

Supplementary information for

Operando Insights on Stable Cu²⁺ Active Sites for Efficient

Electrochemical CO₂-to-C₂H₄ Conversion

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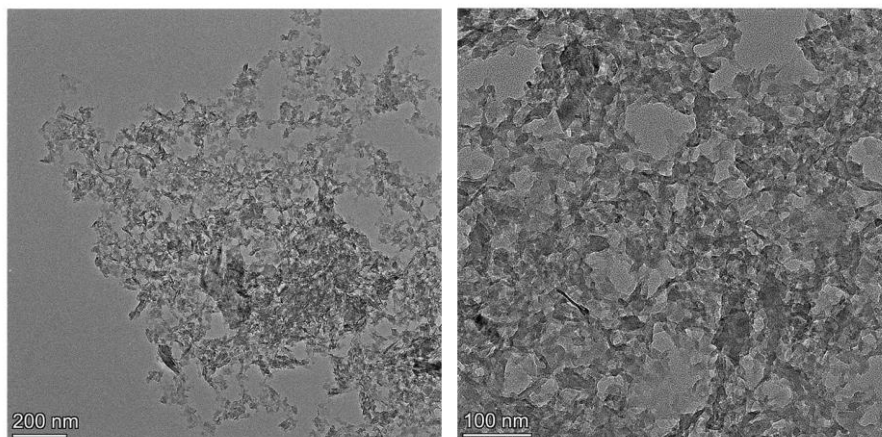
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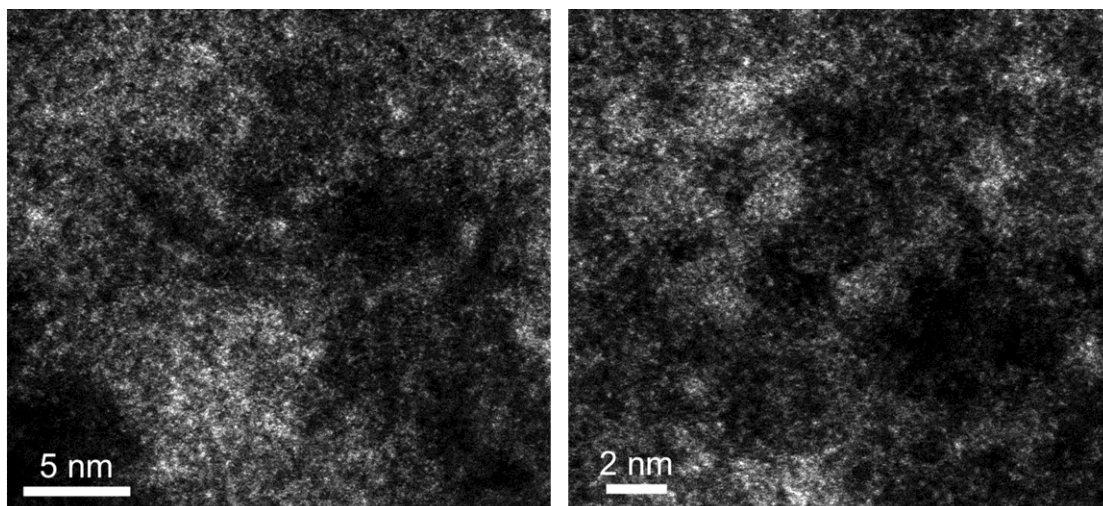
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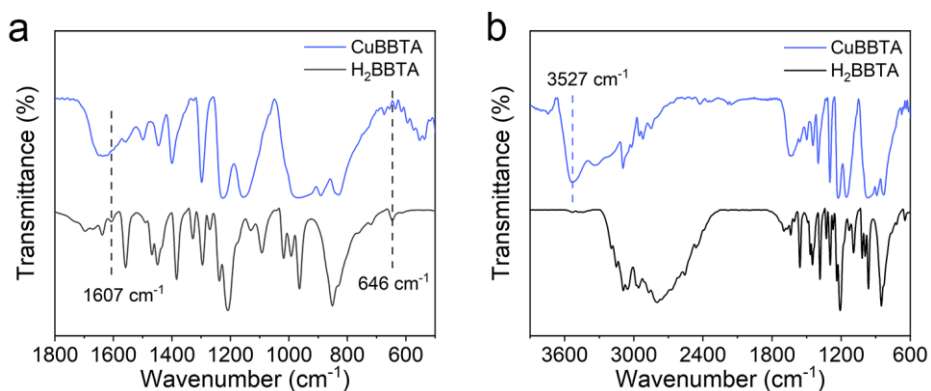
Supplementary Figures



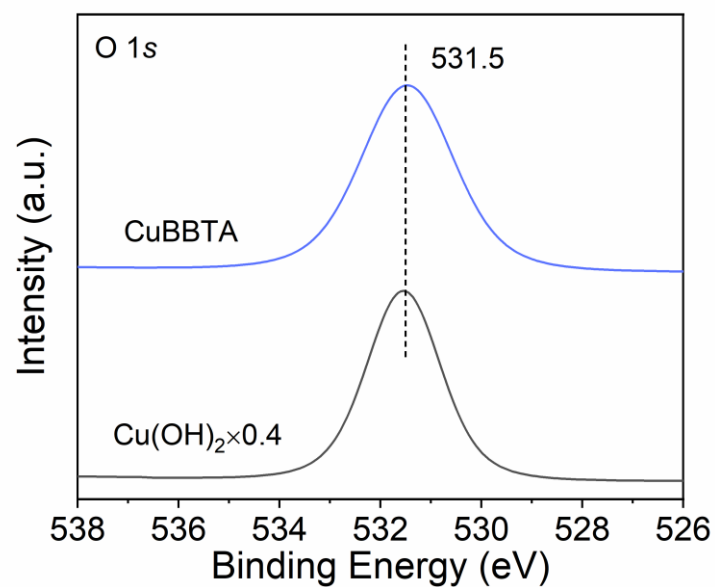
Supplementary Fig. 1 | TEM images of CuBBTA in different magnifications.



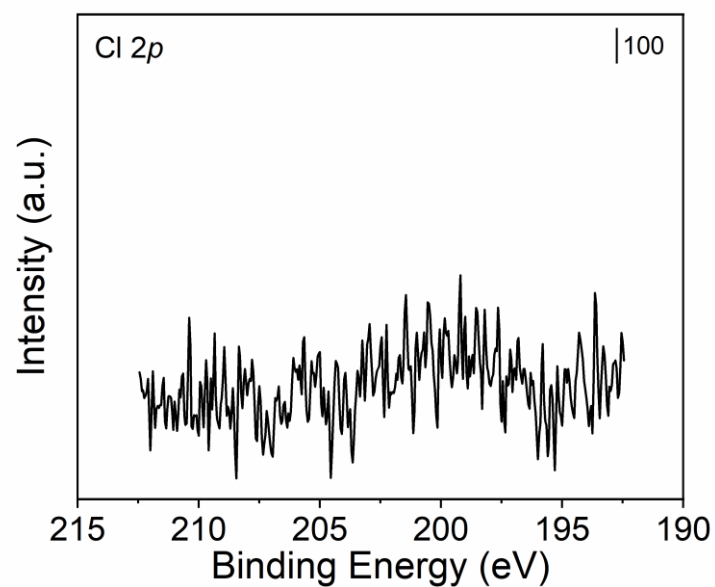
Supplementary Fig. 2 | High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image of CuBBTA in different areas.



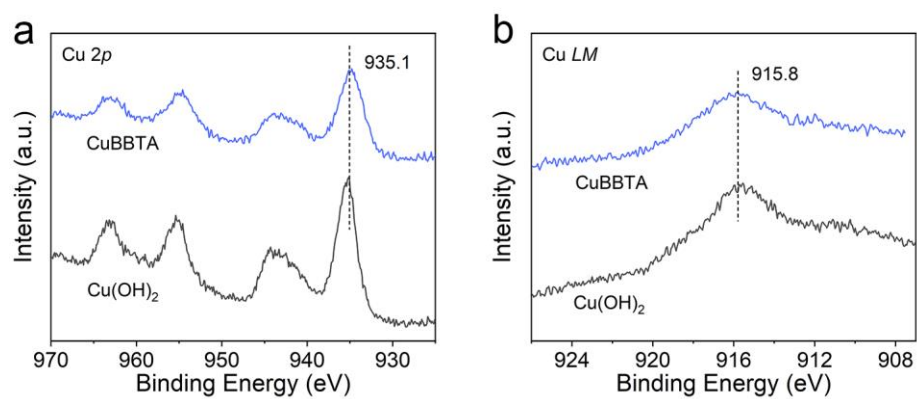
Supplementary Fig. 3 | Fourier-transform infrared spectroscopy (FT-IR). The magnified spectra of H₂BBTA and CuBBTA (a) and full spectra (b). The wide N-H stretching (from 3300 to 2600 cm⁻¹) is absent in CuBBTA. The peak at 3527 cm⁻¹ in CuBBTA is attributed to the hydroxyl group.¹ The absence of N-H in-plane bending (~1607 cm⁻¹) and N-H out-of-plane bending (~646 cm⁻¹) in CuBBTA indicates that the N atom in H₂BBTA is deprotonated.²



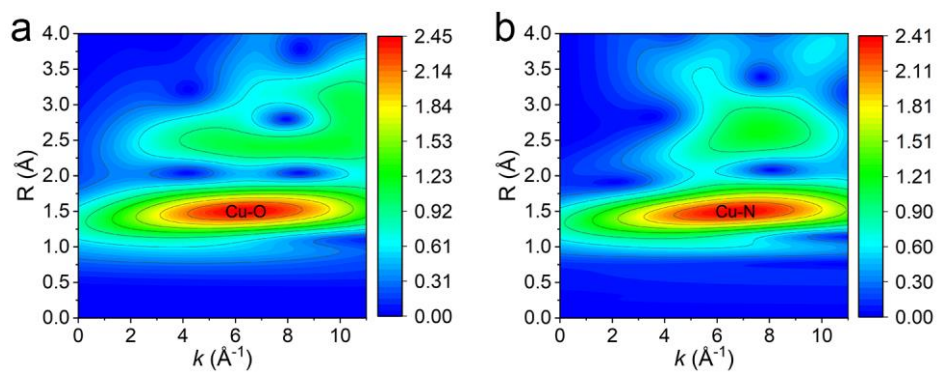
Supplementary Fig. 4 | O 1s XPS of CuBBTA. CuBBTA showed the same O 1s binding energy as that in the reference Cu(OH)₂ sample.



Supplementary Fig. 5 | Cl 2p of CuBBTA. The absence of Cl 2p signal illustrated that the chloride ions in the CuCl₂ precursor were completely replaced and did not involve coordination in CuBBTA.

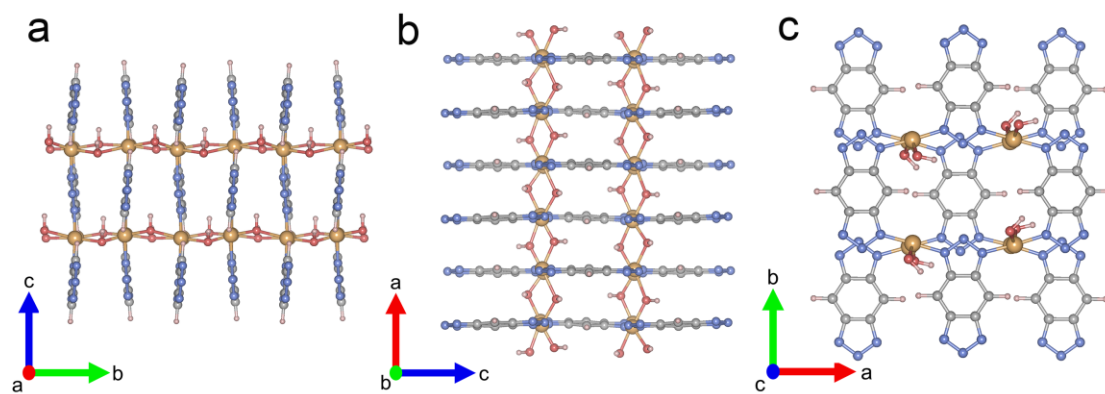


Supplementary Fig. 6 | High-resolution Cu XPS. Cu 2p spectra (a) and Cu LMM spectra (b) of CuBBTA and Cu(OH)₂.

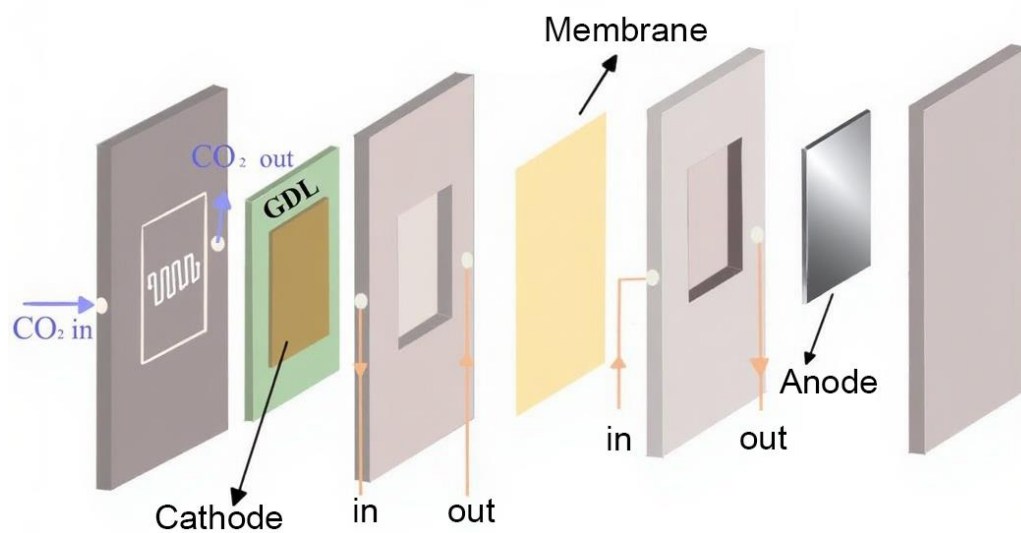


Supplementary Fig. 7 | XAFS wavelet transform (WT) for the reference samples.

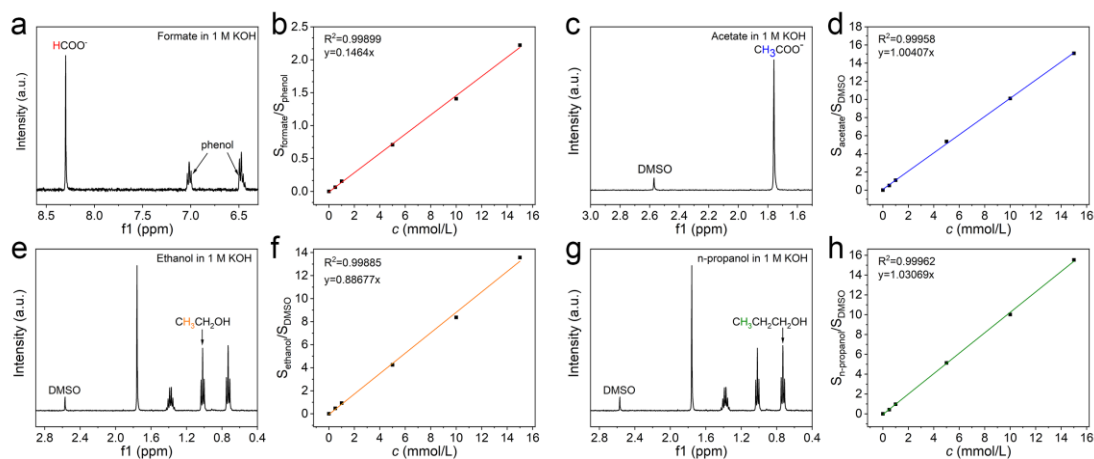
(a) Commercial CuO. (b) Commercial CuPc. The y-axis of the WT plots shows the radial distance, and the x-axis reflects the k -space resolution of the backscattering atom.



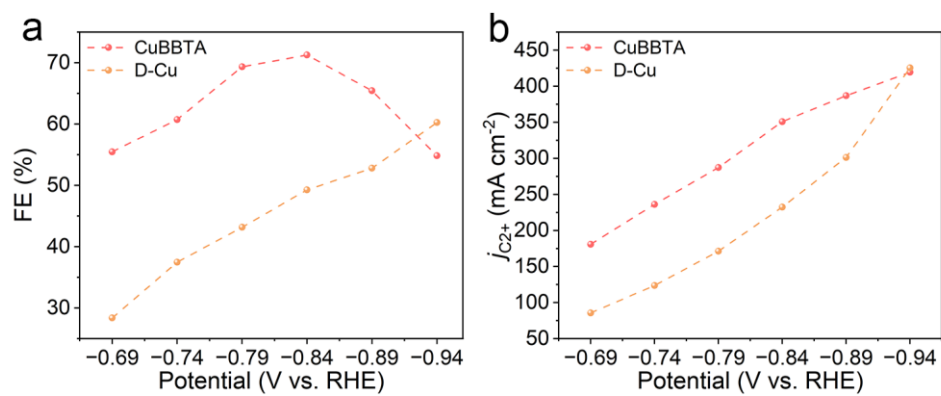
Supplementary Fig. 8 | Model of the CuBBTA. Views from the a-axis (a), b-axis (b), and c-axis (c). The calculated theoretical mass percentage of elements in CuBBTA (Calc.: Cu: 39.82%, C: 22.57%, N: 26.33%, O: 10.2%, H: 1.26%).



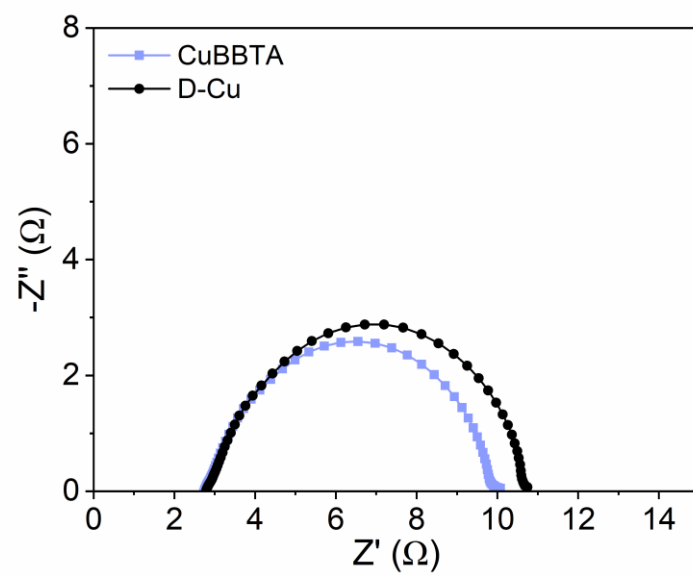
Supplementary Fig. 9 | The schematic diagram of the electrochemical flow cell.



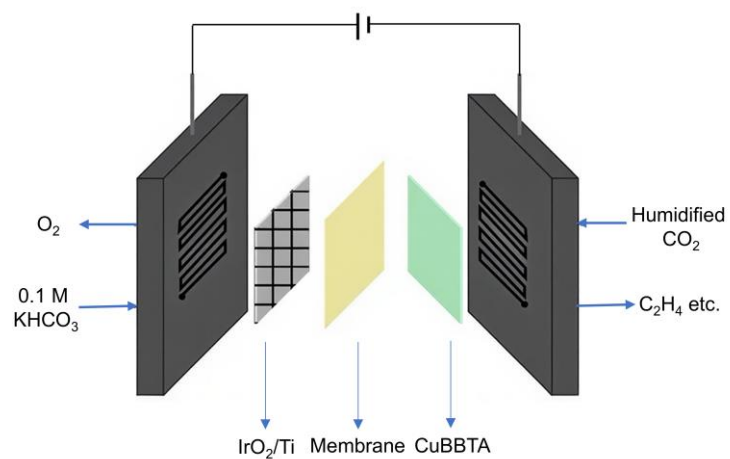
Supplementary Fig. 10 | Magnified view of the ^1H -NMR spectrum highlighting characteristic peaks of various liquid products. ^1H -NMR spectrum (a) and calibration plot (b) for formate measured in 1 M KOH electrolyte. ^1H -NMR spectrum (c) and calibration plot (d) for acetate measured in 1 M KOH electrolyte. ^1H -NMR spectrum (e) and calibration plot (f) for ethanol measured in 1 M KOH electrolyte. ^1H -NMR spectrum (g) and calibration plot (h) for n-propanol measured in 1 M KOH electrolyte. Phenol (triplet, $\delta=7.03$) and DMSO (singlet, $\delta=2.6$) were used as internal standards for quantification of formate and other liquid products, respectively.



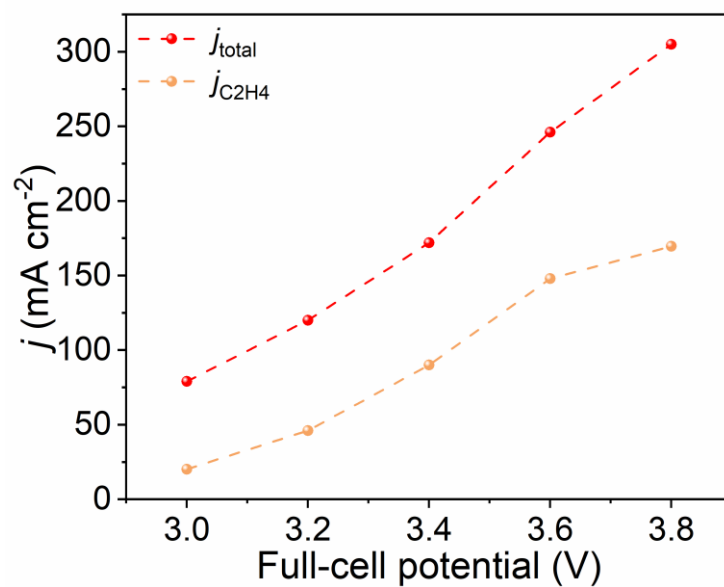
Supplementary Fig. 11 | FE and Partial current densities for C₂₊ products over CuBBTA and D-Cu catalysts.



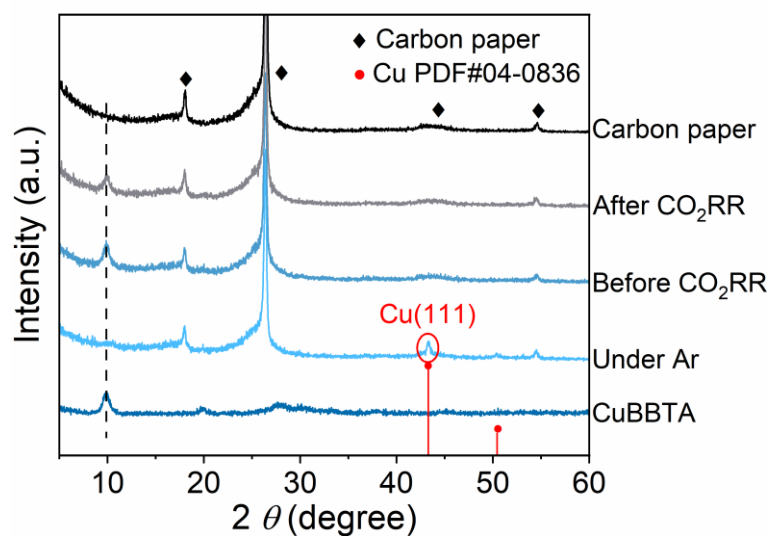
Supplementary Fig. 12 | Nyquist plots of CuBBTA and D-Cu.



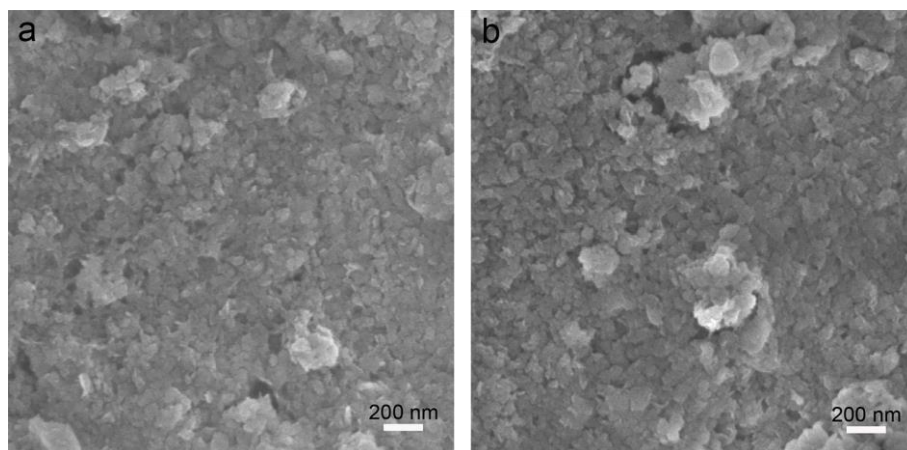
Supplementary Fig. 13 | Schematic illustration of the MEA system.



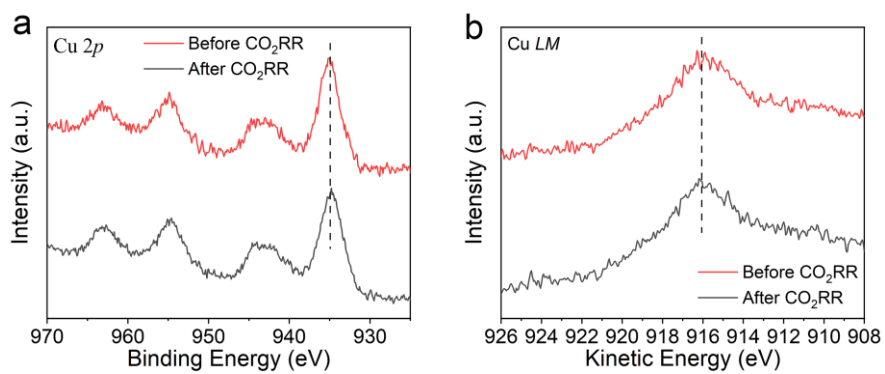
Supplementary Fig. 14 | Total current density and C₂H₄ partial current density over CuBBTA at different full-cell potentials measured in the MEA system.



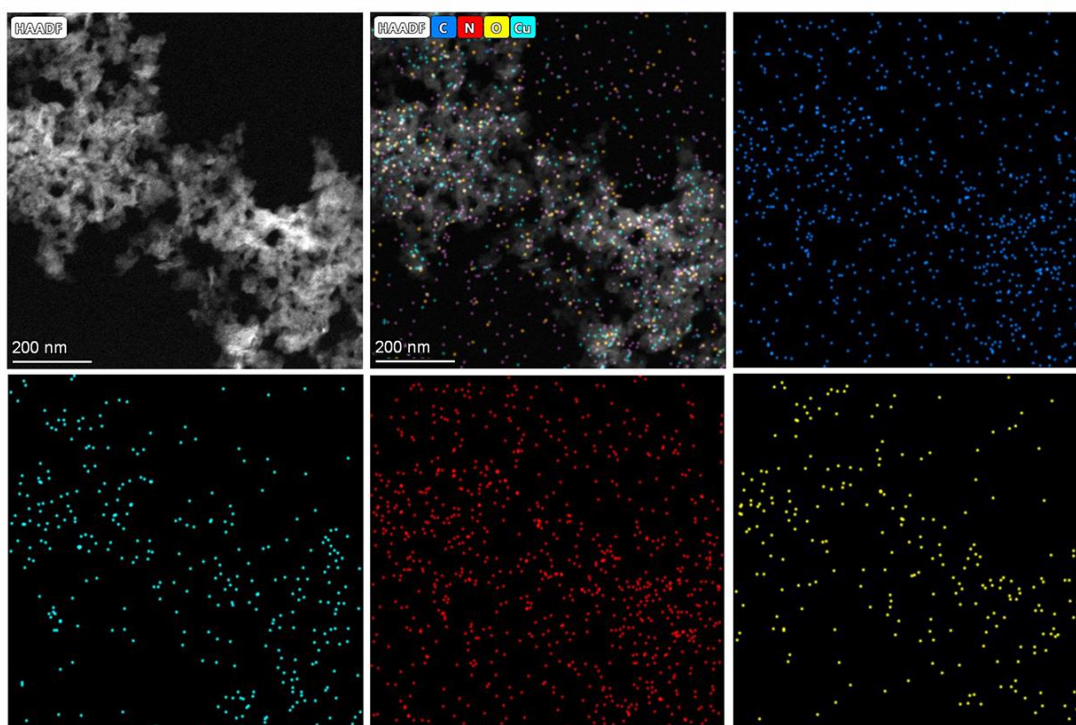
Supplementary Fig. 15 | XRD of CuBBTA, before the CO₂RR electrolysis, after the CO₂RR electrolysis, electroreduction at -300 mA cm^{-2} for 10 min under an Ar atmosphere, carbon paper. The XRD before and after the CO₂RR electrolysis was unchanged and retained the main peak of CuBBTA. The peak of Cu(111) was clearly observed after electrolysis at -300 mA cm^{-2} for 10 min under argon atmosphere. The Cu standard pattern (PDF#04-0836) was used as the reference.



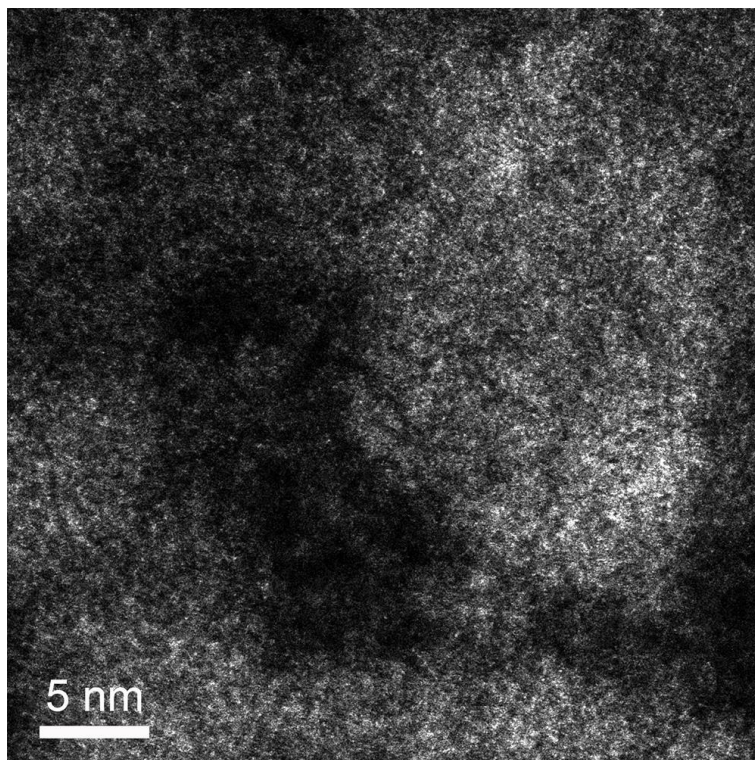
Supplementary Fig. 16 | Scanning electron microscopy (SEM) images of CuBBTA before and after stability test in the MEA system. (a) the CuBBTA on the carbon cloth before CO₂RR process. (b) the CuBBTA on the carbon cloth after CO₂RR process. The structure of CuBBTA remained the same after the stability test.



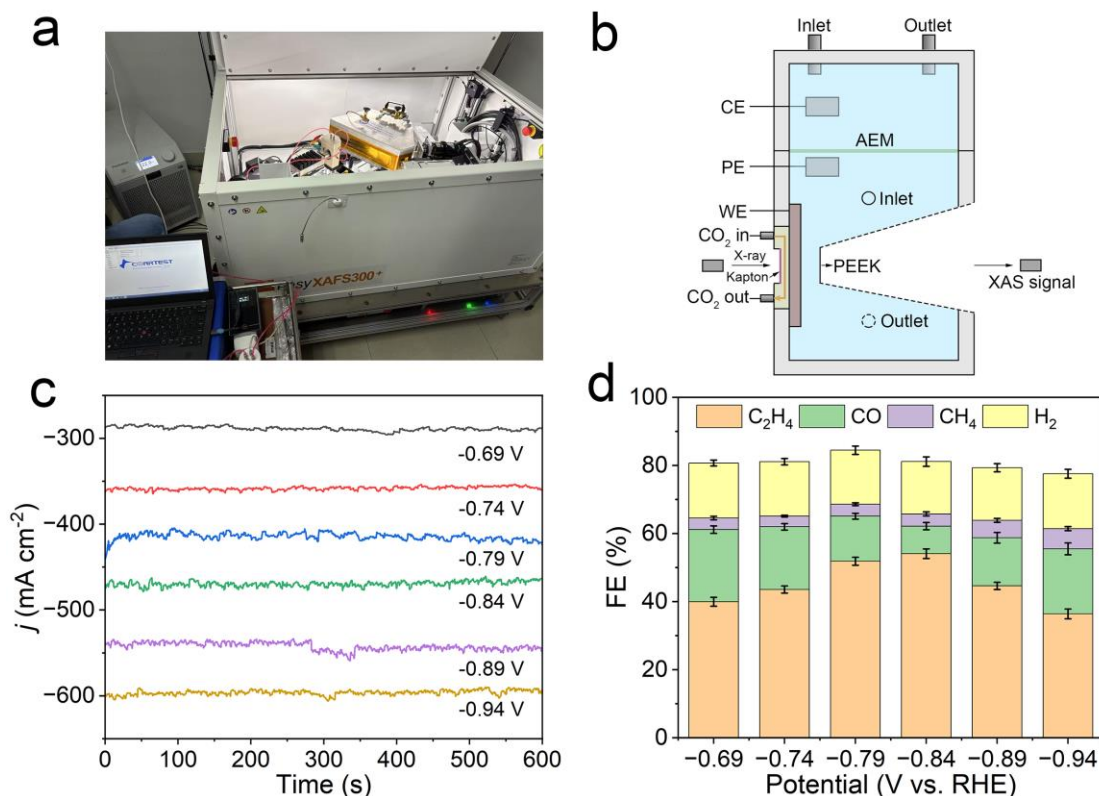
Supplementary Fig. 17 | High-resolution Cu XPS of CuBBTA before and after CO₂RR stability test. (a) Cu 2p spectrum. (b) Cu LMM spectrum.



Supplementary Fig. 18 | Scanning transmission electron microscopy (STEM) elemental mapping of CuBBTA after CO₂RR stability test. No copper nanoclusters appeared.

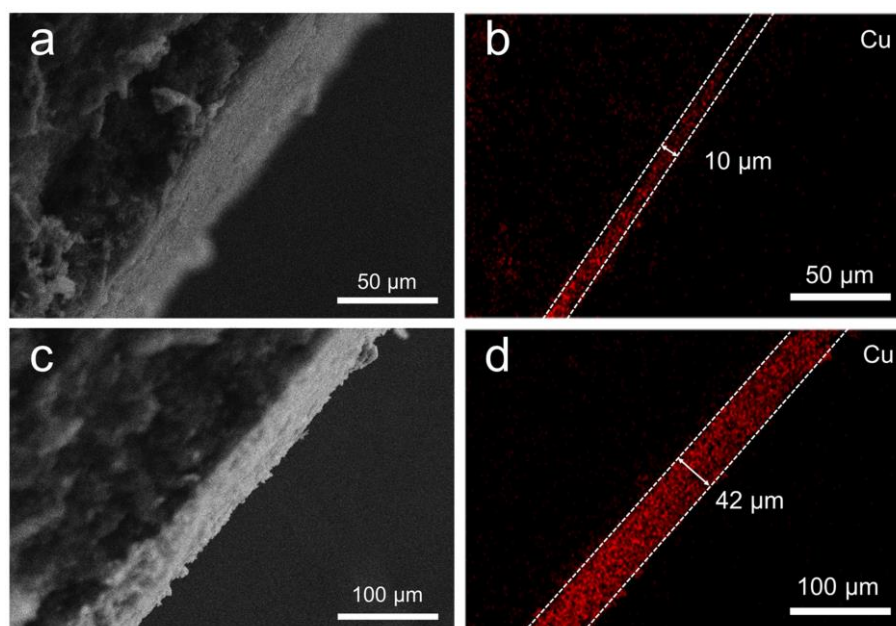


Supplementary Fig. 19 | HAADF-STEM image of CuBBTA after CO₂RR stability test. Copper is distributed as single atoms.

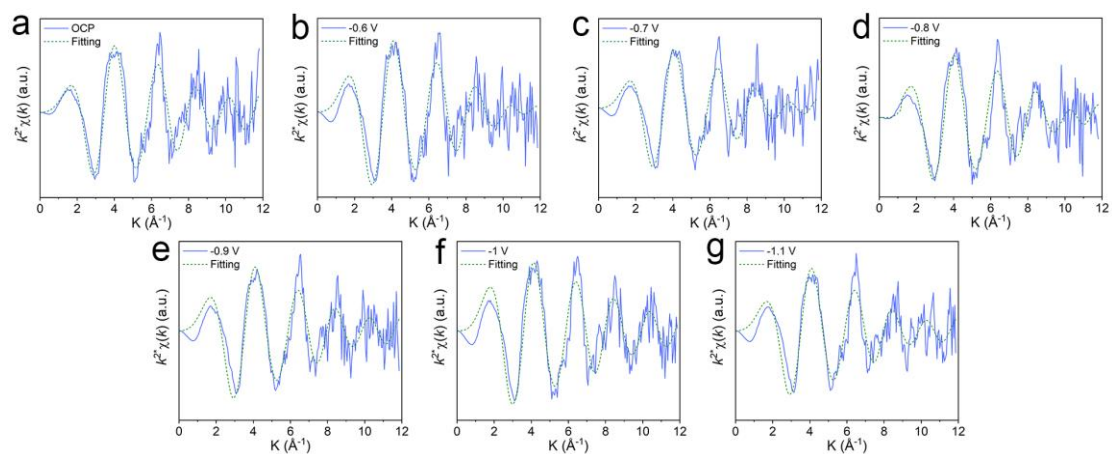


Supplementary Fig. 20 | Operando XAS experiments on the easyXAFS300+ (a) The photograph of operando XAFS. (b) Illustration of in situ XAS electrochemical cells for transmittance mode. (c) The current densities corresponding to different applied potentials in the flow cell in the operando flow-cell electrolyzer. (d) The CO₂RR performance of CuBBTA performed in the operando flow-cell electrolyzer. The error bars represent standard deviations from at least three independent measurements.

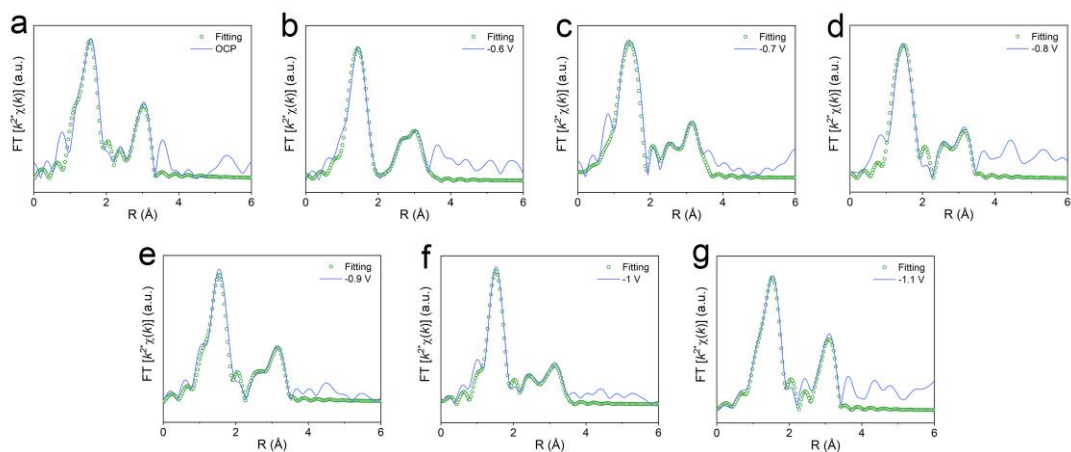
The operando XAS experiments were performed using a flow cell configuration. The flow cell used for evaluating carbon dioxide reduction performance differs from conventional flow cells in that it employs polyimide tape to seal the gas chamber and utilizes PEEK material with adjustable electrolyte thickness, enabling X-ray irradiation and detection of transmitted signals. we evaluated the CO₂ reduction reaction (CO₂RR) performance using the same operando XAS flow cell under identical experimental conditions. The Faradaic efficiencies of each gaseous product and the corresponding current densities at each applied potential were found to be nearly identical to those obtained using the standard flow cell.



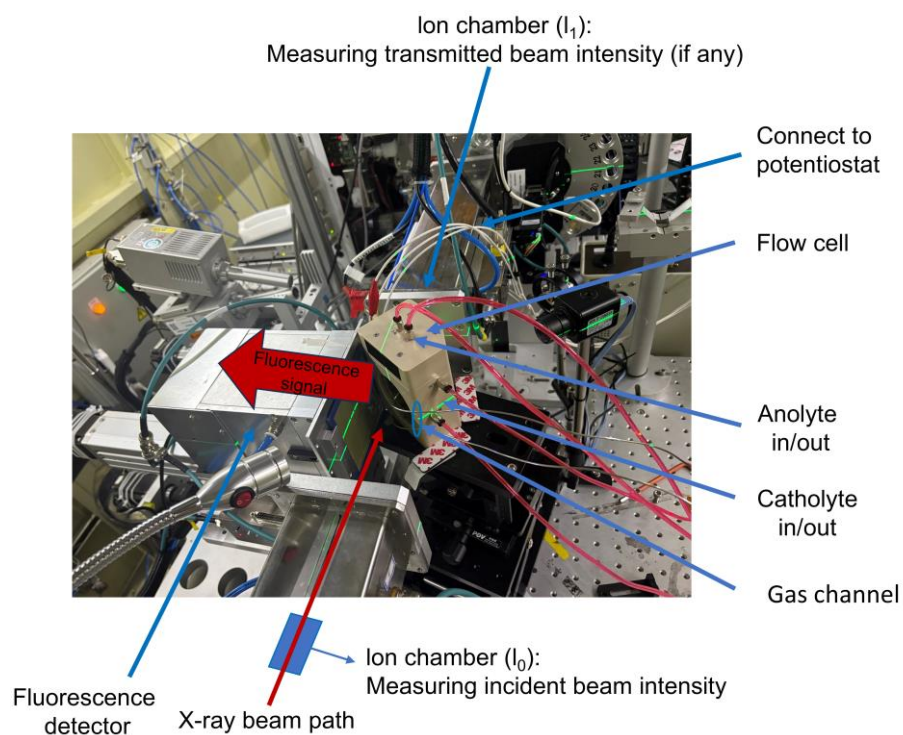
Supplementary Fig. 21 | The cross-section SEM images and the energy dispersive spectroscopy mappings of (a-b) a layer of catalyst in flow cell or (c-d) a layer of catalyst in table-XAS spectrometer flow cell. Due to the low photon flux and limited detection sensitivity in table-XAS spectrometer, it is necessary to increase the catalyst loading and film thickness to enhance the absorption signal intensity, thereby obtaining resolvable spectral features.



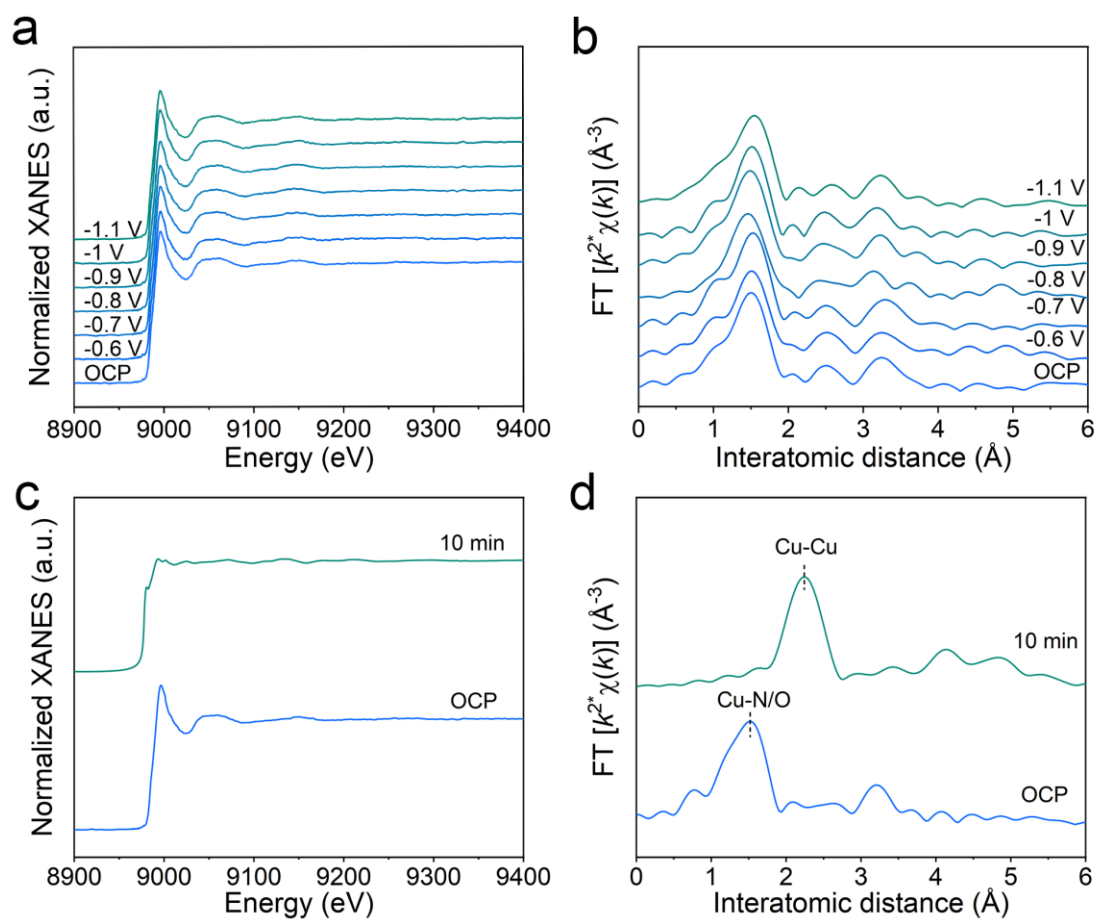
Supplementary Fig. 22 | Operando k^2 -weighted Cu K-edge EXAFS spectra for CuBBTA under at representative potentials. (a) Under open-circuit voltage. (b) At -0.6 V vs. RHE. (c) At -0.7 V vs. RHE. (d) At -0.8 V vs. RHE. (e) At -0.9 V vs. RHE. (f) At -1 V vs. RHE. (g) At -1.1 V vs. RHE.



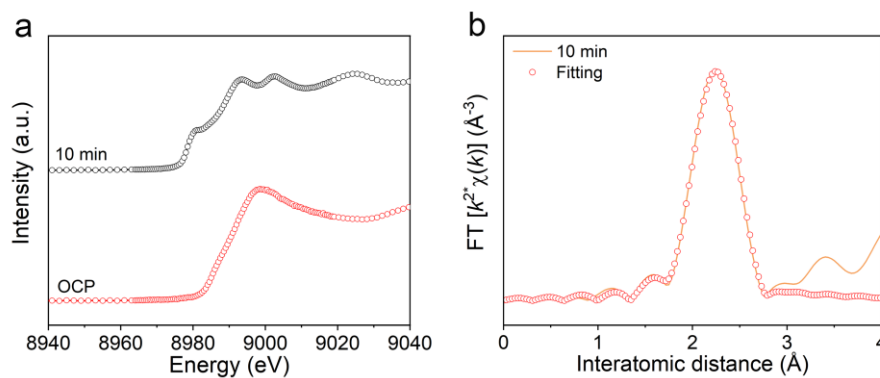
Supplementary Fig. 23 | Fourier-transformed magnitudes for CuBBTA under at representative potentials. (a) Under open-circuit voltage. (b) At -0.6 V vs. RHE. (c) At -0.7 V vs. RHE. (d) At -0.8 V vs. RHE. (e) At -0.9 V vs. RHE. (f) At -1 V vs. RHE. (g) At -1.1 V vs. RHE.



Supplementary Fig. 24 | The photograph of operando XAFS experiments at the BL17B1 beamline in operation. The red arrows show the beam path.



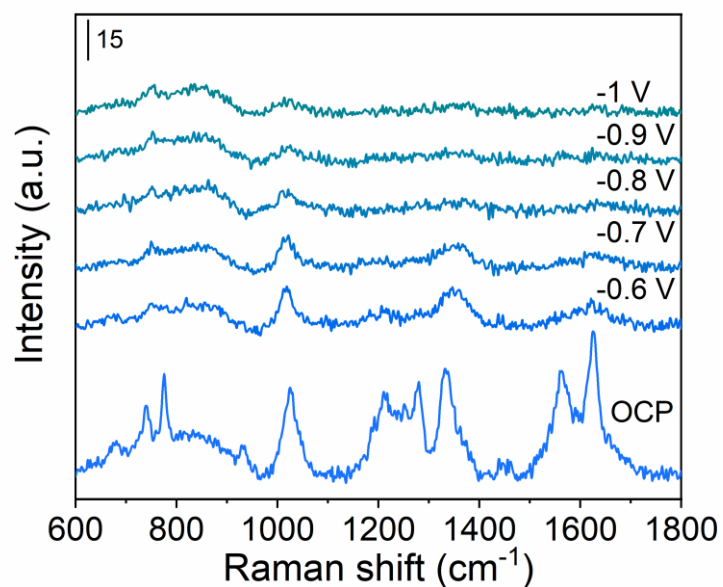
Supplementary Fig. 25 | Operando Cu K-edge XANES at the BL17B1 beamline (a) and EXAFS (b) spectra of CuBBTA at the applied potentials of -0.6 to -1.1 V under CO_2 atmosphere. Cu K-edge XANES (c) and EXAFS (d) spectra of CuBBTA recorded under Ar at a constant current density of -300 mA cm^{-2} (corresponding to -0.7 V) for 10 min.



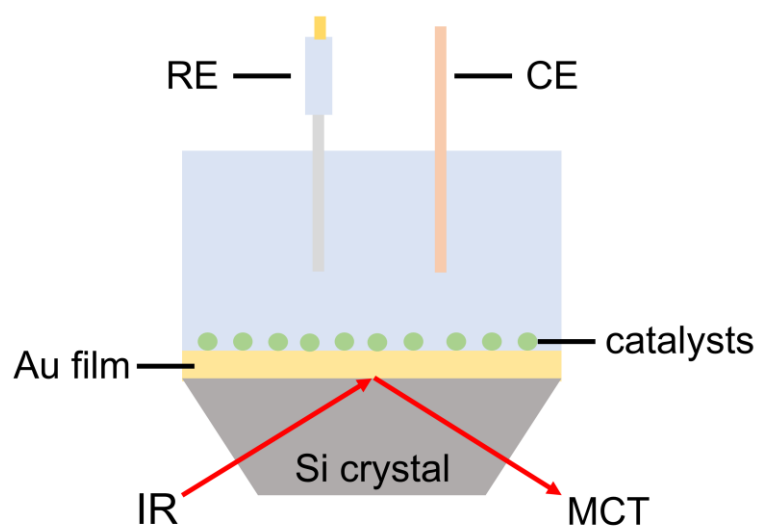
Supplementary Fig. 26 | Operando XAFS measurements. Cu K-edge XANES of CuBBTA catalysts at a constant current density of -300 mA cm^{-2} under Ar atmosphere. (a) Cu K-edge XANES spectra after electroreduction for 10 min. (b) The Cu K-edge EXAFS fitting spectrum of as-reduced CuBBTA after electroreduction for 10 min. The phase of metallic Cu was formatted quickly under Ar atmosphere, which was consistent with the result of XRD.



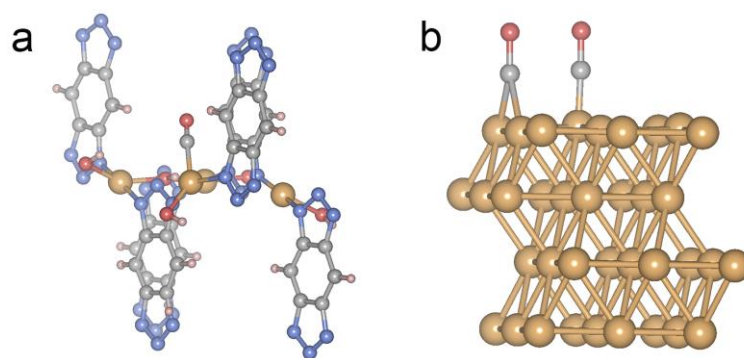
Supplementary Fig. 27 | The electrochemical cell for Operando Raman measurements. A water immersion objective and a 532 nm laser were used. An Ag/AgCl (saturated KCl) electrode and a Pt wire were used as the reference and counter electrodes, respectively.



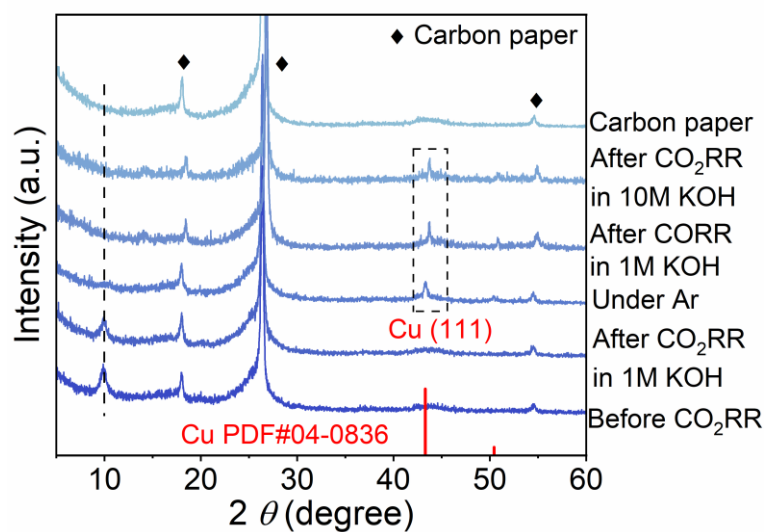
Supplementary Fig. 28 | Operando Raman spectra of CuBBTA at the applied potential of -0.5 V to -1 V under Ar atmosphere. At open-circuit potential (OCP), CuBBTA exhibited characteristic Raman shifts corresponding to its vibrational modes; these signals diminished with increasingly negative potentials and disappeared entirely below -0.5 V.



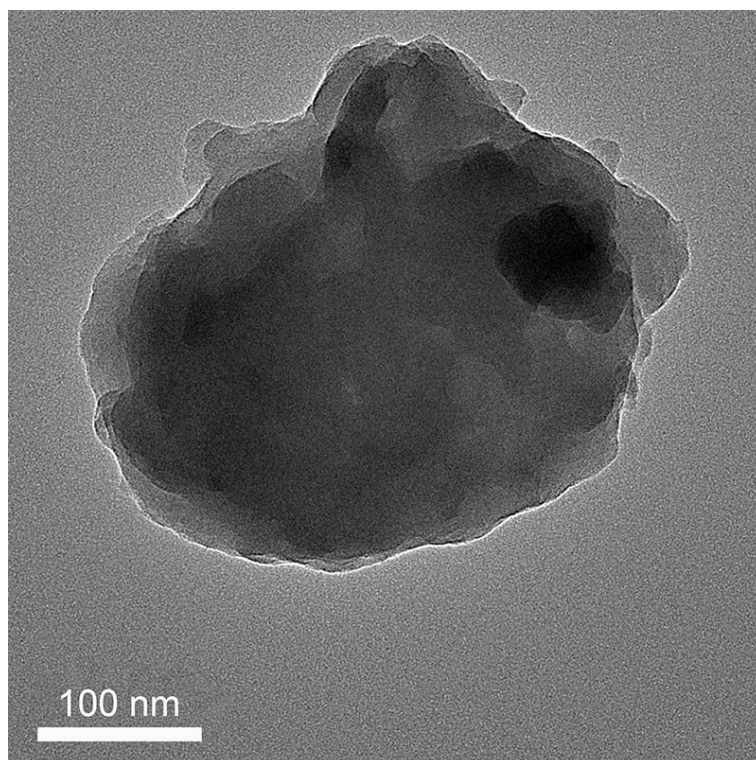
Supplementary Fig. 29 | Schematic diagram of ATR-SEIRAS device.



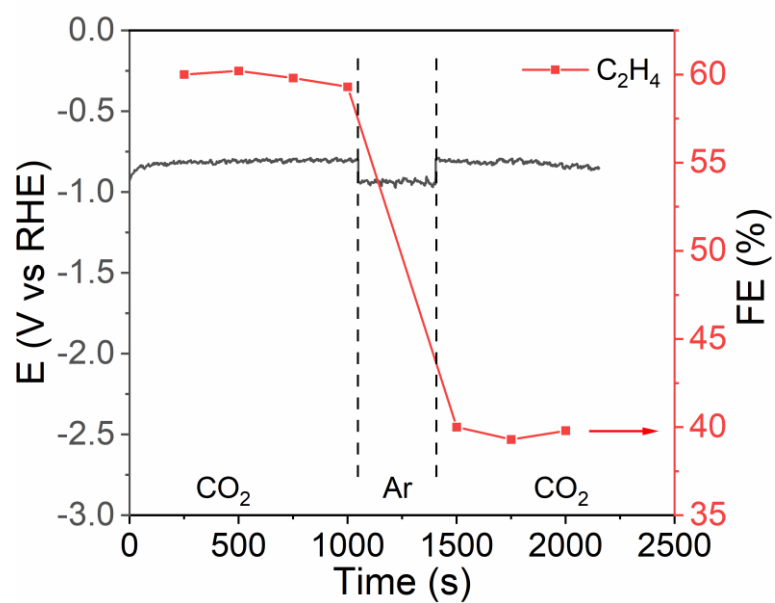
Supplementary Fig. 30 | DFT-predicted $^*\text{CO}$ intermediate configuration on CuBBTA (a) and D-Cu slab (b).



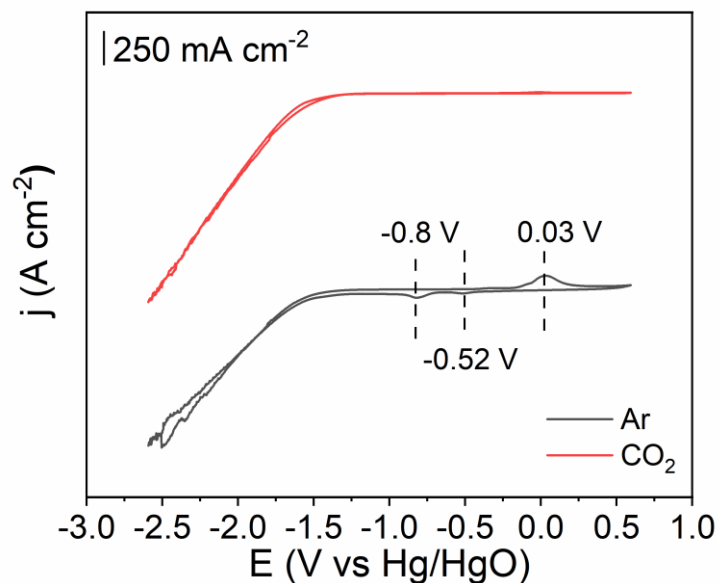
Supplementary Fig. 31 | XRD under different reaction conditions. XRD patterns of the sample under different reaction conditions, including before and after CO₂RR electrolysis, after electroreduction at -300 mA cm^{-2} for 10 min under an Ar atmosphere, after CORR measurement in 1 M KOH, after CO₂RR measurement in 10 M KOH, as well as the carbon paper. A distinct Cu(111) peak is observed after electrolysis at -300 mA cm^{-2} under Ar, after CORR in 1 M KOH, and after CO₂RR in 10 M KOH. The Cu standard pattern (PDF#04-0836) is shown for reference.



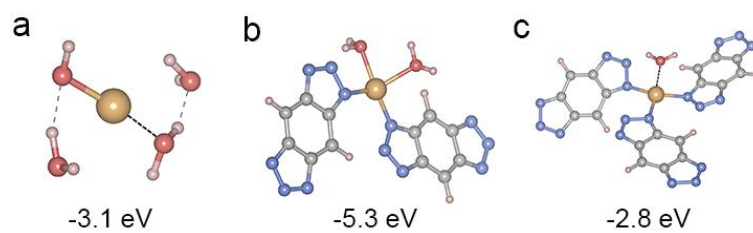
Supplementary Fig. 32 | TEM image of CuBBTA after electroreduction under Ar atmosphere.



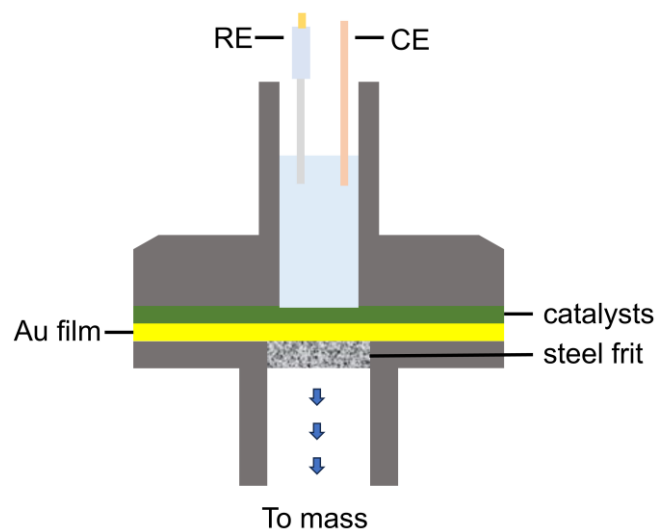
Supplementary Fig. 33 | The CO₂RR performance of CuBBTA at -300 mA cm^{-2} exhibited distinct trends under different atmospheres.



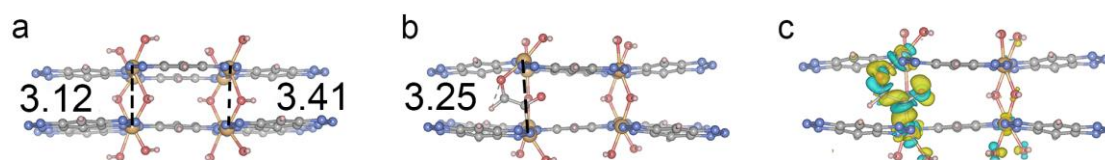
Supplementary Fig. 34 | Cyclic voltammetry (CV) curves of the CuBBTA electrode were recorded in 1 M KOH at a scan rate of 100 mV s⁻¹ over a potential range of -2.5 V to 0.5 V (vs. Hg/HgO) under CO₂ and Ar atmospheres, respectively. Obvious reduction peak at -0.52 V (vs. Hg/HgO) (Cu²⁺ to Cu¹⁺) and -0.8 V (vs. Hg/HgO) (Cu²⁺ to Cu⁰ and Cu¹⁺ to Cu⁰), and oxidation peak at 0.03 V (vs. Hg/HgO) (Cu⁰ to Cu²⁺) appeared under Ar atmosphere.³⁻⁵



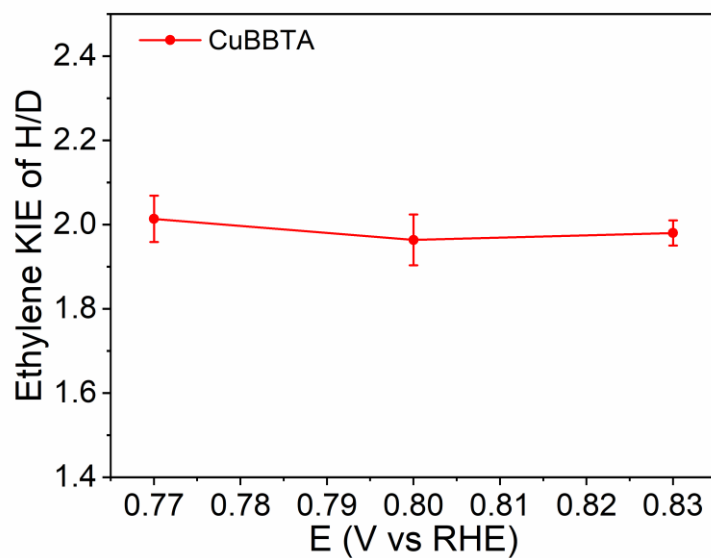
Supplementary Fig. 35 | DFT calculation of free energy of the intermediates were conducted as a reference during the formation of CuBBTA.



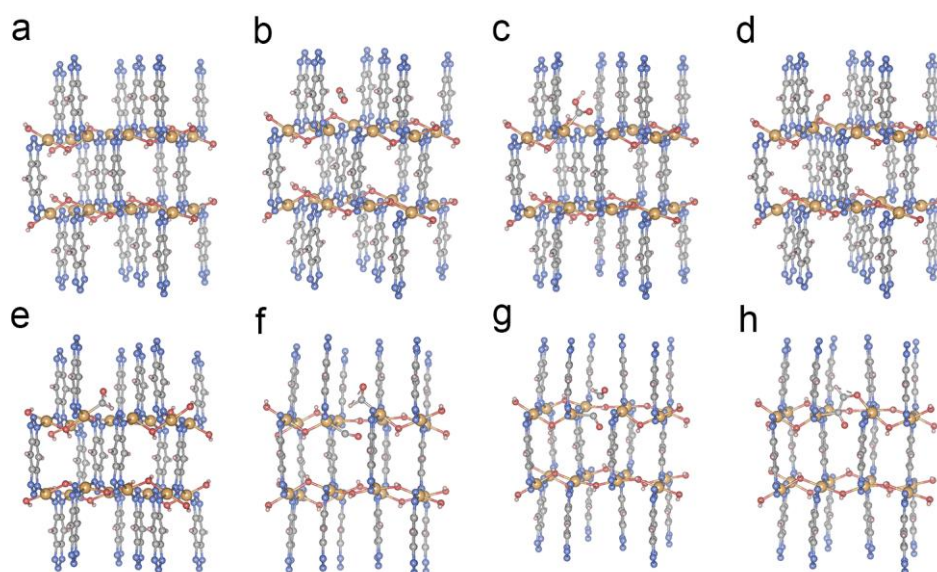
Supplementary Fig. 36 | Schematic illustration for DEMS measurement.



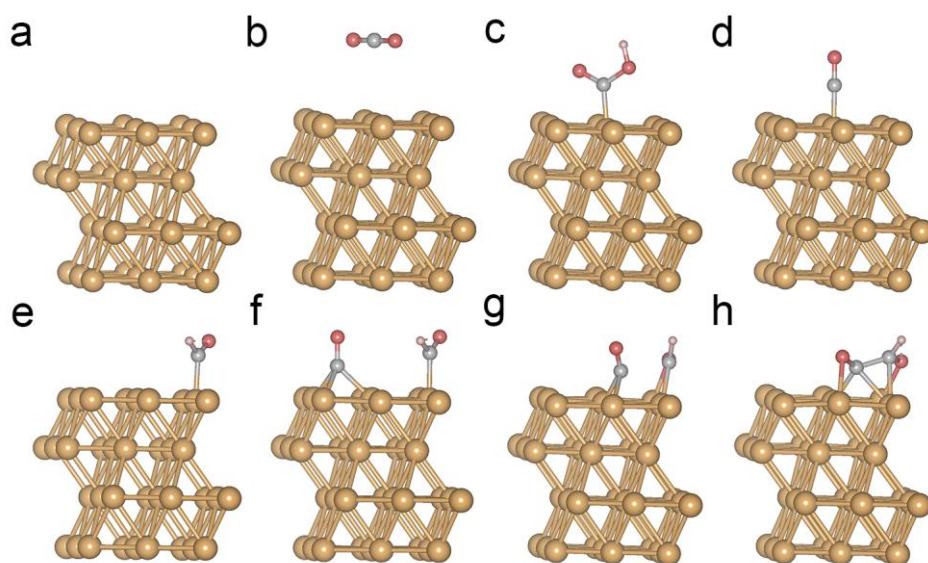
Supplementary Fig. 37 | DFT-predicted $^*\text{COCHO}$ configuration on CuBBTA and Cu-Cu distance before (a) and after (b) $^*\text{COCHO}$ adsorption. (c) Top view of charge difference of $^*\text{COCHO}$ in CuBBTA slab. Cyan and yellow contours present electron depletion and electron accumulation, respectively. The iso-surface level is set to be $0.003 \text{ eV Bohr}^{-3}$.



Supplementary Fig. 38 | KIE of H/D in CO₂RR on CuBBTA under the potential range from -0.77 to -0.83 V. The error bars for ethylene KIE uncertainty represent one standard deviation based on three independent samples. The error bars represent standard deviations from at least three independent measurements.



Supplementary Fig. 39 | The evolution of main intermediates from *CO_2 to *COCHO over CuBBTA during the CO_2 to C_2H_4 process. Side views of (a) CuBBTA; (b) *CO_2 ; (c) *COOH ; (d) *CO ; (e) *CHO (f) $\text{*CHO} + \text{*CO}$; (g) transition state of *COCHO ; (h) *COCHO configurations.



Supplementary Fig. 40 | The evolution of main intermediates from *CO_2 to *COCHO over Cu(111) during the CO_2 to C_2H_4 process. Side views of (a) Cu(111); (b) *CO_2 ; (c) *COOH ; (d) *CO ; (e) *CHO (f) $\text{*CHO} + \text{*CO}$; (g) transition state of *COCHO ; (h) *COCHO configurations.

Supplementary Tables

Supplementary Table 1 | Summary of the amount of Cu in CuBBTA obtained by ICP-AES. The error bars for the data uncertainty represent one standard deviation based on three independent samples.

CuBBTA	Cu (wt.%) ^a
1	38.8
2	40.2
3	39.2
average	39.4±0.7

^amass percentage.

Supplementary Table 2 | The metal loadings of selected Cu SACs from the available literature.

Sample	Synthetic strategy	Loading [wt%]	References
CuBBTA	One-pot synthesis approach	39.4	This Work
Cu/CN	Metal Coordination Route	16.3	6
CCPA	high-concentration precursors strategy	13-15	7
Cu-SACs	General negative pressure annealing approach	29.8	8
UHDCu-N-C SACs	metal sulfide-mediated atomic trapping	26.9	9
Cu ₁ /PCN	Scalable two-step annealing method	21.8	10
Cu SA nanoforest	a micellar brush-derived soft nanoforest system to immobilize SAs	18	11
Cu-N-C	high temperature pyrolysis	20.9	12

Supplementary Table 3 | EXAFS fitting data at the Cu K-edge of CuBBTA. First shell: green lines; Second shell: yellow lines.

Catalyst	Scatter path	CN _{EXAFS} / CN _{DFT}	R _{EXAFS} /R _{DFT} (Å)	ΔE (eV)	σ ² (Å ²)
CuBBTA	Cu-O	2.2±0.3/2.0	1.88±0.12/1.76	3.3±1.8	0.006±0.001
	Cu-N	2.0±0.4/2.0	2.01±0.05/1.98	6.9±4.7	0.008±0.002
	Cu-N	2.1±0.3/2.0	2.85±0.12/2.74	5.2±0.9	0.011±0.008
	Cu-C	2.0±0.2/2.0	3.18±0.05/3.16	6.0±1.3	0.015±0.006
	Cu-Cu	2.1±0.3/2.0	3.15±0.08/3.08	5.4±2.3	0.017±0.010

CN_{DFT}: coordination numbers calculated by DFT. R_{DFT}: bond distance calculated by DFT. CN_{EXAFS}: coordination numbers simulated by EXAFS fitting. R_{EXAFS}: bond distance simulated by EXAFS fitting. σ²: the Debye-Waller factor. ΔE₀: the inner potential shift. S₀² was fixed as 1. data ranges: 2.5 ≤ k ≤ 12 Å⁻¹, 1.0 ≤ R ≤ 3.0. R factor for this fit is 1.5%.

Supplementary Table 4 | Element analysis of CuBBTA. The error bars for the data uncertainty represent one standard deviation based on three independent samples.

Elements	Calc. ^a	Found ^a
C(%)	22.57	21.6±0.2
N(%)	26.33	25.6±0.5
H(%)	1.26	1.35±0.06

^amass percentage.

Supplementary Table 5 | Comparison of half-cell C₂H₄ power conversion efficiency (PCE) over CuBBTA and D-Cu under different applied potential.

catalysts	Applied potential (vs. RHE)	PCE _{ethylene} (%)
CuBBTA	-0.69	26.7
	-0.74	28.9
	-0.79	33.0
	-0.84	34.4
	-0.89	29.4
	-0.94	21.9
D-Cu	-0.69	13.0
	-0.74	16.1
	-0.79	17.7
	-0.84	19.5
	-0.89	20.0
	-0.94	21.5

Supplementary Table 6 | Performance comparison of state-of-the-art Cu-based catalysts for CO₂RR to C₂H₄ reported in the literature.

Catalyst	Potential (V vs. RHE)	PCE _{ethylene} (%)	Current density (mA cm ⁻²)	Reference
CuBBTA	-0.84	34.4	305.2	This work
Au NWs-P1	-1.1	28.6	70	13
Cu ₂ -C ₂ N	-1.4	23.5	318.5	14
Cu ^{δ+} NCN	-1.4	31.7	~400	15
Ln-Cu	-0.95	26.9	~350	16
Cu-DEA-KB	-1.1	24.9	155.7	17
Cu ₂	-1.6	20.7	~225	18
Cu ₃ N-Ag	-1	20	26.7	19
Cu@C _{C=O} ,1	-0.93	35.4	295	20
Cu ₁ Ni-BDP	-1.3	24	279	21
TA-Cu	-1.2	30	316.2	22

Supplementary Table 7 | Interatomic distances and coordination numbers determined by EXAFS analysis of CuBBTA under reaction potential. First shell: green lines; Second shell: yellow lines.

potential	Scatter path	CN	R (Å)	ΔE (eV)	σ^2 (Å ²)	R-factor
OCP	Cu-O	2.2±0.4	1.86±0.08	7.6±1.2	0.005±0.001	0.56%
	Cu-N	2.1±0.2	2.11±0.11	5.2±2.2	0.009±0.002	
	Cu-N	2.0±0.2	2.84±0.14	6.2±1.3	0.013±0.005	
	Cu-C	2.0±0.2	3.15±0.05	4.5±1.2	0.010±0.004	
	Cu-Cu	2.1±0.2	3.18±0.04	3.8±1.5	0.011±0.003	
-0.6 V	Cu-O	2.1±0.2	1.90±0.23	4.5±0.5	0.012±0.004	1.22%
	Cu-N	2.2±0.2	1.98±0.12	7.2±1.3	0.018±0.005	
	Cu-N	2.0±0.3	2.92±0.02	6.3±2.1	0.012±0.002	
	Cu-C	2.1±0.1	3.23±0.11	4.5±1.2	0.014±0.003	
	Cu-Cu	2.2±0.2	3.18±0.21	6.3±0.8	0.012±0.008	
-0.7 V	Cu-O	2.2±0.2	1.79±0.08	4.5±1.2	0.012±0.004	0.86%
	Cu-N	2.1±0.5	2.08±0.04	6.5±2.1	0.006±0.002	
	Cu-N	2.1±0.3	2.75±0.11	7.6±0.5	0.010±0.002	
	Cu-C	2.0±0.2	3.20±0.12	7.5±1.2	0.015±0.002	
	Cu-Cu	2.1±0.3	3.20±0.11	6.5±1.8	0.015±0.006	
-0.8 V	Cu-O	2.0±0.2	1.87±0.06	2.9±0.8	0.012±0.001	0.52%
	Cu-N	2.1±0.1	2.06±0.06	5.5±2.3	0.015±0.005	
	Cu-N	2.1±0.3	2.82±0.08	6.8±1.2	0.015±0.005	
	Cu-C	2.2±0.4	3.16±0.04	6.5±0.8	0.009±0.002	
	Cu-Cu	2.0±0.2	3.14±0.06	4.6±1.8	0.016±0.006	
-0.9 V	Cu-O	2.2±0.1	1.88±0.08	6.5±1.8	0.011±0.001	0.79%
	Cu-N	2.0±0.2	2.03±0.05	6.4±4.2	0.008±0.001	
	Cu-N	2.0±0.4	2.82±0.12	6.3±0.5	0.015±0.008	
	Cu-C	2.1±0.2	3.16±0.11	4.6±1.0	0.012±0.005	
	Cu-Cu	2.1±0.2	3.20±0.10	8.2±2.3	0.012±0.010	
-1 V	Cu-O	2.0±0.3	1.76±0.12	3.2±1.2	0.008±0.001	1.15%
	Cu-N	2.1±0.2	2.11±0.08	4.3±1.5	0.008±0.005	
	Cu-N	2.0±0.4	2.90±0.12	5.5±0.8	0.020±0.008	
	Cu-C	2.0±0.2	3.09±0.10	6.5±1.0	0.006±0.002	
	Cu-Cu	2.1±0.4	3.18±0.08	6.2±2.0	0.016±0.003	
-1.1 V	Cu-O	2.2±0.2	1.89±0.02	6.3±1.1	0.009±0.005	0.88%
	Cu-N	2.0±0.2	2.06±0.05	6.9±2.2	0.010±0.002	
	Cu-N	2.1±0.1	2.89±0.13	4.9±0.8	0.013±0.008	
	Cu-C	2.2±0.2	3.18±0.12	6.7±2.3	0.009±0.006	
	Cu-Cu	2.1±0.1	3.19±0.10	6.4±1.3	0.012±0.008	

CN: coordination numbers simulated by EXAFS fitting. R: bond distance simulated by EXAFS

fitting. σ^2 : the Debye-Waller factor. ΔE_0 : the inner potential shift. S_0^2 was fixed as 1. data ranges: $2.5 \leq k \leq 12 \text{ \AA}^{-1}$, $1.0 \leq R \leq 4.0$.

Supplementary Table 8 | Peak assignments of CuBBTA in Raman spectroscopy.²³

Raman shift (cm ⁻¹)	Vibrational assignments
1625	[ν CC + σ HCC] in benzene
1559	ν NC in triazole + ν CC in benzene
1446	ν NC in triazole
1332	σ HCC
1280	ν CC in triazole
1212	ν CC in benzene + ν CC in triazole
1205	ν NN in triazole
775	σ CCC
737	λ HCCC
679	ν NN in triazole

Abbreviations in the table: ν , stretching; σ , in-plane bending; λ , torsion.

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