Electronic Supplementary Information

Heterostructured bimetallic CuSn Alloy Catalyst: High Performance towards the Electrochemical Reduction of CO₂ to Formate

Jigang Wang^a[†], Jiasui Zou^a[†], Xiao Hu^a, Shunlian Ning^a, Xiujun Wang^b, Xiongwu Kang^{a*} and Shaowei Chen ^{c*} ^aNew Energy Research Institute, School of Environment and Energy, South China University of Technology, Higher Education Mega Center, 382 East Waihuan Road, Guangzhou 510006, China ^bSchool of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510640, China ^{a*}University of California, Santa Cruz, 1156 High Street, CA, 95064 USA [†]These authors contribute equally to the paper.

Corresponding Author

*E-mails: esxkang@scut.edu.cn, shaowei@ucsc.edu

Electrochemical characterization:

An electrochemical workstation (CH Instrument 660 C, Chenhua, China) was used for all electrochemical experiments. CO₂ reduction experiments were performed both performed in a H-type three-electrode cell and flow cell at room temperature. In a typical H-type threeelectrode cell, the two electrode compartments were separated by a Nafion-117 proton exchange membrane to prevent the re-oxidation of CO₂ reduction products. The catalysts on Cu foam were used directly as the working electrode, a Pt wire as the counter electrode and a Ag/AgCl as the reference electrode. The electrochemical performance of pure-phase Cu₆Sn₅ and Cu₃Sn intermetallic compounds was equally performed on copper foam, which were denoted as Cu₆Sn₅-foam and Cu₃Sn-foam respectively. The reference electrode was calibrated against a reversible hydrogen electrode (RHE) and all potentials in the present study were

referred to this RHE unless otherwise stated. iR drop was compensated before electrolysis. A CO_2 -saturated 0.1 M NaHCO₃ solution (pH 6.8) was used as the supporting electrolyte.

Before the tests of CO2RR, the electrolyte in the cathodic compartment was saturated with CO₂ by bubbling CO₂ gas for at least 30 min. During the reduction experiments, the CO₂ gas was delivered at an average rate of 24 mL min⁻¹ (at room temperature and ambient pressure) and routed directly into the gas sampling loop of a gas chromatograph (GC 9560) for quantification of the gas products. The GC was installed with a thermal conductivity detector (TCD) to detect H₂ and flame ionization detector (FID) to detect hydrocarbons. A methanizer (Agilent) was equipped in front of FID for CO detection. High-purity Ar gas was used as the carrier gas for all compartments of the GC. The liquid products of CO2RR were identified and quantified by nuclear magnetic resonance (NMR, 400 MHz, Bruker) measurements.

Flow cell measurements were performed in a custom-designed flow cell reactor. The carbon paper with a microporous layer (Sigracet 29 BC, Fuel Cell Store) was used as the gas diffusion layer (GDL) for supporting catalyst. The CuSn-coated GDL was applied as the working electrode, a piece of anion exchange membrane (SELEMION) as the separator, a 20 wt% IrO₂/C-loaded GDL as the anode and Ag/AgCl (saturated KCl) as the reference electrode. During the measurements, CO₂ flow rate into the flow cell was set as 20 sccm via a mass flow controller (Brooks GF40). The catholyte (1 M KOH) flow rates were controlled via a peristaltic pump

(Cole-Parmer) with 65 rpm.

The Faradaic efficiency was calculated using the following equation:



Where,

Q_{total}: the charge passed, C;

Q_i: the charge used for the reduction of certain product, C;

N_i: the number of moles for a specific product (measured by NMR and GC), mol; n: the number

of electrons exchanged for product formation, which is 2 for CO $\$ H₂ and HCOOH;

F: Faradaic constant, which is 96485 C mol⁻¹.



Fig. S1 SEM images of (a, b) Cu@Sn5, (c) CuSn-5C, (d, e) Cu@Sn15 and (d) CuSn-15C.



Fig. S2 TEM (a) CuSn-5C, (c) CuSn-15C and HRTEM (b) CuSn-5C, (d) CuSn-15C images.



Fig. S3 TEM (a) and EDX mappings (b)(c) of CuSn-10C sample.



Fig. S4 XRD patterns of (a) Cu@Sn5, CuSn-5C; (b) Cu@Sn15, CuSn-15C.



Fig. S5 XPS full survey spectra of CuSn-5C, CuSn-10C and CuSn-15C.



Fig. S6 LSV curves in N₂-saturated (dotted lines) and CO₂- saturated (solid lines) 0.1 M NaHCO₃ electrolyte at a scan rate of 10 mV s⁻¹.



Fig. S7 Reduction potential dependent FEs of CH4 and C2H4 for Cu foam.



Fig. S8 FE of CO2RR products on (a) Cu@Sn5, CuSn-5C; (b) Cu@Sn15, CuSn-15C and (c) CuSn-5C, CuSn-10C, CuSn-15C. Total current (d, e, f) and partial current density of HCOOH on (g) Cu foam, Cu@Sn10 and CuSn-10C; (h) Cu@Sn5 and CuSn-5C; (i) Cu@Sn15 and CuSn-15C.



Fig. S9 Electrochemical double-layer capacitance measurements to determine the surface area of the various electrodes: (a, b) Cu@Sn5, CuSn–5C; (d, e) Cu@Sn10, CuSn–10C; (g, h) Cu@Sn15, CuSn–15C and (j) Cu foam. Variations of current density with scan rate are shown in panels (c, f, i, k), where the corresponding capacitance and ECSA are shown in the insets.

The electrochemical surface area (ECSA) of these catalysts were derived from double layer capacitance, as shown in Fig. S6, which is calculated from the double layer capacitance according: ECSA = C_{DL}/Cs , where C_{DL} is double layer capacitance, Cs is the specific capacitance of the sample or the capacitance of an atomically smooth planar surface of the material per unit area under identical electrolyte conditions. For our estimates of surface area, general specific capacitances of Cs = 0.029 mF cm⁻² was used. ¹⁻³



Fig. S10 Partial current density of HCOOH on Cu@Sn5, CuSn-5C (a), Cu@Sn15 and CuSn-15C (b) and CuSn-5C, CuSn-10C and CuSn-15C.



Fig. S11 XRD patterns of (a) Cu_3Sn and (b) Cu_6Sn_5 .



Fig. S12 TEM images of (a) Cu₃Sn and (b) Cu₆Sn₅.



Fig. S13 Electrochemical capacitance measurements to determine the ECSA of (a) Cu_3Sn -foam and (b) Cu_6Sn_5 -foam. (c) Linear fitting of current density as function of scan rate. The capacitance and ECSA of the Cu_3Sn -foam and Cu_6Sn_5 -foam are shown in the inset.



Fig. S14 (a) FE and partial current density of (a) Cu_6Sn_5 , (b) Cu_3Sn and (c) CuSn-10C.



Fig. S15 Tafel analysis of Cu@Sn-X and CuSn-XC in CO₂-purged 0.1 M NaHCO₃ solution (a, b, c). The Nyquist plots of electrodes in CO₂-purged electrolyte in a frequency range from 1 MHz to 0.01Hz with 10 mV amplitude at -0.8V vs RHE (d).



Fig. S16 Adsorption affinities of OH⁻ surrogate ion on the prepared CuSn alloys.



Fig. S17 LSV (a) and XRD (b) of CuSn-10C before and after CO2RR.



Fig. S18 SEM images of CuSn-10C after CO2RR for 42 h at low (a) and high (b) magnification.



Fig. S19 HRTEM images of CuSn-10C after CO2RR for 42 h.



Fig. S20 Partial current density comparison of various CO₂ electroreduction catalysts.



Fig. S21 HCOOH FE and total current density for electrolysis of CuSn-10C in 1 M KOH electrolyte conducted on a flow cell.



Fig. S22 FE (a) and partial current density (b) of HCOOH on CuSn-5C, CuSn-10C and CuSn-15C in 1 M KOH electrolyte conducted on a flow cell.



Fig. S23 Optimized structures of Cu_3Sn (111) surface and the adsorbed COOH*, HCOO*, CO*, and HCOOH*.



Fig. S24 Optimized structures of Cu_6Sn_5 (111) surface and the adsorbed COOH*, HCOO*, CO*, and HCOOH*.



Fig. S25 Optimized structures of heterostructured Cu_3Sn/Cu_6Sn_5 surface and the adsorbed COOH*, HCOO*, CO*, and HCOOH*.



Fig. S26 Energy diagrams of CO2RR intermediates to CO (blue) and HCOOH (brown) on (a) Cu_3Sn (111), (b) Cu_6Sn_5 (111).



Fig. S27 Gibbs free energy (eV) of adsorbed H* on Cu3Sn(111), Cu6Sn5(111) and Cu₃Sn/Cu₆Sn₅ respectively.

Table S1 Comparison of catalyst performance in selective CO_2 reduction to formate with leading results in the literature.

Catalyst	Electrolyte	Major products	Faradaic Efficiency (%)	Partial current density (mA cm ⁻²)	Potential (V) vs. RHE	Reference
Sn–Cu alloy	0.1M KHCO3	НСООН	82	18.9	-1.0	This Work

Sn/Cu	0.1M KHCO ₃	НСООН	91	0.91	-0.85	4
Sn dendrite	0.1M KHCO ₃	НСООН	55.6	6.4	-1.1	5
nO ₂ /C aerogels	1M KHCO ₃	НСООН	76	12.2	-1.0	6
nO ₂ nanowires	0.1M NaHCO ₃ HCOOH		80	4.8	-0.8	7
Ag ₃ Sn alloy	0.5M NaHCO ₃	НСООН	80	12.8	-0.8	8
SnO ₂ wires	0.1M KHCO ₃	НСООН	87.3	13.7	-1.15	9
Sn nanowires	0.5M KHCO ₃	НСООН	90.3	17.3	-1.0	10
SnIn	0.1M KHCO ₃	НСООН	67.1	7.5	-1.0	11
ltra-small SnO	0.5M KHCO ₃	НСООН	66	13.2	-0.9	12
Cu, S Co-doped SnO ₂	0.5M NaHCO ₃ HCOOH		58.5	3.2	-0.75	13
CuxO–Sn nanowire	0.1M KHCO ₃	СО	90	4	-0.8	14
Cu-Sn foam	0.1M KHCO ₃	СО	93	5.7	-0.9	15
Cu-Sn alloy	0.1M KHCO ₃	СО	90	0.9	-0.6	16

References

- 1. C. W. Li, J. Ciston and M. W. Kanan, *Nature*, 2014, **508**, 504-507.
- X. Zheng, P. De Luna, F. P. García de Arquer, B. Zhang, N. Becknell, M. B. Ross, Y. Li, M. N. Banis, Y. Li, M. Liu, O. Voznyy, C. T. Dinh, T. Zhuang, P. Stadler, Y. Cui, X. Du, P. Yang and E. H. Sargent, *Joule*, 2017, 1, 794805.
- 3. X. Zheng, Y. Ji, J. Tang, J. Wang, B. Liu, H.-G. Steinrück, K. Lim, Y. Li, M. F. Toney, K. Chan and Y. Cui, *Nat. Catal.*, 2018, DOI: 10.1038/s41929-018-0200-8.
- 4. C. Zhao and J. Wang, *Chem. Eng. J.*, 2016, **293**, 161-170.
- 5. H. Won Da, H. Choi Chang, J. Chung, W. Chung Min, E. H. Kim and I. Woo Seong, *ChemSusChem*, 2015, **8**, 3092-3098.
- 6. J. Yu, H. Liu, S. Song, Y. Wang and P. Tsiakaras, *Appl. Catal., A*, 2017, **545**, 159-166.
- 7. B. Kumar, V. Atla, J. P. Brian, S. Kumari, T. Q. Nguyen, M. Sunkara and J. M. Spurgeon, *Angew. Chem., Int. Ed.*, 2017, **56**, 3645-3649.

- 8. W. Luc, C. Collins, S. Wang, H. Xin, K. He, Y. Kang and F. Jiao, *J. Am. Chem. Soc.*, 2017, **139**, 1885-1893.
- 9. S. Liu, J. Xiao, X. F. Lu, J. Wang, X. Wang and X. W. Lou, *Angew. Chem., Int. Ed.*, 2019, **58**, 8499-8503.
- 10. J. Wang, Y. Ji, Q. Shao, R. Yin, J. Guo, Y. Li and X. Huang, *Nano Energy*, 2019, **59**, 138-145.
- 11. W. J. Dong, C. J. Yoo and J.-L. Lee, ACS Appl. Mater. Interfaces, 2017, 9, 43575-43582.
- 12. J. Gu, F. Héroguel, J. Luterbacher and X. Hu, Angew. Chem., Int. Ed., 2018, 57, 2943-2947.
- 13. X. Hu, H. Yang, M. Guo, M. Gao, E. Zhang, H. Tian, Z. Liang and X. Liu, *ChemElectroChem*, 2018, **5**, 13301335.
- 14. Y. Zhao, C. Wang and G. G. Wallace, *J. Mater. Chem. A*, 2016, **4**, 10710-10718.
- 15. J. Zeng, K. Bejtka, W. Ju, M. Castellino, A. Chiodoni, A. Sacco, M. A. Farkhondehfal, S. Hernández, D. Rentsch, C. Battaglia and C. F. Pirri, *Appl. Catal., B*, 2018, **236**, 475-482.
- 16. S. Sarfraz, A. T. Garcia-Esparza, A. Jedidi, L. Cavallo and K. Takanabe, ACS Catal., 2016, 6, 2842-2851.