Electronic supplementary information

Cubic quantum dot/hexagonal microsphere $ZnIn_2S_4$ heterophase junction for exceptional visible-light-driven photocatalytic H_2 evolution

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Electronic Supplementary Information (ESI) available: Material characterization and performance test of the some catalysts. See DOI: 10.1039/x0xx00000x
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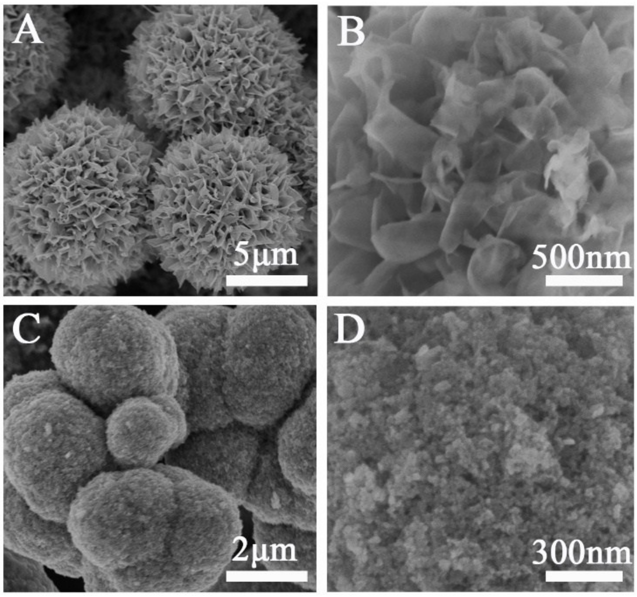

Fig. S1. SEM images of the H-$ZnIn_2S_4$ (A,B) and C-$ZnIn_2S_4$ (C,D) with different magnifications.

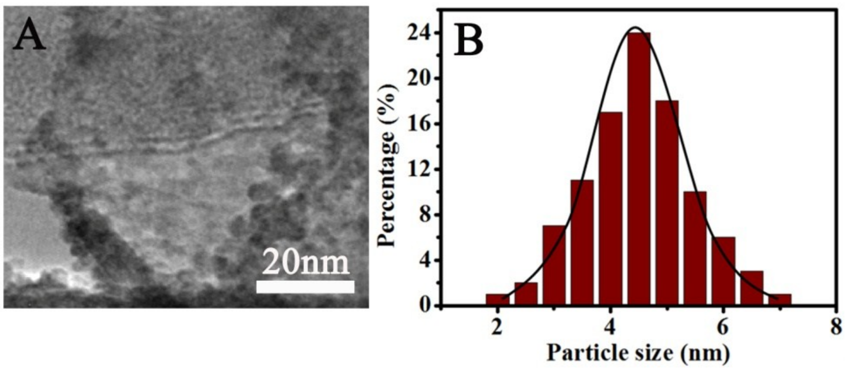

Fig. S2. The TEM image (A) of the 1/6J-$ZnIn_2S_4$ and corresponding size distribution histogram (B) of the cubic quantum dots in the 1/6J-$ZnIn_2S_4$.

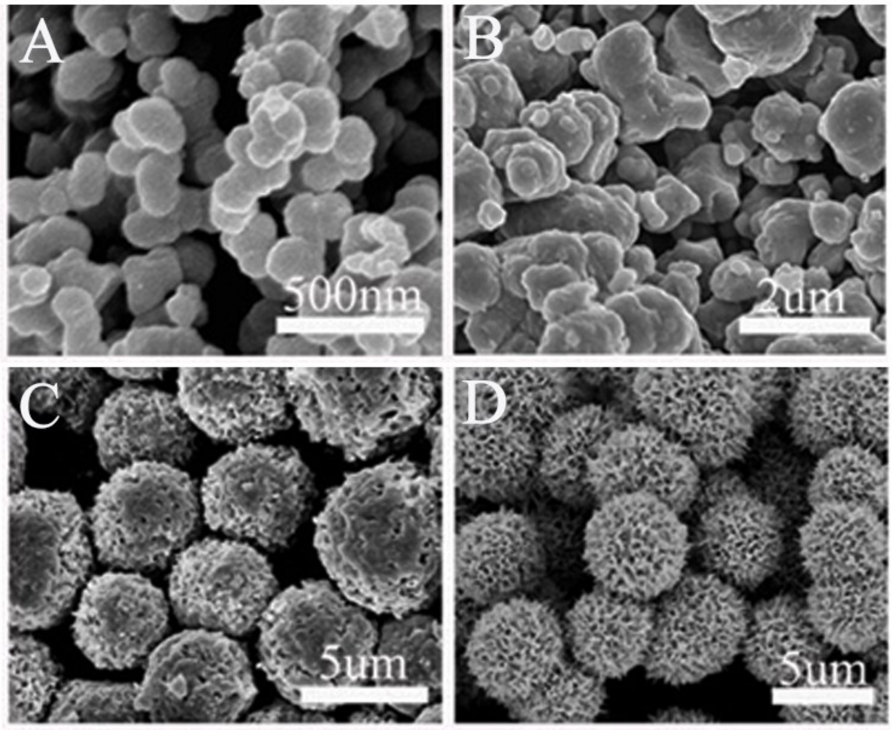

Fig. S3. SEM patterns of the prepared $ZnIn_2S_4$ samples obtained from different solvothermal reaction time: (A) 0.5 h, (B) 1 h, (C) 6 h, and (D) 12 h.

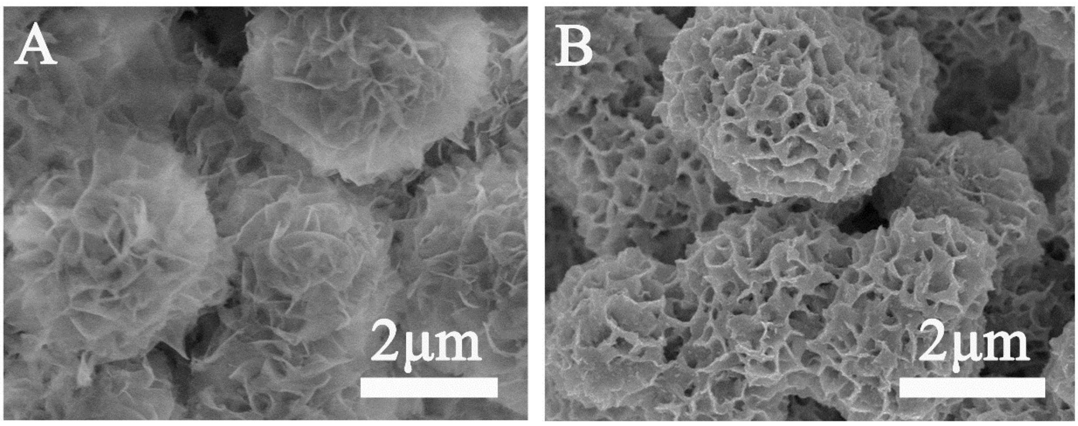

Fig. S4. (A) and (B) are the SEM images of the 1/8J-$ZnIn_2S_4$ and 1/4J-$ZnIn_2S_4$, respectively.

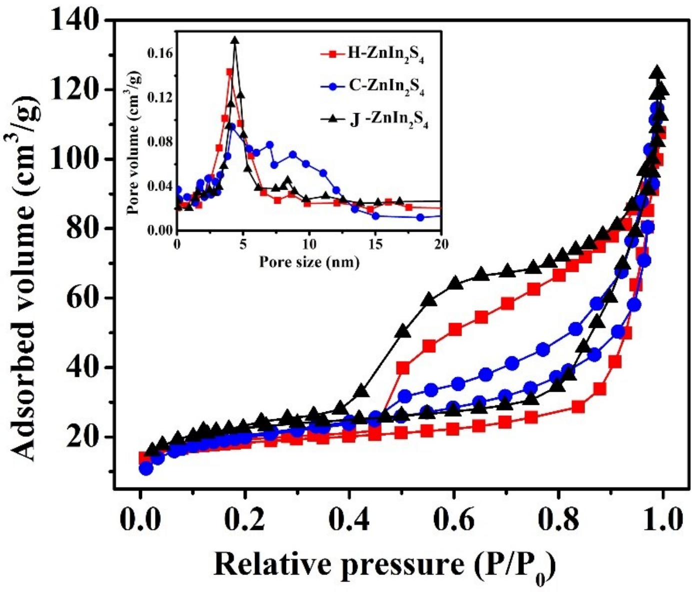

Fig. S5. Nitrogen adsorption–desorption isotherms and the pore size distribution plots (inset) of H-$ZnIn_2S_4$, C-$ZnIn_2S_4$ and J-$ZnIn_2S_4$ (1:6).

Table S1 The results of N_2 adsorption–desorption isotherm test of the different samples.

Samples	S_{BET}(m^2 g^{-1})	Pore volume (cm^3 g^{-1})	Average pore size (nm)
H-$ZnIn_2S_4$	63.8	0.15	3.2
J-$ZnIn_2S_4$	75.5	0.17	3.0
C-$ZnIn_2S_4$	32.3	0.10	2.8

Table S2 Summary of the photoluminescence decay time (τ) and their relative intensities of the different samples.

sample	τ_1(ns)	τ_2(ns)	I_1 (%)	I_2 (%)	Average lifetime (τ, ns)
J-$ZnIn_2S_4$	2.19	9.78	27.97	72.03	9.35
H-$ZnIn_2S_4$	1.68	8.16	32.68	67.32	8.47
C-$ZnIn_2S_4$	1.55	7.65	33.55	66.45	5.48

The average lifetime was calculated using equation: $\langle\tau\rangle=(I_1\tau_1^2+I_2\tau_2^2)/(I_1\tau_1+I_2\tau_2)$

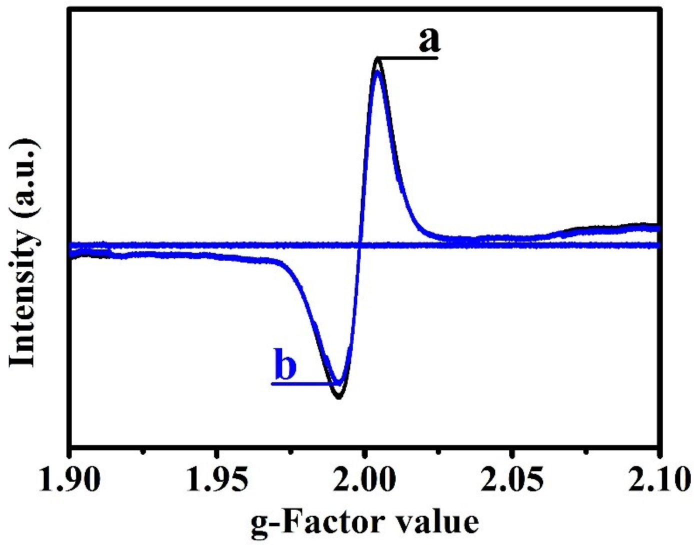

Fig. S6. Room-temperature electron spin resonance (ESR) lines of H-$ZnIn_2S_4$ (a) and the control sample after further hydrothermal process under pure water of H-$ZnIn_2S_4$ (b).

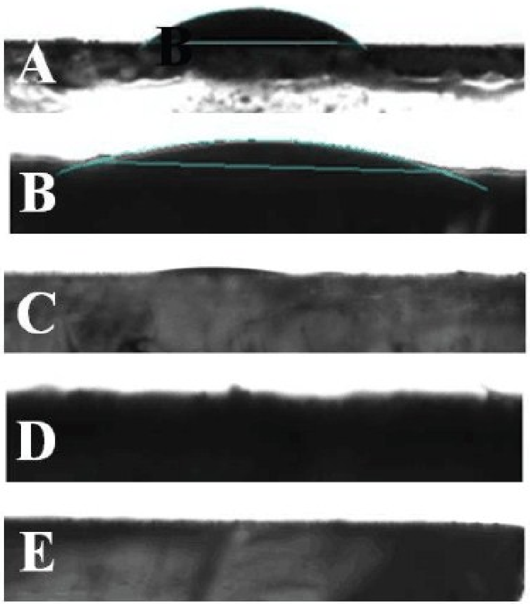

Fig. S7. (A)-(E) are the water contact angle photographs of C-$ZnIn_2S_4$, H-$ZnIn_2S_4$, 1/8J-$ZnIn_2S_4$, 1/6J-$ZnIn_2S_4$, and 1/4J-$ZnIn_2S_4$ under dark, respectively.

Table S3 Values of the parameters resulted from fitting the impedance spectra of the different samples using the equivalent circuit Figure 5C.

Samples	R_S (Ω cm^2)	CPE1 (F cm^{-2})	R_1 (Ω cm^2)	CPE2 (F cm^{-2})	R_{ct} (Ω cm^2)
J-$ZnIn_2S_4$	58.03	7.565×10^{-4}	18.86	5.065×10^{-4}	150. 5
H-$ZnIn_2S_4$	59.35	2.967×10^{-3}	20.55	6.416×10^{-4}	241.2
C-$ZnIn_2S_4$	59.98	4.856×10^{-3}	22.73	6.815×10^{-4}	320.2

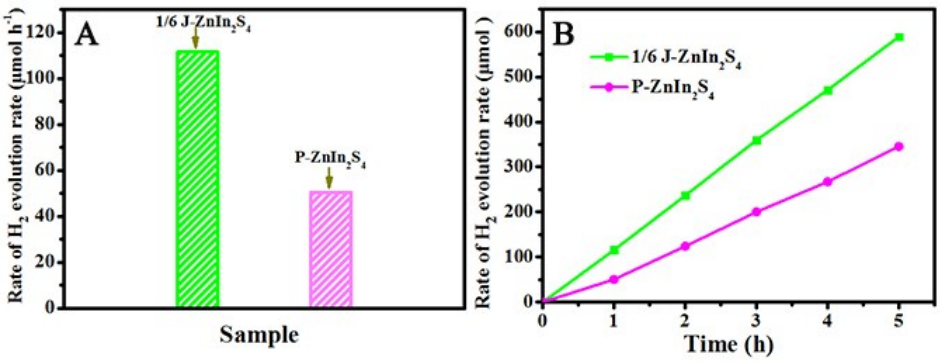

Fig. S8. Comparison of the photocatalytic H_2 evolution rate of 1/6J-$ZnIn_2S_4$ and the P-$ZnIn_2S_4$ (physically mixed C-$ZnIn_2S_4$ and H-$ZnIn_2S_4$) (A), different reaction times (B).

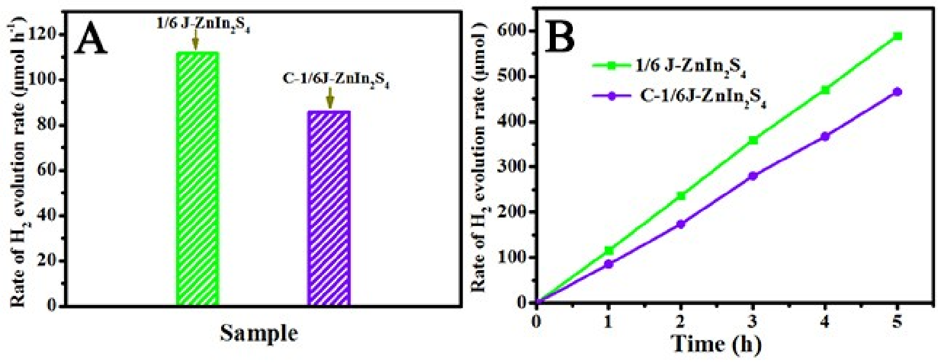

Fig. S9. Comparison of the photocatalytic H_2 evolution rate of 1/6J-$ZnIn_2S_4$ and the crushed 1/6J-$ZnIn_2S_4$ (C-1/6J-$ZnIn_2S_4$) (A), different reaction times (B).

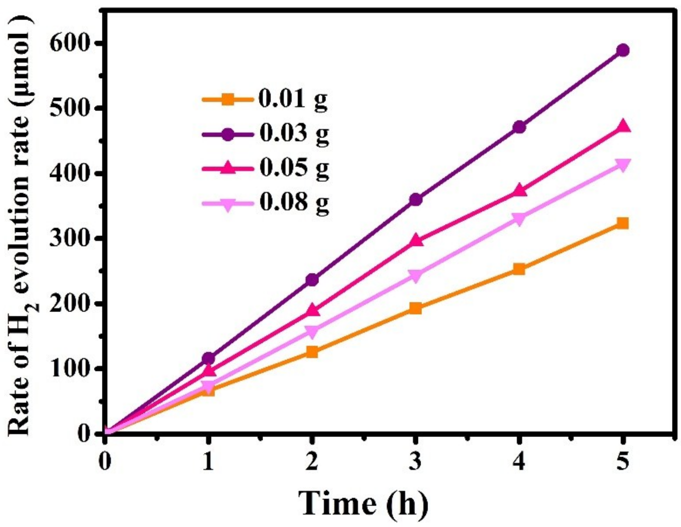

Fig. S10. Photocatalytic H_2 evolution of the 1/6J-$ZnIn_2S_4$ samples with different amounts.

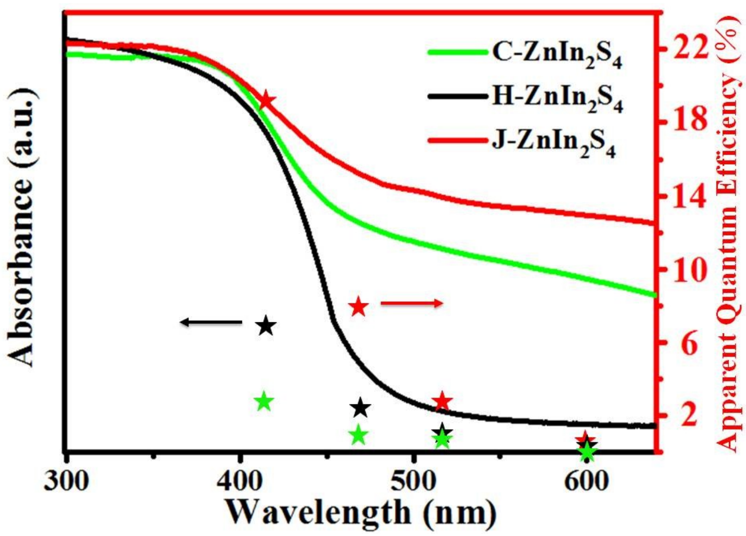

Fig. S11. The H_2 evolution rates of the different samples plotted against wavelength of monochromatic light.

Table S4 The apparent quantum efficiency (AQE) of the different samples under different illumination wavelength.

Sample	Apparent Quantum Efficiency (AQE)			
	420 nm	470 nm	520 nm	600 nm
J-$ZnIn_2S_4$	18.67%	8.20%	2.12%	0.91%
H-$ZnIn_2S_4$	6.43%	2.01%	0.69%	0.15%
C-$ZnIn_2S_4$	3.18%	1.17%	0.12%	0.08%

Table S5 The perfromance comparision of the catalysts from the different references.

Catalyst	Apparent Quantum Efficiency (AQE) at 420 nm	Photocatalytic H_2 Evolution Rate (μmol h^{-1})	Reference
J-$ZnIn_2S_4$	18.67%	114.2	This Work
La-$ZnIn_2S_4$	8.83%	116.68	(1)
$ZnIn_2S_4$	4.11%	49.78	(2)
RGO-$ZnIn_2S_4$	--	81.6	(3)
$ZnIn_2S_4$-CTAB	11.9%	122.2	(4)
$MoS_2/ZnIn_2S_4$	--	47.71	(5)
$Ag/ZnIn_2S_4/TiO_2$	0.18%	33.1	(6)
$ZnIn_2S_4$/g-C_3N_4	0.28%	14.1	(7)

References

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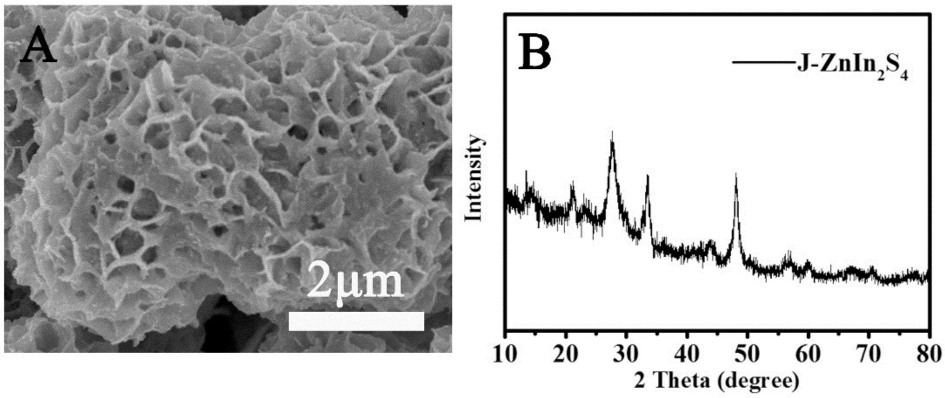

Fig. S12. SEM image (A) and XRD pattern of the J-$ZnIn_2S_4$ after photocatalytic H_2 evolution reaction.