

Efficient CO₂ electroreduction on tin modified cuprous oxide synthesized via a one-pot microwave-assisted route

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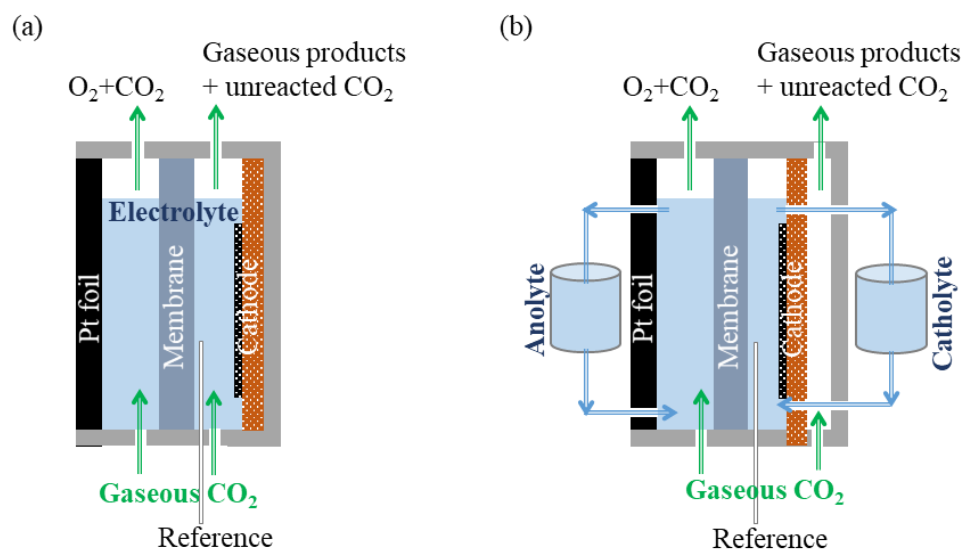
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Scheme S1. Electrochemical cells for the CO₂ electrolysis: (a) batch cell and (b) semi-flow cell

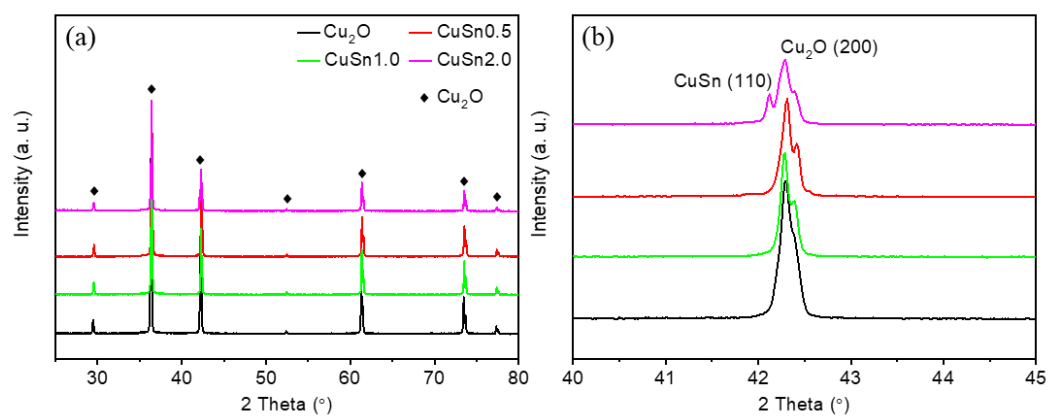


Figure S1. XRD patterns of Cu_2O , CuSn0.5 , CuSn1.0 and CuSn2.0 samples (a) and a view of (200) peak (b).

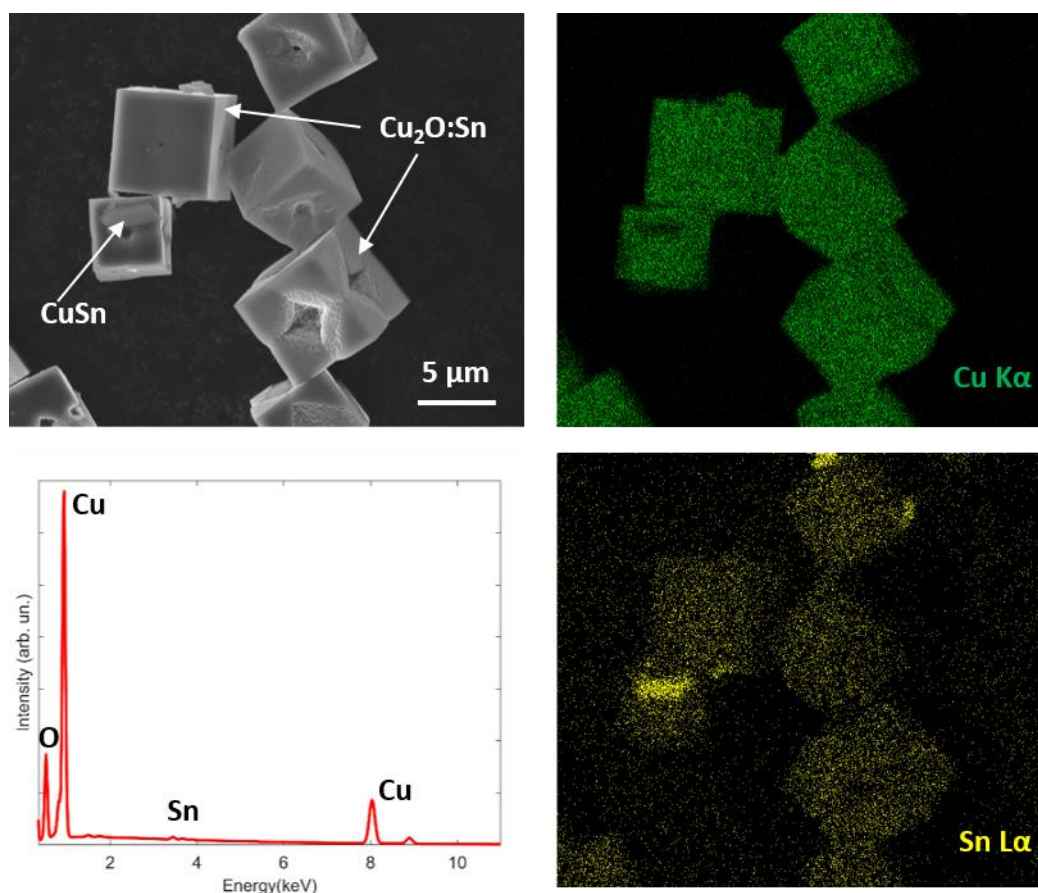


Figure S2. EDX characterization of the region of sample Sn-Cu₂O depicted in the FESEM image, consisting of an EDX spectrum, Cu K α and Sn L α elemental maps.

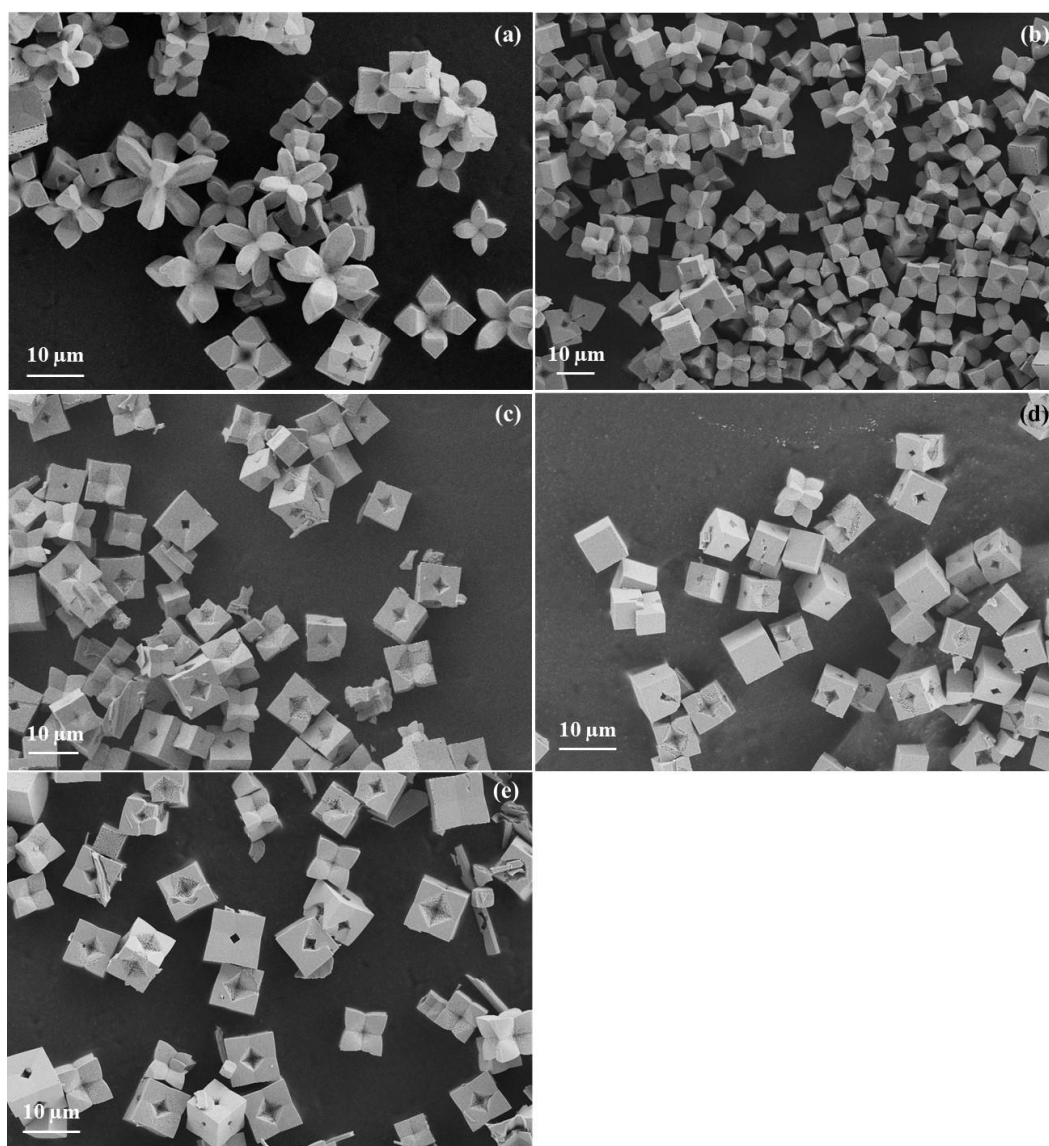


Figure S3. FESEM images of the samples. (a) Cu₂O, (b) CuSn_{0.5}, (c) CuSn_{1.0}, (d) Sn-Cu₂O and (e) CuSn_{2.0}.

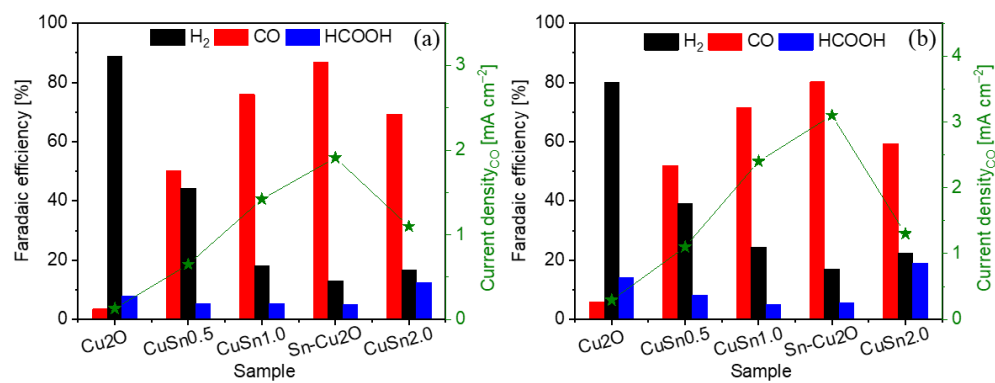


Figure S4. CO₂RR in a batch cell in a CO₂-saturated 0.1 M KHCO₃ aqueous solution on various samples. The dark green line is a guide to the eye for CO partial current density.

Table S1. Current density for CO formation on the Sn-Cu₂O electrode at various potentials in different electrolytes.

| Electrolyte (KHCO₃) | 0.1 M | 0.5 M | 1.0 M | 2.0 M |
|---|---|---|---|---|
| Potential (V vs. RHE) | Current density _{CO} (mA cm ⁻²) | Current density _{CO} (mA cm ⁻²) | Current density _{CO} (mA cm ⁻²) | Current density _{CO} (mA cm ⁻²) |
| -0.35 | 0.097 | 0.14 | 0.28 | 0.36 |
| -0.4 | 0.25 | 0.33 | 0.47 | 0.68 |
| -0.45 | 0.52 | 0.73 | 0.88 | 0.98 |
| -0.5 | 0.78 | 1.37 | 1.82 | 1.88 |
| -0.55 | 1.27 | 2.03 | 2.61 | 3.36 |
| -0.6 | 1.76 | 3.88 | 5.45 | 6.23 |
| -0.7 | 3.17 | 5.95 | 11.25 | 12.28 |
| -0.8 | 4.87 | 9.09 | 16.73 | 24.40 |
| -0.9 | 9.90 | 14.80 | 22.66 | 36.38 |
| -1.0 | 13.87 | 22.00 | 29.30 | 47.16 |

Table S2. Faradaic efficiency for CO formation on the Sn-Cu₂O electrode at various potentials in different electrolytes.

| Electrolyte (KHCO₃) | 0.1 M | 0.5 M | 1.0 M | 2.0 M |
|---|--------------------------------|--------------------------------|--------------------------------|--------------------------------|
| Potential (V vs. RHE) | FE_{CO} (%) | FE_{CO} (%) | FE_{CO} (%) | FE_{CO} (%) |
| -0.35 | 45 | 42 | 72 | 51 |
| -0.4 | 56 | 58 | 79 | 55 |
| -0.45 | 79 | 70 | 81 | 64 |
| -0.5 | 84 | 78 | 81 | 70 |
| -0.55 | 85 | 85 | 83 | 74 |
| -0.6 | 90 | 87 | 86 | 75 |
| -0.7 | 90 | 90 | 83 | 79 |
| -0.8 | 90 | 89 | 80 | 76 |
| -0.9 | 82 | 88 | 76 | 71 |
| -1.0 | 80 | 83 | 73 | 68 |

Table S3. Comparison of different CuSn-based electrocatalysts in liquid-phase CO₂ electrolysis.

| Electrocatalyst | Potential (V vs RHE) | Electrolyte | j_{CO} (mA cm ⁻²) | FE _{CO} (%) | Reference |
|--------------------------------|-------------------------|-------------------------|---|-------------------------|-----------|
| Electrodeposited Cu-Sn | -0.6 | 0.1 M KHCO ₃ | 0.9 | 90 | 1 |
| Dendritic Cu-Sn | -0.8 | 0.1 M KHCO ₃ | 4.7 | 90 | 2 |
| Electrodeposited Cu-Sn | -0.99 | 0.1 M KHCO ₃ | 0.9 | 60 | 3 |
| Dendritic Cu-Sn | -1.1 | 0.1 M KHCO ₃ | 11.5 | 75 | 4 |
| 3D-hierarchical Cu-Sn | -1.0 | 0.1 M KHCO ₃ | 9.6 | ≈70 | 5 |
| Cu/patterned-Sn | -1.0 | 0.1 M KHCO ₃ | 1.9 | 58 | 6 |
| Core/Shell Cu/SnO ₂ | -0.7 | 0.5 M KHCO ₃ | ≈4.3 | 93 | 7 |
| Sn/Cu-Nanofiber-GDE | -1.2 | 0.1 M KHCO ₃ | 100 | ≈80 | 8 |
| Sn-Cu ₂ O | -1.0 | 2.0 M KHCO ₃ | 47 | 70 | This work |
| Sn-Cu ₂ O | -0.7 | 0.5 M KHCO ₃ | 5.9 | 90 | This work |

References

1. Sarfraz, S.; Garcia-Esparza, A.T.; Jedidi, A.; Cavallo, L.; Takanabe, K. Cu-Sn Bimetallic Catalyst for Selective Aqueous Electroreduction of CO₂ to CO. *ACS Catal.* **2016**, *6*, 2842-2851.
2. Zeng, J.; Bejtka, K.; Ju, W.; Castellino, M.; Chiodoni, A.; Sacco, A.; Farkhondeh, M.A.; Hernández, S.; Rentsch, D.; Battaglia, C.; Pirri, C.F. Advanced Cu-Sn foam for selectively converting CO₂ to CO in aqueous solution. *Appl. Catal. B Environ.* **2018**, *236*, 475-482.
3. Morimoto, M.; Takatsuji, Y.; Yamasaki, R.; Hashimoto, H.; Nakata, I.; Sakakura, T.; Haruyama, T. Electrodeposited Cu-Sn Alloy for Electrochemical CO₂ Reduction to CO/HCOO⁻. *Electrocatalysis*, **2018**, *9*, 323-332.
4. Ju, W.; Zeng, J.; Bejtka, K.; Ma, H.; Rentsch, D.; Castellino, M.; Sacco, A.; Pirri, C.F.; Battaglia, C. Sn-Decorated Cu for Selective Electrochemical CO₂ to CO Conversion: Precision Architecture beyond Composition Design. *ACS Appl. Energy Mater.* **2019**, *2*(1), 867-872.
5. Yoo, C.J.; Dong, W.J.; Park, J.Y.; Lim, J.W.; Kim, S.; Choi, K.S.; Ngome, F.O.O.; Choi, S.-Y.; Lee, J.-L. Compositional and Geometrical Effects of Bimetallic Cu-Sn Catalysts on Selective Electrochemical CO₂ Reduction to CO. *ACS Appl. Energy Mater.* **2020**, *3*, 4466-4473.
6. Dong, W.J.; Lim, J.W.; Hong, D.M.; Park, J.Y.; Cho, W.S.; Baek, S.; Yoo, C.J.; Kim, W.; Lee, J.-L. Evidence of Local Corrosion of Bimetallic Cu-Sn Catalysts and Its Effects on the Selectivity of Electrochemical CO₂ Reduction. *ACS Appl. Energy Mater.* **2020**, *3*, 10568-10577.
7. Li, Q.; Fu, J.; Zhu, W.; Chen, Z.; Shen, B.; Wu, L.; Xi, Z.; Wang, T.; Lu, G.; Zhu, J.J.; Sun, S. Tuning Sn-Catalysis for Electrochemical Reduction of CO₂ to CO via the Core/Shell Cu/SnO₂ Structure. *J. Am. Chem. Soc.* **2017**, *139*, 4290-4293.
8. Ju, W.; Jiang, F.; Ma, H.; Pan, Z.; Zhao, Y.-B.; Pagani, F.; Rentsch, D.; Wang, J.; Battaglia, C. Electrocatalytic Reduction of Gaseous CO₂ to CO on Sn/Cu-Nanofiber-Based Gas Diffusion Electrodes. *Adv. Energy Mater.* **2019**, *9*, 1901514.