

Electronic Supplementary Information (ESI)

Simultaneous production of CO and H₂O₂ by paired electrolysis coupling CO₂ reduction and water oxidation

1. Experimental section

1.1 Chemical and materials

Cobalt phthalocyanine (CoPc) was purchased from Sigma-Aldrich. The single-wall carbon nanotubes were purchased from XFNANO. *N,N*-dimethylformamide (DMF) (99.5%), dimethyl sulfoxide (DMSO), Deuterium oxide(D₂O) and ethanol (99.8%) were purchased from Energy Chemical. Potassium bicarbonate (99.7%) and potassium carbonate (99.5%) were purchased from Macklin. Potassium permanganate was purchased from XIHUA. Fluorine-doped tin oxide (FTO) was sourced from N-buliv. Nafion solution (5 wt. %) was purchased from DuPont. All chemicals were used without any further purification.

1.2 Preparation of CoPc/CNT

2 mg of CoPc was ultrasonically dispersed in 20 mL DMF for 10 minutes, followed by adding 40 mg of carbon carrier and ultrasonicated for another 30 minutes, and then stirred for 3 hours. To remove the unsupported CoPc, the stirred solution was washed by DMF (2 times) and H₂O (1 times). The wet solid was freeze-dried to get the final molecular hybrid.

1.3 Preparation of CO₂R electrode

The catalyst ink was prepared by dispersing 1mg of CoPc/CNT in 1ml of ethanol with 50 μl 5% Nafion solution, and then sonication for 1 hour. Then 200 μl of ink were drop-casted onto a 2×1 cm² carbon fiber paper (Sigracet 39 AA) to cover an area of 1×1 cm² (catalyst mass loading, 0.2 mg cm⁻²). The prepared electrodes were dried by infrared heating lamps.

1.4 CO₂R measurements

All electrolytes were prepared with ultrapure water (18.2 MΩ·cm). All electrochemical measurements were carried out in H-type cells (GaossUnion, China) separated by a Nafion 117 membrane between the cathodic and anodic chambers. Pt sheet and saturated Ag/AgCl serve as counter and reference electrodes, respectively. Before electrolysis experiment, the cathodic electrolyte(0.5 M KHCO₃) was bubbled with CO₂ for 30 min under stirring (400 rpm). The pH of the electrolyte was measured by a pH meter (SevenDirect SD20). The ohmic resistance was measured at open-circuit voltage by electrochemical impedance spectroscopy. The potential range of -0.47 to -0.87 V vs. RHE (step size = 0.1 V) was applied during the CO₂R test and calculated the FE(CO) and current density. The yield of CO and H₂ was quantified by gas chromatography (FULI GC-9790Plus, China). The liquid products were quantified after electrocatalysis using ¹H NMR spectroscopy with solvent (H₂O) suppression. 450 μl of electrolyte was

mixed with 50 μl of a solution of 5 mM DMSO in D_2O as internal standards for the ^1H NMR analysis. The concentration of liquid products was calculated using the ratio of the area of the liquid products peak to that of the DMSO internal standard. The linear sweep voltammetry (LSV) curves were recorded at a scanning rate of $10 \text{ mV}\cdot\text{s}^{-1}$ on a CHI-660E electrochemical workstation. All potentials were reported with respect to the RHE scale and corrected by internal resistance drop compensation. All potentials measured were calibrated to RHE using the following equation:

$$E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.197 \text{ V} + 0.059 \text{ pH}$$

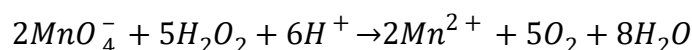
The FE(CO) was calculated according to the following equation:

$$FE_{\text{products}} = \frac{N \times F \times n_{\text{products}}}{Q} \times 100\%$$

Where N is the number of electrons transferred for products. ($N = 2$ for CO and H_2), F is the Faraday constant (96485 C mol^{-1}), n_{products} is the moles of produced products (mol), Q is the total charge obtained from chronoamperometry (C).

1.5 $2e^-$ WOR measurements

The $2e^-$ WOR performance evaluation was conducted similarly to the CO_2R , except the bicarbonate/carbonate-based aqueous solutions (0.5 M KHCO_3 , 2.0 M KHCO_3 , 0.5 M $\text{KHCO}_3 + 3.5 \text{ M K}_2\text{CO}_3$, 2 M K_2CO_3 and 5 M K_2CO_3) were used as the electrolyte. Commercial FTO ($2 \times 1 \text{ cm}^2$, without pretreatment) was used as the working electrode, Pt sheet and saturated Ag/AgCl serve as counter and reference electrodes, respectively. The potential range of 3.1 V to 3.5 V vs. RHE (step size = 0.1 V) was applied during the $2e^-$ WOR test and calculated the FE(H_2O_2) and current density. After electrolysis, The H_2O_2 produced by $2e^-$ WOR electrochemistry was determined by titration of standard potassium permanganate (0.02 M KMnO_4 , standardized against oxalate (Macklin)) titration using sulfuric acid solution (Guangzhou Chemical Reagent Factory) as the proton source, diluted in a 8:92 (H_2SO_4 : H_2O) ratio. A volume of 10 mL of the sample is added to a 250 mL conical flask, after which a volume of 50-100 mL of diluted H_2SO_4 is added into the flask. The mixture is subsequently slowly titrated with 0.02 M KMnO_4 until a color change (from an initial colorless state to a pink solution) is observed at the end point. The overall reaction is described based on the following equation:



The ohmic resistance was measured at open-circuit voltage by electrochemical impedance spectroscopy. The LSV curves were recorded at a scanning rate of $10 \text{ mV}\cdot\text{s}^{-1}$ on a CHI-660E electrochemical workstation. All potentials were reported with respect to the RHE scale and corrected by internal resistance drop compensation.

The FE(H_2O_2) was calculated according to the following equation:

$$FE = \frac{\text{generated } \text{H}_2\text{O}_2(\text{mol}) \times 2 \times 96485 (\text{C mol}^{-1})}{\text{total amount of charge passed (C)}} \times 100\%$$

1.6 CO₂R coupling 2e⁻WOR measurements

All electrochemical measurements were carried out in H-type cells (GaossUnion, China) separated by a Nafion 117 membrane between the cathodic and anodic chambers. A three-electrode system is still adopted, with CoPc/CNT as the CO₂R cathode, FTO as the 2e⁻WOR anode, Ag/AgCl serve as reference electrodes, and the CO₂R coupled 2e⁻WOR test was carried out on CHI-660E electrochemical workstation, and the CO₂-saturated 0.5 M KHCO₃ and 5 M K₂CO₃ were used as electrolytes. In CO₂R coupled 2e⁻WOR test, by carefully adjusting the cathode-to-anode area ratio to 10:1, the potential range of 3.4 ~ 3.6 V vs. RHE (step size = 0.1 V) is used to calculate Faraday efficiency and current density. CO and H₂ yields were determined by gas chromatography (FULI GC-9790Plus, China). The yield of H₂O₂ was detected by using the standard potassium permanganate titration process. All potentials were reported with respect to the RHE scale and corrected by internal resistance drop compensation.

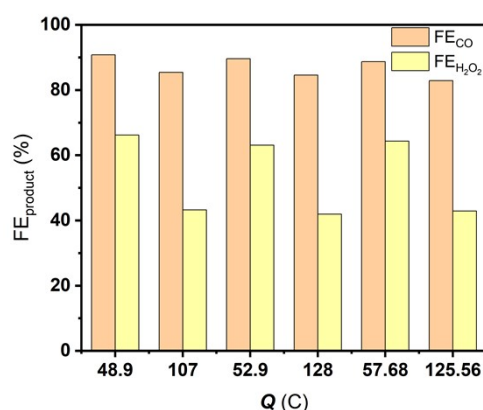


Figure S1. Stability test of 2e⁻WOR. The recycling experiments were conducted by refreshing the electrolyte solution, while using the same cathode and anode throughout the testing process. In the first run of electrolysis, the charge consumption was controlled at approximately 50 C, followed by product selectivity analysis. Subsequently, the electrolyte was replaced for another electrolysis, with charge consumption controlled at about 100 C, followed by another selectivity assessment. This procedure was repeated three times. The results indicated that the selectivity for H₂O₂ decreased with extended testing time; however, it could be restored by replacing the electrolyte solution. This also suggests that the decline H₂O₂ selectivity along with time is attributed to the accumulation of H₂O₂ in the solution.

Table S1. FE_{products} at different current densities. (electrode area of cathode and anode is 1×1 cm²)

Potential (V vs.RHE)	Current density (mA cm ⁻²)	FE(CO)	FE(H ₂ O ₂)
2.73	9.6	83.1%	18.4%
2.94	41	50.5%	30.2%
3.44	83	34.0%	50.6%
3.51	99	23.5%	58.7%

The calculation of the electrical energy consumption (EEC), described in the Methods section of the main manuscript, and summarized later on in Table S2, shows, that the

paired electrochemical production of 1 mol H₂O₂ is invariably accompanied by 1.49 mol CO, requiring just 0.60 kWh. This is 40% less than the 0.99 kWh of electrical energy needed to electrochemically produce the same number of products, separately.

$$2e^- \text{WOR}_{\text{Separate}}: z_{\text{Real}} = \frac{z_{\text{Theoretical}}}{FE} = \frac{2e^-}{71.2\%} = 2.80 e^-$$

$$\text{CO}_2\text{R}_{\text{Separate}}: z_{\text{Real}} = \frac{z_{\text{Theoretical}}}{FE} = \frac{2e^-}{94.1\%} = 2.13 e^-$$

$$2e^- \text{WOR}_{\text{Paired}}: z_{\text{Real}} = \frac{z_{\text{Theoretical}}}{FE} = \frac{2e^-}{60.5\%} = 3.31 e^-$$

$$\text{CO}_2\text{R}_{\text{Paired}}: z_{\text{Real}} = \frac{z_{\text{Theoretical}}}{FE} = \frac{2e^-}{90.2\%} = 2.21 e^-$$

The separate processes refer to the generation of 1 mole of the respective product. For paired electrosynthesis, as the current runs through both half-cells successively, and is therefore equal, the charge required to produce 1 mole of H₂O₂ (using 3.31e⁻),

$$\text{simultaneously generates 1.49 mole of CO: } n_{\text{CO}} = \frac{3.31 e^-}{2.21 e^-} = 1.49 \text{ mol CO.}$$

The calculation of the energy efficiency (EE) of the cell, also described in the Methods section of the main manuscript, as well as the individual EEs for the cathodic (CO electrosynthesis) and anodic (H₂O₂ electrosynthesis) processes, is made under an assumed equal division of the cell potential between the cathode and anode.

$$\text{Thus, } E_{\text{Total}} = E_{\text{Anode}} + E_{\text{Cathode}} = 6.8 \text{ V,}$$

$$\text{Where } E_{\text{Anode}} = E_{\text{Cathode}} = 3.4 \text{ V}$$

Where E° is the thermodynamic potential of the electrosynthesis of CO (-0.103 V vs RHE,) and H₂O₂ (1.76 V vs RHE).

$$\text{Consequently, from the equation } EE (\%) = \left(\frac{E^\circ}{E} \right) \times FE, \text{ found in the main}$$

manuscript under Methods, the following EE values are quantified:

$$EE_{\text{Total Paired}} = EE_{\text{CO Paired}} + EE_{\text{H}_2\text{O}_2 \text{ Paired}} = 2.7\% + 31.3\% = 34\%$$

Table S2. Electrical energy consumption calculations for the individual and paired electrosynthesis of CO and H₂O₂. (Battery voltage (E_{cell}) was measured with an external multimeter)

	E _{cell} /V	FE/%	Z _{Theoretic}	Z _{Real}	X / mol	EEC /kWh mol ⁻¹
2e ⁻ WOR	7.2	71.2	2	2.8	1	0.54
CO ₂ R	5.11	94.1	2	2.13	1	0.30

Σ <i>Separate</i>	\	\	\	\	1 H ₂ O ₂ +1.49 CO	0.99
Paired (Normalised to 1 mole of H ₂ O ₂)	6.8	60.5	2	3.31	1 H ₂ O ₂ +1.49 CO	0.60