

Supporting Information

Broad-Spectrum Response of NiCo₂O₄-ZnIn₂S₄ p-n Junction Synergies Photothermal and Photocatalytic Effects for Efficient H₂ Evolution

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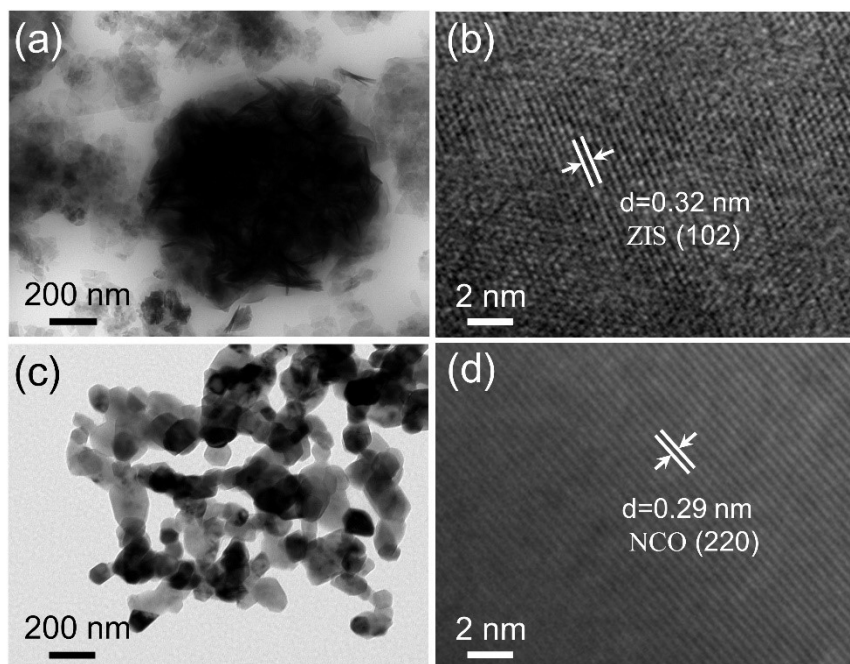


Fig. S1 (a) TEM, and (b) HRTEM images of ZIS. (c) TEM, and (d) HRTEM images of NCO.

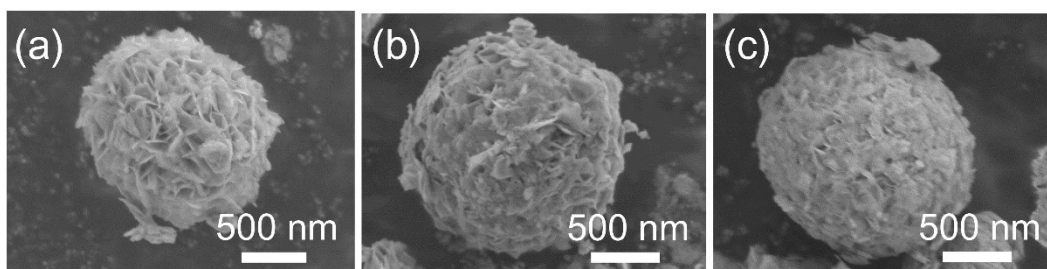


Fig. S2 SEM images of NCO-ZIS-X. (a) NCO-ZIS-1. (b) NCO-ZIS-10. (c) NCO-ZIS-20.

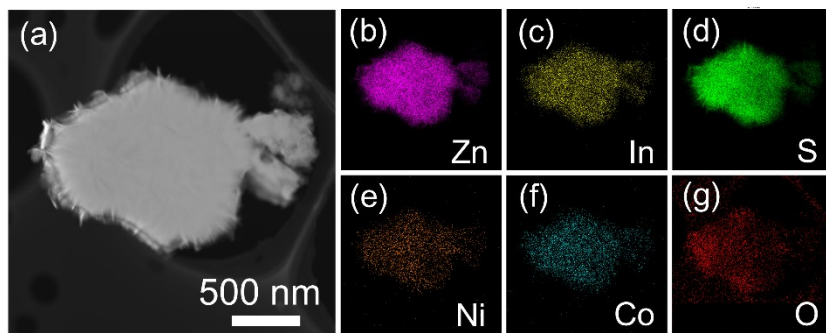


Fig. S3 EDS and corresponding element mapping images of Zn, In, S, Ni, Co, and O in NCO-ZIS-5.

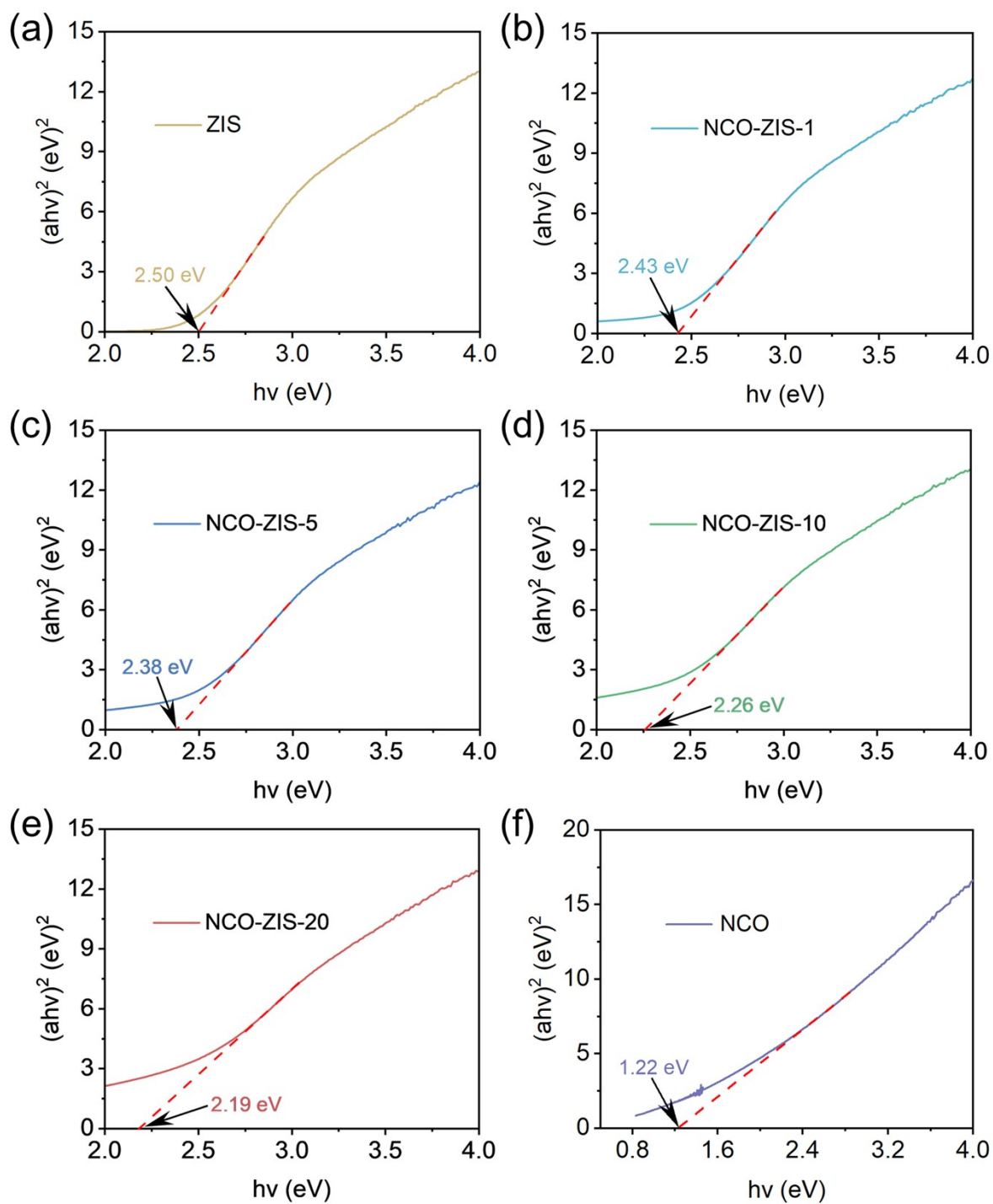


Fig. S4 Tauc plots deriving from the absorbance spectra to evaluate the band gaps of (a) ZIS, (b) NCO-ZIS-1, (c) NCO-ZIS-5, (d) NCO-ZIS-10, (e) NCO-ZIS-20, and (f) NCO.

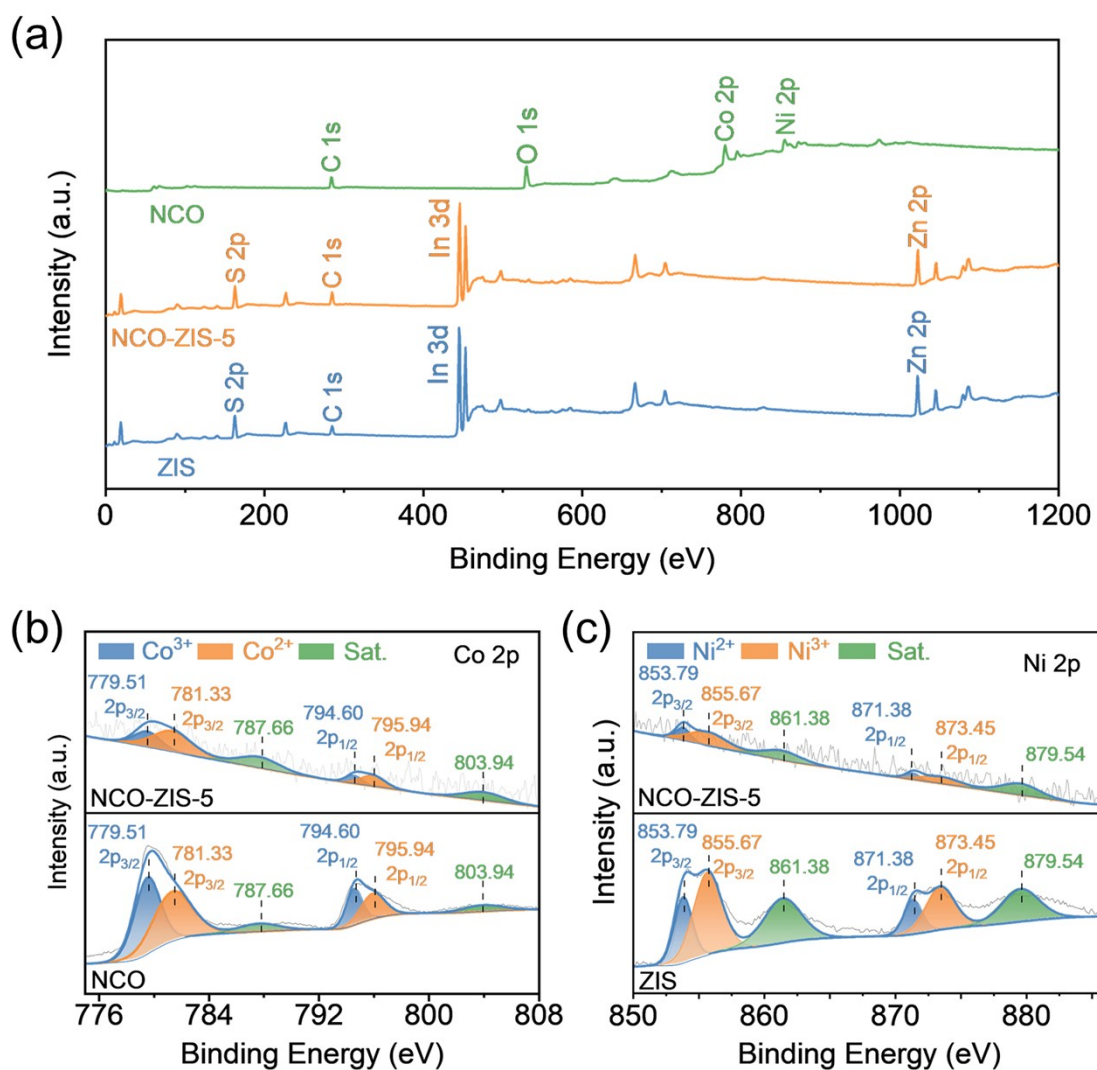


Fig. S5 (a) XPS survey spectra and high-resolution XPS spectra of (b) Co 2p and (c) Ni 2p of the as-prepared samples.

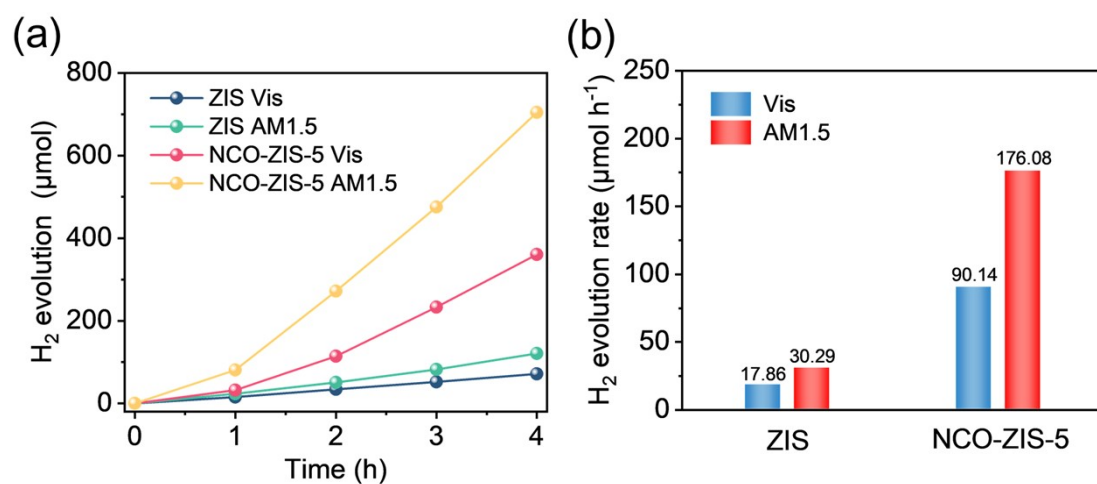


Fig. S6 (a) Time-course photocatalytic H₂ evolution over ZIS and NCO-ZIS-5 and (b) the corresponding H₂ evolution rates under visible light irradiation and full spectrum.

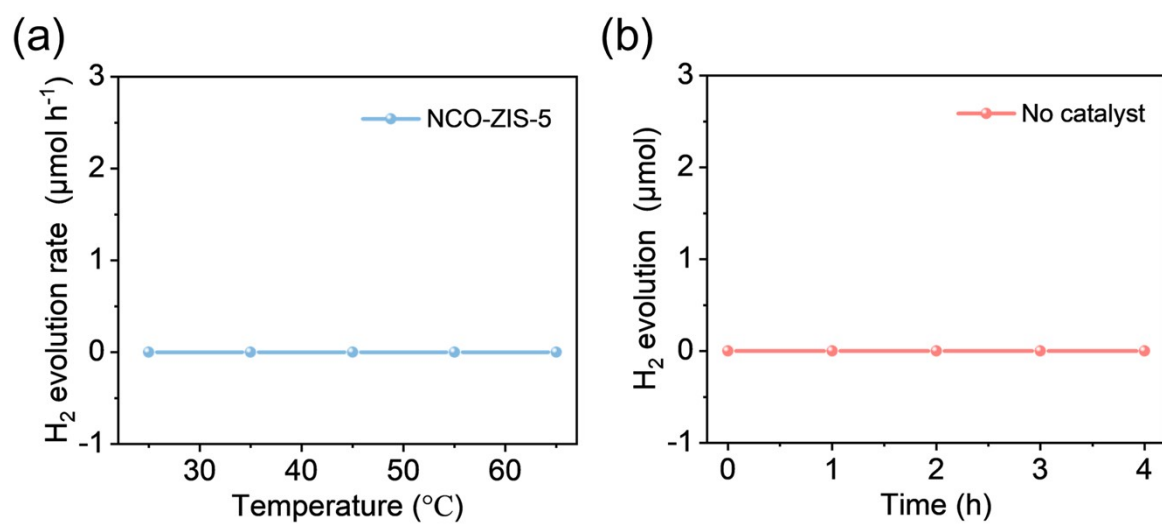


Fig. S7 The blank experiments of hydrogen evolution under (a) dark condition and (b) without catalyst.

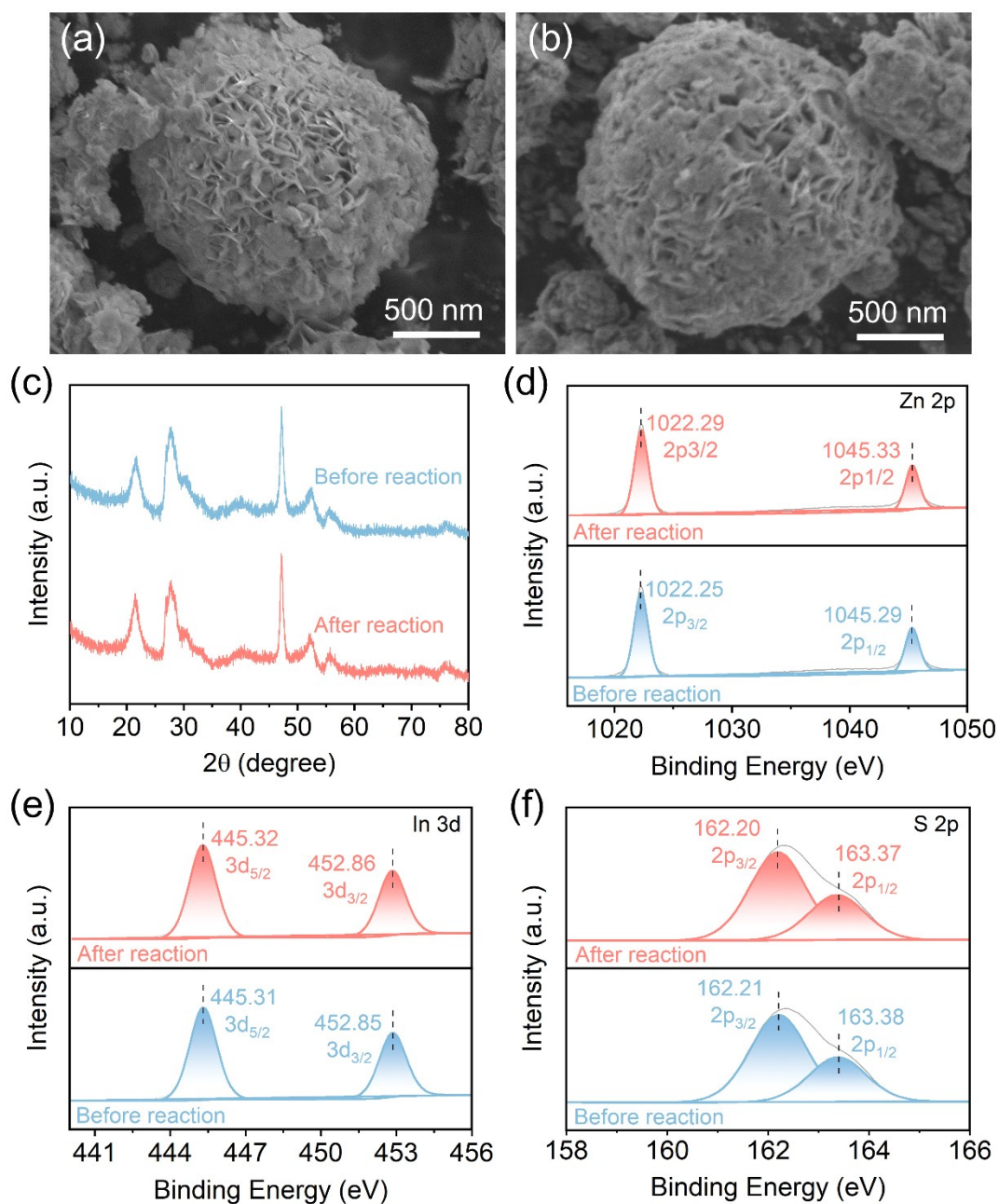


Fig. S8 SEM images of NCO-ZIS-2 (a) before and (b) after photocatalytic reaction. (c) XRD patterns and (d-f) XPS spectra of Zn 2p, In 3d, and S 2p before and after photocatalytic reaction.

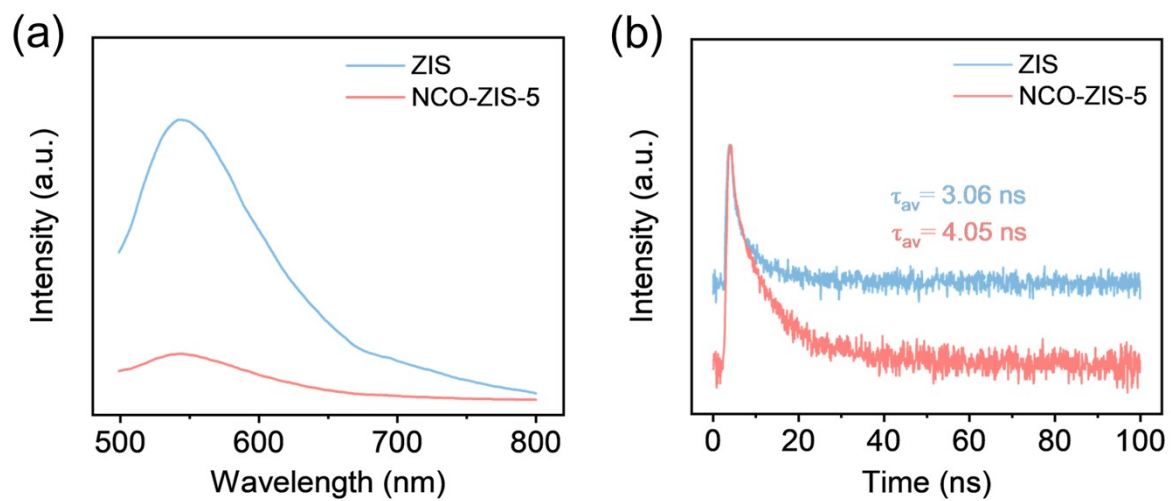


Fig. S9 (a) Steady-state PL spectra and (b) TRPL spectra of ZIS and NCO-ZIS.

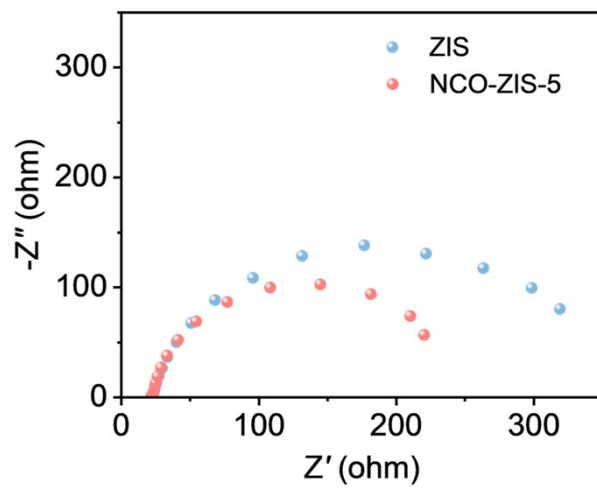


Fig. S10 EIS of ZIS and NCO-ZIS.

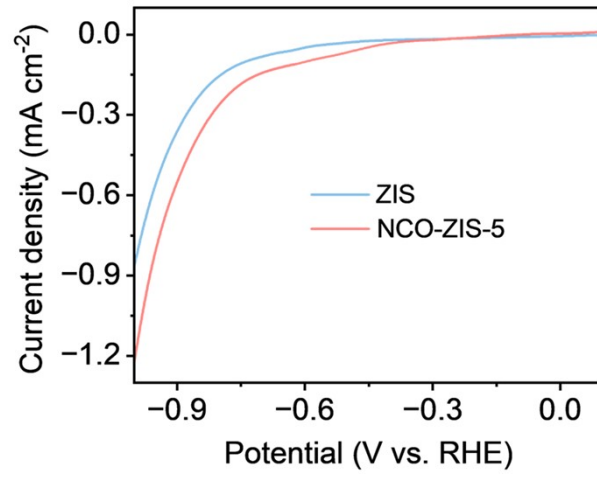


Fig. S11 LSV curves of ZIS and NCO-ZIS.

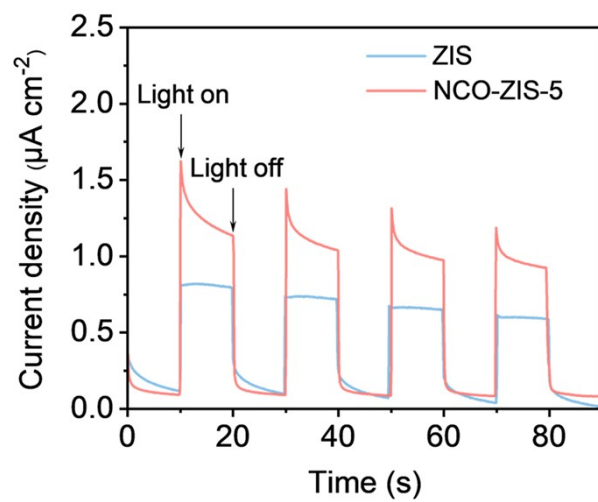


Fig. S12 Transient photocurrent spectra of ZIS and NCO-ZIS.

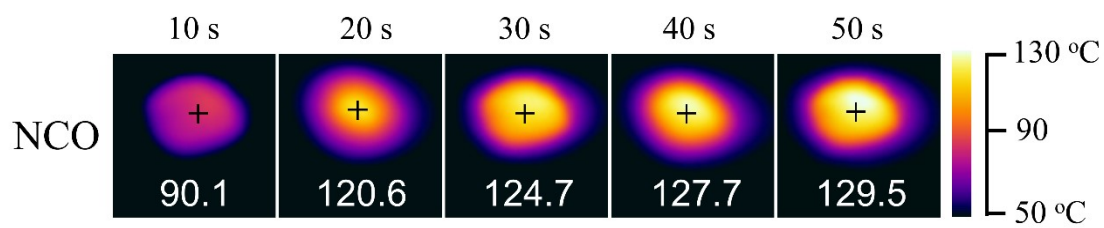


Fig. S13 The temperature fluctuation of NCO under visible light irradiation.

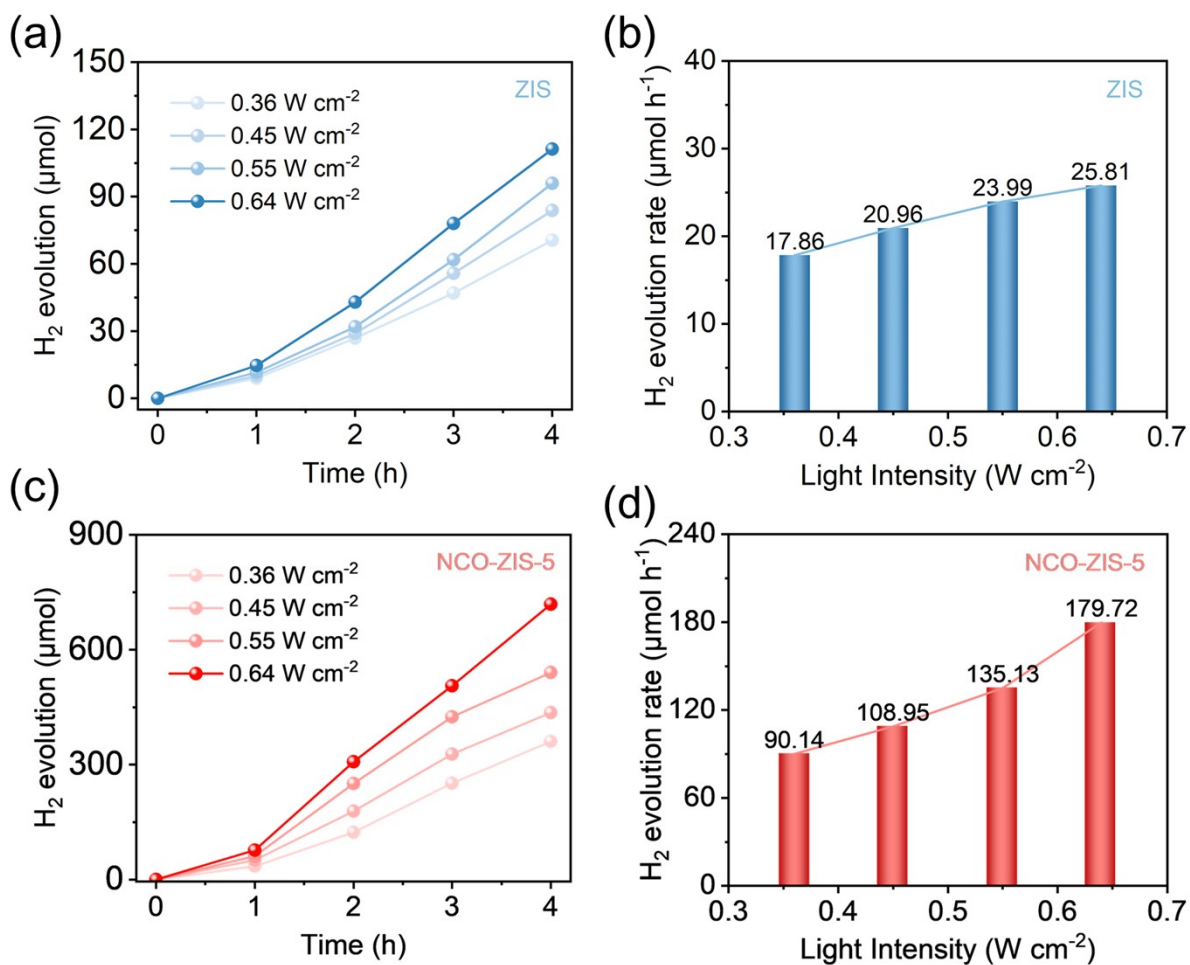


Fig. S14 The photocatalytic hydrogen production rate of (a-b) ZIS and (c-d) NCO-ZIS under different light intensities.

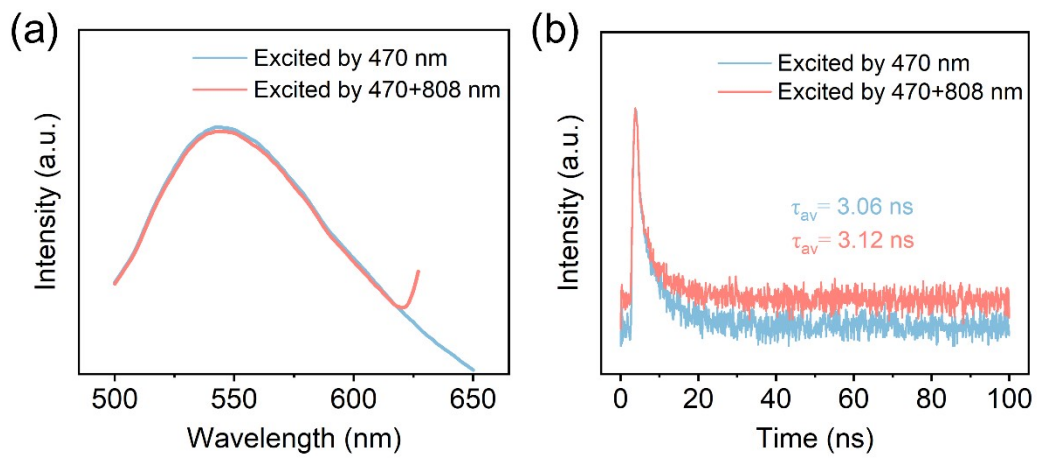


Fig. S15 (a) PL spectra and (b) TRPL decay spectra of ZIS under different excitation.

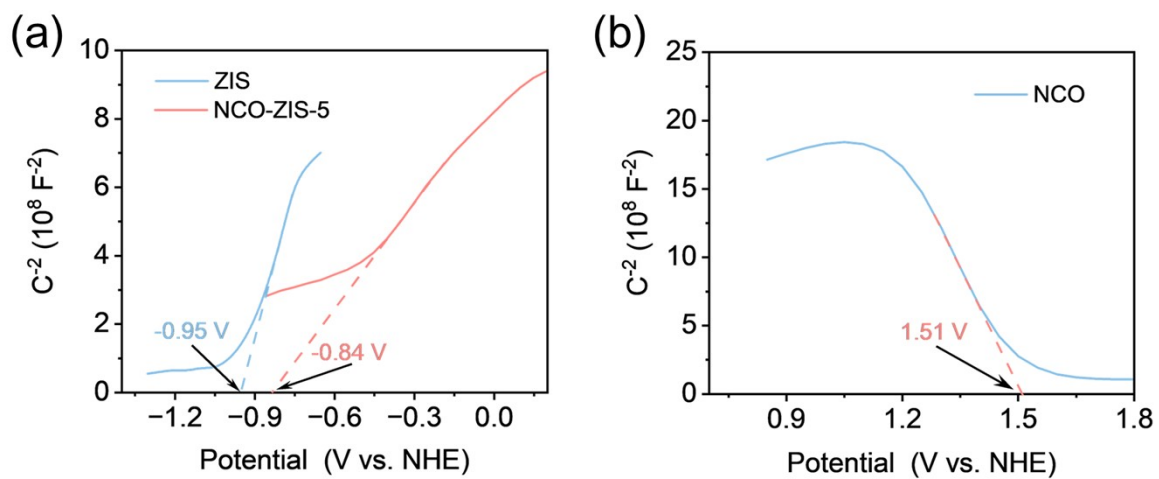


Fig. S16 M-S plots of (a) ZIS and NCO-ZIS, (b) NCO.

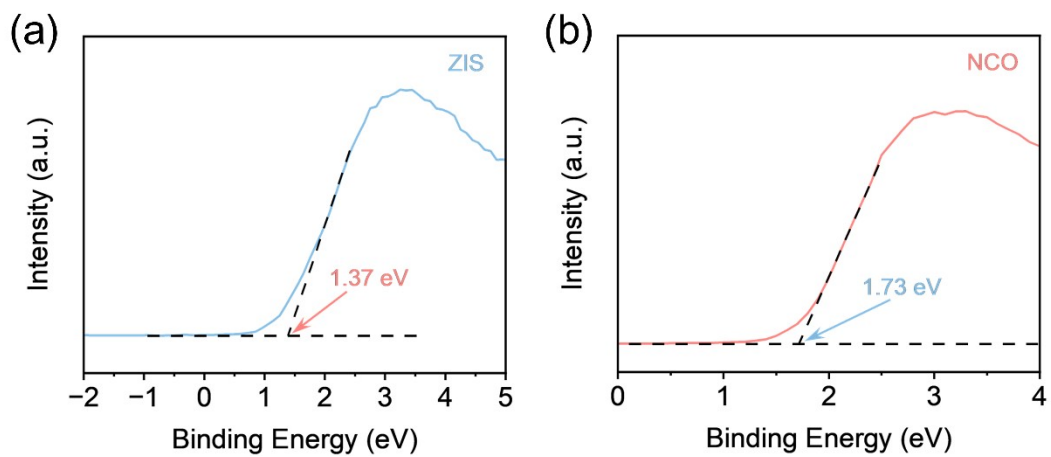


Fig. S17 The XPS valence band spectra of (a) ZIS and (b) NCO.

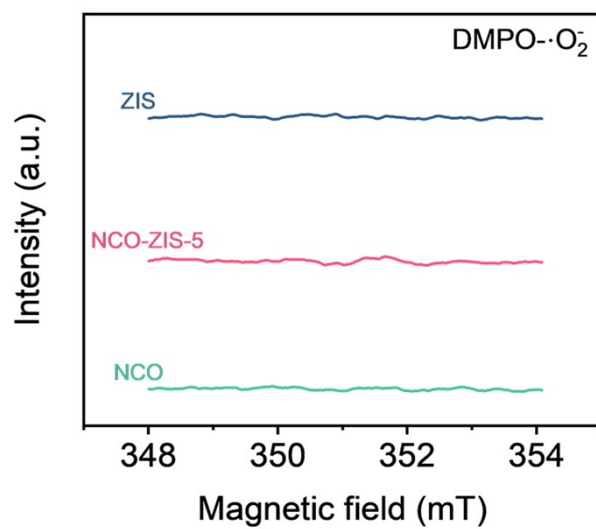


Fig. S18 DMPO spin-trapping EPR spectra of DMPO·O₂⁻ under dark condition.

Table S1 Comparison of the photocatalytic H₂ generation over ZnIn₂S₄-based photocatalysts.

| Photocatalysts | Light source | Sacrificial agent | co-catalyst | H ₂ evolution rate (umol/h/g) | Ref. |
|-------------------------------------------------------------------------------------|--------------------------------------|---------------------------------------------------|-----------------------------------------------|------------------------------------------|----------------------|
| ZnIn ₂ S ₄ @PCN-224 | 300 W Xe amp (λ>420 nm) | Triethanolamine | / | 526 | 1 |
| Mo ₂ C/ZnIn ₂ S ₄ | 300 W Xe amp (λ>400 nm) | Triethanolamine | Mo ₂ C | 4093 | 2 |
| Ti ₃ C ₂ T _x / ZnIn ₂ S ₄ | 300 W Xe amp (λ>400 nm) | Triethanolamine | Ti ₃ C ₂ T _x | 2035 | 3 |
| BC/ZnIn ₂ S ₄ | 150 W Xe amp | Triethanolamine | / | 4466 | 4 |
| TiO ₂ /ZnIn ₂ S ₄ | 300 W Xe lamp | Triethanolamine | / | 215 | 5 |
| dZni-ZnIn ₂ S ₄ | 300 W Xe lamp (λ>420 nm) | Triethanolamine | / | 42.8 | 6 |
| CeO ₂ /ZnIn ₂ S ₄ | 300 W Xe lamp | Na ₂ S/Na ₂ SO ₄ | / | 1497 | 7 |
| Ni _x P/CuWO ₄ /ZnIn ₂ S ₄ | 300 W Xe lamp | Triethanolamine | Ni _x P | 3015 | 8 |
| CNF _S -ZnIn ₂ S ₄ | 300W Xe lamp (λ >420nm) | Triethanolamine | / | 3166 | 9 |
| Ti ₃ C ₂ T _x / ZnIn ₂ S ₄ | 300W Xe lamp (λ >420nm) | Triethanolamine | / | 3280 | 10 |
| C ₃ N ₄ -ZnIn ₂ S ₄ | 300W Xe lamp (λ >420nm) | Triethanolamine | / | 2780 | 11 |
| RGO/ZnIn ₂ S ₄ | 350W Xe lamp (λ >420nm) | Na ₂ S/Na ₂ SO ₄ | Pt/RGO | 1210 | 12 |
| NiCo₂O₄/ ZnIn₂S₄ | 300W Xe lamp (λ>420nm) | Triethanolamin e | / | 4507 | This work |

Table S2 Lifetime Parameters of ZIS and NCO/ZIS-2 from the TRPL results.

| | τ_1 (ns) | A1(%) | τ_2 (ns) | A2 (%) | τ_3 (ns) | A3(%) | τ_{av} (ns) |
|-----------------------------|---------------|-------|---------------|--------|---------------|-------|------------------|
| ZIS (470 nm) | 0.63 | 41.74 | 4.80 | 58.26 | / | / | 3.06 |
| ZIS (470 nm+808 nm) | 0.63 | 42.87 | 4.99 | 57.13 | / | / | 3.12 |
| MC-ZIS-2 (470 nm) | 0.47 | 22.22 | 2.69 | 52.41 | 10.00 | 25.37 | 4.05 |
| MC-ZIS-2 (470 nm+808 nm) | 0.65 | 47.04 | 4.33 | 52.96 | / | / | 2.60 |

Table S3 The hydrogen evolution rate growth multiple of NCO-ZIS relative to ZIS under different light intensities.

| Light intensity (W cm ⁻²) | Hydrogen production | Hydrogen production | Growth multiple |
|------------------------------------------|-------------------------------------------|-----------------------------------------------|-----------------|
| | rate of ZIS ($\mu\text{mol h}^{-1}$) | rate of NCO-ZIS ($\mu\text{mol h}^{-1}$) | |
| 0.36 | 17.86 | 90.14 | 5.04 |
| 0.45 | 20.96 | 108.95 | 5.29 |
| 0.55 | 23.99 | 135.13 | 5.63 |
| 0.64 | 25.81 | 179.72 | 6.96 |

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