Electronic Supplementary Information:

Rational design of 2D/2D $ZnIn_2S_4/C_3N_4$ Heterojunction Photocatalysts for Enhanced Photocatalytic H_2 production

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Experimental

Sample preparation

Preparation of C_3N_4(180) nanosheets

Typically, 2.0 g melamine were added to 35 mL deionized water and stirred for 1 hour. Then, white melamine precursors were placed in 50 mL Teflon-lined autoclave and heated at 180 °C for 12 h in the oven. The obtained precursors were washed with deionized H_2O and dried in vacuum at 70 °C. Last, the obtained precursors were added to an alumina crucible and heated in muffle furnace (550 °C, 2.3 °C min^{-1}, 4 h). The products were obtained and marked as C_3N_4(180). For comparison, the pristine C_3N_4 was got by thermal calcination of melamine (550 °C, 2.3 °C min^{-1}, 4 h).

Preparation of $ZnIn_2S_4$ nanosheets

The $ZnIn_2S_4$ nanosheet was synthesized by the hydrothermal way, 0.2 mmol $Zn(CH_3COO)_2 \cdot 2H_2O$, 0.4 mmol $InCl_3 \cdot 4H_2O$ and 1.6 mmol TAA were added to 30 mL solution (15 mL H_2O and 15 mL ethanol). The solution was vigorous stirred for 30 min until solution was transparent. Then, the above solution was placed into 50 mL Teflon lined autoclave and heated at 180 °C for 24 h. The obtained sample was washed with deionized water and ethanol, and then dried in vacuum at 80 °C.

Preparation of 2D $ZnIn_2S_4$/2D C_3N_4(180) heterojunction

First, 0.14 mmol $Zn(CH_3COO)_2 \cdot 2H_2O$, 0.28 mmol $InCl_3 \cdot 4H_2O$ and 1.12 mmol TAA were added to 30 mL solution (15 mL H_2O and 15 mL ethanol). The solution was vigorous stirred for 30 min until solution was transparent. Then, 0.1 g C_3N_4(180) nanosheets were added to the above solution and stirred for 30 min. Finally, the mixed solution was placed into 50 mL Teflon lined autoclave and heated at 180 °C for 24 h. The obtained sample was washed with deionized water and ethanol and then dried in vacuum at 80 °C. Various mass ratio of $ZnIn_2S_4$ nanosheets were studied for optimal proportion, including 20, 30, 40 and 50 wt.%, and the samples were marked as $XZnIn_2S_4/C_3N_4$(180), where X = 20, 30, 40 and 50. Besides, the preparation process of $40ZnIn_2S_4/C_3N_4$ is similar to that of $40ZnIn_2S_4/C_3N_4$(180) except that C_3N_4(180) was replaced by C_3N_4.

Characterization

Powder X-ray diffraction (PXRD) was tested by D/MAX-2500 diffractometer (Empyrean-100, Holland). Fourier transform infrared spectra (FT-IR) was tested by Nicolet iS50 spectrometer (America). Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were tested on S-4800 field emission SEM (JSM-7800F, Japan) and transmission electron microscopy (JEM-2100, Japan). The thickness of samples was tested by using Asylum Research MFP930 (America) on the atomic force microscopy (AFM). The X-ray photoelectron spectroscopy (XPS) was tested by Thermofisher Escalab 250 Xi+ instrument (America). UV−vis absorption spectra were tested by Shimadzu UV-2450 spectrophotometer (Japan). The nitrogen adsorption and desorption isotherms were tested by Quadrasorb evo analyzer (America). The steady-state and transient photoluminescence (PL) spectra was tested

by the QM400 instrument (America). The photoelectrochemical performance was tested by the CHI760D (Chenhua, China) electrochemical workstation.

Photocatalytic H_2 production experiments

The photocatalytic H_2 production was studied by the Labsolar-6A system (Beijing Perfectlight Technology Co., Ltd., China). The photocatalytic reactor was irradiated via the 300 W Xenon lamp (PLS-SXE300+, Beijing Perfectlight, China). First, 50 mg photocatalysts sample and 10 mL triethanolamine were added into 90 mL H_2O solution. Then, 2 mL H_2PtCl_6 aqueous solution was added for co-catalyst Pt (~ 3 wt % Pt). Last, the photocatalytic reactor was vacuumed and the temperature was kept at 5 ℃. The photocatalytic H_2 production was checked via the gas chromatography apparatus (GC9790II, Fuli instruments Co., Ltd., China).

The apparent quantum efficiency (AQE) of the photocatalytic H_2 production is calculated from equation as follows:

$$AQE = \frac{2 \times the\ number\ of\ evolved\ H\ molecules}{the\ number\ of\ incident\ photons} \times 100\%$$

The solar-to-hydrogen (STH) conversion efficiency is given by:

$$STH = \frac{R(H_2) \times \Delta G_r}{P \times S} \times 100\%$$

Where $R(H_2)$, ΔGr, P, and S represent the rate of hydrogen evolution, the Gibbs energy for the reaction (H_2O (l) → H_2 (g) + 1/2 O_2 (g)), the energy intensity of the AM1.5G solar irradiation (100mW cm^{-2}) and the irradiated sample area (20 cm^2), respectively.

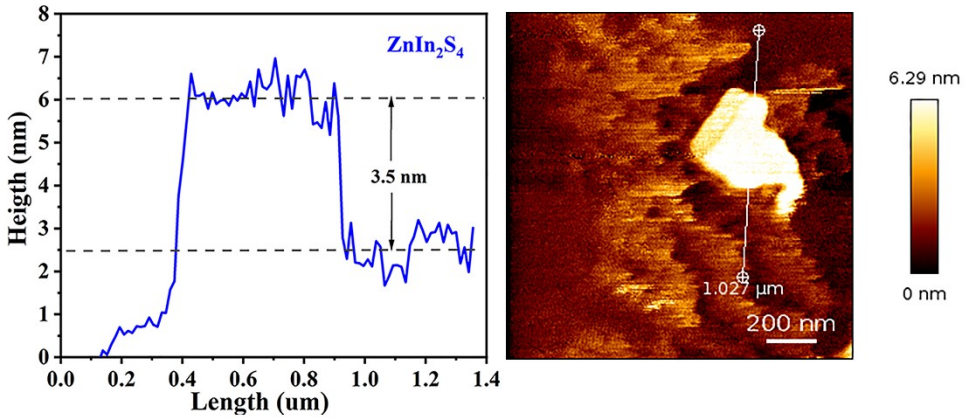

Fig. S1 AFM images and thickness of $ZnIn_2S_4$.

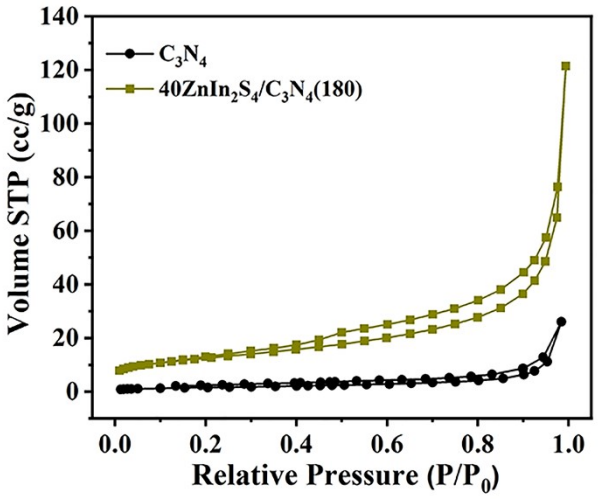

Fig. S2 Nitrogen adsorption-desorption isotherms of C_3N_4 and $40ZnIn_2S_4/C_3N_4(180)$.

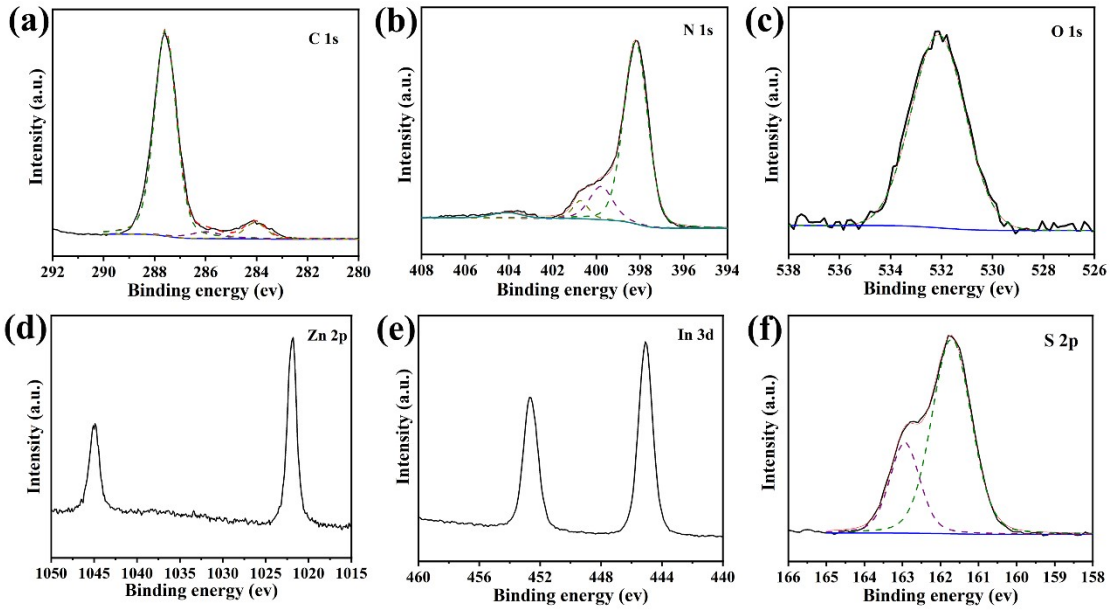

Fig. S3 (a) C 1s XPS spectrum, (b) N 1s XPS spectrum, (c) O1s XPS spectrum, (d) Zn 2p XPS spectrum, (e) In 3d XPS spectrum, (f) S 2p XPS spectrum of $40ZnIn_2S_4/C_3N_4(180)$.

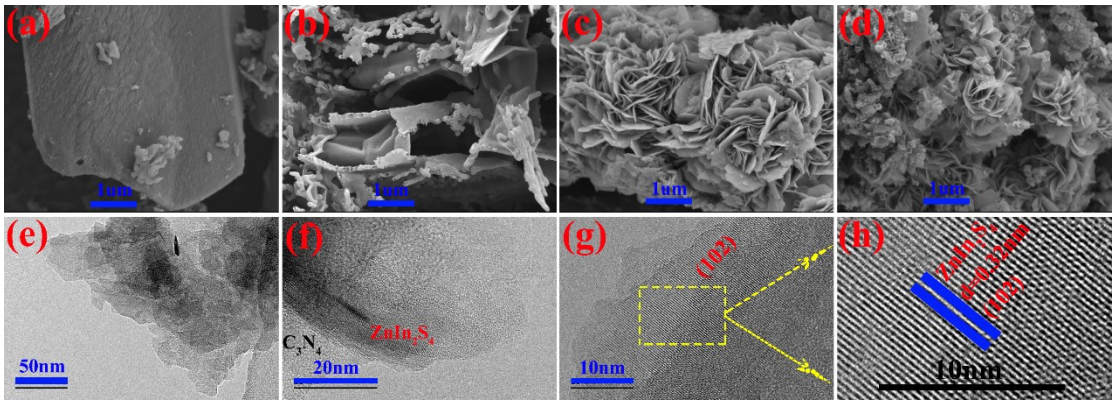

Fig. S4 Typical SEM images of the recycled catalyst (a) C_3N_4, (b) $C_3N_4(180)$, (c) $ZnIn_2S_4$, (d) $40ZnIn_2S_4/C_3N_4(180)$. (e-h) TEM images of the recycled catalyst ($40ZnIn_2S_4/C_3N_4(180)$).

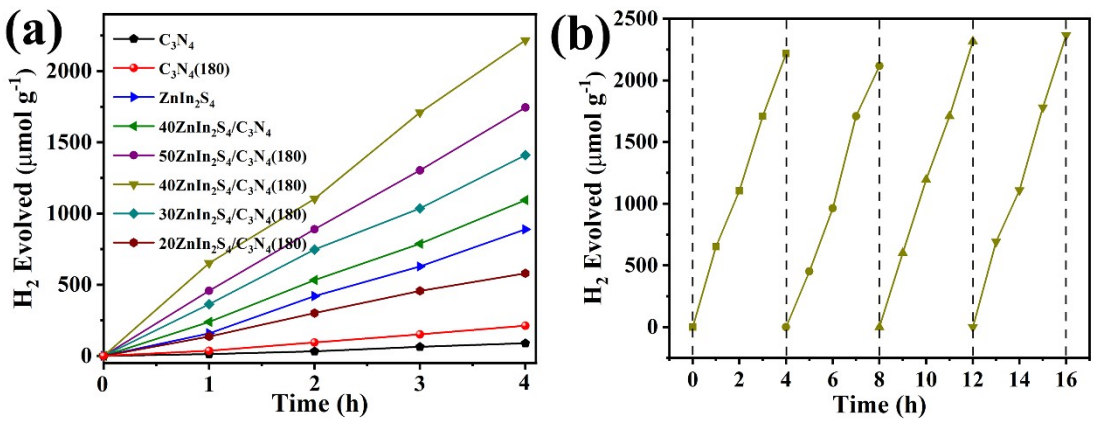

Fig. S5 (a) Time courses of photocatalytic H_2 production without sacrificial agent. (b) Photocatalytic H_2 evolution stability of 40$ZnIn_2S_4$/C_3N_4(180) without sacrificial agent.

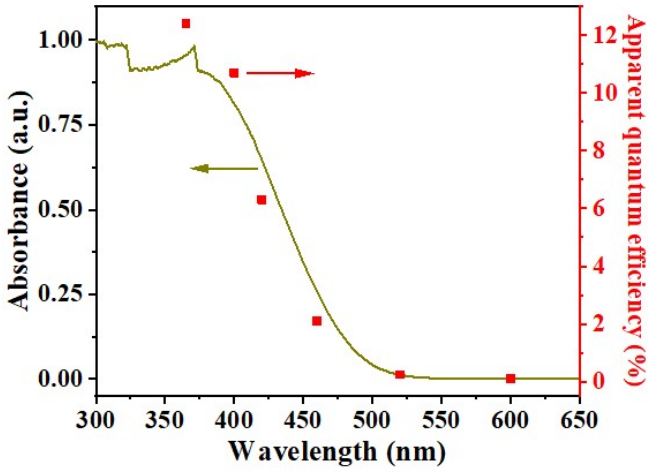

Fig. S6 The wavelength dependent AQE of H_2 evolution over 40$ZnIn_2S_4$/C_3N_4(180).

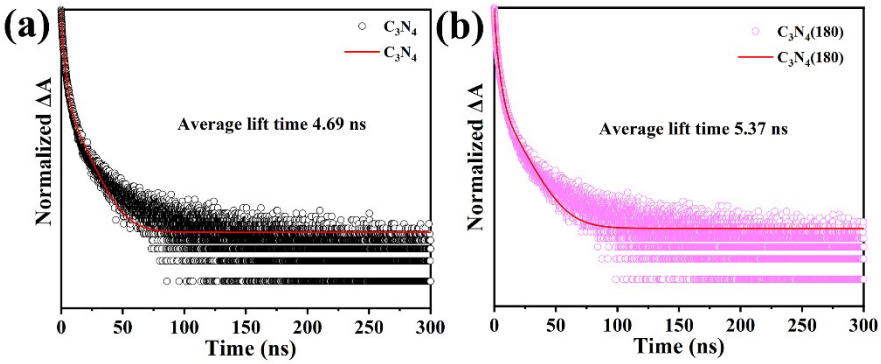

Fig. S7 The time-resolved PL spectra of (a) C_3N_4 and (b) C_3N_4(180).

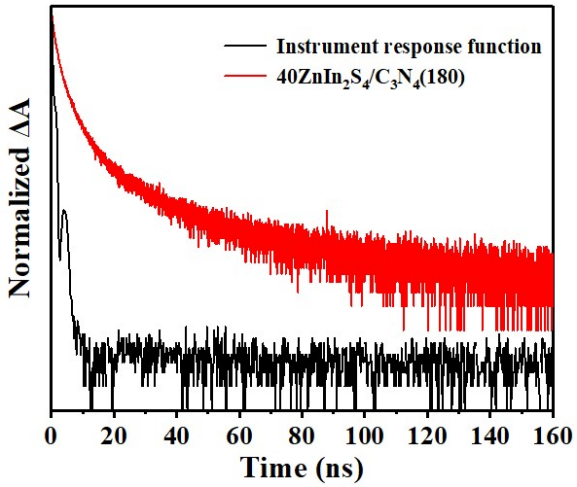

Figure S8 The instrument response function and time-resolved PL spectra of 40$ZnIn_2S_4$/C_3N_4(180).

Table 1

Comparative representation photocatalytic performances of $ZnIn_2S_4$ based photocatalysts reported in other similar works.

Sample	Light Source	Co-catalyst	Sacrificial agent	Activity (μmol h^{-1} g^{-1})	Refs.
$ZnIn_2S_4$/g-C_3N_4/graphene	Solar light irradiation	Not used	Na_2SO_3/Na_2S	477	[1]
$ZnIn_2S_4$/g-C_3N_4	400 W Xe lamp (λ > 420 nm)	Pt	TEOA	450	[2]
Au/g-C_3N_4/$ZnIn_2S_4$	300 W Xe lamp (λ > 420 nm)	Pt	Na_2SO_3/Na_2S	973	[3]
$Zn_3In_2S_6$/FCN	300 W Xe lamp (λ > 420 nm)	Pt	Na_2SO_3/Na_2S	510	[4]
$ZnIn_2S_4$/g-C_3N_4	300 W Xe lamp (λ > 420 nm)	Not used	TEOA	956	[5]
$ZnIn_2S_4$/C_3N_4	300 W Xe lamp (λ > 420 nm)	Pt	TEOA	2016.94	This work

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