

Table S1. Comparison with other catalysts

Semiconductor	Solvothermal method	Morphology	Sacrificial reagent	Light source (nm)	Optimal hydrogen evolution ($\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$)	Refs.
ZnIn ₂ S ₄ @NH ₂ -MIL-125(Ti)	Solvothermal method	Micropores and mesopores	Na ₂ S/Na ₂ SO ₃	300 W Xe lamp	2204.2 40 wt% NH ₂ -MIL-125(Ti)	1
g-C ₃ N ₄ @ZnIn ₂ S ₄	Solvothermal method	2D/2D g-C ₃ N ₄ nanosheet@ZnIn ₂ S ₄ nanoleaf	Triethanolamin e	300 W Xe lamp	2780	2
Co(dmgH) ₂ pyC /ZnIn ₂ S ₄	Impregnating method	Microsphere s	Triethanolamin e	300 W Xe lamp	3840	3
CQDs/ZnIn ₂ S ₄	Microwave hydrothermal method	Microsphere s	N/A	350 W Xe lamp	1032.2	4
MoS ₂ /ZnIn ₂ S ₄	Hydrothermal method	Nanoparticl es	Na ₂ S/Na ₂ SO ₃	300 W Xe lamp	2080 0.5 wt% MoS ₂ /ZnIn ₂ S ₄	5
In ₂ S ₃ /ZnIn ₂ S ₄	Ion-exchange method	Microflower s	Na ₂ S/K ₂ SO ₃	300 W Xe lamp	678	6
CdS/ZnFe ₂ O ₄ /ZnIn ₂ S ₄	Solvothermal processes & Ionic layer adsorption-reaction method	Nanosheet stereoscopic films	Na ₂ S/Na ₂ SO ₃	300 W Xe lamp	79.0 $\mu\text{mol h}^{-1}$ 1-CdS/ZnFe ₂ O ₄ /ZnIn ₂ S ₄	7

- [1] H. Liu, J. Zhang, D. Ao, Construction of heterostructured ZnIn₂S₄@NH₂-MIL-125(Ti) nanocomposites for visible-light-driven H₂ production, *Appl. Catal. B Environ.* 221 (2018) 433–442.
- [2] B. Lin, H. Li, H. An, W. Hao, J. Wei, Y. Dai, C. Ma, G. Yang, Preparation of 2D/2D g-C₃N₄ nanosheet@ZnIn₂S₄ nanoleaf heterojunctions with well-designed high-speed charge transfer nanochannels towards high-efficiency photocatalytic hydrogen evolution, *Appl. Catal. B Environ.* 220 (2018) 542–552.
- [3] Y. Gao, H. Lin, S. Zhang, Z. Li, Co(dmgH)₂pyCl as a noble-metal-free co-catalyst for highly efficient photocatalytic hydrogen evolution over hexagonal ZnIn₂S₄, *RSC*

Adv. 6 (2016) 6072–6076.

- [4] Q. Li, C. Cui, H. Meng, J. Yu, Visible-light photocatalytic hydrogen production activity of ZnIn₂S₄ microspheres using carbon quantum dots and platinum as dual co-catalysts, Chem. Asian. J. 9 (2014) 1766–1770.
- [5] T. Huang, W. Chen, T. Liu, Q. Hao, X. Liu, ZnIn₂S₄ hybrid with MoS₂: a non-noble metal photocatalyst with efficient photocatalytic activity for hydrogen evolution, Powder. Technol. 315 (2017) 157–162.
- [6] Z. Mei, S. Ouyang, D. Tang, T. Kako, D. Golberg, J. Ye, An ion-exchange route for the synthesis of hierarchical In₂S₃/ZnIn₂S₄ bulk composite and its photocatalytic activity under visible-light irradiation, Dalton Trans. 42 (2013) 2687–2690.
- [7] Y. Chen, G. Tian, W. Zhou, Y. Xiao, J. Wang, X. Zhang, H. Fu, Enhanced photo-generated carrier separation in CdS quantum dot sensitized ZnFe₂O₄/ZnIn₂S₄ nanosheet stereoscopic films for exceptional visible light photocatalytic H₂ evolution performance, Nanoscale 9 (2017) 5912–5921.

Figure S1. TG results of the Co₃O₄(20)@ZIS

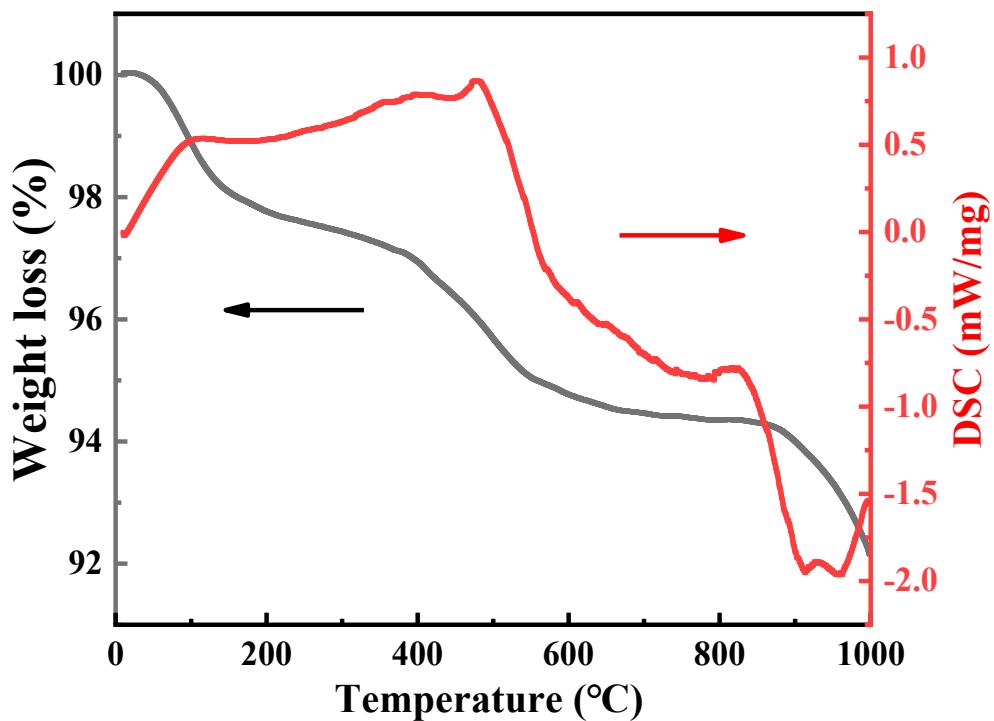


Figure S2. Three cycles of experiment of the $\text{Co}_3\text{O}_4(20)\text{@ZIS}$

