Supplementary Information (SI) for New Journal of Chemistry.

Supporting Information

Copper-tin bimetallic aerogel alloy for the electroreduction of CO_2 to formate

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Experimental Section

Preparation of Cu-Sn Aerogel

Taking the preparation of the Cu-Sn(1:1) aerogel as an example: 1 mmol $CuCl_2 \cdot 2H_2O$, 1 mmol $SnCl_2 \cdot 2H_2O$, 10 mmol NaCA, and 5 mmol NH_4Cl were dissolved in 20 mL of deionized water, followed by stirring for 30 minutes to form a clear solution. Then, 10 mL of 1 mM $NaBH_4$ solution was added to the above solution, and stirring continued for another 30 minutes, during which vigorous bubbling occurred. After stopping the stirring, the mixture was left to stand at room temperature for 6 hours. The black precipitate was then collected, washed four times with deionized water, and freeze-dried to produce the aerogel. The preparation method for the other two aerogels was the same, except that Cu and Sn were used in different molar ratios (2:1 and 1:2) to prepare the Cu-Sn(2:1) and Cu-Sn(1:2) aerogels, respectively. Bulk Sn and granular Cu were also prepared in the absence of Cu and Sn, respectively.

Electrochemical Experiments

Electrochemical tests were conducted using a Shanghai Chenhua electrochemical workstation (CHI760E) in an airtight H-type reaction cell. The cathode and anode compartments of the cell were separated by a Nafion 117 ion-exchange membrane. A graphite rod served as the counter electrode, and a saturated silver/silver chloride electrode (Ag/AgCl) was used as the reference electrode. Carbon paper (TGP-H-60) loaded with the aerogel served as the working electrode. To prepare the working electrode, 5 mg of the catalyst was dissolved in a mixture of 700 μL isopropanol, 270 μL water, and 30 μL 5% Nafion. The resulting mixture was sonicated for 30 minutes to obtain a uniform catalyst ink, which was then evenly drop-cast onto the carbon paper, with a loading of approximately 1 mg/cm². The dried carbon paper was then used as the working electrode.

During the tests, the cathode and anode compartments were filled with 37 mL of 0.5 M $KHCO_3$ solution. Before the tests, CO_2 was bubbled into the cathode compartment at a flow rate of 30 mL/min for 30 minutes to ensure saturation. The scan rate for linear sweep voltammetry (LSV) was set to 50 mV/s. The electrochemical surface area (ECSA) was calculated by recording cyclic voltammetry (CV) curves in the non-Faradaic region at scan rates ranging from 20 to 160 mV/s, and the double-layer capacitance (Cdl) was determined. Electrochemical impedance spectroscopy (EIS) was conducted over a frequency range of 0.01–100 kHz at a testing potential of -1 V vs. RHE. The potential was converted according to the formula:

$$E(\text{vs RHE})=E(\text{vs Ag/AgCl})+0.21\ \text{V}+0.0591\times\text{pH}$$

All test data were reported without IR compensation.

Gas Product Analysis -Electrolysis tests (i-t) were performed for 30 minutes at different potentials. The gas produced in the cathode chamber was introduced into a gas chromatograph (Fuli GC) for online detection via an automatic sampler. The measurement of gas products was conducted using an external standard method, where the gas content was calculated based on the corresponding standard samples. The Faradaic efficiency was calculated as follows[39]:

$$FE = \frac{Z \times F \times V \times \mathrm{t} \times \mathrm{v} \times P / RT}{I\mathrm{t}} \times 100\%$$

$$FE = \frac{\mathrm{n} \times Z \times F}{\mathrm{Q}} \times 100\%$$

Z is the number of electrons transferred to generate a specific product, V is the flow rate of CO_2, v is the volume concentration of the product, I is the total current density, t is the duration of the electrolysis.

Liquid Product Analysis-The electrolyte solution from the cathode after electrolysis was collected for product analysis. The concentration of formate was determined using nuclear magnetic resonance (NMR) spectroscopy with an internal standard method. To perform the analysis, 500 μL of the electrolyte was mixed with 50 μL of deuterium oxide (D_2O) and 50 μL of DMSO. The concentration of formate was calculated based on the peak area of the internal standard in the NMR spectrum. The Faradaic efficiency for formate was calculated using the following formula:

$$FE = C \times \frac{\mathrm{V} \times Z \times F}{\mathrm{Q}} \times 100\%$$

C is the concentration of formate in the electrolyte after electrolysis, V is the volume of the electrolyte, Z is the number of electrons transferred to generate formate, Q is the total charge consumed during the electrolysis process.

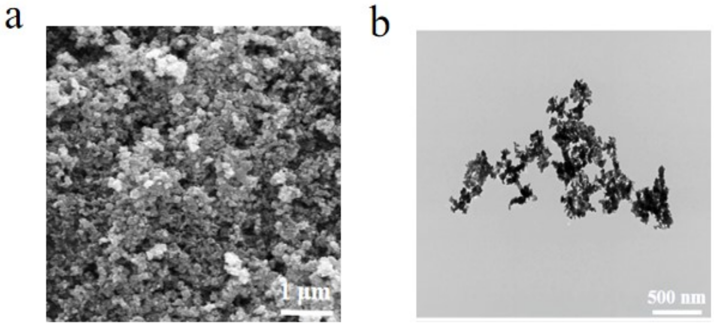

Figure S1 . SEM and TEM images of Cu-Sn (2 : 1) .

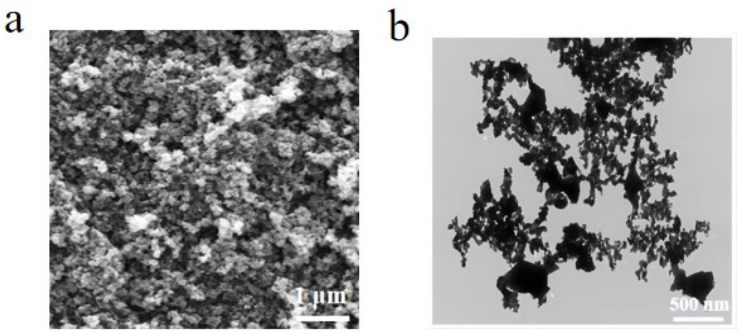

Figure S2 . SEM and TEM images of Cu-Sn (1 : 2) .

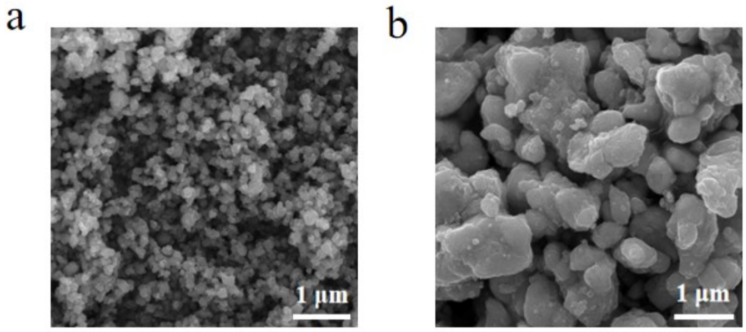

Figure S3. SEM images of Cu and Sn.

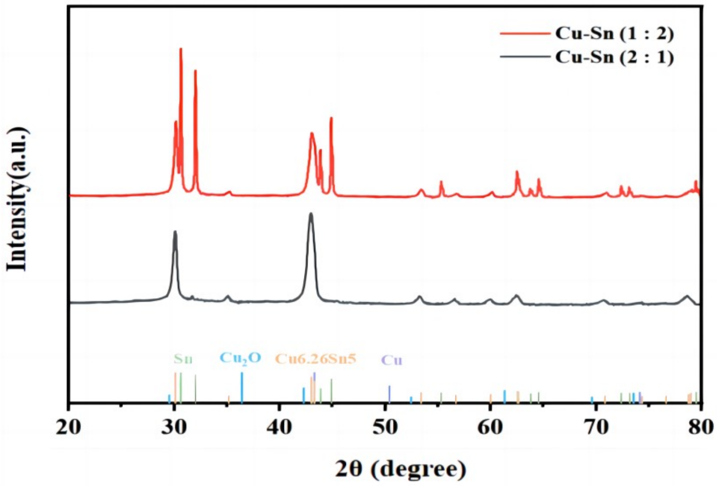

Figure S4. XRD of Cu-Sn (2 : 1) and Cu-Sn (1 : 2).

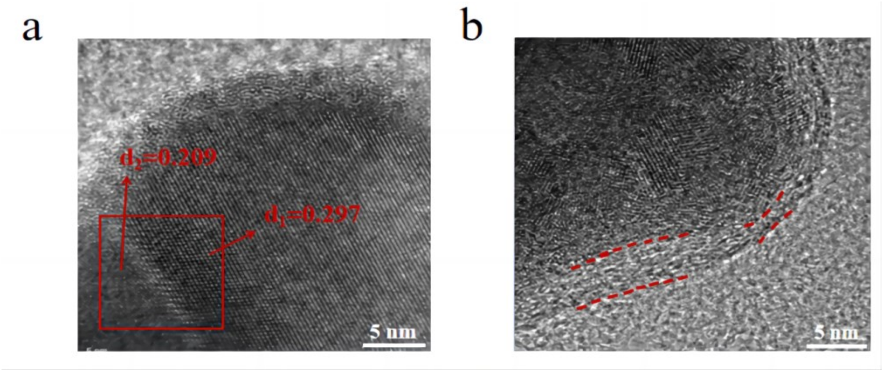

Figure S5. (a) Oxide layer of Cu-Sn (1 : 1) . (b) alloy interface of Cu-Sn (1 : 1).

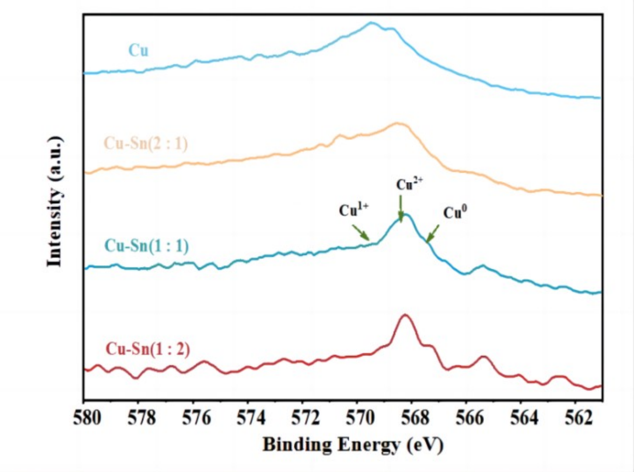

Figure S6. Cu LMM.

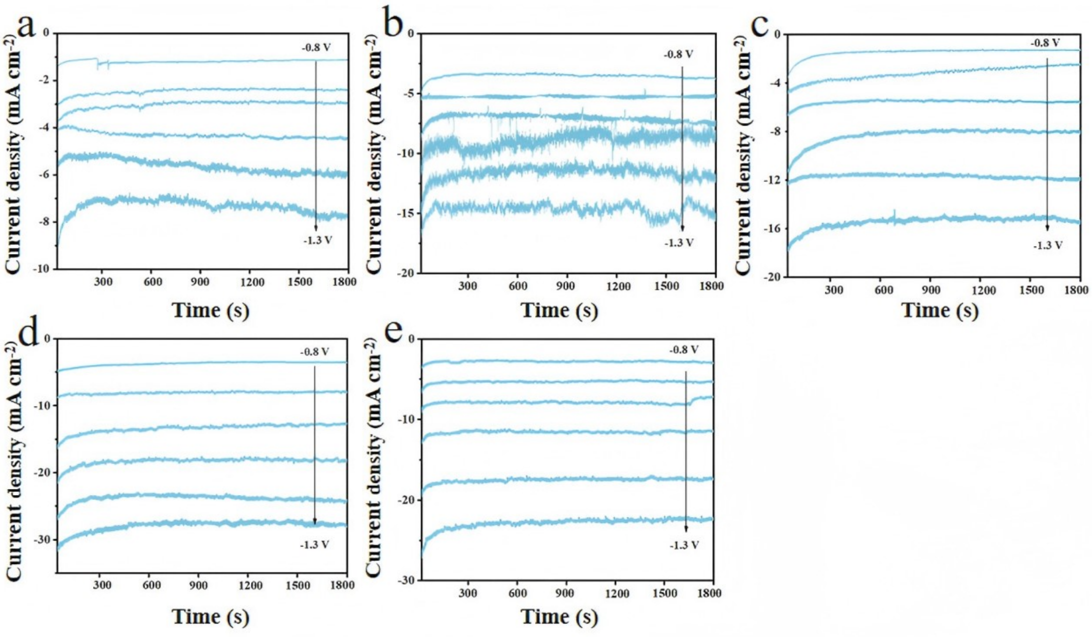

Figure S7. Chronoamperometric testing of five catalysts in the range from -0.8 V to -1.3V.(a) Sn, (b)Cu, (c) Cu-Sn(2 : 1), (d) Cu-Sn(1 : 1), (e) Cu-Sn(1 : 2).

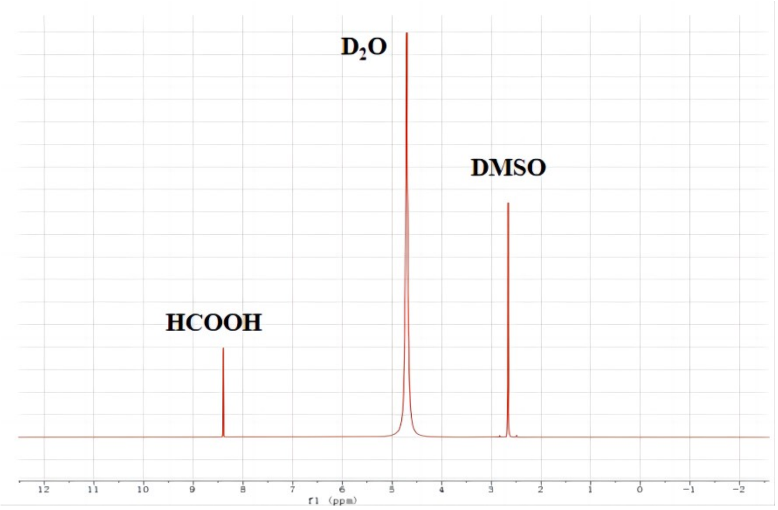

Figure S8. at -1.1V , ^{1}H NMR of Cu-Sn(1 : 1).

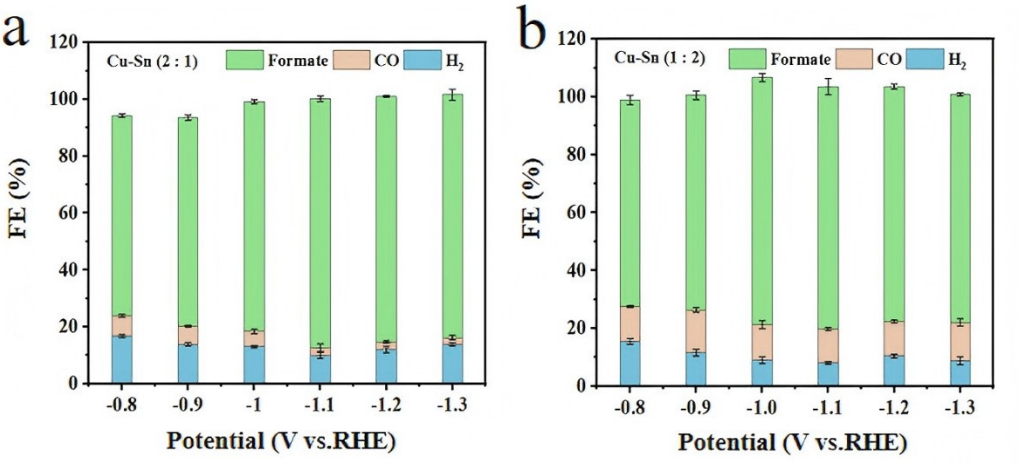

Figure S9. (a) FE of Cu-Sn(1 : 2). (b) FE of Cu-Sn(2 : 1).

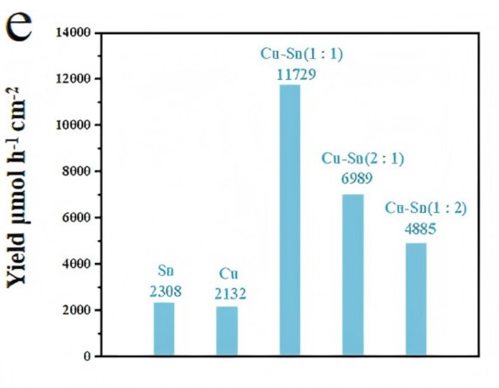

Figure S10. Formate generation rate

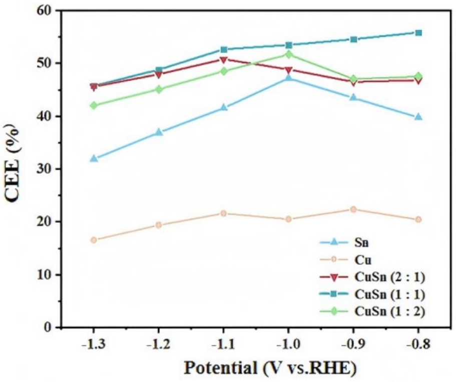

Figure S11. Cathodic energy conversion efficiency

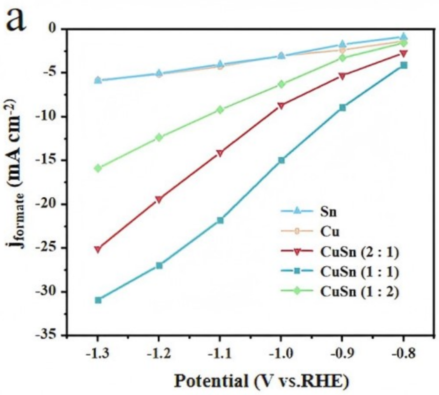

Figure S12. Partial current density for formate of Sn, Cu, Cu-Sn (1:1), Cu-Sn (2:1), Cu-Sn (1:2).

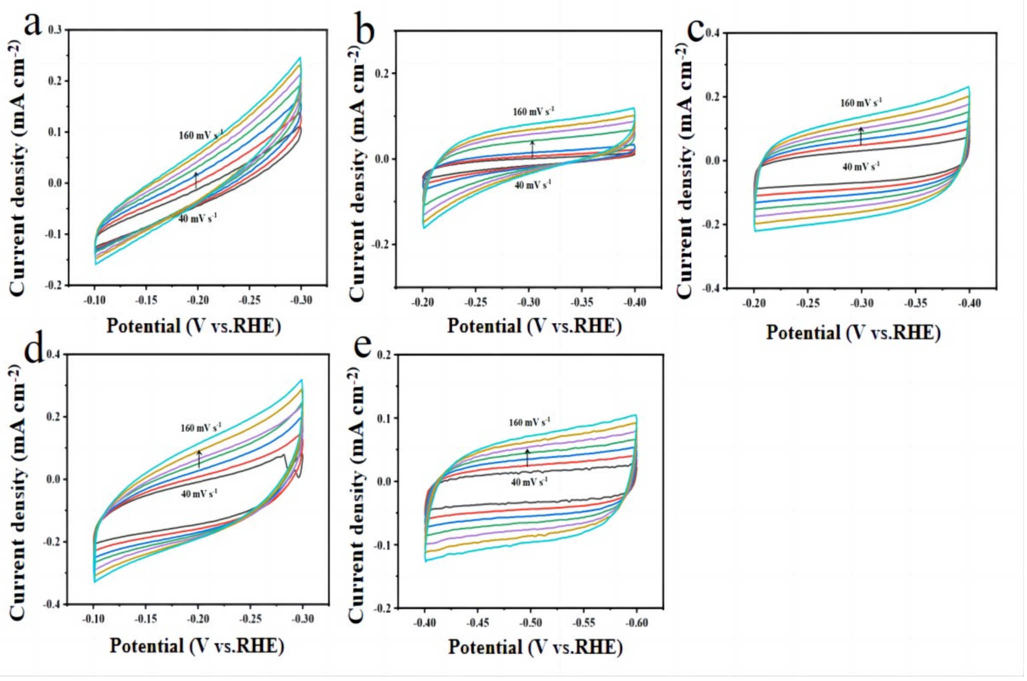

Figure S13. CV (40 -160mV s^{-1}). (a) Sn. (b) Cu. (c) Cu-Sn(1 : 1). (d)Cu-Sn(2 : 1). (e) Cu-Sn(1 : 2)