Supporting information

Polytyped wurtzite-nH ZnS (n=2, 8): Facile synthesis and photocatalytic hydrogen production under sacrificial reagents

Huajuan Ren, Kun Ye, Haoyu Chen, Xuemei Zhou, Feiyu Wang, Qiaofang Shi*, Guowang Diao, Ming Chen*

School of Chemistry and Chemical Engineering, Yangzhou University, Yangzhou 225002, P. R. China

* Corresponding Authors
E-mail address: chenming@yzu.edu.cn (M. Chen); qfshi@yzu.edu.cn (Q. Shi)

Experimental materials

Anhydrous zinc acetate was purchased from Saen Chemical Technology (Shanghai) Co., Ltd. Thiourea and anhydrous sodium sulfite were purchased from Sinopharm Chemical Reagent Co., Ltd. Hydrazine hydrate and ethylenediamine was obtained from Xuchen Chemical Technology Co., Ltd. Sodium sulfide nonahydrate and Cetyl Trimethyl Ammonium Bromide (CTAB) were both purchased from Aladdin. Nafion (5 wt %) was purchased from Sigma-Aldrich Chemical Reagent Co., Ltd. (USA). Deionized water was used throughout the experiments.

Synthesis of $ZnS(en)_{0.5}$

In a typical synthesis, 1 mmol of $Zn(Ac)_2$ and 2 mmol of thiourea were added into an autoclave with an inner Teflon lining which had been filled with 60 mL ethylenediamine of its capacity (100 mL) and heated at 180 ℃ for 18 h. After that, the white precipitate was collected by centrifugation, and then dried in an oven. Here, $ZnS(en)_{0.5}$ precursor was synthesized successfully.

Table S1. Comparison of photocatalytic H_2 production performance of previously reported ZnS-based photocatalysts with the as-prepared ZnS photocatalysts.

Photocatalyst	Synthesis method	Light source	Sacrificial reagent	Activity (μmol h^{-1})	Published year	Ref.
ZnS hollow nanospheres	Hydrothermal	300 W Xe lamp (AM 1.5 G)	0.35 M Na_2S and 0.25 M Na_2SO_3	80.1		This work
ZnS nanosheets	Solvothermal	300 W Xe lamp (AM 1.5 G)	0.35 M Na_2S and 0.25 M Na_2SO_3	9.24		This work
Graphene Oxide-$Zn_xCd_{1-x}S$	Coprecipitation-hydrothermal	Simulated sunlight (AM 1.5 G)	0.35 M Na_2S and 0.25 M Na_2SO_3	1.82	2012	1
5.0 % Pd /ZnS	Co-precipitation	300 W Xe lamp ($\lambda \geq 420$ nm)	0.35 M Na_2S and 0.25 M Na_2SO_3	10.22	2018	2
2.0 % Au ZnO@ZnS	Chemical deposition	300 W Xe lamp ($\lambda \geq 400$ nm)	0.35 M Na_2S and 0.25 M Na_2SO_3	30.43	2019	3
Pt/Mn-ZnS	Solvothermal	300 W Xe lamp ($\lambda \geq 400$ nm)	0.35 M Na_2S and 0.25 M Na_2SO_3	0.42	2017	4
$Zn_{1-x}Cd_xS$/D-ZnS $(en)_{0.5}$	Solvothermal	300 W Xe lamp ($\lambda \geq 400$ nm)	0.35 M Na_2S and 0.25 M Na_2SO_3	463.6	2018	5
ZnS	ionic solutions	150 W Xe lamp (AM 1.5 G)	60 mM Na_2S	1.35	2014	6
CuS/ZnS	Hydrothermal	350 W Xe lamp ($\lambda \leq 420$ nm)	0.35 M Na_2S and 0.25 M Na_2SO_3	257.6	2015	7
Ni-P/defect-rich ZnS	Hydrothermal /Photodeposition	300 W Xe lamp ($\lambda \geq 400$ nm)	0.35 M Na_2S and 0.25 M Na_2SO_3	69.92	2020	8

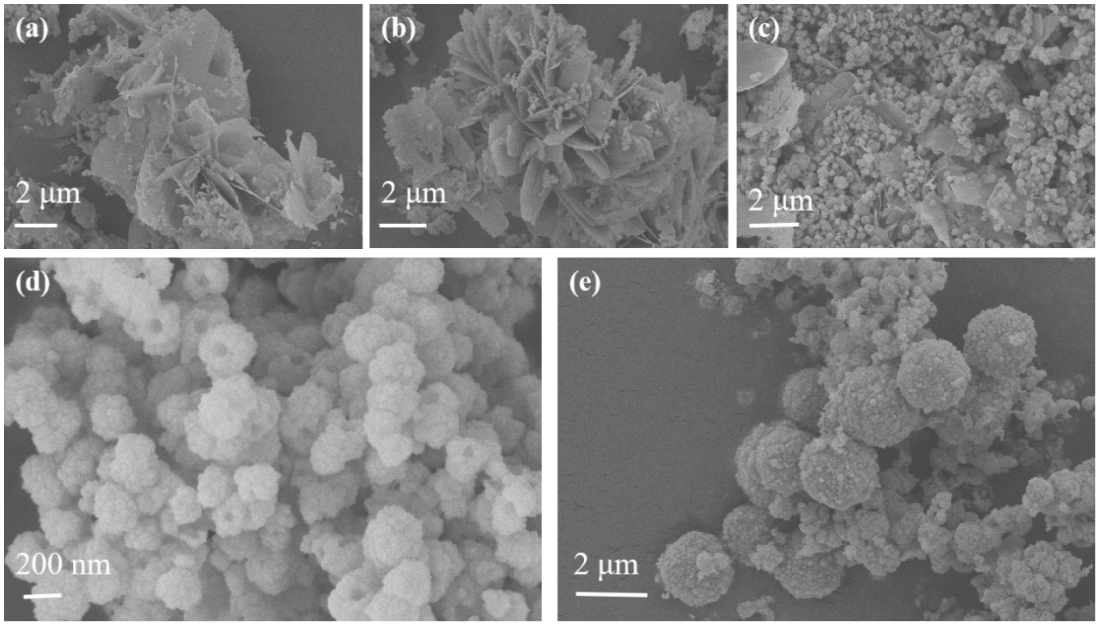

Fig. S1. SEM images of ZnS (a) the molar ratio of Zn to S is 1:1, (b) 1: 2, (c) 1:2.5, (d) 1:3 (ZnS hollow spheres), (e) 1:4.

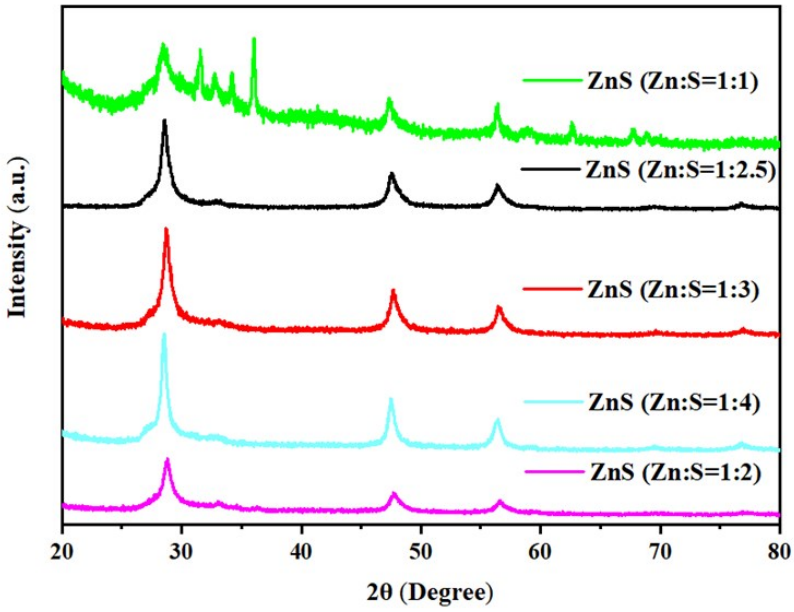

Fig. S2. XRD pattens of ZnS (a) the molar ratio of Zn to S is 1:1, (b) 1: 2, (c) 1:2.5, (d) 1:3 (ZnS hollow spheres), (e)1:4.

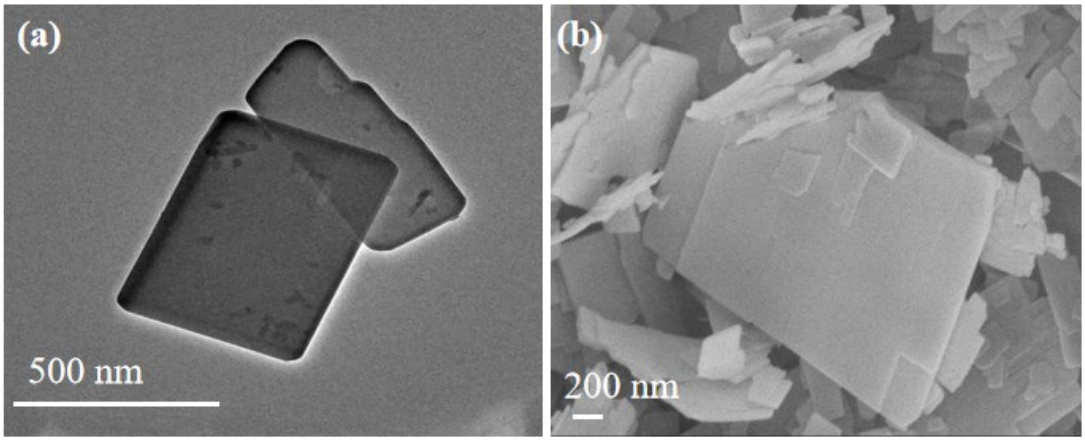

Fig. S3. (a) TEM and (b) SEM images of $ZnS(en)_{0.5}$.

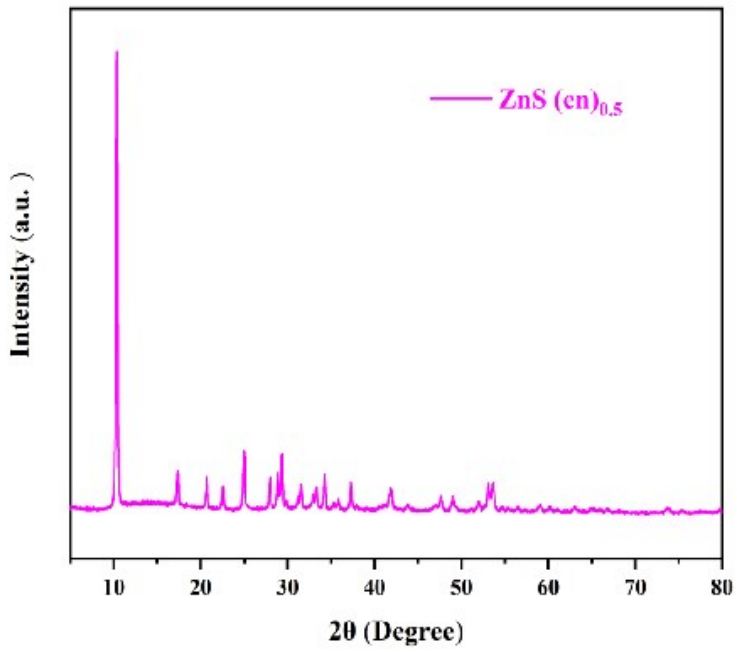

Fig. S4. XRD pattern of $ZnS(en)_{0.5}$.

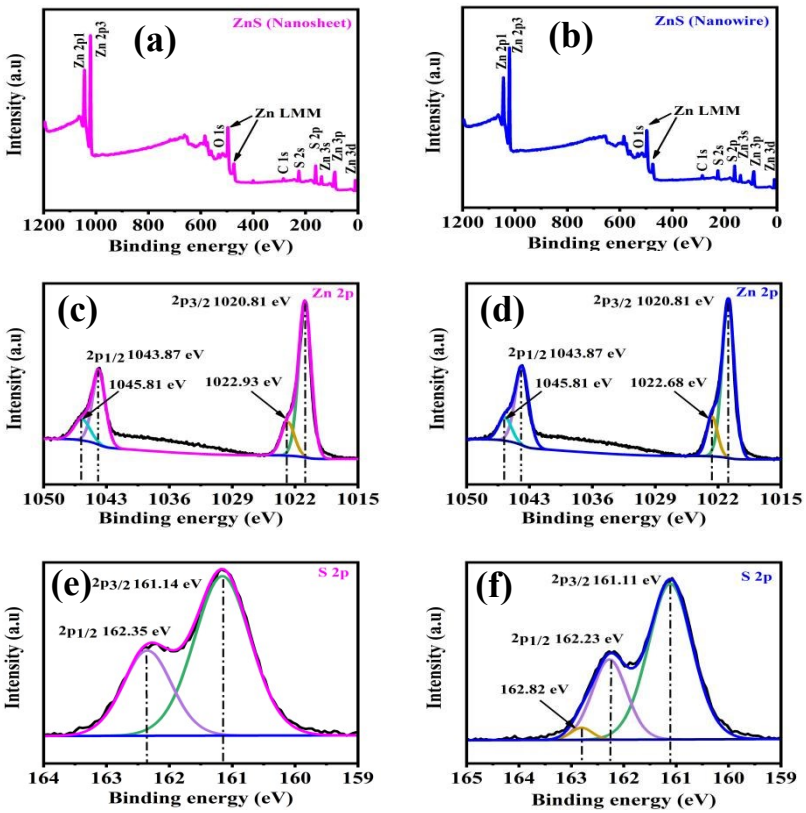

Fig. S5. High-resolution XPS spectra of ZnS nanosheets: (a) fully scanned spectra, (c) Zn 2p, (e) S 2p. High-resolution XPS spectra of ZnS nanowires: (b) fully scanned spectra, (d) Zn 2p, (f) S 2p.

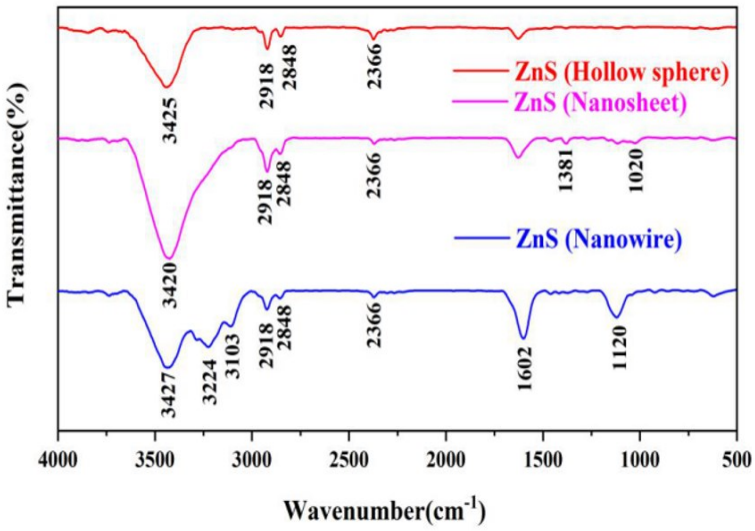

Fig. S6. FT-IR spectroscopy of the three samples.

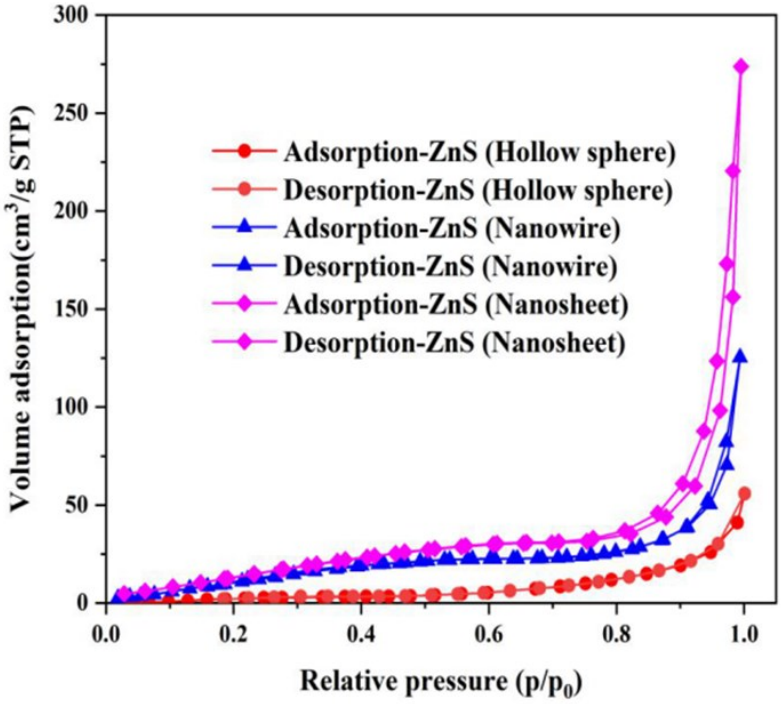

Fig. S7. Nitrogen adsorption/desorption isotherms of the three samples.

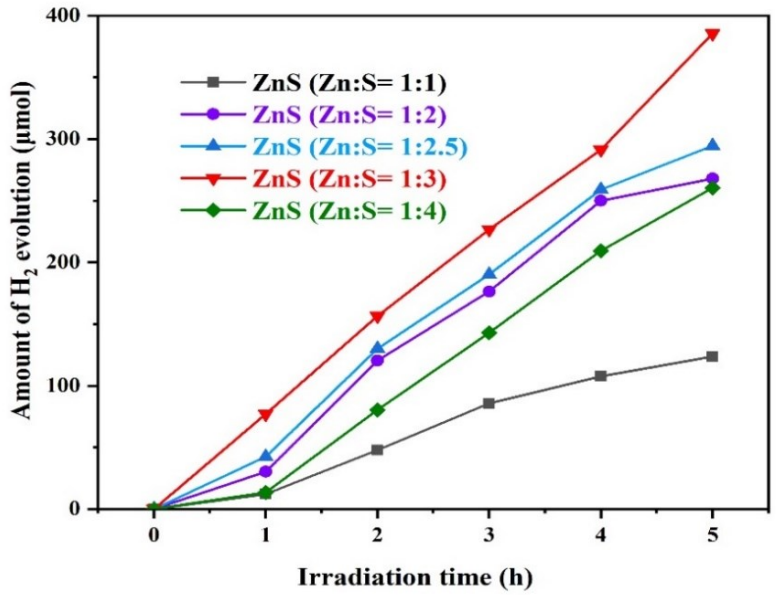

Fig. S8. The photocatalytic hydrogen evolution of ZnS (a) the Molar ratio of Zn to S is 1:1, (b) 1: 2, (c) 1:2.5, (d) 1:3 (ZnS hollow spheres), (e) 1:4.

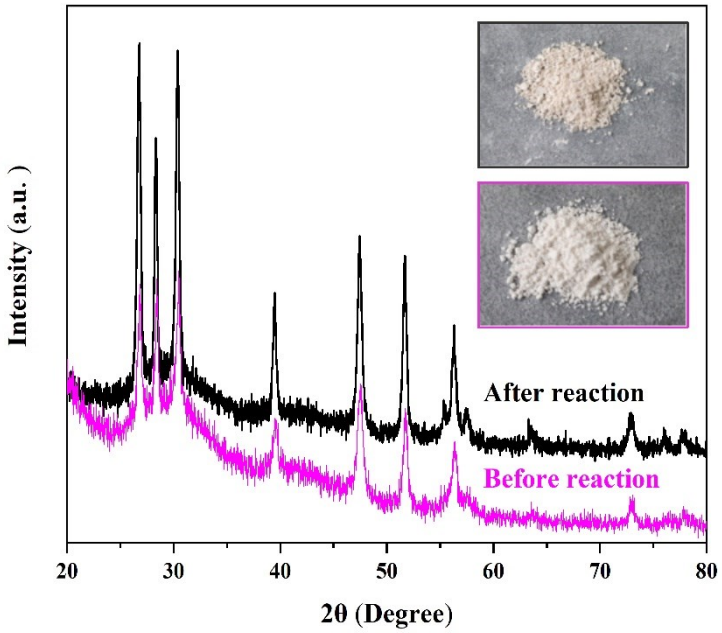

Fig. S9. Comparison of XRD pattern before and after photocatalytic hydrogen production experiment of ZnS nanosheets.

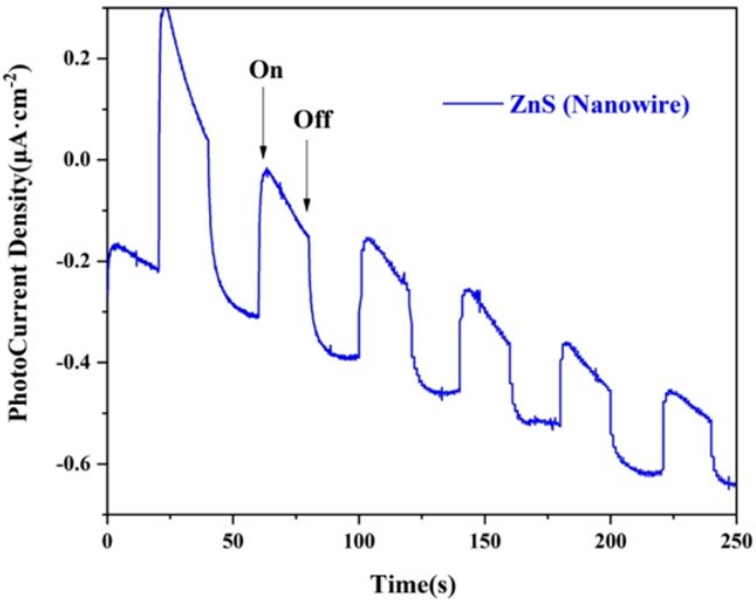

Fig. S10. Transient photocurrent response for the ZnS nanowires in 0.5 M Na_2SO_4 aqueous solution under 300 W light irradiation (AM 1.5 G).

References

1. Zhang, J.; Yu, J.; Jaroniec, M.; Gong, J. R., Noble metal-free reduced graphene oxide-$Zn_xCd_{1-x}S$ nanocomposite with enhanced solar photocatalytic H_2-production performance. *Nano Lett.* **2012,** 12 (9), 4584-4589.

2. Gaikwad, A. P.; Betty, C. A.; Jagannath; Kumar, A.; Sasikala, R., Microflowers of Pd doped ZnS for visible light photocatalytic and photoelectrochemical applications. *Mater. Sci. Semicond. Process.* **2018,** 86, 139-145.

3. Ma, D.; Shi, J.-W.; Sun, D.; Zou, Y.; Cheng, L.; He, C.; Wang, H.; Niu, C.; Wang, L., Au decorated hollow ZnO@ZnS heterostructure for enhanced photocatalytic hydrogen evolution: The insight into the roles of hollow channel and Au nanoparticles. *Appl. Catal., B* **2019,** 244, 748-757.

4. Wang, L.; Wang, P.; Huang, B.; Ma, X.; Wang, G.; Dai, Y.; Zhang, X.; Qin, X., Synthesis of Mn-doped ZnS microspheres with enhanced visible light photocatalytic activity. *Appl. Surf. Sci.* **2017,** 391, 557-564.

5. Feng, W.; Wang, Y.; Huang, X.; Wang, K.; Gao, F.; Zhao, Y.; Wang, B.; Zhang, L.; Liu, P., One-pot construction of 1D/2D $Zn_{1-x}Cd_xS$/D-$ZnS(en)_{0.5}$ composites with perfect heterojunctions and their superior visible-light-driven photocatalytic H_2 evolution. *Appl. Catal., B* **2018,** 220, 324-336.

6. Hong, E.; Kim, D.; Kim, J. H., Heterostructured metal sulfide (ZnS–CuS–CdS) photocatalyst for high electron utilization in hydrogen production from solar water splitting. *J. Ind. Eng. Chem.* **2014,** 20 (5), 3869-3874.

7. Hong, Y.; Zhang, J.; Huang, F.; Zhang, J.; Wang, X.; Wu, Z.; Lin, Z.; Yu, J., Enhanced visible light photocatalytic hydrogen production activity of CuS/ZnS nanoflower spheres. *J. Mater. Chem. A* **2015,** 3 (26), 13913-13919.

8. Zhu, S.; Qian, X.; Lan, D.; Yu, Z.; Wang, X.; Su, W., Accelerating charge transfer for highly efficient visible-light-driven photocatalytic H_2 production: In-situ constructing Schottky junction via anchoring Ni-P alloy onto defect-rich ZnS. *Appl. Catal., B* **2020,** 269, 118806.