Supporting Information

Localized surface plasmon resonance-interface induces ultrafast hot-electron spatiotemporal transfer for boosting photocatalytic H₂ evolution integrated with benzylamine C-N coupling

Jingjing Yang,^{a†} Ziang Chen,^{b†} Jiongrong Wang,^c Bicai Pan,^a Qun Zhang,^{a,b,d*} Chong Xiao, ^{a*} and Yi Xie^{a*}

^a Hefei National Research Center for Physical Sciences at the Microscale, University of Science and Technology of China, Hefei, Anhui, 230026, P. R. China.

^b Department of Chemical Physics, University of Science and Technology of China, Hefei, Anhui, 230026, P. R. China.

^c Key Laboratory of Strongly-Coupled Quantum Matter Physics, Department of Physics, University of Science and Technology of China, Hefei, Anhui, 230026, P. R. China.
^d Hefei National Laboratory, University of Science and Technology of China, Hefei, Anhui, 230088, P. R. China.

[†] These authors contributed equally to this work.

* Corresponding authors. E-mails: yxie@ustc.edu.cn; cxiao@ustc.edu.cn; qunzh@ustc.edu.cn.

Table of Contents

1. Experimental Procedures1
Synthesis of MoO ₃ nanobelts1
Synthesis of MoO _{3-x} nanobelts1
Synthesis of ZnIn ₂ S ₄ nanosheets1
Synthesis of plasmonic MoO _{3-x} @ZnIn ₂ S ₄ heterojunctions2
Synthesis of MoO ₃ @ZnIn ₂ S ₄ heterojunctions2
Synthesis of mixed hybrid with MoO _{3-x} and ZnIn ₂ S ₄ (MoO _{3-x} +ZnIn ₂ S ₄)2
Synthesis of plasmonic noble metal nanoparticles (Au, Ag, Pt, Pd, and Ru) loaded on
ZnIn ₂ S ₄ nanosheets2
Synthesis of plasmonic non-noble metal nanoparticles (Bi and Cu) loaded on $ZnIn_2S_4$
nanosheets
Materials Characterization
Photoelectrochemical measurements4
Photocatalytic measurements for H ₂ evolution integrated with benzylamine C-N
coupling4
Determination of apparent quantum efficiency (AQE)6
Isotope-labeling experiments6
Measurement of surface-enhanced Raman scattering (SERS) performance6
Kelvin probe force microscopy (KPFM) measurements7
Spin-trapping EPR measurements7
In-situ DRIFTS measurements7
Calculation method
2. Figure S1~559
3. Table S1~8
4. References

1. Experimental Procedures

Synthesis of MoO₃ nanobelts: MoO₃ nanobelts were synthetized by virtue of a typical hydrothermal process. All the chemical reagents employed in this study were analytical grade from Aladdin and used without further purification. Firstly, 1.4 g ammonium molybdate tetrahydrate ((NH₄)₆Mo₇O₂₄·4H₂O) was dissolved in 33 mL of deionized water. Then 7 mL of nitric acid was added drop by drop into the above solution under magnetic stirring. After stirring for 30 min, the mixture was transferred into a 100 mL Teflon-lined stainless autoclave and heated at 180 °C for 17 h. Finally, the precipitate was centrifuged and washed with ethanol and deionized water for several times, and then dried in vacuum at 60 °C overnight.

Synthesis of MoO_{3-x} nanobelts: The preparation of MoO_{3-x} nanobelts was obtained from the subsequent treatment of the obtained MoO_3 nanobelts. Specifically, 1g of the synthesized MoO_3 nanobelts were dispersed in 20 mL of ethylene glycol under ultrasonication and then magnetically stirred at room temperature for 30min. Subsequently, the resulting mixtures were heated in a Teflon-lined stainless-steel autoclave at 120 °C for 6 h. Finally, the as-prepared sample were washed with water and ethanol, and then dried at 60 °C in a vacuum oven.

Synthesis of ZnIn₂S₄ nanosheets: ZnIn₂S₄ nanosheets were synthetized by virtue of a mild solvothermal process. All the chemical reagents employed in this study were analytical grade from Aladdin and used without further purification. 1 mmol ZnCl₂ and 2 mmol InCl₃·4H₂O were dissolved in 10 mL of ethylene glycol to form solution A, while 4 mmol thioacetamide was dissolved in 10 mL of ethylene glycol to form solution B. Subsequently, solution B was dropped into solution A slowly and ultrasonicated for 30 min. The obtained suspension was transferred to a Teflon-lined stainless-steel autoclave and heated at 120 °C for 6 h. After cooling naturally to room temperature, the yellow precipitate was collected by centrifugation, washed three times alternately with deionized water and absolute ethanol, and finally dried under vacuum at 60 °C.

Synthesis of plasmonic MoO3-x@**ZnIn2S4 heterojunctions:** The plasmonic MoO3x@ZnIn2S4 heterojunctions were fabricated via a mild solvothermal method for the in-situ growth of ZnIn2S4 nanosheets on plasmonic MoO3-x. In a typical procedure, different amounts of MoO3 nanobelts were dispersed in 15 mL of ethylene glycol under ultrasonication and then 1 mmol of ZnCl2 and 2 mmol of InCl3·4H2O were added and dissolved under vigorous magnetic stirring. Subsequently, 4 mmol of thioacetamide dispersion and ultrasonicated in an ice water bath for 30 min. Afterwards, the resulting mixtures were heated in a Teflon-lined stainless-steel autoclave at 120 °C for 6 h. The resultant product was centrifuged and washed with anhydrous ethanol and deionized water for several times. Finally, the product was dried by lyophilization for further use and characterization. The amounts of MoO3 added were controlled at 25, 50, 75 and 100 mg, and labeled as MoO3-x@ZnIn2S4-1~4.

Synthesis of MoO₃@ZnIn₂S₄ heterojunctions: The MoO₃@ZnIn₂S₄ heterojunctions were fabricated by a mild wet chemical method for the in-situ growth of ZnIn₂S₄ nanosheets on MoO₃. In a typical procedure, 50 mg MoO₃ were dispersed in 30 mL of deionized water under ultrasonication and the pH of the dispersion was adjusted to about 2.5 by adding hydrochloric acid. Then 1 mmol of ZnCl₂, 2 mmol of InCl₃·4H₂O and 4 mmol of thioacetamide were added and dissolved by vigorous magnetic stirring for 30 min. The resulting solution was transferred to an 80 mL round bottom flask, heated to 80 °C in a mantle, and refluxed under continuous stirring for 2 h. After reaction, the resultant product was centrifuged and washed with anhydrous ethanol and deionized water for several times. Finally, the product was dried by lyophilization for further use and characterization.

Synthesis of mixed hybrid with MoO_{3-x} and ZnIn₂S₄ (MoO_{3-x}+ZnIn₂S₄): The mixed hybrid with MoO_{3-x} and ZnIn₂S₄ was fabricated by mixing MoO_{3-x} nanobelts and ZnIn₂S₄ nanosheets (mass ratio: 1:1) via simple physical grinding and labeled as MoO_{3-x}+ZnIn₂S₄.

Synthesis of plasmonic noble metal nanoparticles (Au, Ag, Pt, Pd, and Ru) loaded on ZnIn₂S₄ nanosheets: ZnIn₂S₄ nanosheets were decorated with noble metal nanoparticles through a photo-deposition method. Typically, taking Au NPs/ZnIn₂S₄ as an example, 100 mg of ZnIn₂S₄ powder was suspended in 100 mL of aqueous solution containing 10 vol% methanol by ultrasonic treatment, and then 250 μ L of HAuCl₄· 4H₂O solution (0.01 M) was added and followed by irradiation with a 300 W Xe lamp for 2 h under drastic agitation in Ar. Then the product was collected by centrifugation and washed with deionized water three times. Afterward, the sample was dried at 60 °C in vacuum. For other ZnIn₂S₄ modified with noble metal nanoparticles, the operation is the same as above, except that HAuCl₄· 4H₂O solution (0.01 M) in the reaction system is replaced by AgNO₃ solution (0.02 M), H₂PtCl₆· 6H₂O solution (0.01 M), dilute hydrochloric acid solution of PdCl₂ (0.02 M) and RuCl₃ solution (0.02 M), respectively.

Synthesis of plasmonic non-noble metal nanoparticles (Bi and Cu) loaded on ZnIn₂S₄ nanosheets: ZnIn₂S₄ nanosheets were decorated with non-noble metal nanoparticles through a photo-deposition method. Typically, taking Bi NPs/ZnIn₂S₄ as an example, 100 mg of ZnIn₂S₄ powder was suspended in 100 mL of aqueous solution containing 10 vol% methanol by ultrasonic treatment, and then 250 μ L of 1 M HNO₃ solution containing 0.01 M Bi(NO₃)₃·5H₂O was added and followed by irradiation with a 300 W Xe lamp for 2 h under drastic agitation in Ar. Then the product was collected by centrifugation and washed with deionized water three times. Afterward, the sample was dried at 60 °C in vacuum. For Cu NPs/ZnIn₂S₄ modified with noble metal nanoparticles, the operation is the same as above, except that 1 M HNO₃ solution containing 0.01 M Bi(NO₃)₃·5H₂O in the reaction system is replaced by 0.03M copper acetate (Cu(CH₃COO)₂) solution.

In this work, in order to control the actual final loading mass of different metal nanoparticles to be as same as possible (0.5 mg), we chose to prepare noble metal salt solutions with different molar concentrations to add during the synthesis process, which can ensure that the different metal nanoparticles generated after the photo-deposition reaction will have the same mass.

Materials characterization: The X-ray diffraction (XRD) patterns were recorded on a Philips X'Pert Pro Super diffractometer with Cu K α radiation (λ =1.54178 Å). Scanning electron microscopy (SEM) images were taken on a FEI XL-30 ESEM scanning electron microscope operated at 5 kV. The transmission electron microscopy (TEM) images were obtained using Hitachi-7650 operated at an acceleration voltage of 100 kV. The high-

resolution TEM (HRTEM), and corresponding energy dispersive X-ray spectroscopy (EDS) mapping images were carried out on a Talos F200X with an accelerating voltage of 200 kV. The scanning transmission electron microscopy combined with electron energy loss spectroscopy (STEM-EELS) with the corresponding high angle annular dark-field (HAADF) images were acquired on a JEOL JEM-ARM200F with an accelerating voltage of 200 kV. Fourier transform infrared (FTIR) spectra were obtained on a Magna-IR750 FT-IR spectrometer in a KBr pellet at room temperature. The Raman spectra were acquired on a confocal Raman/PL system (LabRamHR Evolution) equipped with a 532-nm laser source. Brunauer–Emmett–Teller (BET) specific surface areas of the prepared samples were obtained using nitrogen adsorption-desorption isotherms measured at 77 K with an ASAP 2020 adsorption apparatus (Micromeritics, USA). The X-ray photoelectron spectra (XPS) were collected on an ESCALAB MKII with Mg K α (hv = 1253.6 eV) as the excitation source, and all binding energies of samples were corrected by referencing the C 1 s peak to 284.8 eV. For in-situ irradiated XPS measurements, a 300 W Xe lamp (CEL-HXF300, Beijing China Education Au-light Co., Ltd) coupled with a 420 nm cutoff filter was used as the additional light source (λ >420 nm), and its actual illumination intensity was set to 100 mW/cm². Zeta potential was measured by the synchronous Laser Diffraction and Dynamic Image Particle Analyzer (zeta potential detector). Electron Paramagnetic Resonance (EPR) spectra were collected using a Bruker EMX plus 10/12 (equipped with Oxford EPR910 Liquid Helium cryostat) electron spin resonance spectrometer at 150 K (9.405 GHz). The ultraviolet-visible-near-infrared diffuse reflectance spectra (UV-Vis-NIR DRS) were recorded on a PerkinElmer Lambda 950 UV-Vis-NIR spectrophotometer. Room temperature photoluminescence (PL) spectra were recorded on a spectrophotometer (FLS920, Edinburgh Instruments). In this work, the filter used for the photoluminescence spectra measurements were 250 nm long-wavelength-pass filters with a slit width of 5 nm. According to the structural differences of the catalysts, an excitation wavelength of 290 nm was chosen for the pristine MoO_{3-x} and MoO_3 , while the excitation wavelength of 310 nm was used for the ZnIn₂S₄, MoO₃@ZnIn₂S₄, and MoO_{3-x}@ZnIn₂S₄ series samples. Moreover, the sample concentration for the fluorescence quenching experiments was controlled to be 0.1 g/L. Transient photovoltage (TPV) measurements were carried out to study the kinetic features of the photogenerated charges with a 355 nm laser pulse from a

third-harmonic Nd: YAG laser on CEL-TPV2000. The ultrafast transient absorption (TA) measurements were performed on a femtosecond (fs) pump-probe system (Helios, Ultrafast Systems LLC) in combination with an amplified femtosecond laser system (Coherent) under ambient conditions.

Photoelectrochemical measurements: The photoelectrochemical test was measured at the CHI760 electrochemical workstation. In detail, saturated Ag/AgCl and Pt foil were used as the reference electrode and counter electrode, respectively. In a typical process, 5 mg as-synthesized samples were dispersed in 1 mL anhydrous ethanol and evenly grinded to slurry, which was then spread onto a 1 cm×2 cm FTO glass. The prepared FTO/sample was used as the working electrode with 0.5 M Na₂SO₄ aqueous solution as the electrolyte. Then the photocurrent responses of the prepared photoelectrodes were measured under chopped light irradiation (light on/off cycles: 50 s) at a bias potential of 0.7113 V vs. RHE for 550 s. The cathodic polarization curves were performed using the linear sweep voltammetry (LSV) technique with a scan rate of 10 mV s⁻¹. All the electrochemical experiments in this work were carried out under high-purity Ar atmosphere (simulating the atmosphere conditions in the photocatalytic H₂ evolution coupled with benzylamine C-N coupling), and the pH of the test system was 7.

Photocatalytic measurements for H₂ evolution integrated with benzylamine C-N coupling: Typically, 10 mg photocatalyst was dispersed in the mixture of 10 mL acetonitrile, 200 μ L H₂O and 300 μ L BA under ultrasonication in a 50 mL quartz reactor. Before irradiation, the mixture was purged with Ar gas for 30 min to remove air. Subsequently, the above mixture was irradiated by a 300 W Xe lamp (CEL-HXF300, Beijing China Education Au-light Co., Ltd) coupled with a 420 nm cutoff filter. The reaction system was continuously stirred to ensure uniform irradiation and the temperature was maintained at 25 °C by a circulating air blowing system. The amount of produced H₂ was tested by a gas chromatography (GC-8890, Agilent) equipped with thermal conductivity detector (TCD). While the organic products in solution were analyzed by the GC (Shimadzu GC-2014C) with a flame ionization detector (FID), where the photocatalyst is removed by filtration. The concentration of by-product was detected using an ion chromatograph (IC, Dionex Aquion, CS16).

Determination of apparent quantum efficiency (AQE): Under different monochromatic light wavelengths (420, 450, 500, 600 and 700 nm) irradiation, the values of light intensities were measured to 17.8, 16.5, 14.6, 6.5 and 3.7 mW cm⁻² corresponding to the 420, 450, 500, 600 and 700 nm incident wavelength, respectively. H₂ yields were measured after 3 h photoreaction, and calculated as follows:

$$AQE(\%) = \frac{2 \times \text{the number of generated nitric acid molecules}}{\text{the number of incident photons}} \times 100$$
$$= \frac{2 \times n(H_2) \times N_A}{I \times S \times t \times \frac{\lambda}{hc}} \times 100$$

Where $n(H_2)$ is the number of moles of generated H₂; *t* is the irradiation time, N_A and *h* are the Avogadro's constant and Planck constant, respectively, *I* is the light intensity, *S* is the light incident area (19.64 cm²), λ is the light irradiation wavelength, and *c* is speed of light.

Isotope-labeling experiments: In detail, isotope labelling experiments were performed using deuterium water instead of water, while other conditions remained unchanged. Gas detection was conducted through the synchrotron-radiation vacuum ultraviolet photoionization mass spectrometry (SVUV-PIMS) in the combustion end station of the BL03U beamline in the National Synchrotron Radiation Laboratory. In the detection process, helium gas was considered as a carrier gas to identify hydrogen and deuterium gas.

Measurement of surface-enhanced Raman scattering (SERS) performance: Typically, 1 mg of the powder sample was dispersed into 1 mL 10^{-5} mol/L Rhodamine 6G (R6G) aqueous solution by ultrasonication for 10 min, and allowed to settle for 20 min. The mixture was then centrifuged and the precipitate was transferred onto a clean Si wafer, and dried at room temperature. For the blank sample, a 50 µL droplet of the desired solution was simply dropped onto a clean Si wafer and dried at room temperature. The Raman spectra were collected using a confocal Raman/PL system (LabRamHR Evolution) equipped with a 633 nm laser source.

Kelvin probe force microscopy (KPFM) measurements: Kelvin probe force microscopy (KPFM) measurements were implemented based on a Bruker Dimension Icon Multimode V SPM system. A 300 W xenon lamp (CEL-HXF300, Beijing China Education Au-light Co., Ltd) was used as the light source. During the measurement of the surface potential,

the lift mode was used with a lift height of 50-100 nm. In the lift mode, the topography and the surface potential signals were sequentially recorded. The Pt/Ir-coated Si tip was used as a Kelvin tip with a spring constant of $1-5 \text{ N m}^{-1}$ and resonant frequency of 60-100 kHz.

Spin-trapping EPR measurements: The reactive radicals generated in the photocatalytic process are identified by Quasi-in-situ EPR measurements, with adding 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) to trap the reactive species including carbon-centered radical $(\cdot C^+)$, hydroxyl radical $(\cdot OH)$ and superoxide radical $(\cdot O_2^-)$. All of the spin-trapping EPR measurements are carried out with the settings of 5.02 mW microwave power, 9397.615 MHz frequency and 334.5 MT center field by a Bruker EMX plus 10/12 (equipped with Oxford EPR910 Liquid Helium cryostat) on the Steady High Magnetic Field Facilities, High Magnetic Field Laboratory, CAS.

In-situ DRIFTS measurements: In-situ diffuse reflectance infrared Fourier-transform spectroscopy (DRIFTS) measurements were performed using a Bruker IFS 66v Fouriertransform spectrometer equipped with a Harrick diffuse reflectance accessory at the Infrared Spectroscopy and Micro spectroscopy End station (BL01B) in NSRL in Hefei, China. The chamber was constituted with two ZnSe windows, and specifically designed to examine highly scattering powder samples in the diffuse reflection mode. Specifically, 30 mg of the photocatalyst was placed on the sample holder in the test chamber and was sealed in a dynamic vacuum at 160 °C for 1 h to desorb the surface residue. Then the test chamber with the sample cooled to room temperature and was purged with Ar gas for 30 min. Afterwards, the background spectrum for dark adsorption study was acquired. Subsequently, 200 µL of the mixture (100 µL H₂O and 100 µL benzylamine) was injected into the chamber rapidly. The sample was measured by infrared spectroscopy to explore the physical and chemical adsorption states of reactive species on the surface of samples over time in the dark. When the sample surface reaches the saturation adsorption of reactants, the spectra were collected under dark condition and light with a specific irradiation time using a 300 W Xe lamp. The spectra were obtained by subtracting the background from the spectra of samples. Each spectrum was recorded by averaging 256 scans at a resolution of 4 cm^{-1} .

Calculation method: All calculations in this article are performed using VASP (Vienna ab initio simulation package) based on Density Functional Theory (DFT)+U.¹ The electron-ion interaction is described by Projector Augmented Wave (PAW) potentials^{.2} and the exchange-correlation energy functional is represented using the generalized gradient approximation (GGA) in the Perdew-Burke-Ernzerhof (PBE) form.³ A 4×1 {010} supercell containing two O-Mo-O layers and a one-dimensional ZnIn₂S₄ with contact surfaces {001} and exposed surface {102} was used to simulate the MoO_{3-x}@ZnIn₂S₄ interface. In our calculations, the kinetic energy cutoff for the plane-wave basis set is 520 eV and the Brillouin zone is sampled with $2\times2\times1$ k points. During the optimizations, structures were relaxed until an energy convergence of 10^{-5} eV per atom and a force convergence of 0.02 eV Å⁻¹ are reached. In addition, the spin polarization and the van der Waals correction are considered in calculations.

2. Figures



Figure S1. SEM images of (a) $ZnIn_2S_4$, (b) MoO_{3-x} , (c) MoO_3 , (d) $MoO_{3-x}@ZnIn_2S_4$, (e) $MoO_{3-x}@ZnIn_2S_{4-1}$, (f) $MoO_{3-x}@ZnIn_2S_{4-2}$, (g) $MoO_{3-x}@ZnIn_2S_{4-3}$, and (h) $MoO_{3-x}@ZnIn_2S_{4-4}$.



Figure S2. TEM images of (a) $ZnIn_2S_4$, (b) MoO₃, (c) MoO₃@ZnIn₂S₄, (d) MoO_{3-x}@ZnIn₂S₄-1, (e) MoO_{3-x}@ZnIn₂S₄-3 and (f) MoO_{3-x}@ZnIn₂S₄-4.

Discussion: As shown in Figure S1 and S2, Both MoO₃ and MoO_{3-x} are composed of massive and uniform belt-shaped crystals with widths of about 100-300 nm and lengths extending to several micrometers, while the $ZnIn_2S_4$ shows the micro-flower structure assembled by disorder sheet-like structure. For heterojunctions, the densely interlaced $ZnIn_2S_4$ nanosheets grow uniformly along the surface of both MoO_{3-x} and MoO₃ nanobelts, thereby forming unique structures. The morphology of nanosheets and nanobelts is still basically the same as that of the pure $ZnIn_2S_4$, MoO₃ and MoO_{3-x}.

For MoO_{3-x}@ZnIn₂S₄ composites, the morphology of MoO_{3-x}@ZnIn₂S₄ varies slightly with the amount of MoO₃ added. In MoO_{3-x}@ZnIn₂S₄-1, an excess of ZnIn₂S₄ agglomerates and wraps around MoO_{3-x}, resulting in an irregular flower-sphere-like ZnIn₂S₄ dominating the structure, which makes it difficult to identify the one-dimensional nanobelts. When the amount of MoO_{3-x} is too high (MoO_{3-x}@ZnIn₂S₄-3 and 4), a portion of MoO_{3-x} nanobelts are not covered by ZnIn₂S₄ nanosheets. When the MoO₃ precursor was added at 50 mg, the coverage becomes complete and the obtained MoO_{3-x}@ZnIn₂S₄

has the most homogeneous structure. Accordingly, $MoO_{3-x}@ZnIn_2S_{4}-2$ was selected as the standard sample for this study to compare and discuss with other catalysts in various aspects.



Figure S3. (a) HAADF-STEM image of MoO₃@ZnIn₂S₄ in transverse section conditions. (b) HRTEM image and (c) partial enlarged detail for ZnIn₂S₄ part of MoO₃@ZnIn₂S₄. (d) HRTEM image and (e) partial enlarged detail for MoO₃ part of MoO₃@ZnIn₂S₄ in transverse section conditions. (f) EDS elemental mapping images of MoO₃@ZnIn₂S₄ for Mo, O, Zn, In and S in transverse section conditions.

Discussion: As shown in Figure S3a-e, HRTEM images of $MoO_3@ZnIn_2S_4$ heterojunction under its sectioning condition show two groups of lattice stripes with a spacing of 0.324 and 0.387 nm can be ascribed to (102) plane of hexagonal $ZnIn_2S_4$ and (110) plane of orthogonal MoO_3 , respectively.



Figure S4. (a) HAADF-STEM image of $MoO_{3-x}@ZnIn_2S_{4-2}$ in transverse section conditions. (b) EDS elemental mapping images of $MoO_{3-x}@ZnIn_2S_{4-2}$ for Mo, O, Zn, In and S in transverse section conditions.



Figure S5. XRD patterns of (a) different photocatalysts and (b) MoO_{3-x}@ZnIn₂S₄ heterojunctions series. (c) FTIR spectra of MoO₃, MoO_{3-x}, ZnIn₂S₄, MoO₃@ZnIn₂S₄ and MoO_{3-x}@ZnIn₂S₄-2.

Discussion: X-ray diffraction (XRD) patterns were recorded to probe the crystalline structures of representative samples. For pure MoO_3 and MoO_{3-x} , all diffraction peaks can be easily indexed to the orthorhombic α -MoO₃ (JCPDS No. 05-0508). And these characteristic peaks are sharp and well defined, indicating that MoO_3 and MoO_{3-x} are well crystallized. All observed characteristic diffraction peaks in the pristine ZnIn₂S₄ samples can be well matched with those of the hexagonal ZnIn₂S₄ (JCPDS No. 65-2023). Moreover, Figure S5b also shows that the relative intensity for (110) diffraction peak of the MoO_{3-x} increases with increasing amount of the MoO₃ precursor, which implies that the presence of excess MoO_{3-x} nanobelts will result in the failure for uniform coverage of ZnIn₂S₄ on their surfaces and cause an increase in the crystal plane exposure of MoO_{3-x}. The inhomogeneous heterostructure would lead to insufficient photogenerated carrier separation and transfer, thereby causing a decrease in the photocatalytic activity, which is shown in Figure S22. As for the heterojunctions, due to the fact that the (021) and (060) planes of MoO₃ and MoO_{3-x} almost overlap with the (102) and (108) planes of $ZnIn_2S_4$, these diffraction peaks cannot effectively distinguish from each other. Fortunately, the peaks at 24.13° and 47.65° corresponding to the (110) crystal plane of α -MoO₃ and the (110) crystal plane of $ZnIn_2S_4$ can still be clearly identified, respectively.⁴ It is noteworthy that the characteristic diffraction peaks of MoO_{3-x}@ZnIn₂S₄-1~4 are slightly shifted toward high angles compared to single components, which can be attributed to the intimate contact and interaction between the components of heterojunction.⁵ Moreover, the diffraction peaks in MoO_{3-x}@ZnIn₂S₄ are more obviously shifted compared to those in $MoO_3@ZnIn_2S_4$, which is side evidence for the formation of a more intimate interfacial contact with Mo-S bonds in $MoO_{3-x}@ZnIn_2S_4$ heterojunction, thus facilitating the ultrafast interfacial transfer of photoexcited electrons.



Figure S6. XPS spectra of the as-prepared photocatalysts: (a) survey scan spectra and highresolution spectra for (b) O 1s, (c) Zn 2p, (d) In 3d and (e) S 2p.

Discussion: The surface elemental compositions and chemical states of prepared samples were determined by X-ray photoelectron spectroscopy (XPS). The wide-scan survey XPS spectrum in Figure S6a proves the existence of constituent elements Zn, In, S, Mo and O in MoO_{3-x}@ZnIn₂S₄-2 and MoO₃@ZnIn₂S₄. The high-resolution O 1s spectra (Figure S6b) shows that the splitting peaks with the binding energy values of 530.25 eV, 531.23 eV and 532.68 eV in MoO_{3-x}@ZnIn₂S₄-2 can be allocated to lattice oxygen (O-Mo), oxygen vacancies (O_v) and adsorbed H₂O molecules (O_{ads.}), respectively.^{6,7} The appearance of the O_v characteristic peak explains the existence of Mo⁵⁺ and Mo⁴⁺ states, which evidences the abundant localized electrons in MoO_{3-x}@ZnIn₂S₄-2 hybrids and also supports its significant LSPR effect.⁸ The same results were further validated in Electron paramagnetic resonance (EPR) tests (Figure S7).

For pristine ZnIn₂S₄, Zn 2p spectra (Figure S6c) contains two peaks that can be indexed to Zn $2p_{3/2}$ (1022.01 eV) and Zn $2p_{1/2}$ (1045.09 eV).⁹ For the core spectra of In 3d (Figure S6d), two prominent peaks are attributed to In $3d_{5/2}$ (444.88 eV) and In $3d_{3/2}$ (452.47 eV), corresponding to the In³⁺ state.¹⁰ Meanwhile, the S 2p peak (Figure S6e) can be deconvoluted into two component peaks, associated with S $2p_{3/2}$ (161.62 eV) and S $2p_{1/2}$

(162.74 eV), respectively.¹¹ When ZnIn₂S₄ is in contact with MoO_{3-x}, all the peaks of Zn, In, and S experience a shifting trend towards higher binding energy (see Table S1 for details), which implies a possible electron transfer between the two components of the heterojunctions. Combining the result that the binding energy of both Mo and O species decreases in heterojunctions, it can be indicated that ZnIn₂S₄ becomes an electron donor with the decreased electron density, whereas MoO_{3-x} becomes electron acceptors with the increased electron density. These results not only confirm the existence of strong interactions between ZnIn₂S₄ and MoO_{3-x}, but also the formation of an internal electric field originating from the transfer of electrons from ZnIn₂S₄ to MoO_{3-x} via the strong Mo-S bond, which lays the foundation for promoting the separation of photogenerated carriers and suppressing their recombination.

As a supplementary note, Figure 1 and Figure S6 show that the binding energy shift of the Mo 3d orbitals in MoO₃@ZnIn₂S₄ is more significant compared to MoO₃- $_{x}$ @ZnIn₂S₄-2, which can be explained as follows: Firstly, the electron transfer in heterojunctions under dark conditions should be attributed to the difference in the surface work function (Fermi energy level) of MoO_{3-x}, MoO₃ and ZnIn₂S₄. When they come into intimate contact to form the heterojunction, the electrons will be transferred spontaneously from the side with the high surface work function to the side with the low surface work function their Fermi energy levels are aligned, thus leading to a change in the binding energy of elements. Thus, this process is prevalent in numerous heterojunctions, including plasmonic MoO_{3-x}@ZnIn₂S₄-2 and non-plasmonic MoO₃@ZnIn₂S₄ as mentioned in our work, and is not dependent causally on the presence or absence of Mo-S bonding. While the Mo-S binding with LSPR effect produces interfacial near-field enhancement effect upon photoexcitation to provide a unique transport channel for ultrafast spatiotemporal transfer and separation of photoexcited electrons, so the Mo 3d orbital shift in MoO₃- $_{x}$ @ZnIn₂S₄-2 is normal. Although the Mo⁶⁺ 3d orbital shift is more significant in MoO₃@ZnIn₂S₄, it does not appear to have a change in the valence state of Mo, so it is also reasonable that the Mo⁶⁺ 3d orbital shift is significant for MoO₃@ZnIn₂S₄.



Figure S7. EPR spectra of (a) $MoO_{3-x}@ZnIn_2S_4$ heterojunction series and (b) different photocatalysts.

Discussion: EPR is an important method to study unpaired electrons in compounds. As shown in Figure S7, the presence of low valence-state Mo species (Mo^{5+}) and oxygen vacancies (g=2.001) in MoO_{3-x}@ZnIn₂S₄ series was further confirmed by the EPR test.¹² The intensity of these EPR signals in MoO_{3-x}@ZnIn₂S₄-2 are obvious higher than that in MoO₃@ZnIn₂S₄, further confirming that more defects are induced after using ethylene glycol as reducing agent, which is also the source of the LSPR generation.



Figure S8. (a) UV-Vis-NIR DRS pattern of $MoO_{3-x}@ZnIn_2S_4$ heterostructure series (c) Tauc plots of the transformed Kubelka-Munk functions versus the photon energy and (c) VB-XPS spectra for the as-fabricated MoO_3 , MoO_{3-x} and $ZnIn_2S_4$. (d) Schematic illustration for the band structures of the samples simulated by apparent optical properties.

Discussion: The optical property of catalysts is an important factor affecting the photocatalytic effect, so the light-harvesting capability of the as-prepared samples was measured by UV-Vis-NIR diffuse reflection spectroscopy (DRS) as shown in Figure 2a and Figure S8a. In detail, compared to MoO₃ nanobelts, in addition to the intrinsic absorption bands at 200-420 nm, a big plasmon bulge peak in MoO_{3-x} induced by oxygen vacancies located in the visible and NIR regions are also observed.¹³ For MoO₃@ZnIn₂S₄ composite catalyst, the light absorption range showed a significant redshift, which may be influenced by the effect of the heterojunction interface.⁴ Whereas after the depositing of ZnIn₂S₄ onto MoO_{3-x}, not only did the optical absorption edge of samples undergo a redshift compared to that of pure MoO_{3-x}, but they also showed a stronger optical response in the range of Vis-NIR light while retaining the LSPR absorption band of MoO_{3-x}.

Subsequently, the band gap of MoO₃ (2.98 eV), MoO_{3-x} (2.92 eV) and ZnIn₂S₄ (2.58 eV) can be obtained through the corresponding Tauc plots of UV-Vis-NIR DRS according to Kubelka-Munk formula (Figure S8b). Meanwhile, the positions of the valence band (VB) of MoO₃, MoO_{3-x} and ZnIn₂S₄ were confirmed from the VB-XPS spectra (Figure S8c) to be 3.34, 3.20 and 1.58 eV, respectively. Therefore, the conduction band (CB) potentials of MoO₃, MoO_{3-x} and ZnIn₂S₄ samples can be calculated to be 0.36 eV, 0.28 eV and -1.00 eV, respectively. According to the above results, the schematic diagram of the energy band structures of MoO₃, MoO_{3-x} and ZnIn₂S₄ and MoO₃ or MoO_{3-x} makes it possible to form S-scheme heterostructures with high redox capacity after contact.



Figure S9. EPR spectra of free radicals captured by DMPO for $MoO_{3-x}@ZnIn_2S_4$ heterostructure series in different systems under light irradiation (λ >420 nm): (a) DMPO- $\cdot O_2^-$, (b) DMPO- $\cdot OH$. EPR spectra of free radicals captured by DMPO for different samples in different systems under light irradiation (λ >420 nm): (c) DMPO- $\cdot O_2^-$, (d) DMPO- $\cdot OH$.

Discussion: To verify the formation of S-scheme heterojunctions, spin-trapping EPR measurements were performed to detect superoxide radicals $(\cdot O_2^-)$ and hydroxyl radicals $(\cdot OH)$ by using 5,5-dimethyl-1-pyrroline N-oxide (DMPO) as a capture agent. As demonstrated in Figure S9a and S9c, under visible light irradiation, no DMPO- $\cdot O_2^-$ signal peaks appeared due to the positive CB potentials of MoO₃ and MoO_{3-x}. In contrast, almost no DMPO- $\cdot OH$ characteristic signal peaks were observed in Figure S9b and S9d because the VB potential of ZnIn₂S₄ was lower than the redox potential of H₂O/ $\cdot OH$ (2.4 V vs. NHE). Importantly, for both MoO₃@ZnIn₂S₄ and plasmonic MoO_{3-x}@ZnIn₂S₄ heterojunction series, the EPR signal intensities of DMPO- $\cdot O_2^-$ and DMPO- $\cdot OH$ are significantly enhanced and the corresponding characteristic signal intensities in MoO₃-

 $_x$ @ZnIn₂S₄-2 are the strongest, which is convincing evidence that plasmonic MoO₃₋ $_x$ @ZnIn₂S₄ heterojunction series form an S-scheme mechanism with an improved charge separation, which enables the achievement of strong oxidation and reduction abilities.



Figure S10. (a) STEM-HADDF image of the transverse section for MoO_{3-x}@ZnIn₂S₄-2.
(b) LL-EELS spectrum of region A and B mapped from the corresponding STEM image in (a).

Discussion: Electron energy-loss spectroscopy (EELS) can provide insightful information about the composition and electronic structure, as well as the optical properties of semiconductors. In particular, in the low-loss region of EELS (<50 eV), interband transitions and plasmon losses corresponding to the collective oscillations of valence electrons in the materials can be observed.¹⁴ Therefore, Low-loss EELS (LL-EELS) was measured to further confirm the generation of plasmon excitations in MoO_{3-x}@ZnIn₂S₄-2. The STEM-HADDF image (Figure S10a) of the transverse section for MoO_{3-x}@ZnIn₂S₄-2 shows the interface region between MoO_{3-x} and ZnIn₂S₄, while LL-EELS was collected for region A (inside the MoO_{3-x} nanobelts) and region B (at the contact between the edge of MoO_{3-x} and ZnIn₂S₄), respectively.

The intensity of LL-EELS signal in region B is significantly higher than that in region A, which indicates that the LSPR effect at the interface of $MoO_{3-x}@ZnIn_2S_{4-2}$ is stronger than that inside the MoO_{3-x} nanobelts. The enhanced LSPR confirms that the coupling of plasmonic MoO_{3-x} to $ZnIn_2S_4$ can form active 'hot spots' at the interface, which may strongly confine incident light energy to significantly enhance the localized electromagnetic field, thereby increasing the continuous and fast output of localized hot-electrons.¹⁵



Figure S11. In-situ XPS spectra of $MoO_{3-x}@ZnIn_2S_{4}-2$ under dark and Vis-NIR illumination: (a) survey spectra, and high-resolution spectra for (b) O 1s, (c) Zn 2p and (d) In 3d.

Discussion: The charge transfer pathway in plasmonic $MoO_{3-x}@ZnIn_2S_{4}-2$ after light irradiation was investigated by in-situ irradiated XPS measurements. Figure S11a shows that no additional elemental peaks appear after light irradiation, which confirms that light irradiation does not change the structure of $MoO_{3-x}@ZnIn_2S_{4}-2$.

It is well known that defects (e.g., oxygen vacancies) in plasmonic semiconductors can induce collective oscillations of excess free charges and thus exhibit the LSPR effect.¹⁶ As a result, there are a large number of free electrons intrinsically present at the oxygen vacancies of MoO_{3-x}. Upon light irradiation, these massive electrons can be instantaneously excited to a high-energy surface plasmon resonance (SPR) state to generate highly reactive plasmonic hot-electrons. Subsequently, driven by the internal electric field at the heterojunction interface and accelerated by the interfacial near-field enhancement effect

induced by LSPR excitation, the hot-electrons at the oxygen vacancies of MoO_{3-x} are rapidly transferred into $ZnIn_2S_4$ taking O-Mo-S as a bridge. Consequently, the O 1s peak assigned to O-Mo also positively shifts after illumination in Figure S11b.



Figure S12. In-situ XPS spectra of MoO₃@ZnIn₂S₄ under dark and Vis-NIR illumination: (a) survey spectra, and high-resolution spectra for (b) Mo 3d, (c) O 1S, (d) Zn 2p, (e) In 3d and (f) S 2p.

Discussion: As shown in Figure S12 and Table S4, compared with the XPS spectra collected in darkness, after light excitation, the binding energies of Zn 2p, In 3d, and S 2p in MoO₃@ZnIn₂S₄ were shifted by -0.11, -0.08, and -0.06 eV, respectively, whereas the Mo⁶⁺ 3d peaks and the O 1S peaks in the Mo-O species shifted to the high binding energy direction by 0.05 and 0.18 eV, respectively. These results reveal that the electron cloud density increases around ZnIn₂S₄ while decreases around MoO₃, indicating the transfer of photogenerated electrons from MoO₃ to ZnIn₂S₄ under light illumination, which agrees with the charge-transfer mode of S-scheme heterostructure. Although electron transfer also occurs in MoO₃@ZnIn₂S₄ heterojunctions, it is mainly driven by the interfacial internal electric field. Therefore, under controlling variables, the construction of an interfacial structure with LSPR effect to provide an exclusive transport channel for hot electron transfer is the fundamental factor for realizing ultrafast electron transfer from MoO_{3-x} to ZnIn₂S₄ within the timescale of 100 fs.

Furthermore, as illustrated in Figure S12b, a weak signal of the Mo⁵⁺ 3d peaks appeared upon light illumination in compared to the XPS spectra collected in darkness,

which indicate that a portion of Mo^{5+} species is introduced under photoelectron reduction,^{17,18} thus causing the abnormality in the UV-Vis-NIR DRS pattern of $MoO_3@ZnIn_2S_4$. Even though the light absorption edge of $MoO_3@ZnIn_2S_4$ showed a significant redshift, its photocatalytic performance was not the best, which demonstrates that the light absorption property is not the only factor determining the photocatalytic activity in our material system. Therefore, the abnormality in the UV-Vis-NIR DRS pattern of $MoO_3@ZnIn_2S_4$ does not affect the concept and conclusion proposed in this work.



Figure S13. (a) AFM image and corresponding KPFM potential images under (c) darkness and (d) illumination of $ZnIn_2S_4$. (b) Surface potential curves along the lines in the inset of part under darkness and illumination of $ZnIn_2S_4$.



Figure S14. (a) AFM image and corresponding KPFM potential images under (c) darkness and (d) illumination of MoO_{3-x} . (b) Surface potential curves along the lines in the inset of part under darkness and illumination of MoO_{3-x} .



Figure S15. (a) AFM image and corresponding KPFM potential images under (c) darkness and (d) illumination of MoO₃. (b) Surface potential curves along the lines in the inset of part under darkness and illumination of MoO₃.



Figure S16. (a) AFM image and corresponding KPFM potential images under (c) darkness and (d) illumination of $MoO_3@ZnIn_2S_4$. (b) Surface potential curves along the lines in the inset of part under darkness and illumination of $MoO_3@ZnIn_2S_4$.



Figure S17. (a) photocurrent response curves and (b) PL spectra of $MoO_{3-x}@ZnIn_2S_4$ series photocatalysts.



Figure S18. (a) photocurrent response curves, (b) transient photocurrent density curves and (c) PL spectra of as-prepared different samples.

Discussion: The transient photocurrent response curves (Figure S17a and S18a) show a significant enhancement in the current density of the heterojunctions as compared to those of MoO₃, MoO_{3-x} and ZnIn₂S₄ under visible light irradiation. Notably, the photocurrent densities of the MoO_{3-x}@ZnIn₂S₄ series are all higher than that of MoO₃@ZnIn₂S₄ (2.095 μ A cm⁻²), and the photocurrent density of MoO_{3-x}@ZnIn₂S₄-2 (5.348 μ A cm⁻²) is the largest, which indicates that the introduction of the plasmonic MoO_{3-x} has contributed to a great improvement in the transfer and separation of photoinduced charge carriers. In addition, according to Figure S18b, it can be observed that MoO_{3-x}, MoO₃ and ZnIn₂S₄ show spike photocurrent response at the instant of lighting on, which indicates the presence of rapid decay of photoexcited hot-electrons in plasmonic MoO_{3-x} and severe recombination of photogenerated carriers in MoO₃ and ZnIn₂S₄.¹⁹ While the photocurrent of MoO₃@ZnIn₂S₄ and plasmonic MoO_{3-x}@ZnIn₂S₄-2 increases with the light irradiation until it is saturated, which proves the construction of heterojunction promotes the effective separation of photoexcited carriers. Notably, the saturation photocurrent density of plasmonic MoO_{3} - $_{x}$ @ZnIn₂S₄-2 is larger than that of MoO₃@ZnIn₂S₄, which is attributed to the suppression of photoexcited hot-electron decays, resulting in the increase of carrier concentration.

The PL spectra (Figure S17b and S18c) shows that the PL signals of all the heterojunctions are significantly quenched compared with those of the pristine samples, and the lowest PL signals are observed for $MoO_{3-x}@ZnIn_2S_4-2$, implying the rapid transfer of photo-excited electrons from MoO_{3-x} to $ZnIn_2S_4$ and the effective suppression of carrier recombination by the constructed heterojunctions, which is also in good agreement with the results of TPV.



Figure S19. The representative fs-TA kinetics (excitation at 300 nm, probing at 570 nm) recorded on (a) MoO₃ and (b) MoO_{3-x}.


Figure S20. (a) TPV relaxation curves. (b) Maximum charge extraction time, (c) Charge extraction efficiency, (d) attenuation constant and (e) the comparison of A_{eff} from TPV for different photocatalysts.

Discussion: Apart from the fast interfacial charge transfer and effective spatial separation of photogenerated carriers, the efficient extraction is also crucial to ensure the excellent photocatalytic activity. Time-resolved photoluminescence (TPV) measurements were conducted to gain further insights into the kinetics of interfacial charge surface extraction processes in plasmonic MoO_{3-x}@ZnIn₂S₄-2 heterojunctions. As demonstrated in Figure S20a, a significant increase on the surface photovoltage is observed in plasmonic MoO_{3-x}@ZnIn₂S₄-2 and is higher than that of the other samples, suggesting a higher efficiency of carrier transfer at the interface. The maximum charge extraction time (t_{max}, i.e., the time taken for the transient photovoltage to reach its maximum value) can be applied to evaluate the rate of electron extraction. As shown in Figure S20b, the t_{max} of MoO_{3-x}@ZnIn₂S₄-2 (t_{max1}=0.0026 ms) is much smaller than that of MoO₃@ZnIn₂S₄ (t_{max2}=0.0038 ms) and ZnIn₂S₄ (t_{max1}=0.0049 ms), implying that the LSPR-excited ultrafast hot-electron transfer makes MoO_{3-x}@ZnIn₂S₄-2 to possess the fastest charge carrier extraction rate. The integral area (A) of the region consisting of the photovoltage versus the time axis in TPV represents the maximum amount of charge that can be extracted from the sample, which is also

referred to as the charge extraction efficiency. Figure S20c displays that the charge extraction efficiency of MoO_{3-x}@ZnIn₂S₄-2 (A₃=0.0759) is greater than that of MoO₃@ZnIn₂S₄ (A₂=0.0662) and ZnIn₂S₄ (A₁=0.0682), suggesting that the localized electromagnetic field enhancement enables the heterojunction to have the highest amount of charge extraction. The attenuation constant (τ) of TPV relaxation curves was used to estimate the rate of charge recombination process. As shown in Figure S20d, the τ of MoO_{3-x}@ZnIn₂S₄ (0.0753 ms) is obviously shorter than that of ZnIn₂S₄ (0.0770 ms) and MoO₃@ZnIn₂S₄ (0.0787 ms), which proves that the formation of plasmonic heterojunction decelerated the charge recombination process. Eventually, the effective surface charge transfer kinetics. As demonstrated in Figure S20e, the A_{eff} of MoO_{3-x}@ZnIn₂S₄-2 is the highest, which implies that LSPR-interface in MoO_{3-x}@ZnIn₂S₄-2 can accelerate the kinetics of photogenerated carrier transfer, thereby extracting more electrons and holes for participation in the photocatalytic reaction.



Figure S21. Measurement curves of (a) BDA and (c) BBA tested by the gas chromatography. Standard curves of (b) BDA and (d) BBA with gas chromatography.



Figure S22. Time-dependent production of different products for $MoO_{3-x}@ZnIn_2S_4$ series photocatalysts under Vis-NIR (>420 nm) light irradiation: (a) H₂, (b) BDA, (c) BBA and (d) C-N coupling products. (e) H₂ and C-N coupled products generation rate for $MoO_{3-x}@ZnIn_2S_4$ heterojunction series.



Figure S23. Time-dependent production of different products for different photocatalysts under Vis-NIR (>420 nm) light irradiation: (a) H₂, (b) BDA, (c) BBA and (d) C-N coupling products.

Discussion: As exhibited in Figure S23, the yields of both H₂ and C-N coupling products for different photocatalysts increased linearly with irradiation time. Plasmonic MoO_{3-x} x @ZnIn₂S₄-2 heterojunction exhibited superior photoactivity to both ZnIn₂S₄ and MoO_{3-x} for both H₂ evolution and C-N coupling of benzylamine and presented the highest photocatalytic activity with a production rate of 52.35 mmol g⁻¹ h⁻¹ for H₂ and 21.98 mmol g⁻¹ h⁻¹ for C-N coupled products (including BDA: 15.90 mmol g⁻¹ h⁻¹ and BBA: 6.09 mmol g⁻¹ h⁻¹), which are approximately 7.78 and 6.84 times higher than the pristine ZnIn₂S₄ (H₂: 6.73 mmol g⁻¹ h⁻¹, C-N coupling products: 3.21 mmol g⁻¹ h⁻¹), respectively. Only trace amounts of H₂ and C-N coupling products were produced by pure MoO_{3-x} under light irradiation, which can be attributed to the fact that most of hot-electrons and hot-holes prefer to recombine within the catalyst rather than participate in redox reactions. Although

there is a small amount of H_2 production from $ZnIn_2S_4$ in the photocatalytic process, the yield of BBA is higher than that of BDA, which is probably due to the fact that photogenerated electrons are not only involved in the production of H₂, but also combine with H₂ to reduce the generated BDA. Ultimately, the excess production of BBA also inhibits the rate of H₂ evolution and results in a reduction in overall photocatalysis efficiency for $ZnIn_2S_4$. Subsequently, the MoO₃@ZnIn₂S₄ heterojunction with the same surface coverage was carried out as a comparison sample for photocatalytic performance testing to explore the role of plasmonic MoO_{3-x} in the catalytic system. As shown in Figure S23 and Figure 4a, the pristine MoO_3 nanobelts displayed negligible product yields, whereas when MoO₃@ZnIn₂S₄ heterojunctions were formed, the production rates of H₂ and C-N coupling products of benzylamine were significantly enhanced, up to 26.21 and 9.86 mmol g⁻¹ h⁻¹, respectively. It reveals that the construction of heterojunction can improve the spatial separation efficiency of photogenerated carriers to achieve the spatial decoupling of redox reactions, thus enhancing photocatalysis activity. However, the overall photocatalytic coupling reaction performance of MoO₃@ZnIn₂S₄ is still much lower than that of plasmonic MoO_{3-x}@ZnIn₂S₄-2, which implies that the ultrafast hot-electron direct transfer of massive LSPR-excited hot-electrons induced by MoO_{3-x} under the near-field enhancement effect provided by the LSPR-interface is irreplaceable for improving the performance of photocatalytic C-N coupling of benzylamine coupled with H₂ evolution.

Specifically, it should be noted that although the photoexcited electrons in ZnIn₂S₄ nanosheets do not participate in the interface transfer process, it does not mean that they possess better reaction efficiency. For the single semiconductor material (ZnIn₂S₄), the photogenerated electrons and holes exist in the same space, so they are more likely to be recombined, which leads to the inefficient utilization of the photoexcited electrons. It is well known that the photocatalytic reaction efficiency is not only associated with the transport rate of photoexcited electrons, but also inseparable from their quantity. Therefore, when ZnIn₂S₄ is combined with plasmonic MoO_{3-x}, it not only realizes the ultrafast spatiotemporal separation of photoexcited electrons and holes, but also helps to introduce massive high-energy hot-electrons to participate in the photocatalytic reaction.



Figure S24. (a) Time-dependent production of H₂ and BDA for $ZnIn_2S_4$ and MoO_{3-x}@ZnIn₂S₄-2 when BBA is used as a substrate. (b) Time-dependent production of H₂ and BBA for ZnIn₂S₄ and MoO_{3-x}@ZnIn₂S₄-2 when BDA is used as a substrate.

Discussion: The reason for the two products from the benzylamine C-N coupling reaction can be explained by the presence of BBA dehydrogenation and BDA hydrogenation. As seen in Figure S24, the photocatalytic BBA dehydrogenation ability is improved after the combination of ZnIn₂S₄ and MoO_{3-x}, but at the same time the BDA hydrogenation efficiency is also enhanced. For pristine ZnIn₂S₄, the BDA yield is low because the system is constantly hydrogen producing by water splitting, thus limiting the BBA dehydrogenation reaction. In the case of the BDA hydrogenation reaction, the H₂ produced by water splitting is used to hydrogenate BDA, thus making the production of H₂ and BBA to be mutually restrained, which leads to a low performance of both reactions. It can be assumed that the reaction mechanism of C-N coupling in the benzylamine oxidation coupled with hydrogen evolution of heterojunctions may proceed through two simultaneous reaction paths, benzylamine to BBA and benzylamine to BDA, with a certain amount of inter-conversion of the two products.



Figure S25. Wavelength-dependent AQEs of $MoO_{3-x}@ZnIn_2S_{4}-2$ with the optical absorption spectra superimposed for comparison.

Discussion: To evaluate the light utilization efficiency, the wavelength-dependent AQEs of plasmonic MoO_{3-x}@ZnIn₂S₄₋₂ heterojunction were determined by measuring the H₂ production rates under different monochromatic light irradiation. As shown in Figure S25 and Table S7, the AQEs of MoO_{3-x}@ZnIn₂S₄₋₂ heterojunction first decreased and then increased as the wavelength of the monochromatic light increased. Notably, the trend of the determined AQEs is in good agreement with the light absorption spectrum of MoO_{3-x}@ZnIn₂S₄₋₂, which indicates a relatively high utilization efficiency of incident light. In addition, under monochromatic light irradiation at 420 nm and 700 nm, the AQEs were calculated to be 12.56% and 11.26%, respectively, which still exhibits an excellent light utilization efficiency compared with the results of existing literature studies (Table S8).



Figure S26. Time-dependent production of different products for $MoO_{3-x}@ZnIn_2S_4-2$ under different experimental conditions or in the presence of the different trapping species: (a) H₂, (b) BDA, (c) BBA and (d) C-N coupling products.

Discussion: In order to elucidate the mechanisms and affecting factors behind the two halfreactions, controlled experiments under different conditions were performed (Figure 4b and Figure S26). Firstly, no detectable H₂ or C-N coupling products was observed over $MoO_{3-x}@ZnIn_2S_4-2$ in the absence of catalysts or illumination, verifying that both catalysts and light source are necessary to trigger the reaction. It can be discovered that the H₂ evolution rate (11.64 mmol g⁻¹ h⁻¹) is reduced to one-fifth and the production of C-N coupling products (12.47 mmol g⁻¹ h⁻¹) is also significantly suppressed in the absence of water. Water in the coupling reaction can act as a proton mediator to accelerate proton migration or facilitating the adsorption and activation of substrates containing amino groups on the catalyst surface through hydrogen-bonding interaction.²⁰ When benzylamine was absent from the reaction system, the H₂ evolution was greatly limited (269.78 µmol g⁻¹ h⁻¹), from which it can be seen that the consumption of photogenerated holes promotes the electron to participate in the H_2 production via overall water splitting. Subsequently, with an equal amount of triethanolamine (TEOA) in place of benzylamine, it was observed that the H_2 production rate was improved over the absence of any hole sacrificial agent, but was drastically reduced compared to the presence of benzylamine, indicating that benzylamine has a greater electron donation capacity.

Capture experiments were implemented to investigate the reactive species in photocatalytic coupling reaction. Specifically, with the addition of Na₂S₂O₈ as an electron (e⁻) capture agent in the reaction system, the H₂ evolution activity in water splitting was significantly reduced, and the hydrogen was mainly derived from the C-N coupling reaction of benzylamine, which was also suppressed. The presence of Na₂S/Na₂SO₃ as a hole (h⁺) capture agent almost completely prevented the generation of C-N coupling products, but facilitated the evolution of H₂ from H₂O. When isopropanol (IPA) was added to capture \cdot OH, there was a decrease in the photocatalytic production performance of both H₂ and C-N coupled products for MoO_{3-x}@ZnIn₂S₄-2. These results suggest that both e⁻ and h⁺ play vital and major roles in the photocatalytic C-N coupling of benzylamine coupled with H₂ evolution, and \cdot OH is the secondary active species.



Figure S27 Temperature mapping images under Vis-NIR light irradiation ($\lambda \ge 420$ nm) during the real reaction process of photocatalytic benzylamine C-N coupling integrated with H₂ evolution for (a) ZnIn₂S₄, (b) MoO₃@ZnIn₂S₄ and (c) MoO_{3-x}@ZnIn₂S₄-2.



Figure S28. Time-dependent production of different products for $MoO_{3-x}@ZnIn_2S_{4-2}$ under different experimental conditions: (a) H₂, (b) BDA, (c) BBA and (d) C-N coupling products. (e) H₂ and C-N coupled products generation rate for $MoO_{3-x}@ZnIn_2S_{4-2}$ under different experimental conditions.

Discussion: As shown in Figure S27, the dispersion temperature in the photocatalytic coupling reaction system of plasmonic $MoO_{3-x}@ZnIn_2S_{4-2}$ heterojunction was increased from 26.6 °C to 41.8 °C after 3 h of irradiation, whereas for $ZnIn_2S_4$ and $MoO_3@ZnIn_2S_4$, the final temperature reached 39.8 and 40.9 °C under the same conditions, respectively. The small difference in temperature change among the three systems implies that the plasmon-induced photothermal effect may not be the leading factor in enhancing the performance of photocatalytic coupling reaction in our study. Subsequently, the system temperature was kept at about 42 °C and the benzylamine C-N coupling integrated with H₂ evolution test was carried out under darkness. Figure S28 shows that only trace amounts of H₂, BDA and BBA were detected, which is convincing evidence that thermal effect cannot promote photocatalytic H₂ evolution integrated with benzylamine C-N coupling in the plasmonic $MoO_{3-x}@ZnIn_2S_4$ -2 heterojunction photocatalyst system.



Figure S29. Sample characterizations of MoO_{3-x}+ZnIn₂S₄ and other as-prepared catalysts: (a) XRD pattern, (b) SEM image, (c) UV-Vis-NIR DRS pattern, and (d) PL spectra.



Figure S30. Time-dependent production of different products for $MoO_{3-x}+ZnIn_2S_4$ under Vis-NIR (>420 nm) light irradiation: (a) H₂, (b) BDA, (c) BBA and (d) C-N coupling products. (e) H₂ and C-N coupled products generation rate for $MoO_{3-x}+ZnIn_2S_4$.

Discussion: A new set of hybridized samples (MoO_{3-x}+ZnIn₂S₄) were prepared by mixing MoO_{3-x} and ZnIn₂S₄ (mass ratio: 1:1) via simple physical grinding. Then, their structural characterization and photocatalytic benzylamine C-N coupling integrated with hydrogen evolution reaction measurements were carried out to explore the effect of heterojunction formation on electron transfer. From the XRD patterns, SEM images and UV-Vis-NIR DRS pattern of the hybridized samples (Figure S30a-c), it can be clearly seen that MoO_{3-x} and ZnIn₂S₄ had been homogeneously mixed together, but it did not form the morphology of ZnIn₂S₄ nanosheets wrapped around MoO_{3-x} nanobelts. The photoluminescence spectra (Figure S30d) shows that MoO_{3-x}+ZnIn₂S₄, and its emission peak of PL is significant PL quenching in contrast to MoO_{3-x} and ZnIn₂S₄ heterojunction and plasmonic MoO_{3-x}@ZnIn₂S₄-2 heterojunction, which indicates that simple physical mixing without heterojunction formation is not effective in inhibiting the recombination of photogenerated charge carriers. Subsequently, the photocatalytic benzylamine C-N coupling integrated with hydrogen evolution for MoO_{3-x}+ZnIn₂S₄ hybrid was carried out. As depicted in Figure S30e, the

yields of H₂ and benzylamine C-N coupling products for $MoO_{3-x}+ZnIn_2S_4$ hybrid were much lower than those for $MoO_3@ZnIn_2S_4$ and plasmonic $MoO_{3-x}@ZnIn_2S_4-2$ heterojunction under the same catalytic reaction conditions, which strongly illustrates that simple physical grinding and mixing cannot enhance the photocatalytic activity.



Figure S31. SEM images of (a) Au NPs/ZnIn₂S₄, (c) Ag NPs/ZnIn₂S₄, (e) Pt NPs/ZnIn₂S₄, (g) Pd NPs/ZnIn₂S₄ and (i) Ru NPs/ZnIn₂S₄. TEM images of (b) Au NPs/ZnIn₂S₄, (d) Ag NPs/ZnIn₂S₄, (f) Pt NPs/ZnIn₂S₄, (h) Pd NPs/ZnIn₂S₄ and (j) Ru NPs/ZnIn₂S₄.



Figure S32. (a) XRD patterns and (b) UV-Vis-NIR DRS pattern for hybrids of $ZnIn_2S_4$ decorated with plasma noble metal (Au, Ag, Pt, Pd, and Ru) nanoparticles. (c) Enlarged view of the circled portion of each sample in (b).



Figure S33. XPS spectra of Au NPs/ZnIn₂S₄: (a) survey spectra, and high-resolution spectra for (b) Au 4f and Zn 3p, (c) Zn 2p, (d) In 3d and (e) S 2p.



Figure S34. XPS spectra of Ag NPs/ZnIn₂S₄: (a) survey spectra, and high-resolution spectra for (b) Ag 3d, (c) Zn 2p, (d) In 3d and (e) S 2p.



Figure S35. XPS spectra of Pt NPs/ZnIn₂S₄: (a) survey spectra, and high-resolution spectra for (b) Pt 4f, (c) Zn 2p, (d) In 3d and (e) S 2p.



Figure S36. XPS spectra of Pd NPs/ZnIn₂S₄: (a) survey spectra, and high-resolution spectra for (b) Pd 3d, (c) Zn 2p, (d) In 3d and (e) S 2p.



Figure S37. XPS spectra of Ru NPs/ZnIn₂S₄: (a) survey spectra, and high-resolution spectra for (b) Ru 3d, (c) Zn 2p, (d) In 3d and (e) S 2p.



Figure S38. Time-dependent production of different products for hybrids of $ZnIn_2S_4$ decorated with plasma noble metal (Au, Ag, Pt, Pd, and Ru) nanoparticles under Vis-NIR (>420 nm) light irradiation: (a) H₂, (b) BDA, (c) BBA and (d) C-N coupling products. (e) EPR spectra of DMPO-•C_a⁺ for different samples after 10 minutes under illumination.

Discussion: Cheap and easy availability is the economic advantage of plasmonic non-noble metal semiconductors to be invested in large-scale industrial production over noble metal photocatalysts. To demonstrate the high cost-effectiveness of plasmonic MoO_{3-x}@ZnIn₂S₄-2 heterojunctions for photocatalytic production as well as their possibility of replacing noble metal catalysts, hybrids of ZnIn₂S₄ decorated with plasmonic noble metal (Au, Ag, Pt, Pd, and Ru) nanoparticles were prepared and applied to photocatalytic coupling reaction under the same conditions. SEM images, TEM images, XRD patterns and UV-Vis-NIR DRS spectra (Figure S31-32) show that these hybrids possess pure phases and exhibit corresponding specific LSPR absorption. In addition, XPS (Figure S33-37) provided evidence that Au, Ag, Pt, Pd, and Ru were all present in the form of zero-valent nanoparticles, which further illustrated the successful fabrication of noble metal nanoparticles decorated on ZnIn₂S₄ nanosheets. For the performance test of photocatalytic benzylamine oxidation coupled with H₂ evolution (Figure S38a-d), it can be clearly seen that the overall reaction efficiency of Pt NPs/ZnIn₂S₄ is the best among the five noble metal

nanoparticles loaded on ZnIn₂S₄, but the yields of both C-N coupling products and H₂ are much lower than those for plasmonic MoO_{3-x}@ZnIn₂S₄-2. Additionally, Figure S38e displays that the EPR signals of reaction intermediate (carbon-centered radicals) in noble metal nanoparticle-modified ZnIn₂S₄ are all weaker than those in plasmonic MoO_{3-x}@ZnIn₂S₄-2, which is consistent with the generation rate of C-N coupling products. The above results suggest that plasmonic MoO_{3-x}@ZnIn₂S₄-2 possess superior photocatalytic activity and are expected to replace the noble metal plasmonic hybrid catalysts in reducing the cost of photocatalytic coupling reactions and fulfilling the requirements for reliable commercial applications.



Figure S39. SEM images of (a) Bi NPs/ZnIn₂S₄ and (b) Cu NPs/ZnIn₂S₄. TEM images of (c) Bi NPs/ZnIn₂S₄ and (d) Cu NPs/ZnIn₂S₄. (e) XRD patterns and (f) UV-Vis-NIR DRS pattern for hybrids of ZnIn₂S₄ decorated with non-noble metal (Bi and Cu) nanoparticles.



Figure S40. Time-dependent production of different products for hybrids of $ZnIn_2S_4$ decorated with non-noble metal (Bi and Cu) nanoparticles under Vis-NIR (>420 nm) light irradiation: (a) H₂, (b) BDA, (c) BBA and (d) C-N coupling products. (e) H₂ and C-N coupled products generation rate for Bi NPs/ZnIn₂S₄ and Cu NPs/ZnIn₂S₄.

Discussion: As shown in Figure S39, SEM images, TEM images, XRD patterns and UV-Vis-NIR DRS spectra indicated that Bi NPs/ZnIn₂S₄ and Cu NPs/ZnIn₂S₄ had pure phases and exhibited the corresponding specific LSPR absorptions, which demonstrated the successful loading of non-noble metal Bi and Cu nanoparticles on ZnIn₂S₄ nanosheets. Subsequently, we conducted performance tests for photocatalytic benzylamine oxidation integrated with H₂ evolution of Bi NPs/ZnIn₂S₄ and Cu NPs/ZnIn₂S₄ under the same conditions. As illustrated in Figure S40, it can be clearly seen that the overall reaction efficiencies of both Bi NPs/ZnIn₂S₄ and Cu NPs/ZnIn₂S₄ are far lower than those of MoO₃₋ x@ZnIn₂S₄-2, and the yields of both H₂ and C-N coupling products fail to be enhanced compared to those of pristine ZnIn₂S₄. These results indicate that ZnIn₂S₄ loaded with plasmonic non-noble metal nanoparticle has no advantage in enhancing photocatalytic activity.



Figure S41. (a) Measurement curves for standard samples of ammonium ions and byproduct (NH₃) tested by the high-performance ion chromatography. (b) Standard curve of NH₄⁺ with high-performance ion chromatography and the amount of by-product NH₃ produced in the photocatalysis for 1h on MoO_{3-x}@ZnIn₂S₄-2.

Discussion: During the photocatalytic reaction, NH_3 will be present as a by-product. We utilized the flowing atmosphere (Ar) to carry all the gases produced during the reaction into dilute hydrochloric acid solution to collect NH_3 . Then, the amount of NH_3 was detected by ion chromatograph to be approximately 22.06 mmol g⁻¹ h⁻¹ (Figure S41), which is close to the total amount of C-N coupling products. This result clearly demonstrates the redox molar balance of product formation.



Figure S42. (a) Mass spectra of H_2 , HD and D_2 generated from D_2O and BA on plasmonic $MoO_{3-x}@ZnIn_2S_4-2$. (b) Concentration percentage of H_2 , HD and D_2 in the produced hydrogen. (c) Mass spectra of H_2 , HD and D_2 generated from D_2O and BA on different photocatalysts

Discussion: To further clarify the proton source of produced hydrogen, isotope-labeling photocatalytic experiments were carried out. As shown in Figure S42, the main gas products are H₂, HD and D₂ when replacing H₂O with D₂O, which indicates that both benzylamine and water can act as proton contributors. The lower quantities D₂ may be due to the heavier atomic mass of deuterium, which weakens its reactivity.²¹ Moreover, these mass spectra also illustrate the signal of the by-product NH₃ accompanied by its isotopic species. Whereas the structures of C-N coupling products in liquid phase can be detected by mass spectrometry spectroscopy (Figure S43), which indicates the actual occurrence of photocatalytic coupling reaction.



Figure S43. Mass spectra analyses for the liquid products in the reaction bottle after 1h: (a) BA, (b) BDA and (c) BBA.



Figure S44. Nitrogen absorption-desorption isotherms at 77 K for (a) ZnIn₂S₄, (b) MoO₃, (c) MoO_{3-x}, (d) MoO₃@ZnIn₂S₄ and (e) MoO_{3-x}@ZnIn₂S₄-2. The insets show the pore size distribution of the samples.

Discussion: Generally, catalysts with a large specific surface area have more active centers on the surface, which is conducive to the activation of reactants. In order to investigate the specific surface area and pore size distribution of samples, nitrogen (N₂) adsorptiondesorption isotherm tests (Figure S44) were performed. The Brunauer-Emmett-Teller specific surface areas of MoO_{3-x}@ZnIn₂S₄-2 and MoO₃@ZnIn₂S₄ were calculated to be 74.74 and 75.36 m² g⁻¹, respectively, which were much larger than that of pure ZnIn₂S₄ (36.36 m² g⁻¹), MoO₃ (9.37 m² g⁻¹) and MoO_{3-x} (10.76 m² g⁻¹). In contrast, the mesoporous structures in heterojunctions are more abundant than that in pure samples, which will promote fast mass transfer during H₂ evolution.



Figure S45. LSV curves for H₂ evolution reaction.

Discussion: Furthermore, the linear scanning volumetry (LSV) of electrocatalytic H_2 evolution reaction (Figure S45) exhibits that the overpotential of MoO_{3-x}@ZnIn₂S₄-2 is smaller than that of the other samples, which indicates that the introduction of plasmonic semiconductors into heterojunction can significantly boost the kinetics of H_2 generation.



Figure S46. Zeta potential for different photocatalysts.

Discussion: Meanwhile, Figure S46 shows that the zeta potentials of $ZnIn_2S_4$, MoO₃, MoO₃-, MoO₃@ZnIn₂S₄ and MoO_{3-x}@ZnIn₂S₄-2 were -2.0, 22.7, 16.3, -7.3, and -11.3 mV, respectively. Due to the electrostatic interaction between the catalyst surface and the amino group, the more negatively charged the sample surface is, the more favorable the adsorption of benzylamine is. The improvement of the specific surface structure as well as chargenegativity of MoO_{3-x}@ZnIn₂S₄-2 are beneficial to promote the adsorption of reactants and thus improve the photocatalytic performance.



Figure S47. In-situ EPR spectra of $MoO_{3-x}@ZnIn_2S_4-2$ in presence of DMPO and benzylamine in acetonitrile/H₂O under Vis-NIR light irradiation.



Figure S48. In-situ DRIFTS on MoO_{3-x}@ZnIn₂S₄-2 under darkness.

Discussion: In-situ diffuse reflectance infrared Fourier-transform spectroscopy (DRFTS) measurements were carried out using a synchrotron radiation source to unravel the photocatalytic mechanism of benzylamine C-N coupling. After 45 min adsorption of benzylamine and water over $MoO_{3-x}@ZnIn_2S_4-2$ in the dark, the surface of $MoO_{3-x}@ZnIn_2S_4-2$ reached a saturated adsorption state and a series of vibrational bands can be identified (Figure S48): the broad bands between 3680 and 3200 cm⁻¹ due to the stretching vibrations of hydroxyl (v(-OH)) and amidogen groups(v(N-H)), the broad feature in the region of 3140-3000 cm⁻¹ due to C-H stretching vibration of phenyl group (v(C-H)), peaks at 2933, 2907 and 2875 cm⁻¹ due to the C-H symmetric and antisymmetric stretching vibrations of methylene, peaks at 1605 and 1585 cm⁻¹ due to the -NH₂ bending vibration (δ (-NH₂)) of benzylamine and peaks at 1515, 1500, 1465, 1435 and 1380 cm⁻¹ assigned to C-C stretching vibrations of the aromatic ring (v(C-C)).²²⁻²⁷ The intensity of these vibrational bands grew with adsorption time. Furthermore, the peaks at 1220 cm⁻¹ assigned to -NH₂ rocking vibration (ρ (-NH₂)) increased with time.²⁶ The same tendency was

observed for the bands in the region of 1200-1100 cm⁻¹ corresponding to C-N stretching vibrations.^{26,27}



Figure S49. Schematic diagram of the mechanism for photocatalytic dehydrogenation and C-N coupling of benzylamine on $MoO_{3-x}@ZnIn_2S_4-2$.


Figure S50. Schematic diagram of the mechanism for photocatalytic dehydrogenation and C-N coupling of benzylamine on $MoO_3@ZnIn_2S_4$.



Figure S51. Schematic diagram of the mechanism for photocatalytic dehydrogenation and C-N coupling of benzylamine on ZnIn₂S₄.



Figure S52. Schematic diagram of the mechanism for photocatalytic dehydrogenation and C-N coupling of benzylamine on MoO_{3-x}.



Figure S53. Schematic diagram of the mechanism for photocatalytic H_2 evolution integrated with C-N coupling of benzylamine on plasmonic MoO_{3-x}@ZnIn₂S₄-2.

Discussion: In terms of the aforementioned results, a feasible mechanism for photocatalytic H₂ evolution integrated with C-N coupling of benzylamine over MoO_{3-x} $@ZnIn_2S_4-2$ heterojunction is proposed in Figure S53. Under Vis-NIR irradiation, the construction of the S-scheme heterojunction and the introduction of LSPR effect make plenty of electrons aggregate on the CB of ZnIn₂S₄, while holes with high oxidability accumulate on the VB of MoO_{3-x}. As a result, spatial decoupling of the oxidation and reduction reactions is realized. The protons are reduced to H₂ on ZnIn₂S₄, while benzylamine molecules are activated and oxidized on MoO_{3-x}. Firstly, benzylamine molecules are activated by holes on MoO_{3-x} to generate nitrogen-cationic radicals as the active intermediate, and then the holes further acquire protons from nitrogen-cationic radicals to release the *NH intermediates. Finally, after multiple steps of dehydrogenation, a C-N coupling reaction is performed to produce BBA and BDA and evolve NH₃ molecule.

Part of the BBA and BDA may also be interconverted by dehydrogenation and hydrogenation reactions.



Figure S54. Sample characterizations of $MoO_{3-x}@ZnIn_2S_4-2$ after four cyclic tests for photocatalytic C-N coupling of benzylamine coupled with H₂ evolution: (a) XRD pattern, (b) SEM image, (c) TEM image, and (d) UV-Vis-NIR DRS pattern.



Figure S55. XPS spectra of $MoO_{3-x}@ZnIn_2S_4-2$ after four cyclic tests for photocatalytic C-N coupling of benzylamine coupled with H₂ evolution: (a) survey spectra, and high-resolution spectra for (b) Mo 3d, (c) O 1S, (d) Zn 2p, (e) In 3d and (f) S 2p.

3. Tables

Element		Spectra			Binding en	Binding energy (eV)		
		line	MoO ₃	MoO _{3-x}	ZnIn ₂ S ₄	MoO3@ZnIn2S4	MoO _{3-x} @ ZnIn ₂ S ₄ -2	
	M0 ⁶⁺	3d5/2	233.01	232.99		231.97	232.85	
	1010	3d _{3/2}	236.19	236.14		235.15	236.00	
Mo	Mo ⁵⁺	3d5/2		231.82			231.06	
	1,10	3d _{3/2}		234.93		234.17 229.16	234.17	
	Mo ⁴⁺	3d5/2				229. 232.	229.16	
		3d _{3/2}					232.28	
0		O-Mo	530.92	530.79		530.64	530.25	
		Ov		531.34			531.23	
		Oads.		532.45		532.54	532.68	
	Zn	2p _{3/2}			1022.01	1022.13	1022.15	
ZIII		2p _{1/2}			1045.09	1045.21	1045.23	
In		3d _{5/2}			444.88	445.02	445.00	
		3d _{3/2}			452.47	452.61	452.59	
S		2p _{3/2}			161.62	161.81	161.82	
		2p _{1/2}			162.74	162.93	162.94	

Table S1. Detailed high-resolution XPS spectra data of different samples.

Sample	Ecutoff (eV)	Φ (eV)	EF (eV)
ZnIn ₂ S ₄	37.15	2.85	-2.85
МоОз-х	36.51	3.49	-3.49
МоОз	36.67	3.33	-3.33
MoO _{3-x} @ZnIn ₂ S ₄ -2	36.89	3.11	-3.11
MoO3@ZnIn2S4	37.05	2.95	-2.95

Table S2. Detailed data for E_{cutoff} , Φ and E_f of different samples calculated from UPS spectra.

The cut-off energy ($E_{cut-off}$) of the secondary electrons for all samples was obtained by ultraviolet photoelectron spectroscopy (UPS). Then the surface work function (Φ), which can theoretically predict the interfacial electron migration in heterojunctions. was calculated via the formula: Φ =hv- $E_{cut-off}$ (hv=40 eV). As shown in Figure 2d and Table S2, the surface work functions of MoO₃, MoO_{3-x} and ZnIn₂S₄ are calculated to be 3.33, 3.49, and 2.85 eV, respectively. As a result, when MoO₃ or MoO_{3-x} is contacted with ZnIn₂S₄, the energy band of ZnIn₂S₄ will be bent downward, whereas those of MoO_{3-x} and MoO₃ will be bent upward driven by the surface work function difference until their Fermi energy levels are flattened. At this point, the electrons of ZnIn₂S₄ are transferred to MoO_{3-x} or MoO₃, resulting in the formation of a strong interfacial electric field pointing from ZnIn₂S₄ to MoO_{3-x} and MoO₃, which is consistent with the XPS results.

Element		Speetro line —	Binding e	Binding energy (eV)		
	ement	Spectra nne	Dark	Light		
	NA - 6+	3d5/2	232.85	232.95		
	MO	3d _{3/2}	236.00	236.10		
Ма	N# - 5+	3d5/2	231.06	231.26		
NIO	Mo ⁵⁺	3d _{3/2}	234.17	234.37		
	Mo ⁴⁺	3d5/2	229.16	229.31		
		3d _{3/2}	232.28	232.43		
0		O-Mo	530.25	530.34		
		Ov	531.23	531.44		
		O _{ads.}	532.68	532.68		
	7	2p _{3/2}	1022.15	1021.99		
	211	2p _{1/2}	1045.23	1045.07		
In		3d5/2	445.00	444.89		
		3d _{3/2}	452.59	452.48		
S		2p _{3/2}	161.82	161.65		
		2p _{1/2}	162.94	162.77		

Table S3. Detailed high-resolution XPS spectra data for plasmonic MoO3-x@ZnIn2S4-2under dark and illumination.

Element		Spectro line —	Binding er	nergy (eV)
Ele	ement	Spectra line —	Dark	Light
	NA - 6+	3d _{5/2}	231.97	232.02
	MO	3d _{3/2}	235.15	235.20
Ма	N#~5+	3d _{5/2}		230.66
IVIO	MIO	3d _{3/2}		233.77
	Mo ⁴⁺	3d _{5/2}		
		3d _{3/2}		
0		O-Mo	530.64	530.82
		Ov		531.67
		O _{ads} .	532.54	532.55
	7	2p _{3/2}	1022.13	1022.02
	Zn	2p _{1/2}	1045.21	1045.09
In		3d5/2	445.02	444.94
		3d _{3/2}	452.61	452.53
S		2p _{3/2}	161.81	161.75
		2p _{1/2}	162.93	162.87

Table S4. Detailed high-resolution XPS spectra data for non-plasmonic $MoO_3@ZnIn_2S_4$ under dark and illumination.

Sample	Α	t _{max} .	τ	A _{eff.}
ZnIn ₂ S ₄	0.0682	0.0049	0.0770	1.0717
MoO ₃ @ZnIn ₂ S ₄	0.0662	0.0038	0.0787	1.3710
MoO _{3-x} @ZnIn ₂ S ₄ -2	0.0759	0.0026	0.0753	2.1982

Table S5. Detailed data for A, $t_{max.}$, τ and $A_{eff.}$ of different samples tested by TPVmeasurements.

Table S6. Fitting results of fs-TA kinetics recorded on MoO₃ and MoO_{3-x} (Figure S19). The average lifetime is calculated according to $\tau_{ave} = (A_1\tau_1^2 + A_2\tau_2^2)/(A_1\tau_1 + A_2\tau_2)$, where the A_1 and A_2 values are given in the parentheses.

Sample	τ1 (ps)	τ ₂ (ps)	τ _{ave} (ps)
MoO ₃	$2.56 \pm 0.17 \ (55.9\%)$	368 ± 19 (44.1%)	365 ± 19
МоОз-х	$1.06 \pm 0.05 \ (82.5\%)$	167 ± 12 (17.5%)	162 ± 12

Wavelength (nm)	Light intensity (mW cm ⁻²)	H2 yield (µmol h ⁻¹)	AQE (%)
420	17.8	148.32	12.56
450	16.5	107.27	9.15
500	14.6	75.55	6.55
600	6.5	57.92	9.40
700	3.7	46.05	11.26

Table S7. The AQE data of plasmonic $MoO_{3-x}@ZnIn_2S_4$ at different wavelengths.

Note: Catalyst mass:10 mg; Irradiation area: 10.5 cm².

Table S8. Comparison of the photocatalytic H₂ evolution integrated with benzylamine oxidation performance over different photocatalysts.

Entry	Catalyst	Reaction conditions	H ₂ generation rate (mmol g ⁻¹ h ⁻¹)	AQE (%)	C-N coupling products generation rate (mmol g ⁻¹ h ⁻¹)	Ref.
1	MoO _{3-x} @ZnIn ₂ S ₄ -2	300 uL benzylamine 10 mg catalyst 10 mL acetonitrile, 200 uL H ₂ O λ > 420 nm (300 W)	52.35	12.56 (420 nm) 11.26 (700 nm)	21.98	This work
2	MoO ₃ @ZnIn ₂ S ₄	300 uL benzylamine 10 mg catalyst 10 mL acetonitrile, 200 uL H ₂ O λ > 420 nm (300 W)	26.21	6.75 (420 nm)	9.86	This work
3	Pt/PCN-777	0.457 mmol benzylamine (50 uL) 10 mg catalyst 5 mL of DMF, 5 uL of H ₂ O Full spectrum (300 W)	0.33	/	0.47	28
4	EBCN (Embedded edge and bridge units in the carbon nitride framework)	10 mL benzylamine 20 mg catalyst, 1 mL H ₂ PtCl ₆ (1 mg L ⁻¹) 50 mL H ₂ O Full spectrum (300 W)	2.27	3.45 (420 nm)	3.42	29
5	$\frac{2D/2D}{Ti_3C_2T_x/CdS}$	 0.5 mmol benzylamine 10 mg catalyst 5 mL DMF, 2.5 mmol H₂O λ > 420 nm (300 W) 	0.22	/	0.16	30
6	CoP@ZnIn ₂ S ₄	 3.5 mmol benzylamine 10 mg catalyst 20 mL H₂O/acetonitrile solution λ > 400 nm (300 W) 	3.85	1.1 (400 nm) 0.03 (500 nm)	3.82	31
7		200 uL benzylamine 10 mg catalyst 20 mL acetonitrile $\lambda > 400$ nm (300 W)	11.10	/	10.20	20
7	Pd SA/Zhin ₂ 54	200 uL benzylamine 10 mg catalyst 20 mL acetonitrile, 0.5 mL H ₂ O λ > 400 nm (300 W)	16.20	/	13.00	32
8	Z-scheme BaTiO ₃ @ZnIn ₂ S ₄	 400 uL benzylamine 20 mg catalyst 20 mL acetonitrile, 0.5 mL H₂O λ > 400 nm (300 W) 	8.04	/	5.59	33
9	2.0 wt% Pt/CdS/Fe ₂ O ₃	 3.0 mmol benzylamine 25 mg catalyst 30 mL DMF, 3 mL H₂O λ > 420 nm (300 W) 	15.81	18.1 (420 nm)	12.93	34

10	Ni/CdS	2.0 mmol benzylamine 4 mg catalyst 10 mL DMF $\lambda > 420$ nm (300 W)	49.2	44 (420 nm)	BA conversion: 99% (5 h)	35
11	PCN-3 (C ₃ N _{5.4})	10 mL benzylamine 20 mg catalyst 50 mL H ₂ O Full spectrum (300 W)	22.20	14.7 (420 nm) 8.6 (450 nm) 5.9 (500 nm)	41.70	36
12	$In_{4/3}P_2Se_6$	 0.2 mmol benzylamine 20 mg catalyst 20 mL acetonitrile, 100 uL H₂O λ > 300 nm (300 W) 	0.06	/	0.04	37
13	Pd@TiO2@ZnIn2S4	100 uL benzylamine 20 mg catalyst 10 mL acetonitrile, 100 uL H ₂ O Full spectrum (300 W)	5.35	/	11.43	38
14	Pd _{SA+C} /TiO ₂ -V _O	0.5 mL benzylamine 10 mg catalyst 50 mL DMF, 0.5 mL H ₂ O Full spectrum (200 mW·cm ² Xe lamp)	0.59	3.94 (365 nm)	0.26	26
15	Ni/CdS	55 uL benzylamine 10 mg catalyst 5 mL acetonitrile, 300 uL H ₂ O λ > 420 nm (300 W)	12.94	10.8 (420 nm) 11.2 (450 nm)	45.12	39
16	PdS/CdS/MoS ₂	1 mL benzylamine 40 mg catalyst 40 mL DMF, 40 mL H ₂ O $\lambda > 420$ nm (300 W)	6.163	/	BA conversion: 67% (10 h)	40

4. Supporting References

- 1. G. Kresse, J. Furthmüller, Comp. Mater. Sci. 1996, 6, 15-50.
- 2. P. E. Blöchl, Phys. Rev. B 1994, 50, 17953-17979.
- 3. K. Burke, M. Ernzerhof, J. P. Perdew, Phys. Rev. Lett. 1997, 78, 1396.
- 4. Y. Zhang, S. Park, Appl. Catal. B: Environ. 2019, 240, 92-101.
- 5. Y. Zhang, S. Park, J. Mater. Chem. A 2018, 6, 20304-20312.
- X. Liu, L. Yang, M. Huang, Q. Li, L. Zhao, Y. Sang, X. Zhang, Z. Zhao, H. Liu, W. Zhou, *Appl. Catal.* B: Environ. 2022, **319**, 121887.
- 7. S. Patnaik, G. Swain, K. M. Parida, Nanoscale 2018, 10, 5950-5964.
- 8. J. Peng, J. Shen, X. Yu, H. Tang, Zulfiqar, Q. Liu, Chinese J. Catal. 2021, 42, 87-96.
- S. Zhang, X. Liu, C. Liu, S. Luo, L. Wang, T. Cai, Y. Zeng, J. Yuan, W. Dong, Y. Pei, Y. Liu, ACS Nano 2018, 12, 751-758.
- M. Tan, C. Huang, C. Yu, C. Li, R. Yin, C. Liu, W. Dong, H. Meng, Y. Su, L. Qiao, L. Gao, Q. Lu, Y. Bai, *Small* 2022, 18, 2205266.
- 11. C. Wang, C. Lv, X. Sun, F. Huang, W. Wu, C. Li, J. Zhang, S. Li, Appl. Surf. Sci. 2023, 616, 156601.
- 12. B. A. Goodman, M. V. Cheshire, Nature 1982, 299, 618-620.
- 13. S. Xie, H. Zhang, G. Liu, X. Wu, J. Lin, Q. Zhang, Y. Wang, Chinese J. Catal. 2020, 41, 1125-1131.
- 14. V. J. Keast, J. Electron Spectrosc. 2005, 143, 97-104.
- 15. X. Jiang, J. Huang, Z. Bi, W. Ni, G. Gurzadyan, Y. Zhu, Z. Zhang, Adv. Mater. 2022, 34, 2109330.
- H. Wu, X. Li, Y. Cheng, Y. Xiao, R. Li, Q. Wu, H. Lin, J. Xu, G. Wang, C. Lin, X. Chen, Y. Wang, J. Mater. Chem. A 2020, 8, 2827
- 17. H. Su, H. Lou, Z. Zhao, L. Zhou, Y. Pang, H. Xie, C. Rao, D. Yang, X. Qiu, *Chem. Eng. J.* 2022, **430**, 132770.
- 18. F. Xing, R. Zeng, C. Cheng, Q. Liu, C. Huang, Appl. Catal. B 2022, 306, 121087.
- X. Liu, L. Yang, M. Huang, Q. Li, L. Zhao, Y. Sang, X. Zhang, Z. Zhao, H. Liu, W. Zhou, *Appl. Catal.* B 2022, **319**, 121887.
- Q. Wei, C. Yu, X. Song, Y. Zhong, L. Ni, Y. Ren, W. Guo, J. Yu, J. Qiu, J. Am. Chem. Soc. 2021, 143, 6071-6078.
- B. Wu, L. Zhang, B. Jiang, Q. Li, C. Tian, Y. Xie, W. Li, H. Fu, Angew. Chem. Int. Ed. 2021, 60, 4815-4822.
- 22. S. Furukawa, Y. Ohno, T. Shishido, K. Teramura, T. Tanaka, J. Phys. Chem. C 2013, 117, 442-450.
- R. M. Pinto, M. Guerra, G. Copeland, R. I. Olariu, P. Rodrigues, M. T. Barros, M. L. Costa, A. A. Dias, *J. Phys. Chem. A* 2015, **119**, 4118-4126.
- 24. M. A. Leich, N. M. Mackie, K. L. Williams, E. R. Fisher, *Macromolecules* 1998, 31, 7618-7626.
- 25. S. Wei, H. Zhong, H. Wang, Y. Song, C. Jia, M. Anpo, L. Wu, *Appl. Catal. B: Environ.* 2022, **305**, 121032.
- 26. T. Wang, X. Tao, X. Li, K. Zhang, S. Liu, B. Li, Small 2021, 17, 2006255.
- J. Chen, H. Wang, Z. Zhang, L. Han, Y. Zhang, F. Gong, K. Xie, L. Xu, W. Song, S. Wu, J. Mater. Chem. A 2019, 7, 5493-5503.
- 28. H. Liu, C. Xu, D. Li, H. Jiang, Angew. Chem. Int. Ed. 2018, 57, 5379-5383.
- 29. M. Song, X. Deng, G. Li, Q. Wang, H. Peng, P. Chen, S. Yin, J. Mater. Chem. A 2022, 10, 16448-16456.

- H. Wang, P. Hu, J. Zhou, M. B. J. Roeffaers, B. Weng, Y. Wang, H. Ji, J. Mater. Chem. A 2021, 9, 19984-19993.
- 31. W. Liu, Y. Wang, H. Huang, J. Wang, G. He, J. Feng, T. Yu, Z. Li, Z. Zou, *J. Am. Chem. Soc.* 2023, **145**, 7181-7189.
- 32. P. Wang, S. Fan, X. Li, J. Wang, Z. Liu, Z. Niu, M. O. Tadé, S. Liu, Nano Energy 2022, 95, 107045.
- 33. P. Wang, S. Fan, X. Li, J. Wang, Z. Liu, C. Bai, M. O. Tadé, S. Liu, Nano Energy 2021, 89, 106349.
- 34. X. Liu, D. Dai, Z. Cui, Q. Zhang, X. Gong, Z. Wang, Y. Liu, Z. Zheng, H. Cheng, Y. Dai, B. Huang and P. Wang, ACS Catal. 2022, 12, 12386-12397.
- 35. Y. Huang, C. Liu, M. Li, H. Li, Y. Li, R. Su, B. Zhang, ACS Catal. 2020, 10, 3904-3910.
- 36. Q. Wang, X. Deng, H. Pen, F. Liu, M. Song, P. Chen, S. Yin, Nano Res. 2023, 16, 4225-4232.
- B. Wu, X. Zhan, P. Yu, J. Meng, M. G. Sendeku, F. T. Dajan, N. Gao, W. Lai, Y. Yang, Z. Wang, F. Wang, *Nanoscale* 2022, 14, 15442-15450.
- P. She, J. Qin, J. Sheng, Y. Qi, H. Rui, W. Zhang, X. Ge, G. Lu, X. Song, H. Rao, Small 2022, 18, 2105114.
- 39. W. Yu, D. Zhang, X. Guo, C. Song, Z. Zhao, Catal. Sci. Technol. 2018, 8, 5148-5154.
- 40. B. Sun, J. Zheng, D. Yin, H. Jin, X. Wang, Q. Xu, A. Liu, S. Wang, Appl. Surf. Sci. 2022, 592, 153277.