

## Supplementary Data

### **Boosting photocatalytic activity of ZnIn<sub>2</sub>S<sub>4</sub>-based photocatalyst for H<sub>2</sub> evolution using porous ZnWO<sub>4</sub> nanoflakelets as a cocatalyst**

Fengchun Dong<sup>1</sup>, Hui Liu<sup>1</sup>, Lixia Qin<sup>1</sup>, Taiyang Zhang<sup>1,2,\*</sup>, Xiangqing Li<sup>1</sup>, Shi-Zhao Kang<sup>1,\*</sup>

<sup>1</sup>*School of Chemical and Environmental Engineering, Shanghai Institute of Technology, 100 Haiquan Road, Shanghai 201418, China*

<sup>2</sup>*Shanghai Engineering Research Center of Solid Waste Treatment and Resource Recovery, Shanghai Jiao Tong University, Shanghai, 200240, China*

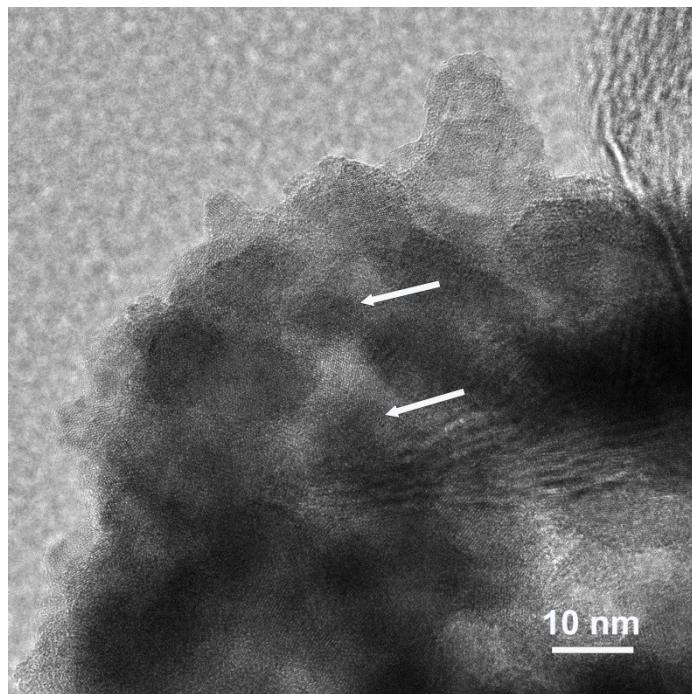
\* Corresponding author: Shi-Zhao Kang, and Taiyang Zhang

Tel./fax: +86 21 60873061.

E-mail address: kangsz@sit.edu.cn (S.-Z. Kang), taiyangzhang@sit.edu.cn (T. Zhang)

---

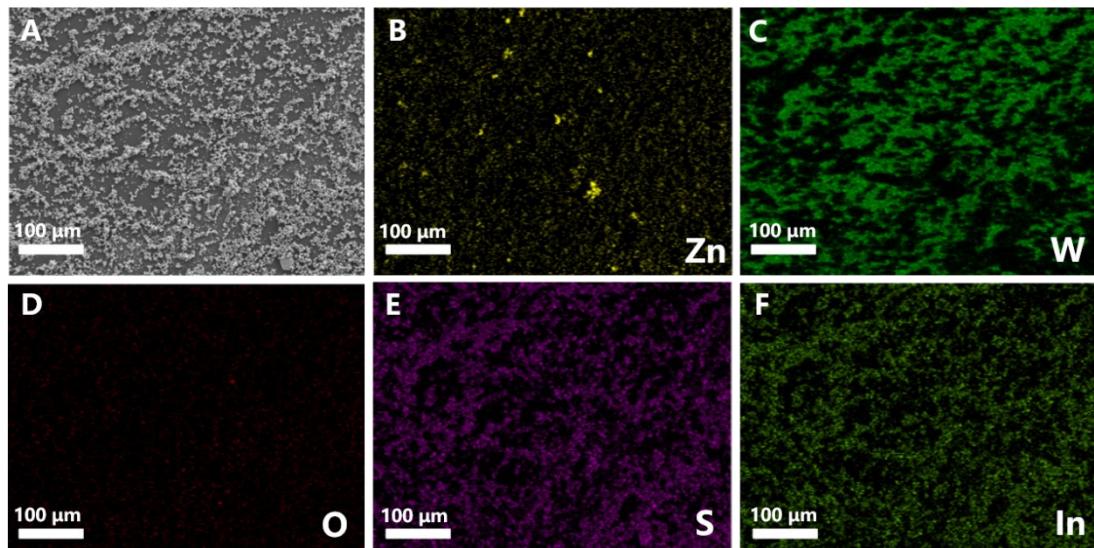
Supplementary Fig. S1



**Fig. S1.** HRTEM image of ZIS/PZW (5%).

---

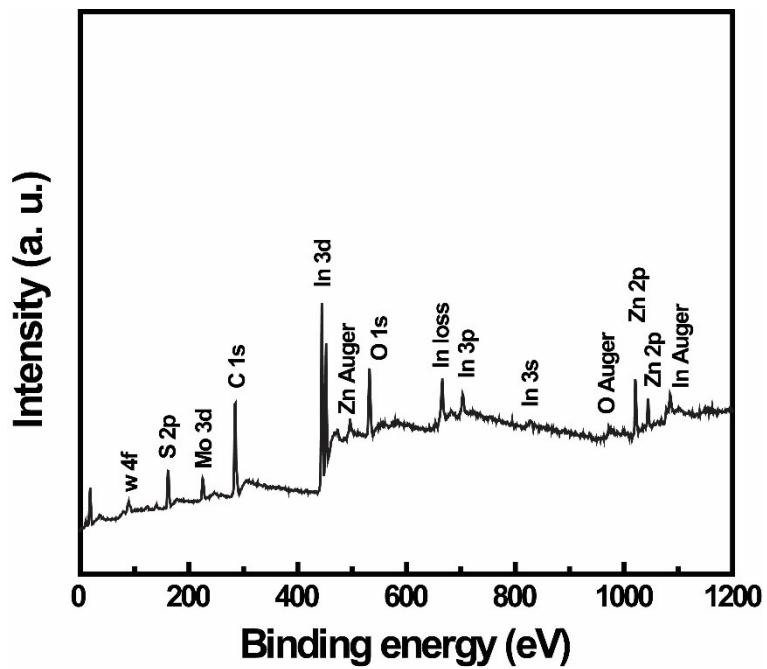
Supplementary Fig. S2



**Fig. S2.** (A) SEM image of ZIS/PZW (5%) and (B, C, D, E and F) corresponding element mappings (Zn, W, O, S and In).

---

Supplementary Fig. S3



**Fig. S3.** XPS survey spectrum of ZIS/PZW (5%).

---

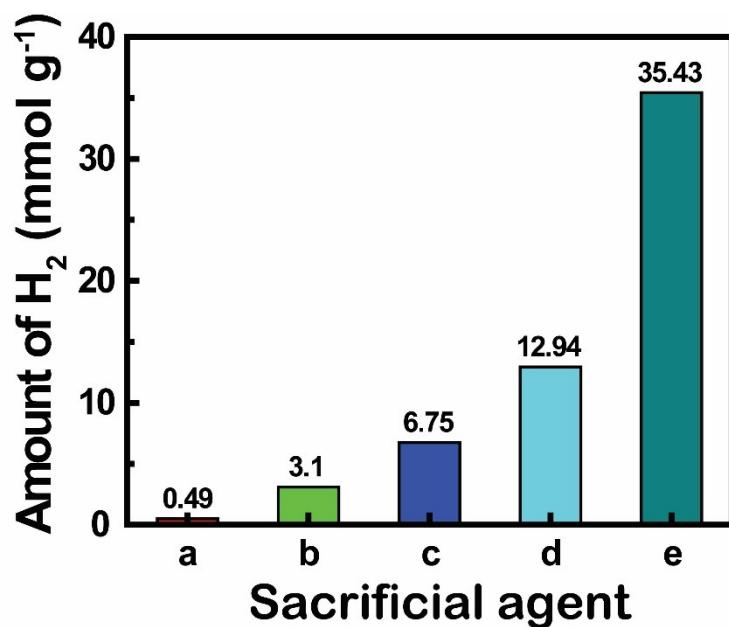
Supplementary Table S1

**Table S1.** Photocatalytic activity of the ZnIn<sub>2</sub>S<sub>4</sub>-based photocatalysts reported recently

| Photocatalysts  | H <sub>2</sub> generation rate (mmol g <sup>-1</sup> h <sup>-1</sup> ) | Ref.      |
|---|--|-----------|
| ZIS/PZW (5%)  | 8.86   | this work |
| ZnIn <sub>2</sub> S <sub>4</sub> nanosheets on FeWO <sub>4</sub> flowers                | 3.53   | 1         |
| NiWO <sub>4</sub> /ZnIn <sub>2</sub> S <sub>4</sub> heterojunction                      | 30.51  | 2         |
| NiS/ZnIn <sub>2</sub> S <sub>4</sub> /AgIn(WO <sub>4</sub> ) <sub>2</sub> nanocomposite | 4.82   | 3         |
| Ag <sub>2</sub> S modified ZnIn <sub>2</sub> S <sub>4</sub> nanosheets                  | 1.00   | 4         |
| ZnIn <sub>2</sub> S <sub>4</sub> /black TiO <sub>2</sub> hollow spheres                 | 5.56   | 5         |

---

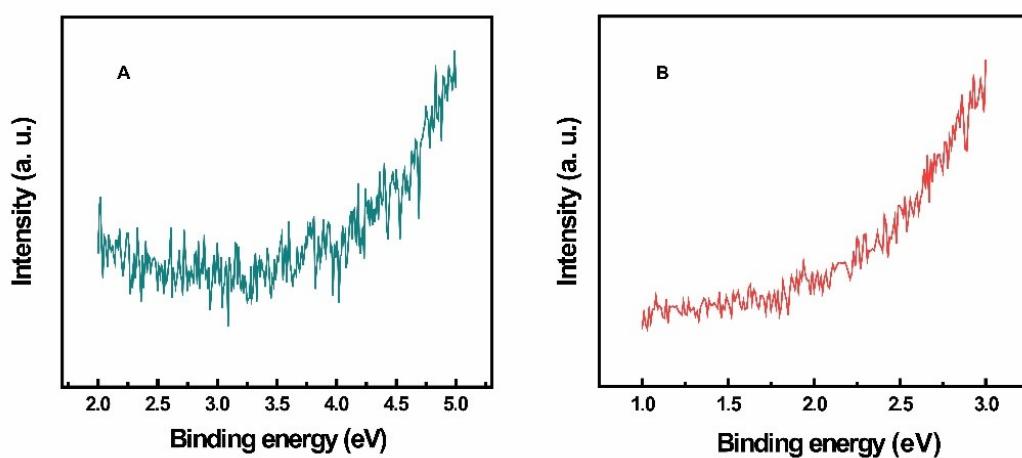
Supplementary Fig. S4



**Fig. S4.** Photocatalytic activity of ZIS/PZW (5%) for H<sub>2</sub> evolution when the sacrificial agent is (a) methyl alcohol, (b) glycol, (c) triethanolamine, (d) Na<sub>2</sub>S/Na<sub>2</sub>SO<sub>3</sub> or (e) lactic acid (photocatalyst 15 mg; temperature 10 °C; irradiation time 4 h).

---

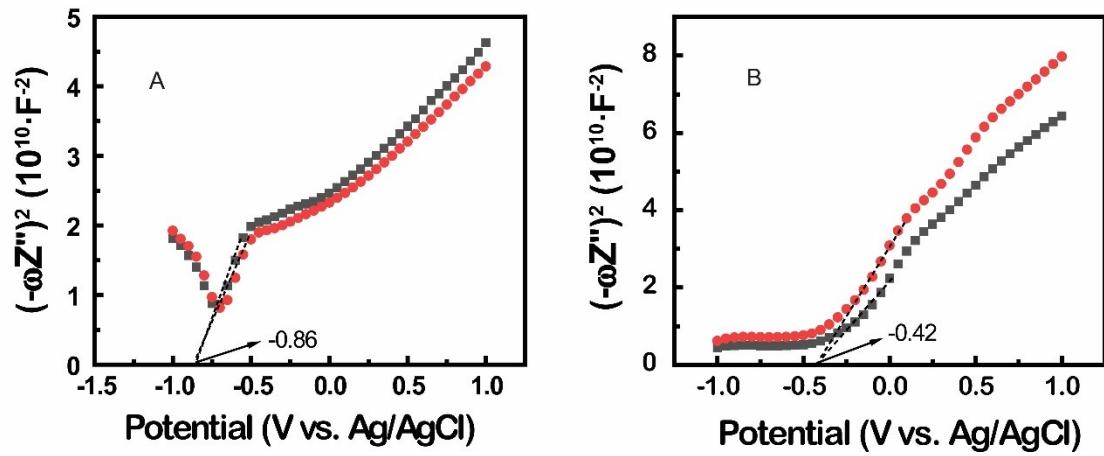
Supplementary Fig. S5



**Fig. S5.** UPS spectra of (A) the porous ZnWO<sub>4</sub> nanoflakelets and (B) the flower-like ZnIn<sub>2</sub>S<sub>4</sub> microspheres.

---

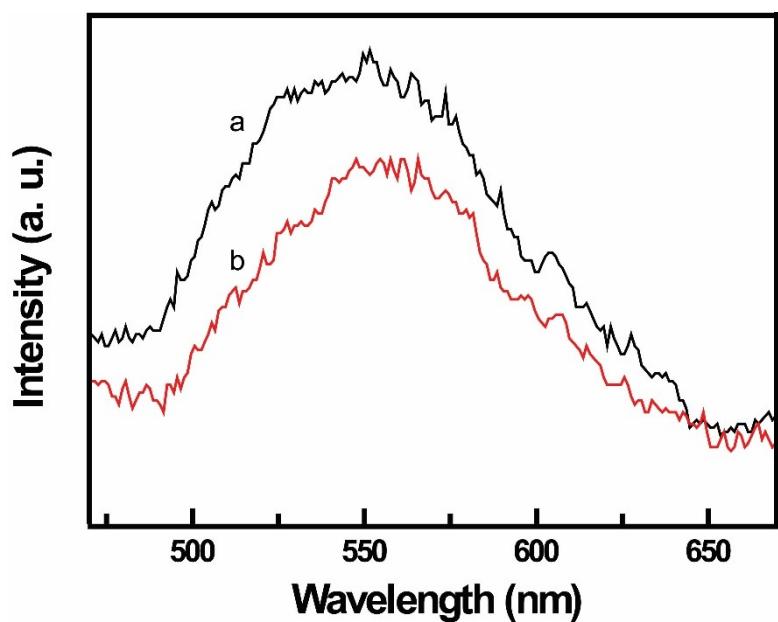
Supplementary Fig. S6



**Fig. S6.** Mott-Schottky curves of (A) the flower-like  $\text{ZnIn}_2\text{S}_4$  microspheres and (B) the porous  $\text{ZnWO}_4$  nanoflakelets.

---

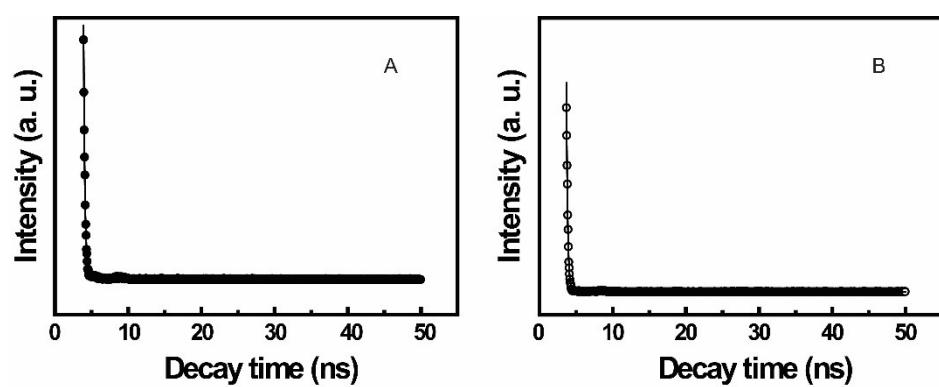
Supplementary Fig. S7



**Fig. S7.** Fluorescence spectra of (a) the  $\text{ZnIn}_2\text{S}_4$  microspheres and (b) ZIS/PZW (5%) when the excitation wavelength is 360 nm.

---

Supplementary Fig. S8



**Fig. S8.** Time-resolved fluorescence spectra of (A) the ZnIn<sub>2</sub>S<sub>4</sub> microspheres and (B) ZIS/PZW (5%).

---

## References

- [1] D. Kong, X. Hu, J. Geng, Y. Zhao, D. Fan, Y. Lu, W. Geng, D. Zhang, J. Liu, H. Li X. Pu, Growing ZnIn<sub>2</sub>S<sub>4</sub> nanosheets on FeWO<sub>4</sub> flowers with p-n heterojunction structure for efficient photocatalytic H<sub>2</sub> production, *Appl. Surf. Sci.*, 2022, **591**, 153256.
- [2] T. Gao, Y. Li, J. Tian, J. Fan, T. Sun, E. Liu, Facile fabrication of NiWO<sub>4</sub>/ZnIn<sub>2</sub>S<sub>4</sub> p-n heterojunction for enhanced photocatalytic H<sub>2</sub> evolution, *J. Alloys Compd.*, 2023, **951**, 169939.
- [3] H. Zhang, H. Gu, X. Wang, S. Chang, Q. Li, W.-L. Dai, Fabrication of noble-metal-free hierarchical rectangular tubular S-scheme NiS/ZnIn<sub>2</sub>S<sub>4</sub>/AgIn(WO<sub>4</sub>)<sub>2</sub> nanocomposite for highly efficient photocatalytic hydrogen evolution, *Chem. Eng. J.*, 2023, **457**, 141185.
- [4] J. Liu, G. Chen, J. Sun, Ag<sub>2</sub>S-modified ZnIn<sub>2</sub>S<sub>4</sub> nanosheets for photocatalytic H<sub>2</sub> generation, *ACS Appl. Nano Mater.*, 2020, **3**, 11017-11024.
- [5] B. Sun, J. Bu, Y. Du, X. Chen, Z. Li, W. Zhou, O. S-dual-vacancy defects mediated efficient charge separation in ZnIn<sub>2</sub>S<sub>4</sub>/black TiO<sub>2</sub> heterojunction hollow spheres for boosting photocatalytic hydrogen production, *ACS Appl. Mater. Interfaces*, 2021, **13**, 37545-37552.