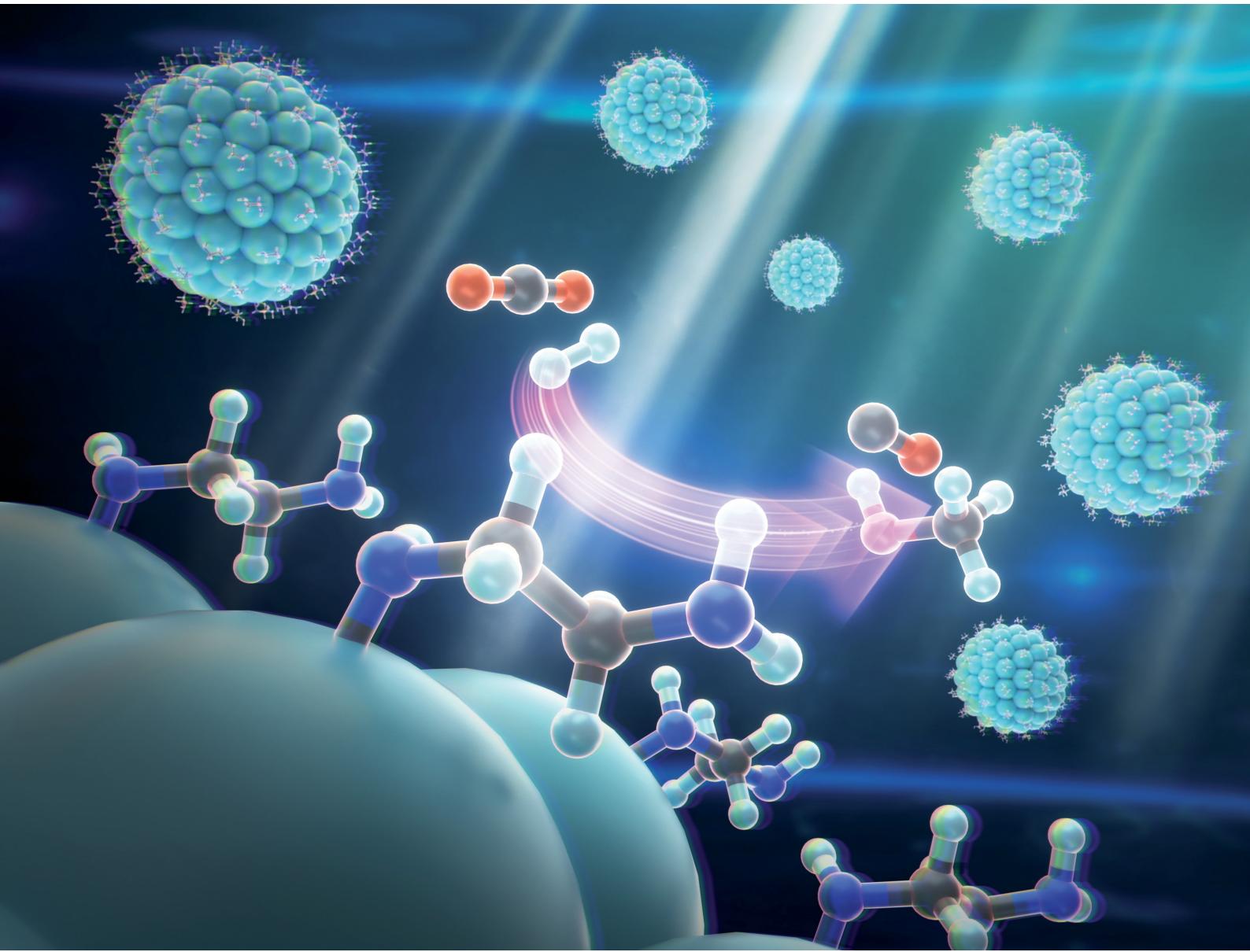


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## Amine functionalized surface frustrated Lewis pairs boost CO<sub>2</sub> photocatalysis†‡

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The archetype surface frustrated Lewis pair (SFLP) that facilitates CO<sub>2</sub> photocatalytic hydrogenation to methanol and carbon monoxide, is an InOH···In site positioned in the surface of a nanoscale indium oxide hydroxide, denoted In<sub>2</sub>O<sub>3-x</sub>(OH)<sub>y</sub>. Proximal Lewis acid In(III) and Lewis base InOH of this genre serve as surface active sites that enable the photochemical heterolytic H<sub>2</sub> dissociation and reduction of CO<sub>2</sub> to the mentioned products. The conversion rate enabled by light has been found to far exceed that enabled by heat. Efforts to enhance the CO<sub>2</sub> photocatalytic performance of the SFLP have involved modifications of the Lewis acidity and basicity through isomorphic substitution of In(III) with Bi(III) and changes in the population of oxygen vacancies through control of oxide non-stoichiometry. Replacement of the Lewis base hydroxide InOH by the stronger Lewis base amine InNH<sub>2</sub> heretofore remains unexplored. The strategy described herein to explore this opportunity begins with the synthesis of In<sub>2</sub>O<sub>3-x</sub>(EDA)<sub>y</sub>. This new material is proven to contain an InNH<sub>2</sub>···In SFLP and its CO<sub>2</sub> photocatalytic performance is demonstrated to outperform that of its In<sub>2</sub>O<sub>3-x</sub>(OH)<sub>y</sub> progenitor. Tailored Lewis acidity and basicity surfaces bring CO<sub>2</sub> photocatalysis another step closer to the vision of solar CO<sub>2</sub> refineries.

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### Broader context

In heterogeneous catalysis the surface frustrated Lewis pair, SFLP, has played a central role in the hydrogenation of CO<sub>2</sub> to commodity chemicals exemplified by syngas, methanol, methane, and higher hydrocarbons. Notably, all prior reports of SFLP in CO<sub>2</sub> catalysis involve a Lewis acid metal M site proximal to a Lewis base hydroxide MOH site, described as M···MOH. The thermochemical and photochemical activity of the SFLP is determined by its electronic ground (thermocatalysis) and excited (photocatalysis) state Lewis acidity and basicity. To this end, the acidity of the Lewis site has previously been investigated by modifying the effective charge on the metal site. This has been curated by changes in the ionic radius, oxidation state, and electronegativity of the metal. This goal has been achieved in the work described herein by switching the Lewis basic hydroxide site M···MOH to a stronger Lewis basic amine M···MNH<sub>2</sub>, a change found to boost photocatalytic CO<sub>2</sub> hydrogenation performance, one more step to the vision of CO<sub>2</sub> refineries powered by light.

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† This paper is dedicated to Professor Geoffrey Ozin on the occasion of his 80th birthday.

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### Introduction

Photocatalytic conversion of CO<sub>2</sub> into valuable chemical fuels has emerged as a potential solution to address both energy and environmental concerns. However, breaking the highly stable C=O bonds in CO<sub>2</sub> molecules remains a challenging task. Previous studies have shown that surface oxygen vacancies (O<sub>vs</sub>) on metal oxides exhibit high catalytic activity and can effectively activate and split CO<sub>2</sub>.<sup>1-3</sup> The thermodynamically metastable O<sub>vs</sub>, which are formed through hydrogen reduction or hydroxyl dehydration, facilitate the incorporation of CO<sub>2</sub> oxygen atoms into the oxide sublattice, enabling subsequent CO<sub>2</sub> hydrogenation. More recently, heterogeneous catalysts with solid surface frustrated Lewis pair (SFLP) have been developed for various significant catalytic reactions, including



$\text{CO}_2$  hydrogenation, hydroamination, and methane conversion.<sup>4,5</sup> SFLP consists of Lewis acidic and Lewis basic sites in close proximity, preventing their interaction and forming Lewis acid–base pair that synergistically activates small molecules such as  $\text{H}_2$ ,  $\text{CO}_2$ , and  $\text{CH}_4$ . The existing solid SFLP systems can be categorized into two types: isolated  $\text{O}_{\text{Vs}}$  systems and  $\text{OH}-\text{O}_{\text{Vs}}$  systems.<sup>6–11</sup> Isolated  $\text{O}_{\text{Vs}}$  systems, represented by  $\text{CeO}_{2-x}$ , exhibit a high density of surface  $\text{O}_{\text{Vs}}$ , which leads to adjacent metal atoms with unsaturated coordination; thus, creating independent Lewis acidic and basic sites.<sup>12</sup> On the other hand,  $\text{OH}-\text{O}_{\text{Vs}}$  systems typically involve a surface metal site with unsaturated coordination (Lewis acid) located near oxygen vacancies and a surface hydroxide site (Lewis base). Examples of such systems include defect-laden hydroxylated oxides like  $\text{In}_2\text{O}_{3-x}(\text{OH})_y$ ,  $\text{TiO}_{2-x}(\text{OH})_y$ , and  $\text{CoGeO}_2(\text{OH})_2$ .<sup>7,13,14</sup> However, achieving a balanced concentration between  $\text{O}_{\text{Vs}}$  and hydroxide sites in this manner is challenging. Although our recent research demonstrated that the reactivity of Lewis acidic sites can be controlled through the replacement of  $\text{In}_2\text{O}_3$  with single-site  $\text{Bi}^{3+}$  ion, maximizing the reactivity of SFLP by simultaneously creating high-level Lewis acidic and basic sites remains a significant challenge.<sup>15</sup>

Incorporating amine functional groups has been widely employed to enhance  $\text{CO}_2$  capture efficiency in  $\text{CO}_2$  photocatalysis. Amine functionalization of various photocatalysts, such as oxides, sulfides, and graphitic carbon nitride, enables substantial  $\text{CO}_2$  adsorption through acid–base interactions.<sup>16–18</sup> The adsorbed amine groups on photocatalysts can activate  $\text{CO}_2$  molecules by forming carbamate intermediates, resulting in a significant distortion of the original linear  $\text{C}=\text{O}$  bond and reducing the energy barrier for  $\text{C}-\text{O}$  bond formation.<sup>19</sup> The previous work by Lu *et al.* demonstrated that amine groups can act as Lewis basic sites, coupling with Lewis acidic sites (e.g., Au surface) to form solid-molecule SFLP. This SFLP configuration enables the activation of  $\text{H}_2$  and subsequent hydrogenation of imines and nitriles.<sup>20</sup> In contrast to the aforementioned SFLP types, amine-functionalized SFLP systems circumvent the reliance on hydroxyl groups to generate  $\text{O}_{\text{Vs}}$ , potentially maximizing the reactivity of SFLP. Moreover, the amine group possesses higher electronegativity than the hydroxyl group, suggesting its potential as a more active Lewis basic site. Consequently, grafting amine groups onto defect-laden oxides by replacing hydroxyl groups could result in the formation of  $\text{NH}_2-\text{O}_{\text{Vs}}$  systems, offering enhanced reactivity and providing strong Lewis acid and base sites to facilitate  $\text{CO}_2$  adsorption and activation, thereby improving photocatalytic  $\text{CO}_2$  reduction performance.

In this study, we present a one-pot solvothermal approach for synthesizing amine-functionalized  $\text{In}_2\text{O}_3$  catalysts for gas-phase  $\text{CO}_2$  hydrogenation photocatalysis. Extensive characterization techniques, coupled with density functional theory (DFT) calculations, are employed to gain valuable insights into the formation of  $\text{InNH}_2\cdots\text{In}$  SFLP systems, the surface and electronic nature of the active sites, and the identification of key intermediates during photocatalytic  $\text{CO}_2$  hydrogenation. The findings of this study provide a foundation for sustainable

chemical fuel production through the engineering of molecule-functionalized metal oxide-based heterogeneous  $\text{CO}_2$  photocatalysis.

## Results and discussion

A facile one-pot solvothermal method was employed to synthesize amine-functionalized  $\text{In}_2\text{O}_3$  nanocrystals (E-IO) using  $\text{In}(\text{NO}_3)_3$  as the indium precursor and ethylenediamine (EDA) as both the reaction medium and functionalizing agent. As illustrated in Fig. 1A, EDA initially chelates with indium ions in the precursor solution, forming  $\text{In}_n(\text{EDA})_m^{3+}$  complexes. These complexes then react with  $\text{OH}^-$  ions, derived from the hydrolysis of EDA, resulting in the generation of  $\text{In}_n(\text{EDA})_{m-x}(\text{OH})_x^{(3-x)^+}$  intermediates. These intermediates gradually dissociate and condense, forming small  $\text{In}_2\text{O}_3$  nuclei with EDA attached to the surface through hydrogen bonding by single coordination according to the previous reports.<sup>21,22</sup> The newly formed  $\text{In}_2\text{O}_3$  nuclei tend to rapidly attach together, minimizing surface energy. Subsequently, they undergo further rearrangement and crystallization through a “self-assembly” aggregation growth mechanism.<sup>23,24</sup> SEM and TEM images of the amine-functionalized  $\text{In}_2\text{O}_3$  nanocrystals are shown in Fig. 1B and C, respectively. These images reveal a predominantly spherical morphology with an average diameter of approximately 30 nm. The  $\text{In}_2\text{O}_3$  nanospheres are composed of small agglomerated nanoparticles with average diameters around 6.50 nm (Fig. 1D). HRTEM analysis in Fig. 1E shows well-defined lattice fringes with an interplanar distance of 0.293 nm, corresponding to the (222) facet of the cubic structure of  $\text{In}_2\text{O}_3$ . The SAED pattern displayed in Fig. 1F exhibits multiple rings composed of individual spots, indicating the polycrystalline nature of the amine-functionalized  $\text{In}_2\text{O}_3$  nanocrystals. EDS mapping of the nanospheres confirms the homogeneous distribution of In, O, and N elements in the  $\text{In}_2\text{O}_3$  nanocrystals (Fig. 1G). The atomic content of N in the E-IO sample was determined to be approximately 5.51 wt% (Fig. S1, ESI‡).

To gain a deeper understanding of the role played by amine groups in the active  $\text{In}_2\text{O}_3$ -based photocatalysts, we synthesized indium hydroxide *via* a hydrothermal method (Scheme S1, ESI‡), where only water was used as the reactant solvent. The resulting indium hydroxide was then calcined to produce  $\text{In}_2\text{O}_3$  with a fresh surface.<sup>25</sup> TEM images of the hydrothermally synthesized  $\text{In}_2\text{O}_3$  sample (H-IO) (Fig. S2A–C, ESI‡) reveal that it is a cube-shaped nanoparticle with an edge length exceeding 400 nm. The significant difference in particle size between E-IO and H-IO makes it challenging to determine whether the variation in photocatalytic activity is attributable to particle size or surface amine groups. To directly compare the  $\text{In}_2\text{O}_3$  samples with and without amine functionalization, we further synthesized  $\text{In}_2\text{O}_3$  (Si-IO) with smaller particle size using  $\text{SiO}_2$  nanospheres as templates in an aqueous solution. The resulting  $\text{In}_2\text{O}_3$  sample consists of small agglomerated nanorods with a diameter of approximately 10 nm (Fig. S2D–F, ESI‡), which is comparable in particle size to the E-IO sample.



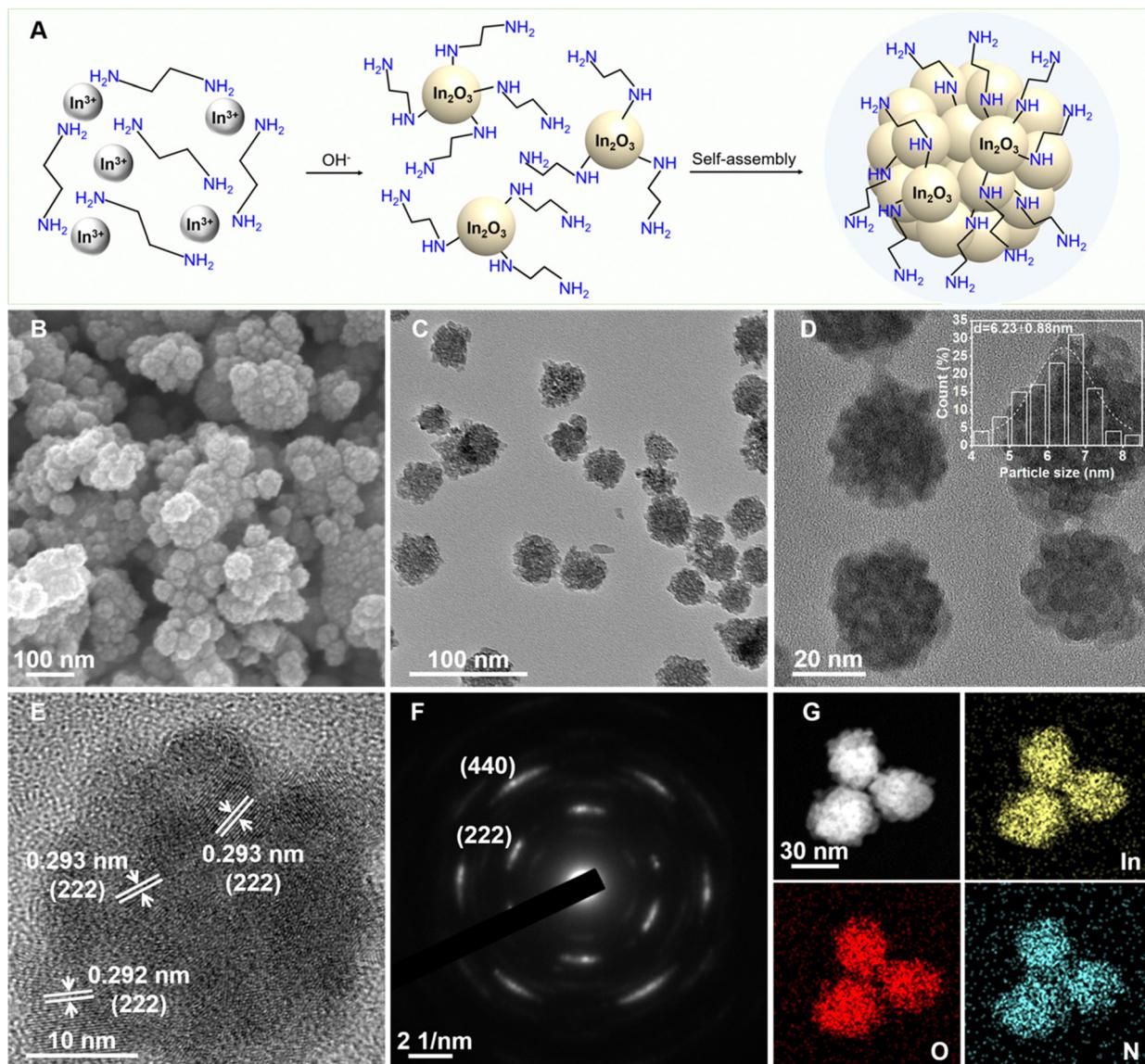
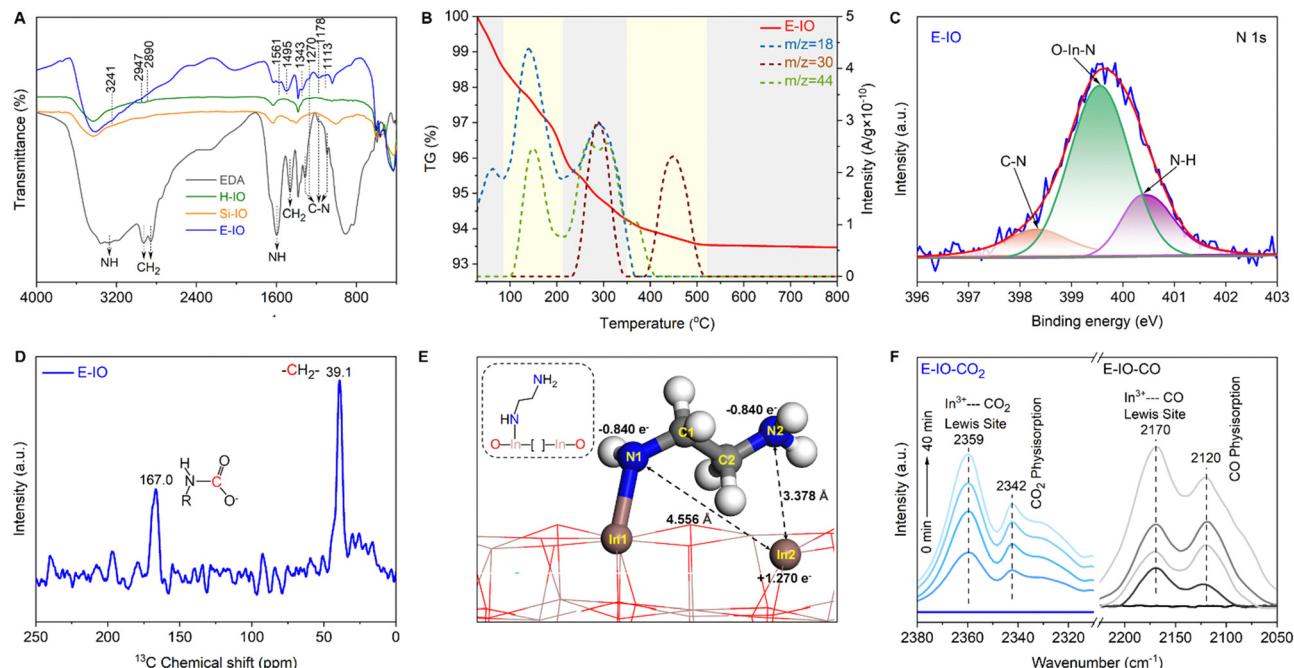


Fig. 1 Synthesis and morphology of amine-functionalized  $\text{In}_2\text{O}_3$  nanocrystals. (A) Schematic of the synthetic route. (B) SEM images. (C)–(E) TEM images, particle size distribution (inset) and HRTEM images. (F) SAED pattern. (G) EDS mapping.

Fig. S3 (ESI<sup>‡</sup>) presents the XRD patterns of the  $\text{In}_2\text{O}_3$  samples with and without amine functionalization. The patterns of all three samples exhibit similar diffraction peaks that can be assigned to the cubic phase of indium oxide ( $\text{c-In}_2\text{O}_3$ ) (JCPDS no. 71-2195). The crystallite sizes estimated using the Scherrer equation are 6.41 nm for E-IO, 29.95 nm for H-IO, and 9.47 nm for Si-IO (Table S1, ESI<sup>‡</sup>). Nitrogen adsorption/desorption isotherms of the three samples are shown in Fig. S4 (ESI<sup>‡</sup>), revealing the presence of mesopores in all  $\text{In}_2\text{O}_3$  samples. The specific surface area follows the order of Si-IO ( $94.97 \text{ m}^2 \text{ g}^{-1}$ ) > E-IO ( $50.54 \text{ m}^2 \text{ g}^{-1}$ ) > H-IO ( $15.67 \text{ m}^2 \text{ g}^{-1}$ ). Although a larger surface area may facilitate  $\text{CO}_2$  adsorption, the subsequent photocatalytic results indicate that surface area is not the primary factor contributing to the improved photocatalytic activity in  $\text{CO}_2$  hydrogenation.

To confirm the successful functionalization of amine groups on the surface of  $\text{In}_2\text{O}_3$  nanocrystals, several characterizations,

including FTIR, TG-MS, XPS, and NMR were conducted on the collected samples. In the FTIR spectra of the three  $\text{In}_2\text{O}_3$  samples (Fig. S5, ESI<sup>‡</sup>), four intense peaks centered at 602, 565, 538, and  $428 \text{ cm}^{-1}$  are observed, corresponding to the vibration peaks of In–O bonds in cubic  $\text{In}_2\text{O}_3$ .<sup>26</sup> The peak at  $1383 \text{ cm}^{-1}$  corresponds to the stretching vibration of OH bonds, with the H-IO sample exhibiting the strongest OH peak due to the abundance of surface OH groups. Notably, the E-IO sample displays several new peaks centered at 3241, 2947, 2890, 1561, 1495, 1343, 1270, 1178 and  $1113 \text{ cm}^{-1}$  (Fig. 2A). According to previous studies and the measured IR spectra of EDA reference, the peaks at 3241 and 1561  $\text{cm}^{-1}$  correspond to the symmetric bending vibration of NH,<sup>27,28</sup> while the peaks at 1343, 1270, 1178 and  $1113 \text{ cm}^{-1}$  can be attributed to the stretching vibration of C–N.<sup>29–32</sup> Additionally, peaks centered at 2947, 2890 and 1495  $\text{cm}^{-1}$  can be assigned to



**Fig. 2** Characterization of samples (A) FTIR spectra of H-IO, Si-IO and E-IO. (B) TGA-MS curves of E-IO in air condition. (C) High resolution N 1s XPS spectra of E-IO. (D)  $^{13}\text{C}$  MAS NMR spectra of E-IO at room temperature. (E) *In situ* DRIFTS spectra of the adsorption of  $\text{CO}_2$  (left) and CO (right) on the E-IO surface at 298 K.

$\text{CH}_2$  vibrational bands.<sup>27,28,32</sup> TG-MS analysis was further performed to confirm the presence of amine groups in the E-IO samples. It is evident that E-IO exhibits significant weight loss during thermal treatment in the temperature range of 30 to 520 °C, compared to the other two samples (Fig. S6, ESI‡). This weight loss can be attributed to the release of ethylenediamine molecules bonded to the surface of E-IO upon thermal treatment. The TG-MS data (Fig. 2B) reveal that the E-IO sample has a substantial amount of physically and chemically absorbed  $\text{H}_2\text{O}$  on the surface, which is desorbed at around 150 and 280 °C, respectively. Physically absorbed  $\text{CO}_2$  is completely removed at approximately 200 °C. Additionally, the observed  $\text{CO}_2$  in the range of 200–400 °C can be attributed to the decomposition of amine groups, which is supported by the presence of a mass spectrometer signal for NO with  $m/z$  value of 30 starting from 245 °C.<sup>33–35</sup> Of note, the additional Raman (Fig. S7, ESI‡) and wide-range N 1s XPS (Fig. S8, ESI‡) results can exclude the possibility of the generation of NO deriving from salt anion ( $\text{NO}_3^-$ ). Furthermore, according to the previous reports shown in Table S2 (ESI‡), the N 1s XPS spectrum of E-IO exhibits three distinct peaks: O-In-N bonding at 399.55 eV,<sup>36</sup> C-N bonding at 398.30 eV and coordinately-bound NH groups at 400.39 eV (Fig. 2C).<sup>37,38</sup> What's more, as shown in Fig. S9 and S10 (ESI‡), the three peaks detected in the C 1s XPS spectrum of E-IO can be attributed to the C-C bonding (284.60 eV), C-N bonding (285.98 eV) and O-C=O bonding (288.83 eV), respectively,<sup>39,40</sup> and the In 3d<sub>5/2</sub> and In 3d<sub>1/2</sub> peaks of E-IO are conventionally deconvoluted to In-N bonding (443.59 eV and 251.18 eV), and In-O bonding (444.17 eV and 451.73 eV).<sup>41</sup> Through these results, the existence state of EDA on the surface

of E-IO can be confirmed: the amine group at one end of EDA is coordinated with the indium atom of  $\text{In}_2\text{O}_3$ , while the amine group at the other end exists in an uncoordinated  $\text{NH}_2$  group state. Solid-state NMR experiment can further provide strong evidence for the successful grafting of EDA molecular onto the catalyst surface. As shown in Fig. 2D, the  $^{13}\text{C}$  magic angle spinning nuclear magnetic resonance ( $^{13}\text{C}$  MAS NMR) spectrum for the E-IO presents the characteristic carbon resonance signals at 39.1 ppm, which can be assigned to the C atom in  $\text{CH}_2$  groups arising from EDA molecular. Moreover, an additional resonance peak at 167.0 ppm is clearly observed and should be attributed to the C atom in carbamate groups that are formed by the binding of  $\text{NH}_2$  groups with  $\text{CO}_2$  in the air.<sup>42–44</sup> Collectively, all these results confirm the successful grafting of amine groups onto the surface of E-IO nanoparticles during the solvothermal process.

Ethylenediamine was employed as both an appropriate amine-modifying reagent and a facilitator for generating a significant quantity of oxygen vacancies during the synthesis of amine-functionalized  $\text{In}_2\text{O}_3$  nanocrystals. The presence and semi-quantitative analysis of oxygen vacancies were determined using XPS and EPR techniques. Fig. S11A–C (ESI‡) shows the high-resolution XPS spectra of the O 1s region in the H-IO, Si-IO, and E-IO samples. The spectra exhibit three distinct peaks at binding energies of 529.35, 530.86, and 531.81 eV, corresponding to lattice oxides, oxygen vacancies, and hydroxyl groups, respectively.<sup>9,45</sup> Notably, E-IO displays a significantly higher oxygen vacancy concentration of 34.43% compared to H-IO (20.68%) and Si-IO (18.15%). Additionally, the binding energy of the In 3d core level in E-IO exhibits a noticeable shift



toward lower binding energy (Fig. S11D, ESI‡), indicating an unsaturated state of indium in the amine-functionalized  $\text{In}_2\text{O}_3$  nanocrystals and a higher surrounding electron density. This observation further confirms the presence of a substantial number of oxygen vacancies in the amine-functionalized  $\text{In}_2\text{O}_3$  sample. EPR spectroscopy is an effective semi-quantitative characterization method for evaluating oxygen vacancies. As depicted in Fig. S12 (ESI‡), all three samples exhibit an EPR signal related to oxygen vacancies, appearing at the *g*-value of 2.003.<sup>46</sup> Notably, E-IO displays the strongest EPR signal, indicating that the presence of ethylenediamine promotes the formation of  $\text{O}_{\text{vs}}$  during the solvothermal synthesis. Consequently, based on the XPS and EPR findings, it can be concluded that the amine-functionalized  $\text{In}_2\text{O}_3$  sample possesses a substantial number of surface oxygen vacancies. As a higher population of oxygen vacancies corresponds to a lower oxygen coordination number around the  $\text{In}^{(\text{III})}$  sites, the coordinately unsaturated  $\text{In}^{(\text{III})}$  becomes more Lewis acidic. Furthermore, the substitution of hydroxyl groups with amine groups, which possess stronger electronegativity in the amine-functionalized  $\text{In}_2\text{O}_3$  nanocrystals, makes them more Lewis basic. Consequently, the amine-functionalized  $\text{In}_2\text{O}_3$  (E-IO) should have intensified Lewis acid and Lewis base sites, showing promising potential in enhancing photocatalytic performance for  $\text{CO}_2$  reduction.

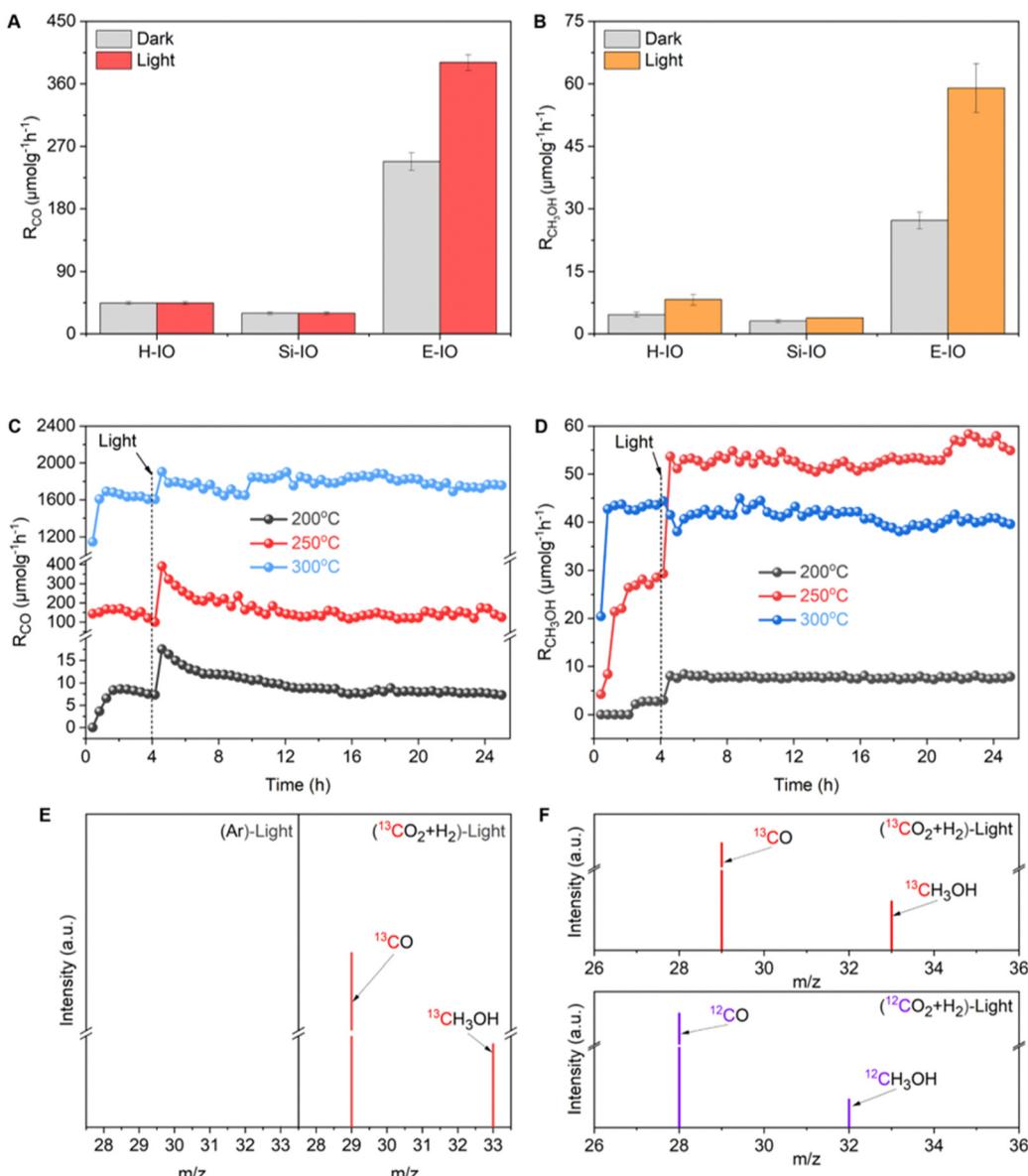
Density functional theory (DFT) slab calculations were conducted to validate the SFLP property achieved by substituting EDA for hydroxide groups on the  $\text{In}_{2-x}(\text{OH})_y$  surface. Previous studies have demonstrated that SFLP, consisting of an unsaturated In atom as the Lewis acid site and a hydroxide group as the Lewis base site, can be constructed by removing a surface oxygen atom and introducing a hydroxide group on the (110) facet of cubic  $\text{In}_2\text{O}_3$ .<sup>15,47,48</sup> Herein, we investigate the optimized structure of the substitution of EDA at the hydroxide group site. As shown in Fig. 2E, two kinds of surface configurations, In2-N1 and In2-N2, are identified on the amine-functionalized surface. The In2-N1 and In2-N2 with respective distances of 4.556 Å and 3.378 Å fall in the domain of solid SFLP. The Bader charge calculations indicate that the related In2, N1 and N2 pairs have atomic local charges of +1.27e, -0.84e and -0.84e, respectively. Compared with In2-N1 configuration, In2-N2 with a shorter distance may deliver a higher capability to activate reactant molecules.<sup>49</sup>

The existence of unsaturated In atom as Lewis acid site is essential for the construction of  $\text{InNH}_2\cdots\text{In}$  SFLP, where the  $\text{NH}_2$  in the  $\text{InNH}_2\cdots\text{In}$  SFLP systems refers to the non-coordinated  $\text{NH}_2$  group of EDA, while the other  $\text{NH}_2$  group being coordinated with the In atom in  $\text{In}_2\text{O}_3$ . To prove this, *in situ* diffuse reflectance infrared Fourier-transform spectroscopy (DRIFTS) of adsorbed CO and  $\text{CO}_2$  at 298 K were investigated, respectively. After thermal treatment of the E-IO at 423 K for 2 h, saturated doses of CO or  $\text{CO}_2$  were introduced into IR cells. The spectrum (Fig. 2F, right) of adsorbed CO on E-IO shows a diagnostic peak centered at 2170  $\text{cm}^{-1}$ , which can be assigned to the C–O stretching vibration of CO interacting with the coordinatively unsaturated In sites.<sup>50–52</sup> In addition, in

the adsorption spectrum of  $\text{CO}_2$  (Fig. 2F, left), the diagnostic peak at 2359  $\text{cm}^{-1}$  can be clearly observed and this peak is usually ascribed to the linear adduct of  $\text{CO}_2$  coordinated to Lewis acidic sites.<sup>53,54</sup> Moreover, the diagnostic peaks at 2120 and 2342  $\text{cm}^{-1}$  can be attributed to the physical adsorption of CO and  $\text{CO}_2$ , respectively. These two spectroscopic characterizations clearly highlight that CO/ $\text{CO}_2$  can be able to interact with unsaturated In atoms that act as Lewis acid sites, providing strong evidence for the presence of grafting state  $\text{InNH}_2\cdots\text{In}$ .

The catalytic performance of  $\text{CO}_2$  hydrogenation was assessed in a flow reactor under reaction temperatures of 200, 250, and 300 °C with and without simulated solar light irradiation, using a gas mixture of  $\text{CO}_2$  and  $\text{H}_2$  in a 1:3 ratio, within a miniaturized photothermal catalytic microreactor system (Fig. S13, ESI‡). All three  $\text{In}_2\text{O}_3$  samples (E-IO, Si-IO, H-IO) exhibited catalytic activity for the reverse water gas shift (RWGS) reaction to produce CO and were capable of synthesizing  $\text{CH}_3\text{OH}$ , although the production rate and selectivity of the products varied among the catalysts. At 200 °C, regardless of light irradiation, all  $\text{In}_2\text{O}_3$  samples showed negligible CO activity, while the E-IO sample exhibited significantly higher  $\text{CH}_3\text{OH}$  activity compared to the other catalysts (Fig. S14 and S15, ESI‡). When the reaction temperature was increased to 250 °C, the Si-IO and H-IO catalysts displayed poor CO and  $\text{CH}_3\text{OH}$  production rates similar to those observed at 200 °C (Fig. 3A and B). Remarkably, the amine-functionalized E-IO catalyst showed a substantial improvement in both CO and  $\text{CH}_3\text{OH}$  formation under these reaction conditions. Specifically, at this temperature, E-IO demonstrated CO production rates of 248.07  $\mu\text{mol g}_{\text{cat}}^{-1} \text{h}^{-1}$  in the dark and 390.74  $\mu\text{mol g}_{\text{cat}}^{-1} \text{h}^{-1}$  under light irradiation, with a photo-enhancement rate of 158%. A significant photo-enhancement rate of approximately 217% was also observed for  $\text{CH}_3\text{OH}$  on E-IO. The solar-powered  $\text{CH}_3\text{OH}$  production rate of 59.02  $\mu\text{mol g}_{\text{cat}}^{-1} \text{h}^{-1}$  was more than 15.4 higher than that of the reference cubic  $\text{In}_2\text{O}_3$  catalyst (Si-IO). This photo-enhancement activity can be attributed to the lower activation energy of the photocatalytic process compared to the thermochemical process.<sup>15</sup> Furthermore, when the reaction temperature was further increased to 300 °C (Fig. S13, ESI‡), although both H-IO and Si-IO samples exhibited improved activities for CO and  $\text{CH}_3\text{OH}$  production, the E-IO sample still exhibited the best catalytic performance among the three catalysts. In particular, under light irradiation, the CO production rate on E-IO reached a high value of 1814.73  $\mu\text{mol g}_{\text{cat}}^{-1} \text{h}^{-1}$ , which is nearly 2.3 times higher than that of H-IO and Si-IO, and comparable to the reported rhombohedral polymorph of  $\text{In}_2\text{O}_3$ .<sup>15</sup> However, due to the exothermic nature of the  $\text{CH}_3\text{OH}$  production reaction, the production rate of  $\text{CH}_3\text{OH}$  on E-IO decreased to 37.57 and 41.06  $\mu\text{mol g}_{\text{cat}}^{-1} \text{h}^{-1}$  under dark and light conditions, respectively, showing almost no photo-enhancement at this high reaction temperature. The estimated turnover number (TON) of the three samples shows a similar activity trend towards CO and  $\text{CH}_3\text{OH}$  production (Fig. S15, ESI‡), further demonstrating that the amine functionalization





**Fig. 3** CO<sub>2</sub> hydrogenation performance (A) CO production rate at 250 °C with and without solar irradiation. (B) CH<sub>3</sub>OH production rate at 250 °C with and without solar irradiation. (C) Long-term (20 h) CO production over E-IO at different reaction temperatures with solar irradiation. (D) Long-term (20 h) CH<sub>3</sub>OH production over E-IO at different reaction temperatures with solar irradiation. (E) GC-MS data from Ar and <sup>13</sup>CO<sub>2</sub>/H<sub>2</sub> atmosphere under irradiation condition at 250 °C. (F) <sup>13</sup>CH<sub>3</sub>OH and <sup>13</sup>CO obtained from <sup>13</sup>CO<sub>2</sub> hydrogenation, and <sup>12</sup>CH<sub>3</sub>OH and <sup>12</sup>CO as a reference.

of In<sub>2</sub>O<sub>3</sub> can significantly enhance the performance of photo-catalytic CO<sub>2</sub> hydrogenation.

Based on the catalytic results, it can be concluded that the amine functionalization of In<sub>2</sub>O<sub>3</sub> significantly enhances the performance of CO<sub>2</sub> hydrogenation, exhibiting remarkable photo-enhancement in both CO and CH<sub>3</sub>OH production. In light of the superior catalytic performance of E-IO, we conducted long-term stability tests under atmospheric pressure conditions at 200, 250, and 300 °C. Prior to the long-term light irradiation testing, a 4 hour thermal catalytic process was performed to establish a steady-state activity. As depicted in Fig. 3C and D, the E-IO catalyst demonstrated excellent photo-catalytic stability for both CO and CH<sub>3</sub>OH production. Notably,

optimal CO production and CH<sub>3</sub>OH formation were achieved at 300 and 250 °C, respectively. After 20 h of continuous light irradiation testing, no significant decrease in production rate was observed, with a CO rate of 1787.18 μmol g<sub>cat</sub><sup>-1</sup> h<sup>-1</sup> and a CH<sub>3</sub>OH rate of 53.38 μmol g<sub>cat</sub><sup>-1</sup> h<sup>-1</sup>. Furthermore, the selectivity of CH<sub>3</sub>OH was evaluated throughout the tests (Fig. S16, ESI†). The results revealed a CH<sub>3</sub>OH selectivity of approximately 49%, 30%, and 2% at 200, 250, and 300 °C under light irradiation, respectively. Notably, the E-IO catalyst exhibited both a high CH<sub>3</sub>OH production rate (53.38 μmol g<sub>cat</sub><sup>-1</sup> h<sup>-1</sup>) and excellent CH<sub>3</sub>OH selectivity (30%) at 250 °C reaction conditions, demonstrating outstanding overall performance compared to reported indium oxide catalysts.<sup>9</sup> Moreover, the

spent E-IO catalyst after 20 h of reactions at 250 °C showed no significant changes in crystal phase, surface chemical groups, and chemical oxidation states, confirming its structural stability (Fig. S17 and S18, ESI‡). It should also be noted that when the E-IO catalyst suffered from catalytic reaction at a higher temperature (300 °C), the surface coordinated EDA molecules disappeared (Fig. 2B and Fig. S18c, ESI‡) and the  $\text{InNH}_2 \cdot \cdot \cdot \text{In}$  SFLP was destroyed, which then contributes to a remarkably decreased photocatalytic activity.

To substantiate that the CO and  $\text{CH}_3\text{OH}$  products were from the photocatalytic reaction, we conducted two parallel control experiments: one was using high-purity Ar instead of  $\text{CO}_2$ , and the other was using carbon-13-labeled carbon dioxide ( $^{13}\text{CO}_2$ ). Fig. 3E demonstrated that no product was observed in the Ar condition, indicating that both carbon products were exclusively derived from  $\text{CO}_2$  reduction. When the reaction atmosphere changed into  $^{13}\text{CO}_2$  and  $\text{H}_2$ , obvious M/S signals of  $^{13}\text{CO}$  ( $m/z = 29$ ) and  $^{13}\text{CH}_3\text{OH}$  ( $m/z = 33$ ) products were detected, supporting the conclusion that the products were generated via  $\text{CO}_2$  reduction. As compared, under  $^{12}\text{CO}_2$  and  $\text{H}_2$  atmosphere, unequivocal signals of  $^{12}\text{CO}$  and  $^{12}\text{CH}_3\text{OH}$  products were detected (Fig. 3F). All these results collectively confirm that the carbon source in the  $\text{CO}_2$  hydrogenation originates from the  $\text{CO}_2$ , rather than the decomposition of EDA molecules grafted on the catalyst surface. To further reflect the strong

chemical interaction of EDA molecule grafting on the  $\text{In}_2\text{O}_3$  surface, we also prepared amine-modified  $\text{In}_2\text{O}_3$  samples *via* the impregnation method. As shown in FTIR spectra (Fig. S19, ESI‡), there exhibited nearly absent characteristic absorption peaks related to EDA on the catalyst surface, indicating efficient removal of surface-grafted EDA molecules during the washing process. To maintain the residual of the EDA molecules, the impregnated catalyst without washing was also prepared and the characteristic absorption peaks related to EDA can be clearly detected. However, the photocatalytic  $\text{CO}_2$  hydrogenation performance of all the impregnated amine-modified  $\text{In}_2\text{O}_3$  showed almost the same as the pristine  $\text{In}_2\text{O}_3$  samples (Fig. S20, ESI‡), suggesting the minimal effect of physical impregnation.

Fig. 4A illustrates the UV-visible DRS spectra and corresponding bandgaps of the H-IO, Si-IO, and E-IO catalysts. All samples exhibit solar light absorption in the ultraviolet region (wavelengths below 440 nm). Notably, E-IO demonstrates significantly stronger UV light absorption, approximately double that of the other two samples. This observation suggests an increase in surface charge of the indium oxide material due to the introduction of surface amine groups. Furthermore, by employing the Kubelka–Munk equation and Mott–Schottky analysis (Fig. S21, ESI‡), we calculated the band gap ( $E_g$ ) and conduction band (CB) of the samples, resulting in

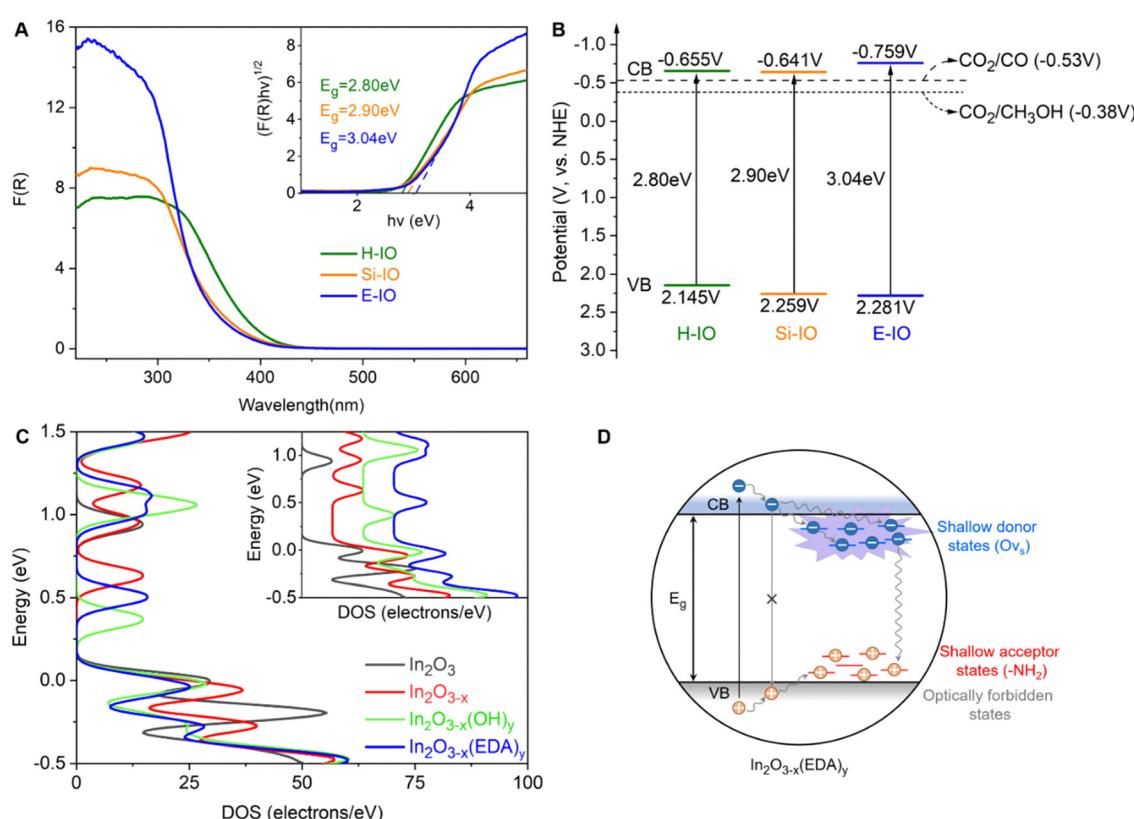


Fig. 4 Photocatalytic and photoelectrochemical characterizations (A) DRS and corresponding Tauc plots (inset) of H-IO, Si-IO, and E-IO. (B) Band diagrams. (C) The total DOS for  $\text{In}_2\text{O}_3$ ,  $\text{In}_{2-x}\text{O}_3$ ,  $\text{In}_{2-x}\text{O}_3\text{-}(\text{OH})_y$ , and  $\text{In}_{2-x}\text{O}_3\text{-}(\text{EDA})_y$  (110) surface, expanded view of the DOS in the conduction band region (inset). (D) A schematic illustration of charge carrier recombination pathways in  $\text{In}_{2-x}\text{O}_3\text{-}(\text{EDA})_y$  nanoparticles.



the band diagrams (Fig. 4B).<sup>55</sup> It is important to note that  $\text{In}_2\text{O}_{3-x}(\text{EDA})_y$  (E-IO) exhibits a more moderate band gap energy with a value of 3.04 eV, compared to  $\text{In}_2\text{O}_{3-x}(\text{OH})_y$  (H-IO) with a band gap energy of 2.80 eV and Si-IO with an  $E_g$  of 2.90 eV), as well as pristine cubic indium oxide (with an  $E_g$  of 3.6 eV as a direct semiconductor).<sup>56</sup> This indicates that E-IO enhances light absorption while avoiding excessive recombination of electron–hole pairs caused by a narrow band gap, thereby improving the transfer efficiency of photogenerated charge carriers. Moreover, E-IO exhibits a more negative conduction band at approximately  $-0.759$  eV compared to the other two samples, indicating a better reduction potential that facilitates  $\text{CO}_2$  photocatalytic reduction.

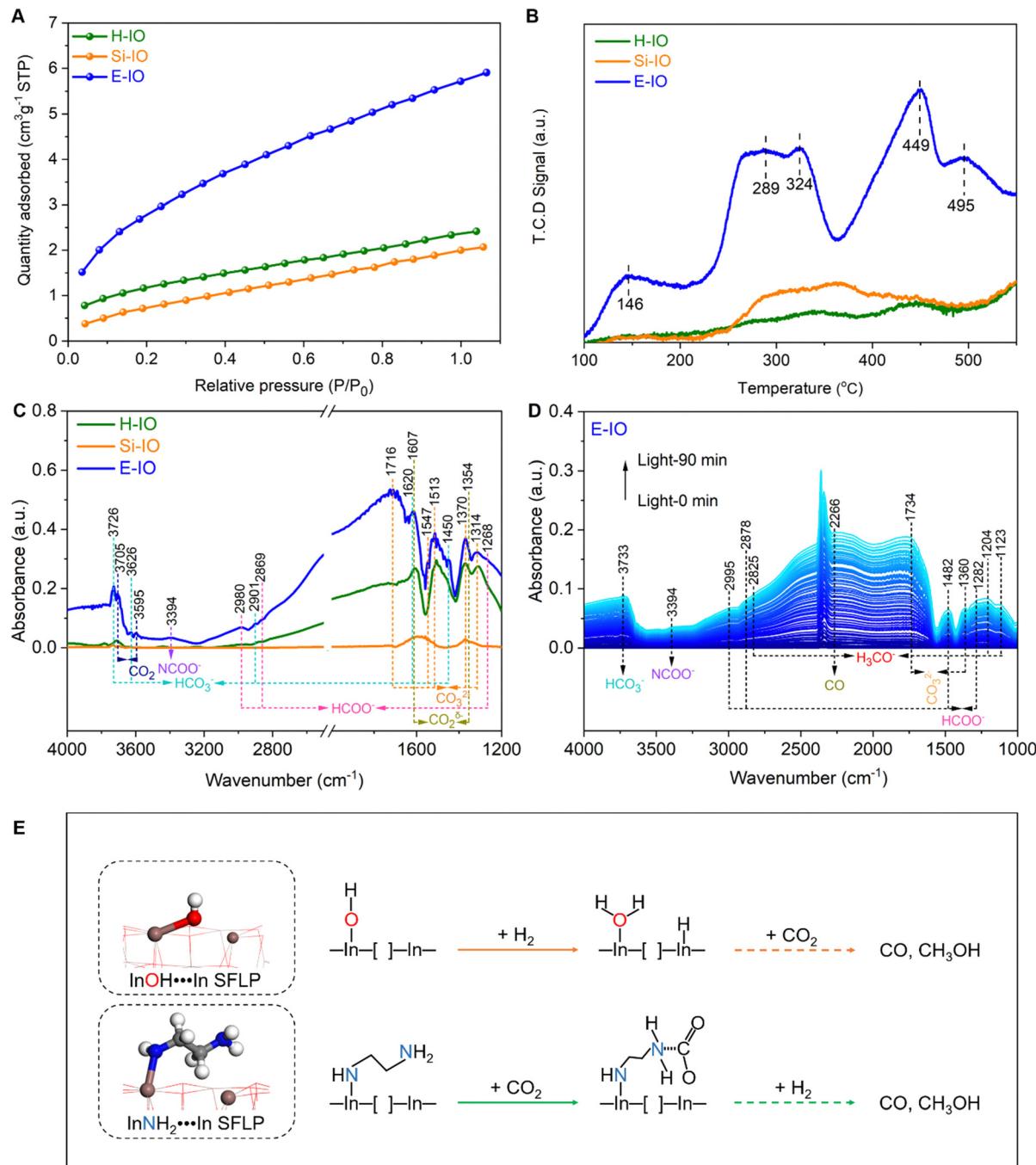
To investigate the photogenerated charge transfer mechanism, the room-temperature photoluminescence (PL) spectra of the H-IO, Si-IO, and E-IO samples are presented in Fig. S22A (ESI‡). All three samples display a green emission peak centered around 460 nm. However, E-IO exhibits a weaker PL emission peak compared to the other two samples. This can be attributed to the fact that amine groups and oxygen vacancies, similar to hydroxide and oxygen vacancies, act as traps, creating more moderate mid-gap states. These mid-gap states effectively capture photo-excited electrons and inhibit electron–hole recombination, leading to a reduction in PL emission intensity. Furthermore, Fig. S22B and C (ESI‡) demonstrate that E-IO exhibits the highest photocurrent density and lowest impedance, indicating superior charge separation and transfer efficiency. These photoelectrochemical characterizations substantiate that the construction of  $\text{InNH}_2\cdot\cdot\cdot\text{In}$  SFLP can enhance the transport of photogenerated charges, thereby improving the photocatalytic performance of amine-functionalized  $\text{In}_2\text{O}_3$ .

To gain a deeper understanding of how surface-grafted  $\text{NH}_2$  groups and oxygen vacancies affect the electronic band structure of amine-functionalized  $\text{In}_2\text{O}_3$ , we conducted density of states (DOS) calculations and partial density of states (PDOS) for four types of surfaces: pristine  $\text{In}_2\text{O}_3$ ,  $\text{In}_2\text{O}_{3-x}$ ,  $\text{In}_2\text{O}_{3-x}(\text{OH})_y$ , and  $\text{In}_2\text{O}_{3-x}(\text{EDA})_y$ , using hybrid DFT calculations (Fig. 4C). On the surface of  $\text{In}_2\text{O}_{3-x}$  with only oxygen vacancies, new states near the original conduction band were observed, closer to the Fermi level compared to the defect-free  $\text{In}_2\text{O}_3$  surface. These states were fully occupied, indicating an increase in electron surface charge due to the donor properties of oxygen vacancies. However, the introduction of oxygen vacancies also pushed the valence band further away from the Fermi level, somewhat diminishing the overall advantage of introducing an oxygen vacancy. Fortunately, these drawbacks can be effectively mitigated when oxygen vacancies are introduced together with amine or hydroxyl groups. Similar to the hydroxyl group, the amine group induced the accumulation of p electrons at the edge of the valence band and shifted the Fermi level toward the edge, exhibiting typical acceptor properties (Fig. S23, ESI‡). The simplified schematic in Fig. 4D illustrates that in the  $\text{In}_2\text{O}_{3-x}(\text{EDA})_y$  specimen, oxygen vacancies create shallow donor states below the conduction band edge, while surface amine groups act as shallow acceptor states above the valence band edge. The presence of surface amine groups and oxygen

vacancies alters the relaxation dynamics of charge carriers, enhancing non-radiative relaxation processes and facilitating the separation of electron–hole pairs, thereby improving the catalytic efficiency of photogenerated electrons in reduction reactions. These findings align with the results obtained from the DRS and PL experiments discussed earlier.

Besides the electronic structure and charge transfer efficiency, the enhanced Lewis acid–base pairs in amine-functionalized  $\text{In}_2\text{O}_3$  are also expected to improve the adsorption and activation capacity for  $\text{CO}_2$ . To investigate the  $\text{CO}_2$  uptake ability, we recorded the  $\text{CO}_2$  adsorption profiles on H-IO, Si-IO, and E-IO catalysts. As shown in Fig. 5A, E-IO exhibits the highest adsorption capacity of  $5.72 \text{ cm}^3 \text{ g}^{-1}$  for  $\text{CO}_2$ , which is 2.44 and 2.86 times higher than that of H-IO and Si-IO, respectively. It is evident that the superior  $\text{CO}_2$  adsorption capacity of E-IO cannot be attributed solely to its surface area, as E-IO has a moderate surface area ( $50.54 \text{ m}^2 \text{ g}^{-1}$ ) compared to the other catalysts. Considering the significant enhancement of Lewis acid–base pairs due to  $\text{NH}_2$  substitution, the improved  $\text{CO}_2$  adsorption capacity can be mainly attributed to the strong chemical interaction between  $\text{CO}_2$  molecules and Lewis basic  $\text{NH}_2$  sites, as well as the abundance of oxygen vacancies. To gain further insight into the effect of  $\text{NH}_2$  substitution on the interaction between  $\text{CO}_2$  and the catalysts, we conducted  $\text{CO}_2$  temperature-programmed desorption ( $\text{CO}_2$ -TPD) tests. As depicted in Fig. 5B, the TPD peak intensity is higher for the amine-functionalized  $\text{In}_2\text{O}_3$  compared to the other catalysts. Notably, the TPD profile of E-IO can be divided into three regions: a low-temperature region ( $100$ – $200$  °C), a medium-temperature region ( $200$ – $360$  °C), and a high-temperature region ( $360$ – $550$  °C). The weak desorption peak at 146 °C corresponds to physically adsorbed  $\text{CO}_2$ . The significant desorption peak observed at 289 °C is attributed to the desorption of  $\text{CO}_2$  that is bound to  $\text{NH}_2$  groups, forming carbamate ( $\text{H}_2\text{NCOO}^-$ ) species.<sup>57,58</sup> The additional peak at 324 °C can be associated with the chemical desorption of bent  $\text{CO}_2\delta^-$  species, which is related to oxygen vacancies.<sup>59,60</sup> Furthermore, the desorption peaks at higher temperatures (449 and 495 °C) are primarily attributed to the decomposition of surface carbonates and bicarbonates.<sup>15,61</sup>

*In situ* DRIFTS experiments were conducted to investigate the adsorption of  $\text{CO}_2$ . It is evident that E-IO exhibits superior adsorption capacity for  $\text{CO}_2$  compared to H-IO and Si-IO, resulting in the formation of a greater number of intermediate species through bonding interactions (Fig. S24, ESI‡). The transient evolution of surface species during  $\text{CO}_2$  adsorption on H-IO, Si-IO, and E-IO samples is depicted in Fig. 5C. In the case of E-IO, the observed features at  $3394 \text{ cm}^{-1}$  can be attributed to the  $\text{NCOO}^-$  skeletal vibration and N–H stretching of carbamate formation, indicating that surface amine groups adsorb and activate  $\text{CO}_2$  by forming carbamates.<sup>62,63</sup> The peaks at 1716, 1513, 1370, and  $1314 \text{ cm}^{-1}$  correspond to the asymmetric and symmetric OCO stretching modes of carbonates ( $\text{CO}_3^{2-}$ ), and the appearance of four peaks at 3726, 3626, 2901, 1620 and  $1450 \text{ cm}^{-1}$  indicates the formation of bicarbonate species ( $\text{HCO}_3^-$ ).<sup>15,64,65</sup> Peaks at 1607 and  $1356 \text{ cm}^{-1}$  represent



**Fig. 5** CO<sub>2</sub> adsorption and activation on H-IO, Si-IO, and E-IO (A) CO<sub>2</sub> adsorption isotherms. (B) CO<sub>2</sub>-TPD profiles. (C) *In situ* DRIFTS spectra of the adsorption of CO<sub>2</sub> at 40 minutes. (D) *In situ* DRIFTS spectra of surface species under reaction conditions on E-IO with light. (E) The traditional InOH...In SFLP photocatalytic CO<sub>2</sub> hydrogenation mechanism (top) and InNH<sub>2</sub>...In SFLP photocatalytic CO<sub>2</sub> hydrogenation mechanism (bottom).

the asymmetric and symmetric stretching modes, respectively, and can be attributed to the bent CO<sub>2</sub><sup>δ-</sup> species adsorbed at oxygen vacancy sites. Peaks at 3705 and 3595 cm<sup>-1</sup> correspond to gaseous CO<sub>2</sub> fingerprint modes.<sup>66</sup> Additionally, peaks at 2980, 2869, and 1268 cm<sup>-1</sup> can be attributed to the asymmetric and symmetric OCO stretching vibrations of adsorbed bidentate formate (HCOO<sup>-</sup>) species.<sup>45,67,68</sup> Although some formate species may also be observed on H-IO and Si-IO, their peak

intensities are weaker compared to E-IO. These collective results indicate that amine-functionalized In<sub>2</sub>O<sub>3</sub> exhibits strong CO<sub>2</sub> adsorption, bonding, and activation abilities due to the presence of grafted NH<sub>2</sub> groups and abundant oxygen vacancies.

To gain a deeper understanding of the enhanced reactivity facilitated by InNH<sub>2</sub>...In SFLP. *In situ* DRIFTS experiments were conducted under reaction conditions (CO<sub>2</sub> + H<sub>2</sub>, 250 °C) to identify reaction intermediates and elucidate the photocatalytic

mechanism involved in the  $\text{CO}_2$  hydrogenation process. Fig. 5D shows the identified surface species on E-IO under reaction conditions with different irradiation times. Vibration absorption peaks of  $\text{HCOO}^-$  were detected at 2995, 2878, 1482, and  $1282\text{ cm}^{-1}$ , which have been previously identified as intermediate species in the generation of CO and  $\text{CH}_3\text{OH}$ .<sup>62,67</sup> The vibration absorption peak of  $\text{H}_3\text{CO}^-$  species, another key intermediate in methanol formation, was indicated by the diagnostic mode at  $2825\text{ cm}^{-1}$ , which corresponds to the  $\text{CH}_3$  stretching modes.<sup>15,68</sup> Additionally, the peaks at 1204 and  $1123\text{ cm}^{-1}$  correspond to the  $\text{C}=\text{O}$  stretching mode of bridged methoxide species. The peak at  $2266\text{ cm}^{-1}$  is attributed to CO, indicating the formation of CO on the surface of E-IO.<sup>69</sup> In contrast, only vibration absorption peaks of CO and a small amount of  $\text{HCOO}^-$  were detected on the surfaces of H-IO and Si-IO (Fig. S25, ESI‡). These results demonstrate that  $\text{In}_2\text{O}_{3-x}(\text{EDA})_y$  catalysts can effectively promote the formation of intermediate species  $\text{HCOO}^-$  and  $\text{H}_3\text{CO}^-$  during the photocatalytic hydrogenation reaction, leading to an enhanced production of  $\text{CH}_3\text{OH}$  and CO.

Based on the comprehensive analysis, a plausible catalytic mechanism for  $\text{CO}_2$  hydrogenation on  $\text{In}_2\text{O}_{3-x}(\text{EDA})_y$  with robust  $\text{InNH}_2\cdots\text{In}$  SFLP can be proposed in Fig. 5E. The traditional  $\text{InOH}\cdots\text{In}$  SFLP with moderate Lewis acid and base sites, can facilitate the heterolysis of  $\text{H}_2$ , in which the proton bound to the hydroxide Lewis base and hydride bound to the coordinately unsaturated indium, and subsequently react with  $\text{CO}_2$  to generate CO and  $\text{CH}_3\text{OH}$ . As for  $\text{InNH}_2\cdots\text{In}$  SFLP, the amine group Lewis base provides a robust adsorption site for  $\text{CO}_2$  molecules, preferentially favouring the activation of  $\text{CO}_2$  into carbamate ( $\text{NHCOO}^-$ ) intermediates. Moreover, the unsaturated In atom acting as Lewis acid can also provide an active site to activate and bond with  $\text{CO}_2$  molecules. This synergistic Lewis acid-base enhancement in the activation ability towards  $\text{CO}_2$  molecules effectively promotes a continuous multi-electron hydrogenation and reduction process, leading to the formation of crucial intermediates and ultimately the production of CO and  $\text{CH}_3\text{OH}$ .

## Conclusions

In summary, this study successfully synthesized amine-functionalized  $\text{In}_2\text{O}_3$  ( $\text{In}_2\text{O}_{3-x}(\text{EDA})_y$ ) nanoparticles, which possess robust  $\text{InNH}_2\cdots\text{In}$  SFLP, using a one-step solvothermal method. In comparison to conventional  $\text{InOH}\cdots\text{In}$ , the  $\text{InNH}_2\cdots\text{In}$  SFLP demonstrates superior performance in the photocatalytic hydrogenation of  $\text{CO}_2$ . This enhanced activity can be attributed to the strong adsorption, binding, and activation capabilities of the Lewis acid-base pairs present in  $\text{InNH}_2\cdots\text{In}$  SFLP. Additionally, the existence of moderate shallow states facilitates the separation of electron-hole pairs, thereby enhancing the reactivity of the Lewis acid-base sites. By leveraging the unique properties of surface  $\text{InNH}_2\cdots\text{In}$  SFLP, it becomes possible to design efficient and sustainable indium oxide catalysts for the conversion of  $\text{CO}_2$  into valuable products.

This research contributes a molecule-functionalized engineering strategy for the development and optimization of heterogeneous photocatalysts, showcasing one more step towards future solar  $\text{CO}_2$  refineries.

## Author contributions

T. Y., N. L. and G. A. O. conceived and designed the experiments. Q. G. and C. N. conducted the catalysts preparation and the catalysts testing flow experiments for  $\text{CO}_2$  hydrogenation. W. R. conducted and analyzed the DFT calculations. Q. G., C. N., Y. Z., W. L., L. Z. and D. Z. performed the structural characterizations and the *in situ* DRIFTS. L. W. and Z. L. performed the carbon-13-labeled carbon dioxide test. T. Y., B. H., and G. A. O. conceived the project and co-wrote the manuscript. The manuscript was written through collective contributions from all authors. All authors approved the final version of the manuscript.

## Conflicts of interest

There are no conflicts to declare.

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