

Supplementary Information

Isolated copper-tin atomic interfaces tuning electrocatalytic CO₂ conversion

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Experimental Section:

Quantification of gas and liquid products. The products and Faradic efficiency (FE) of CO₂ reduction were measured using chronoamperometry at each fixed potential. The gaseous products were quantified by a gas chromatograph (GC) equipped with a flame ionization detector (FID) for CO and CH₄ and a thermal conductivity detector (TCD) for H₂ quantification. Ultrapure Ar (99.999%) was used as the carrier gas. The average flow rate of CO₂ was controlled at 20 ml min⁻¹ by a Cole-Parmer mass flow meter. GC was calibrated using standard gas mixtures under standard conditions (1 atm, 298 K). Liquid products were analysed on a 400 MHz nuclear magnetic resonance spectrometer (NMR, Bruker Avance III HD). A 0.5 ml of product-containing electrolyte was syringed out from the cathodic compartment after electrolysis. It was mixed with 0.1 ml of internal standard of diluted dimethyl sulfoxide (DMSO, Sigma-Aldrich, >99.9%) and 0.1 ml of D₂O (Cambridge Isotope Lab, 99.9%), and then transferred to an NMR sample tube. The calibration curve of formate was made by using sodium formate (Sigma-Aldrich, >99.998%) with different concentrations together with the internal standard and D₂O.

DFT calculations. All of the spin-polarized DFT calculations were performed using the VASP program,¹⁻³ which uses a plane-wave basis set and a projector augmented wave method (PAW) for the treatment of core electrons.² The Perdew, Burke, and Ernzerhof exchange-correlation functional within a generalized gradient approximation (GGA-PBE)⁴ was used in our calculations, and the van der Waals (vdW) correction proposed by Grimme (DFT-D3)⁵ was employed due to its good description of long-range vdW interactions. For the expansion of wavefunctions over the plane-wave basis set, a converged cutoff was set to 450 eV. Spin-polarization effect and dipole correction were considered in all cases.

Figure 5a shows the theoretical models of the studied systems. The structural models of pure Cu, Cu-Sn surface alloy, Cu-Sn bulk alloy, and Cu-Sn core-shell bulk alloy are constructed as 2×4 periodic supercells, which contains six atomic layers with the bottom three layers fixed in their respective bulk positions and all the other atoms

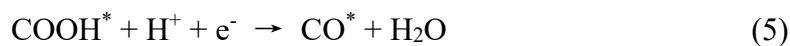
fully relaxed. Here, we considered stepped facets (211) in our models, which have been found to be generally more active for CO₂RR than flat terrace sites. In order to simulate 1% or 3% Sn-doped Cu, a Sn atom replaces a surface Cu atom, which shows much smaller substitution energy rather than in layers below the surface.⁶ The vacuum space was set to larger than 15 Å in the z-direction to avoid interactions between periodic images. In geometry optimizations, all the structures were relaxed up to the residual atomic forces smaller than 0.005 eV/Å, and the total energy was converged to 10⁻⁵ eV. The Brillouin zone integration was performed on the (3×3×1) Monkhorst–Pack k-point mesh.⁷

For CO₂RR on various catalysts, we considered different reaction mechanisms of CO₂RR to formic acid and CO, which have been proposed for CO₂RR on Cu-Sn alloys.⁸

Formic Acid:



Carbon monoxide:



The free energy changes at each electrochemical step involving a proton-electron transfer were computed based on computational hydrogen electrode (CHE) model,⁹ in which the free energy of ($\text{H}^+ + \text{e}^-$) equals to $\frac{1}{2}\text{H}_2(g)$ for standard hydrogen electrode (SHE). The free energy of adsorbates and non-adsorbed gas-phase molecules is calculated as $G = E_{elec} + E_{ZPE} + \int C_p dT - TS$, where E_{elec} is the electronic energy calculated by DFT; E_{ZPE} is the zero point energy (ZPE), C_p is heat capacity, T is temperature and S is entropy. Here, the correction terms are present in Table S3, which are from previous literature.^{9,10} Additionally, a correction of -0.32 and +0.26 eV for non-adsorbed gas-phase CO and HCOOH molecules have

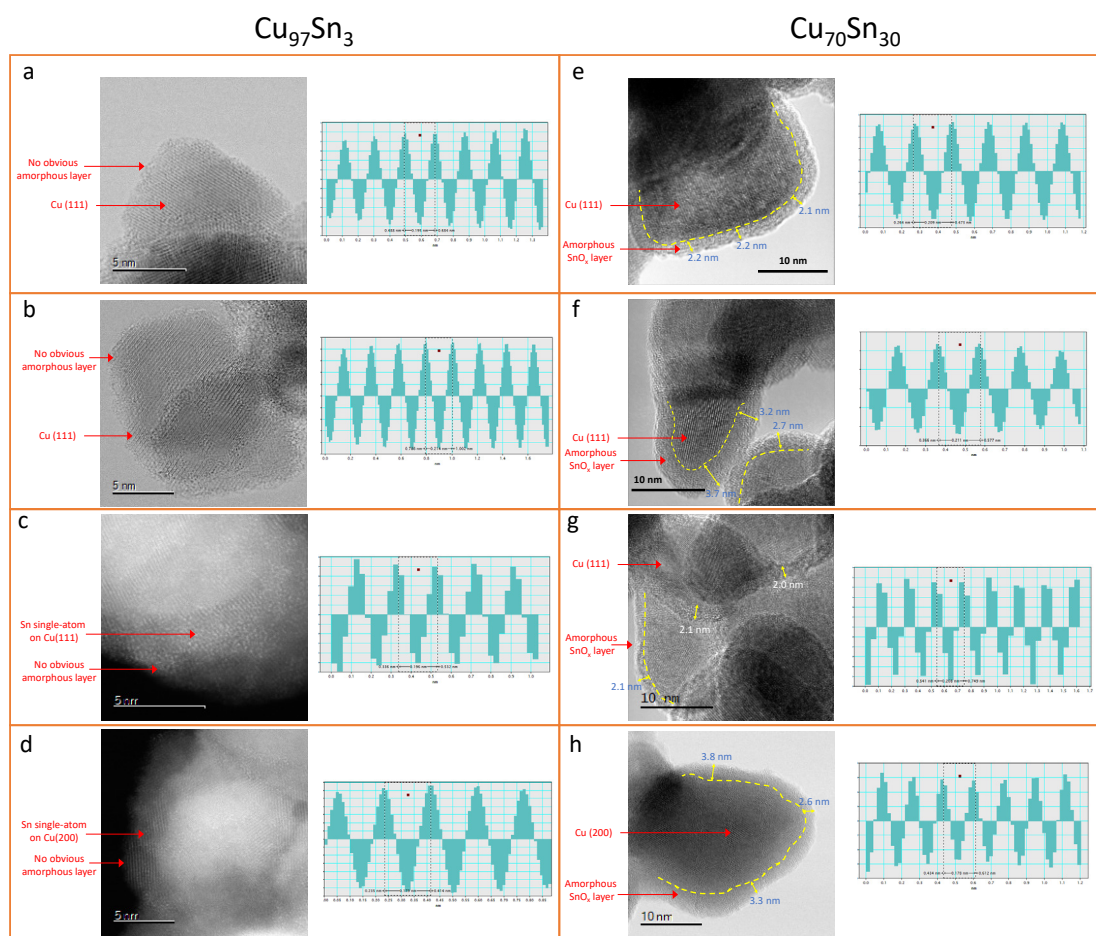
to be made due to the use of PBE functional.⁸ The solvation effects have been included for COOH* and CO* by stabilizing 0.25 and 0.10 eV, respectively.^{9,10}

The overall hydrogen evolution reaction (HER) mechanism is evaluated with a three-state diagram consisting of an initial H⁺ state, an intermediate H* state, and 1/2 H₂ as the final product. The free energy of H* (ΔG_{H^*}) is proven to be a key descriptor to characterize the HER activity of the electrocatalyst. An electrocatalyst with a positive value leads to low kinetics of adsorption of hydrogen, while a catalyst with a negative value leads to low kinetics of release of hydrogen molecule.[11] The optimum value of $|\Delta G_{H^*}|$ should be zero; for instance, this value for the well-known highly efficient Pt catalyst is near-zero as $|\Delta G_{H^*}| \approx 0.09$ eV.[11] The ΔG_{H^*} is calculated as¹¹

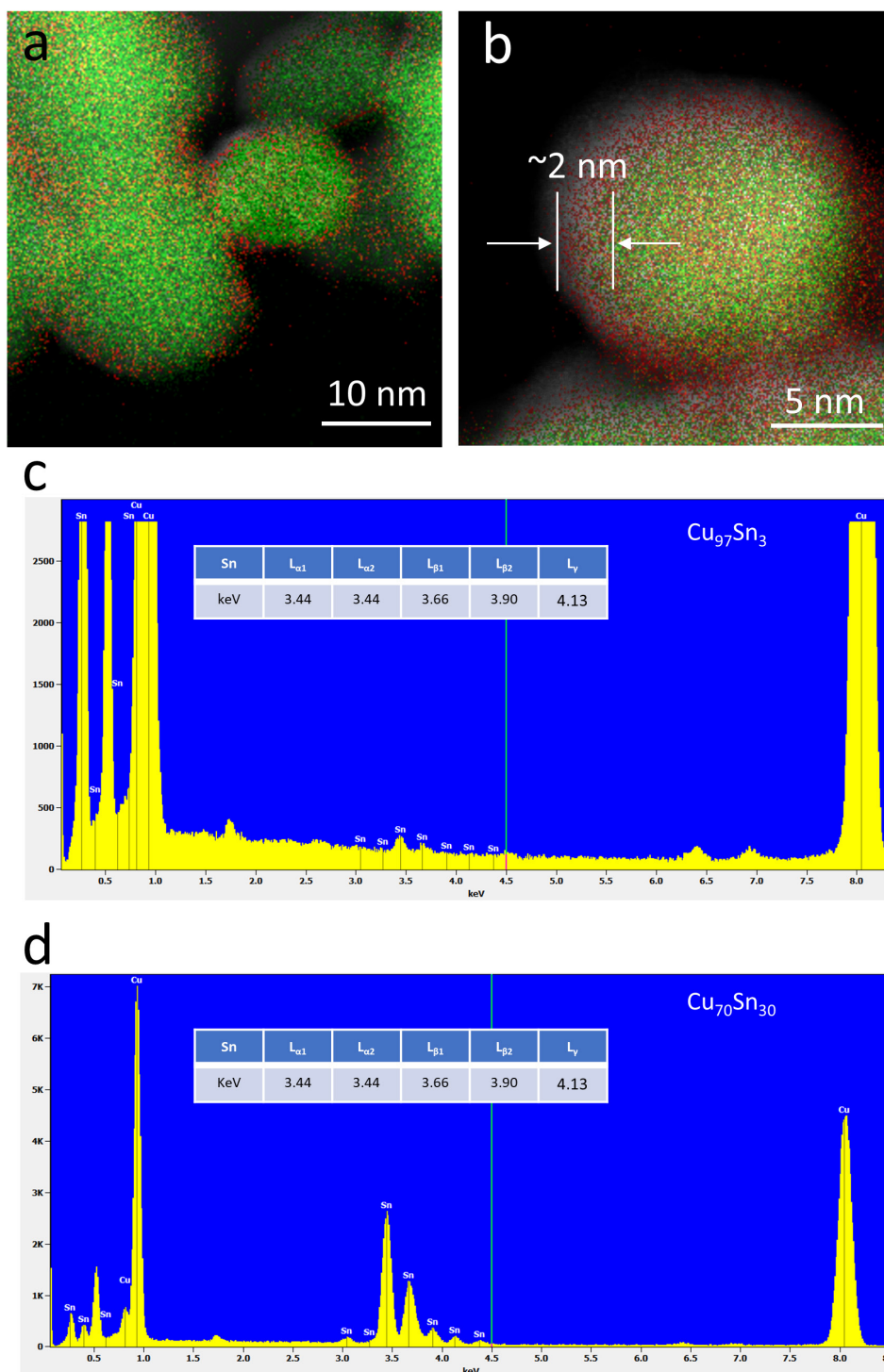
$$\Delta G_{H^*} = \Delta E_{H^*} + \Delta E_{ZPE} - T\Delta S_H \quad (7)$$

where ΔE_{H^*} is the binding energy of adsorbed hydrogen, and ΔE_{ZPE} and ΔS_H are the difference in ZPE and entropy between the adsorbed hydrogen and hydrogen in the gas phase, respectively. As the contribution from the vibrational entropy of hydrogen in the adsorbed state is negligibly small, the entropy of hydrogen adsorption is $\Delta S_H \approx -\frac{1}{2}S_{H_2}$, where S_{H_2} is the entropy of H₂ in the gas phase at the standard conditions. Therefore, Eq. (7) can be rewritten as¹¹

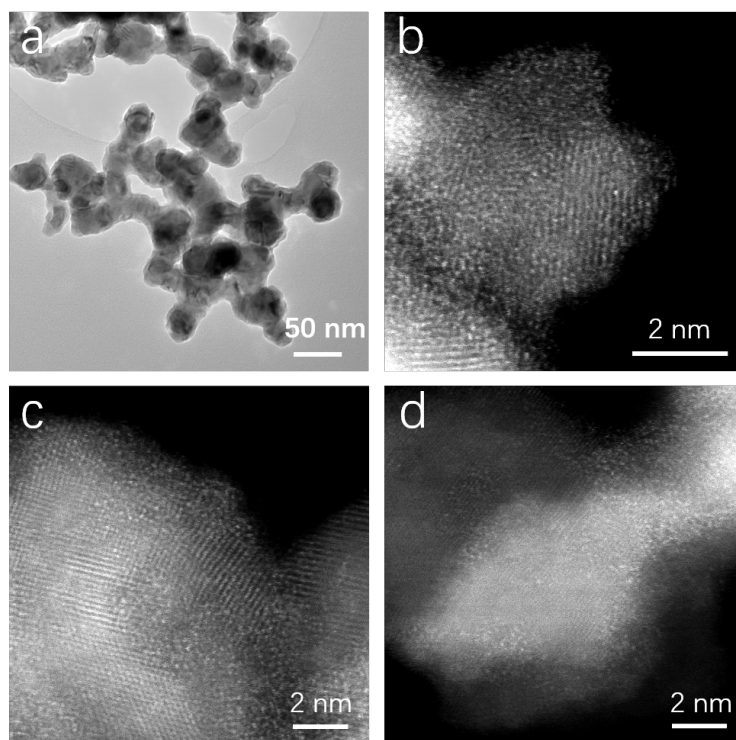
$$\Delta G_{H^*} = \Delta E_{H^*} + 0.24 \text{ eV} \quad (8)$$



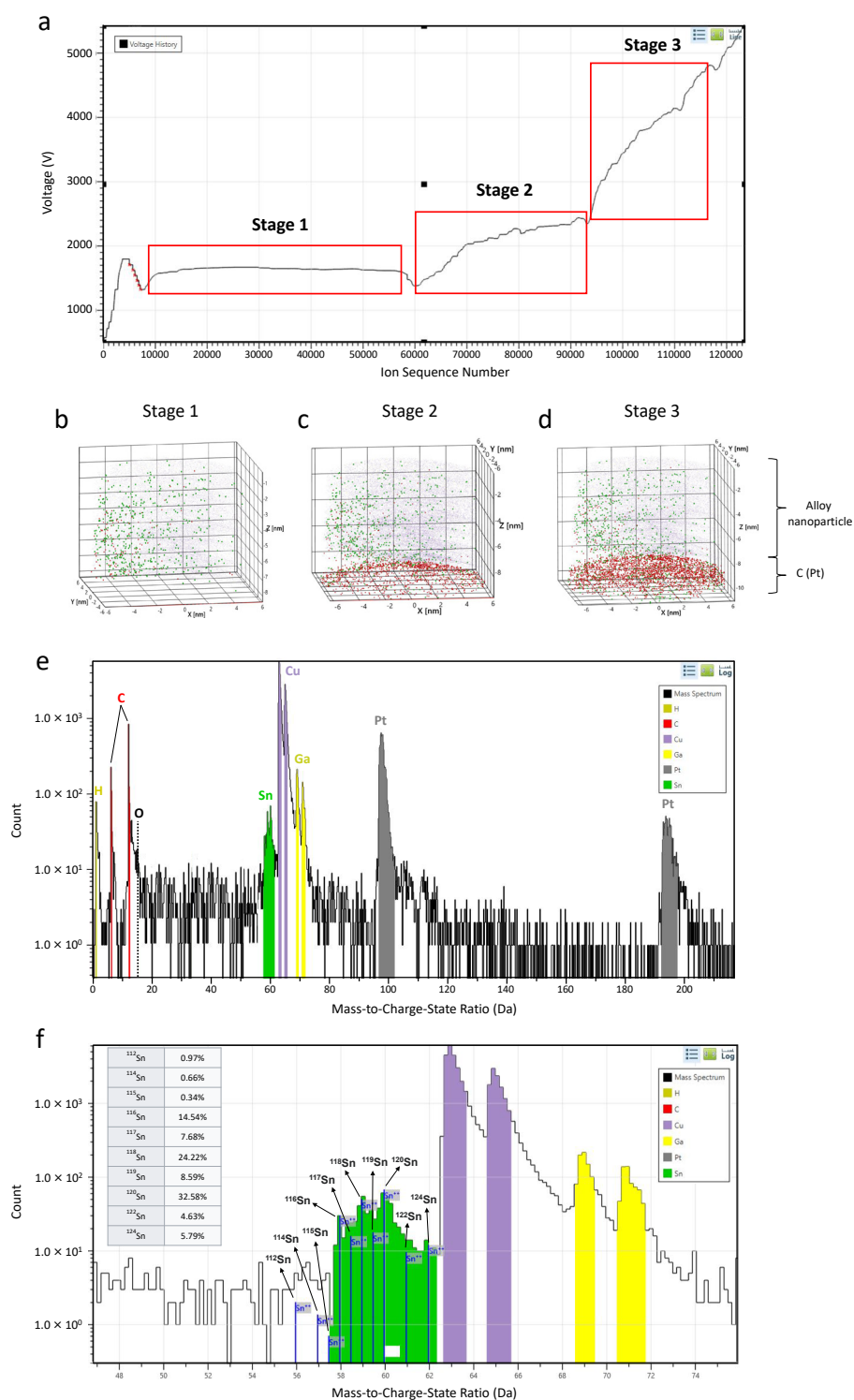
Supplementary Figure 1 | TEM characterizations of $\text{Cu}_{97}\text{Sn}_3$ and $\text{Cu}_{70}\text{Sn}_{30}$. (a-d) The HRTEM and HAADF-STEM images of $\text{Cu}_{97}\text{Sn}_3$ with the spacing analysis of Cu lattice. **(e-h)** The HRTEM images of $\text{Cu}_{70}\text{Sn}_{30}$ with the spacing analysis of Cu lattice. There is a relatively thick amorphous SnO_x shell (2.0-3.8 nm) out of Cu nanoparticles on $\text{Cu}_{70}\text{Sn}_{30}$.



Supplementary Figure 2 | EDS analysis of $\text{Cu}_{97}\text{Sn}_3$ and $\text{Cu}_{70}\text{Sn}_{30}$. (a,b) The overlapped EDX mapping of $\text{Cu}_{97}\text{Sn}_3$ and $\text{Cu}_{70}\text{Sn}_{30}$ based on Fig. 1b,c, respectively. Cu (green) and Sn (red). (c,d) The corresponding mass spectrum analysis.



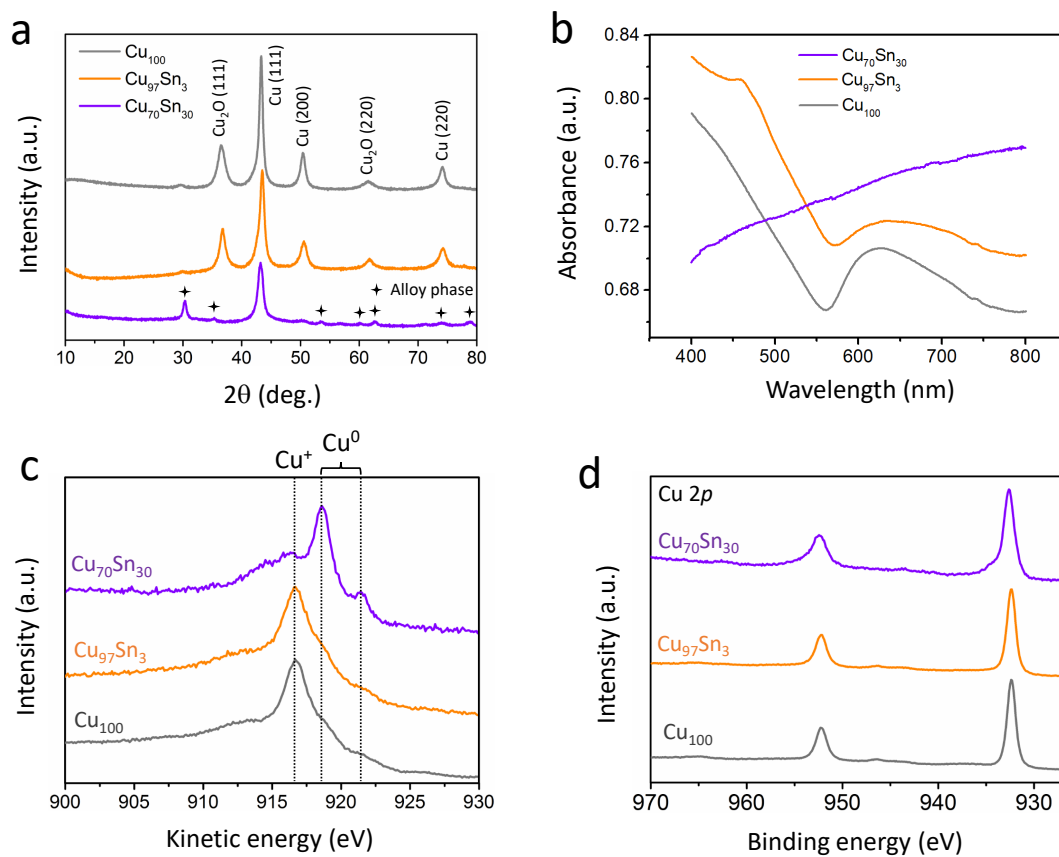
Supplementary Figure 3 | TEM images of $\text{Cu}_{97}\text{Sn}_3$. (a) Typical TEM image $\text{Cu}_{97}\text{Sn}_3$ nanoparticles. (b-d) HAADF-STEM images showing atomically dispersed Sn on the Cu host surface.



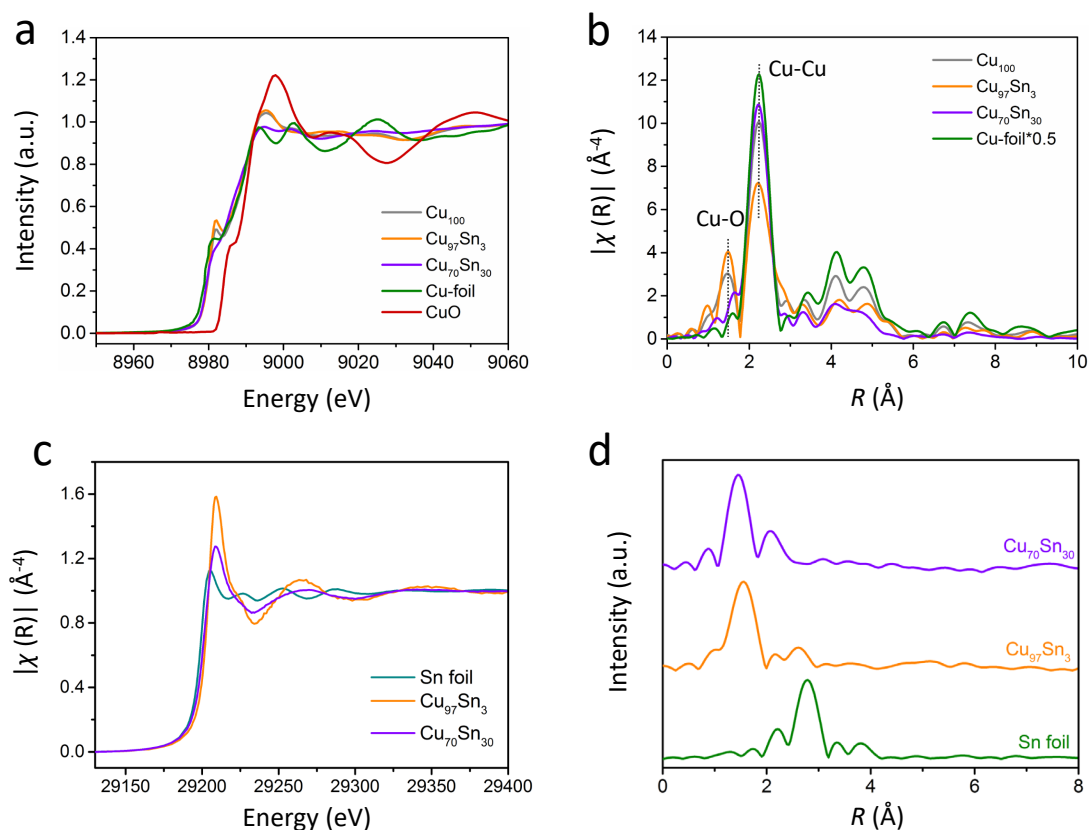
Supplementary Figure 4 | Atom probe tomography analysis of $\text{Cu}_{97}\text{Sn}_3$ specimen. (a) Voltage curves. 3D tomography at the end of Stage 1 **(b)**, Stage 2 **(c)**, and Stage 3 **(d)**. **(e)** The full-range mass to charge spectrum with rebin-treatment to enhance the signal to background ratio. **(f)** The detailed Sn isotopes analysis. Inset is the natural abundance of main isotopes of tin and the ratio is demonstrated as the blue lines, which is in good agreement with the experimental results.

The whole APT experiment includes three stages. During Stage 1, the $\text{Cu}_{97}\text{Sn}_3$ alloy was successfully evaporated by applying electric pulses at the voltage of 1,600 V, which is a common voltage observed for alloy samples (Supplementary Fig. 4a). After the stable evaporation, we obtained the tomography of a single nanoparticle (Supplementary Fig. 4b). Then, the voltage started to increase in Stage 2 because of the detection of the C (Pt) signals (Supplementary Fig. 4c). The C (Pt) comes from our specimen preparation process, during which we incorporated the nanoparticles into a layer of electron-beam-assisted deposition of $(\text{C}_5\text{H}_4)\text{CH}_3\text{Pt}(\text{CH}_3)_3$. This deposition can fill the interspace of each nanoparticle and make the tip compacted. However, the carbon needs higher energy to be evaporated so that the voltage gradually increases.¹² As the experiment continued to run, the carbon layer became thicker and the voltage even increased to above 5,000 V after Stage 3 (Supplementary Fig. 4d). In this case, the APT experiment would automatically end, and we cannot obtain more tomography of nanoparticles.

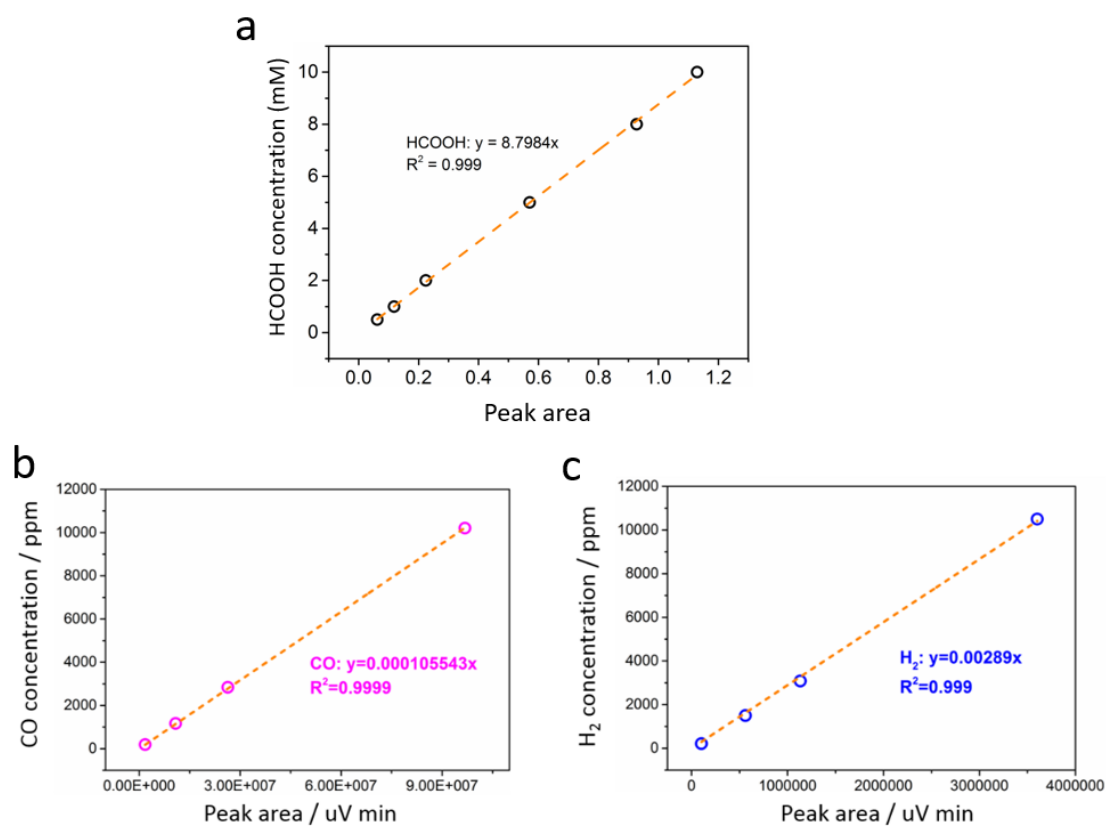
The full-range mass-to-charge spectrum is shown in Supplementary Fig. 4e. Our specimen preparation method use gas-injection-system as adhesive to bond the nanoparticle onto the Mo post, followed by the $(\text{C}_5\text{H}_4)\text{CH}_3\text{Pt}(\text{CH}_3)_3$ deposition and a Ga source FIB annular milling.¹³ As a result, C, Pt, H, and Ga are the primary contamination introduced to the sample. Note that all the elements detected in the spectrum (H, C, Sn, Cu, Ga and Pt) have no overlapping owing to their different mass-to-charge-state ratio. Besides, the overall Sn content is more than 1% in the specimen and the surface content can reach up to ~8%, which is far beyond the detection limit of APT technique (ppm elemental detection capacity).¹⁴ Another strong evidence is that the mass spectrum of Sn matches very well to the corresponding isotopes (Supplementary Fig. 4f). Based on the above analysis, we can firmly claim that the signal peak at ~60 (Da) originating from Sn only, rather than impurities or noise.



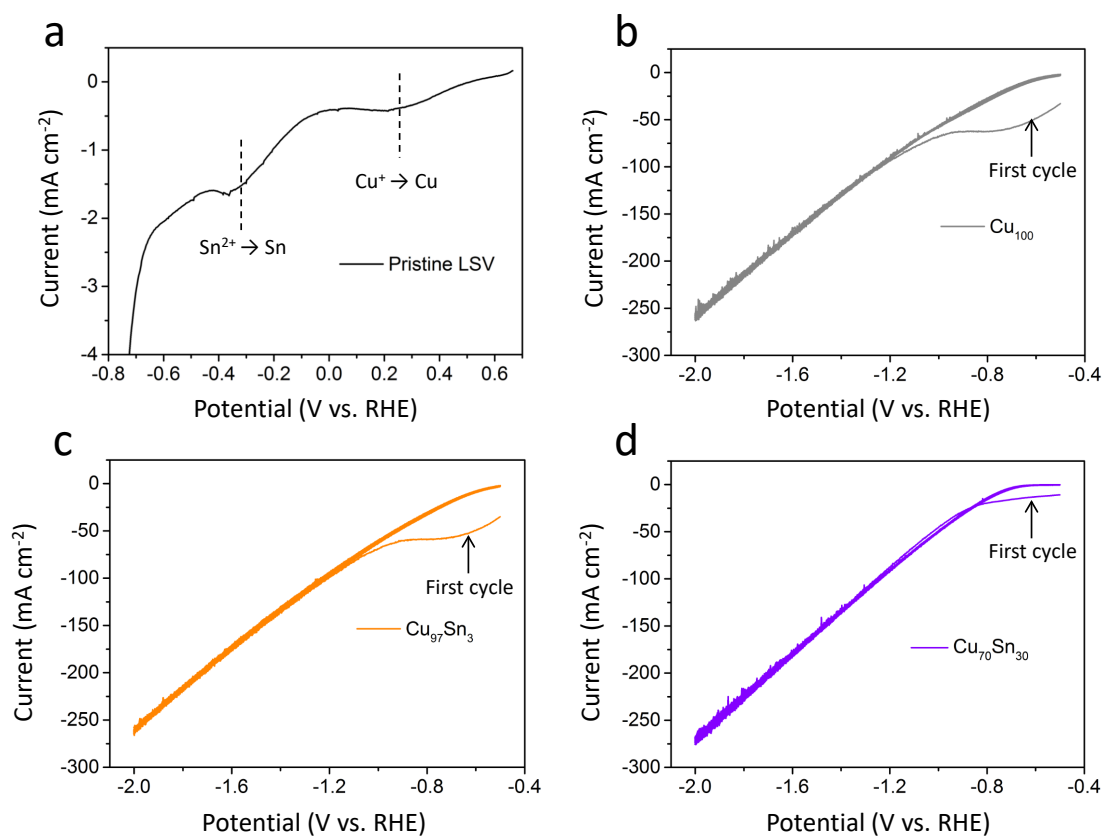
Supplementary Figure 5 | Structural characterizations of Cu_{100} , $\text{Cu}_{97}\text{Sn}_3$ and $\text{Cu}_{70}\text{Sn}_{30}$. (a) XRD patterns. (b) UV-vis spectroscopy. (c) Cu LMM Auger spectra and (d) XPS of Cu 2p spectra.



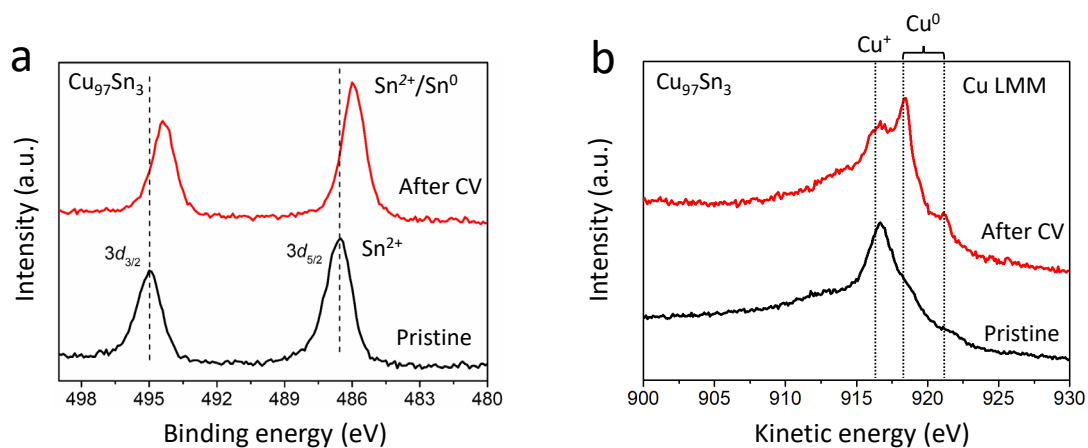
Supplementary Figure 6 | X-ray absorption spectroscopy. (a) Cu K-edge XANES spectra of Cu_{100} , $\text{Cu}_{97}\text{Sn}_3$ and $\text{Cu}_{70}\text{Sn}_{30}$ with the comparison of standard CuO and Cu-foil. (b) The plotted FT-EXAFS spectra obtained from Cu K-edge absorption spectra. (c) Sn K-edge XANES spectra of $\text{Cu}_{97}\text{Sn}_3$ and $\text{Cu}_{70}\text{Sn}_{30}$ with the comparison of standard Sn-foil. (d) The plotted FT-EXAFS spectra obtained from Sn K-edge absorption spectra. As shown in Figure S6c, the near-edge positions of $\text{Cu}_{97}\text{Sn}_3$ and $\text{Cu}_{70}\text{Sn}_{30}$ catalysts are higher than that of Sn foil, indicating the oxidation of Sn in the samples. This is also supported by the Fourier-transformed k^3 -weighted spectra of the samples, where the peaks at 1.4 $\text{\AA}$ correspond to Sn-O coordination shells.



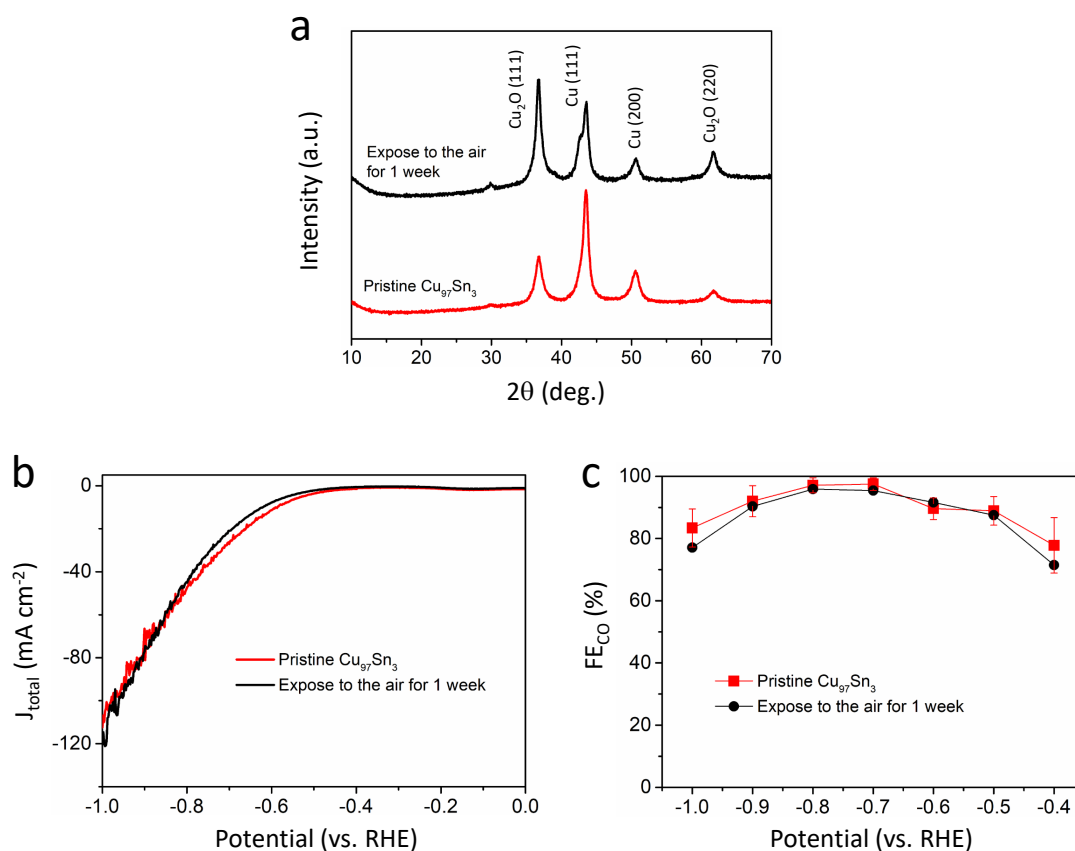
Supplementary Figure 7 | Calibration curves for different products. (a) NMR calibration curves for HCOOH. **(b,c)** GC calibration curves for CO and H₂, respectively.



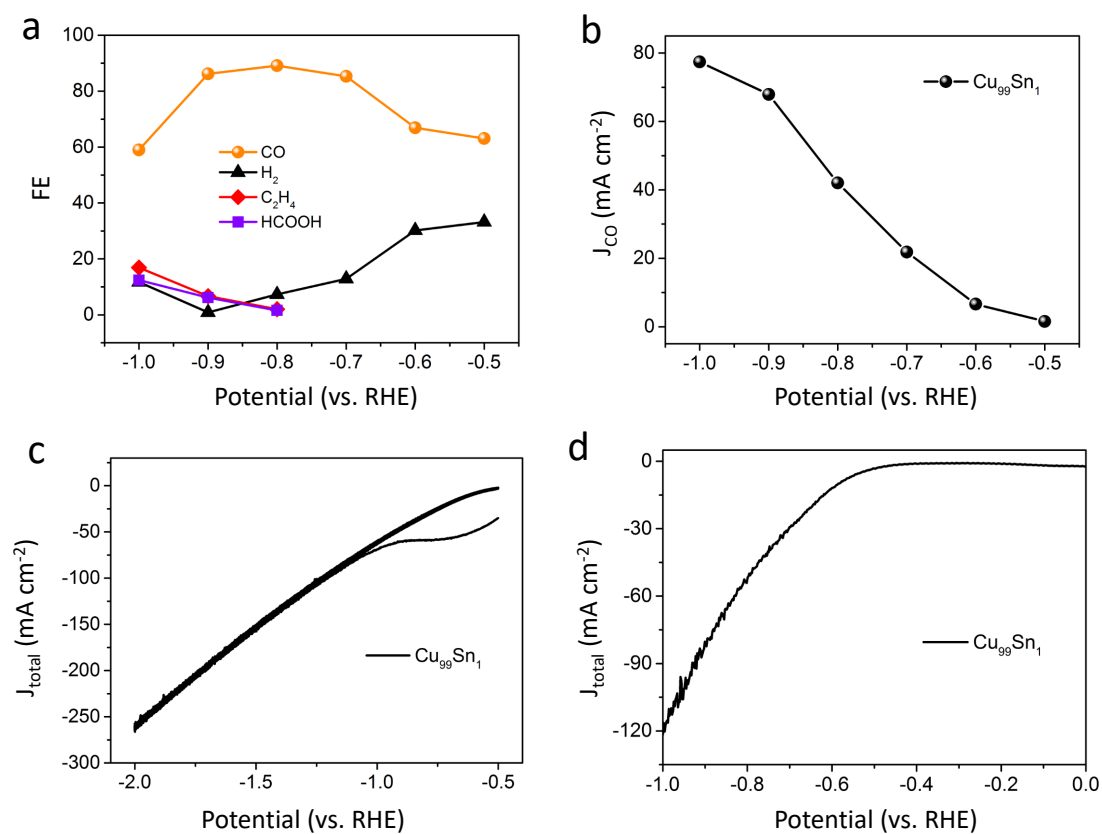
Supplementary Figure 8 | CV pretreatment. (a) Pristine LSV curves of Cu₇₀Sn₃₀. (b-d) CV pretreatment from -0.5 to -2.0 V vs. RHE for 10 cycles at 50 mV s⁻¹.



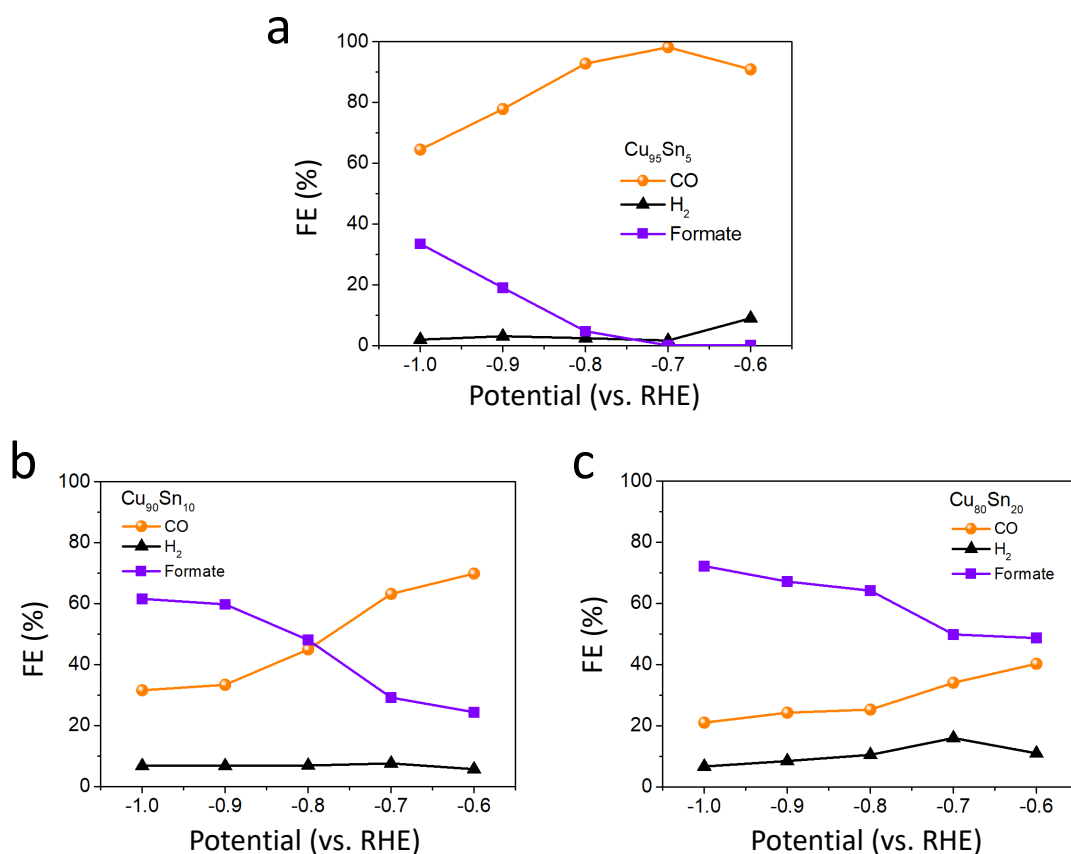
Supplementary Figure 9 | Structural analysis of $\text{Cu}_{97}\text{Sn}_3$ before and after CV treatment. (a) XPS of Sn $3d$ spectra. (b) Cu LMM Auger spectra. *Ex-situ* Sn $3d$ XPS and Cu LMM Auger spectra on $\text{Sn}_{97}\text{Sn}_3$ confirm the reduction of Sn^{2+} to Sn^0 and Cu^+ to Cu^0 after the CV pretreatment. The residual oxides can be attributed to the inevitable oxidation during sample delivery and test. It is expected that most of the Cu and Sn species are reduced to the metallic state after the CV treatment, according to their standard reduction potential ($\text{Sn}^{2+} + 2\text{e}^- \rightleftharpoons \text{Sn}$ at -0.13 vs. SHE, $\text{Cu}^+ + \text{e}^- \rightleftharpoons \text{Cu}$ at +0.52 vs. SHE).^{6,8,15}



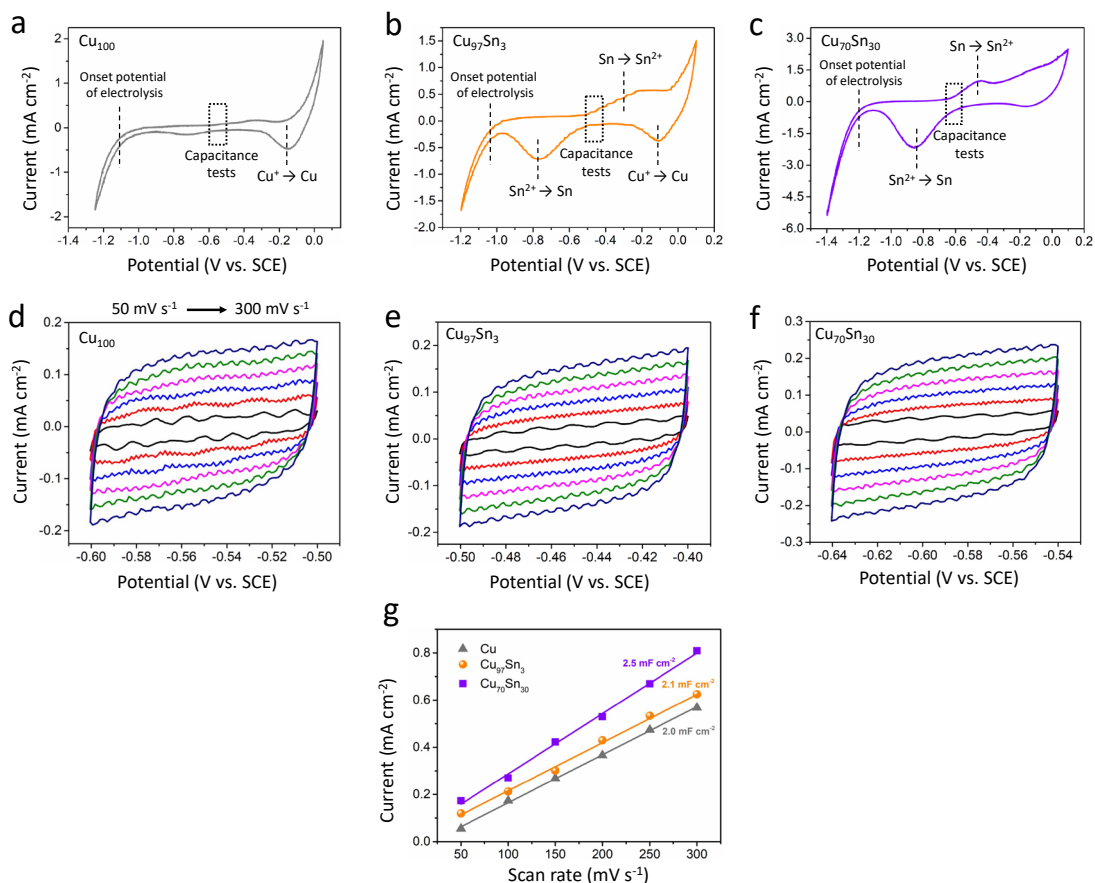
Supplementary Figure 10 | CO_2RR assessment of $\text{Cu}_{97}\text{Sn}_3$ after exposure to the air for 1 week. (a) XRD analysis. (b) LSV comparison. (c) FE_{CO} from -0.4 to -1.0 V vs RHE. To further investigate the influence of the surface oxide layer, the as-synthesized $\text{Cu}_{97}\text{Sn}_3$ sample is exposed to the air and aged for 1 week before CO_2RR testing. As shown in XRD analysis, the $\text{Cu}_{97}\text{Sn}_3$ catalyst is further oxidized after continuous exposure to the air. While, after the CV pretreatment, the aged $\text{Cu}_{97}\text{Sn}_3$ show very close LSV curves and similar FE_{CO} compared with pristine $\text{Cu}_{97}\text{Sn}_3$ for CO_2 electrolysis, indicative of the similar CO_2RR reactivity and the negligible effect of surface oxides after CV pretreatment.



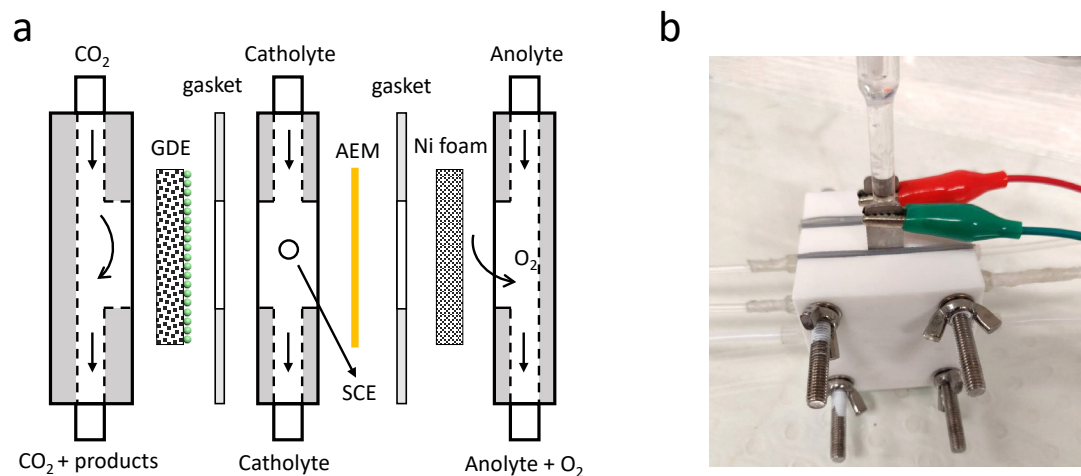
Supplementary Figure 11 | CO₂RR performance of Cu₉₉Sn₁. (a) Potential dependence of Faradaic efficiencies from -0.5 to -1.0 vs. RHE. (b) Potential dependence of j_{CO} . (c) CV pretreatment at 50 mV s⁻¹. (d) LSV curves from 0 to -1.0 V vs. RHE.



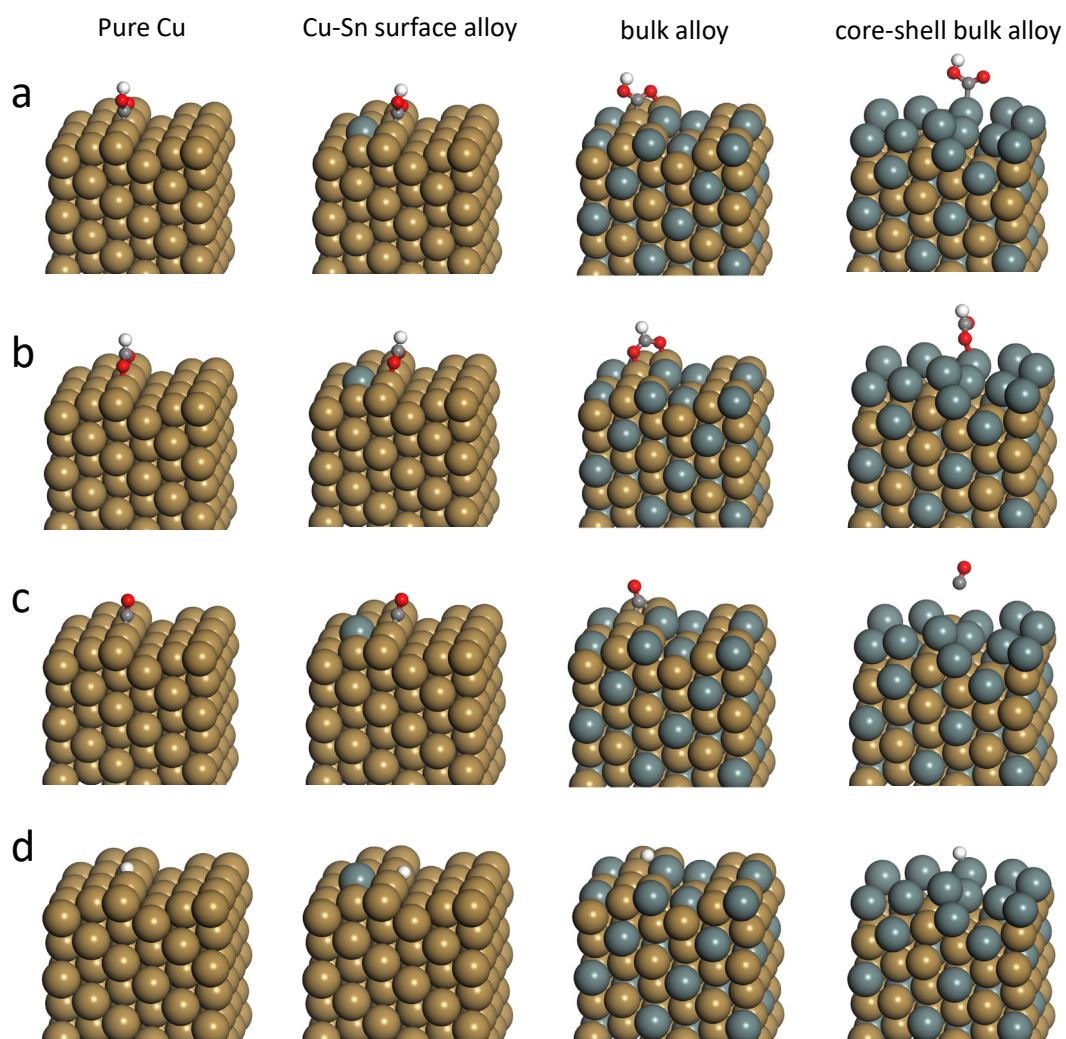
Supplementary Figure 12 | CO₂RR measurements on $\text{Cu}_{95}\text{Sn}_5$ (a), $\text{Cu}_{90}\text{Sn}_{10}$ (b), and $\text{Cu}_{80}\text{Sn}_{20}$ (c). As shown in Supplementary Fig. 12, the $\text{Cu}_{95}\text{Sn}_5$ exhibits CO dominated reactions from -0.6 to -1.0 V vs RHE, and the corresponding FE_{CO} reaches 98% at -0.7 V. As for $\text{Cu}_{90}\text{Sn}_{10}$, the FE_{CO} still outperforms $\text{FE}_{\text{Formate}}$ at low potentials from -0.6 to -0.7 V, and then the production of CO and formate becomes similar at -0.8 V with FE of both products at ~45%. With the further increase of overpotential, the $\text{Cu}_{90}\text{Sn}_{10}$ produces preferentially formate instead of CO. As for $\text{Cu}_{80}\text{Sn}_{20}$, the $\text{FE}_{\text{Formate}}$ exceeds the FE_{CO} in the whole potential range and more approaches to the performance of $\text{Cu}_{70}\text{Sn}_{30}$.



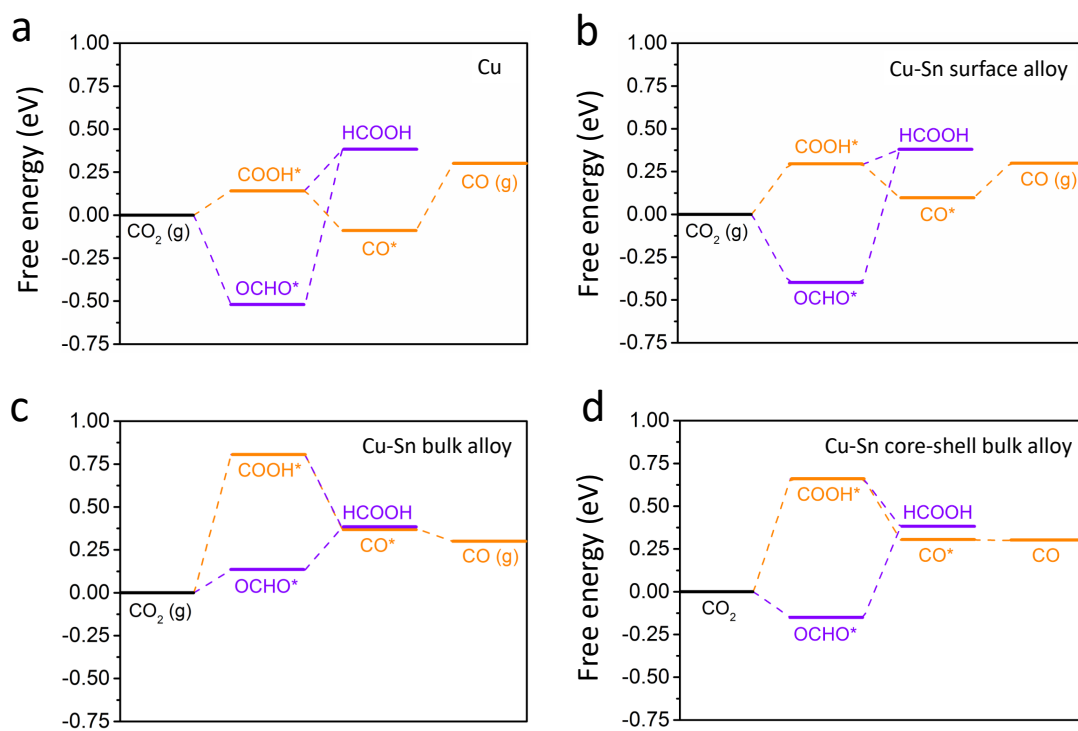
Supplementary Figure 13 | Electrochemically active surface area (ECSA) estimated from the double-layer capacitance. (a-c) CV curves for the identification of the capacitance measurements. (d-f) CV curves at different scan rates from 50 to 300 mV s^{-1} for Cu_{100} , $\text{Cu}_{97}\text{Sn}_3$ and $\text{Cu}_{70}\text{Sn}_{30}$, respectively. (g) Double-layer capacitance of different electrodes. The fluctuation in CV curves can be attributed to the CO_2 gas bubbling during the tests and the Autolab setup is very sensitive to the current change. Note that the fitting error in Supplementary Fig. 13g is very small, which suggests reliable double-layer capacitance calculation.



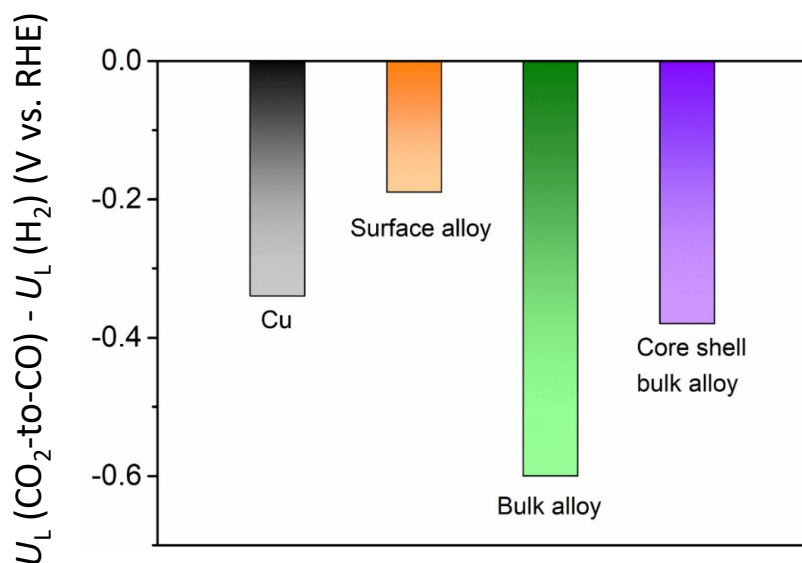
Supplementary Figure 14 | Graphic illustration of a home-customized flow cell.



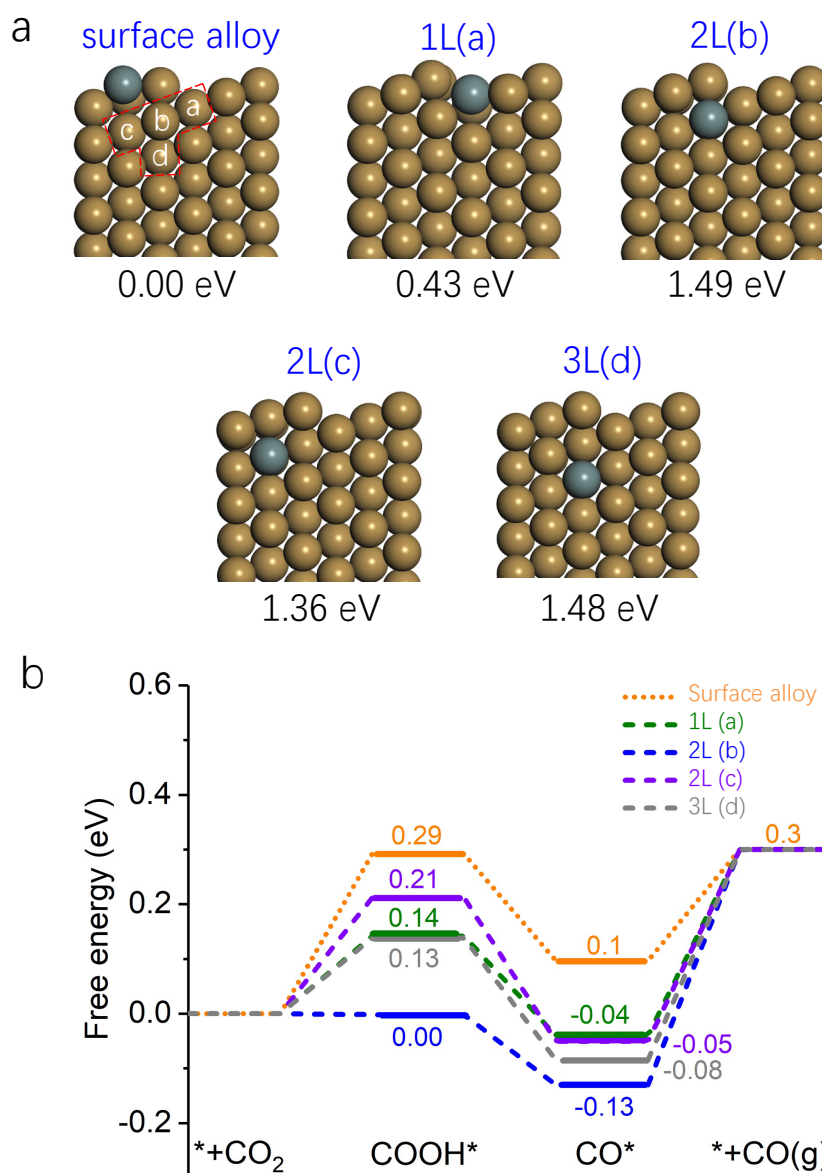
Supplementary Figure 15 | Optimized DFT model with different intermediates. Surface slabs with adsorbed (a) COOH*, (b) OCHO*, (c) CO*, and (d) H* on stepped facets of pure Cu, Cu₉₇Sn₃ and Cu₇₀Sn₃₀. The dark goldenrod, slate grey, grey, red and white balls represent Cu, Sn, C, O and H atoms, respectively.



Supplementary Figure 16 | The calculated free energy diagrams for CO_2 -to- CO and CO_2 -to- HCOOH conversion on four samples.



Supplementary Figure 17 | The difference in limiting potentials for CO₂-to-CO reduction and H₂ evolution on the catalysts. Previous studies have shown that the difference between thermodynamic limiting potentials for CO₂RR and HER (denoted as $U_L(\text{CO}_2) - U_L(\text{H}_2)$, in which U_L is defined as the lowest potential that all reaction steps are downhill in free energy) can reflect the selectivity of CO₂RR. According to this definition, a more positive value indicates a higher selectivity. Figure S17 shows the difference in limiting potentials for four samples, where surface alloy demonstrates a considerably more positive value than other samples, suggesting the greatly enhanced selectivity for CO₂-to-CO conversion.



Supplementary Figure 18 | DFT simulations of CO₂RR on Cu-Sn alloys with Sn atoms in different layers. (a) The relative substitution energy of a Cu atom by an Sn atom at different positions. All are given in eV. **(b)** The calculated free energy diagrams of CO₂-to-CO conversion for Cu-Sn single-atom alloys with different Sn position.

To understand the surface segregation of Sn atoms from the thermodynamical point of view. New density function theory (DFT) simulations have been carried out to investigate the possible position of Sn atom in single-atom Cu-Sn alloy, i.e. if the Sn prefers to sit on the surface or in the bulk. We calculated the relative substitution energy, which corresponds to the difference between the energy of substitution of a Cu atom in an inner layer and the energy of substitution of a Cu

atom at the surface, as shown in Supplementary Fig. 18a. The results suggest that only sit in the sub-surface layers, the substitution energy barrier of Sn atoms significantly increases to ~ 1.5 eV for 2L(b) and 3L(d) position. Therefore, the Sn atoms prefer to anchor on the surface of Cu nanoparticles rather than in bulk from an energetics perspective.

To investigate the effects of Sn atoms from different layers, we also calculated the free energy diagrams of CO₂-to-CO conversion for Cu-Sn single-atom alloys with different Sn positions including 1L(a), 2L(b), 2L(c) and 3L(d) (Supplementary Fig. 18b). For Cu-Sn single-atom alloy with Sn at the surface, the overpotential of CO₂ to-CO conversion is very small (0.29 eV). If the Sn atom locates in the second or the third layer, the electrocatalytic performance also displays a certain degree of enhancement compared with pure Cu, however, the overpotentials of CO₂-to-CO conversion significantly increase to 0.34~0.43 V compared with at the surface. These results indicate that the CO₂RR activities of single-atom Cu-Sn alloys are dependent on Sn atom position, and the single-atom Cu-Sn alloy with Sn at the surface shows the highest CO₂RR activity.

Table S1. Inductively coupled plasma optical emission spectroscopy (ICP-OES) analysis. The influence of oxygen is excluded.

Samples	Cu (at%)	Sn (at%)
Cu ₉₇ Sn ₃	97.3	2.7
Cu ₇₀ Sn ₃₀	72.8	27.2

Table S2. Recently reported Cu-Sn catalysts for CO₂RR in H-cells.

Catalysis	FE _{CO} (%, V vs RHE)	FE _{HCOOH} (%, V vs RHE)	Current density (mA cm ⁻² , V vs RHE)	Ref.
Cu₉₇Sn₃ surface alloy	98% at -0.7 V	/	78 at -1.0 V	Our work
Cu₇₀Sn₃₀ bulk alloy	/	88.8% at -1.0 V	92 at -1.0 V	Our work
CuSn NPs/C-A	~20% at -1.0 V	~70% at -1.0 V	~13 at -1.0 V (HCOOH)	16
CuSn ₃ /carbon paper	/	95% at -0.5 V	31 at -0.5 V (HCOOH)	8
Cu-Sn nanoparticles	/	92% at -0.95 V	9 at -0.95 V (HCOOH)	17
Cu-Sn electrodeposition	/	81% at -1.1 V	13 at -1.1 V (HCOOH)	18
Cu@Sn nanocones	/	90.4% at -1.1 V	57.7 at -1.1 V (HCOOH)	19
7/0.8 Cu/SnO ₂	93% at -0.7 V	/	/	20
Sn/Cu-nanofiber	80% at -1.0 V	/	53 at -1.0 V (CO)	21
Cu-Sn dendrite	~90% at -0.7 V	/	11.5 at -1.1 V (CO)	22
Cu-Sn foam	94% at -0.7 V	/	4.7 at -0.8 V (CO)	23
3D-h Cu-Sn	98.6% at -0.45 V	/	4.5 at -0.45 V (CO)	24
OD-Cu-Sn	90% at -0.6 V	/	1.0 at -0.6 V (CO)	6

Table S3. Performance of recently reported CO₂-to-CO electrocatalysts in flow cells.

Catalysis	E (V vs. RHE)	j_{CO} (mA cm ⁻²)	FE (%)	Electrolyte	Ref.
Cu ₉₇ Sn ₃	-0.45	100	87	1 M KOH	This work
Ni-N/PCFM	-0.7	~115	~80	0.5 M KHCO ₃	25
Ni-N-C	-0.7	~85	~90	1 M KHCO ₃	26
Ni-N-C	-0.8	~110	97%	0.5 M KHCO ₃	27
Fe-N-C	-0.45	94	~90	0.5 M KHCO ₃	28
CoPc@Fe-N-C	-0.55	~100	>90%	0.5 M KOH	29
CoSA/HCNFs	-0.6	~100	~70	1 M KHCO ₃	30
CoPc	-0.65	70.5	94	1 M KOH	31
CoPc-N	-0.66	31	94	1 M KOH	32
Ag/PTFE	-1.0	~160	~90	1 M KHCO ₃	33
	-0.7	~150	~90	1 M KOH	33
Ag/MPL-3C	-0.7	98.5	98.5	0.1 M KHCO ₃	34
Au	-0.7	~110	/	1 M KOH	35
Porous Zn	-0.9	~100	~67%	1 M KHCO ₃	36
	-0.62	100	~70%	1 M KOH	36

Table S4. Contribution to the free energy of adsorbates and non-adsorbed gas-phase molecules from ZPT correction, enthalpic temperature correction, and entropy contribution, respectively. All are given in eV.

Species	ZPE	$\int C_p dT$	-TS
COOH*	0.62	0.10	-0.18
OCHO*	0.62	0.10	-0.23
CO*	0.19	0.08	-0.15
CO ₂	0.31	0.10	-0.65
CO	0.14	0.09	-0.67
H ₂	0.27	0.09	-0.42
H ₂ O	0.58	0.10	-0.65
HCOOH	0.90	0.11	-1.02

Reference

- 1 Kresse, G. & Hafner, J. Ab initio molecular-dynamics simulation of the liquid-metal-amorphous-semiconductor transition in germanium. *Phys. Rev. B* **49**, 14251 (1994).
- 2 Kresse, G. & Joubert, D. From ultrasoft pseudopotentials to the projector augmented-wave method. *Phys. Rev. B* **59**, 1758 (1999).
- 3 Kresse, G. & Furthmüller, J. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Phys. Rev. B* **54**, 11169 (1996).
- 4 Perdew, J. P., Burke, K. & Ernzerhof, M. Generalized gradient approximation made simple. *Phys. Rev. Lett.* **77**, 3865 (1996).
- 5 Grimme, S., Antony, J., Ehrlich, S. & Krieg, H. A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu. *J. Chem. Phys.* **132**, 154104 (2010).
- 6 Sarfraz, S., Garcia-Esparza, A. T., Jedidi, A., Cavallo, L. & Takanabe, K. Cu-Sn bimetallic catalyst for selective aqueous electroreduction of CO₂ to CO. *ACS Catal.* **6**, 2842-2851 (2016).
- 7 Monkhorst, H. J. & Pack, J. D. Special points for Brillouin-zone integrations. *Phys. Rev. B* **13**, 5188 (1976).
- 8 Zheng, X. *et al.* Theory-guided Sn/Cu alloying for efficient CO₂ electroreduction at low overpotentials. *Nat. Catal.* **2**, 55-61 (2019).
- 9 Peterson, A. A., Abild-Pedersen, F., Studt, F., Rossmeisl, J. & Nørskov, J. K. How copper catalyzes the electroreduction of carbon dioxide into hydrocarbon fuels. *Energy Environ. Sci.* **3**, 1311-1315 (2010).
- 10 Ju, W. *et al.* Understanding activity and selectivity of metal-nitrogen-doped carbon catalysts for electrochemical reduction of CO₂. *Nat. Commun.* **8**, 944, doi:10.1038/s41467-017-01035-z (2017).
- 11 Nørskov, J. K. *et al.* Trends in the exchange current for hydrogen evolution. *J. Electrochem. Soc.* **152**, J23-J26 (2005).
- 12 Thuvander, M. *et al.* Quantitative atom probe analysis of carbides. *Ultramicroscopy* **111**, 604-608 (2011).
- 13 Felfer, P. *et al.* New approaches to nanoparticle sample fabrication for atom probe tomography. *Ultramicroscopy* **159**, 413-419 (2015).
- 14 Gault, B., Moody, M. P., Cairney, J. M. & Ringer, S. P. *Atom Probe Microscopy*. Vol. 160 (Springer Science & Business Media, 2012).
- 15 Nguyen-Phan, T.-D. *et al.* Understanding three-dimensionally interconnected porous oxide-derived copper electrocatalyst for selective carbon dioxide reduction. *J. Mater. Chem. A* **7**, 27576-27584 (2019).
- 16 Wang, P. *et al.* Phase and structure engineering of copper tin heterostructures for efficient electrochemical carbon dioxide reduction. *Nat. Commun.* **9**, 1-10 (2018).
- 17 Jiang, X. *et al.* A highly selective tin-copper bimetallic electrocatalyst for the electrochemical reduction of aqueous CO₂ to formate. *Appl. Catal. B: Environ.* **259**, 118040 (2019).
- 18 Li, M. *et al.* Modulated Sn oxidation states over Cu₂O-derived substrate for selective electrochemical CO₂ reduction. *ACS Appl. Mater. Inter.* **12**, 22760, (2020).
- 19 Chen, C. *et al.* Sharp Cu@Sn nanocones on Cu foam for highly selective and efficient

- electrochemical reduction of CO₂ to formate. *J. Mater. Chem. A* **6**, 19621-19630 (2018).
- 20 Li, Q. *et al.* Tuning Sn-catalysis for electrochemical reduction of CO₂ to CO via the core/shell Cu/SnO₂ structure. *J. Am. Chem. Soc.* **139**, 4290-4293 (2017).
- 21 Ju, W. *et al.* Electrocatalytic Reduction of Gaseous CO₂ to CO on Sn/Cu-Nanofiber-Based Gas Diffusion Electrodes. *Adv. Energy Mater.* **9**, 1901514 (2019).
- 22 Ju, W. *et al.* Sn-decorated Cu for Selective Electrochemical CO₂ to CO Conversion: Precision Architecture beyond Composition Design. *ACS Appl. Energy Mater.* **2**, 867-872 (2018).
- 23 Zeng, J. *et al.* Advanced Cu-Sn foam for selectively converting CO₂ to CO in aqueous solution. *Appl. Catal. B: Environ.* **236**, 475-482 (2018).
- 24 Yoo, C. J. *et al.* Compositional and Geometrical Effects of Bimetallic Cu-Sn Catalysts on Selective Electrochemical CO₂ Reduction to CO. *ACS Appl. Energy Mater.* (2020).
- 25 Yang, H. *et al.* Carbon dioxide electroreduction on single-atom nickel decorated carbon membranes with industry compatible current densities. *Nat. Commun.* **11**, 1-8 (2020).
- 26 Möller, T. *et al.* Efficient CO₂ to CO electrolysis on solid Ni-N-C catalysts at industrial current densities. *Energy Environ. Sci.* **12**, 640-647 (2019).
- 27 Zhang, T. *et al.* Nickel-Nitrogen-Carbon Molecular Catalysts for High Rate CO₂ Electro-reduction to CO: On the Role of Carbon Substrate and Reaction Chemistry. *ACS Appl. Energy Mater.* **3**, 1617-1626 (2020).
- 28 Gu, J., Hsu, C.-S., Bai, L., Chen, H. M. & Hu, X. Atomically dispersed Fe³⁺ sites catalyze efficient CO₂ electroreduction to CO. *Science* **364**, 1091-1094 (2019).
- 29 Lin, L. *et al.* Synergistic Catalysis over Iron-Nitrogen Sites Anchored with Cobalt Phthalocyanine for Efficient CO₂ Electroreduction. *Adv. Mater.* **31**, 1903470 (2019).
- 30 Yang, H. *et al.* Highly efficient utilization of single atoms via constructing 3D and free-standing electrodes for CO₂ reduction with ultrahigh current density. *Nano Energy* **70**, 104454 (2020).
- 31 Wang, M. *et al.* CO₂ electrochemical catalytic reduction with a highly active cobalt phthalocyanine. *Nature Commun.* **10**, 1-8 (2019).
- 32 Lu, X. *et al.* High-performance electrochemical CO₂ reduction cells based on non-noble metal catalysts. *ACS Energy Lett.* **3**, 2527-2532 (2018).
- 33 Dinh, C.-T., García de Arquer, F. P., Sinton, D. & Sargent, E. H. High rate, selective, and stable electroreduction of CO₂ to CO in basic and neutral media. *ACS Energy Lett.* **3**, 2835-2840 (2018).
- 34 Wang, R. *et al.* Maximizing Ag utilization in high-rate CO₂ electrochemical reduction with a coordination polymer-mediated gas diffusion electrode. *ACS Energy Lett.* **4**, 2024-2031 (2019).
- 35 Verma, S. *et al.* Insights into the low overpotential electroreduction of CO₂ to CO on a supported gold catalyst in an alkaline flow electrolyzer. *ACS Energy Lett.* **3**, 193-198 (2017).
- 36 Luo, W., Zhang, J., Li, M. & Züttel, A. Boosting CO production in electrocatalytic CO₂ reduction on highly porous Zn catalysts. *ACS Catal.* **9**, 3783-3791 (2019).