

Supporting information

**Inert Basal Plane Activation of Two-Dimensional
ZnIn₂S₄ *via* Ni Atom Doping for Enhanced Co-
catalyst Free Photocatalytic Hydrogen Evolution**

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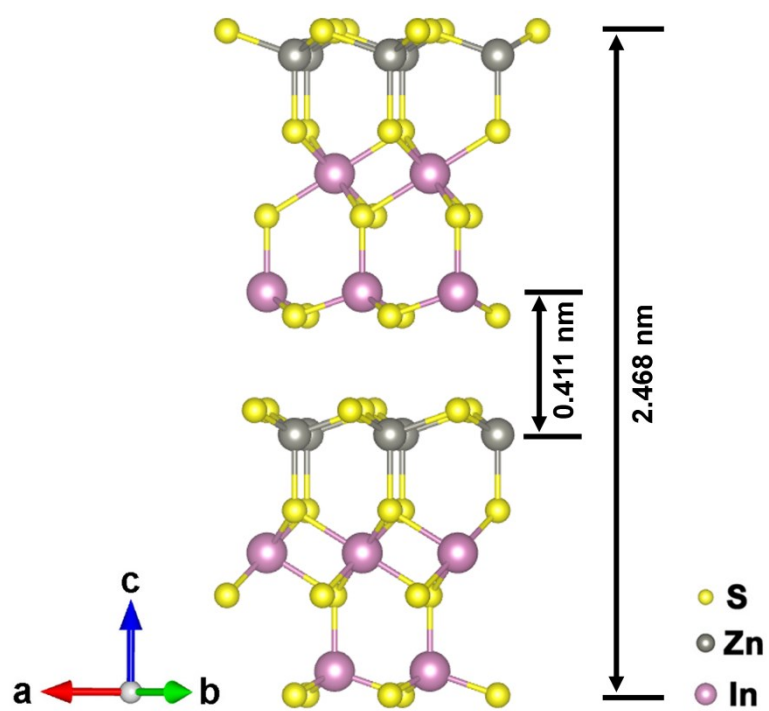


Fig. S1 Crystal structure of hexagonal ZnIn_2S_4 .

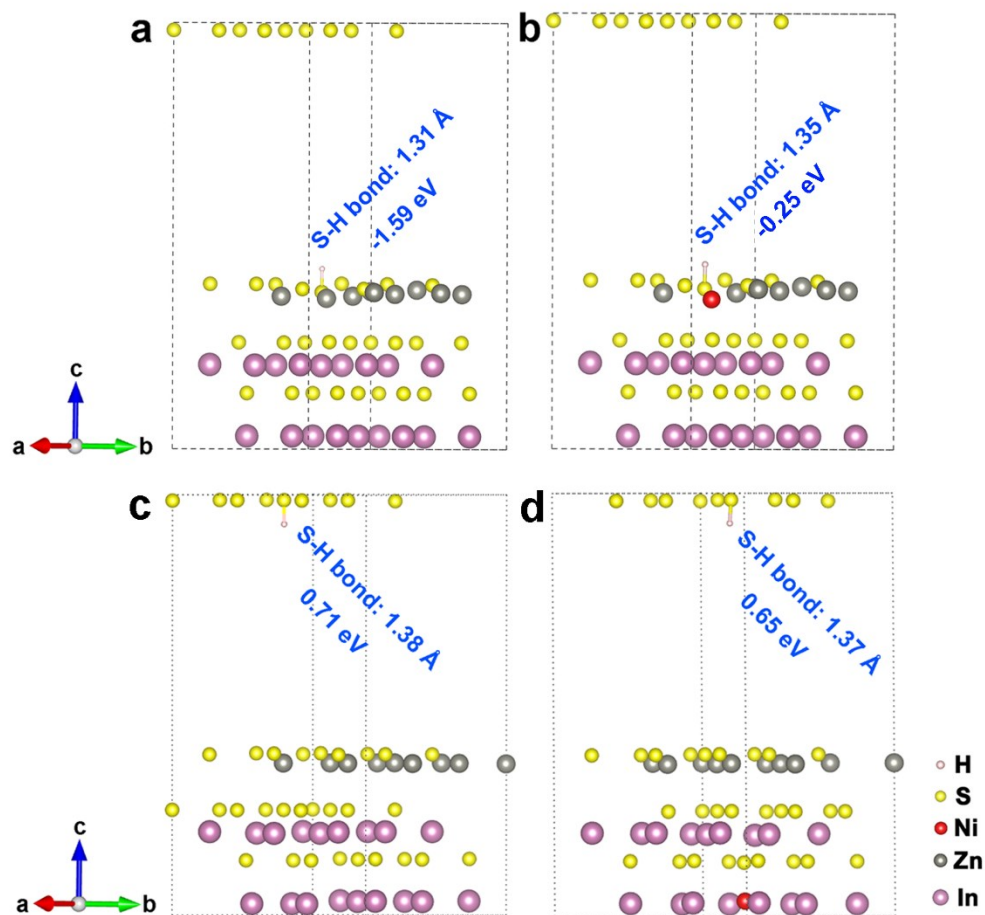


Fig. S2 Bond length of S-H and corresponding ΔG_H^* before (a) and after (b) Ni atom replacing Zn atom. Bond length of S-H and corresponding ΔG_H^* before (c) and after (d) Ni atom replacing In atom.

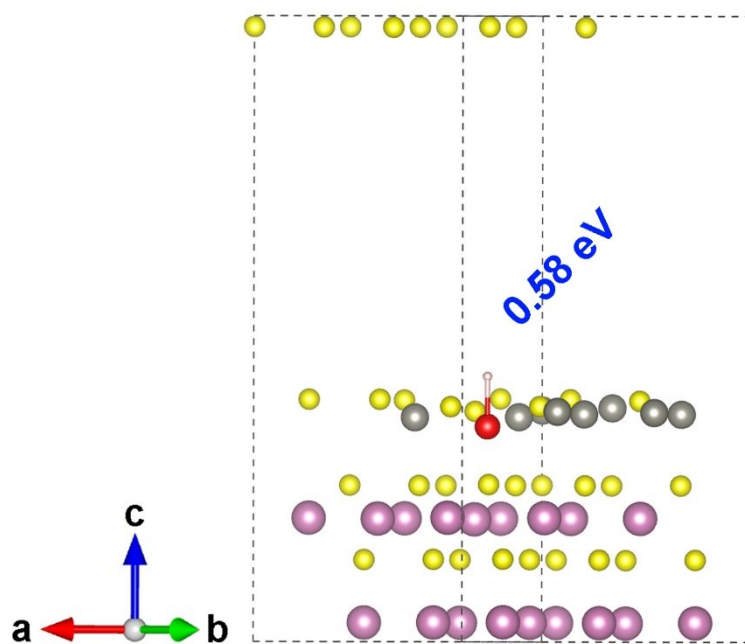


Fig. S3 Calculated ΔG_H^* at Ni atom in Ni-ZIS.

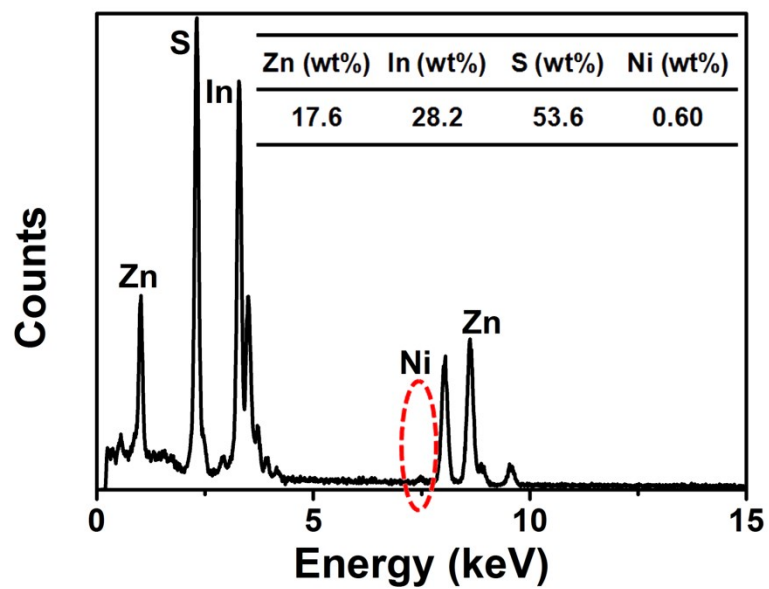


Fig. S4 EDX pattern of Ni_{0.7}-ZIS.

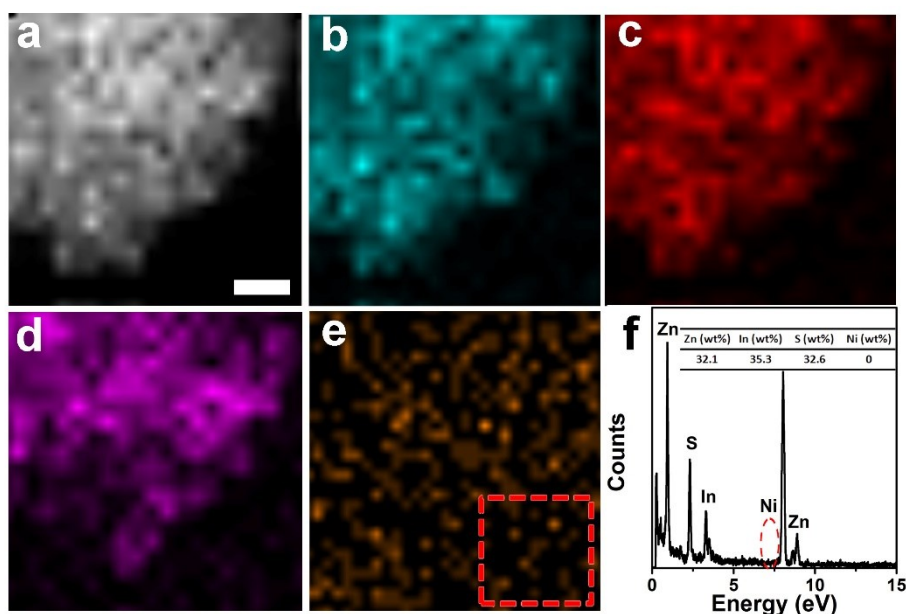


Fig. S5 TEM (a) and elemental mappings of ZIS for Zn (b), S (c) and In (d), the corresponding scale bars are 100 nm. (f) EDX pattern of ZIS

Even though Ni signal is recorded, Ni peak could not be observed in the EDX pattern. More importantly, Ni signal is homogeneously distributed and it is detected even in the place where there is no ZIS nanosheets (red rectangular in Fig. S5e). Therefore, we suppose that the observed Ni signal may be caused by the noise rather Ni element.

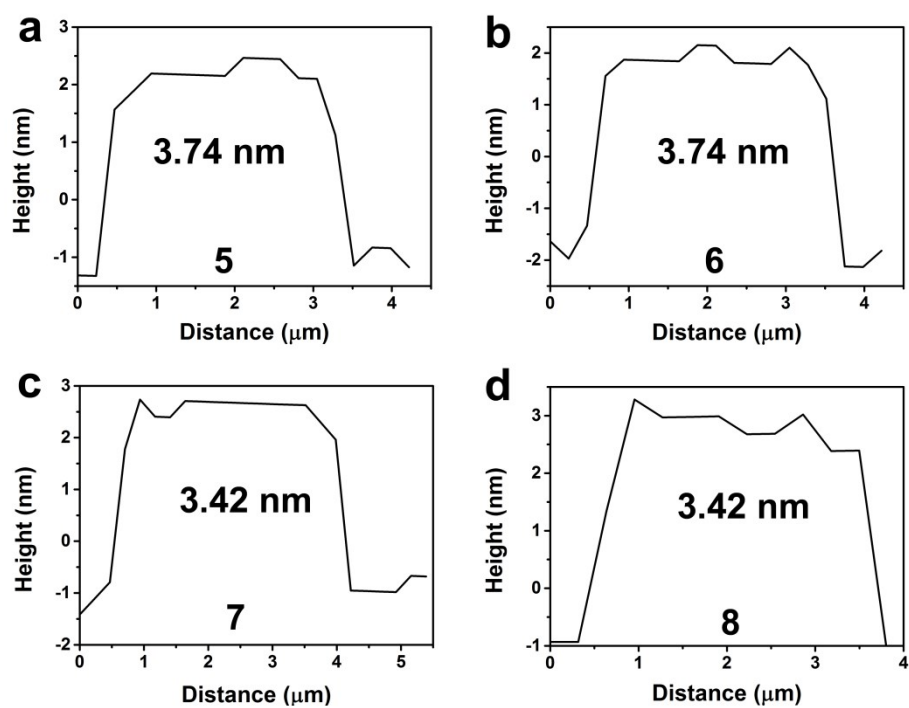


Fig. S6 The corresponding height profiles of $\text{Ni}_{0.7}\text{-ZIS}$ in Fig. 2g.

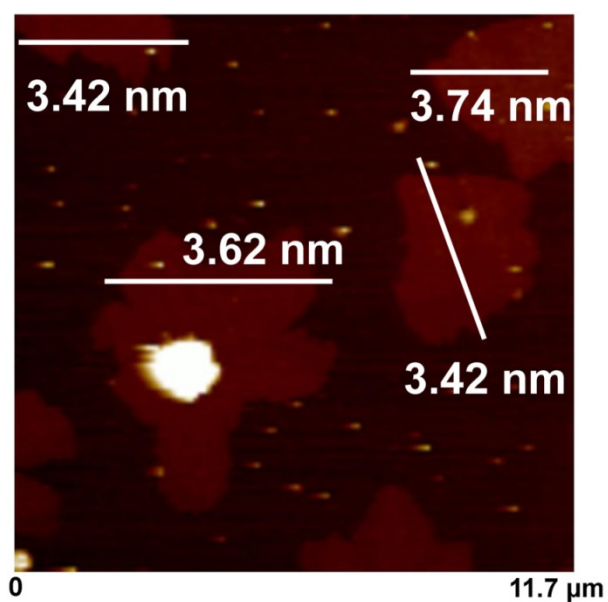


Fig. S7 AFM image and corresponding height profiles of ZIS.

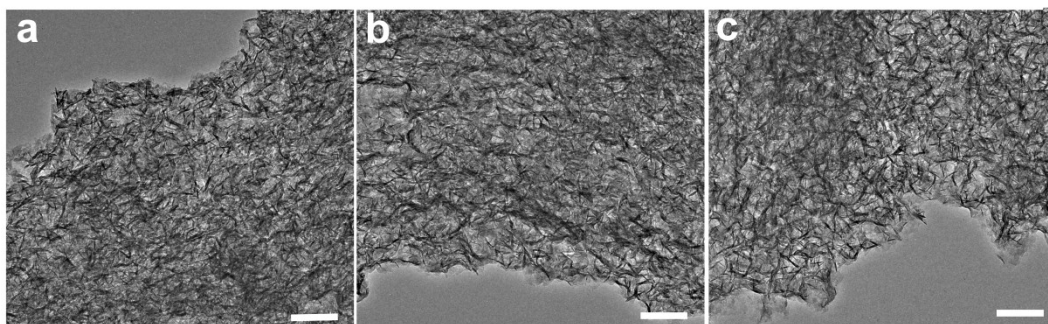


Fig. S8 Morphology of Ni_{0.3}-ZIS (a), Ni_{1.4}-ZIS (b), and Ni_{2.1}-ZIS (c), the scale bar is 100 nm.

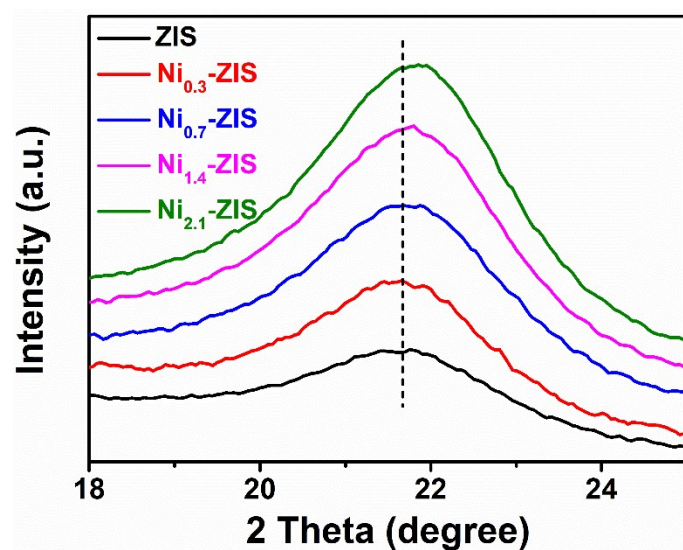


Fig. S9 Enlarged XRD pattern of (006) peak for ZIS and Ni_x-ZIS.

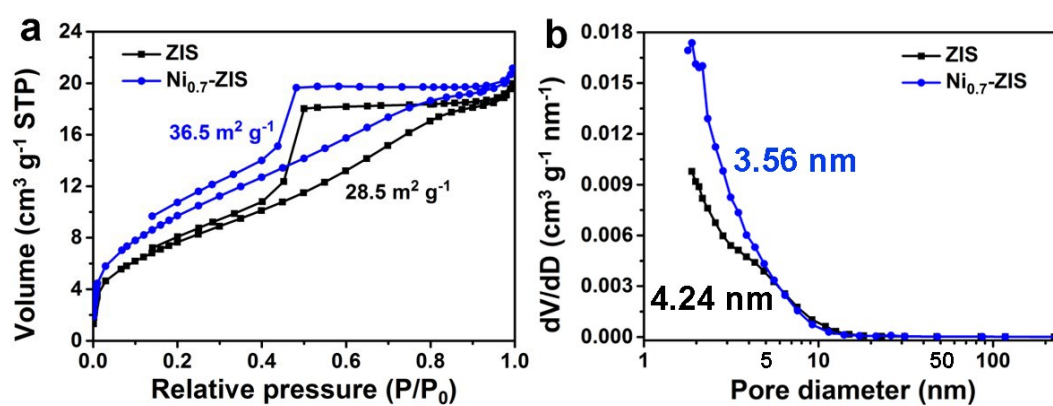


Fig. S10 (a) Nitrogen adsorption/desorption isotherms of ZIS and Ni_{0.7}-ZIS. (b) Pore diameter distribution of ZIS and Ni_{0.7}-ZIS.

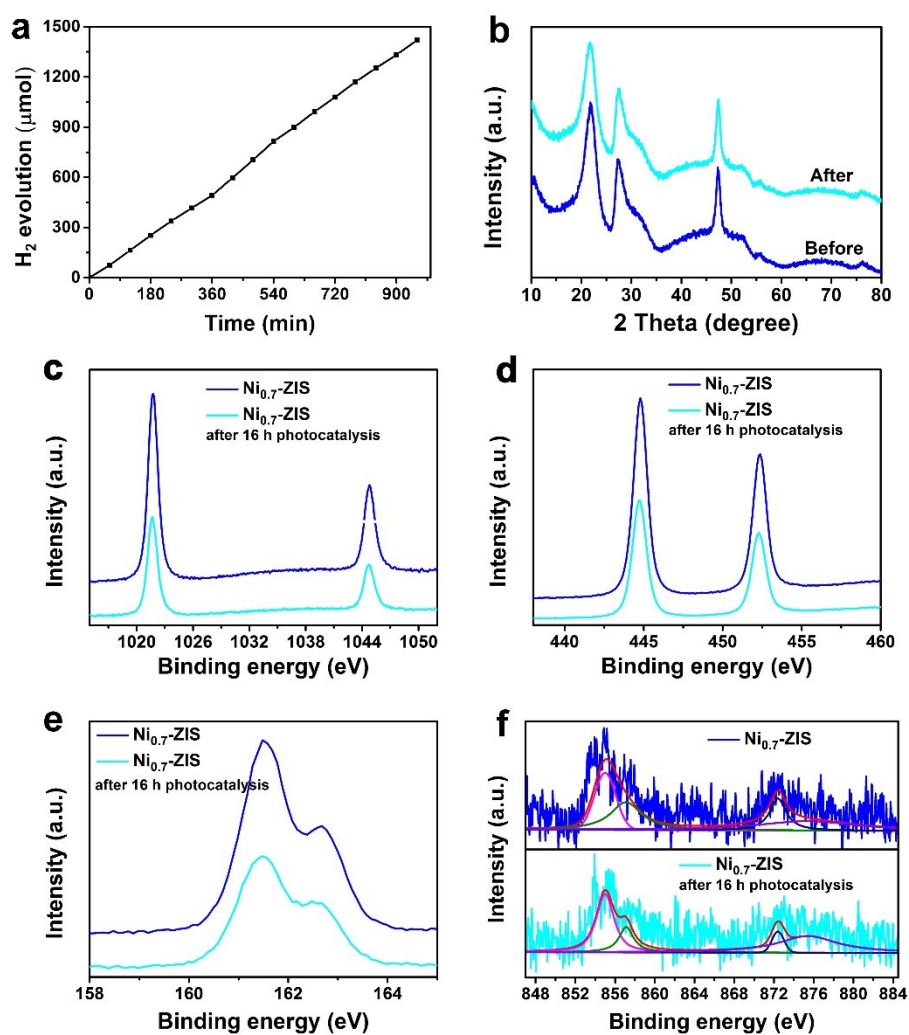


Fig. S11 (a) Photocatalytic activity H_2 evolution of $\text{Ni}_{0.7}\text{-ZIS}$ for 16 h under visible light irradiation. (b) XRD patterns of $\text{Ni}_{0.7}\text{-ZIS}$ before and after 16 h irradiation. High-resolution XPS results: Zn 2p (c), In 3d (d), S 2p (e) and Ni 2p (f) of $\text{Ni}_{0.7}\text{-ZIS}$ before and after photocatalysis for 16 h.

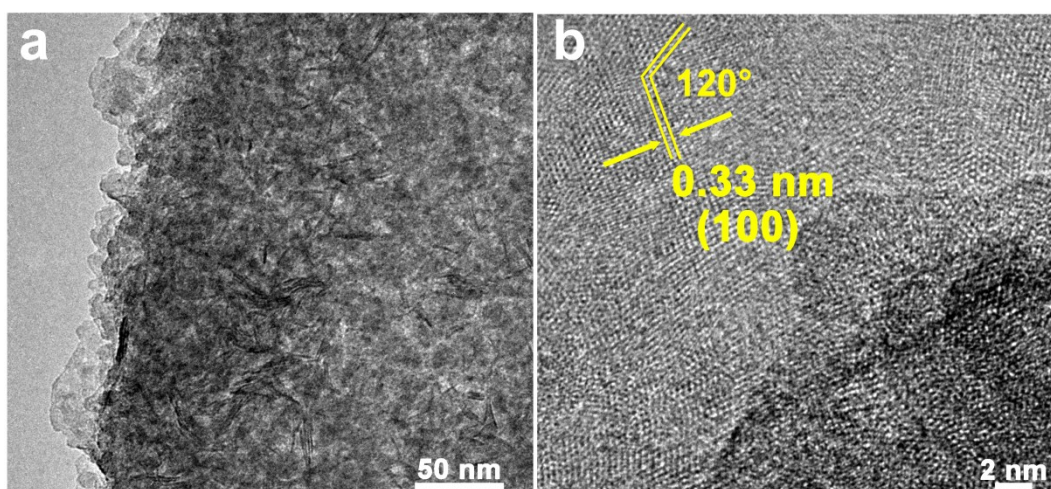


Fig. S12 TEM (a) and HRTEM (b) images of $\text{Ni}_{0.7}\text{-ZIS}$ after 16 h irradiation under visible light irradiation.

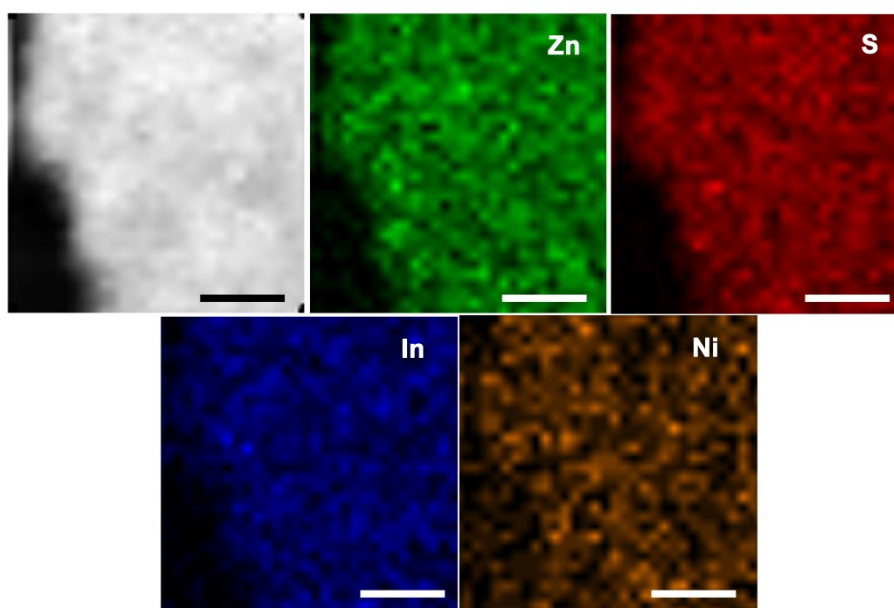


Fig. S13 TEM and elemental mappings for Zn, S, In, and Ni in $\text{Ni}_{0.7}\text{-ZIS}$ after 16 h visible light irradiation, the corresponding scale bars are 100 nm.

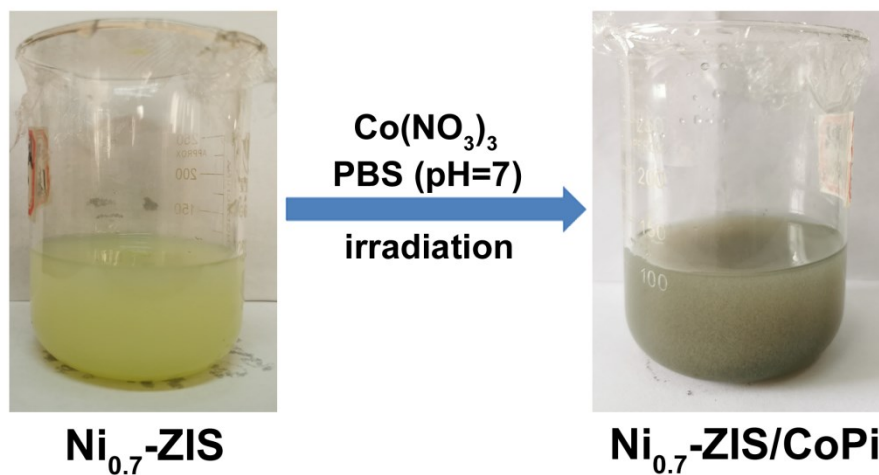


Fig. S14 Photographs of Ni_{0.7}-ZIS before and after photodeposition of CoPi.

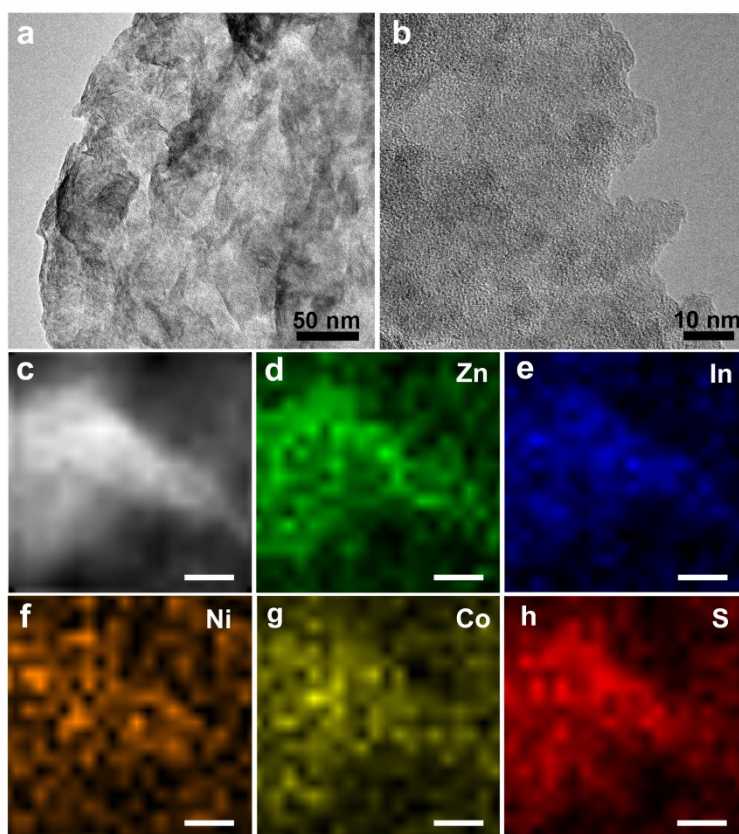


Fig. S15 TEM (a) and HRTEM (b) Ni_{0.7}-ZIS/CoPi. (c-h) TEM and elemental mappings for Zn, In, Ni, Co, and S in Ni_{0.7}-ZIS/CoPi, the corresponding scale bars are 100 nm.

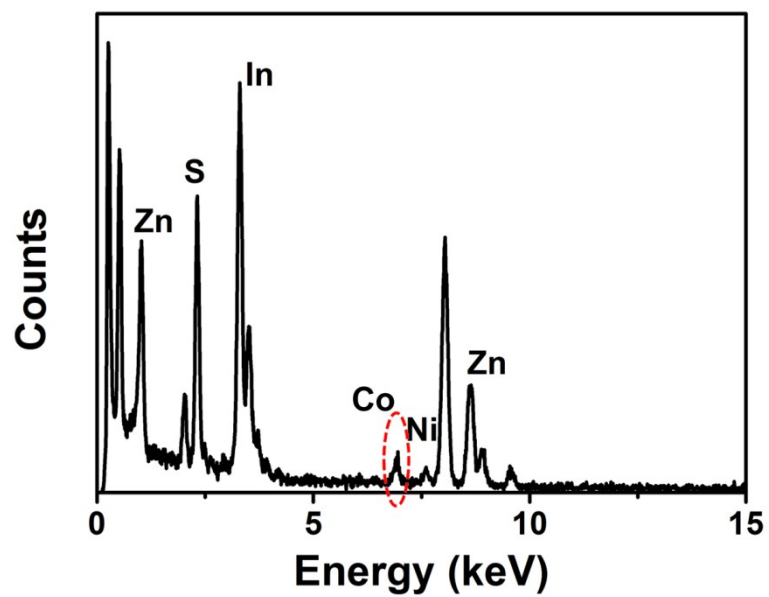


Fig. S16 EDX pattern of $\text{Ni}_{0.7}\text{-ZIS/CoPi}$.

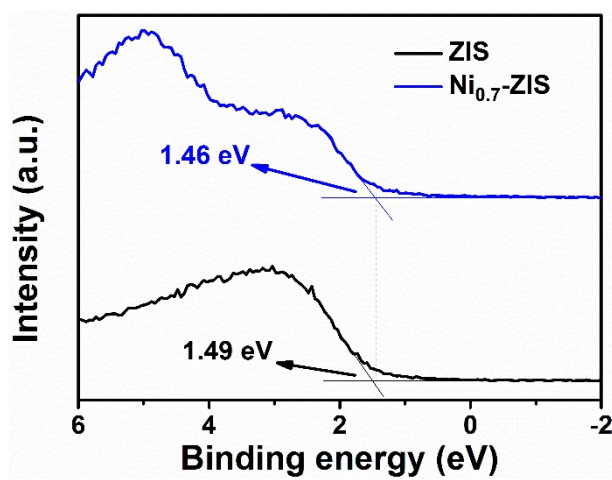


Fig. S17 XPS valence band spectra of ZIS and $\text{Ni}_{0.7}\text{-ZIS}$.

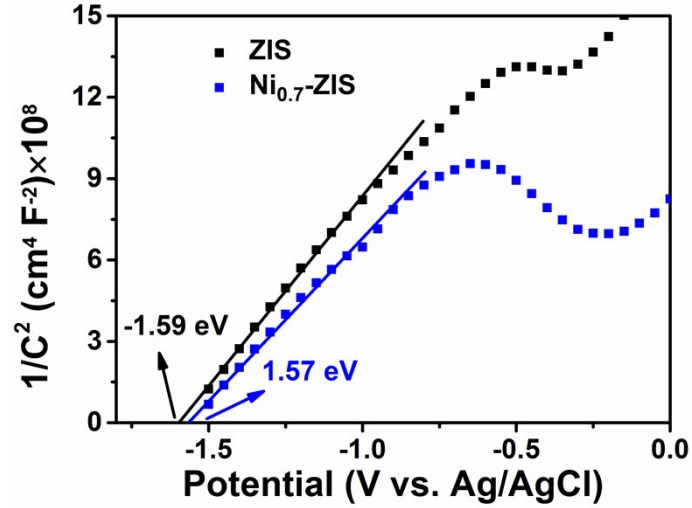


Fig. S18 Mott-Schottky curves of ZIS and Ni_{0.7}-ZIS-300.

To acquire quantitative insight about the charge carrier density of ZIS and Ni_{0.7}-ZIS, the capacitance measurement on the electrode/electrolyte is conducted following the equation¹:

$$\frac{1}{C^2} = \frac{2}{N_d e \epsilon_0 \epsilon} \left[(E_s - E_{fb}) - \frac{kT}{e} \right]$$

Where C is the space charge capacitance in the semiconductor, N_d is the electron carrier density, e is the elemental charge value, ε₀ is the permittivity of the vacuum, ε is the relative permittivity of the semiconductor, E_s is the applied potential, E_{fb} is the flat band potential, T is the temperature and k is the Boltzmann constant.

The carrier density N_d can be determined using the following equation:

$$N_d = - \left(\frac{2}{e \epsilon_0 \epsilon} \right) \left[\frac{d(E_s)}{d\left(\frac{1}{C^2}\right)} \right]$$

where e = 1.6 × 10⁻¹⁹ C, ε₀ = 8.86 × 10⁻¹² F m⁻¹, ε = 4.7.² The calculated carrier densities of ZIS and Ni_{0.7}-ZIS are 2.129 × 10²⁰ and 2.443 × 10²⁰ cm⁻³, respectively, which are

almost the same.

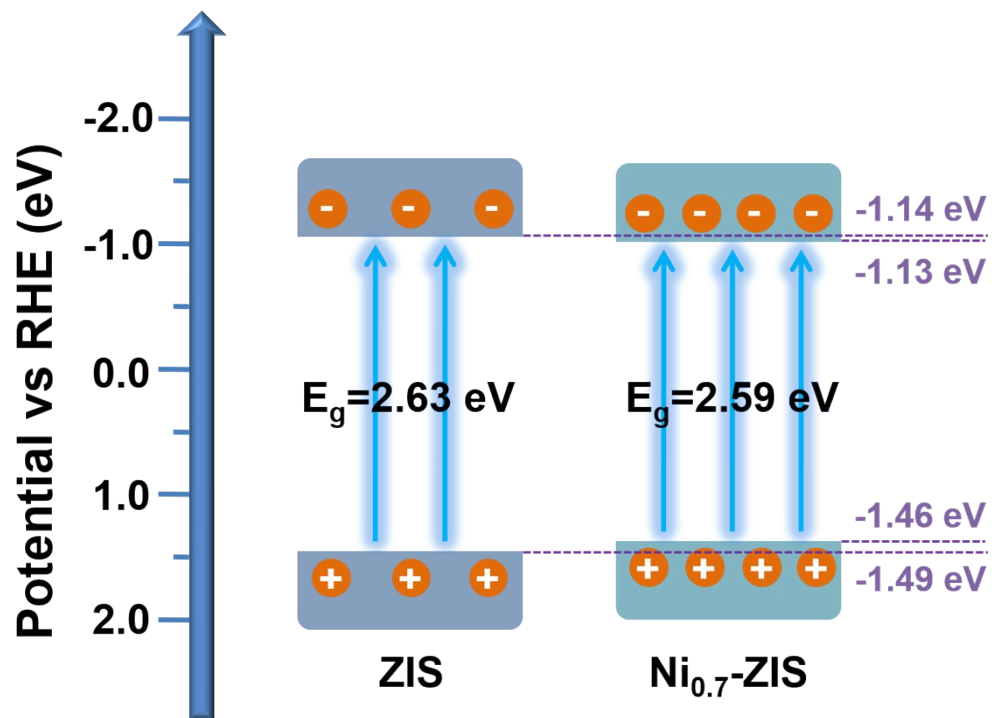


Fig. S19 Schematic illustration of the band structure of ZIS and Ni_{0.7}-ZIS samples.

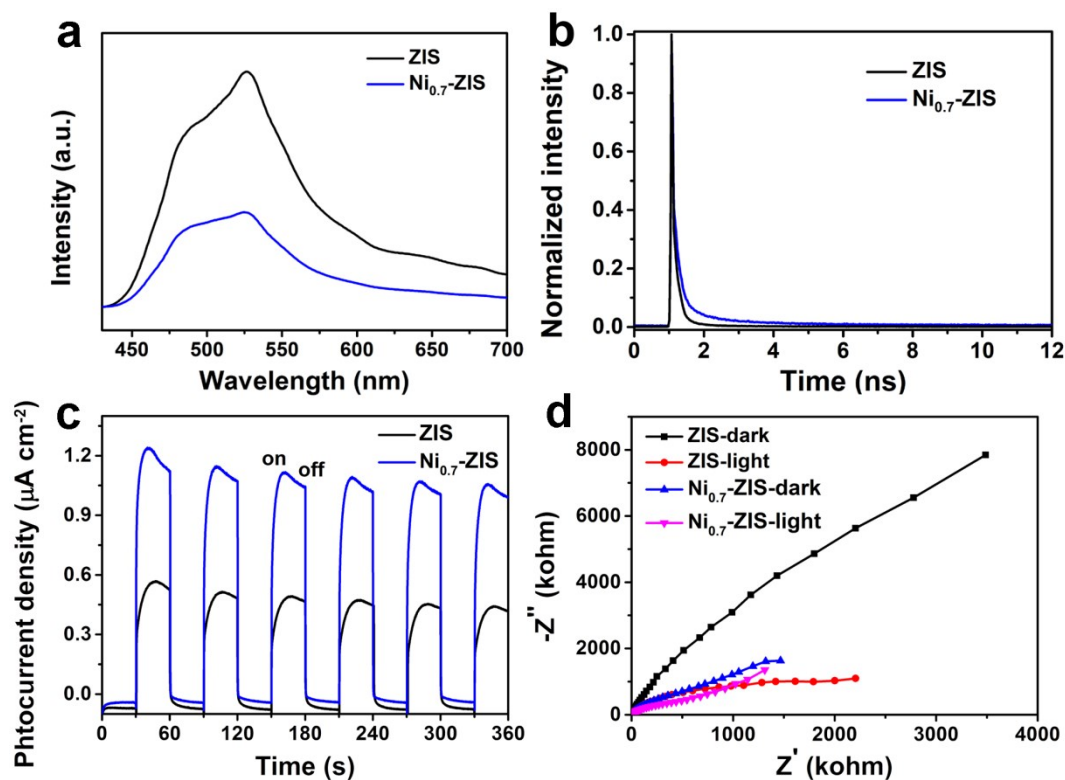


Fig. S20 (a) Steady-state PL spectra of ZIS and Ni_{0.7}-ZIS. (b) Time-resolved transient PL decay of ZIS and Ni_{0.7}-ZIS. (c) Transient photocurrent responses of ZIS and Ni_{0.7}-ZIS. (d) electrochemical impedance spectroscopy of ZIS and Ni_{0.7}-ZIS under dark and visible light irradiation.

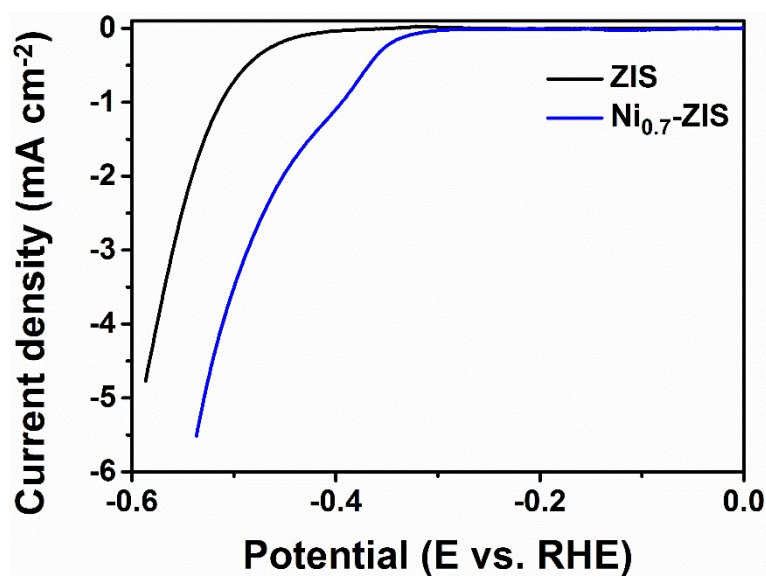


Fig. S21 *J-V* curves of ZIS and Ni_{0.7}-ZIS in 0.1 M NaOH aqueous solution without light irradiation.

Table S1. The different contents in ZIS and Ni-ZIS measured by ICP-MS and theoretical calculation.

Sample	Ni(NO ₃)·6H ₂ O (mL)	Ni (wt%) ICP-MS	Ni (wt%) theoretical
ZIS	0	0	0
Ni _{0.3} -ZIS	0.11	0.26	0.31
Ni _{0.7} -ZIS	0.25	0.67	0.69
Ni _{1.4} -ZIS	0.5	1.25	1.39
Ni _{2.1} -ZIS	0.75	1.96	2.09

Table S2. H₂ evolution at each wavelength of Ni_{0.7}-ZIS.

Wavelength (nm)	H ₂ evolution (μmol)	Light intensity (mW·cm ⁻²)
380	63.6	2
420	61.2	2
450	44.8	3
500	19.7	4.5
550	1.87	8
600	1.27	10
700	0	12

Table S3. Comparison of representative co-catalyst free photocatalysts and their H₂ evolution behaviors.

Catalysts	Sacrificial agent	H ₂ (mmol g ⁻¹ h ⁻¹)	AQE
Ni _{0.7} -ZIS (this work)	TEOA (10 vol%)	4.215	17.1% (420 nm)
Ni _{0.7} -ZIS (this work) (AM 1.5 G)	-	0.237	-
ZnIn ₂ -Au-TiO ₂ ³	-	0.186	-
g-C ₃ N ₄ /nanocarbon/ZnIn ₂ S ₄ ⁴	CH ₃ OH (6 vol%)	0.05	-
2D/2D phosphorene/g-C ₃ N ₄ ⁵	Lactic Acid (18 vol%)	0.571	1.2% (420 nm)
Black phosphorous/g-C ₃ N ₄ ⁶	Methanol	0.427	3.18% (420 nm)
2D black phosphorus/BiVO ₄ ⁷	-	0.27	0.89% (420 nm)
Janus-like g-MnS/Cu ₇ S ₄ ⁸ (full-spectrum irradiation)	Na ₂ S (0.35 M)/Na ₂ SO ₃ (0.25 M)	0.718	18.8% (420 nm)
O-doped ZnIn ₂ S ₄ ⁹	Na ₂ S (0.35 M)/Na ₂ SO ₃ (0.25 M)	2.12	-
Li-EDA treated P-25 ¹⁰ (AM 1.5 G)	Methanol (50 vol%)	3.46	2.57% (420 nm)
ZnIn ₂ S ₄ /g-C ₃ N ₄ ¹¹	TEOA (10 vol%)	2.6408	4.4% (420 nm)
DCN-200 ¹²	TEOA (10 vol%)	0.135	-
Cu _{0.5} -ZIS ¹³ (AM 1.5 G)	Asorbic acid (20% 0.75 M)	1.875	-
In ₂ O ₃ -ZnIn ₂ Se ₄ ¹⁴	Na ₂ S (0.35 M)/Na ₂ SO ₃ (0.25 M)	0.32	-
In ₂ O ₃ -ZnIn ₂ Se ₄ -Mo ¹⁴	Na ₂ S (0.35 M)/Na ₂ SO ₃ (0.25 M)	6.95	-

Notes and references

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