

Supporting information

Mild pyrolysis of ionic self-assembled cobalt porphyrins on carbon toward efficient electrochemical conversion of CO₂ to CO

Xue Zhang,^a Huiyuan Liu,^{a,b,c} Jiaqi Qin,^a Hongsa Han,^a Chenxi Qiu,^a Siyu Zhang,^a Xinyu Hao,^a Wei Liu,^a Yujiang Song^{a,*}

^aState Key Laboratory of Fine Chemicals, School of Chemical Engineering, Dalian University of Technology, 2 Linggong Road, Dalian 116024, China. E-mail: yjsong@dlut.edu.cn.

^bDalian National Laboratories for Clean Energy, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian, Liaoning 116023, China.

^cUniversity of Chinese Academy of Sciences, Beijing 100039, China.

Chemicals

Co(III) meso-tetra(4-sulfonatophenyl) porphyrin chloride (CoTPPS₄) and Co(III) meso-tetra(4-pyridyl) porphyrin chloride (CoTPyP) of the highest purity available were purchased from Frontier Scientific, USA. All aqueous solutions were prepared with ultrapure water (18.2 MΩ cm⁻¹ at 25 °C) obtained from a Millipore Nanopure water system (Synergy UV, France). Carbon black (EC600 JD) was obtained from Akzo Nobel, Holland. Vulcan XC-72 (VXC-72) and Black Pearls 2000 (BP2000) were purchased from Cabot, USA. All of the carbon materials were pretreated in nitric acid (3 M) at 80 °C for 1 h before use. Carbon nanotubes (CNTs) were purchased from XF Nano, Inc. (Nanjing, China) and used as received. KHCO₃ (purity≥99.5%) was purchased from Sinopharm Chemical Reagent, China.

Experimental

100 mL of CoTPPS₄ aqueous solution (200 μM) and 100 mL of protonated CoTPyP aqueous solution (200 μM in 0.02 M HCl) were mixed together and left under stirring for over 6 h at 25 °C. 34.7 mg of pretreated EC600 JD was added to the mixture, followed by sonication for at least 1 h in a water bath to ensure well dispersion. Next, the mixture was filtrated and washed to pH neutral with deionized water to obtain black powder (SACoCo/EC600), followed by drying in an oven at 65 °C for at least 24 h. Next, the dried SACoCo/EC600 was heat-treated in argon by ramping up the temperature to 350 °C with a rate of 5 °C min⁻¹ and holding at 350 °C for 2 h, labelled as H-SACoCo/EC600. For comparison, different heating temperatures (300, 350, 400, 500, 600, 800 °C) were also tried and the SACoCo supported on VXC-72, BP2000 and CNTs were also heat-treated at 350 °C according to the procedure above, respectively.

Additionally, 3.4 mg of CoTPPS₄, 2.4 mg of CoTPyP, and 14.2 mg EC600 were mechanically mixed by grinding in a mortar. Next, the mixture was heat-treated in argon by ramping up the temperature to 350 °C with a rate of 5 °C min⁻¹ and holding at 350 °C for 2 h to obtain H-CoCo/EC600 sample for comparison as well.

Characterizations

Transmission electron microscope (TEM, FEI Tecnai G2 Spirit, 120 keV) was used to characterize the morphology of the samples. Elemental mappings were carried out on Tecnai G2 F30 operated at 300 keV. The samples for TEM analysis and elemental mapping were prepared

by adding several drops of colloidal solution onto a holey carbon-coated copper grid. Powder x-ray diffraction (XRD) patterns were collected on a Rigaku Smartlab 9 powder diffractometer with a Cu K α radiation source (40 kV, 100 mA, $\lambda = 0.15432$ nm) in a 2θ range of 5° – 80° at a scanning rate of 5° min^{-1} . UV-vis spectra were recorded with a spectrophotometer (Analytic Jena, Specord S600) and a 2 mm path length quartz cell. Thermogravimetric analysis (TGA) was conducted on TA Q600 SDT with dried Ar as the processing atmosphere at a heating rate of $10^\circ \text{ C min}^{-1}$. Raman spectra were taken with DXR Microscope from Thermo Fisher, USA. Samples were analyzed by Fourier Transform Infrared Spectrometer (FT-IR, 6700 Thermo Fisher). X-ray photo-electron spectroscopy (XPS) measurements were performed on a Thermo ESCALAB 250Xi spectrometer using monochromatic Al K α line (1486.6 eV) as the x-ray source. N $_2$ adsorption/desorption were measured at 77 K using a Quantachrome Quadrasorb-SI Analyzer, where the BET method was used for surface area determination. Co amount was measured using inductively coupled plasma-optical emission spectrometry (ICP-OES, Perkin Elmer ICP-OES Optima 2000DV). Mass spectrometry (MS) was carried out on MALDI micro MX, Waters, US. Resistivity tests were performed on a powder resistance measuring instrument (ST2722-SD).

Electrochemical conversion of CO $_2$

Typically, an electrocatalyst ink (1 mg mL^{-1}) was prepared by blending certain amount of the electrocatalyst with water, ethanol, and Nafion perfluorinated resin solution (5 wt% in mixture of lower aliphatic ethanol and water, contains 45% water) at $V_{\text{water}}: V_{\text{ethanol}}: V_{\text{Nafion}} = 1:9:0.06$ under sonication for 2 min in a water bath cleaner. The electrocatalyst slurry was sprayed to the microporous layer of gas diffusion layer (GDL, Sunrise Power Co., Ltd., China) to reach a loading of 1.0 mg cm^{-2} on a hot plate (70° C) as the working electrode.

All potentials in this study were referred to that of reversible hydrogen electrode (RHE). Electrochemical CO $_2$ conversion was performed in 0.5 M KHCO $_3$ aqueous solution at 25° C in a house-made H-type electrochemical cell using a graphite rod as the counter electrode, an Hg/Hg $_2$ SO $_4$ as the reference electrode ($E_{\text{RHE}} = E_{\text{Hg}/\text{Hg}_2\text{SO}_4} + 0.65 + 0.059 \cdot \text{pH}$). The working and counter electrode compartment was separated by a Nafion-115 membrane.

The electrolyte in both anodic and cathodic compartment was stirred slightly to aid the diffusion of gas products. The cathodic compartment was continuously purged with CO $_2$ (20 mL min^{-1}) to ensure the saturation of CO $_2$ and vented directly to a gas chromatograph (GC, T7980) for the quantification of gas products every 15 min. The GC was equipped with a packed Molecular Sieve 5A capillary column, a packed Porapak Q column, and a packed GDX-102 column. Nitrogen (99.999%) was used as the carrier gas. Two Flame Ionization Detectors (FIDs) and a Thermal Conductivity Detector (TCD) were used to quantify H $_2$ and CO. HCOO $^-$ was detected by Ion Chromatography (IC) on DIONEX ICS-5000, USA and methanol, ethanol and HCHO were detected by H 1 nuclear magnetic resonance (H 1 NMR) on Bruker AVANCE III 500, Switzerland. The Faradaic efficiencies (FE) of gas products were calculated according to the equation (1):

$$FE_i = \frac{Q_i}{Q_{total}} = \frac{v \cdot x}{22400 \cdot 60} \cdot n \cdot F$$

Where i represents CO or H $_2$, x is the concentration of CO or H $_2$, v is feeding rate of CO $_2$, n is the electron transfer number of 2 for both CO and H $_2$ in this case, F is the Faradaic constant (96485 C

mol⁻¹), I is the average current during certain time of electrolysis.¹

The partial current density of CO or H₂ was calculated according to equation (2) as follows:

$$J_i = J_{total} \cdot FE_i$$

where i represents CO or H₂, J_{total} is the average current density during certain time of electrolysis, and FE_i is the Faradaic efficiency of CO or H₂.

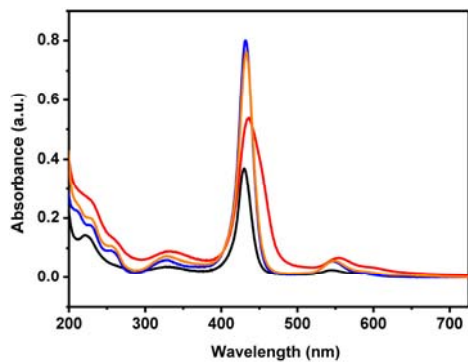


Fig. S1 Typical UV-vis spectra of CoTPPS₄ aq. (black line), CoTPyP aq. (blue line), the aqueous mixture of CoTPPS₄ and CoTPyP (red line), and the supernatant of the mixture of CoTPPS₄ and CoTPyP (orange line).

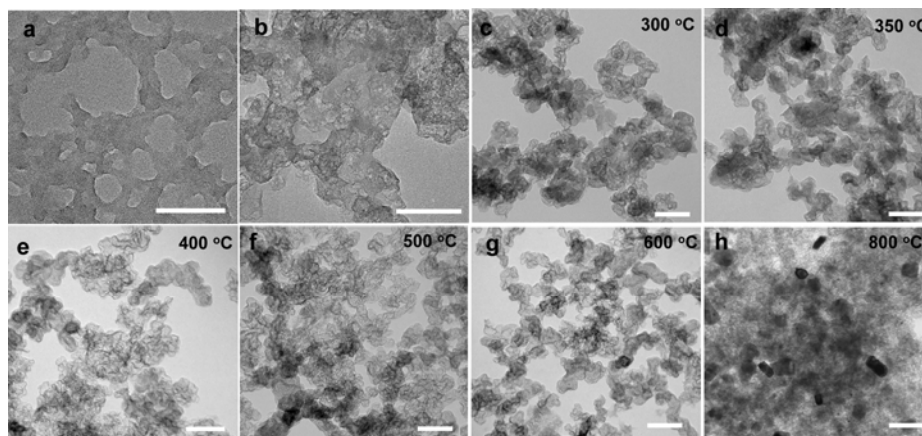


Fig. S2 TEM images of (a) SACoCo, (b) SACoCo/EC600, and (c-h) heat-treated SACoCo/EC600 at different temperatures from 300 to 800 °C. Scale bar, 100 nm.

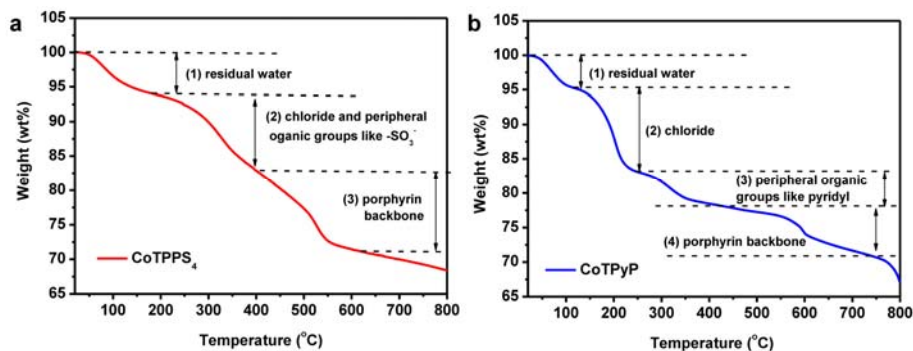


Fig. S3 TGA curves of CoTPPS₄ (a) and CoTPyP (b) with weight-loss assignment^{1, 2} collected in argon atmosphere with a heating rate of 10 °C min⁻¹.

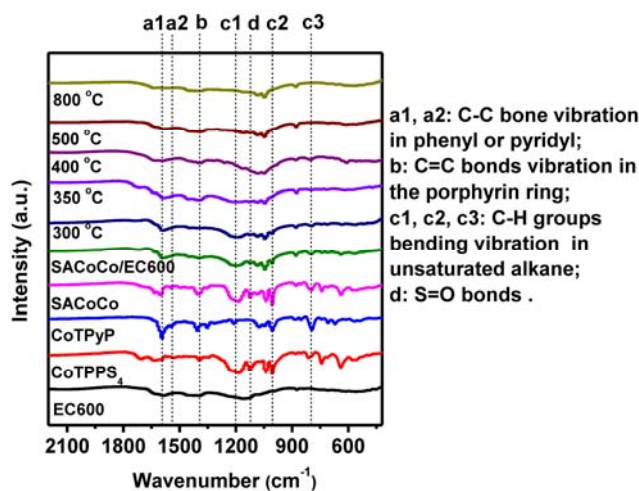


Fig. S4 FT-IR spectra of EC600, CoTPPS₄, CoTPyP, SACoCo, SACoCo/EC600 and heat-treated SACoCo/EC600 with peak assignments³ at different temperatures, indicative of strong interaction of porphyrin ring with the carbon support based on the weakening and loss of certain vibrational modes.

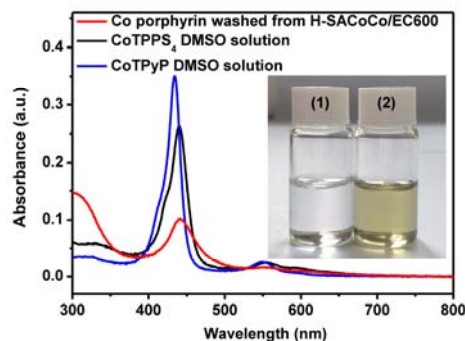


Fig. S5 UV-vis spectra of Co porphyrin washed from H-SACoCo/EC600 with DMSO (red line), CoTPPS₄ DMSO solution (black line), and CoTPyP DMSO solution (blue line). Inset: photographs of DMSO solvent (1) and the Co porphyrin washed from H-SACoCo/EC600 with DMSO (2).

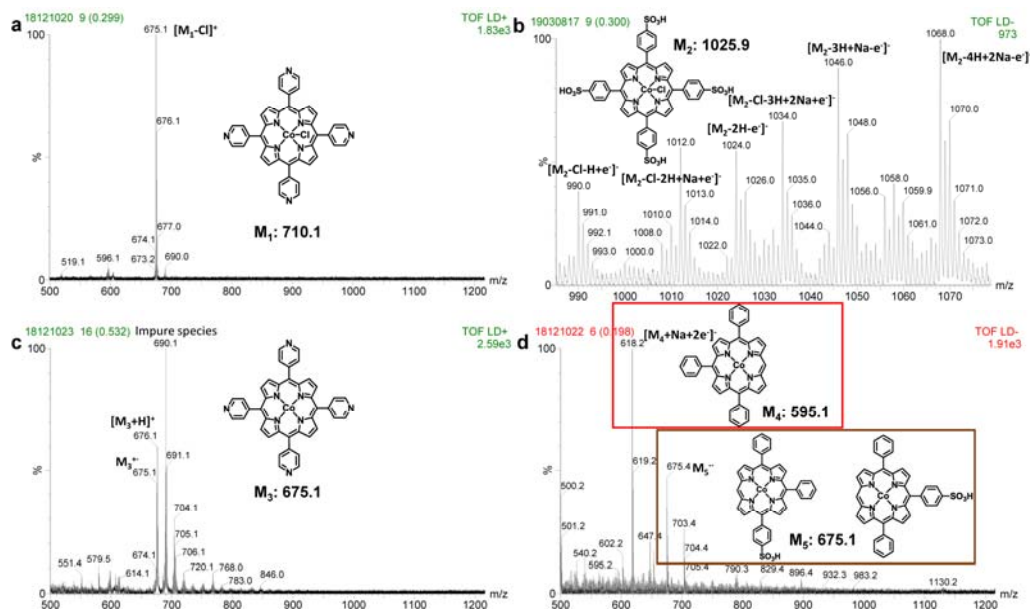


Fig. S6 MALDI mass spectra of CoTPyP (a), CoTPPS₄ (b), and the porphyrins rinsed from H-SACoCo/EC600 with DMSO (c, d) evidenced the maintenance of porphyrin ring and the removal of certain axial ligands and peripheral groups. After heat treatment, the CoTPyP merely loses the axial chloride. The CoTPPS₄ loses axial chloride and some peripheral groups and exists as two forms: (1) losing the axial chloride, four SO₃H, and a phenyl group; (2) losing the axial chloride, three SO₃H, and a phenyl group.

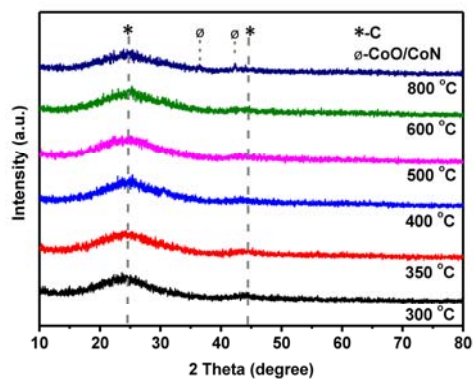


Fig. S7 XRD patterns of heat-treated SACoCo/EC600 at different temperatures.

Table S1 The resistivity (ρ) of EC600, SACoCo/EC600, as well as H-EC600, H-SACoCo/EC600, and H-CoCo/EC600 that heat-treated at 350 °C.

Sample	ρ (Ω cm)
EC600	0.315 \pm 0.001
H-EC600 (350 °C heat treatment)	0.217 \pm 0.001
H-SACoCo/EC600	0.351 \pm 0.001
SACoCo/EC600	0.498 \pm 0.001
H-CoCo/EC600	0.252 \pm 0.001

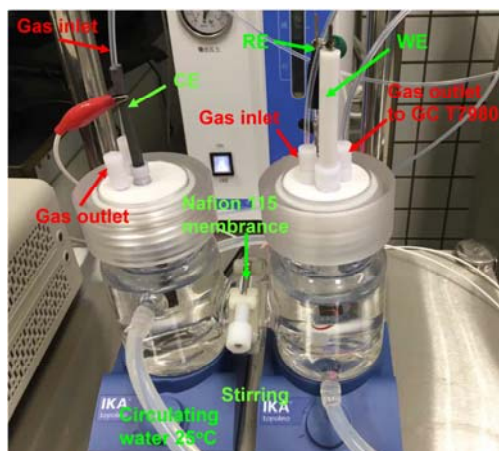


Fig. S8 Photograph of H-type electrolysis cell for CO₂ conversion.

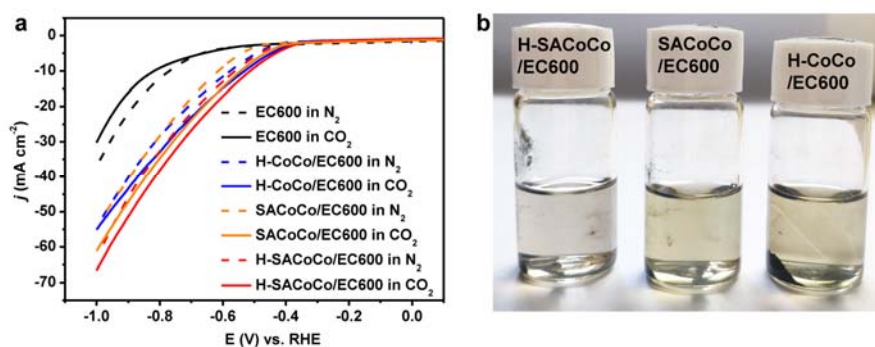


Fig. S9 (a) Linear sweep voltammetry (LSV) curves of electrochemical conversion of CO₂ recorded with EC600 (black line), H-CoCo/EC600 (blue line), SACoCo/EC600 (orange line) and H-SACoCo/EC600 (red line) in CO₂-saturated (solid line) and N₂-saturated (dash line) 0.5 M KHCO₃ aqueous solution, respectively, at a scan rate of 20 mV s⁻¹, (b) photographs of the ink supernatant of H-SACoCo/EC600 (colorless), SACoCo/EC600 (light yellow) and H-CoCo/EC600 (light yellow) obtained by centrifugation, indicative of the difference in the adsorption stability of porphyrins on the carbon support.

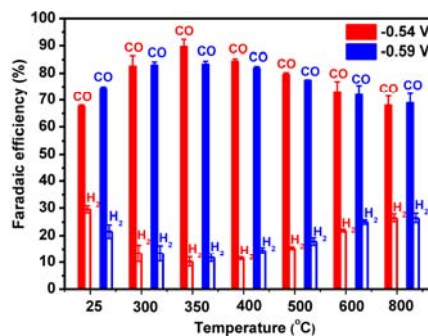


Fig. S10 Faradaic efficiencies of CO₂ conversion products of heat-treated SACoCo/EC600 at different temperatures under -0.54 V (red) and -0.59 V (blue) vs. RHE. The average values and error bars are based on seven measurements during reaction runs.

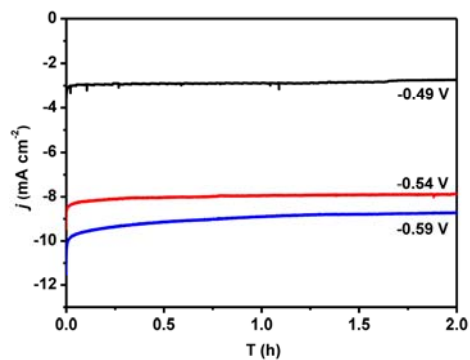


Fig. S11 Representative chronoamperograms of CO₂ electrochemical conversion on the H-SACoCo/EC600 for 2 h at various potentials (vs. RHE) in 0.5 M KHCO₃ aqueous solution.

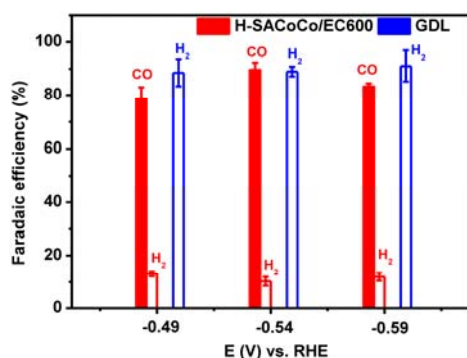


Fig. S12 Faradaic efficiencies of CO₂ conversion products of the H-SACoCo/EC600 and GDL alone at various potentials. The average values and error bars are based on seven measurements during reaction runs.

Table S2 Micropore area, external surface area, and total surface area of H-EC600, H-SACoCo/EC600, SACoCo/EC600, and H-CoCo/EC600 measured by N₂ adsorption/desorption

	Micropore area (m ² g ⁻¹)	External surface area (m ² g ⁻¹)	Total surface area (m ² g ⁻¹)
H-EC600	150.9	1346.6	1497.5
H-SACoCo/EC600	0	487.8	487.8
SACoCo/EC600	0	474.7	474.7
H-CoCo/EC600	52.4	968.5	1020.9

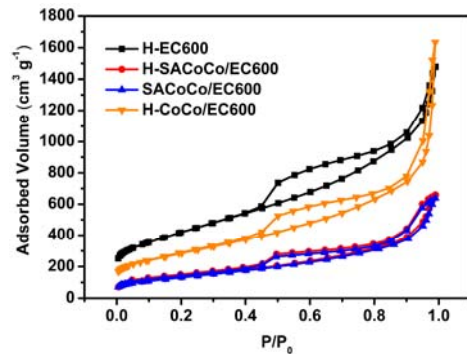


Fig. S13 N₂ adsorption/desorption isotherms of H-EC600, H-SACoCo/EC600, SACoCo/EC600, and H-CoCo/EC600.

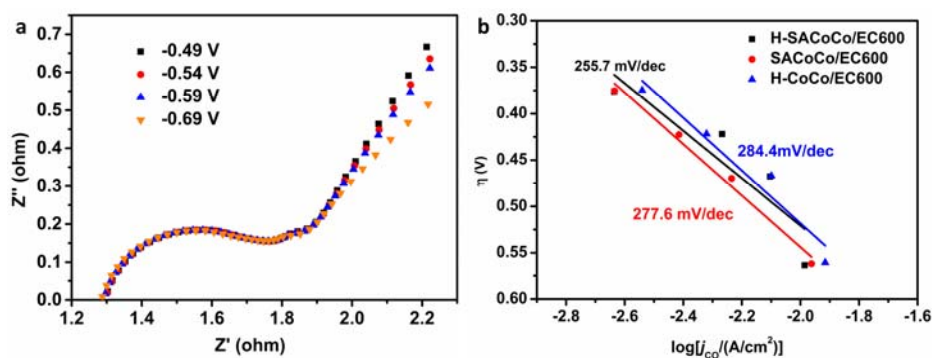


Fig. S14 (a) Nyquist plots of H-SACoCo/EC600 at different applied potentials (vs. RHE), (b) Tafel plots of H-SACoCo/EC600, SACoCo/EC600, and H-CoCo/EC600 loaded on GDL recorded in CO₂-saturated 0.5 M KHCO₃ aqueous solutions (pH 7.2).

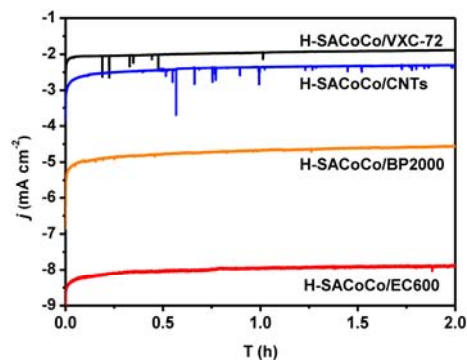


Fig. S15 Representative chronoamperogram curves of CO₂ electrochemical conversion on the H-SACoCo/EC600, H-SACoCo/CNTs, H-SACoCo/BP2000, and H-SACoCo/VXC-72, respectively, for 2 h at -0.54 V vs. RHE in 0.5 M KHCO₃ aqueous solution.

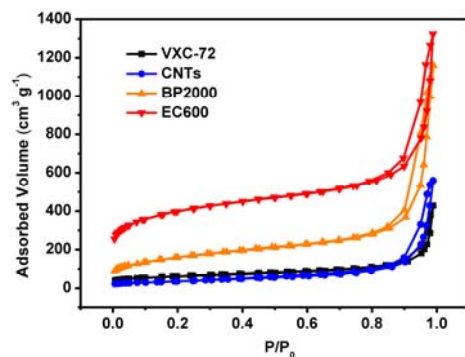


Fig. S16 N₂ adsorption/desorption isotherms of VXC-72, CNTs, BP2000, and EC600.

Table S3 Micropore area, external surface area, and total surface area of four carbon materials measured by N₂ adsorption/desorption.

	Micropore area (m ² g ⁻¹)	External surface area (m ² g ⁻¹)	Total surface area (m ² g ⁻¹)
VXC-72	114.3	107.7	222.2
CNTs	129.6	1.3	130.9
BP2000	955.4	487.7	1443.1
EC600	179.1	1075.8	1254.9

Notes and reference

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