

# Supporting Information

## Interface engineering of noble-metal-free 2D-2D MoS<sub>2</sub>/Cu-ZnIn<sub>2</sub>S<sub>4</sub> photocatalyst for enhanced photocatalytic H<sub>2</sub> production

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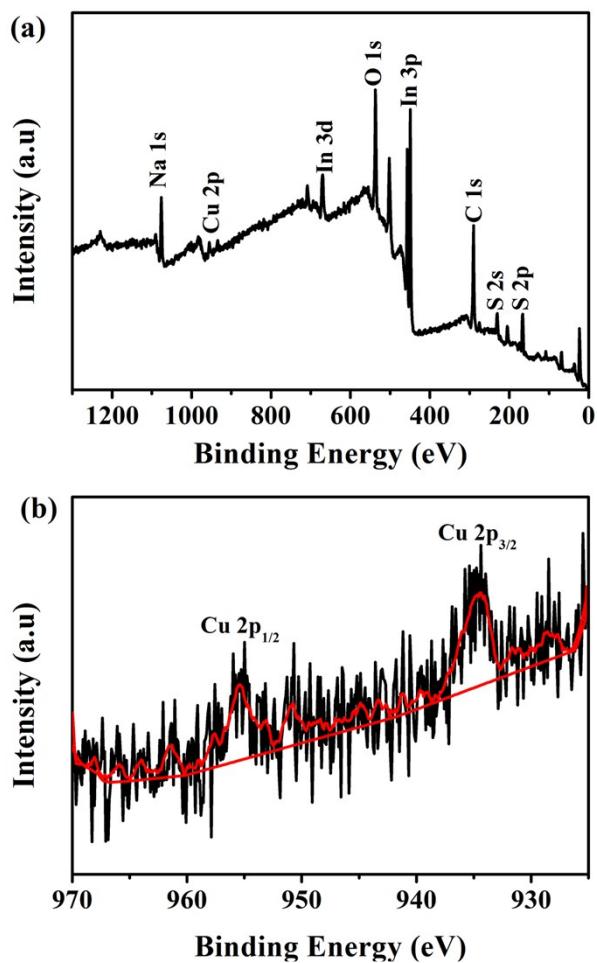
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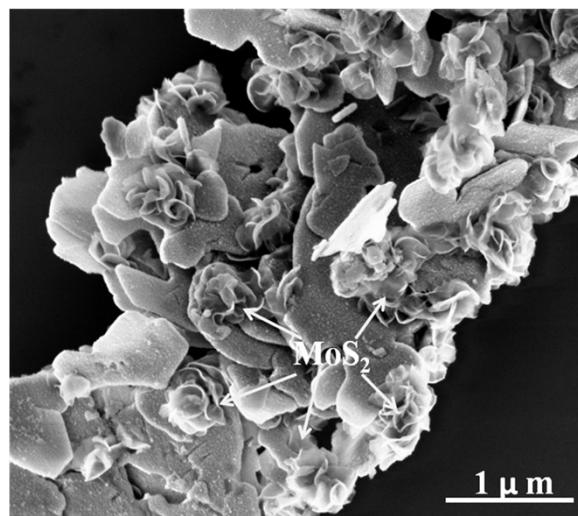
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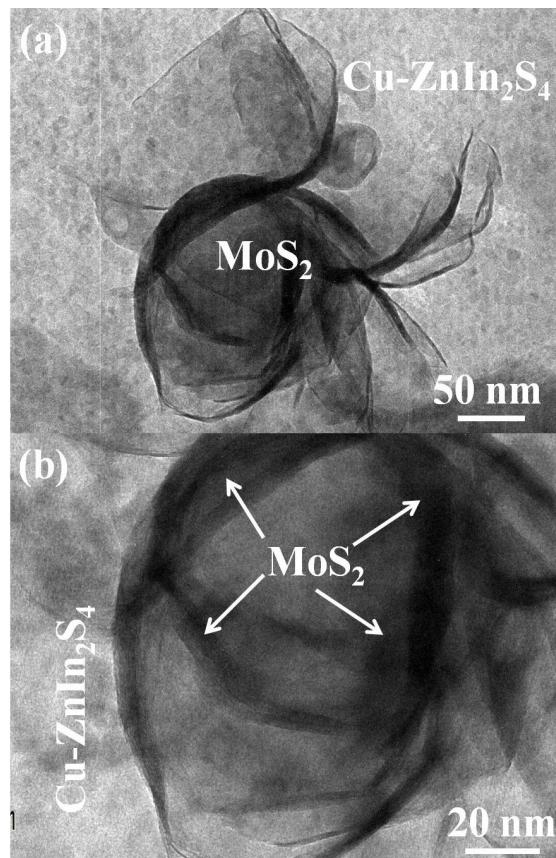
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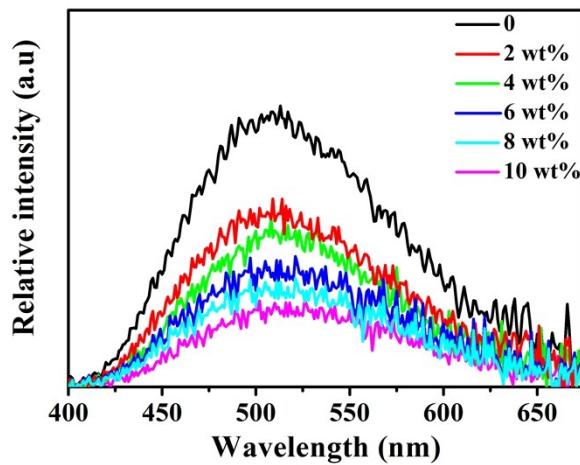
**Figure S1.** (a) Survey XPS spectra of Cu-NaInS<sub>2</sub>. (b) High resolution XPS spectra of Cu 2p.



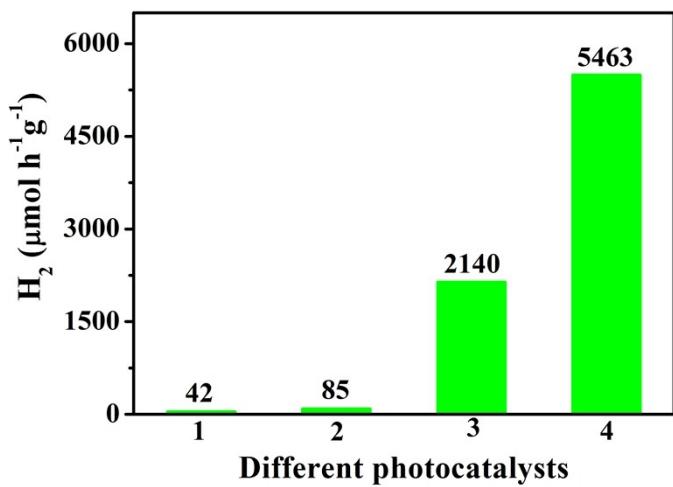
**Figure S2.** SEM image of 10 wt% MoS<sub>2</sub>/Cu-ZnIn<sub>2</sub>S<sub>4</sub> photocatalyst.



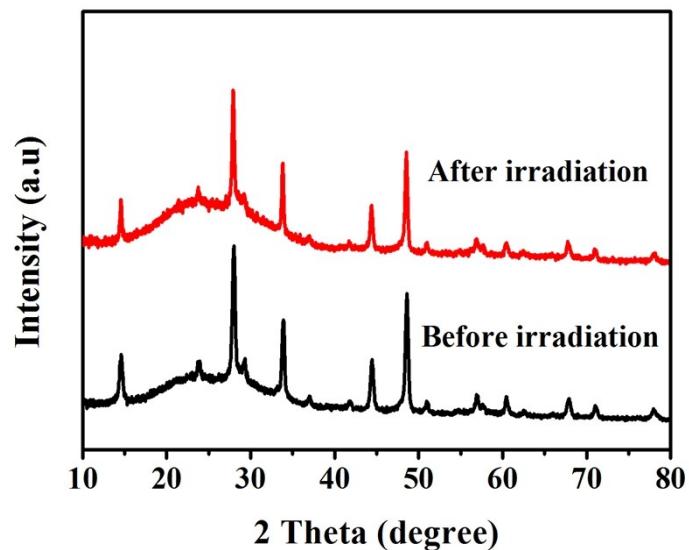
**Figure S3.** (a,b) TEM images of 10 wt% MoS<sub>2</sub>/Cu-ZnIn<sub>2</sub>S<sub>4</sub> photocatalyst.



**Figure S4.** PL emission spectra of pure Cu-ZnIn<sub>2</sub>S<sub>4</sub> and MoS<sub>2</sub>/Cu-ZnIn<sub>2</sub>S<sub>4</sub> photocatalysts in ethanol solutions (0.5 mg ml<sup>-1</sup>) excited at 350 nm.



**Figure S5.** Photocatalytic  $H_2$  evolution rate of  $ZnIn_2S_4$  (1),  $Cu-ZnIn_2S_4$  (2), 6 wt%  $MoS_2/ZnIn_2S_4$  (3) and 6 wt%  $MoS_2/Cu-ZnIn_2S_4$  (4) under visible light irradiation ( $\lambda > 420$  nm) from a 300 W Xe lamp in 250 mL of 0.1 M ascorbic acid aqueous solution.



**Figure S6.** XRD patterns of 6 wt%  $MoS_2/Cu-ZnIn_2S_4$  photocatalyst.

**Table S1.** Analytical results of Cu/In molar ratio in Cu-NaInS<sub>2</sub> and Cu/Cu-ZnIn<sub>2</sub>S<sub>4</sub>.

Sample	Sample concentration (mg/L)	Cu concentration (mg/L)	Cu/In molar ratio (mol%)
Cu-NaInS <sub>2</sub>	420	0.785	0.59
Cu-ZnIn <sub>2</sub> S <sub>4</sub>	480	0.854	0.58

**Table S2.** Comparison of photocatalytic performance for H<sub>2</sub> production between the current work and other reported studies.

Entry	Photocatalyst	Light source	Sacrificial reagent	H <sub>2</sub> evolution rate (μmol h <sup>-1</sup> g <sup>-1</sup> )	Ref
1	Graphene/ZnIn <sub>2</sub> S <sub>4</sub>	300 W Xe lamp (λ>420 nm)	Lactic acid	817	(1)
2	MoS <sub>2</sub> /ZnIn <sub>2</sub> S <sub>4</sub>	300 W Xe lamp (λ>420 nm)	Na <sub>2</sub> S/Na <sub>2</sub> SO <sub>3</sub>	3060	(2)
3	NiS/ZnIn <sub>2</sub> S <sub>4</sub>	300 W Xe lamp (λ>420 nm)	Na <sub>2</sub> S/Na <sub>2</sub> SO <sub>3</sub>	2094	(3)
4	MoS <sub>2</sub> -graphen/ZnIn <sub>2</sub> S <sub>4</sub>	300 W Xe lamp (λ>420 nm)	Na <sub>2</sub> S/Na <sub>2</sub> SO <sub>3</sub>	4169	(4)
5	Pt/ZnIn <sub>2</sub> S <sub>4</sub>	300 W Xe lamp (λ>420 nm)	Na <sub>2</sub> S/Na <sub>2</sub> SO <sub>3</sub>	257	(5)
6	MoS <sub>2</sub> /Cu-ZnIn <sub>2</sub> S <sub>4</sub>	300 W Xe lamp (λ>420 nm)	Ascorbic acid	5463	This work

## References

- (1) L. Ye, J. L. Fu, Z. Xu, R. S. Yuan, Z. H. Li, *ACS Appl. Mater. Interfaces*, 2014, **6**, 3483-3490.
- (2) L. Wei, Y. J. Chen, Y. P. Lin, H. S. Wu, R. S. Yuan, Z. H. Li, *Appl. Catal. B. Environ.* 2014, **144**, 521–527.
- (3) L. Wei, Y. J. Chen, J. L. Zhao, Z. H. Li, *Beilstein J. Nanotechnol.* 2013, **4**, 949-955.
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- (5) Z. B. Lei, W. S. You, M. Y. Liu, G. H. Zhou, T. Takata, M. Hara, K. Domen, C. Li, *Chem. Commun.* 2003, 2142-2143.