# **Supporting Information for**

# Boosting oxygen-resistant CO<sub>2</sub> electroreduction reaction in acidic

## media over conjugated frameworks

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### Section S1. Materials and Synthetic Procedures

#### Materials:

All reagents and chemicals were purchased commercially and used without undergoing further purification.  $CoCl_2 \cdot 6H_2O$ , urea, and  $(NH_4)_2MoO_4 \cdot 4H_2O$  were obtained from General-reagent, FeCl<sub>3</sub>, NiCl<sub>2</sub> \cdot 6H<sub>2</sub>O, acetone, ethanol, isopropyl alcohol, 98 wt% H<sub>2</sub>SO<sub>4</sub>, KOH, and K<sub>2</sub>SO<sub>4</sub> were purchased from Sinopharm Chemical Reagent Co., Ltd., NH<sub>4</sub>Cl, Li<sub>2</sub>SO<sub>4</sub>, and Cs<sub>2</sub>SO<sub>4</sub> were purchased from Macklin Co., Ltd. Besides, pyromellitic dianhydride, polyaniline (PANI), and Na<sub>2</sub>SO<sub>4</sub> were provided by

J&K Scientific Co., Ltd., Alfa, and Xilong Scientific Co. Ltd, respectively. Deionized water was supplied by a UPT-I-5T ultrapure water system (18.2 M $\Omega$ ·cm). Ultrapure CO<sub>2</sub> gas (>99.99%) was purchased from Henan Xinlianxin Shenleng Energy Co., LtD, 95% CO<sub>2</sub> + 5% O<sub>2</sub> gas was purchased from Fujian Nanan Chenggong Gas Co., Ltd.

#### Synthesis of polyphthalocyanine cobalt framework (CoPPc):

CoPPc was prepared by solid-state polymerization reaction while some minor adjustments were made<sup>1-2</sup>. Typically, CoCl<sub>2</sub>·6H<sub>2</sub>O (1.19 g), urea (4.10 g), NH<sub>4</sub>Cl (1.00 g), (NH<sub>4</sub>)<sub>2</sub>MoO<sub>4</sub>·4H<sub>2</sub>O (0.040 g) and pyromellitic dianhydride (2.10 g) were grounded evenly, then the mixture was transferred into a porcelain boat, and heated in a muffle furnace for 3 h at 220 °C with a ramp rate of 2 °C·min<sup>-1</sup>. After cooling down to room temperature, the crude product was wash with ultrapure water, fresh methanol and ethanol several times to get CoPPc, the precipitation finally was dried in vacuum at 70 °C overnight.

### Synthesis of polyphthalocyanine nickel framework (NiPPc):

The preparation of NiPPc was the same as CoPPc, with the exception of using NiCl<sub>2</sub>·6H<sub>2</sub>O (1.19 g) instead of CoCl<sub>2</sub>·6H<sub>2</sub>O (1.20 g).

#### Synthesis of polyphthalocyanine iron framework (FePPc):

The preparation of FePPc was the same as CoPPc with the exception of using FeCl<sub>3</sub> (0.81 g) instead of CoCl<sub>2</sub>·6H<sub>2</sub>O (1.20 g).

#### Section S2 Method:

#### **Characterization methods**

Powder X-ray diffraction (PXRD) patterns were obtained on a Miniflex 600 diffractometer using Cu K $\alpha$  radiation ( $\lambda = 0.154$  nm). Fourier Transform Infrared Spectroscopy (FT-IR) was recorded on a VERTEX70 (Bruker). Raman spectra were recorded on a Labram HR Evolution microscope with a laser excitation wavelength of 633 nm. Ultraviolet-visible (UV-vis) measurements were recorded in a DMF solution of CoPPc in the range of 300 to 800 nm using a Shimadzu UV-2550 spectrophotometer at room temperature. <sup>13</sup>C solid-state Nuclear Magnetic Resonance (ss <sup>13</sup>C NMR) was recorded on an AVANCE III. Scanning electron microscopy (SEM) images were recorded by a FEIT 20 working at 10 KV. Transmission electron microscopy (TEM) images were taken on a FEI TECNAI G2 F20 microscope equipped with an energy dispersive spectrometer (EDS) detector at an accelerating voltage of 200 kV. Aberration-corrected high-angle annular dark-field scanning transmission electron microscopy (AC HAADF-STEM) image was recorded in JEM-ARM300F. Atomic Force Microscope (AFM) images were recorded by Dimension ICON. N<sub>2</sub> sorption isotherms were measured on Micrometrics ASAP 2460. CO<sub>2</sub> sorption isotherms were measured on Micrometrics ASAP 2020. Metal content in CoPPc, NiPPc, and FePPc were detected by inductively coupled plasma atomic emission spectroscopy (ICP-AES) on Avio220Max. X-ray photoelectron spectroscopy (XPS) measurements were performed on an ESCALAB 250Xi X-ray photoelectron spectrometer (Thermo Fisher) using an Al Ka source (15 kV, 10 mA). XAFS measurement and data analysis: XAFS spectra of the Co K-edge were collected at BL14W1 station in Shanghai Synchrotron Radiation Facility (SSRF). The Co K-edge XAFS data of pristine CoPPc was recorded in a transmission mode. <sup>13</sup>CO<sub>2</sub> isotope trace analysis was conducted on Shimadzu GCMS-QP2020 Gas Chromatograph Mass Spectrometer. The gas chromatography measurements were performed on the Fuli Instruments GC9790 Plus gas chromatograph (GC) equipped with FID and TCD. ATR-FTIR experiments were performed on a Nicolet6700 (Thermo Fisher) equipped a liquid nitrogen cooled MCT detector.

#### Working electrode preparation

For feeding with >99.99% CO<sub>2</sub> gas, typically, 5 mg CoPPc and 2 mg Ketjenblack (ECP600JD) were dispersed in 450 µL isopropanol with sonication for 90 minutes, and the 50 µL of Nafion binder solution (5 wt%) were added into the dispersion with sonication for another 30 minutes, a homogeneous ink was made. A total of 80 µL of the ink was then loaded onto the carbon paper electrode (Avcarb GDS3260) with  $0.5 \times$ 2 cm<sup>2</sup> to make the loading of CoPPc was 0.8 mg·cm<sup>-2</sup>. For feeding with 95% CO<sub>2</sub>+5%  $O_2$  gas, however, due to the  $O_2$  reduction reaction occurs at a much less negative reduction potential than the CO<sub>2</sub> reduction reaction. Therefore, a PANI coating strategy<sup>3</sup> with slight modifications to prepare the CoPPc@PANI electrode is necessary. Briefly, PANI (23.2mg) was dispersed in 5 mL of ethanol to make a dispersion. Subsequently, 50 mg CoPPc and 20 mg Ketjenblack were added into the dispersion and sonicated for 120 minutes, followed by 12 hours of shaker treatment (350 rpm), and the dispersion was washed with ultrapure water for 3 times and centrifuged at 12000 rpm for 10 minutes, the precipitate finally was dried in vacuum at 70 °C for 24 h, named as CoPPc@PANI catalyst. Hereafter, 7 mg of the catalyst was dispersed into 630 µL ethanol-water solution with a volume ratio of 3:1, and 70  $\mu$ L of Nafion binder solution (5 wt%) were added at the same time, another 60 minute-sonication was carried out to obtain a homogenous ink. Ultimately, a total of 107 µL of the ink was loaded onto the carbon paper electrode (Avcarb GDS3260) with  $0.5 \times 2 \text{ cm}^2$  to make the loading of CoPPc was 0.8 mg·cm<sup>-2</sup>.

#### **Electrochemical measurements**

The Electrochemical measurements were conducted in a four-part flow cell containing a gas-diffusion electrode (GDE) as the cathode mentioned above, a cation exchange membrane (Nafion–117), a platinum foil electrode  $(1.0 \times 3.0 \text{ cm}^2)$  as the anode, and an Ag/AgCl reference electrode. A copper tape was exploited as the current collector to connect the cathode and anode individually. Either 0.4 M Cs<sub>2</sub>SO<sub>4</sub>, K<sub>2</sub>SO<sub>4</sub>, Na<sub>2</sub>SO<sub>4</sub>, or Li<sub>2</sub>SO<sub>4</sub> were used as both catholyte and anolyte. The pH of the electrolyte was adjusted with 98 wt% H<sub>2</sub>SO<sub>4</sub> when necessary using a pH meter (SX-610, Shanghai

Sanxin Co. Ltd). During electrolysis, 15 mL catholyte and 15 mL anolyte were circulated via a circulation pump at the flow rate of 5 mL·minutes<sup>-1</sup>. Simultaneously, >99.99% CO<sub>2</sub> or 95% CO<sub>2</sub> +5% O<sub>2</sub> gas was directly fed into the cathodic GDE at a rate of 30 sccm. An Ag/AgCl electrode was used to measure against all the electrode potentials according to the equation: E(vs. RHE) = E(vs. Ag/AgCl) + 0.1989 V + 0.059× pH without iR compensation and the measured potentials in this work were all converted to a reversible hydrogen electrode (RHE) scale. Besides, the performance of the catalyst in the flow cell was evaluated by applying different potentials using a chi1140c electrochemical workstation including the use of linear sweep voltammetry (LSV) with a scan rate of 20 mV·s<sup>-1</sup> and potentiostatic electrolysis. During the electrolysis procedure, the effluent gas from the cathode compartment went through the sampling loop (1 mL) of a gas chromatograph. The gas phase composition was analyzed by GC every 5 minutes. The separated gas products were then analyzed by a thermal conductivity detector (for H<sub>2</sub>) and a flame ionization detector (for CO). Additionally, the liquid products were analyzed after electrolysis for 15 minutes by quantitative NMR (ECZ400S) using dimethyl sulphoxide (DMSO) as an internal standard. Solvent presaturation technique was implemented to suppress the water peak.

Faradic efficiency (FE) calculation of a certain gas product was calculated by the equation:

$$FE = \frac{PV}{T \times} \frac{v \times N \times F \times 10^{-6} (\frac{m^3}{mL})}{I \times 60 (s/min)}$$

*v* (vol %): volume concentration of certain gas product in the effluent gas from the cell (GC data);

*V*: gas flow rate measured by a flow meter,  $30 \text{ mL min}^{-1}$ ;

*I*: total steady-state cell current;

*N*: the electron transfer number for product formation;

*F*: Faradaic constant, 96485 C mol<sup>-1</sup>;

- *R*: universal gas constant, 8.314 J mol<sup>-1</sup>·K<sup>-1</sup>;
- *P*: one atmosphere,  $1.013 \times 10^5$  Pa;
- T: room temperature, 298.15 K;
- FE: faradaic efficiency for CO production.

#### Oxygen reduction reaction (ORR) measurements

Typically, all the electrochemical experiments were performed on an IM6ex (Zahner, Germany). The ink was prepared in the same manner as the homogeneous solution for  $eCO_2RR$  feeding with ultra-pure (> 99.99%) CO<sub>2</sub> gas mentioned above, with the only difference being the volume of the as-prepared solution dropped on the subsequent electrode. Specifically, 20 µL of the CoPPc ink or 26.5 µL of the CoPPc@CoPPc ink was dropped onto the surface of a rotating ring-disk electrode (RRDE) with a 5 mm diameter glassy carbon disk and then dried at room temperature. Electrochemical measurements were performed in a three-electrode cell using the Ag/AgCl electrode mentioned above as the reference electrode and Pt mesh as the counter electrode.

Before the electrochemical measurements, the electrolyte (1 M KOH or  $H_2SO_4 + 0.4$  M K<sub>2</sub>SO<sub>4</sub>, pH=3.0) was purged with N<sub>2</sub> or O<sub>2</sub> for 30 minutes to achieve the N<sub>2</sub>-saturated or O<sub>2</sub>-saturated solution, respectively. Subsequently, cyclic voltammetry (CV) with a scan rate of 100 mV·s<sup>-1</sup> was employed to obtain stable polarization curves under these two solutions. Finally, linear sweep voltammograms (LSVs) curves were obtained using the scan rate of 20 mV·s<sup>-1</sup> at a rotation speed of 1600 rpm. Noting that LSV recorded under N<sub>2</sub>-saturated solution was used for background correction.

#### The Isosteric Heats of Adsorption

The isosteric heat of adsorption is an index that measured the strength of the interaction between adsorbent and adsorbed molecules. The isosteric heat of adsorption is calculated according to the Clausius-Clapeyron equation as follows:

$$Q_{st} = RT^2 \cdot \left(\frac{\partial lnP}{\partial T}\right)_q$$

Where  $Q_{st}$  represents the isosteric heats of adsorption, *R* is the gas constant, *T* represents the temperature, which is set as 273 K and 298 K in this work, *P* denotes the pressure of CO<sub>2</sub> adsorption, and *q* represents a certain amount of CO<sub>2</sub> that has been adsorbed.

Section S3. Supplementary Fig. S1-S31 and supplementary Tables S1-S3:



Fig. S1. The FT-IR spectra of NiPPc (a), and FePPc (b) frameworks and correspondingNiPcandFePcmolecules.



**Fig. S2.** The UV-Vis spectra of NiPPc (a), and FePPc (b) frameworks and corresponding NiPc and FePc molecules.



Fig. S3. The ss <sup>13</sup>C NMR spectra of CoPPc.



Fig. S4. The SEM images of NiPPc (a) and FePPc (b), respectively.



Fig. S5. AFM image of CoPPc. (Inset: the corresponding cross-sectional profile of CoPPc nanoflakes.)



Fig. S6.  $N_2$  sorption isotherms of CoPPc measured at 77 K. The amount of  $N_2$  adsorbed by CoPPc is low probably caused by A-B stacking nature, as has been proved by literature reported before<sup>2</sup>, and  $N_2$  uptake is stand with literature<sup>4</sup>.



**Fig. S7.** The LSV curves of CoPPc (a), NiPPc (b), and FePPc (c) under CO<sub>2</sub> or Ar gas feeding when operated in a flow cell using  $H_2SO_4 + 0.4$  M K<sub>2</sub>SO<sub>4</sub> (pH=3.0) as electrolyte.



**Fig. S8.** <sup>1</sup>H NMR full spectrum (a) and corresponding partial enlarged detail (b) of the cathodic electrolyte after 2-hour eCO<sub>2</sub>RR catalysis under 99.99% CO<sub>2</sub> gas feeding.



**Fig. S9.** The mass spectra test of CoPPc of <sup>13</sup>CO recorded under <sup>13</sup>CO<sub>2</sub> atmosphere in  $H_2SO_4 + 0.4 \text{ M K}_2SO_4$  aqueous solution (pH=3.0) in flow cell.



Fig. S10. Faradaic efficiency of CO and  $H_2$  at different potentials for CoPPc (a), NiPPc (b), and FePPc (c) in a flow cell system,  $H_2SO_4 + 0.4$  M K<sub>2</sub>SO<sub>4</sub> (pH=3.0) as the electrolyte.



Fig. S11. Faradaic efficiency of CO and H<sub>2</sub> for CoPPc at different potentials in H<sub>2</sub>SO<sub>4</sub> + 0.4 M M<sub>2</sub>SO<sub>4</sub> (M = Li, Na, K, Cs, pH=3.0). (a) H<sub>2</sub>SO<sub>4</sub> + 0.4 M Li<sub>2</sub>SO<sub>4</sub>, (b) H<sub>2</sub>SO<sub>4</sub> + 0.4 M Na<sub>2</sub>SO<sub>4</sub>, (c) H<sub>2</sub>SO<sub>4</sub> + 0.4 M K<sub>2</sub>SO<sub>4</sub>, (d) H<sub>2</sub>SO<sub>4</sub> + 0.4 M Cs<sub>2</sub>SO<sub>4</sub>.



Fig. S12. Faradaic efficiency of CO and  $H_2$  of CoPPc at different potentials in  $H_2SO_4$  + 0.4 M Cs<sub>2</sub>SO<sub>4</sub> with different pH. (a) pH=1.0, (b) pH=2.0, (c) pH=3.0.



**Fig. S13.** Linear sweep voltammograms (LSVs) of CoPPc catalyst at 1600 rpm in O<sub>2</sub>satuated 1 M KOH or O<sub>2</sub>-satuated H<sub>2</sub>SO<sub>4</sub> + 0.4 M Cs<sub>2</sub>SO<sub>4</sub> (pH=3.0) (scan rate: 20 mV·s<sup>-1</sup>). The reason why the oxygen reduction reaction is performed in the 1 M KOH is that the local environment of eCO<sub>2</sub>RR is considered alkaline<sup>5-7</sup>. From the **Fig. S12**, it could be reduced that the accompanying competitive ORR will be quite severe since the halfwave potential for CoPPc is as positive as 0.98 V *vs*. RHE in 1 M KOH. Even in acidic electrolyte H<sub>2</sub>SO<sub>4</sub> + 0.4 M Cs<sub>2</sub>SO<sub>4</sub> (pH=3.0), the half-wave potential for CoPPc could reach as positive as 0.70 V *vs*. RHE, too, which is much more positive than the potential operated in the eCO<sub>2</sub>RR (below -1.0 V *vs*. RHE).

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Fig. S14 Structure diagrams of the PANI.



**Fig. S15.** The SEM images of (a) CoPPc@PANI catalyst, (b) physically mixed CoPPc and PANI, (c) PANI, and (d) Ketjenblack. Ketjenblack was added into the CoPPc@PANI during the preparation to enhance the conductivity of the electrocatalyst, as described in the **Working electrode preparation**.

The CoPPc@PANI was prepared as a homogeneous ink and then dropped to a silicon wafer and the morphology of the electrocatalyst was observed through SEM. The physically mixed CoPPc and PANI was prepared by dispersing the same proportion of CoPPc and PANI in ethanol first. Then ultrasound treatment was exploited, the same amount of Nafion ionmer was added to make another homogeneous ink, then dropped to a silicon wafer, and the morphology was observed through SEM. The morphology of the PANI behaves as irregularly spherical less than 1  $\mu$ m (**Fig. S14c**). The CoPPc@PANI catalyst formed a smooth platform with some part exposed in the cracks. On the contrary, the physically mixed CoPPc and PANI was randomly dispersed.



**Fig. S16.** (a) The SEM image of CoPPc@PANI. The corresponding EDS mapping of (b) Co, (c) C, (d) N elements of CoPPc@PANI, and (e) the atomic percentage. For ease of comparison, elements that exist in Nafion ionmer such as F, O, and S were omitted.

From the **Fig. S16**, it could be figured out that the Co was evenly distributed in CoPPc@PANI, opposite of the physically mixed CoPPc and PANI, the Co presented irregular distribution in the latter (**Fig. S17**). Furthermore, the atomic percentage of the Co element is far less than the physically mixed CoPPc and PANI, which indicates that the CoPPc is effectively coated by PANI.



**Fig. S17.** (a) The SEM image of the physically mixed CoPPc and PANI. The corresponding EDS mapping of (b) Co, (c) C, (d) N elements of the physically mixed CoPPc and PANI, and (e) the atomic percentage. For ease of comparison, elements that exist in Nafion ionmer such as F, O, and S were omitted.



**Fig. S18.** Electrocatalytic  $CO_2RR$  performance in acidic media (0.4 M  $Cs_2SO_4$  +  $H_2SO_4$ , pH=3.0) in a flow cell system, pure  $CO_2$  as the gas feeding. (a) Faradaic efficiency of CO, (b) CO partial current densities for CoPPc@PANI and parent CoPPc at different potentials.



**Fig. S19.** <sup>1</sup>H NMR full spectrum (a) and corresponding partial enlarged detail (b) of the cathodic electrolyte after half-an-hour eCO<sub>2</sub>RR catalysis under 95% CO<sub>2</sub> + 5% O<sub>2</sub> gas feeding, the CoPPc@PANI served as the electrocatalyst.



**Fig. S20.** <sup>1</sup>H NMR full spectrum (a) and corresponding partial enlarged detail (b) of the cathodic electrolyte after half-an-hour eCO<sub>2</sub>RR catalysis under 95% CO<sub>2</sub> + 5% O<sub>2</sub> gas feeding when the CoPPc@PANI served as the electrocatalyst, with a small amount of extra fresh methanol was added into the cathodic electrolyte. Compared with **Fig. S13**, the peak intensity at the chemical shift of 3.2 ppm has been increased, and no additional peaks was presented in the **Fig. S19**, we conclude that the peak in 3.2 ppm could be assigned to methanol. On the other hand, methanol product was also observed in the eCO<sub>2</sub>RR when 5% O<sub>2</sub> + 95% CO<sub>2</sub> as the gas feeding when the CoPPc@PANI served as the electrocatalyst.



**Fig. S21.** Faradaic efficiency of CH<sub>3</sub>OH, CO, and H<sub>2</sub> of CoPPc@PANI during CO<sub>2</sub>RR process in 5% O<sub>2</sub> and 95% CO<sub>2</sub> gas feeding,  $H_2SO_4 + 0.4$  M Cs<sub>2</sub>SO<sub>4</sub> (pH=3.0) as the electrolyte.



**Fig. S22.** Faradaic efficiency of CH<sub>3</sub>OH, CO, and H<sub>2</sub> of CoPPc during CO<sub>2</sub>RR process in 5% O<sub>2</sub> and 95% CO<sub>2</sub> gas feeding,  $H_2SO_4 + 0.4$  M Cs<sub>2</sub>SO<sub>4</sub> (pH=3.0) as the electrolyte.



Fig. S23. Comparison of the  $CO_2$  adsorption capacity between CoPPc@PANI andCoPPcunder298K(a)and273K(b).



Fig. S24. Isosteric heats of  $CO_2$  adsorption on CoPPc@PANI and CoPPc.



Fig. S25. Linear sweep voltammograms (LSVs) of CoPPc and CoPPc@PANI at 1600 rpm in O<sub>2</sub>-satuated H<sub>2</sub>SO<sub>4</sub> + 0.4 M Cs<sub>2</sub>SO<sub>4</sub> (pH=3.0) (scan rate: 20 mV·s<sup>-1</sup>). In comparison to CoPPc, a significant negative half-wave potential shift was observed in CoPPc@PANI, leading to a failure to achieve the limiting current density at 0.2 V vs. RHE.



**Fig. S26.** Linear sweep voltammograms (LSVs) of CoPPc catalyst at 1600 rpm in  $O_2$ satuated 1 M KOH (scan rate: 20 mV·s<sup>-1</sup>). The reason why the oxygen reduction reaction is performed in the 1 M KOH is that the local environment of eCO<sub>2</sub>RR is considered alkaline<sup>6-8</sup>. In comparison to CoPPc, a significant negative half-wave potential shift was observed in CoPPc@PANI (0.86 *vs.* 0.98 V *vs.* RHE). In addition, the limiting current density is dramatically inhibited after the PANI coating.



Fig. S27. The SEM (a) and TEM (b) images of after-electrocatalysis CoPPc, 95% CO<sub>2</sub> + 5% O<sub>2</sub> as the gas feeding. The after-catalysis CoPPc was obtained by dispersing the after-catalysis CoPPc@PANI in ethanol and separated by differential centrifugation. Besides, the ICP-AES test of after-electrocatalysis electrolyte when 95% CO<sub>2</sub> + 5% O<sub>2</sub> as the gas feeding has been conducted and only  $2.4 \times 10^{-3}$  mg Co metal species were detected.



Fig. S28. The PXRD patterns of CoPPc after electrocatalysis and CoPPc before electrocatalysis. The after-catalysis CoPPc was obtained by dispersing the CoPPc@PANI in ethanol and separated by differential centrifugation.



**Fig. S29.** The FT-IR spectra of CoPPc after electrocatalysis, 95% CO<sub>2</sub> + 5% O<sub>2</sub> as the gas feeding and the corresponding FT-IR spectra of CoPPc before-catalysis. The after-catalysis CoPPc was obtained by dispersing the after-catalysis CoPPc@PANI in ethanol and separated by differential centrifugation.



**Fig. S30**. The high-resolution XPS spectra of Co 2p (a) and N 1s (b) corresponding to CoPPc after electrocatalysis and CoPPc before electrocatalysis. The after-catalysis CoPPc was obtained by dispersing the after-catalysis CoPPc@PANI in ethanol and separated by differential centrifugation.



Fig. S31. The schematic illustration (a) and an assembled image (b) of the home-madecellusedforATR-FTIRmeasurements.

	54165 01 0011 <b>0</b> , 1111 <b>0</b> , 414 1 <b>0</b>	
Sample	Metal Element	Content (wt%)
CoPPc	Со	3.05
NiPPc	Ni	3.77
FePPc	Fe	1.41

**Table S1.** The ICP-AES results of CoPPc, NiPPc, and FePPc.

**Table S2.** The EXAFS fitting results of CoPPc. CN, coordination number; R, distance between absorber and backscatter atoms;  $G^2$ , Debye-Waller factor (a measure of thermal and static disorder in absorber-scatterer distances);  $\Delta E_0$ : the inner potential correction; R factor is used to value the goodness of the fitting.

Sample	Path	CN	R(Å)	$\sigma^2(10^{-3} \text{ Å}^2)$	$\Delta E_0$	R factor
CoPPc	Co-N	3.91	1.91	3.8±3.1	-2.36±2.54	0.011

Catalyst	V <sub>O2</sub> <sup>a)</sup> (%)	V <sub>CO2</sub> <sup>a)</sup> (%)	FE <sup>b)</sup> eCO2RR (%)	$j_{eCO2RR}^{c)}$ (mA·cm <sup>-</sup> <sup>2</sup> )	Potential/Voltag e (V)	Ref.
CoPPc@PAN I	5	95	88.4 (CO + CH <sub>3</sub> OH)	273	-2.1 (vs. RHE)	This work
CoPc/CNT	5	95	~82 (CO)	~26.2	3.4	8
CoPc/CNT	10	90	~71 (CO)	~22.0	3.4	8
Sn	5	95	~99 (HCOOH)	~56.1	-2.4 (vs. Ag/AgCl)	8
PIM- CoPc/CNT	5	95	~76 (CO)	~20.5	3.4	9
AMT-Au	4	15	~66	~24.8	2.7	10
Cu PTFE/Ni- N4	3	15	46.5% (C <sub>2+</sub> )	93	-2.0 (vs. Ag/AgCl)	11
Sputter Cu	4	15	$\sim 20 (C_{2^+})$	~24	2.5	
Cu-PTFE GDE	4	15	~68 (C <sub>2+</sub> ) [10 bar <sup>d)</sup> ]	~146.9	3.0	12
Cu <sub>x</sub> O	4	20	~6 (C <sub>1</sub> ) ~71 (C <sub>1</sub> )	-	-1.17 (vs. RHE)	13
			[20atm, 273K]	~105.0	-1.17 (vs. RHE)	

**Table S3.** Summary and comparison of electrochemical performance under  $O_2$ containing  $CO_2$  gas feed in the flow cell or full cell system.

a)  $V_{O2}$  and  $V_{CO2}$  refer to the volume ratio of  $O_2$  and  $CO_2$ , respectively. the gas is balanced with  $N_2$  or Ar if the total amount of  $V_{O2}$  and  $V_{CO2}$  is less than 100%. b) the FE<sub>eCO2RR</sub> refers to the Faradaic efficiency of products of electroreduction of  $CO_2$ , the corresponding products are in brackets. c) the  $j_{eCO2RR}$  represents the partial current densities of the product of electroreduction of CO<sub>2</sub>.

d) The electrochemical data are obtained under certain pressure conditions. The product is produced at the standard pressure of 1 bar if without any indication.

#### **Section S4. References:**

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