Supporting Information

Cooperative photocatalytic H_2 liberation and benzyl alcohol C-C coupling reactions over $Zn_2In_2S_5$ embracing Zn/In dual vacancies

Ran Wang, ‡abc Minmin Ma, ‡abc Shengyao Qian, abc Li Shi *d and Xiaoxiang Xu *abc

^aClinical and Central Lab, Putuo People's Hospital, Tongji University, Shanghai,

200060, China

Email: xxxu@tongji.edu.cn, telephone: +86-21-65986919

^bDepartment of Neurosurgery, Tongji Hospital, Tongji University School of Medicine,

Tongji University, Shanghai, 200065, P. R. China

^cShanghai Key Lab of Chemical Assessment and Sustainability, School of Chemical

Science and Engineering, Tongji University, Shanghai, 200092, China

^dState Key Laboratory of Organic Electronics and Information Displays & Institute of

Advanced Materials (IAM), Nanjing University of Posts and Telecommunications

Nanjing 210023, China

Email: <u>iamlshi@njupt.edu.cn</u>

‡ These authors have contributed equally to this work.

*Corresponding authors

Experimental Section

Materials synthesis

Zn₂In₂S₅ powders were prepared by a hydrothermal method. Briefly, 0.2876 g ZnSO₄·7H₂O (Aladdin, 99.5%), 0.2212 g InCl₃ (Aladdin, 99.9%), 0.1730 g cetyl trimethyl ammonium bromide (CTAB, SCR, 99.5%), and 0.1878 g thioacetamide (TAA, Aladdin, 99%) were mixed with 20 mL deionized water under magnetic stirring. The resultant solution was transferred into a 50 mL stainless Teflon-lined autoclave for hydrothermal reaction at 160 °C for 18 h. The reaction products were centrifuged, rinsed with distilled water and ethanol, and dried in an oven at 353 K for 12 h. For the construction of cation vacancies, a fraction of distilled water was substituted by ethylene glycol (EG, Aladdin, 99%) for the hydrothermal reactions. The other reaction parameters were kept the same. The sample powders were denoted as ZIS-V where V represented the volume percentage of distilled water being replaced by EG. For example, ZIS-5 represents that sample powders were synthesized using 19 mL distilled water (95 vol%) and 1 mL EG (5 vol%). For comparison, ZIS containing only In vacancies (denoted as V_{In}-ZIS) was synthesized using the same method as ZIS-5, except for a 20% excess of $ZnSO_4 \cdot 7H_2O$ to compensate the Zn deficiency.

Materials analysis

The as-prepared sample powders were analyzed by X-ray powder diffraction (XRD) techniques using a Bruker D8 Focus diffractometer. Cu $K_{\alpha 1}$ ($\lambda = 1.54056$ Å) and Cu $K_{\alpha 2}$ ($\lambda = 1.5444$ Å) were used as the irradiation sources. The light absorption properties of sample powders were examined based on their UV-visible diffuse

reflectance spectra (UV-vis DRS) which were collected using a spectrophotometer (JASCO-V750, Japan). The spectrophotometer was calibrated using BaSO₄ as the non-absorbing reference material. The surface properties of sample powders were inspected by X-ray photoelectron spectroscopy (XPS) which was collected using an X-ray photoelectron spectrometer (Thermo Escalab 250, USA). The XPS data were calibrated based on the signals of the adventitious C 1s at \sim 284.7 eV. The XPS peaks were fitted by the XPS PEAKFIT software, assuming the Gaussian-Lorentzian type (Lorentzian weighting of 20%) peak shape and the Shirley-type background. For the inspection of microstructures, the sample powders were analyzed by a field emission scanning electron microscope (JEOL JSM-7900F, Japan) and a transmission electron microscope (JEOL JEM-2100, Japan). The element distribution of sample powders was analyzed by a Mica energy dispersive X-ray spectroscopy (EDS) system which was equipped with the microscopes. The surface area of sample powders was explored using a specific surface area and porosity analyzer (TisStar 3020, USA) based on the Brunauer-Emmett-Teller (BET) model. The composition of sample powders was examined by inductively coupled plasma optical emission spectrometry (ICP-OES, Agilent 5110, USA). For the monitoring of photocarrier recombination, photoluminescence (PL) spectra were collected using a fluorescence spectrometer (PicoQuant FluoTime 300, Germany) under the excitation of a 420 nm pico-second pulsed laser. The defects within sample powders were detected by collecting their electron paramagnetic resonance (EPR) spectra using a benchtop EPR spectrometer (CIQTEK EPR 200M, China). For the detection of photocarriers and radicals, spintrapping agents were used during EPR analysis. The 2,2-dimethyl-1-oxido-3,4dihydropyrrol-1-ium (DMPO) was used as the spin-trapping agent for the detection of carbon-centered radicals. The 2,2,6,6-tetramethylpiperidinyloxy (TEMPO) was used as a scavenger for the detection of photo-generated electrons and holes according to a previous report.¹ The photocurrent of sample powders was measured by photoelectrochemical (PEC) analysis following our previous setup.² The PEC measurements were controlled by a Zahner electrochemical workstation (Zahner Zennium, Germany) and were carried out in aqueous Na₂SO₄ solution (0.1 M).The light source for illumination was generated by a 300 W xenon lamp source (Beijing Perfectlight Microsolar300, China) whose output was filtered by a 420 nm cut-off filter ($\lambda \ge 420$ nm). The electrochemical impedance spectra at a frequency of 1000 Hz under different potentials were collected and were used for the Mott-Schottky (MS) analysis.

Photocatalytic experiments

The benzyl alcohol (BA) conversion was carried out in a quartz reactor with light illumination from the top window. The reactor has a water jacket that allows water circulation to maintain the temperature at 20 °C. For a typical experiment, 10 mg sample powders were ultrasonically dispersed into a solution containing 0.1 mmol of BA, 7 mL acetonitrile, and 3 mL distilled water. The so-formed suspensions were sealed in the quartz reactor. Ultrapure Ar gas was directed into the reactor for 45 min to remove the air dissolved. Visible light and simulated sunlight illumination were

generated by a 300 W xenon lamp source (Beijing Perfectlight Microsolar300, China) equipped with a 420 nm cut-off filter ($\lambda \ge 420$ nm) and an AM1.5 G filter, respectively. During photocatalytic reactions, the gas composition within the reactor was sampled by a gas chromatography (GC, SHIMADZU GC-2014 C, Japan) at a fixed time period. Likewise, the liquid product within the reactor was sampled by a high-performance liquid chromatography (HPLC, Agilent 1260, USA) and was filtered by a 0.22 µm Nylon syringe filter before HPLC analysis. For the evaluation of the reaction durability, the sample powders at the end of the experiment were collected and reused as the photocatalyst for BA conversion. The performance of the sample powders was evaluated according to their conversion efficiency of BA, yield of the product, and the selectivity for the C-C coupling compounds (Eq.1-3):

$$Conversion = \frac{n_0(BA) - n(BA)}{n_0(BA)} \times 100\%$$
(1)

Yield of target product
$$= \frac{n_c(BA)}{n_0(BA)} \times 100\%$$
 (2)

Selectivity for target product =
$$\frac{n_c(BA)}{n_0(BA) - n(BA)} \times 100\%$$
 (3)

where $n_0(BA)$ is the initial concentration of BA, n(BA) is the concentration of BA at the end of the experiment, and $n_c(BA)$ is the concentration of BA converted to a particulate product, *e.g.*, one of the C-C coupling compounds. The apparent quantum yield (AQY) for the production of the C-C coupling compounds were assessed under monochromic light illumination. The monochromic light was produced by filtering the output of the xenon lamp with a bandpass filter at 420 nm, 450 nm, 500 nm, 550 nm, 600 nm, and 700 nm, respectively. The photon flux at each wavelength was determined by a quantum meter (Apogee MP-300, USA). The AQY was then calculated by the following equation (Eq. 4):

$$AQY = \frac{2 \times moles \ of \ C - C \ coupling \ compounds \ per \ hour}{moles \ of \ photon \ flux \ per \ hour} \times 100\%$$
(4)

Theoretical calculations

The computational analysis in this study was performed using the plane-wave density functional theory (DFT) as implemented in the Quantum Espresso package (QE).³ The Generalized Gradient Approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) functional was adopted to accurately capture the electron exchange-correlation interactions.⁴ To account for long-range Van der Waals (vdW) interactions, the DFT-D3 dispersion correction method, developed by Grimme, was applied.⁵ Structural optimizations were carried out under stringent conditions, employing an energy cutoff of 80 Ry for the plane-wave basis set and a force convergence criterion of 0.02 eV/Å for atomic relaxation. A Monkhorst-Pack k-point grid of 3×3×1 was utilized for the Brillouin zone sampling, while a vacuum layer of 16 Å was included to prevent

spurious interactions between periodic images of the surface.



Fig. S1 XRD patterns of ZIS-V (V = 0, 2.5, 5, 7.5, 10, 20, 50), standard $Zn_2In_2S_5$ patterns are shown at the bottom.



Fig. S2 FE-SEM image of ZIS-0, ZIS-5 and ZIS-50.



Fig. S3 Adsorption-desorption isotherms of ZIS-0, ZIS-5, and ZIS-50.



Fig. S4 UV-vis DRS spectra of ZIS-V (V = 0, 2.5, 5, 7.5, 10, 20, 50).



Fig. S5 High-resolution TEM image of (a) ZIS-0 and (b) ZIS-50, the contrast intensity profile along the dashed yellow arrows is shown on the right.



Fig. S6 XPS spectra of ZIS-0, ZIS-5 and ZIS-50: (a) survey scan; (b) Zn 2*p*; (c) In 3*d*; (d) S 2*p*.



Fig. S7 EPR spectra of V_{In} -ZIS.



Fig. S8 Product yield of deoxybenzoin (DOB), benzoin (BZ), hydrobenzoin (HBZ), benzaldehyde (BAD), H_2 , and the selectivity of the C-C coupling compounds for ZIS-0, ZIS-5 and V_{In} -ZIS.



Fig. S9 The post-mortem analysis of ZIS-5: (a) XRD; (b) FE-SEM images.



Fig. S10 Conversion rate of benzaldehyde (BAD) to C-C coupling compounds over ZIS-0 and ZIS-5 under visible light illumination.



Fig. S11 The reaction mechanisms of photocatalytic conversion of benzyl alcohol to the C-C coupling compounds.



Fig. S12 The OCVD lifetime for ZIS-0 and ZIS-5.



Fig. S13 Bandgap determination of ZIS-0 and ZIS-5 based on the Kubelka-Munk transformation of UV-vis DRS spectra.



Fig. S14 Mott-Schottky plot of ZIS-0 and ZIS-5, capacitance is extracted from electrochemical impedance spectra at a frequency of 1000 Hz.



Fig. S15 The side view geometries at each reaction step for pristine (a) $Zn_2In_2S_5$, (b) $Zn_2In_2S_5$ with V_{Zn} alone, and (c) $Zn_2In_2S_5$ with V_{Zn}/V_{In} dual defects.

Samples	Zn (at%)	In (at%)	S (at%)	Chemical Formula
ZIS-0	21.61 (22.22)	22.62 (22.22)	55.77 (55.55)	$Zn_{1.94}In_{2.03}S_{5.00}$
ZIS-2.5	20.61 (22.22)	22.76 (22.22)	56.62 (55.55)	$Zn_{1.82}In_{2.01}S_{5.00}$
ZIS-5	18.82 (22.22)	22.87 (22.22)	58.31 (55.55)	$Zn_{1.61}In_{1.96}S_{5.00}$
ZIS-7.5	16.71 (22.22)	23.31 (22.22)	59.98 (55.55)	$Zn_{1.39}In_{1.94}S_{5.00}$
ZIS-10	15.61 (22.22)	22.19 (22.22)	62.20 (55.55)	$Zn_{1.25}In_{1.78}S_{5.00}$
ZIS-20	14.92 (22.22)	21.37 (22.22)	63.71 (55.55)	$Zn_{1.17}In_{1.68}S_{5.00}$

Table S1. ICP determined atomic content for as-prepared samples; theoretical values

 are included in the parenthesis.

Table S2. ICP determined atomic content for ZIS and V_{In} -ZIS; theoretical values are

• 1	1 1 1	•	.1		
1100	hohul	111	tho	noront	horic
IIIC	iuucu	111	unc	Darcin	iicsis.
				1	

Samples	Zn (at%)	In (at%)	S (at%)	Chemical Formula
ZIS-0	21.61 (22.22)	22.62 (22.22)	55.77 (55.55)	Zn _{1.94} In _{2.03} S _{5.00}
V _{In} -ZIS	22.04 (22.22)	22.01 (22.22)	55.95 (55.55)	$Zn_{1.97}In_{1.96}S_{5.00}$

Table S3. The moles of photon flux per hour gauged by a quantum meter and the photocatalytic C-C coupling products production rate of ZIS-5 under monochromic light illumination.

λ / nm	Flux / µmol·h ⁻¹	C-C coupling products / µmol·h ⁻¹	AQY (%)
420 ± 20	287	16.5	8.30
450 ± 35	314	3.5	1.50
500 ± 35	481	0.5	0.46
550 ± 35	612	0.1	0.08
600 ± 40	724	0	0.03

Table S4. Comparisons of the photocatalysts for the C-C coupling conversion of

Catalyst	Light source	Reaction conditions	Conversi	Selectivity of	H_2	AQY	References
			on of BA	C-C coupling	(µmol)		
			(%)	compounds			
				(%)			
$Zn_2In_2S_5$ with	300 W Xe	0.1 mmol BA, 10 mg	~100	~100	59.5	8.3% at	This work
$V_{Zn} \! / V_{In}$	lamp	catalysts, 7 mL				420 nm	
	$(\lambda \ge 420 \text{ nm})$	CH ₃ CN, 3 mL H ₂ O,					
		Ar, 8 h					
	Simulated	0.1 mmol BA, 10 mg	~100	~100	86.5	_	
	AM 1.5G	catalysts, 7 mL					
		CH ₃ CN, 3 mL H ₂ O,					
		Ar, 2 h					
$Zn_{0.6}In_2S_{3.6}$	6 W LEDs	0.2 mmol BA, 10 mg	>99	98	134	-	6
7. I. C	$(455\pm5~nm)$	catalysts, 1 mL	> 00	01	172		
$\Sigma n_{0.2} In_2 S_{3.2}$		CH ₃ CN, Ar, 12 h	>99	91	172	-	
$Zn_{0.6}In_2S_{3.6}$	Sunlight	0.2 mmol BA, 10 mg	92	70	126	-	
		catalysts, 1 mL					
		CH ₃ CN, Ar, 36 h					
$ZnIn_2S_4$	8 W LEDs	0.1 mmol BA, 10 mg	~100	>95	-	-	7
	(440-460 nm)	catalysts, 3 mL					
		CH ₃ CN, 7 mL H ₂ O,					
		Ar, 10 h					
Ag ₂ S@CdS	6 W LEDs	0.1 mmol BA, 5 mg	~100	97	-	-	8
	(445 nm)	catalysts, 1 mL					
		CH ₃ CN, Ar, 4h					
2%NiS - P	300 W Xe	0.2 mmol BA, 20 mg	99	67.6	119.4	-	9
doped g-C ₃ N ₄	lamp	catalysts, 10 mL					
	$(\lambda \ge 420 \text{ nm})$	CH ₃ CN, N ₂ , 6 h					
Co-CdS	Visible light	0.25 mmol BA, 10 mg	92	97	99	-	10
	(λ=420 nm)	catalysts, 10 mL					
		CH ₃ CN, Ar, 9 h					
Cd-CdS QDs	2.6 mW laser	2 mM BA, 1.4 mM	83	91	-	0.95% at	11
	405 nm	Na ₂ SO ₃ , 2.8 µM CdS				405 nm	
		QDs, solvent (80:20					
		D ₂ O:CD ₃ OD), Ar, 10					
		h					
CdS-ZnS	300 W Xe	0.1 mmol BA, 10 mg	91.61	98.93	28.52	2.84% at	12
	lamp	catalysts, 7 mL				420 nm	
	$(\lambda \ge 420 \text{ nm})$	CH ₃ CN, 3 mL H ₂ O,					
		Ar, 10 h					

benzyl alcohol (BA) reported in the literature.

2.5%	300 W Xe	0.24 mmol BA, 20 mg	85.4	99.1	107.4	$\sim 1.0\%$ at	13
CdS/SiO ₂	lamp	catalysts, 10 mL				420 nm	
		CH ₃ CN, Ar, 12 h					
Ni doped	300 W Xe	76.9 µmol BA, 5 mg	86	98.5	41.9	-	14
$ZnIn_2S_4$	lamp	catalysts, 5 mL					
nanosheet		CH ₃ CN, vacuum, $2 h$					
STAB-	300 W Xe	0.35 mmol BA,	99	96.5	-		15
$Zn_3In_2S_6$	lamp	20 mg catalysts,					
	$(\lambda{\geq}400~nm)$	5 mL CH ₃ CN,					
		N ₂ , 11 h					
$Zn_2In_2S_5$ with	300 W Xe	0.1 mmol BA, 10 mg	~100	~100	16.1	7.7% at	2
V_{Zn}	lamp	catalysts, 7 mL				420 nm	
	$(\lambda{\geq}420~nm)$	CH ₃ CN, 3 mL H ₂ O,					
		Ar, 8 h					
	Simulated	0.1 mmol BA, 10 mg	~100	~100	77.8		
	AM 1.5G	catalysts, 7 mL					
		CH ₃ CN, 3 mL H ₂ O,					
		Ar, 2 h					

References

- J. Wan, Y. Wang, J. Q. Liu, R. Song, L. Liu, Y. P. Li, J. Y. Li, J. Low, F. Fu and Y. J. Xiong, Full-Space Electric Field in Mo-Decorated Zn₂In₂S₅ Polarization Photocatalyst for Oriented Charge Flow and Efficient Hydrogen Production, *Adv. Mater.*, 2024, **36**, 2405060.
- M. Ma, R. Wang, L. Shi, R. Li, J. Huang, Z. Li, P. Li, E. Y. Konysheva, Y. Li, G. Liu and X. Xu, Defect-Expedited Photocarrier Separation in Zn₂In₂S₅ for High-Efficiency Photocatalytic C-C Coupling Synchronized with H₂ Liberation from Benzyl Alcohol, *Adv. Funct. Mater.*, 2024, 34, 2405922.
- P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, G. L. Chiarotti, M. Cococcioni, I. Dabo, A. Dal Corso, S. de Gironcoli, S. Fabris, G. Fratesi, R. Gebauer, U. Gerstmann, C. Gougoussis, A. Kokalj, M. Lazzeri, L. Martin-Samos, N. Marzari, F. Mauri, R. Mazzarello, S. Paolini, A. Pasquarello, L. Paulatto, C. Sbraccia, S. Scandolo, G. Sclauzero, A. P. Seitsonen, A. Smogunov, P. Umari and R. M. Wentzcovitch, QUANTUM ESPRESSO: a modular and open-source software project for quantum simulations of materials, *J. Phys-Condens. Mat.*, 2009, 21, 395502.
- 4. J. P. Perdew, K. Burke and M. Ernzerhof, Generalized gradient approximation made simple, *Phys. Rev. Lett.*, 1996, 77, 3865-3868.
- S. Grimme, S. Ehrlich and L. Goerigk, Effect of the Damping Function in Dispersion Corrected Density Functional Theory, *J Comput Chem*, 2011, 32, 1456-1465.
- N. C. Luo, T. T. Hou, S. Y. Liu, B. Zeng, J. M. Lu, J. Zhang, H. J. Li and F. Wang, Photocatalytic Coproduction of Deoxybenzoin and H2 through Tandem Redox Reactions, *ACS Catal.*, 2020, 10, 762-769.
- G. Q. Han, X. W. Liu, Z. Cao and Y. J. Sun, Photocatalytic Pinacol C-C Coupling and Jet Fuel Precursor Production on ZnIn2S4 Nanosheets, *ACS Catal.*, 2020, 10, 9346-9355.
- S. G. Lee, M. J. Kang, M. Park, K. J. Kim, H. Lee and H. S. Kim, Selective photocatalytic conversion of benzyl alcohol to benzaldehyde or deoxybenzoin over ion-exchanged CdS, *Appl. Catal. B-Environ.*, 2022, 304, 120967.
- G. Y. Yu, K. Gong, L. Hu, C. W. Xing, Y. J. Hu, D. B. Wang and X. Y. Li, Controllably solar-driven C-C coupling organic synthesis integrated with H₂ production over P-doped g-C₃N₄ with NiS nanoparticles modification, *Appl. Mater. Today*, 2023, **32**, 101794.
- M. Y. Zhang, K. M. Li, C. L. Hu, K. W. Ma, W. J. Sun, X. Q. Huang and Y. Ding, Co nanoparticles modified phase junction CdS for photoredox synthesis of hydrobenzoin and hydrogen evolution, *Chin. J. Catal.*, 2023, 47, 254-264.
- K. P. McClelland and E. A. Weiss, Selective Photocatalytic Oxidation of Benzyl Alcohol to Benzaldehyde or C-C Coupled Products by Visible-Light-Absorbing Quantum Dots, *Acs Appl Energ Mater*, 2019, 2, 92-96.
- R. Wang, Z. D. Zheng, Z. Li and X. X. Xu, Photocatalytic C-C coupling and H₂ production with tunable selectivity based on Zn_xCd_{1-x}S solid solutions for benzyl alcohol conversions under visible light, *Chem. Eng. J.*, 2024, **480**, 147970.
- M. Y. Qi, Y. H. Li, M. Anpo, Z. R. Tang and Y. J. Xu, Efficient Photoredox-Mediated C-C Coupling Organic Synthesis and Hydrogen Production over Engineered Semiconductor Quantum Dots, ACS Catal., 2020, 10, 14327-14335.
- 14. J. Y. Li, M. Y. Qi and Y. J. Xu, Efficient splitting of alcohols into hydrogen and C-C coupled

products over ultrathin Ni-doped ZnIn2S4 nanosheet photocatalyst, *Chinese J. Catal.*, 2022, **43**, 1084-1091.

 S. N. Zhao, S. Song, Y. You, Y. T. Zhang, W. Luo, K. J. Han, T. Ding, Y. Tian and X. A. Li, Tuning redox ability of Zn₃In₂S₆ with surfactant modification for highly efficient and selective photocatalytic C-C coupling, *Mol. Catal.*, 2022, **528**, 112429.