

## Supporting Information

### Construction of $\text{Zn}_{0.65}\text{Cd}_{0.35}\text{S}/\text{SnO}_2$ S-Scheme

#### heterojunctions for efficient photocatalytic $\text{CO}_2$ reduction

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## Materials

Tin chloride pentahydrate ( $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ , 99%), anhydrous ethanol (95%), Sodium hydroxide (NaOH, 95%), Zinc acetate dihydrate ( $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ , 99%), Cadmium acetate dihydrate ( $\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ , 99%), thiourea (99%), PVP ( $K=70000$ ), glycol (99%) is purchased from Shanghai Titan science and technology Co., Ltd, and used as received without further pretreatments. Deionized water is made by our unit.

## Characterization

The morphology and structure of samples were characterized by scanning electron microscopy (SEM, ZEISS Sigma 500, Germany), energy dispersive spectroscopy (EDS) and transmission electron microscopy (TEM, FEI-Tecnai G2, USA) at 200 kV. The crystal structure was characterized by  $\text{Cu K}\alpha$  radiation and X-ray powder diffractometer (XRD, Bruker D8 Advance) and Fourier infrared spectroscopy (FT-IR, Nicolet iS10, USA). The diffuse reflectance spectrum was detected on an UV-visible spectrophotometer (UV-2600, Shimazu, Japan). The surface chemical states were analyzed by X-ray photoelectron spectroscopy (XPS, ESCALAB Xi+, UK). The adsorption capacity and pore size of the material were measured by automatic gas adsorption instrument (BET, ASIQC0000-4, USA). Time-resolved photoluminescence (TRPL) spectroscopy were obtained by fluorescence spectrophotometer (FLS 980, UK).

## Photocatalytic performance test

The prepared sample was accurately weighed 30mg and evenly distributed on the quartz platform. The effective area of the whole sealed reactor is about 250mL. 1 mL of deionized water was placed at the bottom of the container in advance. In order to remove the dissolved gas contained in the ultra-pure water to the maximum extent, vacuum operation was carried out. Then strict nitrogen operation was carried out. This stage was repeated three times, and after the last full of nitrogen, 1 mL of high-purity  $\text{CO}_2$  (99.99%) was injected with a specific standard gas syringe, and stirring was started. Continue for 5 min to ensure that the gas in the reaction vessel is completely mixed evenly. The 300 W Xe lamp (CEL-HXF300, China) was used as the energy source of  $\text{CO}_2$  reduction driven by optical drive. 1 mL of mixed gas was extracted from the reaction vessel every 1 h and injected into the gas chromatograph (HF-900, China). The flame ionization detector (FID) was used for qualitative analysis and quantitative detection of gas products. The product was calibrated by mass spectrometer (HPR-20 R&D).

**Stability testing:** stability testing is a method of performing a cyclic reaction while maintaining normal test conditions. After each reaction is complete, we replace

and clean all substances and containers except the catalyst, and then maintain the same reaction conditions as before for testing. It is worth noting that the catalyst put into the test again is still used the previous time. In this process, a small amount of catalyst will inevitably be wasted, which has an acceptable impact on the experimental results.

### **AQE test for photocatalytic CO<sub>2</sub> reduction**

The apparent quantum efficiency (AQE) of the catalyst was measured based on CO<sub>2</sub>-to-CO conversion under specific excitation wavelength with a specific band pass filter ( $\lambda = 365, 380, 400, 420, 450, \text{ and } 500 \text{ nm}$ ), which was irradiated by the 300 W Xe lamp on the same setup. In general the AQE of CO<sub>2</sub>-to-CO conversion is calculated as follows:

$$AOE (\%) = \frac{\text{numbers of the elections taking part in reduction}}{\text{numbers of incident photons}} \times 100\% = \frac{2 n (CO)}{I} \times 100\%$$

where  $n (CO)$  is the number of CO molecules and  $I$  represents the number of incident photons.

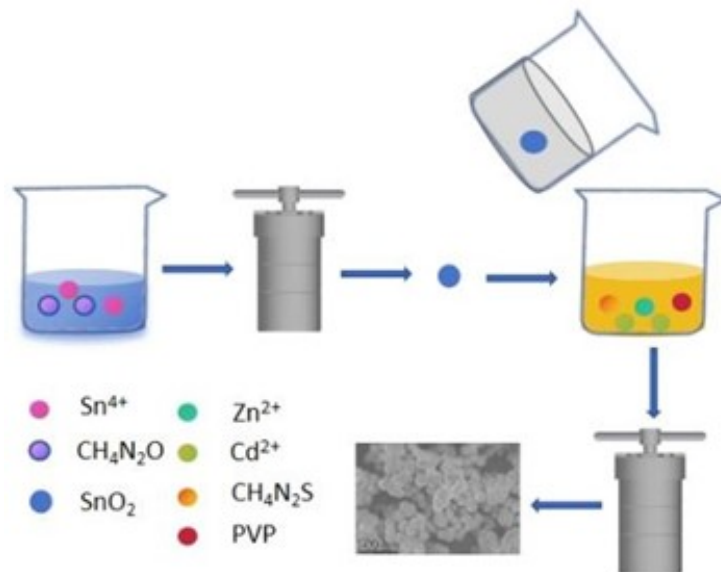
### **Electrochemical test**

All electrochemical tests are performed on an electrochemical workstation (CHI-760, Shanghai Chenhua Instrument Co., LTD. China), using a three-electrode system. The sample is uniformly dispersed on a conductive substrate with an effective area of  $1 \text{ cm} * 1 \text{ cm}$  as the working electrode, platinum sheet and Ag/AgCl electrodes are used as opposite and reference electrodes, respectively. 0.5 M sodium sulfate solution was used as the supporting electrolyte. Mott-schottky test frequency is selected as 500 Hz, 1000 Hz, 1500 Hz. Electrochemical impedance spectroscopy (EIS) was performed the measured frequency range was from 0.1 to 100 kHz. The total duration of the transient photocurrent test is 400 s, and one cycle is completed every 100 s. For OER test, the reference electrode was selected as Hg/HgO electrode, the electrolyte was changed to 1 M KOH, and other test conditions remained unchanged.

### **The analysis of *in situ* diffuse reflectance infrared fourier transform spectroscopy**

The high purity N<sub>2</sub> gas was purged sample cell for 20 min to remove the air and impurities on the surface of the sample (30 mg). A gaseous mixture of CO<sub>2</sub>/H<sub>2</sub>O was

introduced in sample cell for 30 min to achieve adsorption saturation. Then, the catalyst was irradiated 60 min by a 300 W xenon lamp. The FT-IR spectrum was recorded every 10 min. The analysis temperature was 40 °C, and the scanning range was 4000-600  $\text{cm}^{-1}$ .



Scheme 1. Schematic illustration of the synthetic strategy of ZCS/SnO<sub>2</sub>.

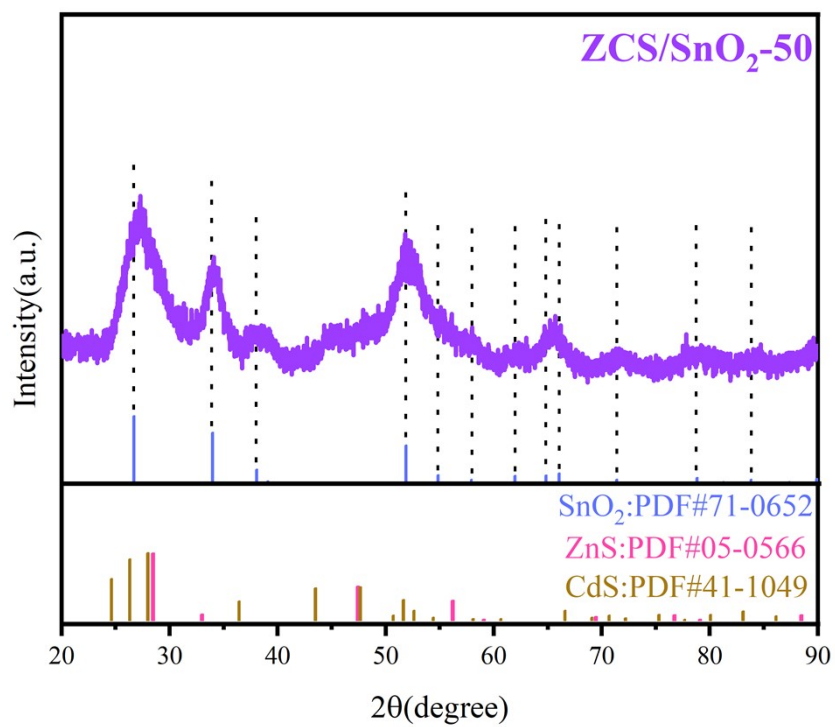


Fig. S1 XRD patterns of ZCS/SnO<sub>2</sub>-50.

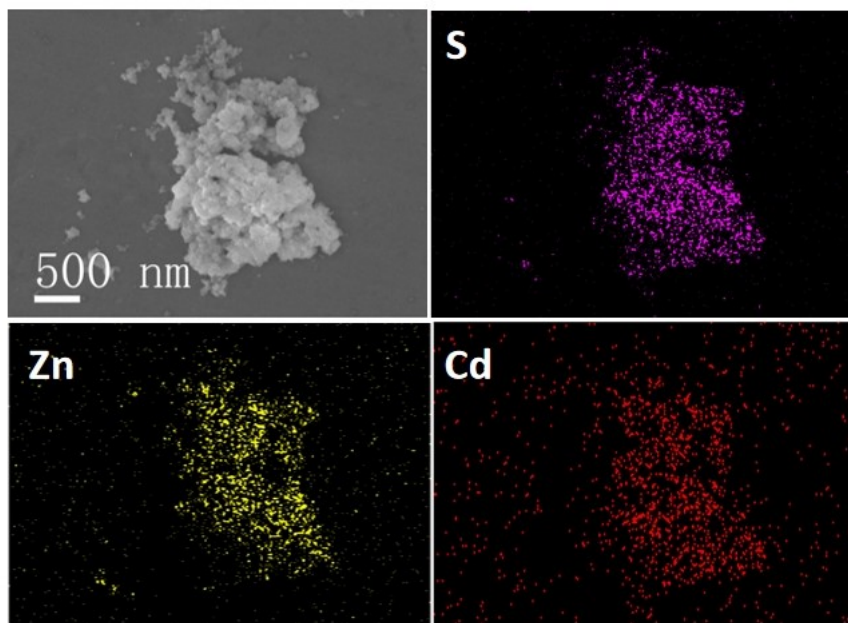


Fig. S2 EDS-mapping images of pure ZCS.

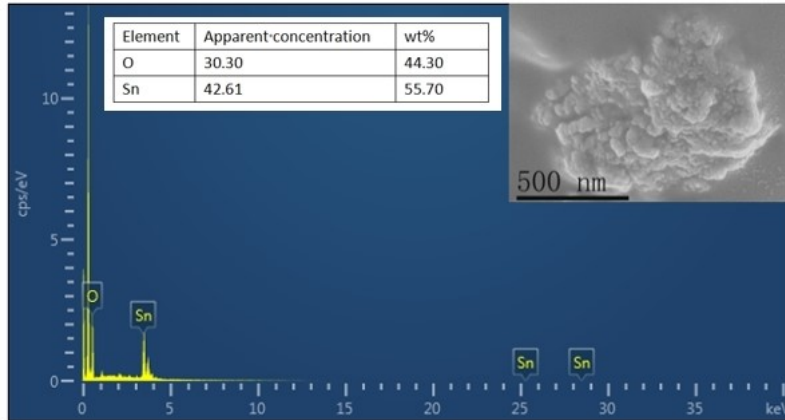


Fig. S3 EDX image of pure SnO<sub>2</sub>.

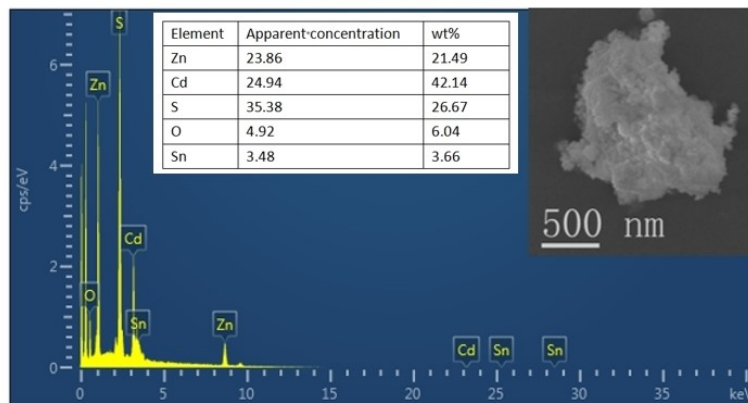


Fig. S4 EDX image of ZCS/SO<sub>2</sub>-1.



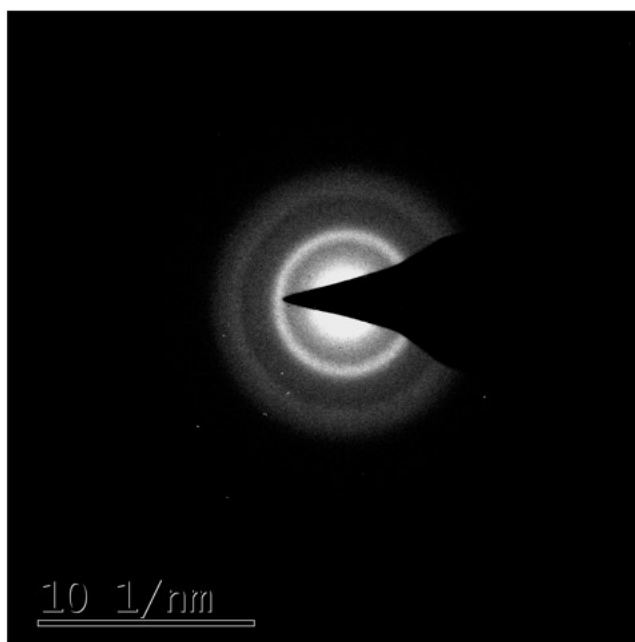


Fig. S5. TEM-SAED pattern of ZCS/SnO<sub>2</sub>-1.

Table. S1 The textural properties of the SnO<sub>2</sub>, ZCS, ZCS/SnO<sub>2</sub>-1.

Material	S <sub>BET</sub> (m <sup>2</sup> /g)	Pore Volume(cm <sup>3</sup> /g)	Average Pore Size(nm)
SnO <sub>2</sub>	3.75	0.01	3.18
ZCS	77.22	0.25	6.45
ZCS/SnO <sub>2</sub> -1	106.08	0.28	5.36

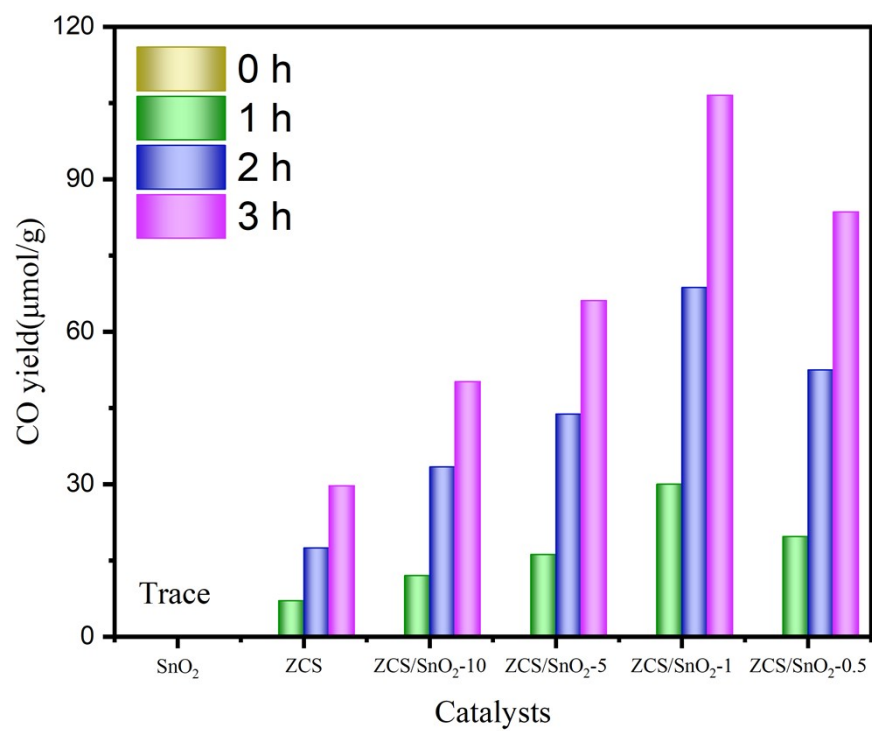


Fig. S6 CO evolution along with irradiation times over ZCS/SnO<sub>2</sub>-10, ZCS/SnO<sub>2</sub>-5, ZCS/SnO<sub>2</sub>-1, ZCS/SnO<sub>2</sub>-0.5 under visible light.

Table. S2 Some metal sulfide-based catalysts for photocatalytic CO<sub>2</sub> reduction are listed (light source is 300 W Xe lamp).

Photocatalyst	Reaction condition	Yield of main product, selectivity	Refs.
Zn <sub>0.65</sub> Cd <sub>0.35</sub> S/SnO <sub>2</sub>	Solid phase	CO= 78.85 μmol/g/h, 98.5% (full spectrum); CO= 35.48 μmol/g/h, ~100% (>420 nm)	This work
Zn <sub>0.2</sub> Cd <sub>0.8</sub> S/g-C <sub>3</sub> N <sub>4</sub>	Liquid phase	CH <sub>3</sub> OH=11.5 μmol/g/h	1
CdS/ZIF-8	Liquid phase	CO=32.13 μmol/h, 83.96%	2
CuInS <sub>2</sub> /C/TiO <sub>2</sub>	Solid phase	CO=7.73 μmol/g/h, about 100%	3
Au@CdS	Liquid phase	CO=3758 μmol/g/h, 70.3%	4
CuCdS	Solid phase	CO= 8.5 μmol/g/h, 92.4%	5
ZnIn <sub>2</sub> S <sub>4</sub> -CdS	Liquid phase	CO= 87.3 μmol(4h)	6
ZnS/ZnO	Solid phase	CO= 38.85 μmol/g/h	7

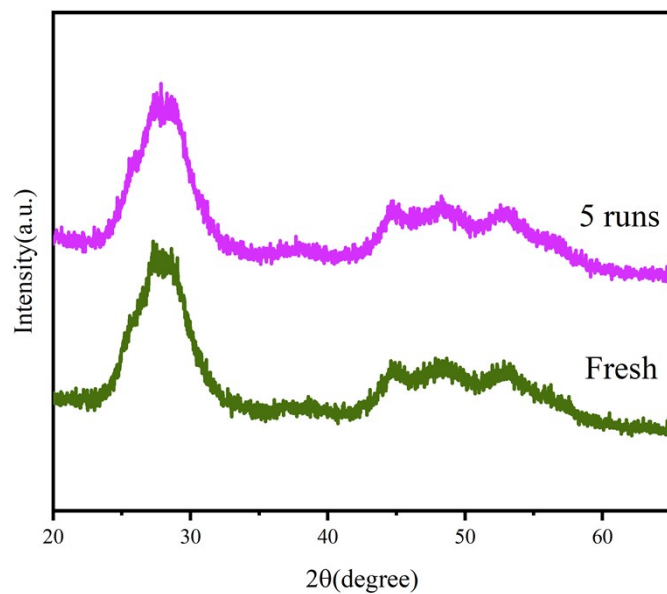


Fig. S7. XRD patterns of fresh sample and after 5 runs of reaction.

Table. S3  $R_{ct}$  supplementary data for EIS.

Sample	$R_{ct}$ (k $\Omega$ )
SnO <sub>2</sub>	18.44
ZCS	25.94
ZCS/SnO <sub>2</sub> -1	48.39

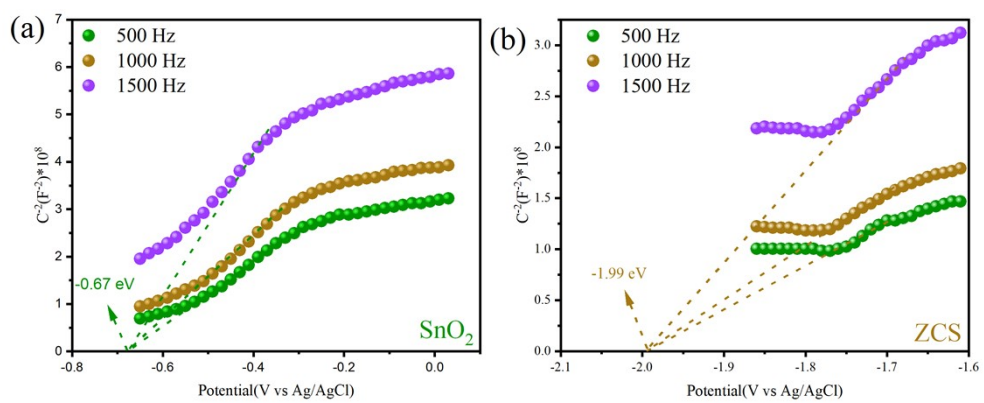


Fig. S8 Mott-Schottky plots of (a) SnO<sub>2</sub> and (b) ZCS.

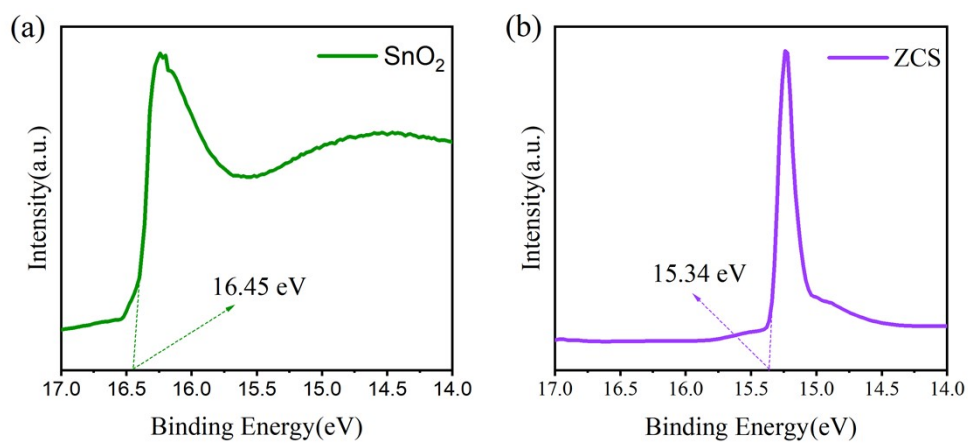


Fig. S9  $E_{\text{cutoff}}$  UPS spectra of (a) SnO<sub>2</sub> and (b) ZCS.



Table. S4 Parameters obtained from TRPL decay curves.

Material	$\tau_1$ (ns) (Rel.%)	$\tau_2$ (ns) (Rel.%)	T (ns)
SnO <sub>2</sub>	1.56 (71.42)	5.56 (28.58)	2.70
ZCS	1.21 (53.06)	4.74 (46.94)	2.87
ZCS/SnO <sub>2</sub> -1	1.41 (45.31)	4.88 (54.69)	3.31

## References

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