Support Information

Promoting Electrochemical CO₂ Reduction by Pyridinium in the Secondary Coordination Sphere of Copper-Sites Anchored on a Covalent Organic Framework

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Experiment Methods

Materials

All reagents and solvents were used as received from commercial sources unless otherwise noted. (2,2'-Bipyridine)-4,4'-diamine (98%) was purchased from TCI. 1,3,5-tri(4-pinacolatoborolanephenyl)benzene (98%), 4,4'-dibromo-2,2'-bipyridine (98%), 1-chloro-2,4-dinitrobenzene (97%), XPhos Pd G4 (95%), cesium carbonate (Cs_2CO_3 , 99%), and deuterium oxide (D_2O) were purchased from Sigma-Aldrich. 1,3,5-tris(4-pyridyl)benzene (98%), copper acetate (98%), potassium bicarbonate (KHCO₃, AR, 99.5%), potassium carbonate (K_2CO_3 , AR, 99%) and potassium hexafluorophosphate (KPF₆, 99%) were purchased from Shanghai Aladdin.

Synthesis of N⁺-COF matrixes

The N⁺-COF matrix was synthesized according to a previously reported method.¹ 1,3,5tris(4-pyridyl)benzene (20 mmol, 6.2 mg) and 1-chloro-2,4-dinitrobenzene (60 mmol, 14.1 mg) were added to acetonitrile solution. The suspension was refluxed under an argon atmosphere for 12 hours. The precipitate was filtered and washed thoroughly with dichloromethane, and then dried under vacuum at 60°C to obtain Zincke salt of N⁺-Cl. ¹H-NMR (400 MHz, D₂O): δ 8.43 (d, *J*= 12 Hz, 3H), 8.98 (dd, *J*1= 4 Hz, *J*2= 4 Hz, 3H), 9.18 (d, *J*= 8 Hz, 6H), 9.28 (s, 3H), 9.34 (d, *J*= 4 Hz, 3H), 9.51 (d, *J*= 4 Hz, 6H), which is in agreement with the previous report. Then the N⁺-Cl (10 mmol, 9.15 mg) and 4,4'-diamino-2,2'-bipyridine (10 mmol, 1.9 mg) were dissolved in 30 mL of ethanol. The suspension was refluxed under an argon atmosphere for 72 hours. The product was filtered and washed thoroughly with ethanol, and then dried under vacuum at 60°C. The resulting N⁺-COF was characterized by various technologies.

Synthesis of COF matrixes

1,3,5-tris(phenylboronic acid pinacol ester)benzene (20 mmol, 13.7 mg) and 4,4'-dibromo-2,2'-bipyridine (30 mmol, 9.42 mg) were added to a solvent mixture of toluene and methanol (10:1 volume ratio). After stirring, 0.1 mL of water, 1wt% of Xphos Pd G4 catalyst, and an appropriate amount of Cs_2CO_3 were introduced. The suspension was refluxed under an argon atmosphere for 72 hours. The product was filtered and washed thoroughly with ethanol and water, and then dried under vacuum at 60°C and characterized by various technologies.

Synthesis of Cu@COF and Cu@COF

The Cu@N⁺-COF was prepared by modifying COF matrixes with Cu²⁺ ions using copper(II) acetate. In detail, the N⁺-COF matrixes (19.4 mg) were dispersed in 20 mL of anhydrous CH₃OH, and the suspension was stirred for 10 min. Then, the copper(II) acetate (11.4 mg; 1.25 eq. concerning bipyridine moieties) in anhydrous CH₃OH solution was slowly added to the suspension, and the mixture was refluxed for 12 hours under Ar atmosphere at 65 °C. The

obtained solid product was filtered and washed with water and ethanol, and then dried under vacuum at 60°C. Finally, the obtained Cu@N⁺-COF was rinsed with a saturated KPF₆ aqueous solution for 2 hours under vigorous stirring to introduce PF_6^- ions as free ions.

The Cu@COF was prepared by the same method as that for Cu@N⁺-COF, with 19.2 mg of COF matrixes and 11.4 mg of copper(II) acetate.

Preparation of working electrode

The 6 mg of Cu@N⁺-COF and 3 mg of carbon black (Ketjenblack ECP600JD) were dispersed in mixed 0.2 mL ethanol and 0.4 mL H₂O solution with 30 μ L Nafion solution added, and then ultrasonicated for 20 min to form a homogeneous catalyst ink. The catalyst ink was dropped onto a hydrophobic gas diffusion electrode (GDE) to obtain the Cu@N⁺-COF electrode as a working electrode, with a loading amount of Cu@N⁺-COF catalyst at approximately 2 mg cm⁻². Similarly, the Cu@COF electrode was prepared by the above steps as well.

Characterizations

The cross-polarized ¹³C solid-state nuclear magnetic resonance (CP ¹³C-SSNMR) spectra were recorded on an Agilent DD2-500MHz instrument at a Larmor frequency of 125.7 MHz. ¹H NMR spectra were measured on a Bruker 400 MHz spectrometer, with chemical shifts (δ in ppm) referenced to the solvent residual proton signal. Fourier transform infrared (FT-IR) spectra were recorded with a Nicolet 6700 Flex (Thermo Fisher). Elemental analysis was performed on an Elementar Vario MICRO cube elemental analyzer. X-ray photoelectron spectroscopy (XPS) spectra were collected using a Thermo Scientific K-Alpha spectrometer equipped with an Al Ka (hv = 1486.6 eV) excitation source. The copper content was measured using ICP-OES with a Thermo Scientific iCAP 6000 series instrument by dissolving Cu@N+-COF and Cu@COF into a concentrated H₂SO₄ and HNO₃ mixture (1:3 by volume). X-band electron paramagnetic resonance (EPR) measurements were performed on a Bruker E500 ELEXSYS spectrometer. Morphological analysis was carried out using atom force microscopy (AFM, Bruker Dimension Icon), and transmission electron microscopy (TEM, JEOL JEM-2100Plus) with an energydispersive X-ray spectrometer (EDX, Oxford). Aberration-corrected high-angle annular dark-field scanning transmission electron microscopy (AC HAADF-STEM) images were collected by a JEM ARM-200F with a spherical aberration corrector.

X-ray absorption fine-structure spectroscopy (XAFS) of copper K-edge was measured at the Shanghai Synchrotron Radiation Facility. This beamline adopts a fixed-exit, double-crystal Si (111) monochromator to provide X-ray energy in the range of 5~23 keV. The X-ray energy was calibrated using a Cu metal foil. Cu K-edge XAFS data were collected in transmission mode using a Lytle detector. The extended X-ray absorption fine structure (EXAFS) data were processed by removing the background and normalizing the edge jump by Athena and Artemis

S3

from the IFEFFIT package. Least-squares EXAFS fitting for Cu@ N⁺-COF and Cu@COF in *R* space was performed to determine the quantitative structural parameters around copper atoms by the ARTEMIS module. The fitting range of *k* space and *R* space in Cu K-edge k^3 -weighted $\chi(k)$ data, as well as the fitting parameters of amplitude reduction factor (s₀²), energy shift (ΔE_0), path length (*R*), coordination number (*N*) and Debye-Waller factor (σ^2) were listed in Table S2.

Electrochemical measurements

The eCO₂RR performance was evaluated in a 1.0 M KHCO₃ solution by a three-electrode system with Ag/AgCI as the reference electrode and IrO_X /Ti-mesh as a counter electrode, using a flow cell assembly with anolyte and catholyte chambers separated by anion exchange membrane (Fumasep® FAA-130). All electrochemical measurements were conducted with a CHI 660e workstation without iR correction. The measured potential was converted to value relative to a reversible hydrogen electrode (RHE) according to the equation:

E (vs RHE) = E (vs Ag/AgCl) + E_1 (ref versus RHE), in which E_1 (ref versus RHE) represents the potential difference between the Ag/AgCl reference electrode and RHE at 25 °C for the 1.0 M KHCO₃ electrolyte, with correction based on a commercialized RHE (HydroFlex[@] of Gaskatel).

For the eCO_2RR performance in the acid electrolyte, measurements were conducted in 0.05 M H_2SO_4 and 0.5 M K_2SO_4 solution using Hg/Hg₂SO₄ as the reference electrode. A Nafion 117 cation exchange membrane (DuPont) was employed to separate the cathode and anode compartments. Similarly, the measured potential was converted to RHE value according to the equation:

E (vs RHE) = E (vs Hg/Hg₂SO₄) + E_2 (ref versus RHE), in which E_2 (ref versus RHE) is the potential difference between the Hg/Hg₂SO₄ reference electrode and RHE at 25 °C for the 0.05 M H₂SO₄ and 0.5 M K₂SO₄ solution, corrected by a commercialized RHE (HydroFlex[@] of Gaskatel).

Calculation of faradaic efficiency

Following eCO₂RR, the gas products were then injected into a gas chromatograph (GC2014, SHIMADZU) for analysis. The GC system was equipped with a thermal conductivity detector (TCD) for analyzing H₂, and a flame ionization detector (FID) for analyzing carbonaceous substances. The liquid products were detected by ¹H NMR spectroscopy on Bruker Avance II 400. For quantification, the NMR sample was prepared by mixing 400 μ L of cathode electrolyte, 100 μ L of D₂O, and 5 μ L of an internal solution (DMSO: D₂O, volume ratio 1:1000). The NMR pulse sequence was specifically designed to pre-saturate and suppress signals from solvents (H₂O/D₂O).

The faradaic efficiency (FE) was calculated as the following equation:

Where, Q_{products} and Q_{total} (C) are the target products' coulomb quantity and the total coulomb quantity at a certain potential during the time of t (s), respectively; V_{products} is the formation rate of target products; n_{e^-} is the number of electrons transferred for production formation; *F* is the Faraday constant (a value of 96485 C mol⁻¹).

Calculation of partial current density and turnover frequency.

The partial current density of CO (j_{CO}) can be calculated by the following equation:

$$j_{\rm CO} = j_{\rm total} \times {\sf FE}_{\rm CO}$$
 eqn. S2

Where j_{total} is the total current density (A cm⁻²) during the test.

The turnover frequency (TOF) is defined as the rate of evolved molecular CO per surface active site per second, which can be calculated by the following equation:

$$\mathsf{FOF}_{\mathsf{CO}}(\mathsf{s}^{-1}) = \frac{\frac{n_{\mathsf{CO}}}{n_{\mathsf{cat.}}}}{t} = \frac{\frac{\mathsf{Q}_{\mathsf{total}} \times \mathsf{FE}_{\mathsf{CO}}}{2F}}{n_{\mathsf{cat.}} \times t} = \frac{j_{\mathsf{total}} \times \mathsf{FE}_{\mathsf{CO}}}{2F \times n_{\mathsf{cat.}}} = \frac{j_{\mathsf{CO}}}{2F \times n_{\mathsf{cat.}}}$$
eqn. S3

Where n_{CO} is the mole number of CO yielded and Q_{total} (C) is the total coulomb quantity at a certain potential during the time of t (s); $n_{cat.}$ is mole number of Cu loading in the catalyst (ICP results); 2 is the number of electrons transferred to evolve a molecule of CO, *F* is the Faraday constant (a value of 96485 C mol⁻¹); j_{total} is the total current density (A cm⁻²) during the test, j_{CO} is the partial current density (A cm⁻²) of CO.

KIEs experiments

Kinetic isotope effects (KIEs) were studied via electrochemical methods by constantpotential electrolysis using a flow cell in the solutions of 1 M KHCO₃ in H₂O and 1 M KDCO₃ in D₂O, or 0.05 M H₂SO₄/0.5 M K₂SO₄ in H₂O and 0.05 M H₂SO₄/0.5 M K₂SO₄ in D₂O. The electrode was prepared by dropping the suspension of Cu@COF and Cu@ N⁺-COF with H₂O and ethanol as dispersants on GDE, in which carbon black was not added to prevent their exact influence on the KIEs test.

KIEs_{H/D} were defined as *eqn. S4*.

$$\mathsf{KIEs}_{\mathsf{H/D}} = \left[\frac{k_{\mathsf{CO},H_2\mathsf{O}}}{k_{\mathsf{CO},D_2\mathsf{O}}}\right]_{\eta} = \left[\frac{j_{\mathsf{CO},H_2\mathsf{O}}}{j_{\mathsf{CO},D_2\mathsf{O}}}\right]_{\eta} = \left[\frac{j_{H_2\mathsf{O}} \times \mathsf{FE}_{\mathsf{CO},H_2\mathsf{O}}}{j_{D_2\mathsf{O}} \times \mathsf{FE}_{\mathsf{CO},D_2\mathsf{O}}}\right]_{\eta} \qquad eqn. \ S4$$

Where, k_{CO,H_2O} and k_{CO,D_2O} are corresponding to the rate constant of eCO₂RR to CO in H₂O and D₂O, respectively. The j_{CO,H_2O} and j_{CO,D_2O} correspond to the current densities of CO, j_{H_2O} and j_{D_2O} correspond to the total current densities in the test at a certain overpotential of η .

As well, FE_{CO,H_2O} and FE_{CO,D_2O} are corresponding to the Faraday efficiency of CO in H₂O and D₂O.

The applied potential for KIE experiments in 1 M KDCO₃ in D₂O, and 0.05 M D₂SO₄/0.5 M K₂SO₄ in D₂O was corrected according to previous reports.^{2, 3}

The temperature-dependence KIEs experiment

The temperature-dependence KIEs were studied using a flow cell under the temperatures of 275, 278, 281, and 289 K, within the solutions of 1 M KHCO₃ in H₂O and 1 M KDCO₃ in D₂O.

The apparent activation energy (E_a) and the pre-exponential factor (A) are obtained by fitting the temperature-dependence of the rate constant or reaction rate to the Arrhenius equation (*eqn.* **S6**).

$$k = Ae^{-E_a/RT}$$
 eqn. S6

Where k is the reaction rate constant at a certain temperature (T), R is the molar gas constant, and this Arrhenius equation could be converted to a partial differential form as **eqn. S7.**

$$\ln k = -\frac{Ea}{RT} + \ln A \qquad eqn. S7$$

Subsequently, the equation could be converted to eqn. S8.

$$E_{a} = RT^{2} \frac{\partial \ln k}{\partial T} = -R \frac{\partial \ln k}{\partial \frac{1}{T}} \qquad eqn. \ S8$$

For eCO₂RR to CO system, the potential-dependent rate constant *k* of the catalyst is the function of corresponding kinetic current density j_{CO} under a certain η , which is equivalent to the turnover frequency (TOF) of the catalytic active site as **eqn. S3**, and thus this Arrhenius equation could be further derivate as **eqn. S9**.

$$E_{a} = \begin{bmatrix} -R \frac{\partial \ln \frac{j_{CO}}{2F \times n_{cat.}}}{\partial \frac{1}{T}} \end{bmatrix}_{\eta} = \begin{bmatrix} -R \frac{\partial \ln j_{CO}}{\partial \frac{1}{T}} \end{bmatrix}_{\eta} eqn. S9$$

Thus, the E_a and corresponding A could be obtained by fitting the experimental kinetics data at different temperatures.

Additionally, based on the eqn. S5, InKIE can be calculated, as shown in eqn. S10.

$$\ln \text{KIE} = \ln \frac{k_{H}}{k_{D}} = \frac{\Delta E_{a}}{RT} + \ln \frac{A_{H}}{A_{D}}$$
 eqn. S10

Where, k_H and k_D are the reaction rate constant in H₂O and D₂O at a certain temperature (T

), $\Delta E_a = E_{a,D} - E_{a,H}$, is the difference between the apparent activation energy in D₂O ($E_{a,D}$) and in H₂O ($E_{a,H}$), A_H and A_D are the pre-exponential factor in H₂O and D₂O.

According to **eqn. S10**, the values of ΔE_a and A_H/A_D are obtained by fitting the experiment data at different temperatures.

In-situ ATR-SEIRAS Experiments

The in-situ ATR-SEIRAS experiment was carried out on a Bruker Vertex 80 infrared spectrometer equipped with an LN-MCT Mid-detector cooled with liquid nitrogen. The spectral resolution was set to 4 cm⁻¹. An Au-deposited Si prism was used as the conductive substrate for the catalysts and the IR reflection element. An appropriate amount of catalyst ink was dropped onto the Au/Si surface as the working electrode and subsequently assembled into a homemade H-type spectroelectrochemical cell, with a graphite rod as the counter electrode and an Ag/AgCl as the reference electrode. The electrochemical experiments were measured by a CHI 660 electrochemistry workstation in 0.1 M KHCO₃ under CO₂ purge, and ATR-SEIRAS spectra were collected during constant-potential electrolysis in the potential range from -0.5 to -1.1 V vs. RHE.



Fig. S1 Synthetic scheme and chemical structure of COF.



Fig. S2 Synthetic scheme and chemical structure of N⁺-COF.



Fig. S3 CP ¹³C-SSNMR spectra of (a) COF and (b) N⁺-COF.



Fig. S4 FT-IR spectra of (a) COF and (b) N⁺-COF.

Sample	Element	¹ Theoretical	² Theoretical	Found		
	С	87.67	79.57	88.14		
COF	Ν	7.86	7.14	6.89		
	Н	5.06	5.13	4.97		
N⁺-COF	С	79.98	72.71	77.98		
	Ν	15.54	14.13	16.10		
	Н	4.47	5.08	5.92		

Table S1 Elemental analysis of COF and N⁺-COF

¹Based on the formula $C_{26}H_{16}N_2$ and $C_{24}H_{16}N_4$ for COF and N⁺-COF, respectively. ²Based on formula $C_{26}H_{16}N_2 \cdot 2H_2O$ $C_{24}H_{16}N_4 \cdot 2H_2O$, where every pyridine unit binds to one H₂O molecule.



Fig. S5 XPS of COF in the (a) survey, (b) N 1s, and (c) C 1s regions.



Fig. S6 XPS of N⁺-COF in the (a) survey, (b) N 1s, (c) C 1s and (d) Cl 2p regions.



Fig. S7 AFM images of (a) Cu@COF and (b) Cu@N⁺-COF.



Fig. S8 TEM images of (a) Cu@COF and (b) Cu@N⁺-COF.



Fig. S9 N_2 absorption-desorption isotherms of (a) Cu@COF, and (b) Cu@N⁺-COF (STP=standard temperature and pressure). Pore size distributions of (c) Cu@COF, and (d) Cu@N⁺-COF were obtained using the non-local density functional theory method.



Fig. S10 FT-IR spectrum of (a) Cu@COF and (b) Cu@N⁺-COF.



Fig. S11 XPS of Cu@COF in (a) survey, (b) C 1s, and (c) O 1s regions



Fig. S12 XPS of Cu@N⁺-COF in (a) survey, (b) C 1s, (c) O 1s, (d) F 1s, and (e) P 2p regions.



Fig. S13 (a) X-band EPR spectra at 298 K and (b) g-factor of Cu@COF and Cu@N⁺-COF.



Fig. S14 (a) Cu K-edge EXAFS (points) and the fitted curves for Cu@COF and Cu@N⁺-COF, shown in k^3 weighted *k*-space, (b) Experimental and fitted Cu K-edge EXAFS curves in R space, inset is the schematic model for FEFF calculation based on DFT results.

Sample	path	<i>d ^b /</i> Å	N	R/Å	σ²/Ų	$\Delta E_0/eV$	R factor
Cu@COF	Cu-N	2.106	2 ^c	1.98	0.004 (1)	7 (2)	1.8%
	Cu-O	2.153	1.8 (4)	2.14	0.004 (1)	- 7(3)	
Cu@N⁺-COF	Cu-N	2.106	2°	2.12	0.003 (1)	6 (2)	1.2%
	Cu-O	2.153	1.8 (3)	2.21	0.005 (1)	- 0(3)	

^a S₀² was fixed as 0.9. Data ranges: $2.5 \le k \le 11.5 \text{ Å}^{-1}$; $1 \le R \le 2.7 \text{ Å}$ for Cu@COF, and $1 \le R \le 2.5 \text{ Å}$ for Cu@N-COF-Cu. ^b The distances for Cu-N and Cu-Cl are from the DFT models. ^c These coordination numbers were constrained as *N* (Cu-N) =2.



Fig. S15 Total current density-time (*I-t*) curves at different potentials (vs. RHE) of (a) Cu@COF and (b) Cu@N⁺-COF in 1.0 M KHCO₃ solutions.



Fig. S16 Average current density-potential (*J*-*V*) curves summarized from *I*-*t* curves of Cu@COF and Cu@N⁺-COF in 1.0 M KHCO₃ solutions.



Fig. S17 ¹H-NMR spectrum of liquid product for (a) Cu@COF and (b) Cu@N⁺-COF in 1.0 M KHCO₃.



Fig. S18 TOFs at different potentials of Cu@COF and Cu@N⁺-COF in 1.0 M KHCO₃ solutions.

Catalyst	Type of Cell	Solution	jco (mA cm⁻²)	FE _{CO} %	Potential (V vs. RHE)	Stability	<i>R</i> ef.
Cu@ N⁺-COF	Flow cell	KHCO ₃	87	93	-1.0	24	This
Cu@COF	Flow cell	KHCO ₃	72	86	-1.1	7	work
Cu@N⁺-COF	Flow cell	H_2SO_4/K_2SO_4	-70	84	-1.5	24	This
Cu@COF	Flow cell	H_2SO_4/K_2SO_4	-45	73	-1.5	24	work
CoPc/GDY/G	Flow cell	KHCO₃	-100	97	-0.82	24	4
CoPc-CTF	Flow cell	H ₃ PO ₄ /KH ₂ PO ₄ /KCI	~ -80	94	-1.2	10	5
CoPPc	Flow cell	H ₂ SO ₄ /CsSO ₄	-200	87	-1.6		6
NiPPc	Flow cell	H ₂ SO ₄ /CsSO ₄	-50	35	-1.6		6
nitro-CoPc/G	H cell	KHCO₃		85	-0.82	30	7
NiPc-NH- TFPN-NH₂	H cell	KHCO ₃		99	-1.0	60	8
NiPc-NH-TFPN	H cell	KHCO₃		~70	-1.0		8
NiPc-NH- TFPN-COOH	H cell	KHCO ₃		71	-1.0		8
CoP@CNT	H cell			> 95	-0.87		9
CoP-Ph@CNT	H cell			80	-0.87		9
CoP-F@CNT	H cell			< 20	-0.87		9

Table S3Catalytic performance comparison of recently reported electrocatalysts for eCO2RR.



Fig. 19 Current density-time (I-t) curve of the stability test for Cu@N⁺-COF in 1.0 M KHCO₃ solution.



Fig. S20 TEM images of (a) tested Cu@COF and (b) tested Cu@N⁺-COF.



Fig. S21 TEM image and corresponding EDX mapping for Cu, C and N elements in tested Cu@COF



Fig. S22 TEM image and corresponding EDX mapping for Cu, C and N elements in tested Cu@N⁺-COF



Fig. S23 AC-HAADF-STEM images of (a) Cu@COF and (b) Cu@N⁺-COF.



Fig. S24 XPS of tested Cu@COF in the (a) survey, (b) Cu 2p (c) N 1s, (d) C 1s, and (e) O 1s regions. Note: in the C 1s region, the C-F bond originates from the addition of Nafion solution, and K^+ ions are derived from the KHCO₃ solution.



Fig. S25 XPS of tested Cu@N⁺-COF in the (a) survey, (b) Cu 2p (c) N 1s, (d) C 1s, (e) O 1s, and (f) P 2p regions. Note: in the C 1s region, the C-F bond originates from the addition of Nafion solution, and K⁺ ions are derived from the KHCO₃ solution.



Fig. S26 Cycle voltammetry (CV) curves of Cu@COF and Cu@N⁺-COF in 0.05 M H_2SO_4 and 0.5 M K_2SO_4 acid solution under CO₂ purge, using a catalyst-coated glass carbon electrode as the work electrode.



Fig. S27 Total current density-time (*I-t*) curves at different potentials (vs. RHE) of (a) Cu@COF and (b) Cu@N⁺-COF in 0.05 M H₂SO₄ and 0.5 M K₂SO₄ acid solution.



Fig. S28 Average current density-potential (*J*-*V*) curves summarized from *I*-*t* curves of Cu@COF and Cu@N⁺-COF in 0.05 M H_2SO_4 and 0.5 M K_2SO_4 acid solution.



Fig. S29 ¹H-NMR spectrum of liquid product for (a) Cu@COF and (b) Cu@N⁺-COF in 0.05 M H_2SO_4 and 0.5 M K_2SO_4 solution.



Fig. S30 TOFs at different potentials of Cu@COF and Cu@N⁺-COF in 0.05 M H_2SO_4 and 0.5 M K_2SO_4 solution.



Fig. S31 Partial current density of hydrogen product ($j_{Hydrogen}$) of Cu@COF and Cu@N⁺-COF in (a) 1.0 M KHCO₃, and (b) 0.05 M H₂SO₄ and 0.5 M K₂SO₄ solutions.



Fig. 32 Linear polarized curves of (a) COF and Cu@COF, and (b) N⁺-COF and Cu@N⁺-COF coated on glass carbon electrode in 1.0 M KHCO₃ solution under CO₂ flow.



Fig. 33 Total current densities and corresponding FE_{CO} of (a) Cu@COF after SCN⁻ treatment and (b) Cu@N⁺-COF after SCN⁻ treatment in 1.0 M KHCO₃ solution.



Fig. S34 Total current densities at different overpotentials of (a) Cu@COF and (b) Cu@N⁺-COF, corresponding FE_{COS} of (c) Cu@COF and (d) Cu@N⁺-COF in KHCO₃/H₂O and KDCO₃/D₂O solutions.



Fig. S35 Total current densities and corresponding $FE_{CO}s$ at different temperatures of (a) Cu@COF and (b) Cu@N⁺-COF, and Arrhenius plots of j_{CO} obtained at the overpotential of -0.9 V (c) Cu@COF and (d) Cu@N⁺-COF in KDCO₃/D₂O and KHCO₃/H₂O acid solutions.



Fig. S36 Total current densities at different overpotentials of (a) Cu@COF and (b) Cu@N⁺-COF, corresponding FE_{CO} s of (c) Cu@COF and (d) Cu@N⁺-COF in K₂SO₄/D₂O and K₂SO₄/H₂O acid solutions.



Fig. S37 j_{CO} and KIE values of (a) Cu@COF and (b) Cu@N⁺-COF in K₂SO₄/D₂O and K₂SO₄/H₂O acid solutions.



Fig. S38 j_{Hydrogen} and corresponding KIE at different overpotentials for (a) Cu@COF and (b) Cu@N⁺-COF in KHCO₃/H₂O and KDCO₃/D₂O solution, for (c) Cu@COF and (d) Cu@N⁺-COF in K₂SO₄/H₂O and K₂SO₄/D₂O solution.

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