CO₂-to-CH₄ electroreduction over scalable Cu-porphyrin based organic polymers promoted by direct auxiliary bonding interaction

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Experimental Procedures

Materials

All chemicals and solvents were commercially available and used without further purification. Potassium hydroxide (KOH), methanol, ethanol, propionic acid and pyrrole were obtained from China National Medicines Corporation Ltd. Dichloromethane was purchased from Shanghai Lingfeng Chemical Reagent Co., Ltd. Copper (II) acetate monohydrate (Cu(Ac)₂·H₂O) was purchased from Shanghai Aladdin BioChem Technology Co., Ltd. Tetraphenylporphyrin-Cu (TPP-Cu) purchased from Jinan Henghua Technology Co., Ltd. Ferrocene was obtained from Xilong Chemical Co., Ltd. 1,1'-ferrocenedicarboxaldehyde and [1,1':4',1"-Terphenyl]-4,4"-dicarboxaldehyde was purchased from Shanghai Tengqian BioChem Technology Co., Ltd. 1,4-benzenedicarbaldehyde and 4,4'-diformylbiphenyl was obtained from Aladdin Industrial Corporation. Nafion solution (5 wt %) was purchased from Sigma-Aldrich. Carbon paper was purchased from Fuel Cell Store. All aqueous solutions were prepared with Millipore water (18.25 M Ω).

Synthesis of Fc-CPP-Cu

Fc-CPP-Cu by the Adler synthesis method¹. was prepared 1,1'ferrocenedicarboxaldehyde (121 mg, 0.5 mmol) and copper (II) acetate monohydrate (52.4 mg, 0.26 mmol) were dissolved in 50 mL propanoic acid in a 150 mL round bottom flask equipped with a condenser. After that, the round bottom flask was purified by high purity nitrogen for three times. The mixture was stirred at room temperature for 20 min. Then, 67.1 mg pyrrole (1.0 mmol) was slowly added drop by drop under stirring and nitrogen atmosphere at room temperature. Afterwards, the temperature was rapidly heated to 130 °C and kept stirring for 10 min. After cooling to room temperature, the crude product was separated from the solution by suction filtration, and then successively washed with aqueous ammonia, dichloromethane, methanol, and water until the filtrate turned colorless. Finally, the product was dried under vacuum overnight at 80 °C. For the microwave synthesis, the reaction condition was identical as the normal synthesis method except that it was heated at 130 °C under 700 W for 10 min.

Synthesis of Bz-CPP-Cu

1,4-benzenedicarbaldehyde (67 mg, 0.5 mmol) and copper (II) acetate monohydrate (52.4 mg, 0.26 mmol) were dissolved in 50 mL propanoic acid in a 150 mL round bottom flask equipped with a condenser. After that, the round bottom flask was purified by high purity nitrogen for three times. The mixture was stirred at room temperature for 20 min. Then, 67.1 mg pyrrole (1.0 mmol) was slowly added drop by drop under stirring and nitrogen atmosphere at room temperature. Afterwards, the temperature was rapidly heated to 130 °C and kept stirring for 10 min. After cooling to room temperature, the crude product was separated from the solution by suction filtration, and then successively washed with aqueous ammonia, dichloromethane, methanol, and water until the filtrate turned colorless. Finally, the product was dried under vacuum overnight at 80 °C.

Synthesis of Bp-CPP-Cu

The synthesis of Bp-CPP-Cu followed similar procedures as that of Fc-CPP-Cu, except that 1,1'-ferrocenedicarboxaldehyde was replaced by 4,4'-diformylbiphenyl (105 mg, 0.5 mmol).

Synthesis of Tp-CPP-Cu

The synthesis of Tp-CPP-Cu followed similar procedures as Fc-CPP-Cu, except that 1,1'-ferrocenedicarboxaldehyde was replaced by [1,1':4',1"-Terphenyl]-4,4"-dicarboxaldehyde (143 mg, 0.5 mmol).

Electrolysis and analysis of CO2 reduction product

The electrolysis tests of the catalyst were carried out in a flow cell. The working electrode was catalyst spray-coated gas diffusion layer (GDL) (Fig. S11). Pt foil and Ag/AgCl electrode were used as the counter and reference electrode, respectively. An anion exchange membrane was inserted between the cathode and Pt foil. Throughout all experiments, 1 M KOH electrolyte was flowed in the cathode and anode chambers separately at 7 mL min⁻¹ with a peristaltic pump, while CO₂ gas was flowed behind the GDL with a flow rate of 20 sccm using a mass flow controller. All the electrolyzer components have verified to be chemically resistant to all the reactants and products under the CO₂ reduction potentials prior to experiments. Chronoamperometry was performed using an electrochemical workstation (SP-150, Bio-Logic) with a standard three-electrode system at room temperature. All potentials were measured versus an Ag/AgCl reference electrode (with saturated KCl) with iR compensation and the results were converted to those versus a reversible hydrogen electrode (RHE) based on the Nernst equation: E (vs. RHE) = E (vs. Ag/AgCl) + 0.197 V + 0.059 \times pH. The gas products (e.g., CO, CH₄, C₂H₄ and H₂) were detected by a gas chromatography (GC, Agilent 7820A) equipped with a flame ionization detector (FID) and a thermal conductivity detector (TCD). The electrolyte solution was collected from the cathode chambers to analyze the liquid products and characterized by ¹H-NMR (Bruker 500 MHz NMR instrument).

Electrochemical measurements

Powder X-ray diffraction (PXRD) patterns of the samples were recorded on a Rigaku SmartLab diffractometer (Japan) equipped with Cu Karadiation ($\lambda = 1.54060$ Å) at 45 kV and 200 mA. Fourier transform infrared spectroscopy (FTIR) was recorded on a Bruker Tensor 27 in the range of 4000-400 cm⁻¹ using the technique of pressed KBr pellets. 273K and 298K CO₂ sorption isotherms were determined by Autosorb IQ2 (Quantachrome Instruments). Metal content analyses was obtained by inductively coupled plasma optic emission spectroscopy (ICP-OES) using Agilent 720ES. X-ray photoelectron spectroscopy (XPS) were recorded using an Escalab 250Xi instrument (Thermo Scientific) equipped with an Al Ka microfocused X-ray source and the C1s peak at 284.6 eV as internal standard. Field emission scanning electron microscopy (SEM, Quanta 250F) was applied to investigate the morphology. Energy dispersive spectrometer (EDS) were recorded on JSM-7600F (JEOL). Transmission electron microscopy (TEM) images, high-resolution TEM (HRTEM) images and STEM-HAADF images coupled to elemental mapping were collected on a JEOL JEM-2100 electron microscope at 200 kV equipped with an Oxford Energy dispersive X-ray spectroscopy. Gas chromatography was performed on GC-7820A equiped a flame ionization detector (FID) with methanizer and a thermal conductivity detector (TCD). The isotope-labeled experiment was performed using ${}^{13}CO_2$ instead of ${}^{12}CO_2$ and the result was analyzed by GC-MS (7890B and 5977B, Agilent). ¹H-NMR was carried out on AVANCE III 400M spectrometer (Bruker). The electrochemical tests were carried out with EC-Lab SP-150 workstation (Bio-Logic). The microwave reaction experiments were conducted on a microwave hydrothermal parallel synthesizer manufactured by Nanjing Xianou Instrument Manufacturing Co., Ltd, model ATPIO-6T, with a rated output power of 1000w. The extended X-ray absorption fine structure (EXAFS) measurements were carried out on the sample at 21A X-ray nanodiffraction beamline of Taiwan Photon Source (TPS), National Synchrotron Radiation Research Center (NSRRC). This beamline adopted 4-bounce channel-cut Si (111) monochromator for mono-beam X-ray nanodiffraction and X-ray absorption spectroscopy. The end-station equipped with three ionization chambers and Lytle/SDD detector after the focusing position of KB mirror for transmission and fluorescence mode X-ray absorption spectroscopy. The photonflux on the sample is range from $1 \times 10^{11} \sim 3 \times 10^9$ photon/sec for X-ray energy from 6 - 27 keV.

The preparation of working electrode

The catalyst ink was prepared by sonicating 10 mg of grinded samples, 100 μ L of Nafion solution (5 wt%) in a 900 μ L solution containing ethanol (500 μ L) and water (400 μ L). After sonicating for 30 min, 50 μ L ink was directly spray-coated on a hydrophobic carbon paper (1 × 2 cm) to form a 0.5×1 cm² catalyst area with a catalyst loading density of ~1 mg cm⁻². The deposited carbon paper was further dried at room temperature.

Evaluation of CO₂RR performance

For gaseous products, the Faradaic efficiency (FE) was calculated as follows. The molar flow of gas from the electrochemical cell was calculated using the concentration of species g measured by GC (x_g (mol mol⁻¹)) and the CO₂ flow rate (f_{CO_2} (mol s⁻¹)). With the number of exchanged electrons to produce species g from CO₂ (Z_g) and Faraday constant (96,485 C mol⁻¹), the partial current towards species g (i_g) was calculated. The Faradaic efficiency for species g (FE_g) is the percentage of the partial current in the total current (i_{tot}):

$$FE_g(\%) = \frac{i_g}{i_{tot}} \times 100\% = \frac{96485 \times x_g \times f_{co_2} \times Z_g}{i_{tot}} \times 100\%$$

Partial current density $(j_{product})$ of each product was calculated as follows:

$$j_{product} = j_{total} \times FE_{product}$$

where j_{total} is the average total current density (mA cm⁻²) during electrolysis.

The turnover frequency (TOF, s⁻¹) of CH₄ was calculated by the equation:

$$TOF = \frac{i_{total} \times FE_{CH4}}{N \times F \times n_{cat}}$$

Where i_{total} is the total current (A), FE_{CH4} is the faraday efficiency of CH₄ (%), N is the number of electrons in the half reaction (N = 4 for CO₂ to CH₄ conversion), F is the Faraday constant (96485 C/mol), n_{cat.} is the moles of catalyst employed in the electrolysis (mol). The TOF of Fc-CPP-Cu at -0.9V is 0.013 s⁻¹ according to Eq.

$$\text{TOF} = \frac{0.0929 \times 0.759}{4 \times 96485 \times 1.36 \times 10^{-5}} = 0.013 \text{ s}^{-1}$$

Other electrochemical measurements

The polarization curves results were obtained by performing linear sweep voltammetry (LSV) mode with a scan rate of 5 mV s⁻¹ during the CO₂ reduction experiments. To estimate the ECSA, CV were tested by measuring C_{dl} under the potential window range from 0.01 V to -0.11 V (vs. Ag/AgCl) with various scan rates from 20 to 100 mV s⁻¹. Electrochemical impedance spectroscopy (EIS) measurement was performed on the electrochemical analyzer in a frequency range from 100 kHz to 100 mHz by applying an AC voltage with 10 mV amplitude at -0.90 V vs. RHE.

DFT details

Spin-polarized DFT calculations were performed with periodic super-cells under the generalized gradient approximation (GGA) using the Perdew-Burke-Ernzerhof (PBE) functional for exchange-correlation and the ultrasoft pseudopotentials for nuclei and core electrons. The Kohn-Sham orbitals were expanded in a plane-wave basis set with a kinetic energy cut-off of 30 Ry and the charge-density cut-off of 300 Ry. The Fermisurface effects has been treated by the smearing technique of Methfessel and Paxton, using a smearing parameter of 0.02 Ry. The convergence criteria are set as 10^{-3} Ry/Bohr of Cartesian force components acting on each atom and 10⁻⁵ Ry of total energy. The Brillouin-zones were uniformly sampled with a gamma k-point mesh, for molecules do not have periodicity. Besides, the reaction barrier and the minimum energy path (MEP) was calculated by the nudged elastic band (NEB) method. The quasi-Newton method was employed to optimize the intermediate images of the NEB calculations, the convergence threshold of which was set at maximum elastic force no larger than 0.015 Ry/Å. Six water molecules were added to stabilize the formed hydroxyl, and we added these water molecules if and only if we did the NEB calculation. When adding these water molecules, the spin-polarization was shut off since spin calculation is expensive but won't affect the water dissociation appreciably. The dispersion correction is applied in all calculations with the semiempirical zero damping D3 method of Grimme. All the calculations were conducted by the PWSCF codes contained in the Quantum ESPRESSO distribution.²

Charge added

As a character in electrocatalysis, the applied potentials will force the catalyst to carry some charges. This impact is different for transiton metal catalysts and molecular catalyst such as porphyrin. For transition metal catalysts, their valence state won't change too much, because their surface are gathered by the metal atoms, which will lead to a large density of state (DOS) around Fermi level. This state is so large that the added charge cannot lead to the rise in Fermi level.³ However, for molecular catalyst such as porphyrin, since these catalysts usually have a much smaller density of state around Fermi level, valence state of metal center may vary seriously with the potential. And because so, the reactivity of metal center may change seriously.⁴ Therefore, we should take charge issue seriously for catalyst in this work. In this paper, the electrode potential we are most interested is at -0.9 V vs RHE, and pH is 14. Thus, if we take the work function (Φ) of electrode at 0 V vs SHE to be 4.44 eV, at the -0.9 V vs RHE, we will have Φ of 4.44-0.059*14-0.9=2.71 eV. On the other hand, for Cu porphyrin molecules, the Φ is calculated to be 4.47, 2.01 and 1.48 eV for neutral case, negatively charged by 1 and 2 additional electrons. This means, it is appropriate to add -1 charge into system during the calculation. So in calculating the adsorption energy, i.e., Eq.S3 to Eq.S11, we used an additional charge of -1, while during NEB calculation, the charge of -2 is used because in it we have OH⁻ that should carry one more electron.

The details for composing the free energy diagram

During calculation, the HER is considered to go through the following mechanism:

$$H^{+} + e^{+} \rightarrow H^{*} (RS1)$$

*H + H⁺ + e → H₂ + * (RS2)

And that for CO₂RR towards CO is:

We also have the mechanism for CO₂RR towards CH₄:

$$CO_{2} + H^{+} + e^{+} \Rightarrow *COOH (RS3)$$

$$*COOH + H^{+} + e^{-} \Rightarrow *CO + H_{2}O (RS4)$$

$$*CO + H^{+} + e^{-} \Rightarrow *CHO (RS6)$$

$$*CHO + H^{+} + e^{-} \Rightarrow *HCOH (RS7)$$

$$*HCOH + H^{+} + e^{-} \Rightarrow *CH + H_{2}O (RS8)$$

$$*CH + H^{+} + e^{-} \Rightarrow *CH_{2} (RS9)$$

$$*CH_{2} + H^{+} + e^{-} \Rightarrow *CH_{3} (RS10)$$

$$*CH_{3} + H^{+} + e^{-} \Rightarrow *CH_{4}(g) (RS11)$$

In calculating the free energy diagrams (FED) from RS1 to RS5, the free energies of proton and electron are treated via the classical computational hydrogen electrode (CHE)

method. ⁵⁻⁷ As for the adsorbates, the associated adsorption free energies of the adsorbates are calculated by the following expression:

$$G_{\rm A} = E_{\rm A} + ZPE - TS + \int C_{\rm p} dT (S1)$$

where E_A is the total energy of a certain molecule A or adsorbate A*. For molecule, E_A can be obtained directly through a gas phase calculation; For a certain adsorbate, E_A is calculated by the difference between the DFT based substrate with (E_{A*}^{DFT}) and without adsorbate A (E_*^{DFT}):

$$E_{\rm A} = E_{\rm A*}^{\rm DFT} - E_{\rm *}^{\rm DFT} (S2)$$

ZPE, TS and $\int C_p dT$ are the correction from zero point energy, entropy and heat capacity, whose values are listed on Table S4. Other than that, H⁺ is calculated by the Gibbs free energy of 1/2H₂, the energy of electron is calculated by -*Ue*. As for the solvation energies, a value of -0.11 eV is added to each O atom of adsorbates. For instance, -0.11 eV and -0.22 eV are added for COOH*. A correction of -0.51 eV is added to CO molecules for the errors for GGA-PBE functional. According to such correction can lead an agreement with experimental overall half reaction of CO₂ reduction. ⁶ Specifically, the standard reaction Gibbs free energy differences of H*, COOH*, CO* are expressed as:

$$\Delta G^{0}_{*COOH} = G_{*COOH} - G_{CO2} - 1/2 \ G_{H2} \ (S3)$$

$$\Delta G^{0}_{*CO} = G_{*CO} - G_{CO2} - G_{H2} + G_{H2O} \ (S4)$$

$$\Delta G^{0}_{H*} = G_{H*} - 1/2 \ G_{H2} \ (S5)$$

$$\Delta G^{0}_{*CHO} = G_{*CHO} - G_{CO2} - 3/2 \ G_{H2} + G_{H2O} \ (S6)$$

$$\Delta G^{0}_{*HCHO} = G_{*HCHO} - G_{CO2} - 2 \ G_{H2} + G_{H2O} \ (S7)$$

$$\Delta G^{0}_{*CH} = G_{*CH} - G_{CO2} - 5/2 \ G_{H2} + 2 \ G_{H2O} \ (S8)$$

$$\Delta G^{0}_{*CH2} = G_{*CH2} - G_{CO2} - 3 \ G_{H2} + 2 \ G_{H2O} \ (S9)$$

$$\Delta G^{0}_{*CH3} = G_{*CH3} - G_{CO2} - 7/2 \ G_{H2} + 2 \ G_{H2O} \ (S10)$$

$$\Delta G^{0}_{*OCHO} = G_{*OCHO} - G_{CO2} - 1/2 \ G_{H2} \ (S11)$$

The standard Gibb free energy differences from RS1 to RS11 are then expressed as:

$$\Delta G^{0}_{RS1} = G_{*H} - 1/2 \ G_{H2} + Ue \ (S12)$$

$$\Delta G^{0}_{RS2} = -G_{*H} + 1/2 \ G_{H2} + Ue \ (S13)$$

$$\Delta G^{0}_{RS3} = \Delta G^{0}_{*COOH} + Ue \ (S14)$$

$$\Delta G^{0}_{RS4} = \Delta G^{0}_{*CO} - \Delta G^{0}_{*COOH} + Ue \ (S15)$$

$$\Delta G^{0}_{RS5} = G_{CO(g)} - \Delta G^{0}_{*CO} + Ue \ (S16)$$

$$\Delta G^{0}_{RS6} = \Delta G^{0}_{*CHO} - \Delta G^{0}_{*CO} + Ue \ (S17)$$

$$\Delta G^{0}_{RS7} = \Delta G^{0}_{*HCHO} - \Delta G^{0}_{*CHO} + Ue \ (S18)$$

$$\Delta G^{0}_{RS8} = \Delta G^{0}_{*CH} - \Delta G^{0}_{*HCHO} + Ue \ (S19)$$

$$\Delta G^{0}_{RS9} = \Delta G^{0}_{*CH2} - \Delta G^{0}_{*CH} + \text{Ue} (S20)$$

$$\Delta G^{0}_{RS10} = \Delta G^{0}_{*CH3} - \Delta G^{0}_{*CH2} + \text{Ue} (S21)$$

$$\Delta G^{0}_{RS11} = G_{CH4} - 4 \ G_{H2} + 2 \ G_{H20} - \Delta G^{0}_{*CH3} + \text{Ue} (S22)$$

$$\Delta G^{0}_{RS12} = \Delta G^{0}_{*OCH0*} + \text{Ue} (S23)$$

Eq.S12-S23 can be used to propose the free energy diagrams.



Fig. S1. The PXRD patterns of Fc-CPP-Cu, Bz-CPP-Cu, Bp-CPP-Cu and Tp-CPP-Cu.



Fig. S2. XPS spectra of Fc-CPP-Cu.



Fig. S3. FTIR spectra of Fc-CPP-Cu, Bz-CPP-Cu, Bp-CPP-Cu, Tp-CPP-Cu and pyrrole.



Fig. S4. XAS measurement. (a) Fe K-edge XANES spectra of Fe foil, FeO and Fc-CPP-Cu. (b) Fe K-edge FT spectra of Fe foil, FeO and Fc-CPP-Cu.



Fig. S5. N₂ sorption test of Fc-CPP-Cu. (a) N₂ sorption curve of Fc-CPP-Cu at 77 K. (b) Pore-size distribution profile of Fc-CPP-Cu.



Fig. S6. N_2 sorption test of Bz-CPP-Cu (a), Bp-CPP-Cu (b) and Tp-CPP-Cu (c) at 77 K.



Fig. S7. CO₂ sorption curves of Fc-CPP-Cu (a), Bz-CPP-Cu (b), Bp-CPP-Cu (c) and Tp-CPP-Cu (d) at different temperatures.



Fig. S8. EDS spectrum of Fc-CPP-Cu.



Fig. S9. High-resolution TEM (HRTEM) image of Fc-CPP-Cu.



Fig. S10. SEM images. a Bz-CPP-Cu. b Bp-CPP-Cu. c Tp-CPP-Cu.



Fig. S11. The schematic representation of the CO_2RR flow cell system applied in this work.



Fig. S12. Linear sweep voltammetric curves of Fc-CPP-Cu, Bz-CPP-Cu, Bp-CPP-Cu and Tp-CPP-Cu.



Fig. S13. Electrocatalytic performance of Fc-CPP-Cu. a Linear sweep voltammetric curves. b Partial current density for CH₄, C₂H₄, CO and H₂.



Fig. S14. Faradaic efficiencies for HER, CO₂RR and CH₄ recorded at different applied potentials of Fc-CPP-Cu.



Fig. S15. Electrocatalytic performance of Bz-CPP-Cu. a Linear sweep voltammetric curves. b Faradaic efficiencies for CH₄, C₂H₄, CO and H₂.



Fig. S16. Electrocatalytic performance of Bp-CPP-Cu. a Linear sweep voltammetric curves. b Faradaic efficiencies for CH₄, C₂H₄, CO and H₂.



Fig. S17. Electrocatalytic performance of Tp-CPP-Cu. a Linear sweep voltammetric curves. b Faradaic efficiencies for CH₄, C₂H₄, CO and H₂.



Fig. S18. Faradaic efficiencies for CH₄, C_2H_4 , CO and H₂. a Physical-mixture of ferrocene and TPP-Cu (molar ratio, ferrocene/TPP-Cu = 2:1). b Fc-CPP (porphyrin center without Cu). c Ferrocene. d TPP-Cu.



Fig. S19. The mass spectra of 13 CO recorded under 13 CO₂ atmosphere.



Fig. S20. Cyclic voltammetry (CV) curves in the region of 0.01 - 0.11 V vs. Ag/AgCl at various scan rates (20 -100 mV s⁻¹) for a, b Fc-CPP-Cu. c, d Bz-CPP-Cu.



Fig. S21. Nyquist plots of electrocatalysts over the frequency ranging from 100 kHz to 0.1 Hz at -0.9 V *vs.* RHE.



Fig. S22. XPS spectra of Fc-CPP-Cu before and after CO₂RR.



Fig. S23. XAS measurement. (a) Cu K-edge XANES spectra of Cu foil, Cu₂O, CuO, and Fc-CPP-Cu samples before and after CO₂RR. (b) Cu K-edge FT spectra of Cu foil, Cu₂O, CuO, and Fc-CPP-Cu samples before and after CO₂RR.



Fig. S24. XAS measurement. (a) Fe K-edge XANES spectra of Fe foil, FeO and Fc-CPP-Cu samples before and after CO_2RR . (b) Fe K-edge FT spectra of Fe foil, FeO and Fc-CPP-Cu before and after CO_2RR .



Fig. S25. The photo image of Fc-CPP-Cu obtained through scale-up synthesis.



Fig. S26. SEM images of Fc-CPP-Cu obtained through scale up production.



Fig. S27. FTIR spectra of Fc-CPP-Cu by normal (blue), scale-up (green) and microwave synthesis (purple).



Fig. S28.Electrocatalytic performance of Fc-CPP-Cu obtained through scale-up synthesis. a Faradaic efficiencies for CH₄, C₂H₄, CO and H₂. b Faradaic efficiencies for HER, CO₂RR and CH₄.



Fig. S29. SEM image of Fc-CPP-Cu obtained through microwave synthesis (10 min).



Fig. S30. Electrocatalytic performance of Fc-CPP-Cu obtained through microwavesynthesis. a Faradaic efficiencies for CH₄, C₂H₄, CO and H₂. b Faradaic efficiencies for HER, CO₂RR and CH₄.



Fig. S31. Free energy profiles for CO₂-to-CH₄ reaction pathway on Bz-CPP-Cu.

Element type	Cal. (wt %)	Found. (wt%)
Fe	15.2	13.1
Cu	8.62	9.4

 Table S1. Metal content analysis results of Fc-CPP-Cu from ICP tests.

Catalyst	Reactor	Electrolyte	Potential	Current	FE CH4	Refe
			(vs. RHE)	density	(%)	renc
				(mA cm ⁻²) ^a		e
Cu NDs	Flow cell	0.1 M	-1.1 V	/	57	9
		KHCO ₃				
La ₂ CuO ₄	Flow cell	1 M KOH	-1.4 V	117	56.3	10
Cuoh	Flow cell	1 M KOH	-0.91 V	100	53	11
Cu-	Flow cell	0.1 M	-1.3 V	3.8	50	12
MOF-74		KHCO ₃				
NGQDs	Flow cell	1 M KOH	-0.74 V	/	4.5	13
NNU-	Flow cell	1 M KOH	-0.9 V	391.79	82.2	14
33(H)						
Pluse	H-cell	0.5 M	-2.8 V vs.	38	85	15
electrode		NaHCO ₃	SCE			
posited						
Cu						
Cu	H-cell	0.1 M	-1.0 V	18	81.7	16
clusters/		KHCO ₃				
DRC						
Cu foil	H-cell	0.5 M	-1.98 V	31	81.6	17
		NaHCO ₃				
n-Cu/C	H-cell	0.1 M	-1.35 V	7	76	18
		NaHCO ₃				
CuS	H-cell	0.1 M	-1.1 V	6	73	19
Cus		KHCO ₃				
Cu ₂ O@	H-cell	0.1 M	-1.4 V	10.8	73	20
CuHHT		KCl/0.1 M				
Р		KHCO ₃				
CuPc/C	H-cell	0.5 M	-1.06 V	13	66	21
NTs		KHCO ₃				
Cu ₂ O@	H-cell	0.1 M	-1.71 V	/	63.2	22
Cu3(BT		KHCO ₃				
C) 2						
Cu-CeO ₂	H-cell	0.1 M	-1.8 V	33.6	58	23
		KHCO ₃				
Cu	H-cell	0.25 M	CV	/	58	24
rhombic		K ₂ CO ₃	method			
dodecah						
edrons						
Polished	H-cell	0.3 M KI +	-1 V	6.7	56	25

Table S2 The performance of various electrocatalysts in the electroreduction of CO_2 to CH_4 .

		0.1.14				
Cu foll		0.1 M				
		KHCO ₃				
Cu	H-cell	0.1 M	-1.05 V	/	56	26
Nanocub		KHCO ₃				
e						
<u> </u>	H-cell	0.1 M	-1 25 V	ΔΔ	55	27
Nanawin	11-0011		-1.23 V	т.т	55	21
nanowir		KIICO3				
es						
	H-cell	0.1 M	-1.8 V vs.	2.6	51	28
CuaDd		TBAPF ₆ /CH ₃	Ag/AgNO			
Cu21 u		CN and 1 M	3			
		H ₂ O				
Cu ^{II} /ade-	H-cell	0.1 M	-1 6 V	15	50	29
MOF		KHCO	1.0 1	10	20	27
nanashaa		KIICO3				
nanosnee						
	~~ 44					
polycryst	H-cell	0.1 M	-1.6 V vs.	/	50	30
alline		KHCO ₃	Ag/AgCl			
copper						
Pd-	H-cell	0.5 M	-0.96 V	57	46	31
decorate		KHCO ₃				
d Cu						
	H cell	0.5 M	1 V vs	3	40	32
Cu	11-0011		$-1 \vee VS$.	3	40	32
water	~~ 44	NaHCO ₃	Ag/AgCl		• • • •	
Cu-N-C	H-cell	0.1 M	-1.6 V	14.8	38.6	33
		KHCO ₃				
Au ₃ Cu	H-cell	0.1 M PBS	-1.6 V	2	36	34
15 nm	H-cell	0.1 M	-1.0 V	/	32	35
Cu		KHCO ₃				
overlave		-				
rs on Pt						
Amino	U coll	0.1 M	1.0 V ug	2	22	26
Amino	H-cell	0.1 M	-1.9 V vs.	2	32	36
Amino acid	H-cell	0.1 M KHCO3	-1.9 V vs. Ag/AgCl	2	32	36
Amino acid modified	H-cell	0.1 M KHCO3	-1.9 V vs. Ag/AgCl	2	32	36
Amino acid modified Cu foil	H-cell	0.1 M KHCO ₃	-1.9 V vs. Ag/AgCl	2	32	36
Amino acid modified Cu foil PDA-Cu	H-cell H-cell	0.1 M KHCO ₃ 0.5 M	-1.9 V vs. Ag/AgCl -0.93 V	2	32	36
Amino acid modified Cu foil PDA-Cu nanowir	H-cell H-cell	0.1 M KHCO ₃ 0.5 M KHCO ₃	-1.9 V vs. Ag/AgCl -0.93 V	2	32	36
Amino acid modified Cu foil PDA-Cu nanowir es	H-cell H-cell	0.1 M KHCO ₃ 0.5 M KHCO ₃	-1.9 V vs. Ag/AgCl -0.93 V	2	32 29	36
Amino acid modified Cu foil PDA-Cu nanowir es Porphyri	H-cell H-cell	0.1 M KHCO3 0.5 M KHCO3 0.5 M	-1.9 V vs. Ag/AgCl -0.93 V -0.976 V	2 2.1 13.2	32 29 27	36 37 38
Amino acid modified Cu foil PDA-Cu nanowir es Porphyri n-Cu	H-cell H-cell H-cell	0.1 M KHCO ₃ 0.5 M KHCO ₃ 0.5 M KHCO ₂	-1.9 V vs. Ag/AgCl -0.93 V -0.976 V	2 2.1 13.2	32 29 27	36 37 38
Amino acid modified Cu foil PDA-Cu nanowir es Porphyri n-Cu Electrod	H-cell H-cell H-cell	0.1 M KHCO ₃ 0.5 M KHCO ₃ 0.5 M KHCO ₃	-1.9 V vs. Ag/AgCl -0.93 V -0.976 V	2 2.1 13.2 3	32 29 27 26	36 37 38 39
Amino acid modified Cu foil PDA-Cu nanowir es Porphyri n-Cu Electrod	H-cell H-cell H-cell H-cell	0.1 M KHCO3 0.5 M KHCO3 0.5 M KHCO3 0.5 M KC1	-1.9 V vs. Ag/AgCl -0.93 V -0.976 V -1.2 V vs. Ag(AgCl	2 2.1 13.2 3	32 29 27 26	36 37 38 39
Amino acid modified Cu foil PDA-Cu nanowir es Porphyri n-Cu Electrod eposited	H-cell H-cell H-cell H-cell	0.1 M KHCO ₃ 0.5 M KHCO ₃ 0.5 M KHCO ₃ 0.5 M KC1	-1.9 V vs. Ag/AgCl -0.93 V -0.976 V -1.2 V vs. Ag/AgCl	2 2.1 13.2 3	32 29 27 26	36 37 38 39
Amino acid modified Cu foil PDA-Cu nanowir es Porphyri n-Cu Electrod eposited Cu	H-cell H-cell H-cell H-cell	0.1 M KHCO ₃ 0.5 M KHCO ₃ 0.5 M KHCO ₃ 0.5 M KC1	-1.9 V vs. Ag/AgCl -0.93 V -0.976 V -1.2 V vs. Ag/AgCl	2 2.1 13.2 3	32 29 27 26	36 37 38 39

		KHCO ₃				
Cu	H-cell	0.1 M	-1.01 V	0.72	18	41
Cu		KHCO ₃				
Cu ₂ O	H-cell	0.25 M	-0.96 V	/	13.4	42
cube		KHCO ₃				
SA-	H-cell	1 M KHCO ₃	-1.8 V	31.8	85	43
Zn/MNC						
МаТа	H-cell	BmimBF ₄ -	-1 V	21.2	83	44
NIO Te2		H_2O				
Zn-BTC	H-cell	BMIMBF ₄	-2.2 V vs.	3	$80.1\pm$	45
MOF/CP			Ag/Ag^+		6.6	
NixGay	H-cell	0.1 M	-0.88 V	0.12	2.1	46
alloys		Na ₂ CO ₃				
N-	Flow cell	1 M KOH	-0.85 V	170	63	47
GQDs-						
UA-3						

^aThe partial current density of CH_4 listed in Table S2 is calculated at the potential at which catalysts exhibit the maximum CH_4 selectivity.

Table S3. ICP-OES and ICP-MS analyses of the solution after CO₂ electroreduction (-0.9 V) for Fc-CPP-Cu.

Electrolyte (af	ter reaction)	μg/L
ICP-OES	Cu	< detection limit
ICP-MS	Cu	< detection limit
ICP-OES	Fe	< detection limit
ICP-MS	Fe	< detection limit

ken from these references. ^{7, 8}				
Species	ZPE	TS	∫C _p dT	
*СООН	0.63	0.17	0.09	
*CO	0.22	0.08	0.05	
H_2	0.27	0.42	0.09	
H_2O	0.58	0.42	0.09	
CH ₄	1.2	0.6	0.10	
*HCOH	0.76	0.068	0.11	
*CH	0.35	0.039	0.028	

0.075

0.096

0.049

0.06

0.59

0.9

*CH₂

*CH₃

Table S4. The correction from the zero-point energy, entropy and heat capacity for ting the total energies to Cibbs free energies (writer aV) All the . 1 1

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