

## Supporting Information

### **Tunable Functional Groups on MXene Regulating Catalytic Property of Anchored Cobalt Phthalocyanine for Electrochemical CO<sub>2</sub> Reduction**

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## Materials.

Titanium aluminum carbide ( $\text{Ti}_3\text{AlC}_2$ , purity 98%, 200 mesh) was bought from Rhawn Company (Shanghai, China). Hydrogen fluoride (HF, AR,  $\geq 40$  wt%), Sodium fluoride (NaF, AR, 97%), Sodium hydroxide (NaOH, AR, 97%) and Dimethyl sulfoxide (DMSO, GC,  $>99.8\%$ ) were bought from Aladdin Company (Shanghai, China). N, N-Dimethylformamide (DMF, AR) and Ethanol absolute (AR) were bought from Kermel Company (Tianjin, China). Cobalt phthalocyanine (CoPc, 97%) was bought from Sigma-Aldrich (Shanghai, China). Proton exchange membrane Nafion 117 was purchased from DuPont. Nafion solution (5 wt.%) was purchased from Sigma-Aldrich (Shanghai, China). All the chemicals were used without further purification. All aqueous solutions were prepared with MilliQ ultrapure water ( $18.2 \text{ M}\Omega \cdot \text{cm}$ ).

## Characterization.

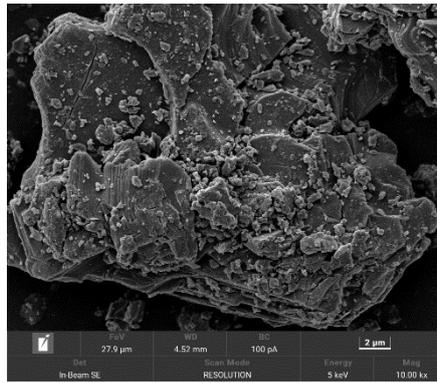
SEM was measured using Quanta 450 FEG microscopy. TEM was measured using FEI Talos F200S microscopy and AC-STEM images were gained on FEI-Titan Cubed Themis G2 300 microscope. The Fourier transform infrared (FTIR) spectra were measured using a Fourier transform infrared spectrometer (Bruker, TENSOR 27FTIR, Germany). XRD (Bruker, D8 Discover, Germany) analysis was carried out to analyze the crystal structure of the material. XPS was carried out using Thermo Scientific ESCALAB 250Xi. UV-vis spectra were obtained using a TU-1900 (Persee, Beijing, China) spectrophotometer. Raman spectra was measured using Renishaw Invia reflex. ICP-MS was performed on Agilent 7800 to detect mass content of Co species. XAFS measurement was collected by Shanghai Synchrotron Radiation Facility.

## DFT calculations.

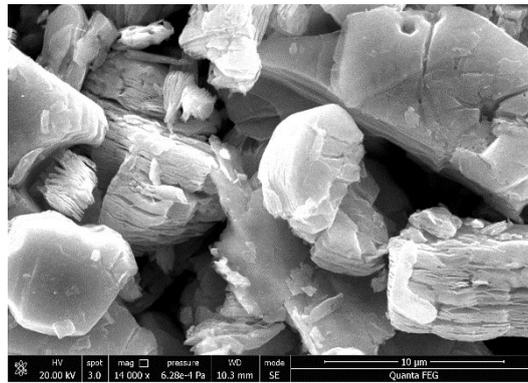
The DFT calculation was performed by Vienna Abinitio Simulation Package (VASP) using the projector augmented wave (PAW) method. Planar wave cut-off energy (ENCUT) is set to 400 eV, graphene substrate, using a  $3 \times 3 \times 1$  super cell containing atoms. The convergence criterion adopts the convergence energy thresholds of EDIFFG =  $-0.02$  and EDIFF =  $1.0 \times 10^{-5}$  eV. The Co-centered k-point sampling grid adopted  $3 \times 3 \times 1$  for the geometric optimization. The  $\Delta G$  of ECRR steps were calculated by:

$$\Delta G = \Delta E_{\text{DFT}} + \Delta E_{\text{ZPE}} - T\Delta S$$

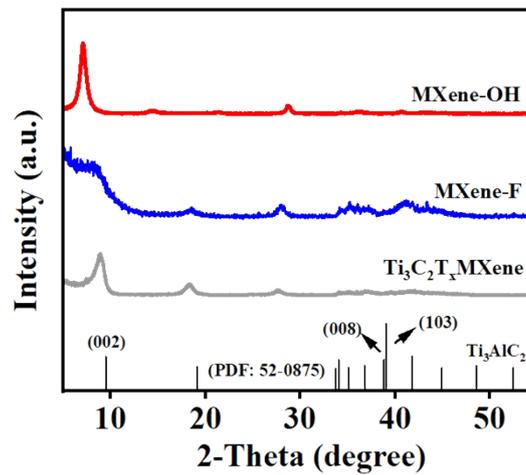
where  $\Delta E_{\text{DFT}}$ ,  $\Delta E_{\text{ZPE}}$  and  $\Delta S$  are the energy from DFT optimization, correction of zero-point energy and the variation of entropy, respectively. T is the temperature ( $T = 298.15 \text{ K}$ ).



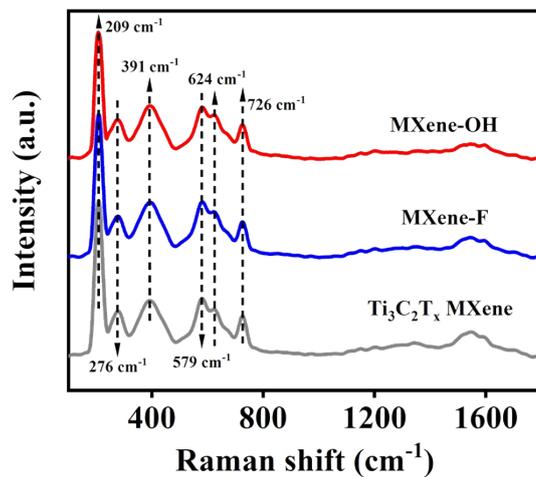
**Figure S1.** SEM image of pristine  $\text{Ti}_3\text{AlC}_2$



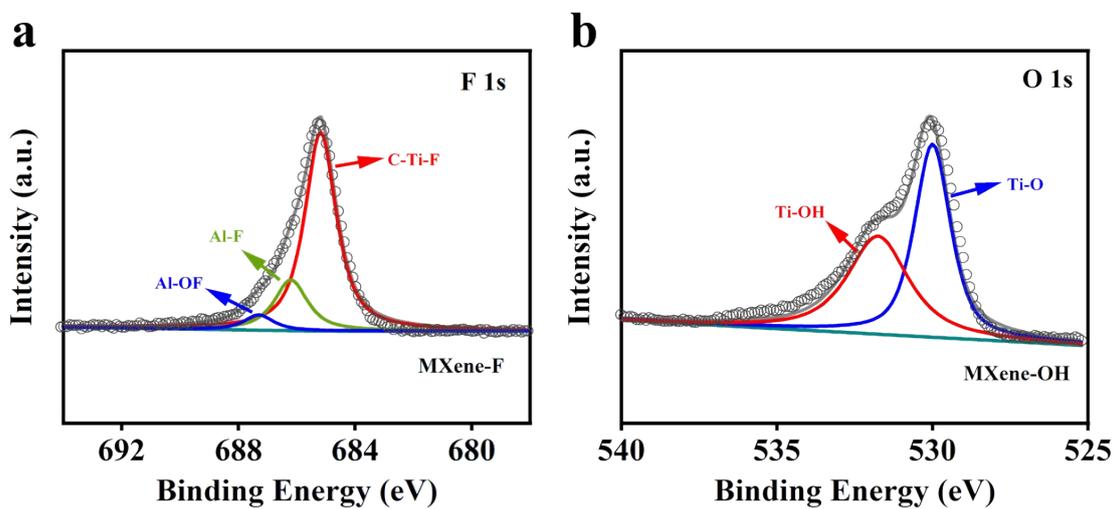
**Figure S2.** SEM image of pristine  $\text{Ti}_3\text{C}_2\text{T}_x$  MXene.



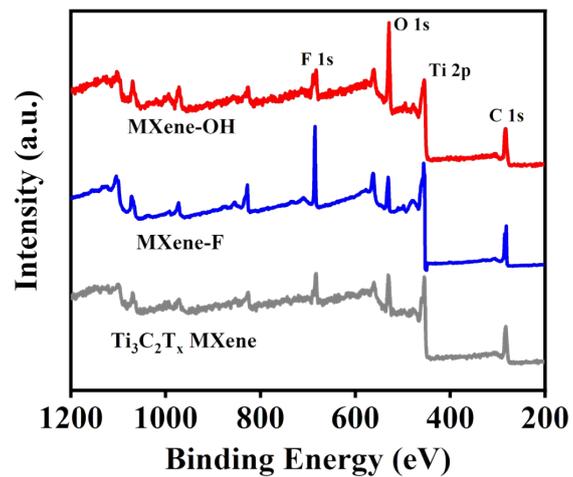
**Figure S3.** XRD patterns of MXene-F, MXene-OH and  $\text{Ti}_3\text{C}_2\text{T}_x$  MXene.



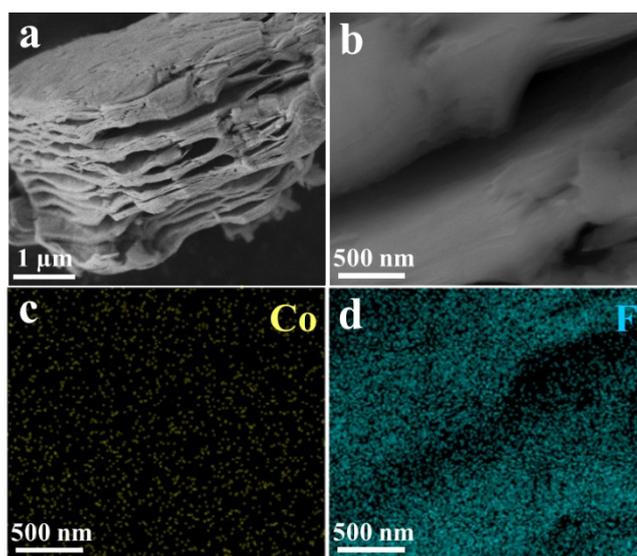
**Figure S4.** Raman patterns of MXene-F, MXene-OH and  $\text{Ti}_3\text{C}_2\text{T}_x$  MXene.



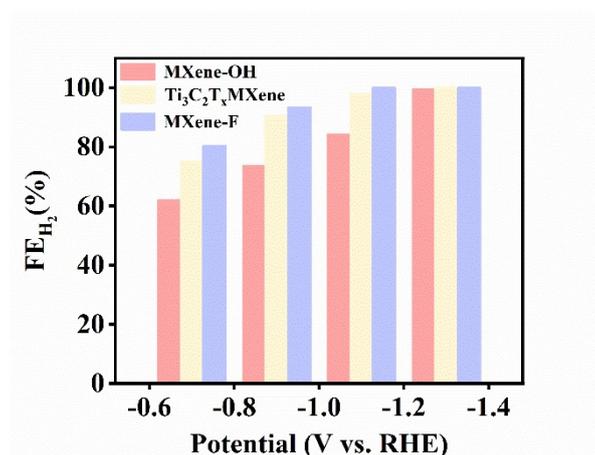
**Figure S5.** (a) XPS spectrum of MXene-F corresponding to F 1s. (b) XPS spectrum of MXene-OH corresponding to O 1s.



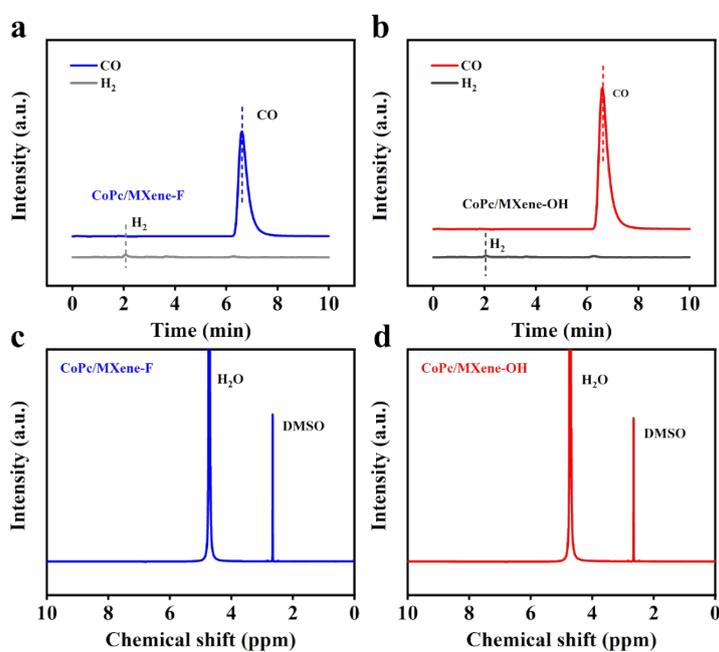
**Figure S6.** XPS spectra of Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>, MXene-F and MXene-OH.



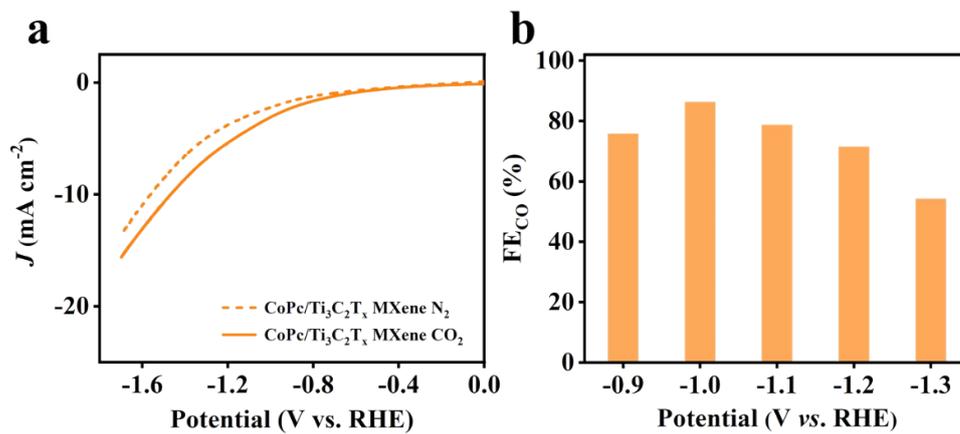
**Figure S7.** EDS of CoPc/MXene-F.



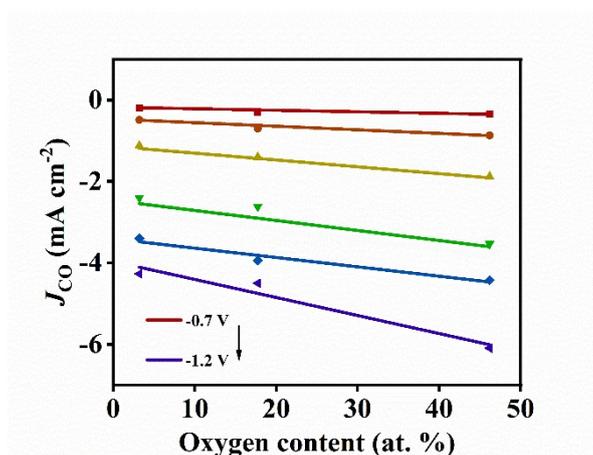
**Figure S8.** FE<sub>H<sub>2</sub></sub> of MXene-OH (red), Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> MXene (yellow) and MXene-F (blue)..



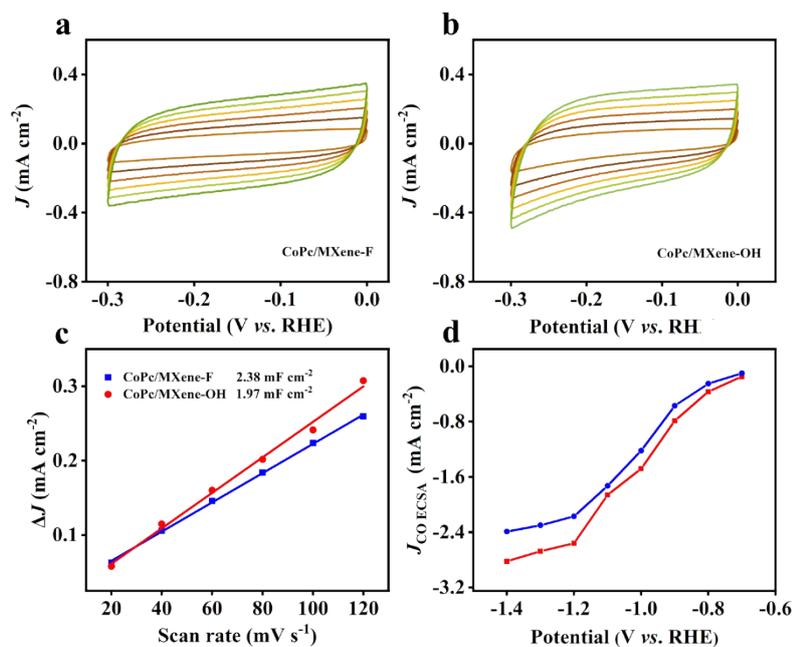
**Figure S9.** (a-b) Curves collected by GC after 30 min of electrolysis at -0.9 V vs. RHE of CoPc/MXene-F and CoPc/MXene-OH, respectively; (c-d) <sup>1</sup>H NMR spectra after 3 h of electrolysis at -0.9 V vs. RHE.



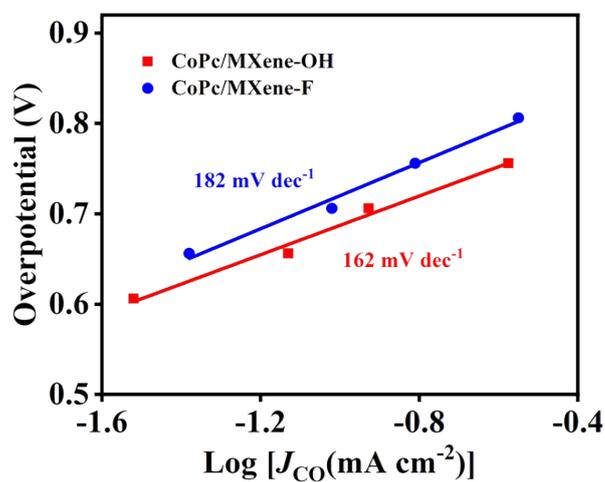
**Figure S10.** (a) LSV curves of CoPc/Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> MXene in CO<sub>2</sub>-saturated or N<sub>2</sub> 0.1 M KHCO<sub>3</sub> solution, (b) FE<sub>CO</sub> at various potentials of CoPc/Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> MXene.



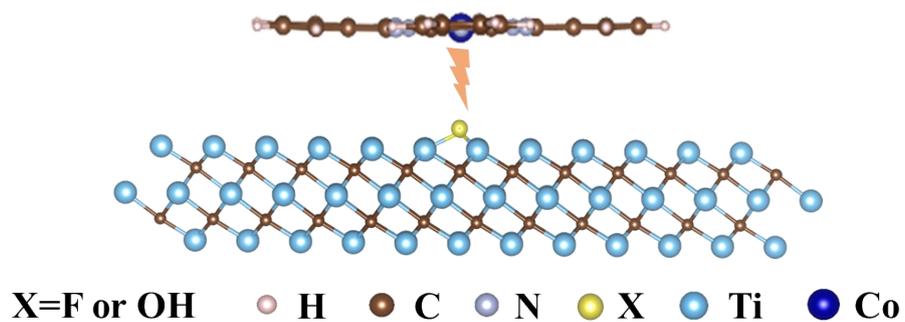
**Figure S11.** Correlation map of -OH content and  $J_{CO}$ .



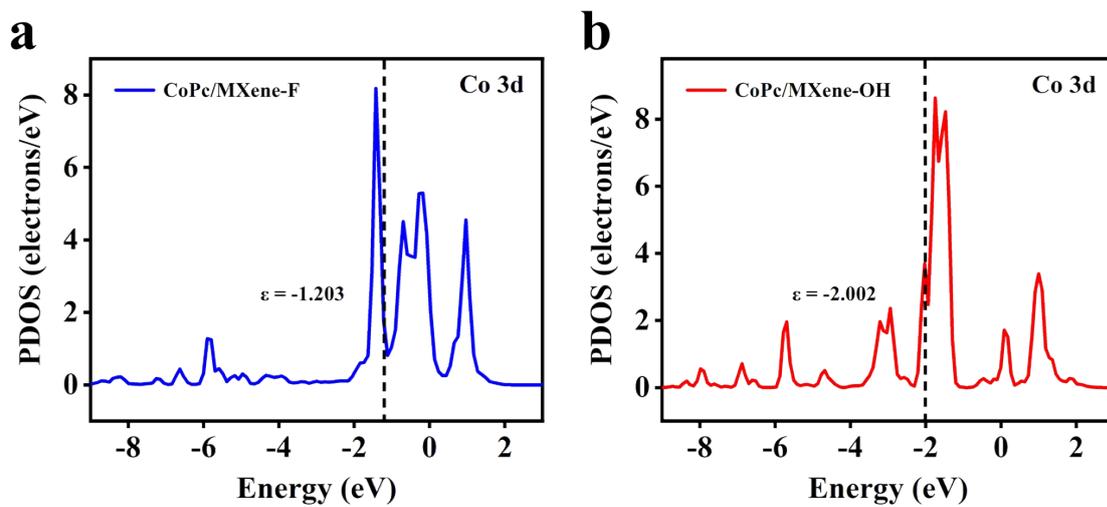
**Figure S12.** Cyclic voltammograms of CoPc/MXene-F (a) and CoPc/MXene-OH (b) at the range of -0.3 to 0 V vs. RHE with different scan rates. (c) Charging current density differences plotted against scan rates. (d) Partial current densities of CO normalized by ECSA of CoPc/MXene-F and CoPc/MXene-OH.



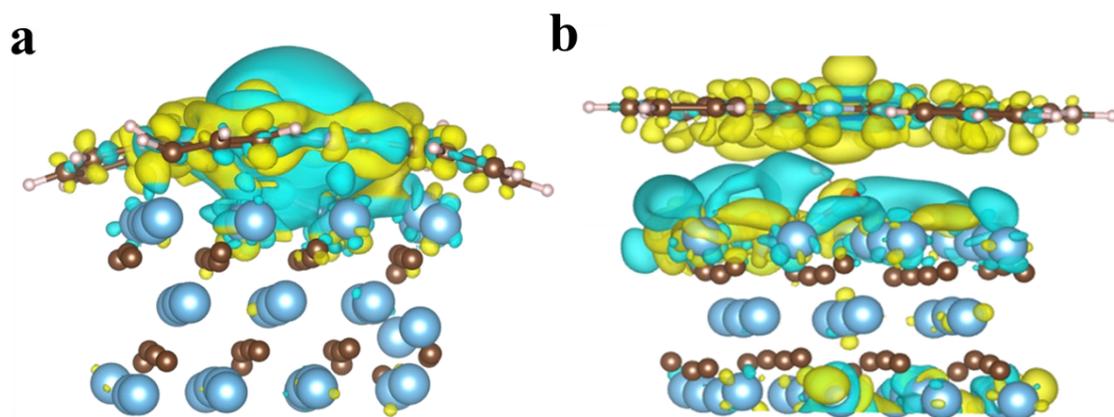
**Figure S13.** Tafel slope of CoPc/MXene-F and CoPc/MXene-OH.



**Figure S14.** Atomic structure schematic of CoPc/MXene-X.



**Figure S15.** PDOS of (a) CoPc/MXene-F, (b) CoPc/MXene-OH.



**Figure S16.** Differential charge density diagram of (a) CoPc/MXene-F and (b) CoPc/MXene-OH.

**Table S1.** Elemental quantification of different catalysts measured by XPS.

Samples	F 1s at %	O 1s at %
MXene-OH	2.16	46.19
MXene-F	38.23	3.20
Ti <sub>3</sub> C <sub>2</sub> T <sub>x</sub> MXene	15.80	17.74

**Table S2.** EXAFS fitting parameters at the Co K-edge for various samples.

Sample	Shell	N <sup>a</sup>	R(Å) <sup>b</sup>	σ <sup>2</sup> (Å <sup>2</sup> ) <sup>c</sup>	ΔE <sub>0</sub> (eV) <sup>d</sup>	R factor
CoPc	Co-N	4.21	1.91	0.0013	0.27	0.0077
	Co-O	6.00	2.12	0.0080	-1.81	
CoO	Co-Co	12.00	3.01	0.0080	-1.81	0.0171
CoPc/MXene-OH	Co-O	0.90	1.33	0.0032	0.36	0.0160
	Co-N	4.10	1.91	0.0002	8.72	