

Pure-water-fed, electrocatalytic CO₂ reduction to ethylene beyond 1,000 h stability at 10 A

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Supplementary Note 1: AEM, PEM and BPM electrolysis systems for ECO₂R

Currently, taking the MEA cell as an example, ECO₂R systems can be divided into three categories (Supplementary Fig. 1): (i) the AEM system, (ii) the PEM system, and (iii) the BPM system. For these three conditions, the strong local alkaline condition is present during ECO₂R, causing a major fraction of the input CO₂ to react with OH⁻ to produce carbonate rather than being reduced into carbon-based products^{S1-S4}, though the PEM system and the BPM system under reverse bias can re-generate CO₂ from carbonate to some extent^{S5,S6}. The different electrolysis systems could influence pH on both sides of the electrodes^{S7-S11}. The AEM system can transport anions (*e.g.*, OH⁻, HCO₃⁻, CO₃²⁻) from the cathode to the anode^{S7,S11} (Supplementary Fig. 1a). The PEM system can transport cations (such as H⁺ and K⁺) from an acidic anode to the cathode^{S8} (Supplementary Fig. 1b). The BPM system can not only transport the anion (OH⁻) but also the cation (H⁺, K⁺) through an anion exchange layer (AEL) and a cation exchange layer (CEL), respectively (Supplementary Fig. 1c,d), which can create a couple of different pH environment in an electrolysis cell^{S9,S10}.

AEM system

Due to the immaturity of AEM technology, some alkali cations (such as K⁺, Cs⁺) in the anolyte can pass through AEM from the anode to the cathode under the electric field (Supplementary Fig. 1a), resulting in carbonate precipitation at the cathode^{S12}. Some anion products from ECO₂R (such as HCOO⁻ and CH₃COO⁻) can also be transferred from the cathode to the anode under the electric field to be re-oxidized to CO₂^{S7,S11,S12}. Although AEM can provide an alkaline environment for ECO₂R, decreasing the thermodynamic driving force for the competing HER, the additional energy input is necessary for the second CO₂ release and capture from the anodic outlet gas. As a result, the AEM system can cause severe CO₂ and anolyte losses and energy penalties^{S12}.

PEM system

For the PEM system, although the acidic cathode environment can alleviate carbonate formation and crossover by using H⁺ to react with carbonate to regenerate CO₂^{S5,S8} (Supplementary Fig. 1b), the anolyte needs to cooperate in supplying alkali cation to surround the cathode catalyst to suppress HER and accelerate the ECO₂R reaction kinetics^{S13}. However, the acidic cathode environment and continuous transfer of the alkali cation from the anode to the cathode lead to burdensome HER and severe anolyte loss during ECO₂R.

BPM system

For the BPM system, there are two situations (Supplementary Fig. 1c,d). When the negatively charged CEL and a positively charged AEL are in contact with the cathode and anode, respectively, it is referred to as “reverse bias” (Supplementary Fig. 1c). When the direction of the electric field across the BPM is reversed (*i.e.*, the CEL is in contact with the anode and AEL with the cathode), it is referred to as “forward bias”

(Supplementary Fig. 1d). Reverse bias and forward bias refer to the movement direction of the charged ions with respect to the charged ion-exchange layers^{S9}.

The BPM with the acidic environment under reverse bias suffers from the same problems as the PEM system, which are burdensome HER and anolyte losses during ECO₂R (Supplementary Fig. 1c). The water dissociation catalyst is generally required at the CEL/AEL interface to lower the overpotential of water dissociation^{S10,S14}.

Under forward bias (Supplementary Fig. 1d), the BPM system with an alkaline cathode environment and an acidic anode environment is generally despised due to higher overpotentials for the redox reaction (such as water splitting)^{S9}. When the metal salt (*e.g.*, KHCO₃) is used as the anolyte for ECO₂R, the BPM system under forward bias will result in carbonate formation and even precipitation and severe anolyte loss due to the local alkaline cathode environment and the transfer of alkali cation from the anode to the cathode^{S6,S10}.

But carbonate formation/precipitation can be suppressed/prevented when using pure H₂O instead of the metal salt electrolyte (Supplementary Fig. 1d). This is for the reason that under forward bias, at the cathode, only cation (H⁺) can form, and it needs to complete charge transfer, taking part in ECO₂R/HER, meaning that there are no additional cations to balance the electrical neutrality of CO₃²⁻ and/or HCO₃⁻. Therefore, under the influence of the electrostatic field, carbonate formation can be suppressed based on an ideal BPM under forward bias. However, due to the immaturity of the BPM technology, the delamination effect of CEL and AEL, ion conductivity and selectivity, and water uptake of the commercial BPM limits its large-scale application^{S9,S15}. Thus, to implement the prototype of our design, the commercially available independent AEM and PEM were integrated (AEM+PEM assembly, named APMA). From a microscopic perspective, APMA is formed mechanically by combining an AEM and a PEM, and there is no physical bonding at the interface. However, the commercial BPM is not where a bipolar junction is presented at the interface. Therefore, when operating ECO₂R, pressure can form due to H₂O formation at the interface, leading to delamination. For our APMA, the delamination situation can be mitigated effectively due to the separated layered structure, which can benefit H₂O transport formed at the interface under the forward bias.

Supplementary Note 2: Manipulations of CN and tensile strain in SS-Cu

To reveal the effect of stacking faults and grain boundaries on CN and strain, we have annealed SS-Cu at various elevated temperatures to tune stacking faults and grain boundaries (250, 350 and 450°C; Cu-250, Cu-350 and Cu-450). The high-temperature treatment can induce rearranging atoms to reach a more thermodynamically favorable state, minimizing the total surface energy^{S16-S18}. *In-situ* heating TEM study explicitly showed the effect of annealing, which demonstrated that stacking faults and grain boundaries in SS-Cu decreased or even disappeared at high temperatures (see Supplementary Videos 1,2 and Supplementary Fig. 8). After each high-temperature treatment, there was no appreciable change in sample size distributions (Supplementary Fig. 4), and all samples stayed as metallic Cu (Supplementary Figs. 9,10). X-ray photoelectron spectroscopy (XPS) measurements showed slight surface oxidation for all the samples (Supplementary Fig. 11). Cu K-edge X-ray absorption spectroscopy (XAS) was conducted to investigate the overall average coordination and strain of Cu (Supplementary Figs. 12-14 and Supplementary Table 2). X-ray absorption near-edge structure (XANES) spectra of samples presented a near-edge feature characteristic of the metallic Cu phase (Supplementary Fig. 12c). Fourier-transformed $\chi(R)$ functions of extended X-ray absorption fine structure (EXAFS) data in the frequency domain (R) revealed an increase in CN as increasing the annealing temperature (Supplementary Fig. 12b). Structural parameters from EXAFS fitting results further indicated that CNs of Cu were increased gradually (from ~ 7.6 to 9.9), and tensile strains were decreased gradually (from $\sim 1.03\%$ to 0.28%) in the order of SS-Cu, Cu-250, Cu-350 and Cu-450 (Supplementary Table 2), consistent with the observed decrease of stacking faults and grain boundaries by *in-situ* heating TEM measurements.

To confirm the probability of surface Cu atoms with low CNs, we first used the lead underpotential deposition (Pb UPD) to identify the exposed facets of SS-Cu, which are Cu(111) and Cu(100) (*refs. S19,S20*) (Supplementary Fig. 15). Then, the atomic structure simulations showed the possible CNs of Cu atoms on the exposed facets (111 and 100) of SS-Cu (Supplementary Figs. 16-19). The perfect Cu(111) plane is composed of the surface atoms with a CN of 9, and depending on the different sliding ways, other CNs (8, 7, 6 and 5) are also possible (Supplementary Figs. 16,17). Similarly, the perfect Cu(100) plane contains surface atoms with a CN of 8 and atomic sites with lower CNs include 7, 6, 5 and 4 (Supplementary Figs. 18,19). As a result, CNs of Cu atoms on the SS-Cu surface vary from 9 to 4 due to abundant and interlaced stacking faults and grain boundaries.

Supplementary Note 3: Effects of CN and tensile strain in SS-Cu on ECO₂R performance

With the increase in the treatment temperature, the samples showed a noticeable decline in the ECO₂R activity (Fig. 3a and Supplementary Figs. 20-24). Such an effect is apparent on ECO₂R-to-C₂H₄/C₂+ (Supplementary Fig. 25), presumably due to the higher CN and lower tensile strain at high temperatures. It prompts our attention to the relationships between CN, tensile strain, and ECO₂R performance. The tensile strain and CNs showed a strong linear correlation with the change in the annealing temperature because of the rearrangement of atoms (Supplementary Fig. 26, black lines). More importantly, a monotonic increase in the partial current density (j_{C2+} , j_{C2H4} or $j_{without H2}$) was observed with the decline of CN and increment of the tensile strain (Supplementary Fig. 26a-c). In other words, the partial current density (j_{C2+} , j_{C2H4} or $j_{without H2}$) showed a strong linear correlation with the function of the tensile strain and CN. This strong linear correlation could reflect that the underlying reason why the stacking fault and grain boundary can improve ECO₂R activity might be derived from the low CN and high tensile strain^{S16,S21,S22}. After excluding the convoluting effects of the size (Supplementary Fig. 4), crystal structure (Supplementary Fig. 10), oxidation state (Cu^{δ+}) (Supplementary Figs. 27-32), the ratio of exposed facets (100/111) (Supplementary Fig. 33) and electrochemical surface area (Supplementary Figs. 34,35), we could explicitly link the low CN and high tensile strain to high ECO₂R activity (especially for ECO₂R-to-C₂H₄/C₂+). In sharp contrast, the function of the tensile strain and CN showed a low correlation to the partial current density of the competing reaction (j_{H2}) (Supplementary Fig. 26d).

Supplementary Note 4: ECO₂R performance over SS-Cu in strong acid

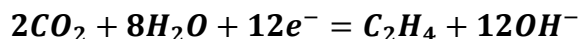
For ECO₂R, the alkaline and neutral electrolytes (such as KOH and KHCO₃) cause carbonate formation, which is fatal to the GDE structure and electrolysis system stability. Although some special strategies to eliminate carbonate have emerged, they result in a severe energy penalty^{S12,S23,S24}. Therefore, Sargent *et al.* carried out ECO₂R in acidic media with concentrated potassium cations to eliminate carbonate formation and crossover^{S5}, effectively boosting the ECO₂R activity and improving input CO₂ utilization. We used a similar K⁺ augmenting strategy based on our high-performance SS-Cu catalyst to enhance the ECO₂R reaction kinetics in the strong acid in a flow cell assembled with PEM (Nafion 117) (Fig. 3c,d, and Supplementary Figs. 36-38).

We sought to operate ECO₂R in a flow cell with acidic media. SS-Cu GDE was directly used as the cathode to perform ECO₂R in a flow cell with 1 M H₃PO₄ as the electrolyte. No ECO₂R product was observed, except H₂ (Supplementary Fig. 36a). Then, in order to slow down OH⁻ diffusion out from the SS-Cu surface and increase the local pH, the cross-linked microporous PMMA layer was assembled on SS-Cu GDEs (SS-Cu/PMMA) (Supplementary Fig. 36c,d). But a similar result shows no ECO₂R product on SS-Cu/PMMA (Supplementary Fig. 36b). According to the cation-augmentation strategy^{S5}, we added concentrated K⁺ to the catholyte, and the ECO₂R performance on SS-Cu/PMMA was boosted.

When using 1 M H₃PO₄ containing 3 M KCl as the catholyte and 1 M H₃PO₄ as the anolyte, SS-Cu/PMMA showed a ~40% C₂₊ FE (~28% toward C₂H₄, ~10% toward C₂H₅OH and ~2% toward CH₃COOH) and a total current density of ~360 mA/cm² at -1.2 V (Supplementary Fig. 37). When using KI instead of KCl, the C₂₊ FE was improved to ~48% (~33% toward C₂H₄, ~14% toward C₂H₅OH and ~1% toward CH₃COOH) with a total current density of ~345 mA/cm² at -1.1 V (Fig. 3c and Supplementary Fig. 38). Considering the practical viability, we performed the acidic-system ECO₂R reaction in an industrially more applicable MEA cell assembled with a Nafion membrane. To enrich K⁺ on the SS-Cu surface, 1 M H₃PO₄ containing 3 M KNO₃ was used as the anolyte. K⁺ and H⁺/H₃O⁺ in the anolyte would pass through the Nafion membrane to the SS-Cu surface under the electric field. Ideally, K⁺ would promote ECO₂R and H⁺/H₃O⁺ would serve as the proton source. Although we did observe the ECO₂R product formation (such as CO and C₂H₄), the ECO₂R reaction was shut down after a few minutes, and HER became dominant. It is due to the continuous K⁺ flow from the anode to the cathode causing severe carbonate precipitation in the flow channel, which blocks CO₂ transport (Supplementary Fig. 39). Thus, the acidic cathode environment combined with alkali metal cation cannot thoroughly eliminate carbonate formation, even resulting in precipitation. Therefore, we believe that ECO₂R in acidic media was not easy to be adopted in the MEA cell.

Supplementary Note 5: Calculation of the theoretical cell voltage at standard conditions

For the thermodynamic potential of ECO₂R-to-C₂H₄ in the alkaline environment and OER in H₂O (Here, about the potential calculations about the half-reaction, the standard potentials of all half-reactions are versus Standard Hydrogen Electrode (SHE), unless otherwise noted):



$$\begin{aligned}\Delta G_{CO_2/C_2H_4}^\theta &= 12 \times (-157.28) + 68.4 - 8 \times (-237.18) - 2 \times (-394.38) \\ &= 867.24 \text{ kJ/mol}\end{aligned}$$

Standard thermodynamic value (Gibbs Free Energy: ΔG^θ) can be obtained from the Table of Thermodynamic Values.

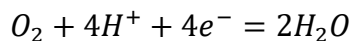
$$\Delta G^\theta = -nFE^\theta$$

where n, F and E^θ are the number of transferred electrons, Faraday's constant and the standard cell voltage, respectively.

$$E_{CO_2/C_2H_4}^{\theta, base} = -\frac{\Delta G_{CO_2/C_2H_4}^\theta}{nF} = -867.24 \times 1000 / 12 / 96485 = -0.75 \text{ V}$$

Anode reaction: $2H_2O = O_2 + 4H^+ + 4e^-$

For the $\Delta G_{O_2/H_2O}^\theta$ and $E_{O_2/H_2O}^{\theta, neutral}$ calculation:



$$\Delta G_{O_2/H_2O}^\theta = -237.18 \times 2 = -474.36 \text{ kJ/mol}$$

$$E_{O_2/H_2O}^{\theta, neutral} = -(-474.36 \times 1000) / 4 / 96485 = 1.23 \text{ V}$$

$$\text{Thus, } E_{CO_2/C_2H_4}^{\theta, base} - E_{O_2/H_2O}^{\theta, neutral} = -1.98 \text{ V}$$

For the thermodynamic potential of H₂O formation by the reaction of H⁺ and OH⁻:



$$\Delta G_{H_2O}^\theta = -237.18 - (-157.28) = -79.90 \text{ kJ/mol}$$

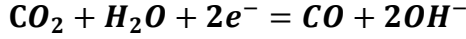
$$\text{Thus, } E_{H_2O}^\theta = -\Delta G_{H_2O}^\theta / nF = -(-79.90 \times 1000) / 1 / 96485 = 0.83 \text{ V}$$

For the voltage loss from the Nernst potential at room temperature (298 K):

$$E_{Nernst\ loss} = 2.303 \frac{RT}{zF} \log_{10} \frac{[H^+]_{Anode}}{[H^+]_{Cathode}} = 0.058 \Delta pH$$

where R , T , z , F , and ΔpH are the ideal gas constant, temperature, valency of ion, Faraday's constant and the pH difference between the anolyte and cathode, respectively.

For the thermodynamic potential of the cathode half-reaction of ECO₂R-to-CO:



$$\begin{aligned} \Delta G_{CO_2/CO}^\theta &= 2 \times (-157.28) + (-137.28) - (-237.18) - (-394.38) \\ &= 179.72 \text{ kJ/mol} \end{aligned}$$

$$E_{CO_2/CO}^{\theta, base} = -\Delta G_{CO_2/CO}^\theta / nF = -179.72 \times 1000 / 2 / 96485 = -0.93 \text{ V}$$

For the calculations of the total overpotential during ECO₂R:

$$E_{Total} = E_{CO_2/C_2H_4}^{\theta, base} - E_{O_2/H_2O}^{\theta, neutral} + \delta_{C_2H_4}^{base} - \delta_{OER}^{neutral} + E_{H_2O}^\theta - \delta_{H_2O} - E_{Ohm} - E_{Nernst\ loss}$$

Here, define the total overpotential is $\delta_{Total} = \delta_{C_2H_4/CO}^{base} - \delta_{OER}^{neutral} - \delta_{H_2O}$ at a given current density and a certain reaction temperature.

$$\begin{aligned} \delta_{Total} &= |\delta_{\frac{C_2H_4}{CO}}^{base} - \delta_{OER}^{neutral} - \delta_{H_2O}| \\ &= E_{Cell\ Voltage} - |E_{CO_2/C_2H_4}^{\theta, base} - E_{O_2/H_2O}^{\theta, neutral} + E_{H_2O}^\theta - E_{Ohm} \\ &\quad - E_{Nernst\ loss}| \end{aligned}$$

The effect of temperature on cell voltage:

Calculations of temperature coefficients for the potentials:

$$\begin{aligned} \left(\frac{\partial E^\theta}{\partial T}\right)_P &= \frac{Q}{zFT} = \frac{T\Delta S}{zFT} = \frac{\Delta H - \Delta G}{zFT} \\ E(T) &= E^\theta + \left(\frac{\partial E^\theta}{\partial T}\right)_P \times (T - 298) \end{aligned}$$

The effect of temperature on Nernst loss:

$$E_{Nernst\ loss} = 2.303 \frac{RT}{zF} \log_{10} \frac{[H^+]_{Anode}}{[H^+]_{Cathode}} = 2.303 \frac{RT}{zF} \Delta pH$$

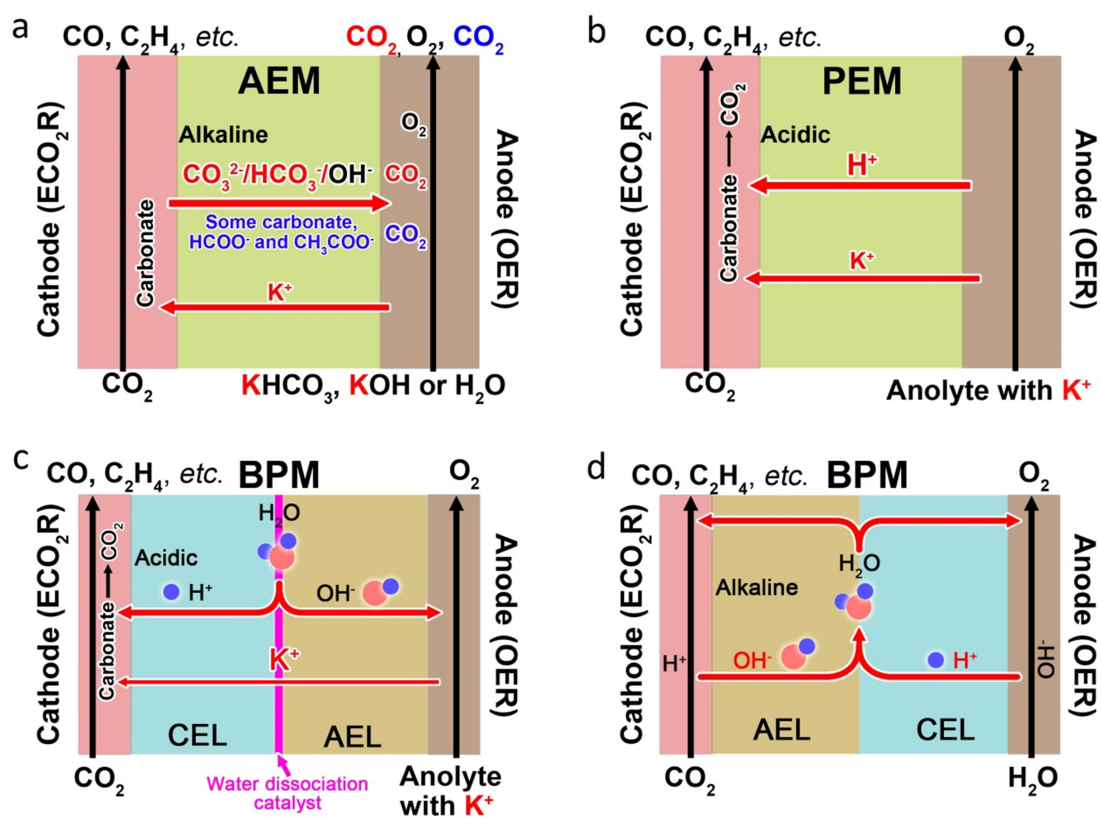
Supplementary Note 6: Identifying the key intermediates of C-C coupling for ECO₂R-to-C₂H₄ on SS-Cu

Density functional theory calculations (DFT) were performed on the perfect Cu(111) and SS-Cu(111) models to reveal the exceptional ECO₂R-to-C₂H₄ performance of SS-Cu. To amplify the impact trend from CN and tensile strain, the unit cell of the SS-Cu model was expanded with a factor of 1.1, meaning 10% tensile strain and CN of the SS-Cu model was set to 7. The reaction energy of CO₂-to-*COOH at the SS-Cu surface is 0.39 eV (Supplementary Fig. 56), much lower than that of the perfect Cu (0.75 eV). Subsequently, the *COOH could be easily converted into *CO due to the negative reaction energies for the perfect Cu and SS-Cu. The *CO intermediate for ECO₂R on SS-Cu was observed by *in-situ* Raman measurements at different potentials (Supplementary Figs. 44, 45, and 55a). The peaks located in the range of 270-360 cm⁻¹ are related to the Cu-CO frustrated rotation and Cu-CO stretch^{S25-S28}. The peaks at 1900-2200 cm⁻¹ can be ascribed to the C≡O stretch of the surface-absorbed CO, including atop-bound CO and bridge-bound CO^{S25,S29}. The vibration of C-H was also observed in the region from 2700 to 3000 cm⁻¹, which can be derived from hydrogenated intermediates (*e.g.*, *CHO, and *COCHO)^{S26}. The more precise assignment of these peaks is highly challenging due to the complexity of hydrogenated intermediates of ECO₂R.

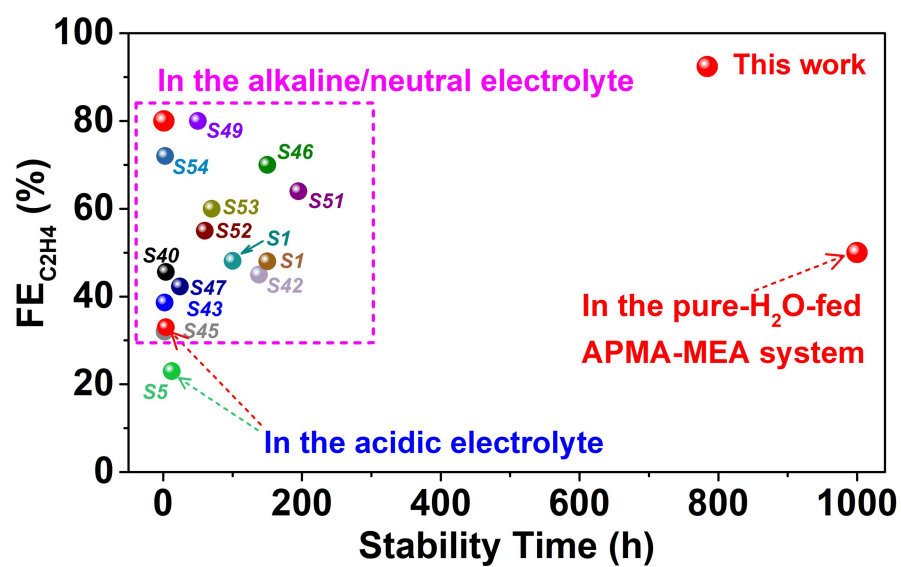
The current consensus regarding the C-C coupling starts with *CO^{S30,S31}. The subsequent dimerization reaction, however, presents some controversies. If the *CO dimerization to *OCCO was the main pathway for C-C coupling, $j_{C_2H_4}/j_{C_2+}$ (productivity) of the electrocatalytic CO reduction (ECOR) to C₂H₄/C₂₊ on SS-Cu should be higher than that of ECO₂R-to-C₂H₄/C₂₊ (*refs.* S30-37). We test the hypothesis of direct *CO dimerization by ECOR experiments. ECOR on SS-Cu was carried out due to the high CO coverage. Interestingly, SS-Cu showed a lower $j_{C_2H_4}/j_{C_2+}$ for the direct ECOR compared with ECO₂R (Supplementary Figs. 55b,c and 57), indicating that the *CO dimerization to *OCCO may not be the main C-C coupling pathway for ECO₂R on SS-Cu. Then, we calculated two hydrogenation paths of *CO (*CO-to-*CHO and *CO-to-*COH) (Supplementary Fig. 58). The *CO-to-*CHO hydrogenation has less reaction energy than that of *CO-to-*COH. And SS-Cu decreased the reaction energy of *CO-to-*CHO hydrogenation from 0.56 to 0.30 eV (Supplementary Figs. 55d and 58). Thus, we proposed two possible pathways, the unoccupied *CO hydrogenation into *CHO to form 2*CHO (*CHO + *CHO) and the direct coupling of the unoccupied *CO and *CHO to form *COCHO. High uphill reaction energy was required to form two *CHO on the perfect Cu and SS-Cu (Supplementary Fig. 58), which indicates that C-C coupling by *CHO dimerization might not be favorable. In contrast, the coupling of *CO and *CHO requires lower reaction energy, and the reaction energy of the coupling of *CO and *CHO to form *COCHO at the SS-Cu surface (0.77 eV) is less than that of the perfect Cu (0.88 eV). The subsequent hydrogenation of *COCHO-to-*COCH₂O is exergonic for the perfect Cu and SS-Cu. Hence, the hydrogenation of *CO-to-*CHO followed

by the subsequent coupling of the unoccupied $^*\text{CO}$ and $^*\text{CHO}$ to $^*\text{COCHO}$ to $^*\text{COCH}_2\text{O}$ should be the most favorable pathway for the C_2H_4 formation. The DFT results showed SS-Cu would electro-catalyze CO_2 reduction to C_2H_4 more easily than the perfect Cu from the thermodynamics, which may be probably mainly due to the lower reaction energy of $^*\text{COOH}$ adsorption for SS-Cu.

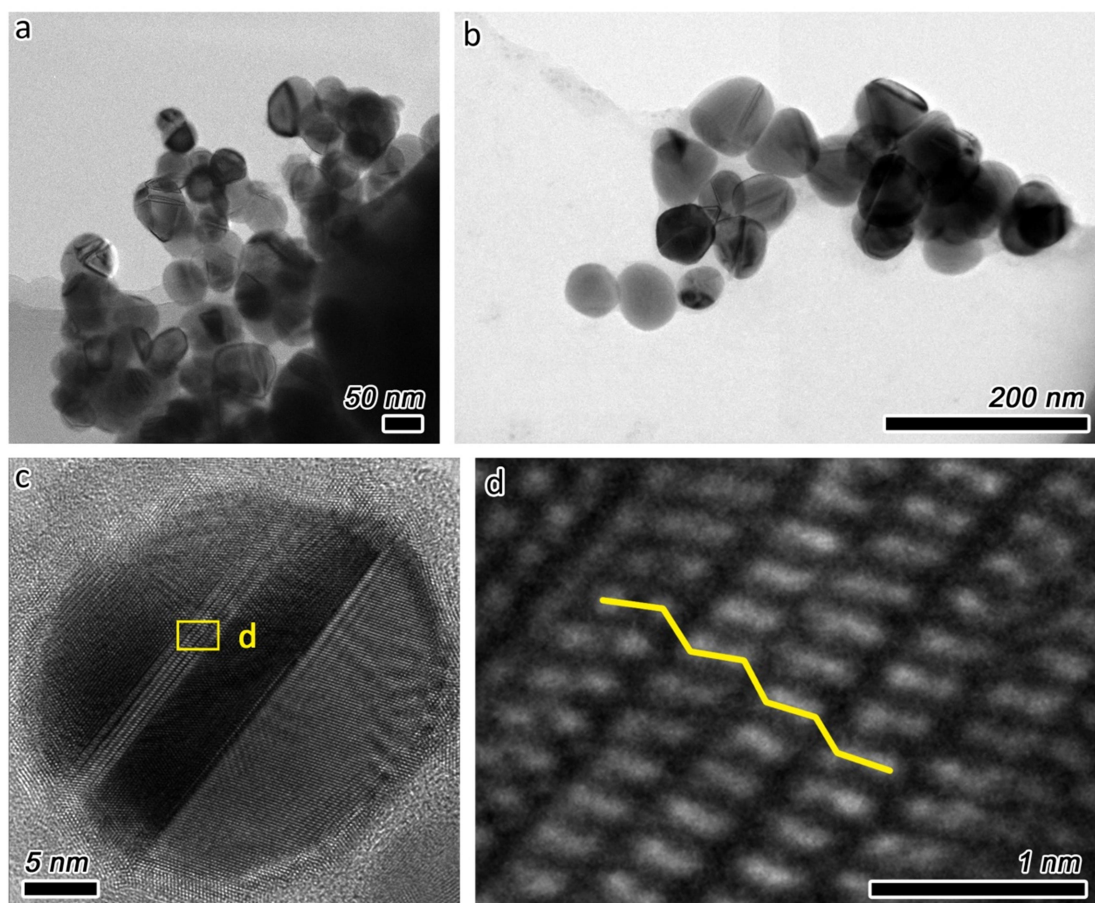
In addition, temperature-programmed desorption (TPD) measurements of CO_2 and CO show that the CO_2/CO adsorption capacities of samples decreased with the increase of treatment temperature of samples ($\text{SS-Cu} > \text{Cu-250} > \text{Cu-350} > \text{Cu-450}$) (Supplementary Fig. 59). The surface Cu atoms with the lower CNs tend to bond/adsorb more CO_2/CO to compensate for the lack of coordination, which could accelerate ECO_2R reaction kinetics. We believe the above thermodynamic and kinetic advantages are ascribed to the effects of the low CN and high tensile strain of SS-Cu.



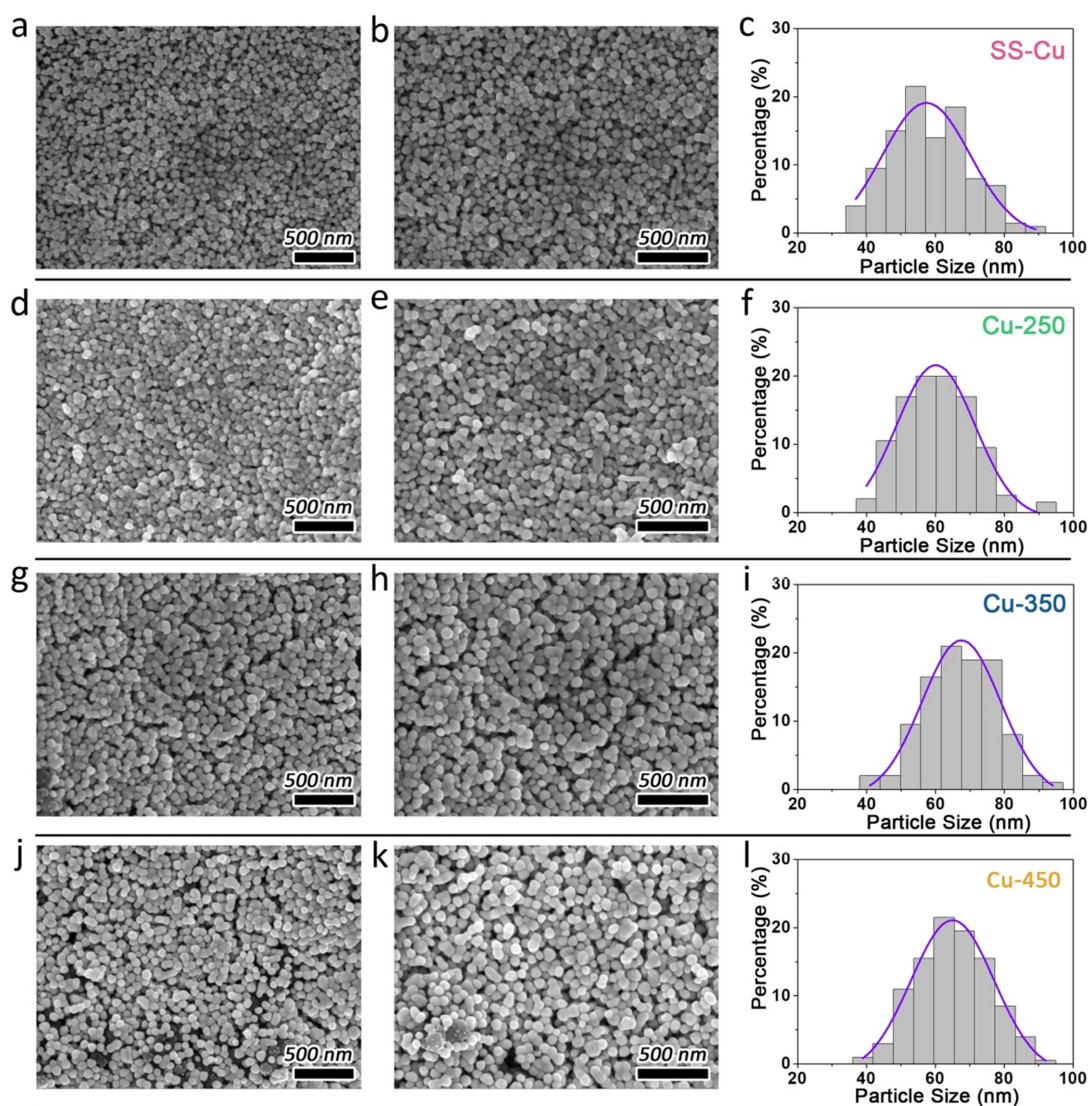
Supplementary Fig. 1 | Comparison of three types of electrolysis systems for ECO₂R. a, AEM system. b, PEM system. c,d, BPM systems under reverse and forward bias, respectively.



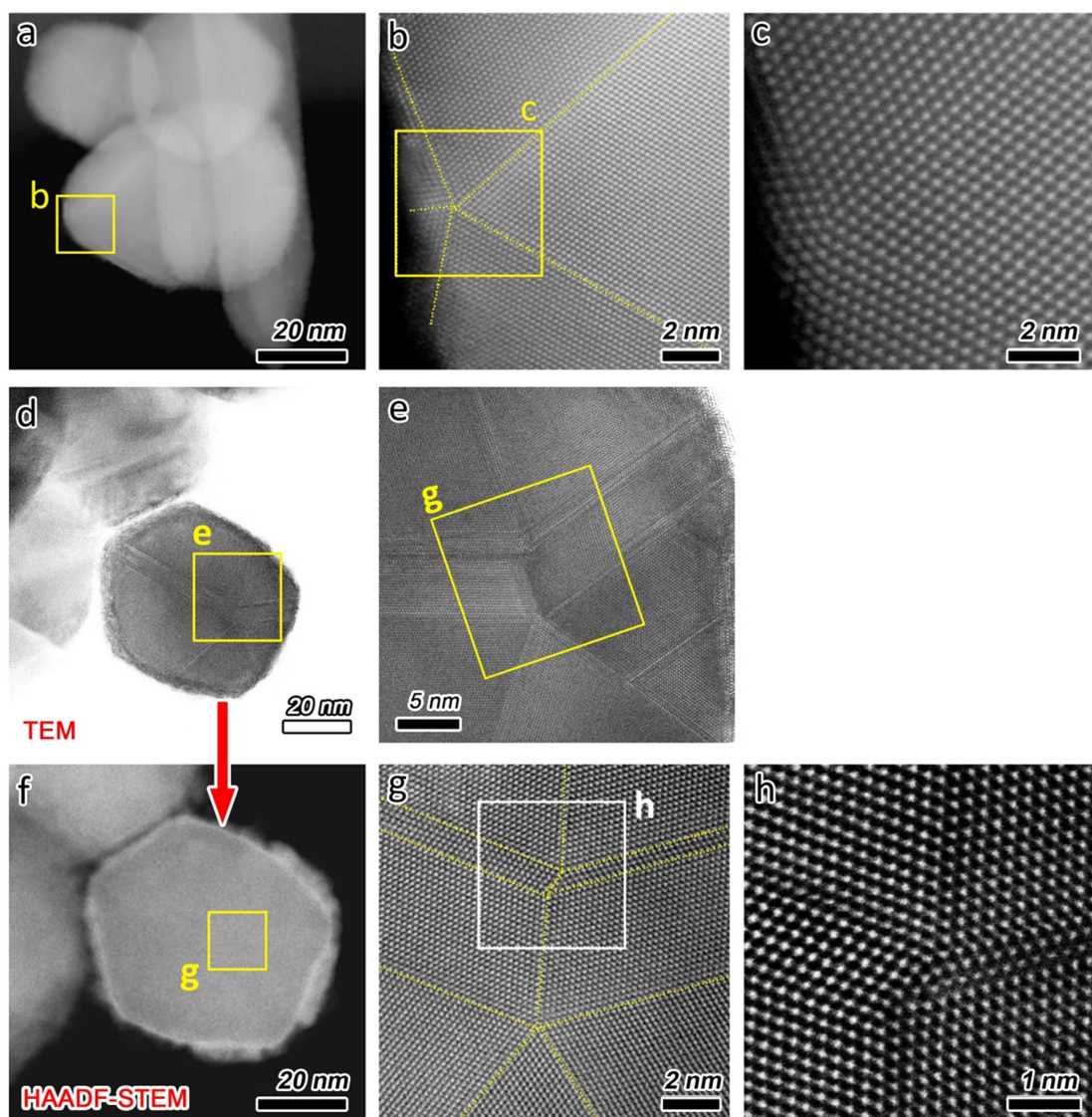
Supplementary Fig. 2 | Stability of ECO₂R-to-C₂H₄ on Cu-based catalysts from literature and SS-Cu in the flow cell or MEA cell with different electrolytes.



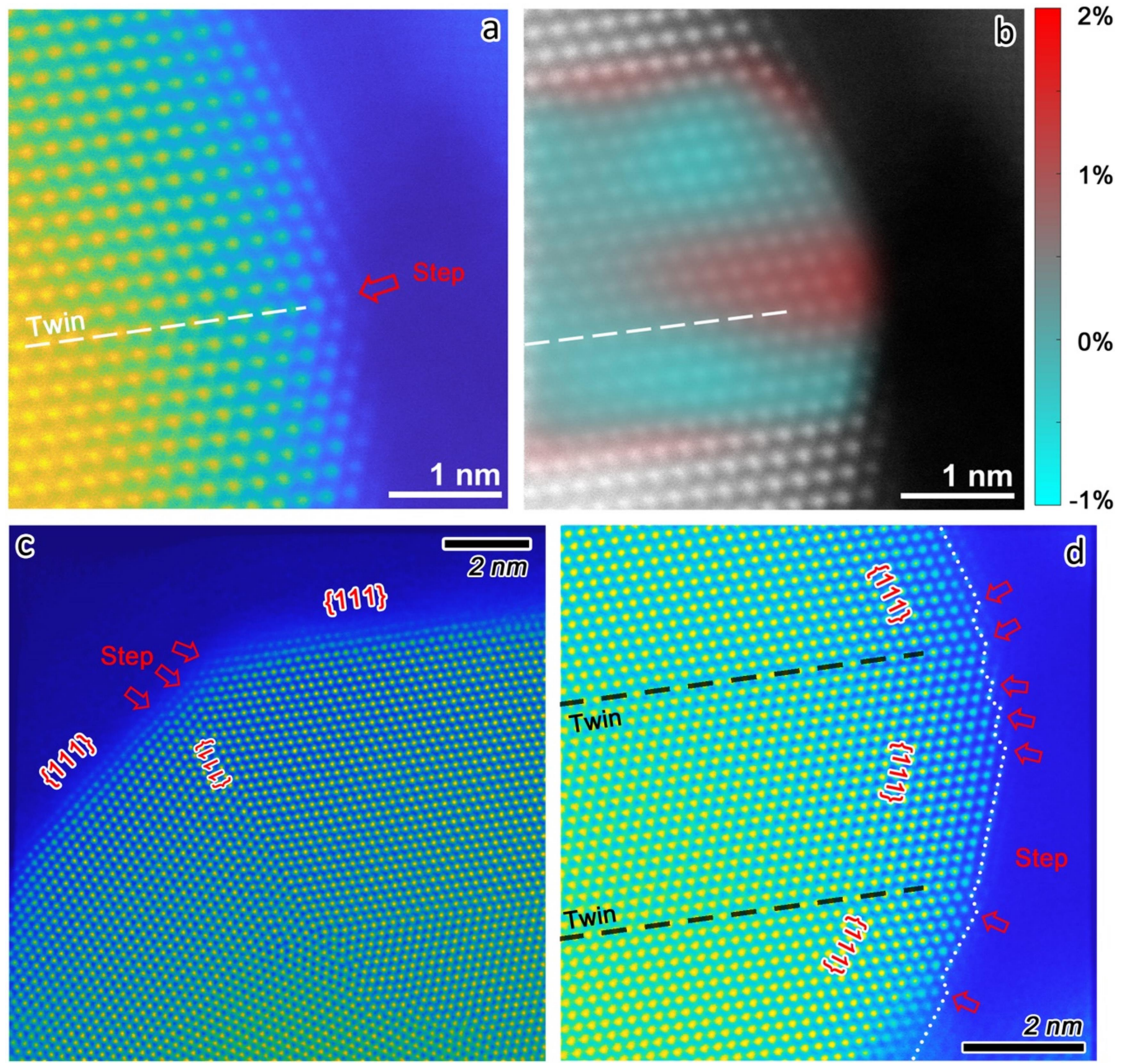
Supplementary Fig. 3 | Fine structure characterization of SS-Cu. a,b, TEM images. c, HRTEM image. d, HAADF-STEM image of stacking faults from the selected area in (c). The yellow line highlights stacking faults.



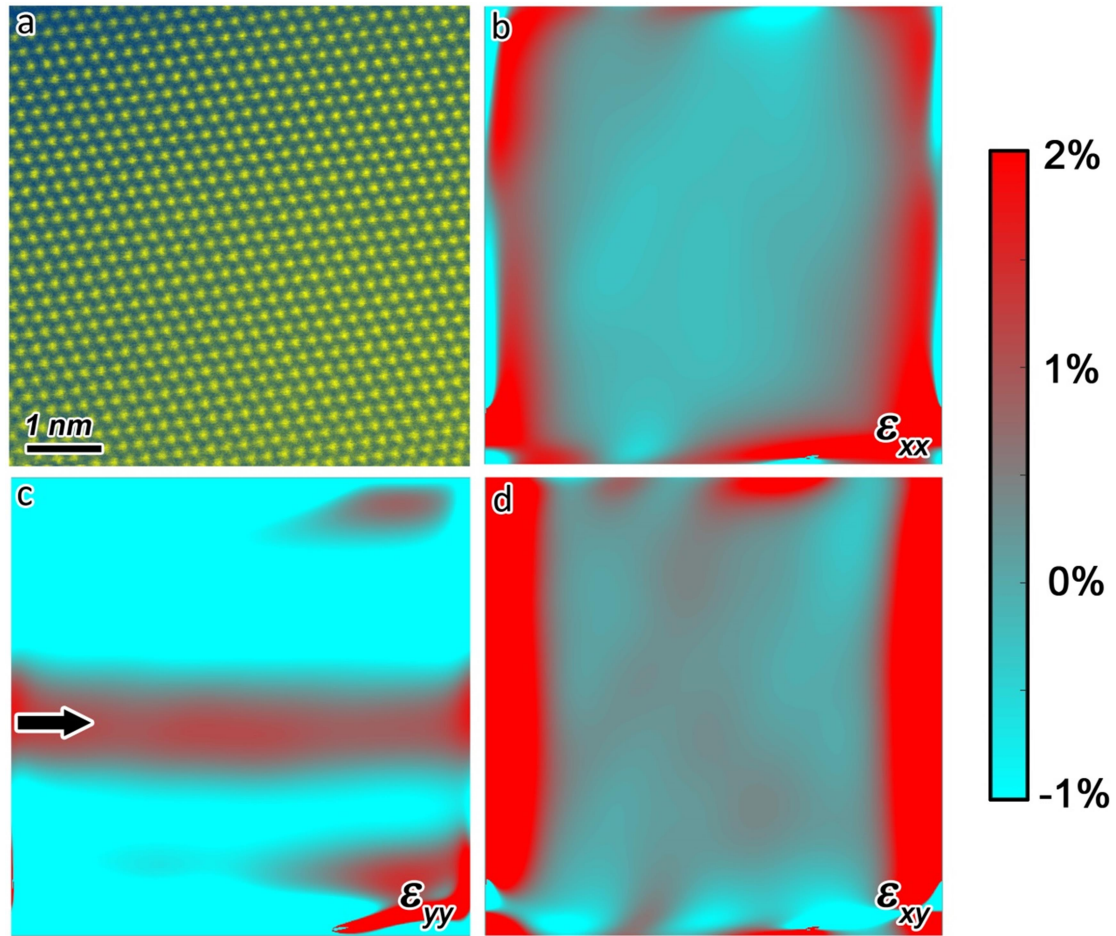
Supplementary Fig. 4 | SEM images and size distributions of samples. a-c, SS-Cu. d-f, Cu-250. g-i, Cu-350. j-l, Cu-450. SS-Cu was annealed at various elevated temperatures to tune stacking faults and grain boundaries (250, 350 and 450°C; Cu-250, Cu-350 and Cu-450).



Supplementary Fig. 5 | Fine structure characterization of SS-Cu. **a,f**, Overview HAADF-STEM images. **b,g**, Atomic-resolution HAADF-STEM images of the selected areas in (a) and (f), respectively. **c,h**, Enlarged atomic-resolution HAADF-STEM images of the selected areas in (b) and (g), respectively. **d,e**, TEM and HRTEM images, respectively. The yellow dashed lines in (b) and (g) highlight the twinning structures.

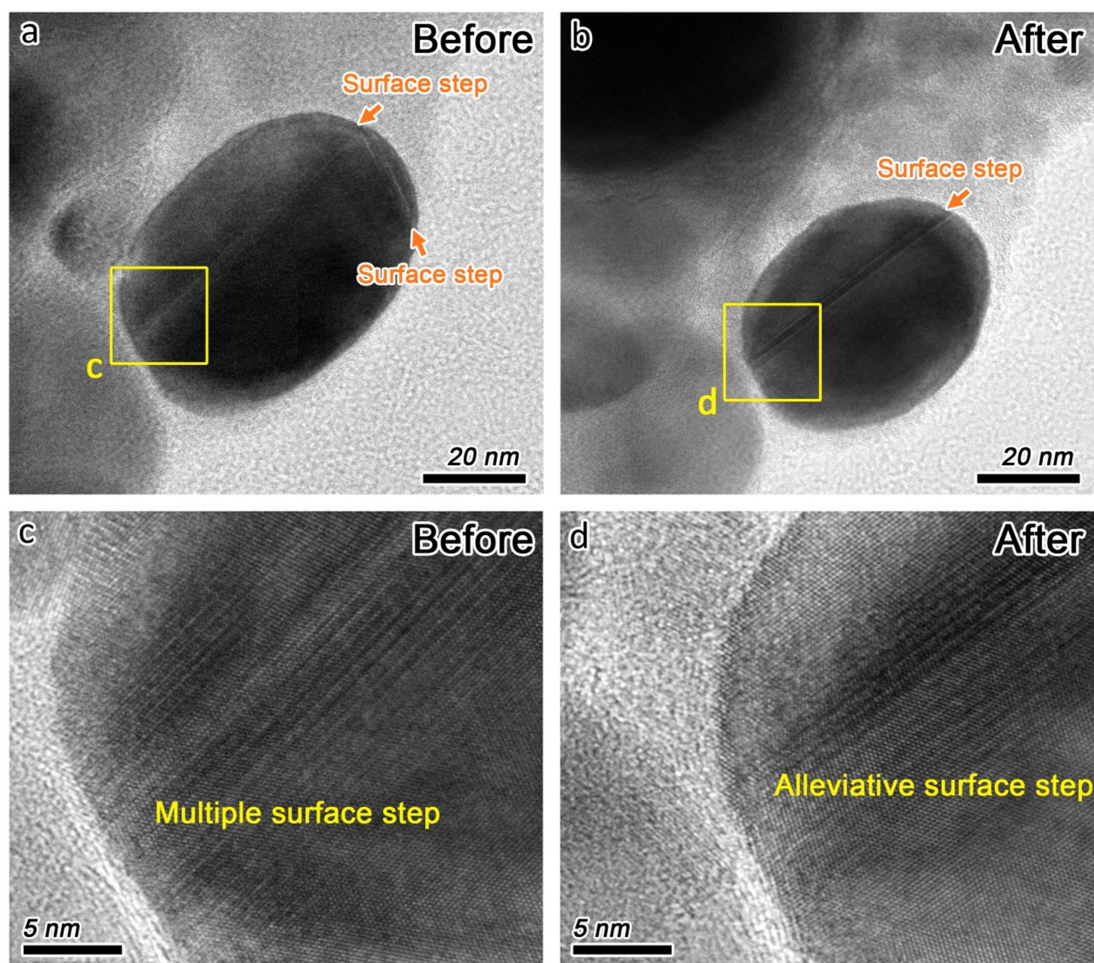


Supplementary Fig. 6 | Analysis of the tensile strain and stepped face of SS-Cu. a, Atomic-resolution HAADF-STEM image showing surface stepped faces induced by a twin boundary along $\{111\}$ as indicated by the white dashed line. **b,** GPA strain mapping on (a) showing tensile strain near the surface exit of the twin boundary. The measured strain is perpendicular to the $\{111\}$ twin boundary. **c,** Atomic-resolution HAADF-STEM image showing stepped faces. **d,** High-resolution atomic-resolution HAADF-STEM image showing stepped faces induced by twin boundaries, both along $\{111\}$ planes as indicated by the black dashed lines.

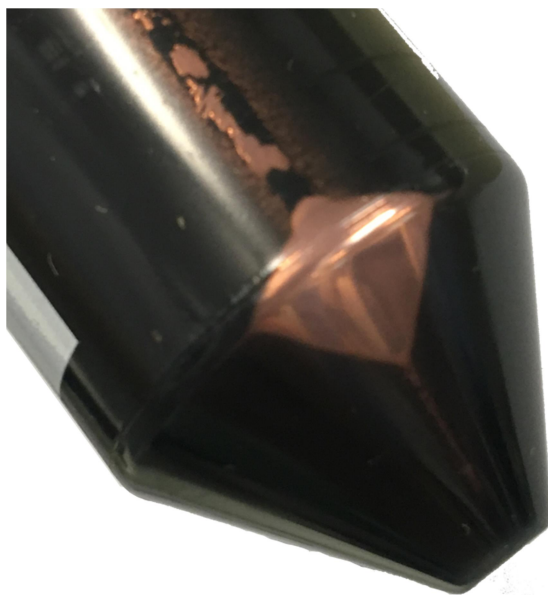


Supplementary Fig. 7 | Analysis of the tensile strain from a defect-free Cu lattice.

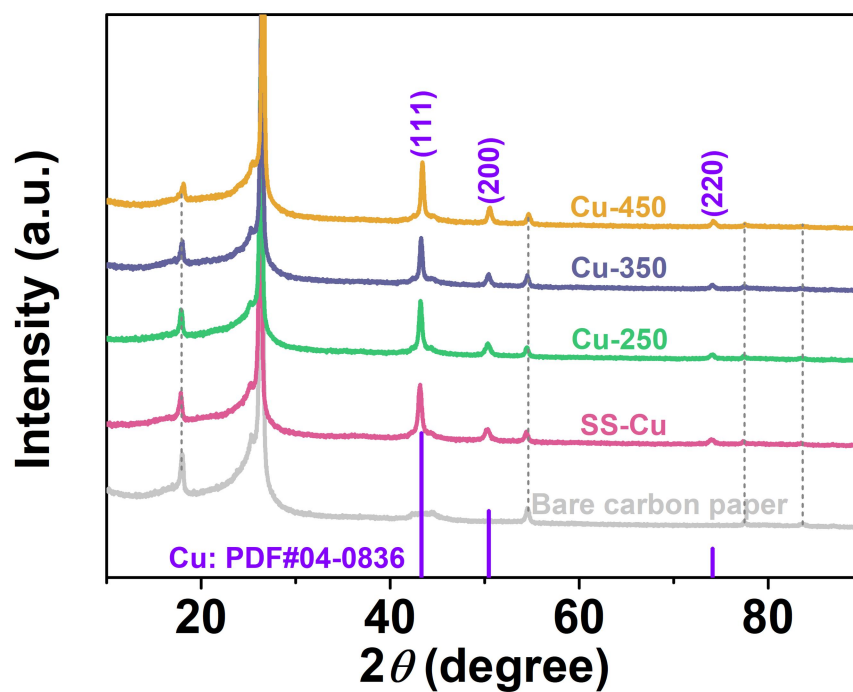
a, Atomic-resolution HAADF-STEM image from a defect-free Cu lattice. **b-d**, GPA strain mapping of (b) ϵ_{xx} , (c) ϵ_{yy} , and (d) ϵ_{xy} on (a) showing negligible strain inside the lattice except for artefacts at the edges of the image. The tensile ϵ_{yy} in the middle of (c), as indicated by an arrow, is due to the sample drift along the vertical direction during STEM image acquisition. It demonstrates the reliability of GPA strain mapping on STEM images.



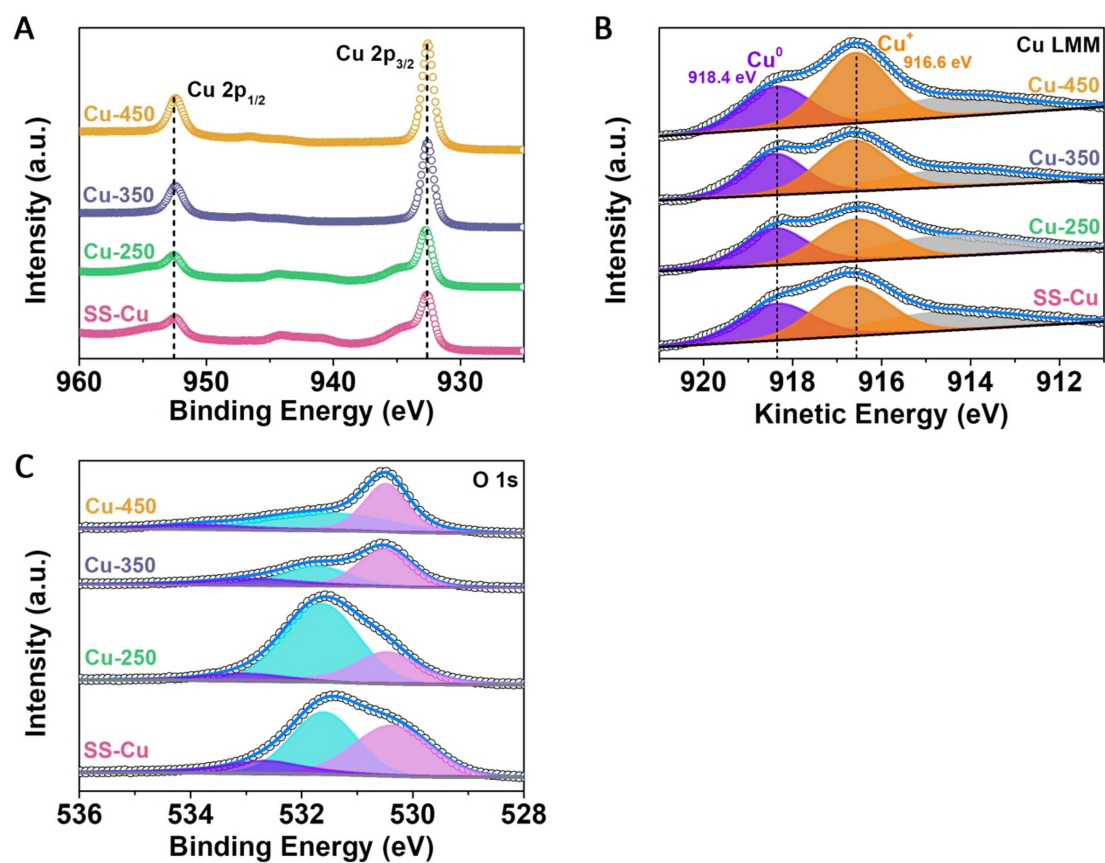
Supplementary Fig. 8 | *In-situ* heating TEM characterization. **a,b**, TEM images of the pristine SS-Cu and the SS-Cu heated at 650°C for 20 min. **c,d**, HRTEM images of the pristine SS-Cu and the SS-Cu heated at 650°C for 20 min. The HRTEM images show that there are ~26 stacking faults in the pristine particle, which are reduced to ~16 after *in-situ* heating, corresponding to a ~38.5% reduction of the stacking fault density. A similar reduction in the stepped face density on the particle surface is expected.



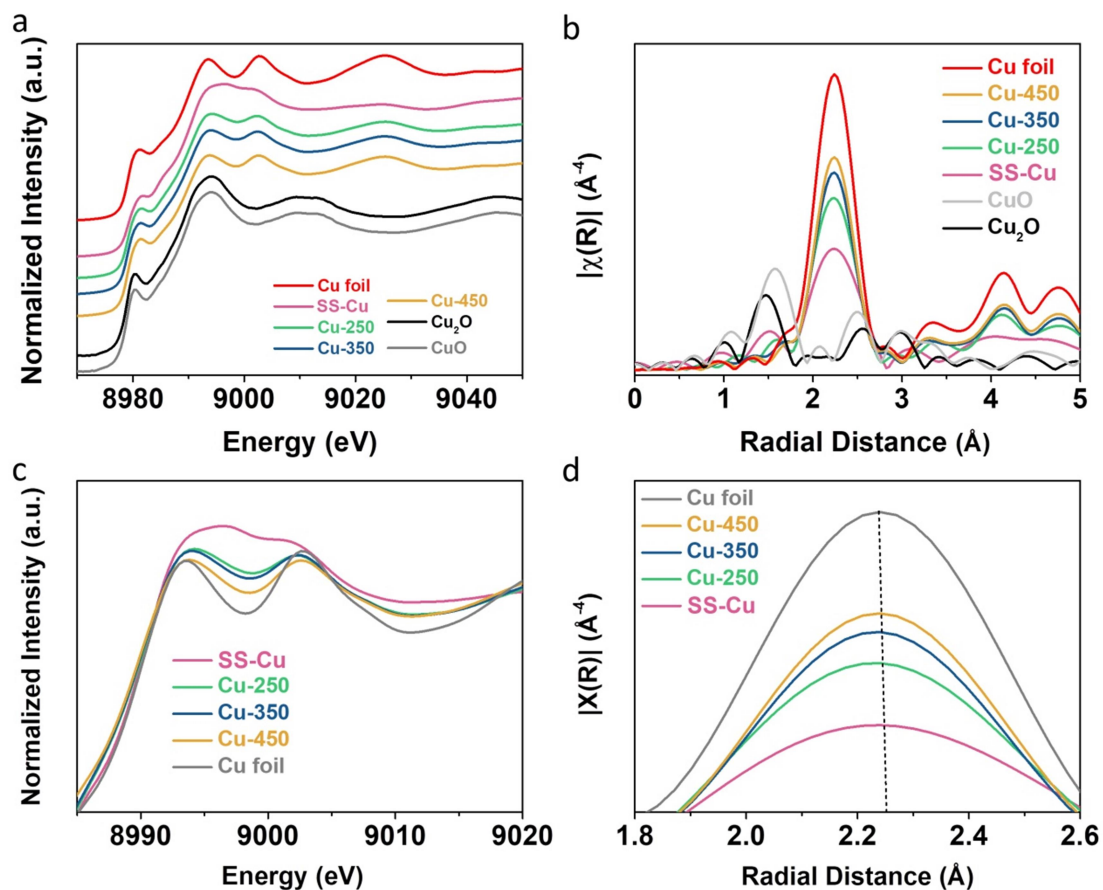
Supplementary Fig. 9 | The digital photograph of SS-Cu nanoparticles after centrifugation.



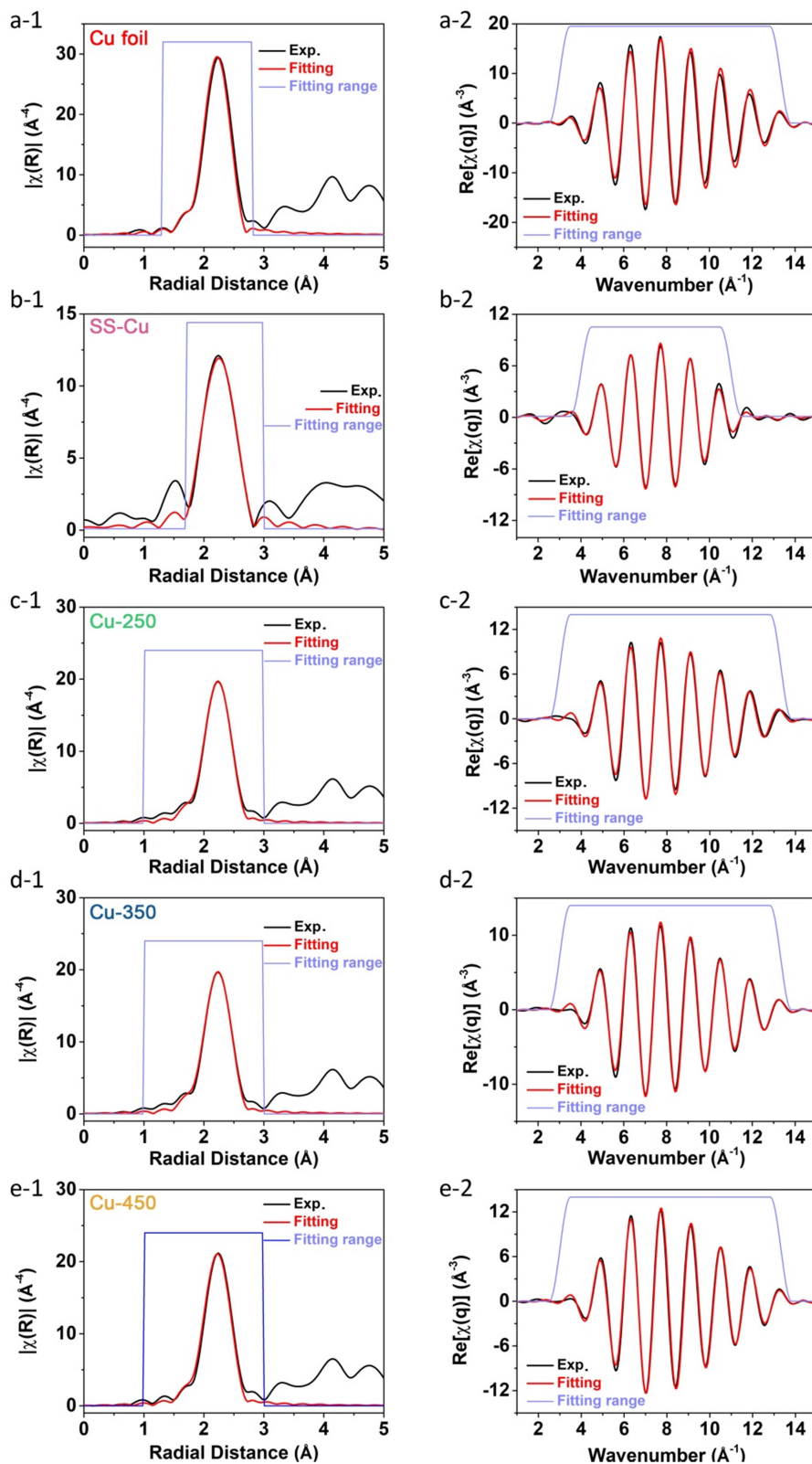
Supplementary Fig. 10 | XRD patterns of SS-Cu, Cu-250, Cu-350 and Cu-450 on the carbon paper, and bare carbon paper.



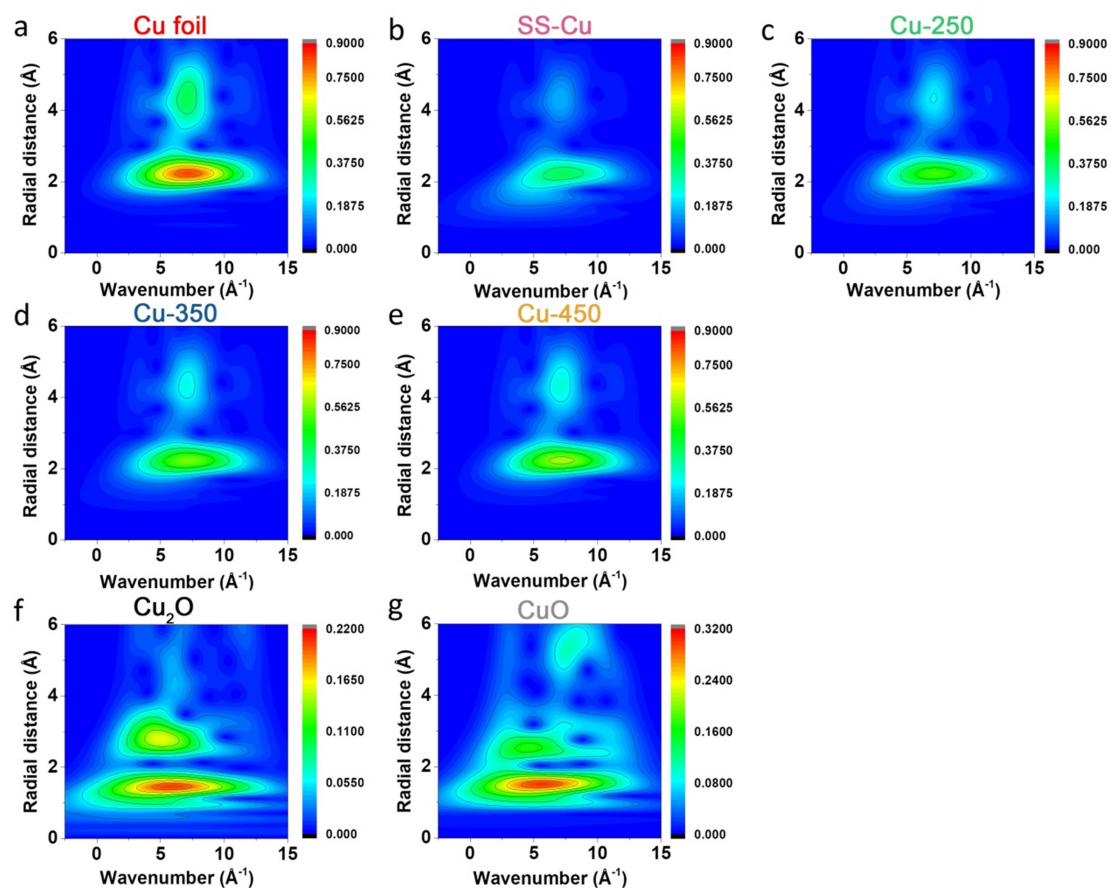
Supplementary Fig. 11 | XPS spectra of SS-Cu, Cu-250, Cu-350 and Cu-450. **a**, Cu 2p XPS spectra. **b**, Cu LMM Auger spectra. **c**, O 1s XPS spectra.



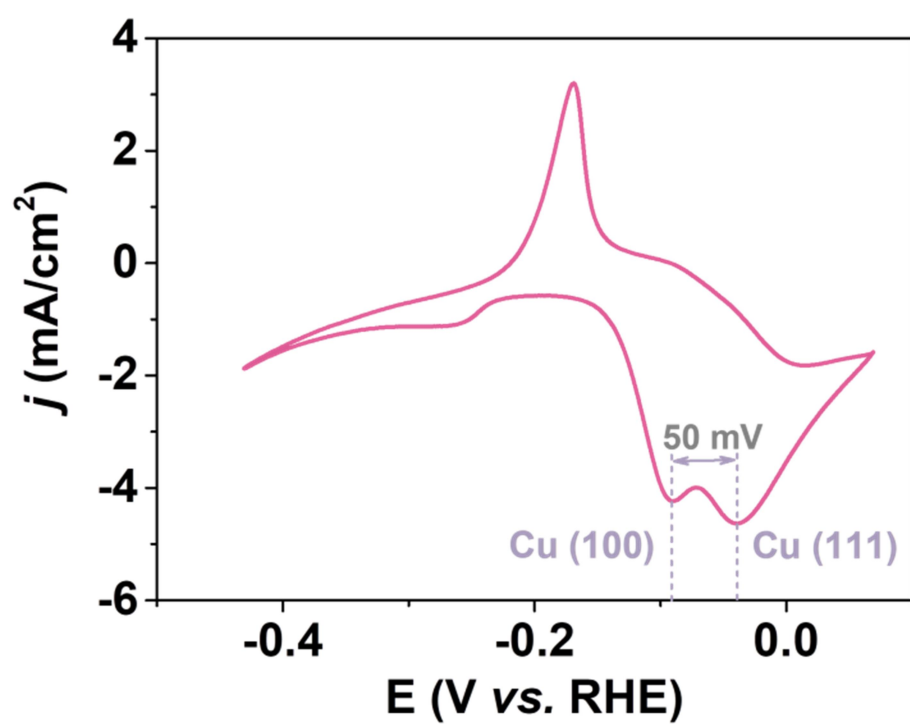
Supplementary Fig. 12 | XAS measurements of SS-Cu, Cu-250, Cu-350 and Cu-450, and the standard Cu foil, CuO and Cu₂O references. a,c, Cu K-edge XANES spectra. b,d, Fourier transform of Cu K-edge EXAFS spectra.



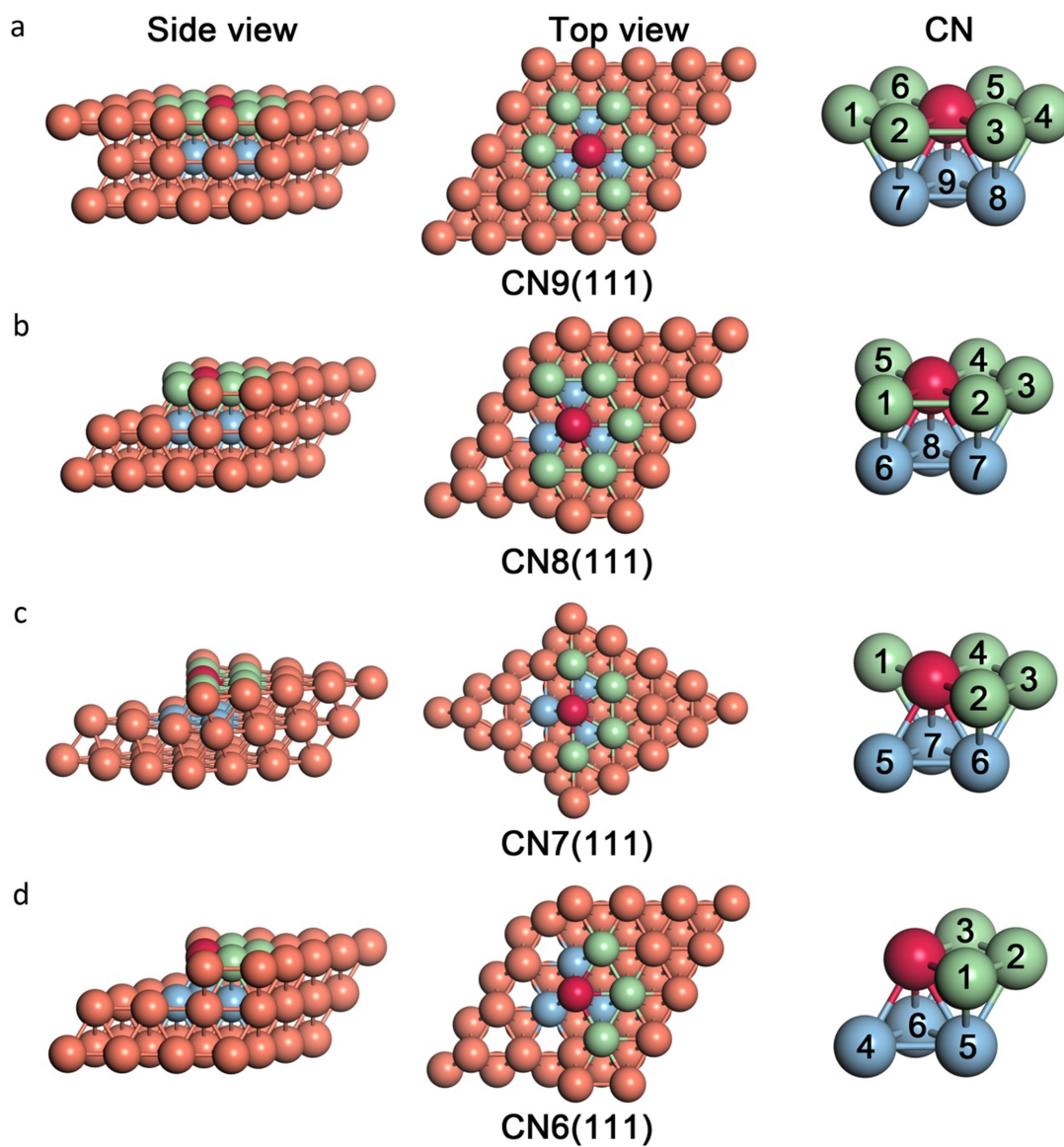
Supplementary Fig. 13 | Cu K-edge EXAFS fitting curves at R and q space, respectively. a, Cu foil reference. b, SS-Cu. c, Cu-250. d, Cu-350. e, Cu-450.



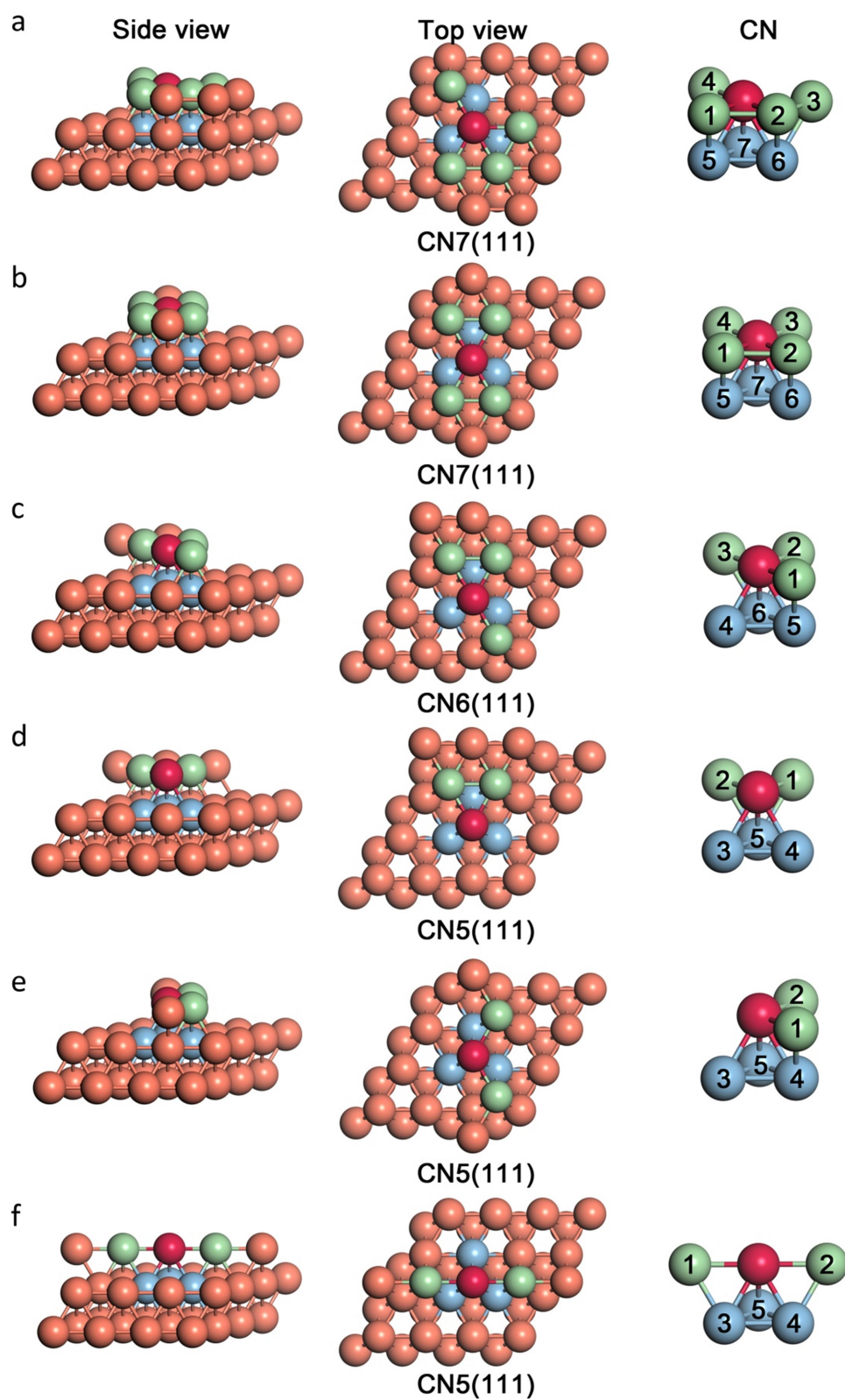
Supplementary Fig. 14 | Two-dimensional plots of wavelet transform EXAFS (2D WT EXAFS). a, Standard Cu foil reference. **b,** SS-Cu. **c,** Cu-250. **d,** Cu-350. **e,** Cu-450. **f,** Standard Cu₂O reference. **g,** Standard CuO reference.



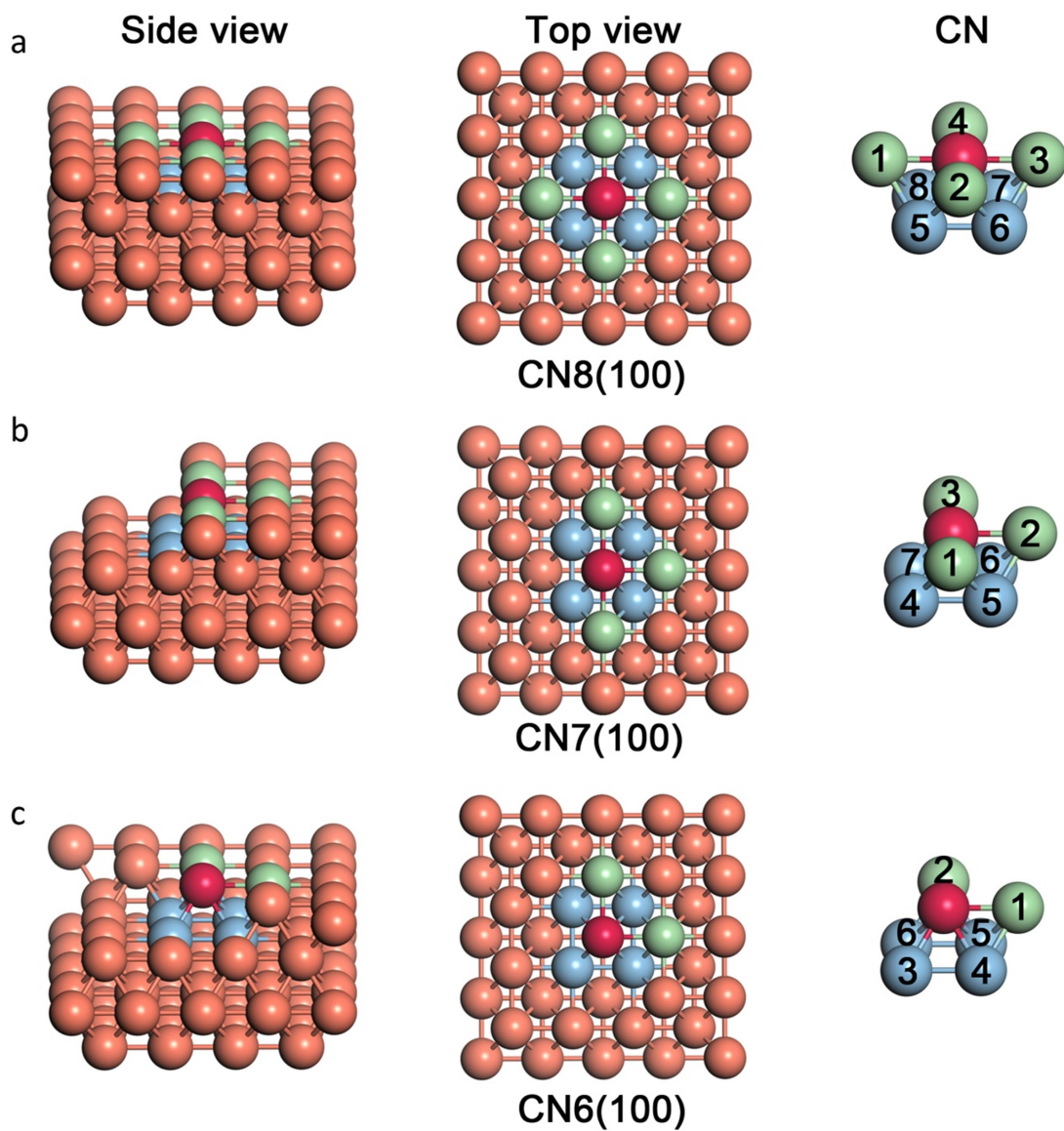
Supplementary Fig. 15 | Exposed facets of SS-Cu determined by Pd-UPD.



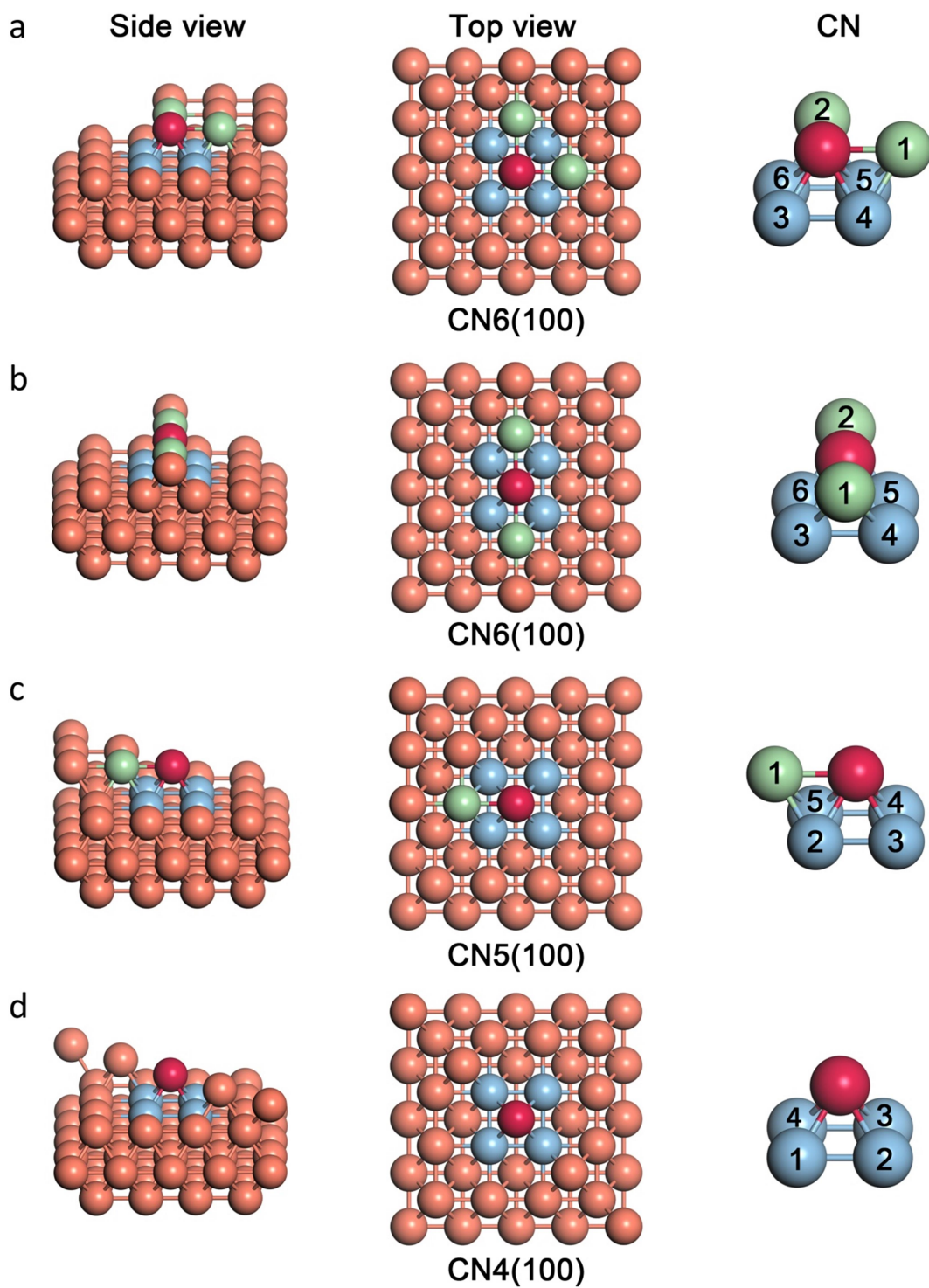
Supplementary Fig. 16 | Atomic models of side view, top view and Cu site with different CNs on Cu(111). a, The perfect Cu(111), CN: 9. b-d, CN: 8, 7 and 6, respectively.



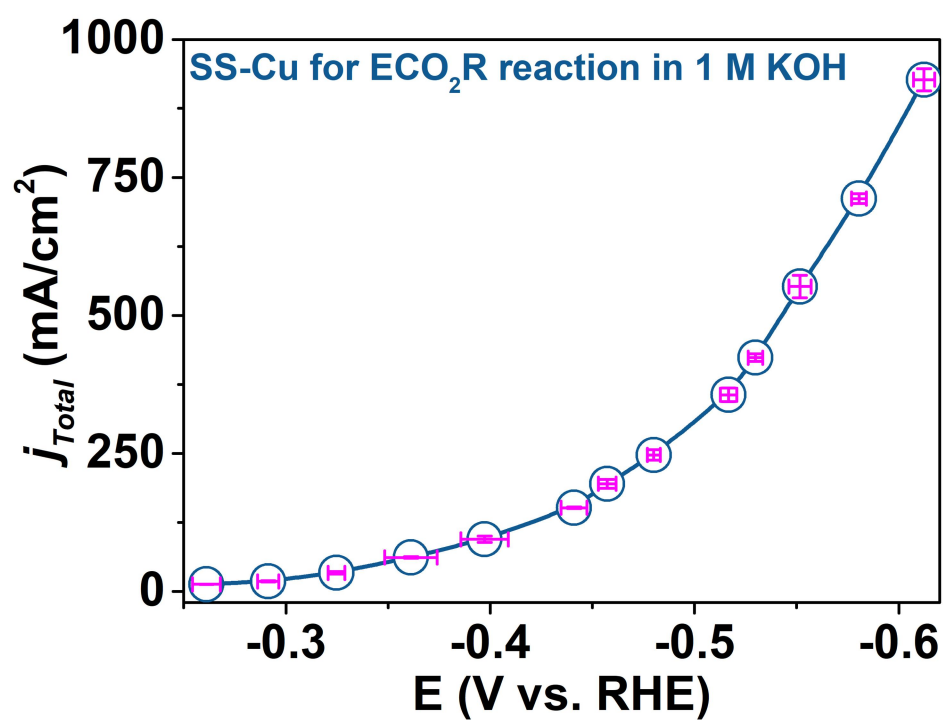
Supplementary Fig. 17 | Atomic models of side view, top view and Cu site with different CNs on Cu(111). a-f, CN: 7, 7, 6, 5, 5 and 5, respectively.



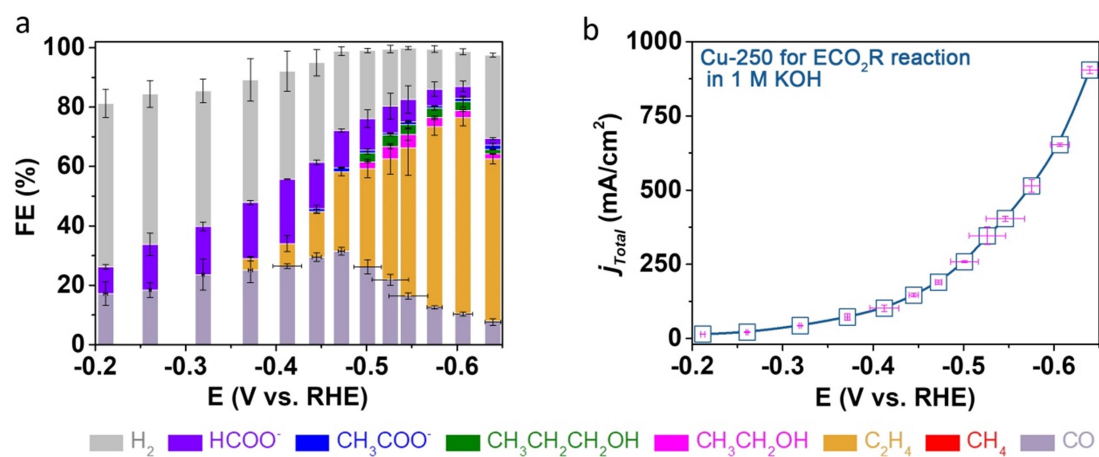
Supplementary Fig. 18 | Atomic models of side view, top view and Cu site with different CNs on Cu(100). a, The perfect Cu(100), CN: 8. b,c, CN: 7 and 6, respectively.



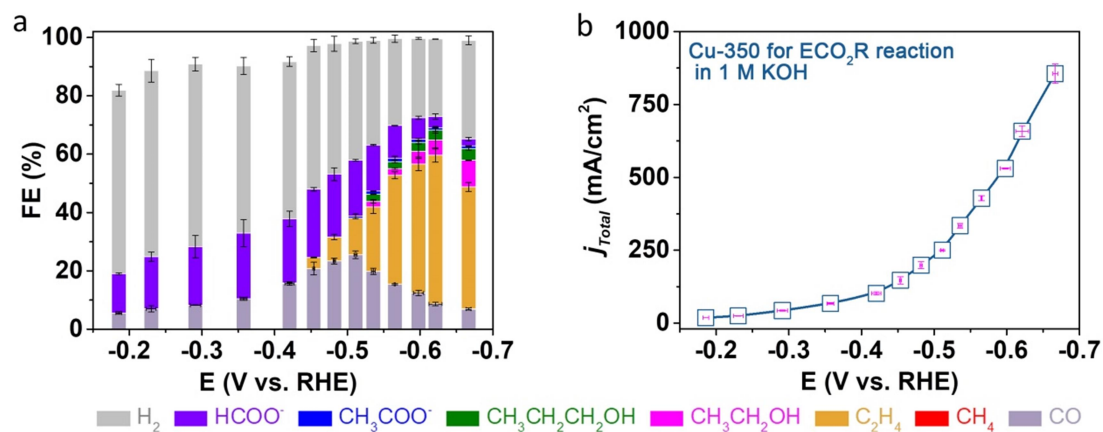
Supplementary Fig. 19 | Atomic models of side view, top view and Cu site with different CNs on Cu(100). a-d, CN: 6, 6, 5 and 4, respectively.



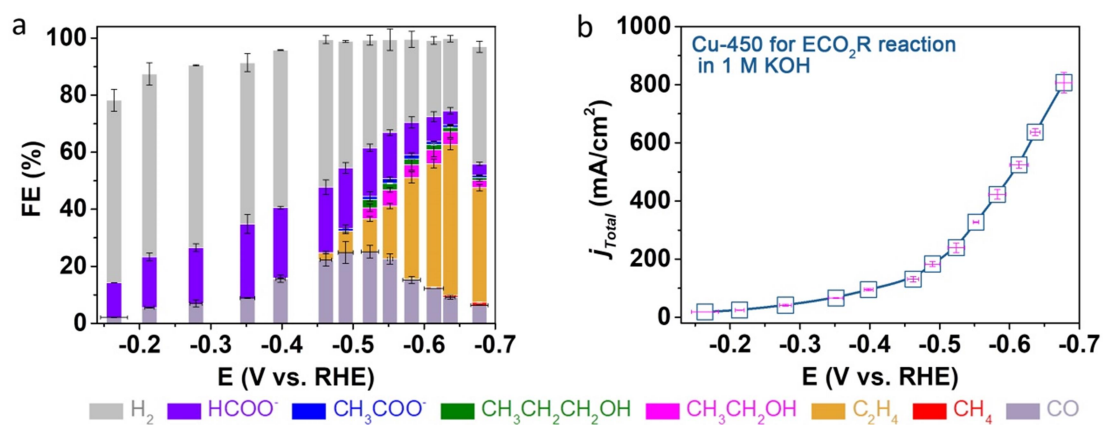
Supplementary Fig. 20 | The total current density of ECO₂R under different applied potentials over SS-Cu in a flow cell with 1 M KOH as the electrolyte. Values are means and error bars indicate SD (n = 3 replicates).



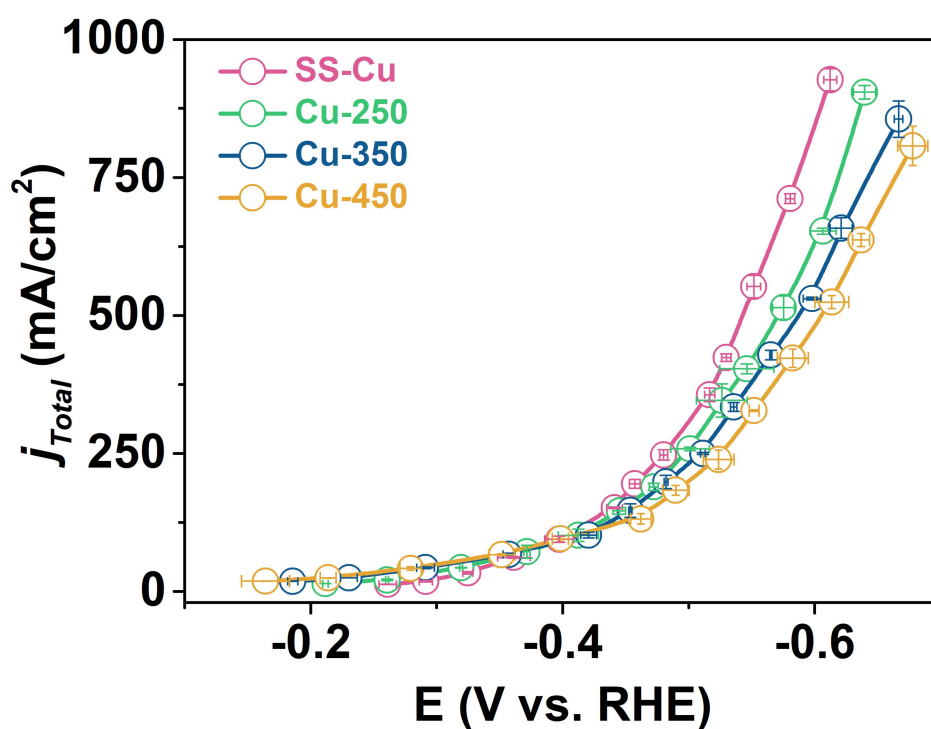
Supplementary Fig. 21 | ECO₂R performance on Cu-250 under different applied potentials in a flow cell with 1 M KOH as the electrolyte. a, FEs toward ECO₂R products. b, Total current density. Values are means and error bars indicate SD (n = 3 replicates).



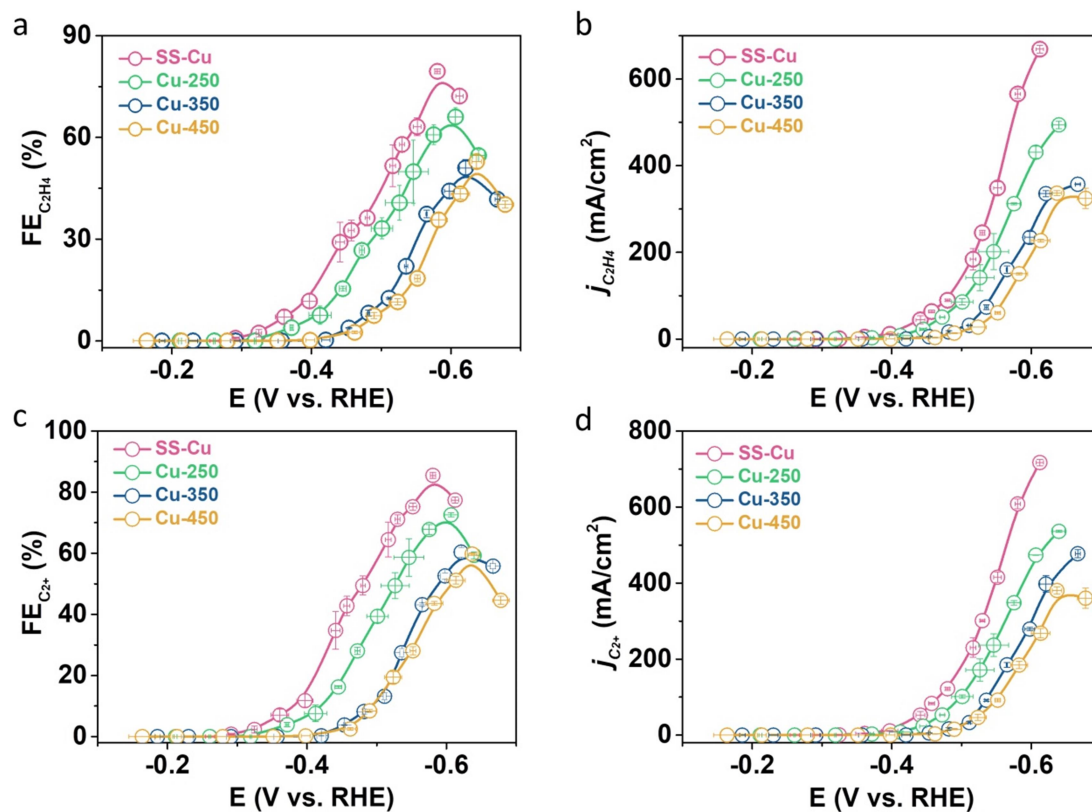
Supplementary Fig. 22 | ECO₂R performance on Cu-350 under different applied potentials in a flow cell with 1 M KOH as the electrolyte. a, FEs toward ECO₂R products. b, Total current density. Values are means and error bars indicate SD (n = 3 replicates).



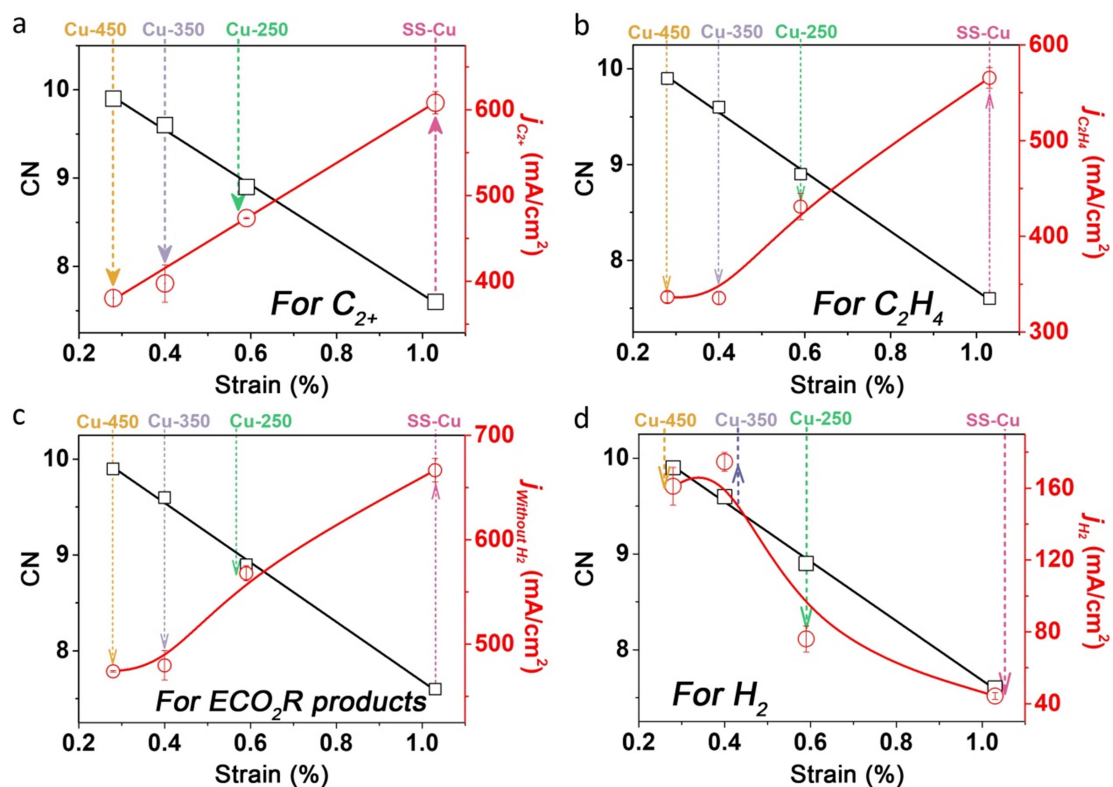
Supplementary Fig. 23 | ECO₂R performance on Cu-450 under different applied potentials in a flow cell with 1 M KOH as the electrolyte. a, FEs toward ECO₂R products. b, Total current density. Values are means and error bars indicate SD (n = 3 replicates).



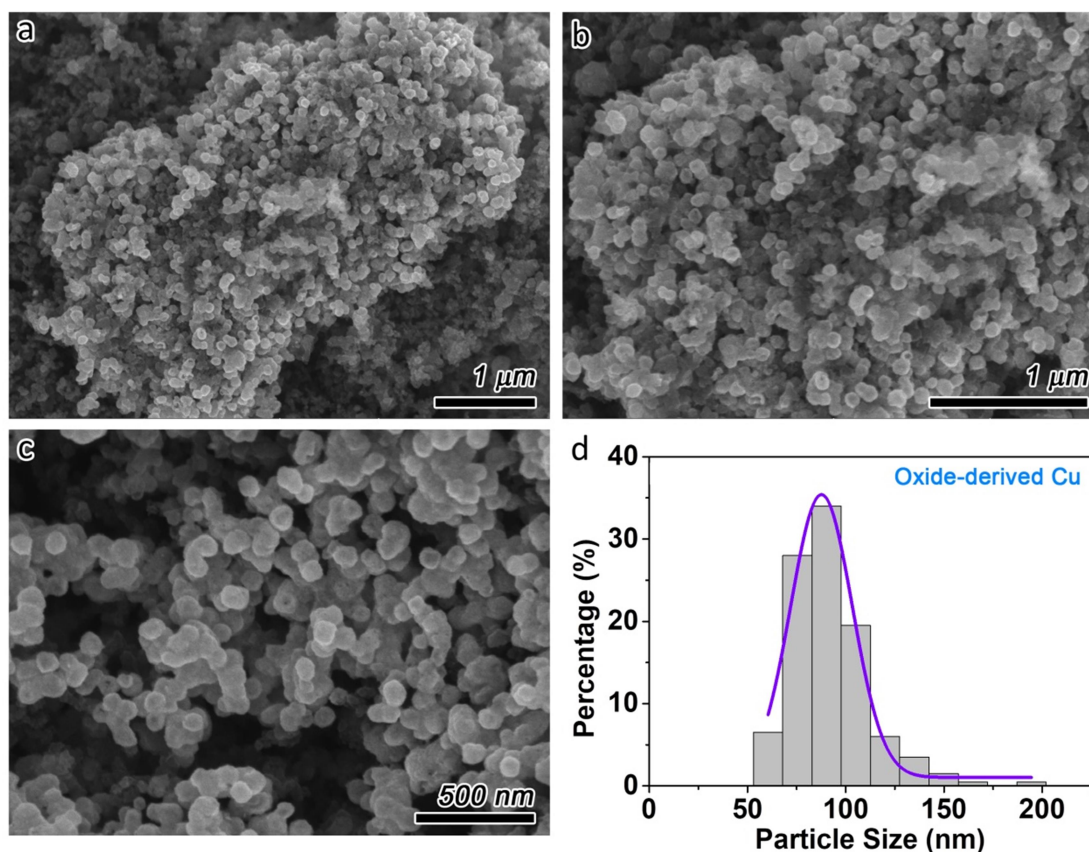
Supplementary Fig. 24 | Comparison of total current densities on SS-Cu, Cu-250, Cu-350 and Cu-450 for the ECO_2R reaction in a flow cell with 1 M KOH as the electrolyte under a range of applied potentials. Values are means and error bars indicate SD ($n = 3$ replicates).



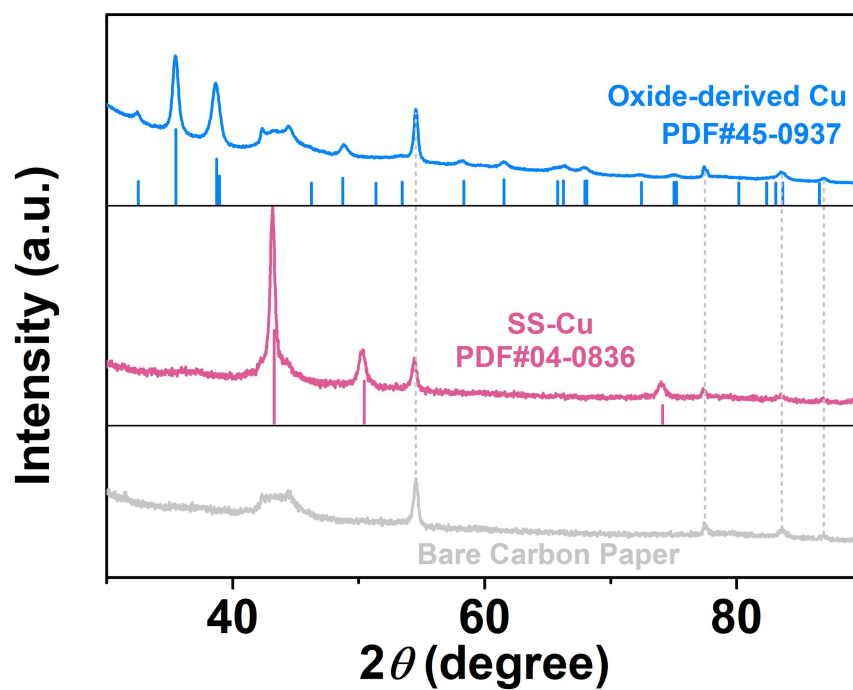
Supplementary Fig. 25 | Comparisons of FEs and partial current densities toward C₂H₄ and C₂⁺ products on SS-Cu, Cu-250, Cu-350 and Cu-450 for the ECO₂R reaction in a flow cell with 1 M KOH as the electrolyte under a range of applied potentials. a,c, FEs toward C₂H₄ and C₂⁺ products, respectively. b,d, Partial current densities of C₂H₄ and C₂⁺ products, respectively. Values are means and error bars indicate SD (n = 3 replicates).



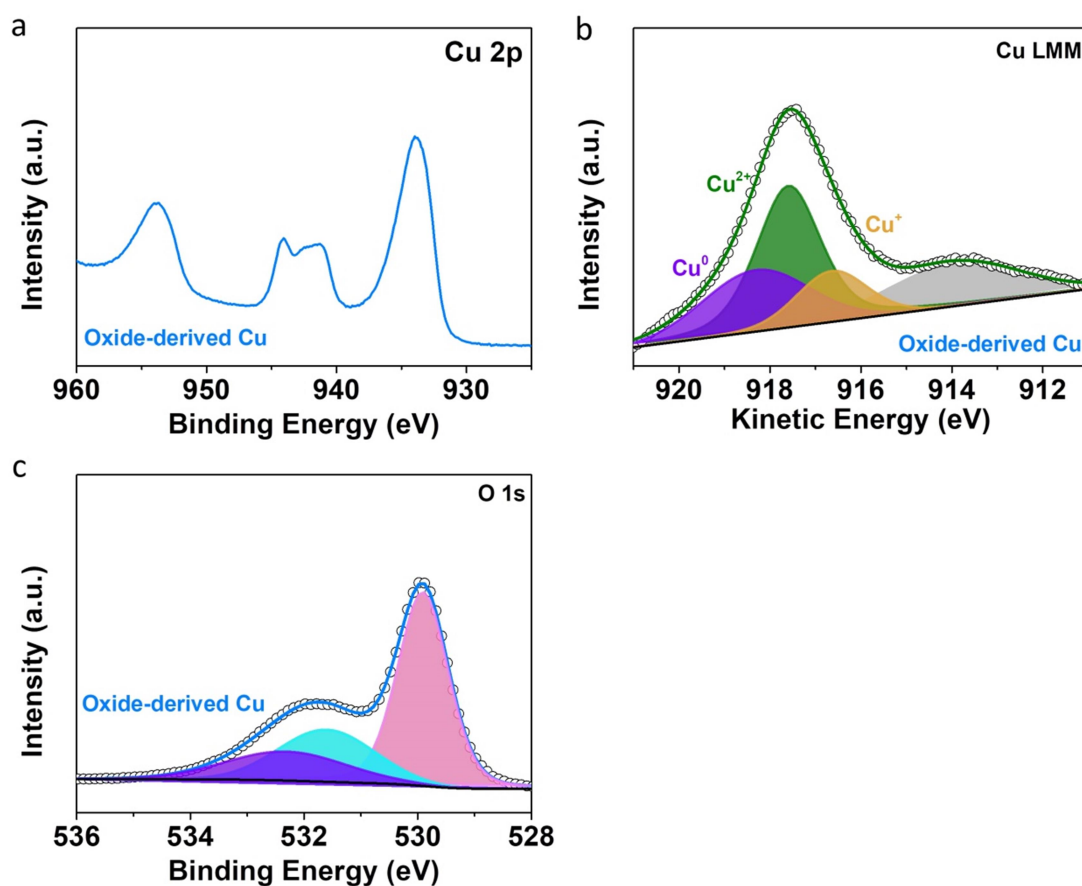
Supplementary Fig. 26 | Relationships between strain, CN and the peak $j_{C_{2+}}$ (a), $j_{C_2H_4}$ (b), $j_{without H_2}$ (c) and j_{H_2} (d) for the ECO₂R reaction in a flow cell with 1 M KOH as the electrolyte. Values are means and error bars indicate SD (n = 3 replicates).



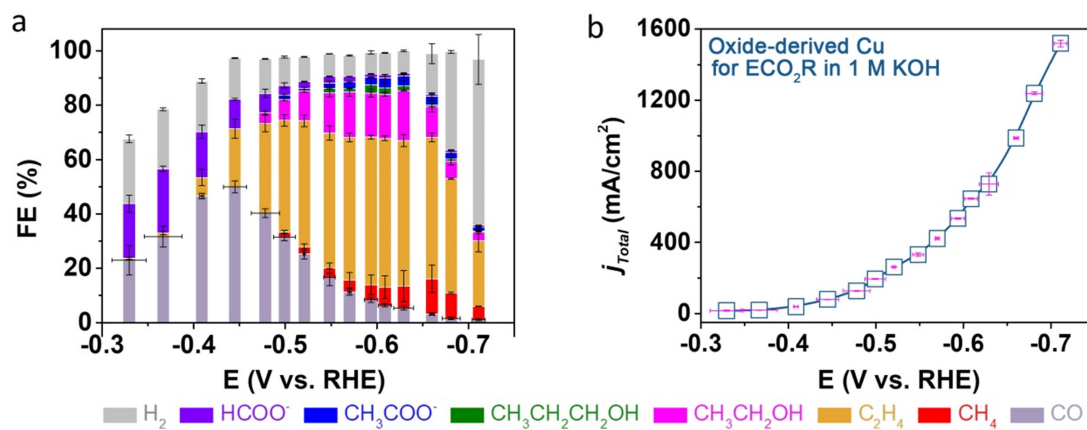
Supplementary Fig. 27 | SEM images (a-c) and size distribution (d) of the oxide-derived Cu. To decouple the effect of the oxidation state ($\text{Cu}^+/\text{Cu}^{2+}$) on ECO_2R performance, we further prepared oxide-derived Cu based on SS-Cu (Supplementary Figs. 27-29). Compared with SS-Cu, the oxide-derived Cu barely showed any improvement in ECO_2R performance on neither FEs nor current densities (Supplementary Figs. 30-32), which mirrored that oxide-derived Cu might not be a crucial factor that determines ECO_2R performance in this system.



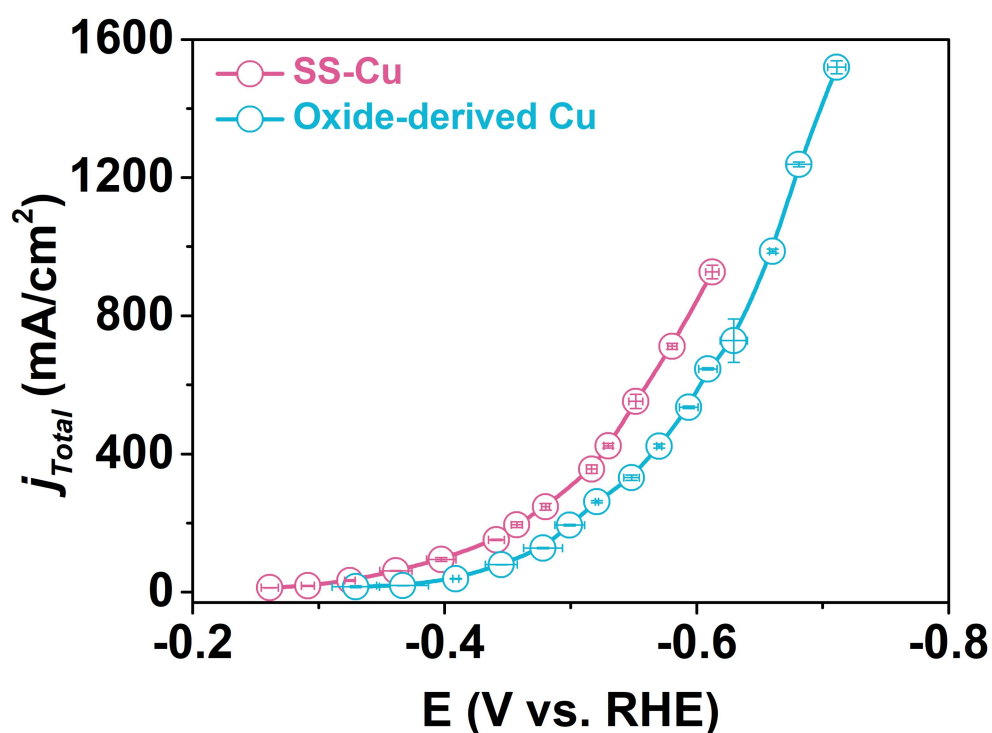
Supplementary Fig. 28 | XRD patterns of SS-Cu, oxide-derived Cu on the carbon paper and bare carbon paper.



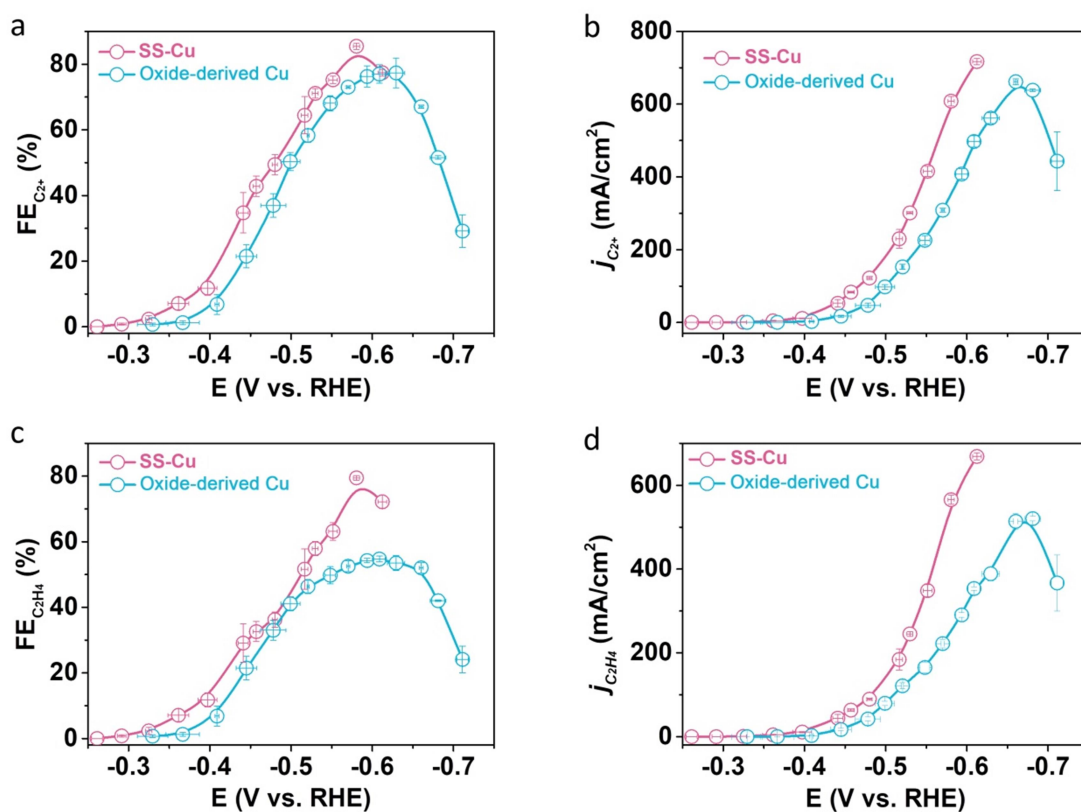
Supplementary Fig. 29 | XPS spectrum of the oxide-derived Cu. **a**, Cu 2p XPS spectrum. **b**, Cu LMM Auger spectrum. **c**, O 1s XPS spectrum.



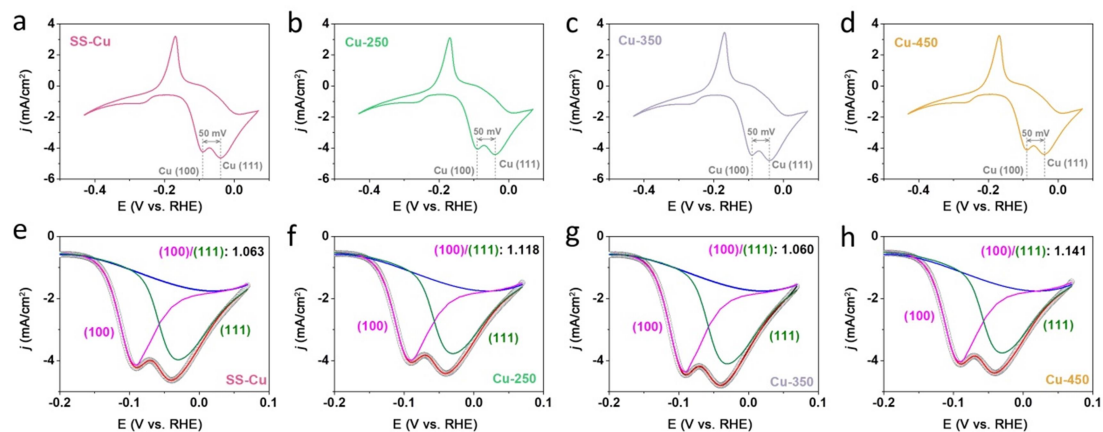
Supplementary Fig. 30 | ECO₂R performance on the oxide-derived Cu under different applied potentials in 1 M KOH. a, FEs toward ECO₂R products. b, Total current density. Values are means and error bars indicate SD (n = 3 replicates).



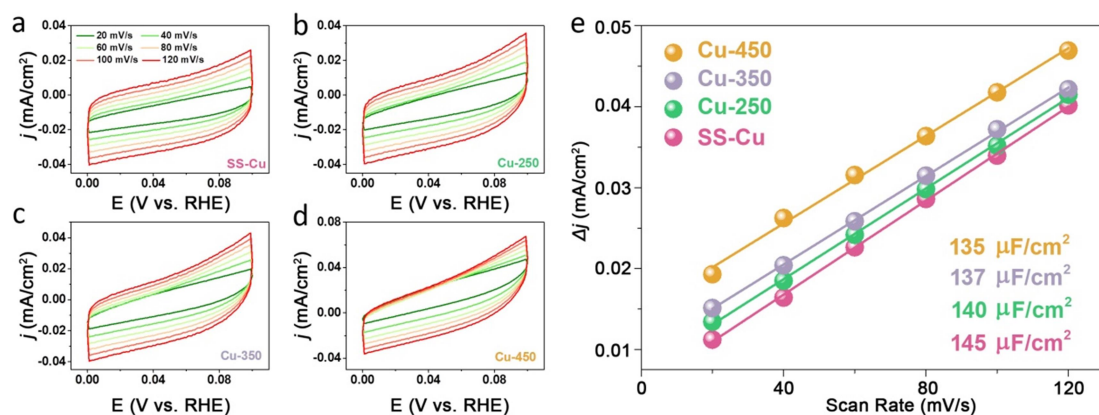
Supplementary Fig. 31 | Comparison of total current densities on SS-Cu and oxide-derived Cu for the ECO₂R reaction in a flow cell with 1 M KOH as the electrolyte under a range of applied potentials. Values are means and error bars indicate SD (n = 3 replicates).



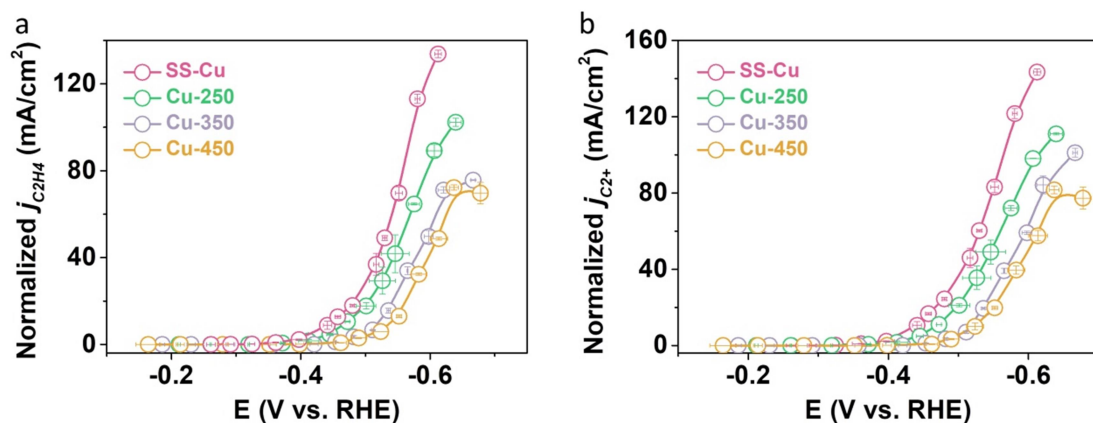
Supplementary Fig. 32 | Comparisons of the ECO₂R performance on SS-Cu and oxide-derived Cu in a flow cell with 1 M KOH as the electrolyte under a range of applied potentials. a,c, Comparisons of FEs toward C₂₊ (a) and C₂H₄ (c), respectively. **b,d**, Comparisons of partial current densities of C₂₊ (b) and C₂H₄ (d), respectively. Values are means and error bars indicate SD (n = 3 replicates).



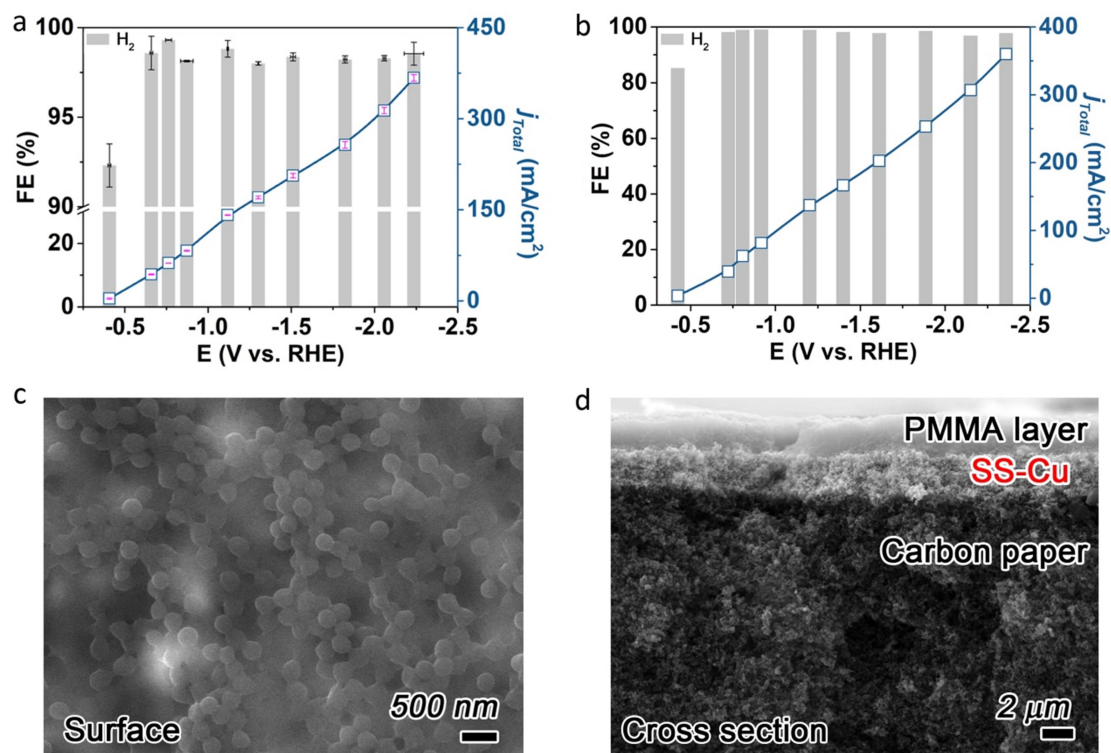
Supplementary Fig. 33 | (100)/(111) ratios of samples determined by Pd-UPD. a-d, SS-Cu, Cu-250, Cu-350 and Cu-450, respectively. **e-h,** (100) and (111) contents of SS-Cu, Cu-250, Cu-350 and Cu-450, respectively. The (100)/(111) ratios of samples showed no relation between the annealing temperature and the (100)/(111) surface population ratio.



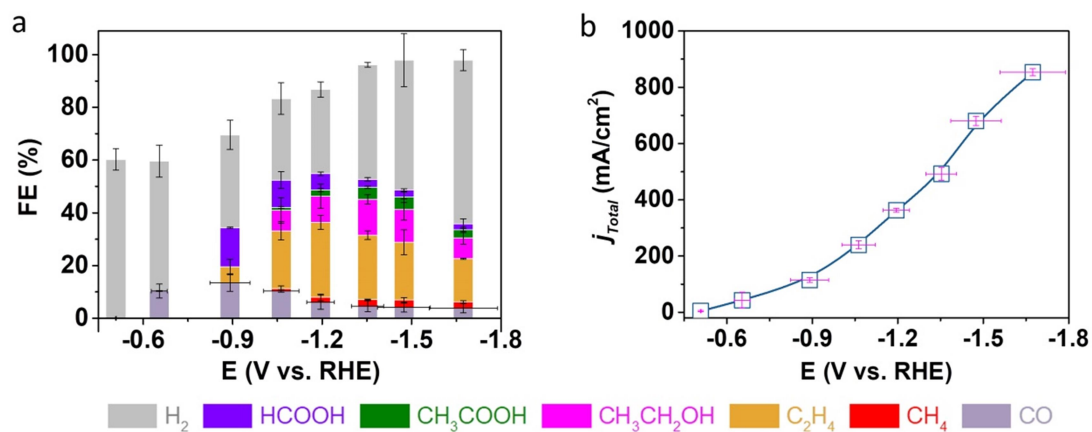
Supplementary Fig. 34 | ECSA measurements of samples. a-d, Cyclic voltammetry curves with various scan rates from 20 to 120 mV/s of SS-Cu, Cu-250, Cu-350 and Cu-450, respectively. e, Double-layer capacitance (C_{dl}) of samples. The C_{dl} was estimated at 0.05 V. Electrochemical surface areas (ECSAs) of samples gradually decreased with the increase of annealing temperature (Cu-450 < Cu-350 < Cu-250 < SS-Cu) due to the increase of CN and decrease of tensile strain, caused by the decrease/absence of stacking faults and grain boundaries.



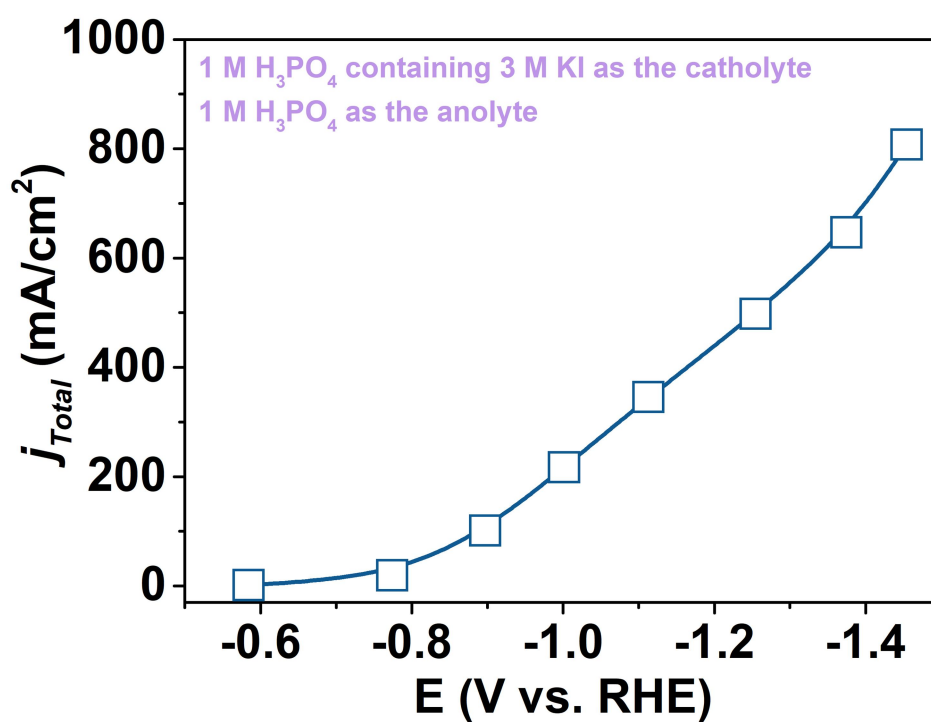
Supplementary Fig. 35 | Comparisons of the ECSA normalized current densities of C_2H_4 and C_{2+} for all samples. **a**, ECSA normalized the current densities of C_2H_4 . **b**, ECSA normalized the current densities of C_{2+} . The ECSA normalized current density was corrected from geometric current density by a factor of C_{dl}/C_{Cu} , where C_{Cu} is the capacitance of polycrystalline Cu foil ($29 \mu F/cm^2$)^{S38}. Although ECSAs of samples gradually decreased, ECSA normalized partial current densities of C_2H_4 and C_{2+} followed the same trend as the geometric partial current densities ($j_{C_2H_4}$ and $j_{C_{2+}}$). Values are means and error bars indicate SD (n = 3 replicates).



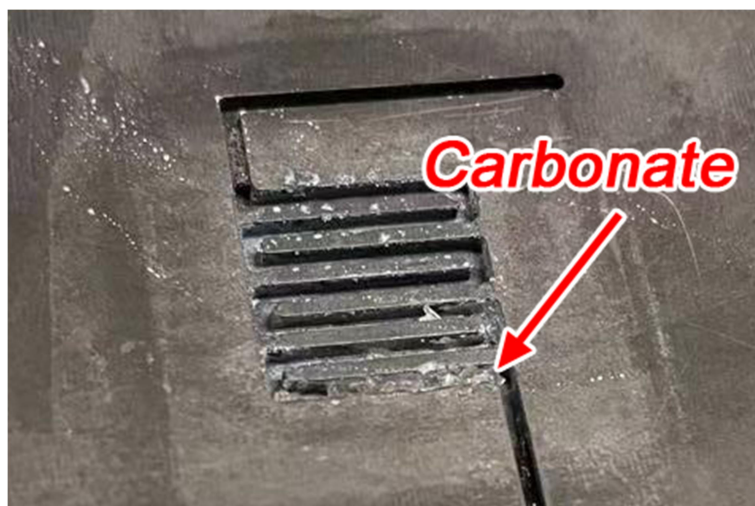
Supplementary Fig. 36 | ECO₂R performance on SS-Cu and SS-Cu/PMMA in a flow cell with 1 M H₃PO₄ as the electrolyte. **a, The FE and total current density on SS-Cu under a range of applied potentials, no ECO₂R product, just H₂. Values are means and error bars indicate SD (n = 3 replicates). **b**, The FE and total current density on SS-Cu/PMMA under a range of applied potentials, no ECO₂R product, just H₂. **c**, SEM image of the surface of SS-Cu/PMMA. **d**, Cross-sectional SEM image of SS-Cu/PMMA.**



Supplementary Fig. 37 | ECO₂R performance on SS-Cu/PMMA in a flow cell with 1 M H₃PO₄ containing 3 M KCl as the catholyte and 1 M H₃PO₄ as the anolyte. a, FEs toward ECO₂R products under a range of applied potentials. b, Corresponding total current density under a range of applied potentials. Values are means and error bars indicate SD (n = 3 replicates).

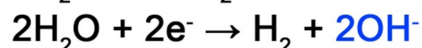
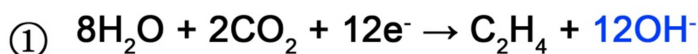


Supplementary Fig. 38 | Total current density under a range of applied potentials for ECO₂R over SS-Cu/PMMA in a flow cell with 1 M H₃PO₄ containing 3 M KI as the catholyte and 1 M H₃PO₄ as the anolyte.



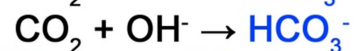
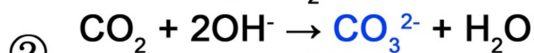
Supplementary Fig. 39 | Digital photograph of the flow channel after the ECO_2R reaction on SS-Cu for ~10 min in an MEA cell with 1 M H_3PO_4 containing 3 M KNO_3 as the anolyte.

At the cathode:



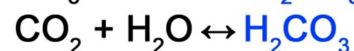
the alkaline cathode environment

Assuming CO_2 could react with the electrogenerated OH^- :



There are no additional cations to balance the electrical neutrality of (bi)carbonate salt (such as K_2CO_3 or KHCO_3) that might be precipitated, except for H^+ .

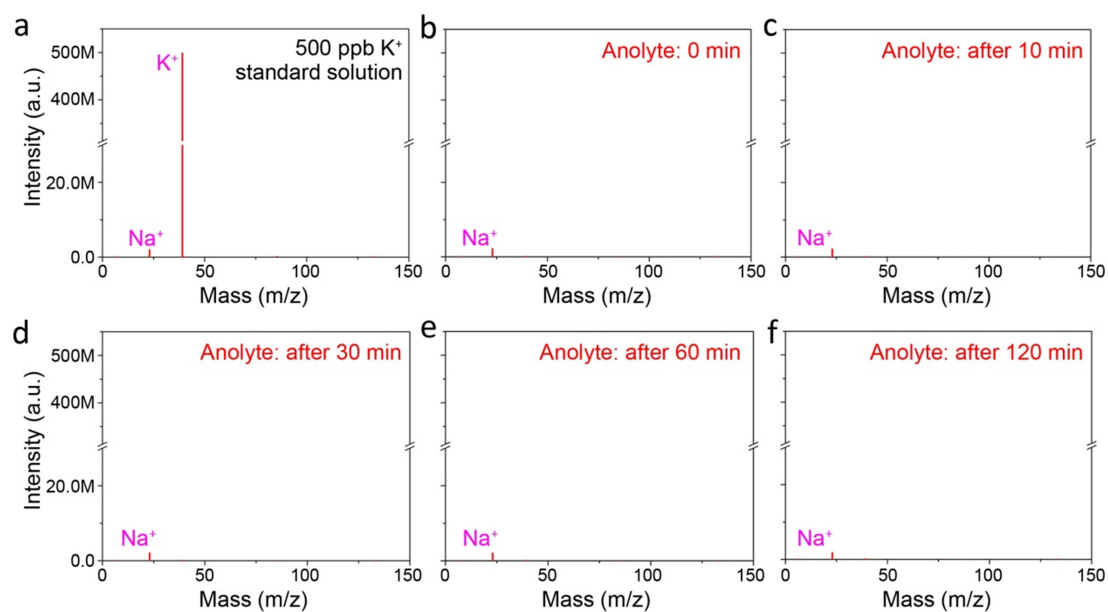
Assuming there would be enough H^+ that could balance the electrical neutrality of (bi)carbonates:



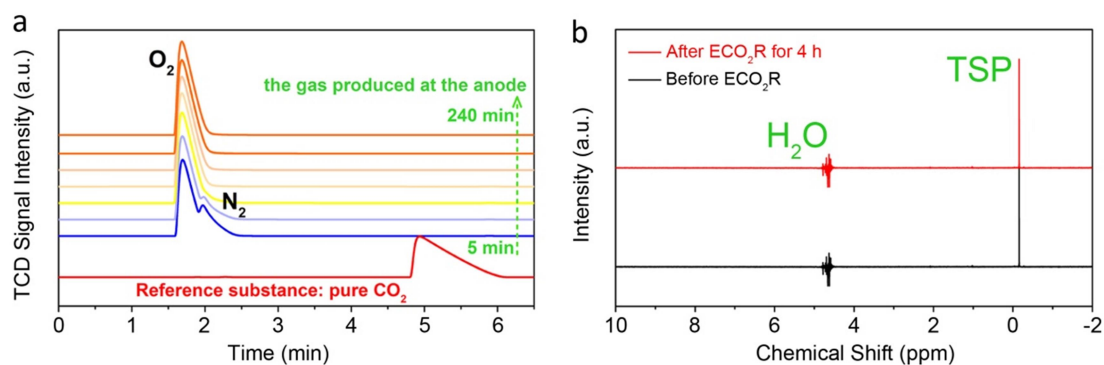
Pure water system would suppress H_2CO_3 formation

Thus, at last, carbonate formation and precipitation can be effectively suppressed and prevented.

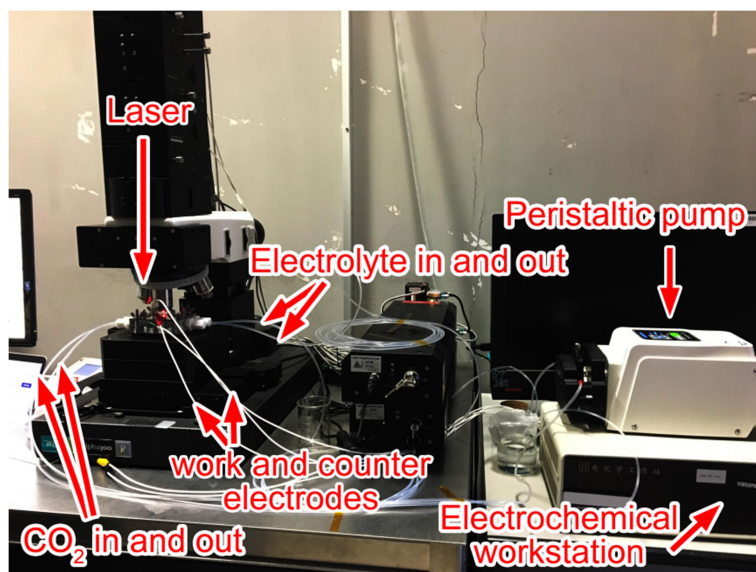
Supplementary Fig. 40 | The reason why carbonate formation/precipitation can be suppressed/prevented in the pure- H_2O -fed APMA-MEA system.



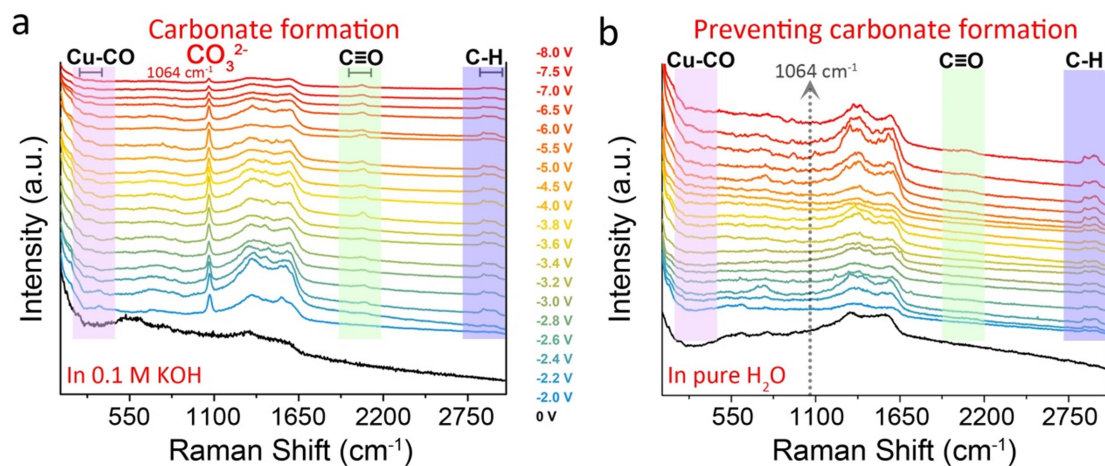
Supplementary Fig. 41 | Time-dependent ICP-MS measurements of pure H₂O anolyte used in the APMA-MEA system for ECO₂R on SS-Cu at 300 mA/cm². a, K⁺ standard solution reference (500 ppb). **b-f,** 0-120 min ICP-MS spectra of the anolyte, respectively.



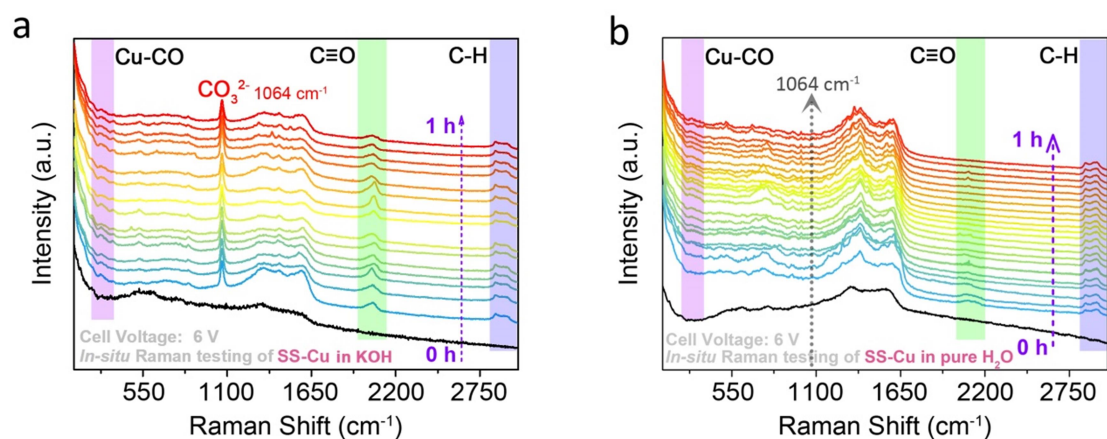
Supplementary Fig. 42 | Anodic products of the pure- H_2O -fed APMA-MEA system at 300 mA/cm^2 for 4 h. a, GC trace of anodic gas products and pure CO_2 as a reference. Initially, a small amount of N_2 was derived from air dissolved in the anolyte (H_2O). The air in H_2O drained away as the reaction went on. **b,** 1H -NMR spectra of the anolyte before and after ECO_2R .



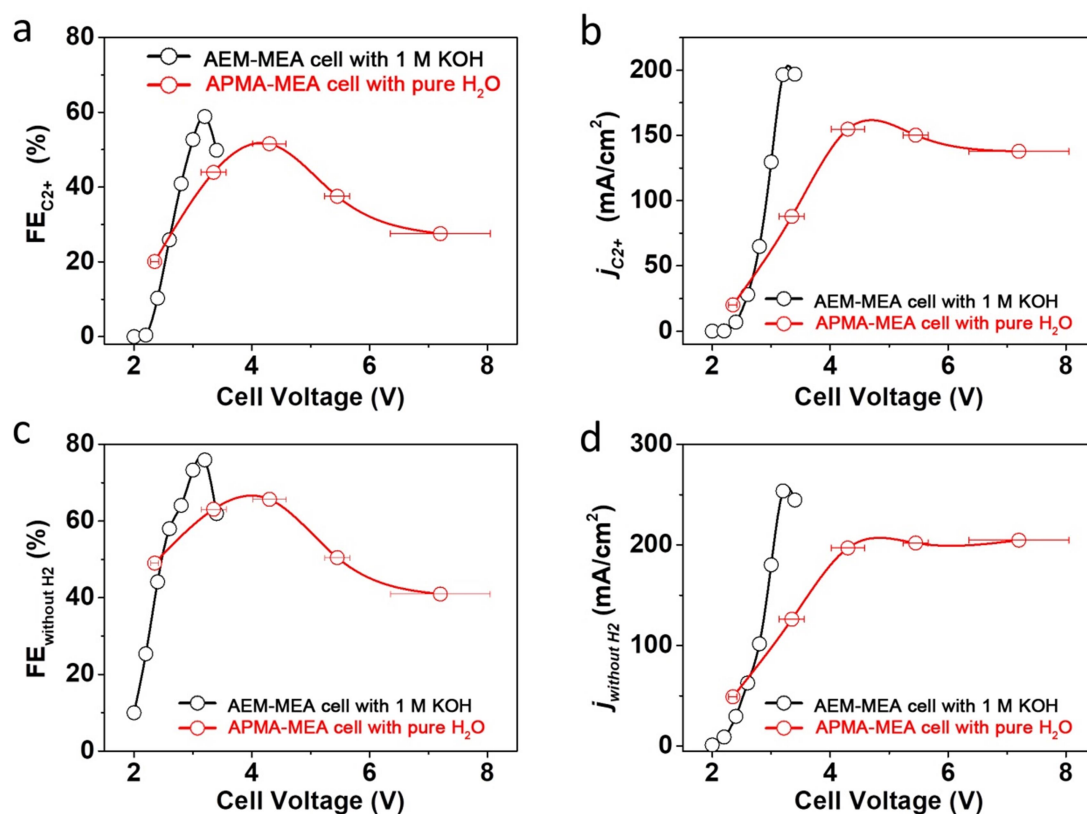
Supplementary Fig. 43 | Digital photographs of the flow cell set-up with a two-electrode system for the *in-situ* Raman measurements during ECO₂R reaction.



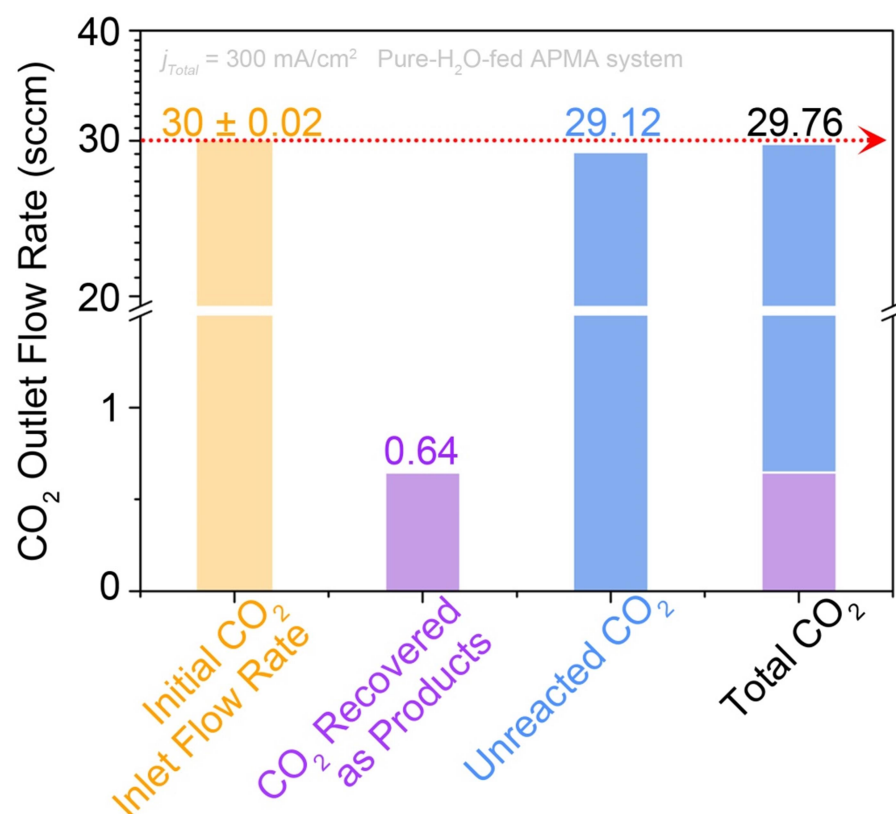
Supplementary Fig. 44 | *In-situ* Raman measurements on SS-Cu for ECO₂R at different cell voltages. a,b, *In-situ* Raman spectra in 0.1 M KOH (a) and pure H₂O (b), respectively.



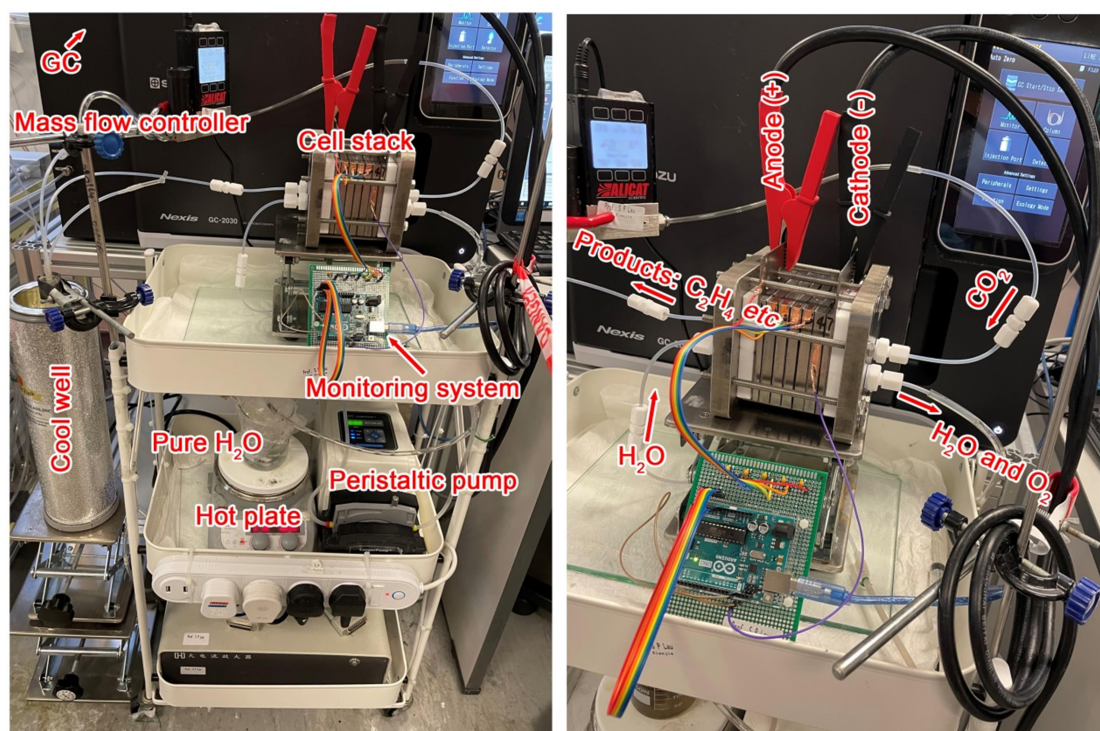
Supplementary Fig. 45 | *In-situ* Raman measurements for ECO₂R on SS-Cu in the different electrolytes at a cell voltage of 6 V. a,b, *In-situ* Raman spectra in 0.1 M KOH (a) and pure H₂O (b) as a function of time, respectively.



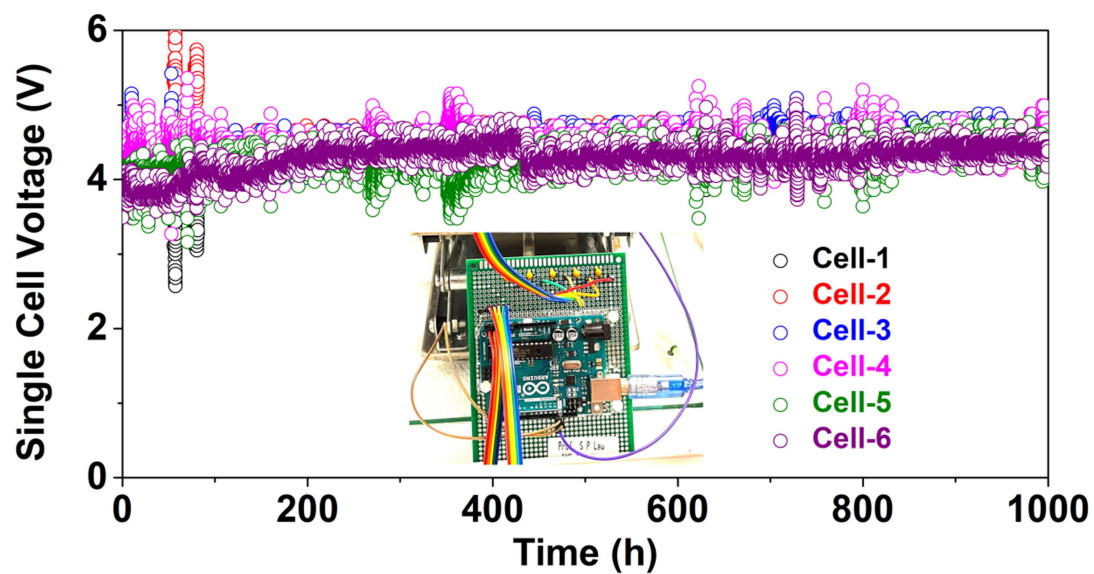
Supplementary Fig. 46 | Comparisons of the ECO₂R performance on SS-Cu in an AEM-MEA cell with 1 M KOH as the anolyte and the pure-H₂O-fed APMA-MEA cell under a range of applied potentials. a,c, Comparisons of FEs toward C₂⁺ (a) and all ECO₂R products (c). **b,d,** Comparisons of partial current densities of C₂⁺ (b) and all ECO₂R products (d). The reaction temperature of the pure-H₂O-fed APMA-MEA system and AEM-MEA system are 60°C and room temperature, respectively. Values are means and error bars indicate SD (n = 3 replicates).



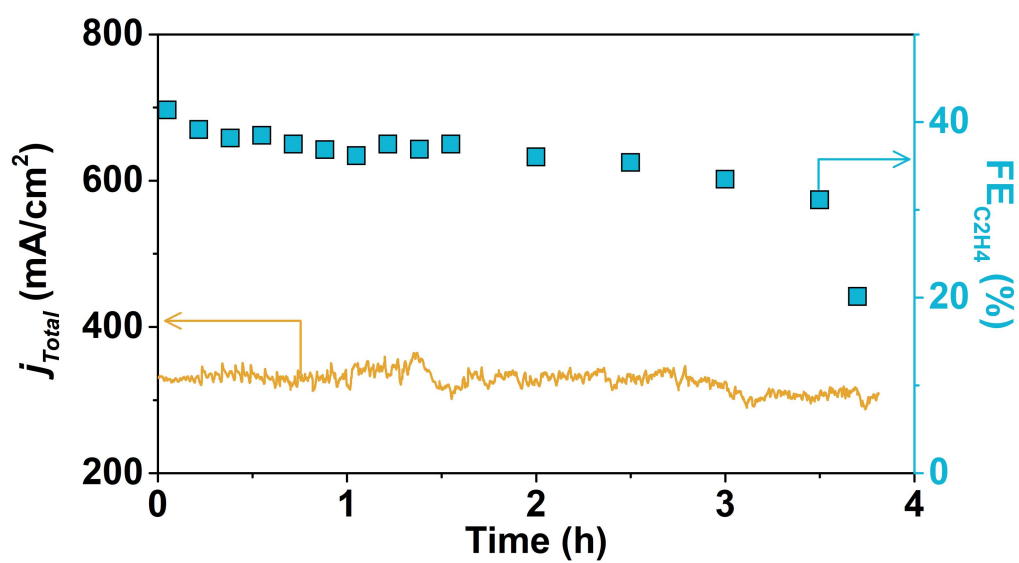
Supplementary Fig. 47 | Carbon balance calculations in the pure- H_2O -fed APMA system at the total current density of 300 mA/cm^2 .



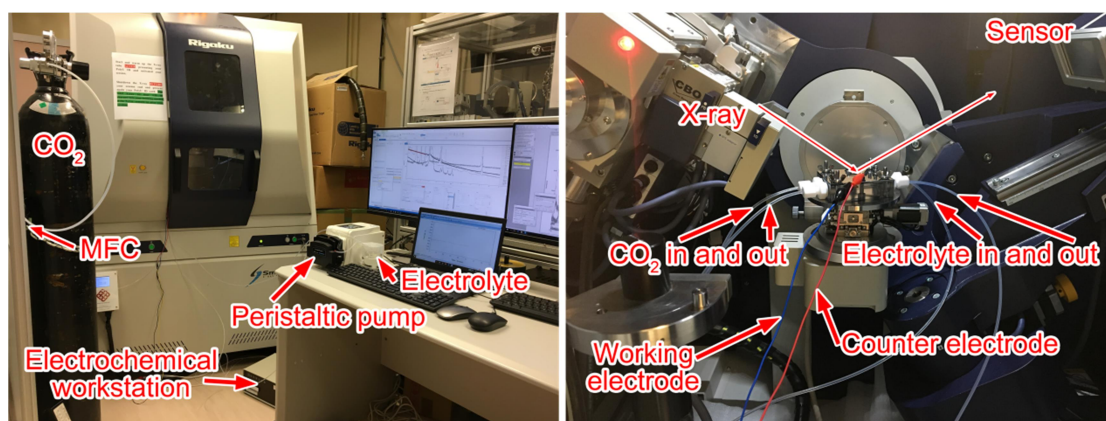
Supplementary Fig. 48 | Digital photographs of the experimental setup for the APMA-MEA stack containing 6 APMA-MEA cells equipped with a monitoring system for performing the ECO₂R reaction.



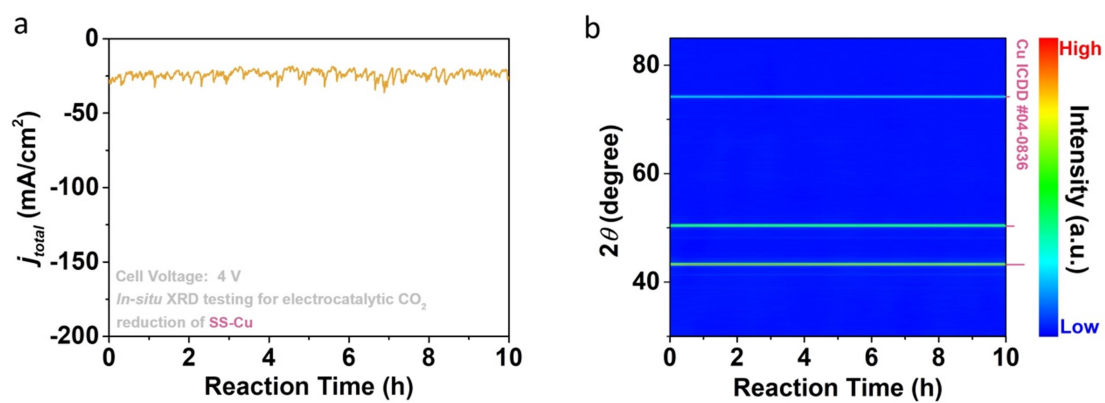
Supplementary Fig. 49 | Stability monitoring of the APMA-MEA stack containing 6 APMA-MEA cells for ECO₂R over SS-Cu at a constant current of 10 A. (Inset) The digital photograph of the monitoring system.



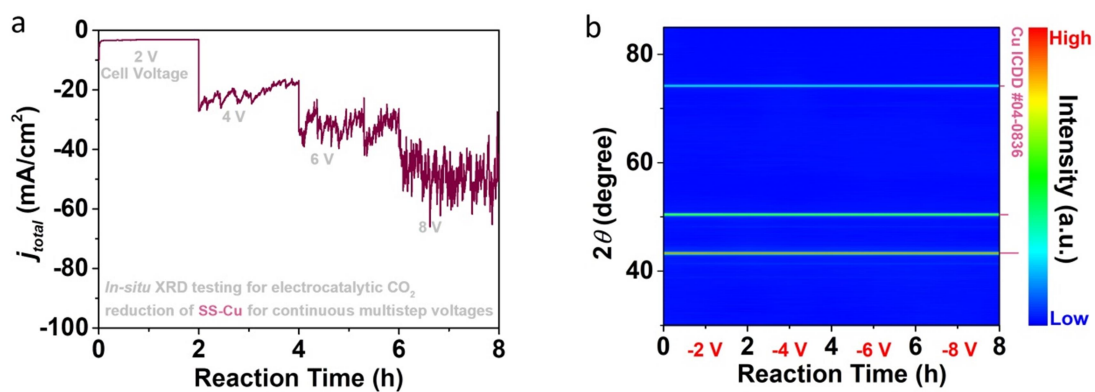
Supplementary Fig. 50 | Stability performance of ECO₂R-to-C₂H₄ on SS-Cu in an AEM-MEA cell with 1 M KOH as the anolyte at 3.2 V cell voltage.



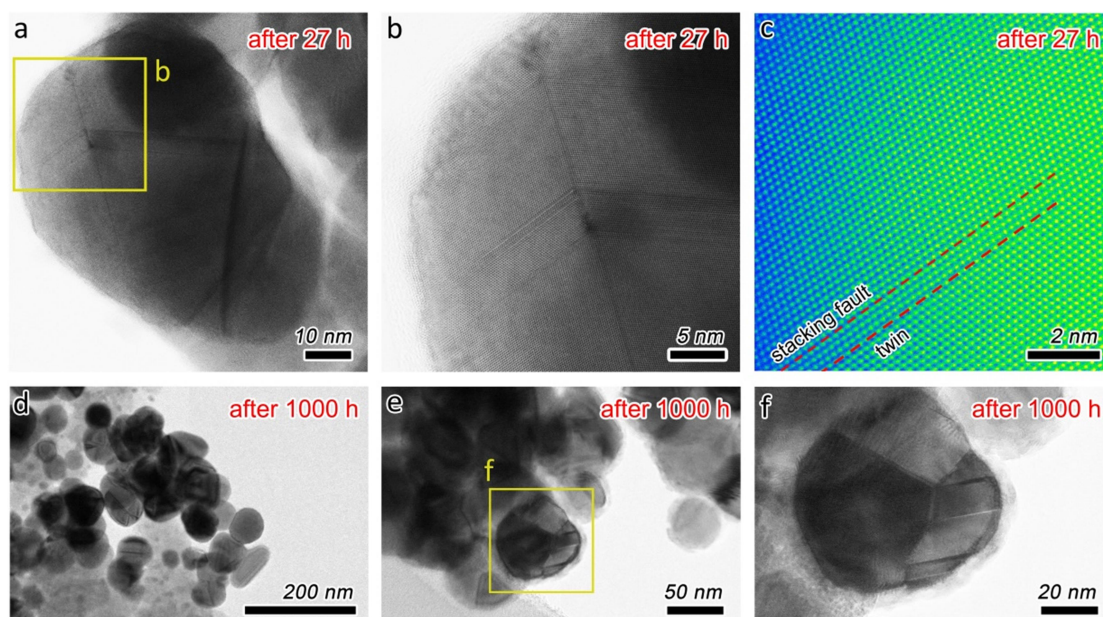
Supplementary Fig. 51 | Digital photographs of the flow cell setup with a two-electrode system for the *in-situ* XRD measurement of the ECO₂R reaction.



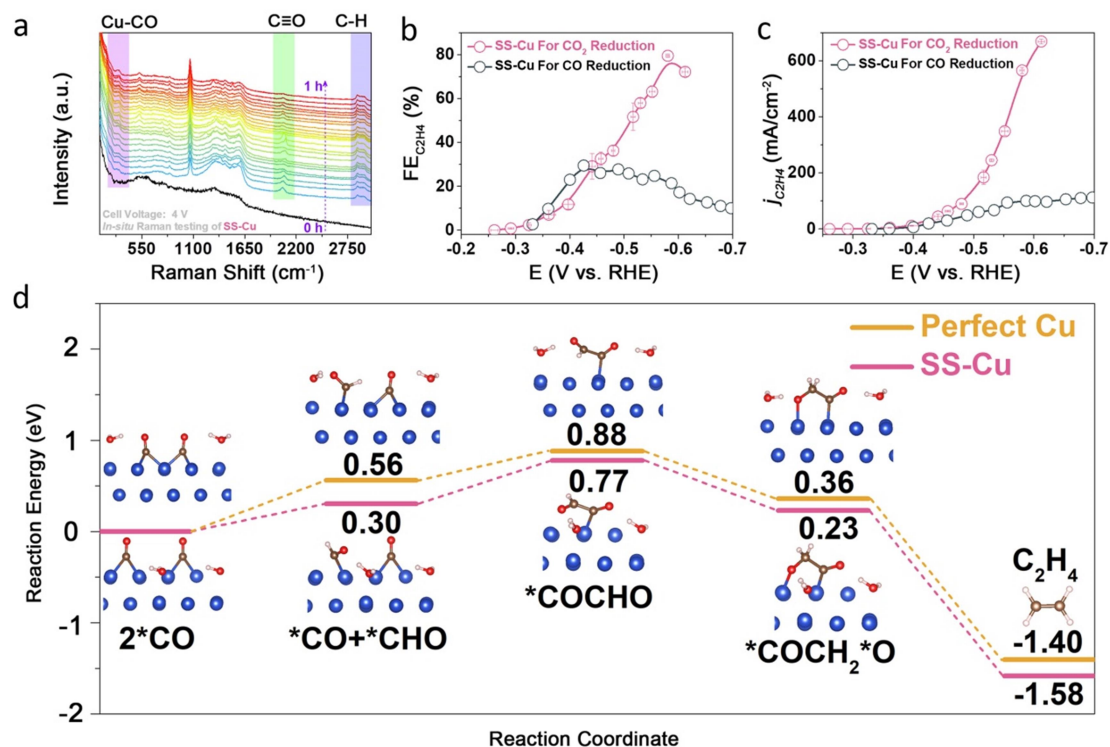
Supplementary Fig. 52 | *In-situ* XRD measurement on SS-Cu for the ECO₂R reaction in 0.1 M KOH at the 4 V cell voltage for 10 h. a, Total current density. b, *In-situ* XRD patterns, corresponding to (a).



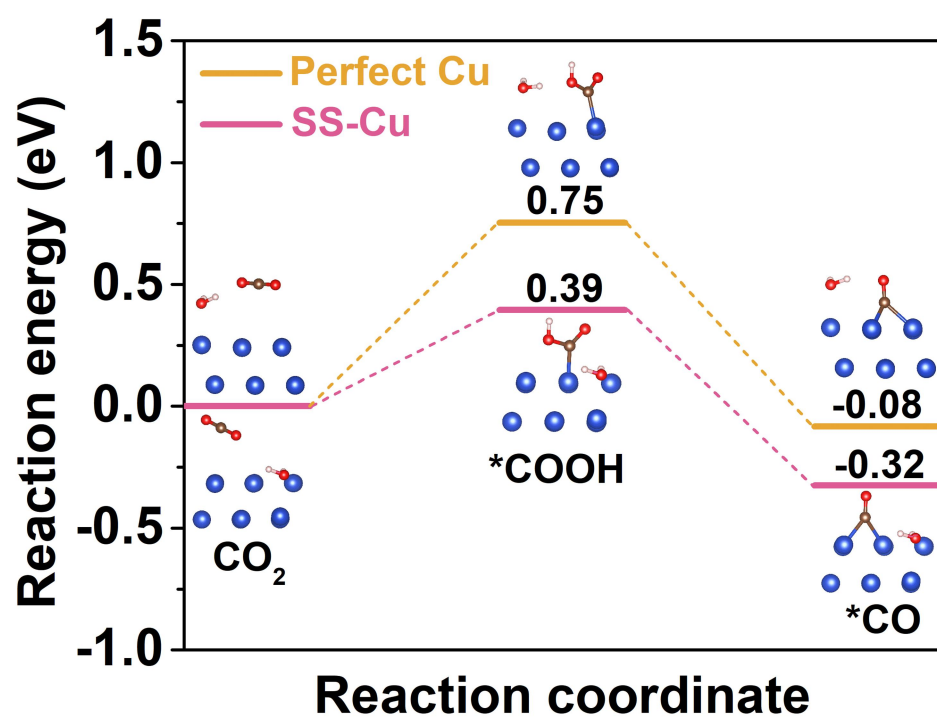
Supplementary Fig. 53 | *In-situ* XRD measurement on SS-Cu for the ECO₂R reaction in 0.1 M KOH at the stepped cell voltages for 8 h. a, Total current density. b, *In-situ* XRD patterns, corresponding to (a).



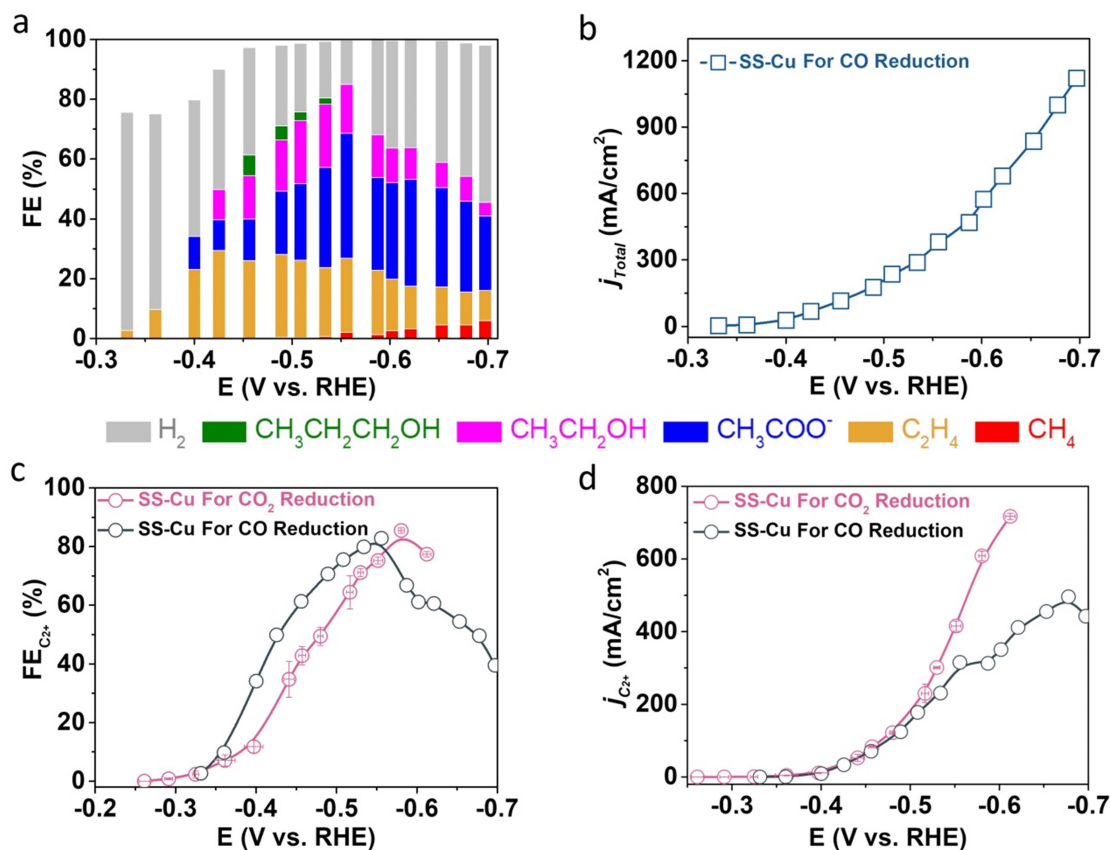
Supplementary Fig. 54 | Structure characterization of SS-Cu after experiencing ECO₂R for 27 h and 1000 h. **a-c**, After 27 h of ECO₂R, ABF-STEM images showing the abundant grain boundaries and stacking faults in SS-Cu (a and b), Atomic-resolution HAADF-STEM image of SS-Cu (c), showing the stacking fault and grain boundary. **d-f**, After 1000 h of ECO₂R, TEM and HRTEM images of SS-Cu, still showing abundant stacking faults and grain boundaries in SS-Cu.



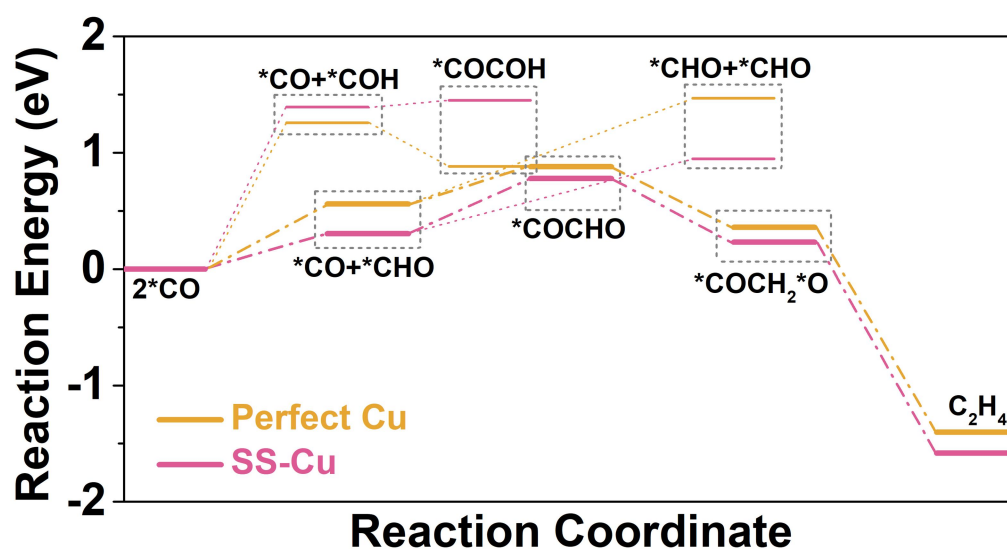
Supplementary Fig. 55 | The studies of the key intermediates of C-C coupling for C₂H₄ formation and effects of CN and tensile strain on ECO₂R by DFT calculations and experiments. **a, *In-situ* Raman spectra of ECO₂R on SS-Cu for 1 h in a customized flow cell with a two-electrode system at 4 V cell voltage. **b,c**, FEs (B) and partial current densities (c) toward C₂H₄ on SS-Cu for ECO₂R and ECOR reactions in 1 M KOH under a range of the applied potentials. Values are means and error bars indicate SD (n = 3 replicates). **d**, A reaction energy diagram for the ECO₂R to C₂H₄ on the perfect Cu and SS-Cu models *via* the direct *CO hydrogenation to *CHO followed by the unoccupied *CO and the *CHO dimerization pathway.**



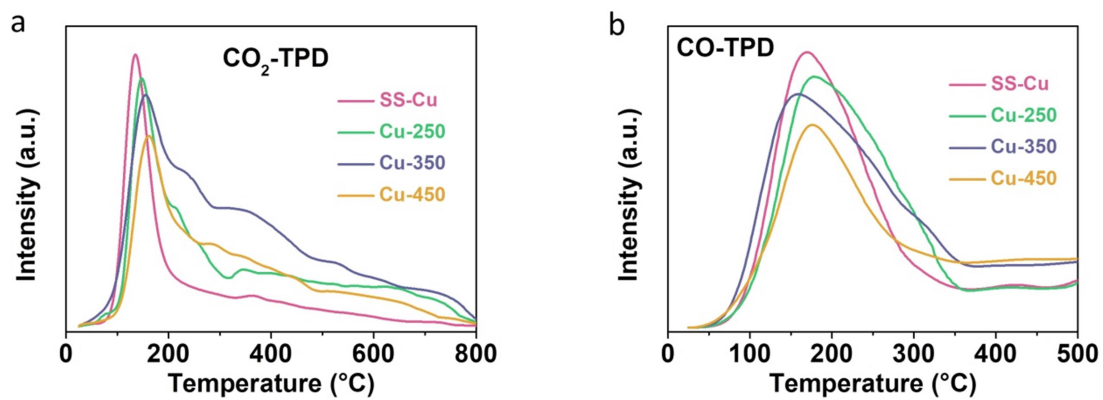
Supplementary Fig. 56 | DFT calculations. A reaction energy diagram for ECO_2R -to- $^*\text{CO}$ intermediate on the perfect Cu and SS-Cu models.



Supplementary Fig. 57 | ECOR performance and comparisons with ECO₂R performance on SS-Cu in the flow cell with 1 M KOH as the electrolyte. **a, FEs toward ECOR products under a range of applied potentials. **b**, Total current density for ECOR under a range of applied potentials. **c,d**, Comparisons of FEs (**c**) and partial current densities (**d**) toward C₂⁺ on SS-Cu for ECO₂R and ECOR in 1 M KOH under a range of applied potentials. Values are means and error bars indicate SD (n = 3 replicates).**



Supplementary Fig. 58 | A reaction energy diagram for the ECO₂R on the perfect Cu and SS-Cu models *via* the direct *CO hydrogenation to *CHO followed by the unoccupied *CO and the *CHO dimerization pathway, or the direct *CO hydrogenation to *COH followed by the unoccupied *CO and the *COH dimerization pathway, or 2*CO hydrogenation to 2*CHO followed by *CHO dimerization pathway.



Supplementary Fig. 59 | Temperature-programmed desorption (TPD) of CO₂ and CO on SS-Cu, Cu-250, Cu-350 and Cu-450. a, CO₂-TPD. b, CO-TPD.

Supplementary Table 1 | Summary of the ECO₂R to C₂H₄/C₂+ performance on different catalysts in the flow cell and MEA cell.

a. Type of Systems	Electrolyte	Potential (V vs. RHE)	$j_{C_2H_4}$ (mA/cm ²)	C ₂ H ₄ Faradaic Efficiency	j_{C_2+} (mA/cm ²)	Total C ₂ + Product Faradaic Efficiency	Stability (h)	Ref.
SS-Cu AEM Flow Cell	1 M KOH	~ -0.58	~569	~80%	~607	~85.48%	<1	This Work
SS-Cu PEM Flow Cell	1 M H ₃ PO ₄ +3 M KI // 1 M H ₃ PO ₄	~ -1.1	~114	~33%	~167	~48.57%	<4	
SS-Cu PEM Flow Cell	1 M H ₃ PO ₄ +3 M KCl // 1 M H ₃ PO ₄	~ -1.2	~101	~28%	~147	~40.71%	-	
SS-Cu AEM-MEA Cell	1 M KOH	~3.2 Cell Voltage	~134	~40%	~196	~58.85%	<4	
SS-Cu APMA-MEA Cell 60 °C	Pure H ₂ O	~4.3 Cell Voltage	~129	~43%	~155	~51.58%	-	
SS-Cu 6-APMA-MEA Stack 60 °C	Pure H ₂ O	~25 Cell Voltage	~167	~50%	-	-	>1000	

a. Type of Systems	Electrolyte	Potential (V vs. RHE)	$j_{C_2H_4}$ (mA/cm ²)	C ₂ H ₄ Faradaic Efficiency	j_{C_2+} (mA/cm ²)	Total C ₂₊ Product Faradaic Efficiency	Stability (h)	Ref.
Cu ₂ S/Cu-V (Cu-Vacancy) AEM Flow Cell	1 M KOH	-0.93	~84.8	21.20%	~223.2	55.80%	-	S39
Cu nanoparticles AEM Flow Cell	1 M KOH	-0.79	~140	45.60%	~215	70%	4	S40
Cu-DAT wires AEM Flow Cell	1 M KOH	-0.6	~75	38.20%	~137.83	70.20%	-	S41
Cu dimer distorted HKUST-1 AEM Flow Cell	1 M KOH	-1.07	262	45%	N/A	N/A	~138	S42
Nanoporous Cu AEM Flow Cell	1 M KOH	-0.67	256	38.60%	411	62%	~2.1	S43
CuAg wire Alloys AEM Flow Cell	1 M KOH	-0.68	172	55.20%	265	85.10%	-	S44
Cu wires AEM Flow Cell	1 M KOH	-0.6	~74	38.20%	~137	70.20%	-	

a. Type of Systems	Electrolyte	Potential (V vs. RHE)	$j_{C_2H_4}$ (mA/cm ²)	C ₂ H ₄ Faradaic Efficiency	j_{C_2+} (mA/cm ²)	Total C ₂₊ Product Faradaic Efficiency	Stability (h)	Ref.
Ag _{0.14} /Cu _{0.86} AEM Flow Cell	1 M KOH	-0.67	80	~32%	195	78% ^b	~2	S45
	1 M KHCO ₃	-0.84	75	~25%	210	70% ^b	-	
Graphite/C NPs/Cu/PTFE AEM Flow Cell	7 M KOH	-0.55	55-70	~70%	60-81	~81%	150	S46
25 nm Cu AEM Flow Cell	3.5 M KOH + 5 M KI	-0.67	~473	~65%	~608	~81%	-	
25 nm Cu AEM Flow Cell	10 M KOH	-0.54	219	66%	275	83%	<0.5	
Cu ₄ O ₃ -rich catalyst AEM Flow Cell	0.5 M Cs ₂ SO ₄ //2.5 M KOH	-0.59	126	42.30%	183.9	61.30%	24	S47
Cu ₂ O films AEM Flow Cell	1.0 M KOH	-0.74	122	67%	-	-	<0.6	S48
Cu-F AEM Flow Cell	0.75 M KOH	-0.89	1040	65%	1280	80%	-	S2
	1.0 M KOH	-0.75	720	~60%	996	~83%	-	
	2.5 M KOH	-0.54	480	60%	672	84%	-	

a. Type of Systems	Electrolyte	Potential (V vs. RHE)	$j_{C_2H_4}$ (mA/cm ²)	C ₂ H ₄ Faradaic Efficiency	j_{C_2+} (mA/cm ²)	Total C ₂₊ Product Faradaic Efficiency	Stability (h)	Ref.
C/De-alloyed Cu-Al/PTFE AEM Flow Cell	1.0 M KOH	~-1.5	400	80%	-	-	50	S49
Surface Reconstructed Cu AEM Flow Cell	3 M KOH	-0.68	-	-	336	84%	-	S50
Tetrahydro-bipyridine-functionalized Cu AEM Flow Cell	1.0 M KHCO ₃	-0.83	230	72%	~261	~82%	-	S51
AEM-MEA Cell	0.1 M KHCO ₃	3.65/5 ^c Cell Voltage	384/5 ^c	64%	-	-	195	
Ionomer-coated Cu AEM Flow Cell	7 M KOH	-0.91	930	60%	1210	~92%	-	S52
AEM-MEA Cell	0.1 M KHCO ₃	3.9/ x^c Cell Voltage	550/ x^c	~55%	-	-	60	

a. Type of Systems	Electrolyte	Potential (V vs. RHE)	$j_{C_2H_4}$ (mA/cm ²)	C ₂ H ₄ Faradaic Efficiency	j_{C_2+} (mA/cm ²)	Total C ₂₊ Product Faradaic Efficiency	Stability (h)	Ref.
Cu (100) AEM Flow Cell	7 M KOH	-0.67	217	-70%	280	90%	-	S53
AEM-MEA Cell	0.15 M KHCO ₃	3.7/5 ^c Cell Voltage	192/5 ^c	~60%	-	-	70	
Polyamine-incorporated Cu AEM Flow Cell	1 M KOH	-0.97	311	72%	389	90%	<3	S54
	5 M KOH	-0.62	- ^d	84%	-	-	-	
	C5	-0.47	~28	87%	-	-	-	
0.8:0.2Cu/Ag AEM Flow Cell	1 M KOH	-0.72	159	48.1%	287	87%	100	S1
0.8:0.2Cu/Ag AEM-MEA Cell	0.5 M KOH	3/1 ^c	106/1 ^c	48%	136/1 ^c	62%	150	
0.8:0.1Cu/Ni-N-C AEM Flow Cell	1 M KOH	-0.70	196	45%	327	75%	-	

a. Type of Systems	Electrolyte	Potential (V vs. RHE)	$j_{C_2H_4}$ (mA/cm ²)	C ₂ H ₄ Faradaic Efficiency	j_{C_2+} (mA/cm ²)	Total C ₂₊ Product Faradaic Efficiency	Stability (h)	Ref.
Cu/CAL PEM Flow Cell	1 M H ₃ PO ₄ +3 M KCl // 1 M H ₃ PO ₄	~ -1.34	276	~23%	480	40%	12.5	S5
Porous Cu AEM-MEA Cell 50 °C	Pure H ₂ O	~3.5 Cell Voltage	420	49.7%	-	-	-	S55
25 nm Cu BPM-MEA Cell 35 °C	0.1 M KHCO ₃	3.8	80	~40%	-	-	-	S10

a. Unless otherwise noted, the ECO₂R reactions were carried out at room temperature.

b. A few percent of the propanol was not calculated.

c. The denominator is the area of the electrode.

x. The area of the electrode is not specified.

d. The current density was not missing.

-. N/A

Supplementary Table 2 | Crystal Structure parameters of SS-Cu, Cu-250, Cu-350, Cu-450 and Cu foil reference from the EXAFS fitting.

Sample	Bond	CN	R (Å)	R-R _{Cu foil} (Å)	D-W factor (Å ²)	ΔE ₀ (eV)	R-factor (%)	Strain (%)
SS-Cu	Cu-Cu	7.6 ± 0.5	2.551 ± 0.004	0.026	0.009 ± 0.001	6.2 ± 0.8	1.4	1.03
Cu-250		8.9 ± 0.4	2.540 ± 0.003	0.021	0.009 ± 0.001	3.8 ± 0.5	1.7	0.59
Cu-350		9.6 ± 0.9	2.535 ± 0.003	0.016	0.009 ± 0.001	3.3 ± 0.4	1.3	0.40
Cu-450		9.9 ± 0.8	2.532 ± 0.002	0.004	0.008 ± 0.001	2.7 ± 0.4	1.2	0.28
Cu foil		12	2.525 ± 0.005	-	0.007 ± 0.001	2.1 ± 0.5	1.8	-

CN: coordination number; R: bond length; ΔE₀: inner potential shift.

Supplementary References

- S1. She, X. J. et al. Tandem electrodes for carbon dioxide reduction into C₂₊ products at simultaneously high production efficiency and rate. *Cell Rep. Phys. Sci.* **1**, 100051 (2020).
- S2. Ma, W. C. et al. Electrocatalytic reduction of CO₂ to ethylene and ethanol through hydrogen-assisted C-C coupling over fluorine-modified copper. *Nat. Catal.* **3**, 478-487 (2020).
- S3. Blommaert, M. A. et al. Orientation of a bipolar membrane determines the dominant ion and carbonic species transport in membrane electrode assemblies for CO₂ reduction. *J. Mater. Chem. A* **9**, 11179-11186 (2021).
- S4. Zhang, F. & Co, A. C. Direct evidence of local pH change and the role of alkali cation during CO₂ electroreduction in aqueous media. *Angew. Chem. Int. Ed.* **58**, 1674-1681 (2019).
- S5. Huang, J. E. et al. CO₂ electrolysis to multicarbon products in strong acid. *Science* **372**, 1074-1078 (2021).
- S6. Yang, K. L. et al. Cation-driven increases of CO₂ utilization in a bipolar membrane electrode assembly for CO₂ electrolysis. *ACS Energy Lett.* **6**, 4291-4298 (2021).
- S7. Liu, Z. C., Yang, H. Z., Kutz, R. & Masel, R. I. CO₂ electrolysis to CO and O₂ at high selectivity, stability and efficiency using sustainion membranes. *J. Electrochem. Soc.* **165**, J3371 (2018).
- S8. O'Brien, C. P. et al. Single pass CO₂ conversion exceeding 85% in the electrosynthesis of multicarbon products via local CO₂ regeneration. *ACS Energy Lett.* **6**, 2952-2959 (2021).
- S9. Pärnamäe, R. et al. Bipolar membranes: a review on principles, latest developments, and applications. *J. Membr. Sci.* **617**, 118538 (2021).
- S10. Xie, K. et al. Bipolar membrane electrolyzers enable high single-pass CO₂ electroreduction to multicarbon products. *Nat. Commun.* **13**, 3609 (2022).
- S11. Salvatore, D. A. et al. Designing anion exchange membranes for CO₂ electrolyzers. *Nat. Energy* **6**, 339-348 (2021).
- S12. Xu, Y. et al. Self-cleaning CO₂ reduction systems: unsteady electrochemical forcing enables stability. *ACS Energy Lett.* **6**, 809-815 (2021).
- S13. Monteiro, M. C. O. et al. Absence of CO₂ electroreduction on copper, gold and silver electrodes without metal cations in solution. *Nat. Catal.* **4**, 654-662 (2021).
- S14. Oener, S. Z., Foster, M. J. & Boettcher, S. W. Accelerating water dissociation in bipolar membranes and for electrocatalysis. *Science* **369**, 1099-1103 (2020).
- S15. Shen, C. H., Wycisk, R. & Pintauro, P. N. High performance electrospun bipolar membrane with a 3D junction. *Energy Environ. Sci.* **10**, 1435-1442 (2017).
- S16. Mariano, R. G., McKelvey, K., White, H. S. & Kanan, M. W. Selective increase in CO₂ electroreduction activity at grain-boundary surface terminations. *Science* **358**, 1187-1192 (2017).
- S17. Huang, W. X. et al. Steam-created grain boundaries for methane C-H activation in palladium catalysts. *Science* **373**, 1518-1523 (2021).

- S18. She, X. J. et al. Grain-boundary surface terminations incorporating oxygen vacancies for selectively boosting CO₂ photoreduction activity. *Nano Energy* **84**, 105869 (2021).
- S19. Ovalle, V. J., Hsu, Y. S., Agrawal, N., Janik, M. J. & Waagele, M. M. Correlating hydration free energy and specific adsorption of alkali metal cations during CO₂ electroreduction on Au. *Nat. Catal.* **5**, 624-632 (2022).
- S20. Hochfilzer, D. et al. In situ analysis of the facets of Cu-based electrocatalysts in alkaline media using Pb underpotential deposition. *Langmuir* **38**, 1514-1521 (2022).
- S21. Feng, X. F., Jiang, K. L., Fan, S. S. & Kanan, M. W. Grain-boundary-dependent CO₂ electroreduction activity. *J. Am. Chem. Soc.* **137**, 4606-4609 (2015).
- S22. Mariano, R. G. et al. Microstructural origin of locally enhanced CO₂ electroreduction activity on gold. *Nat. Mater.* **20**, 1000-1006 (2021).
- S23. Endrődi, B. et al. Operando cathode activation with alkali metal cations for high current density operation of water-fed zero-gap carbon dioxide electrolyzers. *Nat Energy* **6**, 439-448 (2021).
- S24. Ozden, A. et al. Cascade CO₂ electroreduction enables efficient carbonate-free production of ethylene. *Joule* **5**, 706-719 (2021).
- S25. Wang, X. et al. Efficient electrically powered CO₂-to-ethanol via suppression of deoxygenation. *Nat. Energy* **5**, 478-486 (2020).
- S26. Jiang, S., Klingan, K., Pasquini, C. & Dau, H. New aspects of operando Raman spectroscopy applied to electrochemical CO₂ reduction on Cu foams. *J. Chem. Phys.* **150**, 041718 (2019).
- S27. Gao, J. et al. Selective C-C coupling in carbon dioxide electroreduction *via* efficient spillover of intermediates as supported by operando Raman spectroscopy. *J. Am. Chem. Soc.* **141**, 18704-18714 (2019).
- S28. Yang, P. P. et al. Protecting copper oxidation state *via* intermediate confinement for selective CO₂ electroreduction to C₂₊ fuels. *J. Am. Chem. Soc.* **142**, 6400-6408 (2020).
- S29. Li, F. W. et al. Cooperative CO₂-to-ethanol conversion via enriched intermediates at molecule-metal catalyst interfaces. *Nat. Catal.* **3**, 75-82 (2020).
- S30. Calle-Vallejo, F. & Koper, M. T. M. Theoretical considerations on the electroreduction of CO to C₂ species on Cu(100) electrodes. *Angew. Chem. Int. Ed.* **152**, 7282-7285 (2013).
- S31. Liu, X. Y. et al. Understanding trends in electrochemical carbon dioxide reduction rates. *Nat. Commun.* **8**, 15438 (2017).
- S32. Montoya, J. H., Peterson, A. A. & Nørskov, J. K. Insights into C-C coupling in CO₂ electroreduction on copper electrodes. *ChemCatChem* **5**, 737-742 (2013).
- S33. Xiao, H., Cheng, T., Goddard III, W. A. & Sundararaman, R. Mechanistic explanation of the pH dependence and onset potentials for hydrocarbon products from electrochemical reduction of CO on Cu (111). *J. Am. Chem. Soc.* **138**, 483-486 (2016).
- S34. Cheng, T., Xiao, H. & Goddard III, W. A. Free-energy barriers and reaction mechanisms for the electrochemical reduction of CO on the Cu(100) surface,

- including multiple layers of explicit solvent at pH 0. *J. Phys. Chem. Lett.* **6**, 4767-4773 (2015).
- S35. Garza, A. J., Bell, A. T. & Head-Gordon, M. Mechanism of CO₂ reduction at copper surfaces: pathways to C₂ products. *ACS Catal.* **8**, 1490-1499 (2018).
- S36. Cheng, T., Xiao, H. & Goddard III, W. A. Full atomistic reaction mechanism with kinetics for CO reduction on Cu(100) from ab initio molecular dynamics free-energy calculations at 298 K. *PNAS* **114**, 1795-1800 (2017).
- S37. Goodpaster, J. D., Bell, A. T. & Head-Gordon, M. Identification of possible pathways for C-C bond formation during electrochemical reduction of CO₂: new theoretical insights from an improved electrochemical model. *J. Phys. Chem. Lett.* **7**, 1471-1477 (2016).
- S38. Wang, L. et al. Electrochemically converting carbon monoxide to liquid fuels by directing selectivity with electrode surface area. *Nat. Catal.* **2**, 702-708 (2019).
- S39. Zhuang, T. T. et al. Steering post-C-C coupling selectivity enables high efficiency electroreduction of carbon dioxide to multi-carbon alcohols. *Nat. Catal.* **1**, 421-428 (2018).
- S40. Ma, S. C. et al. One-step electrosynthesis of ethylene and ethanol from CO₂ in an alkaline electrolyzer. *J. Power Sources* **301**, 219-228 (2016).
- S41. Hoang, T. T. H., Ma, S. C., Gold, J. I., Kenis, P. J. A. & Gewirth, A. A. Nanoporous copper films by additive-controlled electrodeposition: CO₂ reduction catalysis. *ACS Catal.* **7**, 3313-3321 (2017).
- S42. Nam, D. H. et al. Metal-organic frameworks mediate Cu coordination for selective CO₂ electroreduction. *J. Am. Chem. Soc.* **140**, 11378-11386 (2018).
- S43. Lv, J. J. et al. A highly porous copper electrocatalyst for carbon dioxide reduction. *Adv. Mater.* **30**, 1803111 (2018).
- S44. Hoang, T. T. H. et al. Nanoporous copper-silver alloys by additive-controlled electrodeposition for the selective electroreduction of CO₂ to ethylene and ethanol. *J. Am. Chem. Soc.* **140**, 5791-5797 (2018).
- S45. Li, Y. G. C. et al. Binding site diversity promotes CO₂ electroreduction to ethanol. *J. Am. Chem. Soc.* **141**, 8584-8591 (2019).
- S46. Dinh, C. T. et al. CO₂ electroreduction to ethylene via hydroxide-mediated copper catalysis at an abrupt interface. *Science* **360**, 783-787 (2018).
- S47. Martić, N. et al. Paramelaconite-enriched copper-based material as an efficient and robust catalyst for electrochemical carbon dioxide reduction. *Adv. Energy Mater.* **9**, 1901228 (2019).
- S48. Anastasiadou, D., Schellekens, M., De Heer, M., Verma, S. & Negro, E. Electrodeposited Cu₂O films on gas diffusion layers for selective CO₂ electroreduction to ethylene in an alkaline flow electrolyzer. *ChemElectroChem* **6**, 3928-3932 (2019).
- S49. Zhong, M. et al. Accelerated discovery of CO₂ electrocatalysts using active machine learning. *Nature* **581**, 178-183 (2020).
- S50. Kibria, M. G. et al. A surface reconstruction route to high productivity and selectivity in CO₂ electroreduction toward C₂⁺ hydrocarbons. *Adv. Mater.* **30**, 1804867 (2018).

- S51. Li, F. W. et al. Molecular tuning of CO₂-to-ethylene conversion. *Nature* **577**, 509-513 (2020).
- S52. García de Arquer, F. P. et al. CO₂ electrolysis to multicarbon products at activities greater than 1 A cm⁻². *Science* **367**, 661-666 (2020).
- S53. Wang, Y. H. et al. Catalyst synthesis under CO₂ electroreduction favours faceting and promotes renewable fuels electrosynthesis. *Nat. Catal.* **3**, 98-106 (2020).
- S54. Chen, X. Y. et al. Electrochemical CO₂-to-ethylene conversion on polyamine-incorporated Cu electrodes. *Nat. Catal.* **4**, 20-27 (2021).
- S55. Li, W. Z. et al. Bifunctional ionomers for efficient co-electrolysis of CO₂ and pure water towards ethylene production at industrial-scale current densities. *Nat. Energy* **7**, 835-843 (2022).