

Supporting Information

Universal synthesis of pure-phase IB-group Sn-based alloys with modulable electrocatalytic CO₂ reduction products

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1. Experimental section

1.1 Synthesis of pure phase Ag_4Sn . Commercial Ag powder was washed with ethanol at least three times to eliminate organic contaminants. 15 mmol of SnCl_2 was added to KOH aqueous (30 mL, 3 M), followed by mechanical shock and shaking. After centrifugation, the supernatant was collected and mixed with 0.3 mmol of Ag powder in a 50 mL hydrothermal reactor. The mixture was heated at 180 °C for 13 hours. The resulting solid was washed with deionized water until neutral, then dried in vacuum at 60 °C overnight to obtain the pure phase Ag_4Sn .

1.2 Synthesis of Cu_3Sn and AuSn . The Ag powder was replaced with 0.3 mmol of Cu powder or 0.15 mmol of Au powder, while keeping all other conditions constant. Prior to that, the commercial Cu powder was cleaned with a 10% HCl solution and ethanol separately at least three times to remove surface oxides and organic residues, while the commercial Au powder was cleaned with ethanol alone for at least three times.

1.3 The preparation of electrodes

5 mg of catalyst, 5 mg of conductive carbon black, and 30 μL of 5% Nafion solution were dispersed in 970 μL of isopropanol solution. The obtained ink underwent ultrasonication for 2 h and then was uniformly coated onto $1 \times 1 \text{ cm}^2$ carbon paper and dried on a constant temperature heating table at 80 °C for 30 min. The catalyst loading on the carbon paper was 0.5 mg cm^{-2} .

1.4 Characterizations

The morphology of these materials was characterized using a Hitachi S4800 scanning electron microscope (SEM) and a JEOL JEM-ARM 200F transmission electron microscope (TEM). The crystal structure and physical phases of the materials were analyzed by X-ray diffraction (XRD) using Cu $K\alpha$ radiation on Rigaku SmartLab diffractometer.

1.5 Electrochemical measurements

All electrochemical experiments were carried out on a Biologic VMP3 potentiostat controlled by EC-Lab software using a gastight H-type electrochemical cell separated by a proton-exchange membrane (Nafion 115). In the three-electrode system, the catalyst served as the working electrode, a platinum sheet served as the counter

electrode, and an Ag/AgCl (saturated KCl) electrode served as the reference electrode. The 0.5 M KHCO₃ aqueous solution was used as the electrolyte. During the electrochemical measurements, CO₂ was continuously bubbled through the electrolyte at a rate of 5 mL min⁻¹. All measured potentials were converted to the RHE reference scale according to the following formula:

$$E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.199\text{V} + 0.0591\text{pH} \quad (1)$$

Linear-sweep voltammetry curves were generated at a scanning rate of 5 mV s⁻¹ in 0.5 M KHCO₃ aqueous solution saturated with Ar or CO₂. The CO₂ reduction gas phase products were quantified using a gas chromatograph (Nanjing Hope, GC-9860-5C) equipped with a Valcoplot HayeSep Q column and a Molsieve 5 A column. Liquid products were quantified using ¹H NMR recorded on a Bruker AVANCE AV-300 spectrometer. Typically, 500 μL of electrolyte and 100 μL of dimethyl sulfoxide/D₂O standard solution were mixed.

1.6 Product FE calculation

The FE of products obtained from the electrochemical reduction of CO₂ catalyzed by various catalysts at different voltages refers to the ratio of the electrical charge transferred for the generation of specific products to the total charge passed through the system, which is a crucial parameter for evaluating the electrocatalytic performance of the catalyst. The calculation formulas for the FE of gaseous and liquid products are as follows:

$$FE_{\text{gas}}(\%) = \frac{\alpha \times F \times v \times P_0 \times f_x}{R \times T \times I} \times 100\% \quad (2)$$

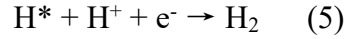
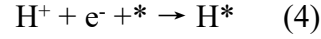
$$FE_{\text{liquid}}(\%) = \frac{\alpha \times F \times c_{x-\text{cell}} \times V_{\text{cell}}}{I \times t} \times 100\% \quad (3)$$

Where, α is the number of electrons transferred in the reduction of CO₂ to a specific product, F is the faradaic constant (96485 C mol⁻¹), v signifies the gas flow rate, P_0 is the ambient pressure (101325 Pa), f_x is the molar fraction of a specific gaseous product, R is the ideal gas constant (8.314 J mol⁻¹ K⁻¹), T is the room temperature (298.15 K), I is the average current during the application of different test potentials, $c_{x-\text{cell}}$ is the

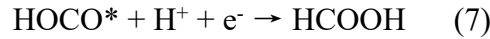
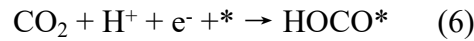
concentration of a specific liquid-phase product in the electrolyte, V_{cell} is the total volume of the electrolyte, and t is the reaction time.

1.7 Theoretical calculation details

The mechanism for the reduction of CO_2 to form H_2 is written as:



The mechanism for the reduction of CO_2 to form formate is written as:



Where, $*$ represents an empty surface catalytically active site or an intermediate species adsorbed on the active site.

All calculations were performed using the Vienna Ab-initio Simulation Package (VASP) for density functional theory (DFT) calculations, with spin polarization effects taken into account. The interaction between ions and electrons is described using the Projector Augmented Wave (PAW) pseudopotential method, with the following electronic configurations for the PAW pseudopotentials: tin (Sn) with s^2p^2 , copper (Cu) with $d^{10}p^1$, gold (Au) with s^1d^{10} , silver (Ag) with s^1d^{10} , oxygen (O) with s^2p^4 , carbon (C) with s^2p^2 and hydrogen (H) with $1s^1$. The exchange-correlation interaction between electrons is described using the Generalized Gradient Approximation (GGA) functional within the Perdew-Burke-Ernzerhof (PBE) scheme. All calculations are performed within the Brillouin zone using a plane-wave cutoff energy of 400 eV. The structures of Ag_4Sn , Cu_3Sn , and AuSn are represented by supercells with the following dimensions: Ag_4Sn with a $2 \times 2 \times 1$ supercell, Cu_3Sn with a $3 \times 2 \times 1$ supercell, and AuSn with a $2 \times 3 \times 1$ supercell, each comprising 64, 64 and 52 atoms, respectively. The convergence criteria for energy and forces are set to 1×10^{-5} eV and 0.01 eV/Å, respectively.

The adsorption energy (E_{ads}) is calculated as follows:

$$E_{\text{ads}} = E_{\text{ad/sub}} - E_{\text{ad}} - E_{\text{sub}} \quad (8)$$

Where, $E_{\text{ad/sub}}$, E_{ad} , and E_{sub} represent the total energies of the optimized adsorbate/substrate system, the adsorbate within the structure, and the substrate, respectively.

2. Experimental results

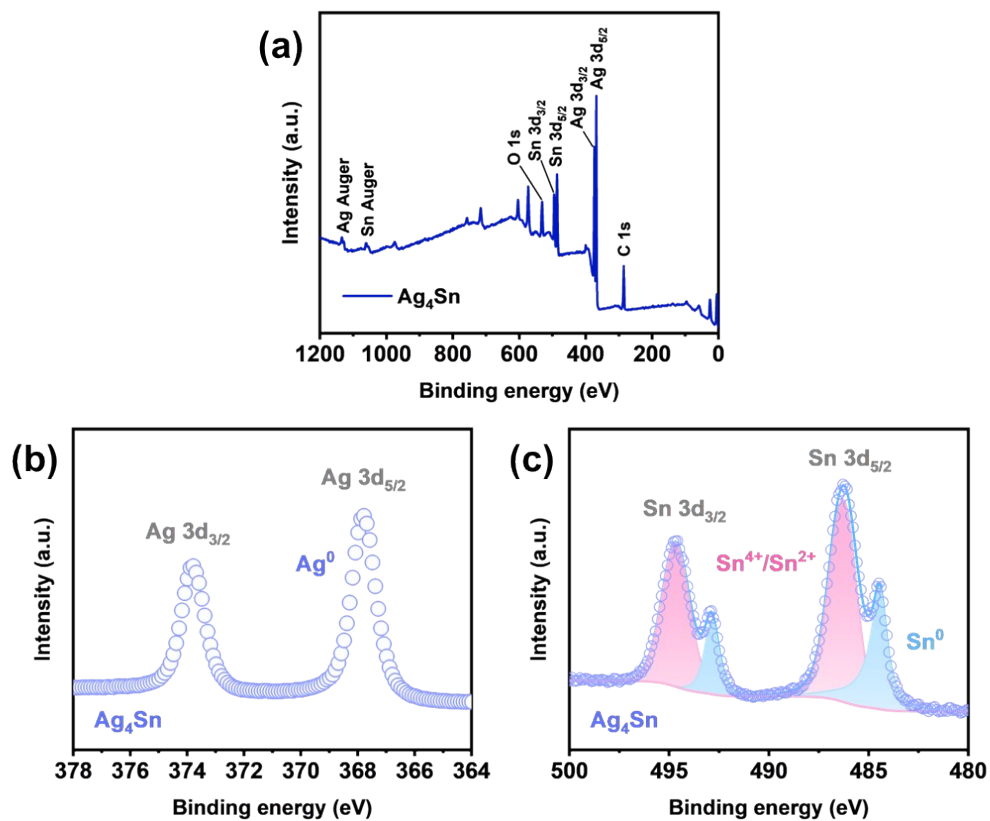


Figure S1. (a) Survey XPS spectrum, (b) Ag 3d and (c) Sn 3d high-resolution XPS spectra of Ag_4Sn catalyst.

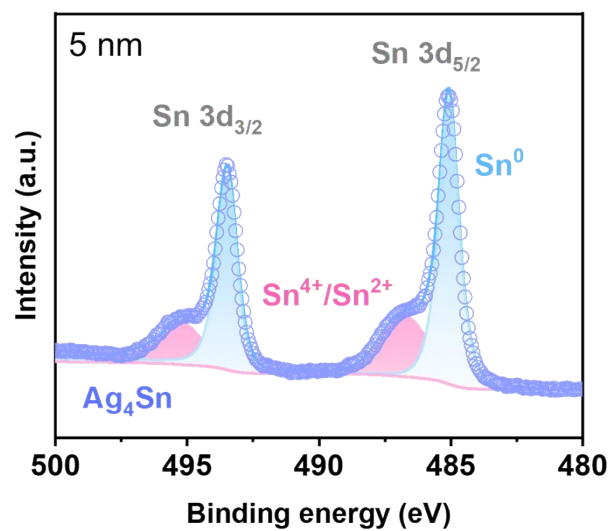


Figure S2. Sn 3d high-resolution XPS spectra of Ag₄Sn after Ar beam etch.

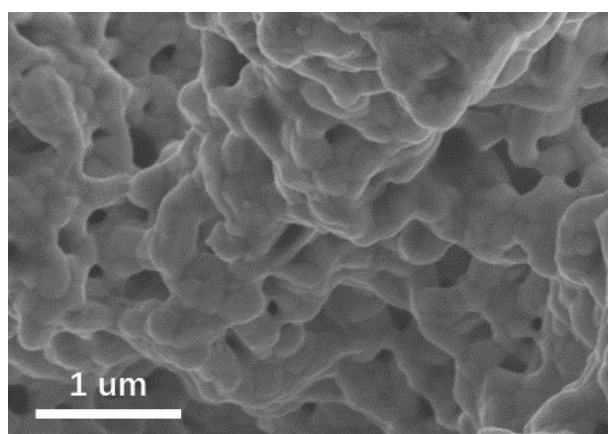


Figure S3. SEM image of Cu₃Sn.

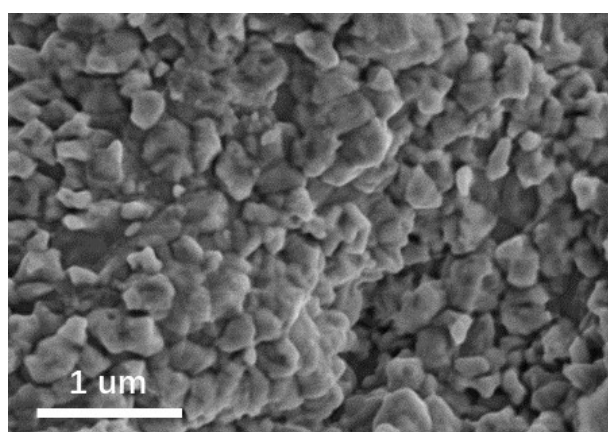


Figure S4. SEM image of AuSn.

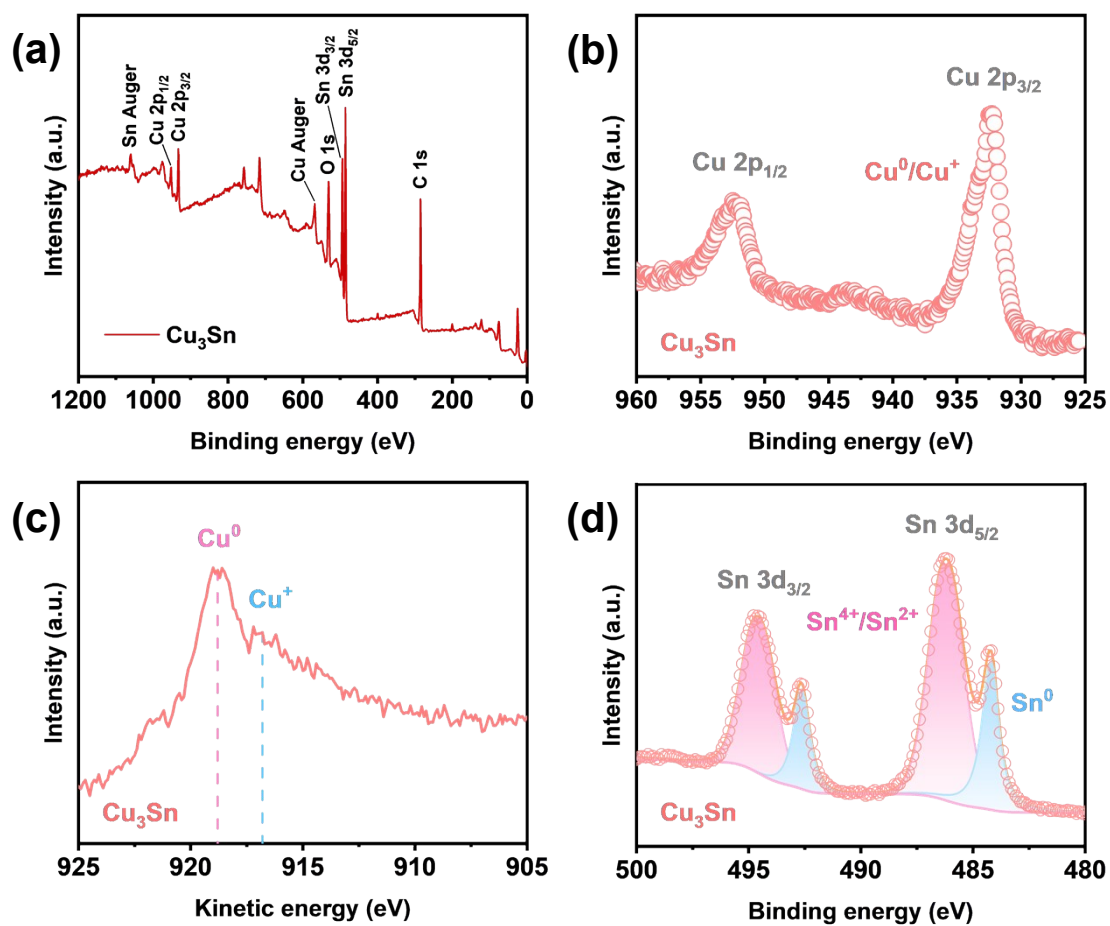


Figure S5. (a) Survey XPS spectrum, (b) Cu $2p$ high-resolution XPS spectra, (c) Cu LMM Auger spectra and (d) Sn $3d$ high-resolution XPS spectra of Cu_3Sn .

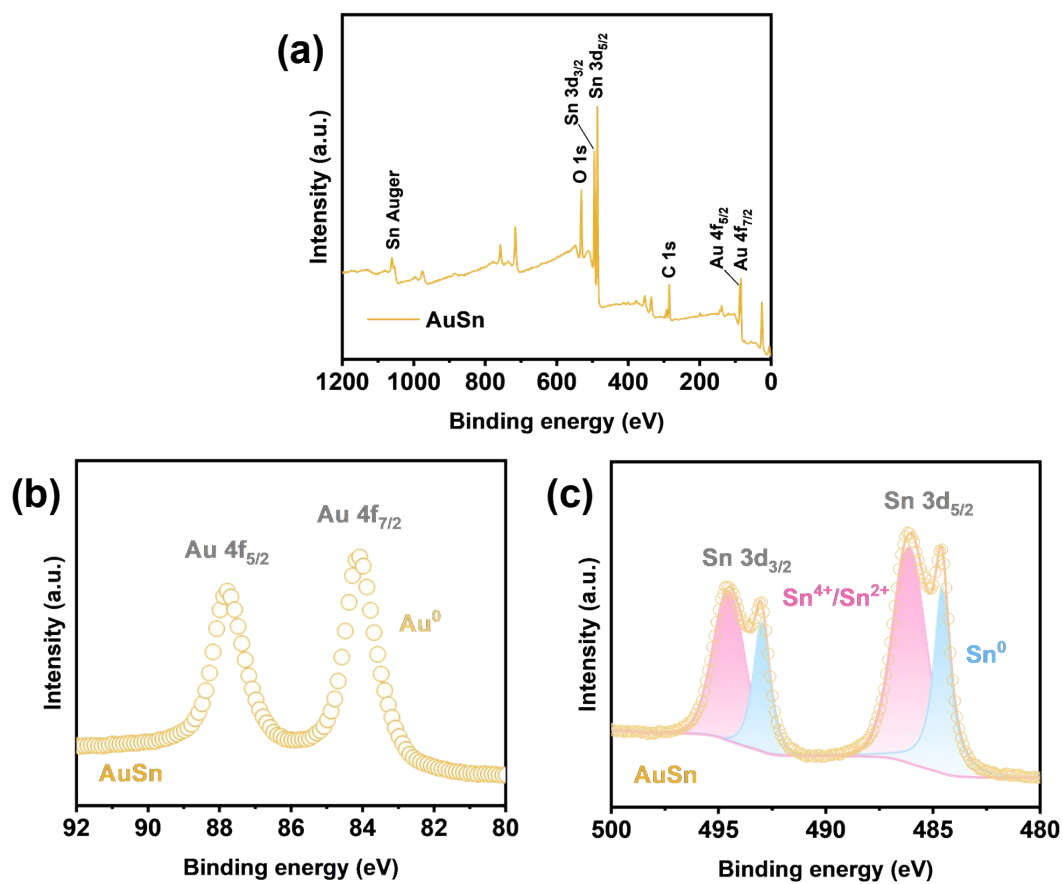


Figure S6. (a) Survey XPS spectrum, (b) Au 4f and (c) Sn 3d high-resolution XPS spectra of AuSn catalyst.

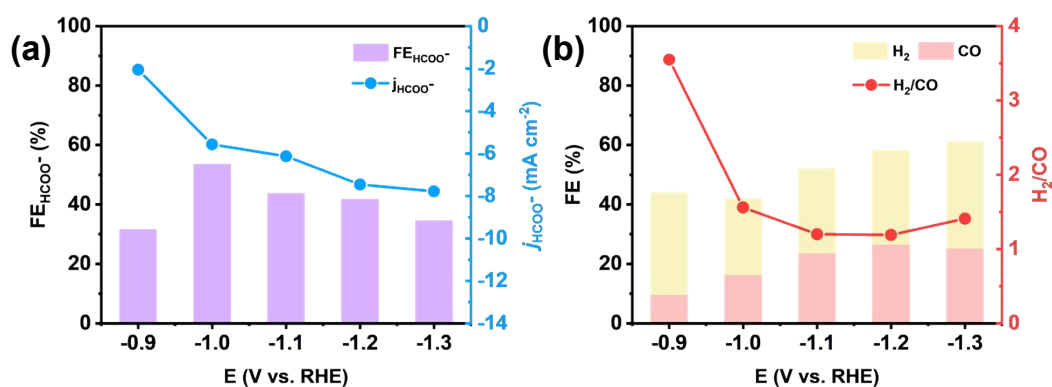


Figure S7. (a) FE_{HCOO^-} , j_{HCOO^-} values, and (b) FE values of H_2 and CO along with H_2/CO ratios of Ag₄Sn catalyst.

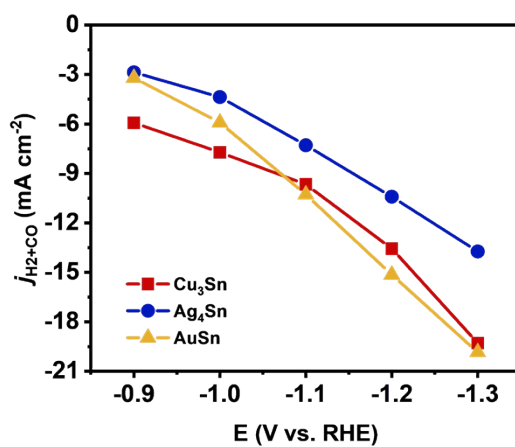


Figure S8. Comparative j_{H_2+CO} values of Cu₃Sn, Ag₄Sn and AuSn catalysts.

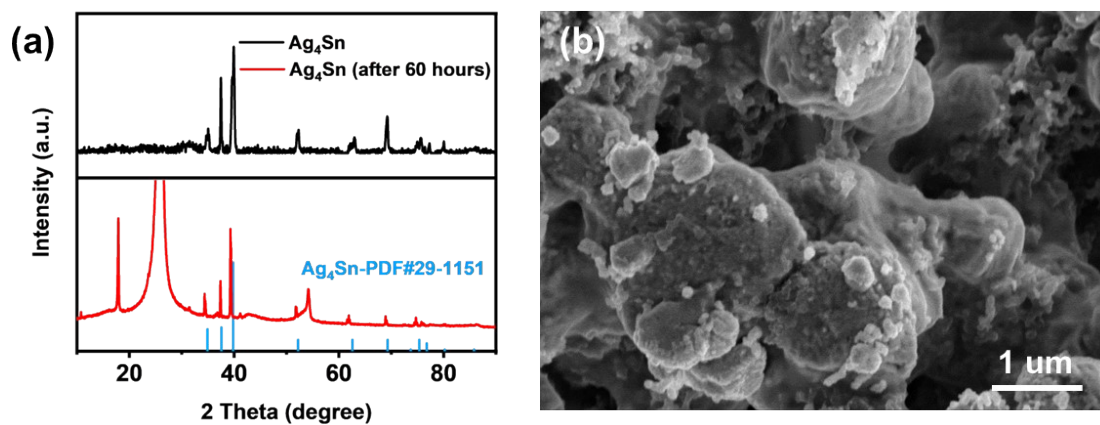


Figure S9. (a) XRD pattern of Ag₄Sn catalyst before and after stability testing. (b) SEM image of Ag₄Sn catalyst after stability testing.

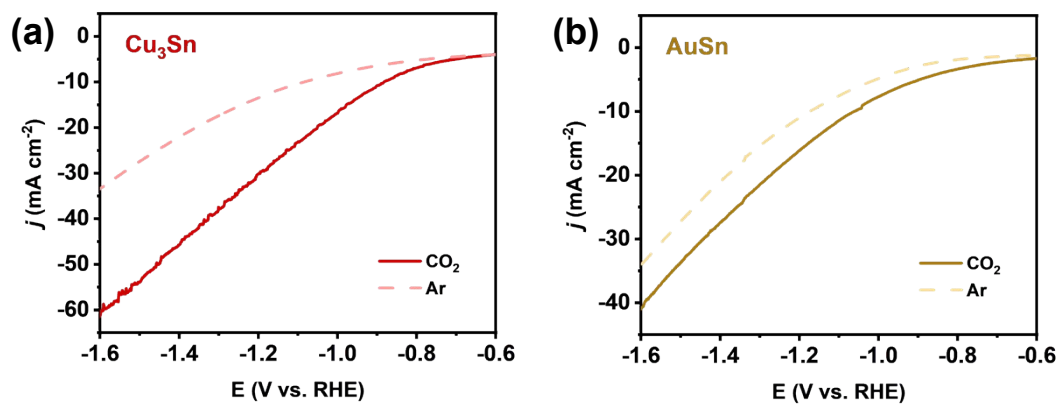


Figure S10. LSV curves of Cu₃Sn (a) and AuSn (b) catalysts in 0.5 M KHCO₃ electrolyte saturated with Ar and CO₂.

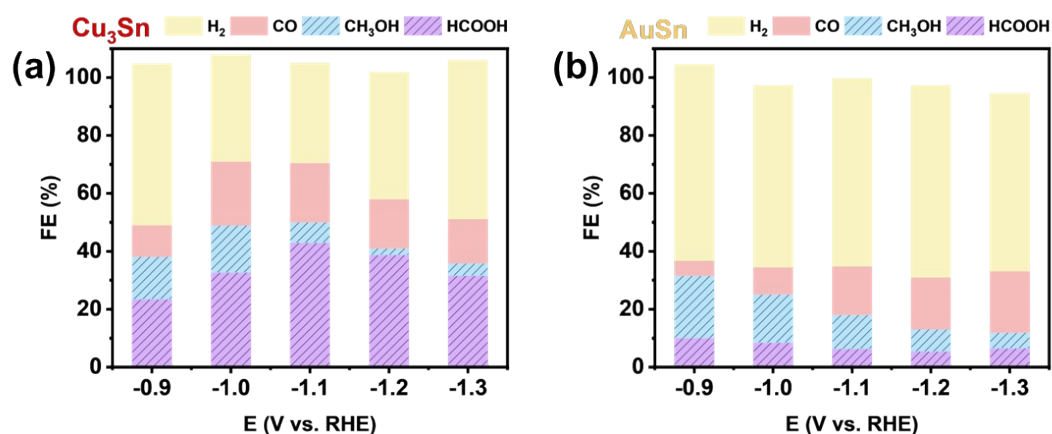


Figure S11. The FE values of all products on (a) Cu_3Sn and (b) AuSn .

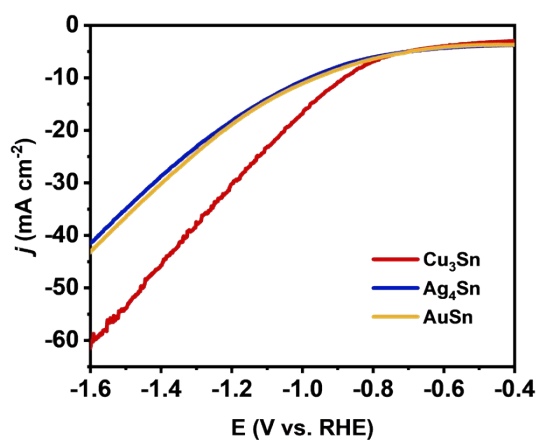


Figure S12. LSV curves of Cu_3Sn , Ag_4Sn , and AuSn in 0.5 M KHCO_3 electrolyte saturated with Ar and CO_2 .

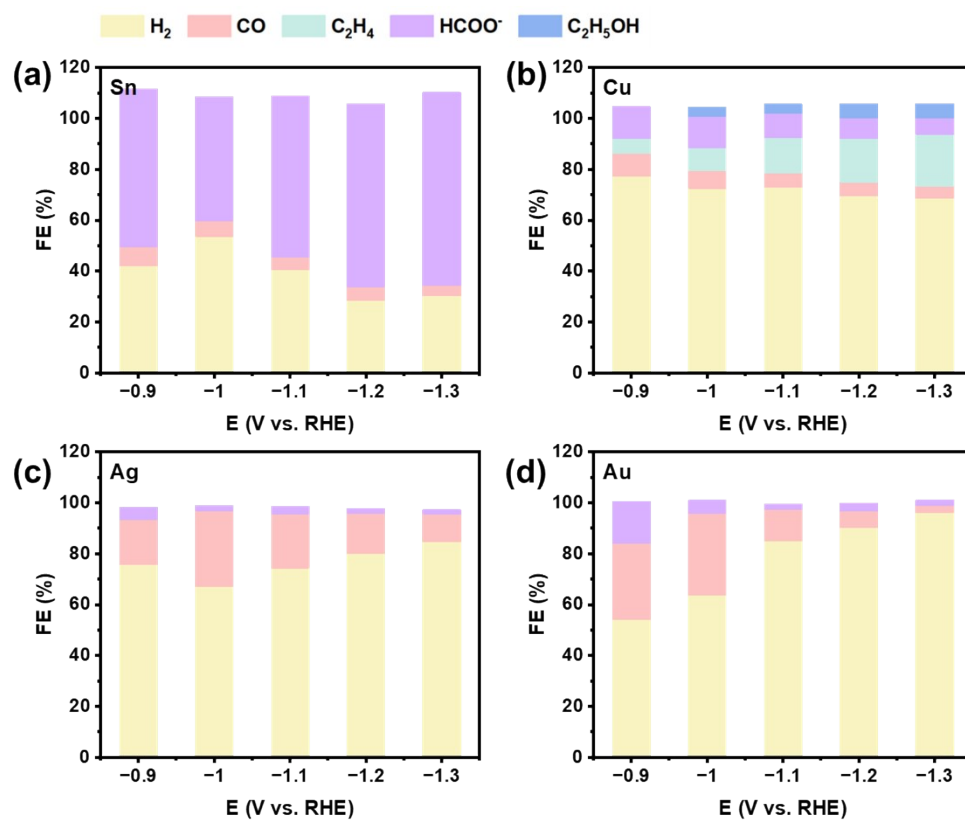


Figure. S13 FE values of all products on (a) Sn, (b) Cu, (c) Ag and (d) Au.

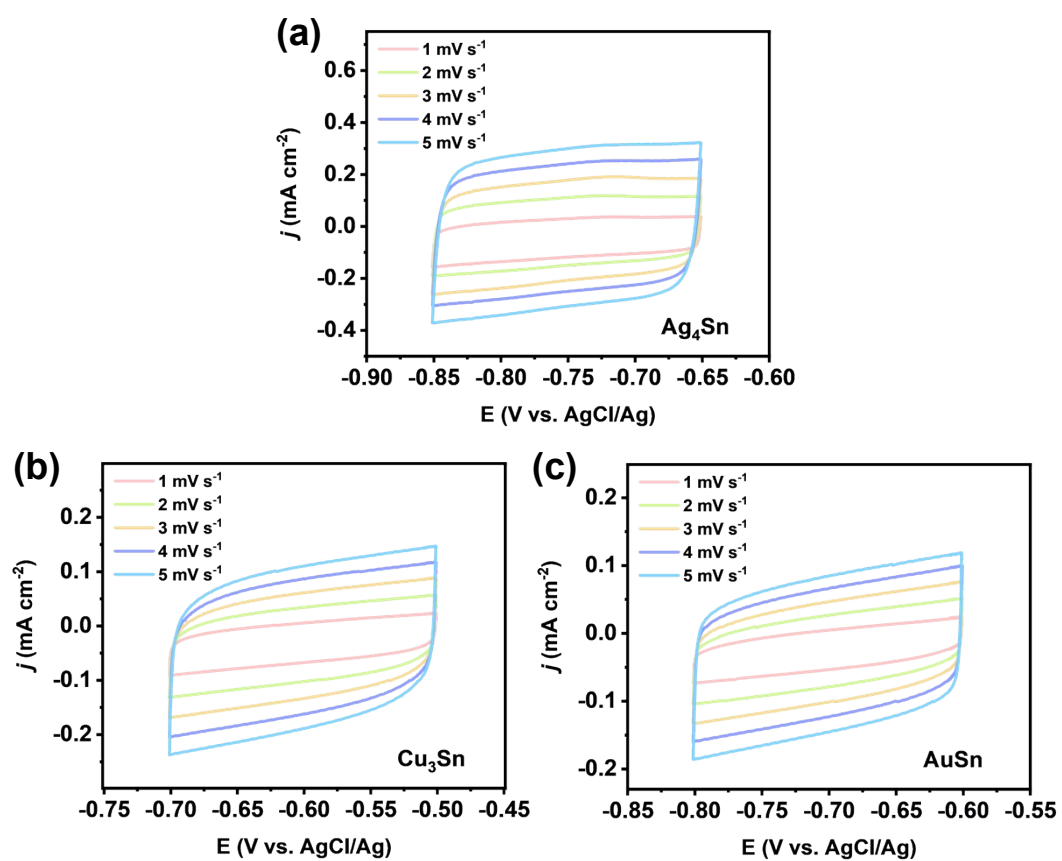


Figure S14. CV curves of (a) Ag₄Sn, (b) Cu₃Sn and (c) AuSn.

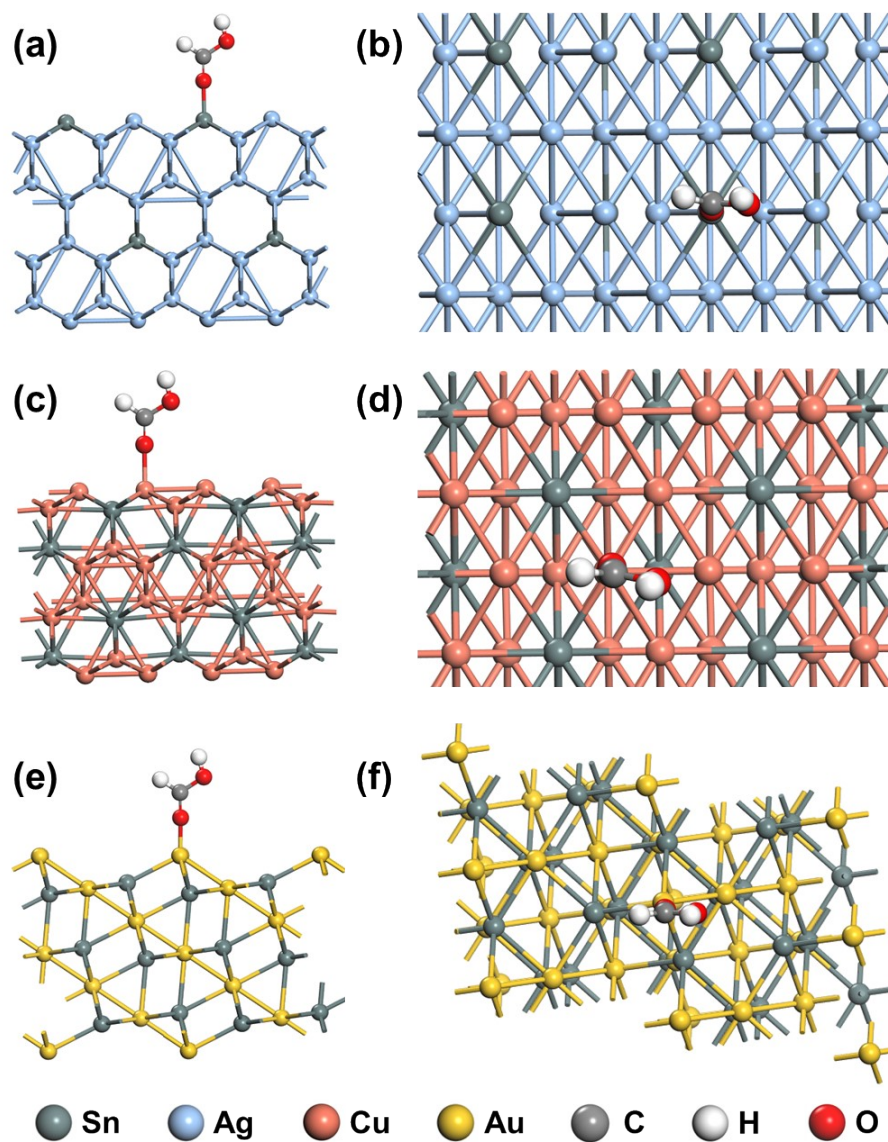


Figure S15. Surface structures and adsorbed HCOOH^* on (a-b) Ag_4Sn (100), (c-d) Cu_3Sn (0 16 0) and (e-f) AuSn (101).

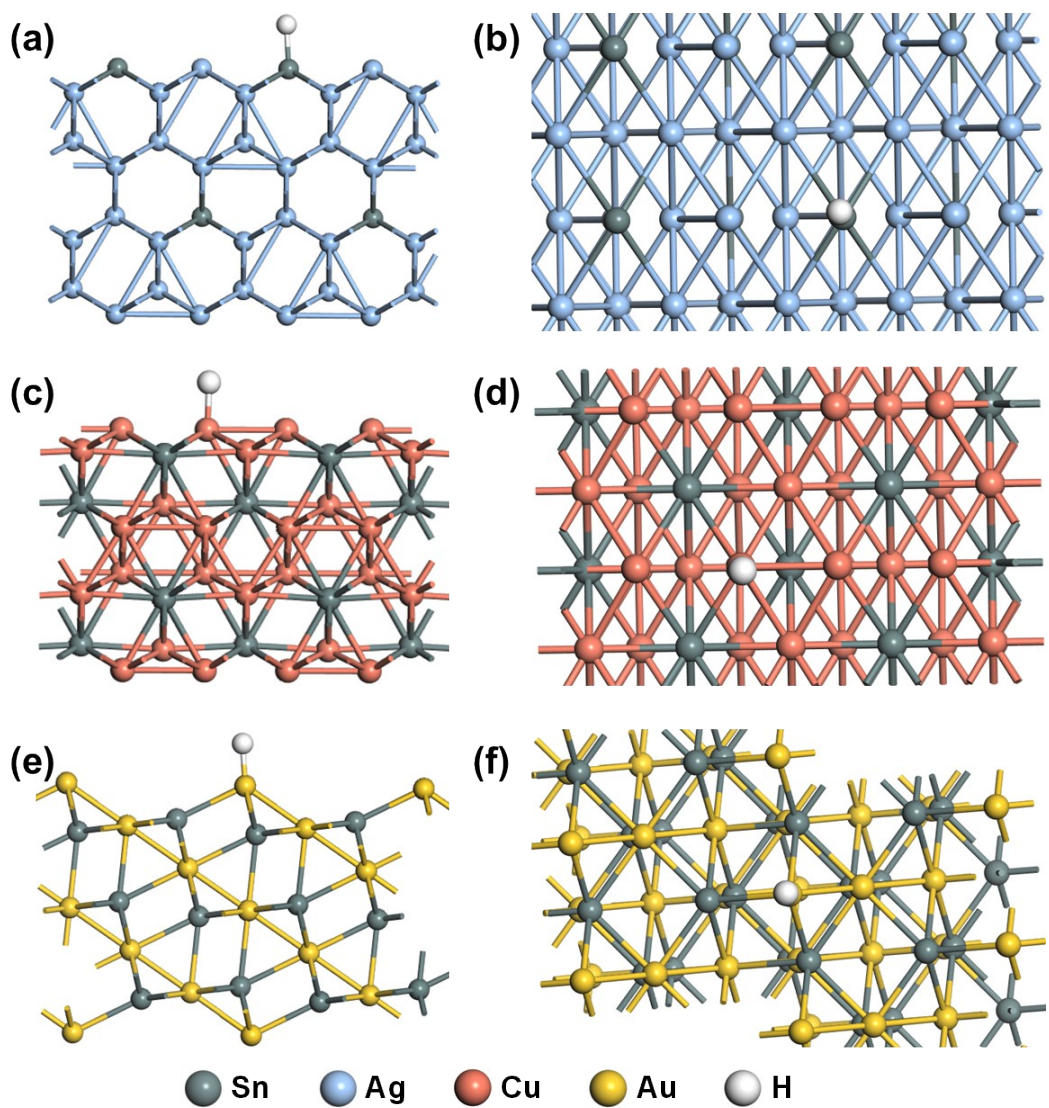


Figure S16. Surface structures and adsorbed H^* intermediates on (a-b) Ag_4Sn (100), (c-d) Cu_3Sn (0 16 0) and (e-f) $AuSn$ (101).