Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information

Highly selective reduction of CO_2 to HCOOH by ZnO/SnO_2 electrocatalyst with heterogeneous interfaces

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1 Experiments

1.1 Materials and Instruments

All reagents were purchased directly from the manufacturer. $Zn(NO_3)\cdot 6H_2O$ (XIYA REAGENT, 99%wt, AR), $SnCl_2\cdot 2H_2O$(TIAN JIN DA MAO, >98%wt, AR), sodium citrate(99.7%wt, AR), $CO(NH)_2$ (99%, AR), $KHCO_3$(Aladdin, >99.5%wt, AR), carbon paper(1cm*2cm), Nafion organic binder, anhydrous ethanol (99.7%wt, AR), deionized water (H_2O, lab homemade), Ar (99%), CO_2 (99%).

The morphology and dimension of as-prepared materials were characterized by Nova NanoSEM 450 equipment. The microstructures of the samples were characterized by TEM (FEI TF30). X-ray diffraction (XRD) pattern was collected by a D/max-2400 diffractometer (Japan Rigaku Rotaflex) using Cu Kα radiation (λ = 154.1 nm). X-ray photoelectron spectroscopy (XPS) measurement was performed on a Thermo ESCALAB XI+ instrument. The binding energy (BE) was calibrated with respect to the C 1s level (284.8 eV) of adventitious carbon. The exact ratio of Zn and Sn elements contained in the material was determined by plasma emission spectroscopy (ICP, Optima2000DV).

1.2 Synthesis of Catalysts

The synthesis of ZnO: $Zn(NO_3)_2\cdot 6H_2O$ (1g), sodium citrate (0.19g) and urea(0.33g) were added a 100mL beaker with 90mL of ultra-pure water. Then the mixture was sonicated for 10min to make it evenly dispersed. Taking 70mL of reaction solution and putting it in the reactor with a 100mL teflon liner. The reactor was put in a blast oven which was set to 130 °C for 12 h. After the reaction, the white solid was washed with ultra-pure water 3 times and dried under vacuum at 50°C for 6h. Then put the solid into a muffle furnace, at a heating rate of 5 °C /min and calcining at 400 °C for 3 h. Finally, the product was collected.

The synthesis of ZnO/SnO_2: ZnO (50mg) and $SnCl_2\cdot 2H_2O$(20mg) were added glass bottle with 11mL ultra-pure water. Then the mixture was sonicated for 10min to make it evenly dispersed. The reaction solution was poured into the reactor with a 20mL teflon liner. The reactor was put in a blast oven which was set to 160 °C for 2h. After the reaction, the solid was washed with ultra-pure water 3 times and dried under vacuum at 50°C for 6h. Finally, the product was collected.

The synthesis of SnO_2: $SnCl_2\cdot 2H_2O$(100mg) was added a glass bottle with 11mL ultra-pure water. Then the mixture was sonicated for 10min to make it evenly dispersed. The reaction solution was poured into the reactor with a 20mL teflon liner. The reactor was put in a blast oven which was set to 160 °C for 2h. After the reaction, the solid was washed with ultra-pure water 3 times and dried under vacuum at 50°C for 6h. Finally, the product was collected.

1.3 Preparation of electrodes

The preparation of ZnO/SnO_2/CP :6 mg ZnO/SnO_2, 1mL anhydrous ethanol and 80μL Nafion 117 solution were added to a small bottle. Then the mixture was sonicated for 30min to make it evenly dispersed. Next, under the illumination of infrared light, the precursor liquid was uniformly coated on the carbon paper (CP) by drip method. Both sides of CP were baked for 10min each after coating. Finally, the ZnO/SnO_2/CP was collected.

The preparation of Z+S/CP (ZnO and SnO_2 was mixed in a ratio of 7:3, 6mg total), ***ZnO/CP and SnO_2/CP*** were similar to the ZnO/SnO_2/CP. Same thing except replacing ZnO/SnO_2 with Z+S, ZnO or SnO_2.

1.4 Electrochemical testing

CO_2 electrochemical performance was tested by CHI660E Electrochemical Workstation in H-type cell which was separated by nafion117 membrane. The ZnO/SnO_2 acted as a working electrode, a platinum mesh electrode as a counter electrode, an Ag/AgCl (in saturated KCl electrolyte) electrode acted as a reference electrode. 35 mL 0.1 M $KHCO_3$ was used as electrolyte, and the electrolyte was bubbled with CO_2 for 20 min (20 ml/min) before starting the test. A flowing atmosphere was used as the experimental condition. Converting all applied potentials to standard potentials (RHE) by the following equation:

$$E\ (V\ vs.\ RHE) = E\ (V\ vs.\ Ag/AgCl) + 0.20 + 0.0591pH.$$

1.5 Product analysis

The type and concentrations of gaseous products were analyzed by gas chromatography (FU LI, 9720 Plus); the type and concentration of liquid products were analyzed by ion chromatography (SHINE, CIC-D100) and NMR. The products obtained from the catalyst designed in this paper were mainly H_2, CO, HCOOH.

The FE(Faraday efficiency) of product is calculated by the following formula:

$$FE = \frac{nFN}{Q} \times 100\%$$

Here, n is molar amount of product, F (=96485C mol^{-1}) is faraday constant, same below; N is number of electrons transferred(the number of electrons transferred in CO, H_2 and HCOOH both is 2), same below; Q is the amount of electricity in the CO_2RR process, same below.

The above formula is a general formula, which will be deformed when used. For liquid products:

$$FE = \frac{CVNF}{Q} \times 100\% = \frac{mVNF}{MQ} \times 100\%$$

Here, C is concentration of product in solution (mol/L), V is Volume of electrolyte (L), same below, m is quality of product in solution (mol/L), M is molar mass of the product.

For gas products (flowing atmosphere):

$$FE = \frac{NFVv \times 101300}{R \times T \times I \times 60} \times 100\%$$

Here, v is volume concentration of gas product from GC, I is the current when GC detects products during electrolysis(A). R is gas constant (8.314 J/(K · mol), T is room temperature (298.15K), 101300 is atmospheric pressure (Pa), 60 is for time conversion.

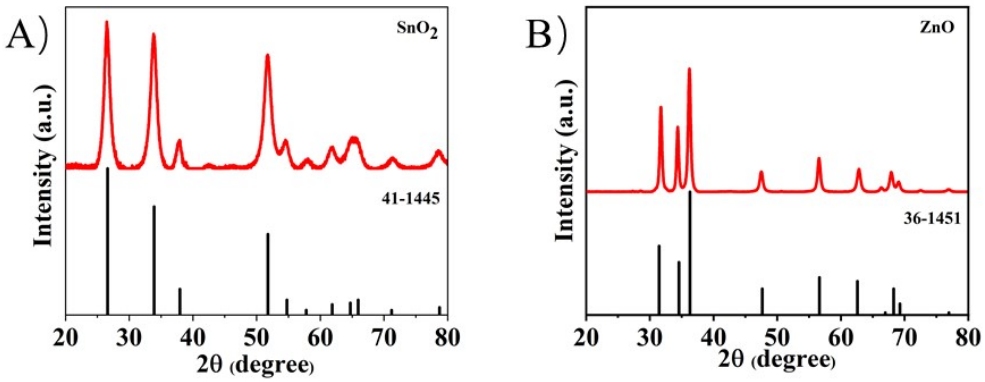

Fig. S1 the XRD spectrum of SnO_2 (A) and ZnO (B) with its standard card

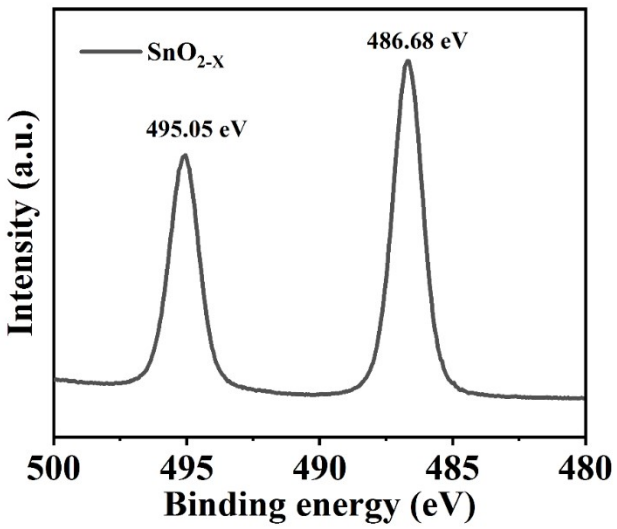

Fig. S2 Sn 3d spectra of SnO_{2-X}

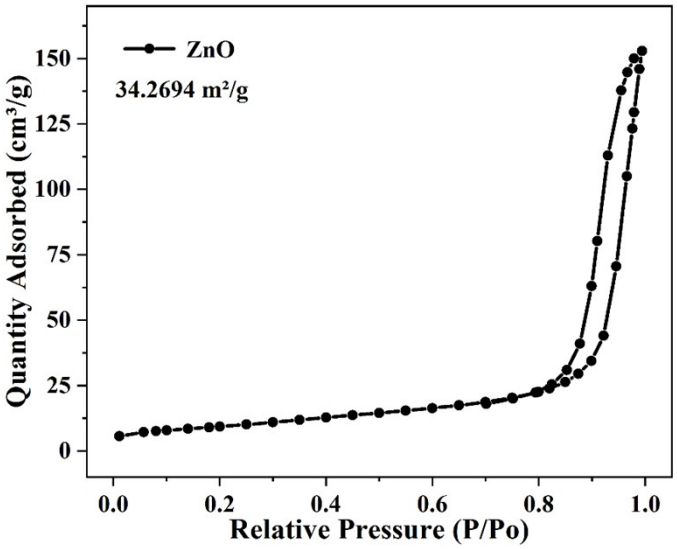

Fig. S3 BET curve of ZnO

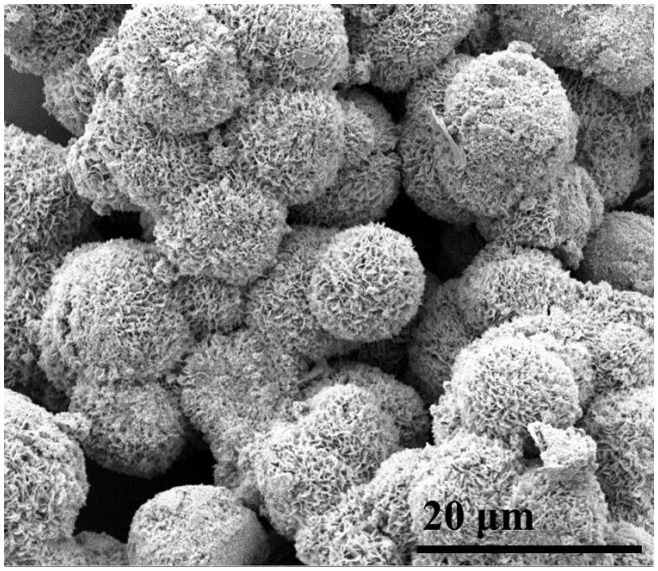

Fig. S4 the SEM images of ZnO

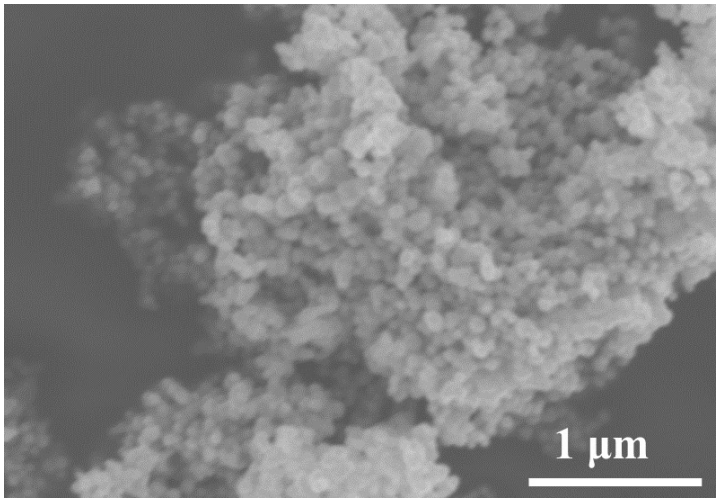

Fig. S5 the SEM images of SnO_2

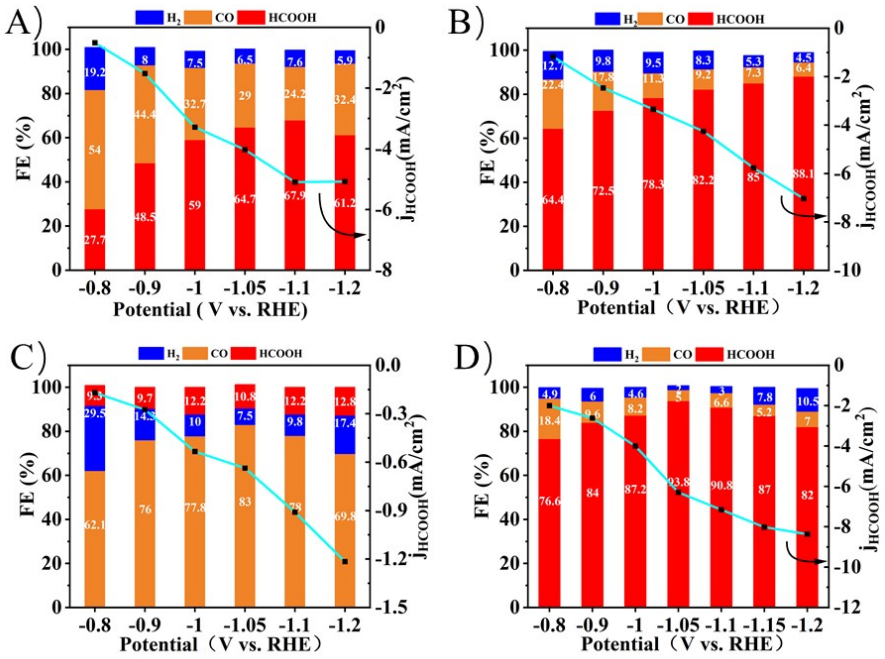

Fig. S6 the FE and current density of HCOOH for (A)SnO_2+ZnO, (B)SnO_2, (C)ZnO and (D)ZnO/SnO_2

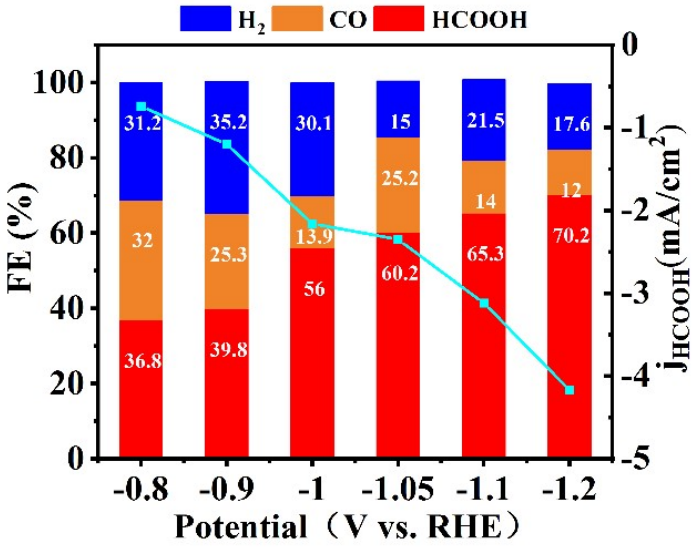

Fig. S7 FE and current density of HCOOH for SnO_2, which was without heat treatment

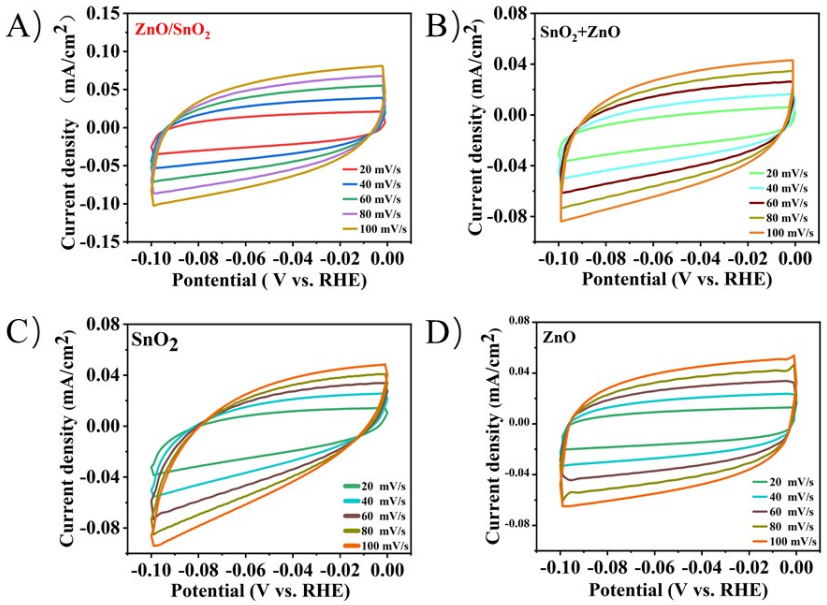

Fig. S8 the CVs of (A) ZnO/SnO_2, (B) SnO_2+ZnO, (C) SnO_2 and (D) ZnO in non-Faraday region

Tab. S1 Mass ratio of ZnO/SnO_2

	ZnO	SnO_2
Results of ICP	70%	30%

Tab. S2 FEs and Yields of HCOOH

	ZnO/SnO_2	ZnO	SnO_2	SnO_2+ZnO
FE	93.8%	10.8%	82.2%	64.7%
Yield ($mmol*h^{-1}*cm^{-2}$)	0.16	0.018	0.14	0.11

Tab.S3 Comparison of some Sn-based materials.

Materials	**Potential (V)**	**Current Density (mA/cm^2)**	**FE**	**References**
ZnO/SnO_2	-1.05	-6.72	93.8%	This work
SnO_2	-1.1	-16	84%	1
CuSn	-1	-10.1	93%	2
CC/Sn/SnBi NPs	-1.08	-36	94.9%	3
$Sn_{97}Pd_3$–NCF	-0.92	-12.75	77%	4
Sn-CF1000	-0.89	-11	62%	5
SnO_2 porous nanowires	-0.8	-5.8	80	6
$CuSn_3$	-0.5	-33	95%	7
$Cu_{0.2}Sn_{0.8}$	-0.35		85%	8
SnO_2/graphene	-1.80	-10.2	93.6%	9
Sn(S)/Au	-0.75	-55	93.3%	10
Zn_2SnO_4/SnO_2	-1.08	-6.1	77%	11

Tab. S4 FEs of ZnO/SnO_2 at -1.05V

Times	1	2	3	4	5	6	7	8	9
FE	93.8%	91%	85.3%	88%	89.5%	90.2%	91.3%	87.5%	86.3%

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