Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supplementary material

N-doped hierarchical porous metal-free catalysts derived from covalent triazine frameworks for efficient oxygen reduction reaction

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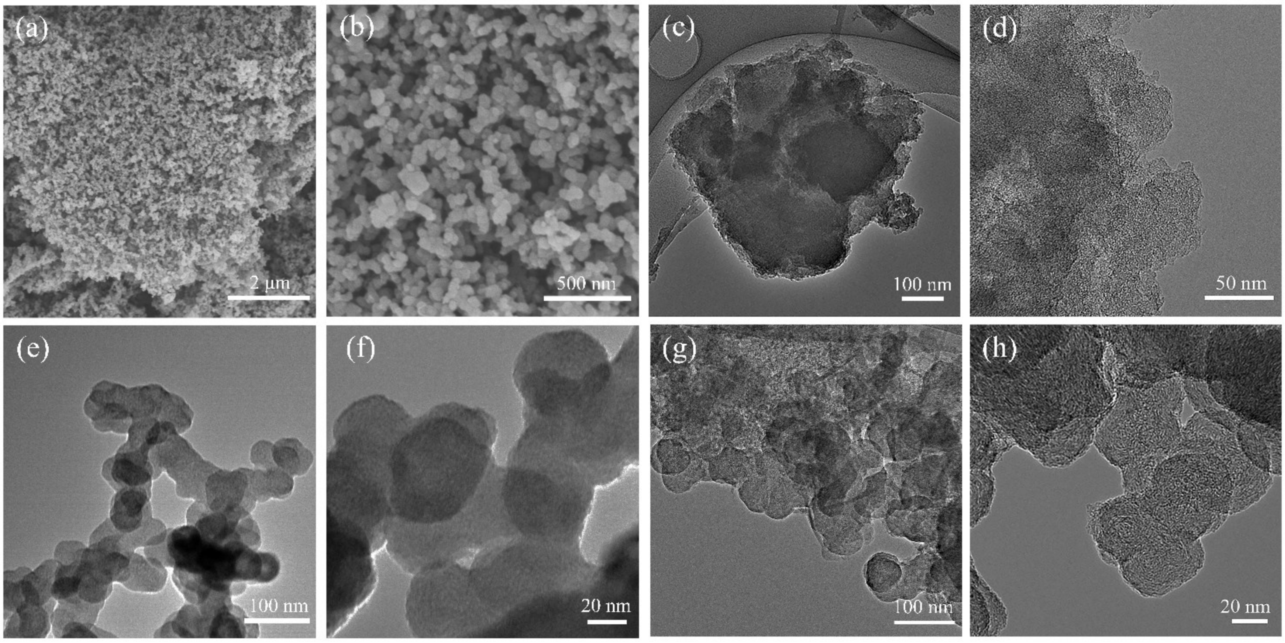

Fig. S1 SEM images of (a–b) Super P; TEM images of (c–d) CTF, (e–f) Super P, and (g–h) CTF-Super P-10.

Table S1. Specific Surface area (SSA) and pore volume characteristics of CTF, CTF-Super P-5, CTF-Super P-10, CTF-Super P-15 and Super P.

Sample	The ratio of 1,4-dicyanobenzene monomer, $ZnCl_2$, and Super P	SSA (m^2/g)	Micropore volume (cm^3/g)	Mesopore volume (cm^3/g)
CTF	1/10/0	1680	0.780	0.600
CTF-Super P-5	1/10/5	1873	0.898	1.568
CTF-Super P-10	1/10/10	1925	0.776	1.852
CTF-Super P-15	1/10/15	835	0.396	1.219
Super P	/	49	0.018	0.374

Table S2. The chemical compositions of catalysts obtained by XPS

Sample	C (at%)	N (at%)	O (at%)
CTF	82.79	6.56	10.36
CTF-Super P-10	87.45	4.16	8.19

Table S3. Summary of the ORR performance of CTF, CTF-Super P-5, CTF-Super P-10, CTF-Super P-15, and 20% Pt/C obtained from LSV curves in O_2-saturated 0.1M KOH at 1600 rpm.

Sample	Onset potential (E_o/V)	Half-wave potential ($E_{1/2}$/V)	Limiting current density (J_m/mA·cm^{-2})
CTF	1.008	0.881	4.76
CTF-Super P-5	0.997	0.882	5.06
CTF-Super P-10	0.981	0.883	5.31
CTF-Super P-15	0.949	0.838	4.55
Pt/C	1.009	0.886	4.54

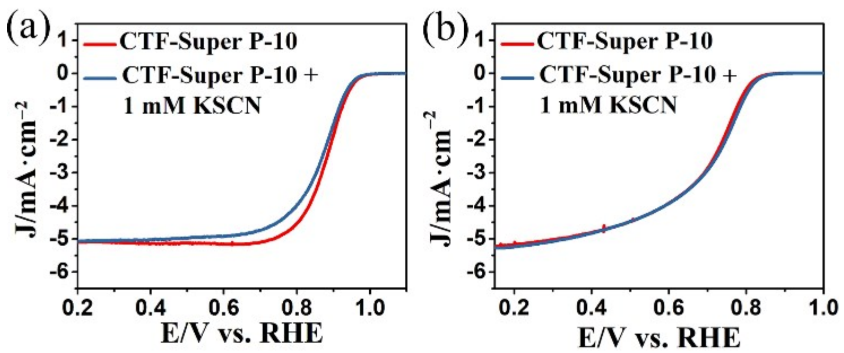

Fig. S2 LSV curves of CTF-Super P-10 before and after the addition of 1mM KSCN at a rotation rate of 1600 rpm with a scan rate of 10 mV s^{-1} (a) in O_2-saturated 0.1 M KOH solution and (b) in O_2-saturated 0.1 M $HClO_4$ solution.

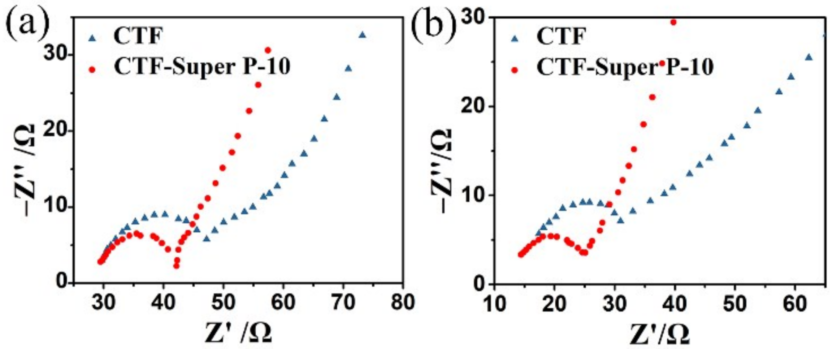

Fig. S3 Nyquist plots of CTF and CTF-Super P-10 (a) in O_2-saturated 0.1 M KOH solution and (b) in O_2-saturated 0.1 M $HClO_4$ solution.

Table S4. Comparison of the onset potential (E_o vs. RHE), half-wave potential ($E_{1/2}$ vs. RHE) and limiting current density (J_m) of N-doped metal-free catalysts for ORR in alkaline and acidic medium.

Catalyst	Mass loading ($mg \cdot cm^{-2}$)	rotation speed (rmp)	Electrolyte	E_o (V)	$E_{1/2}$ (V)	J_m ($mA \cdot cm^{-2}$)	Ref
CTF-Super P-10	0.70	1600	0.1 M KOH	0.981	0.883	5.31	This work
			0.1 M $HClO_4$	0.840	0.717	5.40	This work
VA-NCNT	/	1400	0.1 M KOH	0.885	/	4.1	1
N-graphene	0.11	1000	0.1 M KOH	0.775	0.665	/	2
Meso-EmG	0.82	1600	0.1M KOH	1.0	/	/	3
			0.1 M $HClO_4$	0.829	/	/	
g-C_3N_4@CMK-3	0.09	1500	0.1 M KOH	0.865	/	4.0	4
Carbon-L	0.10	1600	0.1 M KOH	0.861	0.70	4.6	5
NPMC-1000	0.50	1600	0.1 M KOH	0.94	0.85	4.1	6
NPC-F	0.24	1600	0.1 M KOH	0.91	0.84	5.5	7
MPC-np	0.05	1600	0.1 M KOH	0.865	/	5.0	8
TTF-700-96	/	1600	0.1 M KOH	0.828	0.744	5.0	9
N-GQDs/G-12	0.07	1600	0.1 M KOH	0.875	/	3.7	10
N-CNS-120	0.21	1600	0.1 M KOH	0.889	0.755	5.79	11
NHC/rGO-950	0.28	1600	0.1 M KOH	0.95	0.83	5.64	12
			0.1 M $HClO_4$	0.75	/	/	
M1A5-900	12.37	1600	0.1 M KOH	0.99	0.87	5.8	13
			0.5 M H_2SO_4	0.81	0.53	/	
S1N6C900	/	1600	0.1 M KOH	0.95	0.83	4.86	14
			0.5 M H_2SO_4	0.785	0.47	4.50	
CTF-CSU1	0.20	1600	0.1 M KOH	0.79	0.57	5.6	15

C-Zn-MOF-74@CNFs	0.20	1600	0.1M KOH	0.91	0.770	4.466	16
TPOP-900	0.20	1600	0.1 M KOH	0.976	0.875	5.20	17

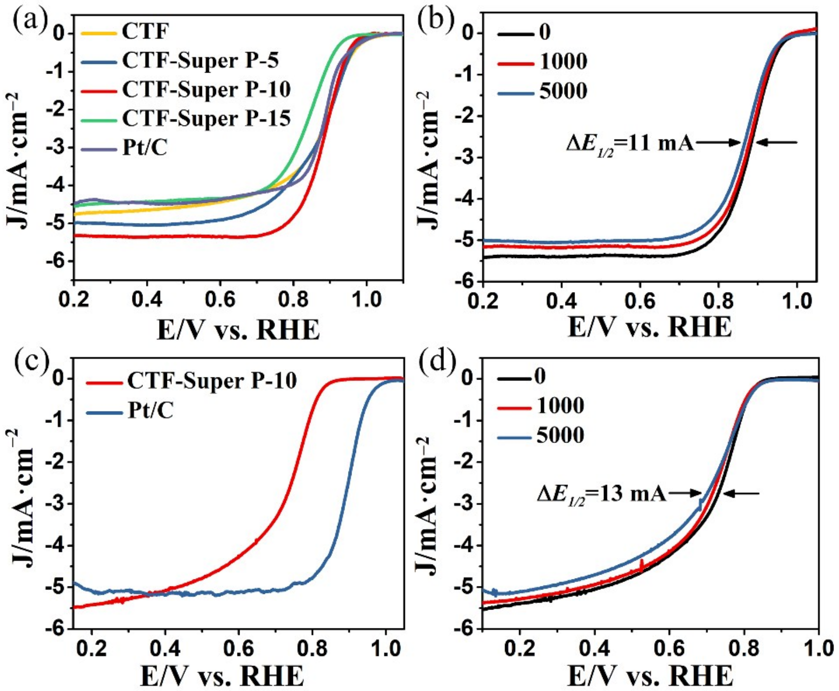

Fig. S4 (a) LSV curves of CTF, CTF-Super P-5, CTF-Super P-10, CTF-Super P-15, and Pt/C, and (b) LSV results of CTF-Super P-10 before and after 5000 potential cycles in O_2-saturated 0.1 M KOH solution. (c) LSV curves of CTF-Super P-10 and Pt/C, and (d) LSV results of CTF-Super P-10 before and after 5000 potential cycles in O_2-saturated 0.1 M $HClO_4$ solution. The above data were tested with a carbon counter electrode.

Table S5. Comparison of the ORR performance obtained from LSV curves using a carbon counter electrode and a Pt counter electrode, respectively.

Catalyst	Electrolyte	Carbon counter electrode			Pt counter electrode		
		E_o (V)	$E_{1/2}$ (V)	J_m ($mA\cdot cm^{-2}$)	E_o (V)	$E_{1/2}$ (V)	J_m ($mA\cdot cm^{-2}$)
CTF	0.1 M KOH	1.015	0.885	4.77	1.008	0.881	4.76
CTF-Super P-5	0.1 M KOH	0.997	0.883	5.00	0.997	0.882	5.06
CTF-Super P-10	0.1 M KOH	0.983	0.885	5.32	0.981	0.883	5.31
	0.1 M $HClO_4$	0.847	0.734	5.45	0.840	0.717	5.40
CTF-Super P-15	0.1 M KOH	0.950	0.839	4.55	0.949	0.838	4.55
Pt/C	0.1M KOH	1.011	0.886	4.48	1.009	0.886	4.54
	0.1 M $HClO_4$	0.994	0.896	5.09	0.989	0.891	5.08

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