**Electronic Supplementary Information for:** 

## A Homojunction-Heterojunction-Homojunction scaffold boosts photocatalytic $H_2$ evolution over $Cd_{0.5}Zn_{0.5}S/CoO$ hybrids

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**Figure S1.** XRD pattern of CZS solid solution. The vertical lines at the top and bottom indicate CdS wurtzite structure (PDF #41-1049) and ZnS zinc blende structure (PDF #05-0566).



Figure S2. The SEM (a), TEM (b), HRTEM (c) and SAED (inset c) images of CZS.



**Figure S3.** XRD patterns of M-CoO at 250°C for 2.5 h, 5 h,7 h (a), as prepared CoO at 250-290°C for 7 h and at 300°C for 0.5 h (b), H-CoO at 300°C for 0.5 h,1.0 h,2.0 h,2.5 h (c).



Figure S4. XRD patterns of CZS/M-CoO-x nanocomposites with variable M-CoO contents.



**Figure S5.** SEM and TEM images of CZS/C-CoO (A, B), CZS/H-CoO(C, D), CZS/M-CoO (E, F), respectively.



Figure S6. EDS mapping of CZS/H-CoO-10% nanocomposite.

Photocatalysts	Light Source	Scavenger	$H_2$ rate (mmol/h)	Ref.
10 mg Twin CZS/M CoO	200 W Valamp	0.25 M No S/0.25 M No SO	1 78	This
10 mg 1 wm CZS/W-COO	500  W Ae lamp	$0.55$ IVI INd <sub>2</sub> 5/ $0.25$ IVI INd <sub>2</sub> 5/ $0_3$	1.70	
	(>420 mm)	0.7536	0.050	WOIK
$1 \text{ mg } Zn_{0.5}Cd_{0.5}S/PdP_{\sim 0.33}S_{\sim 1.67}$	300 W Xe lamp	0.75 M ascorbic acid	0.372	[29]
	(>420 nm)	$0.7 \text{ M Na}_2\text{S}/0.5 \text{ M Na}_2\text{SO}_3$	0.246	
30 mg Zn <sub>0.5</sub> Cd <sub>0.5</sub> S/Pt	500 W Xe lamp	$0.1 \text{ M Na}_2\text{S}/0.1 \text{ M Na}_2\text{SO}_3$	0.114	[26]
	(>400 nm)			
$5 \text{ mg } Zn_xCd_{1-x}S/CdS(2 \text{ at}\%)$	300 W Xe lamp	0.35 M Na <sub>2</sub> S/0.25 M Na <sub>2</sub> SO <sub>3</sub>	0.667	[61]
	(>420 nm)			
50 mg Zn <sub>0.5</sub> Cd <sub>0.5</sub> S/Ni <sub>0.1</sub> Co <sub>0.9</sub> P-	300 W Xe lamp	0.35 M Na <sub>2</sub> S/0.25 M Na <sub>2</sub> SO <sub>3</sub>	0.976	[62
4mol%	(>400 nm)			
20 mg	300 W Xe lamp	10 vol% Lactic acid	0.804	[63]
Zn <sub>0.5</sub> Cd <sub>0.5</sub> S@MoS <sub>2</sub> (10%)	(>420 nm)			
50 mg NiCo <sub>2</sub> O <sub>4</sub> /Zn <sub>0.1</sub> Cd <sub>0.9</sub> S	300 W Xe lamp	0.35 M Na <sub>2</sub> S/0.25 M Na <sub>2</sub> SO <sub>3</sub>	1.72	[57]
	(>400 nm)			
10 mg NiCo <sub>2</sub> O <sub>4</sub> /CdS	5 W LED	10 vol% Lactic acid	0.1098	[58]
25 mg MoO <sub>2</sub> -C/CdS	300 W Xe lamp	10 vol% Lactic acid	0.402	[59]
	(>420 nm)			
50 mg CdS/CoO	300 W Xe lamp	20 vol% Lactic acid	0.0645	[60]
	(>420 nm)			
100 mg g-C <sub>3</sub> N <sub>4</sub> /CoO/Pt	300 W Xe lamp	10 vol% TEOA	0.0651	[42]
	(>400 nm)			
40 mg CoO/C <sub>3</sub> N <sub>4</sub> NTs	300 W Xe lamp	10 vol% TEOA	0.0105	[43]
	(>420 nm)			
40 mg CdS/CoO <sub>x</sub>	350 W Xe lamp	0.35 M Na <sub>2</sub> S/0.25 M Na <sub>2</sub> SO <sub>3</sub>	0.14	[46]
	(>420 nm)			
35 mg CoO <sub>x</sub> /TiO <sub>2</sub> /Pt	UV-light	15 vol% Methanol	0.276	[74]

Table S1. Comparisons of  $H_2$  production rate of recently reported photocatalysts



**Figure S7.** (a) Rate of  $H_2$  evolution with different amount of photocatalysts over a: CZS/M-CoO-1.5%, b: CZS/C-CoO-1.5%, c: CZS/H-CoO-1.5%, d: CZS. (b) Relative light intensity of 300 W Xe lamp with bandpass filter 420 nm.



Figure S8. Wavelength dependent AQY of H<sub>2</sub> evolution for 10 mg of CZS/M-CoO-1.5%.



**Figure S9.** Photocatalytic H<sub>2</sub> generation curves for samples in 0.35 M Na<sub>2</sub>S/0.25 M Na<sub>2</sub>SO<sub>3</sub> aqueous solution under  $\lambda > 510$  nm irradiation, 10 mg of photocatalysts.



Figure S10. XPS survey spectra obtain before and after photocatalysis over CZS/M-CoO-1.5%.



**Figure S11.** Photocatalytic HER activities of CZS/M-CoO-1.5% and CZS measured with different hole scavengers.

## According to the following equations (S1):

$$AQY(\%) = \frac{Number of reacted electrons}{Number of incident photons} \times 100\%$$
$$= \frac{Number of evolved H_2 molecules \times 2}{Number of incident photons} \times 100\%$$
$$= \frac{M \times N_A \times 2}{\frac{P \times t}{E_g \times J}} \times 100\%$$
Where N<sub>A</sub>= 6.02 × 10<sup>23</sup>, I (light intensity) = 0.160 J/s, E<sub>g</sub> = 1240/ $\lambda$  ( $\lambda$  = 420 nm), t (Time) = 3600 s, J = 1.6 × 10<sup>-19</sup> j.



**Figure S12.** (a) Transient photocurrents, (b) Nyquist plots of electrochemical impedance spectra for pristine CZS, CZS/C-CoO-1.5%, CZS/H-CoO-1.5% and CZS/M-CoO-1.5%, using a Pt sheet and carbon rod as counter electrode, respectively.



Figure S13. UV-Vis diffuse reflectance spectra of samples. The inset shows colors of samples.



Figure S14. UV-Vis diffuse reflectance spectra of samples. The inset shows colors of samples.



Figure S15. UV-Vis diffuse reflectance spectra of samples. The inset shows colors of samples.



**Figure S16.** (a) UV-Vis diffuse reflectance spectra of sample. The inset shows the color of samples. (b) The Eg of  $g-C_3N_4$ . (c) XPS survey scan of  $g-C_3N_4/M$ -CoO (inset shows VB XPS of  $g-C_3N_4$ ). (d) The high-resolution of Co 2p in  $g-C_3N_4/M$ -CoO.