

Engineering S-scheme heterojunctions with multichannel charge transfer for efficient photocatalytic hydrogen production

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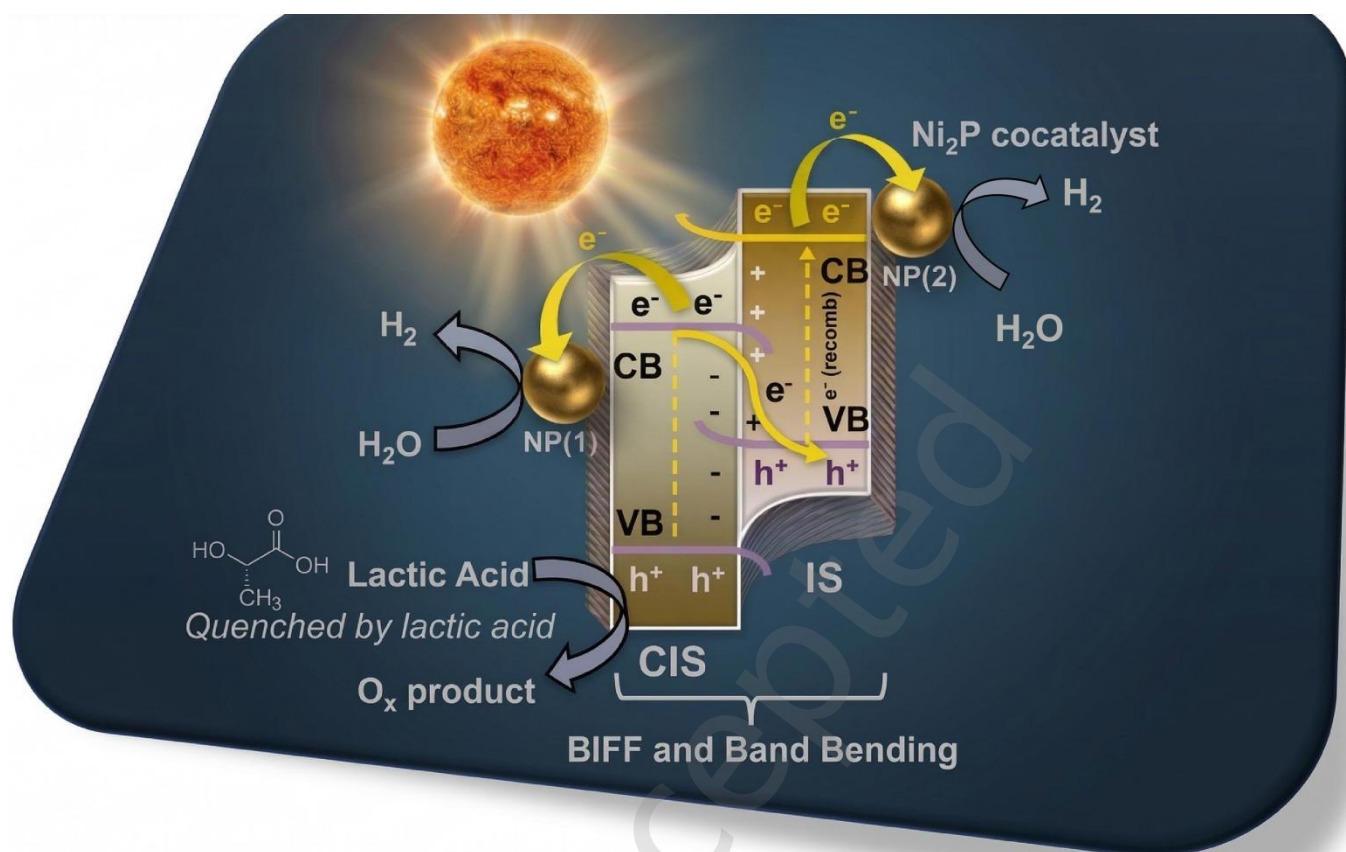
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An S-scheme Ni₂P/CdIn₂S₄/In₂S₃ heterostructure with multiple electron transfer pathways was rationally constructed to promote directional charge migration and efficient spatial separation of photogenerated carriers. The synergistic effect of the built-in electric field and Ni₂P-mediated electron transport enhanced the redox capability and charge transfer dynamics of the photocatalytic system.

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ABSTRACT: Constructing efficient charge separation pathways remains a crucial challenge for advancing photocatalytic hydrogen evolution. In this work, a $\text{Ni}_2\text{P}/\text{CdIn}_2\text{S}_4/\text{In}_2\text{S}_3$ (NP/CIS/IS) heterostructure featuring S-scheme charge separation and multiple electron transfer pathways was constructed through a stepwise assembly approach. Work function analysis, combined with in situ irradiated X-ray photoelectron spectroscopy (ISI-XPS) and density functional theory (DFT) calculations, confirmed the formation of a built-in electric field (BIEF) that drives directional carrier migration across the CIS/IS interface, establishing a typical S-scheme heterojunction. Electron paramagnetic resonance (EPR) studies further revealed significantly enhanced redox activity in the CIS/IS-3 system, attributed to the efficient spatial separation of photogenerated charges. The incorporation of NP nanoparticles remarkably boosted the visible-light-driven hydrogen evolution performance ($\lambda \geq 420$ nm), achieving a high rate of $45,057.1 \mu\text{mol g}^{-1} \text{h}^{-1}$. This enhancement arises from the dual role of NP as the active site and electron mediator, facilitating charge extraction, lowering the Gibbs free energy for H_2 formation, and accelerating hydrogen desorption. Furthermore, three-dimensional charge density mapping validated the presence of multiple synergistic charge transport channels within the 5.7%NP/CIS/IS-3 composite. This study provides new insights into the design of advanced heterostructured photocatalysts for efficient, sustainable hydrogen production from solar energy.

KEYWORDS: S-scheme heterojunctions, multichannel charge transfer, band bending, photocatalyst

1 Introduction

With the rapid advancement of modern industry, humanity is confronted with the dual challenges of global energy shortages and environmental pollution[1]. Therefore, the development of environmentally sustainable energy sources to replace fossil fuels has become a pressing priority. Compared to traditional fossil fuels such as gasoline and coal, hydrogen (H_2) offers a higher energy density per unit and produces clean, environmentally friendly combustion byproducts[2]. Direct solar-to-hydrogen conversion is considered one of the most promising solutions to address the energy crisis. Since 1972, Fujishima and Honda pioneered the use of TiO_2 to convert solar energy into H_2 , marking the birth of semiconductor-based solar-driven water splitting technology[3]. Despite more than fifty years of development, several challenges continue to hinder the widespread industrialization of this technology, including: (1) the issues related to the bandgap structure of semiconductor photocatalysts[4], (2) the low efficiency of photogenerated charge transfer in semiconductor photocatalysts[5], (3) the poor utilization of sunlight by semiconductor photocatalysts[6], and

(4) the suboptimal cycling stability of these photocatalysts[7]. Among these challenges, enhancing the photogenerated charge transfer performance remains a major research focus in the field of photocatalysis. Numerous effective strategies have been proposed to address this issue, such as the construction of semiconductor heterojunctions (e.g., type-II[8], Z-scheme[9, 10], and S-scheme[11-13]) and the selection of suitable cocatalyst.

In the early studies of semiconductor heterojunctions, the construction of type-II heterojunctions was still the predominant research direction. The type-II heterojunction provides an optimal band alignment for efficient photogenerated electron-hole separation, thereby enhancing the photocatalytic performance of the system. However, from a thermodynamic perspective, the charge migration pathway in type-II heterojunctions compromises the inherent redox capabilities of the two semiconductors[14, 15]. To address this limitation, researchers have developed Z-scheme systems by mimicking the photosynthetic processes in nature to further optimize the structure. In these systems, photogenerated electrons in semiconductors with lower conduction band (CB) positions

recombine with photogenerated holes in semiconductors with higher valence band (VB) positions. This structure allows photogenerated electrons and holes to effectively retain their respective energies, thereby reducing energy loss. However, the oxidation-reduction ability of the electrons and holes in the CB and VB involved in photocatalytic reactions remains insufficient[16, 17]. Against this backdrop, Yu and his collaborators proposed a novel heterojunction concept: the S-scheme heterojunction[18]. In the S-scheme heterojunction, the photogenerated electrons are efficiently retained in the CB of the reduced-phase material (RP), while the holes are stored in the VB of the oxidized-phase material (OP). Meanwhile, non-contributory photogenerated charge carriers undergo recombination. Compared to type-II and Z-scheme heterojunctions, the S-scheme heterojunction offers a more rational charge transfer pathway, along with a more defined structural design. Consequently, the construction of S-scheme heterojunctions has emerged as a prominent research focus in the field of semiconductor photocatalysis.[19, 20] Among various semiconductor materials, metal sulfide semiconductors exhibit unique properties, including favorable band gap energies and redox potentials, which have spurred extensive research into their photocatalytic H₂ production applications[21]. In₂S₃ and CdIn₂S₄, distinguished by their well-ordered structures, exceptional electrochemical properties, and high stability, emerge as promising n-type semiconductor photocatalyst candidates with narrow band gaps[22, 23]. The low efficiency of photogenerated charge transfer and the inherent photocorrosion characteristics limit their practical applications. The construction of In₂S₃ and CdIn₂S₄ into S-scheme heterojunctions can effectively address the limitations. However, merely fabricating photocatalysts with S-scheme heterojunctions fails to achieve the optimal charge migration efficiency.

Adding additional cocatalysts is an effective strategy for further enhancing the charge transfer ability of photogenerated charges in S-scheme heterojunctions. Typically, noble metals, such as Pt[24], Pd[25], and Ru[26], are regarded as promising cocatalysts for photocatalytic H₂ production due to their high work functions, which enable them to effectively capture electrons. However, the economic and environmental challenges associated with these metals hinder their large-scale application. Therefore, it is imperative to seek a cheap, efficient, and stable cocatalyst to enhance the transfer efficiency of photogenerated charges in semiconductor photocatalysts. Nickel phosphide (Ni₂P) is a typical transition metal phosphide that exhibits properties similar to those of metalloids and demonstrates excellent electrical conductivity[27, 28]. The phosphorus sites in Ni₂P serve as proton acceptors, while the nickel sites accept hydrides. Additionally, the weak binding of H₂ on the surface of Ni₂P renders it an effective photocatalytic cocatalyst for H₂ evolution reactions. In this study, In₂S₃ was not completely encapsulated by CdIn₂S₄. Therefore, when Ni₂P is loaded on the surface of S-type heterojunctions, it will establish at least two additional electron transfer pathways, significantly enhancing the migration efficiency of photogenerated charges and reducing the recombination rate of photogenerated electrons and holes, thereby improving the photocatalytic H₂ production efficiency.

Herein, Ni₂P/CdIn₂S₄/In₂S₃ (NP/CIS/IS) heterostructures with S-scheme charge transfer and multiple electron pathways were rationally designed via a stepwise assembly approach. Work

function analysis revealed a strong BIEF and band bending at the CIS/IS interface, promoting efficient charge separation. The S-scheme charge migration between CIS and IS was further corroborated by ISI-XPS analysis and DFT simulations. EPR studies indicated that CIS/IS exhibits significantly enhanced redox capability compared to pristine CIS and IS, validating the advantages of the S-scheme configuration. The introduction of NP nanoparticles further boosted photocatalytic H₂ evolution under visible-light irradiation ($\lambda \geq 420$ nm), achieving a remarkable hydrogen production rate of 45057.1 $\mu\text{mol g}^{-1} \text{h}^{-1}$. This improvement is attributed to NP serving as an electron mediator and cocatalyst, which not only lowers the Gibbs free energy barrier for H₂ evolution but also accelerates hydrogen desorption by tuning the H* binding strength. In addition, three-dimensional charge density difference mapping revealed the establishment of multiple interfacial charge transfer channels in 5.7%NP/CIS/IS-3. These results demonstrate the critical role of precise interfacial engineering and cocatalyst integration in constructing high-efficiency photocatalysts for solar-to-hydrogen conversion.

2 Experimental

2.1 Materials

All chemicals were analytical research grade (A.R. grade) and purchased from Aladdin Chemical Reagent Co. without further purification, including indium trichloride tetrahydrate (InCl₃·4H₂O), cadmium acetate dihydrate (Cd(OAc)₂·2H₂O), thioacetamide (CH₃CSNH₂), thiourea (CH₄N₂S), nickel (II) acetate tetrahydrate (Ni(OAc)₂·4H₂O), sodium hypophosphite (NaH₂PO₂), ammonium hydroxide (NH₃·H₂O) and hydrazine monohydrate (N₂H₄·H₂O).

2.2. Synthesis of In₂S₃ (IS) nanoflowers

In₂S₃ nanoflowers were synthesized via a hydrothermal method. The detailed procedure is as follows: 293 mg of InCl₃·4H₂O and 30 mg of thioacetamide were dissolved in 30 mL of a mixed solvent composed of ethylene glycol and deionized water at a volume ratio of 1:5. The solution was stirred thoroughly for 60 min to ensure complete dissolution. Subsequently, the resulting solution was transferred into a 50 mL Teflon-lined stainless-steel autoclave, which was then sealed and placed in an oven at 150°C for 12 h. After naturally cooling to room temperature, the reaction mixture was washed three times with deionized water to remove residual impurities. The obtained red powder was dried in an oven at 60°C for 12 h. The final product, In₂S₃, was denoted as IS.

2.3. Synthesis of CdIn₂S₄/In₂S₃ (CIS/IS)

100 mg of IS was dispersed in 50 mL of deionized water to form a uniform suspension. Predetermined amounts of cadmium acetate (39 mg, 69 mg, 133 mg, and 179 mg) and thiourea (22 mg, 39 mg, 76 mg, and 102 mg) were added to the suspension, followed by ultrasonic treatment for 30 min to ensure thorough mixing. Subsequently, 1 mL hydrazine hydrate was introduced into the mixture, stirring for another 30 min. The solution was then transferred into a 100 mL Teflon-lined stainless-steel autoclave and subjected to hydrothermal treatment in an oven at 160°C for 10 h. After natural cooling to room temperature, the resulting samples were washed three times with deionized water to remove residual impurities. The obtained yellow powders were dried in an oven at 60°C for 12 h. The final products with varying amounts of Cd precursors were denoted as: CIS/IS-1,

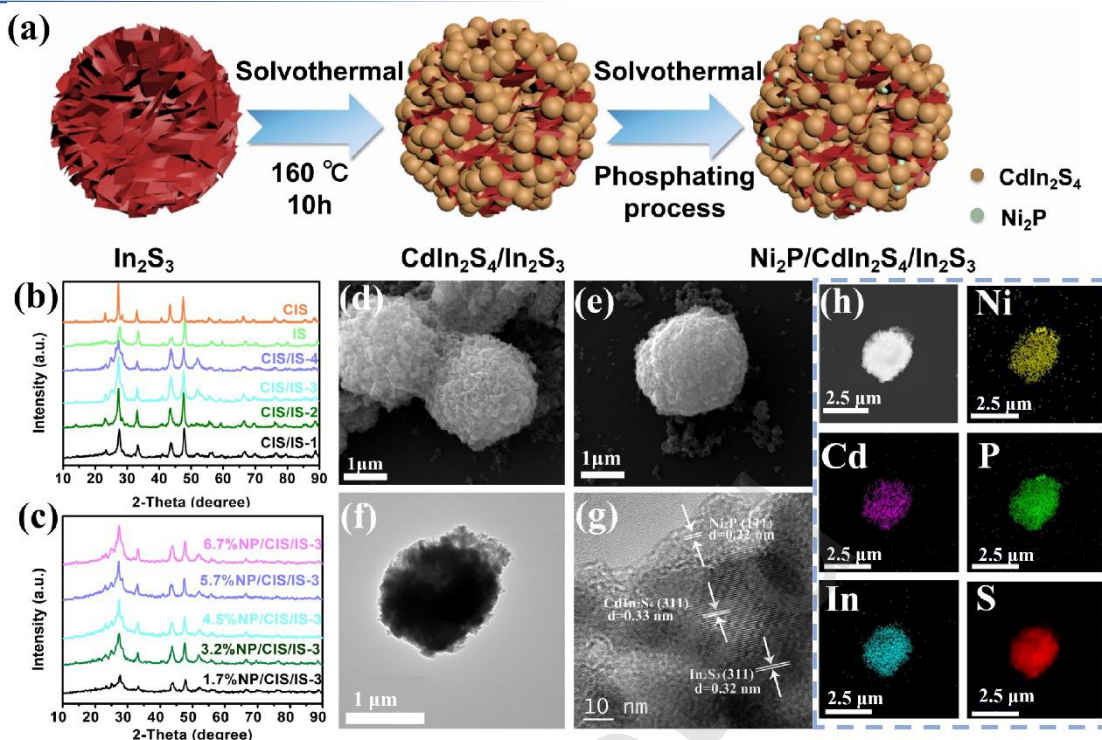


Fig. 1. (a) Schematic preparation process of X%NP/CIS/IS. (b) XRD patterns of IS, CIS and CIS/IS. (c) XRD patterns of X%NP/CIS/IS-3. The SEM image of (d) IS and (e) 5.7%NP/CIS/IS-3. (f) The TEM image of 5.7%NP/CIS/IS-3. (g) The HRTEM image of 5.7%NP/CIS/IS-3. (h) The EDX images of 5.7%NP/CIS/IS-3.

CIS/IS-2, CIS/IS-3, and CIS/IS-4, respectively.

2.4 Synthesis of $\text{Ni}_2\text{P}/\text{CdIn}_2\text{S}_4/\text{In}_2\text{S}_3$ (NP/CIS/IS)

50 mg CIS/IS-3 was dispersed in 20 mL of ethanol solution to form a homogeneous suspension. A specific amount of $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ was dissolved in 0.6 mL of deionized water and added to the above suspension, followed by thorough stirring for 30 min. Subsequently, 0.6 mL of $\text{NH}_3 \cdot \text{H}_2\text{O}$ was dropwise added to the suspension, and the mixture was further stirred for another 30 min. The resulting suspension was then transferred into a 25 mL Teflon-lined stainless-steel autoclave and subjected to hydrothermal treatment in an oven at 180°C for 6 h. After the autoclave was naturally cooled to room temperature, the sample was washed three times with deionized water, and the obtained dark green powder was dried in an oven at 60°C for 12 h.

The obtained precursor was thoroughly ground with NaH_2PO_2 at a mass ratio of 1:2 between precursor and NaH_2PO_2 , and then transferred into a crucible. The crucible was then placed in a tubular furnace under an argon atmosphere and heated to 300°C with a rate of $2^\circ\text{C}/\text{min}$, maintaining this temperature for 2 h. After the furnace was cooled to room temperature, the resulting sample was washed three times with deionized water to remove any residual byproducts and subsequently dried in an oven at 60°C for 12 h. The final samples with varying amounts of Ni precursor were denoted as X%NP/CIS/IS-3, where X% represents the mass fraction of Ni ions. The specific experimental steps are shown in Fig. 1a.

2.5 Photocatalytic H_2 production measurement

Photocatalytic hydrogen production experiments were conducted in a sealed reactor with a total volume of 54 mL. In each experiment, 3.0 mg of the photocatalyst was uniformly dispersed in 20 mL of aqueous solution, to which 2 mL of lactic acid, acting as a sacrificial electron donor, was added. A 300 W

Xe lamp, fitted with a UV cut-off filter ($\lambda \geq 420$ nm), was employed as the visible-light source. The reaction mixture was continuously stirred under ambient temperature conditions. The evolved hydrogen gas was quantified using a gas chromatograph (Fuli GC9790 II) with argon as the carrier gas, equipped with a thermal conductivity detector (TCD). The apparent quantum yield (AQY) was measured under monochromatic light irradiation at $\lambda = 420$ nm. The AQY was determined based on the equation provided below (detail was shown in ESI):

$$\text{A.Q.Y}(\%) = \frac{\text{number of } \text{H}_2 \text{ molecules evolved} \times 2}{\text{number of incident photons}} \times 100\%$$

3 Results and discussion

3.1. Structural analysis

The crystallographic structures of IS, CIS, CIS/IS, and X%NP/CIS/IS-3 were characterized by XRD. As shown in Fig. 1b, the diffraction peaks of the synthesized pure IS and CIS correspond to the standard crystal phases of IS and CIS, respectively[29, 30]. Notably, the characteristic peaks of CIS are similar to those of IS. For CIS/IS composites, as the concentration of Cd^{2+} increases, the diffraction peaks at 27.6° and 33.0° progressively shift to lower angles. Such peak shifts reflect lattice expansion induced by the partial substitution of In^{3+} with Cd^{2+} , confirming the successful formation of the CIS/IS heterostructure. However, in CIS/IS-4, an additional diffraction peak corresponding to CdS emerges, which can be ascribed to the excessive incorporation of Cd^{2+} leading to secondary phase precipitation. Fig. 1c presents the XRD patterns of X%NP/CIS/IS-3. Notably, no additional peaks associated with crystalline Ni_2P are observed in any of the NP-loaded samples. This absence can be attributed to the relatively low NP content, as well as its high dispersion on the CIS/IS surface, which prevents the formation of detectable bulk crystalline domains. Nonetheless, the coexistence of IS, CIS, and highly dispersed NP is further corroborated by complementary analyses, confirming the successful construction of the designed

heterostructures. Importantly, these structural evolutions not only validate the rational design of the CIS/IS-based system but also provide a solid foundation for enhancing interfacial charge transfer and thereby optimizing the photocatalytic H_2 evolution performance.

The morphology of the as-prepared photocatalysts was investigated by SEM and TEM. As shown in Fig. 1d, the pristine IS exhibits a nanosphere-like morphology assembled from thin nanosheets, with a rough surface and an average diameter of approximately 2 μm . Such hierarchical architecture not only provides a large specific surface area but also generates abundant exposed active sites, which are beneficial for subsequent surface reactions. The SEM image of the 5.7%NP/CIS/IS-3 composite is displayed in Fig. 1e. Compared with IS, the composite retains a similar spherical structure, but its surface is non-uniformly decorated with smaller nanoparticles. Due to the incomplete encapsulation of IS by CIS, some NP nanoparticles were observed to grow directly on the exposed IS surface, suggesting that NP can bridge CIS and IS domains, thereby promoting multichannel charge migration. As shown in the TEM image in Fig. 1f, a slight reduction in particle diameter was observed after the high temperature phosphidation process. Fig. 1g presents the HRTEM image of 5.7%NP/CIS/IS-3, in which lattice fringes with interplanar spacings of 0.32 nm, 0.33 nm, and 0.22 nm are observed, corresponding to the (311) plane of IS, the (311) plane of CIS, and the (111) plane of NP, respectively. This observation provides direct structural evidence of the successful integration of IS, CIS, and NP at the atomic scale. The EDX mapping images (Fig. 1h) confirm the uniform distribution of In, Cd, S, Ni, and P elements throughout the composite. Combined with the results from XRD, SEM, TEM, HRTEM, and EDX mapping, it can be concluded that both NP and CIS were successfully deposited onto the surface of IS. The BET results are provided in the ESI.

The XPS spectra were utilized to investigate the chemical composition and chemical state of as-prepared photocatalysts. As shown in Fig. 2a, the full survey spectra of IS, CIS/IS-3, and 5.7%NP/CIS/IS-3 confirm the presence of In and S in pristine IS. Upon further modification with NP, characteristic P signals are clearly detected in 5.7%NP/CIS/IS-3, while the Ni signal appears weak in the survey spectrum, likely due to its relatively low loading amount and strong interaction with P in the Ni_2P

phase. Fig. 2b shows the high-resolution spectrum of In 3d spectra for IS (452.1 eV and 444.5 eV), CIS (451.6 eV and 444.1 eV), CIS/IS-3 (451.9 eV and 444.4 eV) and 5.7%NP/CIS/IS-3 (452.3 eV and 444.7 eV). All four samples exhibit two characteristic peaks corresponding to In 3d_{3/2} and In 3d_{5/2}, respectively[31]. Similarly, Fig. 2c displays the high-resolution spectrum of Cd 3d spectra of CIS (411.3 eV and 404.6 eV), CIS/IS-3 (411.4 eV and 404.7 eV) and 5.7%NP/CIS/IS-3 (411.5 eV and 404.8 eV), where the two symmetrical peaks are assigned to Cd 3d_{3/2} and Cd 3d_{5/2}, respectively, confirming the presence of Cd₂₊[32]. As depicted in Fig. 2d, all S 2p spectra are deconvoluted into two peaks, which should be attributed to S 2p_{1/2} and S 2p_{3/2}, respectively[33]. Fig. 2e presents the Ni 2p spectrum of 5.7%NP/CIS/IS-3, where the two main peaks at 853.6 eV (Ni 2p_{3/2}) and 870.4 eV (Ni 2p_{1/2}) corresponded to Ni^{δ+} of Ni-P bond in Ni_2P [34]. Additionally, the peak located at 856.6 eV of Ni 2p_{3/2} and 874.6 eV of Ni 2p_{1/2} were observed due to the oxidation state of Ni in the Ni_2P [35, 36]. Fig. 2f illustrates the high-resolution P 2p spectrum of 5.7%NP/CIS/IS-3, where the P 2p signals are deconvoluted into two main peaks at 129.6 eV and 133.3 eV, corresponding to P 2p_{3/2} and P 2p_{1/2}, respectively. The peak at 129.6 eV is attributed to the metal-phosphide (M-P) bond, while the peak at 133.3 eV is associated with surface oxidation due to air exposure[37]. As revealed by XPS analysis, compared with IS, the In 3d and S 2p peaks of CIS/IS-3 exhibit a negative shift in binding energy, whereas compared with CIS, they shift toward higher binding energies. Such opposite energy shifts indicate a bidirectional charge redistribution at the CIS/IS heterointerface, suggesting that electrons are partially transferred from CIS to IS until Fermi-level equilibration is achieved. This process induces the formation of an internal built-in electric field (BIEF) at the interface, which facilitates directional electron migration from CIS to IS and promotes charge separation. Consequently, electrons tend to accumulate at the IS surface, providing abundant active sites for subsequent redox reactions. Furthermore, upon NP incorporation, the binding energies of In, Cd, and S exhibit additional positive shifts, implying a further modulation of interfacial electronic structure and enhanced electron accumulation at the CIS/IS-3 interface. Under visible-light irradiation, these findings corroborate a stepwise electron transfer pathway (IS → CIS → NP), where the interfacial BIEF and synergistic coupling among the three components collaboratively optimize charge carrier dynamics, suppress electron-hole

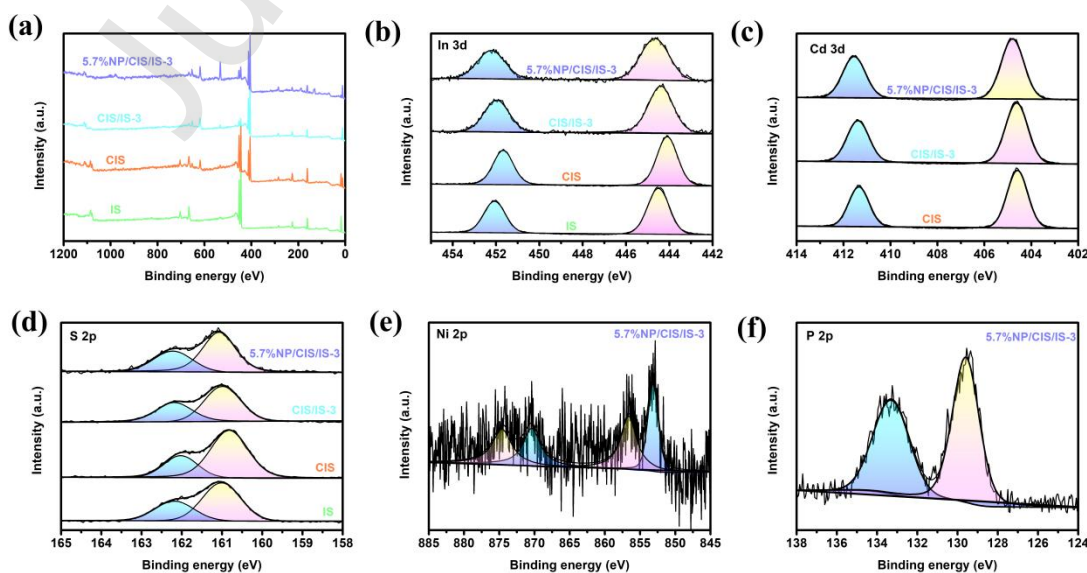


Fig. 2. The XPS spectra of (a) full survey, (b) In 3d, (c) Cd 3d (d) S 2p, (e) Ni 2p and (f) P 2p of the as-synthesized samples.

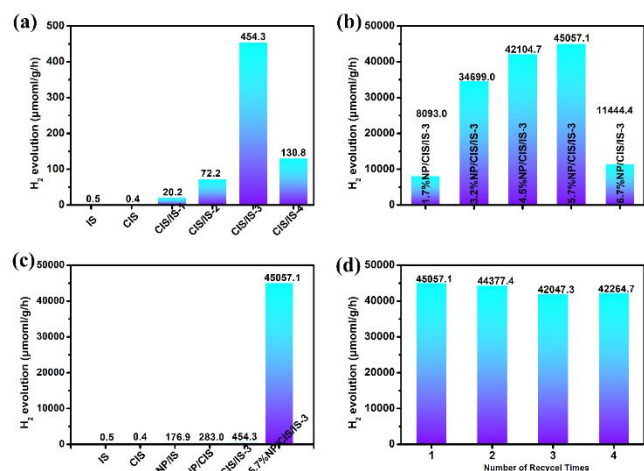


Fig. 3. (a) Photocatalytic performance for H₂ evolution rate of IS, CIS, CIS/IS-1, CIS/IS-2, CIS/IS-3 and CIS/IS-4. (b) The H₂ evolution rate result of X%NP/CIS/IS-3. (c) Comparison of H₂ evolution rate on IS, CIS, NP/IS, NP/CIS and 5.7%NP/CIS/IS-3 under visible-light irradiation. (d) Recycle runs for the photocatalytic H₂ evolution rate of 5.7%NP/CIS/IS-3 under visible-light illumination.

recombination, and thereby enhance the overall photocatalytic efficiency.

3.2. Photocatalytic performance analysis

The photocatalytic H₂ evolution reaction (HER) performance of the as-prepared photocatalysts was evaluated using lactic acid as a sacrificial agent. A 300 W Xe lamp equipped with a 420 nm cut-off filter was employed as the excitation light source. To investigate the influence of different CIS loading amounts on the IS surface, a series of control experiments were conducted, and the results are summarized in Fig. 3a. Pristine IS and CIS exhibited negligible HER activity (0.4 and 0.5 μmol g⁻¹ h⁻¹, respectively), highlighting their limited intrinsic catalytic capability. Remarkably, the HER rate increased significantly with CIS incorporation, reaching a maximum for CIS/IS-3 (454.3 μmol g⁻¹ h⁻¹). In contrast, the HER activity of CIS/IS-4 decreased markedly, which can be attributed to excessive CIS loading leading to a shielding effect that hampers light

absorption and charge separation, ultimately deteriorating the photocatalytic performance. These observations indicate an optimal CIS content is essential for balancing light absorption and interfacial charge transfer.

Although CIS/IS-3 displayed enhanced activity, its HER performance remained far from optimal, suggesting that additional strategies were required to further promote charge separation. Accordingly, NP was introduced as a cocatalyst, and the HER performance of the X%NP/CIS/IS-3 composites was evaluated (Fig. 3b). A volcano-type dependence on NP content was observed, with 5.7%NP/CIS/IS-3 exhibiting the highest HER rate and an AQY of 0.61%, nearly two orders of magnitude higher than that of CIS/IS-3. This remarkable enhancement can be attributed to the synergistic effect of the ternary heterostructure: NP not only facilitates rapid electron extraction and transfer from CIS/IS, but also provides additional active sites for hydrogen evolution. However, further increasing the NP content to 6.7% resulted in a pronounced decrease in HER activity, likely due to the formation of recombination centers that deteriorate the charge separation efficiency. A comparison with representative CdIn₂S₄-based photocatalysts reported in the literature is summarized in Table S2.

To further clarify the role of the ternary heterojunction, comparative studies were performed (Fig. 3c). The H₂ evolution rates for NP/IS, NP/CIS, CIS/IS-3, and 5.7%NP/CIS/IS-3 were 176.9, 283.0, 454.3, and 45057.1 μmol g⁻¹ h⁻¹, respectively, confirming that the rational integration of CIS and NP onto IS dramatically enhances photocatalytic performance by optimizing light absorption, charge separation, and electron transfer pathways.

The long-term stability and recyclability of a photocatalyst are critical factors for practical applications. As shown in Fig. 3d, recycling experiments were conducted under identical reaction conditions. After four consecutive cycles over 20 h of operation, the HER activity of 5.7%NP/CIS/IS-3 remained stable, indicating excellent durability. In addition, the XRD patterns of 5.7%NP/CIS/IS-3 before and after the photocatalytic reactions are presented in Fig. S1. The results reveal that no obvious changes in the crystal structure of 5.7%NP/CIS/IS-3 occurred after the photocatalytic process, indicating its excellent structural stability. This enhanced durability can be attributed to

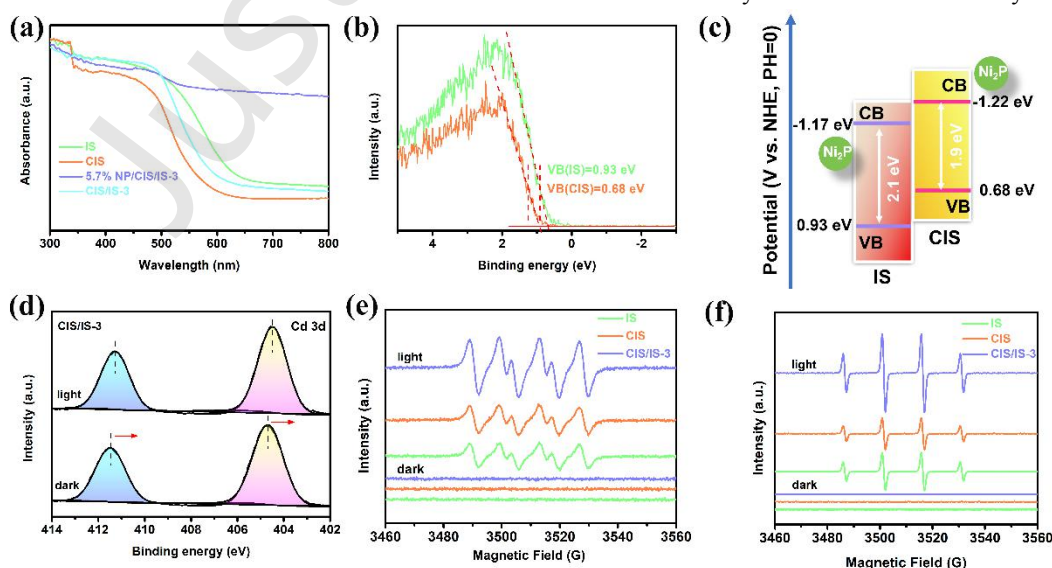


Fig. 4. (a) UV-vis absorption spectra of IS, CIS, CIS/IS-3 and 5.7%NP/CIS/IS-3. (b) The VB-XPS spectra of IS and CIS. (c) The band structure of the 5.7%NP/CIS/IS-3. (d) ISI-XPS spectra of Cd 3d, (e) the DMPO-•O₂- and (f) DMPO-•OH signal EPR signals of CIS, IS and CIS/IS-3 in the dark and under visible-light irradiation, respectively.

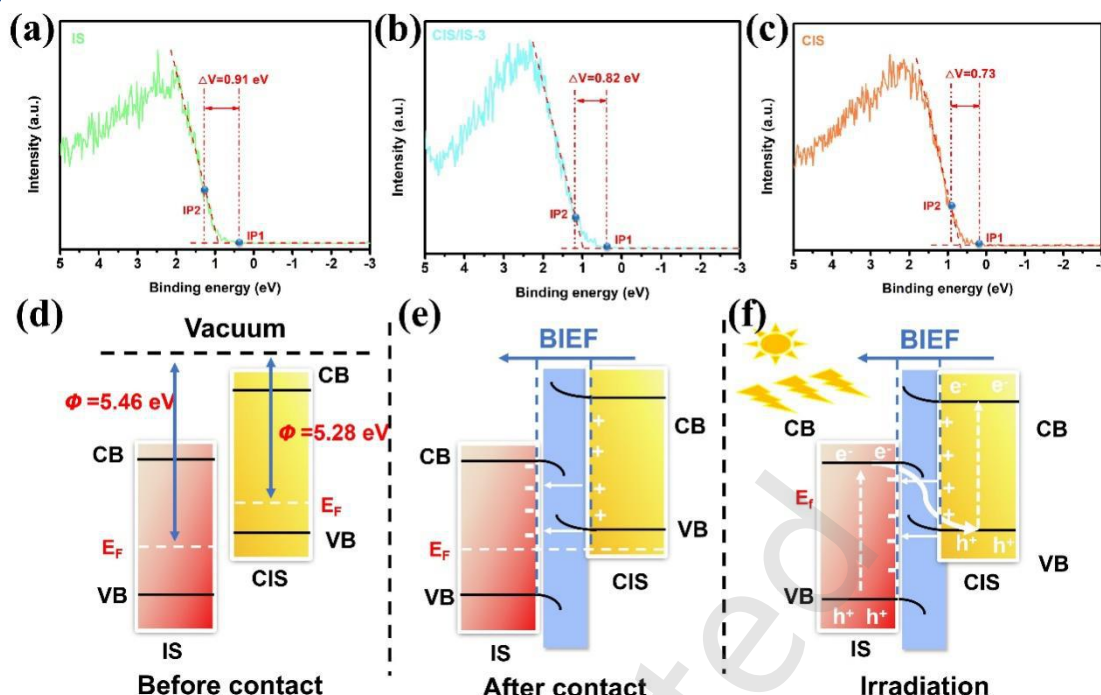


Fig. 5. VB-XPS of (a) IS, (b) CIS and (c) CIS/IS-3; the Φ of IS and CIS (d) before contact, (e) after contact and (f) charge separation and transfer in presence of internal electric field.

the robust ternary heterojunction architecture, in which the intimate interfacial contact effectively suppresses photocorrosion and inhibits the aggregation or detachment of active sites, thereby facilitating efficient charge separation and sustained electron transfer.

3.3. Band structure analysis

Fig. 4a presents the UV-vis absorption spectra of IS, CIS, CIS/IS-3, and 5.7%NP/CIS/IS-3. The absorption edge of IS located at 590 nm, corresponding to a band gap energy of 2.1 eV. CIS exhibits an optical absorption edge at 652 nm, with a corresponding band gap of 1.9 eV. Compared to CIS, the absorption edge of CIS/IS-3 undergoes a red shift, which can be attributed to the formation of CIS on the surface of IS, enhancing light-harvesting capability. Moreover, upon the incorporation of NP with CIS/IS-3, the photoresponse is significantly enhanced within the 500-800 nm wavelength range (as shown in Fig. S2). The valence band maximum (VBM) positions were determined via VB-XPS. As shown in Fig. 4b, the VBM of IS located at 0.93 eV vs. NHE, while that of CIS is positioned at 0.68 eV vs. NHE. Based on these values and the UV-vis absorption spectra results, the conduction band minimum (CBM) of IS and CIS are calculated to be -1.17 eV and -1.22 eV, respectively. Consequently, the band structure of 5.7%NP/CIS/IS-3 is clearly elucidated, as illustrated in Fig. 4c.

The S-scheme heterostructure of CIS/IS-3 was investigated by ISI-XPS and EPR. The ISI-XPS characterization was applied to detect the pathways of photoexcited electron transfer under light irradiation. CIS/IS-3 was measured under 365 nm irradiation. Since both In and S elements are present in CIS and IS, the direction of photogenerated electron flow in the prepared system can only be determined by the presence of Cd elements (the ISI-XPS spectra of In and S elements were presented in ESI, Fig. S3). As shown in Fig. 4d, under illumination conditions, the energy levels of Cd 3d shift to lower angles compared to the dark environment, indicating an increase in the electron cloud density around the Cd element. This demonstrates that, during

the illumination process, electrons will transfer from IS to CIS. Specifically, the BIEF and band bending effects drive the photogenerated electrons from the CB of IS recombination with the photogenerated holes in the VB of CIS. This electron redistribution allows the remaining photogenerated electrons in the CB of CIS to actively participate in the reduction of water.

The characteristics of S-scheme heterojunctions could enhance the capacity of directional charge transfer and can maximize the material's redox capability. Therefore, the EPR was applied to detect the radical intermediates aimed at gaining an insight into the enhanced redox property of CIS/IS heterostructures. As shown in Fig. 4e, the DMPO- $\bullet\text{O}_2^-$ signal of the as-prepared samples are absent in the dark environment. However, CIS and IS presented an obvious DMPO- $\bullet\text{O}_2^-$ signal under the light irradiation. It should be attributed to the suitable CB position for $\text{O}_2/\bullet\text{O}_2^-$ (-0.33 V vs. normal hydrogen electrode (NHE), pH = 0). Meanwhile, due to the close position of the conduction band, the signal strength of $\bullet\text{O}_2^-$ is almost similar. Notably, CIS/IS-3 heterostructures show a prominent DMPO- $\bullet\text{O}_2^-$ signal than CIS and IS. In addition, as shown in Fig. 4f, no obvious DMPO- $\bullet\text{OH}$ signals were detected for the as-prepared samples in the dark environment, whereas clear DMPO- $\bullet\text{OH}$ signals appeared under light irradiation. Compared with individual CIS and IS, CIS/IS-3 exhibited the strongest DMPO- $\bullet\text{OH}$ signal, indicating the enhanced oxidation capability of photogenerated holes in the heterostructure. The EPR results further proved that stronger redox capability of CIS/IS-3 S-scheme heterostructures with respect to individual CIS and IS.

The work function (Φ) plays a crucial role in investigating the internal electric field and interfacial charge transfer behavior within the CIS/IS-3 heterojunction. The kinetic energy of free electrons is modulated by the contact potential difference (ΔV), and due to the intrinsic difference in Φ values between CIS and IS, variations in electron binding energy occur[38, 39]. These changes were characterized through VB-XPS, and ΔV values

were determined based on the distance between inflection points (IP) in the spectra (Fig. 5a-c). The Φ values were obtained by using the equation: $\Phi = \Delta V + \phi$, where $\phi = 4.55$ eV. Accordingly, the Φ values of IS, CIS, and CIS/IS-3 were found to be 5.46 eV, 5.28 eV, and 5.37 eV, respectively (Fig. 5d). Upon establishing direct contact between IS and CIS, the system attains a new equilibrium state. During interfacial electron migration, the region adjacent to the CIS photocatalyst becomes positively charged due to electron depletion, leading to upward band bending and the formation of an electron depletion layer in IS. Conversely, the region near the IS photocatalyst acquires a negative charge as it gains electrons, resulting in an electron accumulation layer and downward band bending (Fig. 5e). Consequently, an internal electric field directed from CIS to IS forms at the CIS/IS-3 heterojunction, effectively inhibiting further electron flow from IS to CIS. Upon visible-light irradiation, electrons in both IS and CIS are photoexcited from the valence band (VB) to the conduction band (CB). Subsequently, the combined influence of the internal electric field and Coulombic interactions facilitates selective charge recombination, whereby photogenerated electrons in the CB of IS recombine with holes in the VB of CIS (Fig. 5f). This charge transfer mechanism follows a S-scheme pathway, wherein the spatial separation of photogenerated holes in the VB of IS and electrons in the CB of CIS preserves strong redox potential, thereby significantly enhancing the photocatalytic reduction capability. The result is consistent with the result of XPS and ISI-XPS.

3.4. Photoelectrochemical characterization analysis

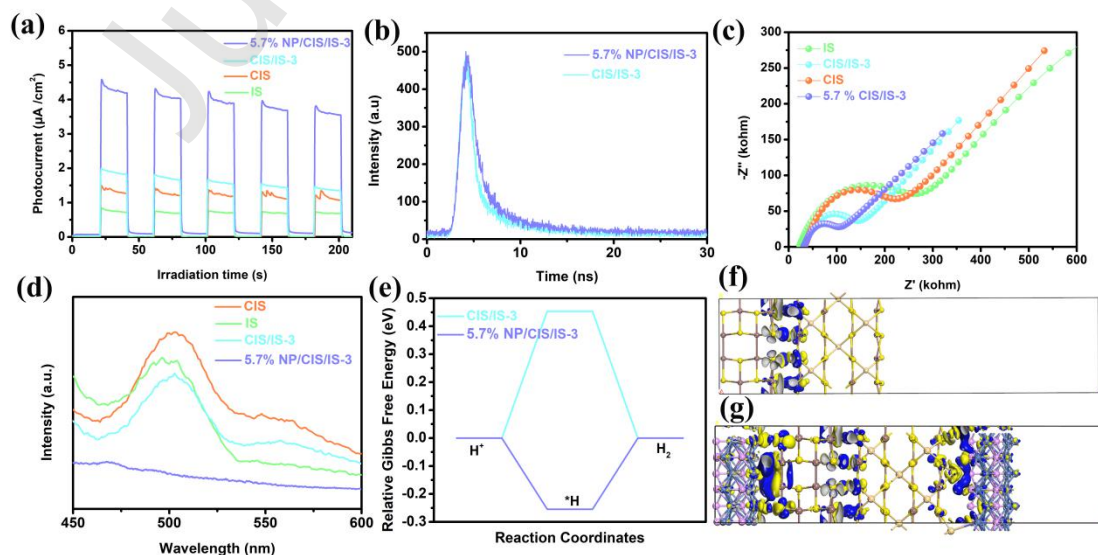
The photoelectrochemical characterizations were conducted to verify that photocatalysts with S-scheme heterostructures and multiple electron transport pathways can efficiently facilitate charge separation and enhance interfacial electron transfer. As shown in Fig. 6a, the transient photocurrent responses of IS, CIS, CIS/IS-3, and 5.7%NP/CIS/IS-3 were recorded under 30 consecutive light on/off cycles. The photocurrent density of CIS/IS-3 was markedly higher than that of IS and CIS, confirming that the construction of the S-scheme heterojunction effectively promotes spatial charge separation and suppresses the recombination of photogenerated carriers. Remarkably, 5.7%NP/CIS/IS-3 exhibited the highest photocurrent intensity

and transfer efficiency. This enhancement can be attributed to the synergistic effects between the S-scheme charge-transfer mechanism and the NP-induced multiple electron transport channels, which collectively accelerate photoinduced charge migration and improve overall photoelectrochemical activity[40].

The TRPL spectra were analyzed to further confirm that 5.7%NP/CIS/IS-3 possesses an additional electronic migration pathway. As shown in Fig. 6b, the average fluorescence lifetimes of 5.7%NP/CIS/IS-3 and CIS/IS-3 were 3.15 ns and 2.95 ns, respectively. The longer fluorescence lifetime of 5.7%NP/CIS/IS-3 compared to CIS/IS-3 suggests that the presence of NP provides an additional electronic migration pathway, which enhances charge-separation efficiency. Consequently, a greater number of photogenerated electrons can participate in the photocatalytic hydrogen production reaction, thereby improving the photocatalytic hydrogen production efficiency[41].

The interfacial charge transfer properties were further evaluated through EIS. As illustrated in Fig. 6c, the Nyquist plots exhibit semicircular radii following the order: IS > CIS > CIS/IS-3 > 5.7%NP/CIS/IS-3. The gradual decrease in arc radius indicates a reduction in charge-transfer resistance, implying improved interfacial conductivity and faster electron transport kinetics. The smallest semicircle radius observed for 5.7%NP/CIS/IS-3 confirms that the integration of S-scheme heterostructures with NP-induced conductive interfaces effectively accelerates interfacial charge exchange and minimizes potential barriers for electron migration.

Furthermore, the PL spectra were employed to evaluate the carrier recombination behavior in the ternary heterostructure composites. As shown in Fig. 6d, 5.7%NP/CIS/IS-3 exhibits the lowest emission intensity, indicating that electron-hole recombination is significantly suppressed due to its unique structural design. By integrating the results from photocurrent response, TRPL, EIS, and PL analyses, it can be conclusively inferred that the formation of S-scheme heterostructures and the introduction of multiple electron transport pathways through NP incorporation synergistically optimize the migration dynamics of photogenerated charge carriers. This cooperative modulation not only enhances charge separation efficiency and interfacial electron transfer but also effectively inhibits recombination, thereby achieving markedly improved photocatalytic H₂ evolution performance.



among all samples, indicating superior charge carrier generation

To further elucidate the underlying photocatalytic mechanism,

Fig. 6. (a) The transient photocurrent curves of CIS, IS, CIS/IS-3 and 5.7%NP/CIS/IS-3, (b) The TRPL spectra of CIS/IS-3 and 5.7%NP/CIS/IS-3, (c) the EIS Nyquist plots and (d) PL spectra of CIS, IS, CIS/IS-3 and 5.7%NP/CIS/IS-3. (e) The calculated free energy diagram of HER a equilibrium potential of 5.7%NP/CIS/IS-3 and CIS/IS-3, The 3D model charge density difference of (f) CIS/IS-3 and (g) 5.7%NP/CIS/IS-3.

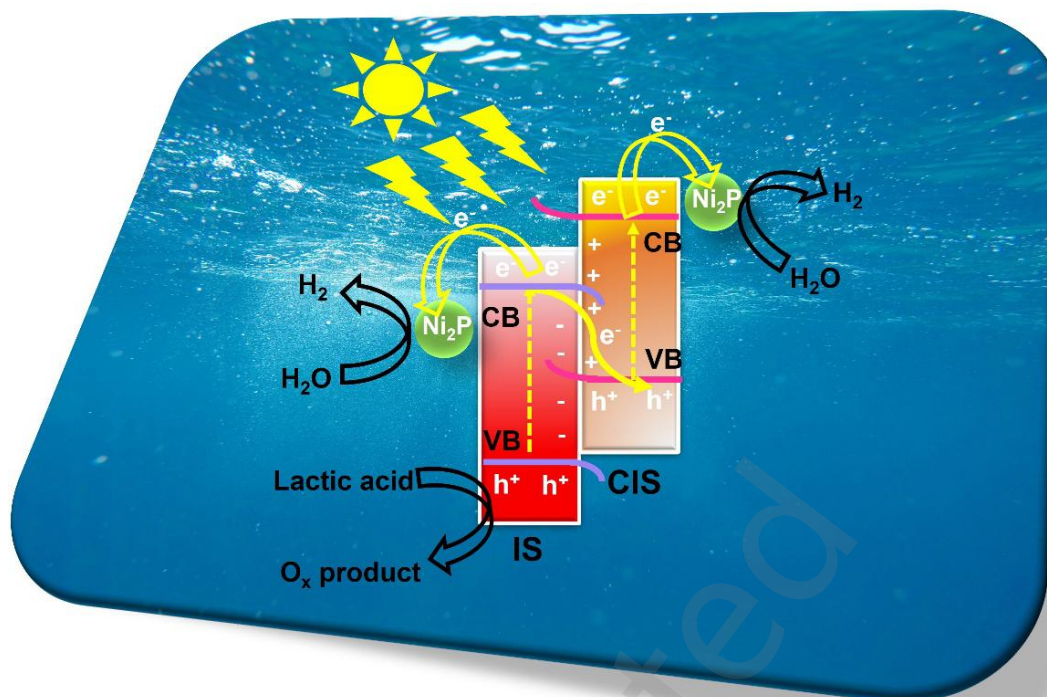


Fig. 7. A proposed photocatalytic mechanism of visible-light-driven H_2 evolution by 5.7%NP/CIS/IS-3 composites.

DFT calculations were performed to analyze the electronic structure and charge redistribution within the heterojunction system. These calculations provided theoretical evidence for the directionality of photogenerated carrier migration, revealed the potential active sites involved in the H_2 evolution reaction, and clarified the role of the internal electric field in facilitating efficient charge separation across the interface (the calculation details were shown in ESI). The HER typically consists of three fundamental steps: adsorption of protons (H^+), formation of the adsorbed hydrogen intermediate (H^*), and generation of hydrogen molecules ($1/2 H_2$). An ideal photocatalyst for HER should possess a ΔG_{H^*} value close to zero, thereby minimizing the kinetic barriers associated with the adsorption and desorption processes. As shown in Fig. 6e, the ΔG_{H^*} value of the 5.7%NP/CIS/IS-3 is more negative than that CIS/IS-3. This result suggests that the introduction of NP significantly enhances the hydrogen adsorption capability of the material, providing more favorable active sites for HER. Consequently, the modified heterostructure exhibits improved catalytic activity, as the optimized ΔG_{H^*} facilitates the adsorption-desorption dynamics essential for efficient H_2 evolution under visible-light irradiation. As illustrated in Fig. 6f and g, the three-dimensional (3D) charge density distributions of the CIS/IS-3 and 5.7%NP/CIS/IS-3 heterostructures were calculated to visualize the spatial behavior of photogenerated carriers. In these plots, blue and yellow regions represent electron accumulation and depletion, respectively. For CIS/IS-3 (Fig. 6f), electron density redistribution reveals a directional migration of photogenerated electrons from IS to CIS under visible-light irradiation, corroborating the results obtained from ISI-XPS analysis and confirming the formation of an S-scheme heterojunction. In the case of 5.7%NP/CIS/IS-3 (Fig. 6g), a more complex and efficient charge transfer behavior is observed. Specifically, three distinct photogenerated electron migration pathways are identified: (i) from IS to CIS, consistent with the intrinsic S-scheme mechanism; (ii) from IS directly to NP, indicating that NP functions as an alternative electron acceptor; and (iii) from CIS to NP, suggesting that NP serves as a terminal electron sink. This multichannel charge migration significantly enhances spatial charge separation and accelerates surface electron

delivery to catalytic sites. The presence of NP not only expands the charge transfer network but also modulates the local charge environment, promoting faster charge extraction and reducing the recombination probability. This synergistic architecture enables more efficient utilization of photogenerated carriers, ultimately contributing to the improved H_2 evolution performance observed experimentally.

Based on the characterizations described above, the mechanism of photocatalytic hydrogen production has been elucidated (as shown in Fig. 7). Due to the effects of band bending and the BIEF, an S-scheme heterojunction was formed between CIS and IS. When visible-light irradiates the NP/CIS/IS system, photoinduced electron-hole pairs are generated in the CB and VB of both CIS and IS. Subsequently, a portion of the photoinduced electrons in the CB of IS transfers to the VB of CIS and recombines with the photoinduced holes in CIS. As a result, photoexcited electrons accumulate in the CB of CIS (The photoexcited holes accumulate in the VB of IS, which were quenched by lactic acid). These accumulated electrons can then migrate to NP, where they participate in the HER. Furthermore, the remaining photoinduced electrons in the CB of IS can also migrate to NP, contributing to the HER. In this way, the NP present in the system acts as a cocatalyst, not only adding an additional photogenerated charge transfer pathway but also facilitating charge extraction, reducing the Gibbs free energy for H_2 formation, and accelerating hydrogen desorption. In summary, both the NP and the CIS/IS S-scheme heterostructures synergistically enhance the separation and migration of charge carriers, significantly improving photocatalytic H_2 evolution performance.

4. Conclusion

In summary, a novel NP/CIS/IS heterostructure with S-scheme charge transfer and multiple electron migration pathways was successfully fabricated via a stepwise assembly method. The formation of a strong built-in electric field at the CIS/IS interface was confirmed by work function analysis, ISI-

XPS measurements, and DFT calculations, leading to efficient spatial separation of photogenerated charge carriers. The construction of the S-scheme heterojunction endowed the CIS/IS system with enhanced redox capability, as evidenced by EPR. The integration of NP nanoparticles further optimized the photocatalytic performance by facilitating rapid charge extraction, lowering the energy barrier for H₂ evolution, and promoting hydrogen desorption. As a result, the 5.7%NP/CIS/IS-3 composite exhibited an impressive H₂ evolution rate of 45057.1 $\mu\text{mol g}^{-1} \text{h}^{-1}$ under visible-light irradiation ($\lambda \geq 420 \text{ nm}$). These findings highlight the crucial role of precise interfacial engineering and cocatalyst modulation in designing high efficiency photocatalysts.

Data availability

All data needed to support the conclusions in the paper are presented in the manuscript and the Electronic Supplementary Material.

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Declaration of competing interest

All the contributing authors report no conflict of interests in this work.

Author contribution statement

Yuwei Ma and **Jinxiao Bao** conceived the idea and designed the experiments. **Senhao Li** prepared the catalysts. **Xiaobo Han** and **Qingchun Wang** performed the photocatalytic reaction studies and analyzed the data. **Xi Zhang** and **Fei Ruan** performed density functional theory calculations. **Yuwei Ma**, **Wenjing Tang** and **Jinxiao Bao** wrote the paper.

Informed consent

Not applicable

Ethics statement

Not applicable

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d.

Electronic Supplementary Material

Engineering S-scheme heterojunctions with multichannel charge transfer for efficient photocatalytic hydrogen production

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Characterization

Powder X-ray diffraction (XRD) analysis was performed using a Rigaku Smartlab diffractometer (Rigaku Corporation, Japan) with Cu-K α radiation ($\lambda = 1.5405 \text{ \AA}$) to examine the crystal structures of the prepared samples. The instrument was operated at a voltage of 45 kV and a current of 200 mA. The scanning was conducted at a rate of $10^\circ/\text{min}$ with a step size of 0.02° , and the XRD patterns were collected over a 2θ range of 10° - 90° . The surface morphology of the samples was analyzed via scanning electron microscopy (SEM) using a TESCAN-MIRA3 instrument. To further elucidate the structural features, transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) were employed, utilizing a JEOL JEM-2100F microscope. Elemental mapping was carried out using energy-dispersive X-ray spectroscopy (EDX) integrated with the TEM setup. X-ray photoelectron spectroscopy (XPS) and ISI-XPS was conducted on a Thermo Scientific ESCALAB 250Xi system equipped with a monochromated Al K α X-ray source ($h\nu = 1486.6 \text{ eV}$), operated at 14.8 kV and 150 W. The binding energy values were calibrated against the C 1s peak of adventitious carbon at 284.8 eV. The chemical states of the constituent elements, including In 3d, Cd 3d, S 2p, Ni 2p, and P 2p, were analyzed by performing peak deconvolution of the high-resolution XPS spectra using XPSPEAK v4.1 software. Photoluminescence (PL) spectra were recorded on a HITACHI F-2500 spectrophotometer with an excitation wavelength of 330 nm to investigate the charge carrier dynamics of the photocatalysts. Photocurrent response measurements (i-t curves) were carried out in a three-electrode cell configuration using a CHI-700D electrochemical workstation. A 300 W Xenon arc lamp served as the light source. The working electrode, counter electrode, and reference electrode were ITO glass coated with the photocatalyst, a Pt flake, and an Ag/AgCl electrode, respectively. A 0.5 M Na₂ SO₄ solution was used as the electrolyte. Electrochemical impedance spectroscopy (EIS) was conducted using an Autolab impedance measurement system in a frequency range of 0.01 - 10^5 Hz , with an AC amplitude of 5 mV at the open-circuit voltage. UV-visible diffuse reflectance spectra (UV-vis DRS) were obtained using a U-3900 solid-state UV-vis spectrophotometer (Hitachi, Japan) to analyze the optical properties of the photocatalysts. ESR spectra were recorded on a Bruker A300-10/12 spectrometer. For $\bullet\text{O}_2^-$ detection, 1 mg/mL methanol sample was O₂-saturated for 30 min, mixed with 100 mM DMPO (1:1), sealed in a capillary, and tested under dark and visible light (300 W Xe lamp, $\lambda > 420 \text{ nm}$) for 80 s.

Calculation of AQY

The photocatalytic hydrogen generation rate in this paper was tested using a cut-off filter at 420 nm ($\lambda \geq 420$ nm); Whereas the AQY was tested using a bandpass filter at 420 nm ($\lambda = 420$ nm).

$$\begin{aligned} \text{AQY} &= \frac{\text{number of H}_2 \text{ molecules evolved} \times 2}{\text{number of incident photons}} \times 100\% \\ &= \frac{2 \times n_{\text{H}_2} \times N_A \times h \times c}{P \times t \times \lambda} \times 100\% \end{aligned}$$

N_A : Avogadro constant, 6.02×10^{23} ;

n_{H_2} (mol): the hydrogen yield, 1.971×10^{-5} mol;

P (W): the optical power of DT 420 filter, 0.15 W (optical power meter: PL-MW2000);

λ (nm): the wavelength of 420 nm (DT 420 filter);

t : the duration of irradiation, 14400 s;

h : Planck constant, 6.626×10^{-34} J·s;

c : the speed of light, 3×10^8 m/s.

$$\text{AQY} = \frac{2 \times 2.3244 \times 10^{-5} \times 6.02 \times 10^{23} \times 6.626 \times 10^{-34} \times 3 \times 10^8}{0.15 \times 14400 \times 420 \times 10^{-9}} \times 100\% = 0.61\%$$

Calculation details

All the density-functional theory (DFT) computations were performed using the Cambridge Sequential Total Energy Package (CASTEP)^[1] based on the pseudopotential plane wave (PPW) method. Electron-ion interactions were described using the ultrasoft (USP) potentials^[2]. A plane-wave basis set was employed to expand the wave functions with a cutoff kinetic energy of 400 eV. For the electron-electron exchange and correlation interactions, the functional parametrized by Perdew-Burke-Ernzerhof (PBE)^[3], a form of the general gradient approximation (GGA), was used throughout. The vander Waals interaction was described using the DFT-D2 method that proposed by Grimme^[4].

During the geometry optimizations, all the atom position were allowed to relax. In this work, the Brillouin-zone integrations were conducted using Monkhorst-Pack (MP) grids^[5] of special points with the separation of $0.05 \text{ \AA}^{-1}$ for the model cell. The convergence criterion for the electronic self-consistent field (SCF) loop was set to $1 \times 10^{-6} \text{ eV/atom}$. The atomic structures were optimized until the residual forces were below $0.03 \text{ eV \AA}^{-1}$.

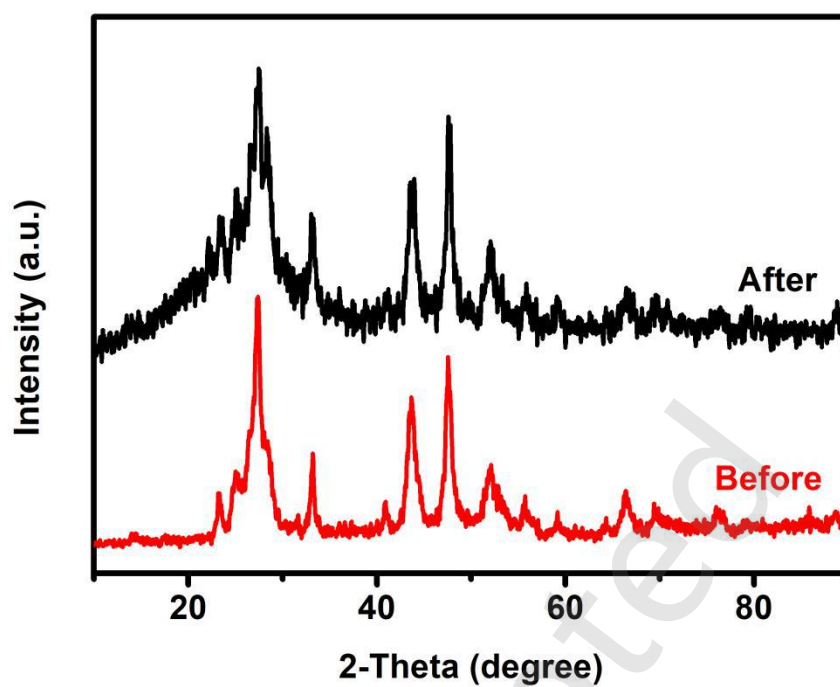


Fig. S1. XRD patterns of 5.7% NP/CIS/IS-3 before and after the photocatalytic H₂ evolution reaction.

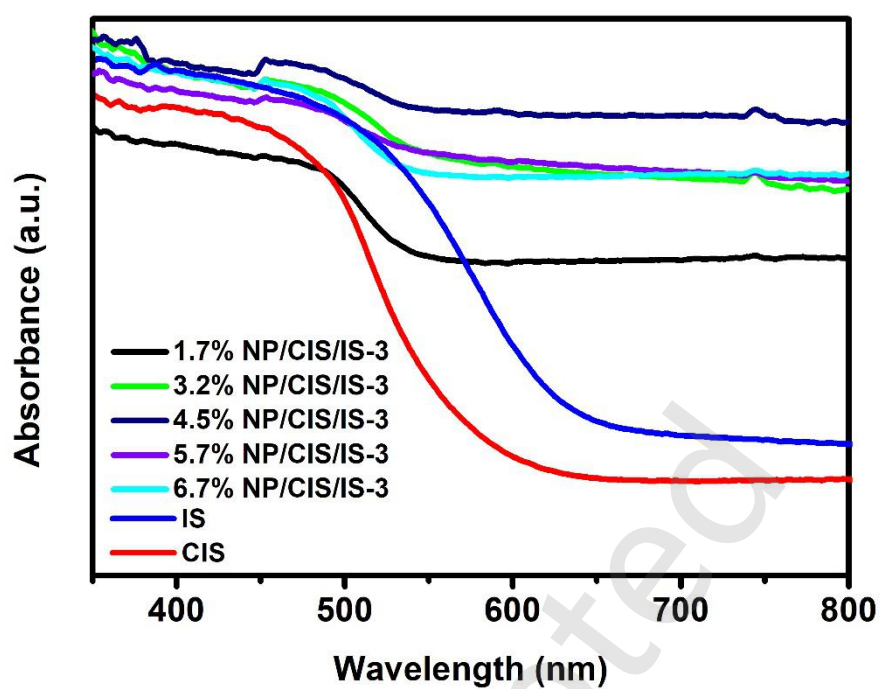


Fig. S2. UV-vis absorption spectra of IS, CIS, CIS/IS-3 and X%NP/CIS/IS-3.

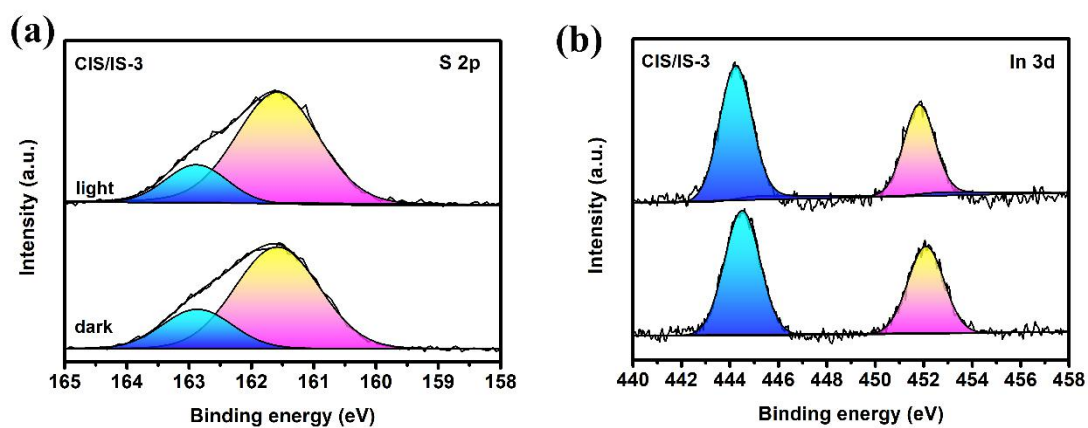


Fig. S3. ISI-XPS spectra of (a) S 2p, (b) In 3d.

Table S1. BET specific surface areas of the samples

Sample	BET specific surface area ($\text{m}^2 \text{g}^{-1}$)
In_2S_3	67.74
$\text{CdIn}_2\text{S}_4/\text{In}_2\text{S}_3$	18.50
$\text{Ni}_2\text{P}/\text{CdIn}_2\text{S}_4/\text{In}_2\text{S}_3$	33.42

To further investigate the surface properties of the samples, Brunauer–Emmett–Teller (BET) specific surface area measurements were conducted, and the corresponding results are summarized in Table S1. After the introduction of NP, the specific surface area of CIS/IS-3 increased, which could expose more accessible active sites and facilitate interfacial photocatalytic reactions. Nevertheless, the surface area of 5.7%NP/CIS/IS-3 remains lower than that of pure IS, while its photocatalytic H_2 evolution performance is significantly superior. This result suggests that the enhanced photocatalytic activity cannot be simply attributed to the increased surface area. Instead, the markedly improved performance mainly originates from the synergistic effect between the efficient charge separation induced by the ternary heterojunction and the cocatalytic function of NP, which together promote charge transfer and accelerate the surface hydrogen evolution reaction kinetics.

Table S2. Comparison of the photocatalytic H₂ evolution performance of Ni₂P/CdIn₂S₄/In₂S₃ with representative CdIn₂S₄-based photocatalysts.

Photocatalyst	Light source	Incident light (λ)	Sacrificial agent	H ₂ (mmol g ⁻¹ h ⁻¹)	Ref
Ni ₂ P/CdIn ₂ S ₄	300W Xe	> 420 nm	lactic acid	6.00	[6]
Ni ₁₂ P ₅ /CdIn ₂ S ₄	300W Xe	> 420 nm	TEOA	5.01	[7]
NiMo ₆ /10N-CdIn ₂ S ₄	LED	> 420 nm	TEOA	30.88	[8]
Co ₉ S ₈ @CdIn ₂ S ₄	300W Xe	> 420 nm	Na ₂ S/Na ₂ SO ₃	4.604	[9]
NiTiO ₃ /CdIn ₂ S ₄	300W Xe	> 400 nm	TEOA	5.169	[10]
UiO-66/CdIn ₂ S ₄ /CaIn ₂ S ₄	250W Xe	> 420 nm	TEOA	4.931	[11]
Mo ₂ C/CdIn ₂ S ₄	300W Xe	> 420 nm	lactic acid	1.178	[12]
Ni ₂ P/CdIn ₂ S ₄ /In ₂ S ₃	300W Xe	> 420 nm	lactic acid	45.05	This work

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