Supporting Information for

3D core-shell porous-structured Cu@Sn hybrid electrodes with unprecedented selective CO₂-into-formate achieving 100%

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1. Chemicals and Materials

All chemicals including Copper(II) sulphate pentahydrate (CuSO₄ 5H₂O), sulfuric acid (H₂SO₄, 98 wt.%), trisodium citrate dihydrate (Na₃C₆H₅O₇ 2H₂O), stannous chloride (SnCl₂ 2H₂O), sodium dodecyl benzene sulfonate (C₁₈H₂₉NaO₃S) were analytical reagents and purchased from Sinopharm Chemical Reagent Co., Ltd. (China). Further purification of above chemicals was not carried out before use.

2. Characterizations and product analysis

2.1 Physics characterizations

Field emission electron microscope (FE-SEM; S-4800, Japan) were employed to observe the morphologies of the Cu@Sn. Images of TEM, HRTEM, and HAADF-STEM were collected on a field-emission transmission electron microscope (JEOL ARM-200F) operating at an accelerating voltage of 200 kV. EDX analysis was conducted using an FEI Talos F200X TEM at an acceleration voltage of 200 kV. X-ray diffraction (XRD; D/max-2550 PC, Japan) with Cu-Ka radiation ($\lambda = 0.154$ nm) and XPS measurements (Thermo-VG Scientific, USA) were applied to explore the changes of crystal face and surface compositions before and after ERC, respectively. The surface profile measurement was performed on a Wyko NT9100 optical profilometer.

2.2 Electrochemical surface area (ECSA) measurement

To evaluate the effect of surface area, we measured the electrochemically active surface area (ECSA) for $Cu@Sn_{(x)}$ from the electrochemical double-layer capacitance of the catalytic surface. The electrochemical capacitance was determined by measuring the non-Faradaic capacitive current associated with double-layer charging from the scan-rate dependence of cyclic voltammograms (CVs).

2.3 Electrocatalytic Reduction of CO₂

All CO₂ reduction experiments were performed using a three-electrode system connected to an electrochemical workstation(CHI660E). A saturated calomel electrode (SCE) and platinum foil (1 cm \times 1.5 cm) were used as reference and counter electrodes, respectively. The prepared Cu@Sn electrode played a role as the working electrode. The electrolyte was 0.5 M KHCO₃ saturated with CO₂. The experiments were performed in a gas-tight two-compartment H-cell separated by an ion exchange membrane (Nafion®117). CO₂ was circulated into the cathode compartment continuously to sustain sufficient gas during the subsequent electrolysis. The pH value of N₂ and CO₂-saturated electrolytes is 8.8 and 7.3, respectively and all figures have been labeled on the RHE scale using E (vs. RHE) = E (vs. SCE) + 0.241 + 0.0591 pH.

2.4 Product analysis

For analysis of the produced formate, the electrolyte after electrolysis was fetched from the compartment with a syringe and diluted 5 ~ 10 times by deionized water. The formate (HCOO⁻) concentration of the diluted samples was quantified by ion chromatography (IC1820, Shanghai Sunny Hengping Scientific instrument Co. Ltd). The Faradaic efficiency towards formate (FE_{HCOO}^{-}) is calculated using Eq. (1):¹

$$FE_{HCOO^{-}} = \frac{2nF}{Q} \tag{1}$$

Where *n* is the moles of generated formate, 2 is the number of transferred electrons from CO₂ to formate, *F* is the Faraday constant (F = 96485 C mol⁻¹), *Q* is the total charge transited across the working electrode (C).

While exploring formate, gases were collected from the top space of the closed cathode compartment with a gas-tight syringe in the process of electrolysis. The gas-phase products were determined with a gas chromatograph (GC1120, Shanghai Sunny Hengping Scientific instrument Co. Ltd). A flame ionization detector (FID) was

employed to detect organic gases such as methane (CH₄) and ethylene (C₂H₄). The concentration of carbon monoxide (CO) and hydrogen (H₂) was detected by a thermal conductivity detector (TCD).

The Faradaic efficiency for the products of H₂, CO, CH₄ and C₂H₄ (*FE_{H2}*, *FE_{C0}*, *FE_{CH4}, and FE_{C2H4}*) is calculated by Equation (2):²

$$FE_{H2/CO/CH4/C2H4} = \frac{10^{-3}mv\%FG}{60RTi} P$$
(2)

Where *m* is the number of transferred electrons for the products H₂, CO, CH₄ and C₂H₄, *v*% is the volume concentration of H₂, CO, CH₄ and C₂H₄ in the collected gases from the top space of the cathode compartment, *i* is the current (mA), *G* is flow rate of CO₂ bubbled into the cathode compartment (mL min⁻¹), $P = 1.01 \times 10^5$ Pa, T = 273.15 K, R = 8.314 J mol⁻¹ K⁻¹.

The partial current density of formate product, $i_{formate}$ (mA cm⁻²), was calculated by Eq. (3):³

$$i_{formate} = \frac{2FcV}{Q}i_{tot}$$
(3)

Where *V* is the volume of the electrolyte in the cathode compartment (L), *c* is the concentration of formate quantified by IC (mol L⁻¹), i_{tot} is the total current density (mA cm⁻²).

3. Tafel slope

The Tafel relationship for CO₂ reduction to formate can be expressed as follows:^{4,5}

$$E = E_0 - \frac{2.303RT}{\alpha n_a F} \log(i_0) + \frac{2.303RT}{\alpha n_a F} \log(i_{formate})$$
(4)

$$b = \frac{2.303RT}{\alpha n_a F}$$
(5)

Where *E* is the applied potential, E_0 is the standard potential for the CO₂/HCOO⁻ couple, α is the electron transfer coefficient, *b* is the Tafel slop, i_0 is the exchange current density, n_{α} is the electron transfer number, $i_{formate}$ is the partial current density for CO₂ reduction to production formate.



 $\label{eq:Fig.S1} \begin{array}{l} \textbf{Fig. S1} \ SEM \ images. \ (a-c) \ Cu, \ (d-f) \ Cu@Sn_{(0.5),} \ (g-i) \ Cu@Sn_{(1),} \ (j-l) \ Cu@Sn_{(2),} \ (m-o) \\ Cu@Sn_{(3),} \ (p-r) \ Cu@Sn_{(5).} \end{array}$



Fig. S2 EDS mapping images of $Cu@Sn_{(1)}$ for Cu, Sn, O.



Fig. S3 XRD patterns of Cu, $Cu@Sn_{(0.5)}$, $Cu@Sn_{(1)}$, $Cu@Sn_{(2)}$, $Cu@Sn_{(3)}$, $Cu@Sn_{(5)}$ electrodes.



Fig. S4 (a) Cu LMM spectra of Cu@Sn₍₁₎ before and after electrolysis. (b) Atomic percentage of Cu⁰, Cu²⁺, Sn⁰, Sn²⁺ and Sn⁴⁺ in Cu@Sn₍₁₎ before and after electrolysis.



Fig. S5 (a-e) Surface areas measured using the capacitance. (a) $Cu@Sn_{(0.5)}$, (b) $Cu@Sn_{(1)}$, (c) $Cu@Sn_{(2)}$, (d) $Cu@Sn_{(3)}$, (e) $Cu@Sn_{(5)}$, recorded in N₂-saturated 0.5 M KHCO₃ solution. Potential scan rates as marked in the figure. Insert shows a linear relationship between the current density (mA cm⁻²) and the potential scan rate.



Fig. S6 cyclic voltammetry (CV) curves in N₂- and CO₂-saturated 0.5 M KHCO₃ electrolytes. (a) Cu; (b) Cu@Sn_(0.5); (c) Cu@Sn₍₂₎;(d) Cu@Sn₍₃₎; (e) Cu@Sn₍₅₎.



Fig. S7 (a,b) high-resolution Sn3d and Cu2p XPS spectra of $Cu@Sn_{(1)}$ after oxidation. (c) LSV curves of $Cu@Sn_{(1)}$ before and after oxidation in N₂- and CO₂-saturated 0.5 M KHCO₃ electrolyte.



Fig. S8 Faradaic efficiency of Sn and Cu@Sn at potential range from -0.68 V to -0.93 V vs. RHE (with 0.05 V intervals) in CO₂ saturated 0.5 M KHCO₃ electrolyte. Electrolysis time: 1 h. (a) Cu; (b) Cu@Sn_(0.5); (c) Cu@Sn₍₁₎; (d) Cu@Sn₍₂₎; (e) Cu@Sn₍₃₎; (f) Cu@Sn₍₅₎; (g) Sn.



Fig. S9 Current-time curves for $Cu@Sn_{(1)}$ at potential range from -0.68 V to -0.93 V vs. RHE (with 0.05 V intervals) in CO₂ saturated 0.5 M KHCO₃ electrolyte. Electrolysis time: 1 h.



Fig. S10 Tafel plot for formate.



Fig. S11 (a) TEM-EDS mapping results of $Cu@Sn_{(1)}$ at high magnification before electrolysis. (b) TEM-EDS mapping results of $Cu@Sn_{(1)}$ after electrolysis.

Catalysts/Elastrada	Electrolyte	Electrolysis	Faradaic	Reference
Catalysts/Electrode		potential	efficiency	
Sn foil	0.25 M KHCO ₃	-2.0 V vs. SCE	94.63	[1]
In-Sn	0.1 M KHCO ₃	-1.2 V vs. RHE	92	6
Sn-GDE	0. 5 M NaHCO ₃	-1.1 V vs. RHE	71	7
Sn/Cu	0.1 M KHCO ₃	-1.8 V vs.	01.5	8
		Ag/AgCl	91.5	
Sn/SnO _x	0.5 M NaHCO ₃	-0.7 V vs. RHE	~40	9
Sn/Pb	0.5 M KHCO ₃	-2.0 V vs.		10
		Ag/AgCl	79.8	
SnO ₂ /carbon aerogel	1.0 M KHCO ₃	-0.96 V vs. RHE	76	11
Cu _x O/Cu	0.5 M KHCO ₃	-0.7 V vs. SHE	59.3	12
SnO ₂ -CuO	0.5M KHCO ₃	-1.0 V vs. SHE	74.1	13
Cu ₂ O/Cu	0.5 M NaHCO ₃	-0.75 V vs. RHE	~33	14
$Cu@Sn_{(1)}$	0.5 M KHCO ₃	-1.6 V vs. SCE	~100	This work

Table S1 Comparison of the performances for electrochemical reduction of CO_2 toformate on $Cu@Sn_{(1)}$ and reported Sn-based and Cu-based catalysts.

	Cu foil	Cu	Cu@Sn before	Cu@Sn after
Ra (µm)	0.73	8.70	8.85	9.44
Rq (µm)	0.88	10.21	10.67	11.09
Rt (µm)	9.27	50.76	51.13	50.33

 Table S2 Roughness comparison of Cu foil, Cu electrode and Cu@Sn (1) before and after
 electrolysis

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