Supplemental Information

**Engineering Surface Oxophilicity of Copper for Electrochemical CO2 Reduction to Ethanol**

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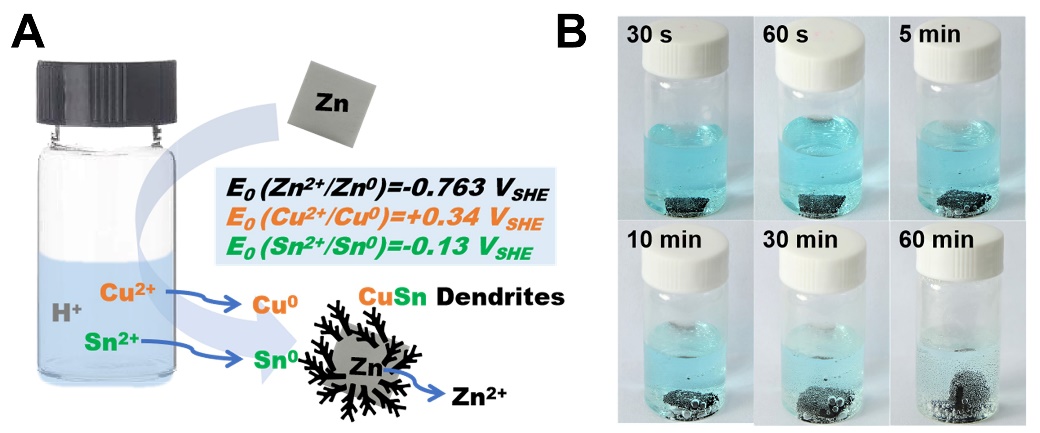
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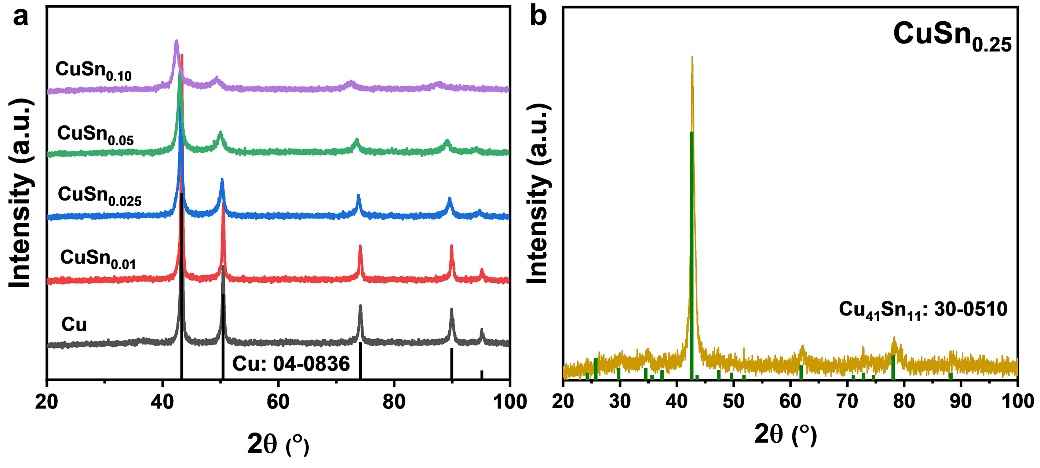
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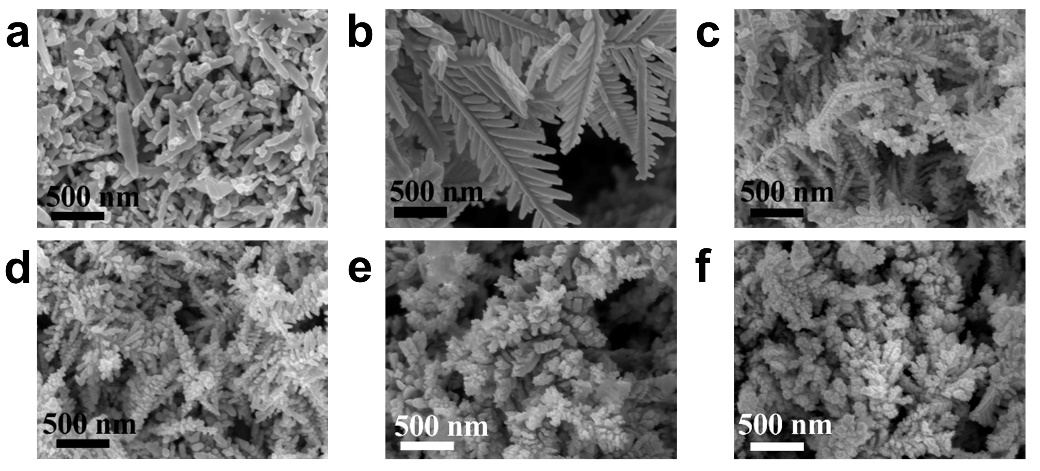
**Figure S1** The oxophilicity of common transition metals and p-block metals determined by the bond dissociation enthalpies of metal oxides.1



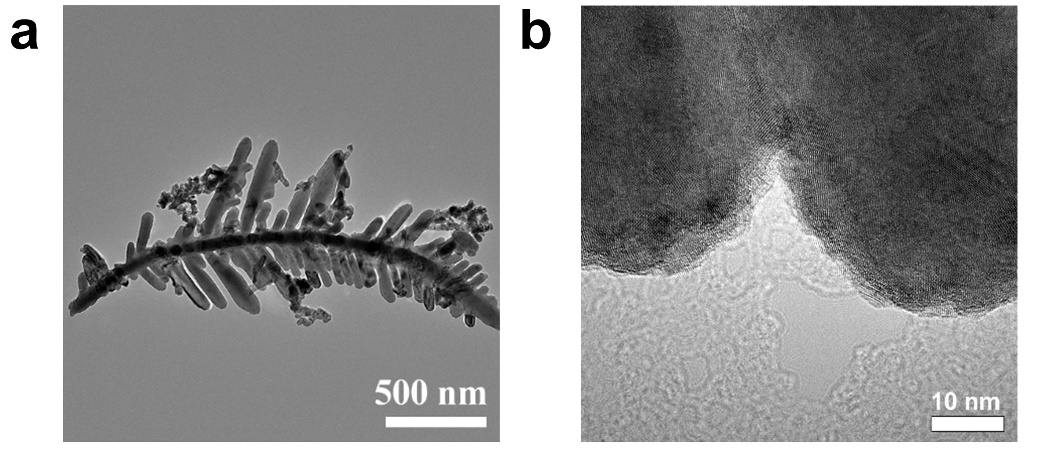
**Figure S2** Schematic diagram of the materials synthesis (a). Photographs illustrate the synthesis procedures (b).



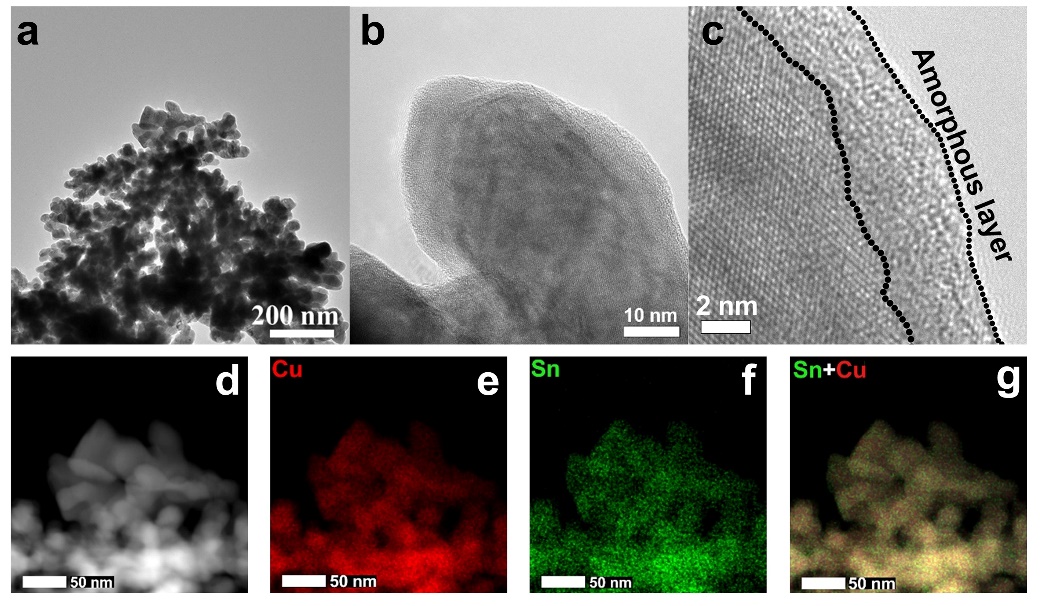
**Figure S3** XRD pattern of Cu to CuSn0.10 catalysts (a) and CuSn0.25 catalyst (b).



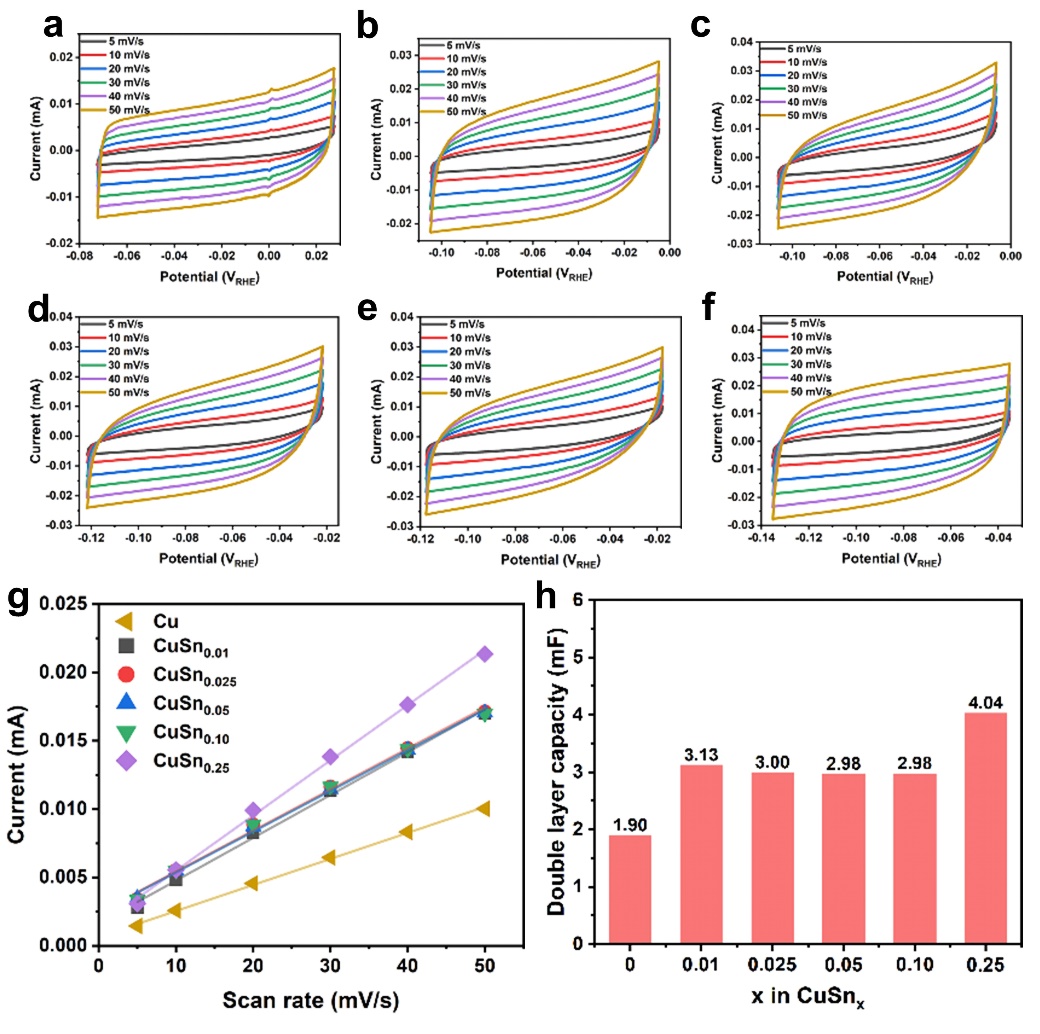
**Figure S4** SEM images of (a) bare Cu, (b) CuSn0.01, (c) CuSn0.025, (d) CuSn0.05, (e) CuSn0.10, and (f) CuSn0.25 catalysts.



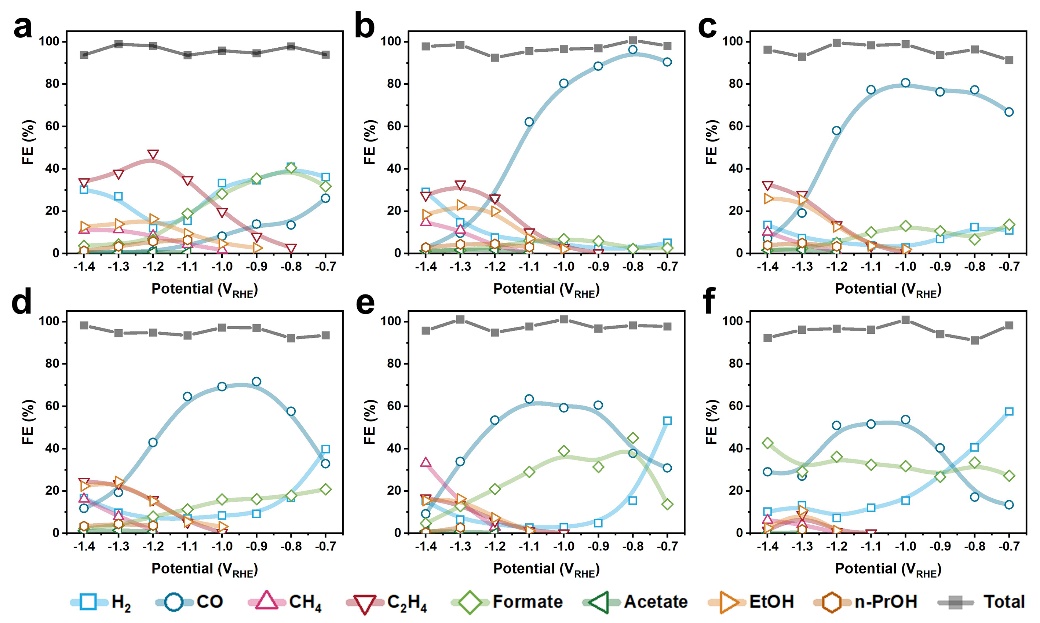
**Figure S5** (a)TEM and (b) HR-TEM images of CuSn0.01 catalyst.



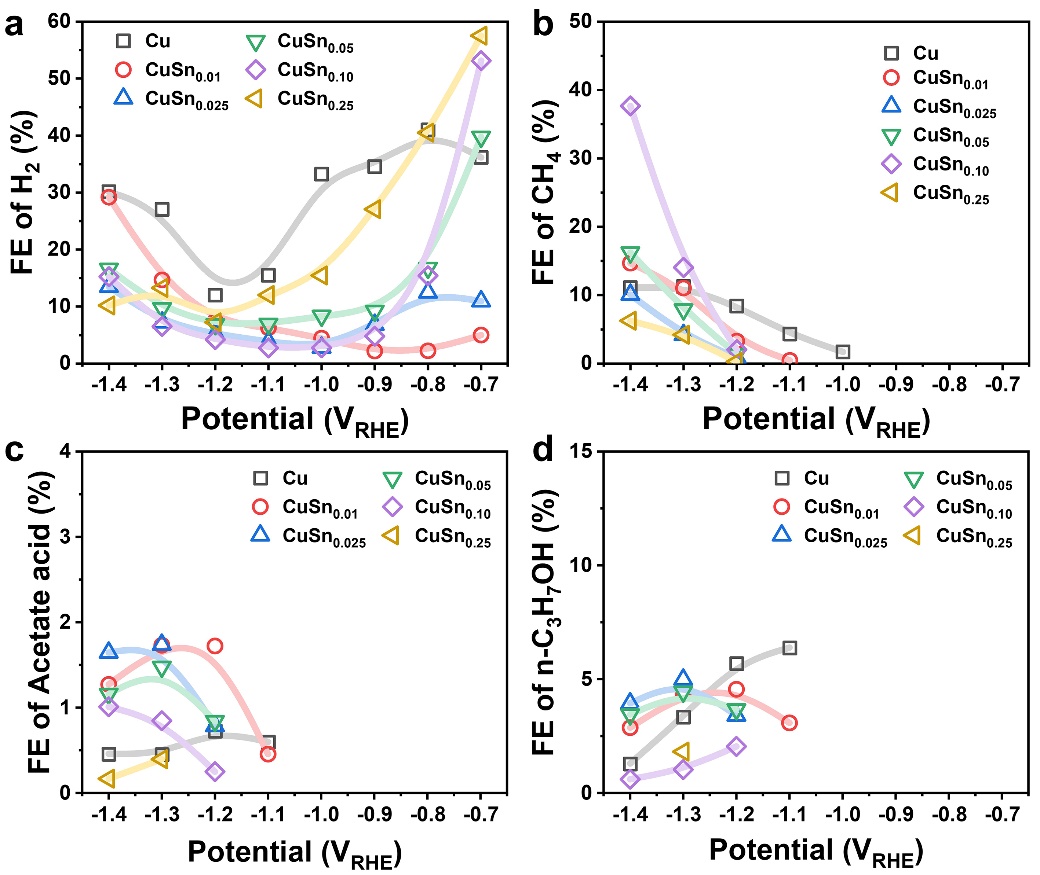
**Figure S6** Characterization of CuSn0.10 catalyst. (a) TEM image, (b-c) HR-TEM images, (d) HAADF-STEM image, and (e-g) EDS elemental mappings of CuSn0.10 catalyst.



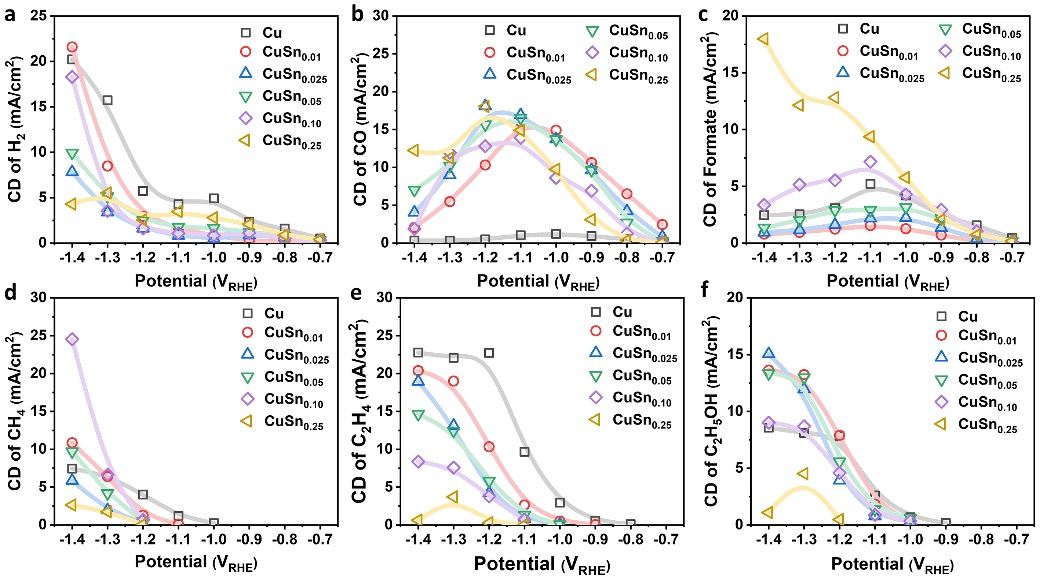
**Figure S7** ECSA measurements of CuSnx catalysts. (a-f) Double layer capacities (Cdl) measured by CV curves in CO2-saturated 0.1 M KHCO3 solution at around open circuit potential (EOC ± 50 mV) of Cu, CuSn0.01, CuSn0.025, CuSn0.05, CuSn0.10, and CuSn0.25 catalysts. (g) Charge current density in CV scans plotted against the scan rates for CuSnx catalysts. (h) ECSA values of CuSnx catalysts.



**Figure S8** The distribution of reduction products at applied potentials on CuSnx catalysts. (a) Cu, (b) CuSn0.01, (c) CuSn0.025, (d) CuSn0.05, (e) CuSn0.10, and (f) CuSn0.25.



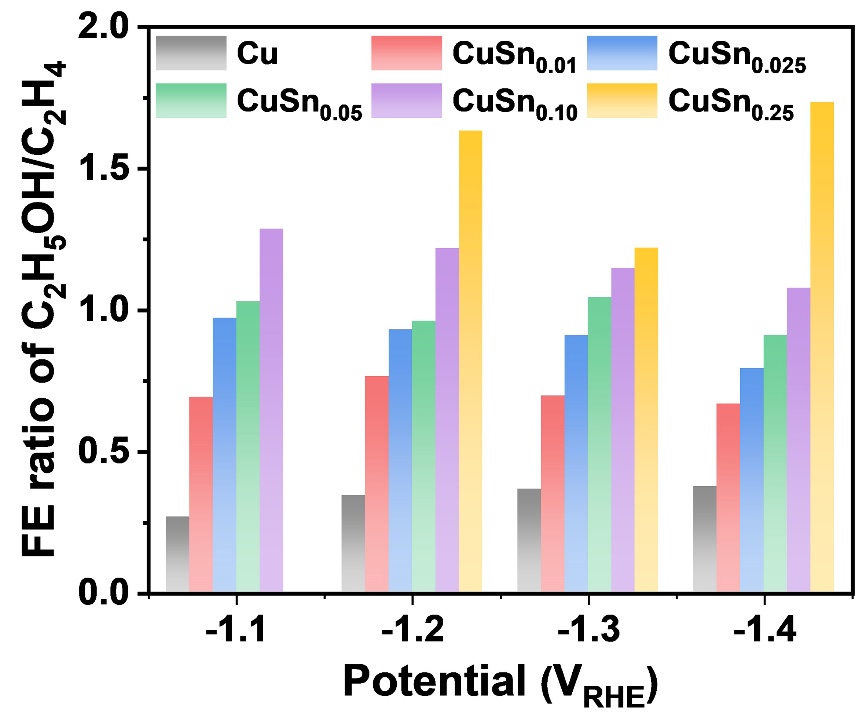
**Figure S9** The FEs of reduction products. (a) H2, (b) CH4, (c) acetate acid, (d) n-C3H7OH.



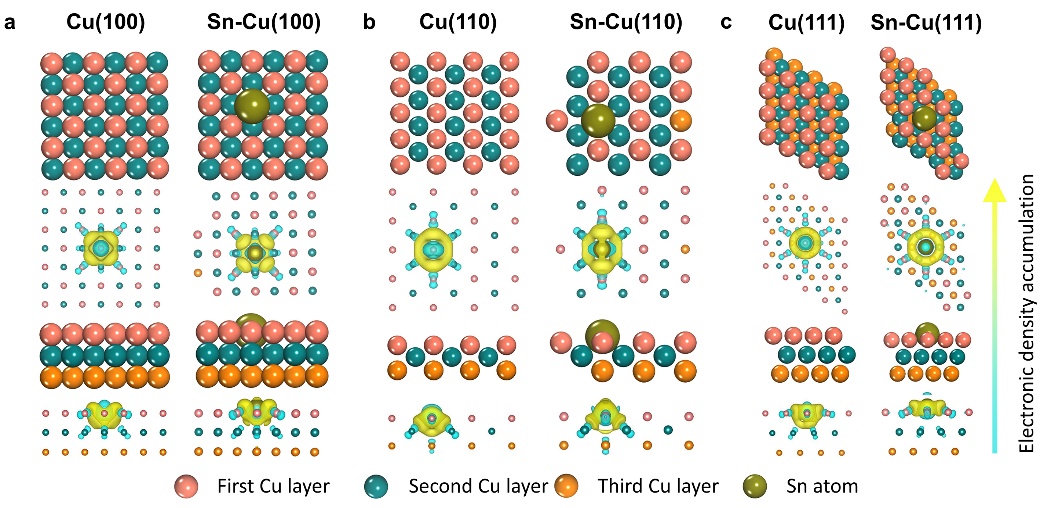
**Figure S10** Current density (CD) of the main reduction products. (a) H2. (b) CO. (c) formate. (d) CH4. (e) C2H4. (f) C2H5OH.



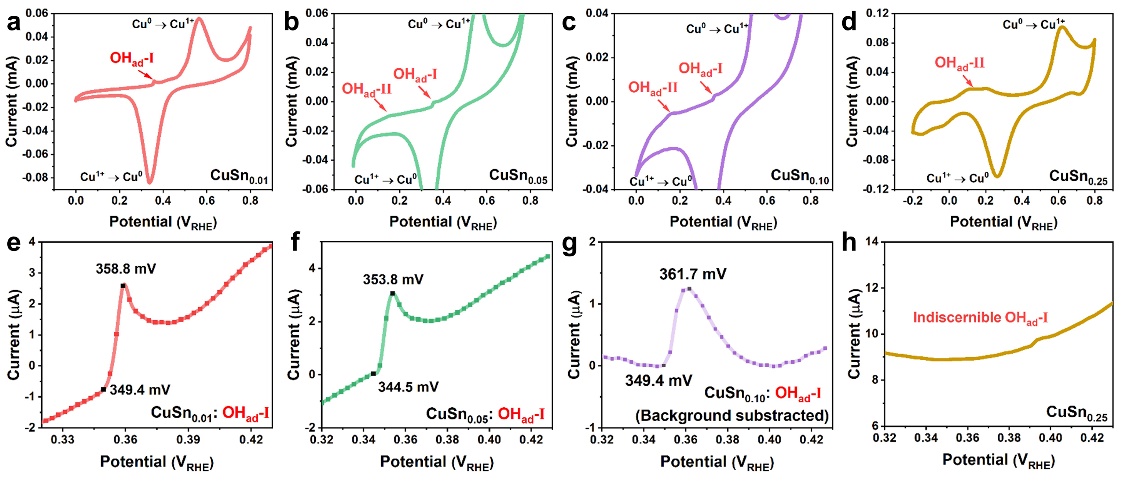
**Figure S11** The typical 1H NMR patterns that shows the peaks for multicarbon liquid products. (a) CuSn0.025 catalysts at different potentials. (b) Different catalysts at -1.3 VRHE.



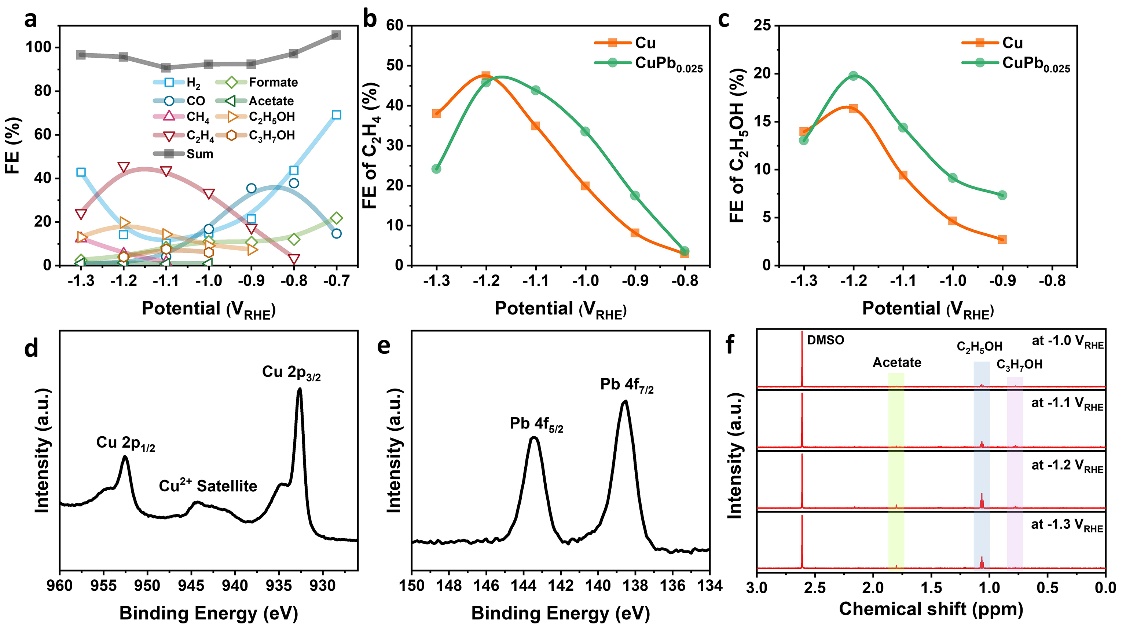
**Figure S12** The FE ratio of C2H5OH/C2H4 on CuSnx catalysts at different potentials.



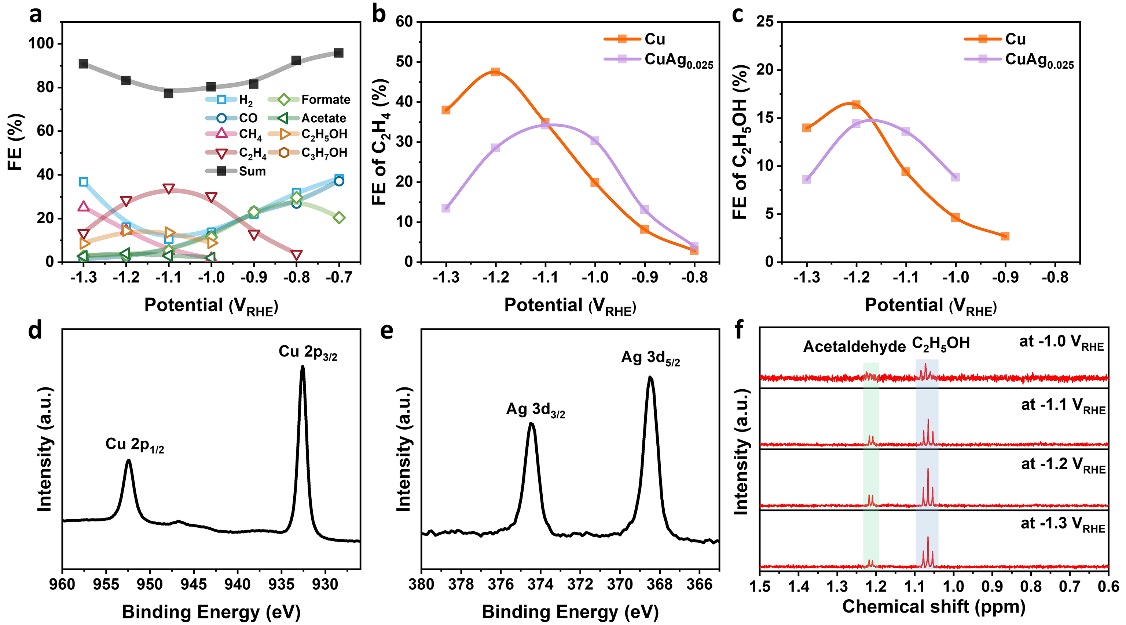
**Figure S13** The slab models of Sn modified Cu facets for calculation and the corresponding differential charge analysis.



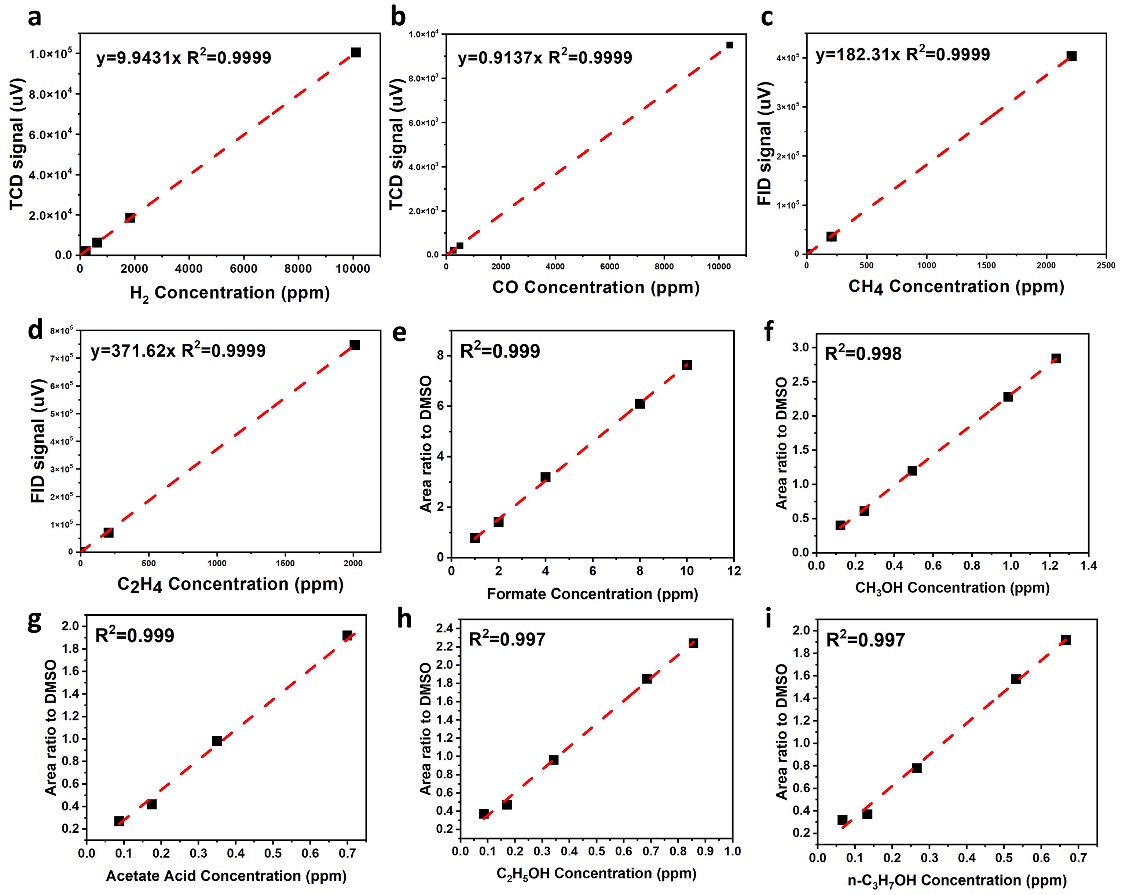
**Figure S14** CV curves of (a) CuSn0.01, (b) CuSn0.05, (c) CuSn0.10, and (d) CuSn0.25 catalysts. Enlarged CV curves showing OHad-I adsorption peaks for (e) CuSn0.01, (f) CuSn0.05, (g) CuSn0.10, and (h) CuSn0.25.



**Figure S15** CO2RR performance and characterization of CuPb0.025 catalyst. (a) FEs of all products at different potentials. (b) Comparison of FE of C2H4 between bare Cu and CuPb0.025 catalysts. (c) Comparison of FE of C2H5OH between bare Cu and CuPb0.025 catalysts. (d) Cu 2p spectra of CuPb0.025 catalysts. (e) Pb 4f spectra of CuPb0.025 catalysts. (f) 1H NMR patterns showing the peaks of multicarbon liquid products for CuPb0.025 catalyst.



**Figure S16** CO2RR performance and characterization of CuAg0.025 catalyst. (a) FEs of all products at different potentials. (b) Comparison of FE of C2H4 between bare Cu and CuAg0.025 catalysts. (c) Comparison of FE of C2H5OH between bare Cu and CuPb0.025 catalysts. (d) Cu 2p spectra of CuAg0.025 catalysts. (e) Ag 3d spectra of CuAg0.025 catalysts. (f) 1H NMR patterns showing the peaks of multicarbon liquid products for CuAg0.025 catalyst.



**Figure S17** Gas and liquid products calibration. (a-d) Gas products. (e-i) Liquid products.

**Table S1** Summary of CO2RR performance of the CuSnx catalysts in this work and the comparison of other Cu-Sn bimetallic catalysts in the literatures.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Catalyst | Reduction product | Faradic efficiency | Partial current density, mA/cm2 | Potential, VRHE | Electrolyte | Reference |
| **CuSn0.01** | **CO** | **96.36 %** | **6.51** | **-0.8** | **0.1 M KHCO3** | **This work** |
| **CuSn0.025** | **C2H5OH** | **25.93%** | **15.05** | **-1.4** | **0.1 M KHCO3** | **This work** |
| Sn/Cu2O | CO | 87.9 % | ~ 15 (total) | -1.3 | 0.1 M KHCO3 | 2 |
| Cu97Sn3 | CO | 98 % | ~ 30 (total) | -0.7 | 0.5 M KHCO3 | 3 |
| CuSn40 | CO | 90.9 % | ~ 3.3 (-0.8 VRHE) | -1.0 | 0.1 M KHCO3 | 4 |
| Cu-Sn form | CO | 93-94 % | 6.2 | -0.9 | 0.1 M KHCO3 | 5 |
| Cu–Sn20 | CO | 82 % | 0.96 | -0.7 | 0.1 M KHCO3 | 6 |
| Cu-Sn dendrite | CO | 74 % | 11.5 | -1.1 | 0.1 M KHCO3 | 7 |
| SnO2/CuS NSs | CO | ~70 % | 15.24 | -1.0 | 0.1 M KHCO3 | 8 |
| Sn/Cu-PVDF | CO | 80 % | 104 (gaseous CO2 feeding) | < -0.9 | 0.1 M KHCO3 | 9 |
| Cu−Sn | CO | 90 % | 1.0 | -0.6 | 0.1 M KHCO3 | 10 |
| C-Cu/SnO2-0.8 | CO | 93 % | 4.6 | -0.7 | 0.5 M KHCO3 | 11 |
| Cu87Sn13 | CO | 59.5 % | ~ 0.9 | -0.99 | 0.1 M KHCO3 | 12 |
| CuO+SnO2 | CO | ~ 90 % | ~ 0.5 | -0.6 | 0.1 M NaHCO3 | 13 |
| Cu/SnOx−CNT  (6.2 % SnOx) | CO | 89 % | 11.3 | -0.99 | 0.1 M KHCO3 | 14 |
| C-Cu/SnO2-1.8 | Formate | 85 % | n.a. | -0.9 | 0.5 M KHCO3 | 11 |
| Cu55Sn45 | Formate | 89.5 % | ~ 2.5 | -1.09 | 0.1 M KHCO3 | 12 |
| Cu/SnOx−CNT  (30.2 % SnOx) | Formate | 77 % | 4.0 | -0.99 | 0.1 M KHCO3 | 14 |
| CuSn0.175-NG | CO+Formate | 93 % | n.a. | -1.0 | 0.5 M KHCO3 | 15 |
| Cu@Sn | Formate | ~ 100 % | 16.52 | -0.93 | 0.5 M KHCO3 | 16 |
| CuSn NPs/C-A | CO | 70.1 % | 1.66 | -0.7 | 0.1 M KHCO3 | 17 |
| Formate | 71.5 % | 12.6 | -1.0 |
| Cu(1)Sn(4)-N-CC | Formate | 90.24 % | 15.56 | -0.97 | 0.5 M KHCO3 | 18 |
| Sn-Cu alloy | Formate | 82.3 % | 79 | -1.14 | 0.5 M KCl | 19 |
| CuSn–10C | Formate | 82 % | 18.9 | -1.0 | 0.1 M NaHCO3 | 20 |
| CuSn NWs/C-Air | Formate | 90.2 % | 17.33 | -1.0 | 0.5 M KHCO3 | 21 |

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