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# Selective conversion of CO<sub>2</sub> to CH<sub>4</sub> enhanced by WO<sub>3</sub>/In<sub>2</sub>O<sub>3</sub> S-scheme heterojunction photocatalysts with efficient CO<sub>2</sub> activation†

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Solar-powered CO<sub>2</sub> reduction is a promising approach for mitigating the energy crisis and environmental issues. However, its efficiency is hindered by challenges including difficult CO<sub>2</sub> activation, rapid charge recombination, and uncontrollable selectivity. Here, we develop WO<sub>3</sub>/In<sub>2</sub>O<sub>3</sub> S-scheme heterojunction photocatalysts by depositing In<sub>2</sub>O<sub>3</sub> nanoparticles onto WO<sub>3</sub> nanosheets for CO<sub>2</sub> photoreduction. The Fermi level difference triggers electron transfer upon coupling, generating an internal electric field pointing from In<sub>2</sub>O<sub>3</sub> to WO<sub>3</sub> 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 CO<sub>2</sub> molecules on the In<sub>2</sub>O<sub>3</sub> surface, the resulting WO<sub>3</sub>/In<sub>2</sub>O<sub>3</sub> heterostructures exhibit enhanced CO<sub>2</sub> photoreduction performance with ~53.7% selectivity for CH<sub>4</sub>, 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 CO<sub>2</sub>-reduction mechanism, and the enhanced CH<sub>4</sub>-selectivity.

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## 1. Introduction

Recently, the incessant combustion of fossil fuels has led to a substantial increase in atmospheric carbon dioxide (CO<sub>2</sub>) concentration, causing grave environmental pollution and concerns about energy scarcity.<sup>1–9</sup> To tackle these issues, a promising strategy is the photocatalytic reduction of CO<sub>2</sub> to valuable solar fuels driven by abundant, clean, and inexhaustible sunlight.<sup>10,11</sup> Nevertheless, the linear CO<sub>2</sub> molecules exhibit thermodynamic stability with a high dissociation energy of the C=O bond (~750 kJ mol<sup>-1</sup>), making their adsorption and activation onto the catalyst surface challenging.<sup>12,13</sup> Additionally, the CO<sub>2</sub> photoreduction process is intricate and involves multiple photoelectron transfer, which leads to diverse reduction products, including CO, CH<sub>4</sub>, CH<sub>3</sub>OH, *etc.*, with unpredictable selectivity. Although CH<sub>4</sub>, 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 CO<sub>2</sub> reduction to CH<sub>4</sub>,<sup>14–21</sup> most still suffer from uncontrollable selectivity and low conversion efficiency. Thus, designing highly active photocatalysts with efficient CO<sub>2</sub> activation and high CH<sub>4</sub> selectivity is still a daunting task.

Indium oxide (In<sub>2</sub>O<sub>3</sub>) is a popular reduction photocatalyst with a high conduction band level, narrow band gap (~2.8 eV) and visible light absorption.<sup>22,23</sup> It has been reported that stable CO<sub>2</sub> molecules can be highly activated on the In<sub>2</sub>O<sub>3</sub> surface to enhance CO<sub>2</sub> photoreduction activity, but the selectivity of CH<sub>4</sub> has not been modulated.<sup>22</sup> In addition, the recombination of photogenerated carriers in unitary In<sub>2</sub>O<sub>3</sub> occurs more readily than transferring to the catalyst surface to participate in photoreactions, leading to poor photocatalytic performance.<sup>24,25</sup> Therefore, the development of In<sub>2</sub>O<sub>3</sub>-based heterojunction photocatalysts that enable efficient spatial separation of electron/hole pairs and selective CO<sub>2</sub>-to-CH<sub>4</sub> 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.<sup>8,26–28</sup> 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.<sup>29–32</sup> Tungsten trioxide (WO<sub>3</sub>) 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.<sup>33,34</sup> Given the interweaved band structures and disparity in work functions, the combination of In<sub>2</sub>O<sub>3</sub> with WO<sub>3</sub> might engender a desirable S-scheme heterojunction photocatalyst with anticipated charge separation, strong redox ability, and heightened CO<sub>2</sub> activation, thereby enhancing CO<sub>2</sub> photo-reduction performance.<sup>22,35,36</sup>

Herein, we synthesized WO<sub>3</sub>/In<sub>2</sub>O<sub>3</sub> S-scheme heterojunction photocatalysts by depositing In<sub>2</sub>O<sub>3</sub> nanoparticles on WO<sub>3</sub> nanosheets through an immersion-annealing technique. Compared to pure WO<sub>3</sub>, the resulting WO<sub>3</sub>/In<sub>2</sub>O<sub>3</sub> heterostructures revealed elevated selectivity in the conversion of CO<sub>2</sub> into CH<sub>4</sub> (53.7%) and enhanced CO<sub>2</sub> reduction efficiency without any molecular cocatalyst or scavenger. Such superior performance was ascribed to the S-scheme charge transfer mechanism and the effective CO<sub>2</sub> activation on the In<sub>2</sub>O<sub>3</sub> 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 CO<sub>2</sub> (CO<sub>2</sub>-TPD). *In situ* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) and theoretical simulations were also employed to elucidate the CO<sub>2</sub> reduction mechanism and the potential causes for the high selectivity of CH<sub>4</sub>. Our work may present a novel perspective for designing exceptional S-scheme heterojunction photocatalysts that facilitate efficient CO<sub>2</sub> activation and improved selective CO<sub>2</sub>-to-CH<sub>4</sub> conversion.

## 2. Experimental details

### 2.1 Synthesis of WO<sub>3</sub>·H<sub>2</sub>O nanosheets

Typically, a total of 3.6 mmol of sodium tungstate dihydrate (Na<sub>2</sub>WO<sub>4</sub>·2H<sub>2</sub>O) and 3.0 mL of tetrafluoroboric acid (HBF<sub>4</sub>, 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 WO<sub>3</sub>·H<sub>2</sub>O nanosheets.

### 2.2 Preparation of WO<sub>3</sub>/In<sub>2</sub>O<sub>3</sub> heterostructures

A certain amount of indium nitrate (In(NO<sub>3</sub>)<sub>3</sub>·4H<sub>2</sub>O) was added to a 30 mL aqueous solution containing 200 mg of WO<sub>3</sub>·H<sub>2</sub>O 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<sup>-1</sup>. The obtained WO<sub>3</sub>/In<sub>2</sub>O<sub>3</sub> heterostructures were labelled as WI $x$  ( $x = 5, 10$  and  $15$ ), where W and I represent WO<sub>3</sub> and In<sub>2</sub>O<sub>3</sub> respectively;  $x$  is the molar ratio of In<sub>2</sub>O<sub>3</sub> in WO<sub>3</sub>/In<sub>2</sub>O<sub>3</sub> nano-hybrids.

## 3. Results and discussion

### 3.1 Activation and photoreduction of CO<sub>2</sub> over WO<sub>3</sub>/In<sub>2</sub>O<sub>3</sub> heterojunctions

The adsorption and activation of CO<sub>2</sub> molecules on catalysts were first investigated by DFT calculations since they are essential steps for CO<sub>2</sub> photoreduction. Fig. 1a and b show that when CO<sub>2</sub> is adsorbed onto the In<sub>2</sub>O<sub>3</sub> 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 CO<sub>2</sub> molecules (1.16 Å). Both the C and O atoms of CO<sub>2</sub> form chemical bonds with the O and In atoms of In<sub>2</sub>O<sub>3</sub>. Moreover, In<sub>2</sub>O<sub>3</sub> donates 0.2 electrons to CO<sub>2</sub> when CO<sub>2</sub> adsorbs on In<sub>2</sub>O<sub>3</sub> (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 CO<sub>2</sub> adsorption capability reveals that pure In<sub>2</sub>O<sub>3</sub> and WI10 exhibit stronger CO<sub>2</sub> adsorption compared to pristine WO<sub>3</sub>, following the same trend as the N<sub>2</sub> adsorption (Fig. S2 and Table S1†). The CO<sub>2</sub>-TPD results demonstrate that pure WO<sub>3</sub>, In<sub>2</sub>O<sub>3</sub> and WI10 all display desorption peaks at 80–200 °C assigned to the physical adsorption of CO<sub>2</sub> (Fig. 1d).<sup>37–39</sup> In the temperature range of 400–800 °C, no significant signals are detected over pristine WO<sub>3</sub>. However, both pure In<sub>2</sub>O<sub>3</sub> and WI10 reveal three prominent desorption peaks corresponding to the decomposition of b-CO<sub>3</sub><sup>2-</sup> (~450 °C) and m-CO<sub>3</sub><sup>2-</sup> (550–750 °C) species, suggesting strong chemisorption interactions between CO<sub>2</sub> molecules and In<sub>2</sub>O<sub>3</sub>.<sup>40–42</sup> Furthermore, *in situ* DRIFTS spectra obtained after adsorption of CO<sub>2</sub> for 15, 30, 45, and 60 min exhibit distinct peaks of formaldehyde (HCHO) (1750 and 1770 cm<sup>-1</sup>), monodentate carbonate (m-CO<sub>3</sub><sup>2-</sup>) (1590, 1560 and 1540 cm<sup>-1</sup>), bidentate carbonate (b-CO<sub>3</sub><sup>2-</sup>) (1425, 1410, 1380, and 1340 cm<sup>-1</sup>), and bicarbonate (HCO<sub>3</sub><sup>-</sup>) (1180, 1110 and 1030 cm<sup>-1</sup>) over In<sub>2</sub>O<sub>3</sub> and WI10 (Fig. S3†). These results indicate that CO<sub>2</sub> can be chemisorbed and activated by In<sub>2</sub>O<sub>3</sub>, and In<sub>2</sub>O<sub>3</sub> is the preferable active site for CO<sub>2</sub> photoreduction in the heterojunctions.

The photocatalytic performance toward CO<sub>2</sub> 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 CH<sub>4</sub> were identified as the reduction products, and O<sub>2</sub> was determined as the oxidation product. Control experiments revealed that no product can be detected in the dark or in the absence of CO<sub>2</sub>. As shown in Fig. 1e and f, pristine WO<sub>3</sub> and In<sub>2</sub>O<sub>3</sub> both reveal lower production yields of CO and CH<sub>4</sub> due to the rapid recombination of photogenerated charge carriers within the unitary photocatalyst. After coupling WO<sub>3</sub> with In<sub>2</sub>O<sub>3</sub>, the CO<sub>2</sub> reduction efficiency is enhanced, reaching the highest evolution yield of 6.6 and 5.4 μmol g<sup>-1</sup> for CO and CH<sub>4</sub> over WI10. Excessive loading of In<sub>2</sub>O<sub>3</sub> nanoparticles on WO<sub>3</sub> 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 CO<sub>2</sub> molecule adsorbed on the In<sub>2</sub>O<sub>3</sub> (111) surface. (d) CO<sub>2</sub>-TPD spectra of In<sub>2</sub>O<sub>3</sub>, WI10 and WO<sub>3</sub>. Photocatalytic CO<sub>2</sub> reduction activities over WO<sub>3</sub>, WI<sub>x</sub>, and In<sub>2</sub>O<sub>3</sub> during the 12 h experiment performed under visible light irradiation: time course of (e) CO and (f) CH<sub>4</sub> production yields. (g) SVUV-PIMS spectra of the products collected after <sup>13</sup>CO<sub>2</sub> photoreduction for WI10 at  $h\nu = 14.2$  eV. (h) The selectivity of CO and CH<sub>4</sub> over WO<sub>3</sub>, WI<sub>x</sub>, and In<sub>2</sub>O<sub>3</sub> samples.

the light shielding effect. During CO<sub>2</sub> photoreduction, the photogenerated holes oxidize H<sub>2</sub>O to produce O<sub>2</sub> in the absence of sacrificial agents, and the evolution rate of O<sub>2</sub> (Fig. S5†) follows the same tendency as that of CO and CH<sub>4</sub>. The apparent quantum efficiency (AQE) of CO<sub>2</sub> photoreduction was measured at different monochromatic wavelengths including 365, 380, 400, 420, 450, and 500 nm over WO<sub>3</sub>/In<sub>2</sub>O<sub>3</sub> nanohybrids. Clearly, the trend of AQE matches well with the light absorption spectrum of WI10 (Table S2, Fig. S6†), affirming the photocatalytic nature of CO<sub>2</sub> reduction.<sup>43–45</sup> 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 (<sup>13</sup>CO<sub>2</sub>) as the substitute source gas. At a photon energy of 14.2 eV, the WO<sub>3</sub>/In<sub>2</sub>O<sub>3</sub> heterojunctions yield a mixture of <sup>13</sup>CH<sub>4</sub> (*m/z* = 17) and <sup>13</sup>CO (*m/z* = 29) as shown in Fig. 1g, which confirms that the evolved reduction products indeed originate from the photoreduction of CO<sub>2</sub> rather than any carbonaceous impurities.<sup>46</sup>

Notably, the selectivity of CH<sub>4</sub> over WO<sub>3</sub>/In<sub>2</sub>O<sub>3</sub> 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 CH<sub>4</sub>, as well as the reaction mechanism, *in situ* DRIFTS experiments along with DFT calculations were carried out. As shown in Fig. 2a, when CO<sub>2</sub>/H<sub>2</sub>O is introduced into the system in the dark, peaks of HCHO, m-CO<sub>3</sub><sup>2-</sup>, b-CO<sub>3</sub><sup>2-</sup> and HCO<sub>3</sub><sup>-</sup> are detected, strongly

remanifesting the chemisorption of CO<sub>2</sub> on the catalyst surface.<sup>47,48</sup> Under light irradiation, new adsorption peaks assigned to \*COOH (1669 cm<sup>-1</sup>), \*CO (2079 cm<sup>-1</sup>), \*CHO (1012 cm<sup>-1</sup>), \*CH<sub>2</sub>O (2855 cm<sup>-1</sup>) and \*CH<sub>3</sub>O (1042 and 1181 cm<sup>-1</sup>) are observed, which are significant intermediates in the conversion of CO<sub>2</sub> to CH<sub>4</sub>.<sup>49–51</sup> Accordingly, a probable CO<sub>2</sub> photoreduction mechanism over WO<sub>3</sub>/In<sub>2</sub>O<sub>3</sub> composites is proposed as follows, where \* stands for the active sites on WO<sub>3</sub>/In<sub>2</sub>O<sub>3</sub> heterojunctions.

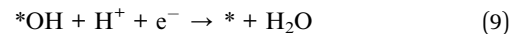
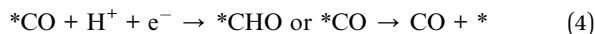


Fig. 2 (a) *In situ* DRIFT spectra of WI10 after adsorption of CO<sub>2</sub>/H<sub>2</sub>O for 15, 30, 45, and 60 min in the dark, and then under light irradiation for 75, 90, 105, and 120 min. (b) Gibbs free energy diagram of CO<sub>2</sub> photoreduction over the In<sub>2</sub>O<sub>3</sub> (111) slab.



Gibbs free energy ( $\Delta G$ ) calculation of  $\text{CO}_2$  photoreduction over the  $\text{In}_2\text{O}_3$  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  $\Delta G$  for the protonation of  $^*\text{CO}$  to  $^*\text{CHO}$  (pathway II,  $-1.61$  eV) is much smaller than that for  $\text{CO}$  desorption from the catalyst surface (pathway I,  $-0.28$  eV), providing a reasonable explanation for the high selectivity of  $\text{CH}_4$  during  $\text{CO}_2$  photoreduction.<sup>52</sup> Overall, the strong adsorption and activation of  $\text{CO}_2$  molecules on the  $\text{In}_2\text{O}_3$  surface are critical factors contributing to the enhanced  $\text{CH}_4$  selectivity and  $\text{CO}_2$  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  $\text{WO}_3$  is consistent with the standard monoclinic phase (JCPDS No. 20-1324), and pristine  $\text{In}_2\text{O}_3$  is indexed to the cubic phase (JCPDS No. 71-2195), respectively (Fig. S7†). In the  $\text{WI}_x$  nano hybrids, the intensity of diffraction peaks attributed to  $\text{In}_2\text{O}_3$  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  $\text{WO}_3$  maintains its nanosheet microscopy with some tiny surface wrinkles (Fig. 3a).<sup>53</sup> In FESEM and transmission electron microscopy (TEM) images of  $\text{WO}_3/\text{In}_2\text{O}_3$  nano hybrids ( $\text{WI}_{10}$ ) (Fig. 3b and c),  $\text{In}_2\text{O}_3$  nanoparticles are clearly observed to be deposited on the surface of  $\text{WO}_3$  nanosheets. The high-resolution TEM image of  $\text{WI}_{10}$  (Fig. 3d) reveals distinct lattice fringes with spacings of 0.292 and 0.375 nm, indicating the presence of  $\text{In}_2\text{O}_3$  and  $\text{WO}_3$  phases, respectively.

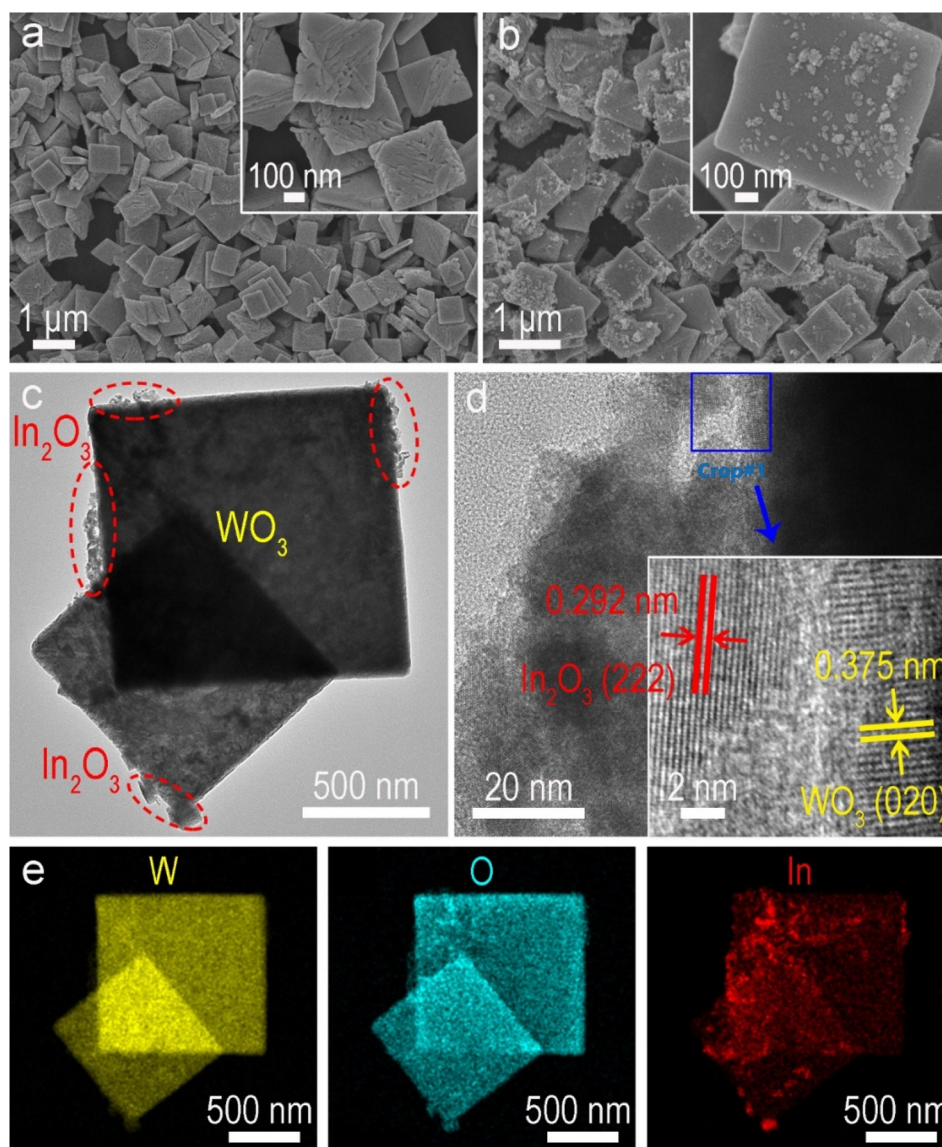


Fig. 3 (a) FESEM image of pure  $\text{WO}_3$  nanosheets. (b) FESEM, (c) TEM and (d) HRTEM images of  $\text{WO}_3/\text{In}_2\text{O}_3$  nanostructures ( $\text{WI}_{10}$ ). (e) EDX elemental mappings of W, O, and In elements in  $\text{WO}_3/\text{In}_2\text{O}_3$  nano hybrids.

corresponding to  $\text{In}_2\text{O}_3$  (222) and  $\text{WO}_3$  (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<sup>†</sup>).

UV-vis diffuse reflectance spectroscopy (DRS) was employed to investigate the optical absorption properties of  $\text{WO}_3$ ,  $\text{In}_2\text{O}_3$  and WI10. The absorption edges of pure  $\text{WO}_3$  and  $\text{In}_2\text{O}_3$  are located at 470 and 465 nm, respectively, corresponding to the bandgap energies of 2.81 and 2.97 eV (Fig. S10<sup>†</sup>). The light harvesting of WI10 is slightly improved compared to pristine  $\text{WO}_3$ , indicating the successful hybridization of  $\text{WO}_3$  and  $\text{In}_2\text{O}_3$ . XPS was carried out to analyze the chemical states and surface

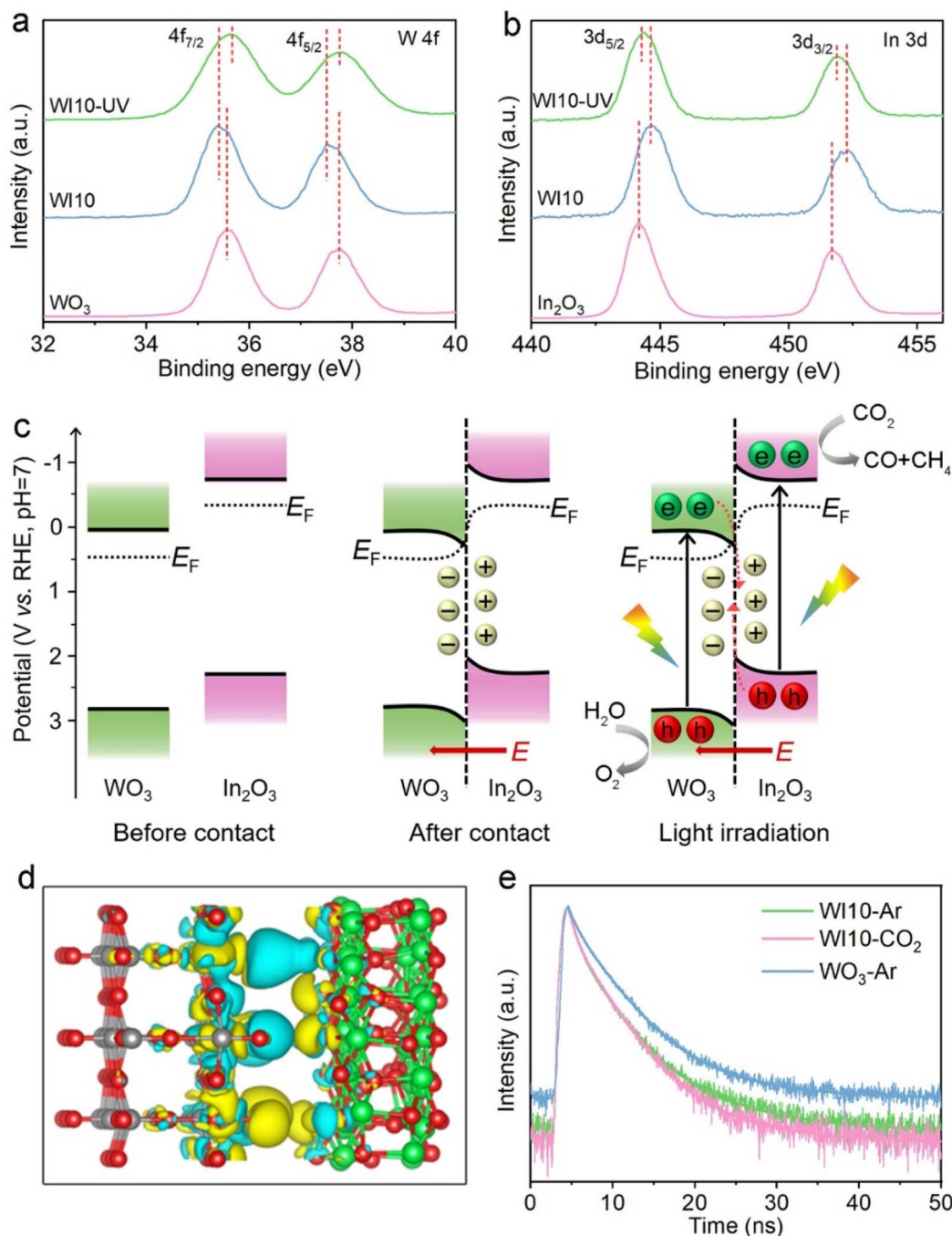


Fig. 4 High-resolution XPS spectra of (a) W 4f, (b) In 3d of  $\text{WO}_3$ ,  $\text{In}_2\text{O}_3$ , and WI10. *In situ* irradiation XPS measurement was conducted under UV light irradiation. (c) Schematic illustration of the formation and charge separation of the  $\text{WO}_3/\text{In}_2\text{O}_3$  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  $\text{WO}_3$  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  $\text{WO}_3$  matrix (Fig. S11a†). The W 4f XPS spectra (Fig. 4a) exhibit two distinct peaks at 35.6 and 37.7 eV, corresponding to hexavalent  $\text{W}^{6+}$ .<sup>54,55</sup> The binding energies (BEs) of In 3d<sub>5/2</sub> and In 3d<sub>3/2</sub> are observed to be 444.2 and 451.7 eV, respectively, confirming the existence of trivalent  $\text{In}^{3+}$  (Fig. 4b).<sup>56,57</sup> 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.<sup>58</sup> Notably, the BEs of W 4f in WI10 display negative shifts in comparison with those in pure  $\text{WO}_3$ , while the peaks of In 3d in WI10 shift positively relative to pure  $\text{In}_2\text{O}_3$ . Such an intriguing phenomenon suggests the migration of electrons from  $\text{In}_2\text{O}_3$  to  $\text{WO}_3$  upon hybridization, creating an IEF with the direction from  $\text{In}_2\text{O}_3$  to  $\text{WO}_3$  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  $\text{WO}_3$  and  $\text{In}_2\text{O}_3$  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  $\text{WO}_3$  and  $\text{In}_2\text{O}_3$  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  $\text{WO}_3$  (001) and  $\text{In}_2\text{O}_3$  (111) (Fig. S14†), the work function ( $\Phi$ ) of  $\text{WO}_3$  and  $\text{In}_2\text{O}_3$  is estimated to be 6.54 and 5.87 eV, respectively, indicating that  $\text{In}_2\text{O}_3$  has a higher Fermi level ( $E_F$ ) than  $\text{WO}_3$ . Additionally, the contact potential difference (CPD) between the samples and the standard gold tip of the Kelvin probe instrument reveals that the calculated  $\Phi$  level of  $\text{WO}_3$  is larger than that of  $\text{In}_2\text{O}_3$  (Fig. S15†), aligning with the DFT results. As a consequence, electrons in  $\text{In}_2\text{O}_3$  will spontaneously diffuse to  $\text{WO}_3$  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  $\text{In}_2\text{O}_3$  to  $\text{WO}_3$  (Fig. 4c). The charge density difference of DFT simulation (Fig. 4d) shows that  $\text{In}_2\text{O}_3$  donates electrons (cyan area) while  $\text{WO}_3$  gains electrons (yellow area) at their interface, further confirming the above electron transfer pathway between  $\text{WO}_3$  and  $\text{In}_2\text{O}_3$ .

Under light irradiation, the electrons in  $\text{WO}_3$  and  $\text{In}_2\text{O}_3$  VBs are initially photoexcited to their CBs. Due to the bent bands and IEF, the photogenerated electrons in the  $\text{WO}_3$  CB tend to transfer to the  $\text{In}_2\text{O}_3$  VB and recombine with its holes, indicating the formation of S-scheme heterojunctions between  $\text{WO}_3$  and  $\text{In}_2\text{O}_3$ . Ultimately, the powerful photoelectrons in the  $\text{In}_2\text{O}_3$  CB and photoholes in the  $\text{WO}_3$  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  $\text{CO}_2$  photo-reduction performance and selectively producing  $\text{CH}_4$ .

*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  $\text{WO}_3$  to  $\text{In}_2\text{O}_3$  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  $\text{WO}_3$  and WI10 were collected under different atmospheres. As shown in Fig. 4e and Table S3,† the shorter lifetime ( $\tau_1$ ) of WI10 is only 0.76 ns in an Ar atmosphere, which is shorter than that of pure  $\text{WO}_3$  (0.96 ns). This suggests that the photoexcited electrons in  $\text{WO}_3$  transfer to  $\text{In}_2\text{O}_3$  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  $\tau_2$  and  $\tau_3$ . 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 ( $\tau_a$ ) of WI10 in a  $\text{CO}_2$  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  $\text{In}_2\text{O}_3$  CB are delivered to  $\text{CO}_2$  molecules for surface photoreduction and fewer photocarriers are involved in detectable recombination.<sup>59,60</sup> 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  $\text{WO}_3$ , 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.<sup>33,61</sup>

Based on the aforementioned analyses, it is suggested that the combination of  $\text{WO}_3$  and  $\text{In}_2\text{O}_3$  to construct S-scheme heterojunctions can effectively promote charge transfer and reduce electron–hole recombination. In concert with the efficient adsorption and activation of  $\text{CO}_2$  molecules on the  $\text{In}_2\text{O}_3$  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  $\text{CO}_2$  photoreduction reaction and produce multi-electron products such as  $\text{CH}_4$ .

## 4. Conclusion

To summarize, an S-scheme  $\text{WO}_3/\text{In}_2\text{O}_3$  heterojunction photocatalyst was constructed by depositing  $\text{In}_2\text{O}_3$  nanoparticles on  $\text{WO}_3$  nanosheets *via* a facile immersion-annealing method. DFT calculations,  $\text{CO}_2$ -TPD and *in situ* DRIFTS revealed that the  $\text{WO}_3/\text{In}_2\text{O}_3$  heterostructures displayed efficient chemisorption and activation of  $\text{CO}_2$  molecules. The difference in Fermi levels caused electrons to transfer from  $\text{In}_2\text{O}_3$  to  $\text{WO}_3$ , 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  $\text{WO}_3$  CB recombined with the holes in the  $\text{In}_2\text{O}_3$



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  $\text{CO}_2$  photoreduction performance with  $\sim 53.7\%$  selectivity for  $\text{CH}_4$ , in the absence of any molecule cocatalyst or scavenger. The  $\text{CO}_2$  photoreduction mechanism and underlying reasons for high  $\text{CH}_4$ -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  $\text{CO}_2$  photoreduction and selective conversion of  $\text{CO}_2$  to  $\text{CH}_4$ .

## 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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