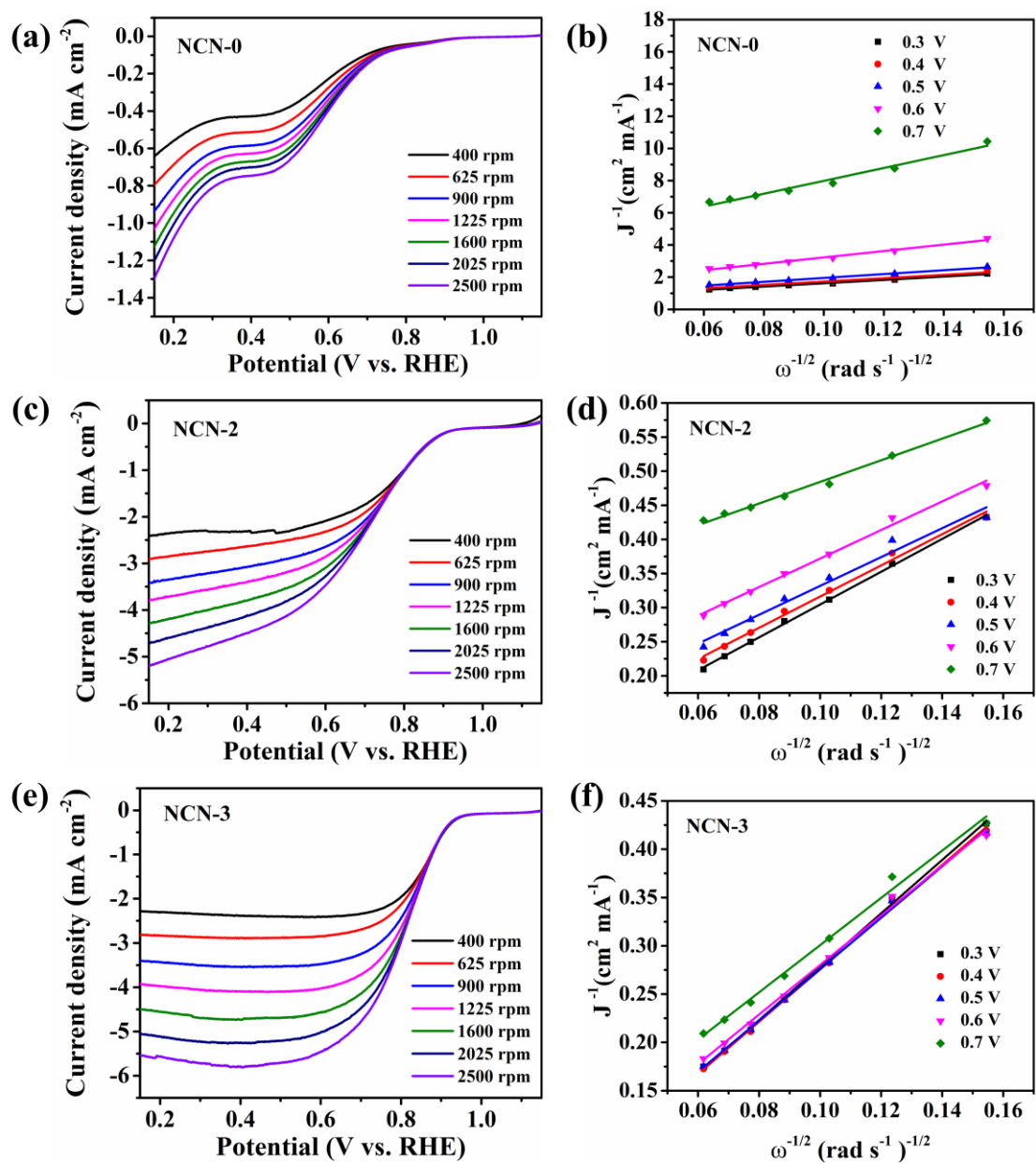


Fig. S9 (a, c, e) LSV curves and (b, d, f) corresponding K-L plots of (a, b) NCN-0, (c, d) NCN-2, and (e, f) NCN-3 in O₂-saturated 0.1 M KOH solution.

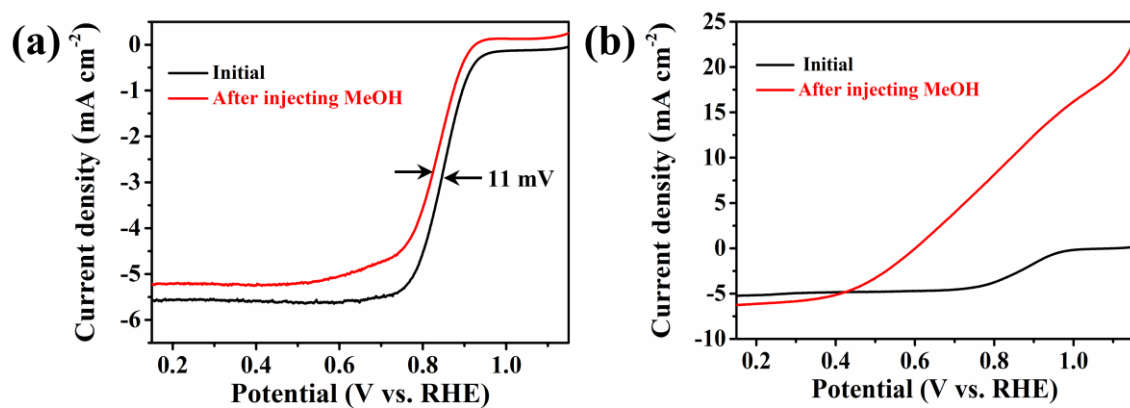


Fig. S10 LSV curves showing the comparison of NCN-7 (a) and 20% Pt/C (b) for ORR in O₂-saturated 0.1 M KOH solution with 5 mV s⁻¹ before (black) and after (red) injecting 10% (volume fraction) methanol.

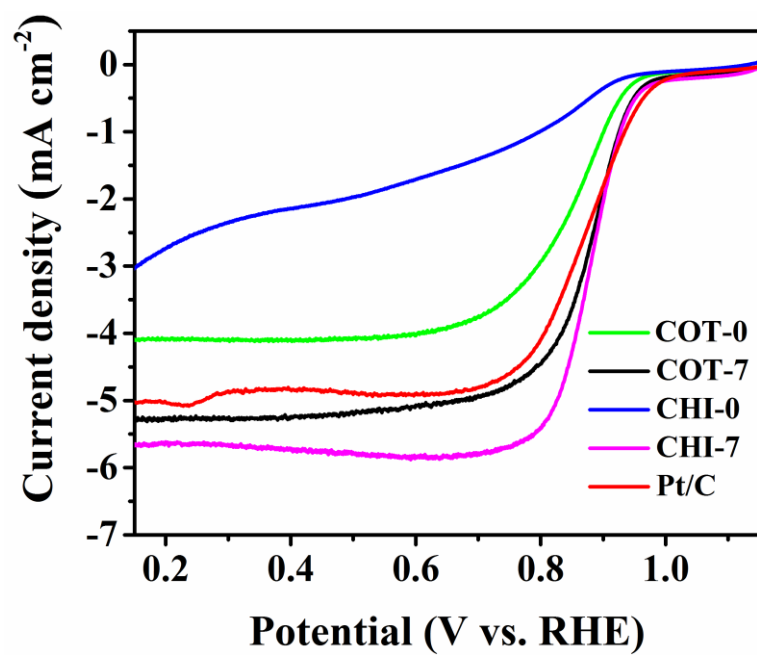


Fig. S11 LSV curves of CHI-0, CHI-7, COT-0, COT-7 and Pt/C recorded at 1600 rpm in O₂-saturated 0.1 M KOH solution with the scan rate of 5 mV s⁻¹.

Table S1 Surface atom contents and porous structural characteristics of different samples.

Sample	C (at.%)	O (at.%)	N (at.%)	Pyridinic N (at. %)	Pyrrolic N (at. %)	Graphitic N (at. %)	Oxidized N (at. %)	S _{BET} /(m ² g ⁻¹)	S _{Micro} /(m ² g ⁻¹)	S _{meso} /(m ² g ⁻¹)	V _{Pore} /(cm ³ g ⁻¹)	V _{Micro} /(cm ³ g ⁻¹)	D _{Ave} /(nm)
NCN-0	68.09	27.83	4.08	1.11	1.99	0.46	0.52	81.0	57.6	23.4	0.061	0.032	2.99
NCN-2	83.94	9.03	7.02	1.95	2.37	2.16	0.55	1,468.0	410.2	1057.8	0.89	0.21	2.43
NCN-3	83.9	7.13	8.97	2.59	3.10	2.25	1.03	1,512.3	448.7	1063.6	1.41	0.28	3.74
NCN-7	85.42	6.03	8.56	3.06	2.33	2.50	0.68	1,655.0	163.2	1491.8	2.08	0.10	5.03
CHI-0	75.93	19.26	4.81	0.78	1.19	2.09	0.75						
CHI-7	86.17	7.96	5.87	1.52	1.43	1.60	1.32						
COT-0	83.53	12.56	3.91	0.79	1.32	1.14	0.66						
COT-7	85.23	9.56	5.21	1.42	1.27	1.46	1.06						

S_{BET}: BET specific surface area, S_{Micro}: Micropore surface area, V_{Pore}: Pore volume, V_{Micro}: Micropore volume, D_{Ads}: Adsorption average pore diameter (4V/A by BET).

Table S2 Comparison of N content and electrocatalytic performances of NCN-7 and biomass-derived carbon materials in other reported work.

Source of biomass	Materials	N content /%	E _{onset} /V	E _{1/2} /V	J _L /(mA cm ⁻²)	Reference
Soybean	Fe/C-SOYB	4.95	0.84	0.68	2.6	J. Power Sources, 2014, 269 , 841-847
Enoki mushroom	N-C@CNT-900	3.2	0.94	0.81	3.98	Nanoscale, 2015, 7 , 15990-15998
Sodium alginate	Ni/NiO/NiCo ₂ O ₄ /N-CNT-As	1.2	0.89	0.74	≈4.9	J. Mater. Chem. A, 2016, 4 , 6376-6384.
Corn silk	N-P-Fe-C	6.55	0.957	0.852	≈5.51	J. Mater. Chem. A, 2016, 4 , 8602-8609
Filter paper	FP-Fe-N-850	7.32	0.98	≈8.3	5.0	Angew. Chem., Int. Ed., 2016, 55 , 1355-1359
Lysine	NCHCs	4	0.92	≈0.80	≈6.0	Nanoscale, 2017, 9 , 1059-1067
Pomelo peel	PPC-NaZnFe	2.92	-	0.86	≈5.9	Carbon, 2018, 130 , 692-700
Chitosan	Co ₁₆ %-NCNT-T800	7.61	-	0.835	6.92	J. Mater. Chem. A, 2018, 6 , 5740-5745.
Glucose	N _{0.54} -Z ₃ /M ₁ -900	3.62	0.94	0.824	4.3	Energy Environ. Sci., 2019, 12 , 648-655
Raw wood	N/E-HPC-900	3.7	-	0.84	≈5.9	Adv. Mater., 2019, 31 , 1900341
Cellulose	NCN-7	8.56	0.99	0.87	5.5	This work