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Uniting Heat and Light in Heterogeneous CO$_2$ Photocatalysis: Optochemical Materials and Reactor Engineering

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CONSPECTUS: The rapid increase in atmospheric CO$_2$ concentration (~420 ppm) has become one of the significant issues threatening human survival. As an effective measure to solve this major problem, renewable energy-powered catalytic CO$_2$ conversion technologies have received vast attention in both academia and industry. Among these techniques, photothermal catalysis is a rising star with promising potential for CO$_2$ conversion even under milder conditions. Indium oxide was among the first to be used in photothermal CO$_2$ catalysis, and through its various forms, stoichiometries, and surface chemistry, it has become one of the most well-studied photothermal catalyst systems. Indium oxide is a highly tunable semiconductor for CO$_2$ photocatalysis, which can be driven by both light photochemically and heat photothermally, thereby serving as an archetype for understanding how to optimize its performance for storing solar as chemical energy, through creative materials chemistry.

Our solar fuel cluster discovered photothermal CO$_2$ catalysis over indium oxide in 2014 and has long been committed to the study of this field. Photothermal catalysis by semiconductors like indium oxide can be deconstructed into three key processes: photochemistry, thermochemistry, and surface chemistry. To be specific, photoexcited electron—hole pairs can enable redox and acid—base surface chemical reactions. Phonons and plasmons can drive these reactions photothermally. Surface active sites, such as surface frustrated Lewis pairs and oxygen vacancies, can amplify product activity and selectivity. Designer synergism between all of these effects ultimately determines the overall performance metrics of photothermal CO$_2$ catalysis. Thus, to design and optimize a photothermal catalyst, the three aforementioned key processes should be considered synergistically.

In this Account, indium oxide-based catalysts are selected as an archetype to introduce the process of photothermal CO$_2$ catalysis and the advancements of indium oxide-based catalysts mainly from our solar fuel cluster are summarized. In detail, the strategies of material design are introduced systematically with the three key processes: photochemistry, thermochemistry, and surface chemistry. Moreover, a foreseeable future of the emerging field of optochemical engineering of photothermal catalysis, ranging from potential reactions to reactor design, is included as the perspective as well. In other words, this Account is dedicated to exploring how chemically tailored indium oxide-based catalyst has served as a platform material for understanding photothermal CO$_2$ catalysis and how this know-how is enabling the design of high quantum efficiency photocatalysts and photoreactors. A comprehensive understanding of these points is the key to the development of the emerging field of optochemical materials and reactor engineering of heterogeneous CO$_2$ photocatalysis.
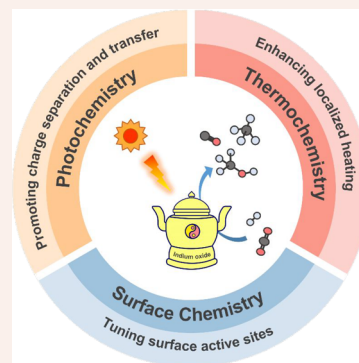
1. INTRODUCTION

Photothermal catalysis is viewed as the progenitor of the emerging field of optochemical materials and reactor engineering.[1] Similar to photoelectrocatalysis which combines two energy sources—light and electricity—to bring new opportunities to catalysis, photothermal catalysis provides an exciting and novel pathway to power the reactions by incorporating both photocatalysis and thermocatalysis.[2,3] The roles of light usually include excitation of photo charge carriers, generation of surface plasmons, and tuning the surface properties,[4−9] while the roles of heat usually include facilitating the diffusion of reactants, ensuring desorption of products, and providing the activation energy for reaction.[2,7] Therefore, the integration of light and heat could drive the reactions under ameliorated

conditions and with elevated yield, faster rates, and novel selectivities.

The ever-increasing atmospheric concentration of CO$_2$ has become one of the significant issues to be resolved urgently. Photothermal heterogeneous catalytic CO$_2$ conversion has received vast attention as a powerful CO$_2$ reduction and utilization technique[3,10] due to its potential to integrate with
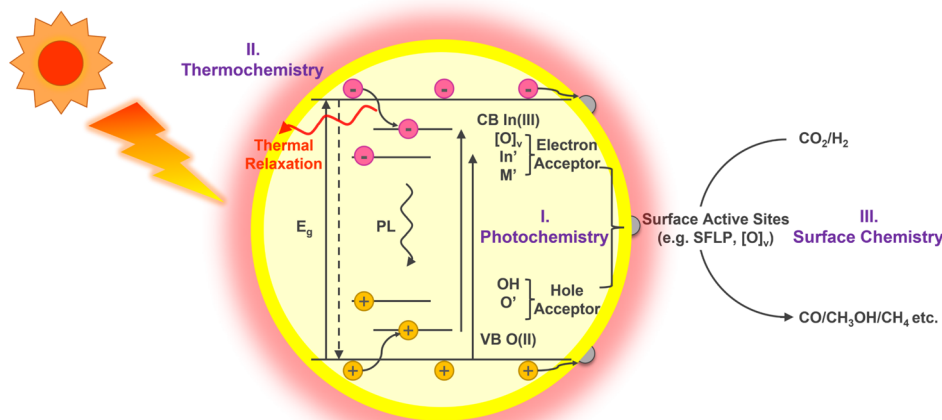
Figure 1. Schematic diagram of the three key processes of photothermal CO_2 catalysis with indium oxide-based catalysts: I. Photochemistry. II. Thermochemistry. III. Surface Chemistry.

the present industrial facilities. The discovery of photothermal CO_2 catalysis can be traced to 2014[11,12] and during the past eight years of fast development, several material systems have demonstrated promise as effective performers for photothermal CO_2 catalysis, including metallic, semiconductors, and plasmonic materials.[8,10,13−15] Indium oxide, a highly tunable semiconductor for CO_2 photocatalysis, which was among the first to be used in photothermal CO_2 catalysis,[11] has become one of the most well-studied photothermal catalyst systems.[4,5,16−18] With the development of indium oxide-based catalysts, a systematic and comprehensive understanding of the synthesis−structure−property relationship of photothermal catalysts has been established,[3] which makes indium oxide a tutorial model for introducing photothermal CO_2 catalysis.

This Account is dedicated to summarizing the advancements of indium oxide catalysts mainly from our solar fuel groups. We explore how chemically tailored indium oxide-based catalysts have served as a platform material for understanding photothermal CO_2 catalysis and how this know-how is enabling the design of high quantum efficiency photocatalysts and photoreactors, key to the development of the emerging field of optochemical materials and reactor engineering of CO_2 photocatalysis.

2. THREE KEY PROCESSES IN PHOTOTHERMAL CO_2 CATALYSIS

Photothermal catalysis has become a rising star in heterogeneous catalysis due to that it demonstrates excellent catalytic performance by uniting light and heat. However, the efficiency and stability of photothermal catalysts have not reached the industrial standard and are major obstacles to further development.[3] In this context, the growing field needs a more comprehensive understanding of the photothermal catalytic process.

Generally, photothermal catalysis is considered an emerging field by uniting light and heat to drive the reaction synergistically.[2,8] Thus, both light-driven photochemical catalysis and heat-driven thermochemical catalysis are essential elements in the process of photothermal catalysis.[2,3,19] On the other hand, for typical heterogeneous catalysis,[3,8] some critical steps in heterogeneous catalysis, adsorption, reaction, and desorption, commonly occur on the catalyst's surface,[20−22] so surface chemistry plays a pivotal role in photothermal

catalysis.[3,21,22] To this end, we believe that the process of photothermal CO_2 catalysis could be divided into three key processes for discussion, including photochemistry, thermochemistry, and surface chemistry, and the schematic diagram using indium oxide-based catalysts as an example is shown in Figure 1. In the following subsections, we will define these aspects, and the specific catalysis cases exploiting them will be elaborated in Section 3.

2.1. Photochemistry

Indium oxide, an archetypal n-type semiconductor with direct and indirect band gaps of 3.7 and 2.6 eV, respectively,[3] exhibits photochemistry akin to other semiconductor materials in traditional photocatalysis.[23−26] Briefly, when the light with photon energy equal to or greater than the band gap energy irradiates a semiconductor, the valence band (VB) electrons are excited and move to the conduction band (CB) of the semiconductor, and leave the free holes in the VB. Then photogenerated electrons with a substantial reduction potential and holes with a significant oxidation potential migrate to the surface to induce redox reactions.[27] Meanwhile, these charge carriers inevitably experience recombination processes, which can be deleterious to the efficiency of photocatalysis.[28] The optoelectronic structure of indium oxide based-catalysts can be affected by their crystal phase, morphology, doping elements, and defect concentrations, which hugely determine the lifetime of photogenerated charge carriers and thus affect the photocatalytic activity.[29,30]

Besides the initiation of a redox reaction, the photochemistry in photothermal catalysis could also enhance the reaction rate by decreasing the activation energy barrier (Figure 2a)[5] via charge transfer to the catalyst surface that leads to the elevation in the active site's acidity and/or basicity, or vibrational modes of energy transfer to transition states inducing the promotion of bond lengths.[2,24,31] The details of the active site will be discussed in Section 2.3.

Furthermore, indium oxide is renowned as a photocatalyst for offering a potential solution to the intermittency limitation of photocatalysis for solar fuel production.[32] It can maintain a persistent photochemical process within the catalyst even after illumination, owing to its "photocapacitor" behavior arising from the extensive continuum of defect states within the band gap. The accumulated charge carriers trapped in the defect
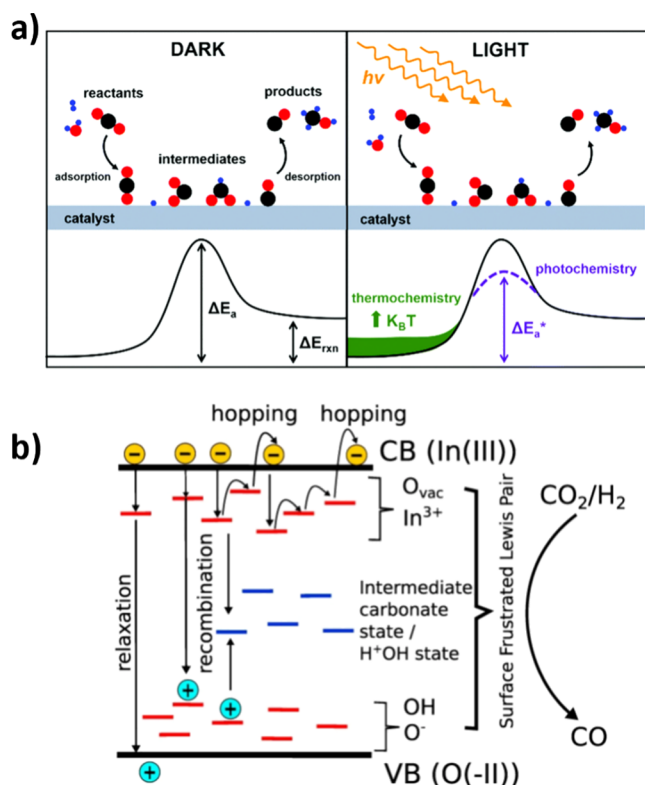
2.2. Thermochemistry

The thermochemical process accelerates the reaction by elevating the reaction temperature, which is the macroscopic manifestation of the accumulation of thermal energy. The increase of the reaction temperature will significantly influence the entire reaction system.[34] Typically, the rise of temperature will facilitate the adsorption, diffusion, and surface chemistry of reactants and enable the rapid desorption of products from active sites.[2,7] Moreover, by tilting the Boltzmann distribution toward higher energies, the primary function of thermal energy (k_BT, k_B is the Boltzmann's constant, and T is the temperature) is to increase the probability of surmounting Arrhenius activation energy barriers, especially for the endothermic reactions (Figure 2a).[35]

In photothermal catalysis, the thermal energy could either be supplied by the external thermal source or generated by light irradiation through the photothermal effect.[9,36,37] In general, nonradiative relaxation of photogenerated electrons and localized surface plasmon resonance (LSPR) are the common mechanisms for converting solar energy into thermal energy via the photothermal effect (Figure 3).[34] Here, we briefly discuss these two mechanisms and will show how they could be employed in the catalytic systems based on indium oxide in Section 3.

2.2.1. Nonradiative Relaxation of Photogenerated Electrons.
The nonradiative relaxation of photogenerated electrons refers to the relaxation of excited electrons to a lower energy state by nonradiative means, which generally occurs in semiconductor materials (Figure 3a). Electrons with a high energy state can relax to a lower energy state, whereas the energy can be released in two processes: nonradiative relaxation to form phonons and radiative relaxation to form photons. In the process of nonradiative relaxation, the excited electrons distribute part of the energy to the crystal lattice, and thermal energy is produced via lattice vibrations.[8,38]

2.2.2. Localized Surface Plasmon Resonance (LSPR).
Light is an electromagnetic wave that can induce excitation of free electrons in metallic nanoparticles and collective oscillation of electrons when the frequency of the photons matches the resonant frequency of CB electrons, and this phenomenon is identified as localized surface plasmon
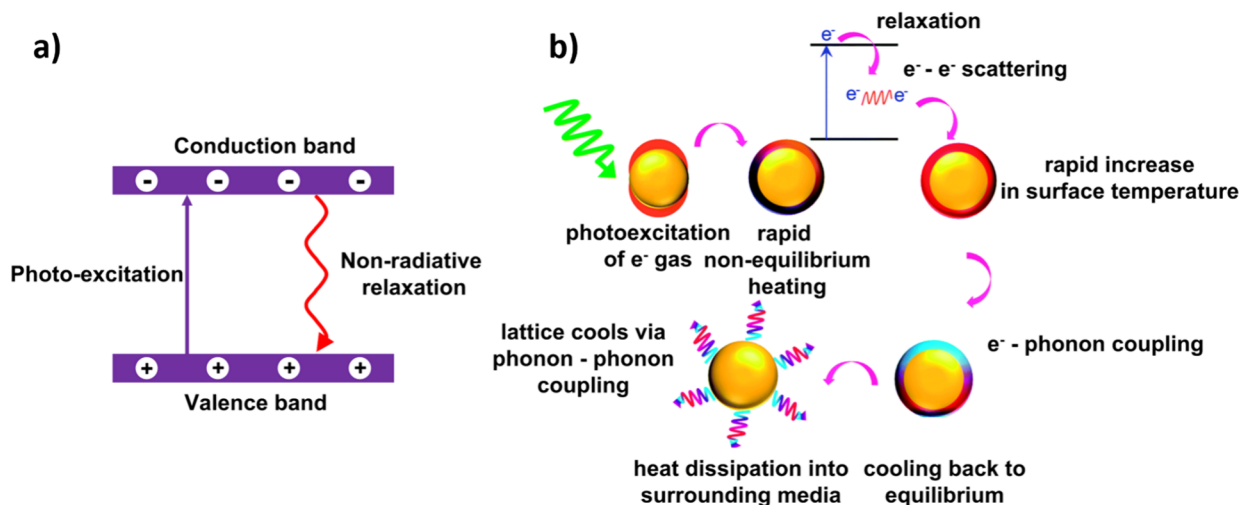
Figure 2. a) Effect of photochemistry and thermochemistry in the photothermal catalytic process.[2] b) Illustration of persistent CO_2 photocatalysis enabled by a defect continuum. The excited electron carriers trapped in the shallow state hop to the conduction band edge with a time interval, resulting in a persistent population of excited carriers after the light illumination is off.[33] Reprinted with permission from refs 2, 33. Copyright 2019 The Royal Society of Chemistry and 2021 Springer Nature.

states during illumination were found to persistently drive the CO_2 conversion after the light is switched off (Figure 2b).[32,33] For defect-laden hydroxylated $In_2O_{3-x}(OH)_y$, it can drive CO production persistently for about 2 h after illumination and increase the CO yield by 19% in the outdoor day and night test compared with day-only test.[33]

Figure 3. Two mechanisms of the photothermal effect. a) Nonradiative relaxation of photogenerated electrons.[8] b) Localized surface plasmon resonance (LSPR).[36] Reprinted with permission from refs 8, 36. Copyright 2022 Elsevier Inc. and 2014 The Royal Society of Chemistry.

resonance (LSPR) (Figure 3b).[2,7,8,39] As a typical metal oxide semiconductor, the pristine indium oxide has no LSPR effect. The LSPR effect is generally introduced into the metal oxide system by doping, including intrinsic doping by oxygen vacancy defects (for example, WO_{3-x} and In_2O_{3-x}[40]) and extrinsic doping by other metal (for example, $Ce:In_2O_3$ and $Sn:In_2O_3$[41]), or forming a heterostructure with plasmonic materials (for example, $Au-In_2O_3$[42]).

The LSPR could significantly enhance the local electric field and the generation of high concentrations of energetic or hot electrons on the surface and is capable of decaying through two competing pathways: radiative and nonradiative decay processes. Thus, the heat is generated by a nonradiative decay process via intra- or interband transitions to form energetic or hot electrons, including electron−electron scattering (<100 fs), electron−phonon scattering (1−10 ps), and phonon−phonon scattering (~100 ps).[43]

2.3. Surface Chemistry

Photothermal CO_2 catalysis is a typical gas−solid heterogeneous catalytic process that occurs on the surface of the solid-phase catalyst. Commonly, the process of surface chemistry in heterogeneous catalysis includes the adsorption of reactants, activation of chemical bonds, formation of intermediates, conversion of intermediates into products, and desorption of products.[2,7,34]

The surface active site, where the adsorption of the reactant occurs and the catalytic reaction further proceeds, is the most critical factor for regulating catalytic activity and product selectivity. Moreover, the surface active site may also accept photogenerated carriers to tune the surface acidity and basicity, and thus initiating the photothermal catalytic reaction.[2,44] As shown in Figure 1, the general charge carrier acceptors contain electron acceptors (oxygen vacancy $[O]_v$, coordinately unsaturated indium (In′), and isomorphic substituted metals (M′)) and hole acceptors (hydroxyl OH and coordinately unsaturated oxygen O′) in indium oxide-based photothermal catalysts. In this section, we mainly focus on the two most common surface active sites in indium oxide-based photothermal catalysts, including oxygen vacancy ($[O]_v$) and surface frustrated Lewis pair (SFLP), in which the SFLP is composed of coordinately unsaturated indium (In′) (adjacent to $[O]_v$) and the proximal OH group.

2.3.1. Oxygen Vacancy ($[O]_v$).
The oxygen vacancy ($[O]_v$) is an intrinsic defect in metal oxides that may exhibit with high reactivity and robust CO_2 adsorption capacity.[45,46] It may also be an extrinsic defect generated by thermal vacuum or chemical reduction of metal oxides. Thus, it becomes the most prevalent surface active site for CO_2 conversion, and is often abundant in indium oxide catalysts. The CO_2 molecules prefer to be adsorbed at $[O]_v$ sites with one O atom of CO_2 located at the bridging $[O]_v$ defect and the interaction between $[O]_v$ with CO_2 may lower the reaction barrier.[39] Furthermore, the presence of $[O]_v$ also results in even higher extent of unsaturation of the coordinately unsaturated surface metal sites and thus higher Lewis acidity. The conduction electrons associated with $[O]_v$ can generate LSPR in the near-infrared spectral region.[41] Mid-gap states will be generated by introducing $[O]_v$ into metal oxide semiconductors, widening the light absorption range. Another advantage of $[O]_v$ as the surface active site is the superior ability to trap photogenerated electrons to prolong the lifetime of charge carriers, which is beneficial for the activity.[2,47] Finally, together with multiple

adjacent atoms, $[O]_v$ can further form a special type of active site, discussed in the following section.

2.3.2. Surface Frustrated Lewis Pair (SFLP).
A unique active site, namely the surface frustrated Lewis pair (SFLP), was first proposed and experimentally validated by our group.[16−18,48] It has well explained the synergistic enhancement of the surface hydroxide group (OH) and oxygen vacancy ($[O]_v$) of $In_2O_{3-x}(OH)_y$ toward photothermal CO_2 catalysis. A frustrated Lewis pair (FLP) the brainchild of Douglas Stephan, is a Lewis acid-Lewis base combination that is sterically prevented from forming a classical Lewis acid−base adduct and is well-known in molecular organometallic compounds in homogeneous catalysis.[49] The SFLP is an outgrowth of the FLP, which involves the synergistic reactivity advantages of Lewis acid and Lewis base sites that permeate heterogeneous (photo)catalyst surfaces.

In the case of hydroxylated indium oxide-based catalysts that enable photothermal CO_2 catalysis, coordinately unsaturated indium (In′) (adjacent to $[O]_v$) on the surface (as the Lewis acid) together with the proximal OH group (as the Lewis base) form an SFLP active site. Such a unique kind of active site could enable heterolytic dissociation of H_2 into a proton bound to the OH and a hydride attached to the In′ site (Figure 4a),[16−18,48] in contrast to previous understanding of homolytic
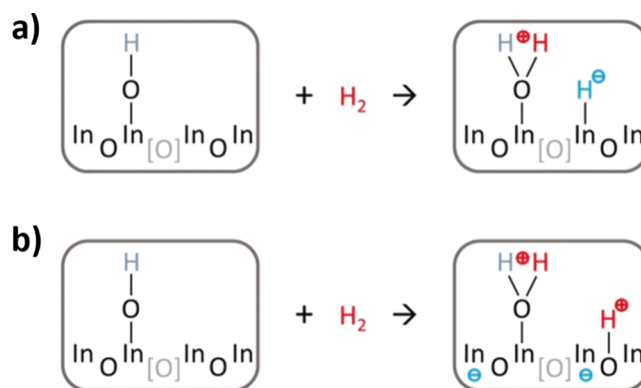

Figure 4. Illustration of the a) heterolysis and b) homolysis reaction pathways for the dissociation of H_2 on the SFLP.[48] ([O], ⊕, and ⊖ represent oxygen vacancies, protons, and electrons, respectively) Reprinted with permission from ref 48. Copyright 2019 Wiley.

dissociation of H_2 (Figure 4b).[48] These transformation processes on SFLP have been confirmed by *ex situ* solid-state ^1H magic angle spinning (MAS) NMR, *in situ* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), and theoretical simulation.[16−18,48]

3. RATIONAL DEVELOPMENT OF INDIUM OXIDE-BASED PHOTOTHERMAL CATALYSTS

Over the past eight years, rapid growth and notable leaps occurred in the burgeoning field of photothermal catalysis, and progress in the development of indium oxide-based catalysts for photothermal CO_2 catalysis is compelling.[3,6,8,14,15,50−52] In this section, we will introduce the rational design and development strategies of indium oxide-based catalysts for photothermal CO_2 catalysis for promoting charge separation and transfer, enhancing localized heating from the photothermal effect, and tuning surface active sites, which correspond to the three key processes discussed in the above
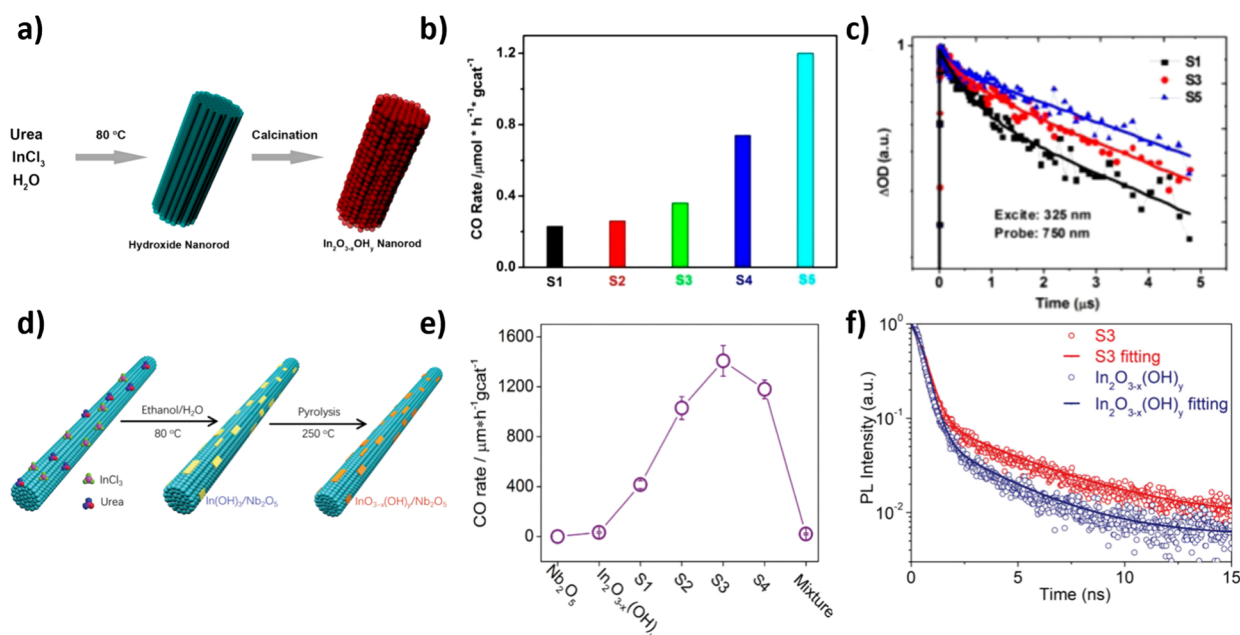
Figure 5. Examples of indium oxide-based catalysts designed by promoting charge separation and transfer. a) Illustration of the preparation of $In_2O_{3-x}(OH)_y$ nanocrystal nanorods, the rod lengths of S1−S5 samples are 800, 1140, 1290, 1810, and 1830 nm, respectively. b) CO production rates of S1−S5 samples under simulated sunlight irradiation. c) Normalized transient absorption traces observed at 750 nm for S1, S3, and S5.[53] d) Illustration of the preparation of $In_2O_{3-x}(OH)_y$@Nb_2O_5 hybrid composite. e) Photothermal catalytic performance of the listed materials. f) Fluorescence decay temporal profiles measured and fit for S3 and pristine $In_2O_{3-x}(OH)_y$.[54] Reprinted with permission from ref 53, 54. Copyright 2016 American Chemical Society and 2019 Wiley.

sections: photochemistry, thermochemistry, and surface chemistry, respectively.

3.1. Promoting Charge Separation and Transfer

The lifetime of the charge carrier is affected by the charge separation and transfer efficiency, which is the dominant factor restricting the performance of photocatalysis.[2,44] It is feasible to use rational catalyst design strategies to promote charge separation and transfer to enhance the photochemical process, thereby improving the photothermal catalytic performance.[3]

Assembling the nanocrystals into superstructures offers a possible route to increasing charge carriers' displacement radius. A nanorod superstructure made of self-assembled nanocrystalline $In_2O_{3-x}(OH)_y$ is a classic example to explain the mechanism of promoting charge separation and transfer by the superstructure (Figure 5a).[53] A set of $In_2O_{3-x}(OH)_y$ nanocrystal nanorods with different lengths were synthesized through the calcination of $In(OH)_3$ precursors prepared by aging urea and $InCl_3$ with different time, and it was found that the CO rate increased with increasing rod length (Figure 5b). Transient absorption traces (Figure 5c) indicated that the lifetime of the charge carrier increases with increasing rod length. The as-prepared $In_2O_{3-x}(OH)_y$ nanorods ensured electrons transfer between neighboring nanocrystals. It could enhance the spatial separation and transfer of excited charge carriers and thus improve the photothermal catalytic activity.

The limited tunability of single-component materials often restricts their further development, therefore the strategy of constructing hybrid nanostructures has been widely applied in enhancing photothermal catalytic performance.[8] An $In_2O_{3-x}(OH)_y$@Nb_2O_5 hybrid composite with a high concentration of $[O]_v$ was synthesized by decorating $In_2O_{3-x}(OH)_y$ on Nb_2O_5 nanorods (Figure 5d).[54] It was observed that the rate of CO_2 to CO over $In_2O_{3-x}(OH)_y$@Nb_2O_5 hybrid composite with a moderate amount of $In_2O_{3-x}(OH)_y$ was

much higher than pristine $In_2O_{3-x}(OH)_y$, Nb_2O_5 and their physical mixture (Figure 5e). Time-resolved fluorescence decay curves (Figure 5f) confirmed a 30% improvement in charge carrier lifetime of $In_2O_{3-x}(OH)_y$@Nb_2O_5 compared with that of pristine $In_2O_{3-x}(OH)_y$, which is caused by the high concentration of $[O]_v$.

Besides the formation of hybrid with other oxides, $In_2O_{3-x}(OH)_y$ can also form a hybrid structure with its different polymorphs. The polymorphic hybrid structure rh/c-$In_2O_{3-x}(OH)_y$ can be prepared by controlling the phase transition from the rhombohedral phase (rh-) to the cubic phase (c-) $In_2O_{3-x}(OH)_y$.[29] As a result, the optimally aligned band gap and mid-band gap defect states of the hybrid structure can be constructed, which facilitates the generation and separation of photogenerated charge carriers and enhances photothermal catalytic performance.

3.2. Enhancing Localized Heating from the Photothermal Effect

Surface localized heating provided by the photothermal effect could save external thermal energy for the reaction and enhance catalytic performance, especially for endothermic processes such as the reverse water gas shift (RWGS) reaction.[2,8,12] To this end, tuning the band gap and interfacing with narrow band gap or plasmonic materials to expand the optical absorption range and enhance localized heating from the photothermal effect are considered as effective approaches for photothermal catalyst design.[2,7,34]

Most semiconductor materials have low utilization efficiency of sunlight due to their low absorption of visible and near-infrared (NIR) light in sunlight, limiting their development in photothermal catalysis. The introduction of $[O]_v$ could generate midgap states, so the band gap of the semiconductor material will be narrowed and the light absorption range will be enhanced.[55,56] In this regard, a black indium oxide, In_2O_{3-x}/
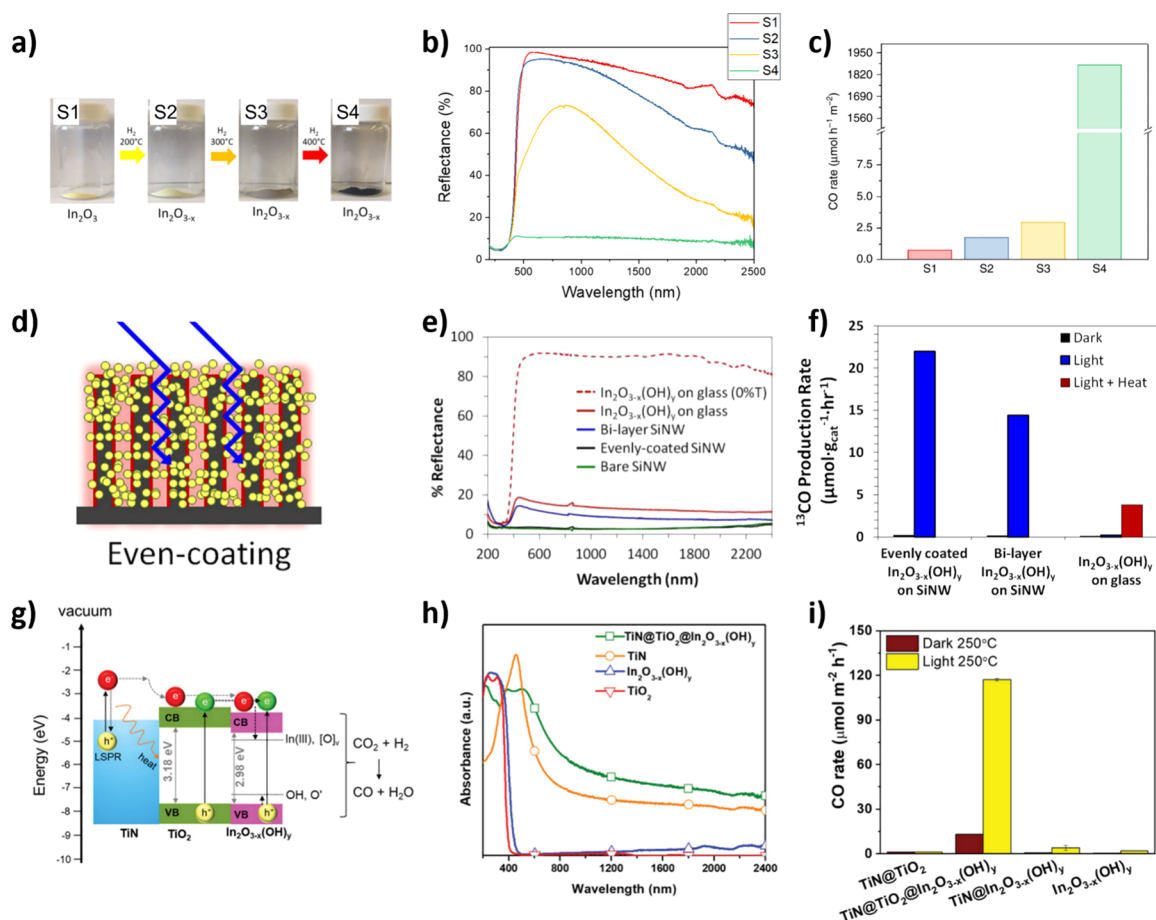
Figure 6. Examples of indium oxide-based catalysts designed by increasing local heating from the photothermal effect. a) Color changes of stoichiometric In_2O_3 (S1) to nonstoichiometric In_2O_{3-x} with different hydrogenation temperatures (S2−S4). b) Optical reflectance spectra (UV−vis-NIR) of S1−S4 samples. c) Photocatalytic CO_2 hydrogenation evaluation in a batch reactor.[4] d) Schematic diagram of the effect of nanostructuring on the film's interaction with incident light. Blue arrows represent incident light, and the red shading illustrates photothermal heat generation. e) UV−vis−NIR diffuse reflectance spectra of the sample films. f) ^{13}CO production rates of the sample films in the dark and under illumination, with or without external heating.[57] g) Schematic diagram of the activation mechanism of $TiN@TiO_2@In_2O_{3-x}(OH)_y$ ternary heterostructure. h) UV−vis absorption spectra of different samples. (i) Surface-area-normalized CO production rates for TiN-based catalyst materials in the flow reactor at 250 °C.[58] Reprinted with permission from refs 4, 57, 58. Copyright 2020 Springer Nature, 2016 American Chemical Society and 2020 Wiley.

In_2O_3 (a nonstoichiometric/stoichiometric heterostructure), with large populations of $[O]_v$ was prepared by thermal treatment of pristine In_2O_3 in 10% H_2/Ar, and the color changed from pale-yellow to gray and even to black indicating the increasing amount of $[O]_v$ in In_2O_{3-x} and an increased population of mid gap states (Figure 6a).[4] The thermal treatment could broaden the absorption of the solar spectrum and achieve about 90% light absorption of Vis-NIR (Figure 6b), and this black indium oxide showed a higher CO rate than pristine In_2O_3 (Figure 6c). Moreover, a new black indium oxide $H_zIn_2O_{3-x}(OH)_y$ was successfully prepared by reducing commercial In_2O_3 with $NaBH_4$, which realized the first photothermal catalytic CO_2 conversion to methanol process without external heating.[5]

The hybrid structure is also an ideal strategy for extending the solar spectrum absorption, and the $In_2O_{3-x}(OH)_y$/SiNW hybrid catalyst is an excellent example (Figure 6d).[57] A parallel vertical array of silicon nanowires (SiNW) is a black-colored semiconductor material with a band gap of 1.1 eV and an excellent support material for photothermal catalysis, and the samples of $In_2O_{3-x}(OH)_y$ interfaced with SiNW had higher light absorption ability and a broader light absorption range

than pristine $In_2O_{3-x}(OH)_y$ (Figure 6e). Therefore, an $In_2O_{3-x}(OH)_y$/SiNW hybrid catalyst had enhanced photothermal catalytic activity toward CO_2 conversion to CO than $In_2O_{3-x}(OH)_y$ on glass, in which the SiNW could improve light harvesting and facilitate heat transfer (Figure 6f).

Heterostructuring with plasmonic materials could effectively broaden the absorption range of sunlight and increase local temperatures and is widely used in catalyst design. Nanoscale TiN is a metallic material with LSPR effect and was used to prepare a ternary heterostructure $TiN@TiO_2@In_2O_{3-x}(OH)_y$ (Figure 6g).[58] The prepared ternary heterostructure has excellent light absorption ability (Figure 6h) and remarkable photothermal catalytic performance (Figure 6i), resulting from the LSPR effect of TiN and the cascade effect of the TiO_2 interlayer.

3.3. Tuning Surface Active Sites

The surface active sites are the key adjustable materials property for the heterogeneous catalytic process, which profoundly affects the catalytic performance.[3] With the development of indium oxide-based catalysts for photothermal CO_2 catalysis, two main strategies, including tuning the types
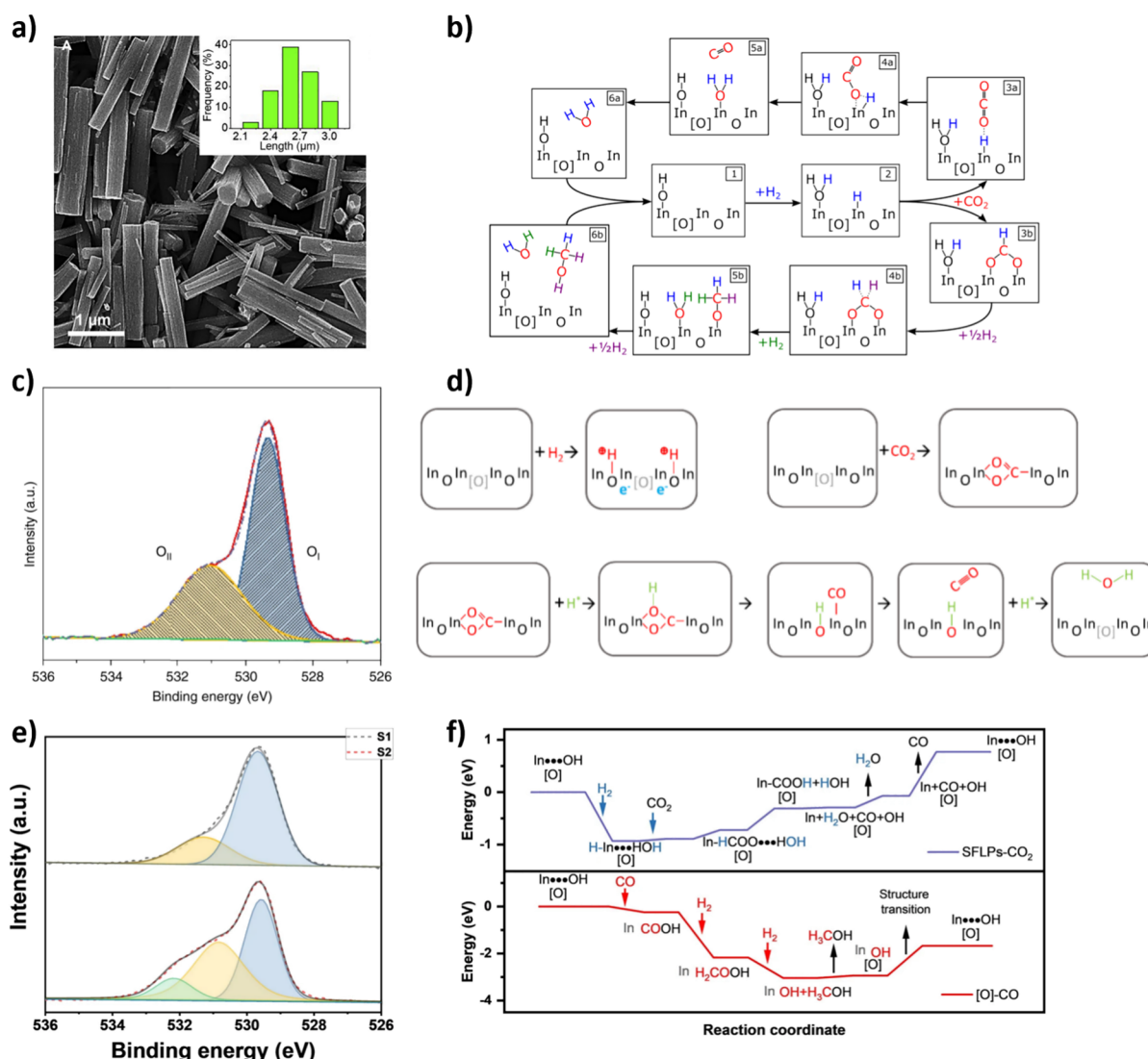
Figure 7. Examples of indium oxide-based catalysts designed by changing the types of surface active sites. a) SEM image of prepared superstructures. Inset in a) shows the statistic histogram of the rod length. b) Proposed reaction pathway for both reverse water gas shift and CO_2 hydrogenation to methanol.[59] c) High-resolution $O1s$ core level XPS spectrum of as-prepared In_2O_{3-x}. d) Proposed reaction pathways for H_2 dissociation, CO_2 adsorption, and CO_2 hydrogenation.[4] e) High-resolution $O1s$ core level XPS spectrum of In_2O_3 and $H_zIn_2O_{3-x}(OH)_y$ (the dashed line is the original XPS spectra, and the solid line is the best fit results). f) Free energy diagram of the RWGS reaction over SFLP sites and subsequent methanol synthesis over the $[O]_v$ site.[5] Reprinted with permission from refs 59, 4, 5. Copyright 2018 Elsevier Inc., 2020 Springer Nature and 2022 Springer Nature.

of surface active sites[4,5,59] and modification of SFLP,[60,61] have been applied to tune the active sites of indium oxide-based catalysts.

3.3.1. Tuning the Types of Surface Active Sites. Tuning the types or combinations of active sites is critical for modulating the reactivity and product selectivity with different reaction mechanisms.[3,14] Three combinations of active sites may be present on the surface of indium oxide-based catalysts, including SFLP, isolated $[O]_v$, and their combination, and distinct mechanisms caused by different active sites will be demonstrated in this section.[4,5,59]

Hydroxylated $In_2O_{3-x}(OH)_y$ nanocrystal was first discovered to be active toward photothermal CO_2 catalysis in 2014. Since then, studies about its surface active site and reaction mechanism have been massively reported. Herein, a rod-like hydroxylated $In_2O_{3-x}(OH)_y$ nanocrystal superstructure (Figure 7a), the first reported photothermal catalyst that could

catalyze CO_2 conversion to methanol at atmospheric pressure, is chosen as an example for discussion.[59] This rod-like $In_2O_{3-x}(OH)_y$ nanocrystal superstructure exhibited a methanol rate of 97.3 μmol g_{cat}^{-1} h^{-1} with methanol selectively of over 50% at 250 °C under light condition. The SFLP-based reaction pathways are shown in Figure 7b. The SFLP heterolytically split H_2 at first, and then the two adsorption configurations of CO_2 led to the different pathways for different products: 1) two O atoms of CO_2 were bonded with In to form bidentate formate configuration HCO_2* and further hydrogenated to produce methanol, summarized as $CO_2 \rightarrow HCO_2* \rightarrow H_2CO_2* \rightarrow CH_3O* \rightarrow CH_3OH$; 2) one of the O atom CO_2 was bonded with H−In to form monodentate configuration HCO_2*, summarized as $CO_2 \rightarrow HCO_2* \rightarrow CO$.

Alternatively, nonstoichiometric black indium oxide In_2O_{3-x}/In_2O_3 with large amounts of $[O]_v$ can be prepared by thermal treatment of pristine In_2O_3 in 10% H_2/Ar.[4] The
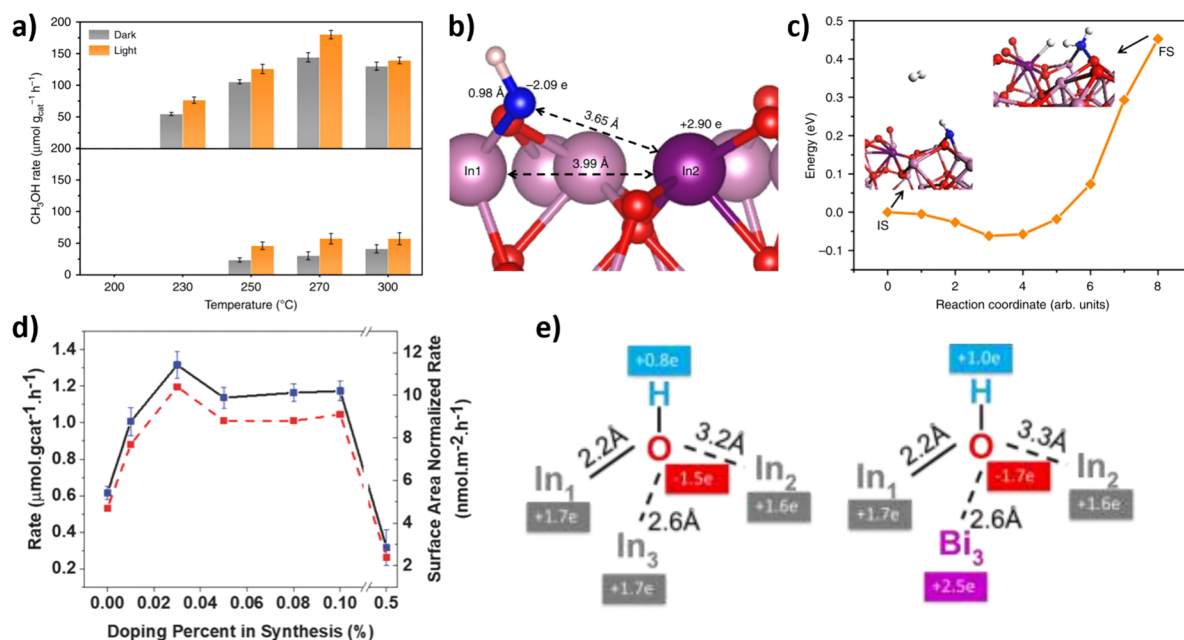
Figure 8. Examples of indium oxide-based catalysts designed by modification of SFLP. a) CH_3OH production rates of rh-$In_2O_{3-x}(OH)_y$ (up) and c-$In_2O_{3-x}(OH)_y$ (down). b) Side view of optimized configuration for (110) rh-$In_2O_{3-x}(OH)_y$. c) Reaction pathway and energy barrier of H_2 dissociation on (110) rh-$In_2O_{3-x}(OH)_y$. White, pink, red, purple, and blue spheres represent H, In, O, Lewis pair In, and Lewis pair O atoms, respectively.[60] d) Plot of average CO production rate (black) and surface-normalized CO production rate (red) as a function of the Bi doping level during synthesis. e) Schematic diagram showing bond lengths and charges for unsubstituted (left), and Bisubstituted $Bi\cdots In_1-OH\cdots In_2$ surfaces (right).[61] Reprinted with permission from refs 60, 61. Copyright 2019 Springer Nature and 2018 Wiley.

absence of OH group was confirmed by X-ray photoelectron spectroscopy (XPS), which indicated that $[O]_v$ is the active site rather than SFLP (Figure 7c). The formation of amorphous regions in the nanocrystal was observed by *in situ* high-resolution environmental transmission electron microscopy (HRETEM). The further density functional theory (DFT) calculation confirmed the mechanism of CO_2 catalysis that occurred on $[O]_v$, where the CO_2 was adsorbed in a $[O]_v$ and proton insertion weakened the C−O bond, promoting the formation of CO. Then, the proton extracted O from In_2O_3 to reform $[O]_v$ and In_2O_{3-x} (Figure 7d).

Recently, a new black indium oxide $H_zIn_2O_{3-x}(OH)_y$ was reported,[5] which was prepared by reducing commercial In_2O_3 with $NaBH_4$ to combine SFLP and $[O]_v$ and enabled a tandem methanol synthesis process via RWGS reaction and CO hydrogenation reaction. The XPS results showed the $H_zIn_2O_{3-x}(OH)_y$ sample has $[O]_v$ and OH group, confirming the presence of the possible dual active sites, $[O]_v$ and the SFLP (Figure 7e). *In situ* DRIFTS measurements of CO_2 and H_2 (1:1) exhibited the formation of methoxy and formate species, and CO and H_2 (1:1) demonstrated the presence of asymmetric HOCO*, which implied that In−OH group assisted the SFLP addition reaction. Thus, the tandem pathway of this new black indium oxide could be proposed as (Figure 7f): H_2 was heterolytically split by SFLP, and CO_2 was converted into CO by a formate intermediate on SFLP via RWGS reaction, and then the produced CO was trapped by $[O]_v$ and further hydrogenated to CH_3OH.

3.3.2. Modification of SFLP. SFLP is the most common surface active site in hydroxylated indium oxide $In_2O_{3-x}(OH)_y$, and the modification of SFLP can be realized by adjusting the SFLP geometry and tuning the distance between Lewis acid and base sites, which in turn can optimize the Lewis acidity/basicity of the SFLP.[3]

Polymorphic materials engineering provides a valuable strategy for optimizing the performance of photothermal catalysts via surface geometry tuning. In_2O_3 has mainly two polymorphic phases: cubic (c-) and metastable rhombohedral (rh-) phases. The rh-$In_2O_{3-x}(OH)_y$ nanocrystal was obtained via calcination of an InOOH precursor and exhibited better catalytic performance than c-$In_2O_{3-x}(OH)_y$ for CH_3OH production (Figure 8a).[60] DFT simulations of the Bader charge (Figure 8b), reaction pathway, and energy barrier of H_2 dissociation (Figure 8c), showed the larger charge difference between the Lewis acid and Lewis base pairs in the (110) rh-$In_2O_{3-x}(OH)_y$, which indicated that the SFLP on the surface of rh-$In_2O_{3-x}(OH)_y$ nanocrystal was more active.

Isomorphous substitution is another effective measure to modify the surface active sites. A series of Bi^{3+}-substituted $In_2O_{3-x}(OH)_y$ nanocrystals $Bi_zIn_{2-z}O_{3-x}(OH)_y$ were prepared via dehydroxylation of Bi^{3+}-substituted $In(OH)_3$, and the photothermal CO rate exhibited accordingly a volcano-shaped trend with the doping concentration (Figure 8d).[61] The DFT calculations suggested that both Lewis acidity and Lewis basicity of the SFLP were increased when Bi substitutes at the neighboring In3 site (the bader charge on O of OH was −1.69e for the substituted system vs −1.50e for the unsubstituted system, and the bader charge on Bi was +2.52e vs +1.55e on In2) (Figure 8e), but acidic In2 atoms could also have been substituted by Bi when excess Bi was doped (the bader charge on O of OH decreased to −1.38e), which led to the reduction of Lewis basicity instead. These two opposing effects adversely determined the rate of H_2 dissociation and thereby the activity of the photothermal catalyst, which explains the volcano-shaped trend of the reaction rate versus the doping content.
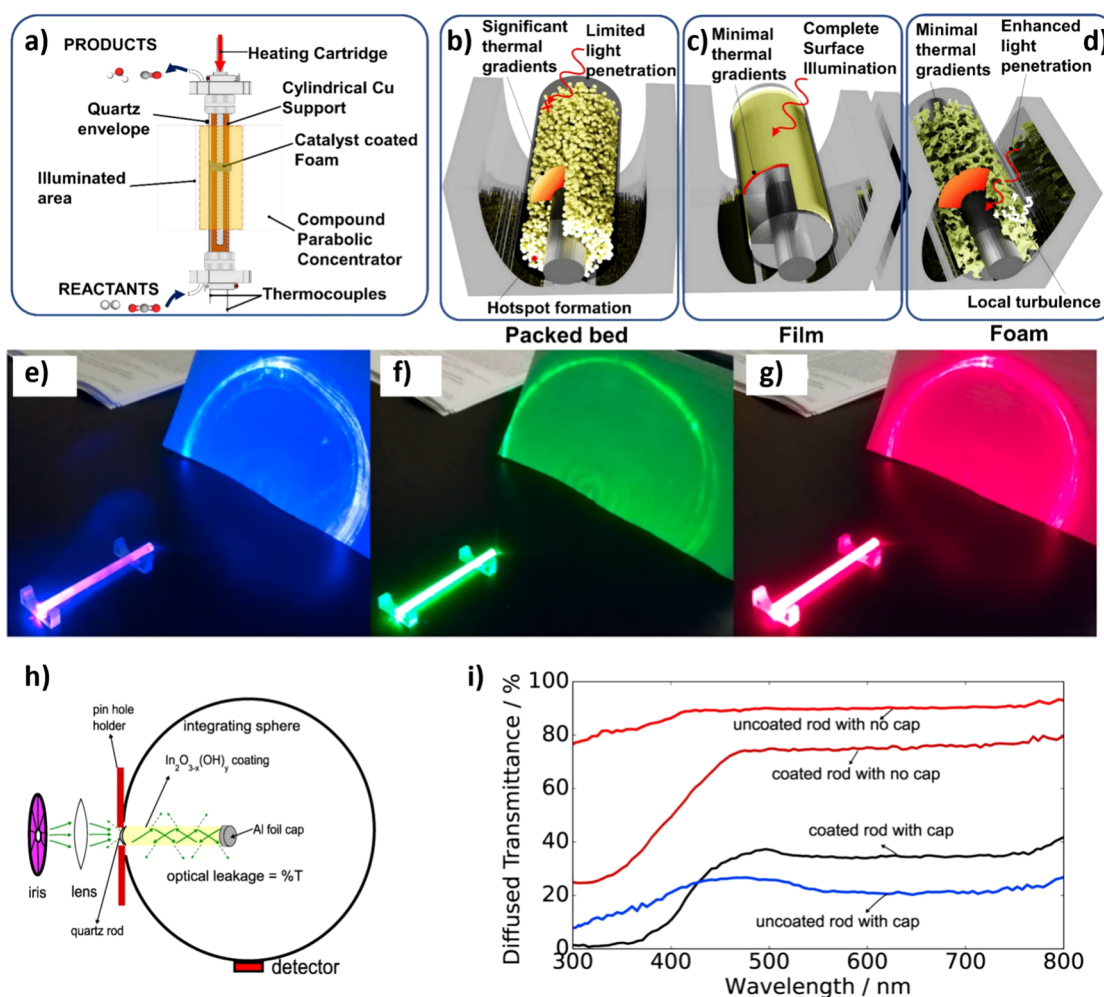
Figure 9. Innovation in optochemical engineering based on indium oxide-based catalysts. a) Simplified scheme of the annular photoreactor employed to conduct the photo- and thermal CO_2 hydrogenation on coated foams. Graphical representation of the physical phenomena catalyzed by $In_2O_{3-x}(OH)_y$ nanorods under solar light for different reactor configurations: b) Packed bed, c) Thin film and d) Coated foam.[62] Waveguide behavior of quartz rod coated by $In_2O_{3-x}(OH)_y$, under e) blue, f) green, and g) red laser illumination. h) Schematic illustration of integrating sphere measurement of the optical leakage. (i) Optical leakage spectra of coated and uncoated waveguides, with and without an aluminum foil end-cap.[33] Reprinted with permission from refs 62, 33. Copyright 2022 Elsevier B.V. and 2021 Springer Nature.

4. INNOVATION IN OPTOCHEMICAL ENGINEERING

Complementary to the design and development of catalysts, judicious optochemical engineering confer new viabilities onto photothermal catalytic CO_2 hydrogenation. Numerous optochemical engineering innovations based on indium oxide-based catalysts have been reported. Photon sponges such as Ni foam were successfully applied as the catalyst support (Figure 9a).[62] A light-enhanced CO production rate of up to 130% was realized due to the minimal thermal gradients and high light penetration of foams (Figure 9d) in contrast to traditional packed beds and film (Figure 9b,c). In addition, the internal reflection in quartz waveguide rod supports could maximize light absorption by $In_2O_{3-x}(OH)_y$ (Figure 9e–h).[33] The catalyst coating increases the visible light lateral scattering compared to uncoated quartz rods (Figure 9i), and the waveguide technology significantly improved photon-to-yield efficiencies and photothermal CO_2 catalysis rates.

5. CONCLUSIONS AND PERSPECTIVE

Indium oxide in its myriad guises has taught us the chemical and physical principles of photothermal CO_2 catalysis. It has also informed us that the ultimate efficiency of converting photons to product depends not just on the materials discovery process but the multiscale architecture and integration of the photocatalyst and photoreactor for capturing solar irradiation. This boils down to an optochemical materials and reactor engineering design problem to optimize light, charge, heat, and mass transport in a photothermal CO_2 photoreactor.

Interest in optochemical engineering of gas-phase heterogeneous CO_2 photocatalysis is on the rise and is anticipated to become mainstream research and development for producing sustainable commodity chemicals from small molecule precursors, such as H_2O, N_2, CH_4, and C_2H_6. This trend is apparent in reports of high light capture efficiency photocatalysts and photoreactors. Recently, optical waveguide,[33,63] photon sponges,[62] ultrablacks,[64] and optofluidics[65] are making their debut all aimed at boosting the performance metrics of photothermal CO_2 catalysis. Moreover, developing a photo-ocapacitor persistent photocatalyst system is an emerging trend to solve the intermittent availability of sunlight.[30]

We see the field pivoting away from a decade of CO_2 photocatalysis materials discovery more toward the industrialization of photons to products. This endeavor requires

optochemical engineering of high-efficiency photocatalysis and photoreactors. Ultimately, the energy and economic metrics of the cost of a mole of photons to produce a mole of products will decide on the viability of any gas-phase heterogeneous CO_2 photocatalysis process.

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Notes

The authors declare no competing financial interest.

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Junchuan Sun studied at Chiba University as an exchange student in 2019 and obtained his bachelor degree from Beijing Institute of Technology (BIT) in 2020. After his graduation, he joined the Chinese University of Hong Kong, Shenzhen as a Ph.D. student under the supervision of Prof. Lu Wang. His current research interest is photothermal catalysis for CO_2 reduction.

■ DEDICATION

Dedicated to the 79th birthday of Professor Geoffrey Ozin.

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