

*Electronic Supplementary Information for*

**Self-assembled Transition Metal Chalcogenides@CoAl-LDH 2D/2D  
Heterostructures with Enhanced Photoactivity for Hydrogen  
Evolution**

Linfen Peng<sup>a</sup>, Changqiang Yu<sup>a</sup>, Yuheng Ma<sup>a</sup>, Guanshun Xie<sup>a</sup>, Xiuqiang Xie<sup>a, \*</sup>,  
Zhenjun Wu<sup>b, \*</sup>, Nan Zhang<sup>a, \*</sup>

<sup>a</sup>*College of Materials Science and Engineering, Hunan University, Changsha 410082,  
China*

<sup>b</sup>*College of Chemistry and Chemical Engineering, Hunan University, Changsha  
410082, China*

\*Corresponding author, E-mail: [xiuqiang\\_xie@hnu.edu.cn](mailto:xiuqiang_xie@hnu.edu.cn); [wooawt@hnu.edu.cn](mailto:wooawt@hnu.edu.cn);  
[nanzhang@hnu.edu.cn](mailto:nanzhang@hnu.edu.cn)

## Contents list

**Figure S1.** Zeta potentials.

**Figure S2.** XRD patterns of the synthesized  $\text{In}_2\text{S}_3$ ,  $\text{In}_2\text{S}_3@\text{CoAl-LDH}$ ,  $\text{ZnIn}_2\text{S}_4$ , and  $\text{ZnIn}_2\text{S}_4@\text{CoAl-LDH}$ .

**Figure S3.** SEM images of  $\text{In}_2\text{S}_3$  (a),  $\text{In}_2\text{S}_3@\text{CoAl-LDH}$  (b),  $\text{ZnIn}_2\text{S}_4$  (c), and  $\text{ZnIn}_2\text{S}_4@\text{CoAl-LDH}$  (d).

**Figure S4.** XPS survey spectra of  $\text{CdIn}_2\text{S}_4$  NSs, CoAl-LDH and CIS@CA composites.

**Figure S5.** DRS spectra of bare  $\text{CdIn}_2\text{S}_4$ , bare CoAl-LDH, and CIS@CA composites.

**Figure S6.** Photocatalytic activity of  $\text{ZnIn}_2\text{S}_4@\text{CoAl-LDH-20\%}$  composites for  $\text{H}_2$  production under SSL irradiation.

**Figure S7.** Long-time stability of  $\text{ZnIn}_2\text{S}_4@\text{CoAl-LDH-20\%}$  and  $\text{In}_2\text{S}_3@\text{CoAl-LDH-20\%}$  for photocatalytic  $\text{H}_2$  production.

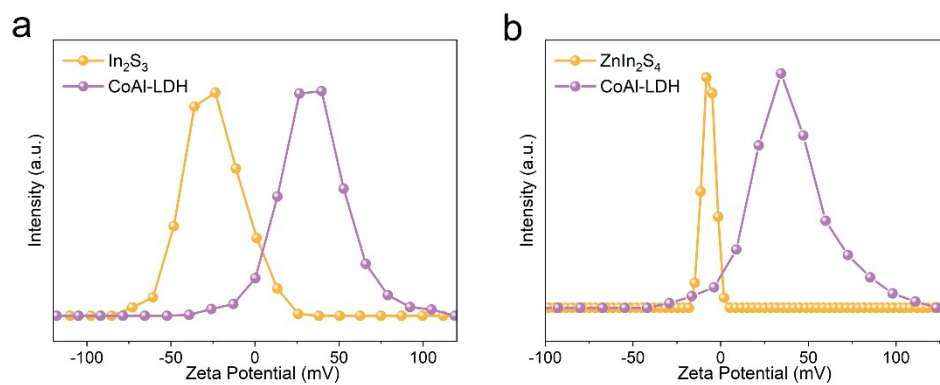
**Figure S8.** XRD patterns of fresh and used CIS@CA composites.

**Figure S9.** Decay curves of photovoltage.

**Figure S10.** Mott-Schottky plots for  $\text{CdIn}_2\text{S}_4$  (a) and CoAl-LDH (b).

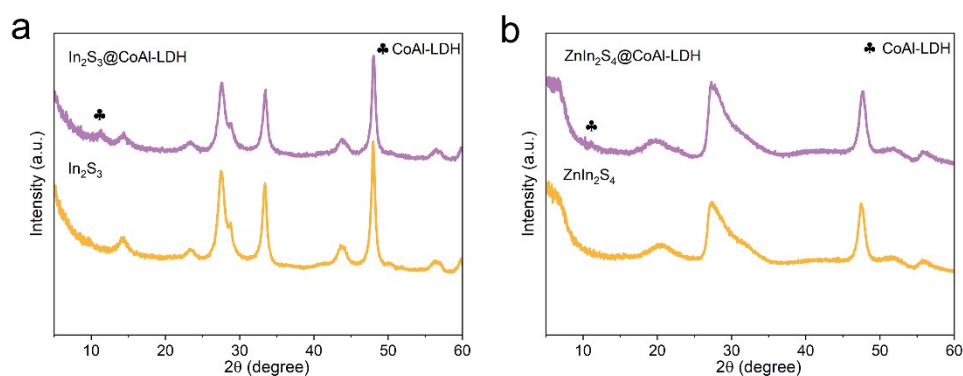
**Figure S11.** (a) VB XPS curves of  $\text{CdIn}_2\text{S}_4$  and (b) CoAl-LDH.

**Figure S12.** The estimated band gap energy of  $\text{CdIn}_2\text{S}_4$  (a) and CoAl-LDH (b) based on the Kubelka-Munk function plot transformed from the absorbance.



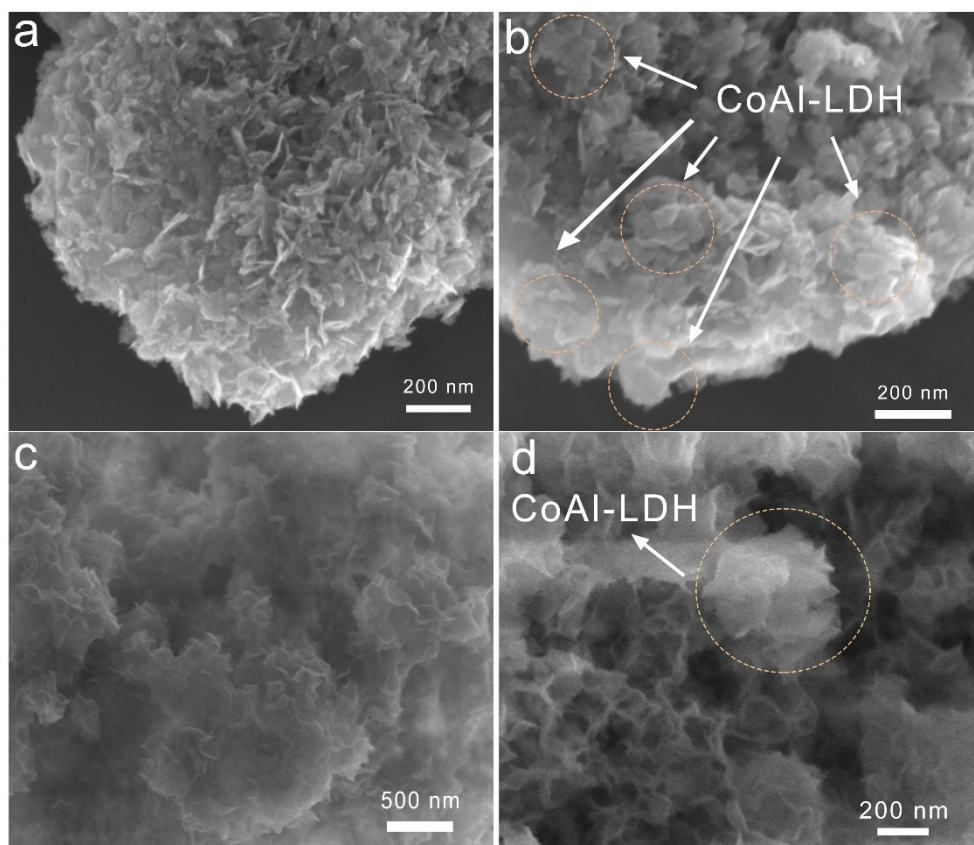
**Figure. S1.** Zeta Potentials.

**Note:** The CoAl-LDH nanosheets have a positive zeta potential of +49.3 mV, whereas the  $\text{In}_2\text{S}_3$  nanosheets have a negative zeta potential of -19.6 mV and the  $\text{ZnIn}_2\text{S}_4$  nanosheets have a negative zeta potential of -8.1 mV.

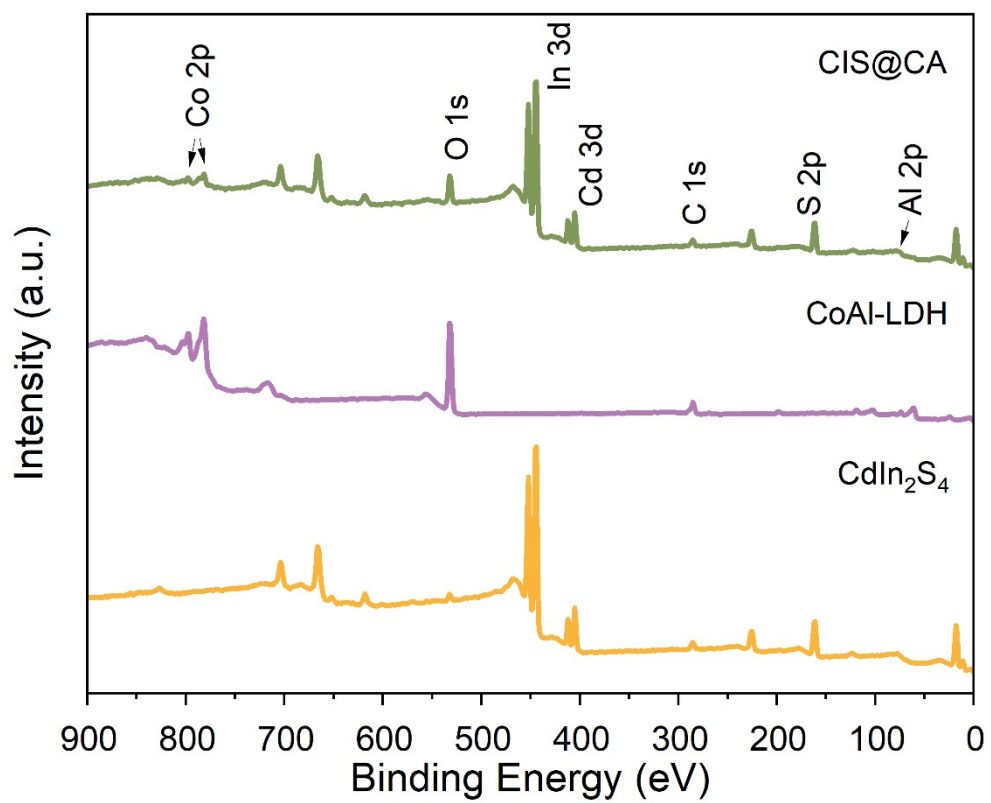


**Figure. S2.** XRD patterns of the synthesized  $\text{In}_2\text{S}_3$ ,  $\text{In}_2\text{S}_3@\text{CoAl-LDH}$ ,  $\text{ZnIn}_2\text{S}_4$ , and  $\text{ZnIn}_2\text{S}_4@\text{CoAl-LDH}$ .

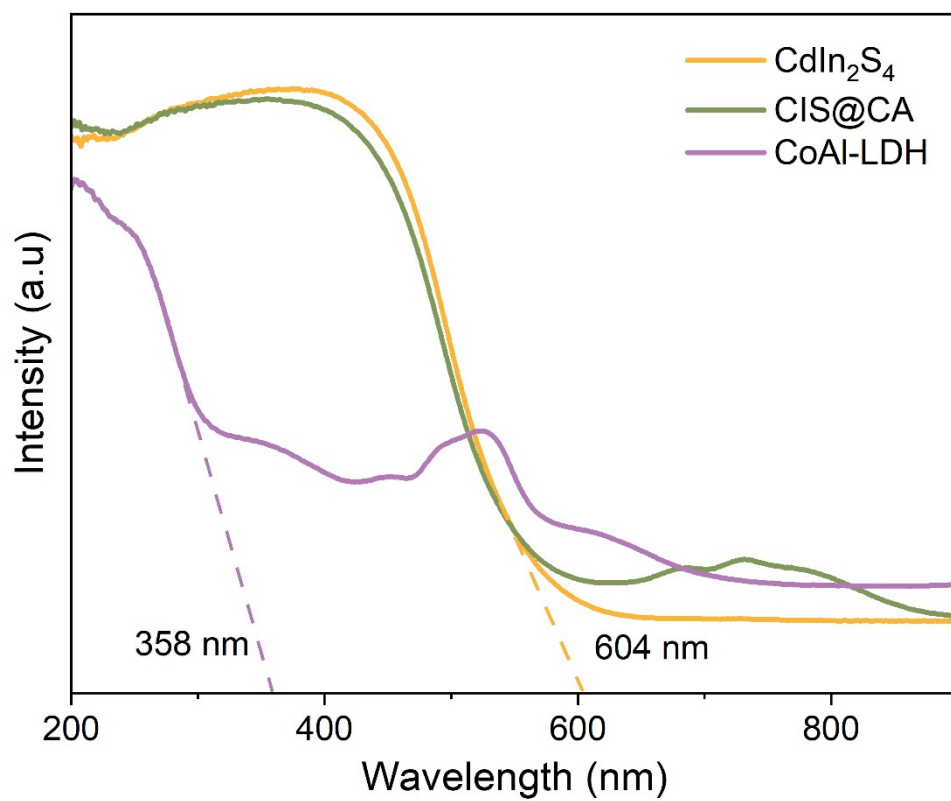
**Note:** As shown in Figure. S2a, The XRD patterns of  $\text{In}_2\text{S}_3@\text{CoAl-LDH}$  and pristine  $\text{In}_2\text{S}_3$  could be indexed to the cubic phase of  $\text{In}_2\text{S}_3$  (JCPDS No. 65-0459)<sup>1</sup>, the peaks at  $2\theta = 14.2^\circ, 23.3^\circ, 27.4^\circ, 28.7^\circ, 33.2^\circ, 43.6^\circ, 47.7^\circ, 56.6^\circ, 59.4^\circ$  of bare  $\text{In}_2\text{S}_3$  are indexed to the (111), (220), (311), (222), (400), (511), (440), (622) and (444) crystal planes, respectively. Figure. S2b shows the XRD patterns of  $\text{ZnIn}_2\text{S}_4$  and  $\text{ZnIn}_2\text{S}_4@\text{CoAl-LDH}$  heterostructure, wherein obvious diffraction peaks at  $20.5^\circ, 27.6^\circ, 47.6^\circ$  and  $56^\circ$  correspond to the (006), (102), (112) and (202) crystal planes of hexagonal  $\text{ZnIn}_2\text{S}_4$  (JCPDS No. 01-072-0773)<sup>2</sup>, respectively.



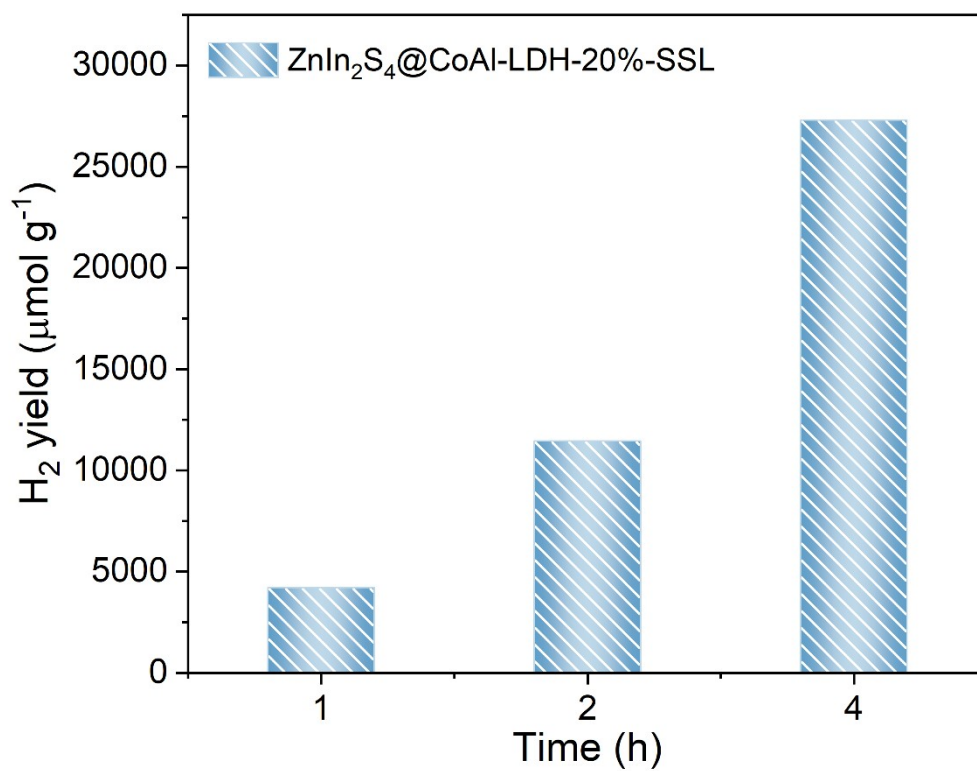
**Figure. S3.** SEM images of In<sub>2</sub>S<sub>3</sub> (a), In<sub>2</sub>S<sub>3</sub>@CoAl-LDH (b), ZnIn<sub>2</sub>S<sub>4</sub> (c), and ZnIn<sub>2</sub>S<sub>4</sub>@CoAl-LDH (d).



**Figure. S4.** XPS survey spectra of CdIn<sub>2</sub>S<sub>4</sub> NSs, CoAl-LDH and CIS@CA composites.

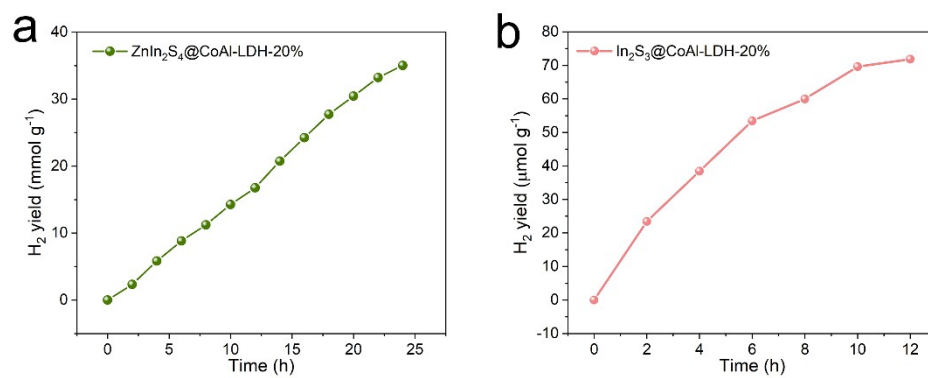


**Figure. S5.** DRS spectra of bare CdIn<sub>2</sub>S<sub>4</sub>, bare CoAl-LDH, and CIS@CA composites.

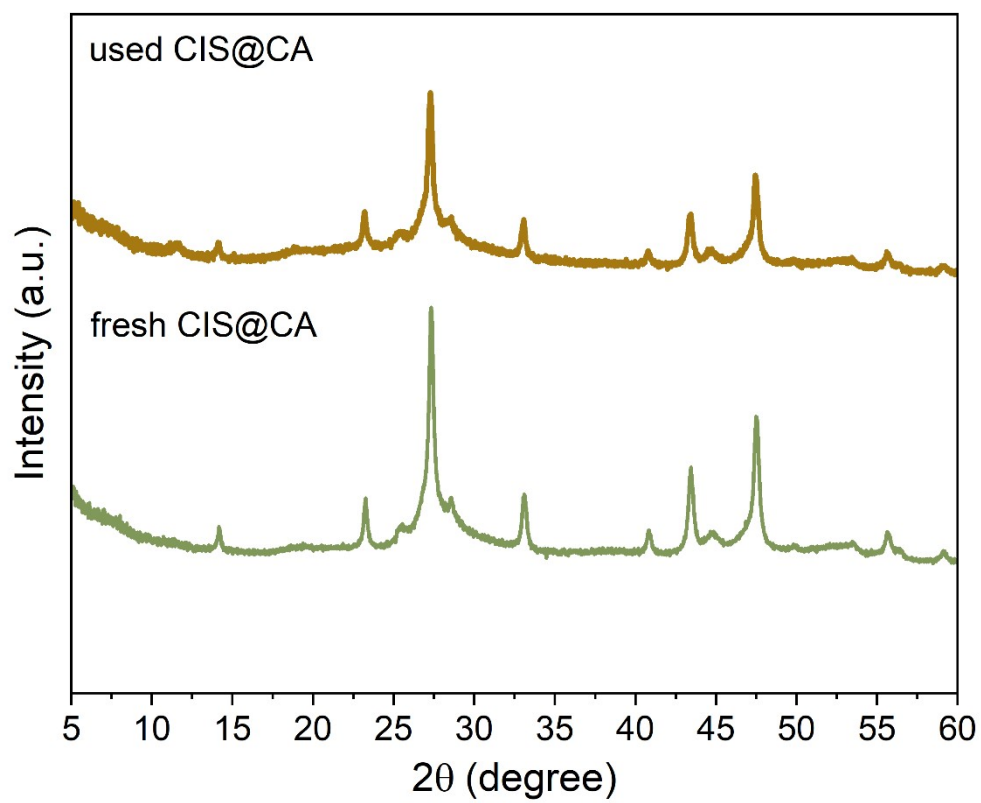


**Figure. S6.** Photocatalytic activity of ZnIn<sub>2</sub>S<sub>4</sub>@CoAl-LDH-20% composites for H<sub>2</sub> production under SSL irradiation.

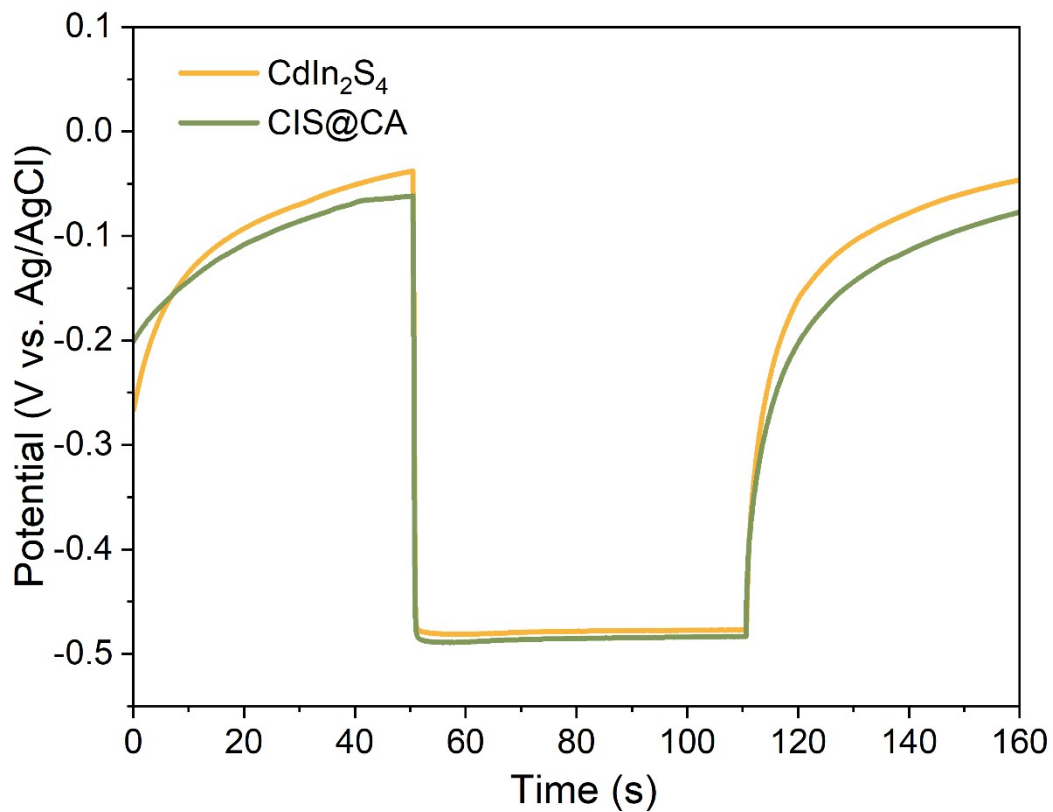




**Figure S7.** Long-time stability of ZnIn<sub>2</sub>S<sub>4</sub>@CoAl-LDH-20% and In<sub>2</sub>S<sub>3</sub>@CoAl-LDH-20% for photocatalytic H<sub>2</sub> production.



**Figure. S8.** XRD patterns of fresh and used CIS@CA composites.

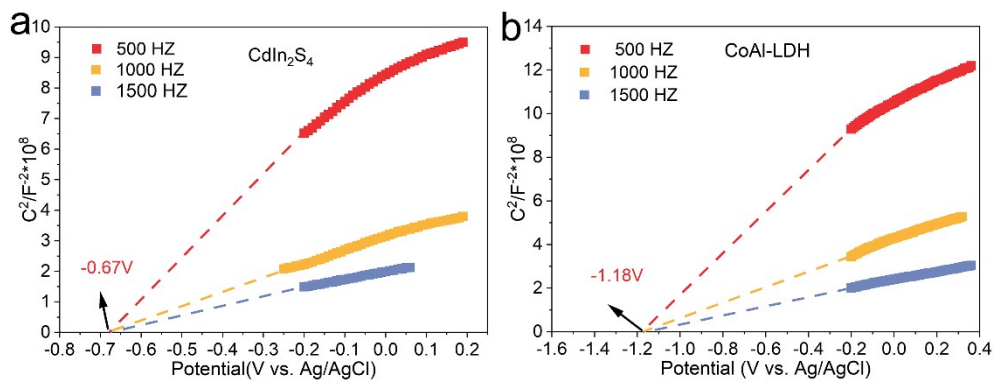


**Figure. S9.** Decay curves of photovoltage.

**Supplementary Note:** The photoelectron lifetime ( $\tau_n$ ) is calculated by the following formula<sup>3</sup>:

$$\tau_n = (k_B T / e) (dV_{OC} / dt)^{-1}$$

where  $k_B$ ,  $T$ ,  $e$ ,  $V_{OC}$  and  $t$  are Boltzmann's constant ( $1.3806 \times 10^{-23}$  J/K), charge of one electron ( $1.602 \times 10^{-19}$  C), temperature (298.15 K), open circuit photovoltage and time, respectively.

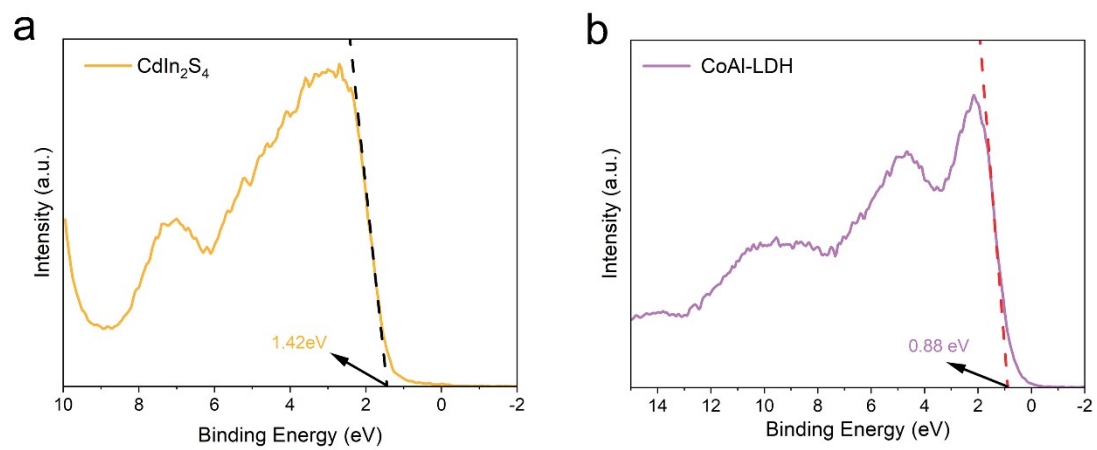


**Figure. S10.** Mott-Schottky plots for CdIn<sub>2</sub>S<sub>4</sub> (a) and CoAl-LDH (b).

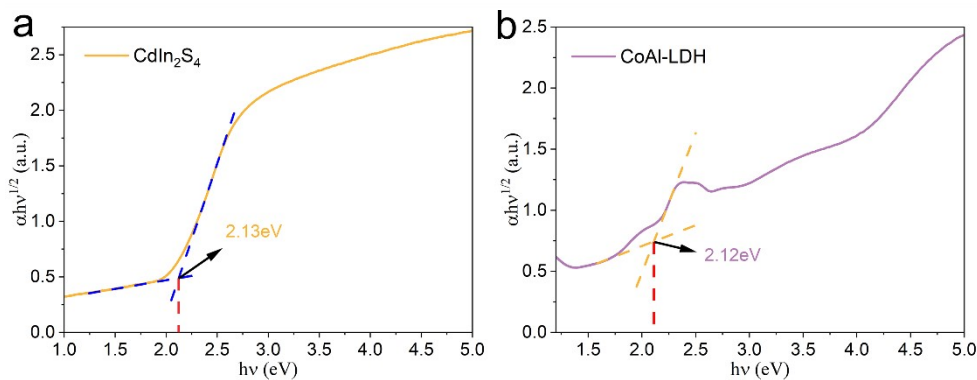
**Supplementary Note:** The flat-band potential values ( $E_{fb}$ ) can be determined by the following Mott-Schottky equation<sup>4</sup>:

$$\frac{1}{C^2} = \frac{2}{\epsilon \epsilon_0 N_D} \left( E - E_{fb} - \frac{k_B T}{q} \right)$$

where  $\epsilon$  and  $\epsilon_0$  are the dielectric constants of free space and the film electrode, and  $N_D$ ,  $C$ ,  $E$ ,  $T$ ,  $k_B$ , and  $q$  represent the donor density, space charge capacitance, applied potential, temperature, Boltzmann's constant, and electronic charge, respectively.



**Figure. S11.** (a) VB XPS curves of CdIn<sub>2</sub>S<sub>4</sub> and (b) CoAl-LDH.



**Figure. S12.** The estimated band gap energy of CdIn<sub>2</sub>S<sub>4</sub> (a) and CoAl-LDH (b) based on the Kubelka-Munk function plot transformed from the absorbance.

**Supplementary Note:** The Kubelka–Munk equation is employed to calculate the band gap energy of the as-obtained solid solutions<sup>4, 5</sup>:

$$(\alpha h\nu)^{1/n} = A(h\nu - E_g)$$

where  $h$ ,  $\alpha$ ,  $\nu$ ,  $A$ , and  $E_g$  represent Planck's constant ( $6.63 \times 10^{-34} \text{ J} \cdot \text{s}$ ), optical absorption coefficient, photon frequency, a constant, and photonic energy band gap, respectively.

In addition,  $n$  is 2 for a direct band gap and 1/2 for an indirect band gap.

## References

1. Y. Zhu, G. Xie, G. Li, F. Song, C. Yu, Z. Wu, X. Xie and N. Zhang, Facial synthesis of two-dimensional  $\text{In}_2\text{S}_3/\text{Ti}_3\text{C}_2\text{T}_x$  heterostructures with boosted photoactivity for the hydrogenation of nitroaromatic compounds, *Mater. Chem. Front.*, 2021, **5**, 6883-6890.
2. H.-J. Lin, Q.-L. Mo, S. Xu, Z.-Q. Wei, X.-Y. Fu, X. Lin and F.-X. Xiao, Unlocking photoredox selective organic transformation over metal-free 2D transition metal chalcogenides-MXene heterostructures, *J. Catal.*, 2020, **391**, 485-496.
3. J.-Y. Li, Y.-H. Li, F. Zhang, Z.-R. Tang and Y.-J. Xu, Visible-light-driven integrated organic synthesis and hydrogen evolution over 1D/2D CdS- $\text{Ti}_3\text{C}_2\text{T}_x$  MXene composites, *Appl. Catal. B: Environ.*, 2020, **269**, 118783.
4. C. Zeng, H. W. Huang, T. R. Zhang, F. Dong, Y. H. Zhang and Y. M. Hu, Fabrication of Heterogeneous-Phase Solid-Solution Promoting Band Structure and Charge Separation for Enhancing Photocatalytic  $\text{CO}_2$  Reduction: A Case of  $\text{Zn}_x\text{Ca}_{1-x}\text{In}_2\text{S}_4$ , *ACS Appl. Mater. Interfaces*, 2017, **9**, 27773-27783.
5. C. Zeng, Y. M. Hu, T. R. Zhang, F. Dong, Y. H. Zhang and H. W. Huang, A core-satellite structured Z-scheme catalyst  $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}/\text{BiVO}_4$  for highly efficient and stable photocatalytic water splitting, *J. Mater. Chem. A*, 2018, **6**, 16932-16942.