# **Supporting Information**

# Topological Transformation Constructed c-SnO<sub>2</sub>/a-ZnSnO<sub>3</sub> Heterostructure with Abundant Interfaces for Efficient Electrocatalytic CO<sub>2</sub> Reduction

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# **Experimental section**

#### Chemicals

SnCl<sub>4</sub>.5H<sub>2</sub>O was purchased from Aladdin. ZnCl<sub>2</sub> was purchased from Generalreagent®. 2-Aminoethanol (C<sub>2</sub>H<sub>7</sub>NO, analytical reagent 99.7%) was purchased from Aladdin.

#### Synthesis of ZnSn

0.15 mmol of SnCl<sub>4</sub>.5H<sub>2</sub>O and 0.2 mmol of ZnCl<sub>2</sub> was dissolved in 15 mL of deionized water. Then the solution was dropwise added by 0.5 mL of 2-aminoethanol, followed by sonication for 15 min. Subsequently, the mixture was left undisturbed for 12 h at room temperature. The resulting precipitate was then centrifuged and washed three times with deionized water and dried in an oven at 60°C for 12 h.

### Synthesis of ZnSn-200, ZnSn-550 and ZnSn-700

ZnSn-200, ZnSn-550, and ZnSn-700 were prepared by annealing ZnSn in air at 200, 550, and 700 °C for 2h, respectively.

## Material Characterization.

The crystal structure of the samples was determined by an X-ray diffractometer

(Bruker D8 Advance). The morphology of the samples was observed using scanning electron microscopy (SEM, TESCAN MIRA LMS) and transmission electron microscopy (TEM, JEOL-JEM-F200). The Raman spectra of the samples were obtained on a LabRAM Soleil Nano Raman spectrometer using an argon ion laser at 532 nm as the excitation source. Fourier transform infrared (FTIR) spectra were obtained with a Bruker INVENIO spectrometer. The X-ray photoelectron spectroscopy (XPS) data were collected using a Thermo Scientific K-Alpha, and all binding energies were calibrated concerning a standard carbon C1s = 284.8 eV. UV spectra were measured using a Shimadzu UV-3600PLUS. Simultaneous TG/DTA analysis was performed (HQT-4) up to 800 °C with a heating rate of 10 °C/min in air atmosphere.

#### Detailed electrochemical measurements.

The electrocatalytic CO<sub>2</sub> reduction measurements were carried out in CO<sub>2</sub>saturated 0.5 M KHCO<sub>3</sub> electrolyte using a two compartment H-type cell separated by a piece of proton exchange membrane (Nafion117) and a three-electrode system. Pt foil and saturated Ag/AgCl electrode were used as the counter electrode and reference electrode, respectively. The working electrode was prepared as the following procedures: 2.5 mg of the as-prepared sample and 0.5 mg of ketjenblack carbon (ECP-600JD) were dispersed in 250 µL of ethanol and 6 µL of Nafion solution (5%). The solution was vigorously sonicated for about 60 min to form a homogeneous ink and the ink was dropped onto a carbon paper (YLS-26, from Japan toray) with a size of  $1 \times 1$ cm<sup>2</sup>. Then, the electrode was dried at 40 °C for overnight. Before the measurement, the cathode chamber (with 35 mL of 0.5 M KHCO<sub>3</sub>) was flowed with CO<sub>2</sub> (99.99%) for 30 min to remove the air and make the CO<sub>2</sub>-saturated electrolyte. Then, the electrocatalysis was carried out with a CO<sub>2</sub> flow rate of 20 mL min<sup>-1</sup>. The gaseous products were delivered to an on-line connected gas chromatograph (GC, Shandong rainbow Chemical Co Ltd, SP-7820) equipped with a thermal conductivity detector (TCD) and a flame ionization detector (FID). And liquid products were characterized by a <sup>1</sup>H nuclear magnetic resonance (NMR) spectrometer (AVANCE III 400 MHz).

In situ attenuated total reflection-infrared (ATR-IR) spectra were measured by an INVENIO R FT-IR spectrometer equipped with a liquid nitrogen cooled mercury cadmium telluride (MCT) detector. The spectro-electrochemical cell furnished with a SPEC-I ATR (Shanghai Yuanfang Technology CO., Lad.) was filled with 0.5 M KHCO<sub>3</sub> electrolyte. The spectro-electrochemical cell was equipped with a silica prism at the bottom as an infrared transmittance window. The silica prism was cleaned by

nitrohydrochloric acid and polished before vacuum coating of a gold conducting layer (the surface resistance reaches 10-20  $\Omega$ ). The working electrode was made by depositing the catalyst slurry (2.5 mg of catalyst dispersed in a 250 µL ethanol and 6 µL Nafion mixture) on the Au-plated silicon prism, so that the IR beam can probe the intermediate species produced during the electrocatalytic CO<sub>2</sub>RR. Ag/AgCl electrode and graphite rod electrode were used as reference electrode and counter electrode, respectively. During the test, CO<sub>2</sub> was kept bubbling into the electrolyte with a flow rate of 20 mL/min. The background spectra were first collected at the open-circuit potential, followed by potential step experiments were performed at different applied potentials. The ATR-IR spectra were simultaneously collected at each potential to analyze the dynamic evolution of the reactive species.



Figure S1. (a, b) SEM images and (c) the size distribution of ZnSn.



Figure S2. (a, b) SEM images and (c) the size distribution of ZnSn-200.



Figure S3. (a, b) SEM images and (c) the size distribution of ZnSn-550.



Figure S4. (a, b) SEM images and (c) the size distribution of ZnSn-700.



Figure S5. XRD patterns of (a) ZnSn, (b) ZnSn-200 and (c) ZnSn-700. The corresponding standard XRD PDF cards of  $ZnSn(OH)_6$ ,  $ZnSnO_3$ ,  $Zn_2SnO_4$  and  $SnO_2$  are also provided.



Figure S6. TG/DTA curves of ZnSn.



**Figure S7.** The overall XPS survey spectra of ZnSn, ZnSn-200, ZnSn-550 and ZnSn-700.



Figure S8. LSV curves of the ZnSn-200 and ZnSn-700 in Ar or  $CO_2$  saturated 0.5M KHCO<sub>3</sub>.



**Figure S9.** The gas products are measured by a GC instrument equipped with TCD and FID. (a) FID and (b) TCD curves of ZnSn-550 at -1.3  $V_{RHE}$ .

The electrocatalytic  $CO_2$  reduction tests were carried out at constant potential electrolysis mode. During the electrolysis process, the gaseous products were continuously delivered into an online connected GC equipped with a TCD and FID and measured per 30 min. The gas products (H<sub>2</sub> was detected by the TCD, CO and CH<sub>4</sub> were detected by the FID equipped with a converter) could be quantitatively analyzed through the FID and TCD curves and calibrated by standard gas (containing H<sub>2</sub>, CO, CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>2</sub>) at known concentration.

The Faraday efficiency of gas products was calculated by Eq. (1):

$$FE = \frac{enF}{Q} = \frac{e \times 96485 \left(\frac{c}{mol}\right) \times V\left(\frac{mL}{min}\right) \times 10^{-6} \left(\frac{m^3}{mL}\right) \times v(vol\%) \times 1.013 \times 10^{-6} \times 10^{-6}$$

where e = the number of electron transfer, which is 2 for the H<sub>2</sub> and CO. v(vol%) = volume concentration of the produced gas in the H-cell, which is measured by the GC and calibrated by standard gas (containing H<sub>2</sub>, CO, CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>2</sub>) at known concentrations. V (mL/min) = flow rate of the CO<sub>2</sub> gas (20 mL min<sup>-1</sup>). I = steady-state cell current.



**Figure S10.** (a) <sup>1</sup>H NMR spectrum of ZnSn-550 at -1.3 V<sub>RHE</sub> for 1.5 h. (b) The standard curve of formate/DMSO <sup>1</sup>H-NMR peak area vs concentration of formate. The standard solution was prepared by mixing 0.1 mL of D<sub>2</sub>O with 0.49 mL of KHCO<sub>3</sub> solution containing formic acid (0.1, 0.5, 1, 3, 6, and 20 mM) and 0.01 mL of KHCO<sub>3</sub> solution containing DMSO (0.15% vol.). The ratio of formate ( $\delta \approx 8.23$  ppm) peak area to DMSO ( $\delta \approx 2.50$  ppm) peak area measured by <sup>1</sup>H-NMR was compared to standard curve to quantify the concentrations of the formate products.

The liquid product was measured by <sup>1</sup>H NMR spectra after the electrolysis: 0.49 mL of the reaction electrolyte was mixed with 0.1 mL of  $D_2O$  and 0.01 mL of KHCO<sub>3</sub> solution containing DMSO (0.15% vol.) to prepare the sample for the <sup>1</sup>H NMR test.

The Faraday efficiency of formate was calculated by Eq. (2):

$$FE = \frac{2F \times n_{formate}}{Q} \#(2)$$

where  $n_{formate}$  is the total moles of formate in the cell, which can be calculated by the <sup>1</sup>H NMR results and the standard curve. *F* is Faraday's constant, 96485 C mol<sup>-1</sup>. *Q* is the total charge consumed during electrolysis at a single voltage.



Figure 11. (a)  $FE_{H2}$ , (b)  $FE_{CO}$ , and (c)  $FE_{C1}$  of ZnSn, ZnSn-200, ZnSn-550 and ZnSn-700 at varied applied potentials.



Figure S12. (a, b) SEM images and (c) the size distribution of the ZnSn-550 after electrocatalytic  $CO_2RR$  test.



**Figure S13.** (a) XRD pattern of the ZnSn-550 after electrocatalytic  $CO_2RR$ , (b, c) Highresolution Zn 2p and Sn 3d XPS spectra of ZnSn-500 before and after electrocatalytic  $CO_2RR$  test.



**Figure S14.** CV curves of (a) ZnSn, (b) ZnSn-200, (c) ZnSn-550 and (d) ZnSn-700 with various scan rates (20, 40, 60, 80, 100, 120 and 160 mV/s).



Figure S15. (a)  $BE_{Zn 2p3/2}$  of the ZnSn, ZnSn-200, ZnSn-550 and ZnSn-700 obtained from Figure 2d. (b)  $FE_{formate}$  and  $FE_{CO}$ , and (c)  $FE_{H2}$  of the ZnSn, ZnSn-200, ZnSn-550 and ZnSn-700 at -1.3  $V_{RHE}$  obtained from Figure 3b and Figure S11.



**Figure S16.** (a) UV-vis diffuse reflectance spectra and (b) Kubelka-Munk plots of the ZnSn, ZnSn-200, ZnSn-550 and ZnSn-700.

Catalysts	Electrolyt e	Potential (vs. RHE)	FE <sub>formate</sub> /%	FE <sub>C1</sub> %	J <sub>formate</sub> /mA cm <sup>-2</sup>	Ref.
c-SnO <sub>2</sub> /a-ZnSnO <sub>3</sub>	0.5 M KHCO <sub>3</sub>	-1.1 V	63.6	75.0	17.7	This work
Sn5-HTBBA/C	0.5 M KHCO <sub>3</sub>	-1.1 V	47.3			1
Sn-MOF	0.5 M KHCO <sub>3</sub>	-1.2 V	92%		21.344	2
SnS NSs	0.5 M KHCO <sub>3</sub>	-1.1 V	82.1%		18.9	3
o-ZSO	0.5 M KHCO <sub>3</sub>	-1.1 V		71.8	7.31 J <sub>C1</sub>	4
ZSO HSs	0.1 M KHCO <sub>3</sub>	-1.1 V	90.2		3.9	5
Zn-Bi	0.5 NaHCO <sub>3</sub>	-0.8 V	94		3.6	6
ZnSn/Zn foil	0.5 M KHCO <sub>3</sub>	-1.1 V	94		9.95	7
$Zn_{2.33}Sb_{0.67}O_4$	0.5 M KHCO <sub>3</sub>	-1.0 V	92		7.6	8
SnOx nanosheets	0.5 M KHCO <sub>3</sub>	-1.25 V	77		9.24	9
Reduced SnO <sub>2</sub> porous nanowires	0.1 M KHCO <sub>3</sub>	-0.8 V	80.1		4.8	10
Mesoporous SnO <sub>2</sub>	0.1 M KHCO <sub>3</sub>	-1.15 V	75		10.8	11
SnO <sub>2</sub> nanotube	0.5 M KHCO3	-1.0 V	72.6		8	12

**Table S1.** Electrocatalytic CO<sub>2</sub>RR performances of recently reported Zn/Sn-based catalysts.

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