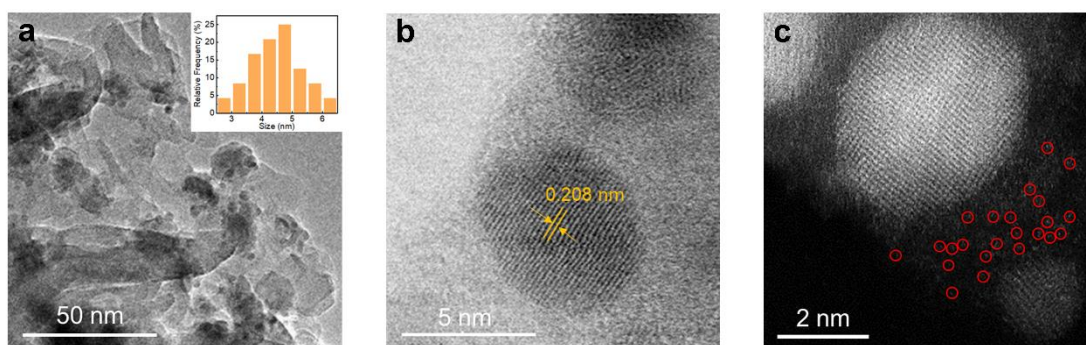


Supplementary Information for

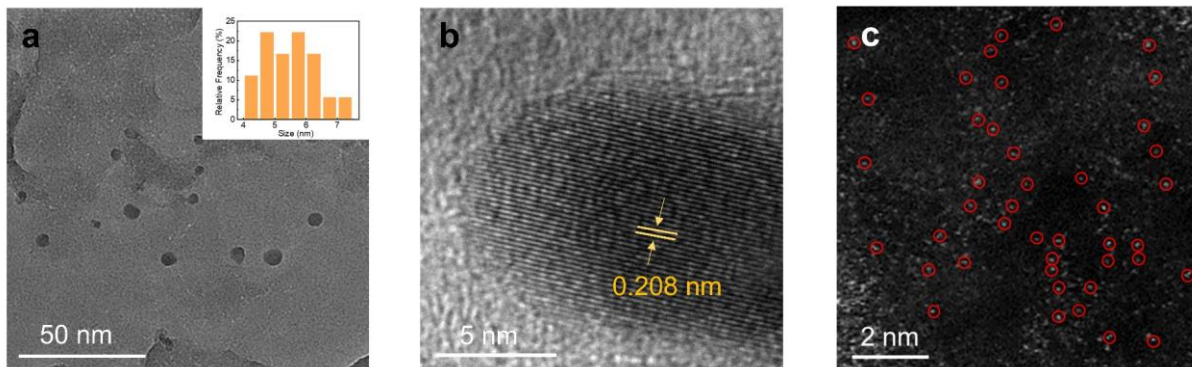
## **Modulating Adsorbed Hydrogen Drives Electrochemical CO<sub>2</sub>-to-C<sub>2</sub> Products**

Jiaqi Feng, Libing Zhang, Shoujie Liu, Liang Xu, Xiaodong Ma, Xingxing Tan, Limin Wu, Qingli Qian, Tianbin Wu, Jianling Zhang, Xiaofu Sun\*, Buxing Han\*

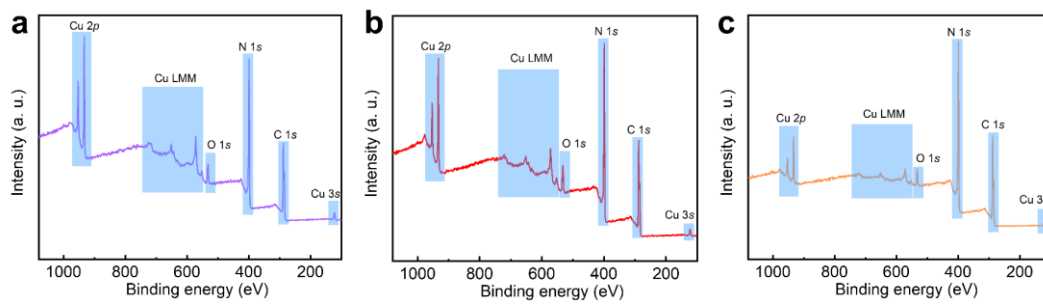
## Supplementary Figures and Tables



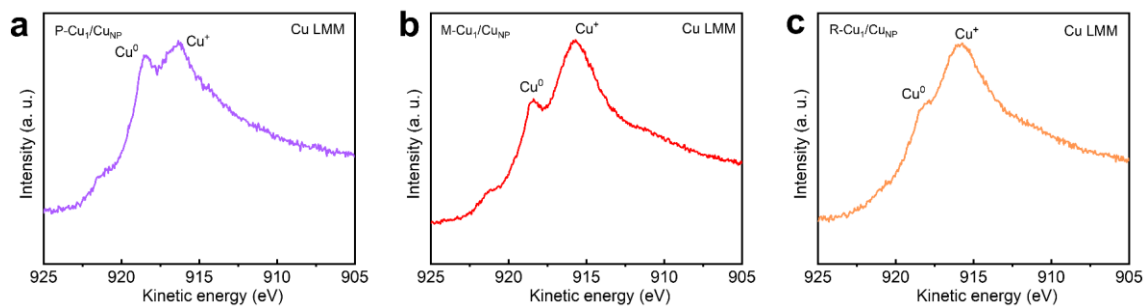
**Figure S1.** (a) TEM image (inset shows particle size distribution), (b) HRTEM image and (c) aberration-corrected HAADF-STEM image of P-Cu<sub>1</sub>/Cu<sub>NP</sub>.



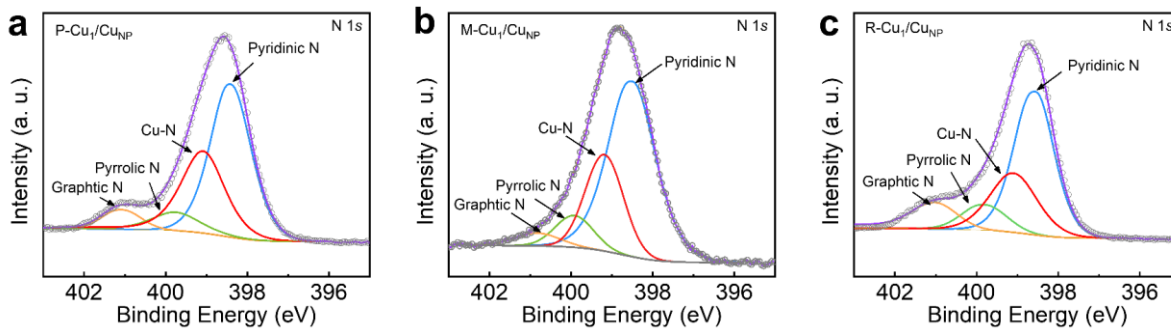
**Figure S2.** (a) TEM image (inset shows particle size distribution), (b) HRTEM image and (c) aberration-corrected HAADF-STEM image of R-Cu<sub>1</sub>/Cu<sub>NP</sub>.



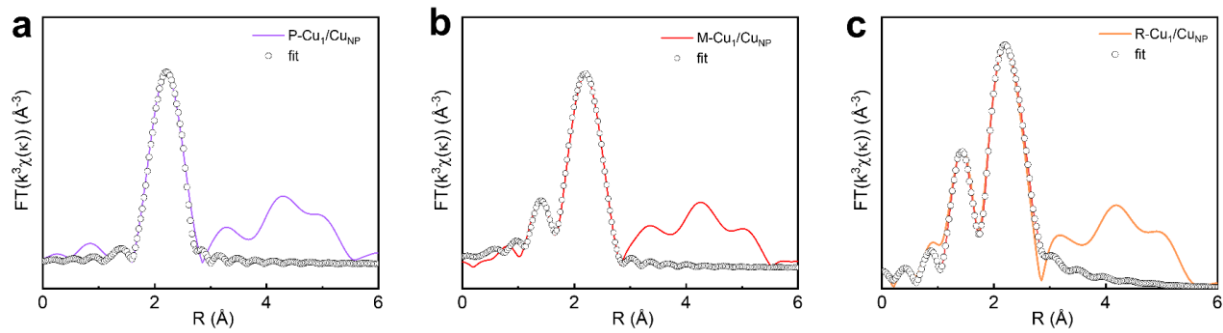
**Figure S3.** XPS survey spectra of (a) P-Cu<sub>1</sub>/Cu<sub>NP</sub>, (b) M-Cu<sub>1</sub>/Cu<sub>NP</sub> and (c) R-Cu<sub>1</sub>/Cu<sub>NP</sub>.



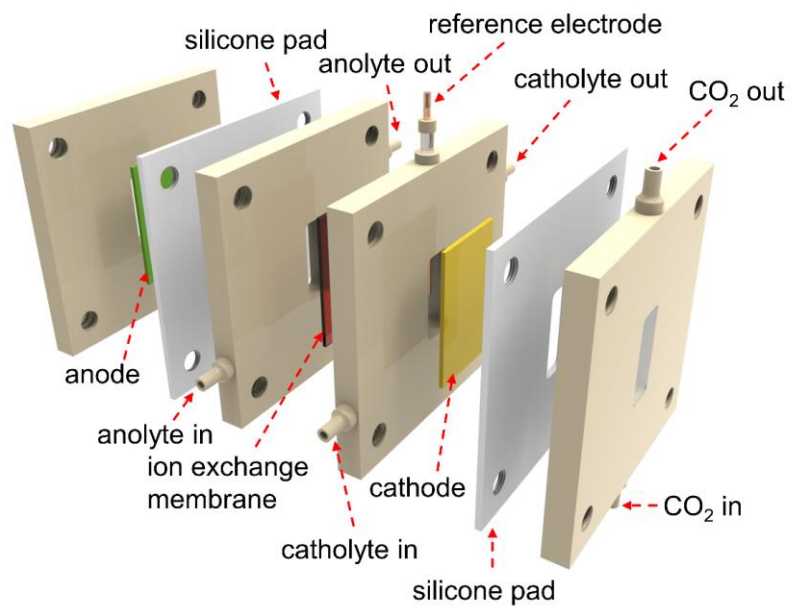
**Figure S4.** Cu Auger LMM spectra of (a) P-Cu<sub>1</sub>/Cu<sub>NP</sub>, (b) M-Cu<sub>1</sub>/Cu<sub>NP</sub> and (c) R-Cu<sub>1</sub>/Cu<sub>NP</sub>.



**Figure S5.** XPS spectra of N 1s orbits of (a) P-Cu<sub>1</sub>/Cu<sub>NP</sub>, (b) M-Cu<sub>1</sub>/Cu<sub>NP</sub>, and (c) R-Cu<sub>1</sub>/Cu<sub>NP</sub>.

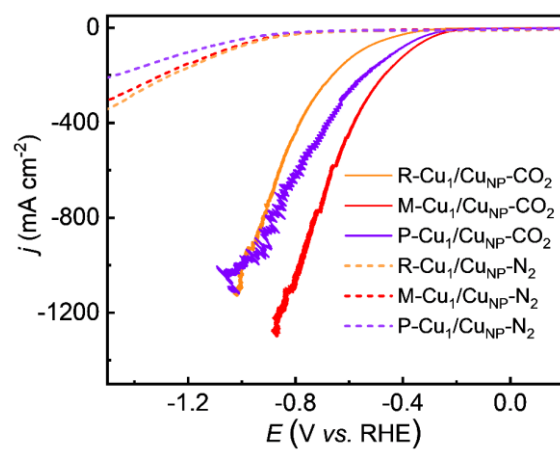


**Figure S6.** Least-squares EXAFS fittings of (a) P-Cu<sub>1</sub>/Cu<sub>NP</sub>, (b) M-Cu<sub>1</sub>/Cu<sub>NP</sub>, and (c) R-Cu<sub>1</sub>/Cu<sub>NP</sub>.

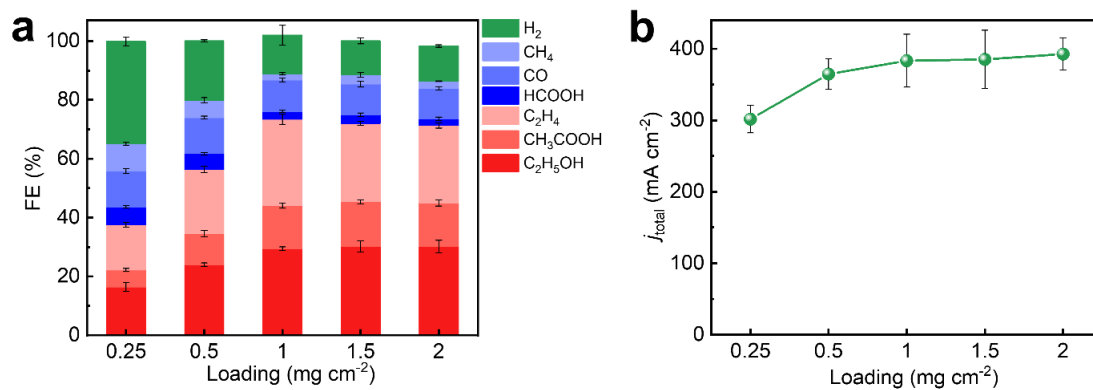


**Figure S7.** The scheme of flow cell used for CO<sub>2</sub>RR tests.

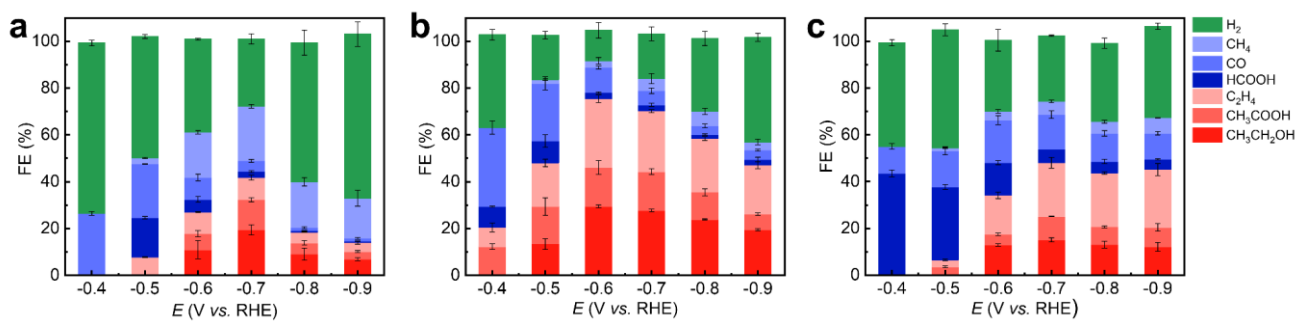




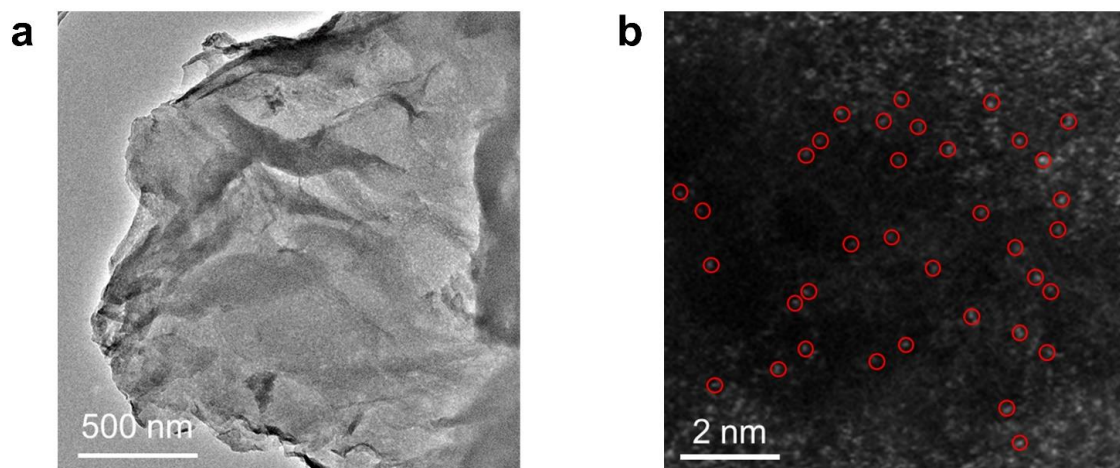
**Figure S8.** LSV curves of R-Cu<sub>1</sub>/Cu<sub>NP</sub>, M-Cu<sub>1</sub>/Cu<sub>NP</sub> and P-Cu<sub>1</sub>/Cu<sub>NP</sub> in CO<sub>2</sub> or N<sub>2</sub> atmosphere, the experiments were performed in 5 M KOH electrolyte with 20 mV s<sup>-1</sup> scan rate and 80% ohmic compensation.



**Figure S9.** (a) Product FEs and (b) current density of M-Cu<sub>1</sub>/Cu<sub>NP</sub> at -0.6V in 5 M KOH electrolyte with various catalyst loading. Both C<sub>2</sub> products selectivity and total current density increased as the increasing loading of M-Cu<sub>1</sub>/Cu<sub>NP</sub> until 1 mg cm<sup>-2</sup>, and no obvious difference was observed among 1, 1.5 and 2 mg cm<sup>-2</sup>. Therefore, we chose 1 mg cm<sup>-2</sup> as the catalyst loading to conduct activity experiments.

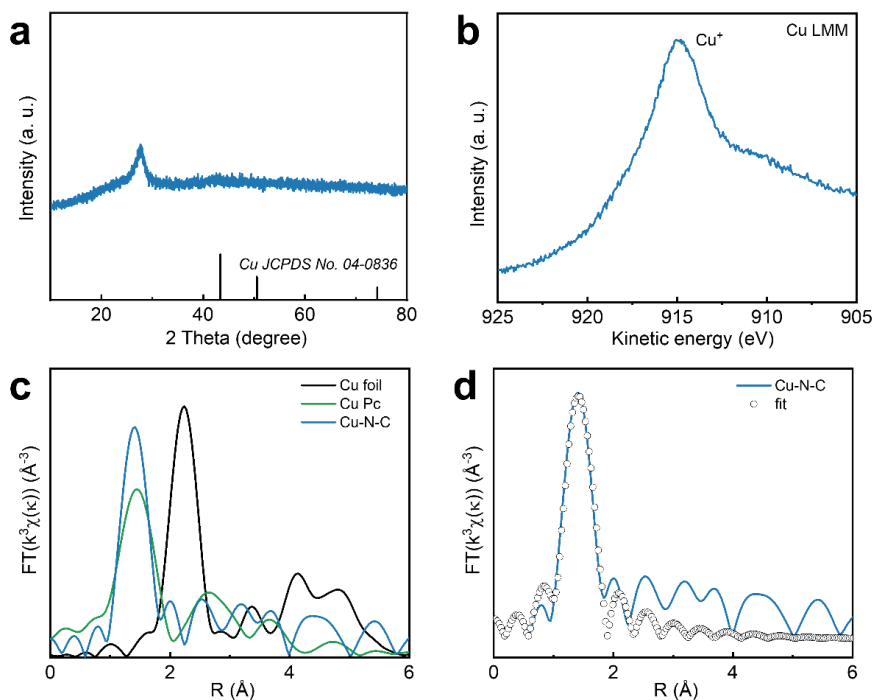


**Figure S10.** The CO<sub>2</sub>RR product FEs of (a) R-Cu<sub>1</sub>/Cu<sub>NP</sub>, (b) M-Cu<sub>1</sub>/Cu<sub>NP</sub> and (c) P-Cu<sub>1</sub>/Cu<sub>NP</sub> under different applied potentials, the experiments were performed in 5 M KOH electrolyte with 80% ohmic compensation. Values are means and error bars indicate s.d. ( $n = 3$  replicates).



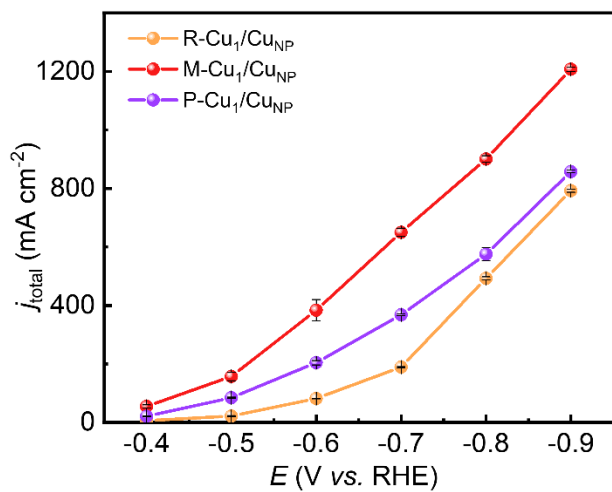
**Figure S11.** (a) TEM and (b) aberration-corrected HAADF-STEM images of Cu-N-C. The Cu-N-C was obtained by acid treatment of M-Cu<sub>1</sub>/Cu<sub>NP</sub>: the M-Cu<sub>1</sub>/Cu<sub>NP</sub> was added into 50 mL 1 M sulfuric acid aqueous solution and heated at 80 °C for 48 h, then washed with deionized water several times and dried at 80°C overnight.

No obvious nanoparticles were observed in TEM image and a large amount of isolated bright dots recognized as Cu single atoms were observed in aberration-corrected HAADF-STEM image.

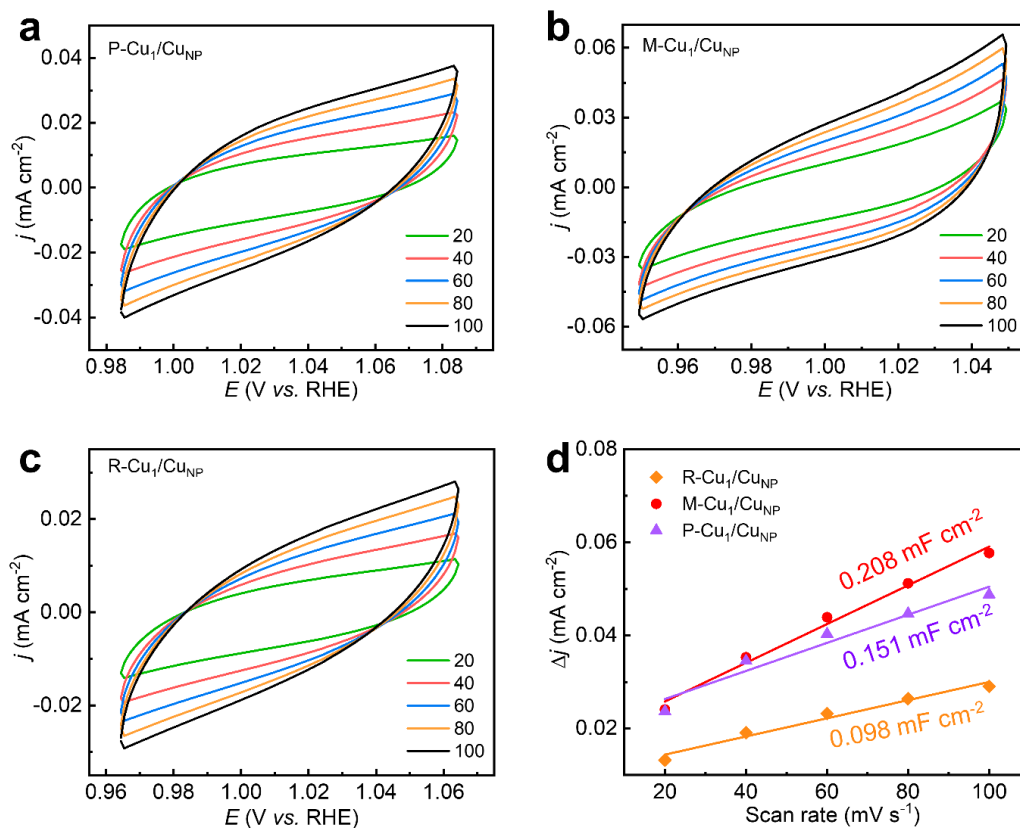


**Figure S12.** (a) XRD pattern, (b) Cu Auger LMM spectrum, (c) EXAFS spectra, and (d) least-squares EXAFS fittings of Cu-N-C. The Cu-N-C was obtained by acid treatment of M-Cu<sub>1</sub>/Cu<sub>NP</sub>: the M-Cu<sub>1</sub>/Cu<sub>NP</sub> was added into 50 mL 1 M sulfuric acid aqueous solution and heated at 80 °C for 48 h, then washed with deionized water several times and dried at 80°C overnight.

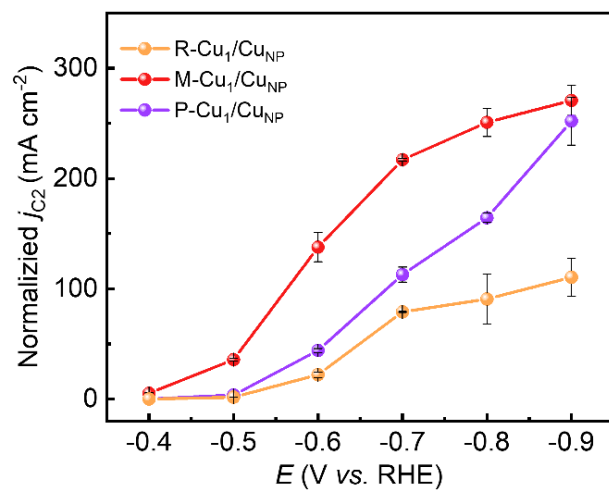
No diffraction peaks related to crystalline Cu species can be identified in XRD pattern. XPS spectra showed that Cu element existed in Cu-N-C catalyst and Cu<sup>+</sup> was main specie. More importantly, the EXAFS profiles in the R-space of Cu-N-C suggested that only the peak attributed to Cu-N coordination located at around 1.4 Å, while the Cu-Cu coordination peak at around 2.2 Å disappeared, which confirmed that the Cu species only existed as single atom form. The results of least-squares EXAFS fitting confirmed that the Cu-N coordination numbers in Cu-N-C was 4.0 (Table S2), implying that the atomic Cu species mainly existed as Cu-N<sub>4</sub> structure.



**Figure S13.** Total current density of R-Cu<sub>1</sub>/Cu<sub>NP</sub>, M-Cu<sub>1</sub>/Cu<sub>NP</sub> and P-Cu<sub>1</sub>/Cu<sub>NP</sub> at different applied potentials in 5 M KOH electrolyte. Values are means and error bars indicate s.d. ( $n = 3$  replicates).

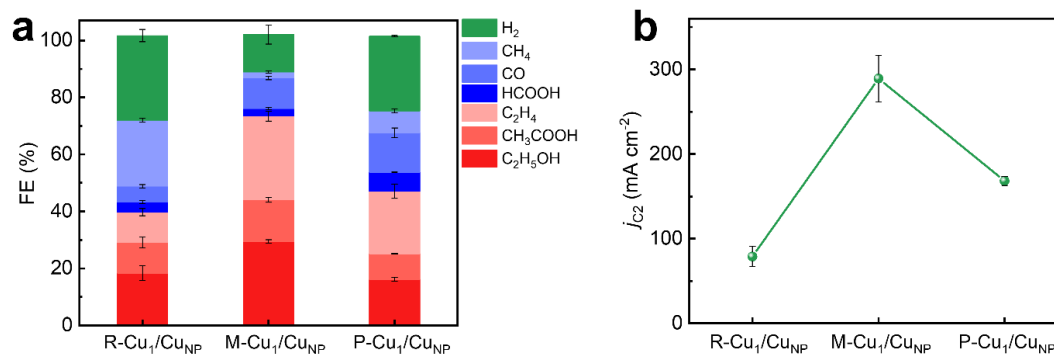


**Figure S14.** Cyclic voltammograms with different scan rates (20, 40, 60, 80, 100 mV s<sup>-1</sup>) for (a) P-Cu<sub>1</sub>/Cu<sub>NP</sub>, (b) M-Cu<sub>1</sub>/Cu<sub>NP</sub>, and (c) R-Cu<sub>1</sub>/Cu<sub>NP</sub> in 0.5 M KHCO<sub>3</sub> electrolyte. (d) Linear fitting of double-layer capacitive currents  $\Delta j$  versus scan rate.

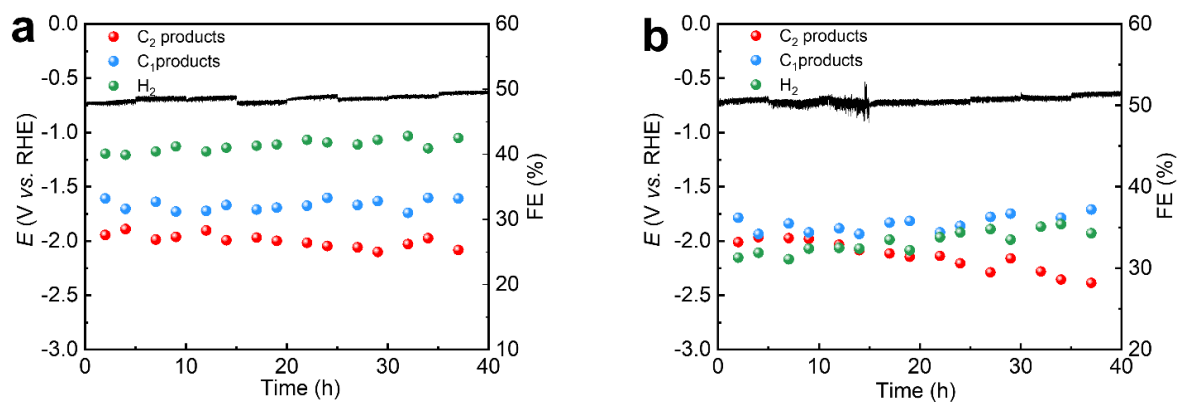


**Figure S15.** The  $j_{C_2}$  of R-Cu<sub>1</sub>/Cu<sub>NP</sub>, M-Cu<sub>1</sub>/Cu<sub>NP</sub> and P-Cu<sub>1</sub>/Cu<sub>NP</sub> after normalized by ECSA in 5 M KOH electrolyte.

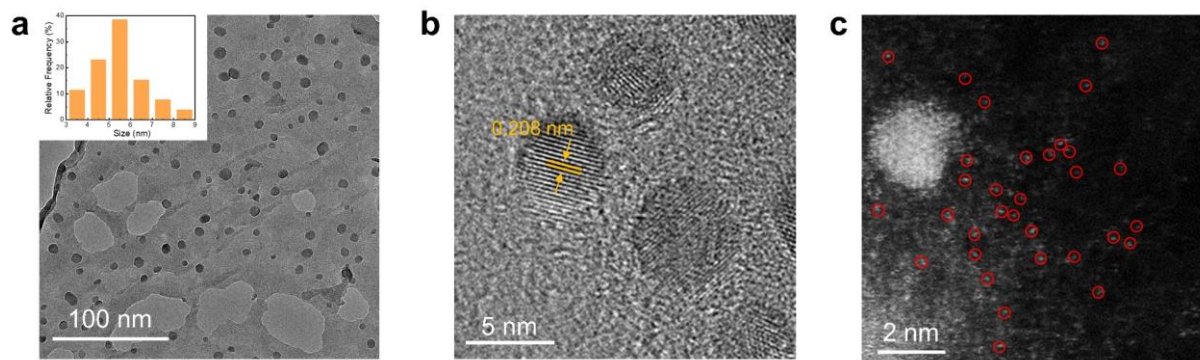




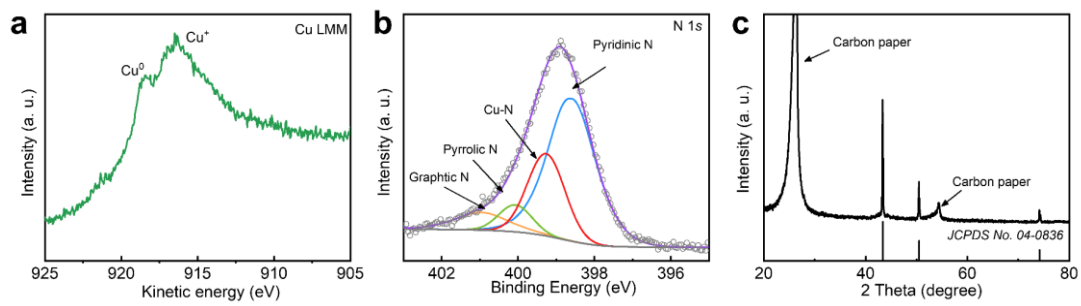
**Figure S16.** The (a) products FE and (b)  $j_{C_2}$  of R-Cu<sub>1</sub>/Cu<sub>NP</sub>, M-Cu<sub>1</sub>/Cu<sub>NP</sub> and P-Cu<sub>1</sub>/Cu<sub>NP</sub> under similar ECSA condition in 5 M KOH electrolyte.



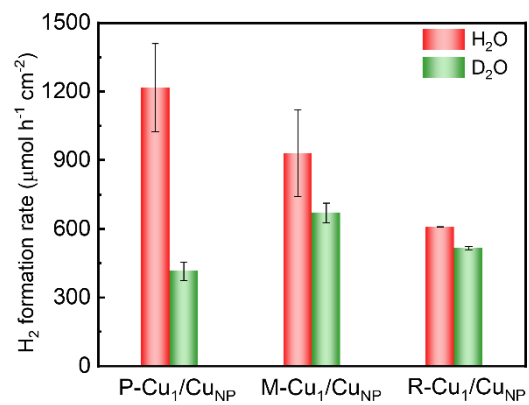
**Figure S17.** Long-term stability of (a) R-Cu<sub>1</sub>/Cu<sub>NP</sub> at a constant current density of 200 mA cm<sup>-2</sup> and (b) P-Cu<sub>1</sub>/Cu<sub>NP</sub> at a constant current density of 400 mA cm<sup>-2</sup> in 5 M KOH electrolyte (the electrode was washed, then dried and the electrolyte was refreshed at intervals 5 h to address the issues of flooding and carbonation).



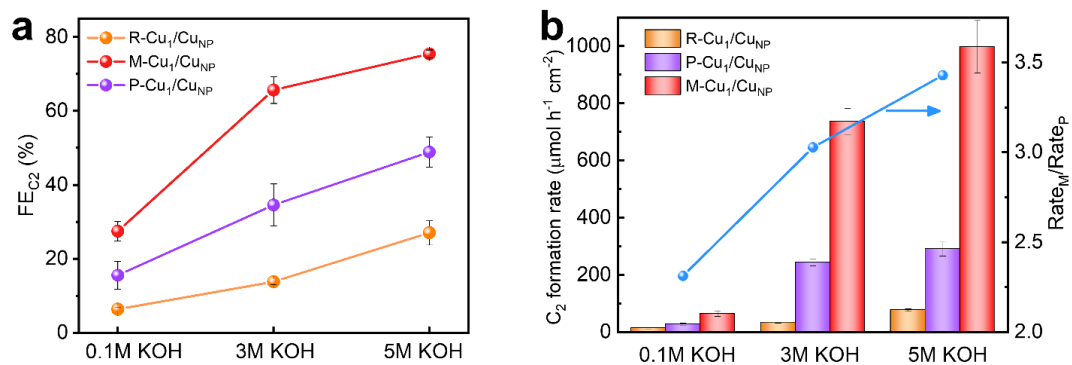
**Figure S18.** (a) TEM image (inset shows particle size distribution), (b) HRTEM image and (c) aberration-corrected HAADF-STEM image of M-Cu<sub>1</sub>/Cu<sub>NP</sub> after 40 h electrolysis.



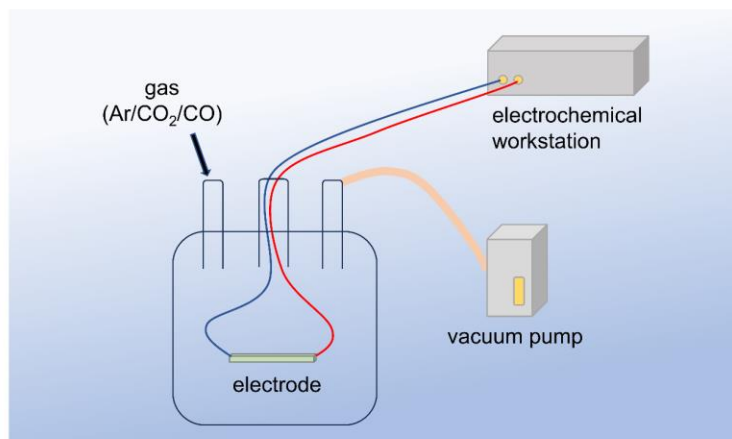
**Figure S19.** (a) Cu Auger LMM spectrum (b) XPS spectra of N  $1s$  orbits and (c) XRD pattern of M-Cu<sub>1</sub>/Cu<sub>NP</sub> after 40 h electrolysis.



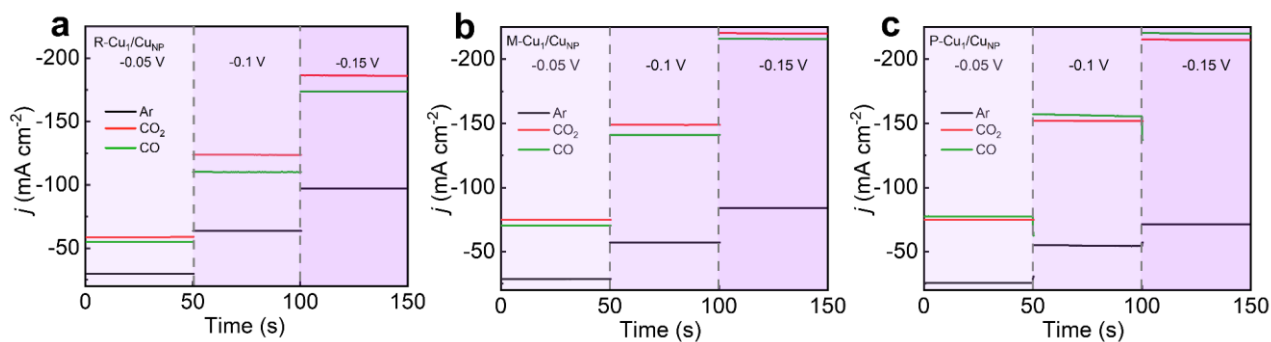
**Figure S20.** The kinetic isotope effect of H<sub>2</sub>O/D<sub>2</sub>O on P-Cu<sub>1</sub>/Cu<sub>NP</sub> M-Cu<sub>1</sub>/Cu<sub>NP</sub> and R-Cu<sub>1</sub>/Cu<sub>NP</sub> at -0.6 V in flow cell with 5 M KOH electrolyte. Values are means and error bars indicate s.d. ( $n = 3$  replicates).



**Figure S21.** (a) FE<sub>C2</sub> of R-Cu<sub>1</sub>/Cu<sub>NP</sub>, M-Cu<sub>1</sub>/Cu<sub>NP</sub> and P-Cu<sub>1</sub>/Cu<sub>NP</sub> in different concentrations KOH electrolyte at -0.6 V. (b) C<sub>2</sub> formation rate of R-Cu<sub>1</sub>/Cu<sub>NP</sub>, M-Cu<sub>1</sub>/Cu<sub>NP</sub> and P-Cu<sub>1</sub>/Cu<sub>NP</sub> in different concentrations KOH electrolyte at -0.6 V and Rate<sub>M</sub>/Rate<sub>P</sub> of M-Cu<sub>1</sub>/Cu<sub>NP</sub> to P-Cu<sub>1</sub>/Cu<sub>NP</sub>. Values are means and error bars indicate s.d. ( $n = 3$  replicates).



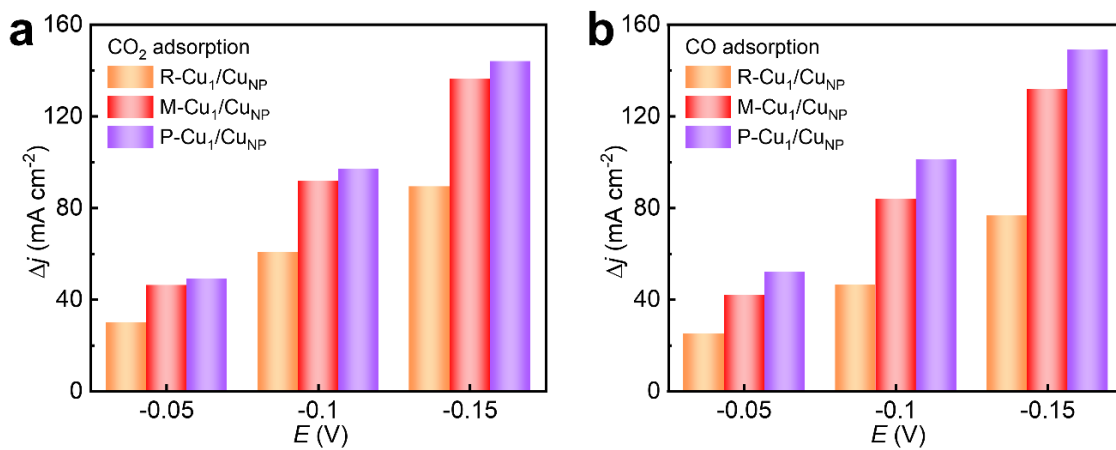
**Figure S22.** The device scheme of gas electro-response experiments.



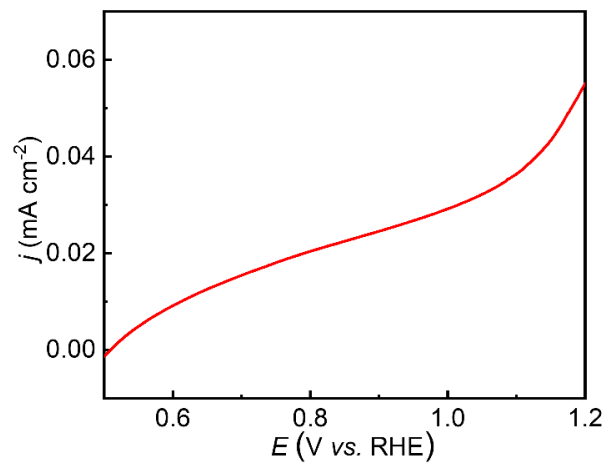
**Figure S23.** The CO<sub>2</sub> and CO gas adsorption electroresponse current density of (a) R-Cu<sub>1</sub>/Cu<sub>NP</sub>, (b) M-Cu<sub>1</sub>/Cu<sub>NP</sub> and (c) P-Cu<sub>1</sub>/Cu<sub>NP</sub>.

The capacity adsorption of CO<sub>2</sub> and CO molecules on the catalysts surface was tested by a self-designed gas adsorption electroresponse device. The Cu foam sprayed with the catalyst was used as electrode. The as-prepared electrode was placed in a sealed container and connected with the electrochemical workstation. Various gas (CO<sub>2</sub>, CO and Ar) were injected into the container and the curve of current was monitored under different applied potentials (-0.05, -0.1 and -0.15 V).

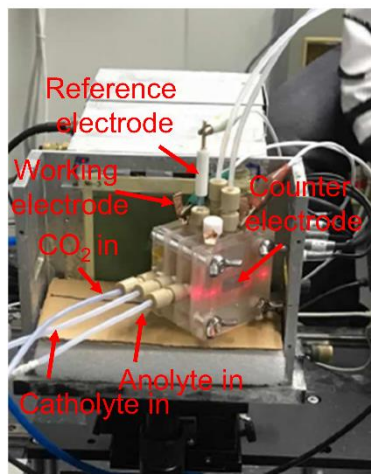




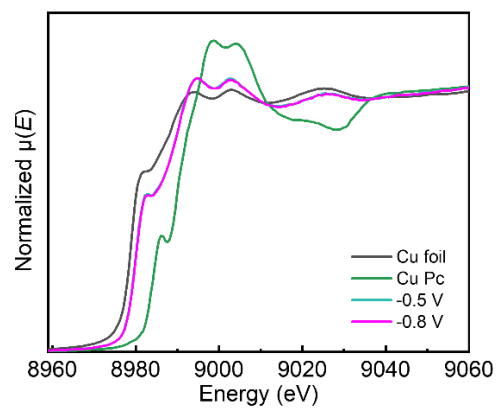
**Figure S24.** Results of (a) CO<sub>2</sub> and (b) CO adsorption responses under different applied voltages over R-Cu<sub>1</sub>/Cu<sub>NP</sub>, M-Cu<sub>1</sub>/Cu<sub>NP</sub> and P-Cu<sub>1</sub>/Cu<sub>NP</sub>.



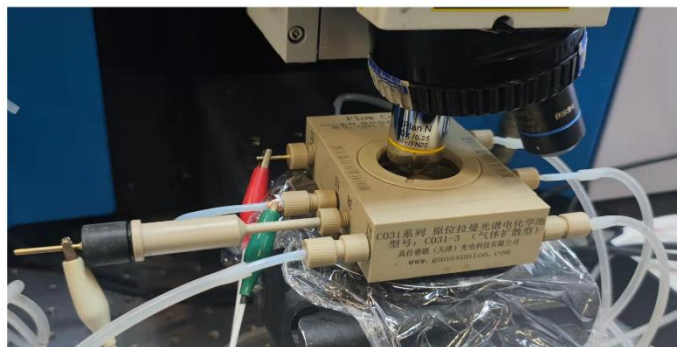
**Figure S25.** The LSV curve of M-Cu<sub>1</sub>/Cu<sub>NP</sub> in 0.1 M Na<sub>2</sub>SO<sub>4</sub> aqueous solution without CO adsorption.



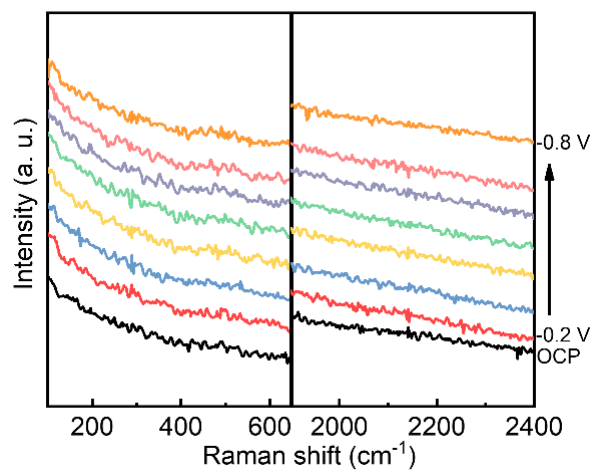
**Figure S26.** The optical photo of flow cell used for *in situ* XAS experiment.



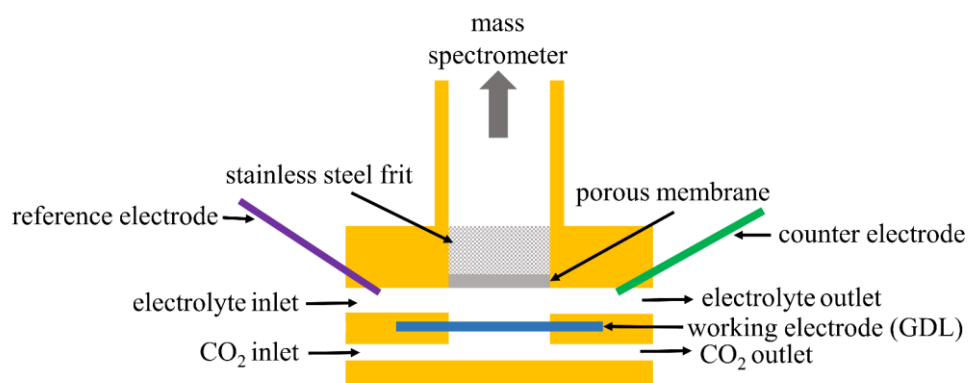
**Figure S27.** The *in situ* XANES spectra at Cu K-edge over M-Cu<sub>1</sub>/Cu<sub>NP</sub> at -0.5 and -0.8 V in 5 M KOH electrolyte.



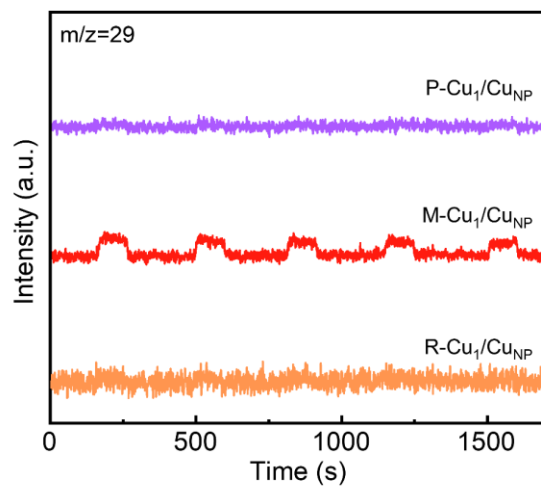
**Figure S28.** The photograph of cell used for *in situ* SERS spectroscopy.



**Figure S29.** *In situ* surface-enhanced Raman spectra recorded at different applied potentials for Cu-N-C during  $\text{CO}_2\text{RR}$ .

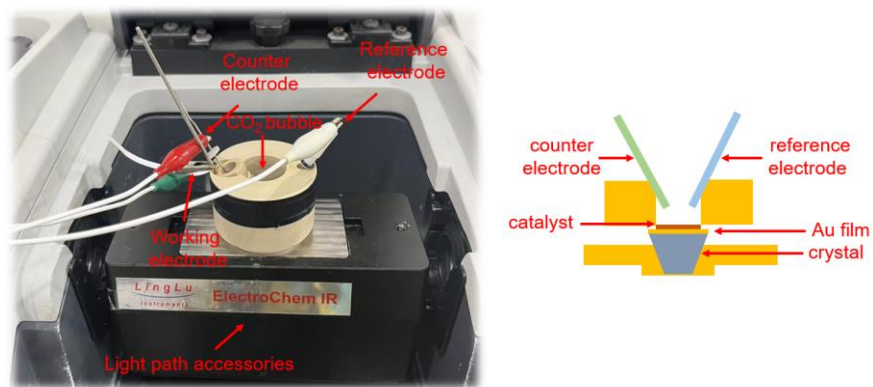


**Figure S30.** The scheme of cell used for online DEMS measurements.

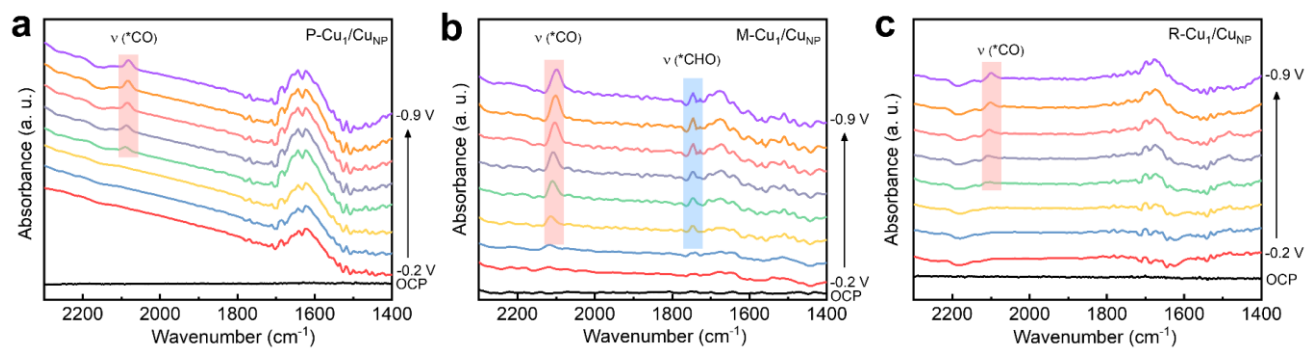


**Figure S31.** The  $m/z$  signal of 29 of P-Cu<sub>1</sub>/Cu<sub>NP</sub>, M-Cu<sub>1</sub>/Cu<sub>NP</sub> and R-Cu<sub>1</sub>/Cu<sub>NP</sub> during online DEMS measurements for CO<sub>2</sub>RR at -0.6 V in five continuous cycles in 5 M KOH electrolyte.

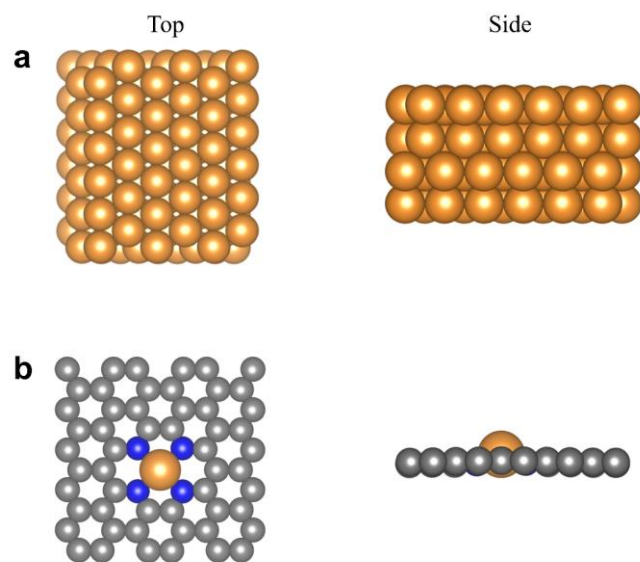




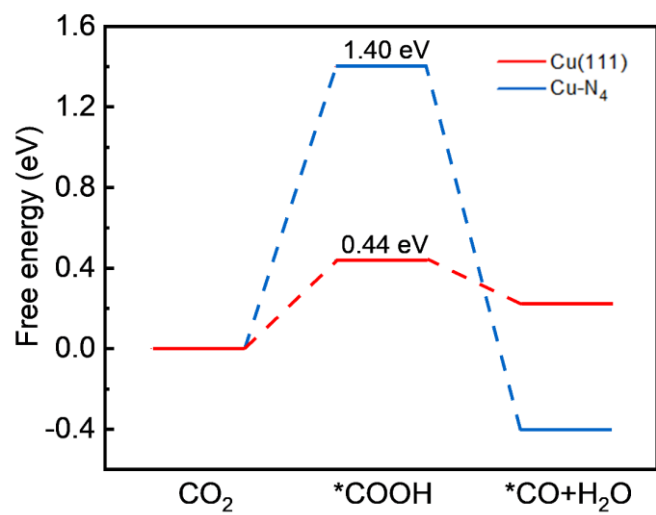
**Figure S32.** The photograph and scheme of cell used for *in situ* ATR-SEIRAS spectroscopy.



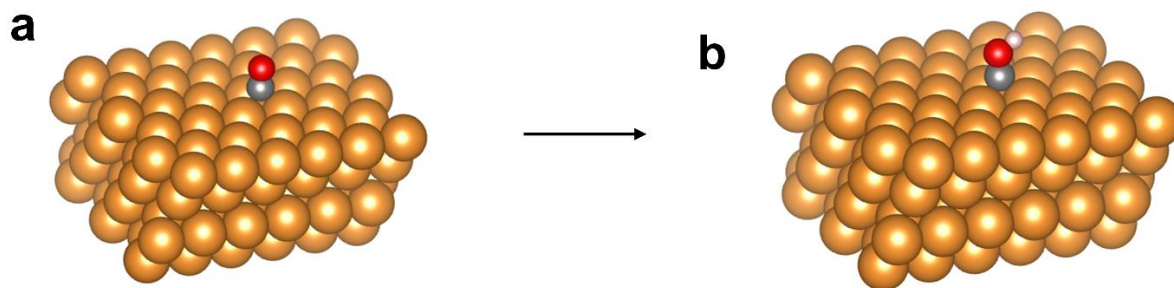
**Figure S33.** *In situ* ATR-SEIRAS spectra recorded at different applied potentials for (a) P-Cu<sub>1</sub>/Cu<sub>NP</sub>, (b) M-Cu<sub>1</sub>/Cu<sub>NP</sub> and (c) R-Cu<sub>1</sub>/Cu<sub>NP</sub> during CO<sub>2</sub>RR in CO<sub>2</sub>-saturated 3 M KOH electrolyte.



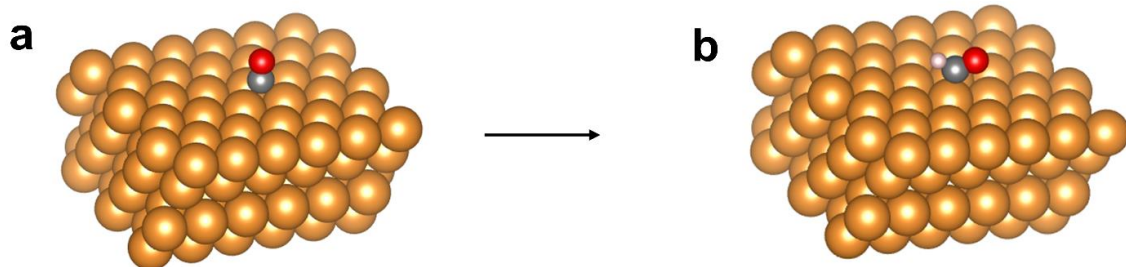
**Figure S34.** The top and side views of (a) Cu(111) and (b) Cu-N<sub>4</sub> models.



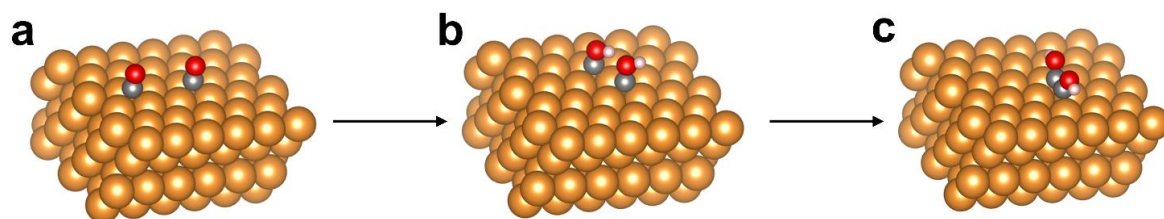
**Figure S35.** The free energy diagram for CO<sub>2</sub>RR to describe the activation of CO<sub>2</sub> over Cu(111) and Cu-N<sub>4</sub>.



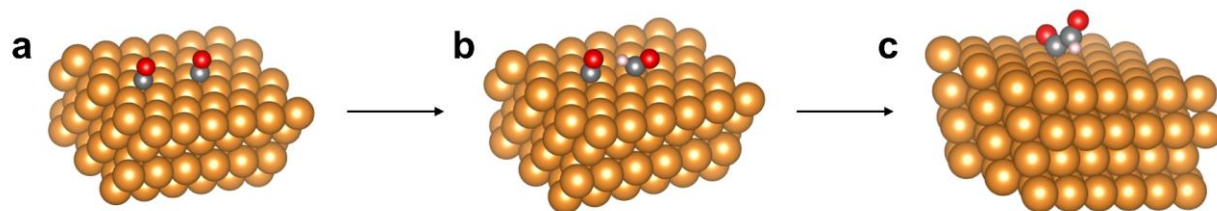
**Figure S36.** Side views of (a) \*CO and (b) \*COH on the Cu(111) facet.



**Figure S37.** Side views of (a) \*CO and (b) \*CHO on the Cu(111) facet.

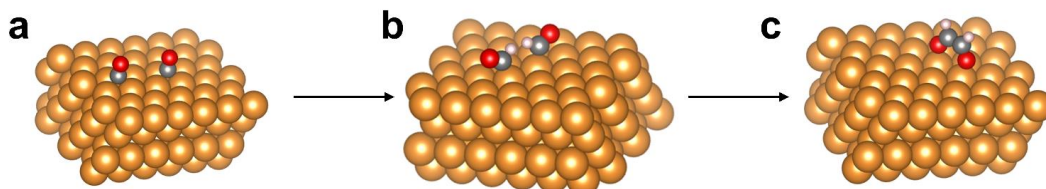


**Figure S38.** Side views of (a)  $^*CO-^*CO$ , (b)  $^*COH-^*COH$  and (c)  $^*COH^*COH$  on the Cu(111) facet.

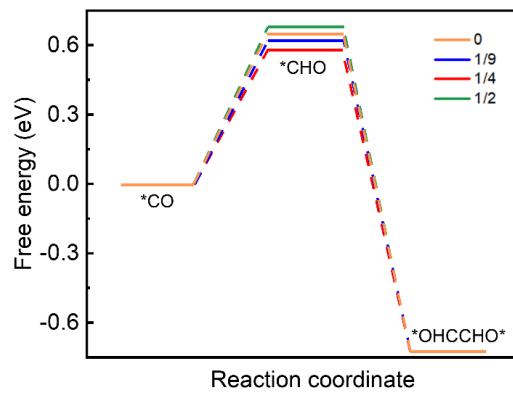


**Figure S39.** Side views of (a)  $^*CO-^*CO$ , (b)  $^*CO-^*CHO$  and (c)  $O^*CCHO$  on the Cu(111) facet.





**Figure S40.** Side views of (a) \*CO-\*CO, (b) \*CHO-\*CHO and (c) \*OHCCHO\* on the Cu(111) facet.



**Figure S41.** Free energy of \*CO hydrogenation to \*CHO on Cu(111) under different \*H coverage.

**Table S1.** The contents of Cu, N and C of the catalysts measured by XPS

Sample	Cu at%	N at%	C at%
P-Cu <sub>1</sub> /Cu <sub>NP</sub>	7.4	33.5	59.1
M-Cu <sub>1</sub> /Cu <sub>NP</sub>	4.3	40.5	55.2
R-Cu <sub>1</sub> /Cu <sub>NP</sub>	1.9	47.2	50.9

**Table S2.** Structural parameters extracted from the EXAFS fitting. ( $S_0^2=0.80$ )

Sample	Scattering pair	CN <sub>real</sub>	R(Å)	$\sigma^2(10^{-3}\text{Å}^2)$	$\Delta E_0(\text{eV})$	P (%)
R-Cu <sub>1</sub> /Cu <sub>NP</sub>	Cu-N	3.9	1.96	5.8	-3.5	28 (Cu <sub>1</sub> )
	Cu-Cu	8.6	2.56*	4.9	2.1	72 (Cu <sub>NP</sub> )
M-Cu <sub>1</sub> /Cu <sub>NP</sub>	Cu-N	3.8	1.96	5.1	-3.4	20 (Cu <sub>1</sub> )
	Cu-Cu	8.6	2.56*	5.4	2.1	80 (Cu <sub>NP</sub> )
P-Cu <sub>1</sub> /Cu <sub>NP</sub>	Cu-N	0.4	1.96	6.0	-3.5	5 (Cu <sub>1</sub> )
	Cu-Cu	8.4	2.56*	4.8	2.1	95 (Cu <sub>NP</sub> )
Cu-N-C	Cu-N	4.0	1.96	5.9	-3.5	-

$S_0^2$  is the amplitude reduction factor  $S_0^2=0.8$ ; CN<sub>real</sub> is the coordination number; R is interatomic distance (the bond length between central atoms and surrounding coordination atoms);  $\sigma^2$  is Debye-Waller factor (a measure of thermal and static disorder in absorber-scatterer distances);  $\Delta E_0$  is edge-energy shift (the difference between the zero kinetic energy value of the sample and that of the theoretical model). R factor is used to value the goodness of the fitting. \* represents a fixed value for the parameter. P represents the percentage of Cu-N<sub>4</sub> (Cu<sub>1</sub>) and Cu NPs Cu in total Cu species of catalyst.

**Table S3.** Product FEs, total current density and error bar of R-Cu<sub>1</sub>/Cu<sub>NP</sub> at various potentials in 5 M KOH electrolyte.

Potential (V)	C <sub>2</sub> H <sub>5</sub> OH FE (%)			Error bar
-0.4	0.0	0.0	0.0	0.00
-0.5	0.0	0.0	0.0	0.00
-0.6	14.8	11.3	7.0	3.90
-0.7	17.2	21.6	19.2	2.20
-0.8	9.0	11.7	6.4	2.65
-0.9	6.3	7.1	7.5	0.61

Potential (V)	CH <sub>3</sub> COOH FE (%)			Error bar
-0.4	0.0	0.0	0.0	0.00
-0.5	0.0	0.0	0.0	0.00
-0.6	5.5	8.2	6.8	1.35
-0.7	12.7	12.0	13.7	0.85
-0.8	3.8	5.7	4.7	0.95
-0.9	2.8	3.3	3.7	0.45

Potential (V)	C <sub>2</sub> H <sub>4</sub> FE (%)			Error bar
-0.4	0.0	0.0	0.0	0.00
-0.5	7.6	7.7	7.9	0.15
-0.6	9.1	9.5	9.2	0.21
-0.7	9.6	8.5	10.6	1.05
-0.8	4.8	4.5	4.5	0.17
-0.9	3.2	4.4	4.0	0.61

Potential (V)	HCOOH FE (%)			Error bar
-0.4	0.0	0.0	0.0	0.00
-0.5	17.4	17.1	16.4	0.51
-0.6	4.1	6.7	5.5	1.30
-0.7	2.7	2.1	3.0	0.46
-0.8	0.5	0.7	0.6	0.10
-0.9	0.5	0.6	0.7	0.10

Potential (V)	CO FE (%)			Error bar
-0.4	22.3	23.1	21.4	0.85
-0.5	23.1	22.8	23	0.15
-0.6	7.9	10.8	9.2	1.45
-0.7	4	4.5	5.1	0.55
-0.8	0.8	1.8	1.2	0.50
-0.9	1.2	1.6	0.9	0.35

Potential (V)	CH <sub>4</sub> FE (%)			Error bar
-0.4	0.0	0.0	0.0	0.00
-0.5	2.8	2.2	2.4	0.31
-0.6	19.4	18.6	20.0	0.70
-0.7	22.6	24.0	22.9	0.74
-0.8	17.8	21.3	20.0	1.77
-0.9	13.7	20.5	17.5	3.41

Potential (V)	H <sub>2</sub> FE (%)			Error bar
-0.4	71.8	73.7	74.0	1.19
-0.5	51.1	52.7	52.1	0.81
-0.6	40.2	39.5	40.1	0.38
-0.7	30.9	28.5	26.6	2.15
-0.8	64.8	54.2	59.8	5.30
-0.9	76.4	64.0	70.5	6.20

Potential (V)	Total current density (mA cm <sup>-2</sup> )			Error bar
-0.4	5.7	6.2	6.0	0.25
-0.5	21.3	22.9	19.8	1.55
-0.6	81.1	82.3	81.5	0.60
-0.7	191.0	187.0	189.0	2.00
-0.8	493.2	487.0	497.2	5.14
-0.9	798.0	787.0	792.0	5.51

**Table S4.** Product FEs, total current density and error bar of M-Cu<sub>1</sub>/Cu<sub>NP</sub> at various potentials in 5 M KOH electrolyte.

Potential (V)	C <sub>2</sub> H <sub>5</sub> OH FE (%)			Error bar
-0.4	0	0	0	0
-0.5	10.8	15.3	14	2.30
-0.6	30.1	29.2	29	0.59
-0.7	27	28	28	0.58
-0.8	24.1	23.9	23.6	0.25
-0.9	19.6	19.9	19	0.46

Potential (V)	CH <sub>3</sub> COOH FE (%)			Error bar
-0.4	12.7	13.1	10.9	1.17
-0.5	18.3	11.8	18	3.67
-0.6	15.5	14.4	20	2.97
-0.7	17.7	16.7	15.3	1.21
-0.8	11.8	13.1	10	1.56
-0.9	7.2	6.3	6.5	0.47

Potential (V)	C <sub>2</sub> H <sub>4</sub> FE (%)			Error bar
-0.4	6.9	7.3	10.5	1.97
-0.5	17.6	17.9	20.5	1.59
-0.6	29.8	30.8	27.5	1.69
-0.7	26.7	25.7	25.4	0.68
-0.8	22.1	23.9	22.9	0.90
-0.9	22.6	20.4	19.7	1.51

Potential (V)	HCOOH FE (%)			Error bar
-0.4	8.6	8.9	9.2	0.30
-0.5	12.5	7.5	7.9	2.78
-0.6	2.4	3.1	2.5	0.38
-0.7	3.5	2.2	2.3	0.72
-0.8	1.5	2.1	1.5	0.35
-0.9	1.2	2.7	3.2	1.04

Potential (V)	CO FE (%)			Error bar
-0.4	35.3	35.6	30.4	2.92
-0.5	23.7	27.8	22.4	2.82
-0.6	10.1	11.3	10.7	0.60
-0.7	7.4	5.4	5.3	1.18
-0.8	3.2	3.4	4.7	0.81
-0.9	4.1	3.6	4.5	0.45

Potential (V)	CH <sub>4</sub> FE (%)			Error bar
-0.4	0	0	0	0.00
-0.5	1.6	1.3	1.9	0.30
-0.6	2.2	1.7	4.5	1.49
-0.7	2.9	7.3	5.3	2.20
-0.8	4.9	5.8	7.6	1.37
-0.9	4.5	3.7	2.2	1.17

Potential (V)	H <sub>2</sub> FE (%)			Error bar
-0.4	37.4	39.8	41.8	2.20
-0.5	18.3	20.9	17.8	1.66
-0.6	11.1	11.3	17.0	3.35
-0.7	17.3	17.7	22.6	2.95
-0.8	33.8	27.9	31.7	2.99
-0.9	42.8	46	45.3	1.68

Potential (V)	Total current density (mA cm <sup>-2</sup> )			Error bar
-0.4	58.4	49.5	56.5	4.69
-0.5	166.8	163.6	140	14.64
-0.6	426	365.5	358.7	37.05
-0.7	635.2	650.5	663.5	14.17
-0.8	895.6	913.5	892.7	11.27
-0.9	1211.83	1212.3	1198.8	7.66



**Table S5.** Product FEs, total current density and error bar of P-Cu<sub>1</sub>/Cu<sub>NP</sub> at various potentials in 5 M KOH electrolyte.

Potential (V)	C <sub>2</sub> H <sub>5</sub> OH FE (%)			Error bar
-0.4	0.0	0.0	0.0	0.00
-0.5	0.0	0.0	0.0	0.00
-0.6	13.4	12.3	12.6	0.57
-0.7	14.2	16.0	15.2	0.90
-0.8	14.5	13.1	11.6	1.45
-0.9	12.2	10.2	13.9	1.85

Potential (V)	CH <sub>3</sub> COOH FE (%)			Error bar
-0.4	0.0	0.0	0.0	0.00
-0.5	3.5	3.9	3.2	0.35
-0.6	4.0	4.5	5.1	0.55
-0.7	10.0	10.1	10.3	0.15
-0.8	8.0	7.2	7.5	0.40
-0.9	8.3	6.7	9.9	1.60

Potential (V)	C <sub>2</sub> H <sub>4</sub> FE (%)			Error bar
-0.4	0.0	0.0	0.0	0.00
-0.5	3.1	2.9	3.5	0.31
-0.6	16.2	17.2	14.5	1.37
-0.7	21.1	24.7	20.3	2.34
-0.8	23.0	23.2	24.0	0.53
-0.9	27.8	23.9	22.9	2.59

Potential (V)	HCOOH FE (%)			Error bar
-0.4	42.0	45.0	44.0	1.53
-0.5	30.1	32.2	31.0	1.05
-0.6	13.4	14.6	15.0	0.83
-0.7	5.7	5.7	5.7	0.00
-0.8	5.7	3.9	4.5	0.92
-0.9	4.2	4.5	4.0	0.25

Potential (V)	CO FE (%)			Error bar
-0.4	10.6	11.4	13.0	1.22
-0.5	16.9	14.1	17.0	1.65
-0.6	16.9	17.0	20.4	1.99
-0.7	16.5	13.2	14.7	1.65
-0.8	12.0	11.1	13.5	1.21
-0.9	11.6	10.8	12.2	0.70

Potential (V)	CH <sub>4</sub> FE (%)			Error bar
-0.4	0.0	0.0	0.0	0.00
-0.5	1.0	1.2	1.4	0.20
-0.6	4.5	3.1	3.4	0.74
-0.7	5.9	5.1	6.2	0.57
-0.8	4.5	5.5	5.5	0.58
-0.9	6.7	6.6	6.5	0.10

Potential (V)	H <sub>2</sub> FE (%)			Error bar
-0.4	45.6	43.1	44.0	1.27
-0.5	48.1	53.1	51.1	2.52
-0.6	30.5	28.2	37.1	4.62
-0.7	28.4	28.0	28.5	0.26
-0.8	31.5	33.7	35.8	2.15
-0.9	40.4	38.1	40.5	1.36

Potential (V)	Total current density (mA cm <sup>-2</sup> )			Error bar
-0.4	21.2	19.8	20.4	0.70
-0.5	83.4	85.9	84.3	1.27
-0.6	211.2	196.0	204.5	7.62
-0.7	367.0	365.7	370.0	2.21
-0.8	554.0	598.3	573.2	22.22
-0.9	860.1	860.0	852.0	4.65

**Table S6.** Product FEs, total current density and error bar of Cu-N-C at various potentials in 5 M KOH electrolyte.

Potential (V)	CO FE (%)			Error bar
-0.4	0	0	0	0
-0.5	3.1	2.7	2.5	0.30
-0.6	2.4	3.4	2.4	0.57
-0.7	2	3.5	2	0.86
-0.8	1.3	3.2	1.4	1.06
-0.9	0	1.8	0	1.03

Potential (V)	CH <sub>4</sub> FE (%)			Error bar
-0.4	0	0	0	0.00
-0.5	2.7	4.3	4.4	0.95
-0.6	2.1	7.8	4.4	2.87
-0.7	3.2	8.8	3.8	3.07
-0.8	1.4	8.6	2.7	3.84
-0.9	0	1.4	1.2	0.76

Potential (V)	H <sub>2</sub> FE (%)			Error bar
-0.4	98.1	98.2	98.5	0.21
-0.5	93.8	92.0	94.2	1.17
-0.6	95.1	87.8	93.3	3.80
-0.7	95.4	87.9	92.1	3.76
-0.8	98.4	87.4	95.7	5.73
-0.9	99.8	97.6	98.3	1.12

Potential (V)	Total current density (mA cm <sup>-2</sup> )			Error bar
-0.4	33.3	32.6	27.9	2.95
-0.5	81.1	64.7	73.7	8.19
-0.6	114.3	99.0	101.8	8.14
-0.7	153.2	136.4	149.4	8.82
-0.8	196.2	168.2	187.0	14.26
-0.9	249.2	228.3	241.0	10.52

**Table S7.** Performance comparison of various catalysts for CO<sub>2</sub> electroreduction to C<sub>2+</sub> products.

Samples	E (V vs. RHE)	FE <sub>C2+</sub> (%)	<i>j</i> <sub>C2+</sub> (mA cm <sup>-2</sup> )	References
M-Cu <sub>1</sub> /Cu <sub>NP</sub>	-0.60	75.4	289.2	This work
Nanoporous Cu	-0.67	62.0	404.8	1
Reconstructed Cu	-1.80	77.0	346.5	2
NGQ/Cu-nr	-0.90	~74.0	~208.0	3
F-Cu	-0.89	80.0	1280.0	4
Multihollow Cu <sub>2</sub> O	-0.61	75.0	267.0	5
CuAg wire	-0.70	85.0	255.0	6
FeTPP[Cl]/Cu	-0.82	85.0	257.0	7
OD-Cu-III	-	74.9	224.7	8
Cu dendrites	-0.68	64.0	255.0	9
Cu	-	80.4	120.6	10
Cu(0)@PIL@Cuba(I)	-0.85	76.1	304.2	11
3-shell HoMSs	-0.88	77.0	513.7	12
Cu-PTFE	-1.50	86.0	~250.0	13
CuS/Cu-V	-0.92	52.8	147.8	14
Ce(OH) <sub>x</sub> -doped-Cu	-0.70	80.3	211.2	15
Cu-KI	-1.09	~72.6	29.0	16
Graphite/Cu/PTFE	-0.54	83.0	275.0	17
Polyamine- incorporated Cu	-0.47	87.0	~35.0	18

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