Supporting Information

Simultaneously tuning charge separation and surface reaction kinetics on $ZnIn_2S_4$ photoanode by P-doping for highly efficient photoelectrochemical water splitting and urea oxidation

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Results and Discussion

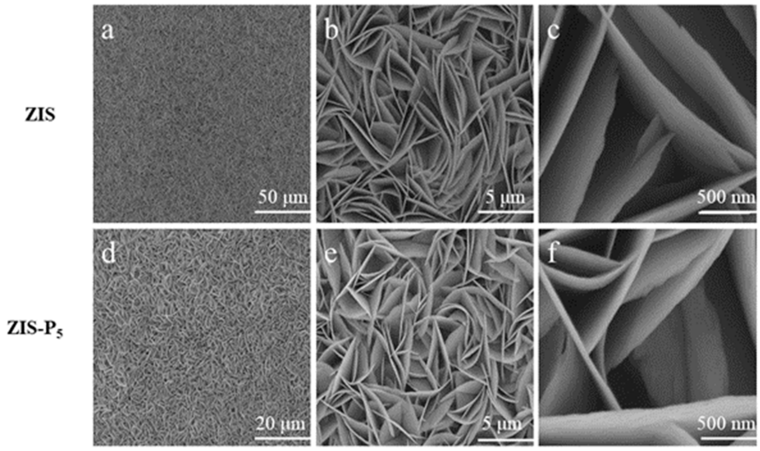

Figure S1. Field emission scanning electron microscopy images of ZIS and ZIS-P_5.

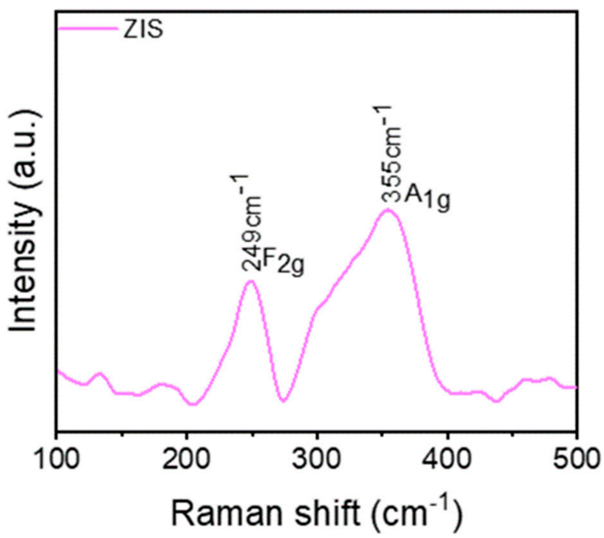

Figure S2. Raman spectra of different samples.

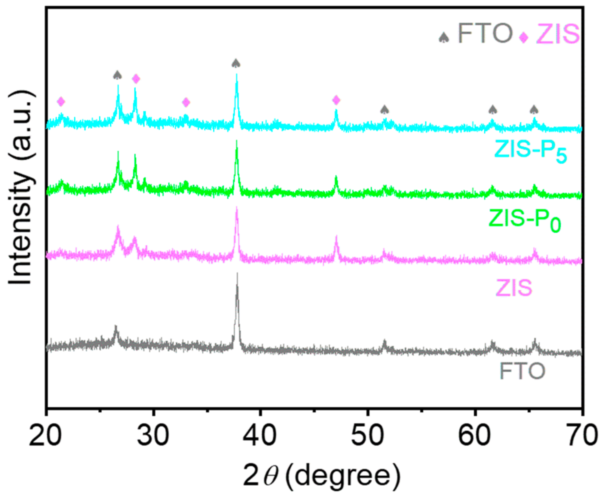

Figure S3. X-ray diffraction (XRD) patterns of different samples.

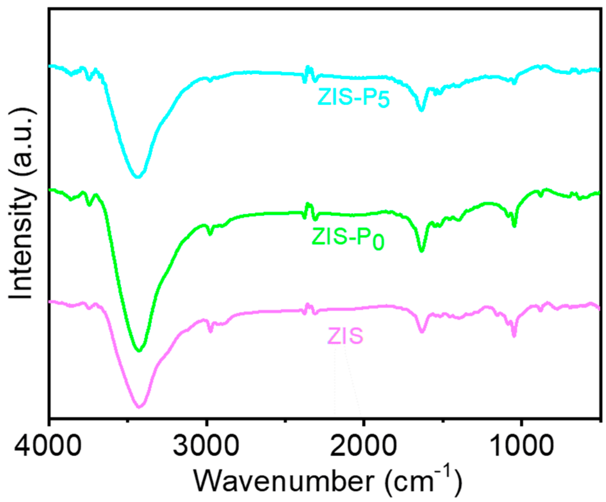

Figure S4. Fourier transform infrared (FT-IR) spectra of different photoanodes.

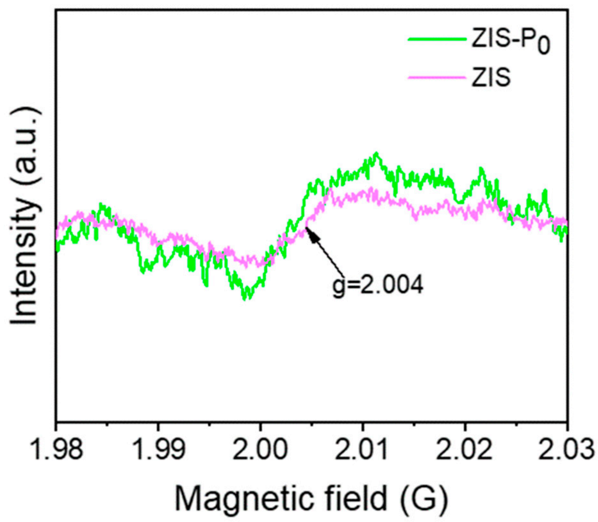

Figure S5. Electron paramagnetic resonance (EPR) spectra of different samples.

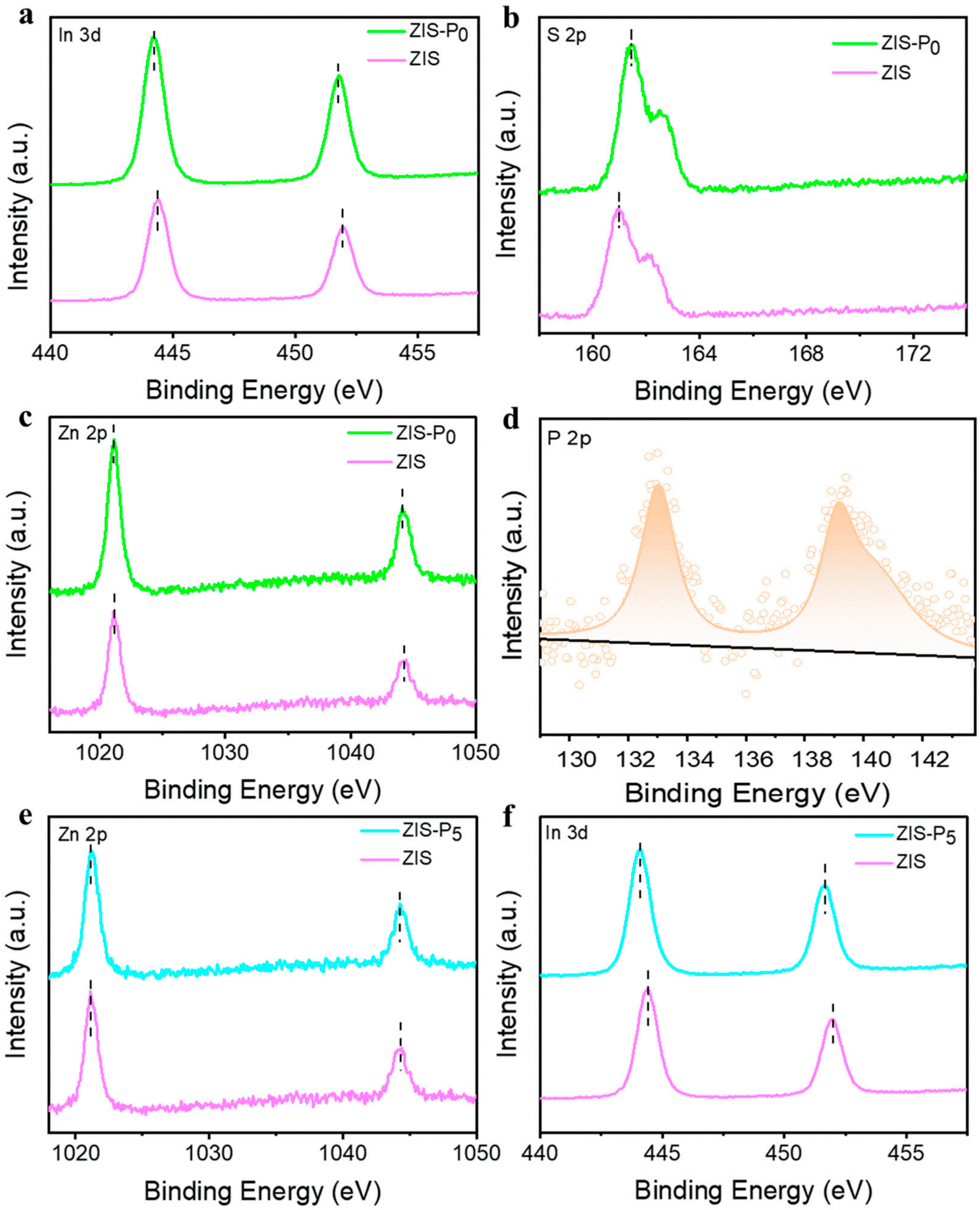

Figure S6. (**a, b, c**) X-ray photoelectron (XPS) spectra of ZIS based photoanodes. (**d, e, f**) X-ray photoelectron (XPS) spectra of different samples.

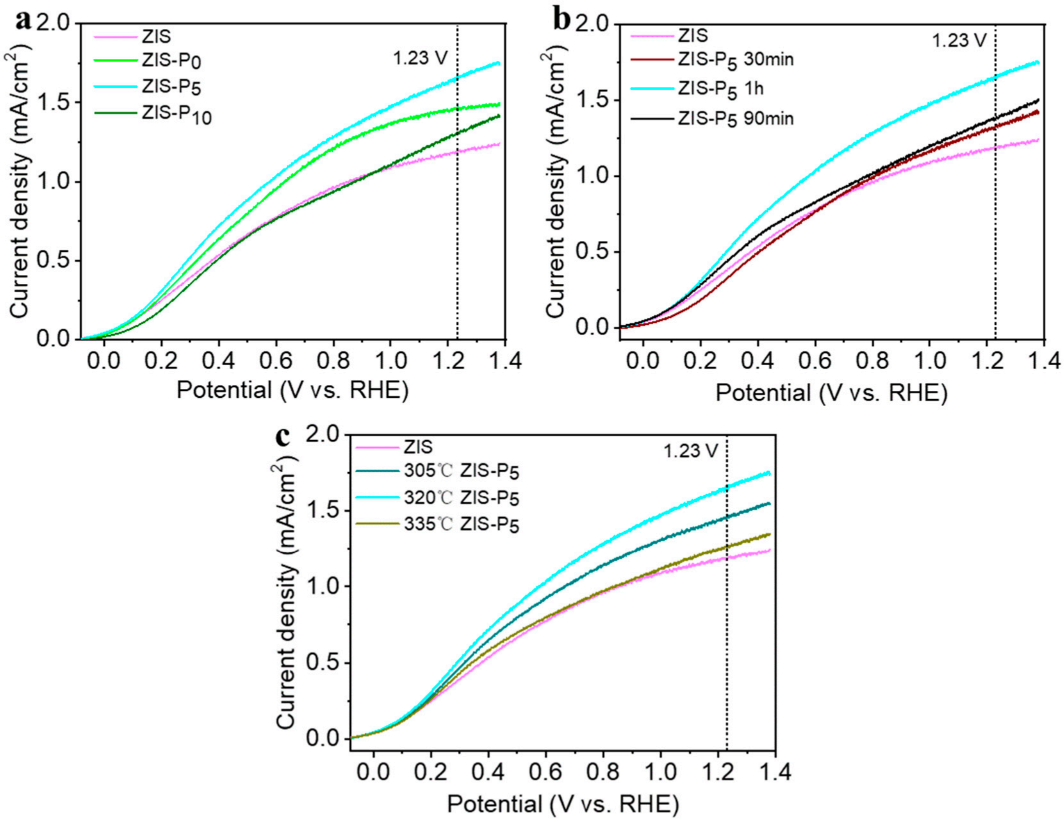

Figure S7. (**a, b, c**) Linear sweep voltammetry (LSV) curves of different samples.

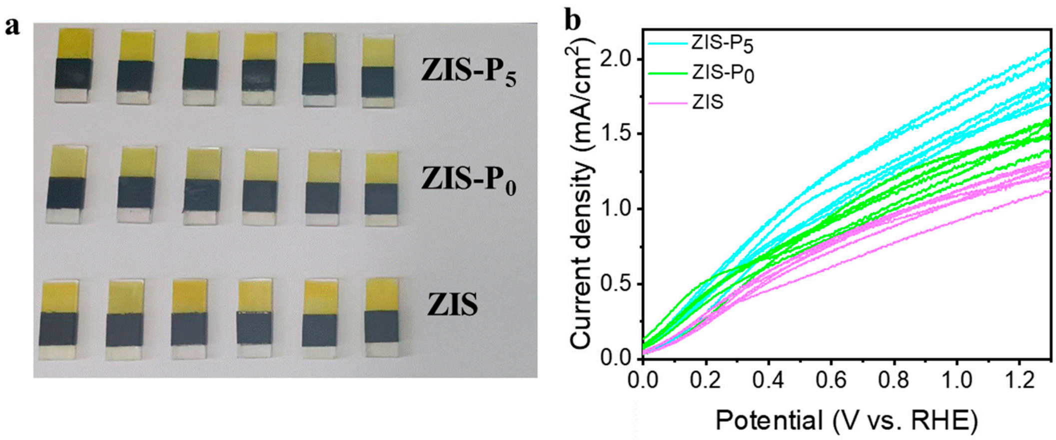

Figure S8. (**a**) Images of different samples. (**b**) Linear sweep voltammetry (LSV) curves of different samples.

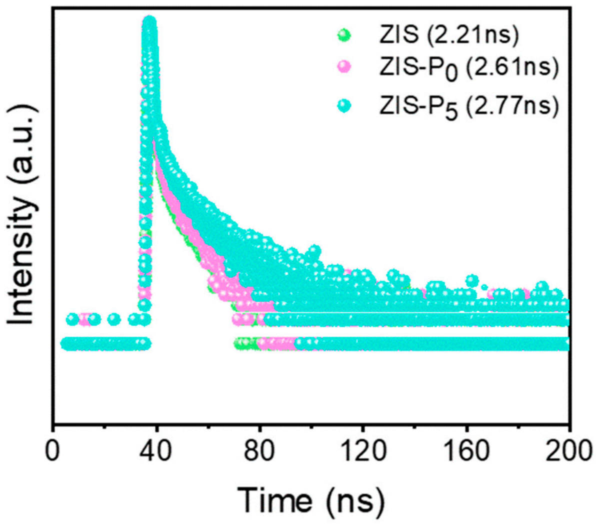

Figure S9. Time-resolved photoluminescence (TRPL) spectra of different samples.

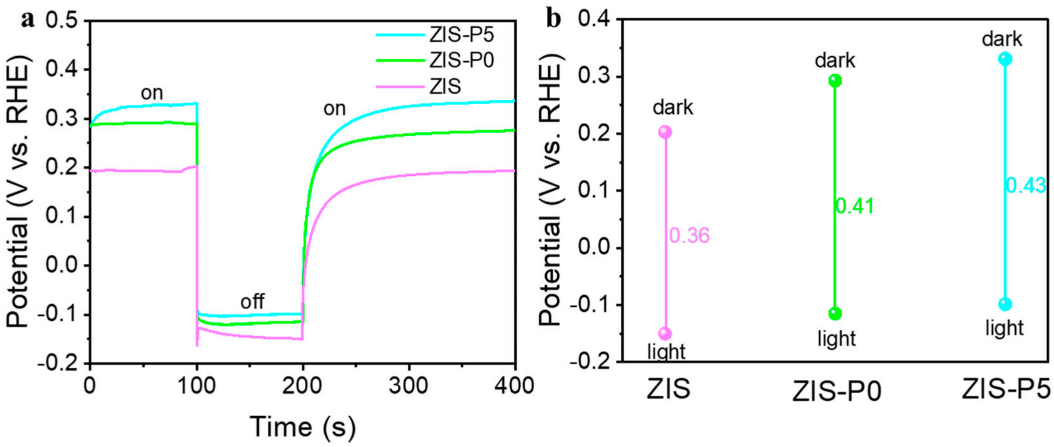

Figure S10. The open circuit potential (OCP) versus time curves measured in 0.5 M PBS solution. (b) The OCP values under both dark and light conditions.

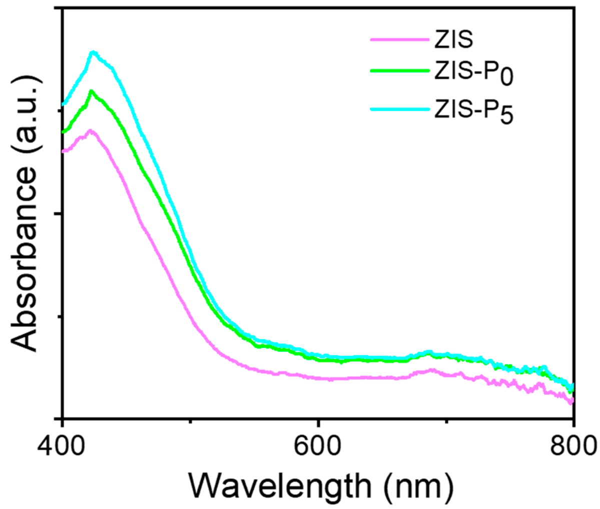

Figure S11. Ultraviolet-visible absorption spectra of different samples.

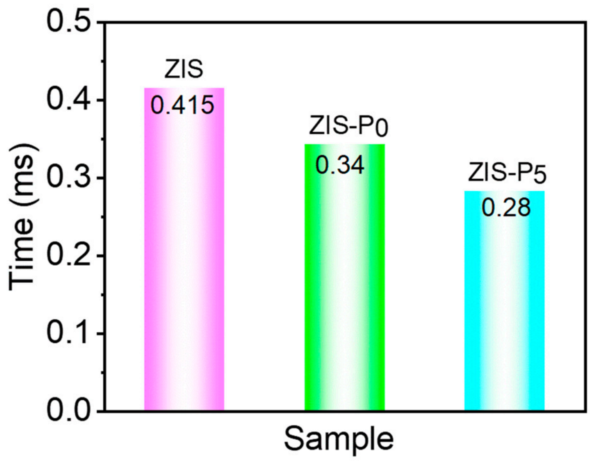

Figure S12. Transient times of different samples.

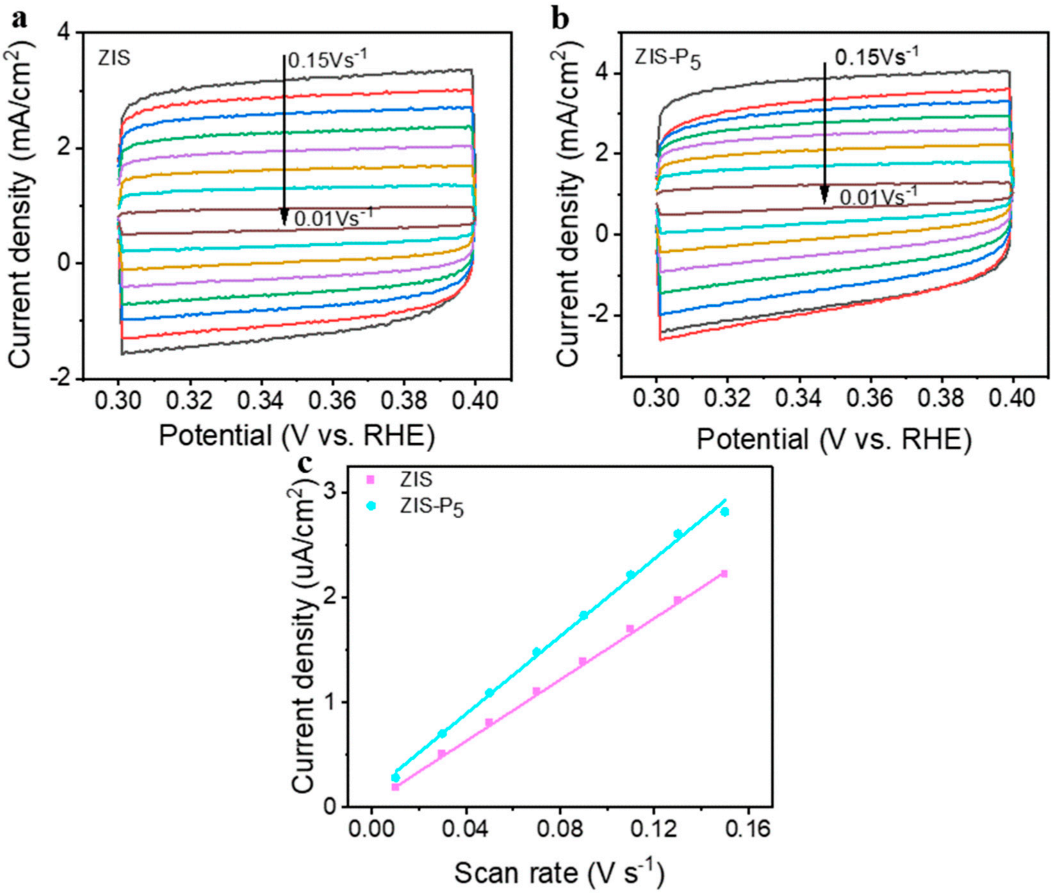

Figure S13. (**a, b, c**) Cyclic voltammograms curves of different samples measured at scan rate ranging from 0.01-0.15V s^{-1}.

Table S1. Summary of recent significant progress of ZIS-based photoanodes.

Photoanodes	Photocurrent at 1.23 V vs. RHE	Journal	Year
Co-Pi/$ZnIn_2S_4$/Pt	0.89 mA/cm^2	*Applied Catalysis B: Environmental*	2019
$ZnIn_2S_4$ homojunction	0.53 mA/cm^2	*Journal of Alloys and Compounds*	2020
Co-Mg: $ZnIn_2S_4$	0.92 mA/cm^2	*Journal of Alloys and Compounds*	2021
TiO_2/$ZnIn_2S_4$/$Zn_{0.6}Ca_{0.4}In_2S_4$	1.07 mA/cm^2	*Surfaces and Interfaces*	2021
$ZnIn_2S_4$/Cu_2S/NiFe-LDH	1.56 mA/cm^2	*Chemical Engineering Journal*	2023
MODs/$ZnIn_2S_4$	1.47 mA/cm^2	*Angewandte Chemie International Edition*	2024
$ZnIn_2S_4$-P_5	1.66 mA/cm^2	*This work*	2024

Table S2. Electrochemical impedance spectra of different samples under light conditions.

Sample	ZIS	ZIS-P_0	ZIS-P_5
R_s / (Ω)	42.3	41.9	40.9
R_{ct} / (KΩ)	4.04	1.77	0.931

Table S3. Electrochemical impedance spectra of different samples under dark conditions.

Sample	ZIS	ZIS-P_0	ZIS-P_5
R_s / (Ω)	49.9	47.4	49.9
R_{ct} / (KΩ)	22.5	19.8	14.9

Table S4. Electrochemical impedance spectra of different samples under light conditions.

Sample	ZIS	ZIS-P_0	ZIS-P_5
R_s / (Ω)	38.6	40.8	35.6
R_{ct} / (KΩ)	3.48	1.61	0.664

Reference

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2. Qian H, Liu Z, Guo Z, et al. Hexagonal phase/cubic phase homogeneous $ZnIn_2S_4$ nn junction photoanode for efficient photoelectrochemical water splitting. *Journal of Alloys and Compounds* **2020**, 830: 154639.
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4. Shi X, Dai C, Wang X, et al. Facile construction $TiO_2/ZnIn_2S_4/Zn_{0.4}Ca_{0.6}In_2S_4$ ternary hetero-structure photo-anode with enhanced photo-electrochemical water-splitting performance. *Surfaces and Interfaces* **2021**, 26: 101323.
5. Hao Z, Wang R, Zhang L, et al. More comprehensive heterojunction mechanism: Enhanced PEC properties originated from novel $ZnIn_2S_4/Cu_2S$ heterojunction assisted by changed surface states. *Chemical Engineering Journal* **2023**, 468: 143568.
6. Zhang S, Du P, Xiao H, et al. Fast Interfacial Carrier Dynamics Modulated by Bidirectional Charge Transport Channels in $ZnIn_2S_4$ - based Composite Photoanodes Probed by Scanning Photoelectrochemical Microscopy. *Angewandte Chemie International Edition* **2024**, 63(3): e202315763.