SUPPORTING INFORMATION

Efficient Ethane Production via $SnCl_4$ Lewis Acid-Enhanced CO_2 Electroreduction in a Flow Cell Electrolyser

Sankeerthana Bellamkonda[1,2*], Ian Brewis[1], Venkateswar Rao Gadela[1], Rana Faisal Shahzad[1], Mohamed Mamlouk[2], Shahid Rasul[1*]

[1]School of Engineering and Environment, Northumbria University, Newcastle upon Tyne, United Kingdom

[2]School of Engineering, Newcastle University, Newcastle upon Tyne, United Kingdom

Synthesis of Cu3Sn: The Cu3Sn GDE has been synthesised by a facile in-situ electrochemical spontaneous precipitation (ESP) method in 25 min. As shown in Figure S2, the synthesis process starts from injecting the acidified Sn^{4+} solution (0.05 M $SnCl_4.5H_2O$ and 0.4 M citric acid, pH = 2.0) into a container until immersing the two electrodes, a Cu_2O-binded GDL and pure In foil, which are externally connected by a 2 Ω cable.

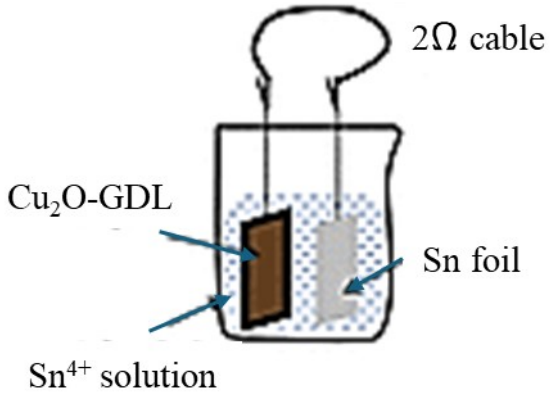

Figure S1. Experiment set-up schematic and process for 25 min ESP.

*Corresponding author; Tel.: +91 9445435743; +44 7471042866;

E-mail address: sankeerthana999@gmail.com *(Sankeerthana B.); and*

shahid.rasul@northumbria.ac.uk *(Shahid Rasul).*

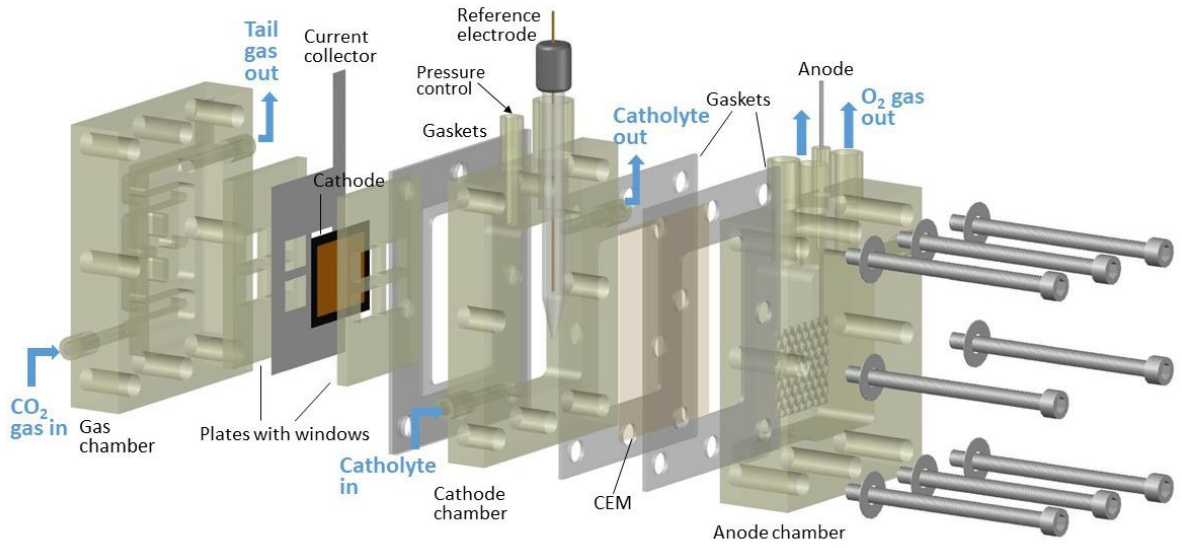

Figure S2. 3D drawing of the CO_2 electrolyser and its components we used in this study.

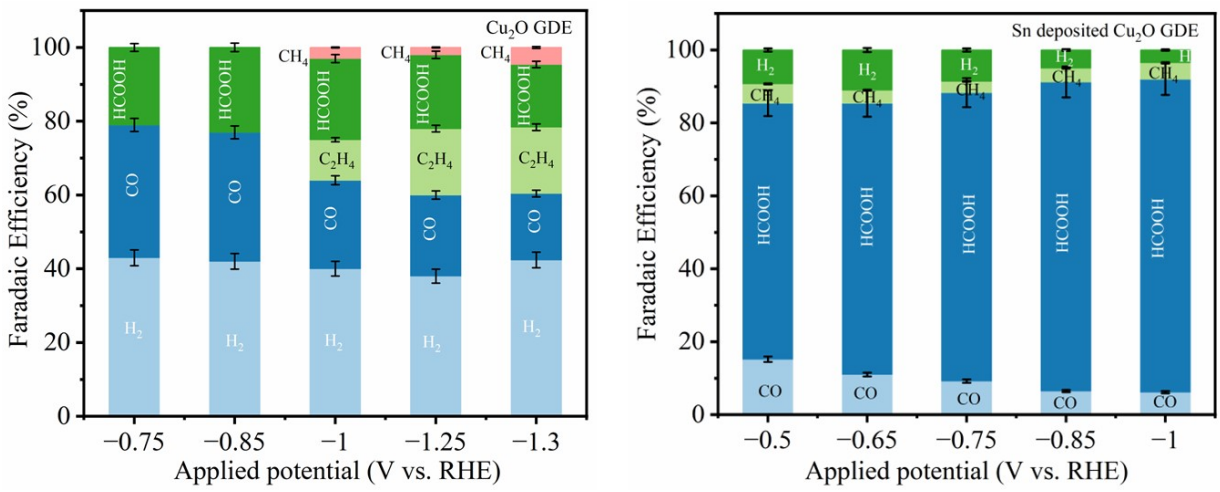

Figure S3. FEs of CO_2 reduced various products as a function of potential for the Cu_2O and Cu_3Sn GDEs during electrochemical reduction using flow cell electrolyser

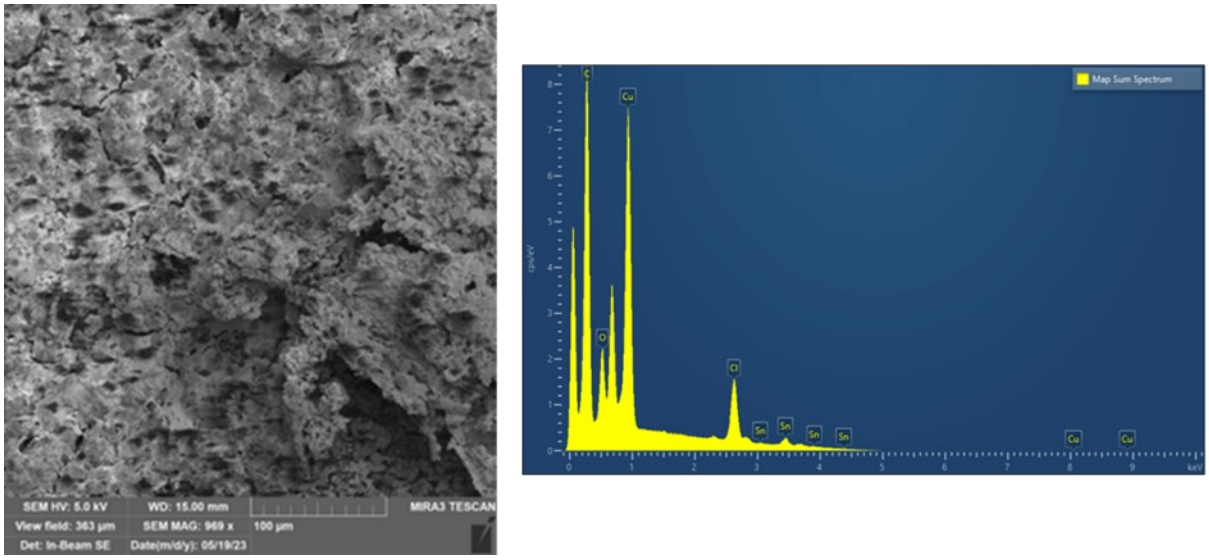

Figure S4. SEM and EDAX images of post CO_2-electrolysed CTC-65 GDE.

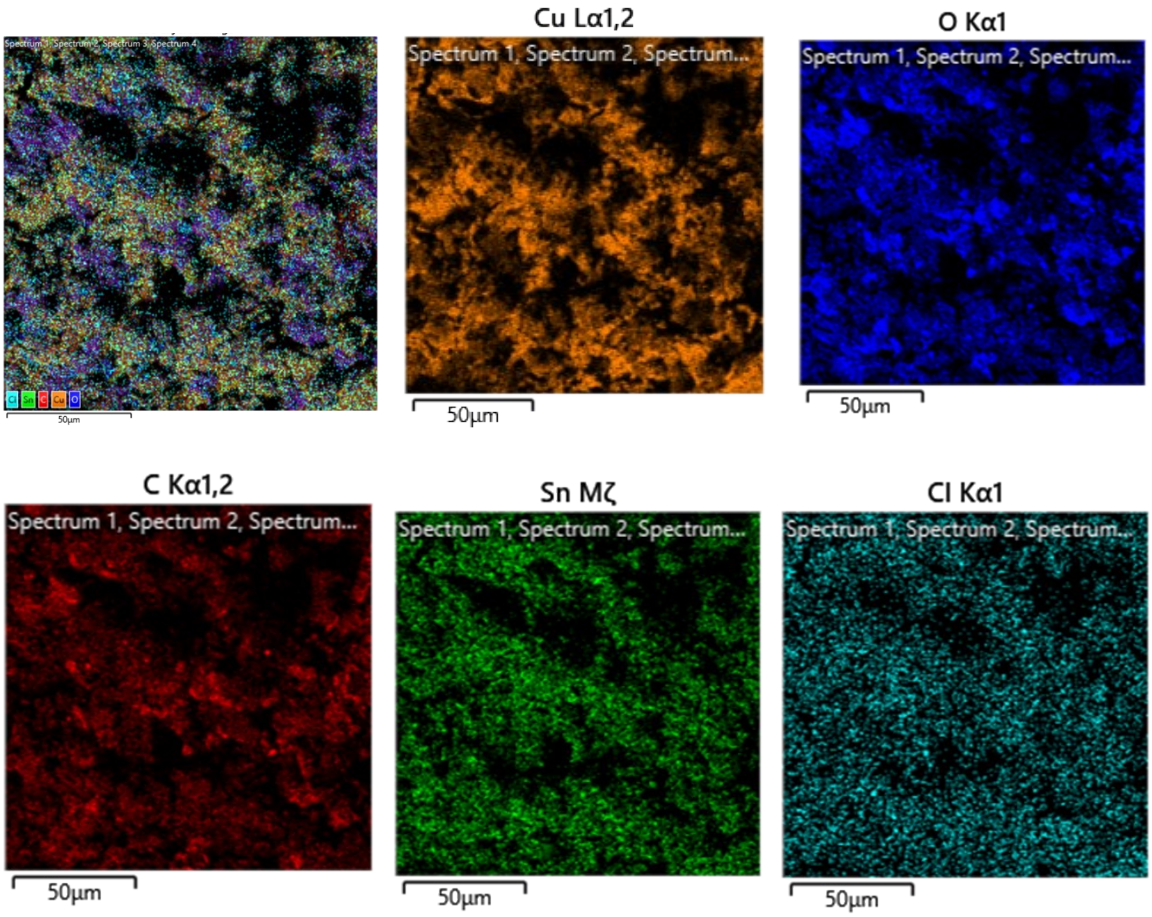

Figure S5. Elemental mapping of post-CO_2 electrolysed CTC-65 GDE.

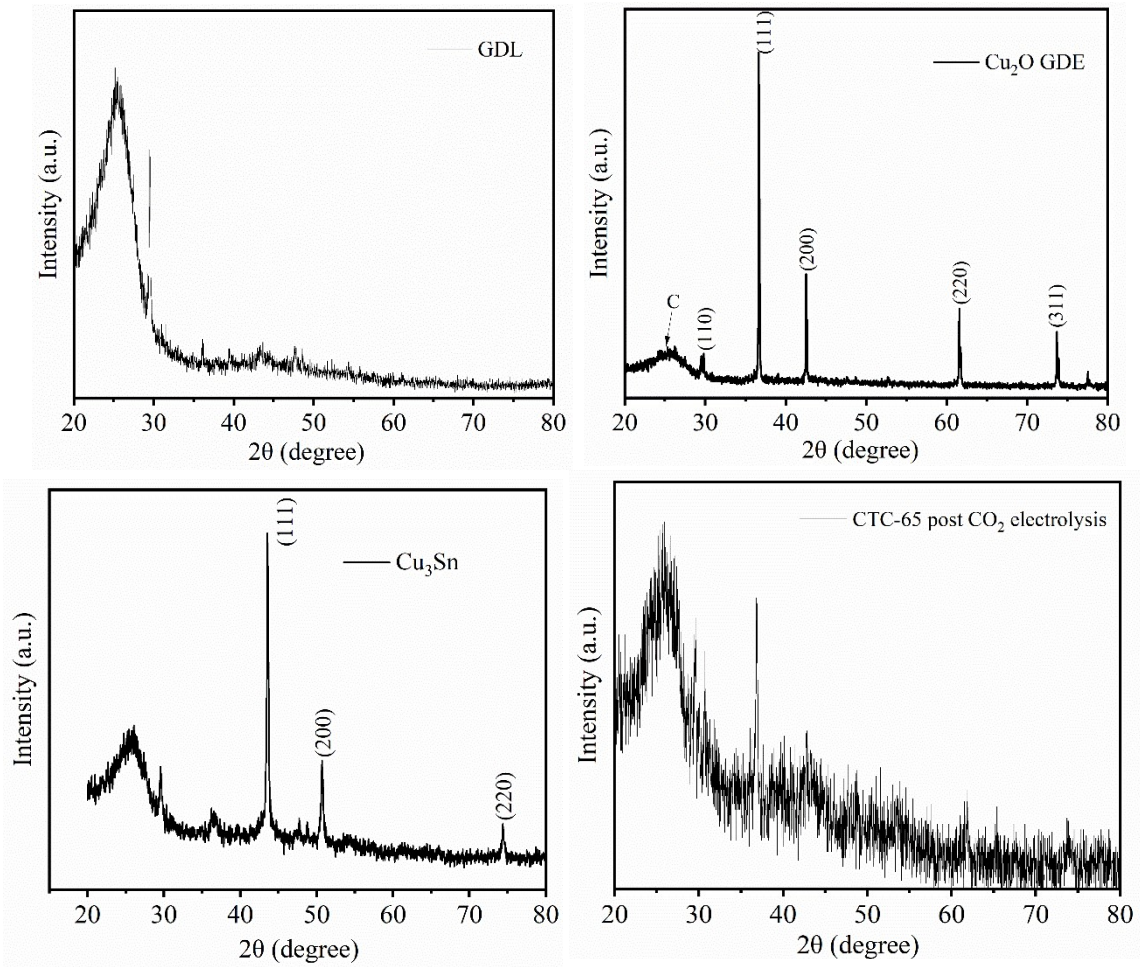

Figure S6. XRD spectra of GDL, Cu_2O GDE, Cu_3Sn GDE and post CO_2 electrolysed CTC-65 GDE.

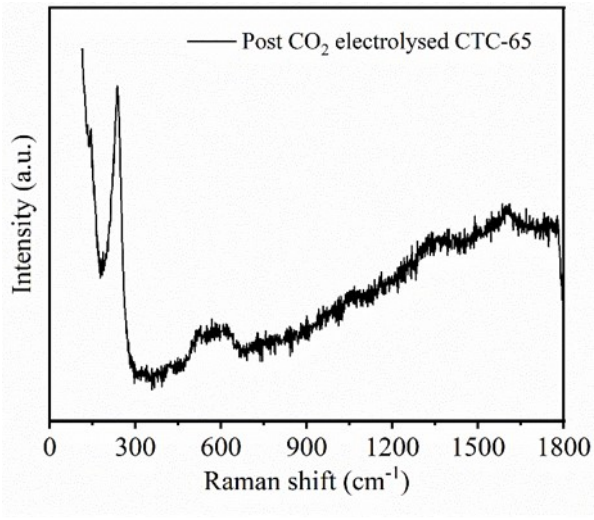

Figure S7. Raman spectrum of post CO_2 electrolysed CTC-65

Computational details on Density Functional Theory (DFT)-type calculations are performed for bulk and slab unit cells. Below we report the unit cell relaxed geometries and k-grid and plane-wave energy cut-offs used for each cell. All provided geometries are in the following format.

Atom types, number of atoms, atom positions, according to QUANTUM ESPRESSO standard input.

1. CO and K adsorbed CTC-65 relaxed geometry – calculated with a 6x6x1 gamma-centered k-grid and a 400 eV plane-wave energy cut-off:

Cu	10.27391	7.149756	4.223283
Cu	10.27391	4.18406	18.26513
Cu	10.27391	1.225918	2.090626
Cu	10.27391	8.634781	18.27262
Cu	10.27391	5.677143	2.088991
Cu	10.27391	2.703721	4.202593
Cu	1.282939	7.895676	2.093938
Cu	1.275522	4.926614	4.204834
Cu	1.284088	1.961471	18.26095
Cu	1.277731	0.47698	4.207403
Cu	1.28683	6.41052	18.26134
Cu	1.285606	3.446337	2.082031
Cu	2.534522	2.700174	4.195092
Cu	2.566275	5.660248	2.080421
Cu	2.569649	8.628428	18.25894
Cu	2.554307	7.146759	4.204055
Cu	2.56671	4.182125	18.24201
Cu	2.570439	1.218011	2.077651
Cu	3.85605	3.432221	2.068884
Cu	3.851974	6.404802	18.25511
Cu	3.833618	0.446238	4.194408
Cu	3.832337	4.949705	4.190887
Cu	3.851843	7.881885	2.08538
Cu	3.85187	1.951731	18.24142
Cu	5.136952	1.21464	2.070055
Cu	5.136953	4.176139	18.24048
Cu	5.136953	7.144073	4.199775
Cu	5.136953	5.649895	2.073959
Cu	5.136952	8.621686	18.25141
Cu	6.422036	1.951731	18.24142
Cu	6.441569	4.949705	4.190886
Cu	6.422062	7.881885	2.085378
Cu	6.417855	3.432221	2.068884
Cu	6.421932	6.404802	18.25511

Cu	6.440287	0.446238	4.194407
Cu	7.704257	8.628428	18.25894
Cu	7.739383	2.700173	4.195088
Cu	7.70763	5.660247	2.08042
Cu	7.703466	1.21801	2.077651
Cu	7.707194	4.182125	18.24201
Cu	7.719598	7.146759	4.20405
Cu	8.996174	0.47698	4.207403
Cu	8.988299	3.446337	2.082031
Cu	8.987074	6.41052	18.26134
Cu	8.998383	4.926615	4.204834
Cu	8.990967	7.895676	2.093936
Cu	8.989817	1.961471	18.26095
Sn	5.136952	2.700019	4.938216
C	5.136952	4.924383	5.852792
O	5.136952	4.924383	6.950279
Cl	4.09963	3.767116	5.298744
Cl	5.948933	3.767116	5.298744
K	5.1369	4.9243	8.9564

2. CO adsorbed Cu – relaxed geometry - Pd/Fe_2O_3 relaxed geometry - calculated with a 6x6x1 gamma-centered k-grid and a 400 eV plane-wave energy cut-off:

Cu	10.27391	7.149756	4.223283
Cu	10.27391	4.18406	18.26513
Cu	10.27391	1.225918	2.090626
Cu	10.27391	8.634781	18.27262
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Cu	1.285606	3.446337	2.082031
Cu	2.534522	2.700174	4.195092
Cu	2.566275	5.660248	2.080421
Cu	2.569649	8.628428	18.25894
Cu	2.554307	7.146759	4.204055
Cu	2.56671	4.182125	18.24201
Cu	2.570439	1.218011	2.077651
Cu	3.85605	3.432221	2.068884
Cu	3.851974	6.404802	18.25511
Cu	3.833618	0.446238	4.194408
Cu	3.832337	4.949705	4.190887

Cu	3.851843	7.881885	2.08538
Cu	3.85187	1.951731	18.24142
Cu	5.136952	1.21464	2.070055
Cu	5.136953	4.176139	18.24048
Cu	5.136953	7.144073	4.199775
Cu	5.136953	5.649895	2.073959
Cu	5.136952	8.621686	18.25141
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Cu	6.421932	6.404802	18.25511
Cu	6.440287	0.446238	4.194407
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Cu	7.739383	2.700173	4.195088
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Cu	8.989817	1.961471	18.26095
C	5.136952	4.924383	5.852792
O	5.136952	4.924383	6.950279

Figure S8 illustrates the electronic dispersion along high-symmetry directions in the Brillouin zone (Gamma, X, M, R), highlighting the evolution of electronic states with the addition of Sn and $SnCl_2$ in bulk Cu crystal structure. The band structures of bulk Cu, Cu with Sn, and Cu with $SnCl_2$ highlights the significant impact of Sn and Cl on the electronic dispersion, directly reflecting changes in the underlying crystal structure. In pure Cu, the metallic band structure exhibits high dispersion along all high-symmetry directions, indicating isotropic electron transport and strong metallic bonding. Upon adding Sn onto surface of the Cu lattice, new localized flat bands appear near the Fermi level, particularly along the M and R directions, suggesting a reduction in isotropy and the introduction of states associated with d-orbitals of Sn. These localized states are linked to enhanced intermediate stabilization due to the crystal field effect of Sn. The inclusion of $SnCl_2$ further modifies the electronic structure, as evident from the increased density of states near the Fermi level and the presence of additional flat bands. The interaction between p-orbitals of Cl and Sn coordination in the Cu lattice introduces

asymmetry in the band dispersion, particularly along the Gamma-X and M-R directions, reflecting the anisotropic electronic environment created by the $SnCl_2$ unit. This anisotropy and the directional nature of band modifications emphasize the role of Sn and Cl in tailoring the electronic structure of CuSnCl, enabling efficient charge transfer and selective CO_2 reduction pathways.

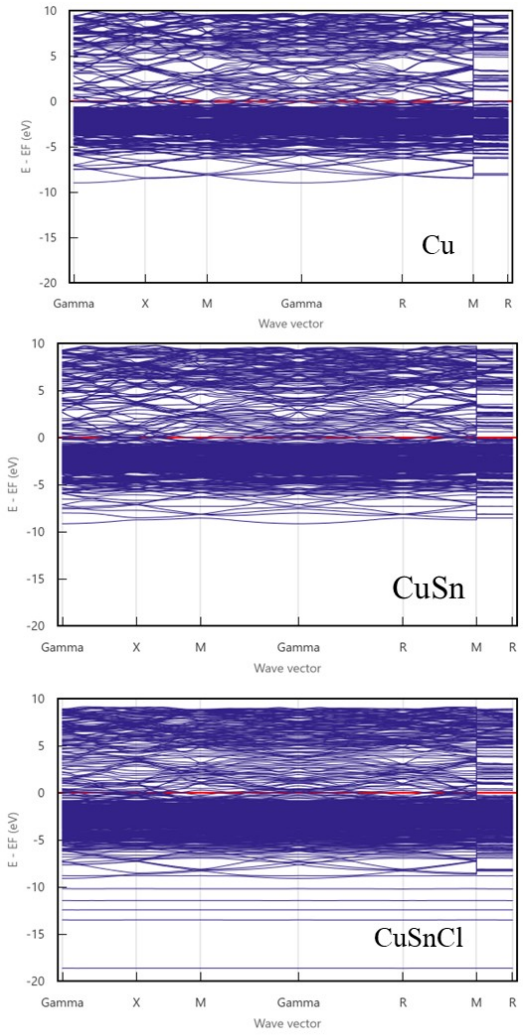

Figure S8. Band structures of bulk Cu slab, Cu with a Sn atom, and Cu with $SnCl_2$ incorporated into the lattice.