Supporting Information

Porous ZnIn₂S₄ with confined sulfur vacancies for highly efficient visiblelight-driven photocatalytic H₂ production

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Experimental section

Chemical and reagents

Commercially available reagents were of analytical grade and employed without further purification. Zinc sulfate heptahydrate (ZnSO₄·7H₂O, 99%) was purchased from Sigma Aldrich. Indium chloride tetrahydrate (InCl₃·4H₂O, 99.995%, trace metals basis) and thioacetamide (TAA, 99%) were bought from Alfa Aesar. 1,3,5cyclohexadriol (C₆H₁₂O₃, >95%) was obtained from Aladdin. Anhydrous ethanol (CH₃CH₂OH) was acquired from Shanghai Titan Technology Co., Ltd. Nafion solution was gained from Sigma Aldrich. High purity argon (Ar) and hydrogen (H₂) gases were purchased by Shanghai Shangnong Gas Co., Ltd. Deionized (DI) water (> 18.25 MΩ cm) was obtained by Millipore System (Millipore, Billerica, MA).

Synthesis of photocatalysts

ZnIn₂S₄ (labeled as ZIS) photocatalyst was achieved by hydrothermal strategy reported by literature¹, the procedure was as follows: 0.294 g ZnSO₄·7H₂O, 0.471 g InCl₃·4H₂O and 0.6048 g TAA were added to 20 mL deionized water with continuous stirring at room temperature for 30 minutes (min) for complete dissolution. Subsequently, the solution was transferred to a 50 mL Teflon-lined autoclave and maintained at 180 °C for 18 hours (h) and cooled to ambient temperature naturally. The yellow product was gathered by centrifugation at 9000 rpm for 5 min and washed by deionized water and CH3CH2OH several times and then dried at 60 °C in vacuum overnight. To fabricate a series of porous ZnIn₂S₄ photocatalysts with sulfur vacancies confined in, 22 mg 1,3,5-cyclohexadriol introducing the theoretical value of 5 wt% were dispersed into the mixed suspension before transferring into the autoclaves and kept at 180 °C for 14, 16, 18, 20, 22 and 24 h. Under the optimal reaction time, different contents of 1,3,5-cyclohexadriol (44, 66, 88, and 110 mg) in the range of 5-25 wt% were added into the mixed solution and then transferred into autoclaves and heated at 180 °C for 18 h. The formation of the porous $ZnIn_2S_4$ with sulfur vacancies confined in (with the theoretical value of 10 wt% and reaction time of 18 h) was abbreviated as Vs-BPZIS-OH. ZIS and Vs-BPZIS-OH were further selected as the research objects.

Characterization of photocatalysts

X-ray diffraction (XRD) analysis was analyzed by Bruker D8 Advanced Diffractometer with Cu K α radiation ($\lambda = 1.5406$ Å) at the scanning speed of 4 °/min to characterize the crystal structure of the as-prepared samples. Morphology and structure of as-obtained samples were examined by Field emission scanning electron microscope (FE-SEM, HITACHI S4800). TEM characterization was performed on a ThermoFisher Talos F200X under 200 kV. High angle annular dark field (HAADF)-STEM images were recorded using a convergence semi angle of 11 mrad, and inner- and outer collection angles of 59 and 200 mrad, respectively. Energy dispersive X-ray spectroscopy (EDS) was carried out using 4 in-column Super-X detectors. Raman spectra were recorded on a Renishaw InVia Raman microscope in the range of 200-1200 cm⁻¹ under a 325 nm laser excitation. The light absorption range of the photocatalysts were carried out by ultraviolet-visible spectrophotometry (UV-vis) with a UV-vis spectrophotometer (CARY 500). Photoluminescence (PL) spectra was recorded on an Edinburgh Instruments (FLSP 920) system at room temperature under the excitation of 350 nm to measure the recombination of photoinduced electron-hole pairs. Time-resolved PL spectra was conducted on Fluorolog-3 (HORIBA) to investigate the precise life time of electron-hole pairs. Infrared transmission was collected on a Fourier transform infrared (FTIR) spectrophotometer Spectrum (Nicolet). The N₂ adsorption-desorption isotherms were measured on a BET analyzer (BELSORP-Max, MicrotracBEL) with the relative pressure (P/P_0) range from 0.0 to 1.0 to determine specific surface area and porosities, and pore size distribution was tested by Barrett-Joyner-Halenda (BJH) methods. X-ray photoelectron spectroscopy (XPS) was performed on ESCALAB 250 Xi X-ray photoelectron spectrometer using a monochromatized Al K α X-ray source (hv = 1486.6 eV) to investigate surface elements content and valence of as-obtained samples. The XPS data were calibrated by the binding energy of C 1s peak at 284.6 eV. X-ray absorption fine structure spectroscopy (XAFS) at Zn K-edge was performed on the 1W1B beamline station of the Beijing Synchrotron Radiation Facility (BSRF), China, operated at ~ 200 mA and ~ 2.5 GeV at 298 K under transmission mode. Standard Zn foil and ZnO powder were used as reference samples. X-band electron paramagnetic resonance (EPR) spectra was performed with a Bruker ER200D instrument at 9.86 GHz and 20 mW to analyze electronic structural changes. Ultraviolet photoelectron spectroscopy (UPS, PHI 5000 Versaprobe II) was conducted to determine the work function (Φ) of semiconductors using He I (21.21 eV) as the excitation source at an applied bias voltage of 5 eV. Inductively coupled plasma-optical emission spectroscopy (ICP-OES) analyses was measured using an Agilent ICP-OES 725 to determine the actual contents of Zn²⁺ and In³⁺ ions. The concentrations of O and S were carried out using an elemental analyzer (EA, VARIO EL III). Thermogravimetric (TG) analyses were performed to determine the composition of the samples using a NETZSCH STA449C instrument under air atmosphere. Atomic force microscopy (AFM) measurements were performed using a Scanning Probe Microscope (Veeco/DI*) to determine the thicknesses of as-prepared samples.

Evaluation of photocatalytic activity

Photocatalytic hydrogen production reaction was carried out in a top-illumination type reactor (LabSolar H₂) at constant temperature (10 °C) maintained by a flow of cooling water, which connected to glass-closed circulation system (CEL-SPH2N, CEAULight, China) under irradiation with 300 W xenon lamp (CEL-HXBF 300) equipped with an ultraviolet cut off filter of 420 nm. Pt as co-catalyst was *in situ* photodeposited on the photocatalysts using H₂PtCl₆·6H₂O as Pt source under 300 W Xe lamp irradiation for 1 h. Typically, 25 mg of the prepared sample was suspended in 50 mL of mixed solution containing triethanolamine (10 vol%) as the sacrificial reagent. Then, the reactant solution was purged for 30 min to expel the dissolved O₂ and irradiated with visible light (> 420 nm). The amount of generated H₂ was determined by an online gas chromatograph (GC 2060, TCD detector), which used Ar as carrier gas, and monitored every 30 min. In order to determine the photocatalytic stability of the sample, a long term photocatalytic H₂ evolution experiment was performed on the as-prepared sample for 20 h.

The apparent quantum efficiency (AQE) was measured under the 300 W Xenon lamp with different band-pass filters of 350 ± 15 , 405 ± 15 , 420 ± 15 , 435 ± 15 , 475 ± 15 , 520 ± 15 and 630 ± 15 nm (errors of wavelength were determined by Guass Simulation of full width at half maximum). The irradiation area was controlled as 1.0 \times 1.0 cm². The average intensity was 51.48, 42.80, 35.91, 51.83, 46.58, and 47.48 mW cm⁻² respectively (CEL-NP 2000). The AQE was calculated according to the following equation (1).

$$AQE[\%] = \frac{Number of reacted electrons}{Number of incident photons} \times 100\% = \frac{2 \times C \times N_A}{s \times P \times t \times \frac{\lambda}{h \times C}} \times 100\%$$
(1)

Where, *C* is the amount of H₂ molecules (µmol) per hour; N_A is the Avogadro constant (6.022 × 10²³ mol⁻¹); *S* is the irradiation area (cm²); *P* is the monochromatic light intensity (W cm⁻²); *t* is the light irradiation time (s); λ is the wavelength of the monochromatic light (nm); *h* is the Plank constant (6.626 × 10⁻³⁴ J s); *c* is the speed of light (3 × 10⁸ m s⁻¹).

Turnover numbering (TON) and turn frequency (TOF) of catalysts

The TON and TOF of photocatalysts were estimated by the following equations (2) and (3):

$$TON = \frac{Moles \ of \ evoluted \ H_2}{Moles \ of \ Pt \ on \ photocatalyst}$$
(2)

$$TOF = \frac{TON}{Reaction time (h)}$$
(3)

Photoelectrochemical activity measurements

The fabrication of the working electrodes was as follows: 4 mg photocatalyst powder was dispersed into mixed solution containing 1 mL isopropanol and 20 μ L Nafion and formed a homogeneous suspension by ultrasonic treatment for 30 minutes. Next, the slurry was drop-casted onto fluorine-doped tin oxide (FTO, 9 Ω sq⁻¹, 1 × 2 cm²) substrates, which had an exposure area of 1 × 1 cm² by masking with an epoxy resin, and heated for 30 min at 60 °C.

Photoelectrochemical properties of the as-prepared electrodes were recorded on electrochemical workstation (CHI 660E), using a standard three-electrode system (a working electrode, an Ag/AgCl electrode reference electrode and a Pt foil counter

electrode). The electrolyte was 0.5 M Na₂SO₄ solution. The reference was converted to standard hydrogen electrode (SHE) scale, using the Nernst equation: $V_{\text{SHE}} = V_{\text{Ag/AgCl}} + V_{\text{Ag/AgCl}}^0$, where, $V_{\text{Ag/AgCl}}$ was acquired by experimental measurement and $V_{\text{Ag/AgCl}}^0$ = 0.1976 V at 25 °C. A 300 W Xe lamp was used as a light source. Electrochemical impedance spectroscopy (EIS) was carried out over the frequency range of 10⁵ to 0.1 Hz, and the sinusoidal voltage amplitude was 5 mV. Transient photocurrent measurements using chopper illumination were collected at an applied potential of 5 mV under the 300 W Xe lamp illumination. Mott-Schottky plots were measured in the range of -1.2 to +1.2 V (vs. Ag/AgCl) reference electrode under frequencies of 1, 1.5 and 2 kHz with AC amplitude of 10 mV in 0.5 M Na₂SO₄ aqueous solution.



Fig. S1. An illustration of the preparation of Vs-BPZIS-OH.



Fig. S2. (a, c) SEM images of ZIS and Vs-BPZIS-OH and (b, d) the corresponding particle diameter distribution of ZIS and Vs-BPZIS-OH, respectively.



Fig. S3. (a, c) AFM images of ZIS and Vs-BPZIS-OH and (b, d) the corresponding height profile of ZIS and Vs-BPZIS-OH, respectively.



Fig. S4. HAADF-STEM image and corresponding EDS elemental maps of Zn, In, S and O in ZIS photocatalyst.



Fig. S5. (a-c) TEM images and (d) HRTEM image of Vs-BPZIS-OH, displaying the 2D layered structure and numerous nanopores.



Fig. S6. (a-b) TEM images of ZIS at different magnifications, displaying the layered structure. (c) HRTEM images of ZIS, showing that the distance between lattice fringes is 0.32 nm, corresponding to the (102) space of hexagonal ZnIn₂S₄. Inset is FFT pattern of ZIS.



Fig. S7. Raman spectra of ZIS and Vs-BPZIS-OH, showing Vs-BPZIS-OH with better crystallinity.



Fig. S8. TG curves of as-synthesized Vs-BPZIS-OH samples, showing that the as-synthesized samples are the pure phase $ZnIn_2S_4$.



Fig. S9. The XPS spectra of Vs-BPZIS-OH and ZIS. (a) Zn 2p spectra. (b) In 3*d* spectra. The binding energies of Vs-BPZIS-OH become lower and broader compared with ZIS, indicating the escape of S atoms.



Fig. S10. Zn K-edge extended XAFS $k^3\chi(k)$ oscillation curves of Vs-BPZIS-OH, ZIS, ZnO and Zn foil, indicating the unique local atomic arrangement of Vs-BPZIS-OH and ZIS compared to ZnO.



Fig. S11. (a) FTIR spectra of ZIS and Vs-BPZIS-OH, revealing that the peaks at 3430, 1620 and 1394 cm⁻¹ are contributed to the surface absorbed water molecules and hydroxyl groups, respectively. (b) XPS spectra in O 1*s* regions with the peaks at 532.79 eV ascribed to O-H bonds, indicating the increased surface hydroxyl groups content in Vs-BPZIS-OH.



Fig. S12. (a) The XPS survey spectra and (b) EDS spectra of ZIS and Vs-BPZIS-OH, unveiling that the as-prepared samples are mainly composed of Zn, In, S and O, respectively, and a stronger peak of O in Vs-BPZIS-OH was observed.



Fig. S13. Water contact angles for as-prepared (a) ZIS and (b) Vs-BPZIS-OH samples, showing the improved hydrophilicity of the Vs-BPZIS-OH.



Fig. S14. UPS spectra of (a) ZIS and (b) Vs-BPZIS-OH (Inset: UPS spectra in the onset (right) and the cutoff (left) energy regions of samples), indicating Vs-BPZIS-OH has lower work function.



Fig. S15. Mott-Schottky plots for the (a) ZIS and (b) Vs-BPZIS-OH samples at fixed frequencies of 1, 1.5 and 2 kHz in 0.2 M Na₂SO₄ aqueous solution (pH = 7), displaying the flat band potential derived from MS plots are about -1.24 and -1.02 V vs. Ag/AgCl for ZIS and Vs-BPZIS-OH, respectively.



Fig. S16. H₂ evolution rate of ZIS and Vs-BPZIS-OH photocatalysts with different amount of Pt.



Fig. S17. (a) Nitrogen adsorption-desorption isotherms and (b) corresponding pore size distribution curves of the various samples with 1,3,5-cyclohexadriol concentrations in the range of 5–25 wt%.



Fig. S18. EPR spectra of series samples with 1,3,5-cyclohexadriol concentrations in the range of 5–25 wt%.



Fig. S19. Time courses of H₂ evolution for ZIS and Vs-BPZIS-OH samples under visible light irradiation without TEOA, indicating the photocatalytic hydrogen performance of Vs-BPZIS-OH still has satisfying photocatalytic hydrogen activity, under the lack of sacrificial agents. Reaction conditions: 25 mg catalyst; 50 mL H₂O; 300 W Xenon lamp ($\lambda > 420$ nm).



Fig. S20. XRD patterns of Vs-BPZIS-OH sample before and after photocatalysis.



Fig. S21. (a) Zn 2*p* XPS spectra, (b) In 3*d* XPS spectra and (c) S 2*p* XPS spectra for Vs-BPZIS-OH before and after stability test.



Fig. S22. (a) Nitrogen adsorption-desorption isotherms and (b) corresponding pore size distribution curves of Vs-BPZIS-OH before and after stability test.

Sample	BET Surface Area (m²/g)	Adsorption average pore diameter (Å)
ZIS	14.14	97.18
Vs-BPZIS-OH (before reaction)	146.58	68.24
Vs-BPZIS-OH (after reaction)	143.53	70.47

Table S1. Specific surface areas and adsorbed average pore diameters for ZIS and Vs-BPZIS-OH.

sample	Zn content (at%)	In content (at%)	S content (at%)	O content (at%)
ZIS	13.51%	25.87%	58.24%	2.38%
Vs-BPZIS-OH	13.12%	24.98%	55.38%	6.52%

Table S2. Composition of ZIS and Vs-BPZIS-OH determined by ICP-OES and EA.

Notes: the contents of Zn and In were tested by ICP-OES; The contents of S and O were determined by EA.

1,3,5-cyclohexadriol concentrations (wt%)	BET Surface Area (m²/g)	Adsorption average pore diameter (Å)
5%	74.76	81.41
10%	141.89	74.50
15%	164.28	64.48
20%	170.98	69.41
25%	188.77	87.54

Table S3. Specific surface areas and adsorbed average pore diameters for a series of samples with1,3,5-cyclohexadriol concentrations in the range of 5–25 wt%.

λ (nm)	W (mW·cm ⁻²)	S (cm ²)	t (h)	H_2 production (µmol)	AQE
350	51.48	13.30	1	258.55	72.24%
405	42.80	13.30	1	240.94	70.00%
420	35.91	13.30	1	169.36	56.53%
435	39.41	13.30	1	164.62	48.34%
475	51.83	13.30	1	108.56	22.20%
520	46.58	13.30	1	44.94	9.37%
630	47.48	13.30	1	10.07	1.70%

Table S4. The calculated AQE of Vs-BPZIS-OH with different band-pass filters.

Photocatalyst	Irradiation light	Sacrificial agent	H ₂ generation	AQE
-	_	_	rate	
Vs-BPZIS-OH this work	300 W Xe lamp, λ > 420 nm	10 vol% TEOA	1537.65 ± 118.65 µmol h ⁻¹ (25 mg) (61506 ± 4746 µmol g ⁻¹ h ⁻¹)	56.53%, 420 ± 15 nm
Co/NGC@ZnIn ₂ S ₄ ²	300 W Xe lamp, $\lambda > 400 \text{ nm}$	TEOA	$11270 \ \mu mol g^{-1}$ $h^{-1} (4 \ mg)$	
$2D\ ZnIn_2S_4/g\text{-}C_3N_4{}^3$	300 W Xe lamp, $\lambda > 400 \text{ nm}$	TEOA	11914 μ mol h ⁻¹ g ⁻¹	33.4%, 420 nm
Sv-CdS ⁴	350 W Xe lamp, $\lambda > 420 \text{ nm}$	Na ₂ S/Na ₂ SO ₃	41730 μ mol h ⁻¹ g ⁻¹	18.84%, 420 nm
NCDs/g-C ₃ N ₄ ⁵	300 W Xe lamp, $\lambda > 400$ nm	TEOA	13499 μ mol h ⁻¹ g ⁻¹	7.6%, 420 nm
P-Cd/CdS/HNTs ⁶	300 W Xe lamp, $\lambda \ge 420 \text{ nm}$	LA	$32110 \ \mu mol \ g^{-1} \ h^{-1}$	45.13%, 420 nm
$g-C_2N_3-2^7$	350 W Xe lamp, $\lambda > 420 \text{ nm}$	$0.25 \text{ M} \text{Na}_2 \text{SO}_3$ and $0.35 \text{ M} \text{Na}_2 \text{S}$	14900 μ mol g ⁻¹ h ⁻¹	19.9%, 420 nm
PC-PEG5 ⁸	300 W Xe lamp, $\lambda > 420 \text{ nm}$	AA	$11600 \ \mu mol \ h^{-1} \ g^{-1}$	5.3%, 365 nm
UT-g-C ₃ N ₄ ⁹	300 W Xe lamp, $\lambda \ge 420 \text{ nm}$	glucose	$12160 \ \mu mol \ g^{-1} \ h^{-1}$	
Tp-nC/BPy ²⁺ - COFs ¹⁰	300 W Xe lamp, $\lambda > 420 \text{ nm}$	AA	34600 μ mol h ⁻¹ g ⁻¹	6.93%, 420 nm
CDs/PCN NVs ¹¹	300 W Xe lamp, $\lambda \ge 420 \text{ nm}$	TEOA	$14022 \ \mu mol \ h^{-1}$	11.84%, 420 nm
NSNOCN ¹²	300 W Xe lamp, $\lambda > 420 \text{ nm}$	TEOA	13990 μ mol h ⁻¹ g ⁻¹	10.8%, 420 nm
CdS-Cu _{2-x} S/MoS ₂ ¹³	300 W Xe lamp, $\lambda > 400 \text{ nm}$	0.3 M Na ₂ S and 0.3 M Na ₂ SO ₃	14184.8 μmol g ⁻¹ h ⁻¹	
NH ₂ -Ti ₃ C ₂ T _x ¹⁴	300 W Xe lamp, $\lambda > 420 \text{ nm}$	AA	14228.1 μmol g ⁻¹ h ⁻¹	7.75%, 420 nm
$CdS@CoS_x^{15}$	300 W Xe lamp, $\lambda > 420 \text{ nm}$	0.25 M Na ₂ S and 0.35 M Na ₂ SO ₃	39200 μ mol g ⁻¹ h ⁻¹	67.3%, 420 nm
SACs ¹⁶	300 W Xe lamp, $\lambda > 420 \text{ nm}$	AA	11 320 μmol g ⁻¹ h ⁻¹	
CdS decorated 2D NMF ¹⁷	300 W Xe lamp, $\lambda > 420 \text{ nm}$	LA	45201 μ mol h ⁻¹ g ⁻¹	
BOC-MS ¹⁸	300 W Xe lamp, $\lambda > 420 \text{ nm}$	AA	33000 μ mol h ⁻¹ g ⁻¹	
CT2.5 ¹⁹	300 W Xe lamp, $\lambda \ge 420 \text{ nm}$	LA	14342 μ mol h ⁻¹ g ⁻¹	40.1%, 420 nm
$g-C_3N_4@C^{20}$	300 W Xe lamp,	TEOA	16885 μmol h ⁻¹	14.3%,

Table S5. Comparison of H_2 -evolution by different materials.

	$\lambda > 420 \text{ nm}$		g^{-1}	420 nm
$GD-C_3N_4{}^{21}$	300 W Xe lamp,	TEOA	$23060 \ \mu mol \ h^{-1}$	31.07%,
	$\lambda > 420 \text{ nm}$	TEOA	g^{-1}	420 nm
V-CN ²²	300 W Xe lamp,	TEOA	$13600 \ \mu mol \ g^{-1}$	12.7%,
	$\lambda > 420 \text{ nm}$	TEOA	h^{-1}	420 nm
CdS/MOF-5(25) ²³	300 W Xe lamp,	$0.25 \text{ M} \text{ Na}_2 \text{S}$ and	$11620 \ \mu mol \ h^{-1}$	11.09%,
	$\lambda > 420 \text{ nm}$	0.35 M Na ₂ SO ₃	g^{-1}	420 nm
NH ₂ -UiO-66/TpPa-	300 W Xe lamp,	Codium accorboto	$23410 \ \mu mol \ g^{-1}$	
1-COF ²⁴	$\lambda > 420 \text{ nm}$	Sodium ascorbate	h^{-1}	
Pt _{ss} -ZIS ²⁵	300 W Xe lamp,	TEOA	$17500 \ \mu mol \ g^{-1}$	50.4%,
	$\lambda > 420 \text{ nm}$	IEUA	h^{-1}	420 nm

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