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A Z-scheme $ZnIn_2S_4$/ ZnS Heterojunction Catalyst: Insight into Enhanced Photocatalytic Performance and Mechanism

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Experimental Section

Materials: Zinc chloride ($ZnCl_2$), indium trichloride tetrahydrate ($InCl_3$•$4H_2O$), thioacetamide (TAA), and anhydrous ethanol were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. Chloroplatinic acid hexahydrate (H_2PtCl_6•$6H_2O$) and Nafion reagent (5 wt%) were bought from Alfa Aesar (China) Chemical Co., Ltd. All the chemicals were not further purified. Deionized water is made by the laboratory.

ZnS: 2 mmol $ZnCl_2$ and 10 mmol TAA were dissolved in EG and deionized water of 60 mL (volume ratio 1:1), stirring until completely dissolved, and then transferred to the Teflon-lined stainless-steel autoclave with a volume of 100 mL and kept at 180 ◦ C for 12 h. After cooling to room temperature, filter the sediment at the bottom and wash it with deionized water. Finally, ZnS can be obtained by drying the filtered sediment at 80 ◦ C for 24 h.

ZIS: 2 mmol $ZnCl_2$, 4 mmol $InCl_3$•$4H_2O$, and 10 mmol TAA were dissolved in EG and deionized water of 60 mL (volume ratio 1:1), stir until completely dissolved, and then transferred to the Teflon-lined stainless-steel autoclave with a volume of 100 mL and kept at 180 ◦ C for 12 h. After cooling to room temperature, filter the sediment at the bottom and wash it with deionized water. Finally, ZIS can be obtained by drying the filtered sediment at 80 ◦ C for 12 h.

ZIS/ZnS: To prepare ZIS/ZnS composites with different molar ratios, 2 mmol $ZnCl_2$, $InCl_3$•$4H_2O$ (0.2,0.6, and 1.2 mmol), and 10 mmol TAA were dissolved in 60 mL EG and deionized water (volume ratio 1:1), stirred until completely dissolved, and then transferred to the Teflon-lined stainless-steel autoclave with a volume of 100 mL and kept at 180 ◦ C for 12 h. After cooling to room temperature, filter the sediment at the bottom and wash it with deionized water and anhydrous ethanol. Finally, the extracted precipitates were dried at 80 ◦ C for 12 h to obtain ZIS/ZnS composites, which were named ZIS/ZnS-1, ZIS/ZnS-2, and ZIS/ZnS-3, respectively.

Photodeposition experiment:1.5 wt% platinum was photo-deposited on the surface of the ZIS/ZnS-2 catalyst using chloroplatinic acid as the platinum source. The 100 mg ZIS/ZnS-2 catalyst was dispersed into a 500 mL quartz photoreactor with 300 mL deionized water, then a certain amount of H_2PtCl_6 aqueous solution was added and stirred to dissolve. After degassing for 30 min, photodeposition reduction was carried out under a 300 W Xe-lamp (simulated sunlight AM1.5 G filter; Merry Change, MC-PF300B). After 1 hour, the suspension was separated by centrifugation, and the solid powder was naturally dried overnight in an oven at 80 ◦ C. Finally, the dried ZIS/ZnS-2 catalyst was analyzed by HR-TEM. In the same way, a 100 mg ZIS/ZnS-2 catalyst was used to replace the filter of the 300 W Xe-lamp light source with a CUT 420 filter ($\lambda > 420$ nm) for photodeposition reduction.

Photocatalytic performance evaluation: The experiment of photocatalytic hydrogen production was carried out in a sealed automatic sample injection system (Merry Change, MC-SPH20-A) with a 500 mL quartz photoreactor. Firstly, the 100 mg catalyst was dispersed in a 300 mL mixture solution of 0.35 M Na_2S and 0.25 M Na_2SO_3 by continuous stirring. After degassing for 30 min, the photocatalytic hydrogen production reaction was carried out under 300 W Xe-lamp (AM1.5G filter or cut 420 filter; Merry Change,

MC-PF300B). The reaction temperature was controlled at 5 ◦ C in the cyclic condensation unit. The lamp source is 11 cm from the surface of the solution, and the stirring speed is set to 450 rpm with a magnetic agitator. The hydrogen was analyzed by gas chromatography (GC-2014c, Shimadzu Co., Japan, argon as carrier gas).

Electrochemical test: The mixed suspension of water and ethanol (volume ratio 1:1) was prepared with the prepared catalyst, which contained the target substance of 20 mg and a small amount of Nafion solution. After ultrasonic treatment, the suspension is uniformly sprayed on the pre-cleaned fluorine-doped tin oxide (FTO) conductive glass of 1 × 2 cm, and the effective deposition area is maintained at 1 cm^2. The electrode was tested on the CHI 760E electrochemical workstation. In a typical three-electrode quartz test system, the platinum plate is used as the opposite electrode, the Ag/AgCl ((saturated KCl(aq))) electrode is used as the reference electrode, and the FTO-loaded target is used as the working electrode. The electrolyte is a 0.5 M Na_2SO_4 aqueous solution with a pH of 6.8. Electrochemical impedance spectroscopy (EIS) was collected under simulated sunlight (AM 1.5G), open-circuit potential, and frequency 100 kHz to 0.01 Hz. Under simulated sunlight (AM 1.5G) irradiation, the instantaneous photocurrent was recorded and measured at an applied voltage of 0.6 V (vs. Ag/AgCl (saturated KCl(aq))). The potential (E) was converted to the reversible hydrogen electrode[1]: $E_{RHE} = E^{\theta}(Ag/AgCl) + 0.199\ V + 0.059 \times pH$ (25 ◦ C)

Characterization: The crystal structure of the sample was tested by a powder X-ray diffractometer (Bruker D8 advance diffractometer) equipped with a Cu K-ray source. Scanning electron microscopy (SEM, Smur8100, Hitachi), transmission electron microscopy (TEM, JEM-2800, Hitachi), and energy-dispersive X-ray spectroscopy (EDX; X-MAX 100TLE SDD detector, Oxford Instruments) were used to observe the morphology, structure, and size of the samples. The EPR test was carried out at room temperature using a spectrometer (JES FA200, JEOL). UV-vis diffuse reflect spectroscopy uses a Lambda 1050 spectrometer equipped with an integrating sphere to measure the absorption capacity of the sample to different wavelengths in the 200-800 nm range. The chemical composition of the surface was evaluated by X-ray photoemission spectroscopy (XPS). Time-resolved fluorescence (TRPL) spectra were recorded on a streak camera (Hamamatsu C10910).

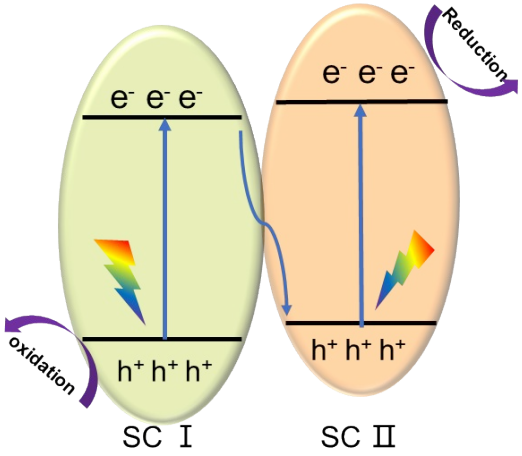

Figure S1. Charge carrier mechanism of Z-scheme heterostructure

sample		ZnS/ZIS-1	ZnS/ZIS-2	ZnS/ZIS-3	ZIS
Atom（wt%）	S	16.73	20.11	24.72	30.33
	Zn	43.24	31.80	21.32	14.33
	In	15.95	33.38	44.54	50.54
Zn/In molar ratio		1.0：0.2	1.0：0.6	1.0：1.2	1.0：2.0
Actual Zn/In atomic molar ratio		1.0：0.21	1.0：0.59	1.0：1.18	1.0：2.01

Table 1. Chemical element datas of ZIS and ZnS/ZIS samples obtained from ICP-MS.

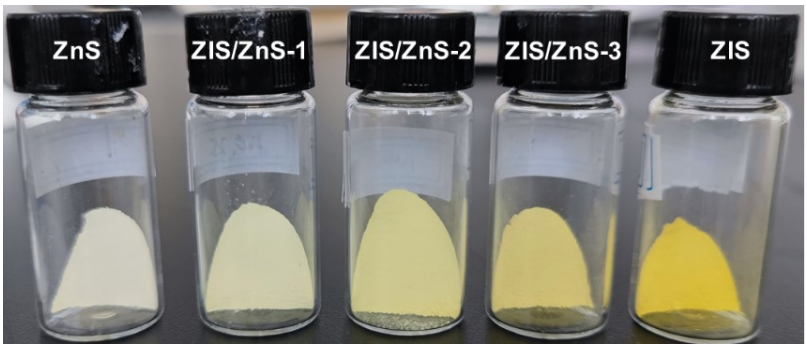

Figure S2. Samples synthesized by solvothermal method

Table 2. Summary table of photocatalytic hydrogen evolution systems with modified $ZnIn_2S_4$ photocatalysts

Photocatalyst	Light source	Photocatalyst concentration	Sacrificial agent	Cocatalyst	Performance	Ref.
ZIS/ZnS	300 W Xe lamp with AM 1.5G	100	0.35 M Na_2S and 0.25 M Na_2SO_3	--	464.1 μmol/h	This work
ZIS/ZnS	300 W Xe lamp，λ > 420 nm	100	0.35 M Na_2S and 0.25 M Na_2SO_3	--	263.3 μmol/h	This work
Cubic quantum dot/hexagonal $ZnIn_2S_4$	300 W Xe lamp，λ > 420 nm	30	0.35 M Na_2S and 0.25 M Na_2SO_3	--	114.2 μmol $h^{-1}g^{-1}$	2
Ni_3S_2/ $ZnIn_2S_4$	300 W Xe lamp，λ > 420 nm	25	TEOA	--	60 μmol $h^{-1}g^{-1}$	3
SnSe/ $ZnIn_2S_4$	300 W Xe lamp，λ = 400-1000 nm	20	TEOA	--	5656 μmol $h^{-1}g^{-1}$	4
$ZnIn_2S_4$/CdS	300 W Xe lamp，λ > 420 nm	20	0.35 M Na_2S and 0.25 M Na_2SO_3	--	1208.81 μmol $h^{-1}g^{-1}$	5
FeS_2/$ZnIn_2S_4$	300 W Xe lamp with AM 1.5G	25	TEOA	--	5050 μmol $h^{-1}g^{-1}$	6
$ZnIn_2S_4$/$Ti_3C_2T_x$	300 W Xe lamp，λ > 400 nm	20	0.35 M Na_2S and 0.6 M Na_2SO_3	--	3058 μmol $h^{-1}g^{-1}$	7
MOF-5/CuO@ $ZnIn_2S_4$	300 W Xe lamp with AM 1.5G	20	TEOA	--	1938.3 μmol $h^{-1}g^{-1}$	8
$SnIn_4S_8$/$ZnIn_2S_4$	300 W Xe lamp，λ > 400 nm	20	TEOA	Pt	2988 μmol $h^{-1}g^{-1}$	9
$Cu_{2-x}S$/$ZnIn_2S_4$	300 W Xe lamp	100	0.35 M Na_2S and 0.25 M Na_2SO_3	--	4653 μmol $h^{-1}g^{-1}$	10
$CoS_{1.097}$/$ZnIn_2S_4$	300 W Xe lamp，λ > 420 nm	20	TEOA	--	2632 μmol $h^{-1}g^{-1}$	11
CeO_x/$ZnIn_2S_4$	UV light emitting	50	0.35 M Na_2S and 0.25 M	--	69 μmol/h	12

	diodes (3 W) (λ > 420 nm)		Na_2SO_3			
g-C_3N_4/$ZnIn_2S_4$	300 W Xe lamp	10	methanol	--	4075 μmol $h^{-1}g^{-1}$	[13]
$ZnIn_2S_4$/CdS/PdS	225 W Xe-lamp	10	0.35 M Na_2S and 0.25 M Na_2SO_3	--	191.9 μmol/h	[14]

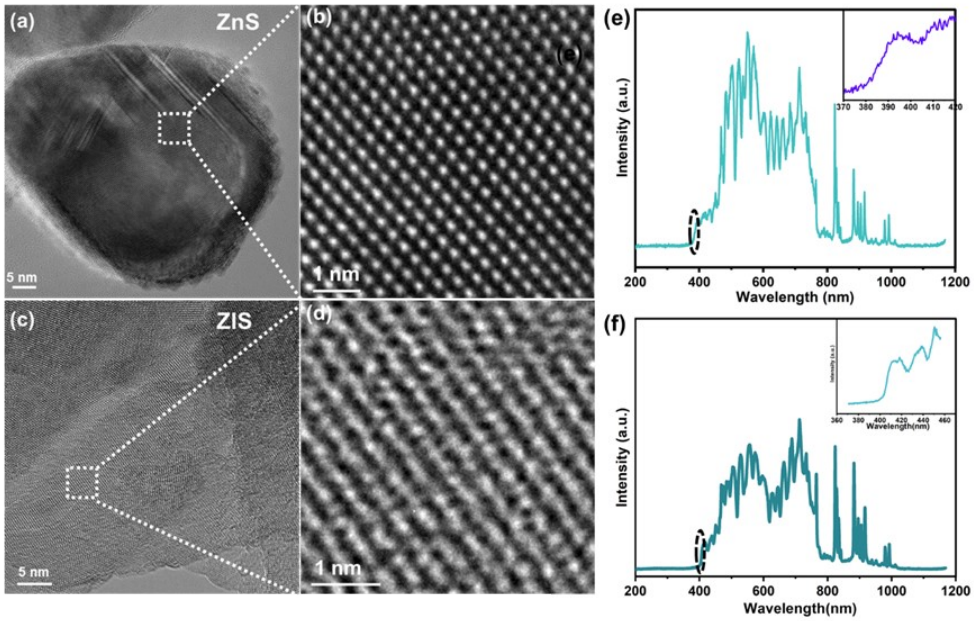

Figure S3. (a) HR-TEM image of ZnS;(b) HR-TEM IFFT image of ZnS; (c) HR-TEM image of ZIS;(d) HR-TEM IFFT image of ZIS;(e) The spectrum of the 300 W Xenon lamp with an AM 1.5G filter used in water splitting research process ;(f) The spectrum of the 300 W Xenon lamp with a CUT420 filter used in water splitting research process

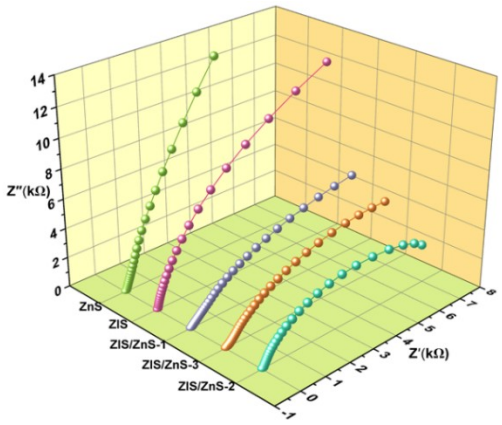

Figure S4. EIS spectra of as-prepared samples under simulated AM 1.5G irradiation

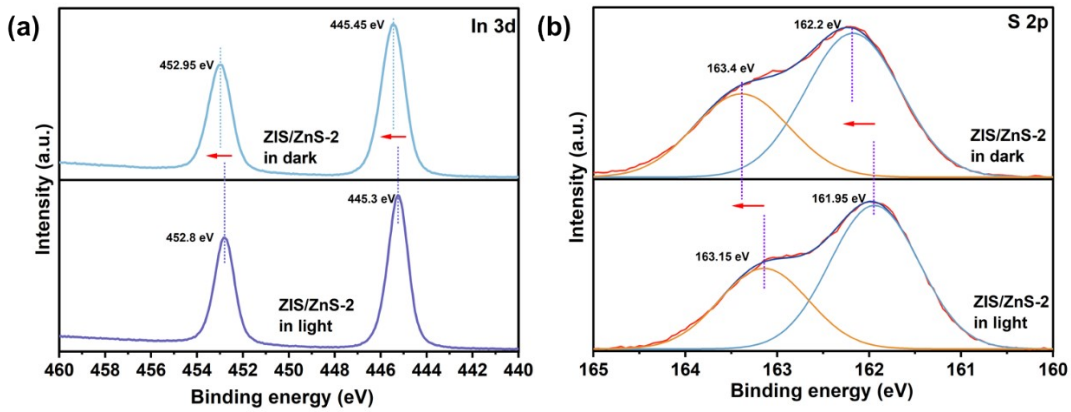

Figure S5. XPS spectra of (a) In 3d and (b) S 2p of ZIS/ZnS in the dark or in light (under full spectrum light source)

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