Electronic Supplementary Material (ESI) for Nanoscale.

Supporting information

Facile In Situ Formation of Ternary 3D $ZnIn_2S_4$-MoS_2 Microsphere/1D CdS Nanorod Heterostructure for the High-efficiency Visible-light Photocatalytic H_2 Production

Lan Wang,*[a] Hanghang Zhou,[a] Hongzhong Zhang,*[a] Yali Song,[a] Huan Zhang,[a] Lingkun Luo,[a] Yifan Yang,[a] Shiqi Bai,[a] Yue Wang,[a] and Shuaixia Liu*[b]

[a]*Henan Collaborative Innovation Center of Environmental Pollution Control and Ecological Restoration, School of Material and Chemical Engineering, Zhengzhou University of Light Industry, Zhengzhou 450001, China*

[b]*School of Resources and Environment, Henan University of Engineering, Zhengzhou 450001, China*

Tel: 86-10-63556510; E-mail: lwang2017@zzuli.edu.cn, zhz@zzuli.edu.cn and lsx94528@163.com

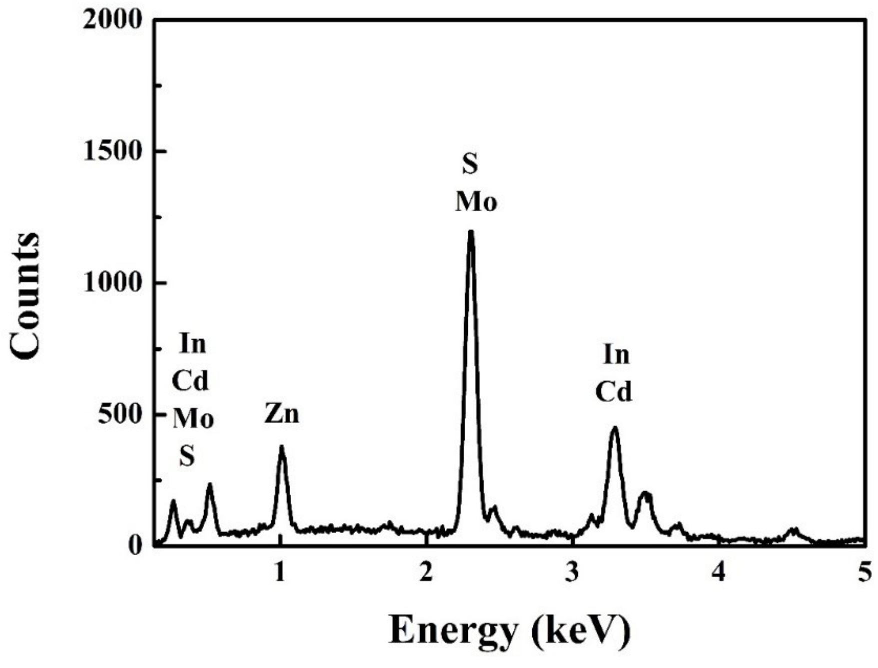

Figure S1 EDS spectrum of ZIS/MoS_2/CdS composite

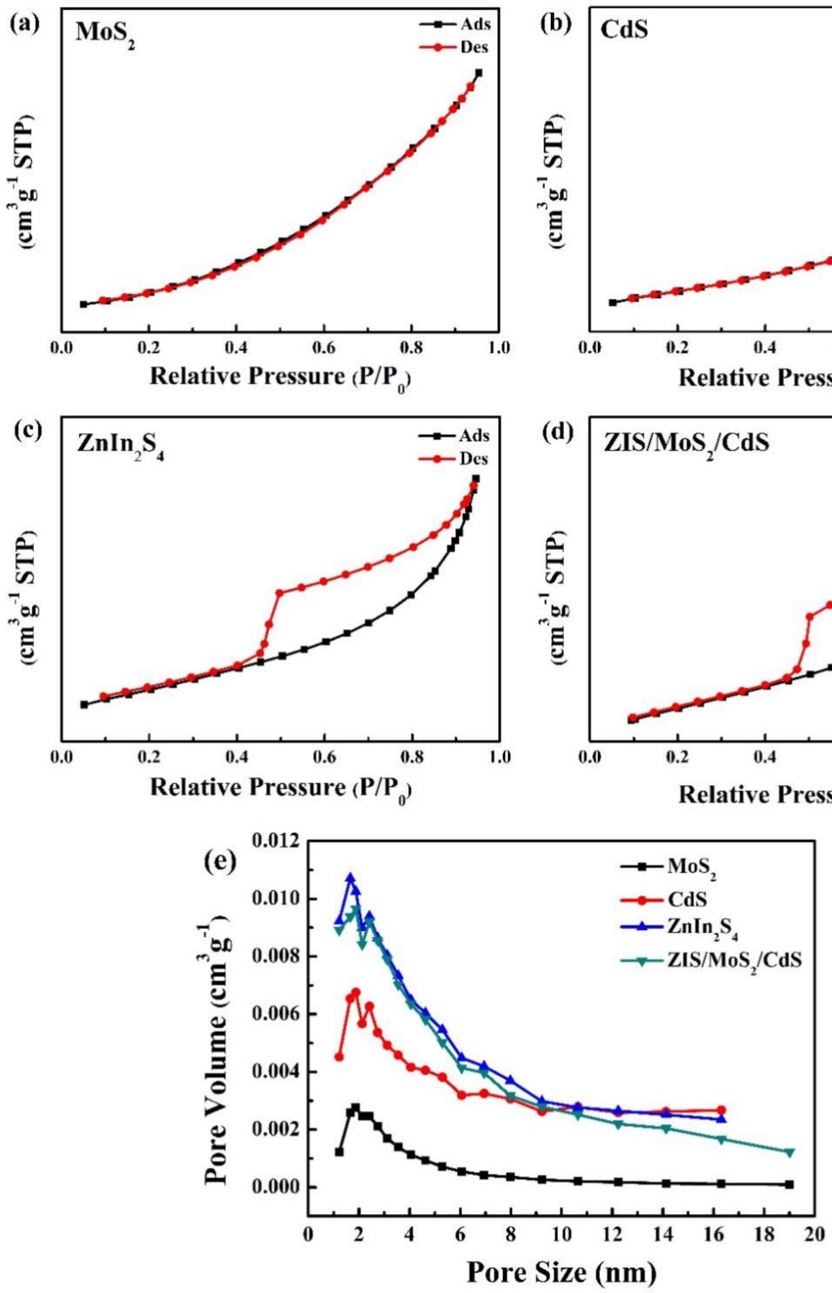

Figure S2 (a-d) Nitrogen adsorption-desorption isotherms and

(e) corresponding the Barrett-Joyner-Halenda (BJH) pore size distribution curves of

MoS_2, CdS, $ZnIn_2S_4$ and ZIS/MoS_2/CdS samples

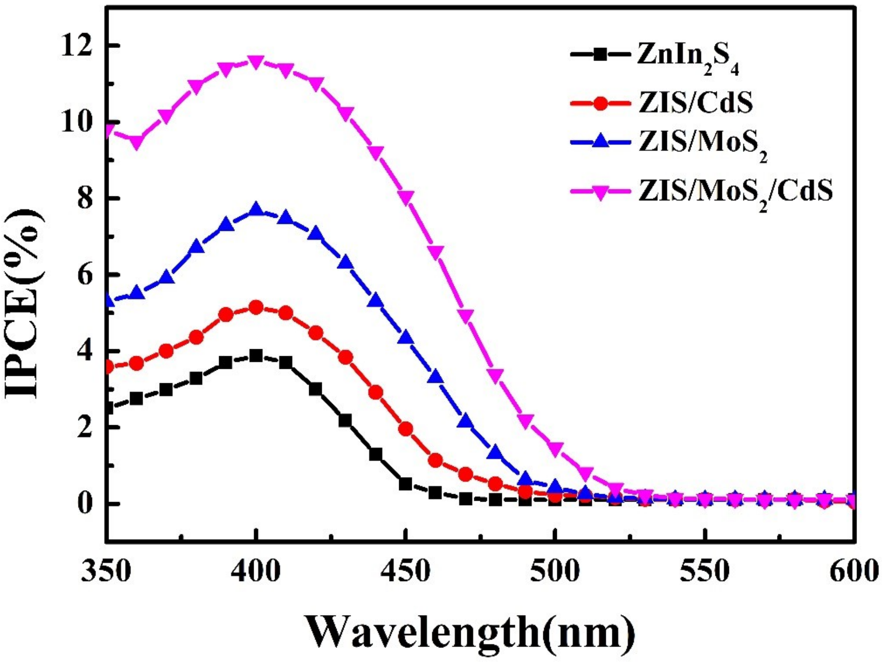

Fig. S3. IPCE spectra of the samples collected at the incident wavelength range from 350 nm to 600 nm at a potential of 1.23 V vs. RHE in 0.1M NaOH electrolyte.

Table S1. BET surface area, pore size, pore volume of the synthesized composite.

Samples	S_{BET} (m^2/g)	Pore Size (nm)	Pore volume (cm^3/g)
MoS_2	3.1665	10.754	0.008513
CdS	22.558	10.864	0.061268
$ZnIn_2S_4$	34.924	8.5996	0.075082
ZIS/MoS_2/CdS	37.629	7.7897	0.07328

Table S2. The apparent quantum efficiency (AQE) of MoS_2, CdS, $ZnIn_2S_4$, ZIS/CdS, MoS_2/CdS, ZIS/MoS_2 and ZIS/MoS_2/CdS

The apparent quantum efficiency (AQE) was analyzed with a wavelength of 420 nm under the 300 W Xe lamp (PLS-SXE300) irradiation. The other experimental conditions were similar to the photocatalytic hydrogen evolution measurement as described before. The light intensity was obtained with an optical power meter (PL-MW2000, Beijing Perfectlight Co. Ltd., China). For example, if 420 nm is used, the average light intensity is 20.4 mW cm^{-2}. The irradiation area is 19.625 cm^2 (2.5 cm radius). The number of incident photons (N) is 1.8×10^{22} calculated by equation (1). The amount of H_2 molecules generated for 6 h were about 4542.3 μmol. The AQE was then calculated in equation (2).

$$N=\frac{E\lambda}{hc}=\frac{20.4\times19.625\times10^{-3}\times6\times3600\times420\times10^{-9}}{6.626\times10^{-34}\times3\times10^{8}}=1.8\times10^{22} \qquad (1)$$

$$
\begin{aligned}
AQE &= \frac{the\ number\ of\ reacted\ electrons}{the\ number\ of\ incident\ photons} \times 100\% \\
&= \frac{2 \times the\ number\ of\ evolved\ H_2\ molecules}{N} \times 100\% \qquad (2) \\
&= \frac{2 \times 6.02 \times 10^{23} \times 4542.3 \times 10^{-6}}{1.8 \times 10^{22}} \times 100\% = 30.38\%
\end{aligned}
$$

Samples	AQE (%)
MoS_2	0
CdS	0.44
$ZnIn_2S_4$	0.78
ZIS/CdS	1.56
MoS_2/CdS	1.14
ZIS/MoS_2	17.21
ZIS/MoS_2/CdS	30.38

Table S3. AQE over some $ZnIn_2S_4$-based photocatalysts in reported work in contrast with this work.

Sample	Light source	Sacrificial agents	AQE	Reference
ZIS/MoS_2/CdS	λ > 420 nm	10% TEOA	30.38%	In this paper
3wt% MoS_2/CQDs/$ZnIn_2S_4$	λ > 420 nm	0.1 M Na_2S/Na_2SO_3	25.6%	1
6wt%MoS_2/Cu-$ZnIn_2S_4$	λ > 420 nm	0.1M	13.6%	2

		ascorbic acid		
1wt%MoS_2/$ZnIn_2S_4$	λ > 420 nm	10vol% lactic acid	3.08%	3
RGO/$ZnIn_2S_4$	λ > 420 nm	10vol% TEOA	4.4%	4
$ZnIn_2S_4$/g-C_3N_4	λ > 420 nm	20vol% TEOA	7.05%	5
$ZnIn_2S_4$/pCN	λ > 400 nm	20vol% TEOA	0.92%	6
$ZnIn_2S_4$@NH_2-MIL-125(Ti)	λ > 420 nm	0.25 M Na_2SO_3 &0.35 M Na_2S	4.3%	7
Ni_2P/$ZnIn_2S_4$	λ > 400 nm	10vol% lactic acid	7.7%	8
$CuInS_2$/$ZnIn_2S_4$	λ > 420 nm	Na_2S&Na_2SO_3	12.4%	9
$ZnIn_2S_4$/$Ni_{12}P_5$	λ > 420 nm	0.25 M Na_2SO_3 &0.35 M Na_2S	20.5%	10
$ZnIn_2S_4$/$MoSe_2$	λ > 420 nm	0.25 M Na_2SO_3 &0.35 M Na_2S	21.39%	11

Table S4. Photocatalytic degradation of organic pollutant with simultaneous hydrogen evolution over the reported $ZnIn_2S_4$/X composite

Sample	Hydrogen production rate (μ mol g^{-1} h^{-1})	The hydrogen production rate ratio ($ZnIn_2S_4$/X vs $ZnIn_2S4$)	Condition: sacrificial agents, cocatalyst light	Reference
ZIS/MoS_2/CdS	7570.4	39.8	10vol% TEOA	In this paper
$ZnIn_2S_4$	190.1		λ > 420 nm	
3wt% MoS_2/CQDs/$ZnIn_2S_4$	3000	17.8	0.1 M Na_2S/Na_2SO_3	1
$ZnIn_2S_4$	168		λ > 420 nm	
1wt%MoS_2/$ZnIn_2S_4$	2512.5	8.7	8% lactic acid	3
$ZnIn_2S_4$	287.5		λ > 420 nm	
MoS_2-QDs/$ZnIn_2S_4$	7156	9	TEOA	12
$ZnIn_2S_4$	794.7		λ > 420 nm	
$ZnIn_2S_4$/MoS_2-RGO	425.1	34.6	20vol% lactic acid	13
$ZnIn_2S_4$	12.3		λ > 420 nm	
2wt% 1T-Li_xMoS_2/$ZnIn_2S_4$	6648	2.4	0.25 M Na_2SO_3 & 0.35 M Na_2S	14
$ZnIn_2S_4$	2270		λ > 420 nm	
MoS_2/$ZnIn_2S_4$	8898	16	10vol% TEOA	15
$ZnIn_2S_4$	556		λ > 400 nm	
CdS/QDs/$ZnIn_2S_4$	2107.5	62	20vol% lactic acid	16
$ZnIn_2S_4$	33.9		λ > 420 nm	

5%-MoS_2/$ZnIn_2S_4$ $ZnIn_2S_4$	3891.6 10.2	381	0.25 M Na_2SO_3 &0.35 M Na_2S λ > 420 nm	17
RGO/$ZnIn_2S_4$ $ZnIn_2S_4$	2640.8 625.6	4.2	10vol% TEOA 0.3 wt% Pt λ > 420 nm	4
$ZnIn_2S_4$/g-C_3N_4 $ZnIn_2S_4$	2780 180.6	15.4	20vol% TEOA λ > 420 nm	5
$ZnIn_2S_4$/pCN $ZnIn_2S_4$	8601 3739	2.3	20vol% TEOA λ > 400 nm	6
$ZnIn_2S_4$@NH_2-MIL-125(Ti) $ZnIn_2S_4$	2204.2 339	6.5	0.25 M Na_2SO_3 &0.35 M Na_2S λ > 420 nm	7
$ZnIn_2S_4$/$Ni_{12}P_5$ $ZnIn_2S_4$	2263 1115	2	0.25 M Na_2SO_3 &0.35 M Na_2S λ > 420 nm	10
$ZnIn_2S_4$/$MoSe_2$ $ZnIn_2S_4$	2228 1023	2.2	0.25 M Na_2SO_3 &0.35 M Na_2S λ > 420 nm	11
NiS/$ZnIn_2S_4$ $ZnIn_2S_4$	3333 1133	2.9	50vol% lactic acid λ > 420 nm	18

$AgIn_5S_8/ZnIn_2S_4$	949.9	3.6	0.25 M Na_2S & 0.25 M Na_2SO_3 2 wt% Pt $\lambda > 420$ nm	19
$ZnIn_2S_4$	263.8			
$3\%WS_2/ZnIn_2S_4$	199.1	6	0.25 M Na_2SO_3 & 0.35 M Na_2S $\lambda \geq 420$ nm	20
$ZnIn_2S_4$	33.2			

REFERENCE

1 B. Wang, Z. Deng, X. Fu and Z. Li, *J. Mater. Chem. A*, 2018, **6**, 19735-19742.

2 Y. J. Yuan, D. Chen, J. Zhong, L. X. Yang, J. Wang, M. J. Liu, W. G. Tu, Z. T. Yu and Z. G. Zou, *J. Mater. Chem. A*, 2017, **5**, 15771-15779.

3 C. Liu, B. Chai, C. Wang, J. Yan and Z. Ren, *Internat. J. Hydrogen Energ.*, 2018, **43**, 6977-6986.

4 Y. Xia, Q. Li, K. Lv, D. Tang and M. Li, *Appl. Catal., B*, 2017, **206**, 344-352.

5 B. Lin, H. Li, H. An, W. Hao, J. Wei, Y. Dai, C. Ma and G. Yang, *Appl. Catal., B*, 2018, **220**, 542-552.

6 H. Yang, R. Cao, P. Sun, J. Yin, S. Zhang and X. Xu, *Appl. Catal., B*, 2019, **256**, 117862.

7 H. Liu, J. Zhang and D. Ao, *Appl. Catal., B*, 2018, **221**, 433-442.

8 X. l. Li, X. j. Wang, J. y. Zhu, Y. p. Li, J. Zhao and F. t. Li, *Chem. Eng.g J.*, 2018, **353**, 15-24.

9 Z. Guan, J. Pan, Q. Li, G. Li and J. Yang, *ACS Sustain. Chem. Eng.*, 2019, **7**, 7736-7742.

10 D. Zeng, Z. Lu, X. Gao, B. Wu and W. J. Ong, *Catal. Sci. Technol.*, 2019, **9**, 4010-4016.

11 D. Zeng, L. Xiao, W.-J. Ong, P. Wu, H. Zheng, Y. Chen and D. L. Peng, *ChemSusChem*, 2017,

10, 4624-4631.

12 Y. Liu, C. F. Li, X. Y. Li, W. B. Yu, W. D. Dong, H. Zhao, Z. Y. Hu, Z. Deng, C. Wang, S. J. Wu, H. Chen, J. Liu, Z. Wang, L. H. Chen, Y. Li and B. L. Su, *J.Colloid Interf. Sci.*, 2019, **551**, 111-118.

13 Z. Guan, P. Wang, Q. Li, G. Li and J. Yang, *Dalton T.*, 2018, **47**, 6800-6807.

14 J. Liu, W. Fang, Z. Wei, Z. Qin, Z. Jiang and W. Shangguan, *Catal. Sci. Technol.*, 2018, **8**, 1375-1382.

15 W. Li, Z. Lin and G. Yang, *Nanoscale*, 2017, **9**, 18290-18298.

16 W. Chen, R. Q. Yan, J. Q. Zhu, G. B. Huang and Z. Chen, *Appl. Surf. Sci.*, 2020, **504**, 144406.

17 Z. Zhang, L. Huang, J. Zhang, F. Wang, Y. Xie, X. Shang, Y. Gu, H. Zhao and X. Wang, *Appl. Catal., B*, 2018, **233**, 112-119.

18 A. Yan, X. Shi, F. Huang, M. Fujitsuka and T. Majima, *Appl. Catal., B*, 2019, **250**, 163-170.

19 Z. Guan, Z. Xu, Q. Li, P. Wang, G. Li and J. Yang, *Appl. Catal., B*, 2018, **227**, 512-518.

20 J. Zhou, D. Chen, L. Bai, L. Qin, X. Sun and Y. Huang, *Internat. J. Hydrogen Energ.*, 2018, **43**, 18261-18269.