Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supporting Information

Regulating surface state of $ZnIn_2S_4$ by gamma-ray irradiation for enhanced photocatalytic hydrogen evolution

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Calculation methods

The $ZnIn_2S_4$ models with/without γ-ray irradiation were simulated by constructed with a 3×3×1 supercell with a 15 Å vacuum layer. The S vacancy in $ZnIn_2S_4$ with γ-ray irradiation was simulated by remove a surface S atom on Zn side. All first-principle calculations were performed within Vienna ab-initio Simulation Package (VASP), while the projector augmented wave (PAW) method [1] and generalized gradient approximation (GGA) functional of Perdew, Burke, and Enzerhof (PBE) were employed in the all calculations [2]. The interactions between adsorbent and $ZnIn_2S_4$ were treated by the semi-empirical London dispersion corrections of D-3 corrections of Grimme et al [3]. The cut-off for all calculations were set as 400 eV in all the calculation, the SCF tolerance level was as 1.0×10^{-6} eV in geometry optimization, while SCF tolerance was set as 1.0×10^{-8} eV for energy calculation. The K points were set as 4×4×1 and 6×6×2 in geometry optimizations and single point calculations, respectively. The free energy of the adsorbed state is calculated as follows based on the adsorption energy

$$\Delta G = \Delta E_{ad} + \Delta E_{ZPE} - T\Delta S$$

where ΔE_{ad} is the adsorption energy, and Δ_{EZPE} is the difference corresponding to the zero point energy between the adsorbed state and the gas phase. [4]

Fig. S1 SEM images of the as-synthesized $ZnIn_2S_4$ before and after γ-ray irradiation: (a) ZIS, (b) ZIS-10, (c) ZIS-20, (d) ZIS-30, (e) ZIS-40, (f) ZIS-50.

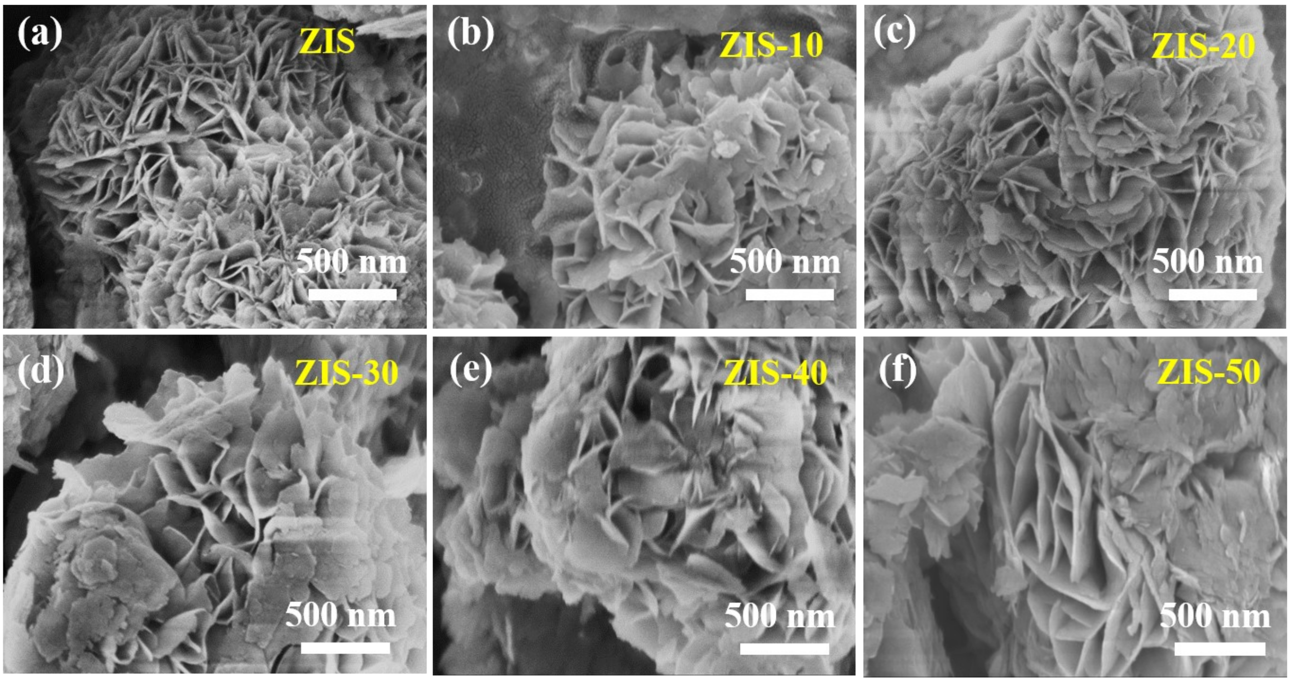

Fig. S2 The SEM image and the corresponding elemental mapping images of S, Zn and In of the as-synthesized $ZnIn_2S_4$.

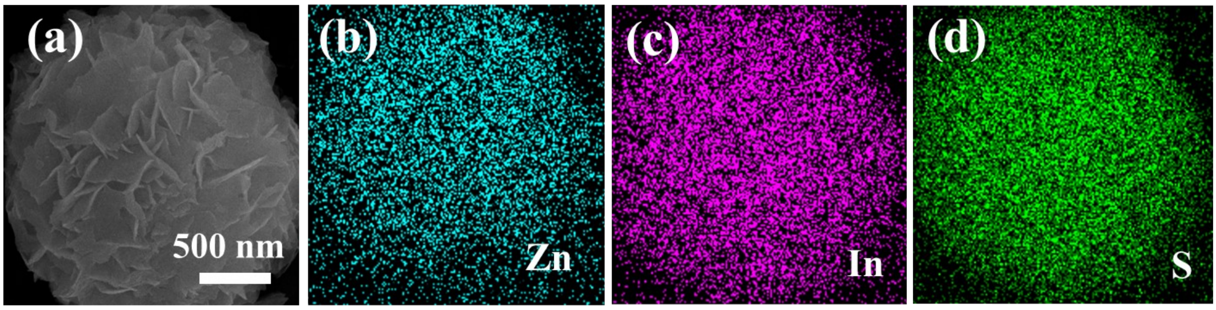

Fig. S3 Isothermal curve (a) and the corresponding pore size distribution (b) of ZIS; isothermal curve (c) and the corresponding pore size distribution (d) of ZIS-40.

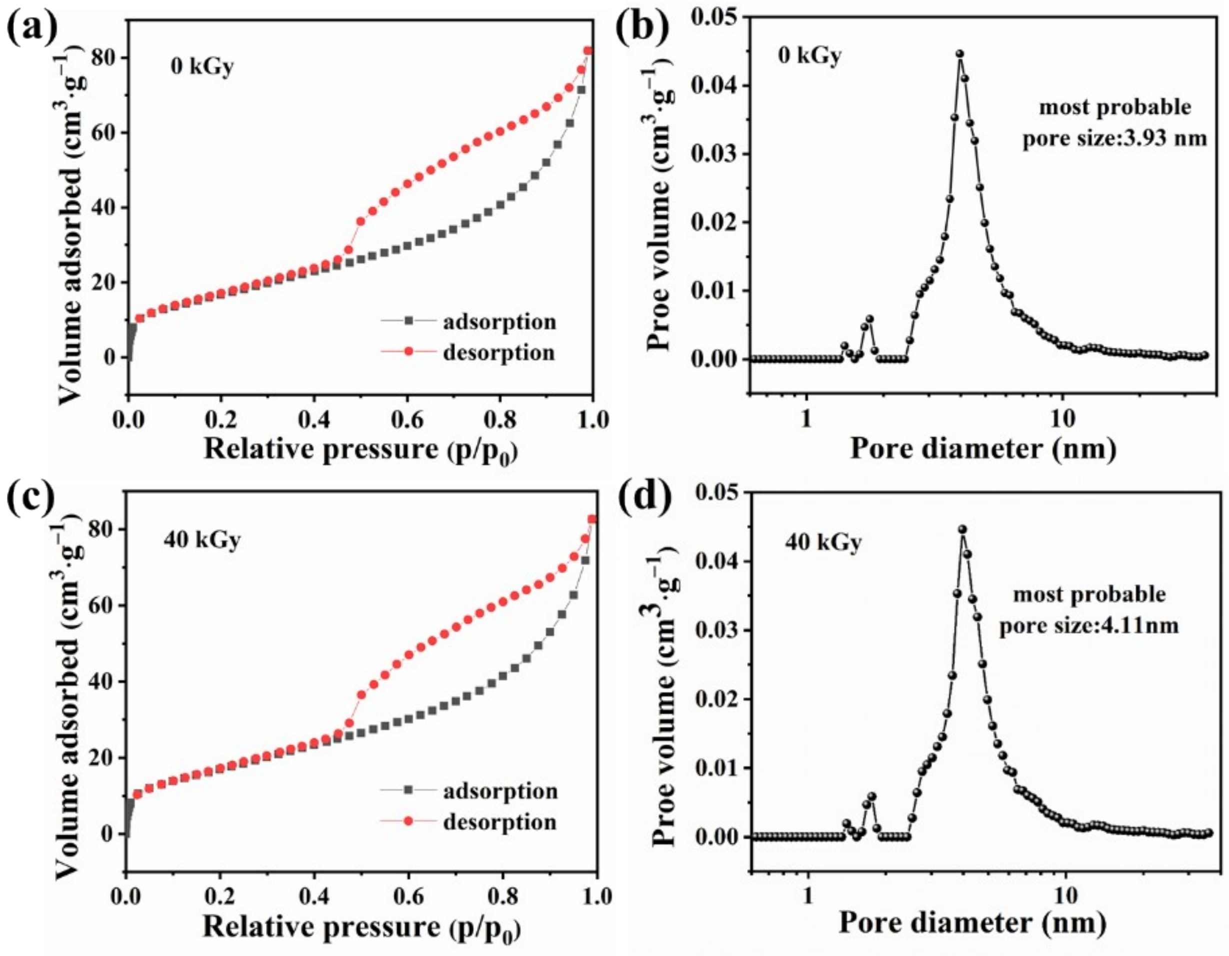

Fig. S4 Photocatalytic H_2 evolution rate over the as-prepared $ZnIn_2S_4$ samples,

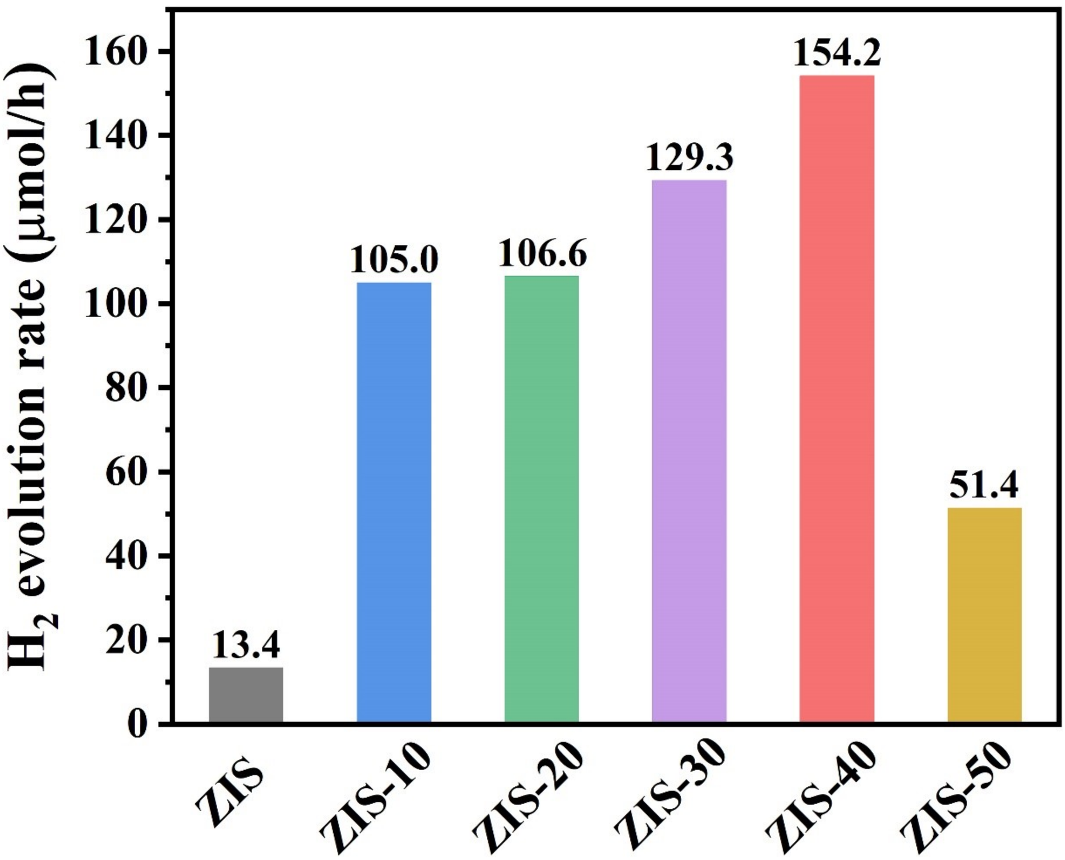

Fig. S5 XRD patterns of ZIS-40 before and after the photocatalytic cycling test.

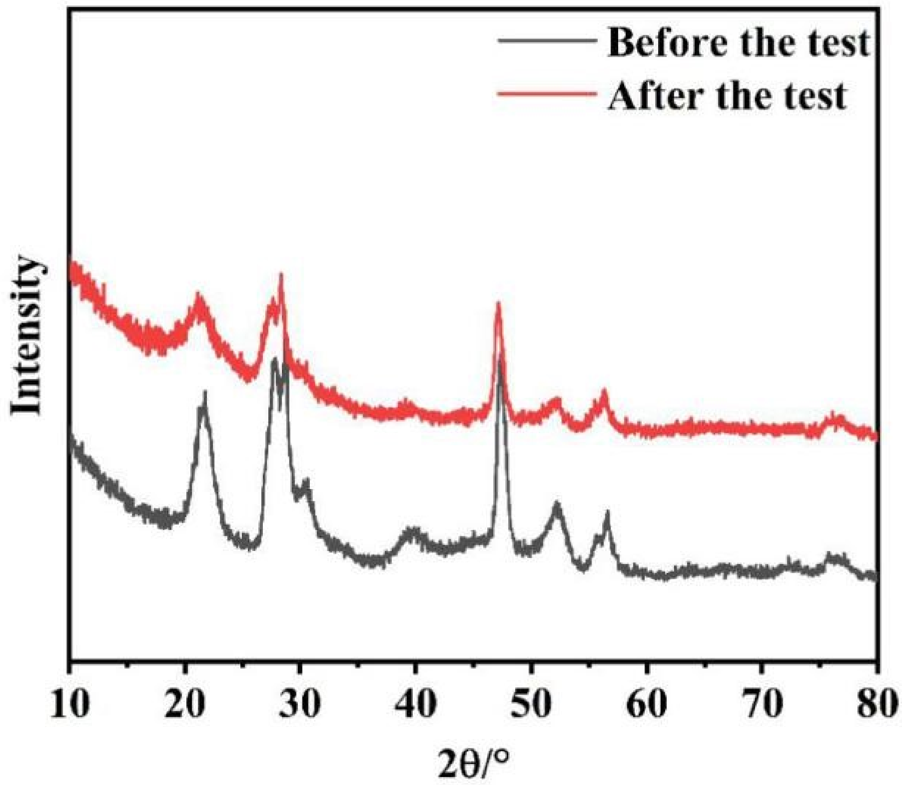

Fig. S6 XPS spectra of ZIS-40 before and after the photocatalytic cycling test.

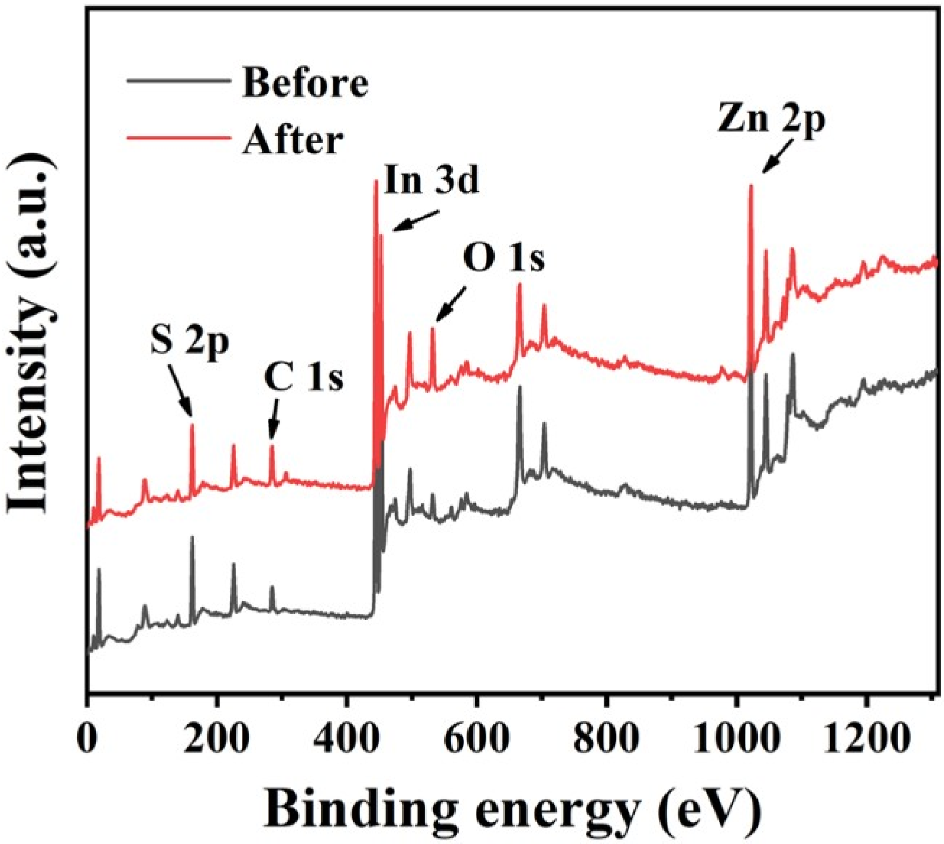

Fig. S7 Nyquist plots of all samples under the irradiation of light at 0 V (vs. SCE) in aqueous 0.5 M Na_2SO_3 solution**.**

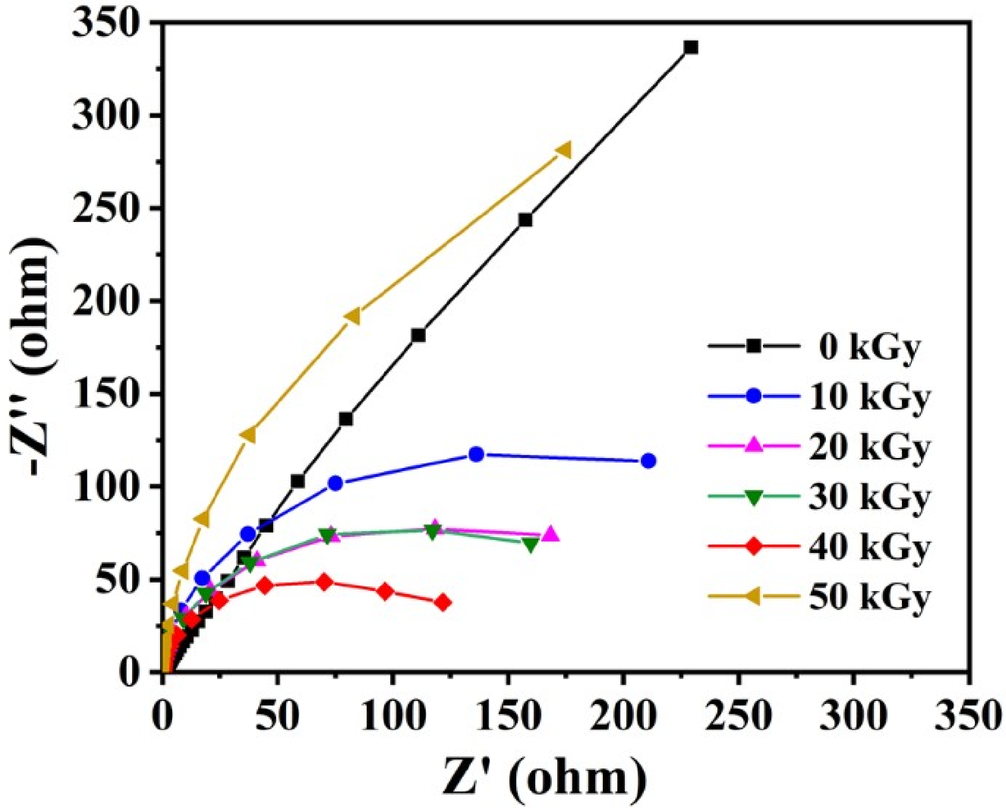

Fig. S8 Calculation models of ZIS (a) and ZIS-V_S (b).

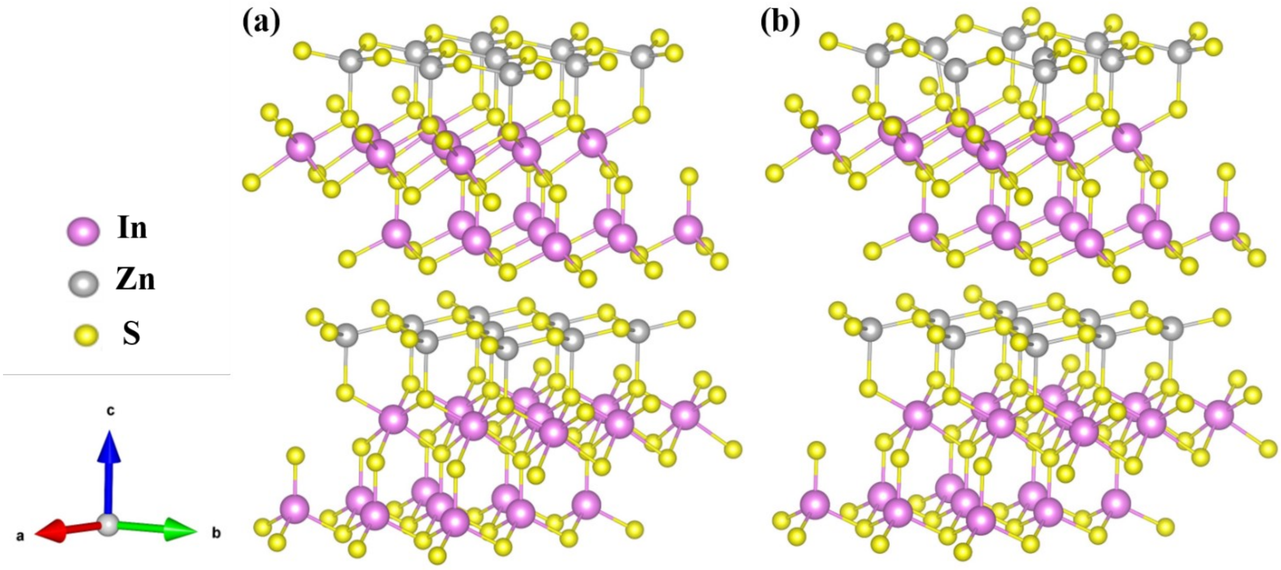

Fig. S9 The adsorption models of H_2O (a) and H (b) on ZIS surface.

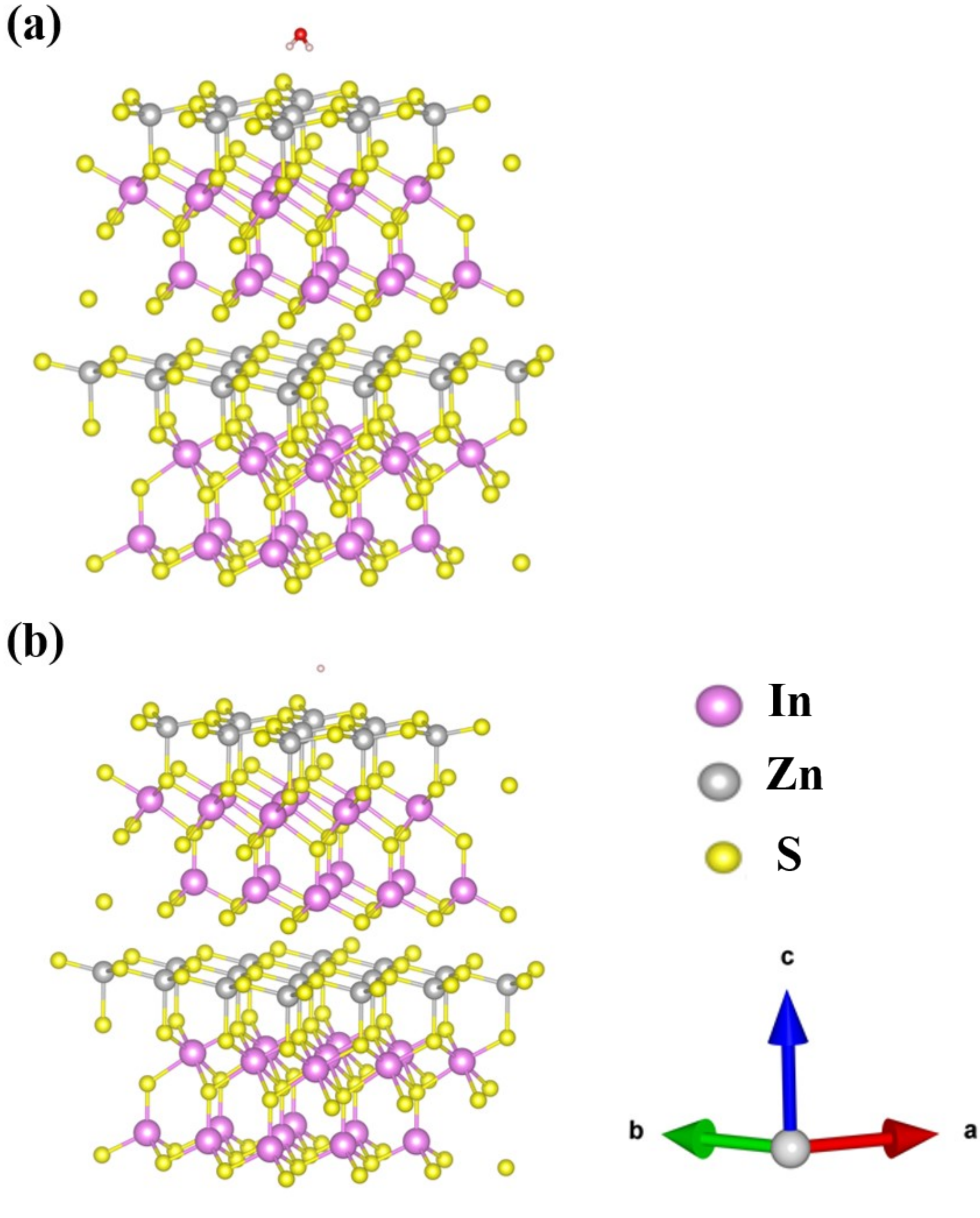

Fig. S10 Charge density difference between ZIS-V_S and ZIS-V_S.

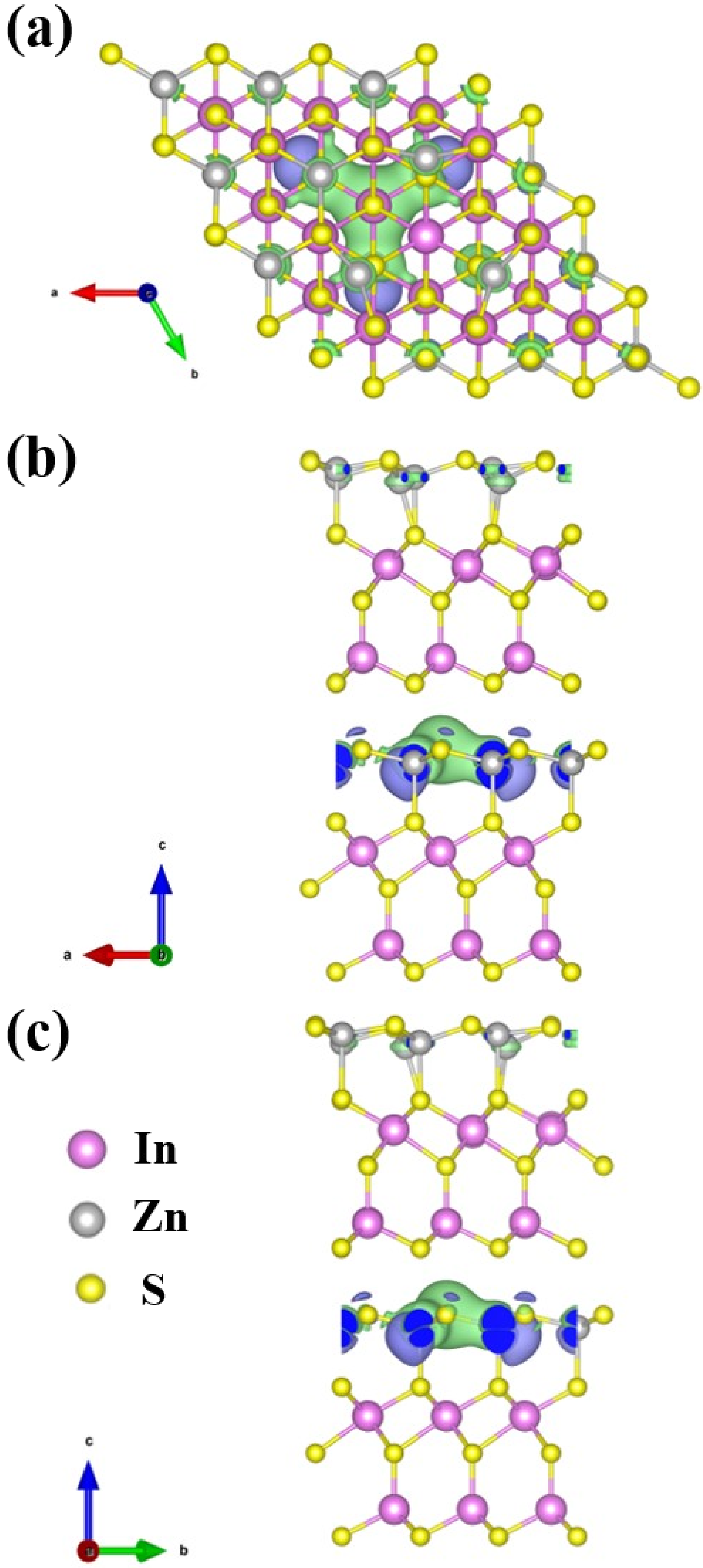

Table S1 Band gaps of the as-synthesized samples observed from Tauc plots

Samples	ZIS	ZIS-10	ZIS-20	ZIS-30	ZIS-40	ZIS-50
Band gaps	2.11	2.07	2.06	2.04	2.01	2.08

Table S2 H_2 evolution performance and apparent quantum of ZIS and ZIS-40 compared with reported $ZnIn_2S_4$

Materials	Condition	H_2 evolution rate	Apparent quantum efficiency	Ref.
$ZnIn_2S_4$	5 mg of the photocatalyst, 300 W Xe lamp (λ > 420 nm) without any cocatalysts.	12.0 μmol h^{-1}	~0.16% at 420 nm	5
N doped $ZnIn_2S_4$	20 mg of the photocatalyst, 300 W Xe lamp (λ > 400 nm) without any cocatalysts.	221.7 μmol h^{-1}	about 17% at 420 nm	6
$ZnIn_2S_4$	20 mg of the photocatalyst, 300 W Xe lamp (λ > 400 nm) without any cocatalysts.	13.478 μmol h^{-1}	~53.68% at 365 nm	7
Hydrogenated $ZnIn_2S_4$	200 mg of the photocatalyst, 300 W Xe lamp (λ > 420 nm) Pt cocatalyst (0.5 wt%)	381.0 μmol h^{-1}		8
$ZnS/ZnIn_2S_4$	50 mg of the photocatalyst, 300 W Xe lamp with AM 1.5 filter, without any cocatalysts.	22.6 μmol h^{-1}		9
$MWCNTs/ZnIn_2S_4$	100 mg of the photocatalyst, 300 W Xe lamp (λ > 420 nm) without any cocatalysts.	68.4 μmol h^{-1}	~23.3% at 420 nm	10
$ZnIn_2S_4$	100 mg of the photocatalyst, 300 W Xe lamp (λ > 400 nm) without any cocatalysts.	13.4 μmol h^{-1}	20.9% at 400 nm 14.6% at 440 nm	This work
$ZnIn_2S_4$ with 40 kGy γ-ray irradiation	100 mg of the photocatalyst, 300 W Xe lamp (λ > 400 nm) without any cocatalysts.	154.2 μmol h^{-1}	69.3% at 400 nm 49.0% at 440 nm	This work

Table S3 Fluorescence lifetime of the as-synthesized samples

Samples	B_1	T_1/ns	B_2	T_2/ns	T/ns
ZIS	1.018345009	48.32527238	3180.928543	5.804645378	5.917672674
ZIS-10	1.734497724	105.2214206	3187.235762	6.52940568	7.387391269
ZIS-20	2767.953771	7.04142596	1.564307707	77.10031095	7.47229263
ZIS-30	1.593868913	112.2975278	3417.606422	7.764480669	8.464842423
ZIS-40	3462.677285	9.443372858	1.293106465	114.7446454	9.91903104
ZIS-50	1.335326429	99.85755348	3187.594636	6.50715211	7.103428418

Table S4 Elemental contents of ZIS and ZIS-40 measured by XPS

Samples	S content	In	Zn content	S/Zn
ZIS	55.01	30.75	14.24	3.86:2.16:1
ZIS-40	51.55	33.02	15.43	3.34:2.14:1

Reference

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