

## Supporting Information

### **Preparation of ZnIn<sub>2</sub>S<sub>4</sub>-AlOOH composite for the photocatalytic reduction of CO<sub>2</sub> to CO**

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## Experimental Section

### Quantitative analysis

Gas product calculation formula:

$$Y_i (\mu\text{mol}) = f_i \times \frac{A_i \times V_{He}}{A_{He} \times V_m} \times 10^3 \quad F_i (\mu\text{mol/g/h}) = \frac{Y_i}{t \times m_{cat}}$$

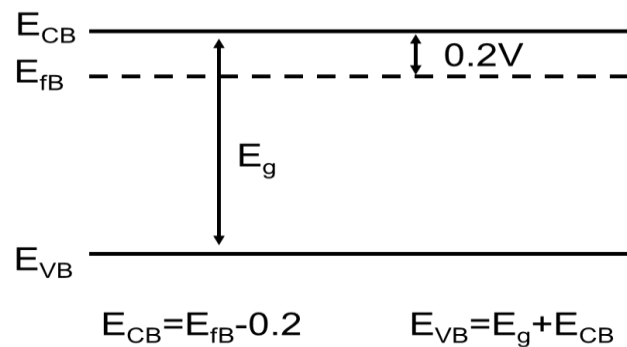
Where  $Y_i$  is the yield of product,  $F_i$  is the rate of product formation,  $A_i$  and  $A_{He}$  are the peak areas of the product and the internal standard He gas respectively, and  $V_{He}$  is the volume of the internal standard He gas (0.1 mL),  $f_i$  is the relative correction factor, 6.2974 for CO and 0.5018 for H<sub>2</sub>,  $V_m$  is the molar volume of the gas (24.5 L mol<sup>-1</sup>, 25°C, 1.01×10<sup>5</sup> pa),  $m_{cat}$  is the mass of the catalyst,  $t$  is the reaction time (12 h).

### Calculation method of band structure

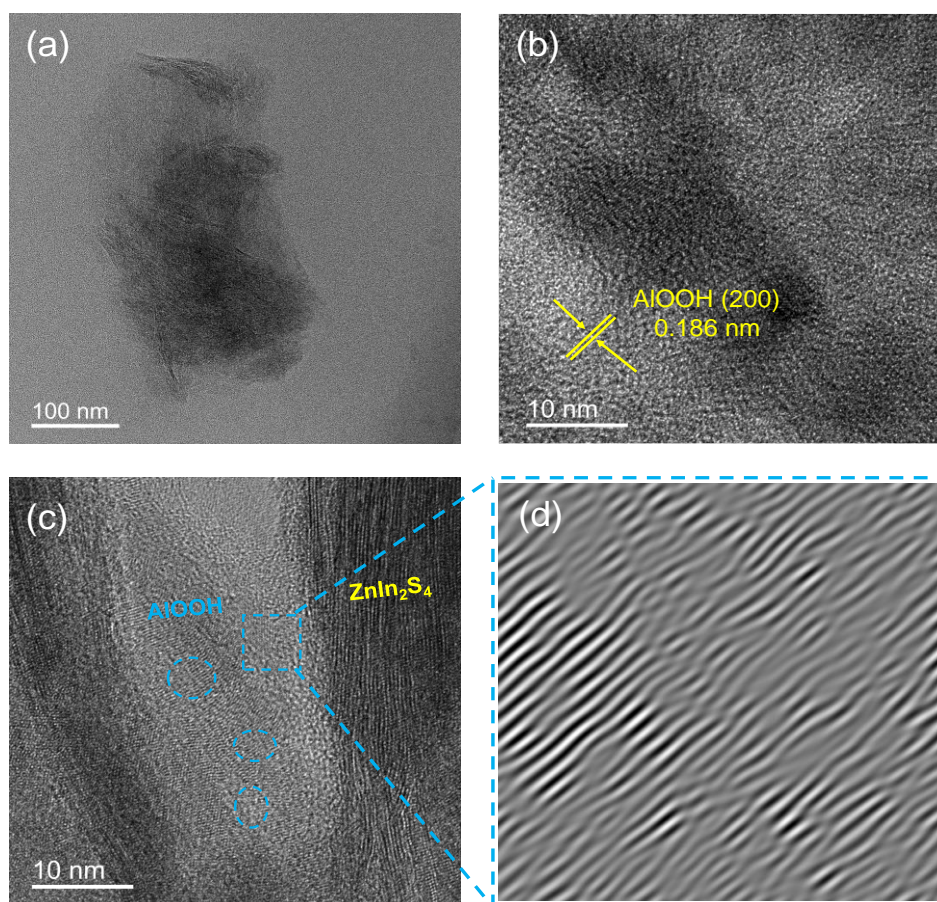
The flat band potential of the sample can be obtained from the Mott-Schottky plot. The positive slope of the curve indicates that the prepared material is an n-type semiconductor. Generally, the flat-band potential of n-type semiconductors is 0.1-0.3 eV higher than the conduction band (CB) potential, and in this paper, 0.2 eV is chosen.

The conduction band potential of the sample can be estimated using the measured flat-band potential. The valence band potential is then calculated using the formula  $E_{VB} =$

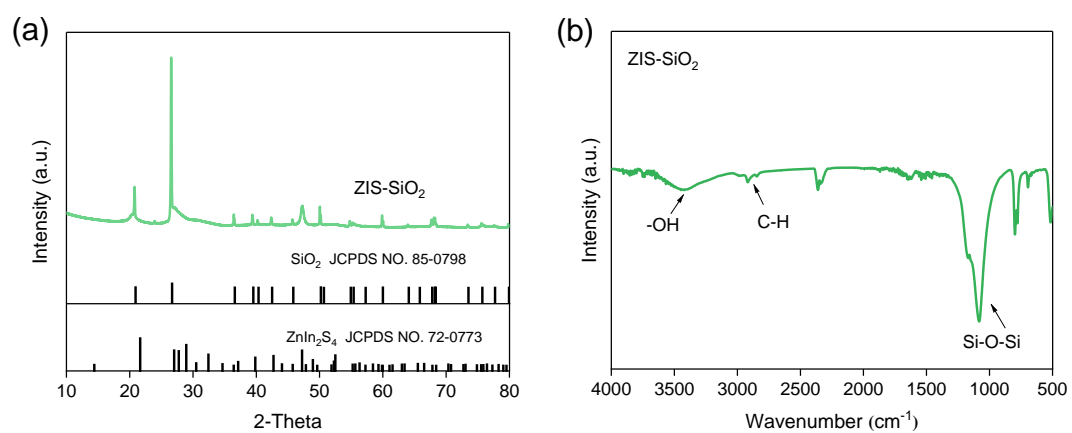
$E_g + E_{CB}$ .<sup>1-3</sup>



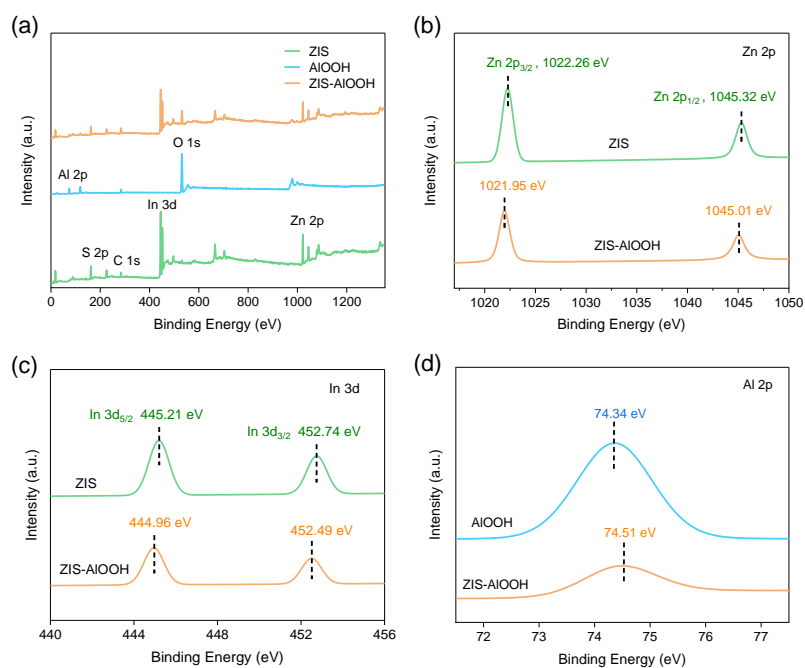
## Supporting Figures



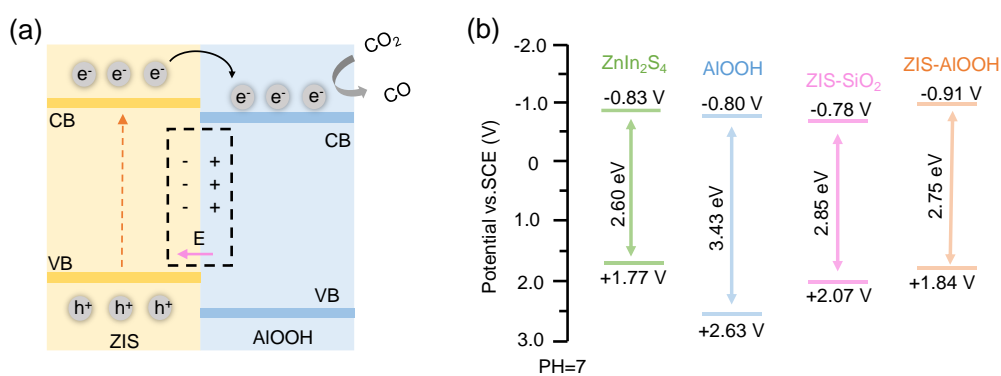
**Fig. S1** (a) TEM images, (b) HRTEM images of AlOOH, (c-d) HRTEM images of ZIS-AlOOH.



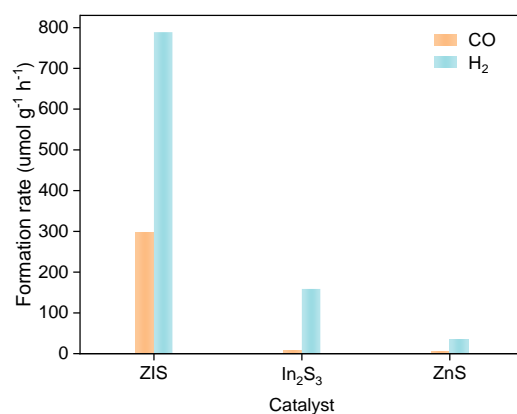
**Fig. S2** (a) X-ray diffraction patterns and (b) FT-IR spectra of ZIS-SiO<sub>2</sub> catalyst.



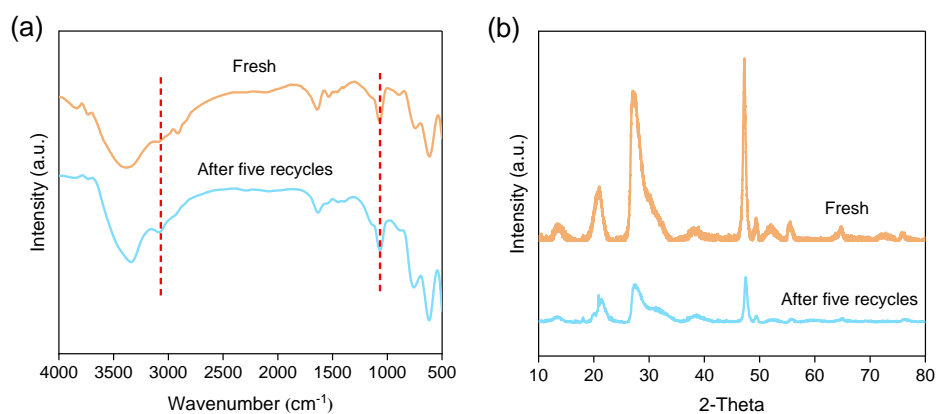
**Fig. S3** (a) XPS survey spectra and corresponding high-resolution XPS spectra of (b) Zn 2p, (c) In 3d, and (d) Al 2p of the ZIS, AIOOH, and ZIS-AIOOH.



**Fig. S4** (a) The schematic illustration of the internal electric field (IEF) induced charge migration of ZIS and AIOOH, (b) the energy band positions of the as-prepared photocatalysts.



**Fig. S5** Photocatalytic activities of ZIS, In<sub>2</sub>S<sub>3</sub>, and ZnS. Reaction conditions: 5 mg of catalyst, 0.9 mL of MeCN, 0.1 mL of H<sub>2</sub>O, 0.1 mL of triethylamine, 1 bar CO<sub>2</sub>, blue LEDs (455 nm), 12 h.



**Fig. S6** (a) FT-IR spectra and (b) X-ray diffraction patterns of ZIS-AIOOH catalyst before and after reaction.

## References

- 1 J. Song, Y. Lu, Y. Lin, Q. Liu, X. Wang and W. Su, *Appl. Catal., B*, 2021, **292**, 120185-120193.
- 2 J. Wang, S. Sun, R. Zhou, Y. Li, Z. He, H. Ding, D. Chen and W. Ao, *J. Mater. Sci. Technol.*, 2021, **78**, 1-19.
- 3 J. Wang, S. Lin, N. Tian, T. Ma, Y. Zhang and H. Huang, *Adv. Funct. Mater.*, 2021, **31**, 2008008-2008046.