

## Supplementary Material

### **Efficient photocatalytic hydrogen production over ZnIn<sub>2</sub>S<sub>4</sub> by construction sulfur vacancies and coupling nickel-based polyoxometalate**

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## 1 Experiment

### 1.1 Equipment and apparatus

All chemicals were analytical, purchased from commercial sources and were utilized without any further purification. Pure water (18.2 M $\Omega$  cm, TOC < 3 ppb) was produced by Molecular Lab Water Purifier. IR spectra (2–4 wt% samples in KBr pellets) were recorded on a Bruker VERTEX 70v FT-IR spectrometer. X-ray diffraction (XRD) spectra were measured by Rigaku D/MAX 2400 diffractometer (Japan) with Cu K $\alpha$  radiation ( $k = 1.5418 \text{ \AA}$ ) operating at 40 kV and 40 mA. The electron paramagnetic resonance (EPR) measurements on ER200DSRC10/12. Photoluminescence (PL) spectra were performed on FLS920 fluorescence spectrometer (Edinburgh Instruments). High resolution X-ray photoelectron spectroscopy (XPS) data were measured by Axis Supra<sup>®</sup> and the binding energy of all the elements were corrected by the C 1s peak (284.8 eV). The optical properties of the solid samples were measured by Shimadzu UV-2600 UV–vis diffuse reflectance spectrophotometer. Diffuse reflectance spectra were measured using a PerkinElmer Lambda 950 UV-vis diffuse reflectance spectrophotometer. The surface morphology of the samples was characterized by a field emission scanning electron microscope (SEM, JSM-6701F, Japan) and transmission electron microscopy (TEM, Tecnai F30, Netherlands). The H<sub>2</sub> amount was detected by gas chromatography (GC) analysis.

### 1.2 Synthesis of Na<sub>12</sub>[( $\alpha$ -SbW<sub>9</sub>O<sub>33</sub>)<sub>2</sub>Cu<sub>3</sub>(H<sub>2</sub>O)<sub>3</sub>] $\cdot$ 46H<sub>2</sub>O (Cu3POM)

Na<sub>9</sub>[ $\alpha$ -SbW<sub>9</sub>O<sub>33</sub>] $\cdot$ 19.5H<sub>2</sub>O was first prepared by dissolving Na<sub>2</sub>WO<sub>4</sub> (40 g, 121 mmol) in 80 ml of boiling water (solution A) and Sb<sub>2</sub>O<sub>3</sub> (1.96 g, 6.72 mmol) in 10 ml of hydrochloric acid (solution B). Solution B is then slowly added to solution A. The mixed solution is heated to boiling and held for 1 hour. After natural cooling, the solution is transferred to a crystallising dish and after a few days a white mass is precipitated and filtered to obtain the product.

A sample of  $\text{CuCl}_2$  (1.0 g, 5.8 mmol) was dissolved in 50 mL of ultrapure water and then added to  $\text{Na}_9[\alpha\text{-SbW}_9\text{O}_{33}] \cdot 19.5\text{H}_2\text{O}$  (10 g, 3.5 mmol) was added. The solution was refluxed at pH 6.2 for 1 hour, cooled and filtered. The solution slowly evaporates at room temperature to produce green crystals, which are separated and air dried to obtain 7.5 g of product.<sup>1</sup>

### 1.3 Synthesis of $\text{K}_6\text{Na}[\text{Ni}_3(\text{H}_2\text{O})_3(\text{PW}_{10}\text{O}_{39}) \text{H}_2\text{O}] \cdot 12\text{H}_2\text{O}$

$\text{Ni}(\text{CH}_3\text{COO})_2$  (2.5 g, 10 mmol) was dissolved in 50 mL of ultrapure water and added to 100 ml of ultrapure water containing  $\text{Na}_2\text{WO}_4$  (9.87 g, 33 mmol) and  $\text{Na}_2\text{HPO}_4$  (0.425 g, 3 mmol), and the pH was adjusted to 6.5 with acetic acid. The resulting yellow solution was refluxed for 2 hours and thermally filtered. Then 4 g of potassium acetate was added to the filtrate at the same time of hot filtration, and the pH value was 6.3. After two days at room temperature, green crystals were obtained by filtration, and the crystals were dried under vacuum to 5.2 g.<sup>2</sup>

### 1.4 Synthesis of $\text{Na}_6\text{K}_4 [\text{Ni}_4(\text{H}_2\text{O})_2(\text{PW}_9\text{O}_{34})_2] \cdot 32\text{H}_2\text{O}$

$\text{Na}_2\text{WO}_4$  (33 g, 100 mmol) and  $\text{Na}_2\text{HPO}_4$  (1.57 g, 11 mmol) were dissolved in 100 mL of ultrapure water and the pH was adjusted to 7.0 using acetic acid. A solution of  $\text{Ni}(\text{CH}_3\text{COO})_2$  (5.5 g, 22 mmol) in 50 mL of ultrapure water was slowly added with vigorous stirring. The resulting mixture was refluxed for 2.5 hours and hot filtered to remove impurities, then 4 g of  $\text{CH}_3\text{COOK}$  was added and the hot yellow solution was left to crystallize. The resulting product was collected by filtration to give 21 g of product<sup>3</sup>

### 1.5 Synthesis of $\text{Na}_{10}[\text{Co}_4(\text{H}_2\text{O})_2(\text{PW}_9\text{O}_{34})_2] \cdot 27\text{H}_2\text{O}$

In 100 ml of ultrapure water,  $\text{Na}_2\text{WO}_4$  (35.62 g, 108 mmol),  $\text{Na}_2\text{HPO}_4$  (3.22 g, 12 mmol) and  $\text{Co}(\text{NO}_3)_2$  (6.98 g, 24 mmol) were mixed. The pH was adjusted from 9 to 7 and the suspension was mixed at 100 °C for two hours. After refluxing, the solution was saturated with NaCl and cooled to room temperature. The resulting purple crystals are collected, washed quickly with about 30 mL of water and recrystallised in hot water to give 33 g of purple crystals.<sup>4</sup>

## 1.6 Synthesis of $K_{10}[Zn_4(H_2O)_2(PW_9O_{34})_2] \cdot 20H_2O$

$Na_8H(PW_9O_{34}) \cdot 19H_2O$  was first prepared by dissolving  $Na_2WO_4$  (120 g, 0.36 mmol) in ultrapure water and stirring until the solid was dissolved, then 4.0 ml of phosphoric acid (0.06 mol, 85 %) was added dropwise. Acetic acid (22.5 ml, 0.4 mol) was added to mixed solutions to produce a large white precipitate at pH 7.5, the suspension is stirred for one hour and filtered to give a white solid of 80 g.

$ZnCl_2$  (0.19 g, 1.4 mmol) was dissolved in 15 ml of ultrapure water and 2.0 g of  $Na_8H[PW_9O_{34}] \cdot 19H_2O$  was slowly added with stirring until the solution was homogeneous. The solution was filtered to remove insoluble matter and excess KCl (5 g) was added to the above solution to produce a white solid. The white solid was filtered and dried. Then the white solid was dissolved in 5 ml of hot water, recrystallised at 5 °C and dried under vacuum to give 1.2 g of white solid.

## 1.7 Synthesis of $ZnIn_2S_4$ -Sv/ $ZnIn_2S_4$

$ZnIn_2S_4$ -Sv was prepared by hydrothermal method by dissolving  $ZnSO_4 \cdot 7H_2O$  (0.29 g, 1 mmol) and  $InCl_3 \cdot 4H_2O$  (0.59 g, 2 mmol) in 70 ml of ultrapure water and adding cetyltrimethylammonium bromide (CTAB) (0.22 g, 0.6 mmol) and thioacetamide (0.34 g, 4.5 mmol) in turn. The mixture was stirred under magnetic stirring for 0.5 h. The milky white solution was transferred to a 100 ml hydrothermal reactor. After the reactor was cooled to room temperature, the yellow solids in the hydrothermal reactor were separated by centrifugation and washed three times with ultrapure water and ethanol. The catalyst was then dried at 60 °C for 12 hours and ground into a powder for subsequent experiments. The sample without adding CTAB in hydrothermal method is named as  $ZnIn_2S_4$ .

## 1.8 Photocatalytic water splitting test

To test the photocatalytic  $H_2$  evolution of the as-prepared samples, 15 mg of catalyst and 20  $\mu$ M POM were dispersed in TEOA (10% v/v) aqueous solution under LED irradiation (Beijing Perfectlight, PLS-LED100B, 100 mW  $cm^{-2}$ ,  $\lambda = 420$  nm). The reaction system is evacuated and replaced with argon gas to remove any residual air

from the solution. To determine the amount of H<sub>2</sub> evolution, 1 mL of the evolved gas was collected and analyzed by a gas chromatograph (GC).

### 1.9 Photoelectrochemical measurement

The photoelectrochemical measurements were investigated on a CHI 760D workstation (CH Instruments Co.) with a three-electrode setup under simulated solar light irradiation (AM 1.5G filter, 100 mW cm<sup>-2</sup>, 300 W Xe lamp, Perfect Light). The fabricated photoanode, Pt plate and Ag/AgCl electrode (3.5 M KCl) were conducted as working electrode, counter electrode and reference electrode, respectively. **0.5M Na<sub>2</sub>SO<sub>4</sub> aqueous solution** was used as the electrolyte and bubbled with Ar gas about 30 min for all photoelectrochemical tests. All measured potentials were converted to V vs. Reversible hydrogen electrode (RHE) ( $E_{\text{RHE}} = E_{\text{Ag/AgCl}} + E_{\text{Ag/AgCl}}^{\theta} + \text{pH} \cdot 0.0591$ ;  $E_{\text{Ag/AgCl}}^{\theta} = 0.197$  V).

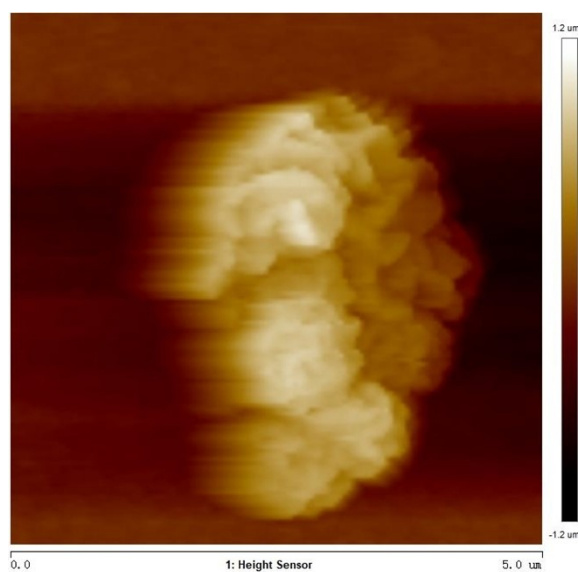
### 2. Relative calculations

The UV diffuse reflectance test is converted to the forbidden band width of the semiconductor using the Tauc plot method (Kubelka-Munk relation):

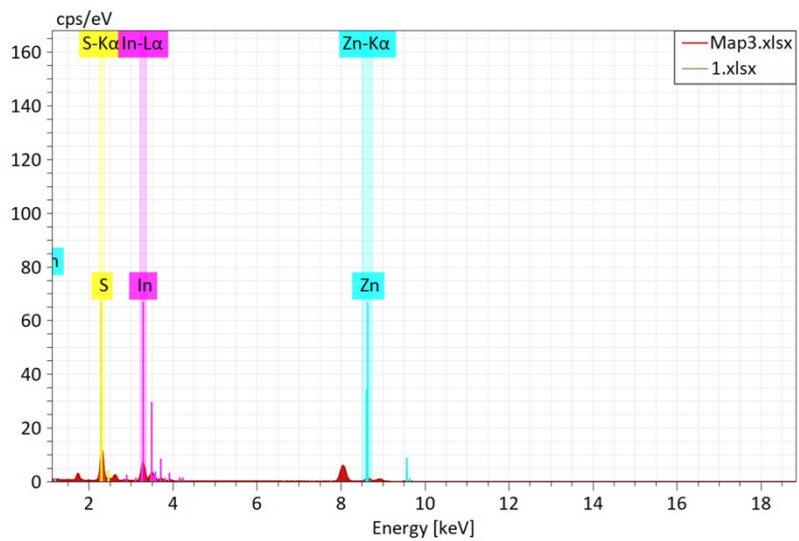
$$(\alpha h\nu)^{1/n} = A(h\nu - E_g)$$

where  $h$  is the Plank constant,  $\nu$  is the optical frequency,  $\alpha$  is the absorption coefficient and  $A$  is a constant.

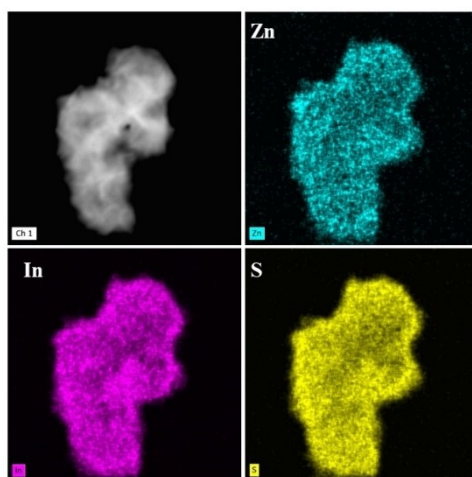
### 3. Figures



**Fig. S1** The AFM image of ZnIn<sub>2</sub>S<sub>4</sub>-Sv photocatalyst.

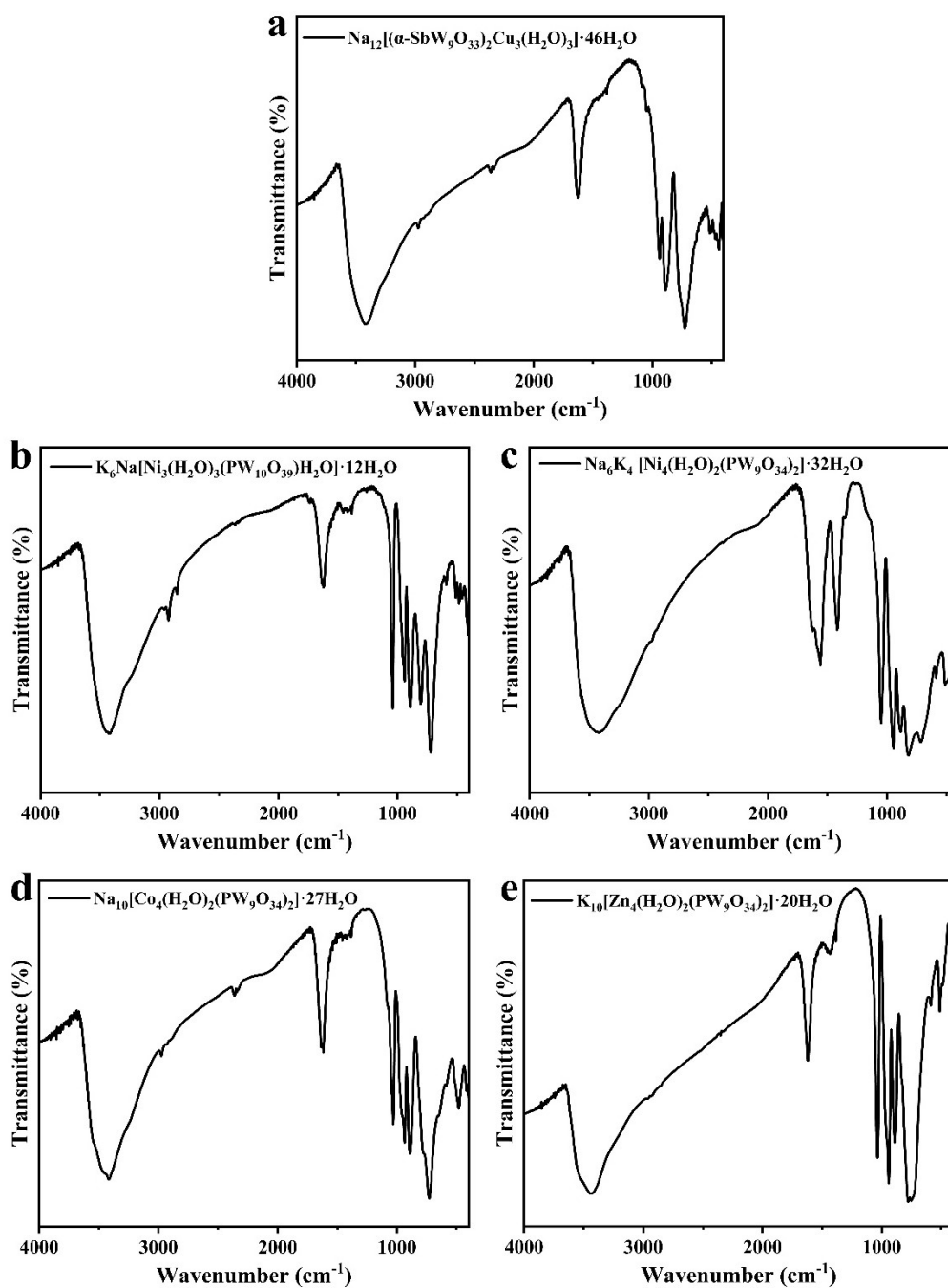


**Fig. S2** The EDS spectrum of ZnIn<sub>2</sub>S<sub>4</sub>-Sv photocatalyst.

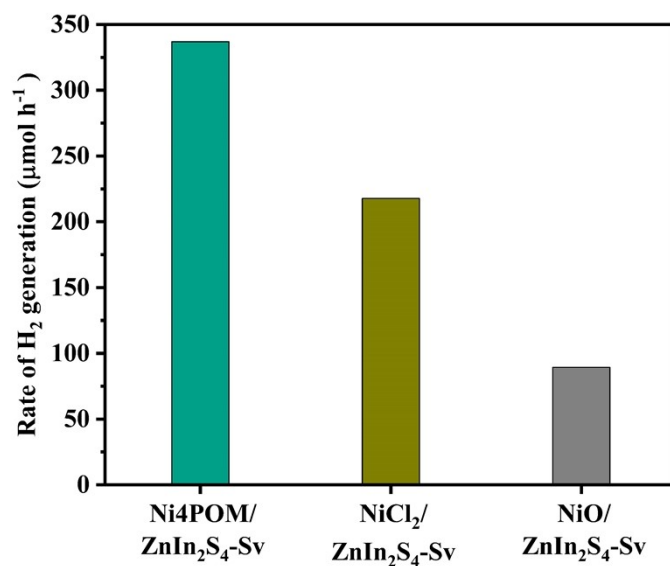


**Fig. S3** EDX elemental mappings of Zn, In and S of  $\text{ZnIn}_2\text{S}_4\text{-Sv}$  photocatalyst.

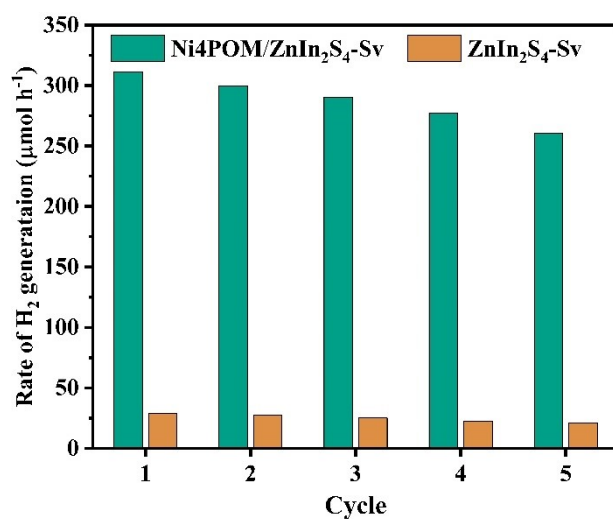




**Fig. S4** FT-IR spectra of (a) Cu3POM, (b) Ni3POM, (c) Ni4POM, (d) Co4POM and (e) Zn4POM



**Fig. S5** The photocatalytic hydrogen production rate of Ni4POM/ZnIn<sub>2</sub>S<sub>4</sub>-Sv, NiCl<sub>2</sub>/ZnIn<sub>2</sub>S<sub>4</sub>-Sv and NiO/ZnIn<sub>2</sub>S<sub>4</sub>-Sv



**Fig. S6** The stability of the photocatalytic hydrogen production rate of Ni4POM/ZnIn<sub>2</sub>S<sub>4</sub>-Sv and ZnIn<sub>2</sub>S<sub>4</sub>-Sv.

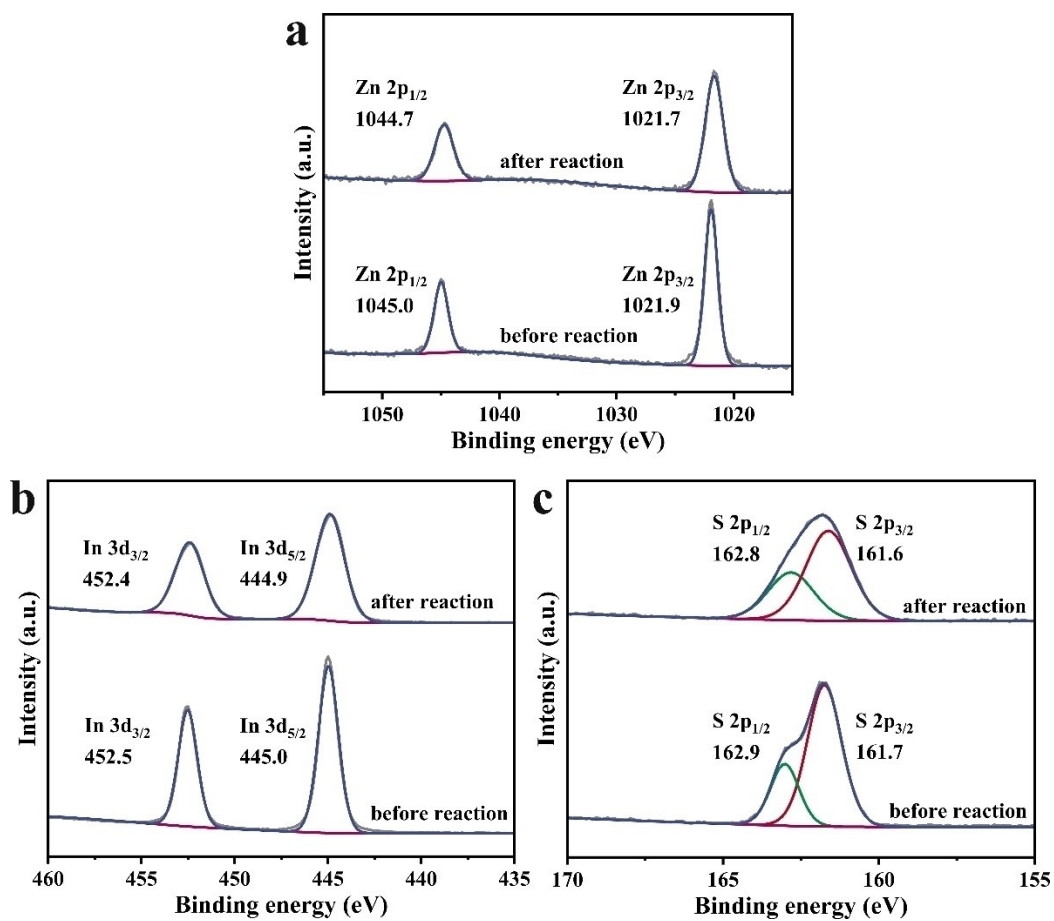


Fig. S7 The XPS spectra of before reaction and after reaction of ZnIn<sub>2</sub>S<sub>4</sub>-Sv.

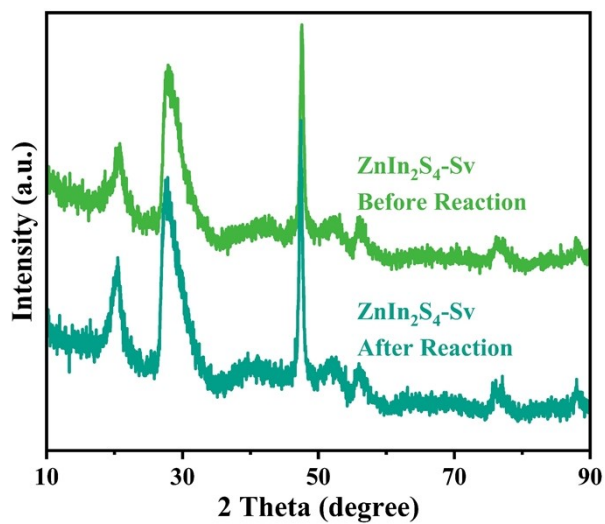
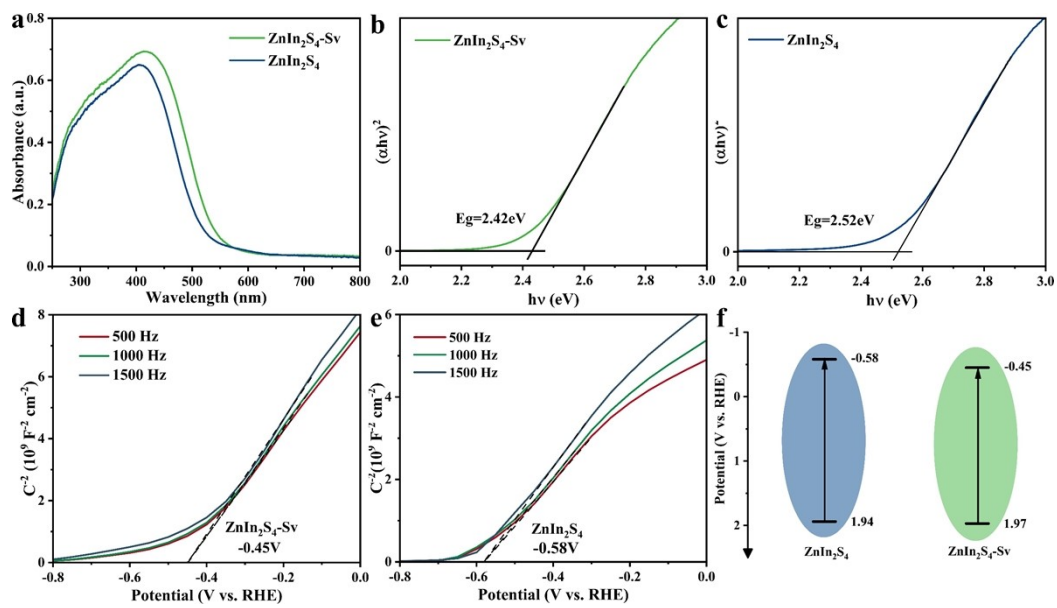
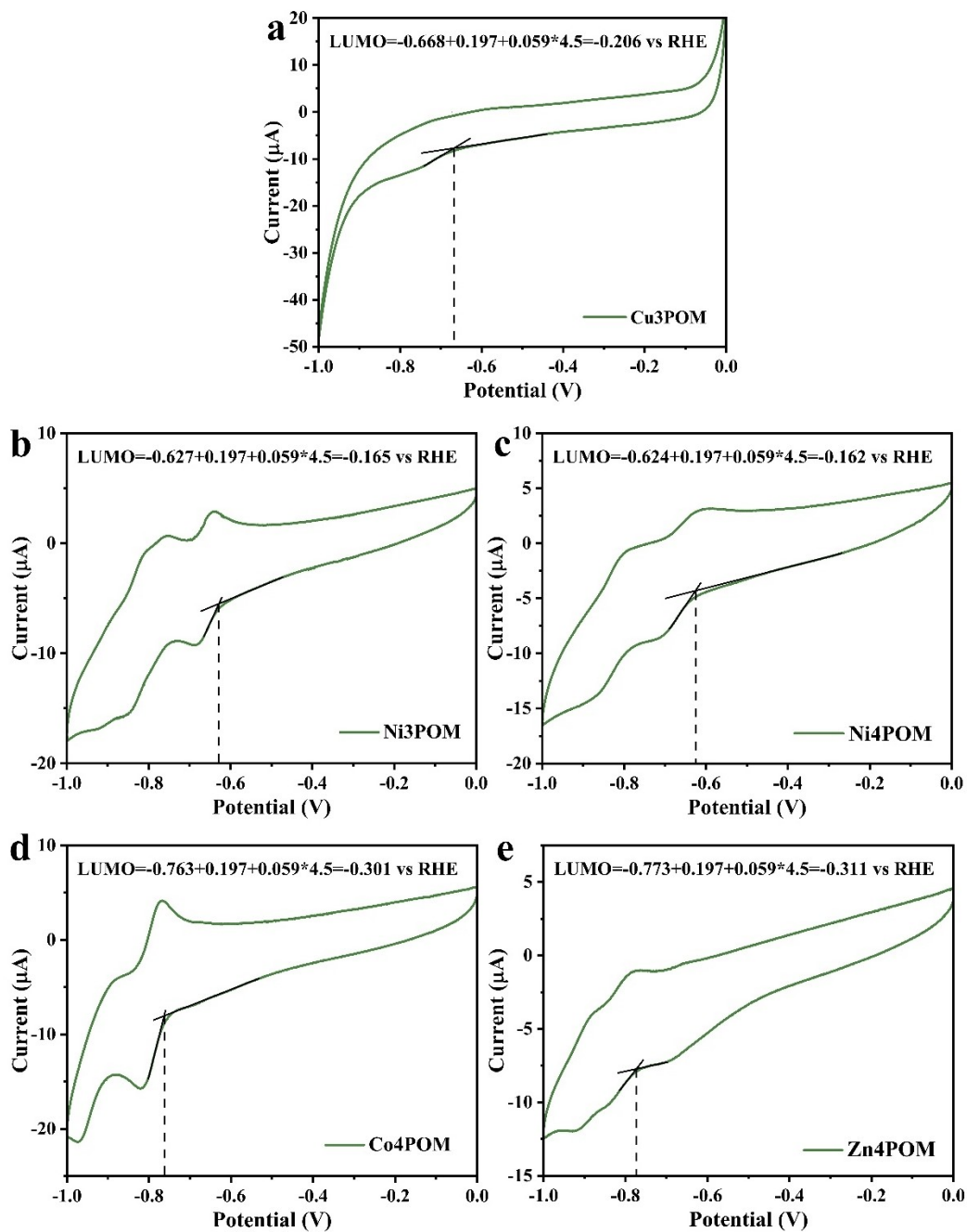


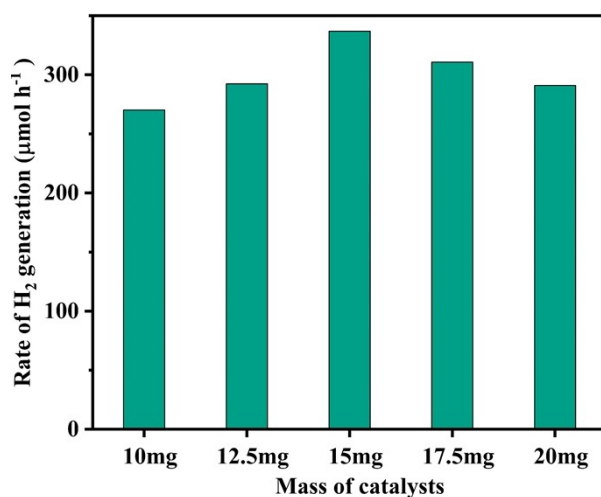
Fig. S8 The powder XRD spectra of before reaction and after reaction of ZnIn<sub>2</sub>S<sub>4</sub>-Sv.



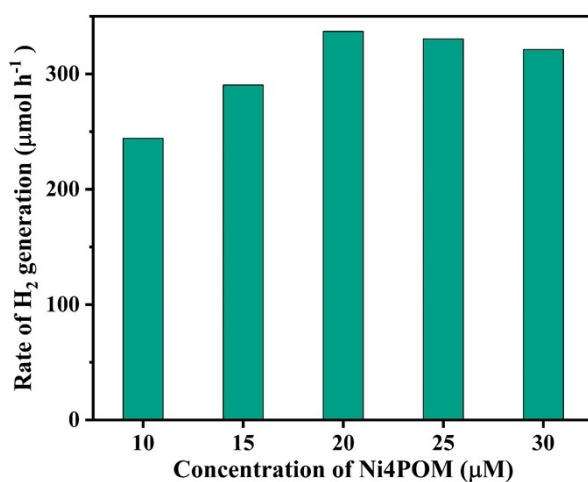
**Fig. S9** (a) Ultraviolet diffuse reflectance spectra of the  $\text{ZnIn}_2\text{S}_4\text{-Sv}$  and  $\text{ZnIn}_2\text{S}_4$ . (b-c)  $\text{Ni}_4\text{POM}/\text{ZnIn}_2\text{S}_4\text{-Sv}$  and  $\text{ZnIn}_2\text{S}_4\text{-Sv}$  curves of  $(\alpha h\nu)^2$  and  $h\nu$ . (d-e) the Mott-Schottky curve of  $\text{ZnIn}_2\text{S}_4\text{-Sv}$  and  $\text{ZnIn}_2\text{S}_4$ . (f) The valence band and conduction band of  $\text{ZnIn}_2\text{S}_4\text{-Sv}$  and  $\text{ZnIn}_2\text{S}_4$ .



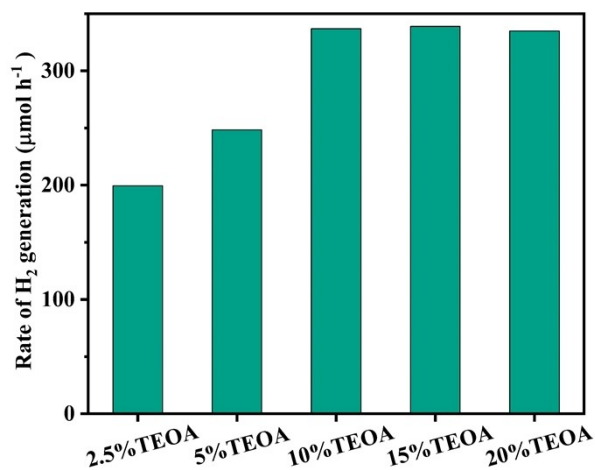
**Fig. S10** The cyclic voltammetry text of (a) Cu3POM, (b) Ni3POM, (c) Ni4POM, (d) Co4POM and (e) Zn4POM. Test conditions: 20  $\mu\text{M}$  polyoxometalates solution with pH=4.5 containing 0.1 M  $\text{Na}_2\text{SO}_4$  and 0.5 M  $\text{CH}_3\text{COONa}/\text{CH}_3\text{COOH}$ . Glassy carbon, Ag/AgCl and Pt electrodes were used as working, reference and counter electrodes respectively.



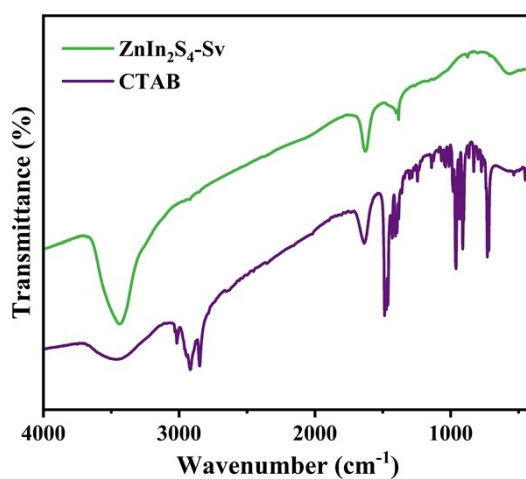
**Fig. S11.** Photocatalytic hydrogen production amounts over different quantity of ZnIn<sub>2</sub>S<sub>4</sub>-Sv. 20 μM POM, 15 mL TEOA (10% v/v) aqueous solution, illumination with 420 nm LED lamp (100 mW·cm<sup>-2</sup>), vigorous agitation using a magnetic stirrer.



**Fig. S12.** Photocatalytic hydrogen production amounts over different concentration of Ni4POM. 15 mg of ZnIn<sub>2</sub>S<sub>4</sub>-Sv, 15 mL TEOA (10% v/v) aqueous solution, illumination with 420 nm LED lamp (100 mW·cm<sup>-2</sup>), vigorous agitation using a magnetic stirrer.



**Fig. S13.** Photocatalytic hydrogen production amounts over the different volumetric concentration of TEOA. 15 mg of ZnIn<sub>2</sub>S<sub>4</sub>-Sv, 20 μM POM, illumination with 420 nm LED lamp (100 mW·cm<sup>-2</sup>), vigorous agitation using a magnetic stirrer.



**Fig. S14.** The FT-IR spectra of ZnIn<sub>2</sub>S<sub>4</sub>-Sv and CTAB.

Table S1 Photocatalytic hydrogen production over different semiconductor catalysts based on ZnIn<sub>2</sub>S<sub>4</sub>

Photocatalyst	Reaction conditions (light resource, amount of photocatalyst and sacrificial agent)	Photocatalytic activity ( $\mu\text{mol h}^{-1}$ )	Ref.
Ni4POM/ZnIn <sub>2</sub> S <sub>4</sub> /Sv	LED lamp ( $\lambda = 420 \text{ nm}$ , $100 \text{ mW cm}^{-2}$ ); 15 mg of catalyst; 20 $\mu\text{M}$ of POM and 15 mL TEOA (10% v/v) aqueous solution	337.5	This article
g-C <sub>3</sub> N <sub>4</sub> /nanocarbon/ZnIn <sub>2</sub> S <sub>4</sub>	LED lamp ( $\lambda = 420 \text{ nm}$ , $80 \text{ mW cm}^{-2}$ ); 50 mg catalyst; 80 mL aqueous solution containing 0.5 M Na <sub>2</sub> S and 0.5 M Na <sub>2</sub> SO <sub>3</sub>	50.3	[5]
RGO-ZnIn <sub>2</sub> S <sub>4</sub>	Xe lamp ( $\lambda > 420 \text{ nm}$ ); 50 mg catalyst; 100 mL aqueous solution containing 0.35 M Na <sub>2</sub> S and 0.25 M Na <sub>2</sub> SO <sub>3</sub>	81.6	[6]
Pt/Ni <sub>12</sub> P <sub>5</sub> /ZnIn <sub>2</sub> S <sub>4</sub> -O	Xe lamp ( $320 \text{ nm} < \lambda < 780 \text{ nm}$ , $300 \text{ mW cm}^{-2}$ ); 30 mg catalyst; 100 mL TEOA (20% v/v)	473.7	[7]
Pt/ZnIn <sub>2</sub> S <sub>4</sub> hollow nanoflowers	Xe lamp ( $\lambda > 420 \text{ nm}$ , $130 \text{ mW cm}^{-2}$ ); 80 mg catalyst; 10 mL TEOA (10% v/v)	301.5	[8]
2D/2D ReS <sub>2</sub> /ZnIn <sub>2</sub> S <sub>4</sub>	LED lamp ( $\lambda = 420 \text{ nm}$ ); 50 mg of catalyst and 80 mL lactic acid (10% v/v) aqueous solution	112	[9]
Heterojunction N-doped ZnIn <sub>2</sub> S <sub>4</sub>	Xe lamp ( $\lambda > 400 \text{ nm}$ , $130 \text{ mW cm}^{-2}$ ); 30 mg catalyst; 60 mL aqueous solution containing 0.35 M Na <sub>2</sub> S and 0.35 M Na <sub>2</sub> SO <sub>3</sub>	7.9	[10]
Li-N co-doped ZnIn <sub>2</sub> S <sub>4</sub>	Xe lamp ( $\lambda > 420 \text{ nm}$ ); 10 mg catalyst; 270 mL aqueous solution containing 0.35 M Na <sub>2</sub> S and 0.25 M Na <sub>2</sub> SO <sub>3</sub>	97.4	[11]
WO <sub>3</sub> @ZnIn <sub>2</sub> S <sub>4</sub>	Xe lamp; 20 mg catalyst; 50 mL TEOA (10% v/v)	170	[12]
CeO <sub>2</sub> /ZnIn <sub>2</sub> S <sub>4</sub>	LED lamp ( $\lambda > 420 \text{ nm}$ , $80 \text{ mW cm}^{-2}$ ); 50 mg catalyst; 80 mL aqueous solution containing 0.5 M Na <sub>2</sub> S and 0.5 M Na <sub>2</sub> SO <sub>3</sub>	69	[13]
Co <sub>6</sub> Mo <sub>6</sub> C <sub>2</sub> -MoO <sub>2</sub> <sup>-</sup> CoNC@ZnIn <sub>2</sub> S <sub>4</sub>	Xe lamp ( $\lambda > 420 \text{ nm}$ ); 10 mg catalyst; 100 mL TEOA (10% v/v)	94.6	[14]
Ce-doped ZnIn <sub>2</sub> S <sub>4</sub>	Xe lamp ( $\lambda > 400 \text{ nm}$ ); 5 mg catalyst; 30 mL TEOA (10% v/v)	37.3	[15]

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