

Supporting Information

Electrochemical Converting CO₂ into HCOO⁻ Synergistically by Nanocomposite of Zn₂SnO₄/ZnO

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Experimental section

Chemicals

SnCl₂ (MW: 189.62), CTAB (364.45), Nafion (5 wt%) and NaOH (AR:96%) were purchased from Sigma-Aldrich Co. Ltd. Sinopharm Chemical Reagent Co., Ltd. Zn(CH₃COO)₂ (MW:183.48), Zn(NO₃)₂·6H₂O (MW:297.48), SnCl₄·5H₂O (MW:350.6) and KHCO₃ (MW:100.12) were obtained from MACKLIN Co., Ltd. All of the reagents were purchased and directly used without further purification.

Synthesis of Zn₂SnO₄/ZnO catalyst

In a typical procedure, 0.24 g of NaOH and 0.73 g of CTAB were added into 40 mL of deionized water under sonication treatment. Then, 2 mL of 0.3 M Zn(CH₃COO)₂ was added dropwise into the solution under vigorous stirring. When the above solution turned into a milky white solution, 16 mg of anhydrous stannous chloride (SnCl₂) was added to the solution. Whereafter, the mixture was transferred into a stainless-steel autoclave and heated to 150 °C for 16 h. After the reaction was completed, the white products were collected and washed alternately with ethanol and deionized water for 4 times. The final products were vacuum-dried at 60 °C for 4 h and directly used for electrochemical measurements.

Synthesis of ZnO catalyst

The synthetic method of ZnO catalyst is according to a previous study.¹⁹ In detail, 0.24 g of NaOH and 0.73 g of CTAB were added into 40 mL of deionized water under sonication treatment. Then, 2 mL of 0.3 M Zn(CH₃COO)₂ was added dropwise into the above solution. After that, the solution was transferred into a stainless-steel autoclave

and heated to 150 °C for 16 h. The obtained white products were collected and washed alternately with ethanol and deionized water for 4 times. The final products were vacuum-dried at 60 °C for 4 h and directly used for electrochemical measurements.

Synthesis of Zn₂SnO₄ catalyst

The synthetic method of Zn₂SnO₄ was according to a previous report.²⁰ Firstly, two solutions were prepared: (1) Solution A: 0.53 g of SnCl₄·5H₂O was dissolved in 10 mL of deionized water and magnetic stirred for 10 minutes. Then, 10 mL of NaOH aqueous solution with concentration of 1 mol·L⁻¹ was added to the above solution, resulting in a uniform transparent solution A. (2) Solution B: 0.446 g of Zn(NO₃)₂·6H₂O was dissolved in 10 mL of deionized water. After magnetic stirring for 10 minutes, the obtained solution was marked as B. Afterwards, a uniform milky-white suspension was produced by slowly adding solution B to solution A. The resultant solution was transferred into a stainless-steel autoclave (50 mL) and heated to 220 °C for 3 h. When the reaction was over, the products were collected and washed with ethanol and deionized water for 4 times. Finally, the products were vacuum dried for 6 h.

Materials characterization

The prepared catalysts were systematically characterized in terms of phase, structure, and morphology. X-ray diffraction (XRD) with a model of Bruker D8 Focus Diffraction system using Cu K α radiation was employed to detect the phase of prepared catalysts. A QUATTRA S field-emission scanning electron microscope (FESEM) was used to observe morphology. TEM, HRTEM and elemental mapping were performed

on a jeol2100F transmission electron microscope at an accelerating voltage of 120 kV. X-ray photoelectron spectroscopy (XPS) was conducted on a K-Alpha Analytical instrument and all obtained XPS spectra were calibrated against the C 1s photoelectron signal at 284.6 eV. The X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) of Sn K-edge and Zn K-edge were measured at room temperature by the BL10c beam line at the Pohang Light Source (PLS-II), Korea. The gas products were detected by GC 9790 plus gas chromatograph. While the liquid products were quantified by ^1H NMR spectra that obtained on a Bruker Advance DPS-2400 spectrometer.

CO₂RR performance evaluation

The electrochemical CO₂ reduction was conducted in a three-chamber flow cell. The anode and cathode was separated by a Nafion 117 membrane. 0.5 M KHCO₃ solution was used as the electrolyte for both anode and cathode. The flow-rate of CO₂ was controlled at 20 sccm by gas mass-flow controller. The Ar (99.999%) was used as the carrier gas. The counter electrode was a piece of Ni foam with an area of $0.5 \times 2 \text{ cm}^2$. The electrochemical data were measured using a CHI760E electrochemical workstation. A solid-state Ag/AgCl electrode was used as reference electrode. All the measured data were calibrated relatively to reversible hydrogen electrode (RHE). All potentials were not iR compensated. The sweep speed of Linear sweep voltammetry (LSV) curves was 5 mV s^{-1} . The products were measured over a one-hour period and repeated at least three times to obtain the average for each applied potential. The response framework, including the electrolyte, was risen with CO₂ for thirty minutes to

arrive at CO₂ immersion before the electrochemical estimations. A gas chromatography system with flame ionization, thermal conductivity, and multiple in-line gas analyzers was used to qualify the gas products.

The Faradic efficiency of gas products was calculated based on the equation of $FE = \frac{nFxV}{j}$, where F is Faraday's constant, n is the electron transfer numbers, V is the total molar flow rate of the gas reactant, x is the mole fraction of the gas product, and j is the total current throughout the CO₂RR process.

A Bruker 400 MHz NMR spectrometer was used to analyze the CO₂RR's liquid products. As the internal standard, 400 mL of the sampled catholyte was added to 50 μL of DMSO solution (80 ppm) and 50 μL of D₂O. The water suppression method was used to measure the ¹H NMR spectrum. The Faradaic efficiency of liquid products was calculated according to the equation of $FE = \frac{nF}{Q}$, where Q is the total quantity of electric charge, n is the molecular amount of the product, and F is the Faraday's constant.

Preparation of working electrode

The working electrode was prepared according to the following steps. 1 mg of the catalyst and 10 μL of Nafion solution were uniformly dispersed in 500 μL ethanol by ultrasonic for 30 min to form a homogeneous ink. Then, the catalyst was dropped onto a piece of gas diffusion layer with the coating area of 0.5 × 2 cm². Finally, the gas diffusion layer was dried naturally and used for electrochemical measurements.

The electrochemical impedance spectroscopy measurements covered a frequency range of 0.01 Hz to 100 KHz. Besides, double-layer capacitances (C_{dl}) were measured

using cyclic voltammetry (CV) at different scan speeds (40, 60, 80, 100, 120, 150 mV s⁻¹) in the potential range of 0.2-0.3 V vs. RHE. Notably, the C_{dl} and EIS measurements were using the typical three electrode system with glassy carbon loaded catalyst as working electrode.

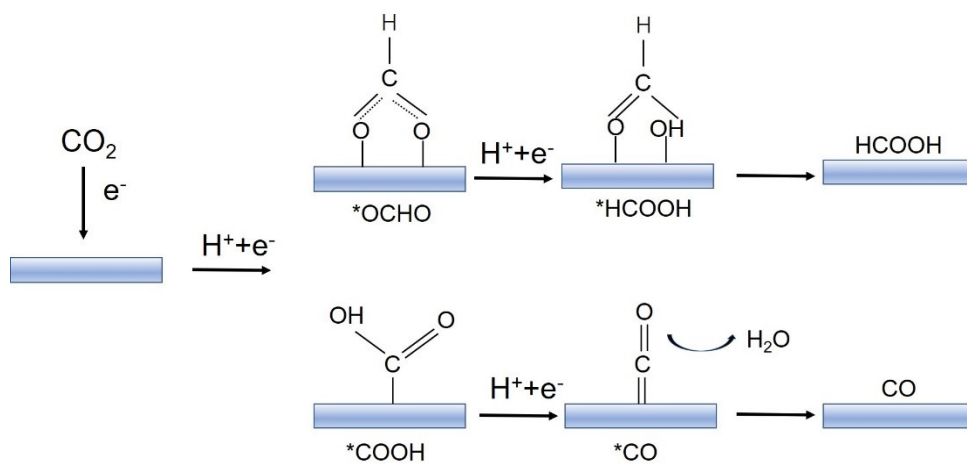


Figure S1. Reaction pathways for HCOOH and CO products.

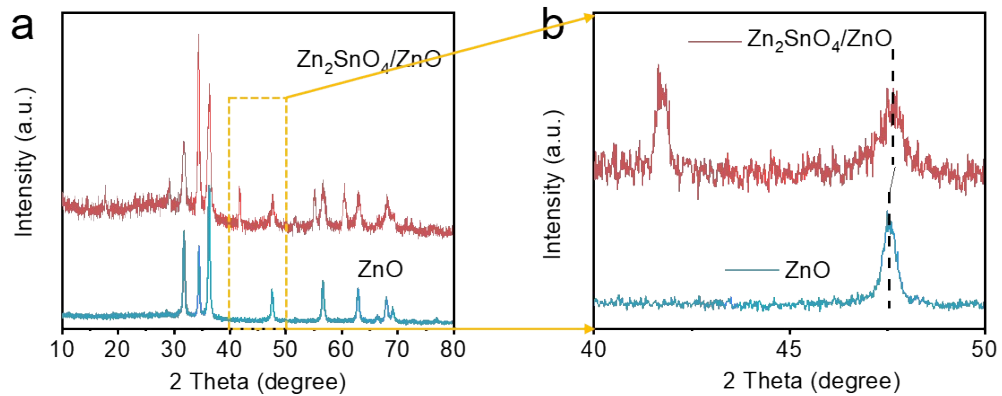


Figure S2. a) XRD patterns of ZnO and Zn₂SnO₄/ZnO, b) Magnified XRD patterns corresponding to the region in a) marked with yellow rectangle.

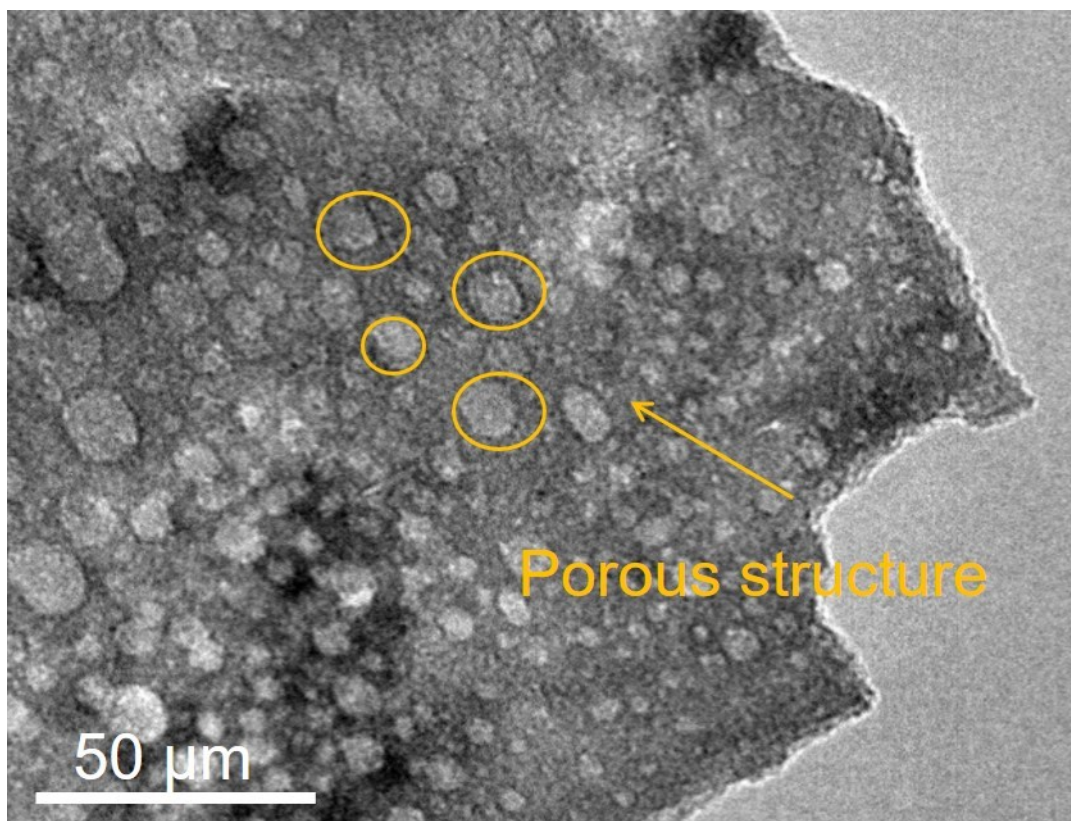


Figure S3. The TEM image of ZnO in Zn₂SnO₄/ZnO.

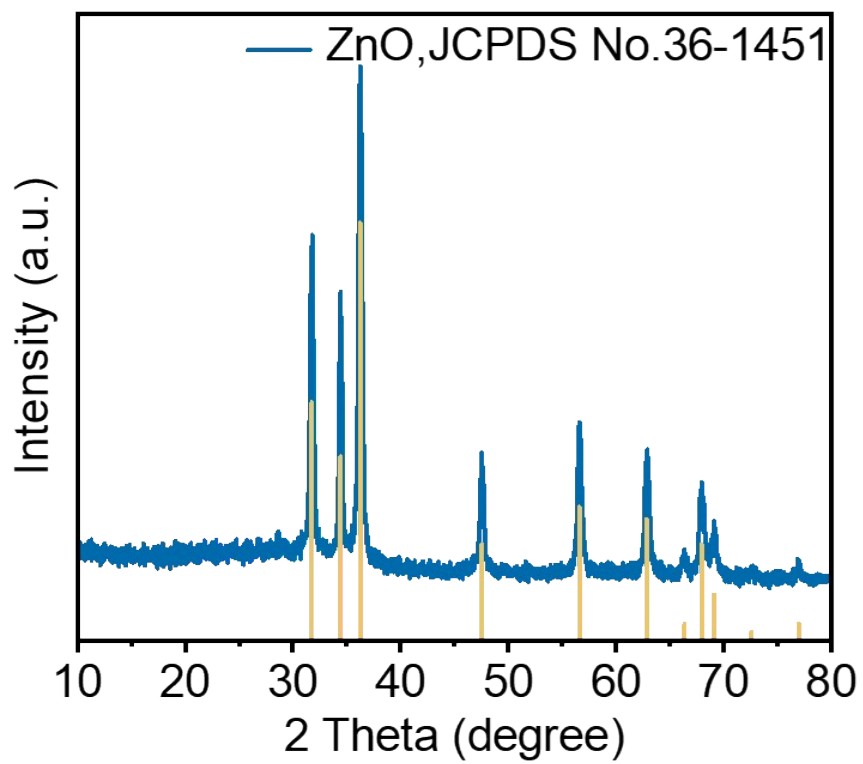


Figure S4. XRD pattern of prepared ZnO catalyst.

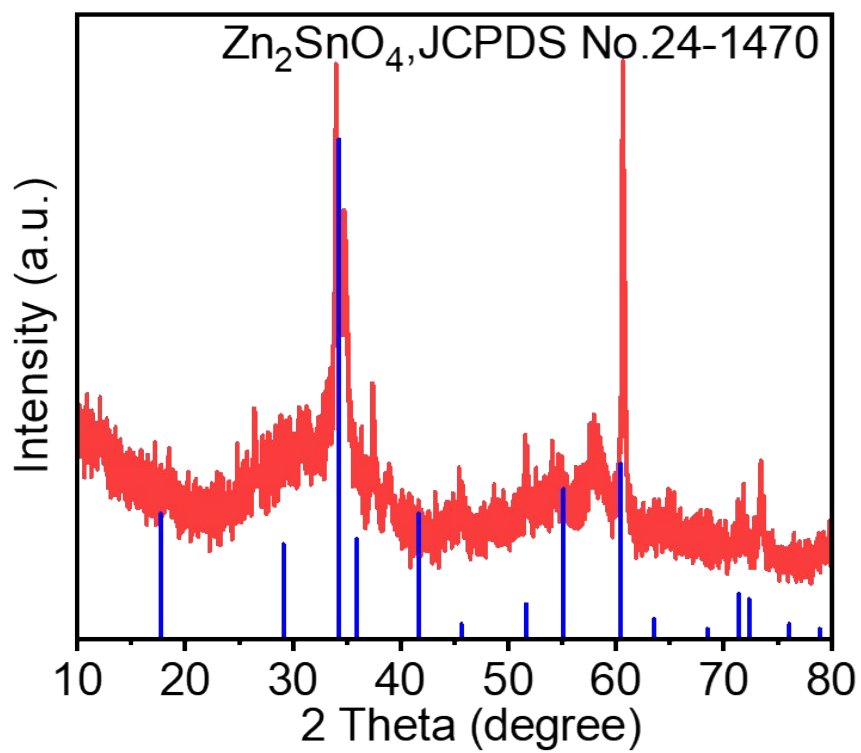


Figure S5. XRD pattern of prepared Zn_2SnO_4 catalyst.

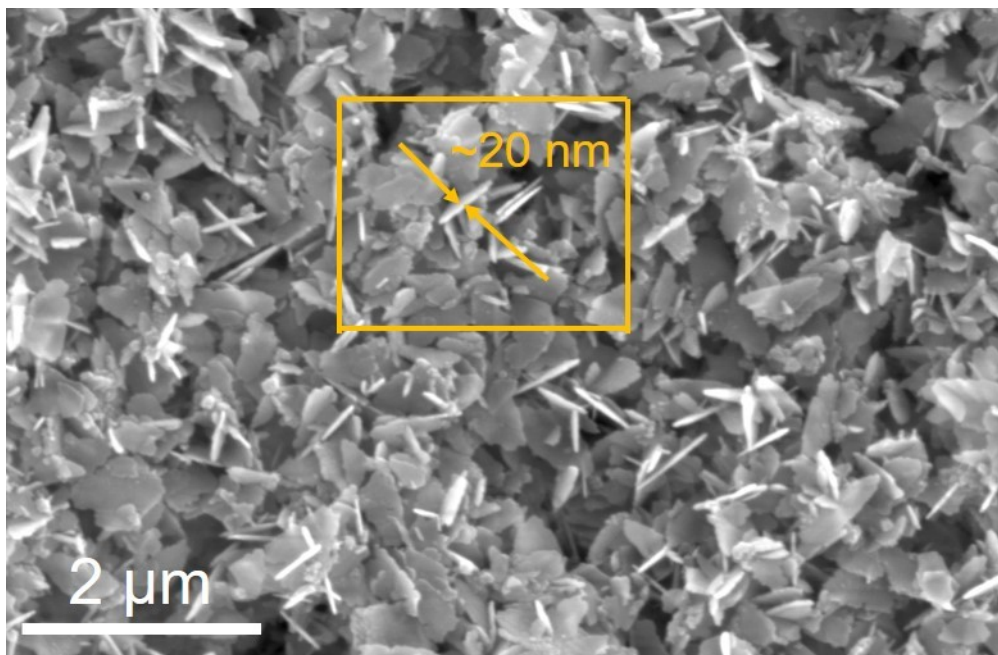


Figure S6. SEM image of ZnO.

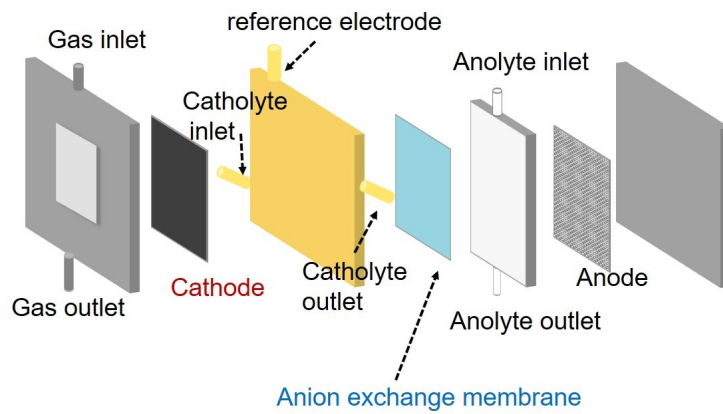


Figure S7. Flow-cell schematic diagram.

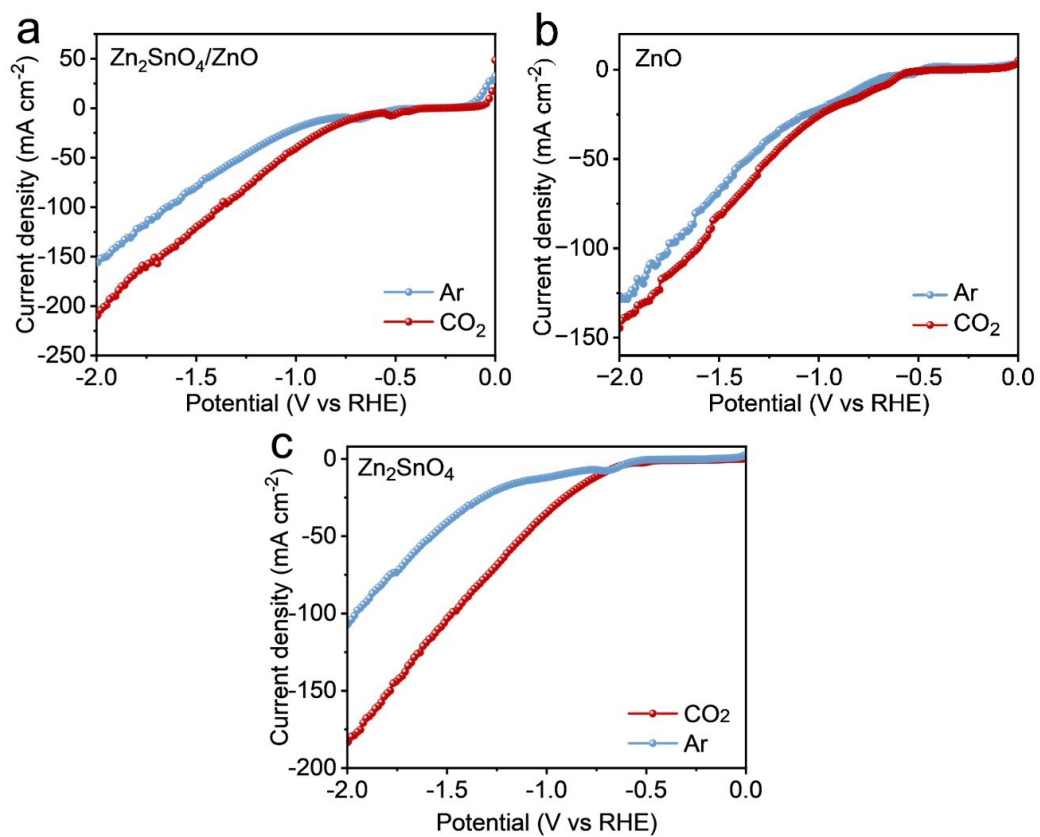


Figure S8. LSV curves of a) $\text{Zn}_2\text{SnO}_4/\text{ZnO}$, b) Syn. ZnO , and c) Zn_2SnO_4 measured at a scan rate of 10 mA cm^{-2} in Ar- or CO_2 -saturated 0.5 M KHCO_3 solution.

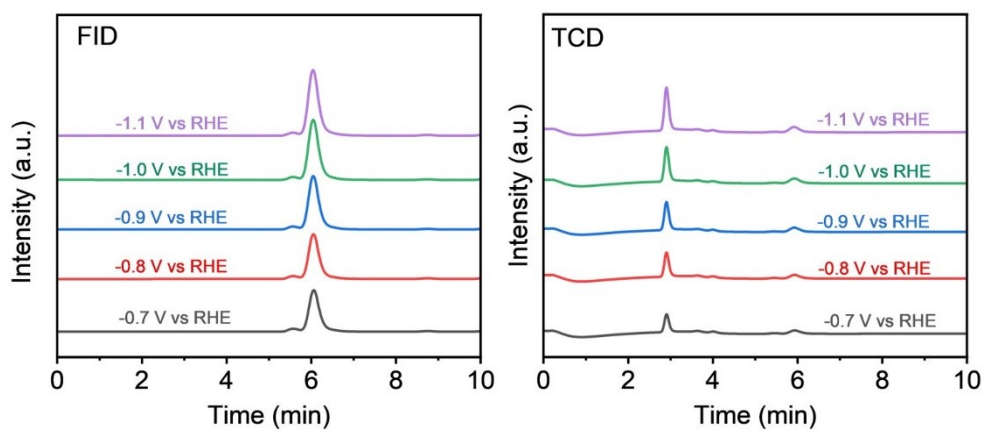


Figure S9. Gas-chromatography of gas product produced by $\text{Zn}_2\text{SnO}_4/\text{ZnO}$ for CO_2RR at various potentials in 0.5 M KHCO_3 solution: a) FID, b) TCD.

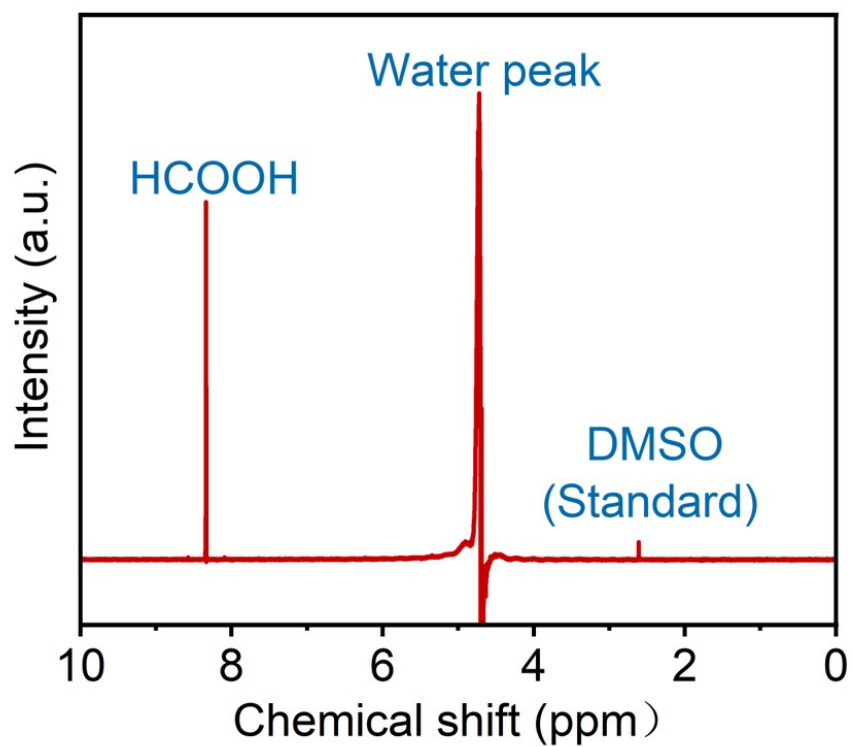


Figure S10. ^1H NMR spectrum of liquid products acquired from $\text{Zn}_2\text{SnO}_4/\text{ZnO}$ for CO_2RR at -1.0 V vs RHE.

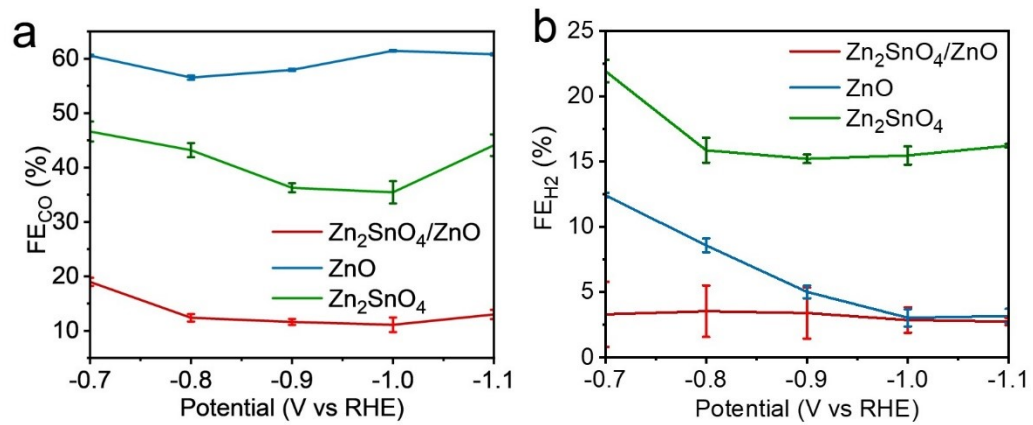


Figure S11. FEs of a) CO, b) H₂ for pristine ZnO, Zn₂SnO₄ and Zn₂SnO₄/ZnO.

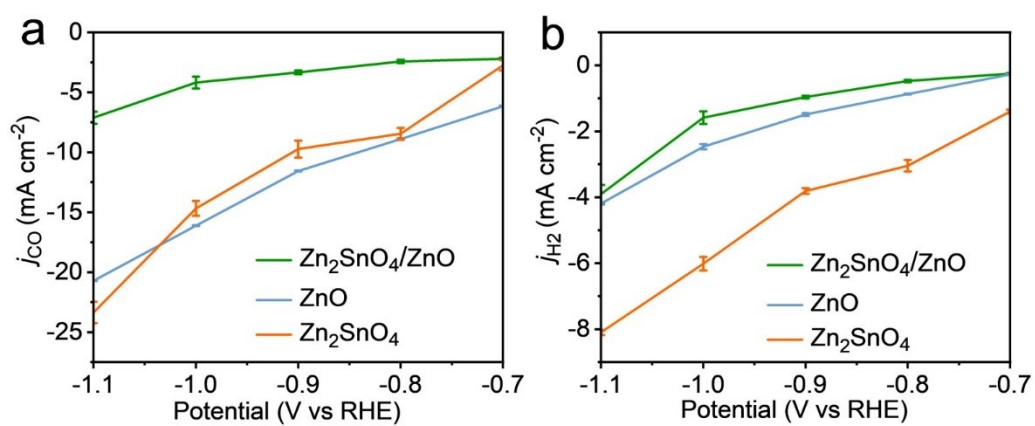


Figure S12. Partial current densities of H₂ and CO for Zn₂SnO₄/ZnO, Syn. ZnO, and Zn₂SnO₄.

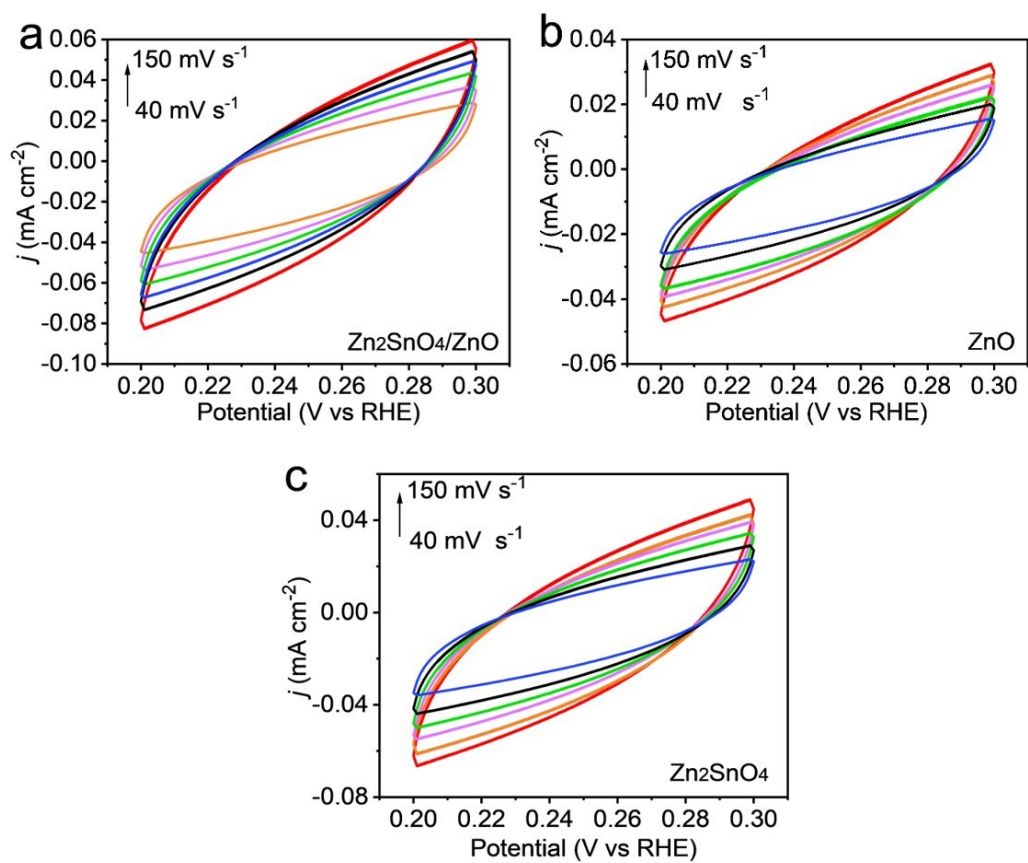


Figure S13. Cyclic voltammograms recorded for a) $\text{Zn}_2\text{SnO}_4/\text{ZnO}$, b) Syn. ZnO , and c) Zn_2SnO_4 electrodes in the approximate region of 0.20 – 0.30 V vs. RHE at various scan rates.

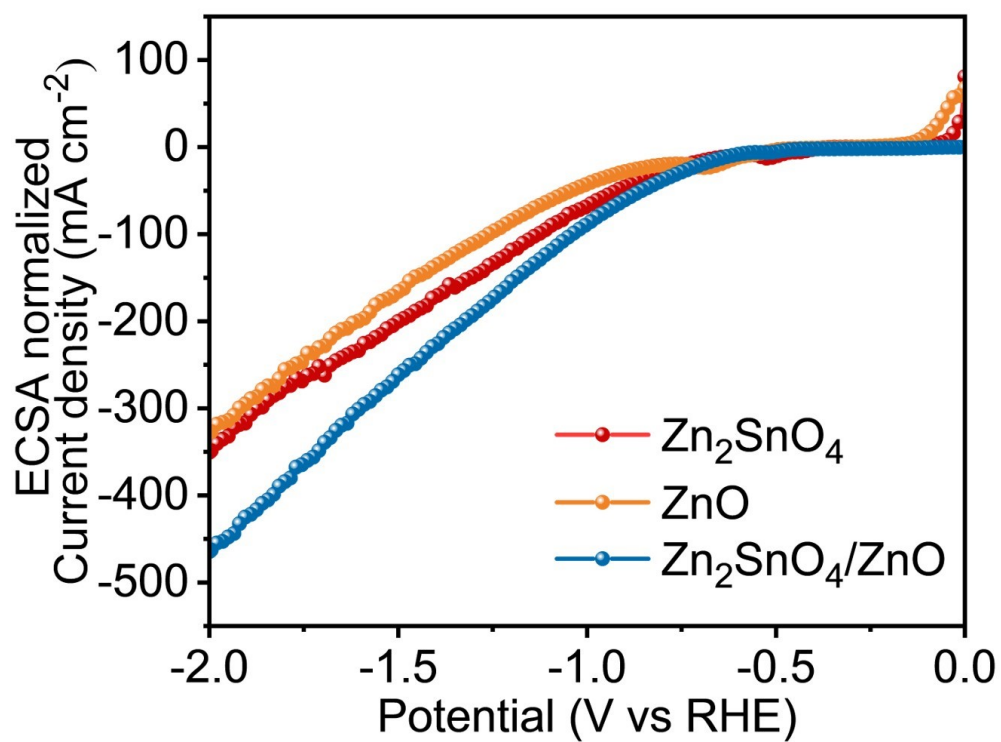


Figure S14. The ECSA normalized specific current density of Zn₂SnO₄/ZnO, Syn. ZnO, and Zn₂SnO₄/ZnO.

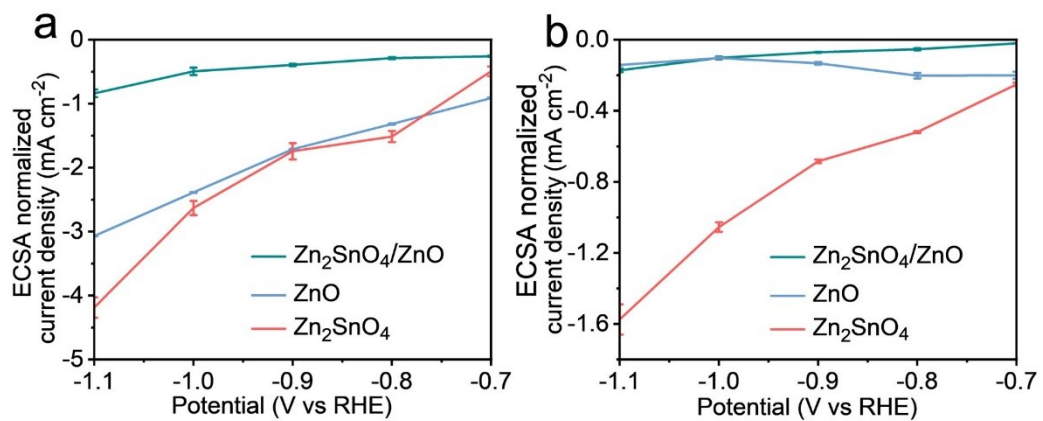


Figure S15. ECSA normalized partial current density of a) CO b) H₂ for Zn₂SnO₄/ZnO, ZnO, and Zn₂SnO₄.