Supporting Information

Achieving long-lived photogenerated holes in $ZnIn_2S_4$ loaded with CoO_x clusters for enhanced photocatalytic pure water splitting

Qingsheng Zhang[a], Shuya Yuan[a], Huabing Yin[b,*], Jianjun Yang[a], Zhongjie Guan[a,*]

[a] National & Local Joint Engineering Research Center for Applied Technology of Hybrid Nanomaterials, Institute of Nanoscience and Engineering, Henan University, Kaifeng 475004, Henan, China

[b] Institute for Computational Materials Science, Joint Center for Theoretical Physics, International Joint Research Laboratory of New Energy Materials and Devices of Henan Province, School of Physics and Electronics, Henan University, Kaifeng 475004, Henan, China

*Corresponding author, E-mail address: yhb@henu.edu.cn; guanzj@henu.edu.cn

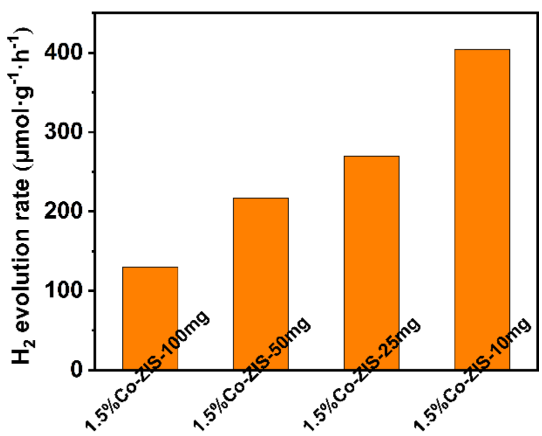

Fig. S1. The H_2 evolution rate of 1.5%Co-ZIS using different usage.

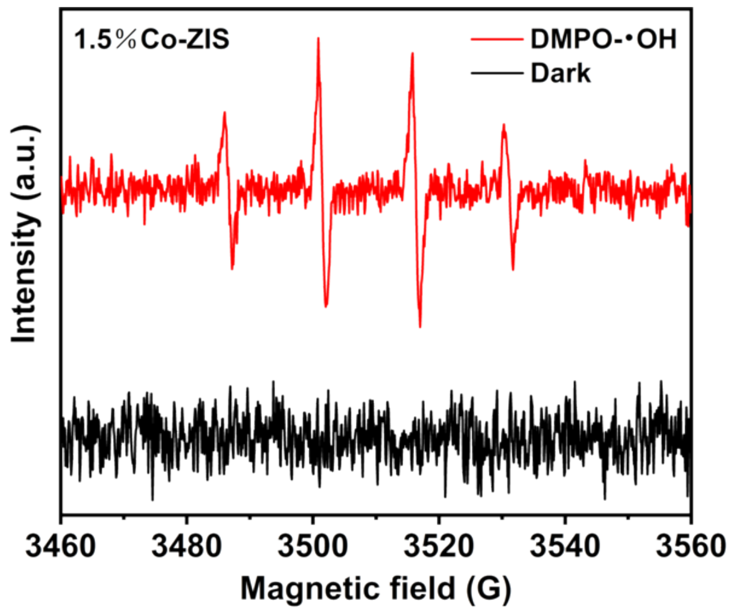

Fig. S2. EPR spectra of 1.5%Co-ZIS.

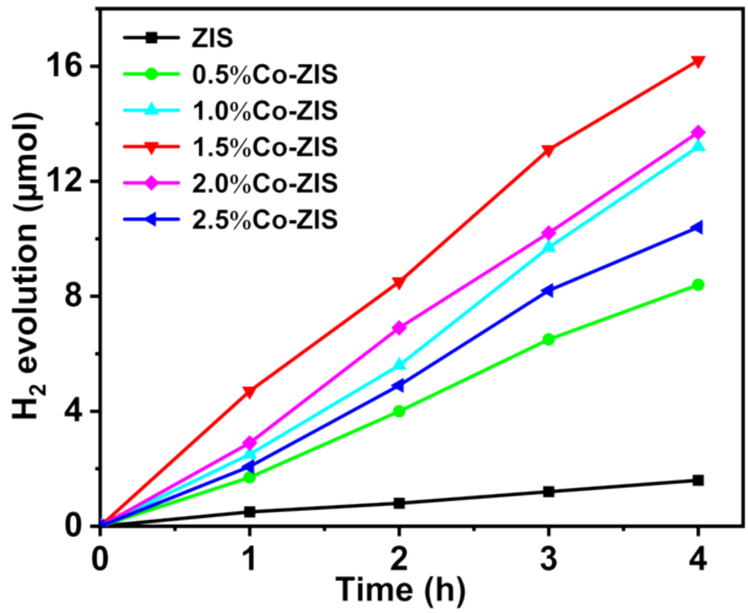

Fig. S3. Time courses of H_2 evolution for ZIS and Co-ZIS composites with different contents of Co.

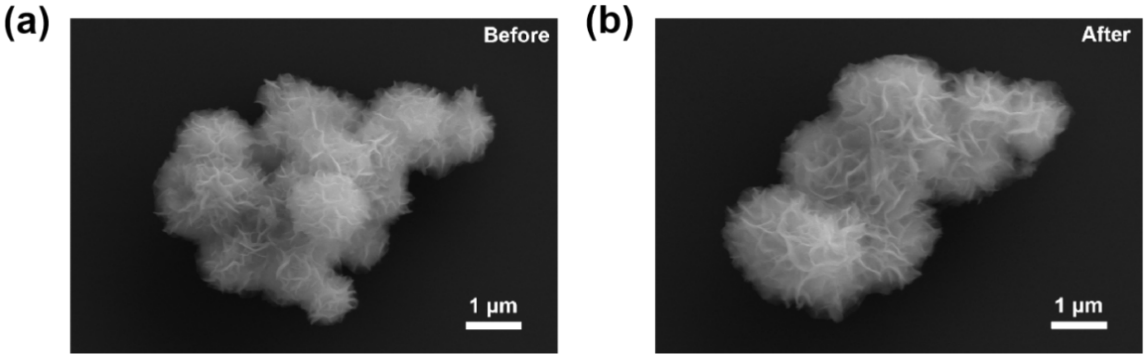

Fig. S4. SEM images of 1.5%Co-ZIS before reaction (a) and after reaction (b).

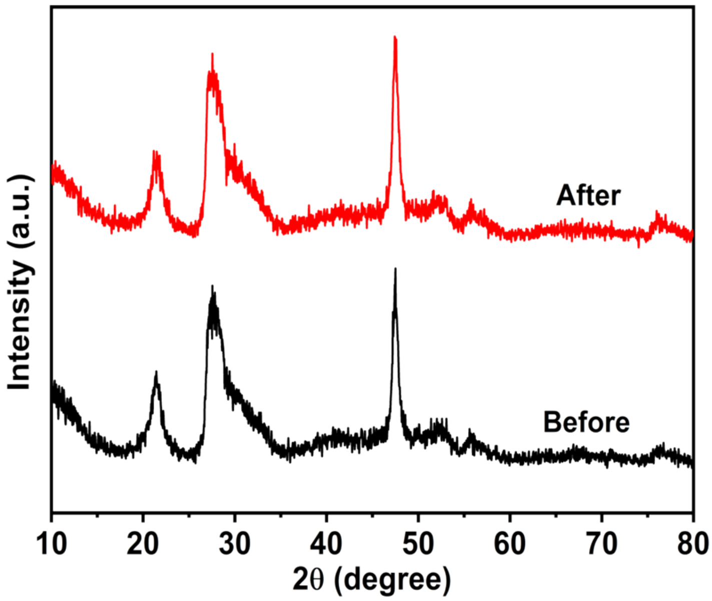

Fig. S5. XRD patterns of 1.5%Co-ZIS before and after the reaction.

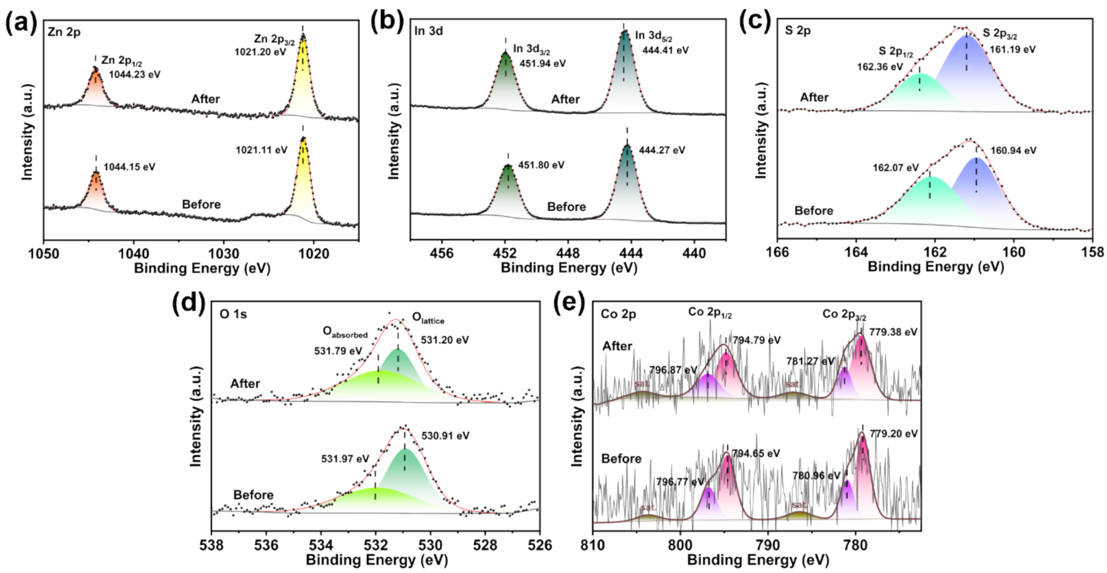

Fig. S6. XPS spectra of Zn 2p (a), In 3d (b), S 2p (c), O 1s (d) and Co 2p (e) for 1.5%Co-ZIS before and after the reaction.

Table S1. Summary of reports on photocatalytic overall water splitting of some common catalysts.

Photocatalyst	Light source	H_2 (μmol·g^{-1}·h^{-1})	O_2/H_2O_2 (μmol·g^{-1}·h^{-1})	AQE	Refs.
p-Co_3O_4/n-TiO_2	300 W Xe-lamp (λ≥420 nm)	8.16	4	/	1
Cu/TiO_2	300 W Xe-lamp (λ≥420 nm)	35.9	16.8	/	2
P-g-C_3N_4-Co_xP	300 W Xe-lamp (λ≥420 nm)	305.2	274.4 (H_2O_2)	3.6% (425 nm)	3
S_v-CdS	350 W Xe-lamp (λ≥420 nm)	363.8	181.9	/	4
Pt/CdS@Al_2O_3	300 W Xe-lamp (λ≥420 nm)	62.1	/	0.11% (430 nm)	5
RuO_2/CdS/MoS_2	300 W Xe-lamp (λ≥420 nm)	52	11	0.32% (365 nm)	6
Ag-$ZnIn_2S_4$	300 W Xe-lamp (λ≥420 nm)	56.6	29.1	0.70% (405 nm)	7
$BiVO_4$@$ZnIn_2S_4$/Ti_3C_2	300 W Xe-lamp (λ≥400 nm)	102.7	50.8	2.40% (410 nm)	8
CdS@$ZnIn_2S$	300 W Xe-lamp (λ≥400 nm)	540.3	604.8 (H_2O_2)	1.63% (400 nm)	9
C-N-g-C_3N_4	300 W Xe lamp	98	84 (H_2O_2)	0.86% (420 nm)	10

	(700nm≥λ≥420nm)				
PCNNi	300 W Xe-lamp (λ≥400 nm)	26.2	24 (H_2O_2)	1.12% (420 nm)	11
$ZnIn_2S_4/WO_3$	300 W Xe-lamp (AM 1.5G)	668.6	328.6	3.18% (380 nm)	12
1.5%Co-ZIS	**300 W Xe-lamp (λ≥400 nm)**	**404.1**	**371.9 (H_2O_2)**	**1.74% (400 nm)**	**This work**

Table S2. Kinetic parameters of TA decay for ZIS and 1.5%Co-ZIS

Sample Name	τ_1 (ps)	τ_2 (ps)	A_1	A_2	χ^2
ZIS	10.15	558.50	0.49	0.51	0.99
1.5Co%-ZIS	23.13	911.60	0.53	0.47	0.99

The life time was used calculated using the following equation:

$$\tau_{ave} = \frac{B_1 \times (\tau_1)^2 + B_2 \times (\tau_2)^2}{B_1 \times \tau_1 + B_2 \times \tau_2}$$

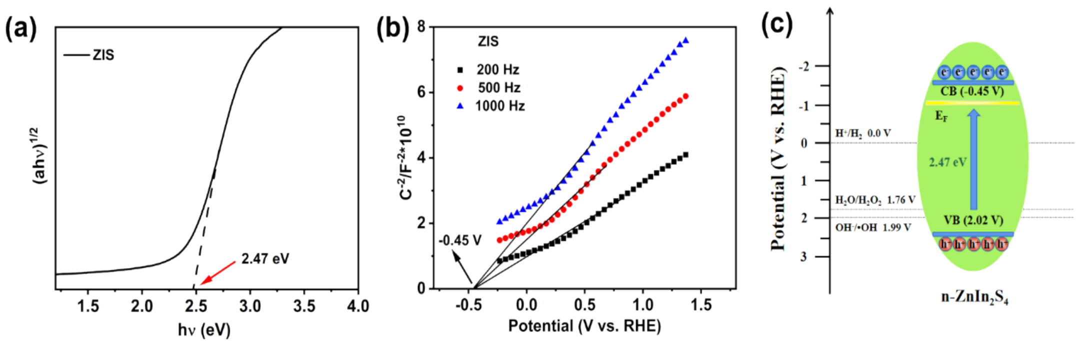

Fig. S7. (a) The plots of $(\alpha h\nu)^{1/2}$ vs. hν for ZIS. (b) Mott-Schottky curves of ZIS. (c) Schematic diagram of ZIS band structure.

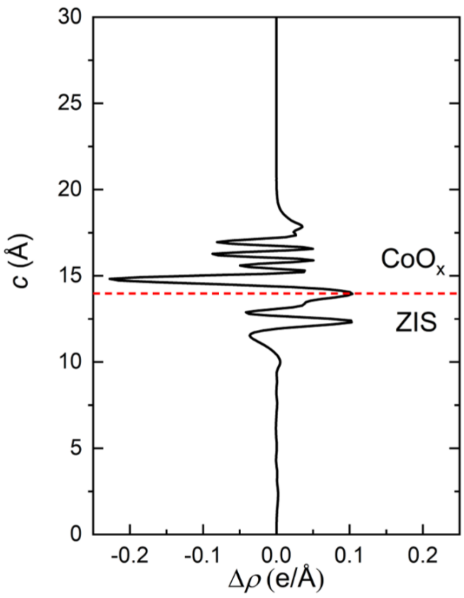

Fig. S8. The planar-averaged electron density difference along the c axis of ZIS/CoO_x interface.

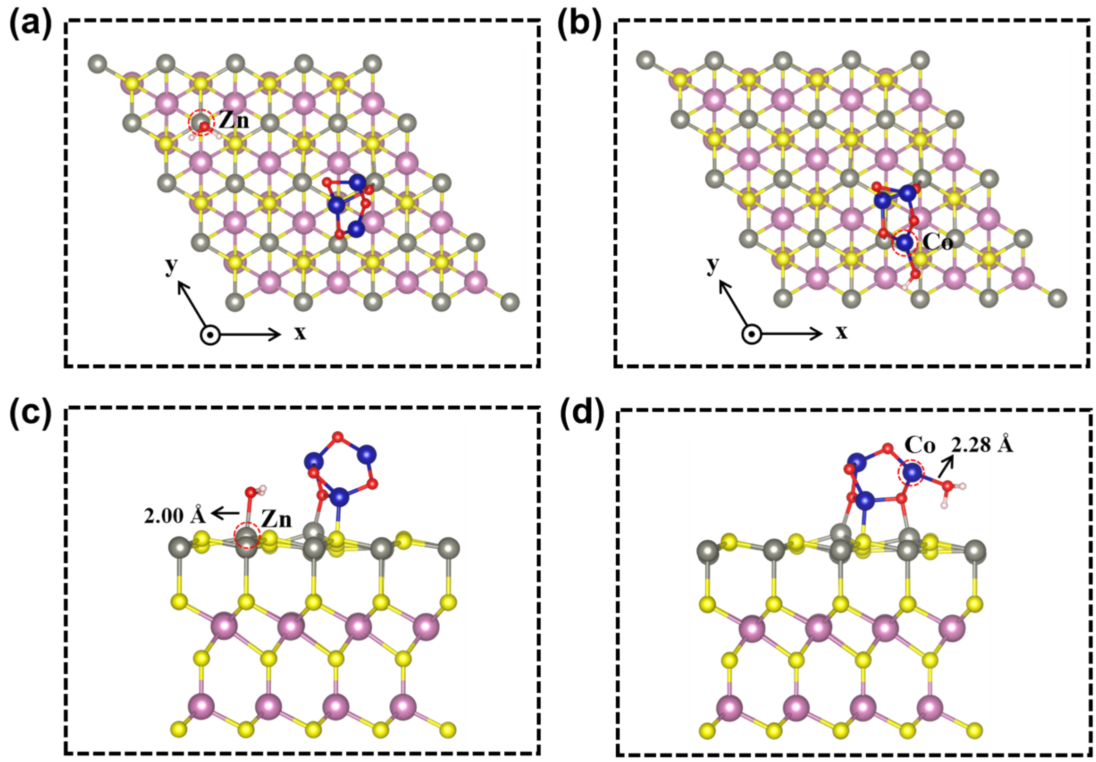

Fig. S9. Top and (b) side view of optimal structure for adsorption H_2O at different sites Zn (a), (c) and Co (b), (d). Gray, purple, yellow, dare blue, red and bright white balls represent Zn, In, S, Co, O and H atoms, respectively.

References

1. Q. Zhang, Z. Hai, A. Jian, H. Xu, C. Xue and S. Sang, *Nanomaterials*, 2016, **6**, 138.
2. D. Wei, Y. Tan, Y. Wang, T. Kong, S. Shen and S. S. Mao, *Sci. Bull.*, 2020, **65**, 1389-1395.
3. F. Xue, Y. Si, C. Cheng, W. Fu, X. Chen, S. Shen, L. Wang and M. Liu, *Nano Energy*, 2022, **103**, 107799.
4. J. He, L. Hu, C. Shao, S. Jiang, C. Sun and S. Song, *ACS Nano*, 2021, **15**, 18006-18013.
5. X. Ning, W. Zhen, Y. Wu and G. Lu, *Appl. Catal. B: Environ.*, 2018, **226**, 373-383.
6. B. Qiu, L. Cai, N. Zhang, X. Tao and Y. Chai, *Adv. Sci.*, 2020, **7**, 1903568.
7. R. Pan, M. Hu, J. Liu, D. Li, X. Wan, H. Wang, Y. Li, X. Zhang, X. Wang, J. Jiang and J. Zhang, *Nano Lett.*, 2021, **21**, 6228-6236.
8. X. Du, T. Zhao, Z. Xiu, Z. Xing, Z. Li, K. Pan, S. Yang and W. Zhou, *Appl. Mater. Today*, 2020, **20**, 100719.
9. E. Zhang, Q. Zhu, J. Huang, J. Liu, G. Tan, C. Sun, T. Li, S. Liu, Y. Li, H. Wang, X. Wan, Z. Wen, F. Fan, J. Zhang and K. Ariga, *Appl. Catal. B: Environ.*, 2021, **293**, 120213.
10. Y. Fu, C. a. Liu, M. Zhang, C. Zhu, H. Li, H. Wang, Y. Song, H. Huang, Y. Liu and Z. Kang, *Adv. Energy Mater.*, 2018, **8**, 1802525.
11. Y. Li, Y. Wang, C. Dong, Y. Huang, J. Chen, Z. Zhang, F. Meng, Q. Zhang, Y. Huangfu, D. Zhao, L. Gu and S. Shen, *Chem. Sci.*, 2021, **12**, 3633-3643.
12. Y. Wang, W. Huang, S. Guo, X. Xin, Y. Zhang, P. Guo, S. Tang and X. Li, *Adv. Energy Mater.*, 2021, **11**, 2102452.