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Selective conversion of CO₂ to CH₄ enhanced by WO₃/In₂O₃ S-scheme heterojunction photocatalysts with efficient CO₂ activation†

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Solar-powered CO₂ reduction is a promising approach for mitigating the energy crisis and environmental issues. However, its efficiency is hindered by challenges including difficult CO₂ activation, rapid charge recombination, and uncontrollable selectivity. Here, we develop WO₃/In₂O₃ S-scheme heterojunction photocatalysts by depositing In₂O₃ nanoparticles onto WO₃ nanosheets for CO₂ photoreduction. The Fermi level difference triggers electron transfer upon coupling, generating an internal electric field pointing from In₂O₃ to WO₃ at the interface. This impels oriented charge transfer and effective separation of the powerful photoinduced carriers. With the unique S-scheme mechanism and the efficient activation of CO₂ molecules on the In₂O₃ surface, the resulting WO₃/In₂O₃ heterostructures exhibit enhanced CO₂ photoreduction performance with ~53.7% selectivity for CH₄, without any molecule cocatalyst or scavenger. *In situ* irradiation X-ray photoelectron spectroscopy, *in situ* diffuse reflectance infrared Fourier transform spectroscopy, along with density functional theory simulations are conducted to elucidate the photocatalytic and CO₂-reduction mechanism, and the enhanced CH₄-selectivity.

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1. Introduction

Recently, the incessant combustion of fossil fuels has led to a substantial increase in atmospheric carbon dioxide (CO₂) concentration, causing grave environmental pollution and concerns about energy scarcity.^{1–9} To tackle these issues, a promising strategy is the photocatalytic reduction of CO₂ to valuable solar fuels driven by abundant, clean, and inexhaustible sunlight.^{10,11} Nevertheless, the linear CO₂ molecules exhibit thermodynamic stability with a high dissociation energy of the C=O bond (~750 kJ mol⁻¹), making their adsorption and activation onto the catalyst surface challenging.^{12,13} Additionally, the CO₂ photoreduction process is intricate and involves multiple photoelectron transfer, which leads to diverse reduction products, including CO, CH₄, CH₃OH, *etc.*, with unpredictable selectivity. Although CH₄, the major component of

natural gas, has the lowest reduction potential among all the products (−0.24 V vs. NHE), it requires eight photoelectrons, making it more difficult to produce than others from a kinetic perspective. Although a variety of photocatalysts have been reported for CO₂ reduction to CH₄,^{14–21} most still suffer from uncontrollable selectivity and low conversion efficiency. Thus, designing highly active photocatalysts with efficient CO₂ activation and high CH₄ selectivity is still a daunting task.

Indium oxide (In₂O₃) is a popular reduction photocatalyst with a high conduction band level, narrow band gap (~2.8 eV) and visible light absorption.^{22,23} It has been reported that stable CO₂ molecules can be highly activated on the In₂O₃ surface to enhance CO₂ photoreduction activity, but the selectivity of CH₄ has not been modulated.²² In addition, the recombination of photogenerated carriers in unitary In₂O₃ occurs more readily than transferring to the catalyst surface to participate in photoreactions, leading to poor photocatalytic performance.^{24,25} Therefore, the development of In₂O₃-based heterojunction photocatalysts that enable efficient spatial separation of electron/hole pairs and selective CO₂-to-CH₄ conversion enhancement is desirable but challenging.

Coupling two semiconductors to fabricate an S-scheme heterojunction offers tremendous potential in augmenting photoactivity, owing to the effective separation of photogenerated carriers and their robust redox capability.^{8,26–28} Generally, S-scheme heterojunctions are constituted of oxidation and reduction photocatalysts. The variance in their Fermi levels

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elicits electron transfer upon contact, thereby resulting in the bending of energy bands and the creation of an internal electric field (IEF) at their interface. As a consequence of the bent bands, IEF, and coulombic attraction, the futile photogenerated electrons in the oxidation photocatalyst and the holes in the reduction photocatalyst amalgamate, accomplishing the efficient spatial separation of charge carriers with adequate redox ability to boost the photocatalytic performance.^{29–32} Tungsten trioxide (WO₃) is an oxidation photocatalyst that exhibits visible-light response and potent oxidizing ability, attributable to its narrow band gap (2.4–2.8 eV) and positive valence band position.^{33,34} Given the interweaved band structures and disparity in work functions, the combination of In₂O₃ with WO₃ might engender a desirable S-scheme heterojunction photocatalyst with anticipated charge separation, strong redox ability, and heightened CO₂ activation, thereby enhancing CO₂ photo-reduction performance.^{22,35,36}

Herein, we synthesized WO₃/In₂O₃ S-scheme heterojunction photocatalysts by depositing In₂O₃ nanoparticles on WO₃ nanosheets through an immersion-annealing technique. Compared to pure WO₃, the resulting WO₃/In₂O₃ heterostructures revealed elevated selectivity in the conversion of CO₂ into CH₄ (53.7%) and enhanced CO₂ reduction efficiency without any molecular cocatalyst or scavenger. Such superior performance was ascribed to the S-scheme charge transfer mechanism and the effective CO₂ activation on the In₂O₃ surface, which were verified through *in situ* irradiation X-ray photoelectron spectroscopy (XPS), time-resolved photoluminescence spectroscopy (TRPL), density functional theory (DFT) calculation and temperature-programmed desorption of CO₂ (CO₂-TPD). *In situ* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) and theoretical simulations were also employed to elucidate the CO₂ reduction mechanism and the potential causes for the high selectivity of CH₄. Our work may present a novel perspective for designing exceptional S-scheme heterojunction photocatalysts that facilitate efficient CO₂ activation and improved selective CO₂-to-CH₄ conversion.

2. Experimental details

2.1 Synthesis of WO₃·H₂O nanosheets

Typically, a total of 3.6 mmol of sodium tungstate dihydrate (Na₂WO₄·2H₂O) and 3.0 mL of tetrafluoroboric acid (HBF₄, 40 wt%) were dissolved in 60 mL of deionized water. The resulting light-yellow solution was transferred to a 100 mL Teflon-lined stainless autoclave and reacted at 100 °C for 12 h. Upon completion of the reaction, yellow precipitates were centrifuged and washed with deionized water and ethanol for three times, followed by drying at 80 °C in an oven to obtain the WO₃·H₂O nanosheets.

2.2 Preparation of WO₃/In₂O₃ heterostructures

A certain amount of indium nitrate (In(NO₃)₃·4H₂O) was added to a 30 mL aqueous solution containing 200 mg of WO₃·H₂O nanosheets. The mixture was magnetically stirred for 2 h, followed by drying in an oven at 90 °C. The resulting solid products

were annealed in air at 500 °C for 2 h, with a heating rate of 2 °C min⁻¹. The obtained WO₃/In₂O₃ heterostructures were labelled as WI_x (*x* = 5, 10 and 15), where W and I represent WO₃ and In₂O₃ respectively; *x* is the molar ratio of In₂O₃ in WO₃/In₂O₃ nano-hybrids.

3. Results and discussion

3.1 Activation and photoreduction of CO₂ over WO₃/In₂O₃ heterojunctions

The adsorption and activation of CO₂ molecules on catalysts were first investigated by DFT calculations since they are essential steps for CO₂ photoreduction. Fig. 1a and b show that when CO₂ is adsorbed onto the In₂O₃ surface, the O=C=O bond is visibly bent at an angle of 129.33°, and the bond length is stretched in comparison with free CO₂ molecules (1.16 Å). Both the C and O atoms of CO₂ form chemical bonds with the O and In atoms of In₂O₃. Moreover, In₂O₃ donates 0.2 electrons to CO₂ when CO₂ adsorbs on In₂O₃ (Fig. 1c), which is further supported by the planar-averaged charge density difference along the Z direction as shown in Fig. S1.† The investigation of the CO₂ adsorption capability reveals that pure In₂O₃ and WI10 exhibit stronger CO₂ adsorption compared to pristine WO₃, following the same trend as the N₂ adsorption (Fig. S2 and Table S1†). The CO₂-TPD results demonstrate that pure WO₃, In₂O₃ and WI10 all display desorption peaks at 80–200 °C assigned to the physical adsorption of CO₂ (Fig. 1d).^{37–39} In the temperature range of 400–800 °C, no significant signals are detected over pristine WO₃. However, both pure In₂O₃ and WI10 reveal three prominent desorption peaks corresponding to the decomposition of b-CO₃²⁻ (~450 °C) and m-CO₃²⁻ (550–750 °C) species, suggesting strong chemisorption interactions between CO₂ molecules and In₂O₃.^{40–42} Furthermore, *in situ* DRIFTS spectra obtained after adsorption of CO₂ for 15, 30, 45, and 60 min exhibit distinct peaks of formaldehyde (HCHO) (1750 and 1770 cm⁻¹), monodentate carbonate (m-CO₃²⁻) (1590, 1560 and 1540 cm⁻¹), bidentate carbonate (b-CO₃²⁻) (1425, 1410, 1380, and 1340 cm⁻¹), and bicarbonate (HCO₃⁻) (1180, 1110 and 1030 cm⁻¹) over In₂O₃ and WI10 (Fig. S3†). These results indicate that CO₂ can be chemisorbed and activated by In₂O₃, and In₂O₃ is the preferable active site for CO₂ photoreduction in the heterojunctions.

The photocatalytic performance toward CO₂ reduction was evaluated in an online closed gas-circulation system (OLPCRS-2, Shanghai Boyi Scientific Instrument Co., Ltd) with a quartz reactor under visible light irradiation (Fig. S4†). CO and CH₄ were identified as the reduction products, and O₂ was determined as the oxidation product. Control experiments revealed that no product can be detected in the dark or in the absence of CO₂. As shown in Fig. 1e and f, pristine WO₃ and In₂O₃ both reveal lower production yields of CO and CH₄ due to the rapid recombination of photogenerated charge carriers within the unitary photocatalyst. After coupling WO₃ with In₂O₃, the CO₂ reduction efficiency is enhanced, reaching the highest evolution yield of 6.6 and 5.4 μmol g⁻¹ for CO and CH₄ over WI10. Excessive loading of In₂O₃ nanoparticles on WO₃ nanosheets, *i.e.*, WI15, deteriorates the photocatalytic performance owing to

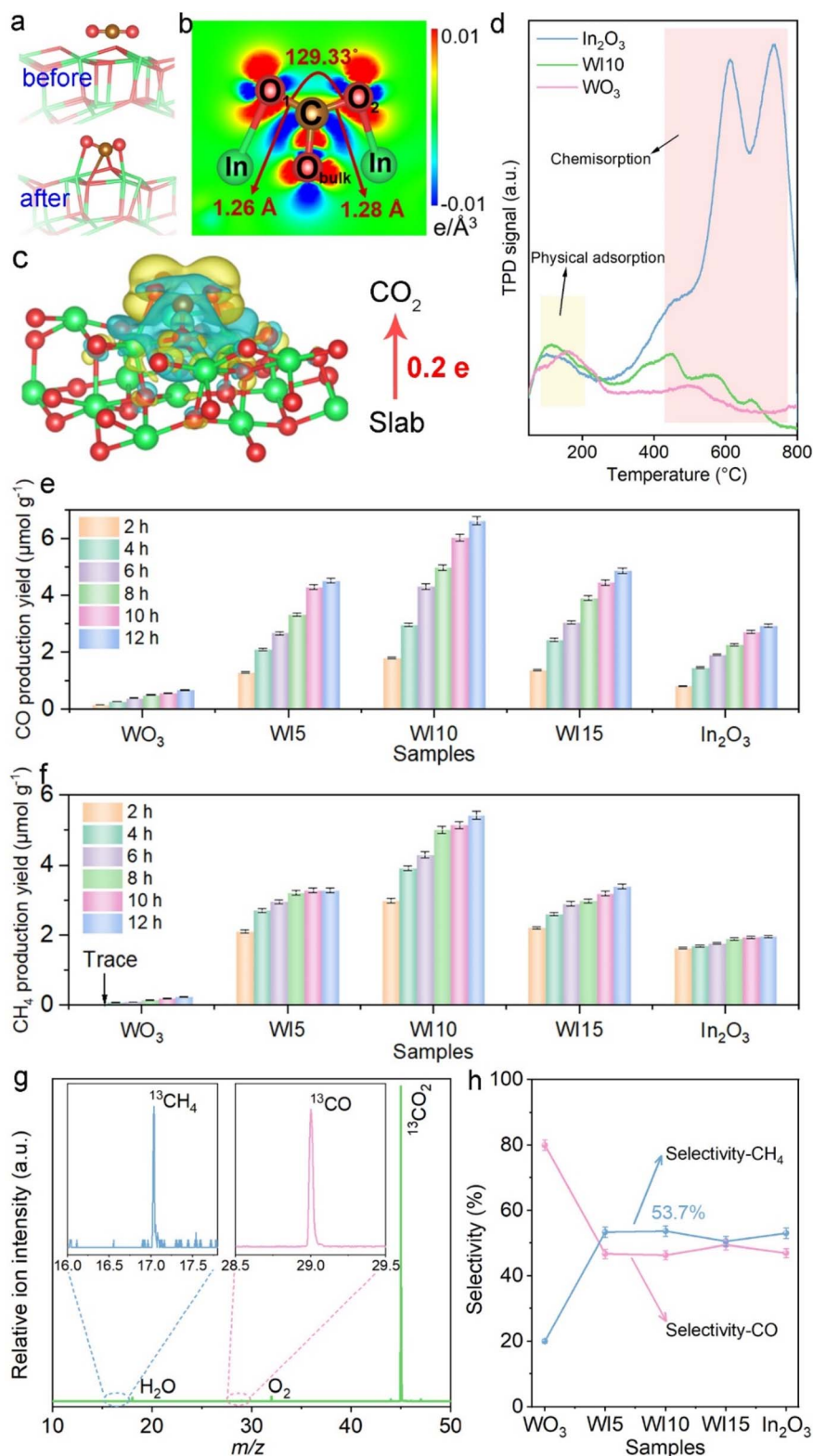


Fig. 1 (a and b) Optimized structure and (c) the corresponding charge density difference images of the CO₂ molecule adsorbed on the In₂O₃ (111) surface. (d) CO₂-TPD spectra of In₂O₃, WI10 and WO₃. Photocatalytic CO₂ reduction activities over WO₃, WI_x, and In₂O₃ during the 12 h experiment performed under visible light irradiation: time course of (e) CO and (f) CH₄ production yields. (g) SVUV-PIMS spectra of the products collected after ¹³CO₂ photoreduction for WI10 at *hν* = 14.2 eV. (h) The selectivity of CO and CH₄ over WO₃, WI_x, and In₂O₃ samples.

the light shielding effect. During CO₂ photoreduction, the photogenerated holes oxidize H₂O to produce O₂ in the absence of sacrificial agents, and the evolution rate of O₂ (Fig. S5†) follows the same tendency as that of CO and CH₄. The apparent quantum efficiency (AQE) of CO₂ photoreduction was measured at different monochromatic wavelengths including 365, 380, 400, 420, 450, and 500 nm over WO₃/In₂O₃ nanohybrids. Clearly, the trend of AQE matches well with the light absorption spectrum of WI10 (Table S2, Fig. S6†), affirming the photocatalytic nature of CO₂ reduction.^{43–45} The synchrotron-radiation vacuum ultraviolet photoionization mass spectrometry (SVUV-PIMS) was employed to disclose the origin of the products by using isotope-labeled carbon dioxide (¹³CO₂) as the substitute source gas. At a photon energy of 14.2 eV, the WO₃/In₂O₃ heterojunctions yield a mixture of ¹³CH₄ (*m/z* = 17) and ¹³CO (*m/z* = 29) as shown in Fig. 1g, which confirms that the evolved reduction products indeed originate from the photoreduction of CO₂ rather than any carbonaceous impurities.⁴⁶

Notably, the selectivity of CH₄ over WO₃/In₂O₃ nanohybrids is higher than that of CO and reaches the maximum of 53.7% over WI10 as revealed in Fig. 1h. In order to uncover the underlying reasons for the high selectivity of CH₄, as well as the reaction mechanism, *in situ* DRIFTS experiments along with DFT calculations were carried out. As shown in Fig. 2a, when CO₂/H₂O is introduced into the system in the dark, peaks of HCHO, m-CO₃²⁻, b-CO₃²⁻ and HCO₃⁻ are detected, strongly

remanifesting the chemisorption of CO₂ on the catalyst surface.^{47,48} Under light irradiation, new adsorption peaks assigned to *COOH (1669 cm⁻¹), *CO (2079 cm⁻¹), *CHO (1012 cm⁻¹), *CH₂O (2855 cm⁻¹) and *CH₃O (1042 and 1181 cm⁻¹) are observed, which are significant intermediates in the conversion of CO₂ to CH₄.^{49–51} Accordingly, a probable CO₂ photoreduction mechanism over WO₃/In₂O₃ composites is proposed as follows, where * stands for the active sites on WO₃/In₂O₃ heterojunctions.

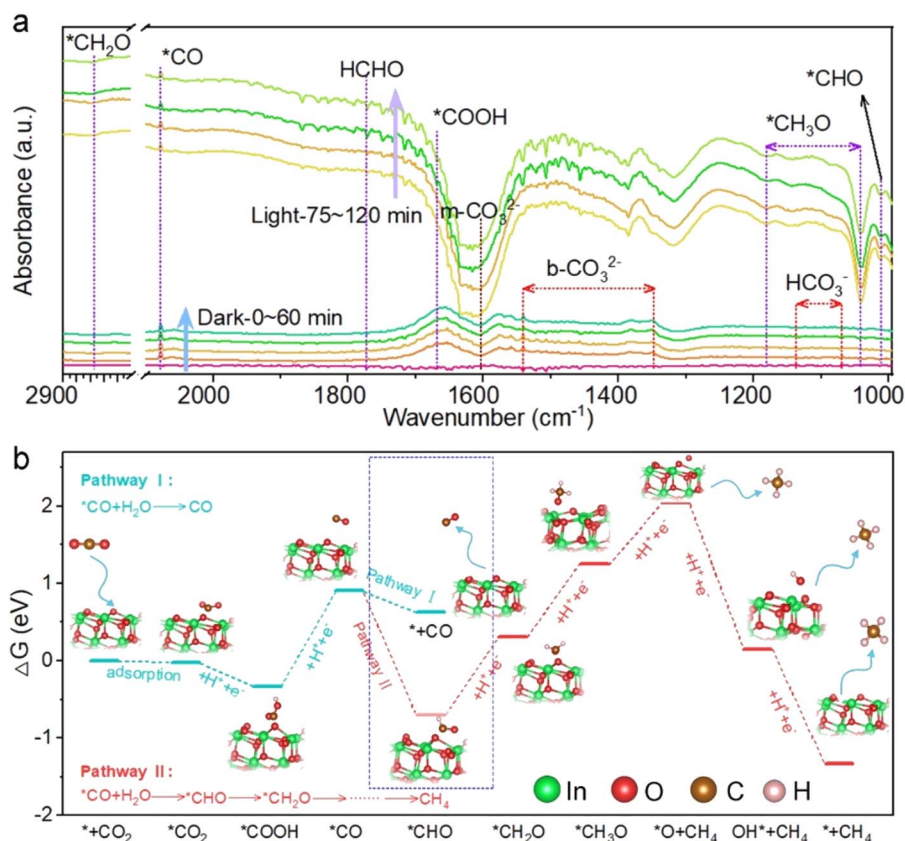
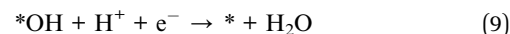
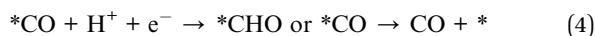
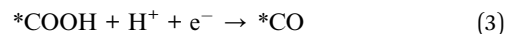


Fig. 2 (a) *In situ* DRIFT spectra of WI10 after adsorption of CO₂/H₂O for 15, 30, 45, and 60 min in the dark, and then under light irradiation for 75, 90, 105, and 120 min. (b) Gibbs free energy diagram of CO₂ photoreduction over the In₂O₃ (111) slab.

Gibbs free energy (ΔG) calculation of CO_2 photoreduction over the In_2O_3 surface was further conducted to confirm the reaction pathway described above, and the results are presented in Fig. 2b. It is worth noting that the change in ΔG for the protonation of $^*\text{CO}$ to $^*\text{CHO}$ (pathway II, -1.61 eV) is much smaller than that for CO desorption from the catalyst surface (pathway I, -0.28 eV), providing a reasonable explanation for the high selectivity of CH_4 during CO_2 photoreduction.⁵² Overall, the strong adsorption and activation of CO_2 molecules on the In_2O_3 surface are critical factors contributing to the enhanced CH_4 selectivity and CO_2 reduction performance.

3.2 Characterization of $\text{WO}_3/\text{In}_2\text{O}_3$ heterojunctions

Structural characterization studies provide additional insights into understanding the boosted photocatalytic activity. The X-

ray diffraction (XRD) pattern of pure WO_3 is consistent with the standard monoclinic phase (JCPDS No. 20-1324), and pristine In_2O_3 is indexed to the cubic phase (JCPDS No. 71-2195), respectively (Fig. S7†). In the WI_x nano hybrids, the intensity of diffraction peaks attributed to In_2O_3 increases with its content (x), indicating the synthesis of $\text{WO}_3/\text{In}_2\text{O}_3$ heterojunctions. The precursor $\text{WO}_3 \cdot \text{H}_2\text{O}$ exhibits uniform square nanosheets with a smooth surface as revealed in the field emission scanning electron microscopy (FESEM) image (Fig. S8†). After dehydration, pristine WO_3 maintains its nanosheet microscopy with some tiny surface wrinkles (Fig. 3a).⁵³ In FESEM and transmission electron microscopy (TEM) images of $\text{WO}_3/\text{In}_2\text{O}_3$ nano hybrids (WI_{10}) (Fig. 3b and c), In_2O_3 nanoparticles are clearly observed to be deposited on the surface of WO_3 nanosheets. The high-resolution TEM image of WI_{10} (Fig. 3d) reveals distinct lattice fringes with spacings of 0.292 and 0.375 nm, indicating the presence of In_2O_3 and WO_3 phases, respectively.

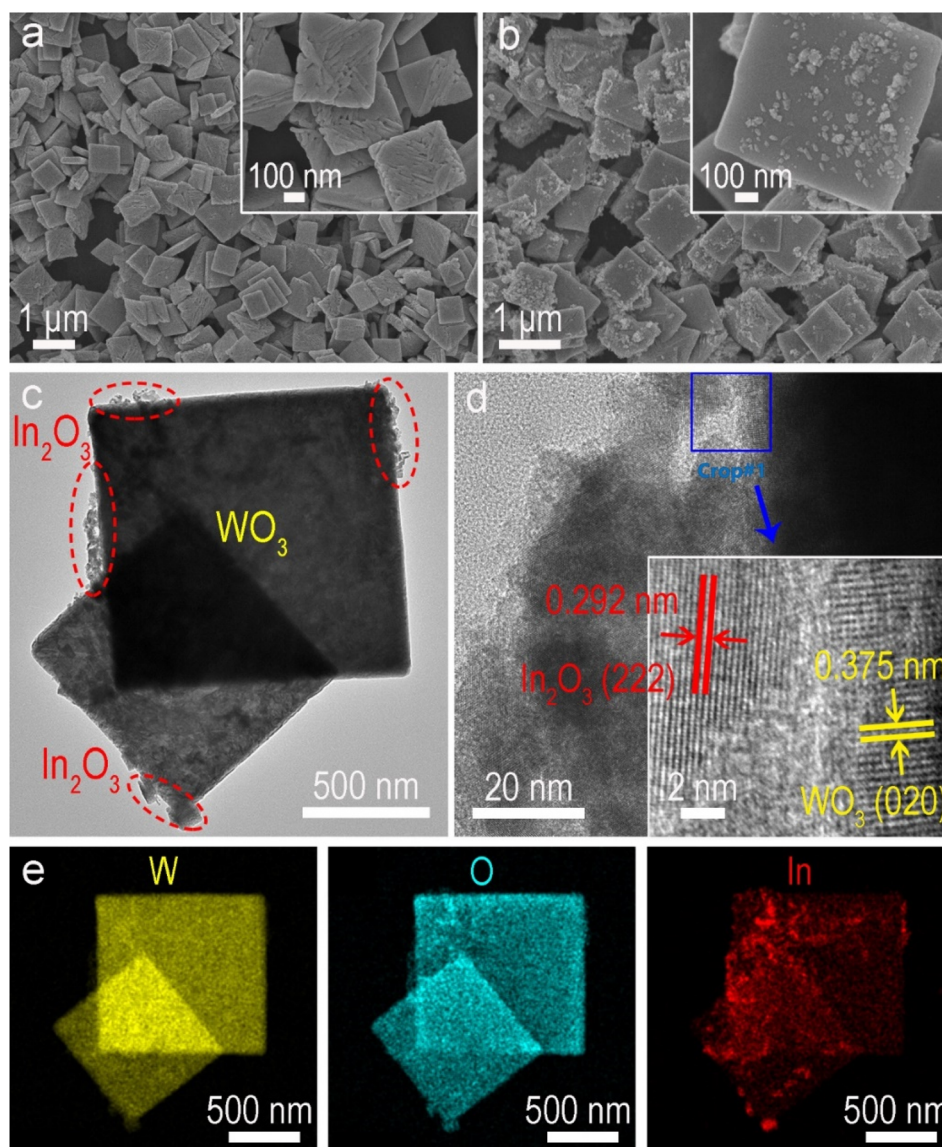


Fig. 3 (a) FESEM image of pure WO_3 nanosheets. (b) FESEM, (c) TEM and (d) HRTEM images of $\text{WO}_3/\text{In}_2\text{O}_3$ nanostructures (WI_{10}). (e) EDX elemental mappings of W, O, and In elements in $\text{WO}_3/\text{In}_2\text{O}_3$ nano hybrids.

corresponding to In_2O_3 (222) and WO_3 (020) planes, respectively. The energy-dispersive X-ray spectroscopy (EDX) elemental mappings of WI10 confirm the existence of W, O and In elements, further affirming the formation of $\text{WO}_3/\text{In}_2\text{O}_3$ nano-hybrids. The phase and morphology of spent WI10 were also evaluated, and there are no detectable changes compared with the fresh sample, indicating substantial photostability of the catalysts (Fig. S9[†]).

UV-vis diffuse reflectance spectroscopy (DRS) was employed to investigate the optical absorption properties of WO_3 , In_2O_3 and WI10. The absorption edges of pure WO_3 and In_2O_3 are located at 470 and 465 nm, respectively, corresponding to the bandgap energies of 2.81 and 2.97 eV (Fig. S10[†]). The light harvesting of WI10 is slightly improved compared to pristine WO_3 , indicating the successful hybridization of WO_3 and In_2O_3 . XPS was carried out to analyze the chemical states and surface

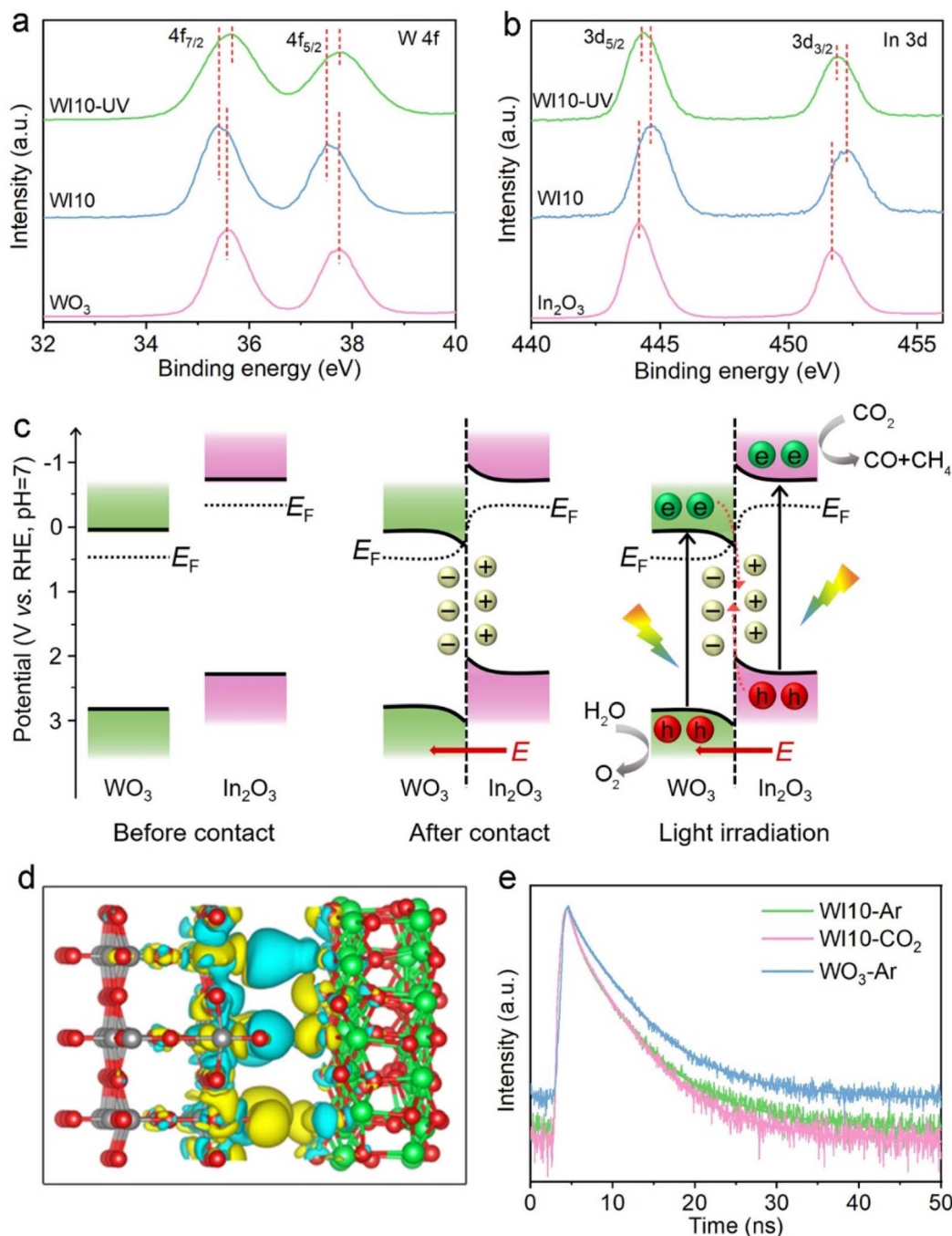


Fig. 4 High-resolution XPS spectra of (a) W 4f, (b) In 3d of WO_3 , In_2O_3 , and WI10. *In situ* irradiation XPS measurement was conducted under UV light irradiation. (c) Schematic illustration of the formation and charge separation of the $\text{WO}_3/\text{In}_2\text{O}_3$ S-scheme heterojunction. (d) The charge density difference of the $\text{WO}_3/\text{In}_2\text{O}_3$ heterojunctions; cyan and yellow regions represent electron depletion and accumulation, respectively; grey, green, and red spheres represent W, In and O atoms, respectively. (e) TRPL spectra of WO_3 and WI10 in different atmospheres.

compositions of the resultant samples. The survey spectrum of WI10 demonstrates the presence of the In element, as well as W and O elements derived from the WO_3 matrix (Fig. S11a†). The W 4f XPS spectra (Fig. 4a) exhibit two distinct peaks at 35.6 and 37.7 eV, corresponding to hexavalent W^{6+} .^{54,55} The binding energies (BEs) of In 3d_{5/2} and In 3d_{3/2} are observed to be 444.2 and 451.7 eV, respectively, confirming the existence of trivalent In^{3+} (Fig. 4b).^{56,57} After the photoreaction, the chemical states of $\text{WO}_3/\text{In}_2\text{O}_3$ heterojunctions exhibit imperceptible changes as manifested by the W 4f and In 3d XPS spectra (Fig. S12†), further confirming the stability of catalysts. The O 1s XPS spectra (Fig. S11b–d†) reveal the presence of lattice oxygen (530.5 eV), adsorbed oxygen (533.2 eV), and surface hydroxyls (531.9 eV) in the samples.⁵⁸ Notably, the BEs of W 4f in WI10 display negative shifts in comparison with those in pure WO_3 , while the peaks of In 3d in WI10 shift positively relative to pure In_2O_3 . Such an intriguing phenomenon suggests the migration of electrons from In_2O_3 to WO_3 upon hybridization, creating an IEF with the direction from In_2O_3 to WO_3 at their interface to facilitate the efficient separation of photogenerated charge carriers (as discussed below).

3.3 Insights into the S-scheme charge separation mechanism

The band structure of WO_3 and In_2O_3 was first investigated to unravel the charge transfer and separation mechanism over $\text{WO}_3/\text{In}_2\text{O}_3$ heterojunctions. The potentials of the VB maximum and CB minimum of WO_3 and In_2O_3 are calculated to be 2.88 and 0.07 V, as well as 2.28 and -0.69 V (vs. RHE), respectively, based on Mott–Schottky plots, valence band XPS spectra (Fig. S13†) and the band gap (Fig. S10b†). According to the electrostatic potentials along the z-axis of WO_3 (001) and In_2O_3 (111) (Fig. S14†), the work function (Φ) of WO_3 and In_2O_3 is estimated to be 6.54 and 5.87 eV, respectively, indicating that In_2O_3 has a higher Fermi level (E_F) than WO_3 . Additionally, the contact potential difference (CPD) between the samples and the standard gold tip of the Kelvin probe instrument reveals that the calculated Φ level of WO_3 is larger than that of In_2O_3 (Fig. S15†), aligning with the DFT results. As a consequence, electrons in In_2O_3 will spontaneously diffuse to WO_3 upon contact until reaching the same E_F at their interface, which will lead to the bending of their energy bands and the creation of an IEF pointing from In_2O_3 to WO_3 (Fig. 4c). The charge density difference of DFT simulation (Fig. 4d) shows that In_2O_3 donates electrons (cyan area) while WO_3 gains electrons (yellow area) at their interface, further confirming the above electron transfer pathway between WO_3 and In_2O_3 .

Under light irradiation, the electrons in WO_3 and In_2O_3 VBs are initially photoexcited to their CBs. Due to the bent bands and IEF, the photogenerated electrons in the WO_3 CB tend to transfer to the In_2O_3 VB and recombine with its holes, indicating the formation of S-scheme heterojunctions between WO_3 and In_2O_3 . Ultimately, the powerful photoelectrons in the In_2O_3 CB and photoholes in the WO_3 VB are reserved to participate in photocatalytic reactions (Fig. 4c). Such an S-scheme charge transfer route not only efficiently separates photoinduced

carriers, but also preserves the strong redox ability of surviving electrons and holes, thereby definitely enhancing CO_2 photo-reduction performance and selectively producing CH_4 .

In situ irradiation XPS was carried out to verify the proposed S-scheme charge transfer pathway within the $\text{WO}_3/\text{In}_2\text{O}_3$ heterostructure. As presented in Fig. 4a and b, the BEs of W 4f shift positively under illumination, while the In 3d BEs show negative shifts with reference to their respective values measured in the dark. These results support the transfer of photogenerated electrons from WO_3 to In_2O_3 and validate the suggested S-scheme photocatalytic mechanism. To gain a better understanding of how charge carriers are transferred in $\text{WO}_3/\text{In}_2\text{O}_3$ heterostructures, TRPL spectra of pure WO_3 and WI10 were collected under different atmospheres. As shown in Fig. 4e and Table S3,† the shorter lifetime (τ_1) of WI10 is only 0.76 ns in an Ar atmosphere, which is shorter than that of pure WO_3 (0.96 ns). This suggests that the photoexcited electrons in WO_3 transfer to In_2O_3 and the radiative recombination is retarded. Consequently, only a small fraction of photoelectrons of WI10 engage in the photocarrier recombination to emit fluorescence, resulting in shorter lifetimes of τ_2 and τ_3 . These results provide further evidence for the S-scheme charge separation mechanism in $\text{WO}_3/\text{In}_2\text{O}_3$ heterojunctions. In addition, the average lifetime (τ_a) of WI10 in a CO_2 atmosphere is shorter compared to that in an Ar atmosphere (3.38 vs. 3.56 ns), which indicates that a great deal of photoinduced electrons in the In_2O_3 CB are delivered to CO_2 molecules for surface photoreduction and fewer photocarriers are involved in detectable recombination.^{59,60} Photoelectrochemical measurements were further conducted to analyze the charge separation efficiency. As shown in Fig. S16,† WI10 displays higher photocurrent density and smaller charge transfer resistance (R_{ct}) as compared with pristine WO_3 , indicating superior electron/hole separation efficiency and lower resistance for charge transfer in the $\text{WO}_3/\text{In}_2\text{O}_3$ S-scheme heterojunctions.^{33,61}

Based on the aforementioned analyses, it is suggested that the combination of WO_3 and In_2O_3 to construct S-scheme heterojunctions can effectively promote charge transfer and reduce electron–hole recombination. In concert with the efficient adsorption and activation of CO_2 molecules on the In_2O_3 surface, the resulting $\text{WO}_3/\text{In}_2\text{O}_3$ S-scheme heterojunctions possess more photoelectrons with high reduction capacity to participate in the CO_2 photoreduction reaction and produce multi-electron products such as CH_4 .

4. Conclusion

To summarize, an S-scheme $\text{WO}_3/\text{In}_2\text{O}_3$ heterojunction photocatalyst was constructed by depositing In_2O_3 nanoparticles on WO_3 nanosheets *via* a facile immersion-annealing method. DFT calculations, CO_2 -TPD and *in situ* DRIFTS revealed that the $\text{WO}_3/\text{In}_2\text{O}_3$ heterostructures displayed efficient chemisorption and activation of CO_2 molecules. The difference in Fermi levels caused electrons to transfer from In_2O_3 to WO_3 , thus forming an IEF and bending the energy bands at the interface, as evidenced by XPS and DFT results. Under light irradiation, photoinduced electrons in the WO_3 CB recombined with the holes in the In_2O_3

VB, driven by the bent bands and IEF, following an S-scheme charge transfer pathway and achieving efficient separation efficiency of powerful photogenerated charge carriers. As a result, the optimized $\text{WO}_3/\text{In}_2\text{O}_3$ heterojunctions exhibited enhanced CO_2 photoreduction performance with $\sim 53.7\%$ selectivity for CH_4 , in the absence of any molecule cocatalyst or scavenger. The CO_2 photoreduction mechanism and underlying reasons for high CH_4 -selectivity were uncovered *via in situ* DRIFTS, along with Gibbs free-energy calculations. This work offers a perspective on designing novel S-scheme heterojunction photocatalysts for efficient CO_2 photoreduction and selective conversion of CO_2 to CH_4 .

Author contributions

Y. H., J. Y., and F. X. conceived and designed the experiments. Y. H. and Z. Y. conducted material synthesis, the characterizations of the materials, and the photocatalytic test. C. L. and Y. P. performed the SVUV-PIMS test. Y. H., J. Y., D. X., W. M., and F. X. contributed to data analysis. Y. H. wrote the manuscript. F. X. supervised the project, performed DFT calculations, and revised the manuscript. All authors discussed the results and commented on the manuscript.

Conflicts of interest

There are no conflicts to declare.

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