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# Tuning the band gap energy of $\text{Cu}_x\text{In}_y\text{S}$ for superior photothermocatalytic $\text{CO}_2$ conversion to $\text{C}_2\text{H}_4$ <sup>†</sup>

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Photothermal catalysis significantly enhances the efficiency of photocatalytic  $\text{CO}_2$  reduction, offering a promising strategy for accelerated  $\text{CO}_2$  resource utilization. Herein, a series of  $\text{Cu}_x\text{In}_y\text{S}$  photocatalysts were synthesized, exhibiting tunable band gap energy by varying the Cu/In/S atomic ratios for photothermocatalytic  $\text{CO}_2$  conversion to  $\text{C}_2\text{H}_4$ . The typical  $\text{CuInS}_2$  catalyst demonstrates a more negative conduction band, significantly enhancing the electron reduction ability and facilitating the multi-electron reduction of  $\text{CO}_2$  to  $\text{C}_2\text{H}_4$ . Additionally, the abundant sulfur vacancies in  $\text{CuInS}_2$  generate additional active sites, enhance charge separation efficiency, and consequently improve catalytic activity. The generation rate of ethylene reaches  $45.7 \mu\text{mol g}^{-1} \text{h}^{-1}$  with a selectivity of 79.7%. This study provides a new avenue for producing ethylene in photothermal catalysis, as well as highlighting the superiorities of the  $\text{CuInS}_2$  catalyst.

Keywords: Photothermal catalysis;  $\text{CO}_2$  reduction; Ethylene; Metal sulfides; Band gap energy.

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## 1 Introduction

The excessive use of fossil fuels has led to excessive emissions of carbon dioxide ( $\text{CO}_2$ ) into the atmosphere, causing severe climate change.<sup>1–4</sup> Photocatalytic conversion of  $\text{CO}_2$  into hydrocarbons, artificial photosynthesis based on  $\text{H}_2\text{O}$  as the electron transfer medium and proton source, is a technology with environmental sustainability values.<sup>5</sup> Nevertheless, the efficiency of traditional photocatalytic  $\text{CO}_2$  reduction remains hindered by the sluggish multi-electron transfer kinetics and suboptimal photon utilization efficiency.<sup>6</sup> Recent research reveals that the photothermal synergistic catalysis strategy can accelerate the photocatalytic conversion of  $\text{CO}_2$ , significantly enhancing the efficiency of  $\text{CO}_2$  conversion and product selectivity.<sup>7,8</sup>

Photocatalytic efficiency of  $\text{CO}_2$  conversion remains unsatisfactory, primarily because of the high thermodynamic stability of  $\text{CO}_2$  molecules ( $\Delta G_{298 \text{ K}}^0 = -394.36 \text{ kJ mol}^{-1}$ )<sup>9</sup> and

the limited photon utilization.<sup>10</sup> To date, the primary products of  $\text{CO}_2$  photothermal conversion have been  $\text{C}_1$  compounds such as carbon monoxide, methane and formic acid.<sup>11–14</sup>  $\text{C}_2\text{H}_4$ , as an important  $\text{C}_2$  chemical, has widespread applications in the synthesis of fibers, rubbers, plastics, and alcohols.<sup>15</sup> C–C coupling to produce  $\text{C}_2\text{H}_4$  remains a significant challenge.<sup>16</sup> Theoretically, the selective photoreduction of  $\text{CO}_2$  to  $\text{C}_2$  products is primarily hindered by the difficulties associated with C–C coupling of key intermediates such as  $^*\text{CO}$  and  $^*\text{COOH}$ , which requires a high kinetic barrier.<sup>17</sup> To achieve efficient photothermal catalysis for the reduction of  $\text{CO}_2$  to  $\text{C}_2\text{H}_4$ , the catalyst should possess several critical properties: efficient electron transfer and utilization, favorable adsorption of  $^*\text{CO}$  intermediates,<sup>18</sup> and low energy barrier for the formation of  $^*\text{OCCO}$ .<sup>19,20</sup> Accordingly, various catalytic strategies to enhance the photothermal catalytic  $\text{CO}_2$  reduction capability have been investigated.

The band gap width is a pivotal factor influencing the performance of photocatalysts. Significant photogenerated electron-hole pairs can only be generated when the photon energy matches or exceeds the band gap energy. Concurrently, the conduction band (CB) potential must be more negative than the surface electron acceptor potential to ensure effective photocatalytic  $\text{CO}_2$  reduction.<sup>21</sup> Bai *et al.*<sup>22</sup> synthesized a series of  $\text{Zn}_m\text{In}_2\text{S}_{3+m}$  catalysts with tailored bandgap energies and constructed  $\text{Zn}_2\text{In}_2\text{S}_5/\text{BiVO}_4$  heterojunctions, which improve the separation of charge carriers and the photocatalytic performance. Chai *et al.*<sup>23</sup> synthesized various metal sulfides and demonstrated  $\text{CuInSnS}_4$  as having the most negative

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conduction band potential, achieving exceptional photocatalytic activity and selectivity for multi-electron  $\text{CO}_2$  reduction. Therefore, tuning the band gap provides an effective strategy for enhancing the selectivity of photocatalytic  $\text{CO}_2$  conversion to  $\text{C}_2\text{H}_4$ .

Metal sulfides have garnered extensive attention due to their structural tunability and broad light absorption capabilities.<sup>24</sup> Among these, Cu-based catalysts are highly efficient for  $\text{CO}_2$  to  $\text{C}_2\text{H}_4$  conversion due to their unique electronic structure and surface properties, which stabilize CO intermediates and promote C–C coupling.<sup>25</sup> Furthermore, In-based materials, as high-performance semiconductors, offer a favorable band structure for efficient electron–hole separation, enhancing photothermal catalytic performance. Gao *et al.*<sup>26</sup> reported  $\text{CuInP}_2\text{S}_6$  nanosheets achieving 56.4% selectivity for the photocatalytic reduction of  $\text{CO}_2$  to  $\text{C}_2\text{H}_4$ . The In sites facilitated the reduction of  $\text{CO}_2$  to  $\text{*CO}$ , and the C–C coupling reaction occurred on the Cu sites. Furthermore, sulfur vacancies are frequently employed as a modulation strategy in metal sulfides. These defects significantly influence catalyst reactivity, modulate the electronic structure, facilitate charge transport, and effectively lower the kinetic barrier.<sup>27,28</sup> Yan *et al.*<sup>29</sup> designed a  $\text{Bi}_2\text{S}_3@\text{In}_2\text{S}_3$  catalyst, with the In–S<sub>v</sub>–Bi active center composed of adjacent Bi and In sites accompanied by abundant S<sub>v</sub> defects, which reduces the energy barrier of  $\text{CO}_2$  activation and C–C coupling, achieving a  $\text{C}_2\text{H}_4$  generation rate of  $11.81 \mu\text{mol g}^{-1} \text{h}^{-1}$ , with a selectivity of approximately 90%. Therefore, regulating the band structure and defect sites of the  $\text{Cu}_x\text{In}_y\text{S}$  photocatalyst holds significant prospects for enhancing the reduction of  $\text{CO}_2$  to  $\text{C}_2\text{H}_4$ .

Herein, we have successfully synthesized a series of metal sulfides, including  $\text{CuInS}_2$ ,  $\text{CuIn}_2\text{S}_4$ ,  $\text{CuIn}_5\text{S}_8$ , CuS and  $\text{In}_2\text{S}_3$  by a simple hydrothermal method. Among these, the  $\text{CuInS}_2$  catalyst demonstrated superior performance in photothermal catalytic  $\text{CO}_2$  reduction, utilizing  $\text{H}_2\text{O}$  as a proton donor. The generation rate of ethylene reached  $45.7 \mu\text{mol g}^{-1} \text{h}^{-1}$  with a selectivity of 79.7%. The high performance was attributed to the photothermal effect, the high amount of sulfur vacancies and the narrow band gap of the  $\text{CuInS}_2$  catalyst, where the

abundant sulfur vacancies create additional active sites, promoting  $\text{CO}_2$  activation, and a more negative conduction band significantly enhancing the electron reduction ability and facilitating the selectivity of  $\text{CO}_2$  conversion to  $\text{C}_2\text{H}_4$ .

## 2 Results and discussion

X-ray diffraction (XRD) analysis was conducted to investigate the crystal structures and compositions of the synthesized samples.<sup>30</sup> As illustrated in Fig. 1a, the diffraction peaks observed at  $27.9^\circ$ ,  $46.5^\circ$ , and  $55.1^\circ$  correspond to the (112), (220), and (312) crystal planes of the  $\text{CuInS}_2$  phase, respectively. Additionally, diffraction peaks at  $14.3^\circ$ ,  $27.7^\circ$ ,  $33.5^\circ$ ,  $44.0^\circ$ , and  $48.1^\circ$  are attributable to the (111), (311), (400), (511), and (440) crystal planes of  $\text{CuIn}_2\text{S}_4$  and  $\text{CuIn}_5\text{S}_8$  phases, respectively. In Fig. 1b, the XRD patterns further reveal the successful synthesis of monometallic sulfides, specifically CuS (PDF#79-2321) and  $\text{In}_2\text{S}_3$  (PDF#73-1366). The diffraction peaks at  $29.3^\circ$ ,  $31.8^\circ$ ,  $32.9^\circ$ ,  $48.0^\circ$ ,  $52.8^\circ$ , and  $59.4^\circ$  are assigned to the (102), (103), (006), (110), (108), and (116) crystal planes of CuS, respectively. Meanwhile, peaks at  $14.2^\circ$ ,  $27.4^\circ$ ,  $33.2^\circ$ ,  $43.6^\circ$ , and  $47.7^\circ$  correspond to the (103), (109), (00 12), (309), and (22 12) crystal planes of  $\text{In}_2\text{S}_3$ , respectively.

The microstructure and structural characteristics of the samples were carefully studied using scanning electron microscopy (SEM). The SEM comparisons of different samples under identical magnifications are shown in Fig. 2a–e. CuS exhibits a basic nanoparticle morphology, whereas  $\text{CuIn}_2\text{S}_4$ ,  $\text{CuIn}_5\text{S}_8$ ,  $\text{In}_2\text{S}_3$  and  $\text{CuInS}_2$  display a microspheres morphology self-assembled by nanosheets. The thicknesses of the catalyst flakes for CuS,  $\text{CuIn}_2\text{S}_4$ ,  $\text{CuIn}_5\text{S}_8$ ,  $\text{In}_2\text{S}_3$  and  $\text{CuInS}_2$  were measured to be 53 nm, 26 nm, 25 nm, 38 nm, and 20 nm, respectively. Notably,  $\text{CuInS}_2$  demonstrates an ultrathin nanosheet morphology offering significant advantages for photocatalytic applications. The reduced thickness effectively shortens the charge transport distance, thereby minimizing the probability of charge recombination, ultimately enhancing the quantum efficiency of the photocatalytic process.<sup>31</sup>

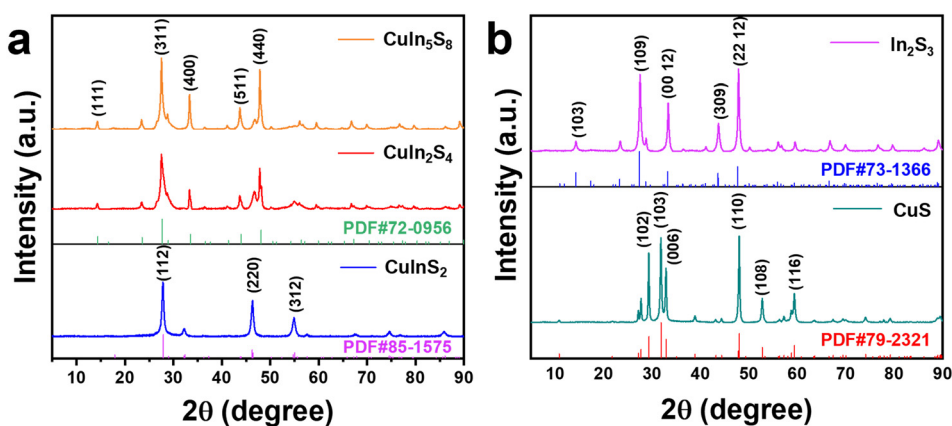


Fig. 1 (a) XRD patterns of  $\text{CuInS}_2$ ,  $\text{CuIn}_2\text{S}_4$  and  $\text{CuIn}_5\text{S}_8$  samples; (b) XRD patterns of CuS and  $\text{In}_2\text{S}_3$  samples.



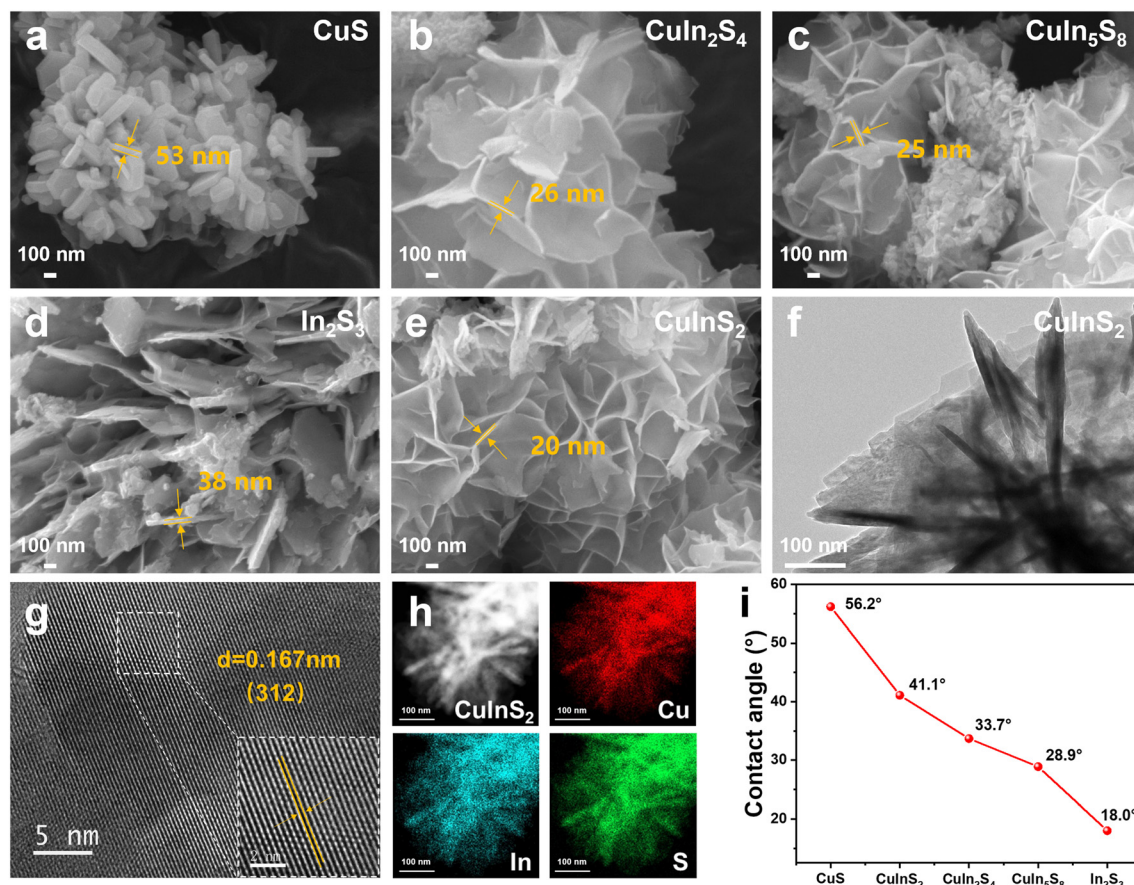


Fig. 2 SEM images of (a) CuS, (b)  $CuIn_2S_4$ , (c)  $CuIn_5S_8$ , (d)  $In_2S_3$  and (e)  $CuInS_2$ ; (f) TEM image, (g) HRTEM image, and (h) EDS mapping of  $CuInS_2$ ; (i) static water contact-angle of  $Cu_xIn_yS_z$ .

The TEM analysis confirms that  $CuInS_2$  consists of nanoflakes (Fig. 2f). Due to the low surface activity of  $CuInS_2$  nanosheets, it is easy to agglomerate together, which forms the microsphere morphology observed in the SEM diagram. The high-resolution TEM image (Fig. 2g) reveals an exposed crystal plane of  $CuInS_2$  with a lattice spacing of 0.167 nm, which corresponds to the (312) crystal face. Additionally, the elemental mapping in Fig. 2h demonstrates a uniform distribution of Cu, In, and S elements across the  $CuInS_2$  nanoparticles. The composition of the  $CuInS_2$  sample was analyzed by energy dispersive spectroscopy (EDS), as presented in Table S1.† The EDS results indicate that the atomic ratio of Cu, In and S is approximately 1:1:2, closely matching the stoichiometric composition of the  $CuInS_2$  compound, indicating the high purity of the  $CuInS_2$  nanocrystal. Furthermore, inductively coupled plasma mass spectrometry (ICP-MS) was employed to determine the metal element content in the  $CuInS_2$  sample, with the results detailed in Table S2.† The Cu and In atomic ratio was found to be approximately 1:1, corroborating the theoretical stoichiometric value of  $CuInS_2$ . Collectively, these results confirm the successful preparation of the  $CuInS_2$  nanocrystal with high-quality exposed (312) crystal faces. The hydrophilicity and hydrophobicity of the catalyst were

examined, as depicted in Fig. 2i, and all the samples demonstrated hydrophilic characteristics, with contact angle measurements following the order:  $CuS > CuInS_2 > CuIn_2S_4 > CuIn_5S_8 > In_2S_3$ . This implies that a certain degree of hydrophilicity is beneficial to the adsorption of water on their surfaces, hence possibly aiding subsequent proton transfer to participate in the  $CO_2$  reduction reactions.<sup>32</sup>

X-ray photoelectron spectroscopy (XPS) was employed to investigate the electronic states of the synthesized samples.<sup>30</sup> The high-resolution XPS spectra (Fig. 3a) reveal that the Cu  $2p_{1/2}$  and Cu  $2p_{3/2}$  binding energies for the  $CuInS_2$  sample are 951.6 eV and 931.8 eV, respectively. Importantly, the Cu 2p binding energy of  $CuInS_2$  is 0.3 eV lower than that observed for CuS. This shift can be attributed to changes in electron distribution and chemical bond strength arising from the interaction between Cu and In, resulting in a reduction in binding energy.<sup>33</sup> Further analysis of the In 3d region (Fig. 3b) shows that the binding energies of In  $3d_{3/2}$  and In  $3d_{5/2}$  in the  $CuInS_2$  sample are 452.1 eV and 444.6 eV, respectively. Compared with  $In_2S_3$ , the In 3d binding energies of  $CuInS_2$  uniformly shift to lower binding energy. This shift is attributed to the distinct coordination environments of In atoms in  $CuInS_2$  and  $In_2S_3$  because the partial In atom in  $In_2S_3$  exists in the state of  $[InS_4]$  tetrahedron.<sup>34</sup> For S 2p, the





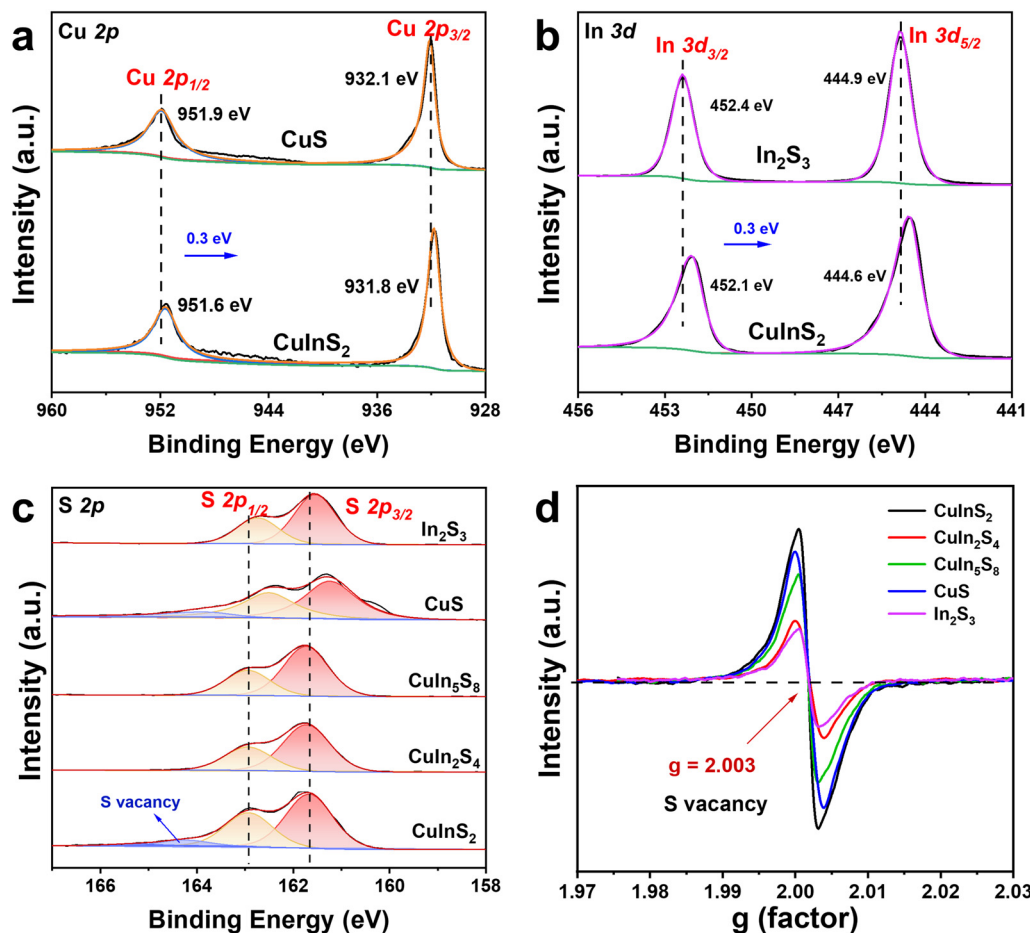


Fig. 3 XPS spectra of  $\text{Cu}_x\text{In}_y\text{S}$ : (a) Cu 2p, (b) In 3d and (c) S 2p; (d) EPR spectra of  $\text{Cu}_x\text{In}_y\text{S}$ .

binding energies of S 2p<sub>1/2</sub> and S 2p<sub>3/2</sub> are measured at 162.9 eV and 161.7 eV, respectively (Fig. 3c). Due to the fact that the average bond length between sulfur and metal atoms in CuInS<sub>2</sub> is slightly longer than that of monometallic sulfides, the S atom in CuInS<sub>2</sub> exhibits the highest binding energy. Notably, an additional peak at 164.5 eV is observed in both CuInS<sub>2</sub> and CuS samples, which has been attributed to sulfur vacancies as reported in the literature.<sup>35</sup> The higher binding energy of S atoms in CuInS<sub>2</sub> relative to monometallic sulfides suggests that the S atoms in CuInS<sub>2</sub> exist in an electron-deficient state. To provide further insights into the formation of sulfur vacancies, the  $g = 2.003$  signal observed in the room-temperature EPR spectra was attributed to sulfur defects (Fig. 3d).<sup>36</sup> The presence of the sulfur vacancy has the potential to act as a reaction site to enhance the ability of CO<sub>2</sub> adsorption and subsequent activation and promote C–C coupling to generate C<sub>2</sub>H<sub>4</sub>.<sup>23,29</sup> Subsequent photo-thermal catalytic CO<sub>2</sub> reduction experiments also confirmed that the catalytic activity is positively correlated with the sulfur vacancy content, with CuInS<sub>2</sub>, which has the highest sulfur vacancy concentration, exhibiting the best catalytic performance.

The photothermal catalytic performance of the sample for CO<sub>2</sub> reduction was evaluated using a flow fixed-bed reactor

(Fig. S1†). In this gas–solid reaction system, CO<sub>2</sub> and H<sub>2</sub>O vapor were continuously introduced. Under illumination from a 300 W xenon lamp with full-spectrum output, the reaction temperature was maintained at 130 °C. After 6 hours of reaction, the only detectable gaseous products were C<sub>2</sub>H<sub>4</sub> and CO, while no liquid-phase products were observed. To address the limitation of recombination of electron and hole pairs, triethanolamine (TEOA) was introduced as a sacrificial agent to effectively consume photogenerated holes formed during the photocatalytic reaction. To preliminarily exclude the impact of TEOA on the products of the CO<sub>2</sub> reduction reaction, its decomposition behavior was investigated under the N<sub>2</sub> atmosphere. As shown in Table S3,† at temperature of 130 °C, neither C<sub>2</sub>H<sub>4</sub> nor CO was detected. Further, the thermal stability of TEOA was evaluated (Fig. S2†). Results show no mass loss at 130 °C, confirming the thermal stability of TEOA at this temperature. These findings collectively indicate that TEOA does not decompose to produce C<sub>2</sub>H<sub>4</sub> or CO at the reaction temperature of 130 °C. Consequently, the influence of TEOA on the photothermal catalytic CO<sub>2</sub> reduction products can be preliminarily excluded.

The photothermal catalytic CO<sub>2</sub> reduction performance of the sample under reaction conditions of 0.5 MPa and 5 mL min<sup>−1</sup> is shown in Fig. 4a. The CuInS<sub>2</sub> sample demonstrates



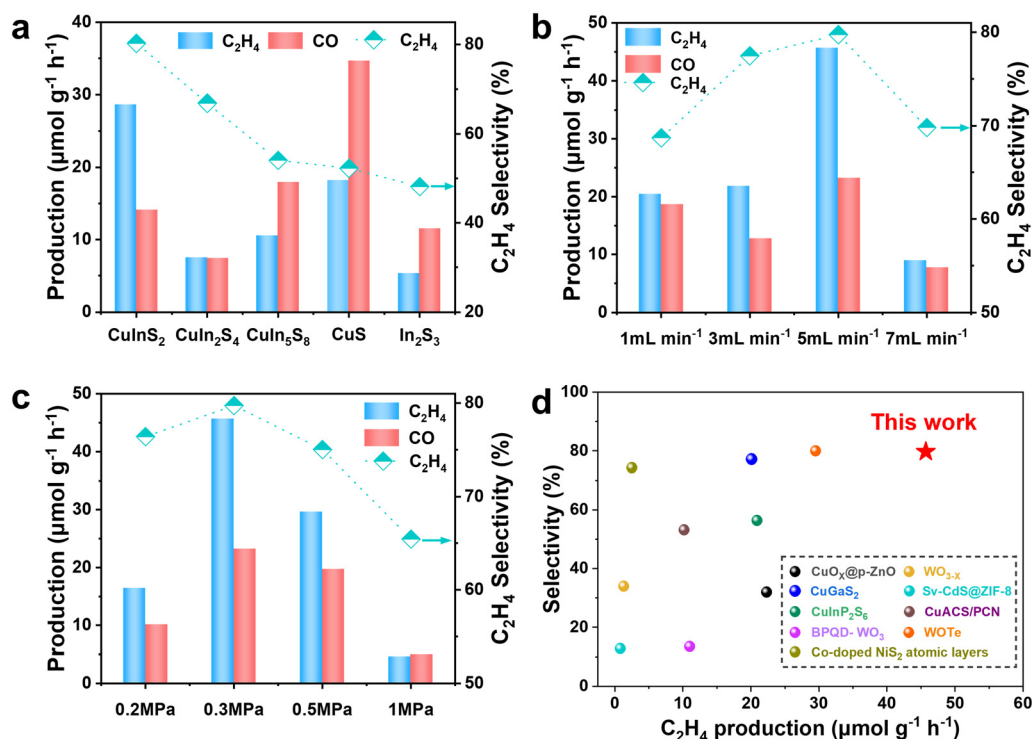


Fig. 4 (a) Photothermal catalytic CO<sub>2</sub> reduction performance of Cu<sub>x</sub>In<sub>y</sub>S<sub>z</sub>; photothermal catalytic CO<sub>2</sub> reduction performance of CuInS<sub>2</sub> catalysts (b) under different flow rates and (c) reaction pressures; (d) the C<sub>2</sub>H<sub>4</sub> production rates and selectivity of different catalysts.

exceptional performance in photothermal catalytic CO<sub>2</sub> reduction, producing C<sub>2</sub>H<sub>4</sub> and CO as the primary products. The generation rate of C<sub>2</sub>H<sub>4</sub> was  $28.6 \mu\text{mol g}^{-1} \text{h}^{-1}$ , while the CO generation rate was  $14.1 \mu\text{mol g}^{-1} \text{h}^{-1}$ . The selectivity to C<sub>2</sub>H<sub>4</sub> was calculated to be 80.2%, based on the carbon-containing product contents. In contrast, monometallic sulfides such as CuS and In<sub>2</sub>S<sub>3</sub> predominantly produce CO as the main product. This variation in product selectivity suggests that bimetallic sulfides and monometallic sulfides differ in their CO<sub>2</sub> reduction mechanisms or exhibit distinct active sites.<sup>23</sup> Thermogravimetric analysis (Fig. S3†) was performed to investigate the thermal stability of the sample. The analysis reveals a degree of mass loss at approximately 130 °C, likely attributable to the presence of trace amounts of H<sub>2</sub>O in the sample. As the temperature increases, the volatilization of H<sub>2</sub>O results in the observed weight loss. The reaction conditions were further explored. The photothermal catalytic CO<sub>2</sub> reduction performance of the CuInS<sub>2</sub> sample under 0.3 MPa pressure and varying flow rates is evaluated in Fig. 4b, with superior photothermal catalytic performance demonstrated at a flow rate of 5 mL min<sup>-1</sup>. This may be because the moderate flow rate enhances the supply of reactants, thereby increasing reaction rates, whereas excessive flow reduces catalyst interaction time, ultimately lowering efficiency.<sup>37</sup> The photothermal catalytic CO<sub>2</sub> reduction performance of the CuInS<sub>2</sub> sample under a flow rate of 5 mL min<sup>-1</sup> and varying pressures is evaluated in Fig. 4c. The results demonstrate excellent photothermal catalytic performance at 0.3 MPa. Within a certain range, an increase

in pressure allows the active sites on the catalyst surface to interact more effectively with reactants, thereby improving catalyst activity.<sup>37</sup> Comparative analysis reveals that at a pressure of 0.3 MPa and a flow rate of 5 mL min<sup>-1</sup>, the CuInS<sub>2</sub> sample exhibits optimal activity. Under these conditions, the rate of C<sub>2</sub>H<sub>4</sub> generation reaches  $45.7 \mu\text{mol g}^{-1} \text{h}^{-1}$ , with a C<sub>2</sub>H<sub>4</sub> selectivity of 79.7%. Notably, compared with previously reported photothermal catalysts, the prepared CuInS<sub>2</sub> catalyst demonstrates superior rate and selectivity for C<sub>2</sub>H<sub>4</sub> production (Fig. 4d, Table S4†).

With the increase in reaction time, the rates of C<sub>2</sub>H<sub>4</sub> and CO exhibited a noticeable upward trend. Notably, after 6 hours of reaction, the rate of C<sub>2</sub>H<sub>4</sub> using the CuInS<sub>2</sub> catalyst was significantly higher compared to the other samples (Fig. S4 and S5†). The durability and stability of the CuInS<sub>2</sub> catalyst were further assessed through cyclic experiments illustrated<sup>38</sup> in Fig. 5a, over five consecutive cycles (6 hours per cycle); the C<sub>2</sub>H<sub>4</sub> production rate remained above 85% of the baseline activity, with the activity decay mainly attributed to catalyst poisoning by CO.<sup>39–41</sup> The XRD patterns of the CuInS<sub>2</sub> catalyst before and after the cyclic reaction (Fig. S6†) revealed no discernible changes in the crystal structure, confirming the structural integrity of the material post-reaction. Furthermore, the XPS results of the CuInS<sub>2</sub> catalyst after the reaction, shown in Fig. S7–S9† indicated that the binding energies of Cu, In, and S in the sample remained relatively unchanged. These findings collectively suggest that the CuInS<sub>2</sub> catalyst maintains robust stability during the photothermal catalytic CO<sub>2</sub> reduction process. To confirm the



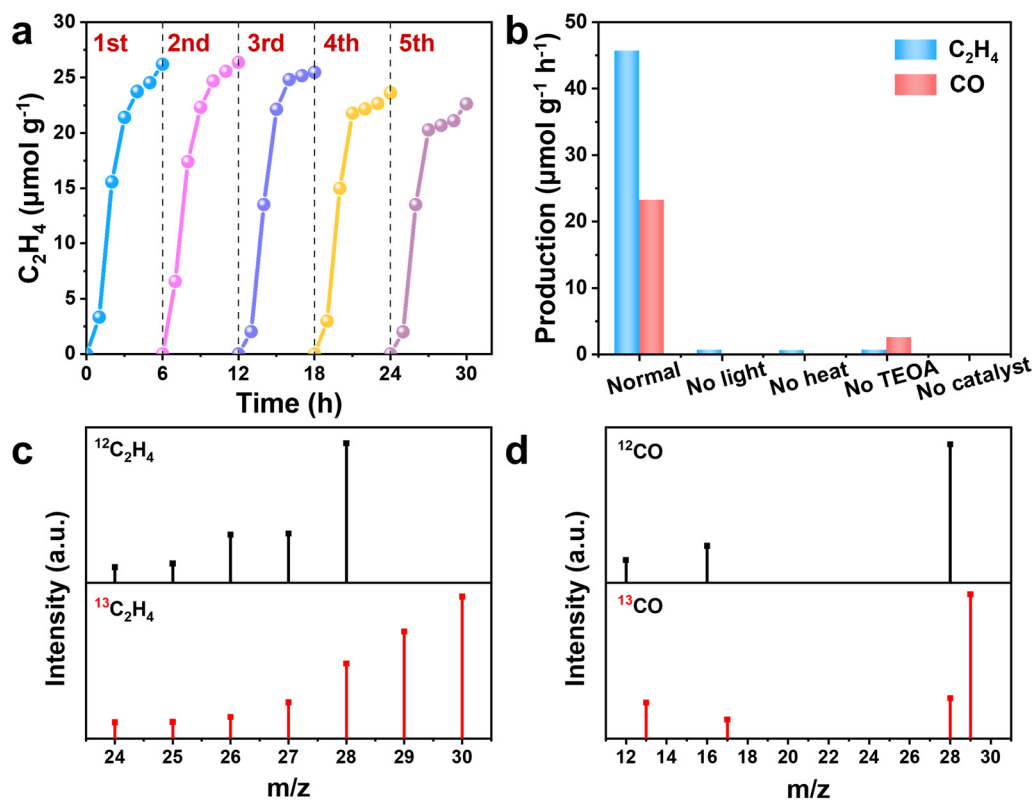


Fig. 5 (a) Stability test of  $\text{CuInS}_2$ ; (b) control experiments of the  $\text{CuInS}_2$  sample under different reaction conditions; GC-MS spectra of the produced (c)  $\text{C}_2\text{H}_4$  and (d)  $\text{CO}$  from the photothermocatalytic reduction of  $^{13}\text{CO}_2$  or  $^{12}\text{CO}_2$  on  $\text{CuInS}_2$ .

occurrence of  $\text{CO}_2$  reduction on  $\text{CuInS}_2$ , blank control experiments under various conditions were conducted. As shown in Fig. 5b, no product was detected in the absence of the catalyst, indicating its essential role in the reaction. When the reaction was performed at 130 °C without light, the rate of  $\text{C}_2\text{H}_4$  generation was only  $0.6 \mu\text{mol g}^{-1} \text{h}^{-1}$ , highlighting the fundamental importance of light as a driving force in the photothermal catalytic system. Similarly, under light irradiation but without external heating, the rate of  $\text{C}_2\text{H}_4$  generation was merely  $0.5 \mu\text{mol g}^{-1} \text{h}^{-1}$ . In contrast, under normal photothermal conditions (0.3 MPa, 5 mL  $\text{min}^{-1}$ , 130 °C, 300 W xenon lamp), the rate of  $\text{C}_2\text{H}_4$  generation reached  $45.7 \mu\text{mol g}^{-1} \text{h}^{-1}$ , demonstrating that thermal energy significantly enhances the production of  $\text{C}_2\text{H}_4$ .<sup>42</sup> The efficiency of photothermal conversion of  $\text{CO}_2$  to  $\text{C}_2\text{H}_4$  was notably higher than that achieved by photocatalysis or thermal catalysis alone. This underscores the indispensable roles of both light and heat in the photothermal reaction system. Importantly, the rate of  $\text{C}_2\text{H}_4$  increased nearly tenfold upon the addition of the sacrificial agent TEOA. Control experiments conducted with  $\text{N}_2$  instead of  $\text{CO}_2$  yielded only trace amounts of  $\text{C}_2\text{H}_4$  and  $\text{CO}$  (Table S5†), directly confirming that the source of the  $\text{C}_2\text{H}_4$  and  $\text{CO}$  products was  $\text{CO}_2$ . To further verify the carbon source of  $\text{C}_2\text{H}_4$  and  $\text{CO}$  in the products, isotope tracer experiments using  $^{13}\text{CO}_2$  were performed.<sup>43</sup> The products were analyzed by gas chromatography–mass spectrometry (GC–MS). As

shown in Fig. 5c and d, the mass spectral fragment ion distributions of  $\text{C}_2\text{H}_4$  and  $\text{CO}$  were systematically characterized. The comparison experiments show that the fragment peaks of  $\text{C}_2\text{H}_4$  ( $m/z = 28 \rightarrow 30$ ) and  $\text{CO}$  ( $m/z = 29 \rightarrow 30$ ) were obviously shifted when  $^{13}\text{CO}_2$  is involved in the reaction. This isotopic shift exclusively confirms that the carbon in  $\text{C}_2\text{H}_4$  and  $\text{CO}$  originates from  $\text{CO}_2$ , rather than carbonaceous components of the catalyst or decomposition of organic sacrificial agents.

The light absorption capacity and charge separation efficiency of catalysts are critical factors influencing the experimental results of photothermal synergistic catalysis. The optical absorption abilities of the  $\text{CuInS}_2$ ,  $\text{CuIn}_2\text{S}_4$ ,  $\text{CuIn}_5\text{S}_8$ ,  $\text{CuS}$ , and  $\text{In}_2\text{S}_3$  samples were investigated using UV-vis diffuse reflectance spectroscopy (UV-vis DRS), as shown in Fig. S10.† Notably, the absorption edges of these materials are not distinct, reflecting full-spectrum absorption characteristics. The broad absorption range of these photocatalysts is advantageous for capturing photons, thereby enhancing photocatalytic reactions.<sup>44</sup>  $\text{CuInS}_2$  exhibits strong light absorption across the spectral range, demonstrating promising potential for photocatalytic activity. Photoluminescence spectroscopy (PL) serves as an effective tool to assess the electron–hole recombination capability in photocatalysts. Lower recombination rates enhance charge utilization efficiency, thereby improving reactivity. As shown in Fig. 6a, the  $\text{CuInS}_2$  sample exhibits the weakest PL signal,



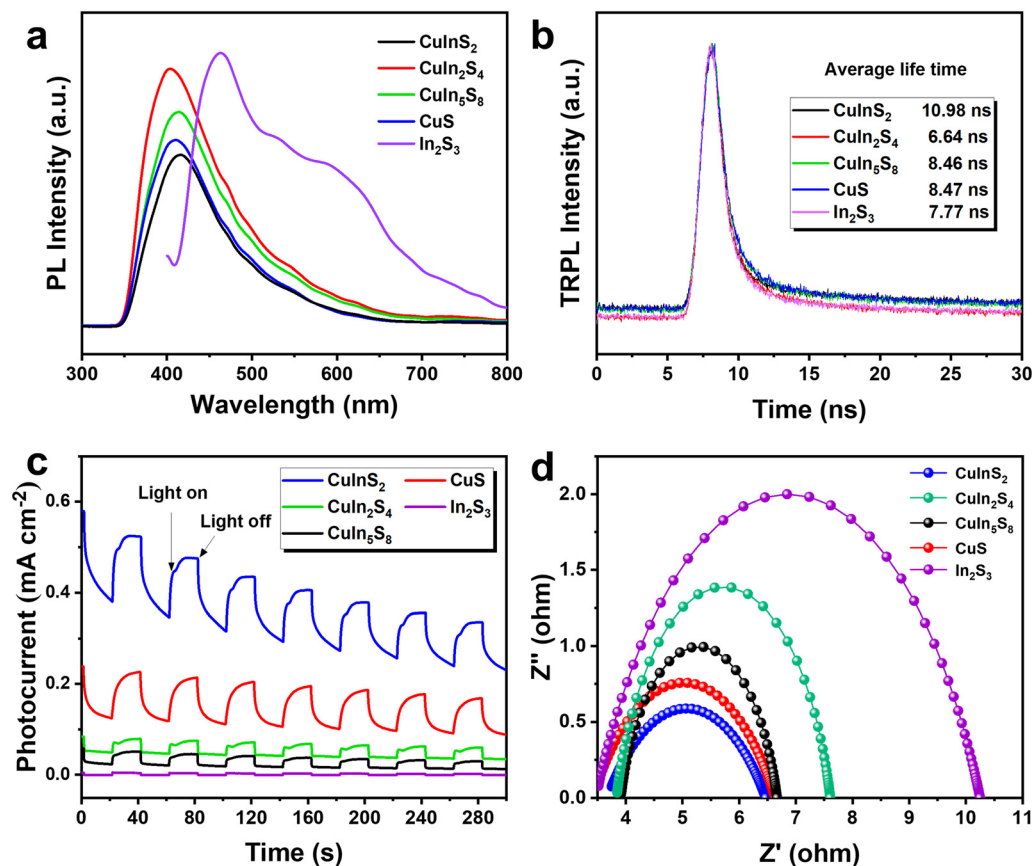


Fig. 6 (a) Steady-state fluorescence spectra, (b) transient fluorescence spectra, (c) transient photocurrent response curves and (d) electrochemical impedance spectra of  $\text{Cu}_x\text{In}_y\text{S}$ .

indicative of the most effective charge separation. Furthermore, the time-resolved photoluminescence (TRPL) spectrum presented in Fig. 6b reveals that the  $\text{CuInS}_2$  sample has an average carrier lifetime of 10.98 ns, which is markedly higher than that of the other samples. This extended carrier lifetime suggests a significant suppression of charge recombination. Additional photoelectrochemical tests corroborated these findings, further elucidating the electron-hole pair separation efficiency of the representative photocatalyst samples. These results underscore the importance of the  $\text{CuInS}_2$  sample's superior charge separation characteristics in promoting photothermal synergistic catalysis.

Transient photocurrent measurements (Fig. 6c) were conducted to investigate the photocurrent response of the as-prepared samples under optical switching conditions. Among the tested samples, the  $\text{CuInS}_2$  sample exhibited the highest photocurrent response, signifying superior separation efficiency of photogenerated electron-hole pairs under illumination conditions.<sup>45,46</sup> These results are consistent with previous studies. Electrochemical impedance spectroscopy (EIS) was employed to gain deeper insights into the electron transfer capabilities of the samples. As illustrated in Fig. 6d, the Nyquist plot for  $\text{CuInS}_2$  demonstrates a smaller semicircle radius compared to the other samples, indicating

a lower charge transfer resistance and enhanced interfacial charge transfer efficiency.<sup>47</sup> Overall, these results suggest that  $\text{CuInS}_2$  exhibits outstanding activity in photothermal catalytic  $\text{CO}_2$  reduction reactions due to its excellent charge separation and electron transport properties.

To elucidate the factors governing the divergent selectivity patterns in catalytic reactions, we conducted a comprehensive analysis of the band gap properties for each candidate catalyst. The conduction band (CB) positions of the samples were evaluated through Mott-Schottky (M-S) analysis,<sup>48</sup> with CB potentials measured as -1.19 eV, -1.01 eV, -0.96 eV, -1.07 eV, and -0.74 eV (V vs. NHE) for  $\text{CuInS}_2$ ,  $\text{CuIn}_2\text{S}_4$ ,  $\text{CuIn}_5\text{S}_8$ ,  $\text{CuS}$  and  $\text{In}_2\text{S}_3$ , respectively (Fig. 7a-e). The positive slopes observed in the M-S curves at multiple frequencies (2000, 3000, and 4000 Hz) confirm that  $\text{CuInS}_2$  is an n-type semiconductor. As revealed by XPS valence band spectra<sup>49</sup> (Fig. 7f), the valence band (VB) potentials were calculated to be 0.14 eV, 0.49 eV, 0.45 eV, 0.08 eV, and 1.64 eV (V vs. NHE) for  $\text{CuInS}_2$ ,  $\text{CuIn}_2\text{S}_4$ ,  $\text{CuIn}_5\text{S}_8$ ,  $\text{CuS}$  and  $\text{In}_2\text{S}_3$ , respectively. Based on the formula  $E_g = E_{\text{VB}} - E_{\text{CB}}$ ,<sup>44</sup> the  $E_g$  values for  $\text{CuInS}_2$ ,  $\text{CuIn}_2\text{S}_4$ ,  $\text{CuIn}_5\text{S}_8$ ,  $\text{CuS}$  and  $\text{In}_2\text{S}_3$  were determined to be 1.33 eV, 1.50 eV, 1.41 eV, 1.15 eV, and 2.38 eV, respectively.

Based on the aforementioned results, an electronic band diagram relative to the standard hydrogen electrode was





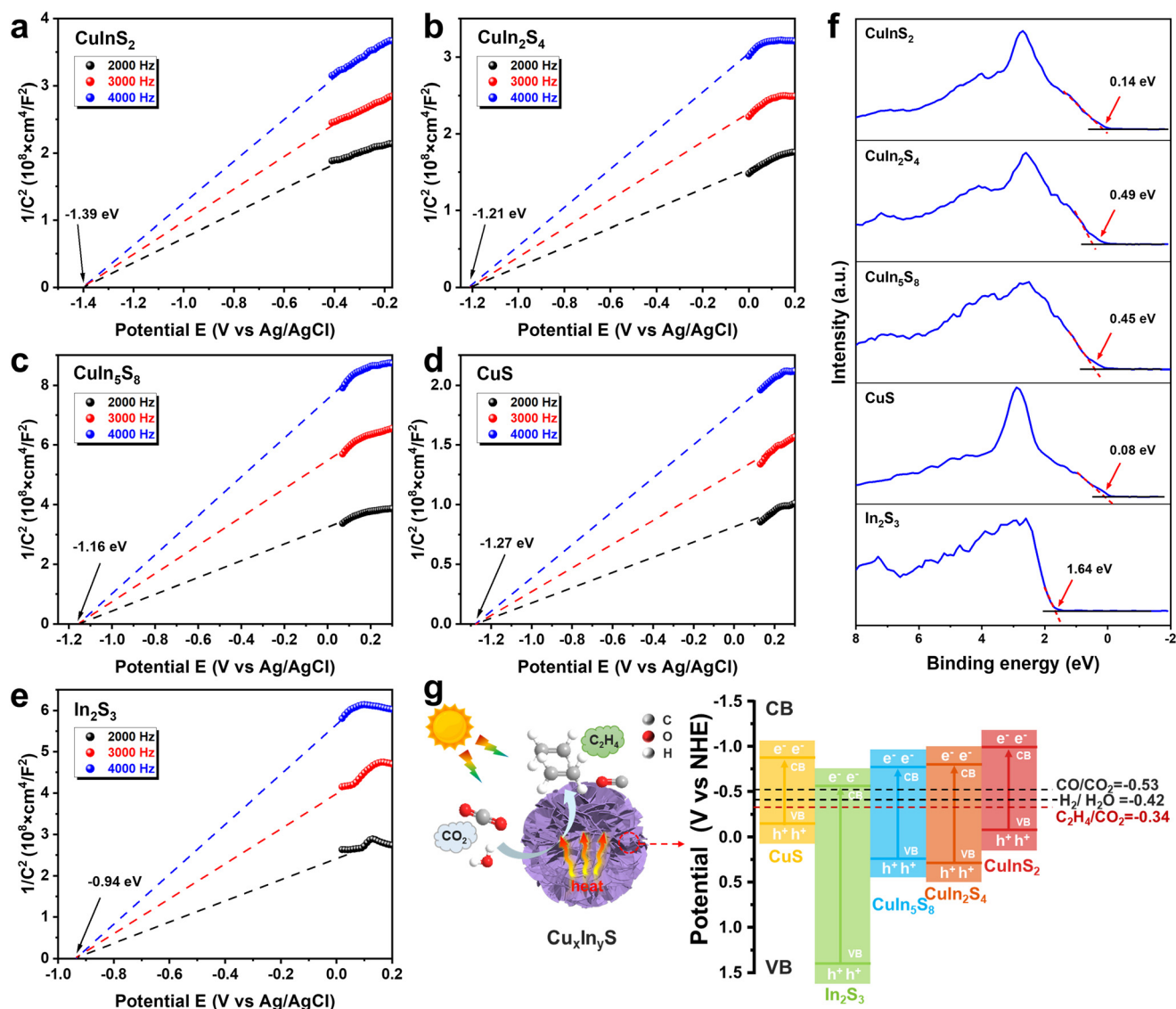


Fig. 7 Mott-Schottky curves of (a) CuInS<sub>2</sub>, (b) CuIn<sub>2</sub>S<sub>4</sub>, (c) CuIn<sub>5</sub>S<sub>8</sub>, (d) CuS and (e) In<sub>2</sub>S<sub>3</sub>; (f) XPS valence band spectra of Cu<sub>x</sub>In<sub>y</sub>S; (g) the optical band gap energy of Cu<sub>x</sub>In<sub>y</sub>S.

constructed (Fig. 7g), which critically determine the driving force for redox reactions. All the samples demonstrated the capability to reduce CO<sub>2</sub> to C<sub>2</sub>H<sub>4</sub> and CO. CuInS<sub>2</sub>, in particular, has a band gap energy that aligns closely with the energy required for CO<sub>2</sub> reduction to C<sub>2</sub>H<sub>4</sub>, and its more negative CB position endows the electrons with stronger reducing power,<sup>23</sup> facilitating multi-electron CO<sub>2</sub> reduction pathways to C<sub>2</sub>H<sub>4</sub>. These findings underscore the potential of CuInS<sub>2</sub> as a highly efficient photocatalyst for CO<sub>2</sub> reduction, supported by its advantageous band structure and strong optical absorption properties.

To gain deeper insight into the band gap structure of Cu<sub>x</sub>In<sub>y</sub>S, projected density of states (PDOS) calculations were performed using density functional theory (DFT),<sup>50</sup> as shown in Fig. 8. The results indicate that the band gap energies of CuS, CuInS<sub>2</sub> and In<sub>2</sub>S<sub>3</sub> follow the order: CuS < CuInS<sub>2</sub> < In<sub>2</sub>S<sub>3</sub>. The band gap of CuInS<sub>2</sub> lies between that of CuS and

In<sub>2</sub>S<sub>3</sub>, enabling efficient visible-light absorption while avoiding the rapid carrier recombination caused by the excessively narrow band gap of CuS and the reduced light absorption efficiency resulting from the overly wide band gap of In<sub>2</sub>S<sub>3</sub>.<sup>51</sup> The PDOS for CuInS<sub>2</sub> reveals that the Cu 3d orbitals are the most active, contributing significantly to the electronic states near the Fermi level.<sup>30</sup> This suggests that during photoexcitation, electrons from the Cu 3p orbitals transition from the valence band maximum (VBM) to the conduction band minimum (CBM), playing a crucial role in the photocatalytic CO<sub>2</sub> reduction reaction.

### 3 Conclusion

In summary, this study has successfully synthesized a series of Cu<sub>x</sub>In<sub>y</sub>S photocatalysts modulating the Cu/In/S atomic ratios by a simple hydrothermal method. The CuInS<sub>2</sub> catalyst



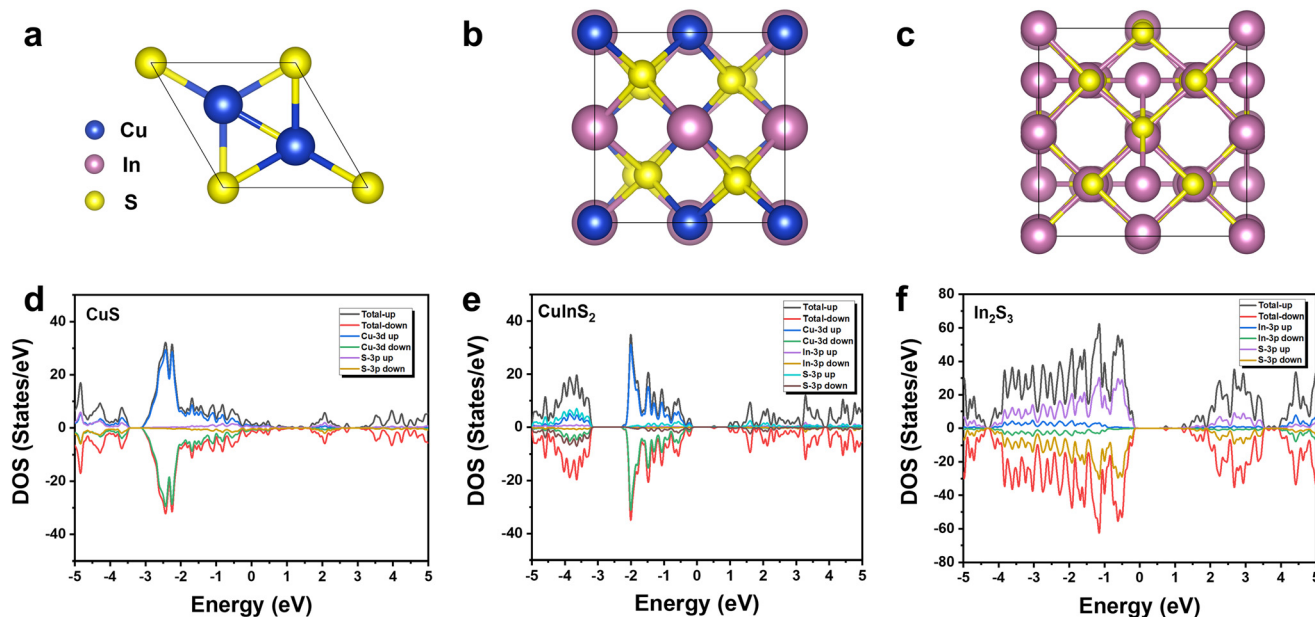


Fig. 8 Structural model diagram of (a) CuS, (b) CuInS<sub>2</sub> and (c) In<sub>2</sub>S<sub>3</sub>; PDOS of (d) CuS, (e) CuInS<sub>2</sub> and (f) In<sub>2</sub>S<sub>3</sub>.

demonstrated a remarkable rate of  $45.7 \mu\text{mol g}^{-1} \text{h}^{-1}$  for photothermal CO<sub>2</sub> reduction with H<sub>2</sub>O to C<sub>2</sub>H<sub>4</sub>, achieving a selectivity of 79.7% and excellent cycle stability. Control experiments conclusively proved the photothermal synergistic catalytic process, which significantly enhanced the efficiency of the reaction, addressing the limitations of single-mode photocatalysis and thermal catalysis. Electrochemical measurements, along with PL and TRPL analyses, confirmed the superior charge transport and separation efficiency demonstrated by the CuInS<sub>2</sub> catalyst. Furthermore, the abundant sulfur vacancies create additional active sites, promoting CO<sub>2</sub> activation, and the more negative conduction band of the CuInS<sub>2</sub> catalyst facilitates the reduction of CO<sub>2</sub> to C<sub>2</sub>H<sub>4</sub>. This work offers valuable insights into the design of metal sulfide catalysts for the photocatalytic conversion of CO<sub>2</sub> into C<sub>2+</sub> products.

## 4 Experimental section

### 4.1 Chemicals and materials

All chemicals were used as received without further purification. Cupric chloride dihydrate (CuCl<sub>2</sub>·2H<sub>2</sub>O), indium chloride tetrahydrate (InCl<sub>3</sub>·4H<sub>2</sub>O, 99.9%), thioacetamide (TAA, ≥98.0%), deionized water and anhydrous ethanol (C<sub>2</sub>H<sub>5</sub>OH, 99.5%) were purchased from Aladdin Reagent Company (Shanghai, China).

### 4.2 Preparation of CuInS<sub>2</sub>

1.8 mmol of CuCl<sub>2</sub>·2H<sub>2</sub>O, 1.8 mmol of InCl<sub>3</sub>·4H<sub>2</sub>O and 3.6 mmol of TAA were dissolved in 80 mL deionized water and 80 mL ethanol, and reacted under hydrothermal conditions of 160 °C for 12 hours. After the reaction, the product was collected and washed with deionized water and ethanol, and

dried under vacuum at 60 °C for 12 hours; the synthesized sample was denoted as CuInS<sub>2</sub>.

The synthesis methods for CuIn<sub>2</sub>S<sub>4</sub> and CuIn<sub>5</sub>S<sub>8</sub> are consistent with the described procedure, with the only modification being the variation in the molar ratios of CuCl<sub>2</sub>·2H<sub>2</sub>O, InCl<sub>3</sub>·4H<sub>2</sub>O, and TAA.

### 4.3 Preparation of CuS

1.8 mmol of CuCl<sub>2</sub>·2H<sub>2</sub>O and 3.6 mmol of TAA were dissolved in 80 mL deionized water and 80 mL ethanol, and reacted under hydrothermal conditions of 160 °C for 12 hours. After the reaction, the product was collected and washed with deionized water and ethanol, and dried under vacuum at 60 °C for 12 hours; the synthesized sample was denoted as CuS.

### 4.4 Preparation of In<sub>2</sub>S<sub>3</sub>

1.8 mmol of InCl<sub>3</sub>·4H<sub>2</sub>O and 3.6 mmol of TAA were dissolved in 80 mL deionized water and 80 mL ethanol, and reacted under hydrothermal conditions of 160 °C for 12 hours. After the reaction, the product was collected and washed with deionized water and ethanol, and dried under vacuum at 60 °C for 12 hours; the synthesized sample was denoted as In<sub>2</sub>S<sub>3</sub>.

### 4.5 Photothermal catalytic reduction of CO<sub>2</sub>

For CO<sub>2</sub> photothermal conversion, 0.2 g catalyst and 0.1 mL TEOA were filled into the reaction tube. Subsequently, the flow fixed-bed reactor was filled with high-purity CO<sub>2</sub> gas to reach the reaction pressure. In the reaction system, deionized water was used as the proton source and a 300 W xenon lamp was used as the light source (Fig. S1†). The reaction products were analyzed in real time online by gas chromatography (GC 9790 II, FuLi, FID and TCD detector). The carbon-based



products of CO and C<sub>2</sub>H<sub>4</sub> were quantified with a flame ionization detector (FID).

The photothermocatalytic CO and C<sub>2</sub>H<sub>4</sub> production amounts and the rate could be calculated as follows:

$$Y = \frac{V}{22.4 \times 1000} \quad (1)$$

$$v = \frac{Y}{m \times t} \quad (2)$$

where  $Y$  represents CO and C<sub>2</sub>H<sub>4</sub> production (μmol),  $V$  is the volume of CO and C<sub>2</sub>H<sub>4</sub> (mL),  $v$  represents the CO and C<sub>2</sub>H<sub>4</sub> production rate (μmol g<sup>-1</sup> h<sup>-1</sup>),  $m$  is the mass of sample (g), and  $t$  is the reaction time (h).

The selectivity for the CO<sub>2</sub> reduction products of CO and C<sub>2</sub>H<sub>4</sub> was calculated using the following equation:

$$\text{CO selectivity (\%)} = \frac{n(\text{CO})}{n(\text{CO}) + 2n(\text{C}_2\text{H}_4)} \times 100\% \quad (3)$$

$$\text{C}_2\text{H}_4 \text{ selectivity (\%)} = \frac{2n(\text{C}_2\text{H}_4)}{n(\text{CO}) + 2n(\text{C}_2\text{H}_4)} \times 100\% \quad (4)$$

where  $n(\text{CO})$  and  $n(\text{C}_2\text{H}_4)$  are the molar yields of generated CO and C<sub>2</sub>H<sub>4</sub> products, respectively.

#### 4.6 Electrochemical measurements

The preparation of the working electrode was as follows. 5 mg photocatalyst was dispersed in a mixed solution of 350 μL C<sub>3</sub>H<sub>8</sub>O, 50 μL Nafion and 100 μL H<sub>2</sub>O, and sonicated for 1 h. Then the mixed liquid was dispersed on FTO glass as a photoelectrode. The transient photocurrent response and electrochemical impedance spectra (EIS) were determined by using a CHI760E electrochemical workstation. 0.5 M Na<sub>2</sub>SO<sub>4</sub> solution was used as the electrolyte and a 300 W xenon lamp was used as the light source. The sample photoelectrode, platinum foil and Ag/AgCl served as the working electrode, counter electrode and reference electrode, respectively.

#### 4.7 Characterization

X-ray diffraction (XRD) was carried out using an X-ray diffractometer (Smartlab (9)) with the  $2\theta$  range from 5° to 90°. The morphology and sizes were examined by field-emission transmission electron microscopy (TEM) and field-emission scanning electron microscopy (SEM) using a JEOL F200 and JSM-7800 (Prime), respectively. X-ray photoelectron spectroscopy (XPS) analyzing the chemical compositions was conducted with an AXIS SUPRA+. The electron paramagnetic resonance (EPR) was measured on a Bruker EMX-Plus ESR spectrometer. The UV-vis diffuse reflectance spectra (DRS) were obtained with a Hitachi UH4150 spectrophotometer using BaSO<sub>4</sub> as the reflectance standard. Steady-state photoluminescence (PL) spectra of the as-prepared samples were detected with a Hitachi F-4700. Time-resolved photoluminescence (TRPL) spectra of the as-prepared samples were detected with an Edinburgh Instruments 980.

## Data availability

The data that support the findings of this study are available from the corresponding author upon reasonable request.

## Author contributions

Longlong Wang: investigation, confirmation, conceptualization, methodology, data analysis and writing – original draft. Ruirui Wang: supervision, formal analysis, data curation and writing – review & editing. Shuang Wei: investigation, confirmation, conceptualization. Kexin Li: methodology, data analysis. Hasnain Nawaz: conceptualization, methodology. Bin He: writing – review & editing. Mengyue Li: investigation. Ruixia Liu: supervision, resources, project administration, funding acquisition, writing – review & editing.

## Conflicts of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Note added after first publication

This article replaces the version published on 17th April 2025, which inadvertently omitted the keywords from the Abstract.

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