Supporting information

Highly Efficient Solar-driven Photocatalytic Hydrogen Evolution by Ternary 3D $ZnIn_2S_4$-MoS_2 Microsphere/1D TiO_2 Nanobelt Heterostructure

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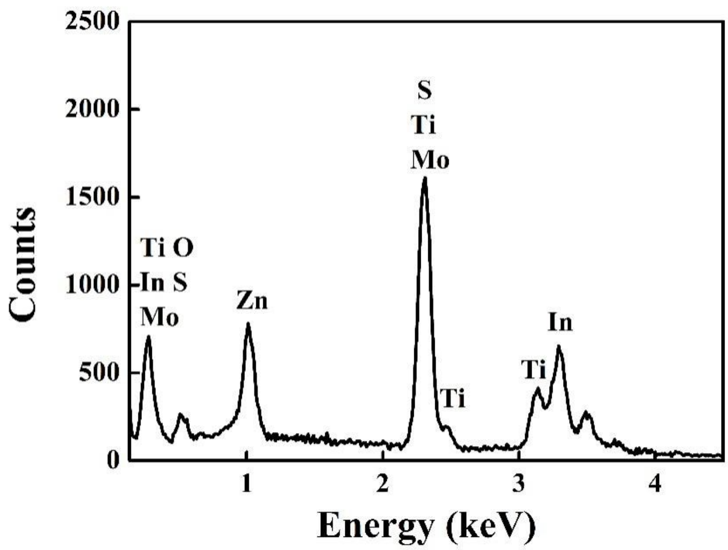

Figure S1 EDS spectrum of 250%-ZIS/25%-MoS_2/TiO_2 composite

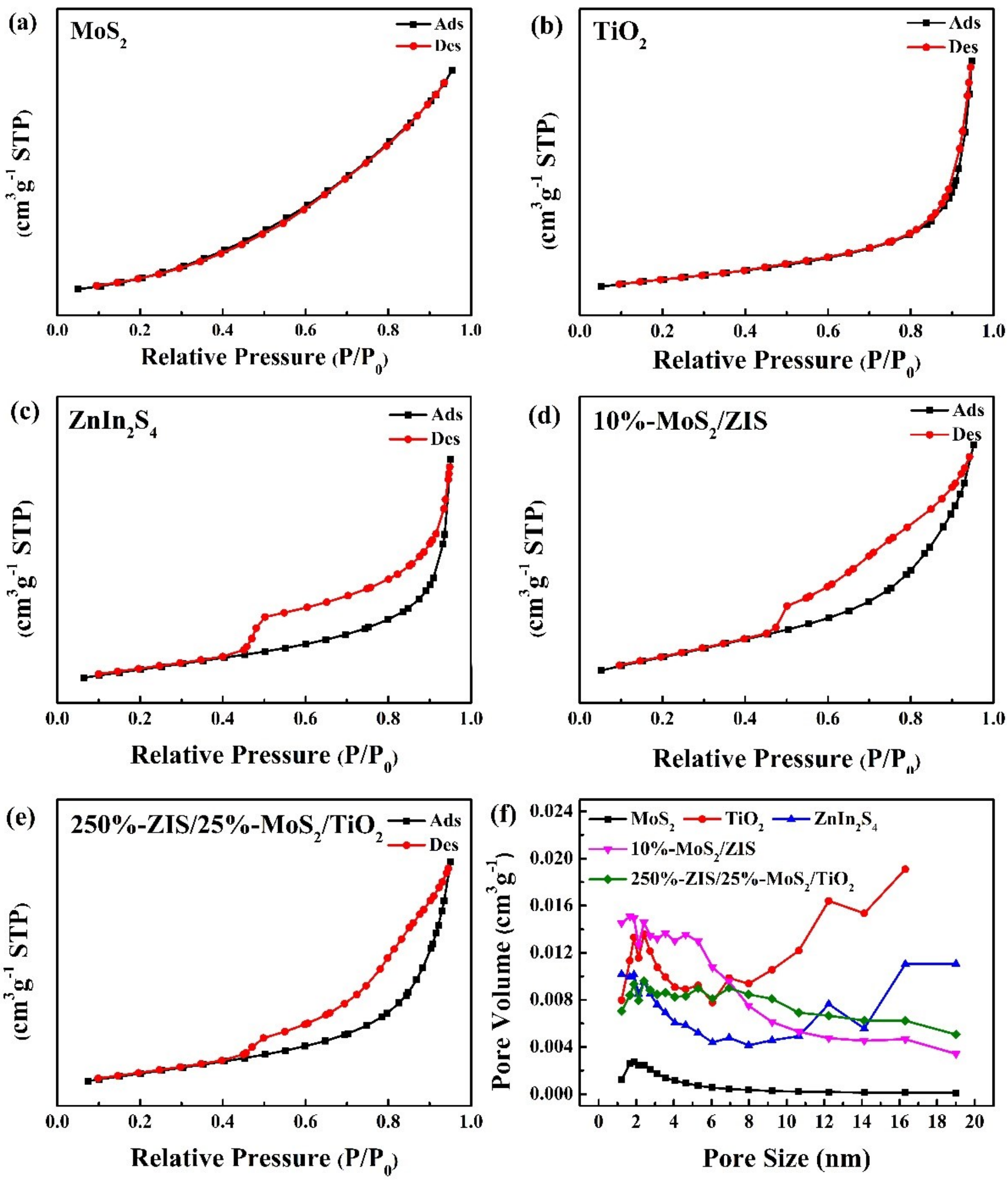

Figure S2 (a-e) Nitrogen adsorption-desorption isotherms and

(f) corresponding the Barrett-Joyner-Halenda (BJH) pore size distribution curves of MoS_2, TiO_2, $ZnIn_2S_4$, 10%-MoS_2/ZIS and 250%-ZIS/25%-MoS_2/TiO_2 samples

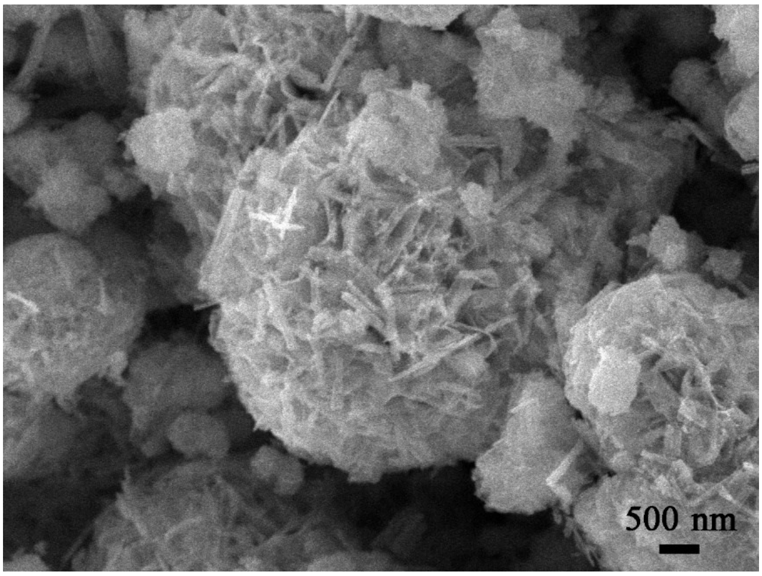

Figure S3 SEM images of 250%-ZIS/25%-MoS_2/TiO_2 after four cycles

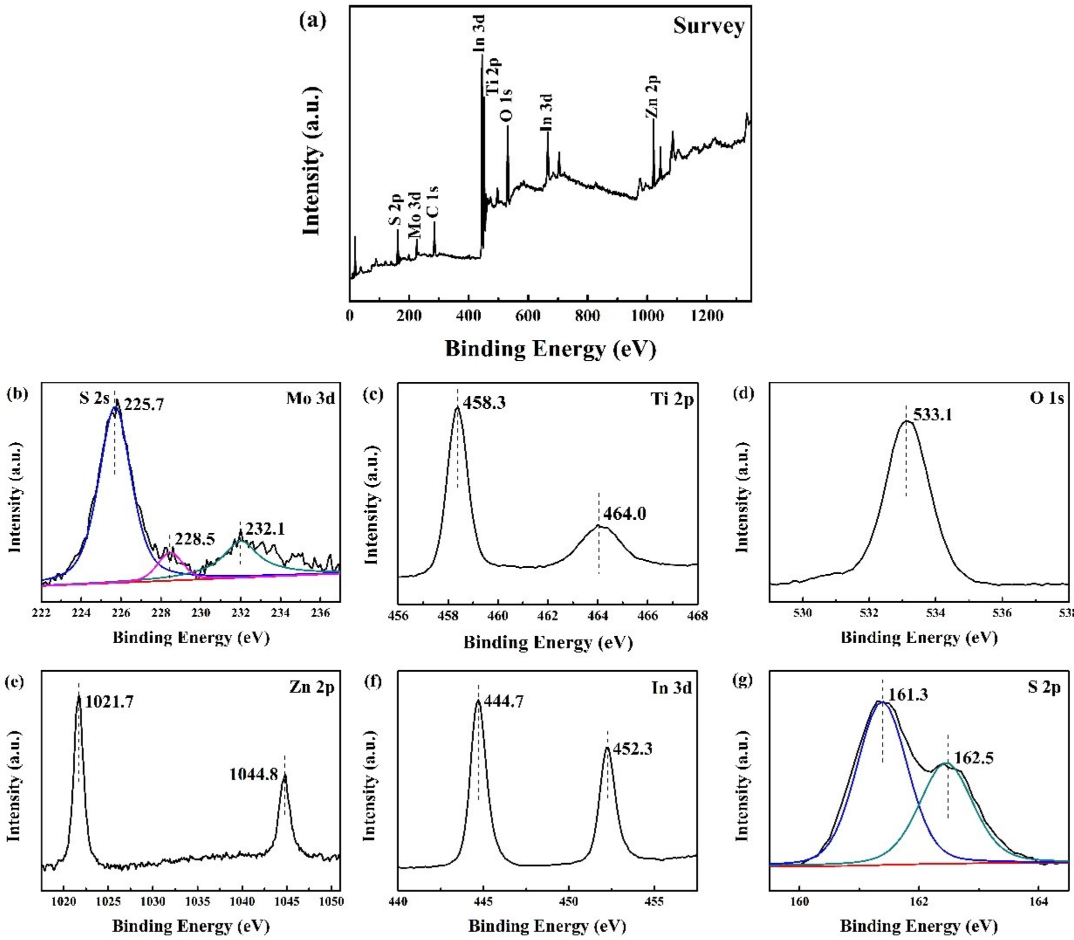

Figure S4 XPS of 250%-ZIS/25%-MoS_2/TiO_2 after four cycles

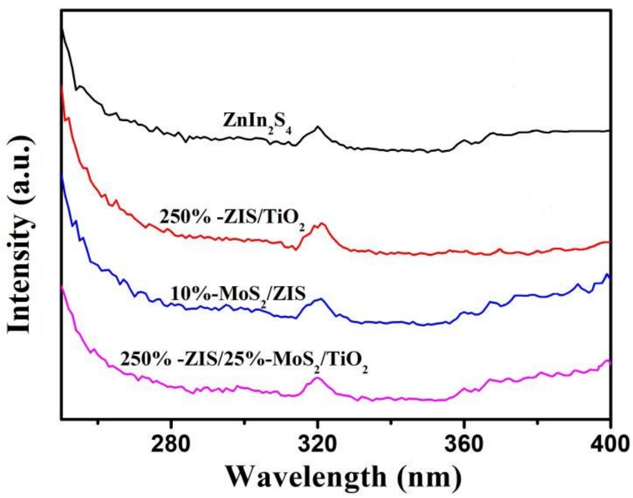

Figure S5 Excitation spectrum of $ZnIn_2S_4$, 250%-ZIS/TiO_2, 10%-MoS_2/ZIS and 250%-

ZIS/25%-MoS_2/TiO_2

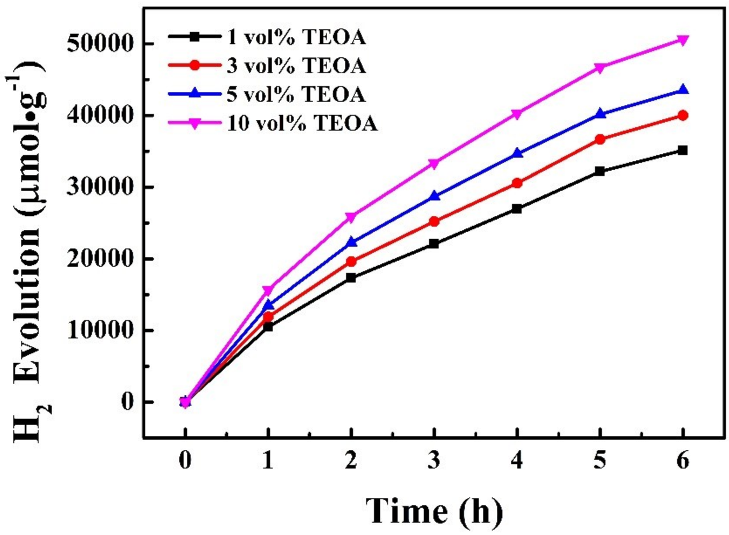

Figure S6 Time courses of H_2 evolution with different TEOA contents

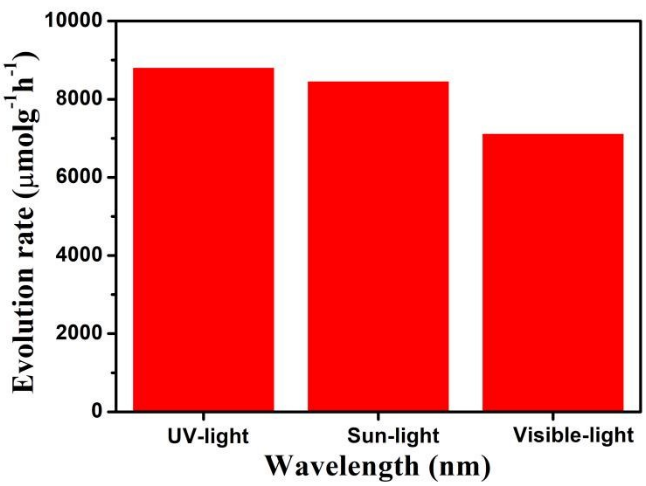

Figure S7 The rate of H_2 evolution of the 250%-ZIS/25%-MoS_2/TiO_2 under UV-light (λ=380 nm), sunlight (AM 1.5) and visible light (λ=380 nm).

Table S1 The atomic ratios (Zn:In:Mo:Ti) of as-synthesized 250%-ZIS/25%-MoS_2/TiO_2 measured by ICP-AES.

Sample	**Element**
Precursor (Zn:In:Mo:Ti)	**Zn:In:Mo:Ti (ICP)**
3.8:7.6:1:8	3:5.8:1:7.5

Table S2. BET specific 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	3.166	10.754	0.008
TiO_2	43.711	19.187	0.242
$ZnIn_2S_4$	34.924	8.599	0.075
10%-MoS_2/ZIS	59.587	10.046	0.149
250%-ZIS/25%-MoS_2/TiO_2	50.372	12.683	0.142

Table S3. The apparent quantum efficiency (AQE) of MoS_2, TiO_2, $ZnIn_2S_4$, 250%-ZIS/TiO_2, 25%-MoS_2/TiO_2, 10%-MoS_2/ZIS and 250%-ZIS/25%-MoS_2/TiO_2. The apparent quantum efficiency (AQE) was analyzed with a wavelength of 380 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 380 nm is used, the average light intensity is 19.1 mW cm^{-2}. The irradiation area is 19.625 cm^2 (2.5 cm radius). The number of incident photons (*N*) is 1.55×10^{22} calculated by equation (1). The amount of H_2 molecules generated for 6 h were about 5064.2 μmol. The AQE was then calculated in equation (2).

$$N = \frac{E\lambda}{hc} = \frac{19.1\times19.625\times10^{-3}\times6\times3600\times380\times10^{-9}}{6.626\times10^{-34}\times3\times10^{8}} = 1.55\times10^{22} \quad (1)$$

$$\begin{aligned} AQE &= \frac{the\ number\ of\ reacted\ electrons}{the\ number\ of\ incident\ photons}\times100\% \\ &= \frac{2\times the\ number\ of\ evolved\ H_2\ molecules}{N}\times100\% \quad (2) \\ &= \frac{2\times6.02\times10^{23}\times5064.2\times10^{-6}}{1.55\times10^{22}}\times100\% = 39.33\% \end{aligned}$$

For example, if 420 nm is used, the average light intensity is 19.1 mW cm^{-2}. The irradiation area is 19.625 cm^2 (2.5 cm radius). The number of incident photons (*N*) is 1.71×10^{22} calculated by equation (1). The amount of H_2 molecules generated for 6 h were about 4262.8 μmol. The AQE was then calculated in equation (2).

$$N = \frac{E\lambda}{hc} = \frac{19.1\times19.625\times10^{-3}\times6\times3600\times420\times10^{-9}}{6.626\times10^{-34}\times3\times10^{8}} = 1.71\times10^{22} \qquad (1)$$

$$\begin{aligned} AQE &= \frac{the\ number\ of\ reacted\ electrons}{the\ number\ of\ incident\ photons}\times100\% \\ &= \frac{2\times the\ number\ of\ evolved\ H_2\ molecules}{N}\times100\% \qquad (2) \\ &= \frac{2\times6.02\times10^{23}\times4262.8\times10^{-6}}{1.71\times10^{22}}\times100\% = 30.0\% \end{aligned}$$

Samples	AQE (%)
MoS_2	0.00
TiO_2	0.02
$ZnIn_2S_4$	0.93
250%-ZIS/TiO_2	1.27
25%-MoS_2/TiO_2	0.11
10%-MoS_2/ZIS	19.99
250%-ZIS/25%-MoS_2/TiO_2	39.33
250%-ZIS/25%-MoS_2/TiO_2 (420 nm)	30.0

Table S4. AQE over some $ZnIn_2S_4$-based photocatalysts in reported work in contrast with this work.

Sample	Light source	Sacrificial agents	AQE	Reference
250%-ZIS/25%-MoS_2/TiO_2	simulated sun-light	10 vol% TEOA	39.33%	In this paper

	λ > 420 nm	10 vol% TEOA	30%	
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 ascorbic acid	13.6%	2
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 S5. Photocatalytic 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 ZnIn2S4)	Condition: sacrificial agents, cocatalyst light	Reference
250%-ZIS/25%-MoS_2/TiO_2	8440.28	44.4	10vol% TEOA	In this paper
$ZnIn_2S_4$	190.1		simulated sun-light	
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	

$MoS_2/ZnIn_2S_4$ $ZnIn_2S_4$	8898 556	16	10vol% TEOA λ > 400 nm	15
$CdS/QDs/ZnIn_2S_4$ $ZnIn_2S_4$	2107.5 33.9	62	20vol% lactic acid λ > 420 nm	16
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
$ZnIn_2S_4/g\text{-}C_3N_4$ $ZnIn_2S_4$	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

$ZnIn_2S_4/MoSe_2$	2228	2.2	0.25 M Na_2SO_3 &0.35 M Na_2S	11
$ZnIn_2S_4$	1023		λ > 420 nm	
$NiS/ZnIn_2S_4$	3333	2.9	50vol% lactic acid	18
$ZnIn_2S_4$	1133		λ > 420 nm	
$AgIn_5S_8/ZnIn_2S_4$	949.9	3.6	0.25 M Na_2S & 0.25 M Na_2SO_3	19
$ZnIn_2S_4$	263.8		2 wt% Pt λ > 420 nm	
$3\%WS_2/ZnIn_2S_4$	199.1	6	0.25 M Na_2SO_3 & 0.35 M Na_2S	20
$ZnIn_2S_4$	33.2		λ ≥ 420 nm	

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