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RESEARCH ARTICLE

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Multi-interfacial catalyst with spatially defined redox reactions for enhanced pure water photothermal hydrogen production

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Abstract

Photocatalytic overall water splitting is a promising strategy to store abundant solar energy as clean fuel, but recombination of photogenerated carriers is the key factor that reduces the efficiency. Herein, we report multi-interfacial ternary CoP@ZnIn₂S₄@Co₃O₄ photocatalyst with coordinated structural and electronic band coupling to concurrently fulfill spatially decoupled redox centers and modulated electric field. For one, the realization of 3D open framework consists of 2D ZnIn₂S₄ nanosheets on 1D CoP co-catalyst maximizes exposures apart from circumvents aggregation and shielding issues. Another is the spatially defined and selective redox reactions where CoP is designated for proton reduction and Co₃O₄ for water oxidation. And finally, constructed type II band structure and p-n junction facilitates directional charge separation, thereby prohibiting the recombination of charge carrier and also increase the local charge density. Besides, small band gap CoP and Co₃O₄ exhibit photothermal effect to further enhance photocatalytic hydrogen production. As a result, the photocatalysts could achieve the respective half reaction and pure water hydrogen evolution rate of 4254 and 145 μ mol g⁻¹ h⁻¹ under visible light illumination and further enhance to 10 740 and 308 μ mol g⁻¹ h⁻¹ when subjected to full spectrum photoheating. This work presents a promising strategy in designing surface and interfacial dominated photocatalytic system to achieve efficient solar energy to chemical conversion.

KEYWORDS

charge transfer, oxidation centers, pure water splitting, redox centers, zinc indium sulfide

1 | INTRODUCTION

Materials constituents and structural design have pivotal influences on catalytic activities.¹⁻⁴ Metal chalcogenides,

specifically in a two-dimensional (2D) form is an ideal material system as a photocatalyst host and scaffold to load co-catalyst^{5,6} owing to its exquisite photo and electrochemical properties, high-specific surface area, short

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SCHEME 1 Schematic diagram of the designed $CoP/ZnIn_2S_4/Co_3O_4$ multi-interfacial catalyst with spatially defined redox centers, builtin electric field, and photoheating

migration path of charge carriers, and also its versatility for further chemical and topographical modifications.⁷⁻¹⁰ Among the candidates, ternary ZnIn₂S₄ is an efficient photocatalyst as it has a relatively narrow band gap and suitable band potentials that coincide the visible light spectrum. Analogous to the chalcogenides, transition metal phosphides have long been studied for catalysis. Among them, CoP, has been widely reported to be an efficient co-catalyst for hydrogen evolution reaction (HER) catalyst in photocatalytic and electrocatalytic water splitting as it can produce a "weak ligand" effect when metal-P bonds are formed and thus promote the release of hydrogen from active sites.¹¹⁻¹⁴ However, previous works are mainly focused on zero-dimensional (0D) CoP nanoparticles loaded on the light absorbing host semiconductors, which limits the contact between the host and co-catalyst as well as restricts the loading mass due to the light shielding outcome.

Moreover, effective charge separation and surface reactivity are two other crucial tactics to boost solar-to-hydrogen conversion efficiency.^{15–20} It has been proven to be an effective strategy to design a single entity photocatalyst with reduction and oxidation co-catalysts to simultaneously localize respective redox active sites and inhibit the recombination of photo-generated electron–hole pairs.^{21–23} However, the main challenge is to prevent random distribution of two different co-catalysts on the host surfaces. Coexistence of reductive and oxidative co-catalysts in an unsegregated space could inevitably lead to random flow of charge carriers. Worse still, close proximity or intercoverage of redox active sites cause severe charge recombination and adverse backward reactions, which defeats the primary purpose of designing selective co-catalysts.24-26 One typical structure design to spatially separate the disparate co-catalysts is the core-shell Janus nanosphere, which utilizes the inner and outer shell surfaces for either electron or hole shuttling purposes.^{27–29} Though the core-shell structure enhances the rate of outer shell redox reaction, it may compromise the rate of charge carrier transfer that is confined in the core, which is highly dependent on the shell thickness and porosity. Besides, the exposed surfaces of the core-shell construct are limited to the spherical bifacial scheme and constrained by its thickness profile. This limitation demands for a tailored photocatalyst that maximizes the surface-to-volume exposure and interfacial contact in addition to spatially separate the redox co-catalysts and possibly implements other strategy to further promote charge separation. In addition, photothermal conversion is one of the most effective strategies to harvest solar energy.³⁰⁻³² Compared to the localized plasmonic resonance of noble metals, which will only absorb a limited bandwidth centered at the plasmonic resonance wavelength of the nanoparticles, broadband light-adsorbing semiconductors are able to self-heat under the irradiation of visible or near

infrared (NIR) light without the requirement of introducing other photothermal materials or external heating devices. Accordingly, it is an effective method to further improve the photocatalytic performance by introducing cocatalysts with extended light absorption for photothermal effect.

Herein, we prepared a multi-interfacial photocatalyst with spatially defined redox reactions and built-in electric field to achieve spontaneous hydrogen production in pure water. The open framework 2D nanosheets photocatalyst on 1D co-catalyst architecture clearly differentiates itself from the typical spherical core-shell configuration as it exemplifies highly exposed multi-facial ZnIn₂S₄ surfaces coupled to 1D CoP nanowire to promote fast vectorial charge transportation. Oxidative Co₃O₄ nanoparticles are successively loaded onto the exterior surfaces of the 2D nanosheets to isolate them from the reductive co-catalysts (Scheme 1). Other than achieving spatial charge separation, a self-built electric field is exploited to induce directional migration of charges. The internal electric field derived from the energy band structures of p-n heterojunction helps to further reduce charge recombination to drive the targeted surface reactions. The multi-facial heterostructure yields half reaction and pure water hydrogen evolution rate of 4254 and 145 μ mol g⁻¹ h⁻¹ under visible light illumination and photothermal assisted hydrogen production enhancement of 10 740 and 308 μ mol g⁻¹ h⁻¹, respectively. These findings highlight rational design of semiconductor with well-constructed heterojunctions and band structures that effectively accelerate the separation of photoexcited charges for efficient photothermal catalytic processes.

2 **RESULTS AND DISCUSSION** 1

Hierarchical CoP nanowires/ZnIn₂S₄ nanosheets heterostructures are first synthesized and optimized for half reactions photocatalytic hydrogen production. As illustrated in Figure S1a, S2 and S3, CoP nanowires maintain the 1D structures after phosphorization of $Co(CO_3)_{0.35}$ $Cl_{0.20}(OH)_{1.10}$ nanowires precursors. The CoP nanowires are observed with lengths of a few micrometers and average diameter of 100 nm. Ultrathin ZnIn₂S₄ nanosheets are subsequently grown on the 1D CoP nanowires to form CoP/ZnIn₂S₄ heterostructures for HER. It can be clearly seen from Figure 1A,B that ZnIn₂S₄ nanosheets are uniformly and densely distributed on the surface of CoP nanowires. In contrast, other CoP/ZnIn₂S₄ composites either present as an overloaded ZnIn₂S₄ nanosheets or uncovered CoP (Figure S4, S5). High resolution transmission electron microscope (HRTEM) of CoP/ZnIn₂S₄ composites in Figure 1C,D indicate that the lattice fringes of 0.285 and 0.32 nm correspond to the (011) crystal facet of CoP and (102) plane of ZnIn₂S₄, respectively, which

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confirm the hybrid heterostructures consist of CoP and ZnIn₂S₄. Besides, TEM and HAADF images as well as EDX mappings in Figure 1E verify that CoP/ZnIn₂S₄ composite is made up of CoP nanowires core and ZnIn₂ S₄ nanosheets shell. The growth of 2D ZnIn₂S₄ nanosheets radially around the 1D CoP endows increased heterojunctions, interfacial contacts and exposure of ZnIn₂S₄ nanosheets.

The phase composition and surface chemical states of CoP/ZnIn₂S₄ composites were investigated using X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). After phosphorization, 31.6°, 35.3°, 36.3°, 48.1° peaks are observed, consistent with the (011), (200), (111), (211) crystal planes of orthorhombic CoP (JCPDS No.29-0497), respectively (Figure 1F, Figure S1b). Moreover, the diffraction peaks of 21.6°, 27.7°, 47.2°, 52.4°, 55.6° can be indexed to the (006), (102), (110), (116), and (022) planes of hexagonal ZnIn₂S₄ (JCPDS No.65-2023), respectively. As expected, the prepared hierarchical CoP/ZnIn₂S₄ composites exhibit both characteristic peaks of orthorhombic CoP and hexagonal ZnIn₂S₄. These results attest that high crystallinity CoP@ZnIn₂S₄ composite is successfully prepared. Furthermore, the XPS survey spectrum of Figure S6a also suggests the presence of Co, P, Zn, In, and S in the composites. The highresolution Co 2p XPS spectrum in Figure 1G reveals two spin orbit doublets and two satellite peaks (identified as "Sat." in the figure). The first doublet with binding energy of 778.6 and 781.2 eV and the second doublet with peaks at 793.6 and 797 eV are ascribed to Co2p_{3/2} and $Co2p_{1/2}$, thereby confirming the co-existence of Co^{2+} and Co^{3+} in the composites. XPS results of P 2p, Zn 3d, In 2p, and S 2p also validate the existence of P, Zn, In, and S, which are in good agreement with the previous report, thus affirming the formation of CoP/ZnIn₂S₄ (Figure S6b, c, d).

The surface area of CoP@ ZnIn₂S₄ sample was measured by Brunauer-Emmett-Teller method (Figure 2A) and was found to be 104.6 m^2g^{-1} , which is higher than pure CoP and $ZnIn_2S_4$ sample (1.9 and 22.92 m²g⁻¹, respectively, Figure S7). This analysis indicated the high-porosity structure of CoP@ ZnIn₂S₄, which would contribute to excellent hydrogen performance and also facilitate subsequent chemical modification. UV/Vis absorption spectroscopy was then performed to study the optical properties of the prepared materials. As shown in Figure 2B, ZnIn₂S₄ presents visible light absorption with a band edge at 520 nm, while CoP exhibits broad absorption of ultraviolet-visible-NIR range. However, due to the extremely narrow bandgap of CoP, the photo-induced electrons and holes suffer a rapid recombination, drastically limit its capability to perform consequential water splitting activity. Instead, CoP plays the role of a cocatalytic reductive center. The co-catalytic function of CoP





FIGURE 1 (A and B) SEM and TEM images of CoP@ZnIn₂S₄ composites. HRTEM images of (C) CoP nanowires part and (D) ZnIn₂S₄ nanosheets part. (E) HAADF-TEM images of CoP@ ZnIn₂S₄ composites and EDX mapping of Co, P, S, In, and Zn. Scale bar: 200 nm. (F) XRD patterns of CoP, ZnIn₂S₄ and CoP@ ZnIn₂S₄ composites. (G) High-resolution XPS spectra of Co 2p, P 2p. XPS, X-ray photoelectron spectroscopy; XRD, X-ray diffraction

and constituent proportion between CoP and $ZnIn_2S_4$ are evaluated using the half reaction hydrogen evolution. By tuning the amount of CoP, it is apparent that HER production rates of all CoP/ZnIn₂S₄ composites increase steadily over time, and the optimum HER rates could achieve $4254 \ \mu\text{mol g}^{-1} \ h^{-1}$ for 5%-CZ sample, which is five times higher than the pristine ZnIn₂S₄ (HER is 745 $\ \mu\text{mol g}^{-1} \ h^{-1}$) (Figure 2C,D). This result demonstrates that CoP is an efficient co-catalyst for H₂ evolution. Moreover, HER of the optimal CoP@ZnIn₂S₄ sample (5%-CZ) can maintain at around $4254 \ \mu\text{mol g}^{-1} \ h^{-1}$ after long cycles, indicating a good stability of the prepared CoP@ZnIn₂S₄ composites (Figure 2E).

To form hole collectors and active sites for oxidation reaction, Co_3O_4 nanoparticles were loaded onto the 2D ZnIn₂S₄ nanosheets. As depicted in the cross-sectional illustration, the ternary CoP@ZnIn₂S₄@Co₃O₄ will form multi-interfacial oxidation and reduction cascade catalysis reactions (Figure 3A). Due to the high length-todiameter ratio of CoP nanowire structure, it will form multi heterojunctions along the CoP structure. Figure 3B shows that diffraction peaks of 31.3°, 36.8°, 44.8°, 59.4°, and 65.2° over CoP/ZnIn₂S₄/Co₃O₄ correspond to the (220), (311), (400), (511), and (440) planes of cubic Co₃O₄ (JCPDS No.43–1003), respectively. The low-magnification TEM images of CoP/ZnIn₂S₄/Co₃O₄ reveal that ZnIn₂S₄ nanosheets are coated on the CoP nanowire while Co₃O₄ nanoparticles are dispersed on the surfaces of ZnIn₂S₄ nanosheets (Figure 3C, Figure S8). The high-magnification TEM and EDX mapping images further confirm that the Co₃O₄ nanoparticles are deposited on the ZnIn₂S₄ nanosheets (Figure S9). The sequential loading of Co₃O₄ nanoparticles instead of in situ growth ensures selective deposition on the ZnIn₂S₄ nanosheets, preventing adventitious coverage of CoP redox sites. Explicitly, the engineered photocatalyst realizes the formation of high-density interfacial active sites, which would promote subsequent oxidation and reduction cascade catalysis reactions.

The pure water splitting photocatalytic reactions without sacrificial agents of CoP/ZnIn₂S₄/Co₃O₄ composites are then evaluated. As illustrated in Figure 3D, CoP/ZnIn₂S₄ without oxidative Co₃O₄ cocatalysts exhibits no pure water splitting activity under visible light irradiation. This can be ascribed to the fast recombination of electrons and holes over ZnIn₂S₄, and photo-induced holes are inclined to oxidize ZnIn₂S₄, leading to a serious photo-corrosion issue. Nevertheless, when the Co₃O₄ (2 wt%) is loaded as oxidative cocatalyst, CoP/ZnIn₂S₄/Co₃O₄ displays H₂ evolution rate of 25.4 µmol g⁻¹ h⁻¹. Optimized loading of 15% Co₃O₄



FIGURE 2 (A) N₂ adsorption-desorption isotherm and pore size distribution curves (inset) of CoP@ ZnIn₂S₄ composites, (B) UV-vis absorption spectra of CoP, ZnIn₂S₄, and CoP@ ZnIn₂S₄ composites. (C) Photocatalytic H₂-evolution performance of CoP@ ZnIn₂S₄ samples over time under visible light illumination. (D) Average photocatalytic H2-evolution performance of CoP@ ZnIn2S4 composites with different amount of CoP. (E) Stability test of H2 evolution performance over 5%-CZ sample

/CoP/ZnIn₂S₄ composite exhibits the highest hydrogen evolution rate of 145 μ mol g⁻¹ h⁻¹. This activity is competitive with the state-of-art representative photocatalysts for overall water splitting, demonstrating the remarkable benefits from the unique structure of dual cocatalysts confined in ZnIn₂S₄ nanosheets (Table S1). However, the half reaction of HER over CoP@ZnIn₂S₄ sample (5%-CZ) dramatically drops to 1340 μ mol g⁻¹ h⁻¹ when 15% Co₃O₄ was introduced, which indicates that Co₃O₄ is not favorable in the redox reactions (Figure S10). Considering the capability of holes capturing ability by the Co₃O₄ and p-n junction formed between Co₃ O₄ and ZnIn₂S₄, the holes on VB of ZnIn₂S₄ are prone to be transferred to Co₃O₄ to participate in the oxidation reaction

under the effect of built-in electric field. As a result, spatially separated dual co-catalysts CoP and Co₃O₄ act as redox and oxidation centers, respectively. By virtue of the distinct and directional flow of electrons and holes over the ZnIn₂S₄ nanosheets with multi-facial heterojunctions, the photocatalytic pure water splitting is augmented.

To demonstrate the importance of the purposefully designed multi-facial heterostructure, two types of control samples of CoP/ZnIn₂S₄/Co₃O₄ composites with randomly distributed co-catalysts (CZC-random) and traditional spherical core-shell construct (CZC-CS) are synthesized for comparisons (Figure S11, 12). Low-hydrogen evolution rate of merely 13 μ mol g⁻¹ h⁻¹ is obtained from the

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FIGURE 3 (A) Cross section view of CoP@ $ZnIn_2S_4@Co_3O_4$ ternary composites. (B) XRD patterns of Co_3O_4 , CoP@ $ZnIn_2S_4$, and CoP@ $ZnIn_2S_4@Co_3O_4$. (C) TEM images of CoP@ $ZnIn_2S_4@Co_3O_4$ samples. (D) Photocatalytic pure water splitting of H₂ evolution performance of CoP/ $ZnIn_2S_4$ with different loading amount of Co₃O₄. (E) EPR responses of the 15% Co₃O₄@ $ZnIn_2S_4@5\%$ CoP samples under visible light and dark conditions. (F) Time dependence of H₂O₂ absorption peaks of 15% Co₃O₄@ $ZnIn_2S_4@5\%$ CoP samples suspension during photocatalytic pure water splitting. XRD, X-ray diffraction

CZC-random sample, which probably arises from the Co₃ O₄ partly covering the CoP redox sites and the CoP nanowires shielding the host $ZnIn_2S_4$ photocatalyst (Figure S11). Similarly, the CZC-CS underperforms as compared to the engineered multi-facial heterostructure. The HER of CoP/ZnIn₂S₄/Co₃O₄ with core-shell structure attains 48 µmol g⁻¹ h⁻¹ (Figure S12, S13). Notably, high length-todiameter ratio nanowire structure enables the formation of high-density anchored heterojunctions and also prevents the inter-coverage of the redox and oxidation centers, contributing to prominent charge separation and highly efficient surface reactivity. We also investigate the oxidative products of photocatalytic pure water splitting using 15% $Co_3O_4/CoP/ZnIn_2S_4$. It was reported that water would be electrochemically and photochemically oxidized into three products: •OH radicals, H_2O_2 or O_2 .³³ Considering the possibility of twoelectron pathway instead of four-electron pathway,^{34,35} the characteristic signal of •OH was studied via in situ EPR spectroscopy. As observed in Figure 3E, compared to dark condition, 15% $Co_3O_4/CoP/ZnIn_2S_4$ shows strong •OH signal after visible light irradiation for 10 min in pure water. In addition, trace amount of H_2O_2 could also be detected when the photocatalytic pure water splitting reaction reaches 3 h. The concentration of H₂O₂ sustainably increases over 28 h (Figure 3F). Collectively, the results suggest the single electron pathway which oxidizes water to •OH in the first stage and then the combination of two •OH radicals that contribute to the formation of H₂O₂, further demonstrating the feasibility of pure water splitting over ternary CoP@ZnIn₂S₄ OCo_3O_4 dual cocatalysts photocatalyst.

At this juncture, light absorption and charge transfer behaviors are characterized via UV/Vis absorption spectroscopy and photo/electrochemical methods to investigate the high-photocatalytic pure water splitting performance of the ternary CoP@ZnIn₂S₄@Co₃O₄ composites. The Co₃O₄ exhibits outstanding light absorption similar to CoP. The light absorption performance of CoP@ZnIn₂S₄@Co₃O₄ dual cocatalysts loaded photocatalyst is further improved compared to CoP@ZnIn₂S₄ surface (Figure S14). However, the optimal sample with the highest hydrogen evolution performance does not correspond to the highest loading amount of CoP or Co₃O₄. This suggests the light absorption is not the dominant factor to significantly influence the photocatalytic water splitting performance.

To further affirm the photothermal effect of CoP, Co₃ O₄, and their contribution to hydrogen production rate, the temperature profiles of the catalysts were obtained in Figure 4A. It can be seen from the infrared thermal images of ZnIn₂S₄, CoP@ZnIn₂S₄, and CoP@ZnIn₂S₄ $@Co_3O_4$ that the temperature of $ZnIn_2S_4$ reached only $36.5^{\circ}C$ after illumination. Compared to bare $ZnIn_2S_4$, the temperature of CoP@ZnIn₂S₄ and CoP@ZnIn₂S₄@Co₃O₄ increased rapidly to 56.8 and 71.2°C, respectively. The results demonstrate both of the CoP and Co₃O₄ contribute to photothermal effect due to their excellent light adsorption from ultraviolet to infrared range. To prove that the photo-to-heat conversion of CoP and Co3O4 leads to improved photocatalyis, hydrogen production perfomances were compared with experiments conducted at controlled temperature of 30°C. As shown in Figure 4B, when temperature was lowered to 30°C, the half reaction of hydrogen generation rate of 5%-CZ sample dramatically dropped to 2223 μ mol g⁻¹ h⁻¹ under visible light illumination, which is less than half the amount of the hydrogen produced without cooling. Similarly, the H₂ generation from pure water splitting of 15% Co₃O₄/CoP/ZnIn₂S₄ composite also dipped from 145 μ mol g⁻¹ h⁻¹ to only 43 μ mol g⁻¹ h⁻¹. However, the respective half reaction and pure water hydrogen evolution rate further enhanced to 10 740 μ mol g⁻¹ h⁻¹ and 308 μ mol g⁻¹ h⁻¹ when subjected to full spectrum photoheating. These results suggest the valid contribution of the photothermal effect of CoP and Co₃O₄ toward improved hydrogen performance over 15% Co₃O₄/CoP/ZnIn₂S₄ photocatalysts.

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Charge separation and transfer kinetics of the pure CoP, ZnIn₂S₄, Co₃O₄, hybrid CoP@ZnIn₂S₄, and ternary CoP@ZnIn₂S₄@Co₃O₄ are then studied. Photoluminescence (PL) is characterized to study the charge separation efficiency. A lower PL intensity infers a reduced recombination of photo-generated electrons and holes, in other words a higher charge separation efficiency. Bare ZnIn₂S₄ shows a strong peak at around 470 nm due to the fast charge recombination of band gap transition (Figure 4C). After the introduction of CoP co-catalyst, the PL peak intensity is apparently lowered, signifying the recombination of photo-generated electrons and holes is efficiently suppressed, thus contributing to the enhancement of photocatalytic hydrogen evolution performance. When dual co-catalysts are loaded, the PL intensity of CoP@ZnIn₂S₄@Co₃O₄ is further decreased. This may be ascribed to the efficient separation of photo-generated electrons and holes due to the spatially separated dual co-catalyst as well as the favorable band structure and built-in electric field. The accelerated charge separation and transfer ability are also disclosed by the photocurrent response and electrochemical impedance spectroscopy (EIS) studies. The higher photocurrent response and smaller semicircle of Nyquist plots of the CoP@ZnIn₂S₄ stems from the efficient electron migration to the cocatalyst CoP (Figure S15). When Co₃O₄ is loaded, the photocurrent response is improved and the optimal sample 15% Co₃O₄/CoP/ZnIn₂S₄ manifests the highest photocurrent and smallest semicircle (Figure 4D,E, Figure S16). In addition, compared to CZC-random and CZC-CS samples, Co₃O₄/CoP/ZnIn₂S₄ reveals a higher photocurrent and lower resistance, in good accordance to the enhanced photocatalytic pure water splitting performance of the spatially distributed dual cocatalyst and electric field directed charge separation (Figure S17).

Based on the above analysis, the possible charge transfer pathway and energy band mechanism are proposed. Mott-Schottky (M-S) characterization was performed to determine the flat band position of CoP, ZnIn₂ S₄, and Co₃O₄. Based on M-S curve, the flat band potentials of pure CoP and ZnIn₂S₄ are -0.61 and -0.83 eV, respectively, and the flat potential of Co₃O₄ corresponds to 0.48 eV (Figure S18). Generally, the flat potential of ntype semiconductor is almost equal to its conduction band, while for p-type semiconductor, it is roughly the valence band potential. In addition, the bandgap of pure CoP, ZnIn₂S₄, and Co3O4 can be calculated to 1.18, 2.56, and 1.04 eV according to UV-vis absorption spectra (Figure S19). Therefore, the band structures of CoP, $ZnIn_2S_4$, Co_3O_4 are obtained based on the equation $E_{VB} = E_{CB} + E_g$, as schematically illustrated in Figure 4F. When the sample is irradiated by an incident light, electrons on the CB of ZnIn₂S₄ will transfer to the CB of CoP.

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(A) Corresponding temperature evolution and infrared images of ZnIn₂S₄, CoP@ZnIn₂S₄ composites and CoP@ ZnIn₂S₄ @Co₃O₄ samples under irradiation. (B) Hydrogen production rate comparison of CoP@ZnIn₂S₄ (5%_CZ) and CoP@ZnIn₂S₄@ Co₃O₄ (5% CZC 15%) samples under visible light, full spectrum illumination and cooling with controlled temperature at 30°C. (C) Photoluminescence spectra of as-prepared ZnIn₂S₄, CoP@ZnIn₂ S₄ composites and CoP@ ZnIn₂S₄ @Co3O4 samples. (D) Nyquist plots and (E) Photocurrent response of CoP@ ZnIn₂S₄, Co₃ O₄, CoP@ ZnIn₂S₄@Co₃O₄ samples. (F) Proposed charge transfer process of CoP@ ZnIn2S4 @Co₃O₄ composites

Thereafter, the electrons at the CoP reduce the water to H_2 , while the holes on $ZnIn_2S_4$ would migrate to Co_3O_4 under the effect of built-in electric field induced by p-n junction between ZnIn₂S₄ and Co₃O₄. As Co₃O₄ has the ability to oxidize water, the holes accumulated on the Co₃ O4 would participate in the oxidation reaction to produce •OH, which would recombine to produce H₂O₂. To further validate electron transfer pathway, Pt deposition experiments are performed to determine the electron trapping sites. As shown in Figure S20, Pt particles are deposited on the surface of CoP, implying that electrons would conceivably flow to CoP instead of Co₃O₄. The interface charge density differences of ZnIn₂S₄ (002)/CoP (002) and ZnIn₂S₄ (002)/Co₃O₄ (111) have been analyzed by DFT calculations. The redistribution of charge mainly occurs at the interface of ZnIn₂S₄/CoP and ZnIn₂S₄/Co₃O₄, while insignificant changes in charge difference away from CoP and Co₃O₄ are observed (Figure S21). The electrons are accumulated near ZnIn₂S₄ and consumed at the interface of CoP. As a result,

there will be a built-in electric field from CoP to $ZnIn_2S_4$, which facilitates the electrons transfer from $ZnIn_2S_4$ to CoP. Similarly, the electrons from Co_3O_4 will transfer to $ZnIn_2S_4$ due to the presence of the built-in electric field. This charge transfer path is also consistent with the experimental analysis of Figure 4f. The type-II heterojunction between CoP and $ZnIn_2S_4$ alongside p-n junction between $ZnIn_2S_4$ and Co_3O_4 forms asymmetric field to realize efficient separation of charges to boost the pure water splitting performance. The complementary photo- and electronic properties of the $CoP/ZnIn_2S_4/Co_3O_4$ catalyst design enhances the dynamics of the charge carriers for kinetics and thermally induced reactivity.

3 | CONCLUSION

In summary, multi-interfacial heterostructures of $ZnIn_2S_4$ nanosheets loaded with dual cocatalysts has been designed with reductive CoP as the interior 1D vectorial redox sites and oxidative Co_3O_4 nanoparticles on the exterior surfaces for photocatalytic hydrogen production in pure water. Also, the internal electric field p-n junction engineering facilitates charge separation and transfer, thus allowing the electrons and holes to partake reduction and oxidation reactions, respectively alongside solar thermal driven assisted photoactivity. This work demonstrated rational materials and electronic design that facilitates prominent charge separation and highly efficient surface reactivity. This study provides a pathway to design and construct efficient photocatalytic water splitting system.

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CONFLICT OF INTEREST

The authors declare no conflict of interest.

AUTHOR CONTRIBUTION

Tianxi Zhang: Conceptualization, Methodology, Formal analysis, Writing - Original draft. Fanlu Meng: Project administration, Formal analysis, Validation, Writing review & editing. Minmin Gao: Formal analysis, Resources, Investigation, Writing - review & editing. Weili Ong: Resources, Investigation. Kok-Giap Haw: Resources, Investigation. Tianpeng Ding: Resources, Investigation. Ghim Wei Ho: Formal analysis, Writing - review & editing, Supervision. Sibudjing Kawi: Supervision.

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SUPPORTING INFORMATION

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