

## *Supplementary Information*

### **S-scheme $\text{Zn}_2\text{In}_2\text{S}_5/\text{CdS}$ nanosheet-on-nanosheet heterostructures with tight interface contacts promote efficient $\text{H}_2\text{O}_2$ photoproduction from pure water**

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## Theoretical calculation

In this study, all calculations were conducted using density functional theory (DFT) as implemented in the Vienna Ab initio Simulation Package (VASP).<sup>[1]</sup> The generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) functional was employed to describe the exchange-correlation interactions.<sup>[2]</sup> The ion-electron interactions were treated using the projector-augmented wave (PAW) method.<sup>[3]</sup> Van der Waals (vdW) interactions were accounted for using the DFT-D3 method to accurately describe the interactions between the substrate and gas molecules.<sup>[4]</sup> To avoid spurious interactions arising from periodic boundary conditions, a vacuum layer of at least 15 Å was introduced in the unit cell.<sup>[5]</sup> The plane-wave cutoff energy was set to 400 eV, and the Brillouin zone was sampled using a 3×3×1 k-point grid. The convergence criteria for energy and force were set to 10<sup>-4</sup> eV per atom and 0.02 eV/Å, respectively.

The Gibbs free energy was calculated by adopting the standard hydrogen electrode model:<sup>[6]</sup>

$$\Delta G = \Delta E + \Delta E_{ZPE} - T\Delta S$$

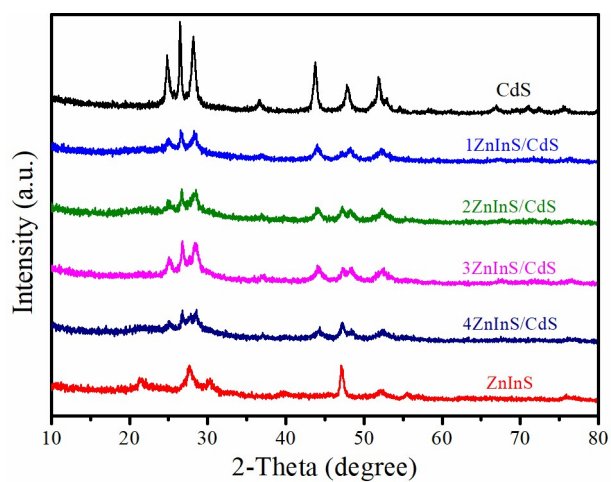
Where  $\Delta E$ ,  $\Delta E_{ZPE}$ , and  $\Delta S$  are the adsorption energy, changes in zero-point energy and entropy, respectively.  $\Delta E_{ZPE}$  and  $\Delta S$  are calculated by vibration frequency. T is temperature (298.15 K). The  $\Delta E$ ,  $\Delta E_{ZPE}$ , and  $\Delta S$  were calculated through the equation:

$$\Delta E = \Delta E_{\text{total}} - E_{\text{surface}} - E_{\text{gas}}$$

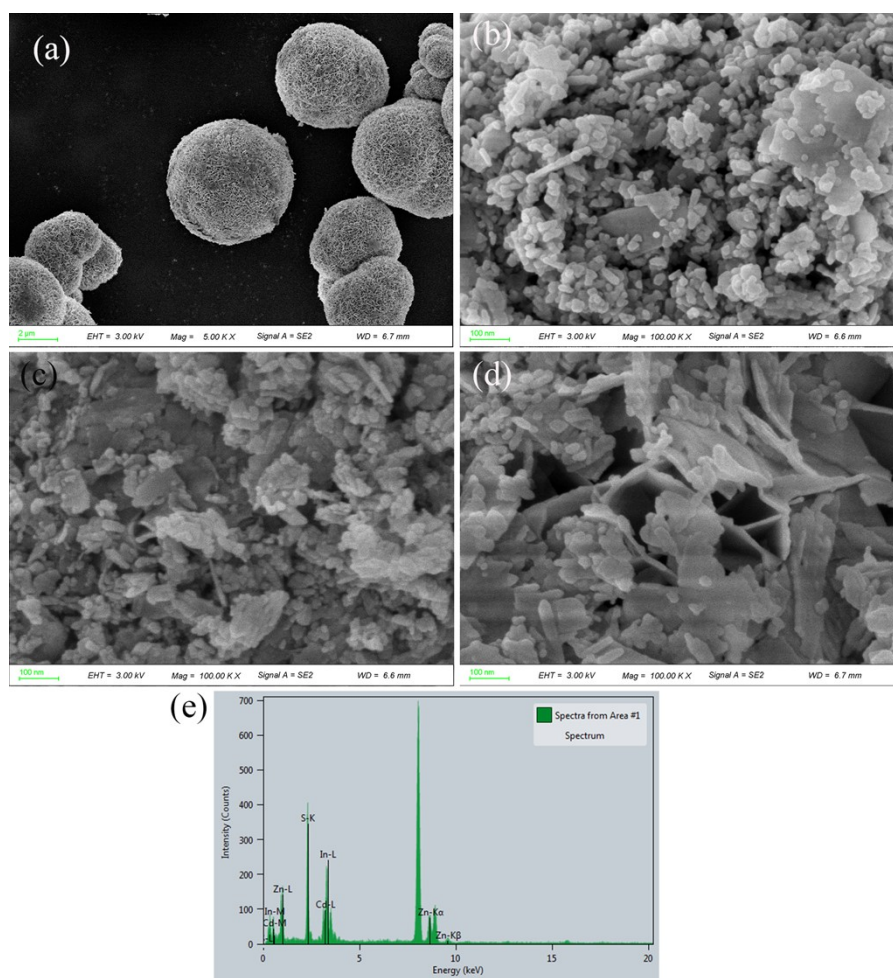
$$E_{ZPE} = \frac{1}{2} \sum_i h\nu_i$$

$$TS = K_B T \sum_i \ln \{ 1 + e^{-h\nu_i / K_B T} \} - \sum_i h\nu_i \{ 1 / (e^{-h\nu_i / K_B T} + 1) \}$$

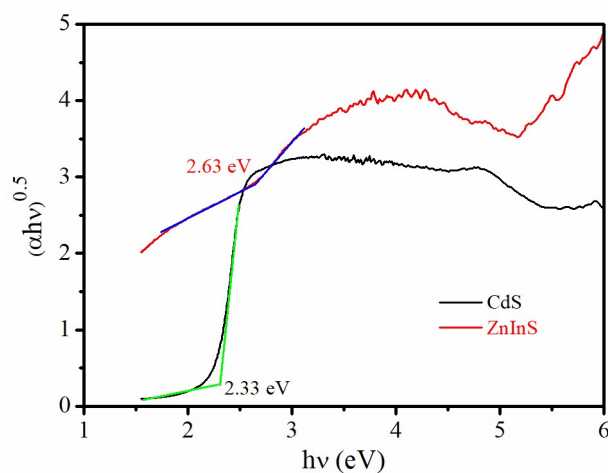
Where  $E_{\text{total}}$ ,  $E_{\text{surface}}$ , and  $E_{\text{gas}}$  are the total energies for different adsorption sites, substrate slab, and adsorbent, respectively. The symbols h and  $\nu$  represent Planck's constant and the vibrational frequency, respectively. Only the vibrational modes of the adsorbate were explicitly calculated, while the catalyst sheet was kept fixed. The Boltzmann constant is denoted as  $K_B$ .



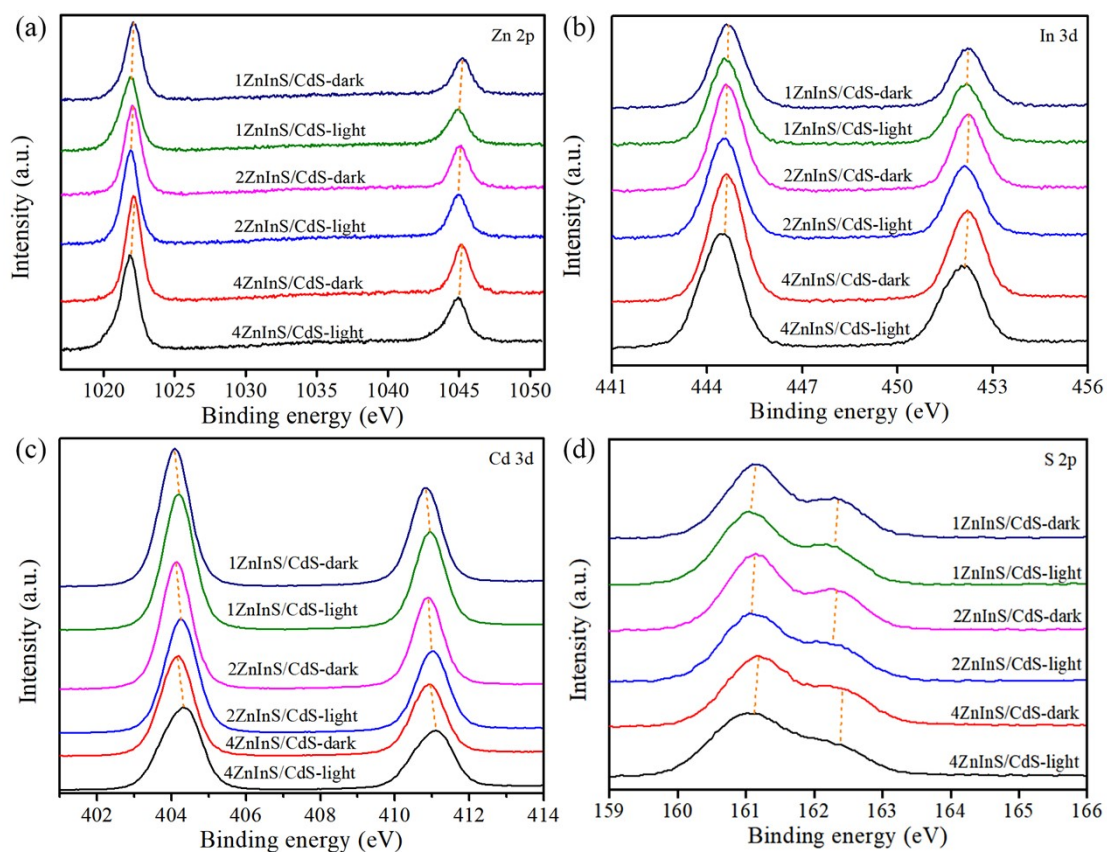
**Fig. S1** XRD patterns of as-synthesized ZnInS, CdS, and ZnInS/CdS samples.



**Fig. S2** SEM images of (a) ZnInS, (b) 1ZnInS/CdS, (c) 2ZnInS/CdS, and (d) 4ZnInS/CdS. (e) EDX spectra of 3ZnInS/CdS sample.



**Fig. S3** Band gaps of ZnInS and CdS.



**Fig. S4** (a) Zn 2p, (b) In 3d, (c) Cd 3d, and (d) S 2p of 1ZnInS/CdS, 2ZnInS/CdS, and 4ZnInS/CdS sample.

**Tab. S1** Surface area, pore diameter and pore volume parameters for CdS, ZnInS, and the ZnInS/CdS samples.

Samples	Surface area <sup>a</sup> (m <sup>2</sup> /g)	Pore size <sup>b</sup> (nm)	V <sub>t</sub> <sup>c</sup> (cm <sup>3</sup> /g)
ZnInS	50.49	7.169	0.275
CdS	34.45	25.942	0.248
1ZnInS/CdS	65.19	12.441	0.337
2ZnInS/CdS	67.13	10.334	0.289
3ZnInS/CdS	70.10	8.392	0.299
4ZnInS/CdS	69.85	7.061	0.362

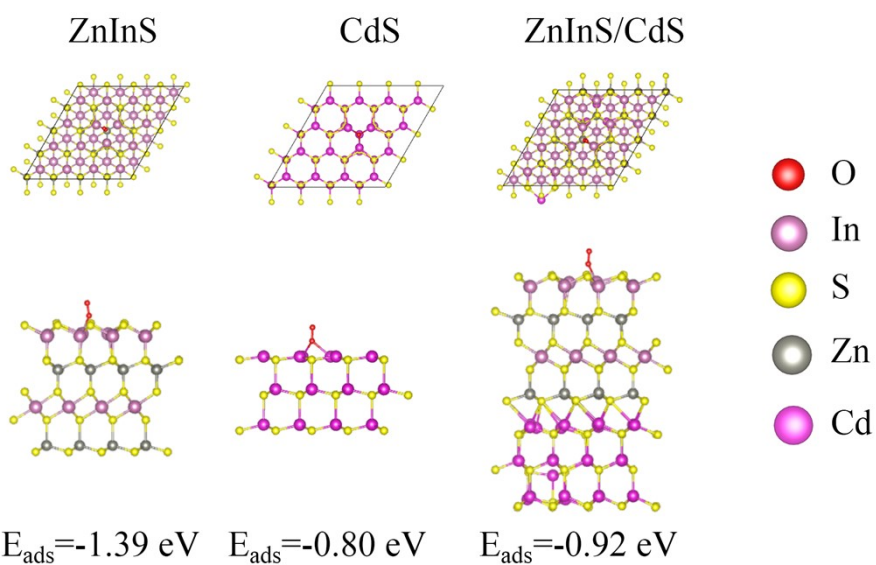
<sup>a</sup>Measured using N<sub>2</sub> sorption with the BET method.

<sup>b</sup>Diameter size of porous structure calculated using the N<sub>2</sub> desorption with Barrett-Joyner-Halenda (BJH) method.

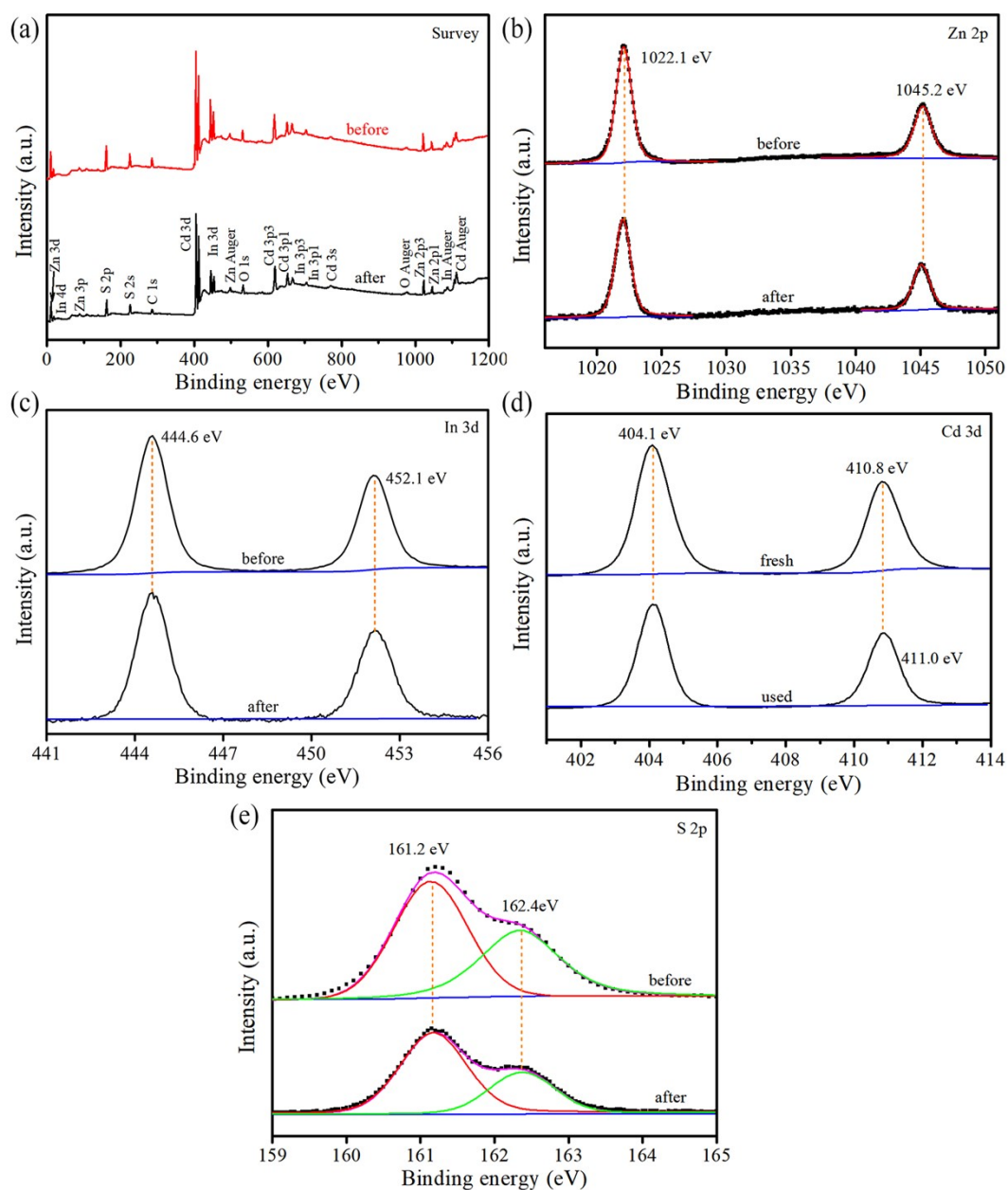
<sup>c</sup>Total pore volume of pores estimated at P/P<sub>0</sub> approaching 0.99.

**Tab. S2** Comparison of photocatalytic synthesis of H<sub>2</sub>O<sub>2</sub> yield (μM·h<sup>-1</sup>) of 3ZnInS/CdS sample with previously reported catalysts.

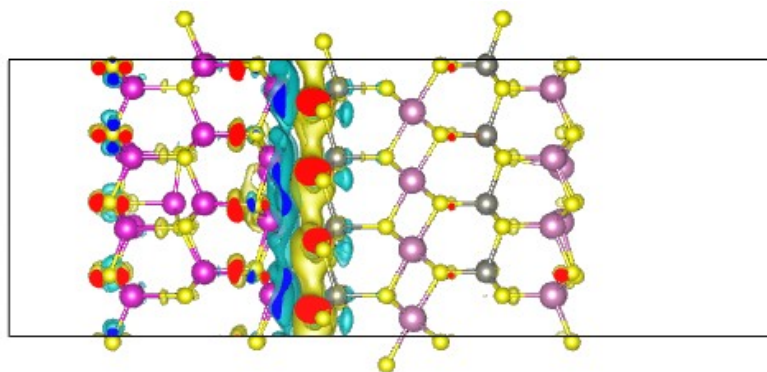
Photocatalysts	Catalyst amount (g/L)	Atmosphere, Sacrificial agent	Light source	H <sub>2</sub> O <sub>2</sub> yield	Ref.
S-CCN	/	O <sub>2</sub> , TEOA	simulated sunlight	136.63	[7]
Bi <sub>4</sub> Ti <sub>3</sub> O <sub>12</sub>	0.67	O <sub>2</sub> , ethanol	λ ≥ 420 nm	55.00	[8]
ZnIn <sub>2</sub> S <sub>4</sub>	0.67	O <sub>2</sub> , ethanol	λ ≥ 420 nm	96.00	
Cu-ZnIn <sub>2</sub> S <sub>4</sub>	0.50	O <sub>2</sub> , methanol	λ > 420 nm	73.75	[9]
Ni <sub>1</sub> -CN	1.00	O <sub>2</sub> , none	λ ≥ 420 nm	52.46	[10]
ZnInS/CdS	0.50	none, none	λ ≥ 420 nm	185.28	This work



**Fig. S5** Model structure for O<sub>2</sub> adsorption on ZnInS, CdS, and ZnInS/CdS.  $E_{\text{ads}}$  is the total adsorption energy of O<sub>2</sub>.



**Fig. S6** (a) Survey spectra, (b) Zn 2p, (c) In 3d, (d) Cd 3d, and (e) S 2p of 3ZnInS/CdS sample before and after recycling reactions for 6 h.



**Fig. S7** Charge density difference of the ZnInS/CdS model.

**Tab. S3** Corresponding kinetic fitted results of ZnInS, CdS, and 3ZnInS/CdS.

Samples	$\tau_1$ (ns)	$A_1$	$\tau_2$ (ns)	$A_2$	$\tau_{ave}$ (ns)
ZnInS	1.91	0.943	17.32	0.057	7.37
CdS	2.14	0.917	16.81	0.083	8.24
3ZnInS/CdS	1.26	0.901	10.03	0.099	5.35

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