

Supporting Information

Transient and General Synthesis of High-density and Ultrasmall Nanoparticles on Two-dimensional Porous Carbon via Coordinated Carbothermal Shock

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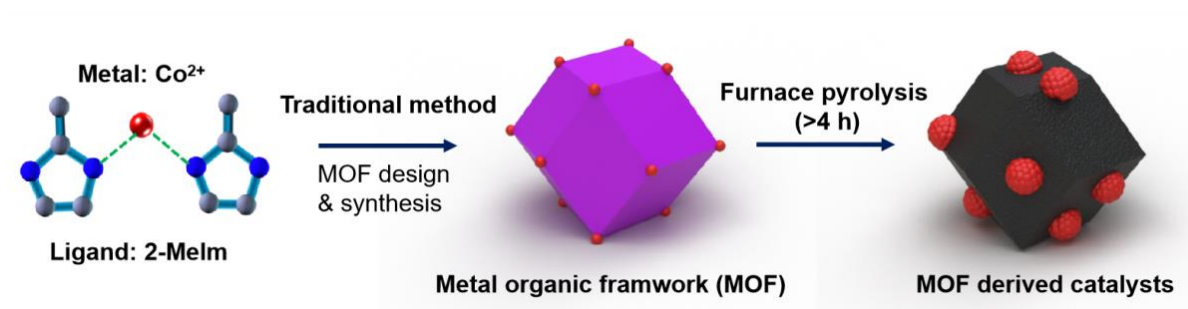
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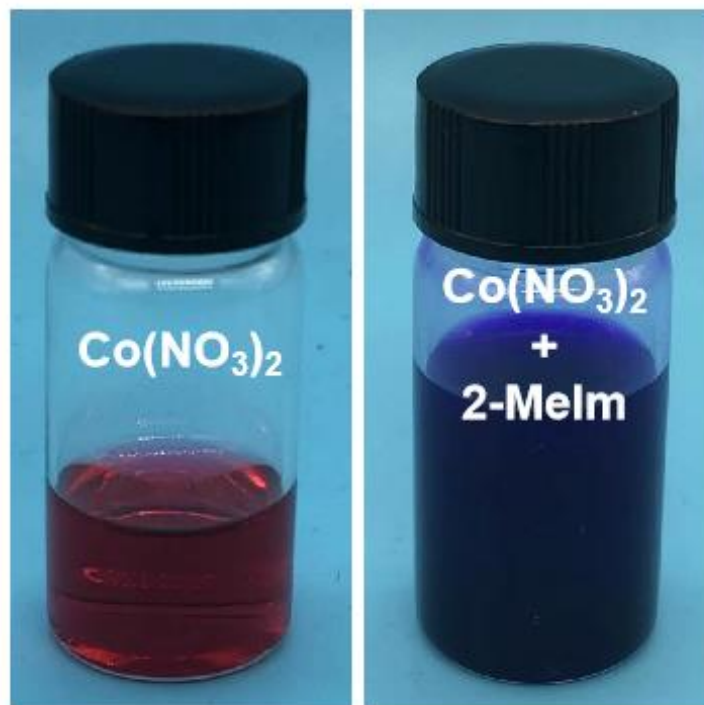
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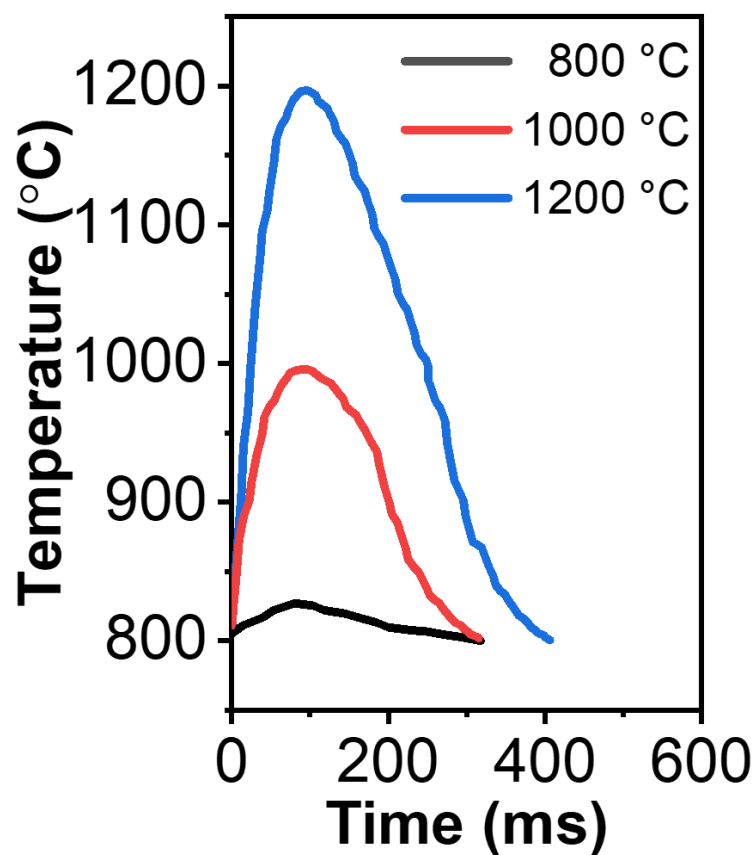
Supplementary Figure 1. MOF-derived catalysts by the traditional method, where both MOF synthesis and thermal pyrolysis take a lot of time and energy. Moreover, furnace pyrolysis leads to particle aggregation and buried in the 3D carbon matrix.



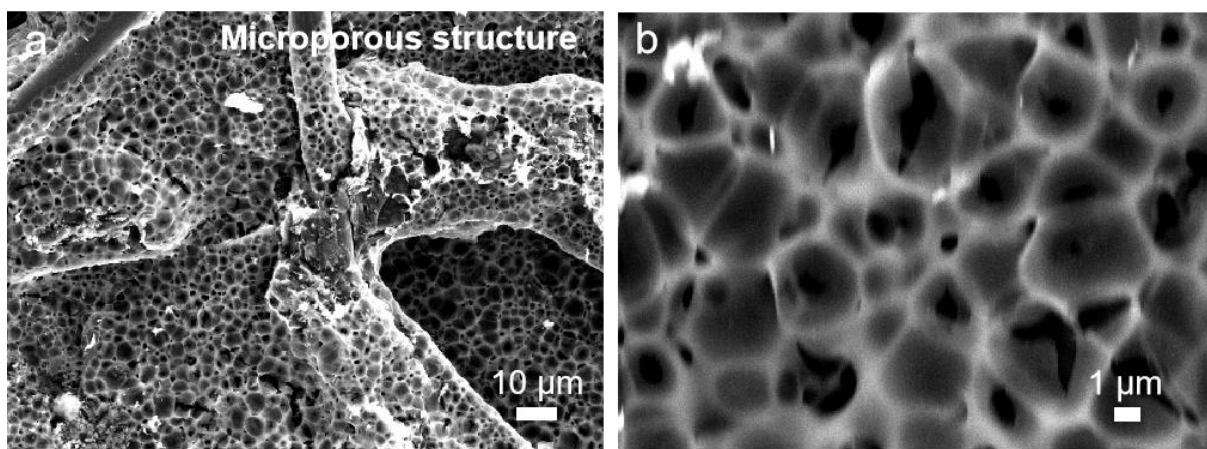
Supplementary Figure 2. The synthesis process of Co-N-CTS.



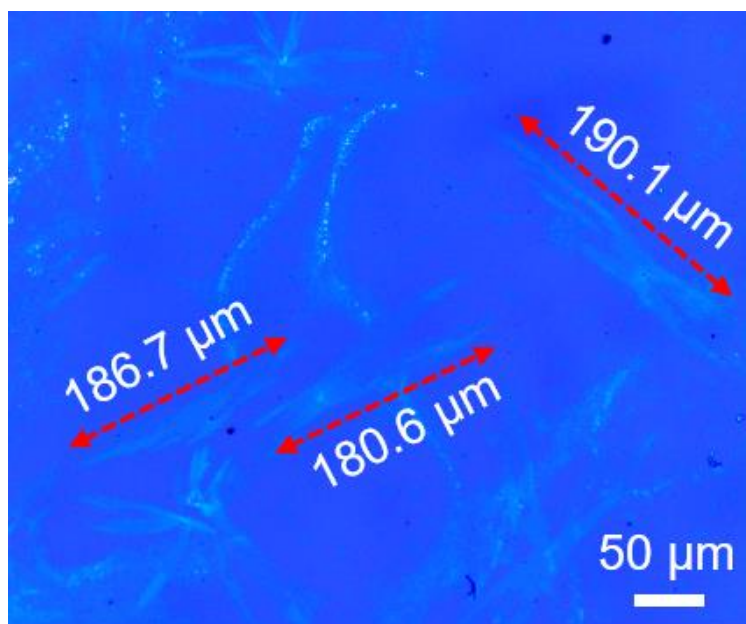
Supplementary Figure 3. Photo image of crimson $\text{Co}(\text{NO}_3)_2$ and blue mixture solution after adding 2-Melm solution.



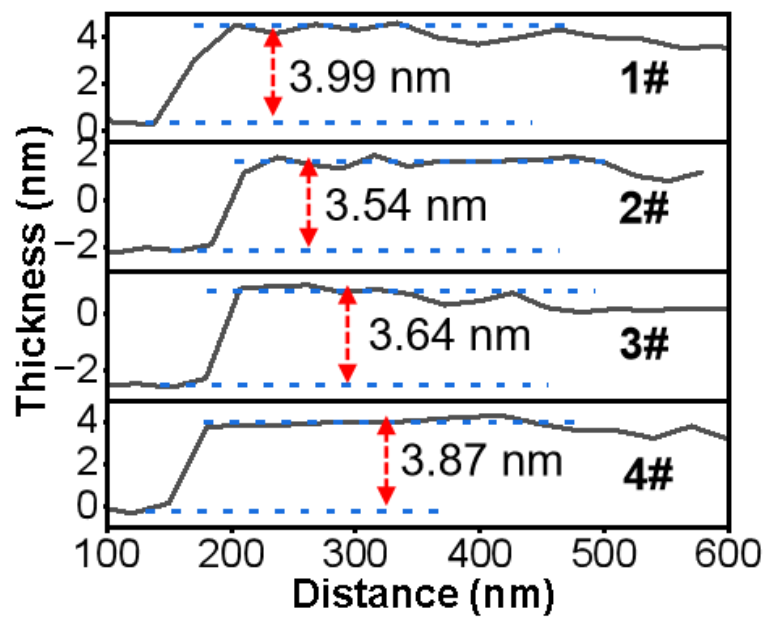
Supplementary Figure 4. The temperature profile of carbothermal shock treatment (800, 1000, and 1200 °C, 100 ms).



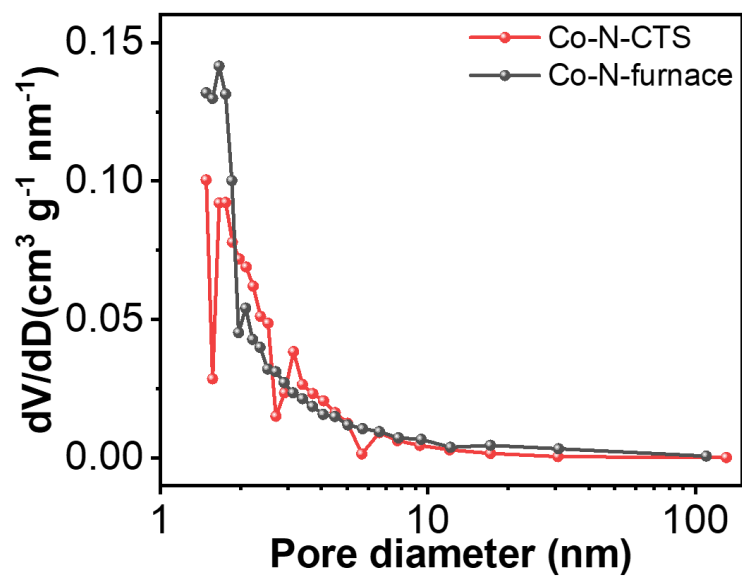
Supplementary Figure 5. SEM image of MOC after carbothermal shock.



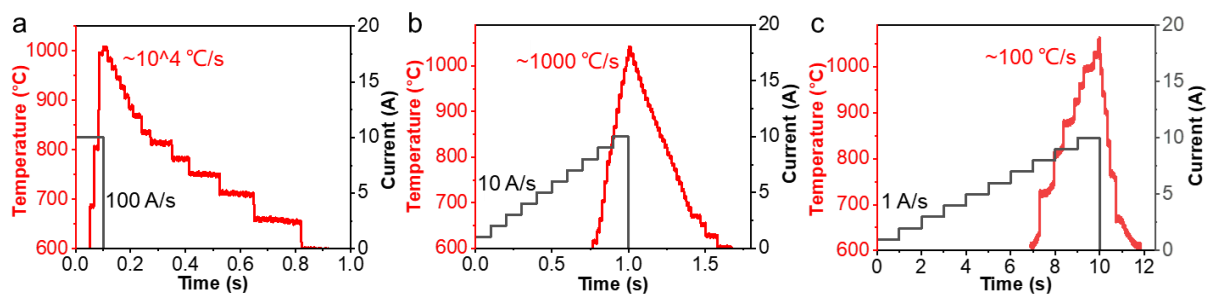
Supplementary Figure 6. The optical microscopy image of Co-N-CTS.



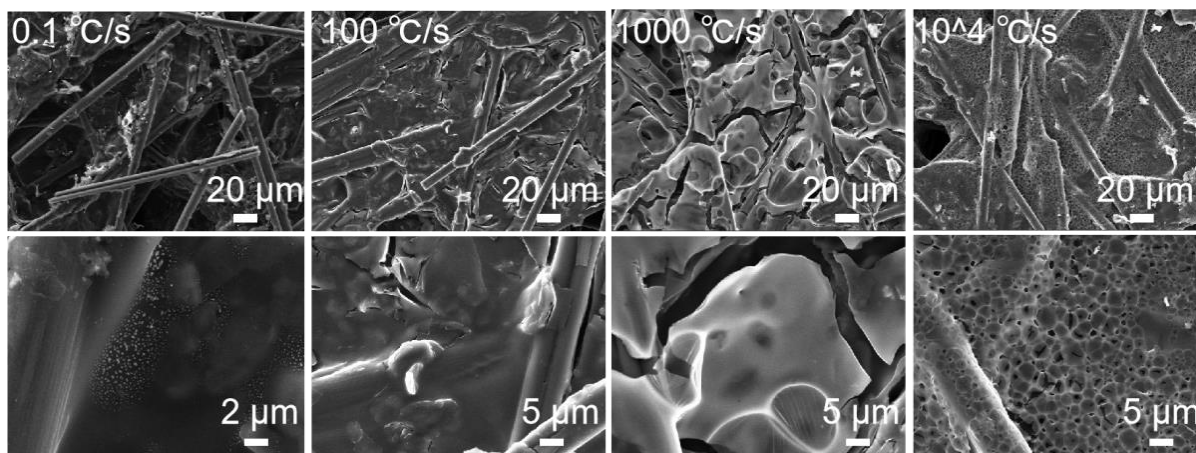
Supplementary Figure 7. The thickness of different carbon films.



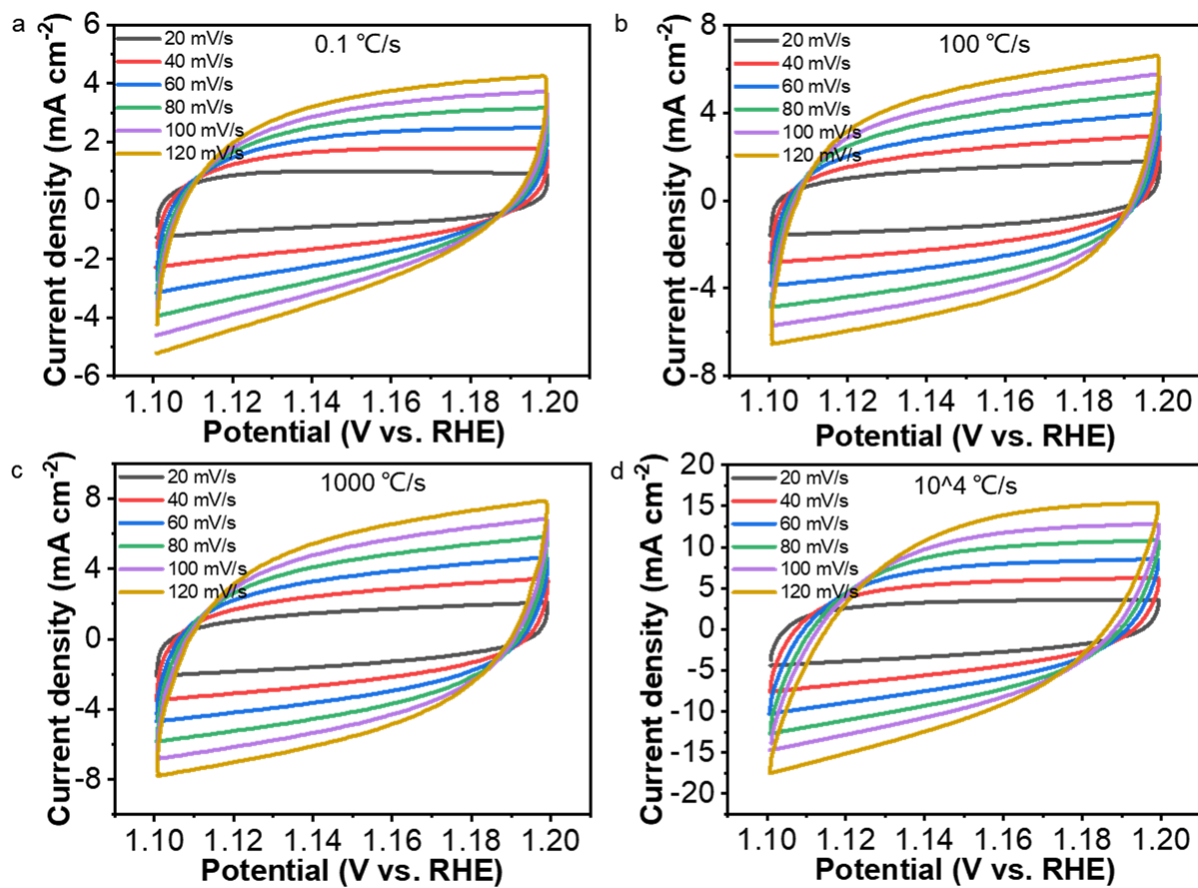
Supplementary Figure 8. The pore size distribution of Co-N-CTS and Co-N-furnace.



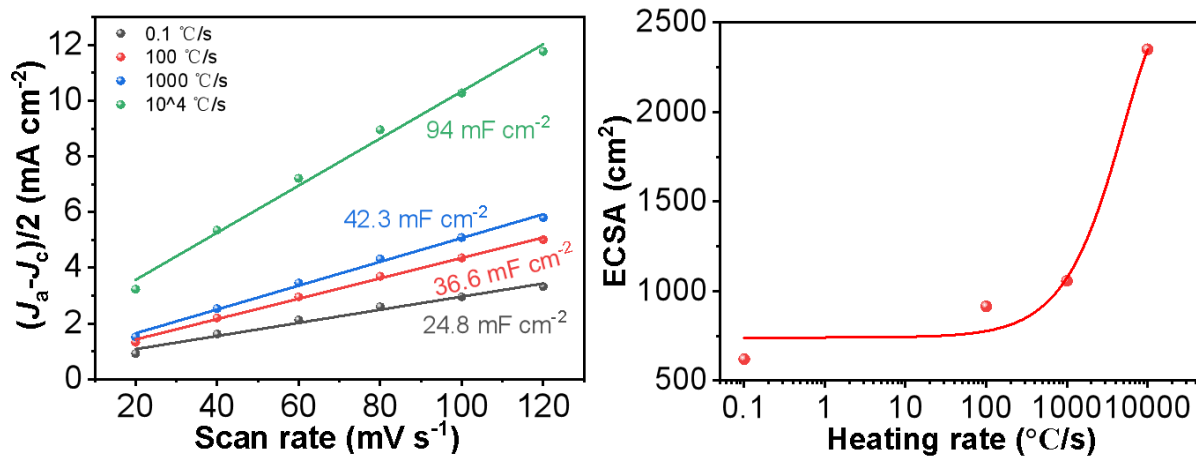
Supplementary Figure 9. The current and temperature profiles at different (designed) heating rates: (a) $\sim 10^4$ °C/s, (b) ~ 1000 °C/s, and (c) ~ 100 °C/s.



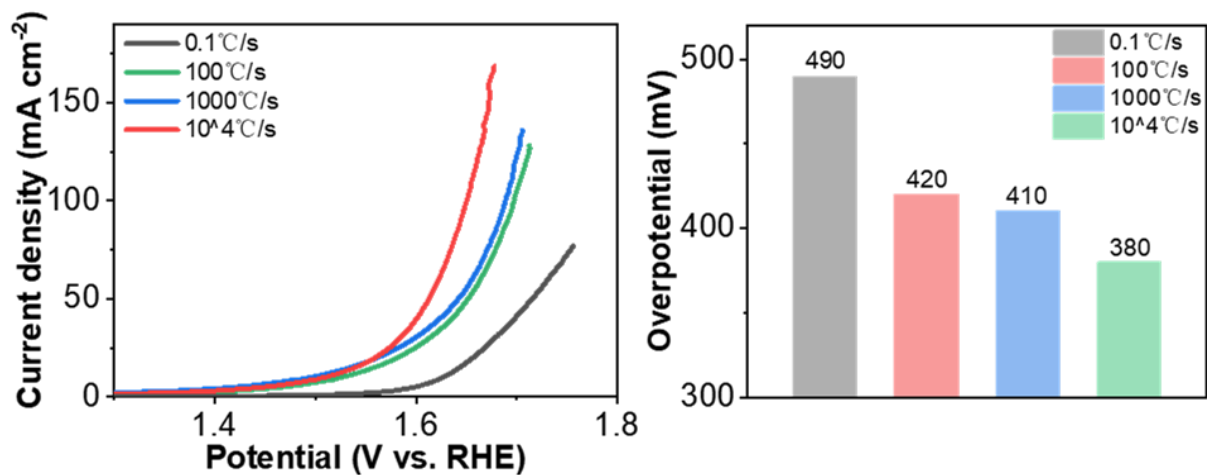
Supplementary Figure 10. SEM images of MOC at different heating rates of 0.1, 100, 1000, and 10⁴ °C/s.



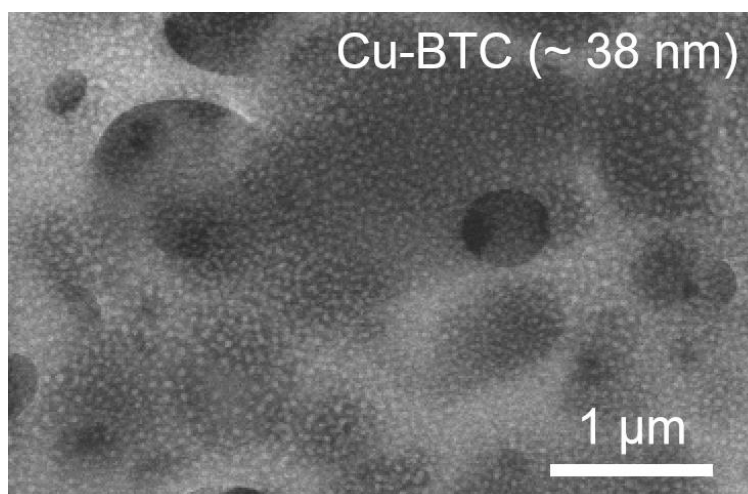
Supplementary Figure 11. CV curves of Co sample at different heating rate 0.1, 100, 1000 and 10⁴ °C/s.



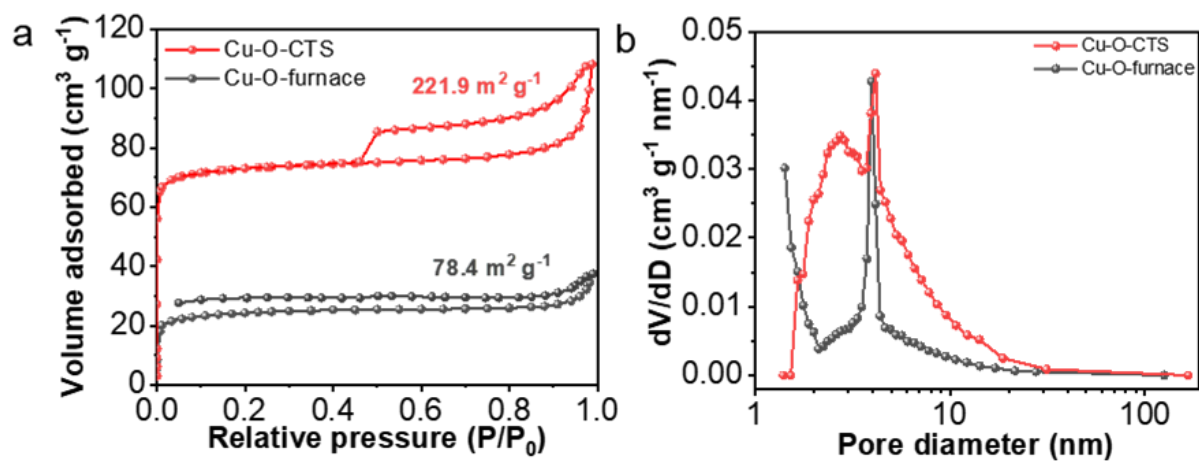
Supplementary Figure 12. (a) the C_{dl} values of Co sample at different heating rate, and (b) the relationship between ECSA and heating rate.



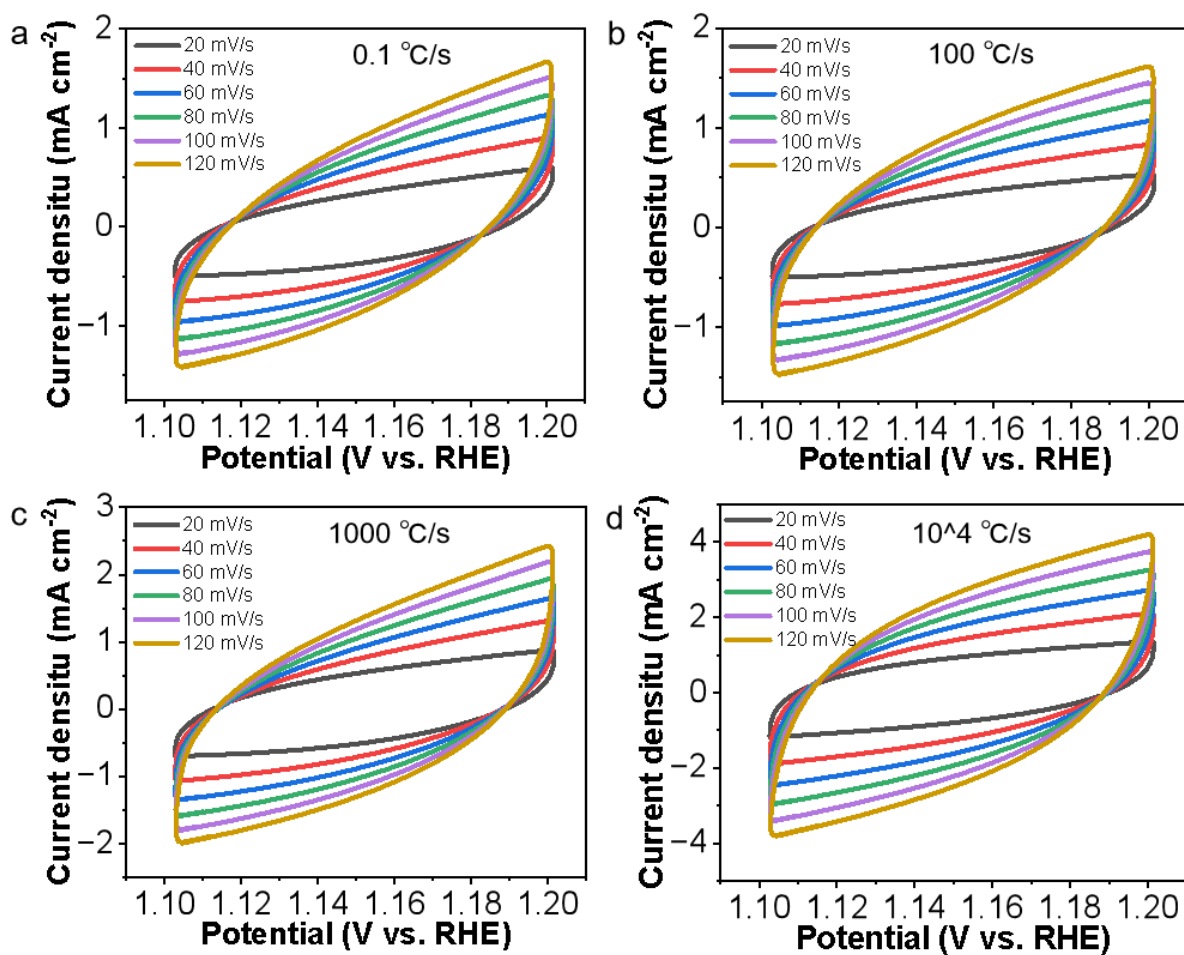
Supplementary Figure 13. The OER performances of Co samples at different heating rates of 0.1, 100, 1000, and 10⁴ °C/s.



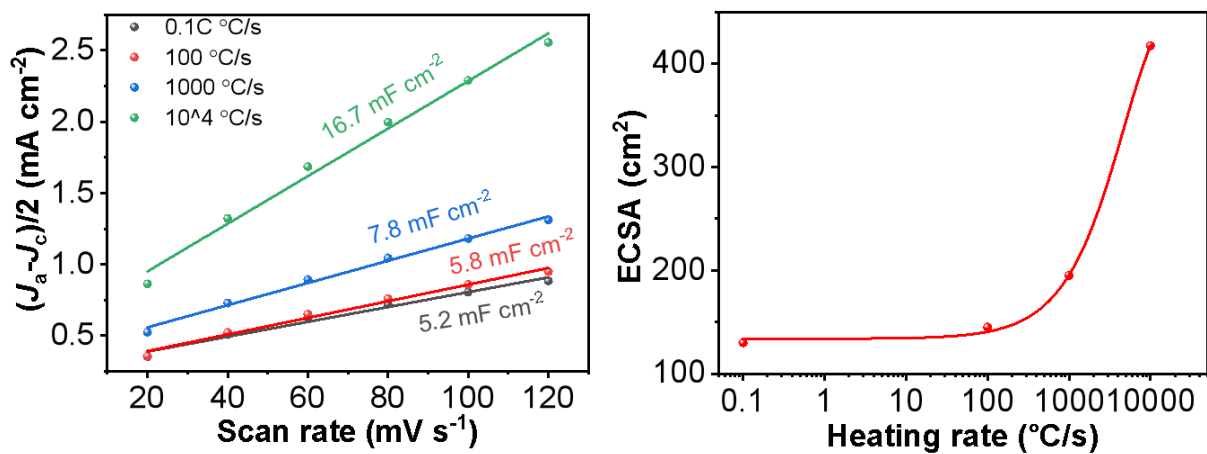
Supplementary Figure 14. SEM images of Cu-BTC (~38 nm) after CTS treatment.



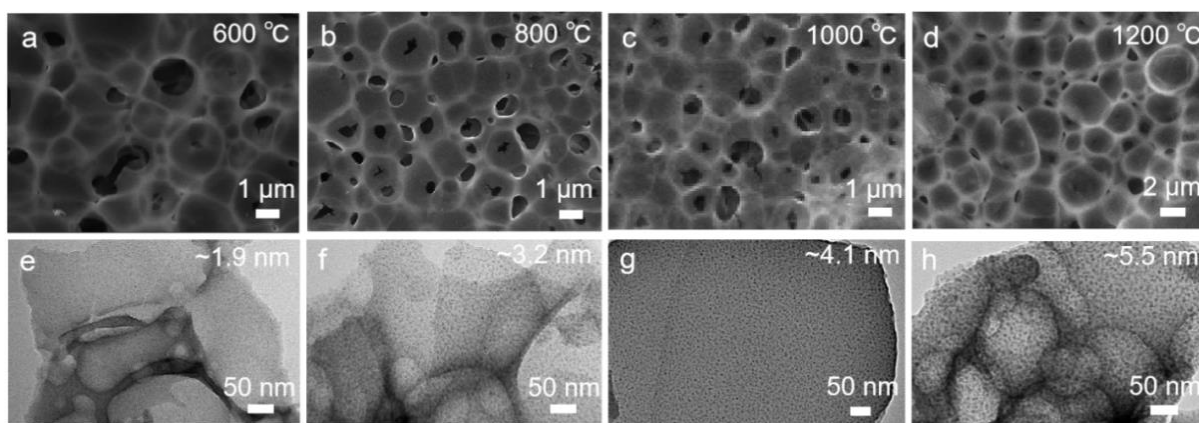
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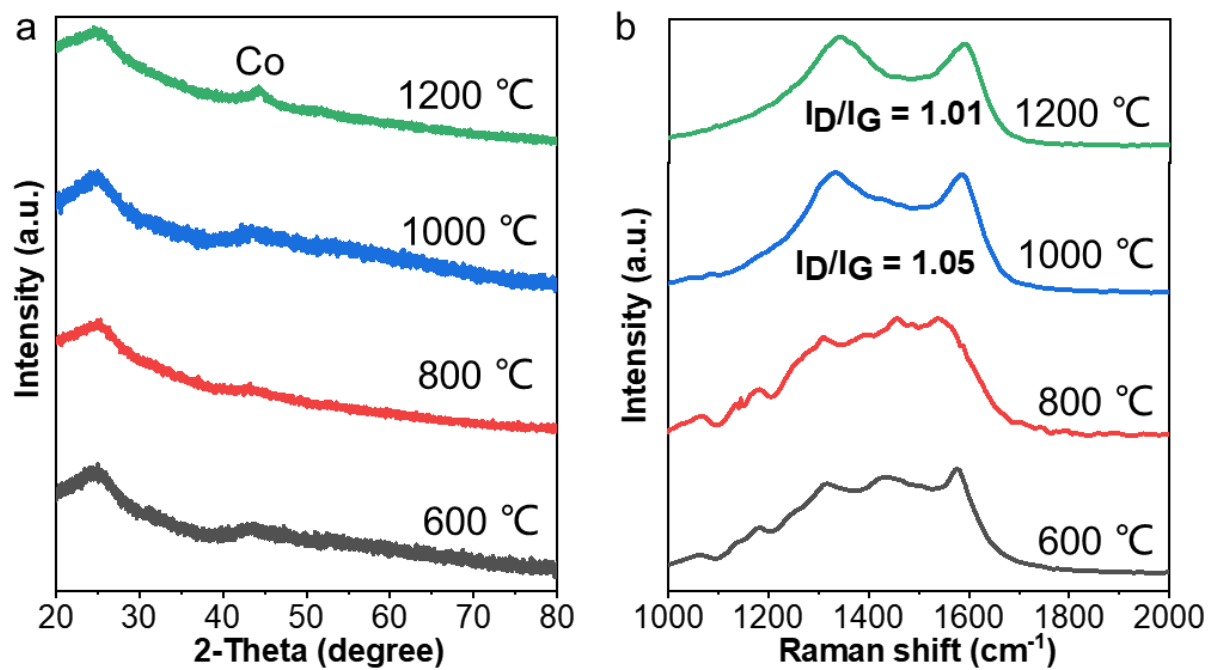
Supplementary Figure 16. The CV curves of Cu sample at different heating rate 0.1, 100, 1000 and 10⁴ °C/s.



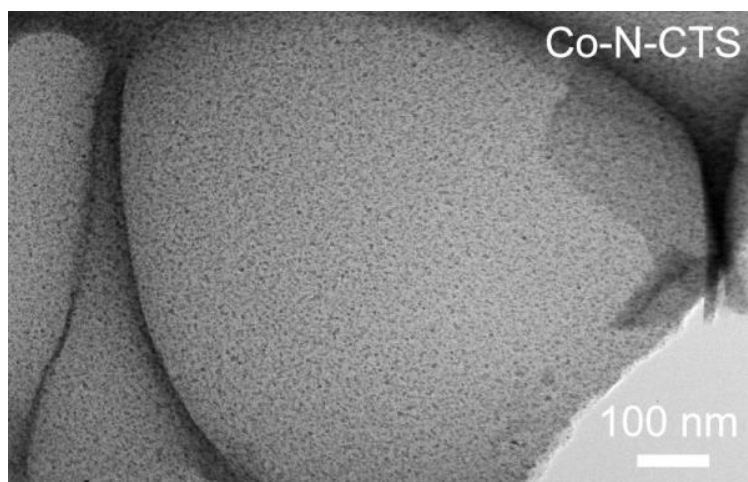
Supplementary Figure 17. (a) the C_{dl} values of Cu sample at different heating rate, and (b) the relationship between ECSA and heating rate.



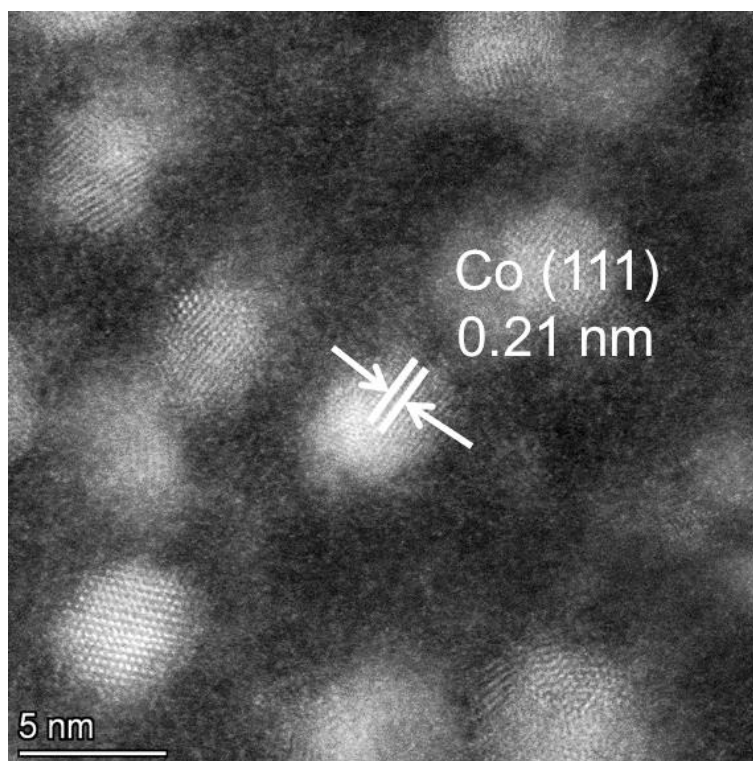
Supplementary Figure 18. (a-d) SEM and (e-f) TEM images of Co-N-CTS samples pyrolyzed at different temperatures (600, 800, 1000, and 1200 °C).



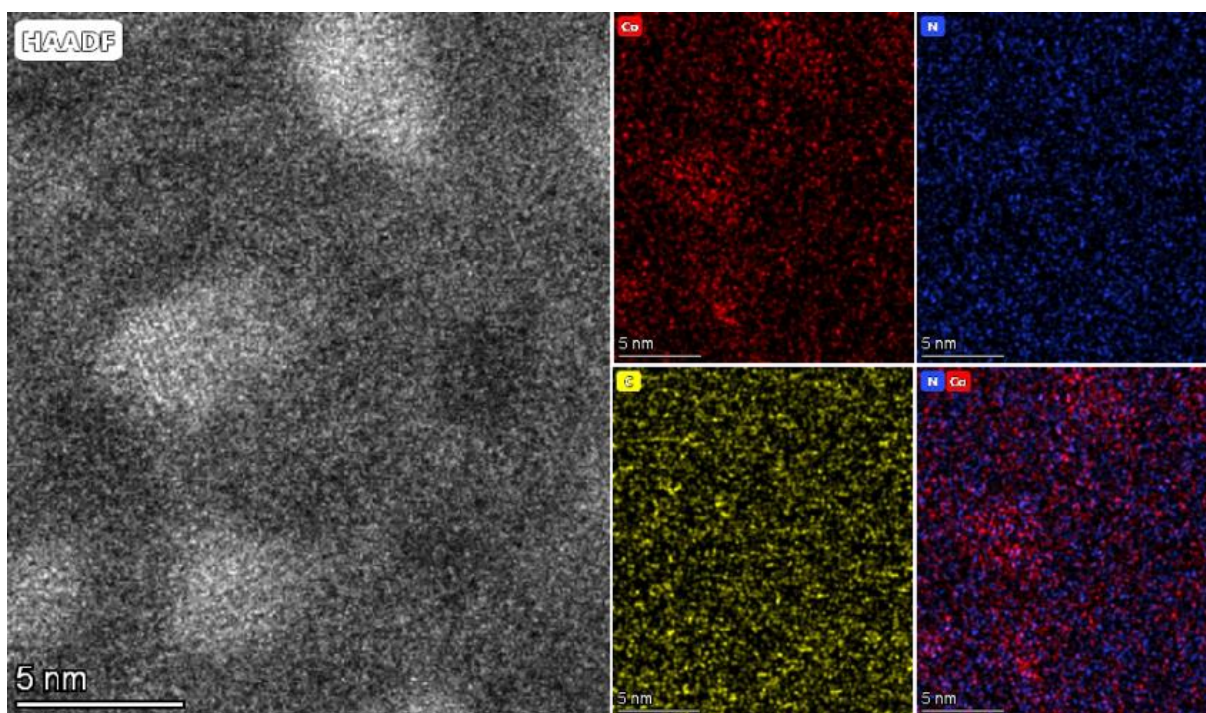
Supplementary Figure 19. (a) XRD and (b) Raman spectrum of Co-N-CTS samples pyrolyzed at different temperatures (600, 800, 1000, and 1200 °C).



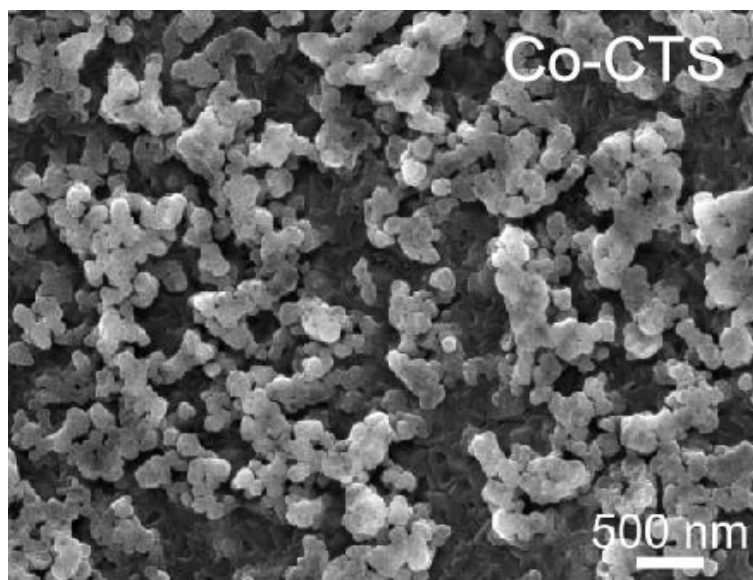
Supplementary Figure 20. TEM image of Co-N-CTS.



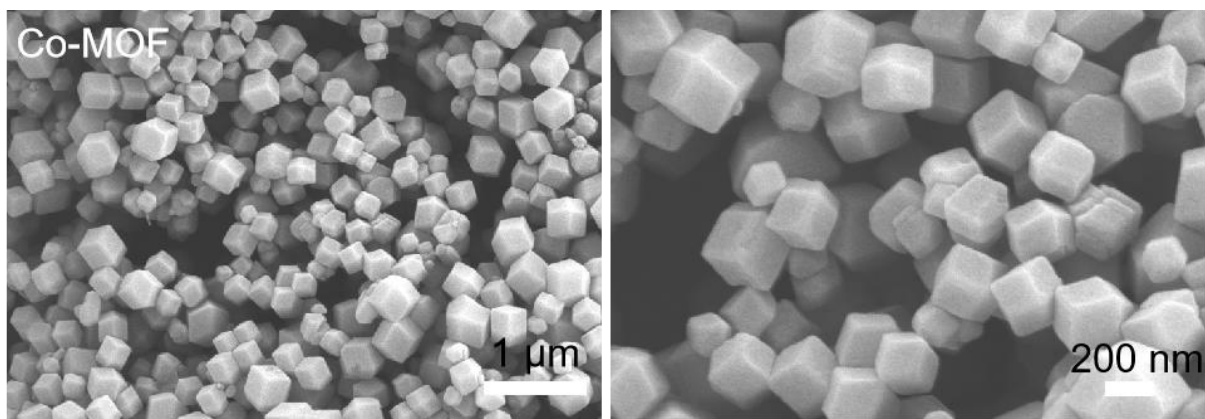
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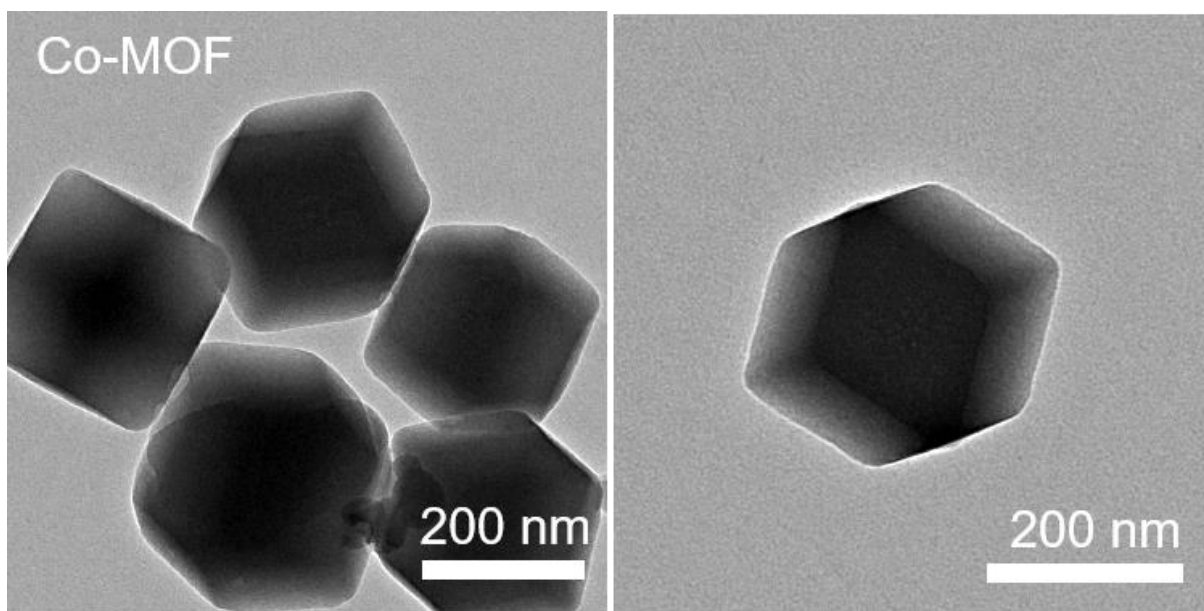
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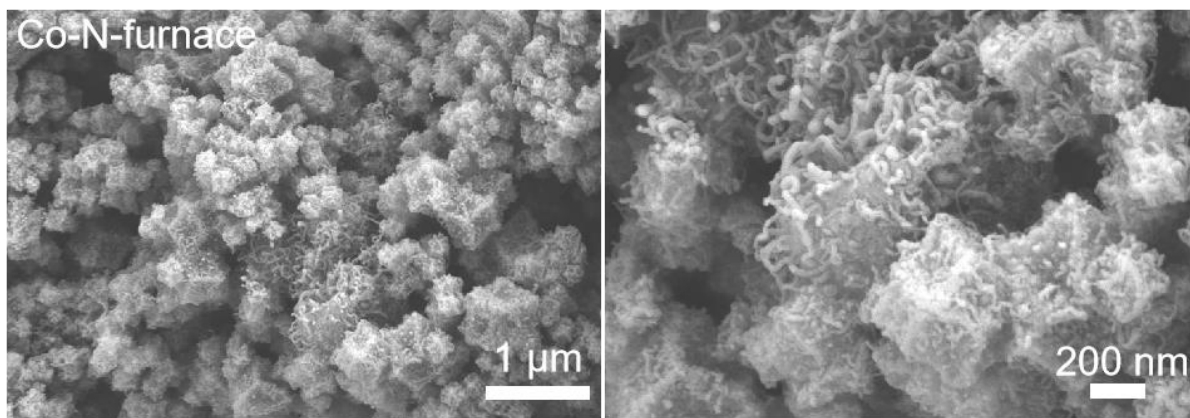
Supplementary Figure 23. SEM image of Co without 2-MeIm after carbothermal shock.



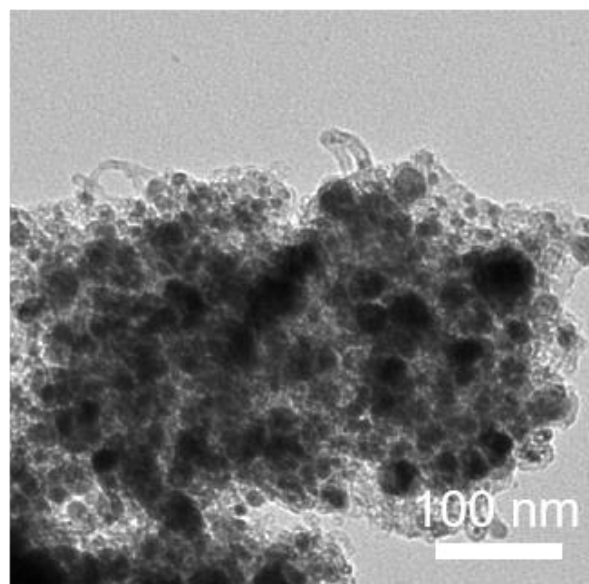
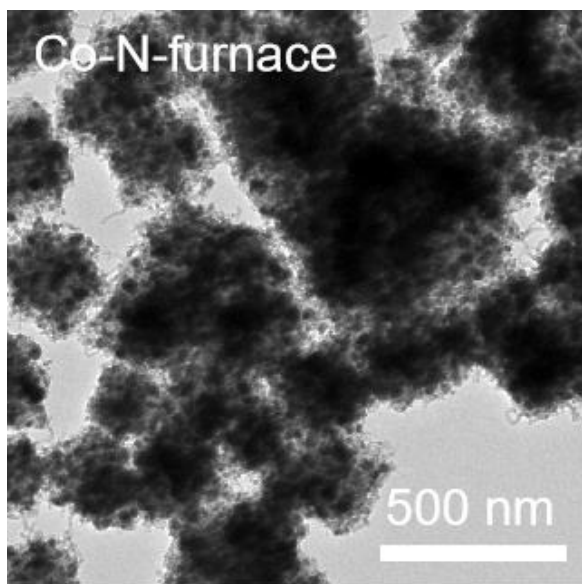
Supplementary Figure 24. SEM image of Co-MOF.



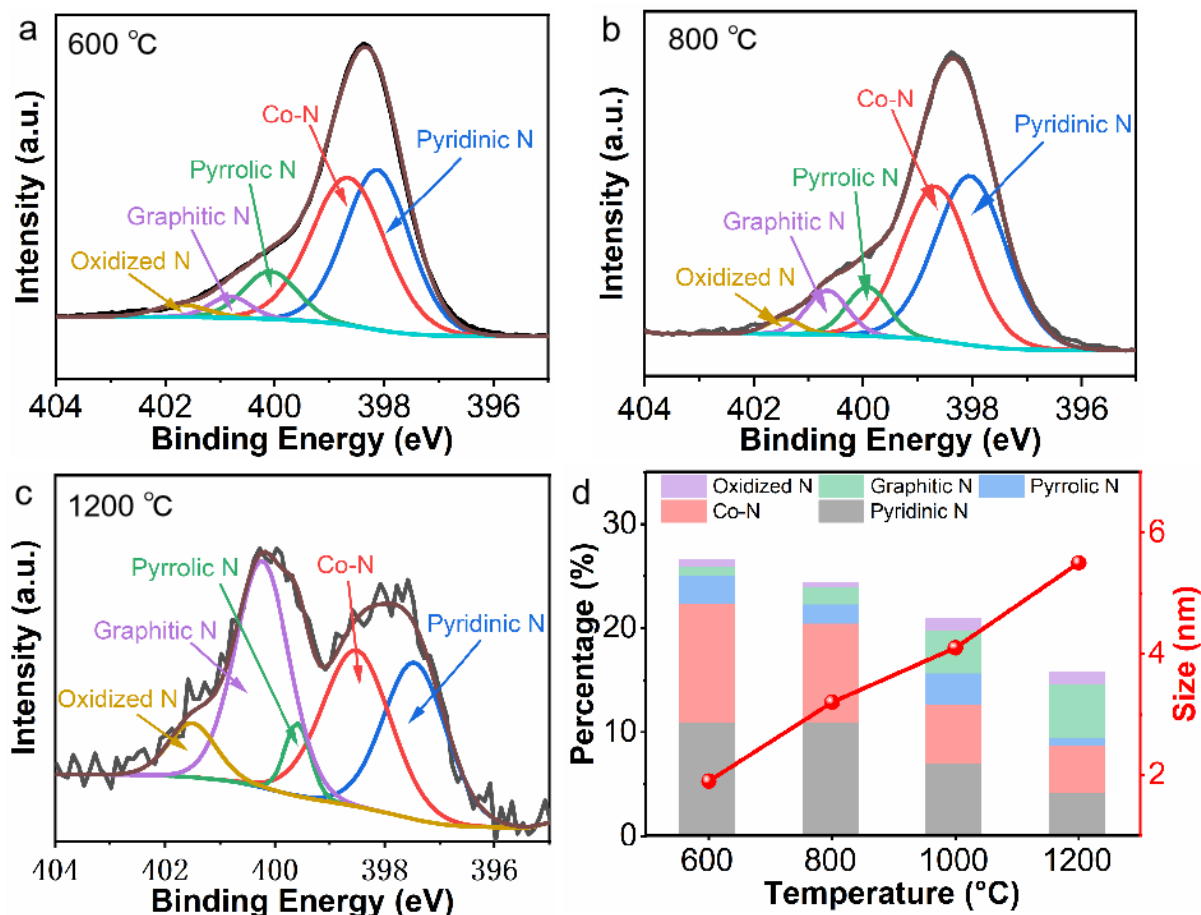
Supplementary Figure 25. TEM image of Co-MOF.



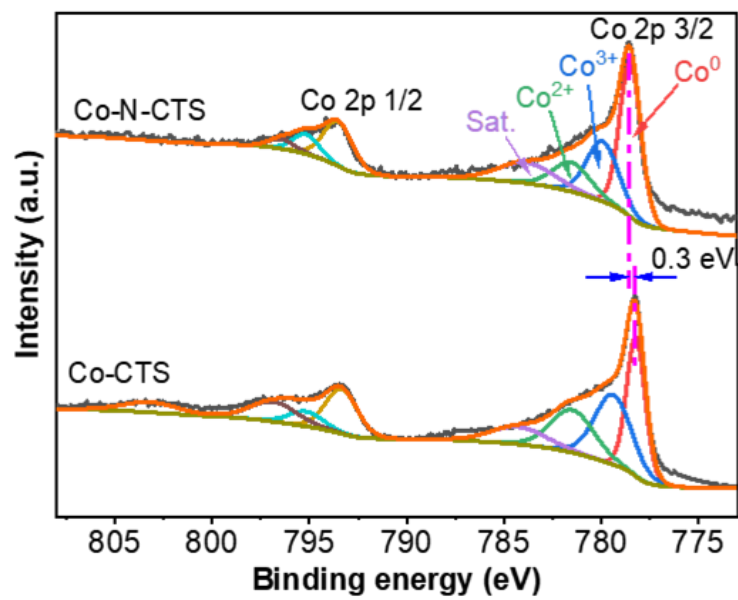
Supplementary Figure 26. SEM image of Co-MOF after furnace heating treatment.



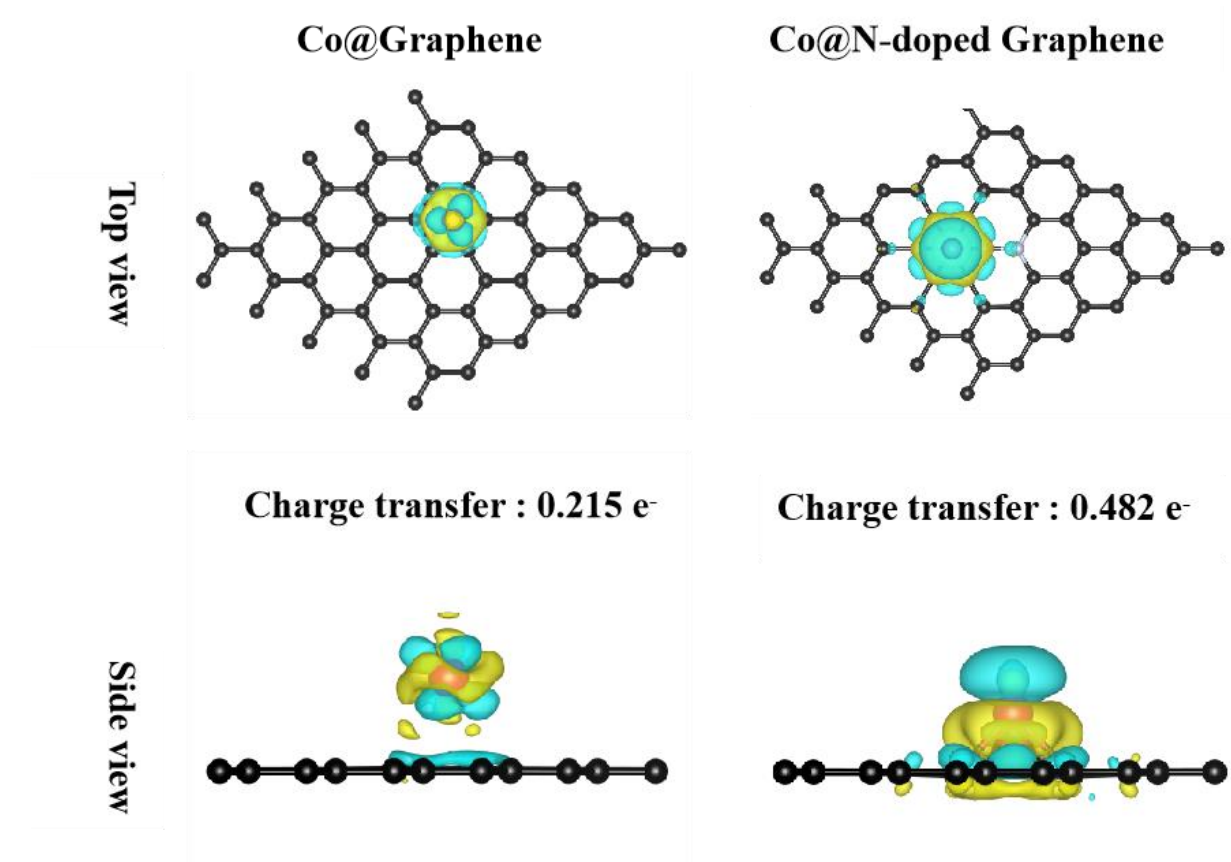
Supplementary Figure 27. TEM image of Co-MOF after furnace heating treatment.



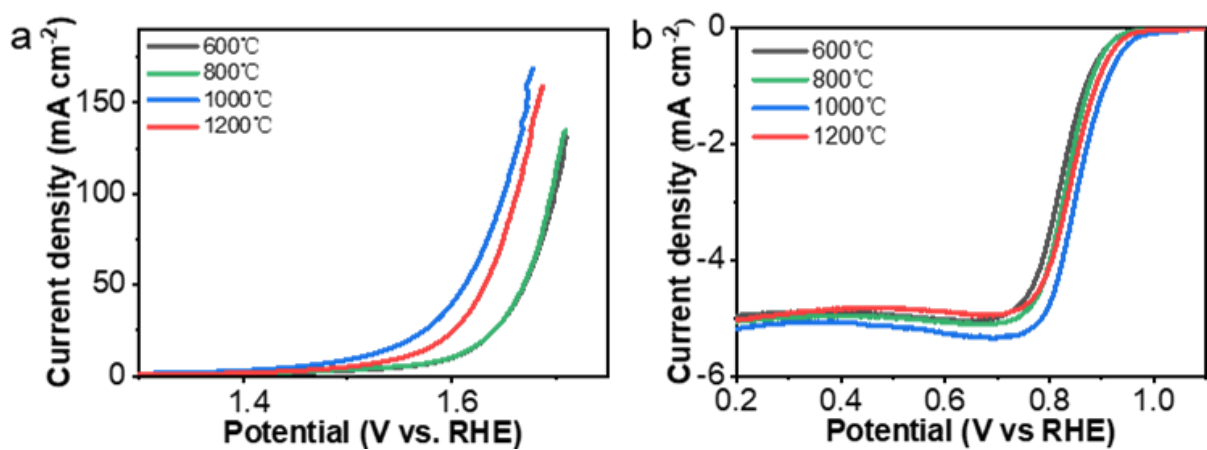
Supplementary Figure 28. The high-resolution XPS of N signal at 600, 800, and 1200 °C and the contents of N species and particle size pyrolyzed at different temperatures.



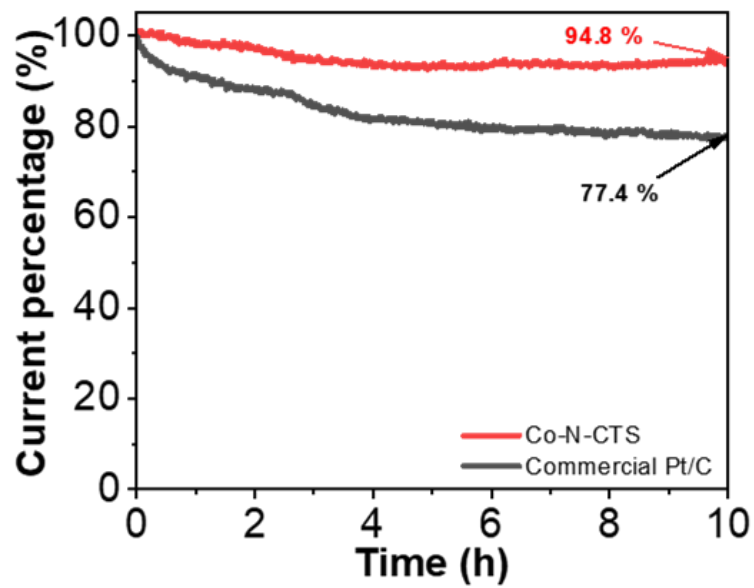
Supplementary Figure 29. The XPS spectrum of Co-N-CTS and Co-CTS.



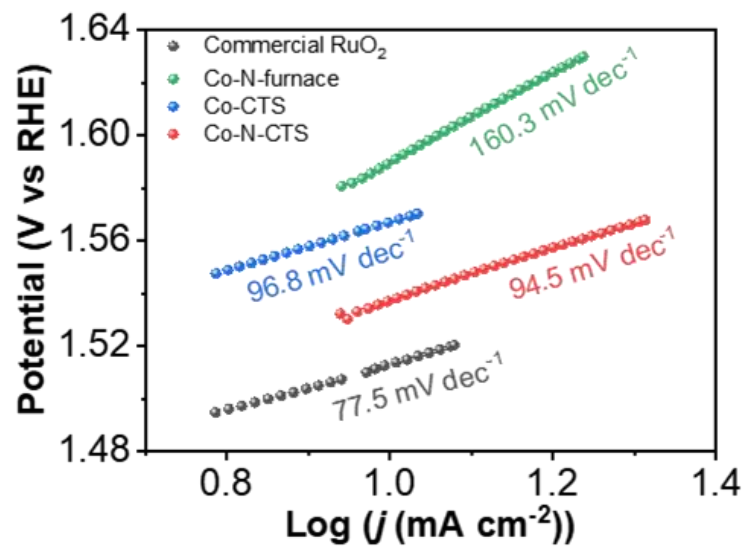
Supplementary Figure 30. The difference of charge density between Co and the rest of the system. Yellow represents the electron-accumulation area and cyan is the electron-depletion area. Isosurface level: 0.002 e/Bohr³.



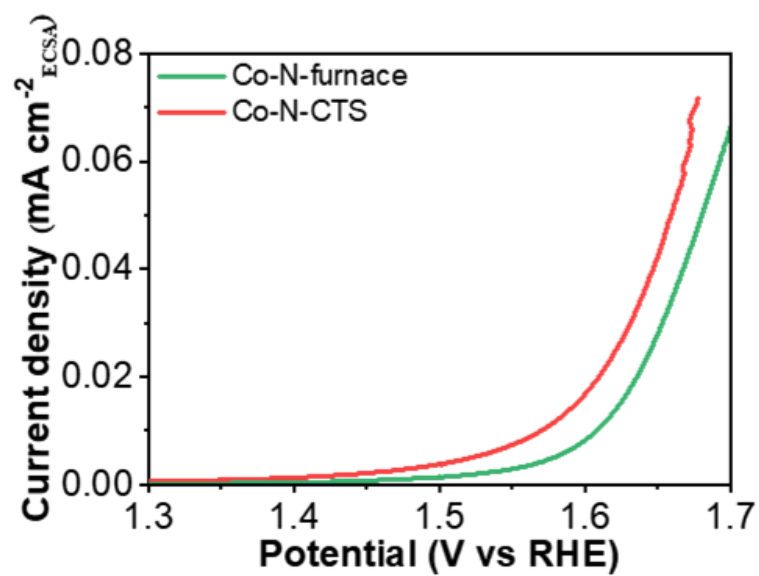
Supplementary Figure 31. (a) OER and (b) ORR performances of Co-N-CTS samples at different pyrolysis temperature of 600, 800, 1000, and 1200 °C.



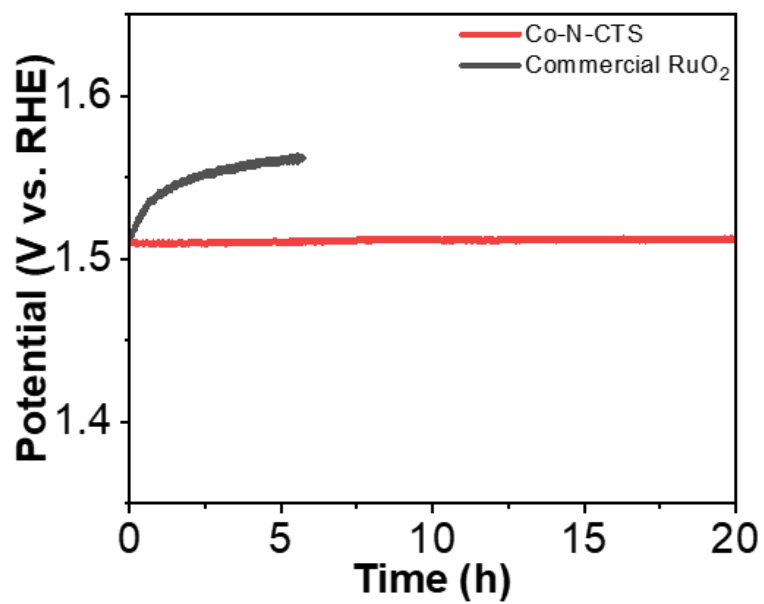
Supplementary Figure 32. The ORR stability tests of commercial Pt/C and Co-N-CTS.



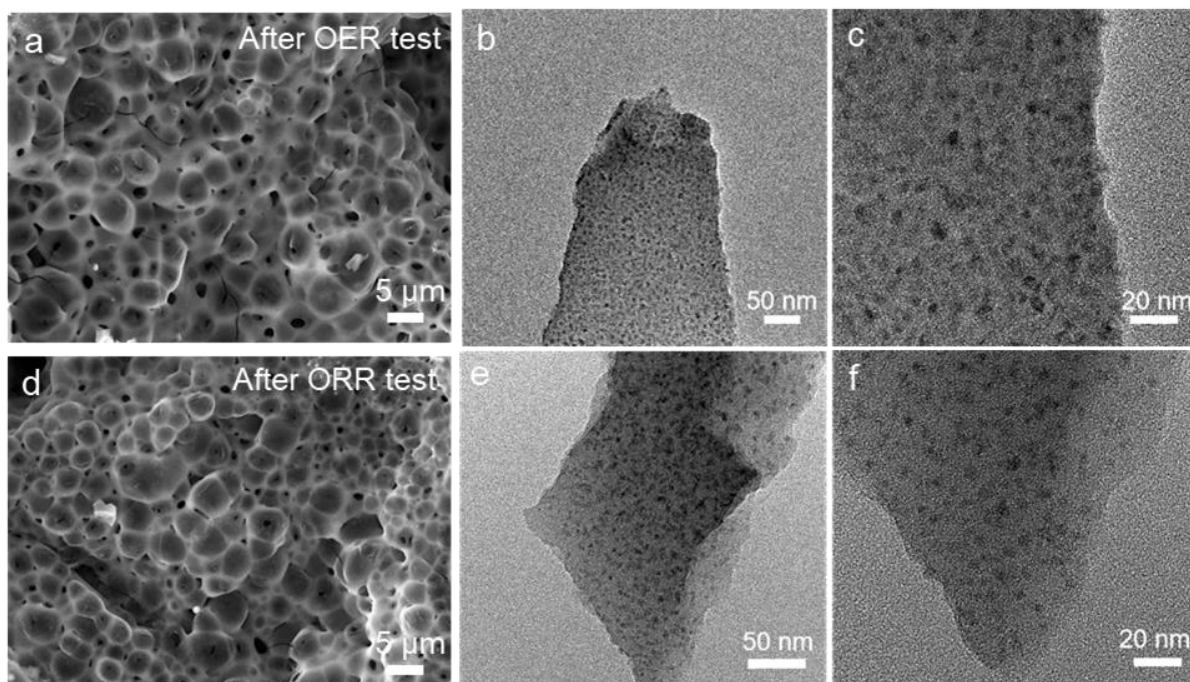
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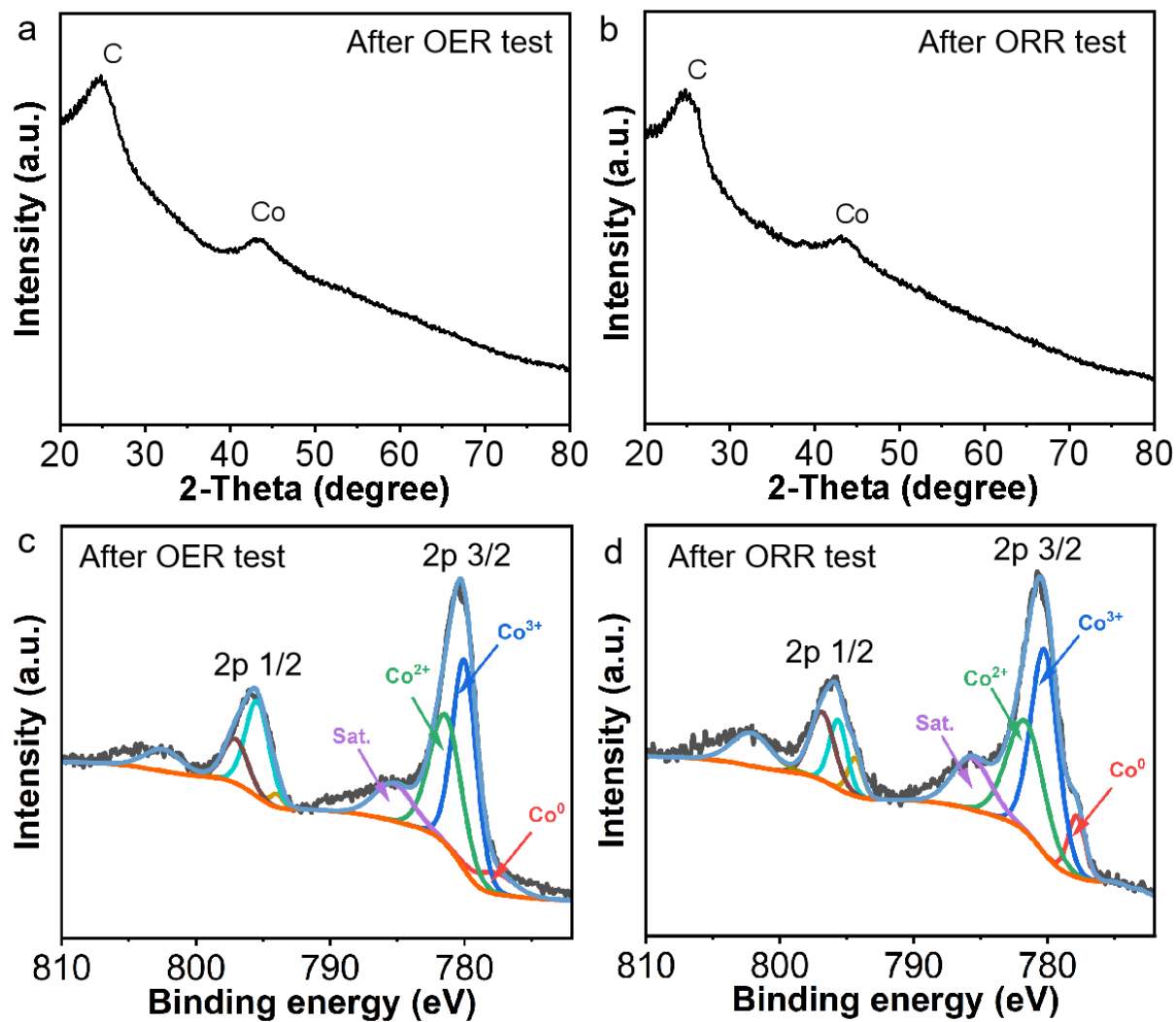
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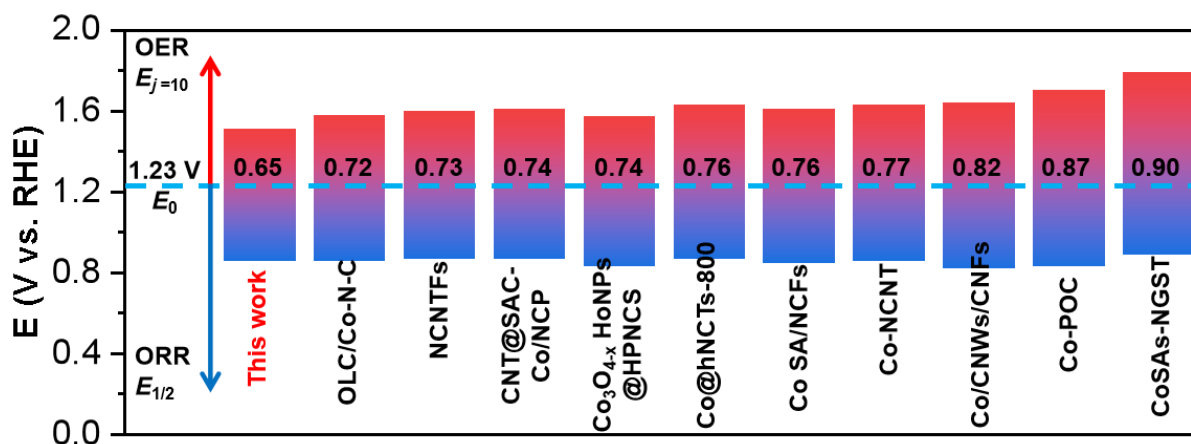
Supplementary Figure 35. The OER stability tests of commercial RuO₂ and Co-N-CTS.



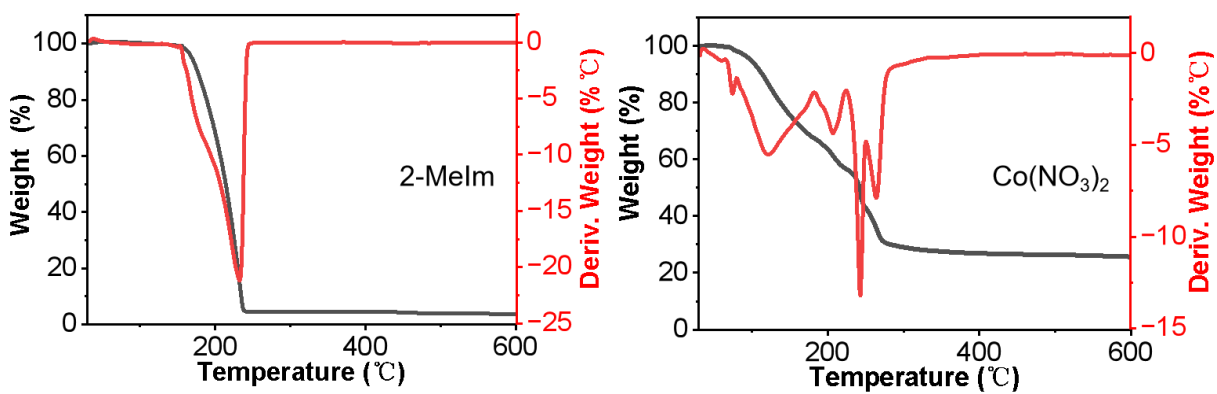
Supplementary Figure 36. SEM and TEM image of Co-N-CTS after 20 h OER and 10 h ORR test.



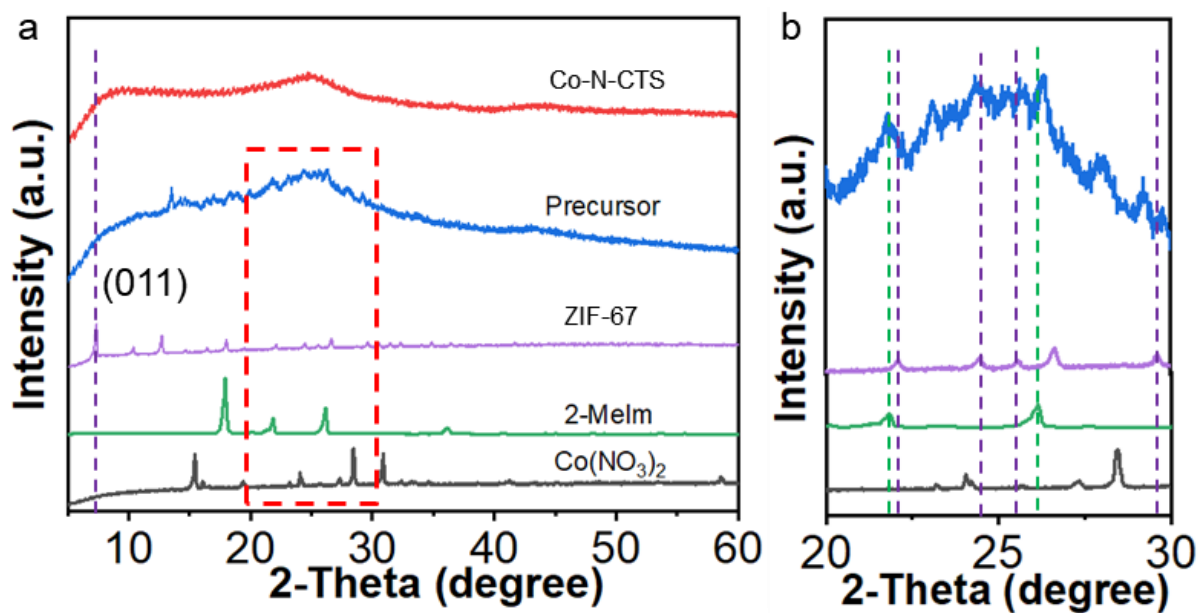
Supplementary Figure 37. The XRD and Co XPS spectrum of Co-N-CTS after 20 h OER and 10 h ORR test.



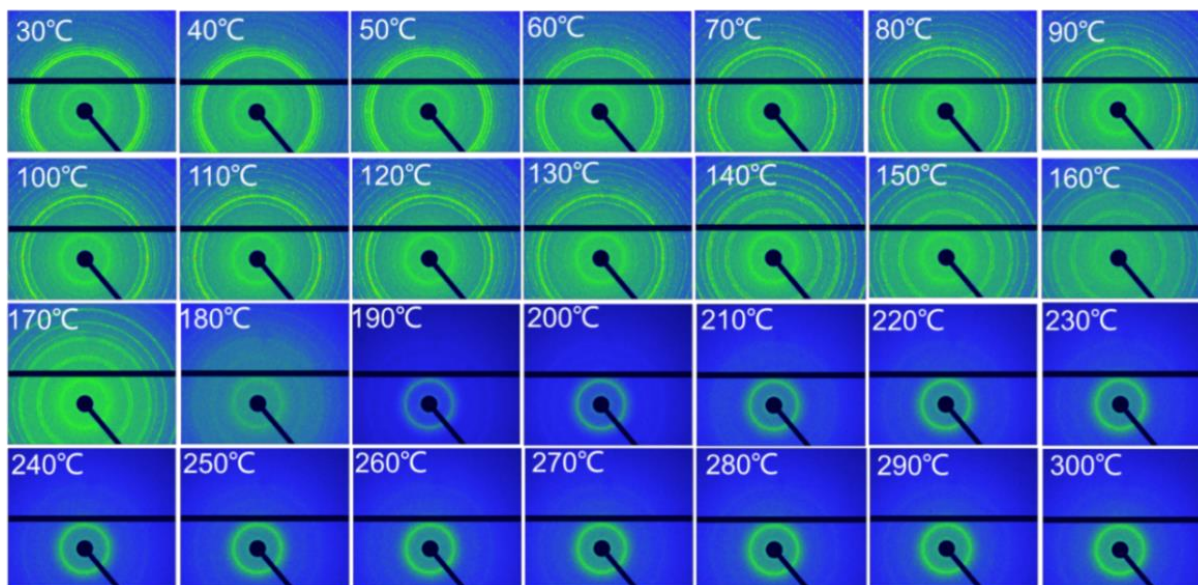
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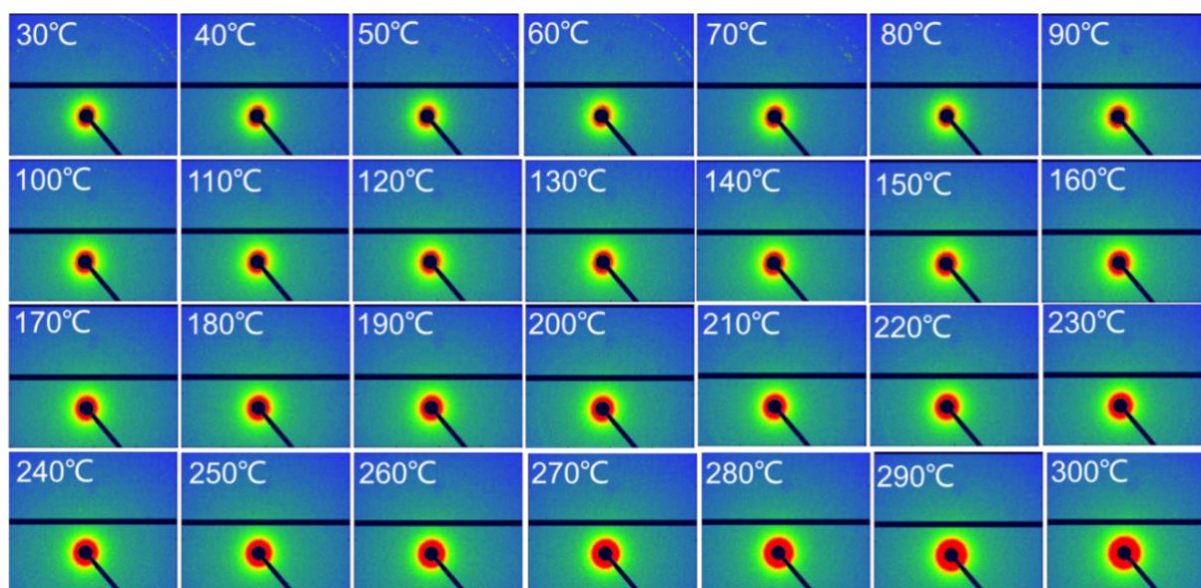
Supplementary Figure 39. The TGA-DTG profile of (a) 2-Melm and (b) $\text{Co}(\text{NO}_3)_2$ from 50 to 600 °C in Ar gas.



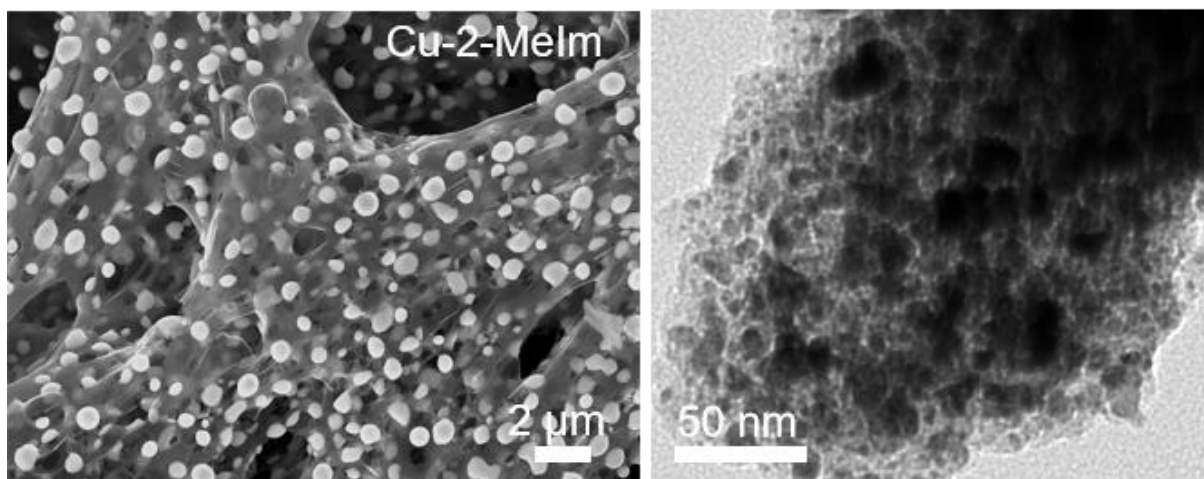
Supplementary Figure 40. (a) and (b) XRD patterns of the metal-ligand precursor, Co-N-CTS, ZIF-67, 2-Melm, and $\text{Co}(\text{NO}_3)_2$.



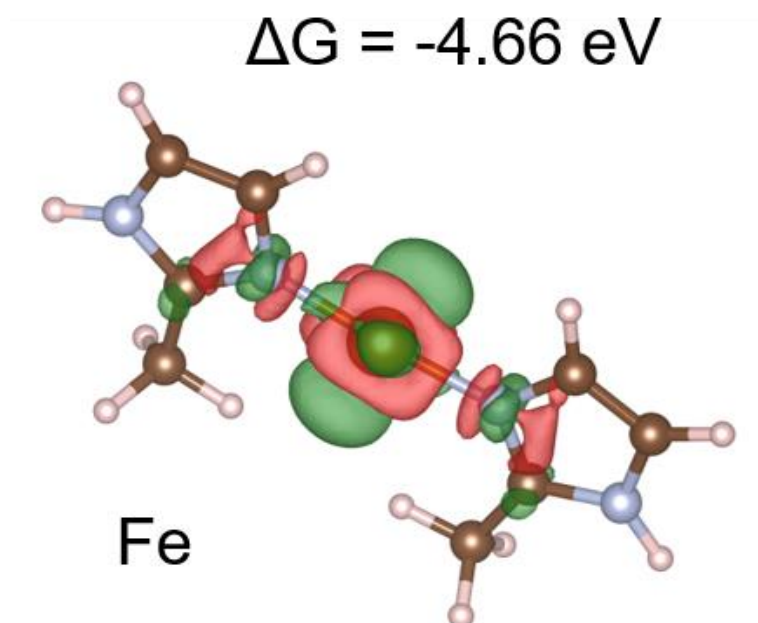
Supplementary Figure 41. The diffraction pattern of MOC from 30 to 300 °C.



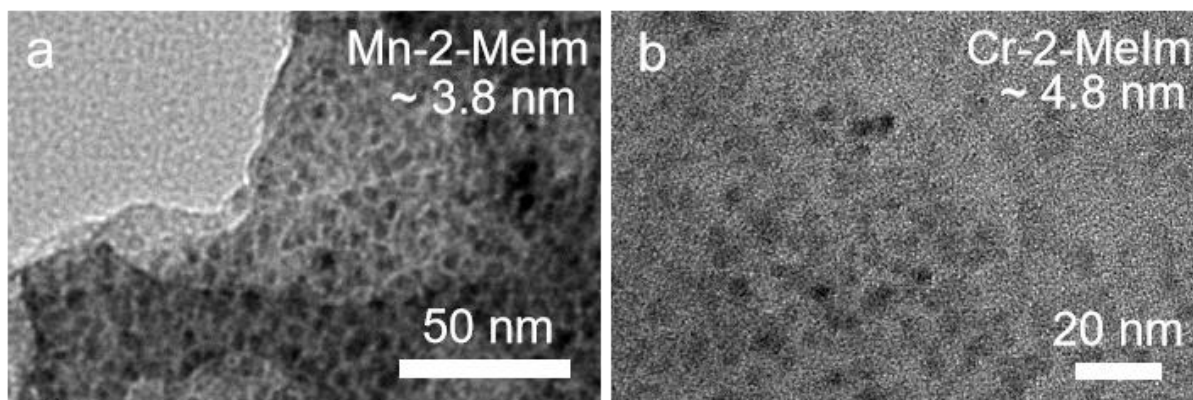
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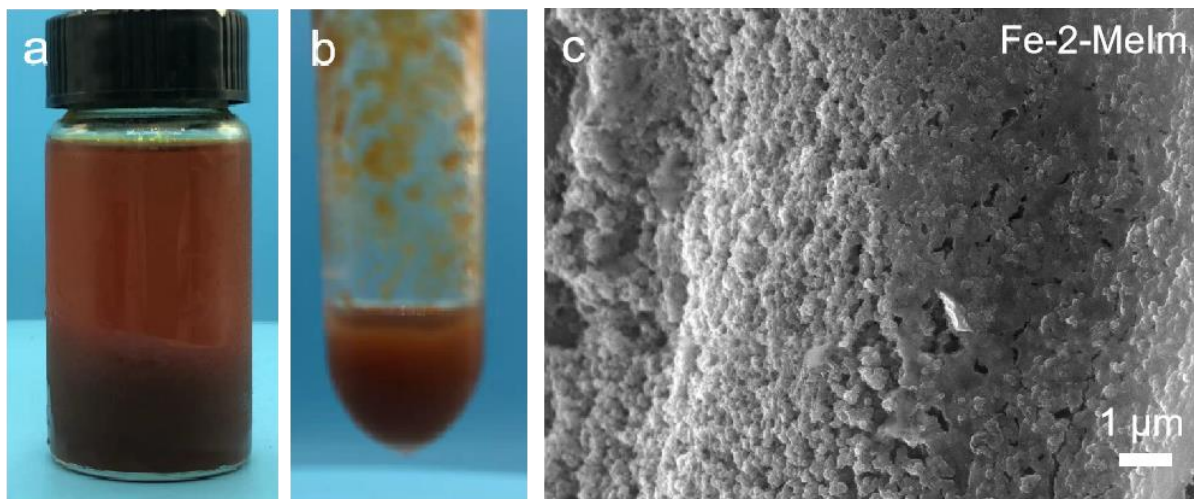
Supplementary Figure 43. SEM and TEM image of Cu-2-MeIm after carbothermal shock.



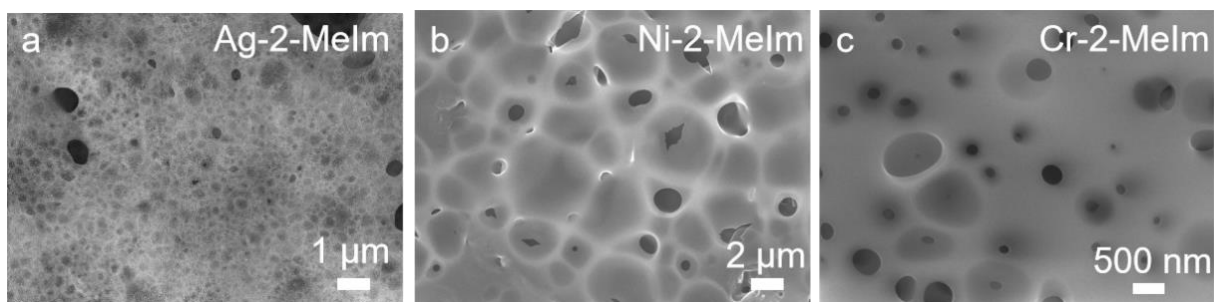
Supplementary Figure 44. The formation energy of Fe with 2-MeIm.



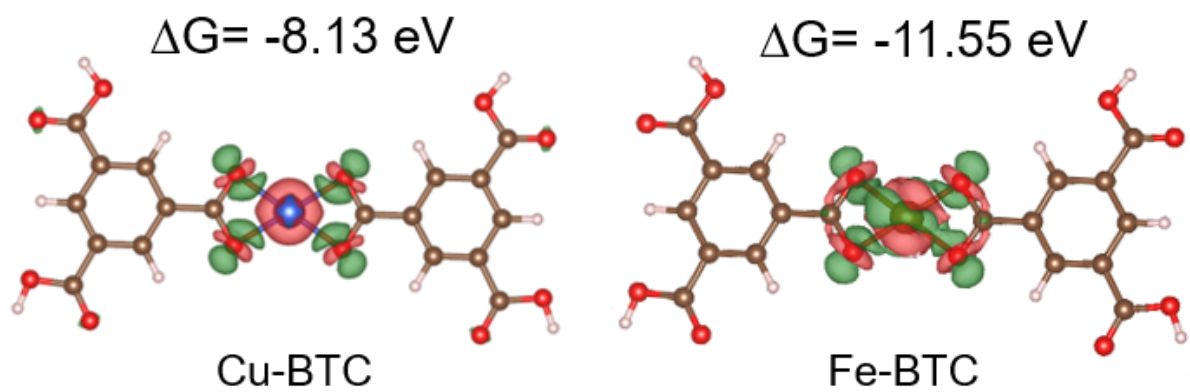
Supplementary Figure 45. TEM image of (a) Mn-2-MeIm and (b) Cr-2-MeIm after carbothermal shock.



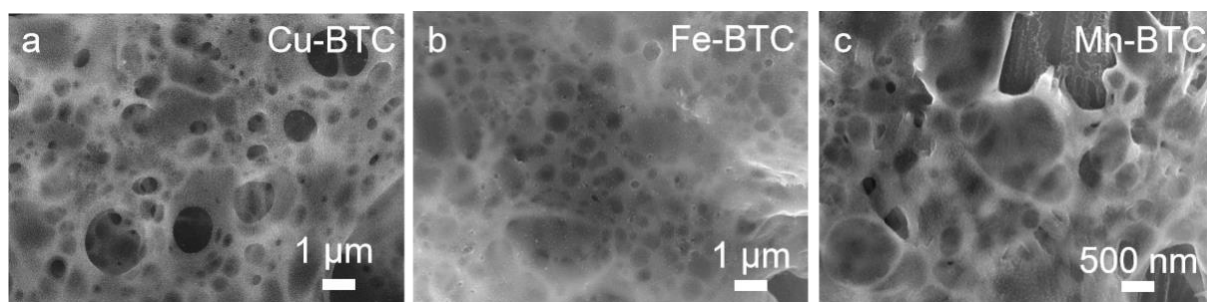
Supplementary Figure 46. Optical image of (a) 0.2 M $\text{Fe}(\text{NO}_3)_3$ ethanol solution, (b) $\text{Fe}(\text{NO}_3)_3$ and 2-MeIm mixed solution, and (c) SEM image of Fe-2-MeIm after carbothermal shock. The $\text{Fe}(\text{OH})_3$ precipitated in 0.2 M $\text{Fe}(\text{NO}_3)_3$ ethanol solution after 2 h, and the $\text{Fe}(\text{OH})_3$ nanoparticles precipitated immediately after the $\text{Fe}(\text{NO}_3)_3$ solution was added to the 2-MeIm solution, indicating that alkaline 2-MeIm promotes $\text{Fe}(\text{OH})_3$ nanoparticle formation.



Supplementary Figure 47. SEM images of (a) Ag-2-MeIm, (b) Ni-2-MeIm, and (c) Cr-2-MeIm after carbothermal shock.



Supplementary Figure 48. The formation energy and charge distribution of Cu and Fe with BTC.



Supplementary Figure 49. SEM images of (a) Cu-BTC, (b) Fe-BTC, and (c) Mn-BTC after carbothermal shock.

Supplementary Table 1. Comparison of various CTS methods.

	1.Substrate	Special substrate?	2.Precursor	Precursor design?	Compositions	In situ assembly / tunable pores?	3. Particles	4.Hierarchical porosity?	Reference
Conventional CTS	Carbon	X	Metal salt (e.g., CoCl ₂)	X	None specific	X	~10-20 nm	X	Science 2018, 359, 1489-1494 (our previous work)
Enhanced CTS (enhancing the metal-substrate interaction)	CO ₂ activated carbon (defective carbon)	✓	Metal salt (e.g., H ₂ PtCl ₆)	X	None specific	X	~5 nm (high density) ~0.8 nm (low density)	X	ACS AMI 2019, 11, 29773 (our previous work)
	3D mesoporous carbon (defective, pore confinement)	✓	Metal salt (e.g., RuCl ₂)	X	None specific	X	~ 3 nm (low density)	X (only mesopores)	Nano Lett. 2019, 19, 8, 5149-5158 (Lacet et. al.)
	Cellulose (maximized defective carbon)	✓	Metal salt (e.g., CuCl ₂)	X	None specific	X	~35 nm (High density coverage > 85%)	X	Sci. Adv. 2021, 7, eabk2984 (Song et. al.)
Coordinated CTS (coordinated metal-ligands in precursor design)	Carbon (carbon for CTS)	X	Crystalline MOF (e.g., ZIF-67)	✓	Only MOF	X	< 3 nm (high density)	X (micropores < 2 nm)	Nano Energy 2022, 97, 107125
	Carbon (carbon for CTS)	X	Metal + ligands (e.g. Co ²⁺ & 2Melm)	✓	Coordination chemistry (Beyond MOF)	✓	~ 3.2 nm (high density)	✓ open/hierarchical pores (μm-nm)	This work

Supplementary Table 2. The heating rates control at different target heating rate.

Target heating rate (°C/s)	Current rate (A/s)	Current range (A)	Heating time (s)	Peak temperature (°C)	Actual heating rate (°C/s)
100	1	0 ~ 10	10	1063	106.3
1000	10	0 ~ 10	1	1042	1042
10000	100	0 ~ 10	0.1	1009	10090

Note: the heater size (carbon paper): length * width * thickness = 3.0 cm * 0.5 cm * 0.03 mm; Power loading mode: current output; Maximum output voltage: 30 V.

Supplementary Table 3. The peak areas (%), binding energy, and FWHM for N species in Co-N-CTS.

	pyridinic N	Co-N	pyrrolic N	graphitic N	oxidized N
Binding energy (eV)	398.22	399.02	400.25	401.1	402.16
FWHM	1.52	1.85	1.3	1.23	0.92
Peak areas (%)	33.5	27.2	14.1	19.8	5.4

Supplementary Table 4. The peak areas (%), binding energy, and FWHM for Co species in Co-N-CTS.

	Co⁰ 2p_{3/2}	Co³⁺ 2p_{3/2}	Co²⁺ 2p_{3/2}	Satellite peaks	Co⁰ 2p_{3/2}	Co³⁺ 2p_{3/2}	Co²⁺ 2p_{3/2}
Binding energy (eV)	778.41	779.83	781.44	783.76	793.42	795.08	796.36
FWHM	1.33	1.99	2.37	3.5	1.86	1.63	1.63
Peak areas (%)	34.5	20.0	11.4	12.1	12.8	5.5	2.8

Supplementary Table 5. The peak areas (%), binding energy, and FWHM for Co species in Co-CTS.

	Co^0 $2p_{3/2}$	Co^{3+} $2p_{3/2}$	Co^{2+} $2p_{3/2}$	Satellite peaks	Co^0 $2p_{3/2}$	Co^{3+} $2p_{3/2}$	Co^{2+} $2p_{3/2}$	Satellite peaks
Binding energy (eV)	778.2 2	779.39	781.48	784.28	793.36	795.19	796.86	903.19
FWHM	1.16	2.33	2.72	3.5	2.02	2.17	2.95	3.5
Peak areas (%)	22.7	22.7	16.0	8.4	12.5	4.5	8.2	5.0

Supplementary Table 6. Performance comparison in ORR and OER between Co-N-CTS and other reported Co-based bifunctional electrocatalysts in literature.

Catalysts	ORR $E_{1/2}$ (V)	OER η_{10} (mV)	ΔE (V)	Reference
Co-N-CTS	0.86	280	0.65	This work
OLC/Co-N-C	0.86	350	0.72	Angew. Chem., Int. Ed. 2021, 60, 12759.
NCNTFs	0.87	370	0.73	Nat. Energy. 2016,1, 15006.
CNT@SAC-Co/NCP	0.87	380	0.74	Adv. Funct. Mater. 2021, 31, 2103360.
Co ₃ O _{4-x} HoNPs @HPNCS	0.83	340	0.74	Angew. Chem. Int. Ed. 2019, 58, 13840-13844.
Co@hNCTs-800	0.87	400	0.76	Nano Energy 2020, 71, 2211.
Co SA/NCFs	0.85	380	0.76	Nano Lett. 2022, 22, 2497–2505.
Co-NCNT	0.86	400	0.77	Energy Storage Mater. 2019, 20, 234-242.
Co/CNWs/CNFs	0.82	410	0.82	Adv. Funct. Mater. 2021, 31, 2105021.
Co-POC	0.83	470	0.87	Adv. Mater. 2019, 31, 1900592.
CoSAs-NGST	0.89	560	0.9	Adv. Funct. Mater. 2021, 31, 2010472.

Supplementary Table 7: The formation energy of metal with 2-MeIm.

Ingredient	Ag	Cu	Co	Mn	Cr	Fe	Ni
Formation energy	-0.87	-2.5	-3.44	-3.55	-4.14	-4.66	-5.8

Supplementary Table 8: The formation energy of metal with BTC.

Ingredient	Cu	Fe
Formation energy	-8.13	-11.55

Supplementary References

1. Yao, Y. *et al.* Carbothermal shock synthesis of high-entropy-alloy nanoparticles. *Science* (80-.). **359**, 1489–1494 (2018).
2. Yao, Y. *et al.* Ultrafast, controllable synthesis of sub-nano metallic clusters through defect engineering. *ACS Appl. Mater. Interfaces* **11**, 29773–29779 (2019).
3. Lacey, S. D. *et al.* Stable multimetallic nanoparticles for oxygen electrocatalysis. *Nano Lett.* **19**, 5149–5158 (2019).
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