Supporting Information

Boosting Oxygen Reduction Activity of Non-metallic Catalysts via Geometric and Electronic Engineering through Nitrogen and Chlorine Dual-Doping

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S1: Materials and Instrumentation:

All chemicals were purchased from commercial sources and used without further treatment unless otherwise stated. zinc chloride ($ZnCl_2$, TCI, 98%),paraformaldehyde ((CH_2O)n, Aladdin, 95%), glyoxal ($C_2H_2O_2$, Sinopharm Chemical Reagent Co., Ltd., 40% in H_2O), hydrochloric acid (HCl, Sinopharm Chemical Reagent Co., Ltd., 38%), perchloric acid ($HClO_4$, Sinopharm Chemical Reagent Co., Ltd., 70.0-72.0%), N,N-dimethylformamide (C_3H_7NO, Sinopharm Chemical Reagent Co., Ltd., AR), acetone (CH_3COCH_3, Sinopharm Chemical Reagent Co., Ltd., AR), methylbenzene (C_7H_8, Sinopharm Chemical Reagent Co., Ltd., AR), Pt-C (Alfa Aesar, 20 wt% metal), nafion solution (Sigma-Aldrich, 5% in lower aliphatic alcohols and water) were purchased from the commercial corporations.

The Raman spectrum was tested on a Labram HR800 Evolution over a range of 300-2000 cm-1. X-ray photoelectron spectroscopy (XPS) measurements were performed on an ESCALAB 250Xi X-ray photoelectron spectrometer (Thermo Fisher) using an Al Ka source (15 kV, 10 mA). Powder X-ray diffraction (PXRD) patterns were recorded on a Miniflex 600 diffractometer using Cu Kα radiation (λ = 0.154 nm) with a scan speed of 2° min^{-1} at room temperature. Transmission electron microscope (TEM) images were recorded by a FEIT 20 working at 200 kV. Aberration-corrected High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images and the EDS of samples were performed with a Titan Cubed Themis G2 300 (FEI) high-resolution transmission electron microscope operated at 200 kV. N_2 adsorption-desorption isotherm were measured using Micromeritics ASAP 2460 instrument at 77 K. Prior to nitrogen adsorption/desorption measurement, the samples were evacuated and activated at 120 °C for 10 h by molecular pump. The Nyquist plots were obtained by the electrochemical impedance spectroscopy (EIS) measurement. It was performed by applying AC voltage with 5 mV amplitude in a frequency range from 0.01 Hz to 100 kHz under open circuit potential condition.

Table S1. Element content catalyzed by XPS

	N %	Cl %
CCTF-500	5.27	0.54
CCTF-600	5.08	0.60
CCTF-700	4.76	0.62

Catalyzed by XPS.

Table S2. Element content catalyzed by element analysis

	C %	N %	H %
CCTF-500	82.02	6.61	2.65
CCTF-600	75.46	5.51	2.2
CCTF-700	72.19	4.55	1.9

Catalyzed by element analysis.

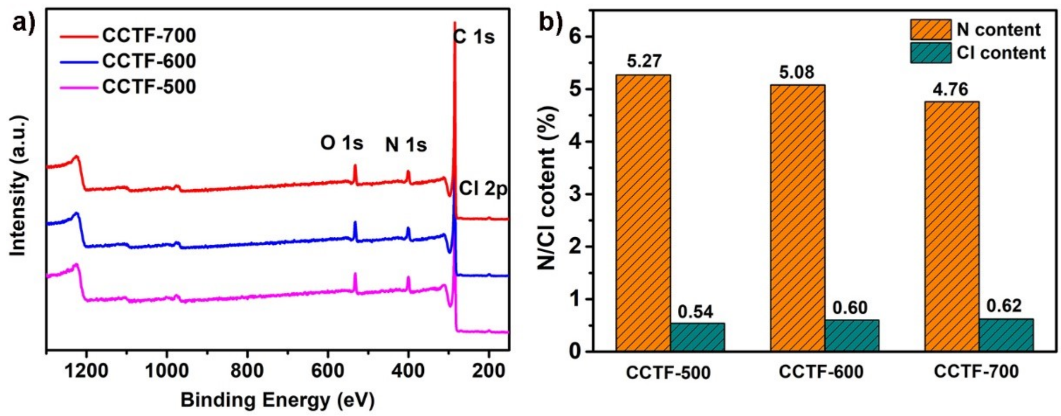


Figure S1. a) XPS survey spectrum, b) N and Cl content determined from XPS of CCTF-500, CCTF-600, CCTF-700.

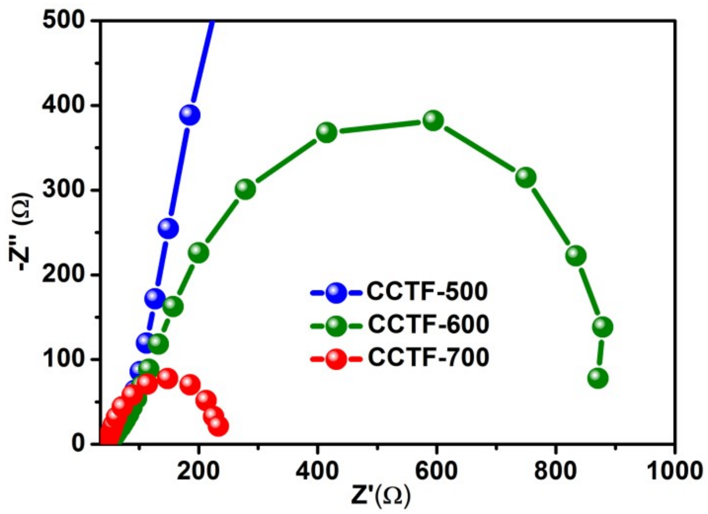


Figure S2. Nyquist plots of CCTF-500, CCTF-600, CCTF-700 over the frequency range from 100 kHz to 10 mHz.

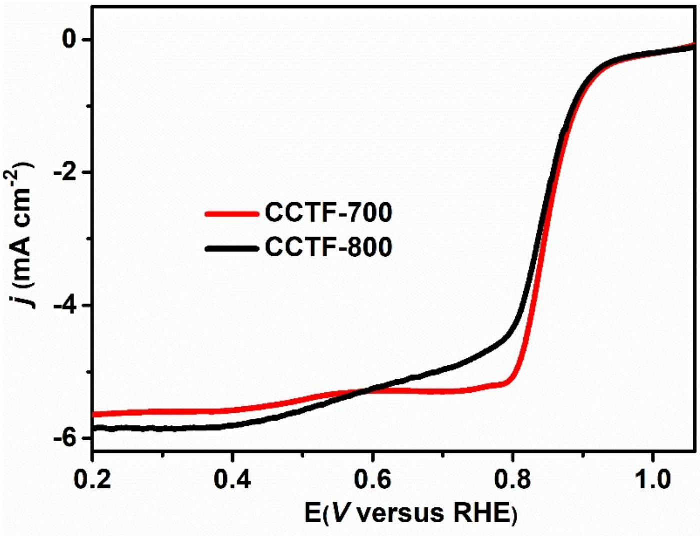


Figure S3. LSV curves of CCTF-700 and CCTF-800.

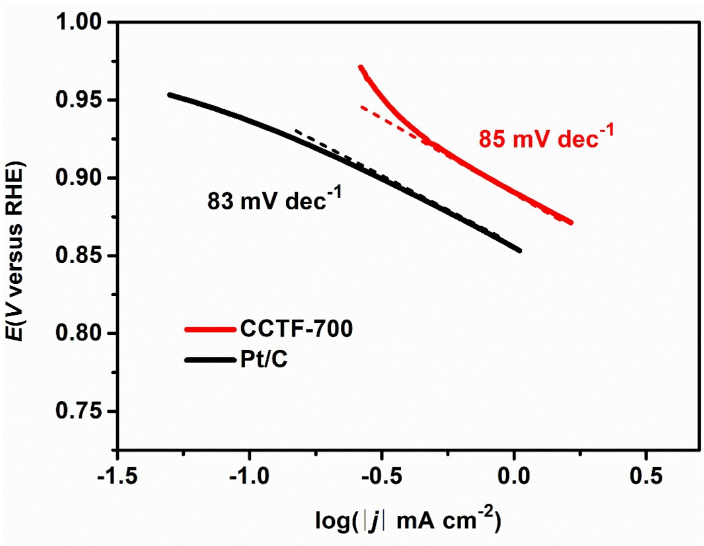
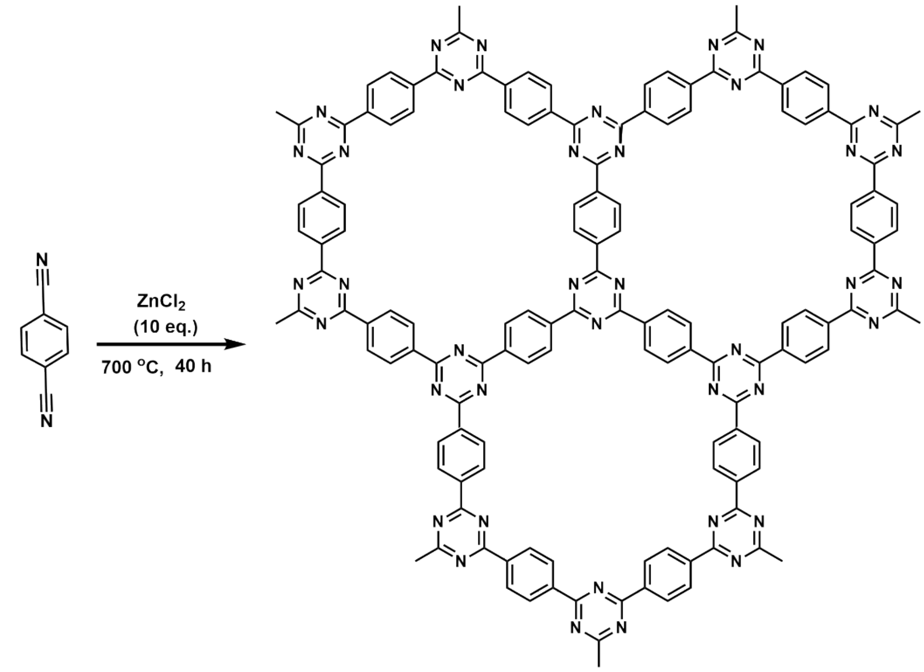


Figure S4. The corresponding Tafel plots obtained from the RDE polarization curves in 0.1 M KOH.



Scheme S1. Schematic representation of CTP-700.

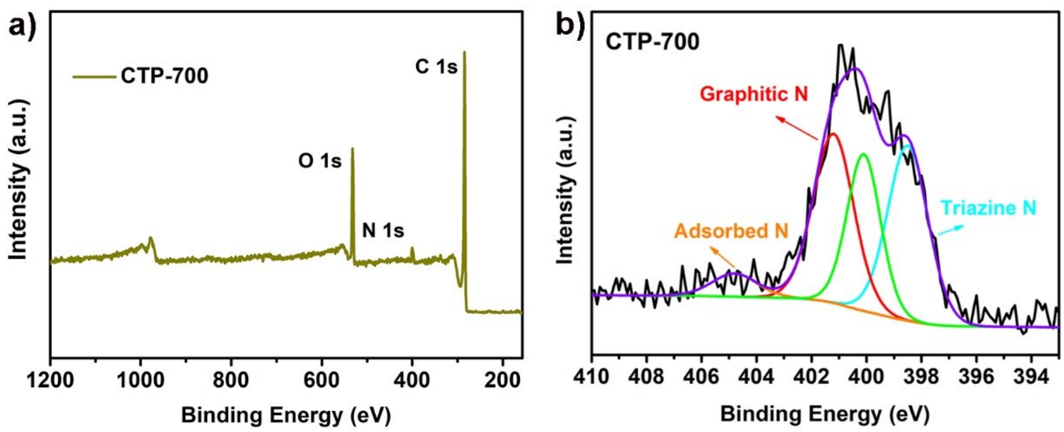


Figure S5. (a) XPS survey spectrum and (b) The high-resolution N 1s XPS spectra of CTP-700.

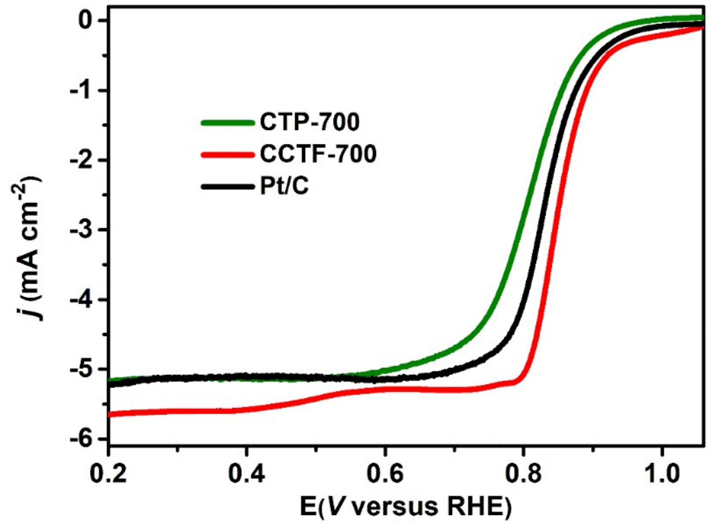


Figure S6. LSVs of different samples at 1600 rpm in 0.1M KOH.

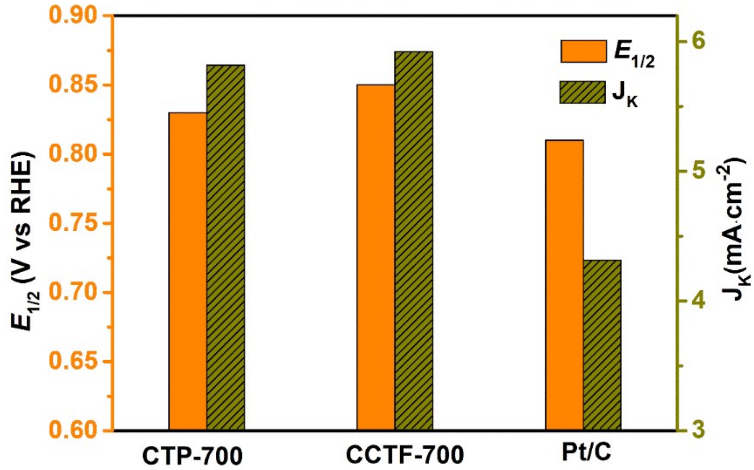


Figure S7. $E_{1/2}$ and J_k at 0.85 V for various catalysts in 0.1 M KOH.

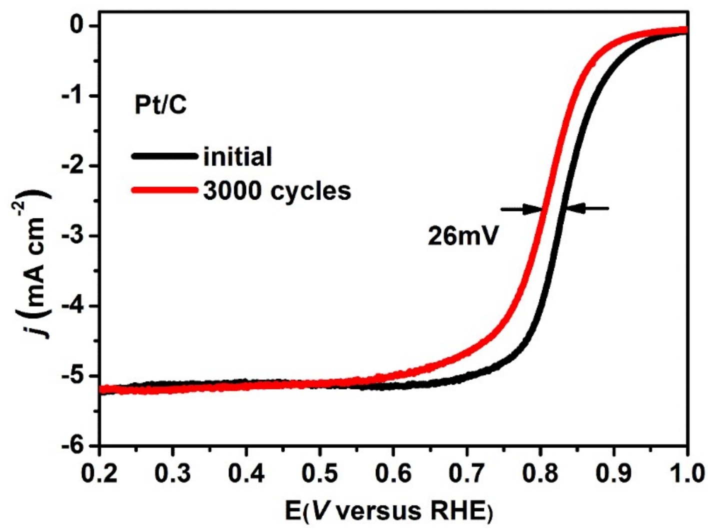


Figure S8. LSV curves of the commercial Pt/C before and after 3000 cycles.

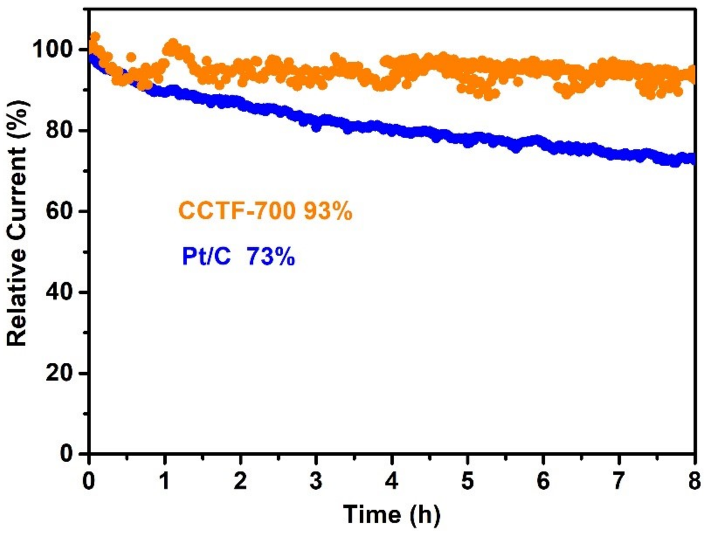


Figure S9. The current-time chronoamperometric responses of CCTF-700 and Pt/C 0.1 M KOH.

Table S3. Comparison of ORR catalytic performances in 0.1M KOH between CTF-700 and other metal-free electrocatalysts.

Class	Catalyst	Heteroatoms	Half-wave potential (V *vs.* RHE)	Onset potential (V *vs.* RHE)	Ref.
One heteroatom doped	CCTF-700	N,Cl	0.85	1.03	This work
	Pt/C		0.81	1.0	This work
	1.13% NCNTs	N	~0.65	0.76	*Small,* 2023, 19, 2302795
	Q3CTP-COFs	N	0.72	0.92	*Nano-Micro Lett.* 2023, *15,*159
	NPCM1000	N	0.755	0.875	*Energy,* 2018, 152, 333–340
	MPSA/GO1000	N	0.82	1.00	*Angew. Chem. Int.Ed.,* 2016, 55, 2230
	BINOL-CTFs	N	0.737	0.793	*ACS Appl. Mater. Interfaces,* 2023, 40, 44689−44699
	N/POPQ800	N	0.728	0.832	*ACS Appl. Energy Mater.,* 2022, 5, 15899−15908
	Trz-COP	N	0.73	~0.8	*Chem. Commun.*, 2022, 58, 5506–5509
	d-pGCS-1000	N	0.82	0.95	*Chem. Eng. Sci.,* 2022, 259, 117816
	NDC1000	N	0.86	0.96	*Angew. Chem. Int.Ed.,* 2020, 59, 11999-12006
	N-MCNs	N	0.78	~0.9	*Angew. Chem. Int.Ed.,* 2015, 54, 15191
	NPC-S1.2	N	0.72	0.9	*J Am Chem Soc.*, 2017, 139, 12931–12934
	NHC/rGO	N	~0.80	~0.94	*J. Mater. Chem. A,* 2017, 5, 23170–23178
	N-hG	N	0.83	0.91	*Carbon,* 2020,162, 66-73

Heteroatoms co-doped	JUC-616	N, Se	0.78	~0.9	*J. Mater. Chem. A,* 2023, 11, 18349-18355
	NSC-10	N,S	0.81	0.94	*Chinese chem. Lett.,* 2023, 34 ,107462
	N,P-CGHNs	N, P	0.82	0.90	*Adv. Mater.* 2016*,28,* 4606
	PSN-G3	P,S,N	0.79	~1.0	*Dalton Trans.,*2023,52,4389–4397
	TTF-F	N,F	0.77	0.86	*Adv. Mater.* , 2015*,*27, *3190-3195*
	S,N-codoped graphene (SNG)	N, S	0.72	0.88	*Carbon*, 2018, 134, 316–325
	NS(3:1)-C-MOF-5	N,S	0.82	0.96	*J Mater Chem A*, 2014, 2, 6316–6319
	NF–MG3	N, F	0.828	1.047	*Nanoscale*, 2015, 7, 10584–10589
	S–N–C	N,S	0.89	0.98	*Dalton Trans.,* 2022, 51,18152–18158
	N/S-2DPC60	N,S	0.75	0.86	*Adv. Funct. Mater.* 2016, 32, *5893-5902*
	CNS	N,S	0.87	0.97	*Carbon,* 2021, 184 *,* 127-135
	L-Cy-rGO	N,S	~0.7	0.77	*Energy Fuels* 2021, 35, 6823−6834

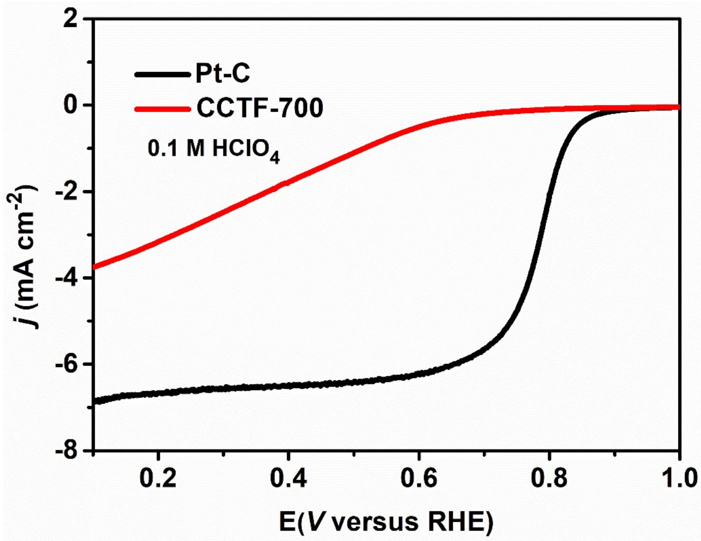


Figure S10. LSVs of CCTF-700 at 1600 rpm in 0.1M $HClO_4$.