

## Supplementary Information

# Zr-Based Metal-Organic Frameworks PCN-222@Defective ZnIn<sub>2</sub>S<sub>4</sub> Core-Shell Z-Scheme Heterojunctions Toward Efficient Charge Separation and Optimized Photocatalytic Performance

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## Materials

N,N-dimethylformamide (DMF) and ethanol (EtOH) were purchased from Tianjin Kemer Chemical Reagent Co. Zinc nitrate hexahydrate ( $\text{ZnNO}_3 \cdot 6\text{H}_2\text{O}$ ), indium nitrate hydrate ( $\text{In}(\text{NO})_3 \cdot x\text{H}_2\text{O}$ ), L-cysteine (L-cys), zinc chloride ( $\text{ZnCl}_2$ ), indium trichloride tetrahydrate ( $\text{InCl}_3 \cdot 4\text{H}_2\text{O}$ ), thioacetamide (TAA), and Zirconium tetrachloride ( $\text{ZrCl}_4$ ) were purchased from Aladdin Industrial. 4,4,4,4-(Porphine-5,10,15,20-tetrayl) tetrakis (TCPP) was purchased from Tianjin Guangfu Science. All chemicals were analytic reagents and used as received. The deionized water was used throughout this study.

## Characterizations

X-ray diffraction (XRD) was obtained by a Bruker D8 Advance diffractometer (using Cu  $K\alpha 1$  radiation,  $\lambda = 1.54056 \text{ \AA}$ , 40 kV, 40 mA). Scanning electron microscopy (SEM) images were obtained with a Philips XL-30-ESEM-FEG instrument operating at 20 kV. Transmission electron microscope (TEM) JEOL JEM-2010 at an accelerating voltage of 200 kV was also used to record the electron micrographs of the samples. X-ray photoelectron spectroscopy (XPS, Kratos, ULTRA AXIS DLD) was carried out with monochrome Al  $K\alpha$  ( $h\nu = 1486.6 \text{ eV}$ ) radiation. UV-vis diffuse reflection spectra (DRS) were recorded on a UV-vis spectrophotometer (UV-2550, Shimadzu) with an integrating sphere attachment, and  $\text{BaSO}_4$  was used as the reference material. The  $\cdot\text{O}_2^-$  radicals were detected by the fluorescence probe technique with coumarin on a RF-5301PC fluorescence spectrophotometer and a 300 W Xenon lamp. The photoluminescence (PL) spectra were measured with a PE LS 55 spectrofluorophotometer at excitation wavelength of 400 nm. The work function of samples was tested by Scanning Kelvin probe (SKP) (SKP5050 system, Scotland). The

electron spin resonance (ESR) spectra under visible light irradiation were tested with ESR spectrometer (Bruker model A300). The temperature of the sample was measured using the Testo 865 infrared thermograph.

### **Photocatalytic hydrogen evolution**

A closed circulation system was utilized to ensure the reaction at room temperature, while a 300 W Xenon lamp (Aulight, CEL-HXF300, Beijing Perfectlight Co. Ltd., China) equipped with a 420 nm cut-off filter (6.0 cm away from the reactor) was used. Typically, 50 mg photocatalyst was finely dispersed in 100 mL deionized water, where  $0.35 \text{ mol L}^{-1} \text{ Na}_2\text{S}\cdot 9\text{H}_2\text{O}$  and  $0.25 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_3$  were added as the sacrificial reagents. Prior to the lighting, the solution was saturated with flowing  $\text{N}_2$  gas for 20 min to remove the oxygen dissolved. The reaction mixture was magnetically kept stirred so as to sustain the uniform dispersion. The  $\text{H}_2$  evolution was determined by using an online gas chromatography (GC9560, Ar carrier, TCD detector, China).

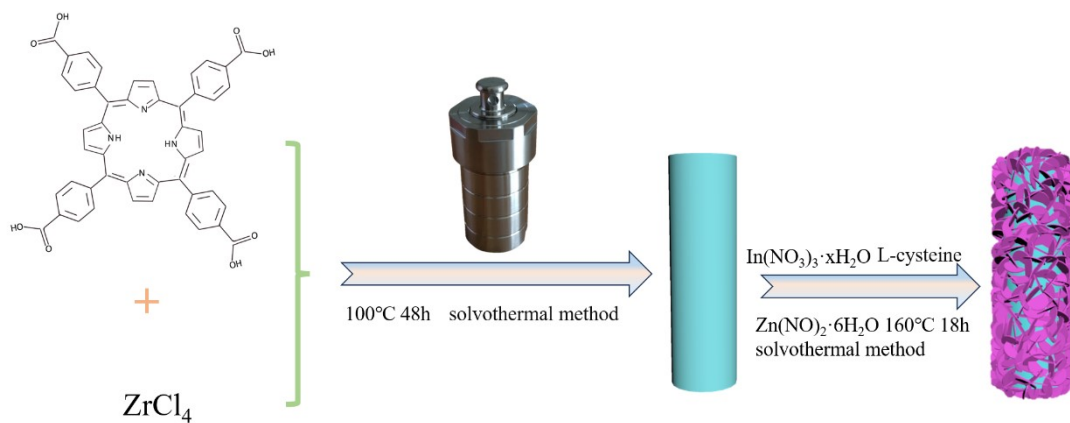
### **Photocatalytic degradation activity tests**

A common antibiotic contaminant, tetracycline (TC), was selected for photocatalytic degradation experiments. The experiments were carried out in winter in Harbin ( $44^\circ 04' \text{N}$ ,  $125^\circ 42' \text{E}$ ) and the room temperature was maintained at  $12 \pm 2 \text{ }^\circ \text{C}$ . In a typical experiment, photocatalyst (30 mg) was added to TC solution (30 mL, 10 mg/L). The suspensions were then placed in dark to ensure adsorption-desorption equilibrium. Then, 300 W Xenon lamps were used to irradiate the suspensions and the residual TC concentrations were analyzed by using a T6 UV-Vis spectrophotometer.

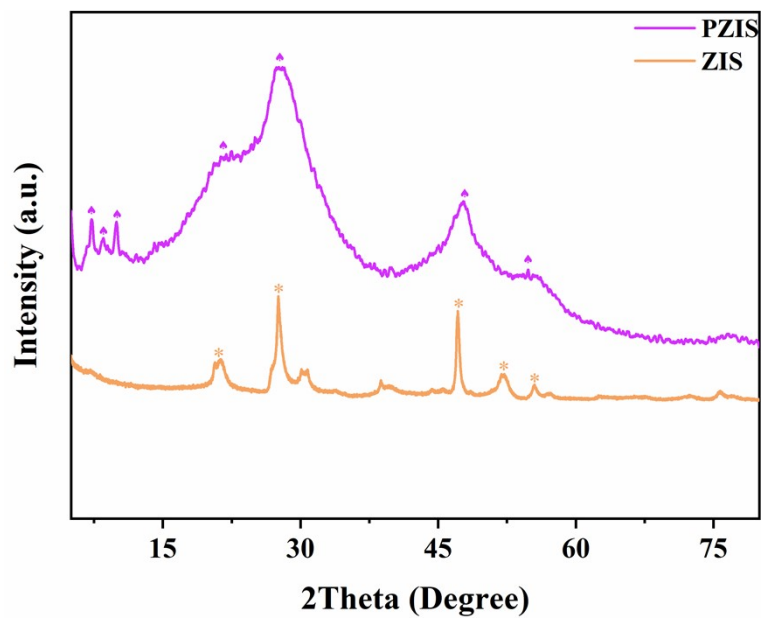
### **Photoelectrochemical measurements**

The electrochemical impedance spectroscopy and photocurrents curves were examined

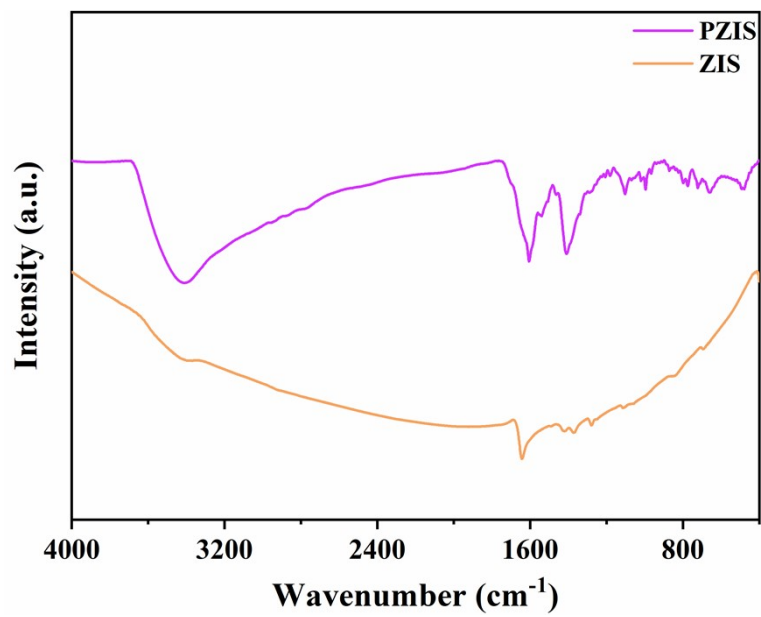
by the Princeton workstation, which employed the three-electrode configuration. KOH (1.0 M) aqueous solution was used as the electrolyte solution. Pt foil was the counter electrode and Ag/AgCl electrode was used as the reference electrode. In order to prepare working electrode, photocatalyst sample (50 mg) was dispersed in ethanol (35 mL), and then the suspension was sprayed onto the FTO glass. Electro-chemical impedance spectroscopy was measured with amplitude of 5 mV and frequencies varying from 0.01 to 10000 Hz.



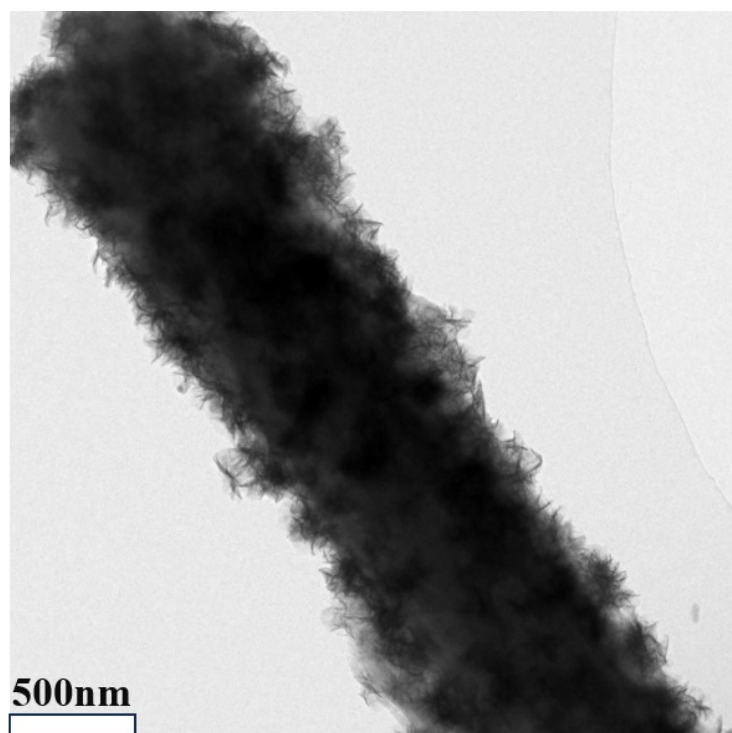
**Scheme S1.** Schematic diagram of the preparation of PV<sub>In</sub>-ZIS heterostructures.



**Fig S1.** XRD patterns of PZIS and ZIS, respectively.

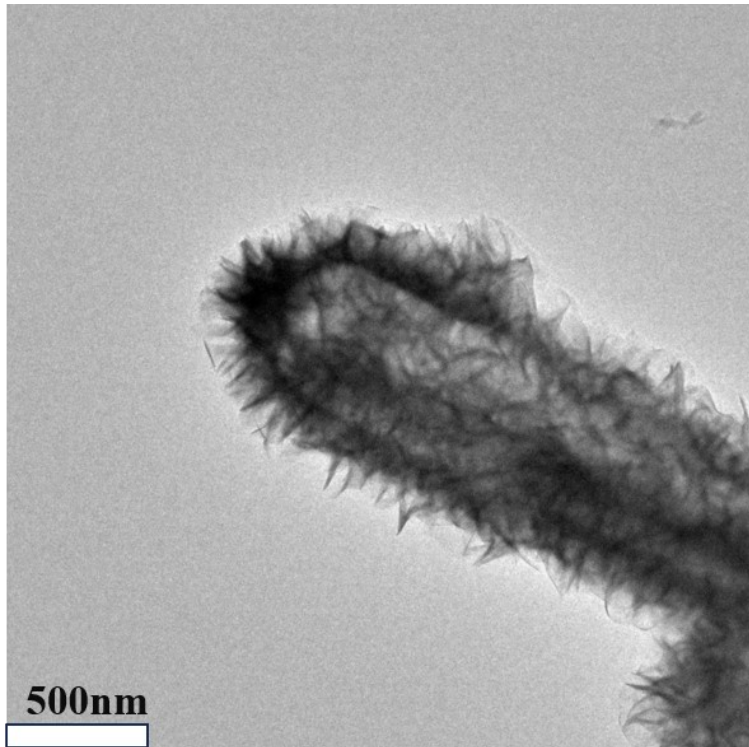


**Fig S2.** FT-IR spectra of PZIS and ZIS, respectively.

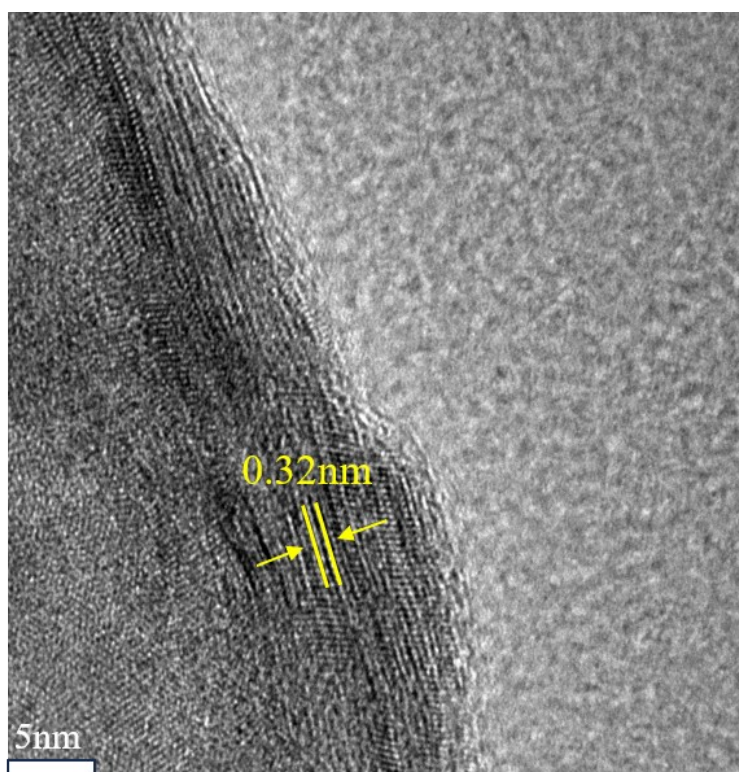


**Fig S3.** TEM image of  $V_{In}$ -PZIS.

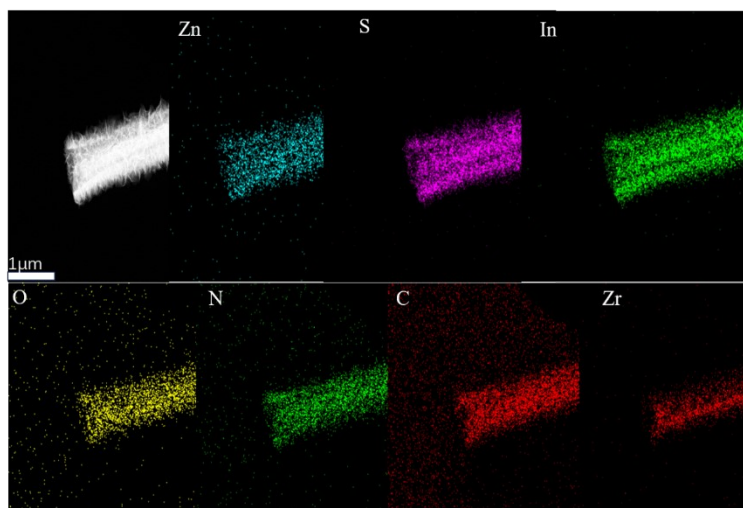




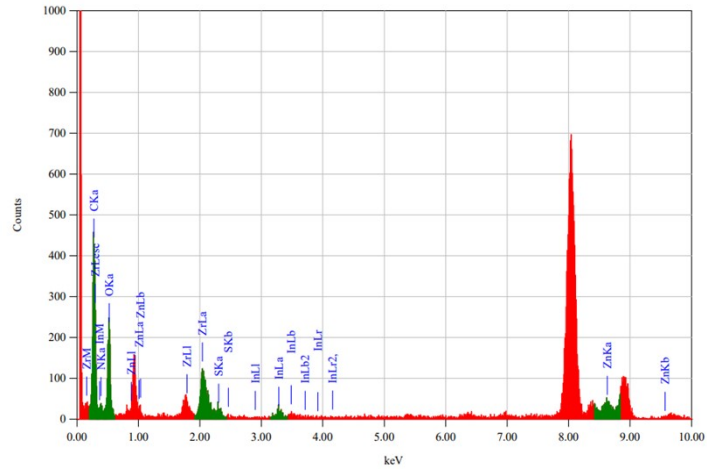
**Fig S4.** TEM image of PZIS.



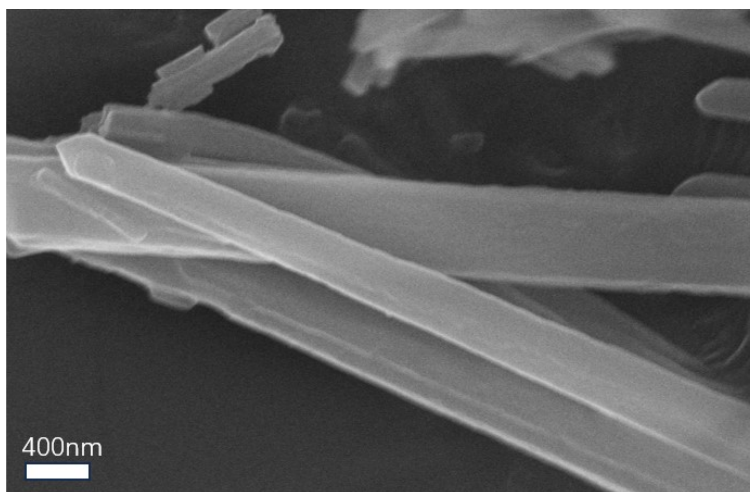
**Fig S5.** HRTEM image of PZIS.



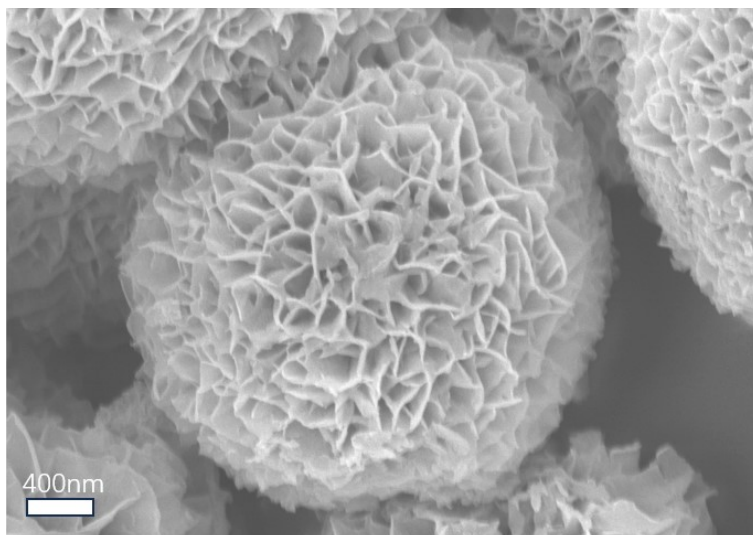
**Fig S6.** TEM image and the element (Zn, S, In, O, N, C, Zr) mappings of PZIS.



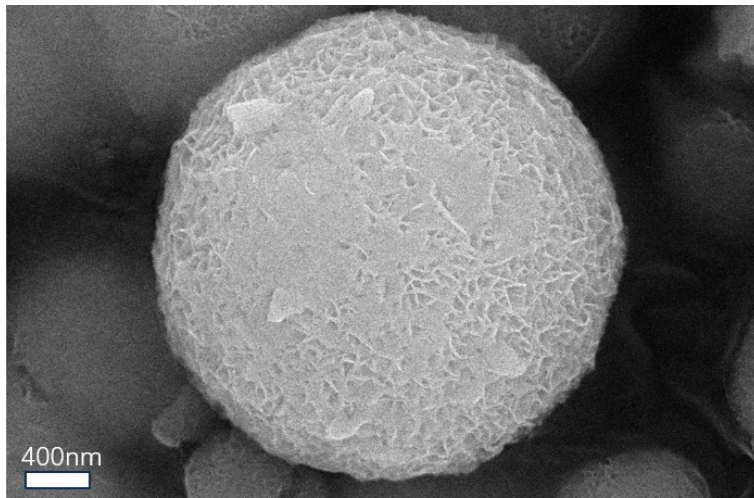
**Fig S7.** EDX of PV<sub>In</sub>-ZIS.



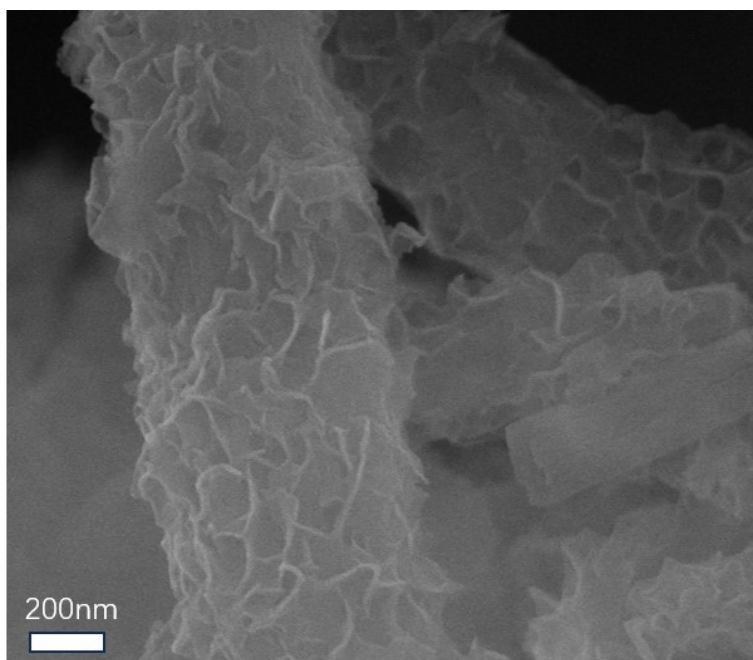
**Fig S8.** SEM image of PCN-222.



**Fig S9.** SEM image of ZIS.

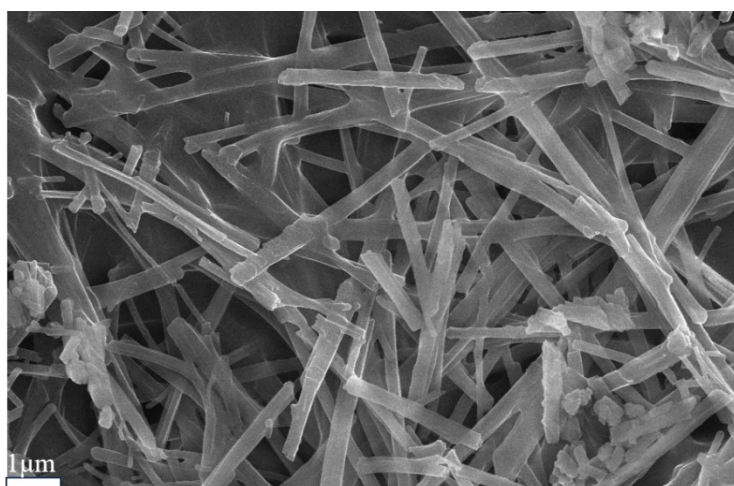


**Fig S10.** SEM image of V<sub>In</sub>-ZIS.

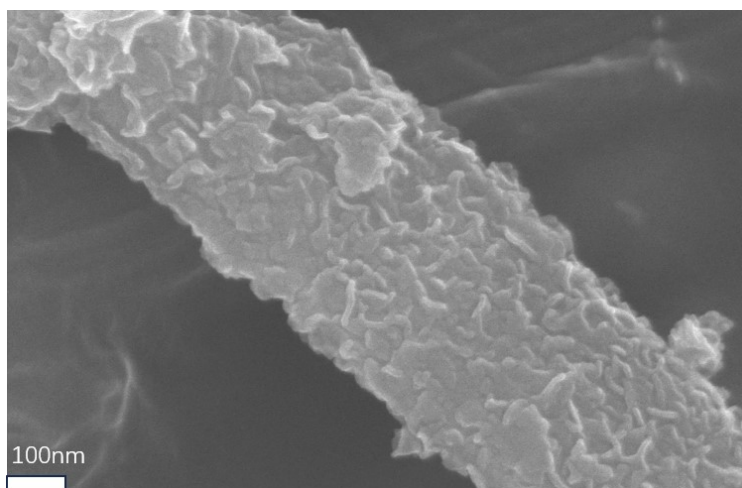


**Fig S11.** SEM image of PV<sub>In</sub>-ZIS.

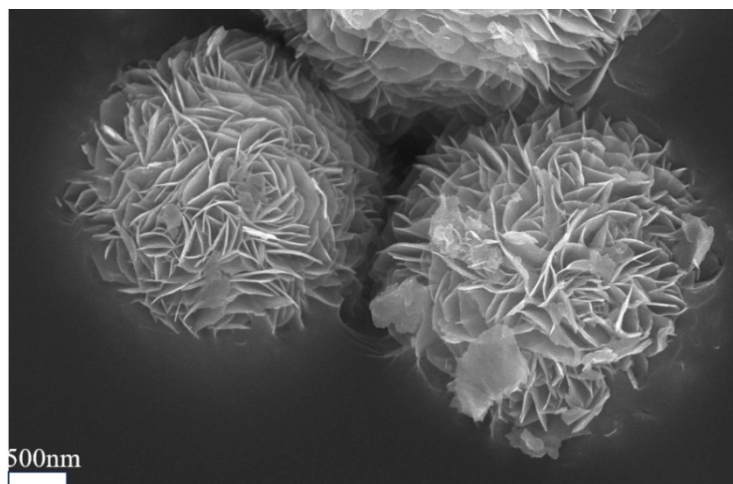




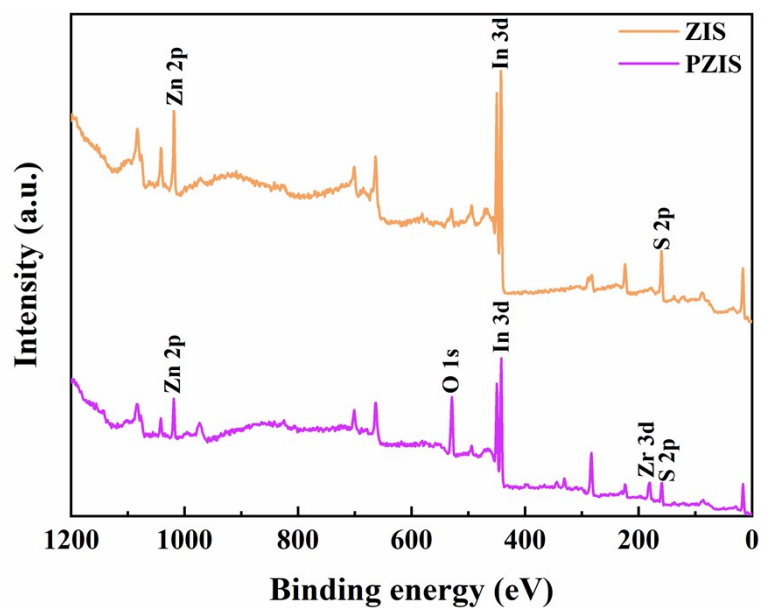
**Fig S12.** SEM image of PCN-222.



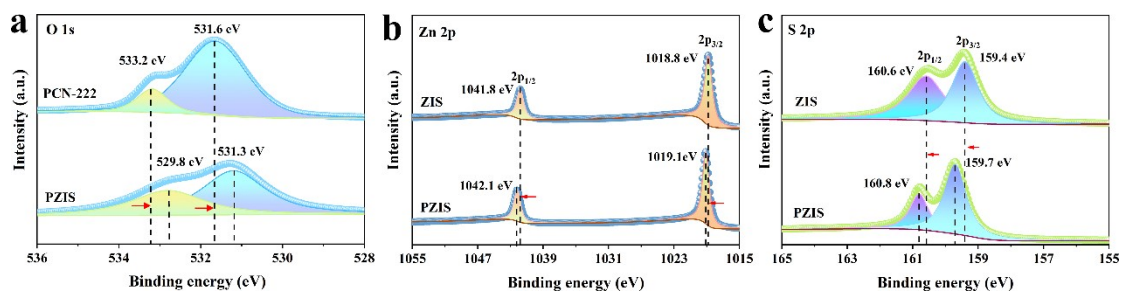
**Fig S13.** SEM image of PZIS.



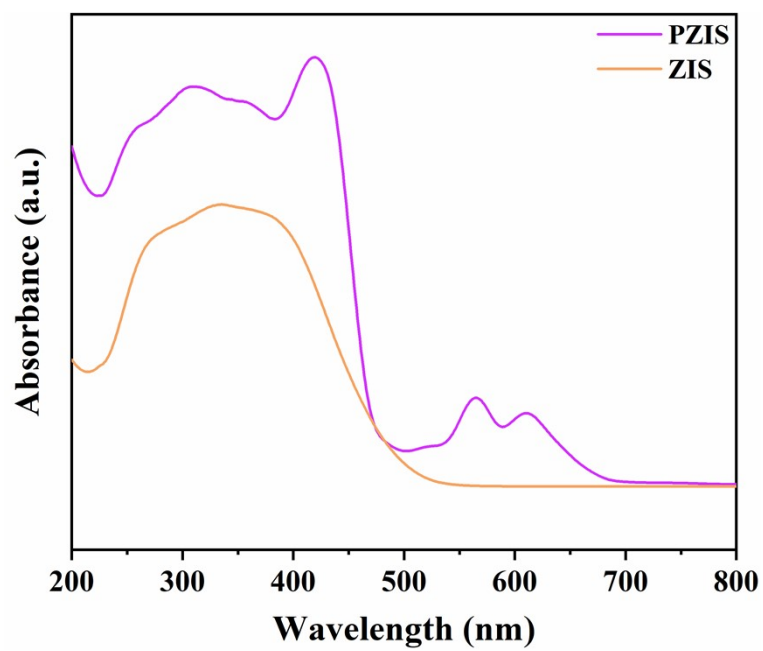
**Fig S14.** SEM image of ZIS.



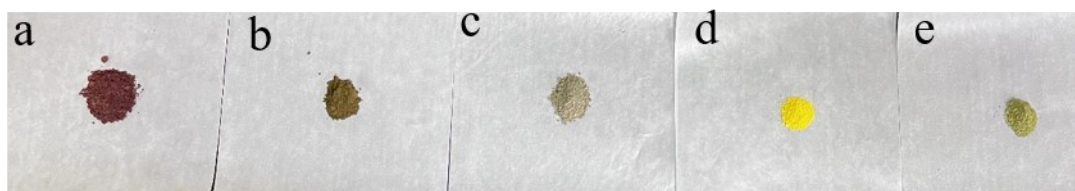
**Fig S15.** XPS spectra of ZIS and PZIS, respectively.



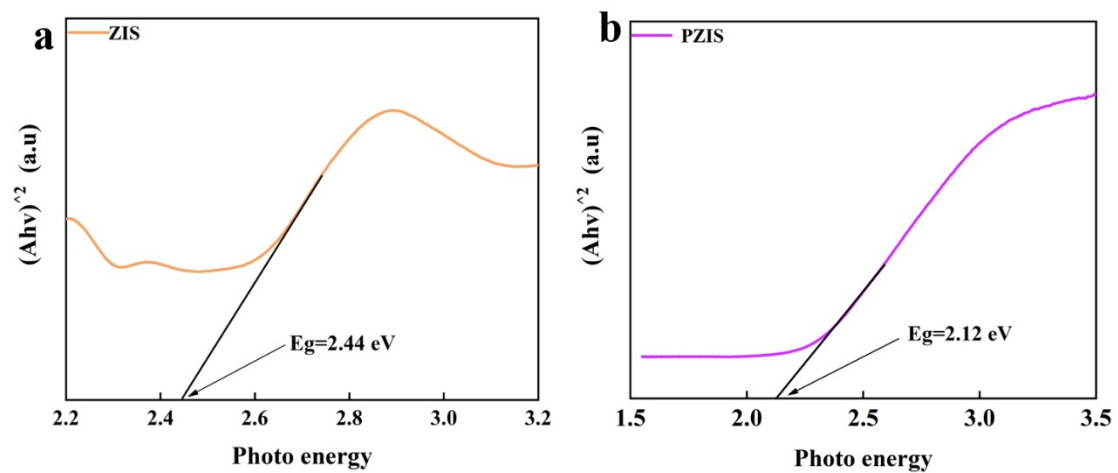
**Fig S16.** XPS spectra of PZIS: (a) O 1s, (b) Zn 2P, (c) S 2p.



**Fig S17.** UV-vis diffuse reflectance spectra of PZIS and ZIS, respectively.

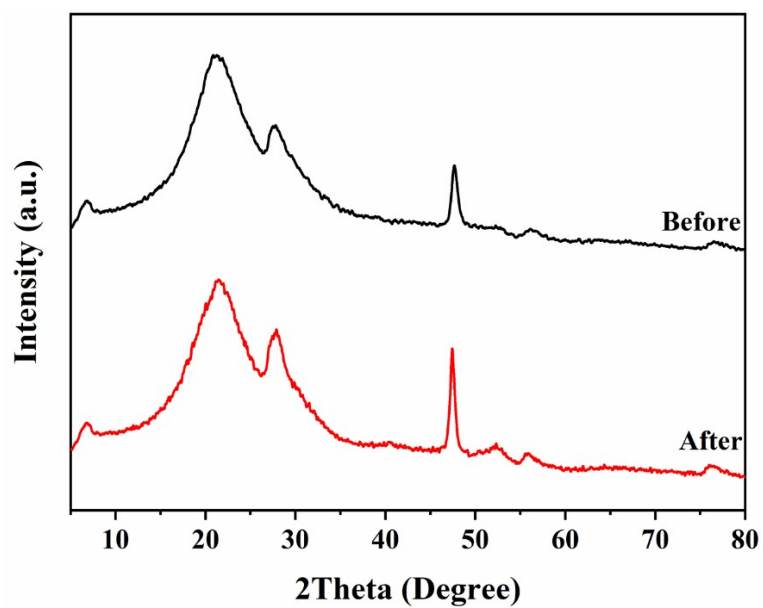


**Fig S18.** Digital photos of (a) PCN-222, (b)  $V_{In}$ -ZI, (c)  $PV_{In}$ -ZIS, (d) ZIS and (e) PZIS.

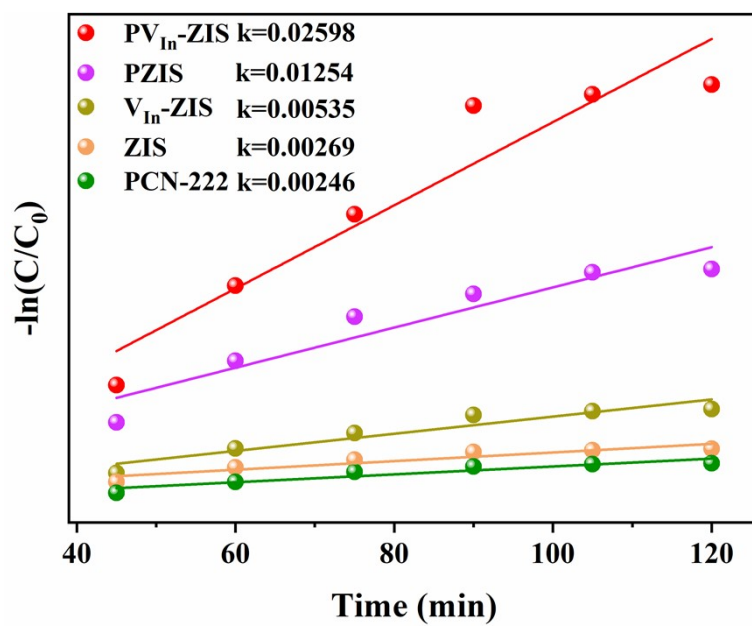


**Fig S19.** Mott-Schottky plots of (a) ZIS, and (b) PZIS, respectively.





**Fig S20.** XRD patterns of PV<sub>In</sub>-ZIS before and after the photocatalytic removal of tetracycline under the visible light irradiation.



**Fig S21.** The pseudo-first-order kinetic fitting curves of PCN-222 for the photocatalytic TC degradation under the visible light irradiation.

**Table S1.** The H<sub>2</sub> evolution of ZIS-based photocatalysts

Photocatalysts	Vacancy structure	H <sub>2</sub> production	References
Ni/ZnIn <sub>2</sub> S <sub>4</sub>	S	703 μmol·g <sup>-1</sup> ·h <sup>-1</sup>	S1
ZnIn <sub>2</sub> S <sub>4</sub> /b-TiO <sub>2</sub>	O, S	278 μmol·g <sup>-1</sup> ·h <sup>-1</sup>	S2
ZnIn <sub>2</sub> S <sub>4</sub> /B-C <sub>3</sub> N <sub>4</sub>	S	876 μmol ·g <sup>-1</sup> ·h <sup>-1</sup>	S3
ZnIn <sub>2</sub> S <sub>4</sub>	Zn	212 μmol ·g <sup>-1</sup> ·h <sup>-1</sup>	S4
PV <sub>In</sub> ZIS	In	1790 μmol ·g <sup>-1</sup> ·h <sup>-1</sup>	<b>This work</b>

**Table S2.** Results of the exponential decay-fitted parameters for the fluorescence lifetime of as prepared samples.

Photocatalyst	B1	$\tau_1(\text{ns})$	B2	$\tau_2(\text{ns})$	$\tau(\text{ns})$
PCN-222	1735.641	0.868	333.559	5.711	3.57
V <sub>In</sub> -ZIS	1821.031	1.114	288.834	7.559	4.45
PV <sub>In</sub> -ZIS	2171.183	1.090	64.035	19.730	7.57

## References

1. H. Chen, M. Li, J. Gao, D. Yang, Z. Li, H. Liu, Y. Xie, L. Guo and W. Zhou, *Appl. Surf. Sci.*, 2023, **628**, 157385.
2. B. Sun, J. Bu, Y. Du, X. Chen, Z. Li and W. Zhou, *ACS. Appl. Mater. Inter.*, 2021 **13**, 37545-37552.
3. P. Tan, M. Zhang, L. Yang, R. Ren, H. Zhai, H. Liu, J. Chen and J. Pan, *Diam. Relat. Mater.*, 2023, **140**, 110456.
4. B. Xu, H. Li, B. Chong, B. Lin, X. Yan and G. Yang, *Chem. Eng. Sci.*, 2023, **270**, 118533.