

Supporting Information

Interfacial Phosphate Like "Bridge" Mediates Bulk Charge and Surface Oxygenated-Intermediates Migration for Efficient Photoelectrochemical Water Splitting

Cheng Wang^a, Wei Zhang^b, Shuo Gu^a, Shengdong Sun^a, Meng Zhou^{b*}, Wei Chen^a, Shikuo Li^{a*}

^aPhotoelectric Conversion Energy Materials and Devices Key Laboratory of Anhui Province, Key Laboratory of Structure and Functional Regulation of Hybrid Materials (Anhui University) Ministry of Education, School of Material Science and Engineering & School of Chemical and Chemical Engineering, Anhui University, Hefei 230601, P. R. China.

^bHefei National Laboratory for Physical Sciences at Microscale, University of Science and Technology of China, Hefei 230026, P. R. China

*Corresponding authors. E-mail: mzhou88@ustc.edu.cn, lishikuo@ahu.edu.cn; Tel: +86-551-63861328

Catalogue

1. Materials	S2
2. Experimental.....	S2
2.1 Synthesis of ZnIn ₂ S ₄ nanoarray.....	S2
2.2 Synthesis of ZnIn ₂ S ₄ -CdS nanoarray.....	S2
2.3 Synthesis of ZnIn ₂ S ₄ -PO/CdS nanoarray.....	S2
2.4 Synthesis of ZnIn ₂ S ₄ -P nanoarray.....	S2
2.5 PEC measurements.....	S2
2.6 fs-TA measurements.....	S2
2.7 Oxygen evolution detection.....	S2
3. Characterization	S2
4 . Density function theory calculation details.....	S3
5. Supplementary figures.....	S4
6. Supplementary tables.....	S11
7. References:.....	S13

1. Materials

Zinc chloride (ZnCl_2), Indium chloride ($\text{InCl}_3 \cdot 4\text{H}_2\text{O}$), Thioacetamide ($\text{CH}_4\text{N}_2\text{S}$) and Cadmium chloride ($\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$) were purchased from Sinopharm Chemical Reagent Co., Ltd. Sodium hypophosphite (NaH_2PO_2) were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. Conductive glass (FTO, 14Ω , $20 \text{ mm} \times 15 \text{ mm}$) was provided by Wuhan Lattice Solar Technology Co., Ltd. All chemicals were used as purchased without further purification.

2. Experimental sections

2.1 Synthesis of ZnIn_2S_4 nanoarray

0.082 g ZnCl_2 , 0.35 g $\text{InCl}_3 \cdot 4\text{H}_2\text{O}$ and 0.18 g $\text{CH}_4\text{N}_2\text{S}$ were first dissolved in 60 mL aqueous solution. Then the precursor solution was transferred into 100 mL autoclave. A piece of clean FTO glass substrate was subsequently putted into the solution. It was heated in the oven at $160 \text{ }^\circ\text{C}$ for 360 min. After cooling, the substrate with uniform light yellow was obtained and washed with deionized water.

2.2 Synthesis of ZnIn_2S_4 -CdS nanoarray

According to the ion exchange method [1, 2], the ZnIn_2S_4 -CdS nanoarrays were synthesized as follows: Firstly, 11.42 g $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$ was dissolved in 30 mL deionized water. Then, 1 mL above solution was diluted into 10 mL in a glass bottle, and which was purged with N_2 gas for 20 min. Finally, the above yellow substrate was immersed into the solution, and the bottle was maintained $100 \text{ }^\circ\text{C}$ for 30 min in an oil bath. After that, the substrate was washed thoroughly with deionized water.

2.3 Synthesis of ZnIn_2S_4 -PO/CdS nanoarray

2.12 g NaH_2PO_2 was first dissolved in 20 mL deionized water. The subsequent step was the similar to synthesis of ZIS-CdS, except for adding 4 mL NaH_2PO_2 solution.

2.4 Synthesis of ZnIn_2S_4 -P nanoarray

2.12 g NaH_2PO_2 was first dissolved in 20 mL deionized water. The uniform yellow substrate with ZnIn_2S_4 nanosheet arrays were then immersed into the above solution and kept in $100 \text{ }^\circ\text{C}$ for 30 min in an oil bath.

2.5 PEC measurements

The PEC performance was measured on an electrochemical workstation CHI 660E (CH Instrument

Inc., Shanghai) using a three-electrode system (photoanode, Ag/AgCl as reference electrode and Pt sheet as counter electrode). The electrolyte was 0.5 M Na₂SO₄ aqueous solution, and the measurements were performed under AM 1.5 G simulated sunlight illumination with a calibrated light intensity of 100 mW cm⁻² (MC-PF300C, MerryChange Technology Co., Ltd). EIS, IPCE and IMPS were all measured by Zahner IM6 (Zahner IM6, Germany). For the stability test, the electrolyte was 0.25 M Na₂S and 0.35 M Na₂SO₃ aqueous solution and carried out at the potential of 0.25 V vs RHE.

2.6 fs-TA measurements

The femtosecond transient spectra were measured using a home-built pump-probe set-up. The laser pulse (800 nm, 35 fs pulse width, 1 kHz repetition rate) was generated by a regeneratively amplified Ti: sapphire laser (Coherent Astrella-Tunalbe-USP, USA). The output of the pulse is then divided into two beams with a beam splitter. For the pump beam, a BBO crystal was used to generate the pulse with central wavelength of 400 nm (0.3 uJ). The probe beam was controlled with an optical delay line and then focused on a thin sappier plate to generate the white light, which split into two beams by using a broadband 50/50 beam splitter as the signal and reference beams (450-800 nm). The focused pump and probe pulses were overlapped into a sample cuvette. The mutual polarization between the pump and probe beams was set to the magic angle (54.7) by placing a half-wave plate in the pump beam. There was no photodegrading after fs-TA experiments by checking the steady-state absorption spectra.

2.7 Oxygen evolution detection

Oxygen evolution of the photoanode was measured in an air-tight reactor connected to a closed gas circulation system (MC-SPB10-AG, Beijing MerryChange Technology Co., Ltd). Prior to measurements, the cell compartments were carefully sealed with rubber septa and glycerin to prevent any gas leakage and then Ar-purged for 1 h. The conditions were similar to the PEC test, 1.2 V vs RHE bias was applied.

3 Characterization

Microscopic morphology of the photoanodes were confirmed by scanning electron microscopy (SEM, Sigma500, Germany). The lattice structure of the photoanode was observed using transmission electron microscope (TEM) (HRTEM, JEM-2100, Japan). The XRD pattern of the

sample was performed on an X-ray polycrystal diffractometer (Smart Lab 9KW, Japan). Raman spectra were obtained by laser confocal Raman spectrometer (inVia-Reflex, UK) at room temperature. Elemental displacements of the photoanode was measured on X-ray photoelectron spectroscopy (XPS) (ESCALAB 250 Xijing, USA). Fourier transform infrared spectra (FTIR) were recorded on a Fourier transform spectrometer (NEXUS-870) with KBr pellets. Room temperature photoluminescence (PL) spectra were carried out on FS5 fluorescence (Edinburgh Instruments, UK). Kelvin probe force microscope (KPFM) measurement was performed on Park atomic force microscope (ParkNX10, Korea). Electron paramagnetic resonance (EPR) and Electron spin resonance (ESR) spectra were taken from a X-band desktop electron paramagnetic resonance spectrometer (Bruker EMXnano, Germany). The surface photovoltage (SPV) of the photoanodes were tested by a surface photovoltage test system (SEO-012, China).

The OCP decay life can be calculated by the following formula:

$$\tau_n = -\frac{k_B T}{q} \left(\frac{dV_{oc}}{dt} \right)^{-1} \quad (S1)$$

where τ_n is the carrier lifetime, k_B is Boltzmann's constant, T is the temperature, and q is the positive charge.

The IPCE was calculated from the equation:

$$\text{IPCE} = \left[\frac{1024 \times J (mAcm^{-2})}{\lambda (nm) I_{light} (mWcm^{-2})} \right] \times 100\% \quad (S2)$$

where λ is the incident light wavelength, J is the photocurrent density at wavelength λ under illumination, and I_{light} is the incident light irradiance intensity.

Free radical capture experiment: 5, 5-Dimethyl-L-pyrroline N-oxide was used to capture $\cdot\text{OH}$, and the active species was detected by ESR after 3 min of light irradiation.

4. Density function theory calculation details

DFT calculations: All calculations are carried out using CASTEP under the spin polarized density functional theory (DFT) scheme.^[3] Specifically, the exchange function is treated by the generalized gradient approximation (GGA) of the Perdew-Burke-Ernzerhof (PBE) function.^[3, 4] The Vanderbilt ultrasoft pseudopotential was used with a cutoff energy of 500 eV. A vacuum layer of 15 Å was established in the direction of the C-axis to avoid interlayer effects.

Under standard conditions, the Gibbs free energy (ΔG) of the OER reaction can be calculated according to the following formula:

$$G = E + E_{ZPE} - TS - eU \quad (\text{S3})$$

where E , E_{ZPE} , and S represent the single-point energy, zero-point energy, and entropy of the ZIS, ZIS-CdS and ZIS-P/CdS, respectively, with and without different oxygen intermediates adsorbed. T indicates a temperature of 298.15 K. U is the potential compared to a typical hydrogen electrode.

For the oxygen evolution reaction, we considered the four elementary steps:



where $*$ represents a surface site and *OH , *O , and *OOH are intermediates adsorbed on an active site on the catalyst surface.

The overpotential (η) are calculated as follows:

$$\eta = \frac{\max \{ \Delta G_1, \Delta G_2, \Delta G_3, \Delta G_4 \}}{e} - 1.23 \quad (\text{S8})$$

Here, ΔG_1 , ΔG_2 , ΔG_3 , and ΔG_4 denote the Gibbs free energy difference for each reaction, (S4)-(S7), respectively.

6 .Supplementary figures

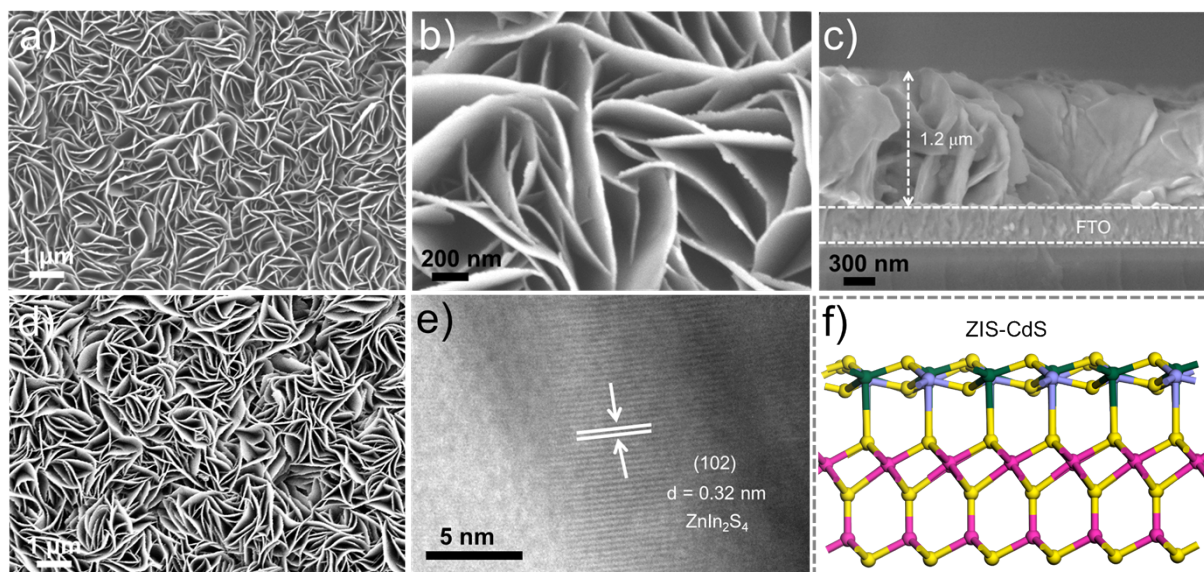


Figure S1. SEM images (a, b) and Cross-sectional SEM image (c) of the ZIS sample. SEM image (d) of the ZIS-P/CdS sample. HRTEM image (e) of the ZIS sample. The optimized molecular structure model of the ZIS-CdS sample (f).

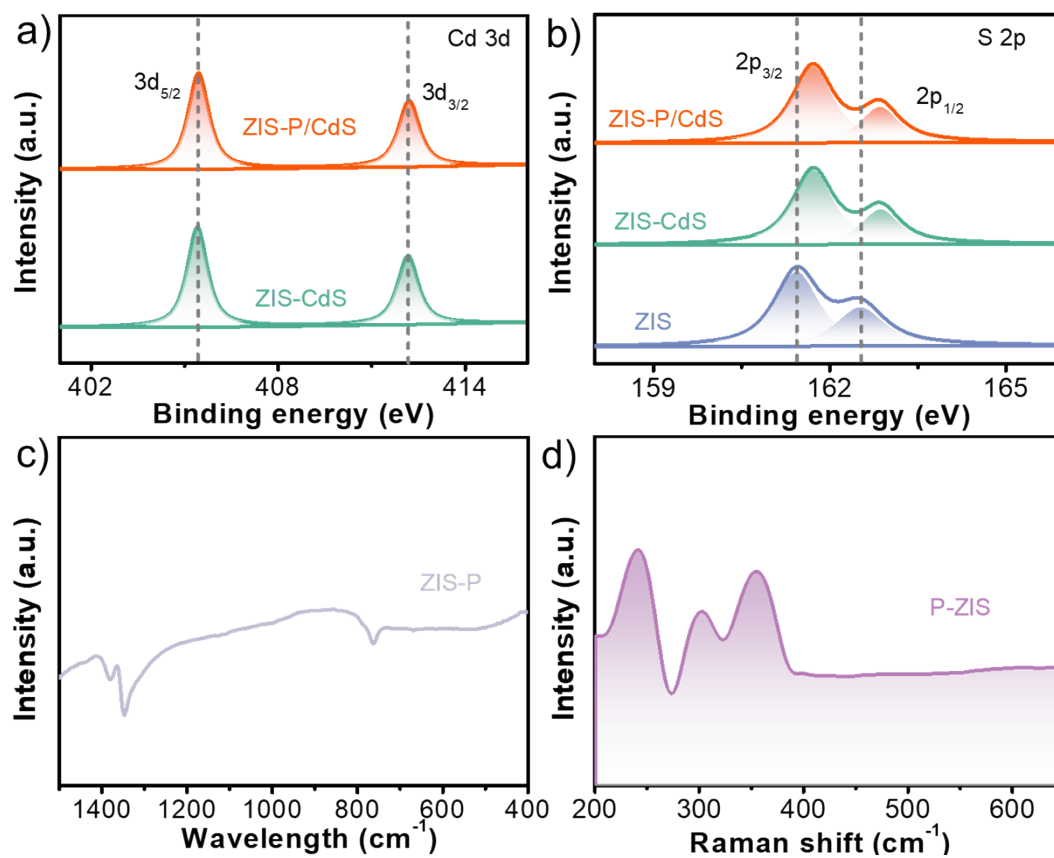


Figure S2. High resolution XPS spectra of Cd 3d (a), S 2p (b) of the samples. FTIR spectrum of the ZIS-P sample (c), and Raman spectrum of the P-ZIS sample (d).

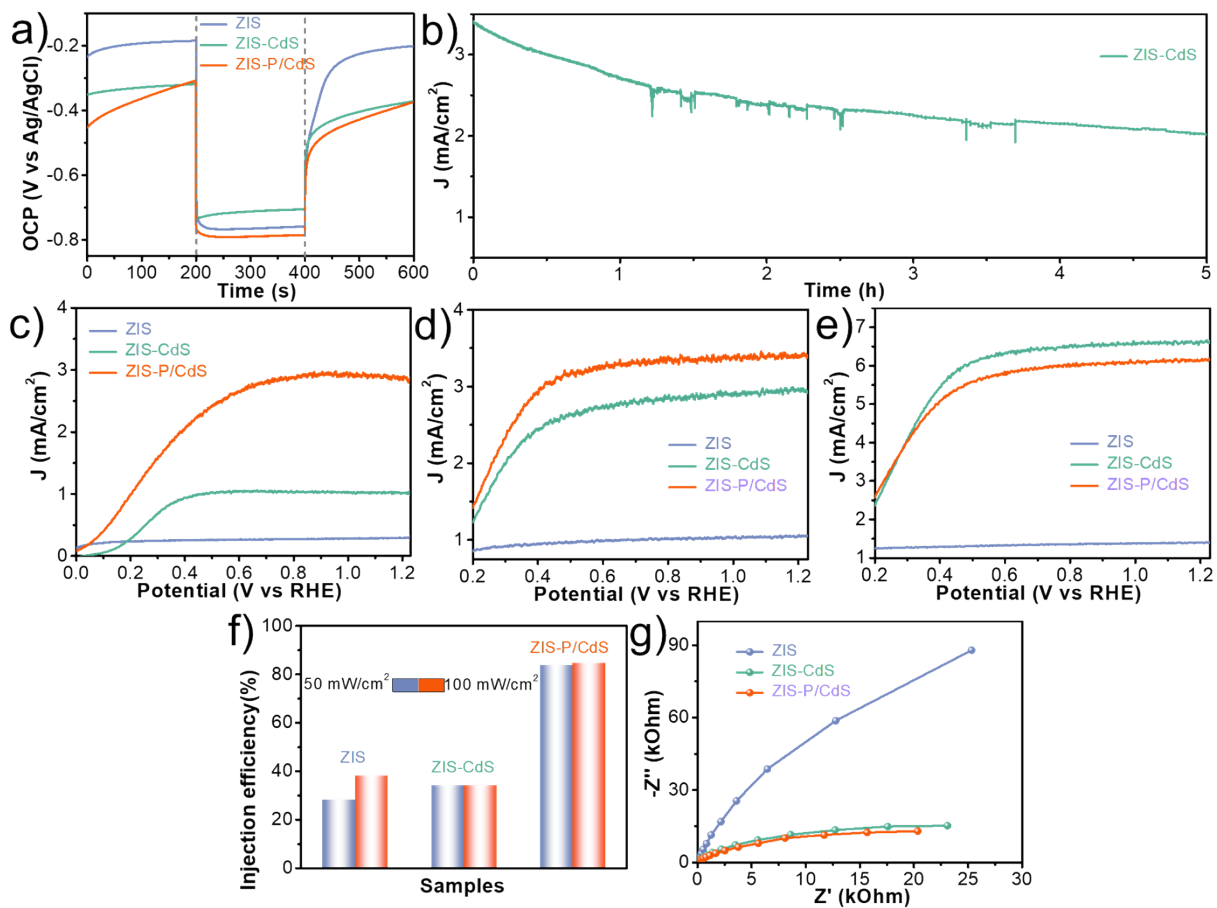


Figure S3. OCP (a), Five-hour operation applied at 0.25 V vs RHE in 0.25 M Na₂S and 0.35 M Na₂SO₃ electrolyte (b), LSV curves in a neutral solution (c), hole scavenger solution (d, e), η_{inj} at 1.23 V vs RHE (f), EIS (g) of the ZIS, ZIS-CdS, and ZIS-P/CdS samples, respectively. Light conditions: 50 mW cm⁻² (c, d) and 100 mW cm⁻² (e).

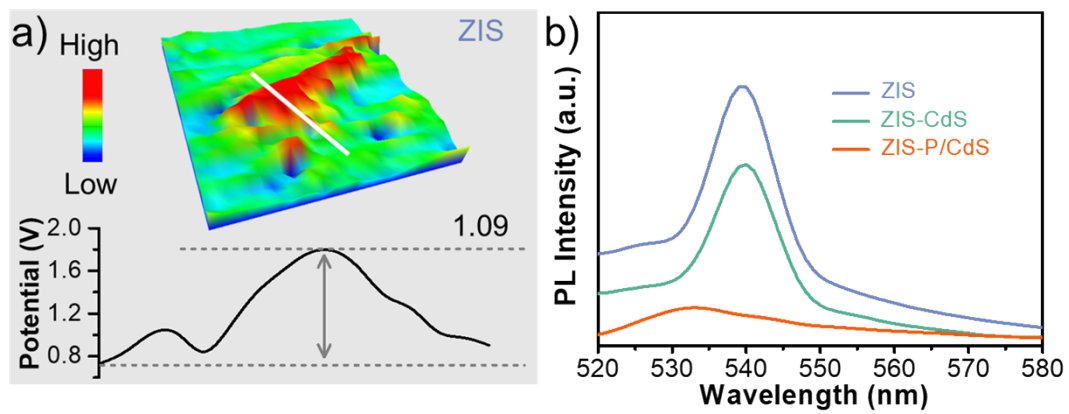


Figure S4. KPFM image of the ZIS sample (a), and steady-state PL spectra of the samples (b).

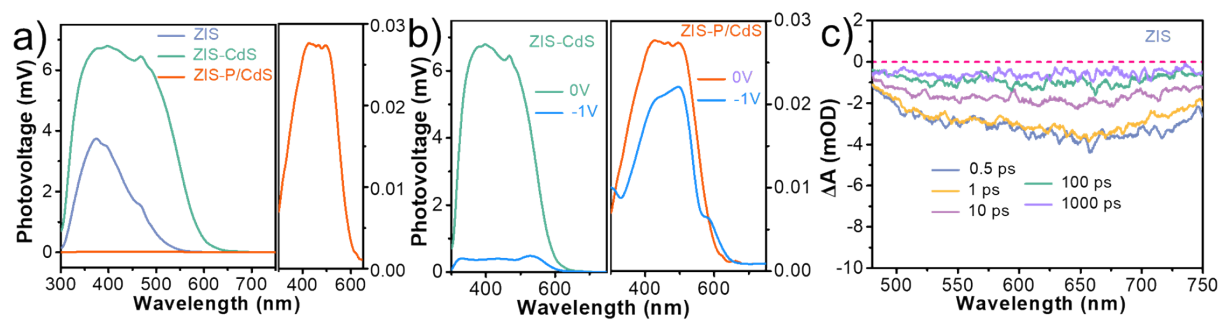


Figure S5. SPV spectra (a), *in situ* SPV spectra (b) of the samples, and fs-TA spectra at differing time delay (c) of the ZIS sample.

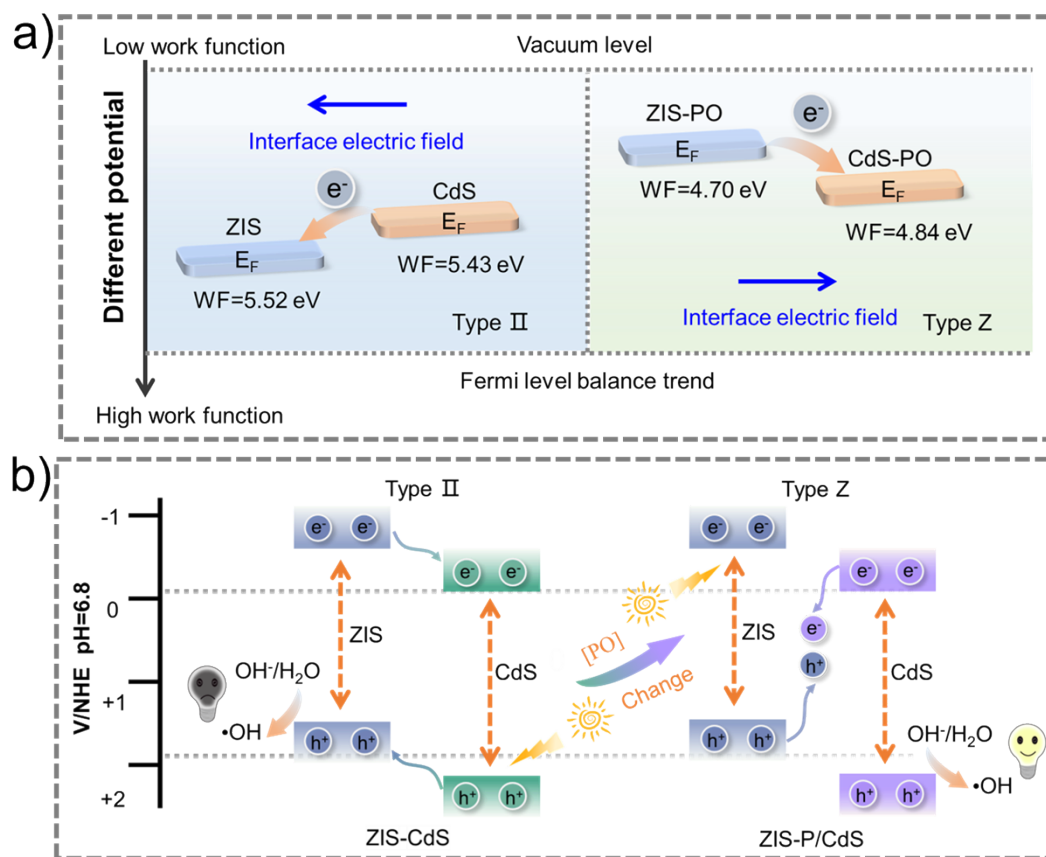


Figure S6. [PO] modulation model for work function (a), and schematic diagram of carrier flow (b)

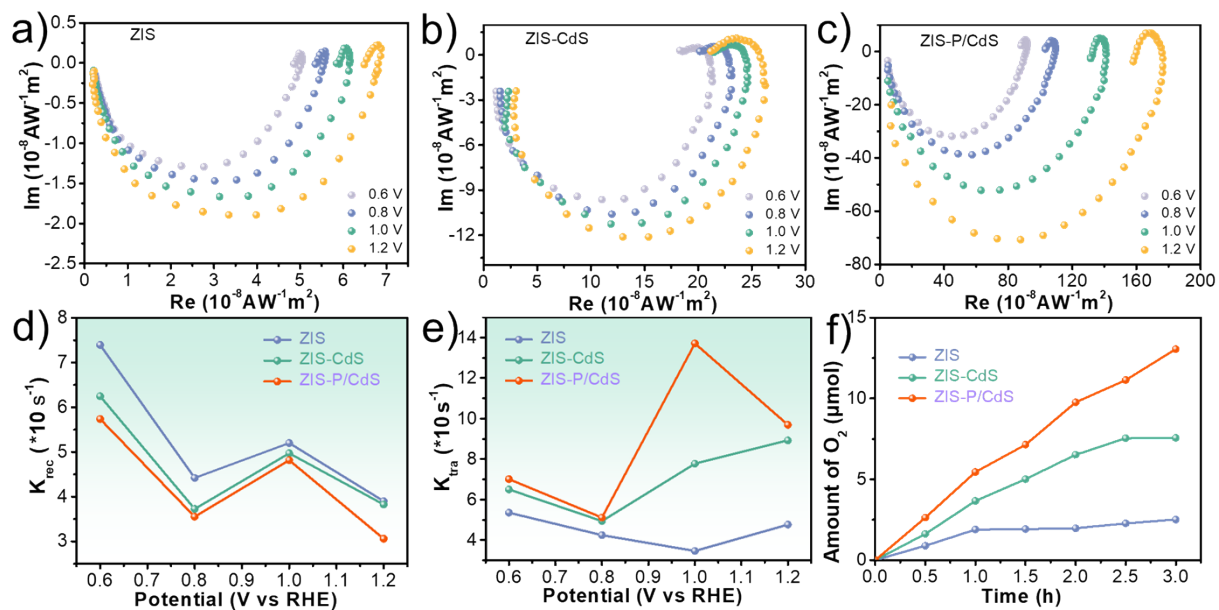


Figure S7. IMPS spectra of the ZIS (a), ZIS-CdS (b) ZIS-P/CdS (c) photoanodes. Calculate k_{rec} (d) and k_{tra} (e) based on the IMPS spectra. Amount of measured oxygen evolution of the samples (f).

7 Supplementary tables

Table S1. Detailed comparisons of ZIS-P/CdS PEC performances with the reported sulfur-based photoanodes.

Photoanodes	J (mA cm ⁻²) at 1.23 V _{RHE}	Electrolyte	References
Zn ₁₀ In ₁₆ S ₃₆	4.63	Na ₂ SO ₃	<i>Angew. Chem. Int. Ed.</i> 2018, 57,16882
ZnInS/Fe-In-S	5.35	Na ₂ SO ₄	<i>Nat. Commun.</i> 2021, 12, 5247
In ₂ S ₃ /Bi ₂ S ₃	2.0	Na ₂ SO ₄	<i>J. Mater. Chem. A</i> 2020, 8, 5612
Vs-CdIn ₂ S ₄	5.73	Na ₂ SO ₄	<i>Nat. Commun.</i> 2020,11, 3078
Vertical SnS ₂	2.6	Na ₂ SO ₄	<i>Adv. Energy Mater.</i> 2019, 9, 1901236
CdIn ₂ S ₄ /InO _x /NiFe-LDH	5.47	KOH	<i>Appl. Catal. B: Environ.</i> 2022, 300, 120717
WO ₃ /In ₂ S ₃	1.61	Na ₂ SO ₄	<i>Adv. Energy Mater.</i> 2020, 10,1903951
CdIn ₂ S ₄ /In ₂ S ₃ /SnO ₂	2.98	Na ₂ SO ₄	<i>Adv. Mater.</i> 2020, 32, 2002893
SnS ₂ plasma	2.15	Na ₂ SO ₄	<i>Angew. Chem. Int. Ed.</i> 2019, 58, 16668
ZIS-O-TS	4.57	Na ₂ SO ₄	<i>Adv. Energy Mater.</i> 2022, 2200629
ZIS-O-S	3.52	NaH ₂ PO ₄ /Na ₂ HPO ₄	<i>Adv. Energy Mater.</i> , 2021: 2101181
ZnIn ₂ S ₄ /CdS/ZnO	3.48	Na ₂ SO ₄	<i>Adv. Energy Mater.</i> 2021, 11(8): 2003500
ZIS-P/CdS	5.2	Na ₂ SO ₄	<i>This Work</i>

Table S2. Fitted parameters for fs-TA signals of the ZIS, ZIS-Cd and ZIS-P/CdS samples.

Samples	τ_1 (ps)	τ_2 (ps)	τ_3 (ps)
ZIS	1.12	22.6	2678
ZIS-CdS	0.68	32.1	2106
ZIS-P/CdS	0.09	48.7	2236

References

1. L. He, C. R. Luan, S. P. Liu, M. Chen, N. Rowell, Z. Wang, Y. Li, C. C. Zhang, J. Lu, M. Zhang, B. Liang, K. Yu, *J. Am. Chem. Soc.*, 2022, **144**, 19060-19069.
2. W. W. Xu, W. Tian, L. X. Meng, F. R. Cao, L. Li, *Adv. Energy Mater.*, 2021, **11**, 2003500.
3. G. C. Zuo, Y. T. Wang, W. L. Teo, A. M. Xie, Y. Guo, Y. X. Dai, W. Q. Zhou, D. Jana, Q. M. Xian, W. Dong, Y. L. Zhao, *Angew. Chem.Int. Edit.* 2020, **59**, 11287.
4. Y. G. Chao, P. Zhou, J. P. Lai, W. Y. Zhang, H. W. Yang, S. Y. Lu, H. Chen, K. Yin, M. G. Li, L. Tao, C. S. Shang, M. P. Tong, S. J. Guo, *Adv. Funct. Mater.* 2021, **31**, 2100923.