

Supporting Information

Metal-organic frameworks derived single-atom catalysts for electrochemical CO₂ reduction

Mengna Xie,^{‡ab} Jiawei Wang,^{‡ab} Xian-Long Du,^{*acd} Na Gao,^{ad} Tao Liu,^e Zhi Li,^e

GuoPing Xiao,^{acd} Tao Li^b and Jian-Qiang Wang^{acd}

^a Key Laboratory of Interfacial Physics and Technology, Shanghai Institute of Applied Physics, Chinese Academy of Sciences, Shanghai 201800

^b Engineering Research Center of Large-Scale Reactor Engineering and Technology, Ministry of Education, State Key Laboratory of Chemical Engineering, East China University of Science and Technology, Shanghai 200237, China

^c University of Chinese Academy of Sciences, Beijing 100049, China

^d Dalian National Laboratory for Clean Energy, Chinese Academy of Sciences, Dalian 116023, China

^e Shandong Energy Group Co., Ltd., Jinan 250014, China

* Corresponding Author

E-mail: duxianlong@sinap.ac.cn

‡These authors contributed equally to this work.

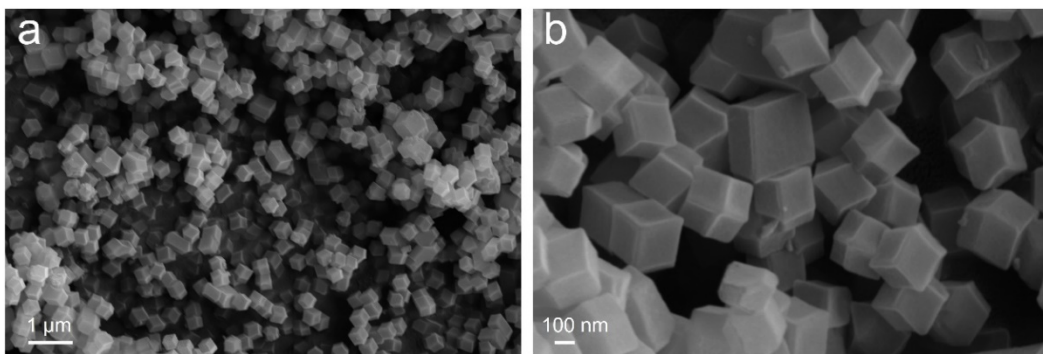


Figure S1. (a) and (b) SEM images of ZIF-8. It is obvious that the synthesized ZIF-8 exhibits a uniform rhomb dodecahedral shape.

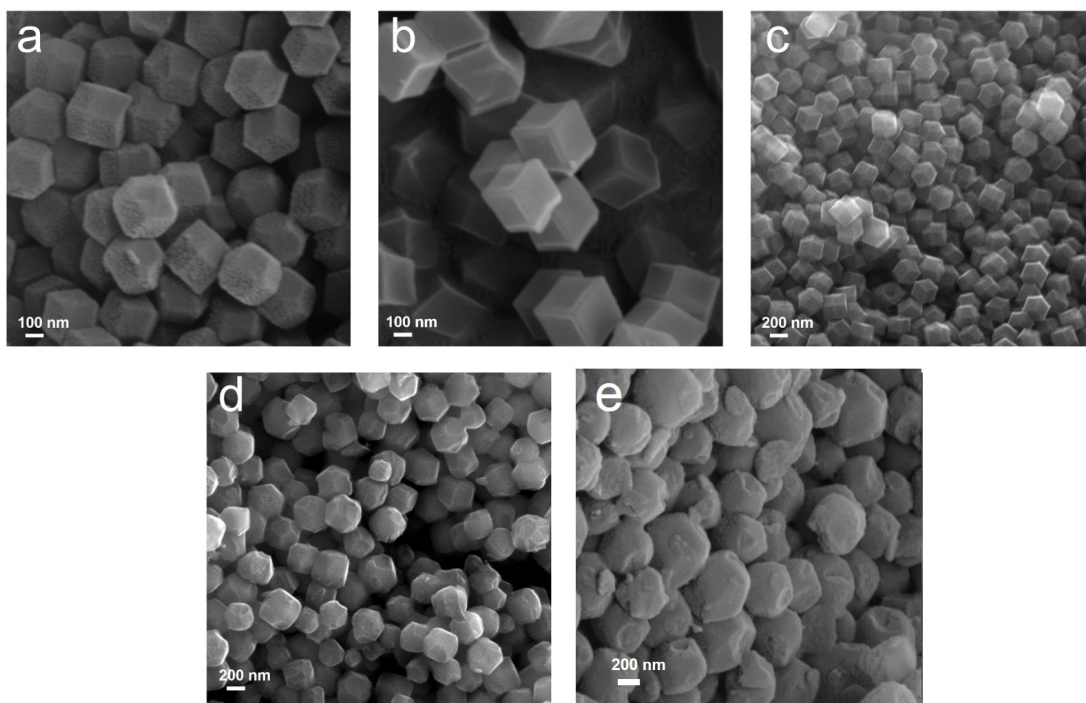


Figure S2. SEM characterization of M-N-C. SEM images of (a) Fe-N-C, (b) Ni-N-C, (c) Mn-N-C, (d) Co-N-C and (e) Cu-N-C.

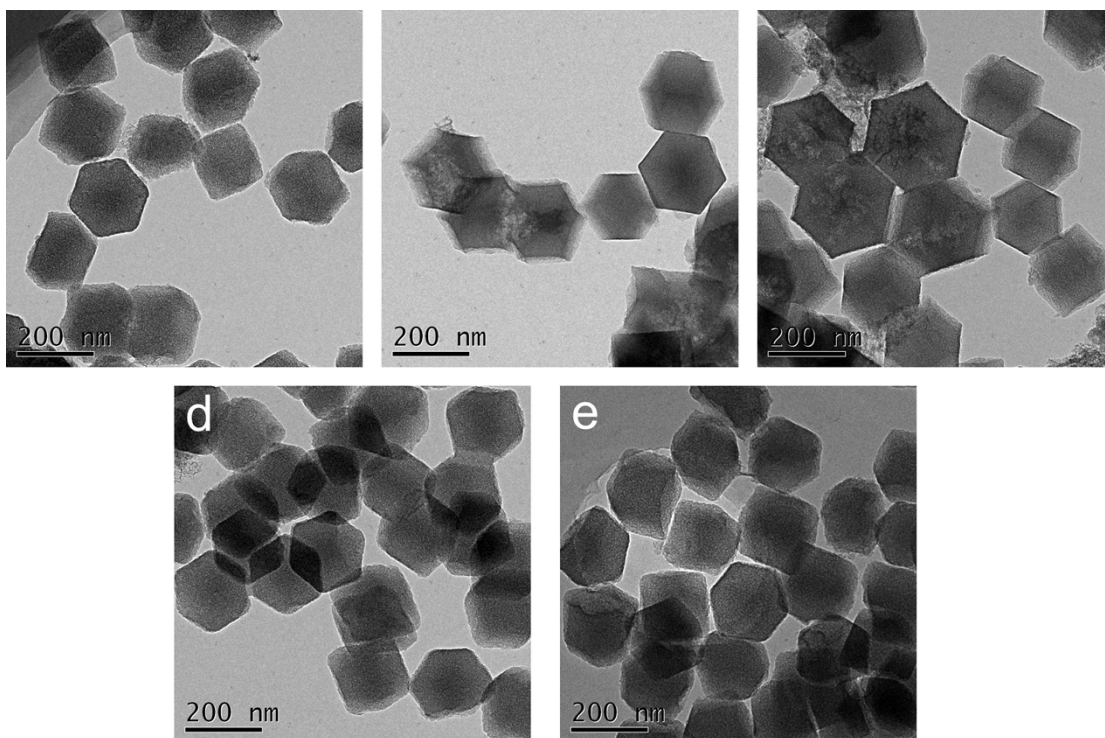


Figure S3. TEM characterization of M-N-C. TEM images of (a) Fe-N-C, (b) Ni-N-C, (c) Mn-N-C, (d) Co-N-C and (e) Cu-N-C.

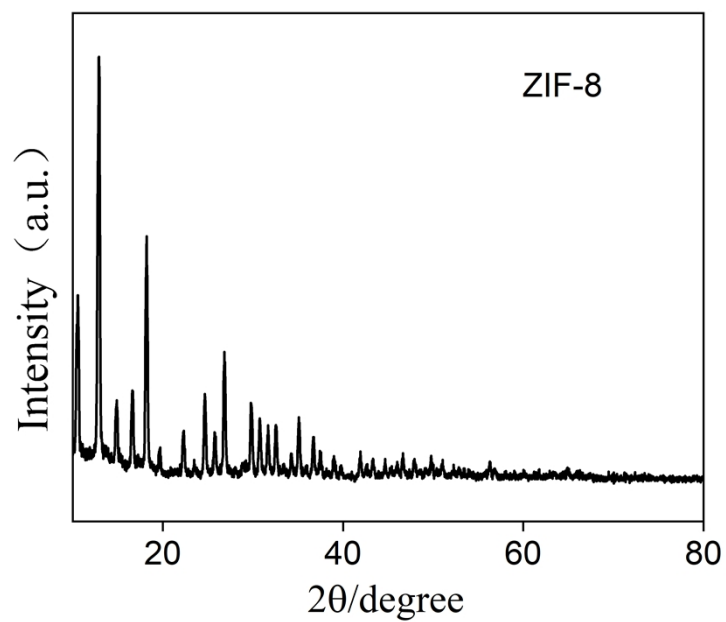


Figure S4. XRD pattern of ZIF-8.

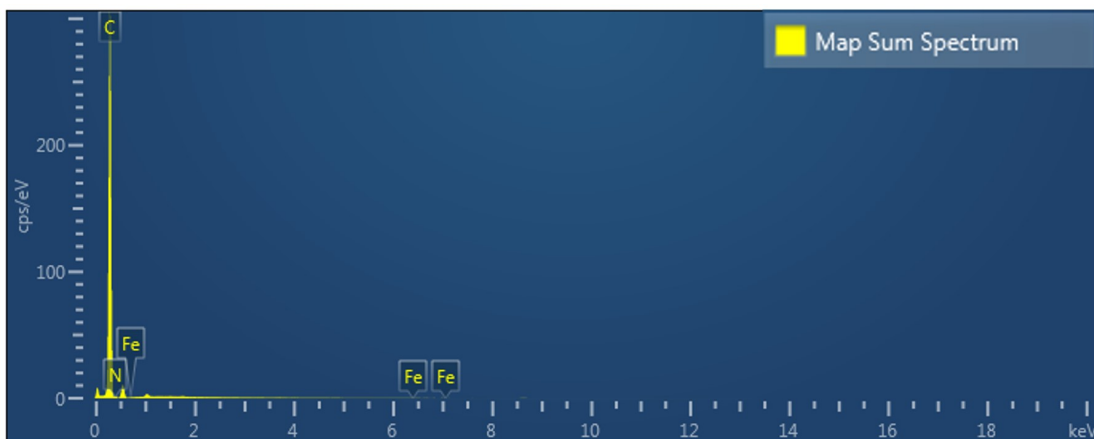


Figure S5. Energy dispersive spectroscopy (EDS) characterization of Fe-N-C. No visible Zn signal locating at 8.63 keV was detected in Fe-N-C, suggesting low residual Zn content.

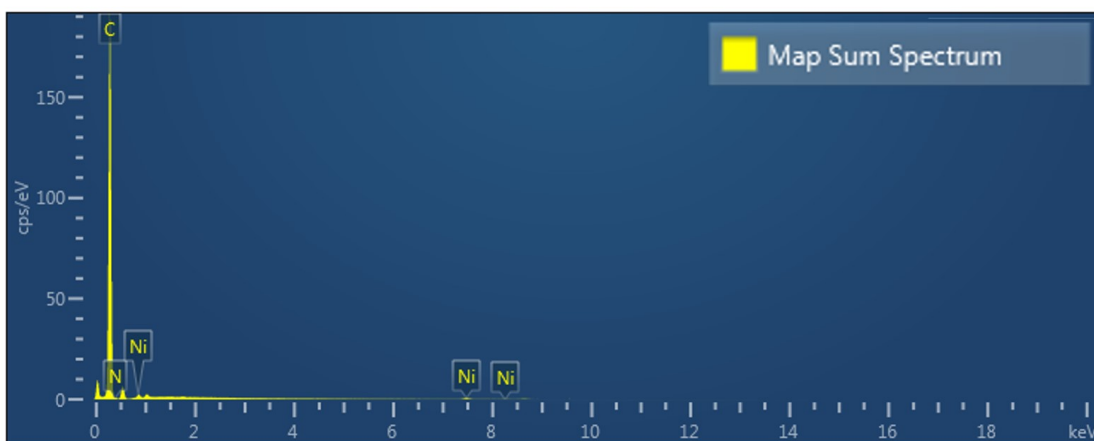


Figure S6. Energy dispersive spectroscopy (EDS) characterization of Ni-N-C. No visible Zn signal locating at 8.63 keV was detected in Ni-N-C, suggesting low residual Zn content.

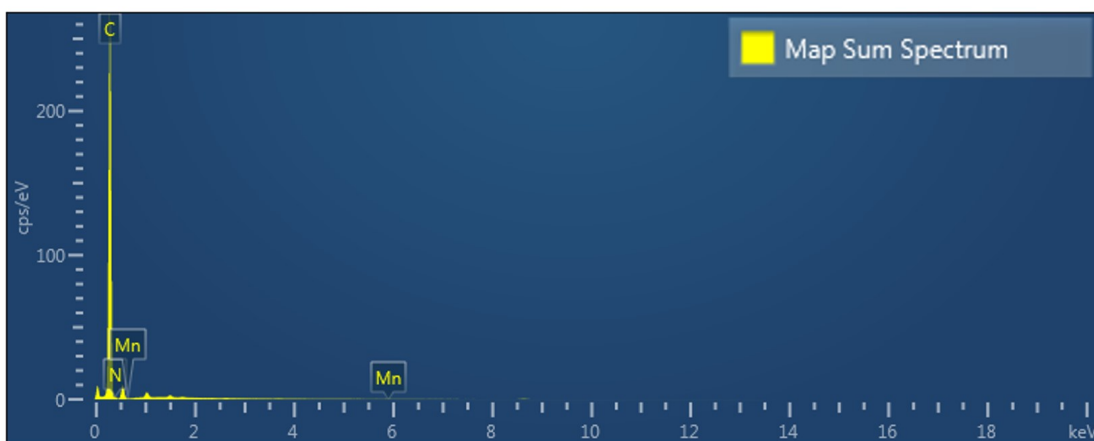


Figure S7. Energy dispersive spectroscopy (EDS) characterization of Mn-N-C. No visible Zn signal locating at 8.63 keV was detected in Fe-N-C, suggesting low residual Zn content.

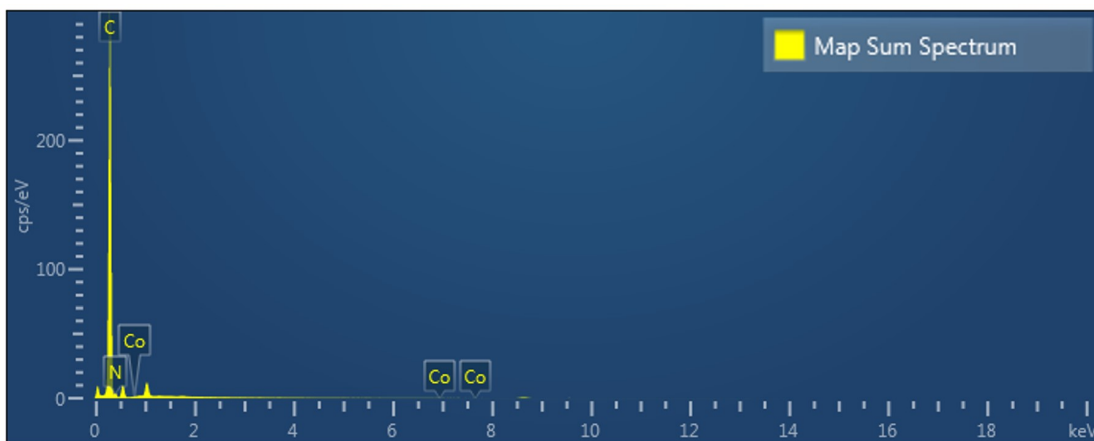


Figure S8. Energy dispersive spectroscopy (EDS) characterization of Co-N-C. No visible Zn signal locating at 8.63 keV was detected in Co-N-C, suggesting low residual Zn content.

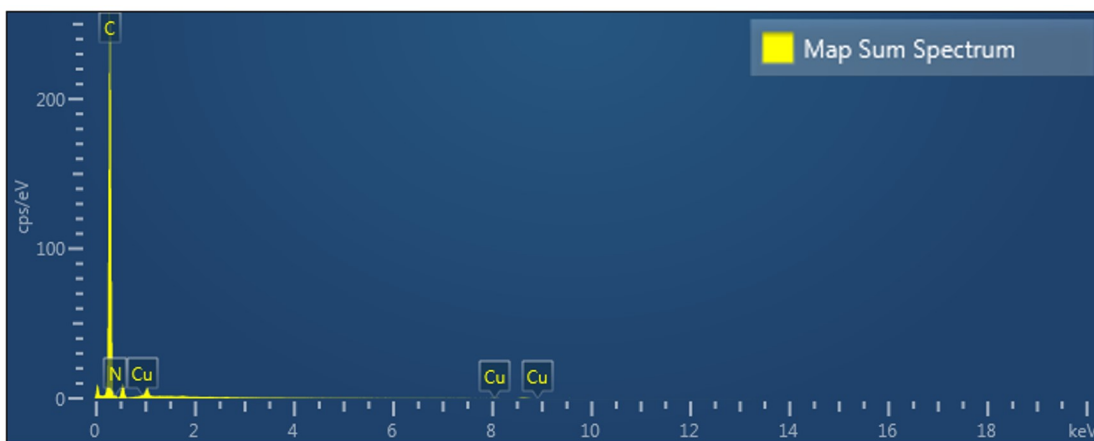


Figure S9. Energy dispersive spectroscopy (EDS) characterization of Cu-N-C. No visible Zn signal locating at 8.63 keV was detected in Cu-N-C, suggesting low residual Zn content.

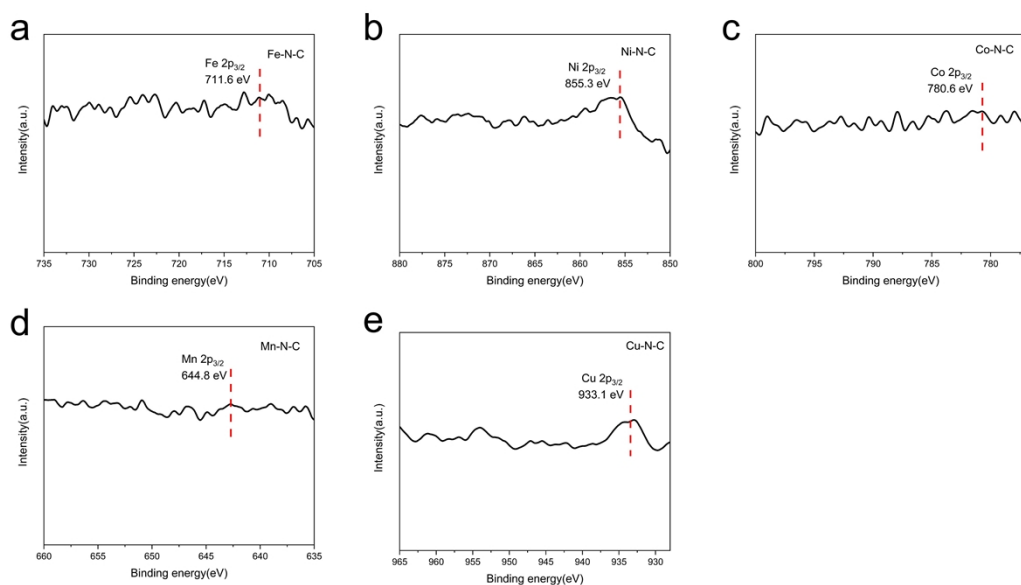


Figure S10. (a) Fe 2p spectrum of Fe-N-C, (b) Ni 2p spectrum of Ni-N-C, (c) Mn 2p spectrum of Mn-N-C, (d) Co 2p spectrum of Co-N-C and (e) Cu 2p spectrum of Cu-N-C

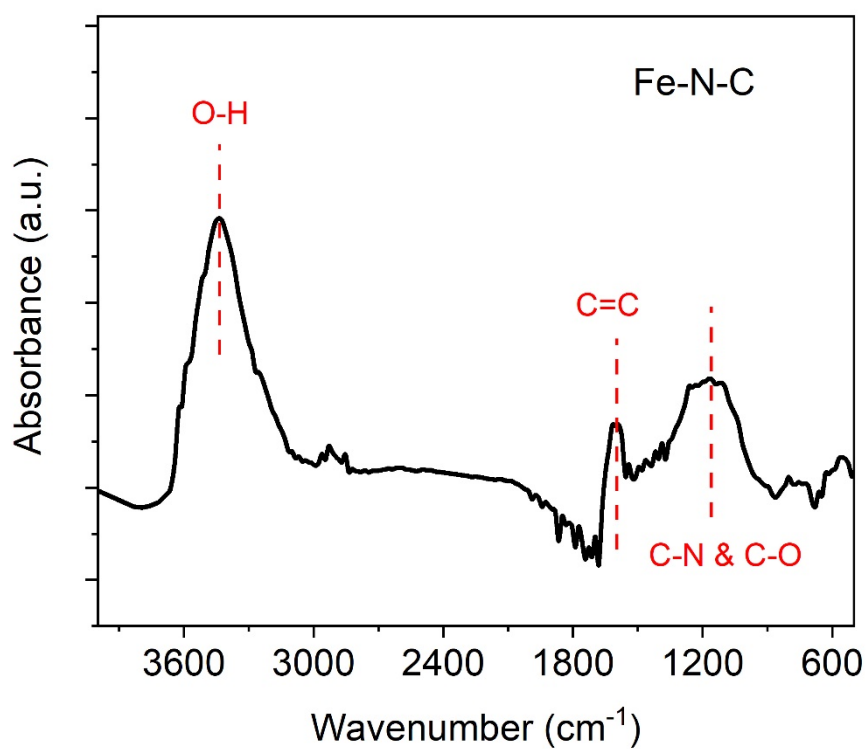


Figure S11. FT-IR spectra of Fe-N-C.

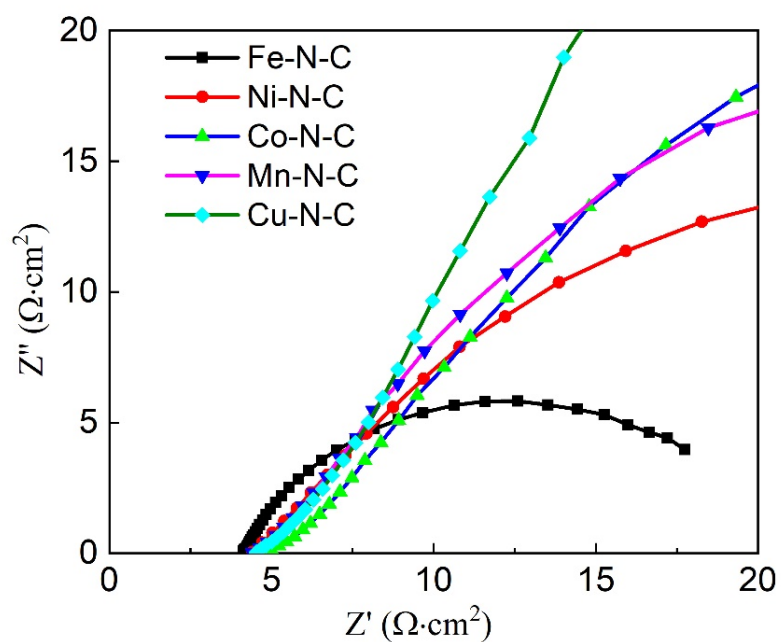


Figure S12. Nyquist plots of M-N-C catalysts in CO_2 -saturated 0.5 M KHCO_3 solution at -0.5 V vs RHE.

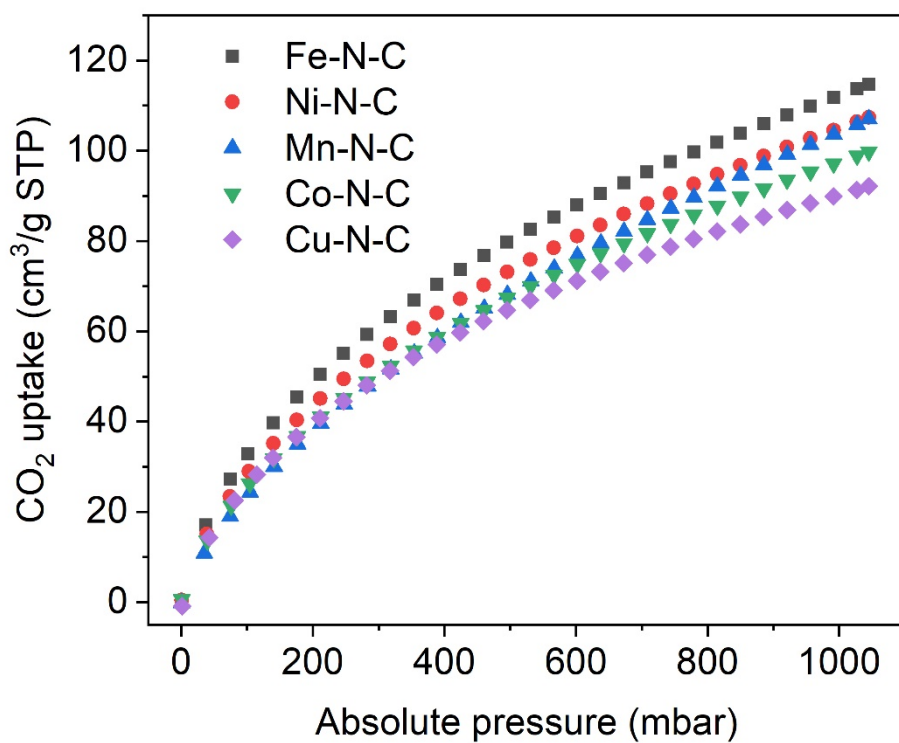


Figure S13. CO_2 physisorption isotherm at 273 K.

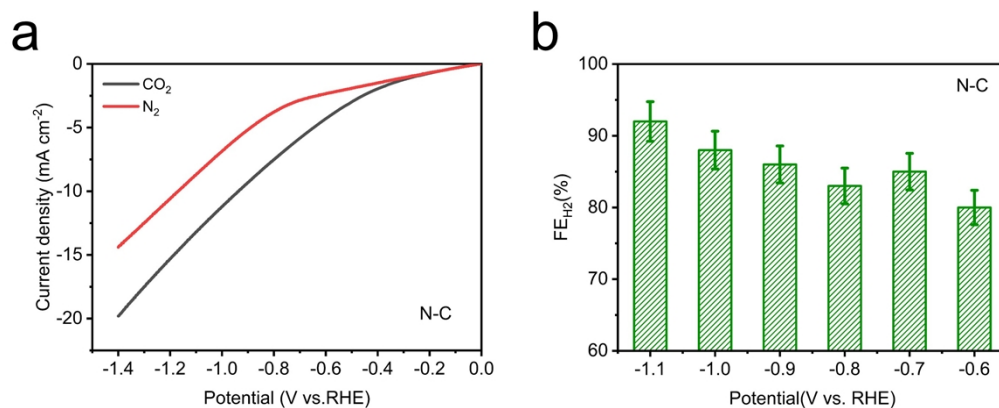


Figure S14. Electrocatalytic CO₂RR Performance of N-C catalyst using a flow cell (a) LSV curves in pure N₂- and CO₂-saturated 0.5 M KHCO₃ at a scan rate of 10 mV s⁻¹. (b) FE for H₂ production measured in CO₂-saturated 0.5 M KHCO₃

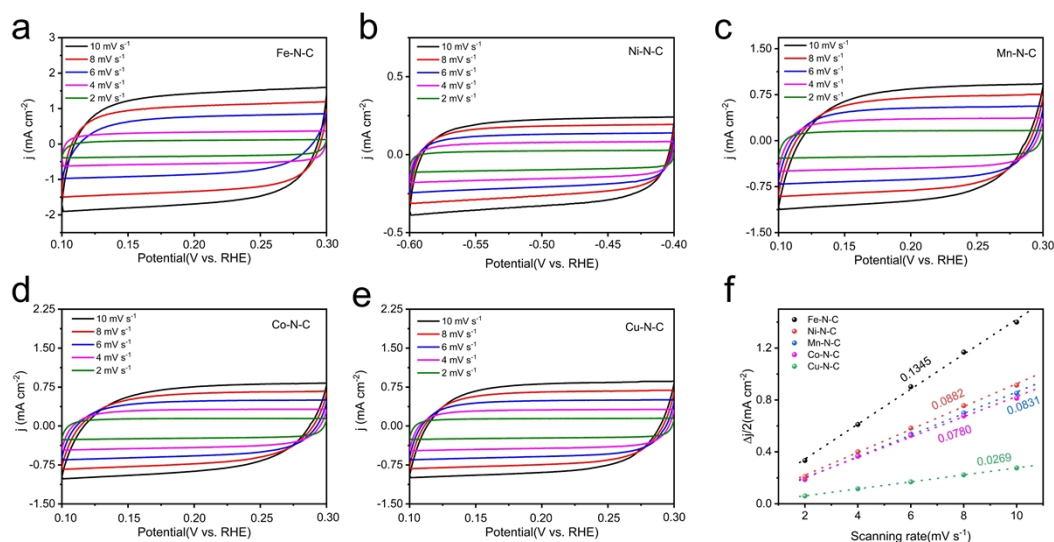


Figure S15. CV curves of (a) Fe-N-C, (b) Ni-N-C, (c) Mn-N-C, (d) Co-N-C and (e) Cu-N-C. The CV measurements were performed in CO₂-saturated 0.5 M KHCO₃ at various scan rates: 2, 4, 6, 8 and 10 mV s⁻¹. (f) A plot of changing current density against scan rates for electrochemically active surface area (ECSA) measurements. As clearly shown, ECSA of the M-N-C catalysts increased in the following order of Fe-N-C > Ni-N-C > Mn-N-C > Co-N-C > Cu-N-C, coinciding with the FE_{CO} results.

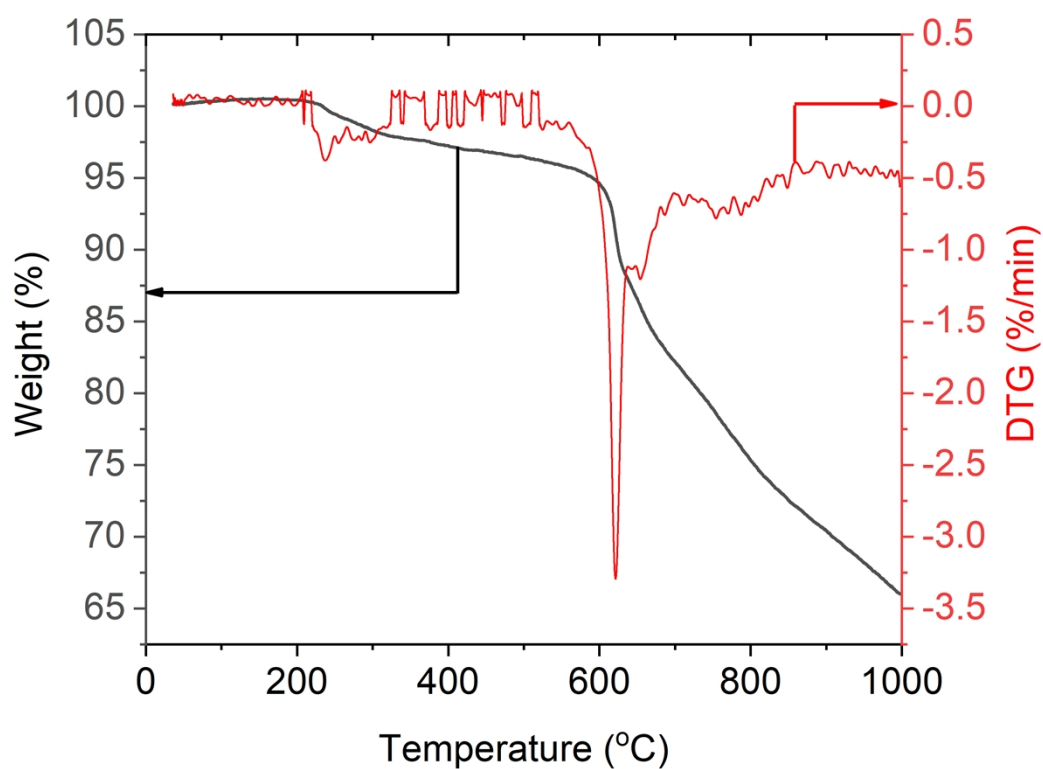


Figure S16. TG-DTG patterns of the composite of $\text{Fe}(\text{NO}_3)_3$ adsorbed within ZIF-8.

Table S1. Metal contents of all M-N-C samples determined by ICP-MS

Sample	Metal content (wt%)
Fe-N-C	0.48
Ni-N-C	0.65
Mn-N-C	0.58
Co-N-C	0.52
Cu-N-C	0.68