

## Supporting Information

### **Integrating Dual-defects and heterojunction in $\text{ZnIn}_2\text{S}_{4-x}$ /g- $\text{C}_3\text{N}_{4-x}$ composite induces breaking-symmetry for photocatalytic hydrogen production**

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## Chemicals

Indium chloride tetrahydrate ( $\text{InCl}_3 \cdot 4\text{H}_2\text{O}$ ), Chloroplatinic acid ( $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ ), Zinc acetate ( $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ ), thioacetamide ( $\text{CH}_3\text{CSNH}_2$ ), triethanolamine (TEOA), ethanol ( $\text{C}_2\text{H}_5\text{OH}$ ) and melamine ( $\text{C}_3\text{H}_6\text{N}_6$ ) are supplied by Aladdin Reagent Company, China, sulfuric acid ( $\text{H}_2\text{SO}_4$ ) is all supplied by Sinopharm Chemical Reagent Co., Ltd. All reagents used in the experiment are analytically pure and can be used directly without further purification.

## Synthesis of defective carbon nitride ( $\text{CN}_{\text{Nv}}$ )

First, 5 g of melamine was added to 100 mL of deionized water and stirred to form a suspension, and then 5 mL of sulfuric acid solution ( $V_{\text{sulfuric acid}}:V_{\text{water}}=1:1$ ) was slowly added dropwise to the suspension. After stirring for 2 hours, the resulting product underwent washing with deionized water and ethanol, followed by filtration to collect. The product was dried in an oven at 80 °C for 8 h. Subsequently, an alumina crucible containing 10 g of sulfuric acid-treated melamine was heated from ambient temperature to 600 °C at a ramp rate of 1 °C  $\text{min}^{-1}$  under an atmosphere of Ar gas using a tube furnace and held for 40h to obtain  $\text{CN}_{\text{Nv}}$ .

## Synthesis of carbon nitride (g- $\text{C}_3\text{N}_4$ )

Thermal polymerization was used to synthesize g- $\text{C}_3\text{N}_4$ . g- $\text{C}_3\text{N}_4$  was obtained by placing 2 g of melamine in a crucible and raising the temperature to 520 °C in air at an elevated rate of 5 °C  $\text{min}^{-1}$  and keeping it there for 4 hours.

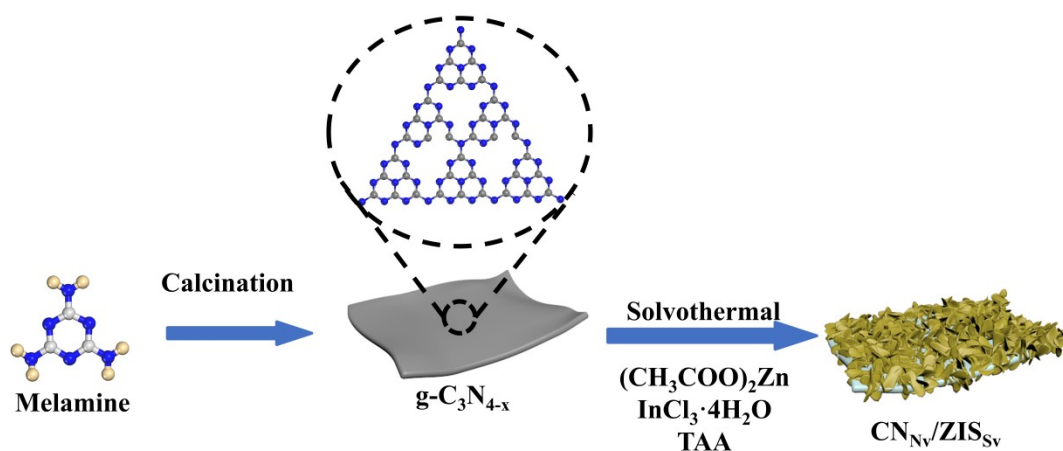
## Synthesis of $\text{ZIS}_{\text{Sv}}/\text{CN}_{\text{Nv}}$ composites

First, 0.4 mmol  $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ , 0.8 mmol  $\text{InCl}_3 \cdot 4\text{H}_2\text{O}$  and 3.2 mmol TAA

are added into 30 mL ethanol solution ( $V_{\text{water}}: V_{\text{ethanol}}=1:1$ ), then stirring for 30 min. Subsequently, X mg ( $X=0, 5, 10, 15, 20$ ) of  $\text{CN}_{\text{NV}}$  was weighed and added to the above solution and stirred for 30 minutes to obtain a homogeneous suspension. The mixed solution was then transferred to an autoclave reactor and reacted at  $180^{\circ}\text{C}$  for 24 hours. The sample obtained was washed three times with deionized water and ethanol and then dried in a vacuum oven at  $60^{\circ}\text{C}$  for 12h. The as-obtained samples were denoted as  $\text{ZIS}_{\text{SV}}/5\text{CN}_{\text{NV}}$ ,  $\text{ZIS}_{\text{SV}}/10\text{CN}_{\text{NV}}$ ,  $\text{ZIS}_{\text{SV}}/15\text{CN}_{\text{NV}}$  and  $\text{ZIS}_{\text{SV}}/20\text{CN}_{\text{NV}}$ , respectively. The detailed preparation procedure is shown schematically in Scheme S1. For comparison,  $\text{ZIS}_{\text{SV}}$  was also prepared via a similar method as that for the preparation of  $\text{ZIS}_{\text{SV}}/\text{CN}_{\text{NV}}$  composites without adding  $\text{CN}_{\text{NV}}$  in the synthesis process.

### Synthesis of $\text{ZnIn}_2\text{S}_4/10\text{CN}_{\text{NV}}$ and $\text{ZIS}_{\text{SV}}/10\text{g-C}_3\text{N}_4$ composites

$\text{ZnIn}_2\text{S}_4/10\text{CN}_{\text{NV}}$  and  $\text{ZIS}_{\text{SV}}/10\text{g-C}_3\text{N}_4$  were prepared similarly to  $\text{ZIS}_{\text{SV}}/\text{CN}_{\text{NV}}$ .  $\text{ZnIn}_2\text{S}_4/10\text{CN}_{\text{NV}}$  was synthesized hydrothermally with the addition of 1.6 mmol of TAA.  $\text{ZIS}_{\text{SV}}/10\text{g-C}_3\text{N}_4$  was prepared under the same other conditions, except that CN was added during the hydrothermal process.



**Scheme S1.** Schematic illustration of a synthetic route for  $\text{CN}_{\text{NV}}/\text{ZIS}_{\text{SV}}$  composite.

## **Characterization**

The crystal structures and microtopography are explored by X-ray diffractometer (XRD, Rigaku SmartLab SE, Japan, Cu-K $\alpha$ , 10°–80°, 2° min<sup>-1</sup>), Scanning electron microscope (SEM, sigma 300), and a high-resolution transmission electron microscope (HRTEM, JEOL JEM-F200, Japan). The light absorption capacity of the samples was investigated by UV-Vis diffuse reflectance spectroscopy (DRS, Shimadzu 2450, Japan) and X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB 250X, U.S., C1S corrected at 284.8 eV) was used to characterize the surface chemistry of the materials. Steady-state fluorescence was tested by photoluminescence spectroscopy (PL, Hitachi F-7000, Japan). Reactive substances and vacancies in the reaction were detected by electron paramagnetic resonance spectroscopy (ESR/EPR, Bruker EMXplus-6/1, Germany). Both the electrochemical impedance spectroscopy (EIS) and photocurrent response were measured on the electrochemical workstation (CHI760E). The electrochemical workstation was a standard three-electrode system, in which the catalyst-coated indium tin oxide (ITO) was the working electrode, the Pt wire was the counter electrode and the Ag/AgCl electrode was the reference electrode. Femtosecond transient absorption spectroscopy (fs-TAS) was tested with a Helios Pump-Probe system (Ultrafast Systems LLC).

## **Photocatalytic H<sub>2</sub> production experiments**

Photocatalytic hydrogen production experiments were performed on an all-glass automated on-line trace gas analysis system (Labsolar-6A, Beijing Perfectlight) equipped with a 300 W xenon lamp fitted with a 420 nm cut-off filter. Typically, 50

mg of photocatalyst was added to a 15% aqueous solution of TEOA with a certain amount of  $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$  (3 wt% Pt), and then transfer to a quartz reactor with a light-transmitting top. Degassing of the entire system by means of a vacuum pump prior to the reaction in order to expel dissolved gases from the suspension. The whole photocatalytic hydrogenolysis reaction lasted for 4 hours, and the temperature of the reaction was maintained at  $5^\circ\text{C}$  using a circulating water system. Hourly collected gases were analyzed using a gas chromatograph.

### **Femtosecond time-resolved transient absorption (fs-TA)**

The fs-TA measurements were accomplished using a femtosecond regenerative amplified Ti-sapphire laser system in which the amplifier was seeded with the 120 fs laser pulses from an oscillator laser system. It was measured in the combined utilization of the Femtosecond Laser System (Coherent) and the Helios Pump-Probe System (Ultrafast Systems LLC). The 360 nm pump pulses were generated from optical parametric amplifier (TOPAS-800-fs), which was pumped by the 800 nm fundamental beam outputted from Femtosecond Laser System. The white light continuum probe beam was generated by focusing a small portion ( $\sim 10 \mu\text{J}$ ) of the regenerative amplifier's fundamental 800 nm laser pulses into a 2 mm sapphire crystal. The pump and probe beams intersected on the sample at a particular angle. In order to achieve high signal-to-noise ratios, the data were collected with the range of 5 to 10 scans in the measurement and the signal amplitudes in the fs-TA measurements were averaged for further analysis.

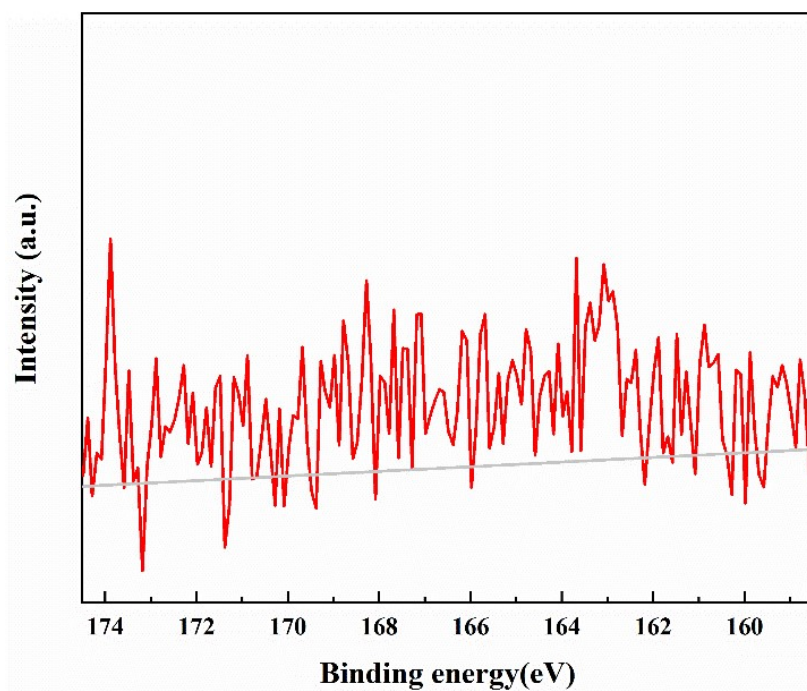


Fig. S1. XPS spectra of the CN<sub>Nv</sub> sample S 2p

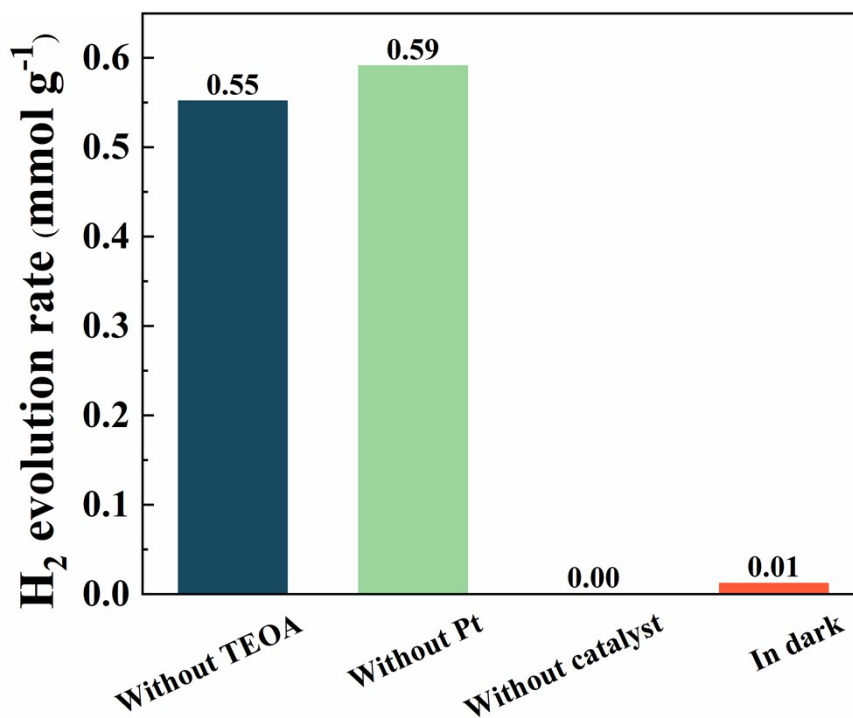


Fig. S2. Blank control experiment

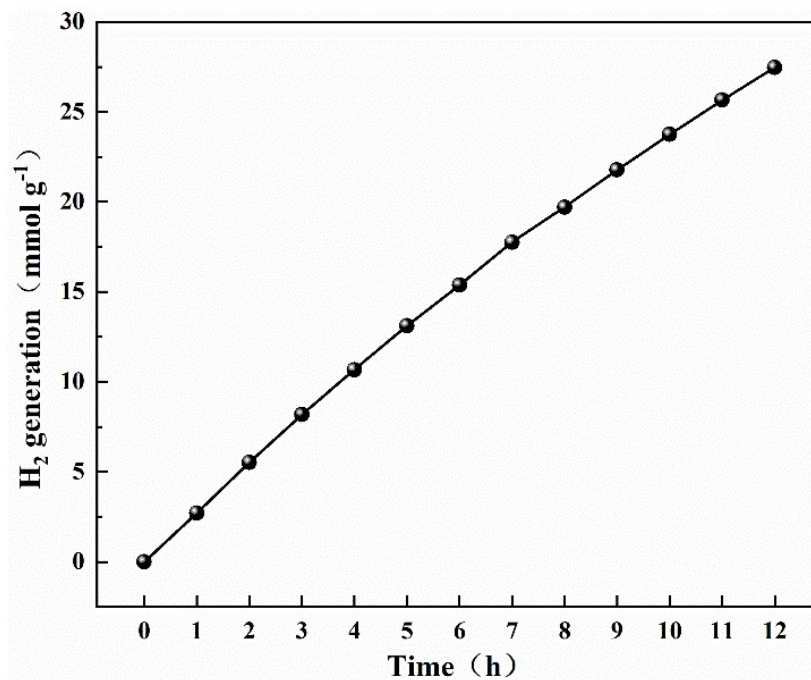


Fig. S3. 12 hours of continuous hydrogen evolution

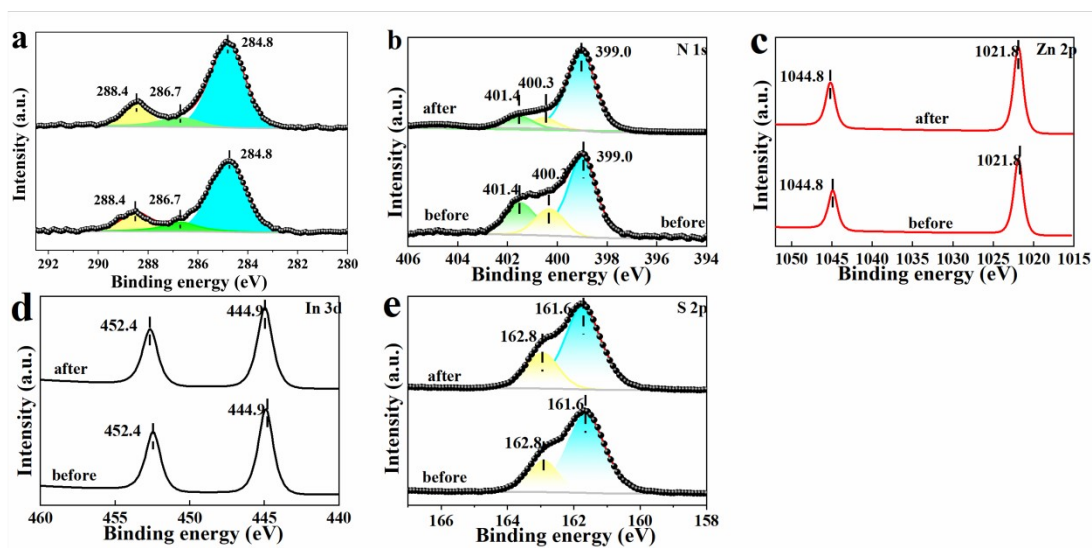


Fig.S4. XPS spectra of ZIS<sub>sv</sub>/10CN<sub>sv</sub> samples before and after use: (a) C 1s, (b) N 1s, (c) Zn 2p, (d) In 3d and (e) S 2p.

**Table. S1.** Comparison of hydrogen yield of 4h from different materials

Sample	Irradiation wavelength range	sacrificial agent	Co-catalyst	H <sub>2</sub> yield of 4h (mmol g <sup>-1</sup> h <sup>-1</sup> )	Ref.
In <sub>2</sub> O <sub>3</sub> /ZnIn <sub>2</sub> S <sub>4</sub>	300W Xe-lamp ( $\lambda \geq 420\text{nm}$ )	TEOA	3wt.%Pt	2.18	1
ZnIn <sub>2</sub> S <sub>4</sub> /CuInS <sub>2</sub>	1000 W Xe-lamp ( $\lambda \geq 420\text{nm}$ )	Na <sub>2</sub> S/ Na <sub>2</sub> SO <sub>3</sub>	2wt.%Pt	1.04	2
Ni- ZnIn <sub>2</sub> S <sub>4</sub> /SnNb <sub>2</sub> O <sub>6</sub>	300 W Xe lamp ( $\lambda > 420 \text{ nm}$ )	Na <sub>2</sub> S/Na <sub>2</sub> SO <sub>3</sub>	3wt.%Pt	2.81	3
WO <sub>3</sub> /ZnIn <sub>2</sub> S <sub>4</sub>	300 W Xe lamp ( $\geq 420 \text{ nm}$ )	Na <sub>2</sub> S/Na <sub>2</sub> SO <sub>3</sub>	1wt.%Pt	1.95	4
In(OH) <sub>3</sub> /ZnIn <sub>2</sub> S <sub>4</sub>	350 W Xe lamp ( $>420 \text{ nm}$ )	TEOA	0.5wt.%Pt	1.47	5
ZnIn <sub>2</sub> S <sub>4</sub> @CNC	300 W Xe lamp ( $>420 \text{ nm}$ )	Lactic acid	1 wt.% Pt	1.80	6
Ni(OH) <sub>2</sub> /g-C <sub>3</sub> N <sub>4</sub>	300 W Xe lamp ( $>420 \text{ nm}$ )	TEOA	1 wt.% Pt	0.152	7
Na(30)-MCN	300 W Xe lamp ( $>420 \text{ nm}$ )	TEOA	3 wt.% Pt	2.80	8
ZIS <sub>Sv</sub> /10CN <sub>Nv</sub>	300 W Xe lamp ( $\geq 420 \text{ nm}$ )	TEOA	3 wt.% Pt	3.1	This work



## References

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