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Photothermal CO₂ hydrogenation for C₁ fuels: fundamentals, reaction pathways and reactor design

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Photothermal CO₂ hydrogenation has emerged as a promising strategy for converting CO₂ into value-added C₁ fuels and chemicals by coupling solar-energy harvesting with catalytic hydrogenation. Compared with conventional thermocatalysis and photocatalysis, photothermal catalysis relies on the synergistic effects of photon-to-heat conversion and photoinduced electronic processes. Localized heating accelerates CO₂ activation, H₂ dissociation, and surface hydrogenation kinetics, while photoexcited charge carriers and interfacial electronic redistribution regulate reactant activation and the evolution of reaction intermediates, thereby directing reaction pathways and product selectivity. Recent advances have demonstrated that rational catalyst design—including the engineering of active sites, oxygen vacancies, metal–support interfaces, hydrogen-transfer pathways, and Lewis acid–base pairs—can selectively steer CO₂ hydrogenation toward CO, CH₄, or CH₃OH through distinct reaction pathways. In parallel, reactor-engineering strategies, such as continuous-flow operation, solar concentration, thermal confinement, structured porous architectures, and 3D-printed reactors, further enhance photon utilization, heat management, and mass transfer, enabling efficient solar-driven catalysis. This review provides an integrated perspective on the fundamental mechanisms of photothermal CO₂ hydrogenation, highlighting photothermal synergistic effects, reaction pathways, catalyst-design principles governing selective C₁ product formation, and emerging reactor-design strategies for practical solar-fuel production. Finally, the remaining challenges and future opportunities for catalyst–reactor co-design and the scalable implementation of photothermal CO₂ hydrogenation are discussed.

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1. Introduction

The continuous rise in anthropogenic carbon dioxide (CO₂) emissions, primarily driven by the large-scale consumption of fossil resources, has intensified global climate change and

accelerated the urgency of developing sustainable carbon management strategies.^{1–4} Beyond carbon capture and storage, the catalytic conversion of CO₂ into fuels and chemicals has attracted increasing attention because it enables the transformation of an abundant greenhouse gas into value-added carbon feedstocks, thereby contributing simultaneously to emission mitigation and renewable energy storage.^{5,6} Among the various CO₂ conversion strategies, CO₂ hydrogenation is particularly attractive because H₂ serves as a more effective reductant than water, enabling faster kinetics, higher productivity, and more controllable product formation.^{7,8} Its compatibility with established catalytic processes further makes it highly promising for practical fuel and chemical synthesis.^{9,10} Correspondingly, research interest in this area has grown sharply, as reflected by the rapid increase in annual publications and citations related to photothermal CO₂ conversion and the more focused subfield of photothermal CO₂ hydrogenation (Fig. 1).

Depending on catalyst composition and operating conditions, CO₂ hydrogenation can yield a variety of products,

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including CO, hydrocarbons, and oxygenates. Among them, single-carbon (C_1) molecules, particularly carbon monoxide (CO), methane (CH_4), and methanol (CH_3OH), are of special importance.^{11,12} These three products represent the predominant and most extensively investigated target products in heterogeneous photothermal CO_2 hydrogenation, as reflected by the current literature. By contrast, other C_1 species, such as formic acid and formaldehyde, are generally more susceptible to further conversion under photothermal conditions and are therefore more frequently reported as intermediates in CO_2 reduction pathways rather than as terminal products. Based on these considerations, the present review focuses primarily on CO, CH_4 , and CH_3OH as the representative C_1 products. CO is a key intermediate for syngas chemistry and Fischer–Tropsch synthesis, CH_4 is compatible with existing natural gas infrastructure, and methanol is a versatile platform molecule for

fuels, hydrogen storage, and downstream chemical manufacturing.^{13–17} Compared with multicarbon products, C_1 products generally involve lower kinetic complexity, clearer reaction pathways, and more mature industrial relevance, making them highly attractive near-term targets for practical CO_2 utilization.^{18,19} Therefore, selectively directing CO_2 hydrogenation toward C_1 products represents both a scientifically meaningful and technologically realistic route toward carbon neutrality.

Despite this promise, efficient CO_2 hydrogenation remains challenging because CO_2 is a thermodynamically stable and kinetically inert molecule with a high $C=O$ bond strength.¹³ Conventional thermocatalytic processes often rely on elevated temperatures and pressures to overcome these barriers, which leads to substantial energy input and may compromise product selectivity through competing reaction pathways and



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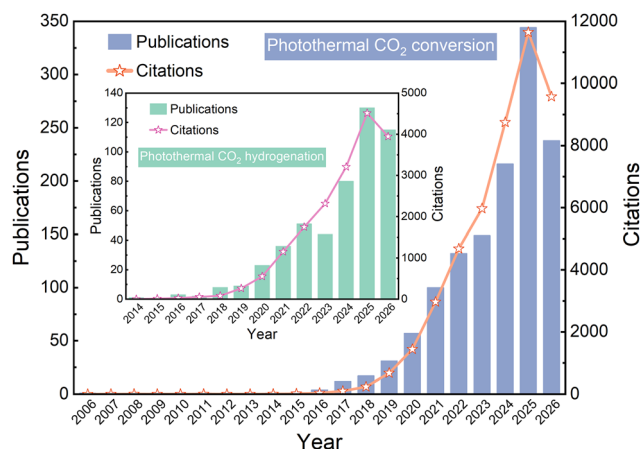


Fig. 1 Annual publication and citation trends in photothermal CO₂ conversion and photothermal CO₂ hydrogenation. Data were retrieved from the Web of Science Core Collection using Topic searches with the search terms photothermal CO₂ conversion and photothermal CO₂ hydrogenation, respectively. The 2026 data include publications and citations available up to August 2026.

thermodynamic constraints.²⁰ In parallel, purely photocatalytic approaches offer solar-driven CO₂ conversion under mild conditions, but their practical performance is frequently limited by narrow light spectral response, insufficient photon flux, fast charge separation-recombination, and slow surface reaction kinetics.²¹ As a result, neither thermal catalysis nor photocatalysis alone fully satisfies the combined requirements of efficiency, selectivity, and scalable solar utilization under mild reaction conditions. Photothermal catalysis has emerged as a promising strategy to bridge this gap by integrating photochemical and thermochemical effects within a single catalytic platform.²² In photothermal CO₂ hydrogenation, incident light can be harnessed through multiple channels: absorption of high-energy photons generates energetic charge carriers that

modulate CO₂ adsorption and activation, while visible and near-infrared photons can be converted into localized heat that accelerates surface kinetics and reduces the external energy demand.^{23,24} This synergistic utilization of photonic and thermal energy enables broader solar-spectrum harvesting than conventional photocatalysis while providing greater flexibility than purely thermal catalysis.^{25,26} More importantly, photothermal fields can regulate the reaction microenvironment through localized heating, charge redistribution, defect activation, and interfacial electronic modulation, creating new opportunities to direct selectivity among competing C₁ pathways.^{12,25}

Recent years have witnessed rapid advances in catalyst design for photothermal CO₂ hydrogenation, including plasmonic nanostructures, transition-metal nanoparticles, oxygen-defective oxides, MOF-derived hybrids, and metal-support interfacial architectures.^{10,21,27–29} These materials have demonstrated increasingly efficient conversion of CO₂ to CO, CH₄, and CH₃OH under light-assisted conditions. Meanwhile, mechanistic studies using *operando* infrared spectroscopy, Raman spectroscopy, X-ray absorption spectroscopy, and theoretical calculations have begun to reveal how photothermal effects influence the formation and evolution of key intermediates, including COOH*, HCOO*, CO*, and CH_xO* species, during CO₂ hydrogenation.^{30,31} While catalyst development and mechanistic understanding have progressed rapidly, reactor engineering is also emerging as a critical factor for translating laboratory photothermal systems into practical technologies.³² Unlike conventional catalytic reactors, photothermal reactors must simultaneously manage photon transport, heat generation and dissipation, gas-solid mass transfer, and catalyst exposure geometry.³³ Light penetration, thermal gradients, residence time, and catalyst geometry can strongly influence activity and selectivity.³⁴ Structured reactors such as monoliths, foams, thin films, and microchannels therefore offer important opportunities to intensify performance through enhanced light utilization, heat transfer, and mass transport efficiency.^{27,35–37} Consequently, understanding photothermal CO₂ hydrogenation requires a multiscale perspective that connects active sites, reaction pathways, and reactor environments.

Nevertheless, several fundamental questions remain unresolved.^{38–40} First, the respective contributions of thermal and non-thermal effects under illumination remain difficult to quantify, leading to ongoing debate regarding the origin of enhanced catalytic performance. Second, although local photon-to-heat and photon-to-charge conversion processes are believed to influence reaction pathways, their roles in governing intermediate evolution and product selectivity have not been fully understood. Third, the coupling of catalyst design and reactor engineering remains largely unexplored, limiting the translation of laboratory-scale advances into practical photothermal CO₂ conversion systems. Addressing these challenges requires a comprehensive understanding that spans energy conversion mechanisms, catalytic reaction pathways, and reactor-level engineering considerations. While previous reviews have summarized photothermal CO₂ conversion systems or specific catalyst families, an integrated perspective connecting photothermal fundamentals,



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reaction chemistry, and reactor design remains less developed. In this review, we therefore focus on the fundamental principles of photothermal CO_2 hydrogenation, the pathways governing the selective formation of CO , CH_4 , and CH_3OH , and the reactor strategies required for efficient solar-driven operation. By linking insights from surface chemistry, reaction engineering, and solar energy utilization, this review aims to provide design principles for the rational development of efficient and scalable photothermal CO_2 hydrogenation systems toward practical C_1 fuel synthesis.

2. Fundamentals of photothermal CO_2 hydrogenation

Photothermal CO_2 hydrogenation integrates light absorption with thermal and photoinduced electronic effects to drive the conversion of thermodynamically stable CO_2 .⁴¹ Unlike conventional thermocatalysis, which relies solely on heat, or photocatalysis, which is primarily governed by photoexcited charge carriers, photothermal catalysis operates through coupled thermal and photonic processes that simultaneously influence catalyst temperature, interfacial electronic structure, and surface reaction kinetics.⁴² As CO_2 hydrogenation involves energy-intensive bond activation and multiple hydrogenation steps, the synergistic utilization of light and heat can enhance catalytic activity and reaction efficiency under comparatively mild conditions.^{43,44} The fundamental processes governing photothermal CO_2 hydrogenation, including energy conversion, reactant activation, surface hydrogenation, and product formation, are summarized in Fig. 2. Upon light irradiation, absorbed photons are converted into localized heat and photoinduced charge carriers, which cooperatively regulate CO_2 adsorption

and activation, H_2 dissociation, intermediate hydrogenation, C–O bond cleavage or retention, and product desorption. Together, these elementary steps determine the selective formation of CO , CH_4 , or CH_3OH .

2.1 Photon-to-heat and charge conversion

A key characteristic of photothermal catalysis is the utilization of solar energy through both photon-to-heat and photon-to-charge conversion pathways. Upon illumination, absorbed photons can be dissipated through non-radiative relaxation processes, generating localized heat, while high-energy photons may also induce charge excitation and redistribution at catalytic surfaces.⁴⁵ Photon-to-heat conversion is generally the dominant contribution in most photothermal CO_2 hydrogenation systems.^{46,47} Recent carrier-dynamics studies have further revealed that efficient photon-to-heat conversion depends not only on broadband light absorption but also on ultrafast non-radiative charge recombination. Using flash-photolysis time-resolved microwave conductivity (TRMC), Nishikubo *et al.* demonstrated that hydrogenation introduces abundant trap states in $\text{H}_x\text{MoO}_{3-y}$, accelerating charge recombination by two to three orders of magnitude compared with pristine MoO_3 .⁴⁸ The rapid conversion of photoexcited carriers into lattice phonons provides direct experimental evidence for localized heat generation in defect-rich oxides, thereby explaining the high photothermal conversion efficiency frequently observed in hydrogenated metal oxides used for catalytic CO_2 hydrogenation. Metals, semiconductors, carbides, nitrides, and defect-rich oxides can efficiently absorb incident solar radiation and convert it into thermal energy, generating localized heating at illuminated catalyst surfaces.^{10,11,20,28,49} Such localized heating accelerates temperature-dependent elementary processes, including H_2 dissociation, surface diffusion, and hydrogenation of reaction intermediates.

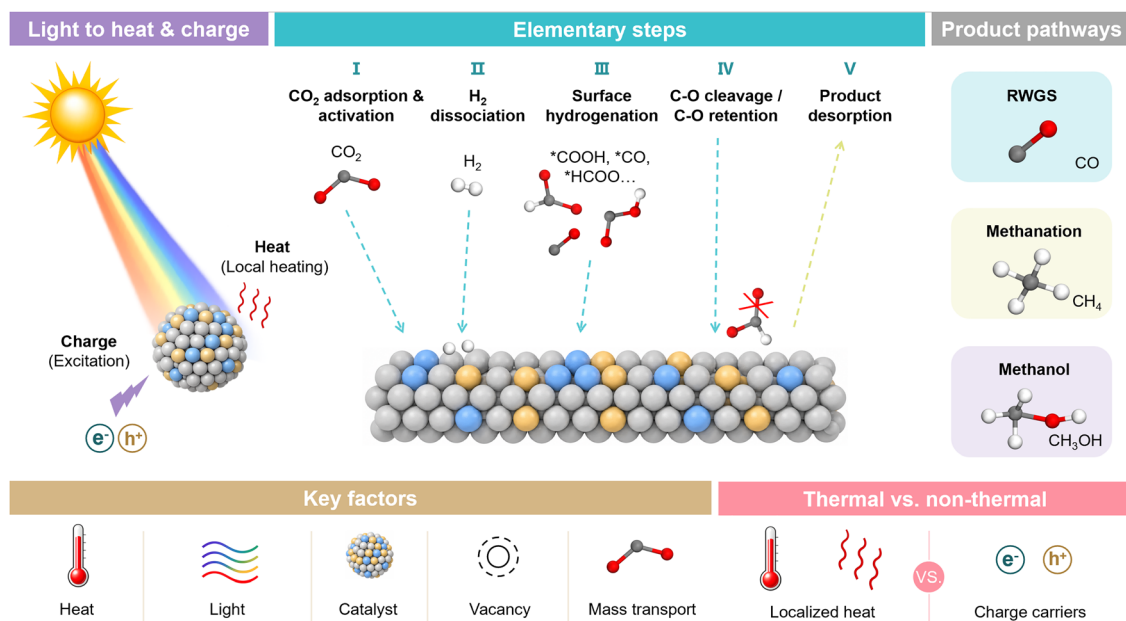


Fig. 2 Fundamental processes governing photothermal CO_2 hydrogenation.

Simultaneously, photon-to-charge conversion can modify the electronic properties of catalytic interfaces. In semiconductor-based catalysts, photoexcitation generates electron-hole pairs, whereas plasmonic metals may produce energetic charge carriers under resonant illumination.^{50,51} These photoinduced electronic effects can influence reactant adsorption, CO₂ activation, H₂ dissociation, and the stability of surface intermediates by altering local electron density and interfacial electronic structures.^{52,53} A representative example is the plasmonic Pt/H_xMoO_{3-y} catalyst featuring localized surface plasmon resonance (LSPR), in which visible-light excitation generates hot electrons together with localized photothermal heating.⁵⁴ Photoelectrochemical measurements confirmed the generation of photoexcited charge carriers, while XPS analysis revealed reversible redox cycling of Mo species associated with oxygen vacancies. These electronic effects facilitate CO₂ activation at oxygen-vacancy sites and cooperate with photothermal heating to enhance the RWGS reaction, illustrating that photon-to-charge conversion can directly regulate interfacial catalytic processes in photothermal CO₂ hydrogenation.

2.2 Elementary steps in photothermal CO₂ hydrogenation

Despite the diversity of products, photothermal CO₂ hydrogenation generally involves four fundamental steps: CO₂ adsorption and activation, H₂ dissociation, surface hydrogenation reactions, and product desorption.^{55,56} Photothermal inputs can influence each of these processes by modifying local temperature and interfacial electronic properties. CO₂ activation is often the first kinetic challenge because of the high thermodynamic stability and linear molecular structure of CO₂. Effective activation typically occurs on oxygen vacancies, basic sites, metal-oxide interfaces, or low-coordination metal centers, where adsorbed CO₂ can be transformed into reactive surface intermediates.^{26,57,58} H₂ activation commonly occurs on metallic sites, including Ni, Ru, Pt, Rh, Co, Cu, Pd, and Fe.^{28,59} Under photothermal conditions, localized heating promotes H-H bond cleavage, while photoinduced electronic effects may further facilitate hydrogen activation and interfacial charge transfer. In bifunctional catalysts, activated hydrogen can migrate from metal sites to adjacent oxide surfaces through hydrogen spillover, coupling H₂ activation with CO₂ conversion.^{31,60,61} Following reactant activation, sequential hydrogenation reactions generate various surface intermediates that ultimately determine product distribution. Depending on catalyst composition and reaction conditions, these pathways may favor CO, CH₄, or oxygenated products.^{41,43,44,52,62} Photothermal operation can accelerate intermediate transformation by enhancing surface diffusion and reaction kinetics through localized heating. According to the Arrhenius relationship, increasing the local temperature increases the reaction rate constant without necessarily changing the intrinsic activation energy.⁴² In contrast, additional photoinduced electronic effects may alter adsorption energetics or reaction pathways, thereby changing the apparent activation energy. Finally, efficient desorption of products and byproducts is essential for maintaining catalytic turnover. Excessively strong adsorption of

reaction products may block active sites, whereas localized heating under illumination can facilitate product release and active-site regeneration.^{63,64}

2.3 Thermal and non-thermal effects

Despite rapid progress in the field, distinguishing intrinsic non-thermal effects from purely thermal contributions remains one of the central challenges in photothermal catalysis.⁷ In many systems, enhanced catalytic performance under illumination can be largely attributed to light-induced heating, particularly when catalysts exhibit strong absorption across the visible and infrared regions. Therefore, claims of hot-carrier-mediated or other non-thermal mechanisms require careful validation.⁶⁵ A major challenge arises from accurate temperature determination.⁶⁶ Conventional thermocouples typically measure bulk or reactor-wall temperatures rather than the actual temperature of illuminated catalyst surfaces. As transient nanoscale or microscale hot spots may form under irradiation, the catalytically relevant temperature can differ substantially from the measured average value, potentially leading to overestimation of non-thermal contributions.

To distinguish thermal and non-thermal effects, multiple complementary approaches are often employed, including dark thermal controls at matched temperatures, wavelength-dependent activity measurements, chopped-light experiments, *operando* spectroscopic characterization, isotopic tracing, theoretical simulations, and advanced temperature characterization techniques such as infrared thermography, Raman thermometry, and Debye-Waller factor analysis from FT-EXAFS for probing element-specific local temperatures in catalysts.^{66,67} However, no single method can unambiguously separate thermal and non-thermal contributions. Matched-temperature dark controls provide a direct kinetic benchmark, but their reliability depends critically on accurate determination of the catalytically relevant surface temperature; unresolved local temperature gradients or hot spots can otherwise produce an apparent photo-enhancement. Wavelength-dependent and chopped-light experiments provide useful evidence for photon-dependent behavior, although variations in optical absorption and heating dynamics can complicate their interpretation. *Operando* spectroscopy can reveal light-induced changes in surface species or electronic states, but such observations alone do not establish a causal relationship with catalytic enhancement. Consequently, reliable mechanistic assignment generally requires converging evidence from temperature-matched kinetics, accurate thermometry, wavelength- or time-dependent responses, and *operando* characterization.

If catalytic enhancement correlates primarily with surface temperature, a thermally dominated mechanism is generally inferred. In contrast, spectral resonance effects, transient photo-responses, or changes in intermediate populations beyond thermal expectations may indicate additional non-thermal contributions. Recent studies have increasingly adopted such multi-technique approaches. For example, Yang and co-workers combined wavelength-dependent activity measurements, surface-temperature analysis, activation-energy comparisons, isotopic

tracing, and *in situ* DRIFTS to evaluate the origin of activity enhancement during photothermal CO₂ methanation over a yolk-shell Ni@NC nanoreactor.⁶⁸ By comparing photothermal and purely thermal reactions at the same catalyst surface temperature, they observed a ~30% higher CH₄ production rate under illumination, providing evidence that photo-assisted effects contribute beyond simple heating. These findings illustrate how complementary characterization and kinetic analyses can provide deeper insight into photothermal reaction mechanisms. A broad methodological consensus is emerging that non-thermal effects should not be assigned on the basis of activity enhancement under illumination alone, but should instead be supported by multiple independent and mutually consistent lines of evidence. Nevertheless, quantitatively separating thermal and non-thermal contributions remains challenging and controversial, particularly for strongly light-absorbing catalysts with heterogeneous local temperatures.

For CO₂ hydrogenation, thermal and non-thermal effects typically operate in concert rather than independently.⁶⁹ Localized heating often provides the primary kinetic driving force, whereas photoinduced electronic perturbations can influence adsorption behavior, interfacial charge transfer, intermediate evolution, and reaction pathways.⁷⁰ The contribution of electronic effects can be assessed by complementary approaches such as *operando* XPS/XAS for monitoring charge redistribution and oxidation-state changes, transient absorption spectroscopy for probing carrier dynamics, and kinetic comparisons under matched-temperature illumination conditions. Understanding the relative contributions of these effects is therefore essential for establishing structure–activity relationships and guiding the rational design of photothermal catalysts and reactors.

3. Reaction pathways and selectivity control

Building on these principles, the product distribution in photothermal CO₂ hydrogenation arises from the competition among

multiple surface hydrogenation, C–O bond cleavage, and oxygenate-retention pathways. Among the reported products, CO, CH₄, and CH₃OH are the most representative C₁ targets because they differ markedly in thermodynamic preference, mechanistic requirements, and downstream application value. Under photothermal conditions, light intensity, local temperature, catalyst composition, and interfacial structure introduce additional variables that can reshape reaction energetics and intermediate coverages beyond those accessible in conventional thermocatalysis. Understanding how these factors steer selectivity is therefore essential for the rational design of catalysts and operating strategies. Recent studies further demonstrate that photothermal catalysts can exhibit substantially different activity–selectivity relationships depending on the targeted C₁ product, highlighting the intrinsic trade-offs between deep hydrogenation, CO desorption, and oxygenate stabilization pathways, as summarized in Fig. 3 and Table 1. In this section, the formation mechanisms, key control parameters, and representative advances for CO, CH₄, and CH₃OH production are discussed.

3.1 CO formation *via* RWGS

CO is one of the most accessible and widely reported products in photothermal CO₂ hydrogenation, primarily generated through the reverse water–gas shift (RWGS) reaction: CO₂ + H₂ → CO + H₂O.^{94–98} As an endothermic reaction, RWGS is thermodynamically favored at elevated temperatures, making it intrinsically compatible with photothermal catalysis, where absorbed photons are converted into localized heat on catalyst surfaces.⁴² Mechanistically, CO formation generally involves CO₂ adsorption and activation, H₂ dissociation, and subsequent conversion through distinct pathways, including *COOH-mediated, *HCOO-mediated, and oxygen-vacancy-mediated redox mechanisms. In associative pathways, *COOH or *HCOO intermediates are ultimately converted into adsorbed *CO prior to rapid CO desorption, whereas in redox pathways, reversible lattice oxygen exchange directly participates in CO formation.³⁸ Selective CO production therefore requires efficient CO₂ activation, rapid

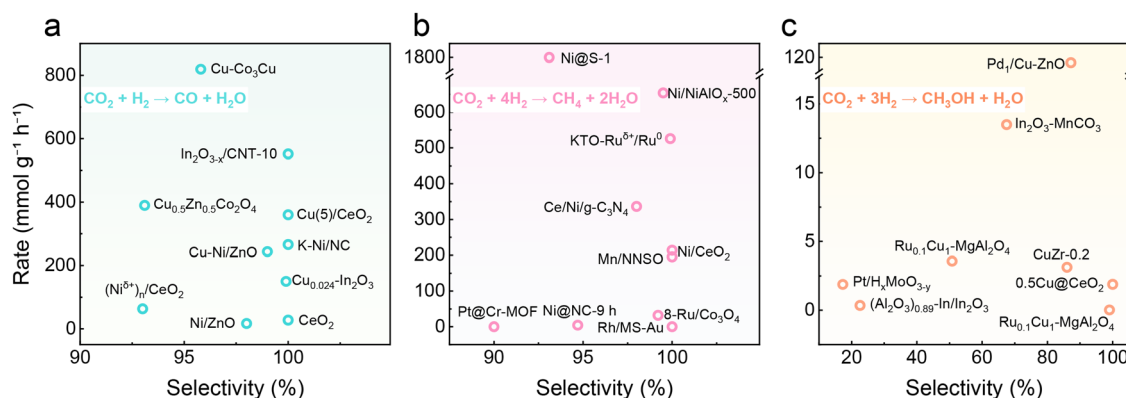


Fig. 3 Selectivity and production rates of representative photothermal catalysts for CO₂ hydrogenation to CO, CH₄ and CH₃OH reported in 2025–2026. (a) Cu(5)/CeO₂,⁷¹ (Ni^{δ+})_n/CeO₂,⁷² Cu–Ni/ZnO,⁷³ K–Ni/NC,⁷⁴ In₂O_{3–x}/CNT-10,⁷⁵ Cu_{0.5}Zn_{0.5}Co₂O₄,⁷⁶ Cu_{0.024}–In₂O₃,⁵⁸ Cu–Co₃Cu,⁶² CeO₂,⁷⁷ Ni/ZnO,⁷⁸ (b) Ni@NC-9 h,⁶⁸ 8-Ru/Co₃O₄,⁷⁹ KTO–Ru^{δ+}/Ru⁰,⁸⁰ Ce/Ni/g–C₃N₄,⁸¹ Rh/MS–Au,⁸² Mn/NNSO,⁸³ Ni/NiAlO_x-500,⁸⁴ Pt@Cr–MOF,⁸⁵ Ni@S-1,⁸⁶ Ni/CeO₂,⁸⁷ (c) Pt/H_xMoO_{3–y},⁴⁷ Pd₁/Cu–ZnO,⁸⁸ CuZr-0.2,⁸⁹ Ru–In₂O₃/g–C₃N₄,⁹⁰ Ru_{0.1}Cu₁–MgAl₂O₄,⁹¹ In₂O₃–MnCO₃,⁴⁴ (Al₂O₃)_{0.89}–In/In₂O₃,⁹² 0.5Cu@CeO₂.⁹³

Table 1 Performance comparison of representative catalysts for photothermal CO₂ hydrogenation to C₁ products

Product	Catalyst	Reaction conditions	Conversion (%)	Selectivity (%)	Rate (mmol g ⁻¹ h ⁻¹)	Ref.
CO	Cu(5)/CeO ₂	1.5 W cm ⁻² Xe lamp, 320.6 °C	25	100	359.9	71
	(Ni ^{δ+}) _n /CeO ₂	Simulated solar irradiation, 2.6 W cm ⁻²	47	93	63.36	72
	Cu–Ni/ZnO	300 W Xe lamp, 30 mW cm ⁻² , 500 °C	—	99	243.6	73
	K–Ni/NC	Simulated solar irradiation (Xe lamp), 4.3 W cm ⁻²	—	100	266	74
	In ₂ O _{3–x} /CNT-10	300 W Xe lamp, batch reactor	65	100	552	75
	Cu _{0.5} Zn _{0.5} Co ₂ O ₄	350 °C, 300 W Xe lamp	—	93.1	389.8	76
	Cu _{0.024} –In ₂ O ₃	3 W cm ⁻² full-spectrum light, 210 °C	7.5	99.9	150	58
	Cu–Co ₃ Cu	3 W cm ⁻² full-spectrum light	—	95.8	820	62
	CeO ₂	1.8 W cm ⁻² light, 400 °C	—	100	27.4	77
	Ni/ZnO	Xe lamp irradiation, 300 °C	36.2	98	16.5	78
CH ₄	Ni@NC-9 h	420 nm LED irradiation, 180 °C, 12.5 vol% CO ₂ , 86.9 mW cm ⁻²	—	94.7	4.33	68
	8-Ru/Co ₃ O ₄	300 W Xe lamp, 318 °C, 0.5 MPa	—	99.21	32.15	79
	KTO–Ru ^{δ+} /Ru ⁰	Xe lamp, 312.6 °C	—	99.9	526	80
	Ce/Ni/g–C ₃ N ₄	Xe lamp (3.36 W cm ⁻²), 300 °C	—	98	336.7	81
	Rh/MS–Au	Simulated sunlight, 100 mW cm ⁻²	—	100	0.00805	82
	Mn/NNSO	Photothermal reactor, 0.1 MPa, 300 W Xe lamp	54.8	100	195.7	83
	Ni/NiAlO _x -500	330 °C, Xe lamp irradiation (2.9 W cm ⁻²)	84.5	99.5	654.2	84
	Pt@Cr–MOF	254 nm UV, 200 °C, atmospheric pressure	—	90	0.1595	85
	Ni@S-1	300 W Xe lamp, 400 °C	—	93.1	1800	86
	Ni/CeO ₂	Natural sunlight/concentrated sunlight, 360–370 °C	99.9	100	214	87
CH ₃ OH	Pt/H _x MoO _{3–y}	Visible light (λ > 450 nm, 750 mW cm ⁻²), 200 °C, 2.0 MPa	10.9	17.3	1.89	47
	Pd ₁ /Cu–ZnO	300 W Xe lamp, 240 °C, 3 MPa	—	87.2	116.2	88
	CuZr-0.2	Xe lamp (2.2 W cm ⁻²), ~220 °C, 3 MPa	98	86	3.14	89
	Ru–In ₂ O ₃ /g–C ₃ N ₄	300 W Xe lamp, 265 °C, 1.0 MPa	5.3	50.8	3.58	90
	Ru _{0.1} Cu ₁ –MgAl ₂ O ₄	Light irradiation, 190 °C	—	99	0.0286	91
	In ₂ O ₃ –MnCO ₃	Light irradiation, 150 °C, 4.0 MPa	13.5	67.5	13.5	44
	(Al ₂ O ₃) _{0.89} –In/In ₂ O ₃	Light irradiation, 250 °C, 0.1 MPa	—	22.6	0.3528	92
	0.5Cu@CeO ₂	Light irradiation, 140 °C, 2 MPa	—	100	1.89602	93

H₂ dissociation, moderate *CO binding, and timely CO desorption before further hydrogenation occurs.⁹⁹ Beyond optimizing these elementary steps, recent studies have increasingly focused on elucidating how localized photothermal heating and photo-induced electronic effects cooperatively regulate RWGS activity and selectivity.⁹ Representative strategies include single-atom/vacancy synergy, hydrogen-spillover-driven defect regeneration, cooperative metal–oxide redox interfaces, dual-site functional separation of H₂ activation and CO formation, heterophase interface engineering, and photothermal chemical-looping reaction engineering, as illustrated by the representative examples discussed below.^{16,58,60,62,71,100}

A representative strategy for promoting photothermal RWGS is to couple oxygen-vacancy engineering with atomically dispersed metal sites. As shown in Fig. 4a, increasing light intensity simultaneously raises the catalyst temperature and CO production rate over Cu–In₂O₃, directly demonstrating the photothermal enhancement of the RWGS reaction under full-spectrum irradiation.⁵⁸ Mechanistic investigations further reveal that this enhanced performance originates from the synergistic interaction between Cu single atoms and oxygen vacancies. Under 3 W cm⁻² full-spectrum illumination, the optimal Cu–In₂O₃ catalyst achieves a CO production rate of 46.17 mol g_{Cu}⁻¹ h⁻¹ with >99% selectivity and maintains stable operation for 450 h in a continuous-flow reactor. Notably, localized photothermal heating raises the catalyst surface temperature

to approximately 210 °C, whereas conventional thermocatalysis requires about 410 °C to achieve the same CO₂ conversion. In addition, the apparent activation energy decreases from 68.25 to 52.30 kJ mol⁻¹, indicating a genuine photothermal enhancement beyond simple bulk heating. Mechanistic studies combining photocurrent measurements, *in situ* EPR, NAP-XPS, *in situ* DRIFTS, and DFT calculations reveal that illumination simultaneously induces localized heating and dynamic electronic regulation. Photocurrent measurements demonstrate enhanced charge separation, while *in situ* EPR shows that light irradiation dynamically increases the concentration of oxygen vacancies during reaction. NAP-XPS further confirms accelerated formation of formate species under illumination, providing direct evidence that photoexcited charge carriers participate in CO₂ activation. Meanwhile, localized photothermal heating accelerates H₂ dissociation on Cu single atoms and promotes subsequent hydrogenation kinetics. Oxygen vacancies serve as the primary adsorption and activation sites for CO₂, whereas Cu single atoms mainly activate H₂. The activated hydrogen subsequently hydrogenates vacancy-bound CO₂ through the *COOH pathway, followed by dehydroxylation to *CO and rapid CO desorption. Therefore, this catalyst demonstrates that photoinduced electronic effects and localized photothermal heating operate cooperatively, with light-enhanced charge dynamics promoting oxygen-vacancy formation and CO₂ activation, while localized heating accelerates hydrogenation kinetics. The positive

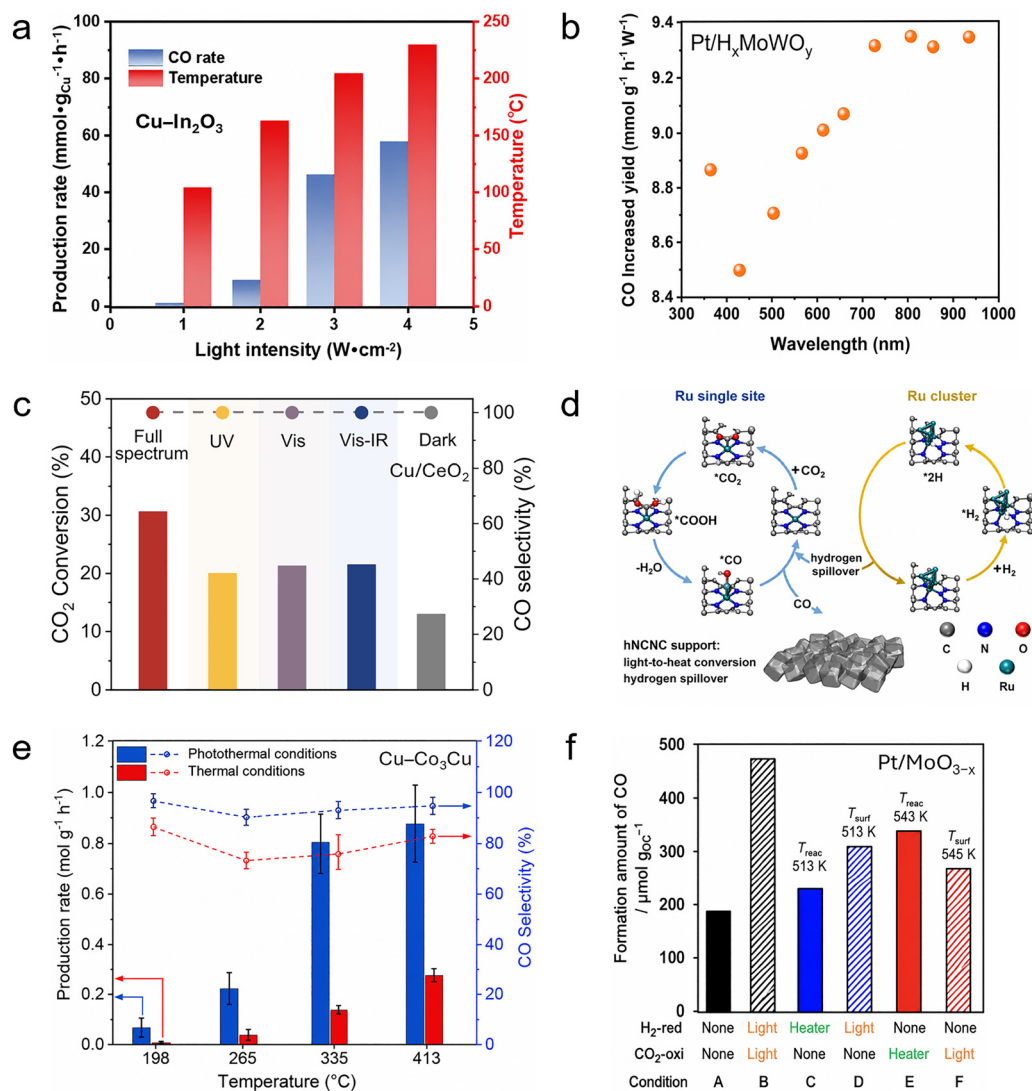


Fig. 4 Representative strategies for selective CO formation in photothermal RWGS systems. (a) Photothermal enhancement of CO production over Cu-In₂O₃ as a function of light intensity. Adapted from ref. 58 with permission from Wiley-VCH, copyright 2025. (b) Wavelength-dependent enhancement of CO production over Pt/H_xMoWO_y under visible-NIR irradiation. Adapted from ref. 16 with permission from the Royal Society of Chemistry, copyright 2022. (c) Wavelength-dependent CO₂ conversion over Cu/CeO₂ under full-spectrum, UV, visible, visible-IR irradiation, and dark conditions. Adapted from ref. 71 with permission from American Chemical Society, copyright 2026. (d) Dual-site Ru catalysts separate H₂ dissociation and CO formation via hydrogen spillover. Adapted from ref. 60 with permission from Wiley-VCH, copyright 2025. (e) Comparison of photothermal and thermocatalytic RWGS performances of Cu-Co₃Cu at identical catalyst temperatures. Adapted from ref. 62 with permission from Wiley-VCH, copyright 2025. (f) Comparison of light irradiation and external heating during the H₂-reduction and CO₂-oxidation steps of Pt/MoO_{3-x} in RWGS chemical looping. Adapted from ref. 100 with permission from the American Chemical Society, copyright 2025.

correlation between light intensity, catalyst temperature, and CO production (Fig. 4a) further confirms that these coupled photothermal and electronic effects jointly determine the highly efficient and selective RWGS performance.

Beyond static vacancy engineering, dynamic defect regeneration under reaction conditions provides another effective strategy for promoting photothermal RWGS. As shown in Fig. 4b, the CO production enhancement strongly depends on the irradiation wavelength, with the largest activity increase occurring in the visible-NIR region, demonstrating that efficient plasmonic light harvesting plays a key role in promoting the photothermal RWGS reaction.¹⁶ Under visible-NIR irradiation ($\lambda > 450$ nm, 0.88 W cm⁻²)

at a reaction temperature of 140 °C, the optimized Pt/H_xMoWO_y catalyst achieves a CO production rate of 3.1 mmol h⁻¹ g⁻¹, which is more than five times higher than that obtained under dark conditions and substantially higher than that of Pt/H_xWO_y. Control experiments further showed that performing the RWGS reaction thermally at 186 °C reproduced approximately 90% of the light-induced activity enhancement, indicating that localized photothermal heating is the dominant contributor to activity promotion, while photoinduced electronic effects provide an additional enhancement beyond thermal heating. Mechanistic investigations combining photoelectrochemical measurements, *operando* XAFS, XPS, and DFT calculations revealed that Mo doping

increases the concentration of free electrons and oxygen vacancies, thereby strengthening visible-NIR plasmonic absorption and facilitating photoinduced electron transfer to adsorbed CO_2 . Meanwhile, Pt nanoparticles efficiently dissociate H_2 and generate spillover hydrogen, which promotes H intercalation and continuous oxygen-vacancy regeneration within the H_xMoWO_y lattice. *Operando* XAFS and XPS further confirmed reversible Mo/W redox cycling during reaction, demonstrating that oxygen vacancies consumed during CO_2 activation are continuously regenerated by hydrogen spillover. Therefore, photothermal heating and photoinduced electronic regulation play complementary roles in this system: localized heating dominates the acceleration of RWGS kinetics, whereas photoexcited electrons facilitate CO_2 activation through dynamic oxygen-vacancy regeneration and interfacial charge redistribution. Their cooperative coupling enables sustained active-site regeneration and efficient CO production under photothermal conditions.

Building upon spillover-assisted vacancy regeneration, similar defect-mediated RWGS chemistry has also been extended to non-noble-metal catalysts through the construction of Cu–O–Ce interfacial sites. As shown in Fig. 4c, Cu/CeO₂ exhibits pronounced wavelength-dependent RWGS activity under full-spectrum, UV, visible, and visible-IR irradiation, demonstrating that both photothermal heating and photoinduced electronic effects contribute to CO_2 conversion.⁷¹ Han and co-workers reported a Cu/CeO₂ photothermal catalyst featuring highly dispersed Cu nanoparticles and Cu–O–Ce interfacial sites, which achieved 100% CO selectivity with a CO production rate of 359.9 mmol g_{cat}^{−1} h^{−1} under 1.5 W cm^{−2} full-spectrum irradiation. More importantly, at the same catalyst surface temperature, illumination produced substantially higher CO formation than thermocatalysis, while the apparent activation energy decreased from 40.6 to 26.5 kJ mol^{−1}, indicating that photoinduced effects contribute beyond thermal heating alone. Mechanistic investigations combining transient kinetic analysis, pseudo *in situ* XPS, EPR, *operando* DRIFTS, and DFT calculations revealed that Cu nanoparticles primarily function as H_2 dissociation sites, whereas the CeO₂ support undergoes reversible Ce⁴⁺/Ce³⁺ redox cycling to continuously regenerate oxygen vacancies for CO_2 activation through a redox RWGS pathway. Unlike associative RWGS mechanisms involving stable *COOH or *HCOO intermediates, CO formation proceeds predominantly through continuous reduction and reoxidation of Ce sites. Meanwhile, the localized surface plasmon resonance (LSPR) of Cu nanoparticles not only generates efficient photothermal heating but also promotes interfacial transfer of photoexcited electrons to the CeO₂ support, thereby accelerating the Ce⁴⁺/Ce³⁺ redox cycle and oxygen-vacancy regeneration under illumination. Therefore, localized photothermal heating mainly accelerates RWGS kinetics, whereas photoexcited electrons facilitate interfacial redox cycling and CO_2 activation through continuous oxygen-vacancy regeneration. Their synergistic coupling at Cu–O–Ce interfacial sites enables highly efficient and selective CO production under photothermal conditions.

A more sophisticated catalyst design is to spatially decouple H_2 activation from CO_2 hydrogenation through a hydrogen

spillover-assisted dual-site architecture. As illustrated in Fig. 4d, Ru clusters and atomically dispersed Ru–N₄ sites perform distinct catalytic functions, where hydrogen generated on Ru clusters continuously migrates to neighboring Ru single sites through hydrogen spillover, enabling efficient coupling of H_2 activation with selective CO_2 hydrogenation.⁶⁰ Sun and co-workers developed a Ru single-site/cluster hybrid catalyst supported on N-doped hierarchical carbon nanocages (hNCNC), which achieved a CO production rate of 3.1 mol g_{Ru}^{−1} h^{−1} with over 98% CO selectivity under 3.8 W cm^{−2} irradiation and maintained stable operation for 15 h. The hNCNC support exhibits broadband solar absorption (>98% over 200–2500 nm) and efficient photon-to-heat conversion, generating localized temperatures of approximately 380 °C under illumination to drive the RWGS reaction. Arrhenius analysis further revealed that the hybrid catalyst possesses the lowest apparent activation energy (45.7 kJ mol^{−1}) compared with Ru single sites (74.3 kJ mol^{−1}) and Ru clusters (54.4 kJ mol^{−1}), demonstrating that the dual-site architecture substantially accelerates RWGS kinetics under photothermal conditions. Mechanistic investigations combining H_2 -TPD, H–D isotope exchange, CO-TPD, *in situ* DRIFTS, DFT calculations, and kinetic analyses revealed that Ru clusters efficiently dissociate H_2 and continuously deliver hydrogen species to adjacent Ru–N₄ sites through hydrogen spillover across the hNCNC support. This abundant hydrogen supply markedly facilitates the formation of the key *COOH intermediate on Ru–N₄ sites, where CO_2 hydrogenation preferentially proceeds through the *COOH pathway (* CO_2 → *COOH → *CO → CO). Meanwhile, the dominant Ru–N₄ sites exhibit moderate CO adsorption, enabling rapid CO desorption while effectively suppressing further hydrogenation to CH₄. The authors further demonstrated that localized photothermal heating provides the primary driving force for RWGS kinetics, whereas the hydrogen-spillover-assisted dual-site architecture efficiently coordinates H_2 activation, hydrogen transfer, and selective CO formation. Therefore, by integrating efficient photon-to-heat conversion with spatially separated catalytic functions, this catalyst establishes hydrogen-spillover-assisted dual-site synergy as an effective strategy for simultaneously enhancing RWGS activity and CO selectivity under photothermal conditions, providing valuable inspiration for the rational design of multifunctional photothermal hydrogenation catalysts.

Reaction-induced phase engineering offers an effective strategy for constructing heterophase interfaces that simultaneously regulate light harvesting, reactant activation, and product desorption in non-noble-metal photothermal catalysts. As shown in Fig. 4e, photothermal catalysis consistently delivers higher CO production rates than thermocatalysis at identical catalyst temperatures while maintaining high CO selectivity, demonstrating that illumination promotes the RWGS reaction beyond thermal heating alone.⁶² Gu and co-workers developed a Cu–Co₃Cu heterophase catalyst through *in situ* photoreduction of oxide precursors under RWGS conditions. Under 3 W cm^{−2} full-spectrum irradiation, the optimized catalyst achieved a CO production rate of 0.82 mol g_{cat}^{−1} h^{−1} with approximately 95% CO selectivity and

exhibited excellent long-term stability. Remarkably, the photo-thermal catalyst produced the same CO yield at approximately 265 °C that required about 413 °C under conventional thermo-catalysis, indicating that light irradiation substantially reduces the operating temperature required for efficient RWGS. Mechanistic investigations combining *in situ* DRIFTS, NAP-XPS, CO-TPD, kinetic isotope experiments, and DFT calculations revealed that CO₂ hydrogenation proceeds through a formate-mediated pathway involving sequential carbonate (CO₃), bicarbonate (HCO₃), and formate (HCOO) intermediates. Unlike metallic Co, methanation-related intermediates (CH₃O and CH_xO*) were absent on the Cu–Co₃Cu catalyst, indicating that the heterophase interface selectively suppresses over-hydrogenation and promotes CO formation. More importantly, the abundant Cu–Co₃Cu heterophase boundaries function as efficient channels for photoinduced charge transfer and localized hot-charge accumulation, enhancing broadband light harvesting and facilitating CO₂ activation. Meanwhile, localized photothermal heating accelerates H₂ activation and surface reaction kinetics, whereas interfacial electronic modulation strengthens CO₂ adsorption while maintaining moderate CO binding, thereby facilitating rapid CO desorption and suppressing methanation. Therefore, photothermal heating and interfacial electronic effects act cooperatively in the Cu–Co₃Cu heterophase catalyst, enabling efficient photon utilization, accelerated RWGS kinetics, and highly selective CO production through reaction-induced phase engineering.

Beyond catalyst design, photothermal promotion has recently been extended to reaction engineering through chemical-looping RWGS (RWGS-CL), where light irradiation can independently regulate the reduction and oxidation steps of the catalytic cycle.¹⁰⁰ As shown in Fig. 4f, light irradiation during the H₂-reduction step produces a substantially larger increase in CO formation than conventional external heating at a comparable catalyst temperature, demonstrating that photothermal promotion is not solely determined by bulk temperature. Takami and co-workers developed a Pt/MoO_{3-x} oxygen carrier for photothermal RWGS-CL, in which visible-NIR irradiation ($\lambda > 450$ nm, 0.75 W cm⁻²) was selectively applied during the H₂ reduction or CO₂ oxidation step. Under photothermal conditions, the defective Pt/MoO_{3-x} catalyst exhibited markedly higher CO production than under dark operation, with the most pronounced enhancement occurring when illumination was introduced during the H₂-reduction step. *Operando* XAFS and kinetic analyses revealed that illumination accelerates the reduction of Mo species and promotes rapid regeneration of oxygen vacancies, thereby providing abundant active sites for subsequent CO₂ activation during the oxidation step. More importantly, comparison between photothermal and externally heated conditions at similar catalyst temperatures demonstrated that light-induced temperature gradients within the catalyst bed regenerate oxygen vacancies more efficiently than uniform external heating, indicating that photothermal enhancement originates not only from elevated temperature but also from localized heat generation and spatially non-uniform thermal distributions. Consequently, the rate-determining process shifts from sluggish oxygen-vacancy migration toward faster lattice

oxygen transport under illumination, leading to enhanced CO production. This work demonstrates that photothermal effects can regulate not only surface catalytic reactions but also solid-state oxygen transport and defect regeneration, extending photothermal RWGS from catalyst design to reaction engineering through the integration of oxygen-carrier chemistry and localized photothermal heating.

Taken together, these representative studies demonstrate that efficient photothermal RWGS is achieved not only through rational catalyst design but also through precise regulation of the coupled light–heat–matter interactions occurring during the reaction. Although the reported systems employ different catalyst architectures and proceed through distinct COOH-mediated, HCOO-mediated, or redox pathways, they consistently show that localized photothermal heating primarily accelerates temperature-dependent reaction kinetics, whereas photoinduced electronic effects facilitate CO₂ activation, interfacial charge transfer, oxygen-vacancy regeneration, or hydrogen spillover. The cooperative coupling of these thermal and electronic contributions enables efficient photon utilization, rapid CO formation, and timely CO desorption while suppressing over-hydrogenation toward CH₄. Recent advances in heterophase engineering and photothermal chemical-looping further demonstrate that photothermal promotion can extend beyond catalyst optimization to reaction engineering by regulating oxygen transport and defect dynamics. These mechanistic insights provide important guidelines for the rational design of next-generation photothermal RWGS catalysts and reactors.

3.2 CH₄ formation *via* methanation

CH₄ formation represents the deepest hydrogenation pathway in photothermal CO₂ hydrogenation and proceeds through the Sabatier reaction: CO₂ + 4H₂ → CH₄ + 2H₂O.^{70,79} Compared with CO formation *via* RWGS, methanation is thermodynamically more favorable but kinetically more demanding because it involves an eight-electron reduction process, multiple C–O bond cleavage and hydrogenation steps, and a continuous supply of reactive hydrogen species.^{86,101} In general, CH₄ can be generated through *CO-mediated pathways, in which CO₂ is first converted into *CO and subsequently hydrogenated through intermediates such as *CHO and *CH_x species, or through formate/carbonate-mediated pathways involving *HCOO, *HCO₃, and related oxygenated intermediates.^{80,85} Unlike RWGS, where rapid CO desorption is desirable, methanation requires the stabilization and further hydrogenation of carbon-containing intermediates beyond *CO. Therefore, the central challenge in photothermal methanation is not only to promote deep hydrogenation while maintaining efficient CO₂ activation and hydrogen supply, but also to elucidate how coupled light–heat effects regulate hydrogen activation, intermediate evolution, and product selectivity. Recent studies have addressed these challenges through complementary catalyst-design strategies and mechanistic investigations, revealing the respective roles of localized photothermal heating, photo-induced electronic effects, and their synergistic interactions.

Recent progress further indicates a shift from isolated active-site optimization toward the coordinated regulation of interfacial electronic structure, defect chemistry, intermediate binding, hydrogen transport, and local energy conversion, enabling more precise control over deep hydrogenation toward CH₄.^{102–107} The representative studies discussed below illustrate this evolution from different perspectives, highlighting how these factors can be individually or cooperatively regulated to promote CH₄ formation (Fig. 5).

A clear example of active-site engineering is provided by isolated Ni atoms anchored on In₂O₃ nanocrystals.⁴¹ In pristine In₂O₃, CO tends to desorb after CO₂ activation, leading predominantly to RWGS products. Upon introducing isolated Ni sites, however, the reaction pathway is redirected toward CH₄ formation. Under photothermal conditions at 250 °C, the optimized In₂O₃@Ni catalyst achieves a CH₄ evolution rate of 1043 μmol g^{−1} h^{−1} with a near-unity CH₄ selectivity of approximately 99%, whereas the CH₄ production rate under thermal-

only conditions is nearly six times lower. Moreover, catalytic activity increases with both reaction temperature and light intensity, confirming that both thermal input and photon flux contribute to the enhanced methanation performance. Femto-second transient absorption spectroscopy, electrochemical impedance spectroscopy, and transient photocurrent measurements further demonstrate that isolated Ni sites promote charge separation and carrier transport under illumination, while differential charge-density calculations reveal that photoexcitation facilitates electron transfer from In₂O₃@Ni to adsorbed CO₂. The resulting enrichment of photoexcited electrons facilitates the reductive activation of adsorbed CO₂, whereas localized photothermal heating accelerates H₂ dissociation and subsequent hydrogenation kinetics. *In situ* DRIFTS and DFT calculations further reveal that CO₂ is first converted to *COOH and then to *CO intermediates. As illustrated in Fig. 5a, isolated Ni sites strengthen *CO adsorption and significantly lower the energy barrier for the key *CO → *CHO

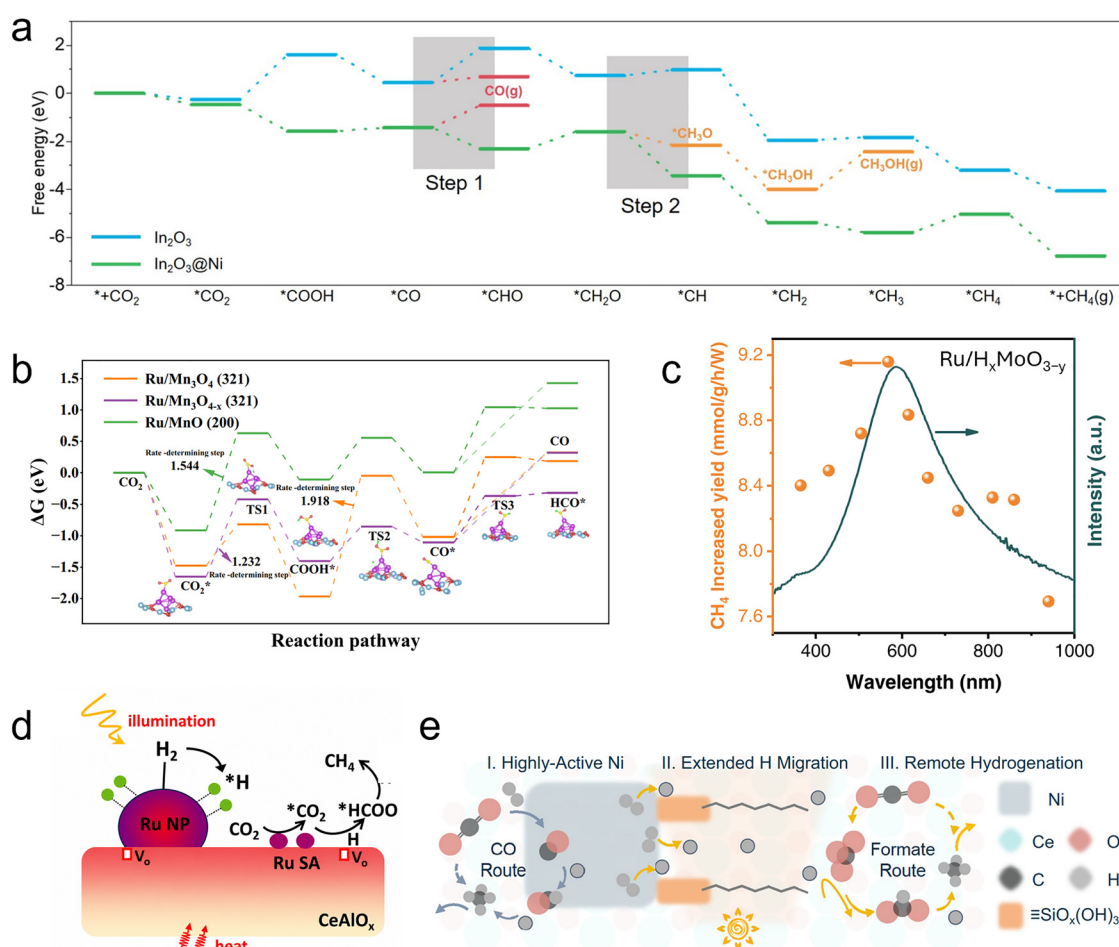


Fig. 5 Representative pathways for selective CH₄ formation in photothermal CO₂ methanation. (a) Ni single sites on In₂O₃ lower hydrogenation barriers, enabling near-unity CH₄ selectivity. Adapted from ref. 41 with permission from the American Chemical Society, copyright 2024. (b) Ru/MnO/Mn₃O₄ interfaces tune methanation energetics under photothermal conditions. Adapted from ref. 108 with permission from Springer Nature, copyright 2024. (c) Wavelength-dependent enhancement of CH₄ production over plasmonic Ru/H_xMoO_{3-y}. Adapted from ref. 110 with permission from Elsevier, copyright 2022. (d) Tandem Ru nanoparticle/single-atom sites separate H₂ activation and CO₂ conversion on CeAlO_x, enhancing methanation. Adapted from ref. 53 with permission from Wiley-VCH, copyright 2025. (e) Hydrogen migration on Ni/CeO₂ promotes direct and remote hydrogenation for efficient Sabatier conversion. Adapted from ref. 87 with permission from Springer Nature, copyright 2026.

hydrogenation step, thereby suppressing CO desorption and promoting sequential hydrogenation through $^*\text{CHO}$, $^*\text{CH}$, $^*\text{CH}_2$, and $^*\text{CH}_3$ intermediates toward CH_4 . In addition, the modified reaction pathway avoids the methanol branch, further contributing to the exceptionally high CH_4 selectivity. This work demonstrates that efficient photothermal methanation arises from the synergistic interplay between photochemical charge activation, photoinduced electronic modulation, and thermally accelerated surface hydrogenation, with isolated Ni atoms steering the reaction pathway toward deep hydrogenation and highly selective CH_4 production.

Phase evolution and photothermal coupling offer another route to enhance CO_2 methanation.¹⁰⁸ Under reaction conditions, Ru/MnO_x evolves into a well-defined $\text{Ru/MnO/Mn}_3\text{O}_4$ structure and achieves a CH_4 production rate of $166.7 \text{ mmol g}^{-1} \text{ h}^{-1}$ with 99.5% selectivity and 66.8% CO_2 conversion at 200°C . Importantly, at the same reaction temperature, photothermal operation produces substantially higher CH_4 yields than thermocatalysis, and the activity further increases with increasing light intensity, confirming that photon irradiation contributes beyond thermal heating alone. The key feature of this system is the dynamic interaction between Ru-mediated H spillover and the reducible MnO_x support. Ru efficiently dissociates H_2 , while spillover hydrogen promotes the reconstruction of MnO_x into catalytically favorable $\text{MnO/Mn}_3\text{O}_4$ phases. Meanwhile, enhanced light absorption together with improved charge separation under illumination facilitates the transfer of photoexcited electrons from MnO_x to Ru sites, thereby promoting CO_2 activation and the formation of the key COOH intermediate. *In situ* FT-IR reveals a COOH -mediated pathway, in which CO_2 is converted into CO_2 , COOH , CO , and finally CH_4 (Fig. 5b). Notably, the characteristic COOH bands appear at lower temperatures under photothermal conditions than during thermocatalysis, indicating that photon irradiation facilitates the elementary $\text{CO}_2 \rightarrow \text{COOH}$ step and accelerates the formation of this key intermediate. Correspondingly, the apparent activation energy decreases from 99.9 to 68.5 kJ mol^{-1} , while DFT calculations identify partially reduced $\text{Ru/Mn}_3\text{O}_{4-x}$ as the most active phase with the lowest barrier (1.232 eV) for COOH formation. This work demonstrates that efficient photothermal methanation arises from the synergistic combination of reaction-induced phase reconstruction, enhanced hydrogen spillover, photoinduced electronic activation, and thermally accelerated hydrogenation.

Another representative example demonstrates how plasmonic oxide supports enhance photothermal CO_2 methanation through efficient light harvesting and localized heat generation. Ge and co-workers developed a $\text{Ru/H}_x\text{MoO}_{3-y}$ catalyst by introducing hydrogen into $\alpha\text{-MoO}_3$ through Ru-assisted hydrogen spillover, which simultaneously generated abundant oxygen vacancies and plasmonic absorption in the visible-near-infrared (Vis-NIR) region.¹¹⁰ Under Vis-NIR irradiation ($\lambda > 450 \text{ nm}$, 0.75 W cm^{-2}) at only 140°C , the catalyst achieved a CH_4 production rate of $20.8 \text{ mmol g}_{\text{cat}}^{-1} \text{ h}^{-1}$ ($520 \text{ mmol g}_{\text{Ru}}^{-1} \text{ h}^{-1}$) with 100% CH_4 selectivity, representing a 4.7-fold enhancement over dark conditions. As shown in Fig. 5c, the enhancement in CH_4 production strongly depends on the irradiation wavelength

and closely follows the plasmonic absorption of $\text{H}_x\text{MoO}_{3-y}$, providing direct evidence that visible-NIR photons efficiently drive the reaction through plasmon-assisted photothermal conversion. Mechanistic investigations combining *in situ* DRIFTS, *in situ* FTIR, *operando* XAFS, photocurrent measurements, and electrochemical impedance spectroscopy revealed that CO_2 methanation proceeds predominantly through a CO-mediated pathway. Ru nanoparticles efficiently dissociate H_2 , whereas oxygen vacancies generated in $\text{H}_x\text{MoO}_{3-y}$ provide active sites for CO_2 adsorption and activation. Upon Vis-NIR excitation, free electrons stored in the defect levels of $\text{H}_x\text{MoO}_{3-y}$ are excited into hot electrons, a fraction of which directly participates in CO_2 reduction, while their non-radiative decay into phonons generates localized heat that further promotes the reaction. *In situ* FTIR further showed that light irradiation accelerates the hydrogenation of CO intermediates on Ru surfaces, thereby facilitating their subsequent conversion toward CH_4 . *Operando* XAFS further demonstrated the reversible evolution of the local coordination environment during reaction, confirming that hydrogen spillover continuously regenerates oxygen vacancies and maintains the plasmonic properties of the catalyst under reaction conditions. Together, the wavelength-dependent activity and *operando* spectroscopic evidence demonstrate that the superior methanation performance originates from the coupled electronic and thermal effects of plasmon excitation, together with dynamic oxygen-vacancy regeneration. This work therefore provides a representative example of integrating plasmonic light harvesting, localized photothermal heating, hydrogen spillover, and oxygen-vacancy engineering to promote efficient photothermal CO_2 methanation.

Electronic-structure regulation provides a complementary strategy for promoting deep hydrogenation by controlling the fate of $^*\text{CO}$ intermediates.¹⁰⁹ A representative example is the PdCo alloy anchored on self-supporting N-doped carbon arrays grown on carbon cloth (PdCo-NC/CC). Under Xe-lamp irradiation without external heating, the catalyst achieved a CH_4 generation rate of $15.23 \text{ mol g}_{\text{metal}}^{-1} \text{ h}^{-1}$ with 100% selectivity, while maintaining stable operation for over 100 h in a continuous-flow photothermal reactor. During irradiation (3.0 W cm^{-2}), the catalyst surface rapidly heated to approximately 355°C , substantially higher than the corresponding Co catalyst (330.5°C), owing to the efficient photo-to-heat conversion of the carbon-cloth-supported architecture. Control experiments further showed that thermocatalysis performed at the same reactor temperature produced significantly lower CH_4 yields, whereas reactions were completely suppressed when the reactor was externally cooled or when UV light ($< 300 \text{ nm}$) was removed, confirming that localized photothermal heating dominates the reaction while photo-assisted electronic effects also contribute to activity enhancement beyond simple bulk heating. Mechanistic investigations combining *in situ* DRIFTS, CO hydrogenation tests, CO-TPD, CO-DRIFTS, and DFT calculations revealed that CO_2 methanation proceeds through both the formate ($^*\text{CO}_2 \rightarrow ^*\text{HCOO} \rightarrow \text{CH}_4$) and CO-mediated ($^*\text{CO}_2 \rightarrow ^*\text{CO} \rightarrow ^*\text{CHO} \rightarrow \text{CH}_4$) pathways, with Pd primarily promoting the latter. Incorporation of Pd induces strong 3d-4d orbital hybridization, shifts the Co d-band center upward, strengthens $^*\text{CO}$ adsorption, suppresses CO desorption, and

lowers the energy barrier for the rate-determining $^*\text{CO} \rightarrow ^*\text{CHO}$ hydrogenation step from 1.32 to 0.86 eV. Consequently, $^*\text{CO}$ is retained on the catalyst surface long enough to undergo further hydrogenation instead of escaping as CO, thereby directing the reaction toward highly selective CH_4 formation. This example demonstrates that efficient photothermal methanation can be achieved through the synergistic integration of localized photothermal heating with orbital-level electronic regulation of key surface intermediates.

Dual-site catalysis provides another effective strategy by spatially separating CO_2 activation from H_2 dissociation. Tang and co-workers developed a $\text{Ru}_1 + \text{NPs/CeAlO}_x$ catalyst consisting of atomically dispersed Ru sites and Ru nanoparticles supported on oxygen-vacancy-rich CeAlO_x .⁵³ Under full-spectrum irradiation (200–1100 nm, 1.8 W cm^{-2}) at 200 °C, the catalyst achieved a CH_4 production rate of $131.4 \text{ mmol g}_{\text{cat}}^{-1} \text{ h}^{-1}$ with nearly 100% selectivity, which further increased to $197.2 \text{ mmol g}_{\text{cat}}^{-1} \text{ h}^{-1}$ when the light intensity was raised to 3.1 W cm^{-2} , substantially outperforming the corresponding Ru single-atom and Ru nanoparticle catalysts. Mechanistic studies combining H_2 -TPR, CO_2 -TPD, *in situ* DRIFTS, and DFT calculations demonstrated a clear functional division between the two Ru species. Ru nanoparticles efficiently dissociate H_2 with a lower activation barrier (0.30 eV) than isolated Ru atoms (0.57 eV), whereas Ru single atoms preferentially adsorb and activate CO_2 . Hydrogen atoms generated on Ru nanoparticles subsequently migrate to neighboring Ru single atoms through hydrogen spillover, where CO_2 -derived intermediates are sequentially hydrogenated *via* the $^*\text{HCOO}$ pathway (Fig. 5d). Importantly, the authors distinguished thermal and photochemical contributions by comparing reactions at identical catalyst surface temperatures under dark and illuminated conditions. Light irradiation nearly doubled the CH_4 production rate and reduced the apparent activation energy from 103.9 to 83.3 kJ mol^{-1} . Wavelength-dependent experiments further showed that full-spectrum irradiation produced higher activity than visible-IR irradiation despite similar catalyst temperatures, indicating that UV-generated charge carriers contribute beyond photothermal heating by promoting reactant activation and intermediate conversion. This work demonstrates that efficient photothermal methanation can be achieved through the synergistic combination of spatially separated active sites, hydrogen spillover, localized heating, and photoinduced charge-carrier effects.

Beyond active-site engineering, regulating hydrogen transport across catalyst surfaces provides another effective strategy for improving photothermal CO_2 methanation. Lu and co-workers developed an alkylsilane-modified Ni/CeO_2 catalyst, in which a small amount of surface alkylsilane acts as an extended hydrogen-migration network while simultaneously improving Ni dispersion, reducing the average particle size from approximately 13 to 7 nm.⁸⁷ Under photothermal conditions using a 300 W Xe lamp ($\sim 1.5 \text{ W cm}^{-2}$), the optimized catalyst exhibited a markedly higher CO_2 conversion than pristine Ni/CeO_2 and achieved a maximum solar-to-chemical efficiency of $\sim 43.4\%$ at 250 °C. Outdoor experiments further demonstrated 99.9% CO_2 conversion, nearly 100% CH_4

selectivity, and an energy conversion efficiency of $\sim 25\%$ under concentrated natural sunlight, with stable operation for over 100 h. Mechanistic investigations combining reaction kinetics, H_2 -TPR, H_2/D_2 -switching *in situ* DRIFTS, and isotope exchange experiments revealed that the alkylsilane chains provide an efficient hydrogen-transport pathway beyond conventional oxide-mediated spillover. The optimized catalyst exhibited a near-zero H_2 reaction order (0.08 under illumination), indicating highly efficient hydrogen activation and migration. Hydrogen atoms generated on Ni nanoparticles migrate through the alkylsilane network to remotely hydrogenate adsorbed carbonate and formate species, thereby accelerating the overall methanation kinetics (Fig. 5e). Importantly, light irradiation further enhanced hydrogen migration and promoted the hydrogenation of carbonate species into the key HCOO intermediate, as evidenced by *in situ* DRIFTS. This light-promoted process was associated with hot-electron contributions, locally enhanced electric fields, and interfacial charge redistribution, which facilitate hydrogen redistribution and accelerate carbonate-to-formate hydrogenation. This work demonstrates that engineering long-range hydrogen transport, together with photothermally enhanced hydrogen migration and photoinduced electronic effects, provides an effective strategy for maximizing CO_2 methanation activity beyond conventional active-site optimization.

Taken together, these representative studies demonstrate that highly efficient CH_4 formation in photothermal CO_2 hydrogenation arises from the cooperative interplay between catalyst design and coupled light–heat effects rather than from thermal catalysis alone. Although different catalysts operate through distinct mechanistic pathways, they share common principles, including efficient H_2 activation, stabilization and hydrogenation of carbon-containing intermediates, and suppression of CO desorption. More importantly, mechanistic investigations increasingly reveal that light contributes not only localized heating but also photoinduced electronic effects, including enhanced charge separation, plasmon-assisted energy conversion, interfacial charge redistribution, and promoted hydrogen migration, which collectively facilitate intermediate evolution and deep hydrogenation. While growing evidence supports a contribution from photoexcited carriers beyond photothermal heating, their mechanistic roles are not yet fully established.^{111–114} In particular, the respective involvement of electrons and holes in individual elementary steps remains highly system-dependent and insufficiently understood in photothermal CO_2 methanation.^{115–117} These findings highlight that future photothermal methanation catalysts should be designed by simultaneously optimizing catalytic active sites, photothermal energy conversion, and light-induced electronic processes to maximize both activity and CH_4 selectivity.

3.3 CH_3OH formation *via* oxygenate pathway

Methanol formation in photothermal CO_2 hydrogenation predominantly proceeds through oxygenate-mediated pathways, in which CO_2 is sequentially hydrogenated *via* surface intermediates such as $^*\text{COOH}$, $^*\text{HCOO}$, $^*\text{CHO}$, CH_2O , and CH_3O before forming CH_3OH .^{118–121} Unlike RWGS pathways that terminate

with CO desorption, oxygenate-mediated routes retain carbon-containing intermediates on the catalyst surface, thereby enabling deep hydrogenation and high methanol selectivity.^{92,122} Because this process requires multiple proton-coupled electron-transfer and hydrogenation steps while preserving the C–O bond, efficient methanol synthesis relies on catalysts capable of simultaneously activating CO₂, dissociating H₂, stabilizing oxygenated intermediates, and promoting hydrogen transfer.^{90,123} Recent advances further demonstrate that photothermal catalysis enhances this process not only through localized heating but also through light-induced modulation of interfacial electronic structures, thereby facilitating reactant activation, hydrogen spillover, and oxygenate hydrogenation. Accordingly, catalyst design has evolved from conventional oxygen-vacancy engineering toward more sophisticated active-site architectures, including surface frustrated Lewis pairs (SFLPs), molecularly dispersed metal centers, bimetallic alloy interfaces, defect-engineered FLPs, and interfacial Lewis acid–base pairs, which cooperatively regulate the adsorption, transformation, and hydrogenation of oxygen-containing intermediates to achieve highly selective CH₃OH formation.^{43,44,47,88,91,93,124}

A representative oxide-based strategy for photothermal CO₂ hydrogenation to CH₃OH was demonstrated by black indium oxide, H₂In₂O_{3–x}(OH)_y, which contains surface frustrated Lewis pairs (SFLPs) consisting of adjacent In sites and hydroxylated

oxygen species.¹²⁴ Under photothermal conditions at ambient pressure, this catalyst achieves CH₃OH selectivities of 33–49%, exceeding the equilibrium limitation of conventional thermal CO₂ hydrogenation. Importantly, kinetic analysis under dark and light irradiation revealed that illumination not only provides thermal heating but also modifies the reaction kinetics. As shown in Fig. 6a, the apparent activation energy for CH₃OH formation decreases from 97.11 kJ mol^{–1} under dark conditions to 73.61 kJ mol^{–1} under light irradiation in the high-temperature regime, indicating an additional light-induced contribution beyond conventional thermal activation. At lower temperatures, the apparent activation energies under dark and light conditions are comparable, suggesting that the enhancement mainly originates from photothermal heating. These results demonstrate that light irradiation accelerates methanol synthesis through both photothermal and light-induced kinetic effects. Mechanistic investigations further revealed that the enhanced methanol formation originates from a tandem reaction pathway involving spatially coupled SFLP sites and oxygen-vacancy sites. SFLP sites first promote H₂ activation and CO₂ adsorption, leading to the formation of CO intermediates through a RWGS-like process. Instead of desorbing as gaseous CO, the surface-bound CO intermediates are subsequently transferred to adjacent oxygen-vacancy sites, where they undergo sequential hydrogenation through oxygenated intermediates to

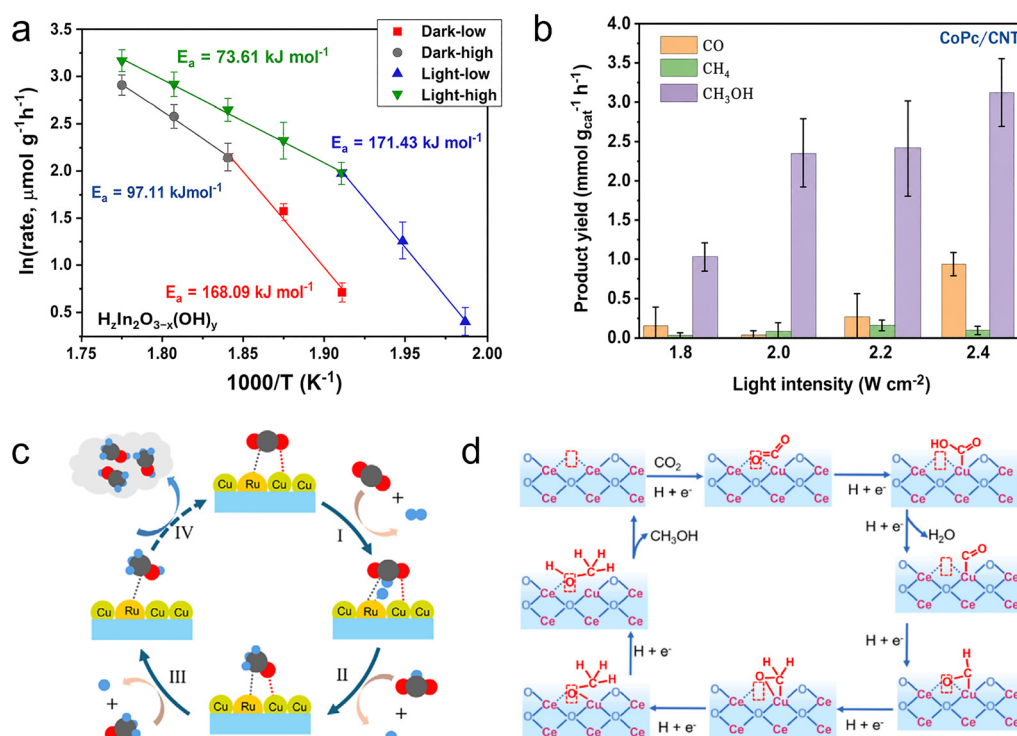


Fig. 6 Representative pathways for selective CH₃OH formation in photothermal CO₂ hydrogenation. (a) Arrhenius plots of CH₃OH formation over black indium oxide (H₂In₂O_{3–x}(OH)_y) under dark and illuminated conditions. Adapted from ref. 124 with permission from Springer Nature, copyright 2022. (b) Effect of light intensity on CO, CH₄, and CH₃OH production over the CoPc/CNT photothermal catalyst. Adapted from ref. 43 with permission from Wiley-VCH, copyright 2024. (c) Cooperative CO₂ activation and hydrogenation over RuCu alloy dual sites under light irradiation. Adapted from ref. 91 with permission from Wiley-VCH, copyright 2025. (d) Frustrated Lewis pair-assisted oxygenate hydrogenation on Cu@CeO₂ catalysts. Adapted from ref. 93 with permission from Elsevier, copyright 2024.

produce CH_3OH . DFT calculations indicate that this tandem pathway is energetically more favorable than direct CO_2 hydrogenation on isolated oxygen-vacancy sites. Therefore, the cooperative interplay between SFLP sites and oxygen vacancies establishes an *in situ* tandem RWGS–methanol pathway, in which CO generated on SFLP sites is immediately consumed for methanol synthesis rather than being released as a by-product. This work demonstrates that coupling light-induced kinetic enhancement with tandem active-site engineering provides an effective strategy for overcoming the thermodynamic limitations of conventional CO_2 hydrogenation and achieving highly selective photothermal CH_3OH production.

More direct evidence for a sequential RWGS–hydrogenation route was demonstrated in a molecularly dispersed CoPc/CNT photothermal catalyst.⁴³ In this system, cobalt phthalocyanine molecules anchored on carbon nanotubes serve as isolated Co– N_4 active sites, while the CNT support functions as an efficient broadband photothermal absorber. Under simulated solar irradiation, the catalyst achieved a CH_3OH production rate of $2.4 \text{ mmol g}_{\text{cat}}^{-1} \text{ h}^{-1}$ with nearly 99% selectivity, representing one of the most selective photothermal methanol synthesis systems reported to date. As shown in Fig. 6b, increasing light intensity markedly enhances CH_3OH production while maintaining excellent methanol selectivity, demonstrating that efficient photothermal heating provided by the CNT support effectively promotes CO_2 hydrogenation. The catalyst operates at an optimal reaction temperature of approximately 250°C , where methanol formation is kinetically favored over competing CO and CH_4 production. *Operando* DRIFTS combined with DFT calculations further revealed that CO_2 hydrogenation proceeds through a RWGS-derived oxygenate pathway. CO_2 is first activated to form $^*\text{CO}_2$ and $^*\text{COOH}$ species, followed by the generation of adsorbed $^*\text{CO}$. Instead of desorbing as gaseous CO, the $^*\text{CO}$ intermediate remains coordinated to the isolated Co– N_4 center and undergoes sequential hydrogenation through $^*\text{CHO}$, $^*\text{CH}_2\text{O}$, and $^*\text{CH}_3\text{O}$ intermediates before finally producing CH_3OH . Unlike conventional Cu-based catalysts, the molecularly dispersed CoPc active sites stabilize oxygenated intermediates and suppress CO desorption, thereby directing the reaction toward selective methanol formation. In this system, photothermal heating mainly regulates the reaction environment by maintaining the optimal operating temperature, whereas the well-defined Co– N_4 coordination environment governs the reaction pathway and product selectivity. This work demonstrates that integrating efficient photothermal energy harvesting with molecularly defined active sites provides an effective strategy for highly selective photothermal CO_2 hydrogenation to CH_3OH .

Bimetallic alloy catalysts provide another route to promote methanol formation through light-driven electronic restructuring. As illustrated in Fig. 6c, a RuCu alloy supported on MgAl_2O_4 was developed for highly selective photothermal CO_2 hydrogenation under ambient pressure and simulated solar irradiation.⁹¹ Under illumination, the localized surface plasmon resonance (LSPR) of Cu stabilizes metallic Cu^0 and drives the *in situ* formation of a RuCu alloy, resulting in pronounced

interfacial electronic restructuring. Under simulated solar irradiation, the optimized catalyst achieves a CH_3OH selectivity of approximately 99% with a productivity of $640 \mu\text{L g}^{-1} \text{ h}^{-1}$, substantially outperforming the corresponding thermocatalytic process. The superior activity under illumination confirms that light contributes not only localized photothermal heating but also light-induced electronic restructuring of the RuCu alloy. *In situ* spectroscopic analyses together with DFT calculations revealed that Ru incorporation induces electron redistribution between Ru and Cu, modifies the adsorption geometry of CO_2 , and strengthens CO_2 activation through dual Ru–O and Cu–O interactions. As illustrated in Fig. 6c, CO_2 hydrogenation proceeds through a formate-mediated oxygenate pathway ($^*\text{CO}_2 \rightarrow ^*\text{HCOO} \rightarrow ^*\text{CH}_3\text{O} \rightarrow \text{CH}_3\text{OH}$), while hydrogen species generated on Ru sites continuously migrate to adjacent Cu-bound intermediates. Importantly, alloy formation lowers the overall reaction barrier and shifts the rate-determining step from CH_3O formation on Cu to HCOO formation on RuCu, facilitating deep hydrogenation toward methanol. This study demonstrates that light-driven electronic restructuring not only regulates the energetics of surface intermediates but also dynamically reconstructs alloy active sites under reaction conditions, providing an effective strategy for directing photothermal CO_2 hydrogenation toward highly selective CH_3OH production.

Defect-engineered ceria catalysts provide another strategy for promoting methanol synthesis through frustrated Lewis pair (FLP) chemistry. As illustrated in Fig. 6d, atomically dispersed Cu species were introduced into the CeO_2 lattice to construct abundant FLPs consisting of adjacent $\text{Ce}^{3+}/\text{Cu}^{\delta+}$ Lewis acid sites and lattice oxygen Lewis base sites around oxygen vacancies.⁹³ Under photothermal conditions, the optimized $0.5\text{Cu}@ \text{CeO}_2$ catalyst achieved a methanol yield of $1896.02 \mu\text{mol g}_{\text{cat}}^{-1} \text{ h}^{-1}$, which was 5.61 times higher than that obtained without light irradiation. The markedly enhanced activity under illumination demonstrates that light not only supplies localized photothermal heating but also promotes photogenerated charge separation and electron transfer. *In situ* DRIFTS, photoelectrochemical measurements, and DFT calculations revealed that Cu incorporation increases the oxygen-vacancy concentration, strengthens CO_2 adsorption, and facilitates H_2 activation on FLP sites. As illustrated in Fig. 6d, CO_2 hydrogenation proceeds through a carboxyl-mediated pathway ($^*\text{CO}_2 \rightarrow ^*\text{COOH} \rightarrow ^*\text{CO} \rightarrow ^*\text{HCO} \rightarrow ^*\text{H}_2\text{CO} \rightarrow ^*\text{CH}_3\text{O} \rightarrow \text{CH}_3\text{OH}$). The formation of FLPs alters the adsorption configuration of reaction intermediates, substantially lowers the energy barrier for the COOH -to- CO conversion, and shifts the conduction band to more negative potentials, thereby enhancing the reducing capability of photogenerated electrons for deep hydrogenation. Collectively, the synergistic integration of FLP-assisted reactant activation, oxygen-vacancy engineering, and enhanced photogenerated charge transfer enables highly selective methanol synthesis, providing an effective strategy for directing photothermal CO_2 hydrogenation toward CH_3OH through defect-engineered acid–base pair regulation.

Interfacial Lewis acid–base pair engineering has also proven highly effective for low-temperature methanol synthesis. In the recently reported $\text{In}_2\text{O}_3\text{--MnCO}_3$ composite, strong interfacial coupling generates covalent In–O–Mn linkages, in which electron-deficient In centers function as Lewis acids while neighboring oxygen atoms serve as Lewis bases, forming robust interfacial Lewis acid–base pairs.⁴⁴ Under photothermal conditions, the optimized 30In–Mn catalyst achieved a CH_3OH selectivity of 67.5% at 13.5% CO_2 conversion at only 150 °C and maintained stable performance for more than 500 h, demonstrating that interfacial Lewis acid–base engineering effectively promotes low-temperature CO_2 hydrogenation. Kinetic analyses further revealed that light irradiation substantially lowers the apparent activation barrier for CO_2 hydrogenation, indicating that photothermal heating together with interfacial electronic modulation accelerates reactant activation beyond conventional thermal catalysis. Spectroscopic investigations showed that the In–O–Mn Lewis acid–base pairs promote polarized CO_2 adsorption and facilitate the formation of surface carbonate and carboxylate intermediates, whose concentrations correlate directly with methanol production rates. Meanwhile, interfacial electron redistribution strengthens the Lewis acid–base interaction, enhances both CO_2 activation and H_2 dissociation, and thereby facilitates the subsequent oxygenate-mediated hydrogenation pathway. This work demonstrates that constructing covalently coupled oxide–carbonate interfaces enables simultaneous regulation of interfacial electronic structure, Lewis acid–base chemistry, and oxygenated intermediate formation, providing an effective strategy for highly selective photothermal CO_2 hydrogenation to CH_3OH under low-temperature conditions.

Overall, despite their diverse compositions and active-site structures, the representative catalysts discussed above converge on a common design principle: the rational integration of complementary catalytic functions within cooperative active-site architectures. Rather than relying on a single multifunctional active center, these systems spatially and electronically coordinate CO_2 activation, H_2 dissociation, hydrogen transfer, and oxygenate hydrogenation, thereby overcoming the intrinsic kinetic limitations associated with deep CO_2 reduction while maintaining high methanol selectivity. Photothermal inputs further reinforce this cooperative catalytic network by coupling localized heating with interfacial electronic regulation, which accelerates elementary hydrogenation steps and optimizes the evolution of oxygenated intermediates. Collectively, these studies demonstrate that synergistically integrating photothermal energy utilization with cooperative active-site engineering represents a general design strategy for directing CO_2 hydrogenation toward highly selective CH_3OH synthesis.

4. Photothermal reactor design

While catalyst design determines the intrinsic activity and reaction pathways of photothermal CO_2 hydrogenation, efficient solar-driven conversion also depends critically on reactor

engineering, which governs how light energy is delivered to catalytic interfaces and transformed into useful reaction environments.²⁴ Unlike conventional thermocatalytic systems that rely on externally heated reactor walls, photothermal reactors couple light irradiation, heat generation, and gas transport within the same reaction space, creating localized and dynamic reaction environments that cannot be achieved under purely thermal conditions.¹²⁵ Consequently, reactor design directly influences photon utilization, heat management, reactant transport, and catalyst accessibility, ultimately affecting reaction kinetics, C_1 product selectivity, and overall solar-to-chemical energy conversion efficiency.^{126,127} Therefore, photothermal reactor engineering should be regarded not merely as a supporting component for catalysts, but as an essential strategy for coordinating coupled light–heat–flow fields and regulating catalytic microenvironments. The following sections summarize recent advances in continuous-flow operation, light and thermal management, structured reactor architectures, and representative reactor designs for efficient photothermal CO_2 hydrogenation.

4.1 Continuous-flow photothermal reactors

Continuous-flow reactors have become the predominant platform for photothermal CO_2 hydrogenation because they provide continuous reactant supply, controllable residence time, and efficient product removal under steady-state operation.^{126,128} More importantly, continuous-flow operation enables simultaneous coupling of light irradiation, localized heat generation, and gas transport within the reaction zone, thereby establishing stable photothermal reaction environments that are difficult to achieve in conventional thermocatalytic reactors.²⁷ In continuous-flow photothermal reactors, incident light continuously irradiates the catalyst bed while CO_2/H_2 mixtures flow through illuminated catalytic channels, enabling continuous production of CO , CH_4 , or CH_3OH under coupled light–heat–flow conditions.

A key feature of continuous-flow photothermal reactors is that heat is generated directly at illuminated catalyst surfaces rather than being transferred uniformly from an external heat source. Consequently, catalyst surface temperatures may differ substantially from the bulk gas temperature, generating localized thermal gradients that promote non-equilibrium reaction microenvironments. These localized environments accelerate surface reaction kinetics while regulating the adsorption, hydrogenation, and desorption of reaction intermediates. At the same time, continuous gas flow continuously replenishes reactants and removes gaseous products, preventing excessive accumulation of strongly adsorbed intermediates and helping maintain stable catalytic performance during prolonged operation.³³

Beyond ensuring steady-state operation, continuous-flow reactors also provide an effective means of regulating reaction pathways through controllable operating parameters.⁴⁰ Gas hourly space velocity, residence time, H_2/CO_2 ratio, irradiation intensity, and reaction temperature collectively determine the evolution of local reaction microenvironments and the lifetime of surface intermediates. In general, shorter residence times favor rapid CO desorption and promote the RWGS pathway,

whereas longer residence times combined with hydrogen-rich conditions facilitate further hydrogenation toward CH_4 or CH_3OH . Therefore, continuous-flow reactor design is not simply intended to improve mass transport; instead, it provides a practical strategy for coordinating coupled light-heat-flow fields to regulate local reaction microenvironments and selectively direct photothermal CO_2 hydrogenation toward desired C_1 products.

4.2 Light and thermal management

4.2.1 Solar concentration strategies. After establishing stable continuous-flow operation, the next challenge is to maximize the utilization of incident solar energy. Because photothermal CO_2 hydrogenation relies on direct photon-to-heat conversion at catalyst surfaces, increasing the photon flux reaching catalytic interfaces is an effective strategy for improving reactor performance.^{32,129,130} Solar concentration enhances the energy density delivered to illuminated catalysts, enabling higher interfacial temperatures under moderate solar irradiation without proportionally increasing the temperature of the entire reactor.

Besides increasing photon flux, optical management also determines how solar energy is distributed throughout the catalyst bed. Illumination geometry, focal distance, irradiation angle, optical penetration depth, and spectral composition collectively influence photon distribution and therefore the spatial distribution of photothermal energy. Proper optical design helps maintain more uniform irradiation, reduces local energy loss, and improves catalyst utilization during continuous-flow operation. Conversely, non-uniform light penetration can create spatially heterogeneous reaction zones within the catalyst bed, where differences in photon flux lead to variations in local temperature and photoinduced carrier generation. Such heterogeneity can alter the relative rates of CO_2 activation, intermediate hydrogenation, and product desorption, thereby affecting both overall activity and C_1 product distribution. Beyond controlling light intensity, wavelength management has recently emerged as another effective strategy for improving photothermal performance. Recent studies have shown that different spectral regions can contribute to distinct elementary steps during CO_2 hydrogenation. For example, wavelength-resolved experiments on Ru/ TiO_2 revealed that ultraviolet irradiation primarily promotes CO_2 adsorption and the formation of bicarbonate and formate intermediates on the TiO_2 support, whereas visible-near-infrared irradiation mainly accelerates the hydrogenation of adsorbed CO species on Ru through enhanced photothermal heating and photoinduced electronic effects.¹³¹ Consequently, full-spectrum illumination achieves superior catalytic performance by coupling the complementary functions of different wavelength ranges, rather than simply increasing the total energy input. Therefore, solar concentration should be regarded not simply as a means of increasing temperature, but as an integrated optical strategy for simultaneously optimizing photon flux, spectral utilization, and overall photothermal energy conversion efficiency.

4.2.2 Thermal confinement strategies. Increasing photon input alone cannot maximize photothermal performance if the generated heat is rapidly dissipated. Therefore, thermal

confinement has become an equally important design strategy for improving reactor efficiency.^{33,132} Rather than generating additional heat, thermal confinement aims to retain photothermally generated energy near catalytic interfaces by minimizing conductive, convective, and radiative heat losses, thereby sustaining efficient photothermal conversion under continuous operation.

Selective solar absorbers, thermally insulating substrates, and multilayer heat-retention structures have been widely employed to confine thermal energy within illuminated catalytic regions. These approaches improve solar-to-thermal energy utilization while avoiding unnecessary heating of the reactor body. Effective thermal management also contributes to catalyst stability by reducing excessive bulk temperatures that may induce catalyst sintering or undesired side reactions. Temperature distribution is equally important because excessive thermal gradients can generate kinetically distinct reaction zones within the same catalyst bed. Local hot regions may accelerate deep hydrogenation or undesired side reactions, whereas cooler regions can favor incomplete conversion or accumulation of intermediates; therefore, controlling the magnitude and spatial distribution of temperature gradients is critical for maintaining both catalytic efficiency and product selectivity. Therefore, efficient photothermal reactor design requires coordinated optimization of light absorption and heat retention, enabling sustained energy utilization and stable catalytic performance during long-term solar-driven CO_2 hydrogenation.

4.3 Structured architectures

While continuous-flow operation establishes stable reaction fields and light/thermal management improves energy utilization, structural design further determines how photons, heat, and reactants are distributed within the catalytic bed. Therefore, structured architectures have emerged as an effective strategy for regulating local reaction microenvironments through rational control of light transport, heat transfer, and mass diffusion. Compared with conventional packed-bed reactors, structured architectures provide more uniform catalyst exposure, lower pressure drop, and improved transport efficiency, thereby enhancing overall photothermal performance.⁶³ Representative structured architectures are summarized in Fig. 7.

4.3.1 Monolithic and porous architectures. Monolithic architectures represent one of the most widely adopted structured configurations for continuous photothermal CO_2 hydrogenation (Fig. 7a). Their ordered channel structures reduce pressure drop while enabling continuous gas transport and uniform catalyst exposure under steady-state operation.³⁷ At the same time, regular channel geometries improve light penetration and heat distribution throughout the catalytic bed, making monolithic architectures particularly attractive for continuous-flow and large-scale applications. Porous and foam architectures further enhance transport performance by introducing interconnected three-dimensional transport networks. As illustrated in Fig. 7b, multiple light scattering within porous frameworks increases photon utilization, while hierarchical

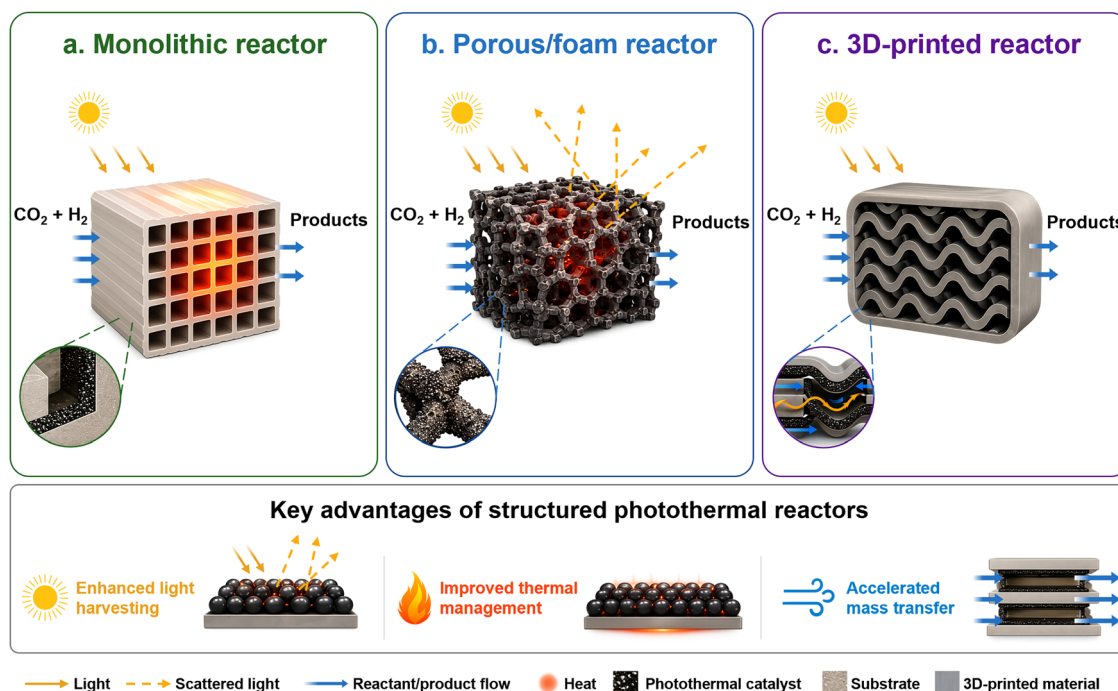


Fig. 7 Representative structured architectures for continuous photothermal CO_2 hydrogenation. (a) Monolithic reactor, (b) porous/foam reactor, and (c) 3D-printed reactor.

pore structures facilitate rapid reactant diffusion and efficient removal of gaseous products. In addition, interconnected conductive frameworks improve heat redistribution without eliminating localized photothermal heating. These combined effects strengthen the coupling of light harvesting, heat transfer, and mass transport, making porous architectures active regulators of reaction microenvironments rather than passive catalyst supports.

4.3.2 3D-printed architectures. Recent advances in additive manufacturing have further expanded the design flexibility of photothermal reactors. Unlike conventional monolithic structures with fixed geometries, 3D printing enables precise control over channel configuration, pore architecture, and flow pathways, allowing reactor geometry itself to be optimized for photothermal operation.^{17,133} As illustrated in Fig. 7c, catalytic layers, heat-conduction pathways, and gas-flow channels can be integrated into a single reactor body, improving photon utilization, thermal management, and reactant accessibility simultaneously. More importantly, programmable reactor geometries enable localized regulation of residence time, flow distribution, and heat transfer, providing new opportunities for tailoring reaction microenvironments according to different C_1 products.

Overall, structured architectures demonstrate that structural design extends beyond mechanical support or catalyst immobilization. By simultaneously regulating light harvesting, thermal management, and mass transport, these architectures create well-controlled reaction microenvironments that maximize catalyst utilization and improve photothermal CO_2 hydrogenation. From a catalyst–reactor coupling perspective, the

optimal transport environment is intrinsically linked to the kinetic requirements of the target reaction. Catalysts favoring rapid CO formation require efficient product removal to suppress further hydrogenation, whereas CH_4 or CH_3OH formation generally benefits from sufficient H_2 supply and residence time to sustain sequential hydrogenation of surface intermediates. Structured architectures should therefore be matched with catalyst-specific reaction kinetics and pathways, rather than optimized solely for maximum light absorption or heat retention. The emergence of programmable reactor structures also reflects a broader transition from catalyst optimization alone toward integrated catalyst–reactor co-design for efficient solar-driven C_1 production.

4.4 Representative photothermal reactor designs

The reactor engineering strategies discussed above have been successfully implemented in a series of representative photothermal CO_2 hydrogenation systems (Fig. 8 and 9). Rather than relying on a single design principle, these reactors combine optical concentration, thermal management, structural optimization, and microenvironment regulation to improve solar energy utilization, reaction efficiency, and product selectivity. The representative examples below illustrate how reactor-level engineering complements catalyst design to achieve efficient and practical photothermal CO_2 hydrogenation.

Optical concentration represents one of the most direct reactor engineering strategies for increasing solar energy utilization in photothermal CO_2 hydrogenation. Wu and co-workers designed a concentrated solar reactor using Fresnel lenses to focus incident sunlight onto a Pt/ZnO catalyst bed, thereby

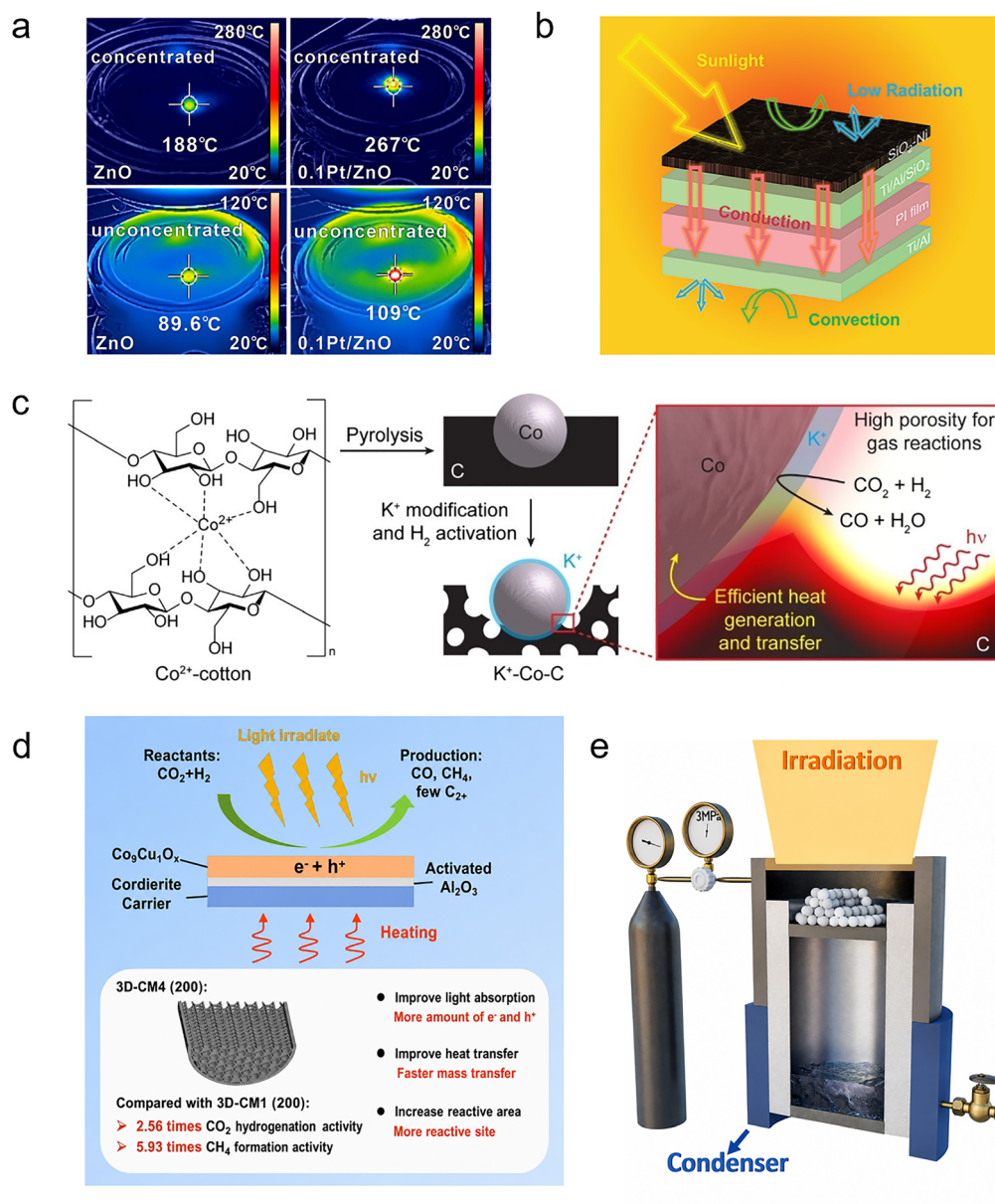


Fig. 8 Representative reactor engineering strategies for practical photothermal CO₂ hydrogenation. (a) Concentrated solar photothermal reactor. Adapted from ref. 134 with permission from American Chemical Society, copyright 2023. (b) Metamaterial-enabled thermal confinement strategy. Adapted from ref. 95 with permission from Wiley-VCH, copyright 2024. (c) Hierarchical porous photothermal architecture. Adapted from ref. 135 with permission from Wiley-VCH, copyright 2023. (d) 3D-printed monolithic photothermal reactor. Adapted from ref. 35 with permission from Royal Society of Chemistry, copyright 2026. (e) LOGIC photothermal reactor for equilibrium-shifted methanol synthesis. Adapted from ref. 89 with permission from Science China Press, copyright 2024.

generating highly localized photothermal heating (Fig. 8a).¹³⁴ Compared with unconcentrated irradiation, concentrated illumination increased the solar-to-chemical energy conversion efficiency from 0.012% to 0.264% and enhanced the CO production rate by nearly 120-fold, from 0.96 to 115.32 $\mu\text{mol g}^{-1} \text{h}^{-1}$. Infrared thermal imaging further confirmed that concentrated irradiation raised the catalyst surface temperature from approximately 109 to 267 °C for Pt/ZnO, creating localized hot spots that substantially accelerated CO₂ conversion. Importantly, concentrated irradiation also reduced the apparent activation energy

from 48.19 to 37.23 kJ mol^{-1} , indicating that localized photothermal heating directly facilitated reaction kinetics. This work demonstrates that optical concentration is an effective reactor-level strategy for intensifying local heat generation and improving solar energy utilization in photothermal CO₂ hydrogenation.

Thermal management through spectrally selective solar absorbers provides an effective strategy to minimize heat dissipation and maximize photothermal conversion within reactor systems. Liu and co-workers developed a Ni-based selective metamaterial absorber by integrating an Al reflective layer, a

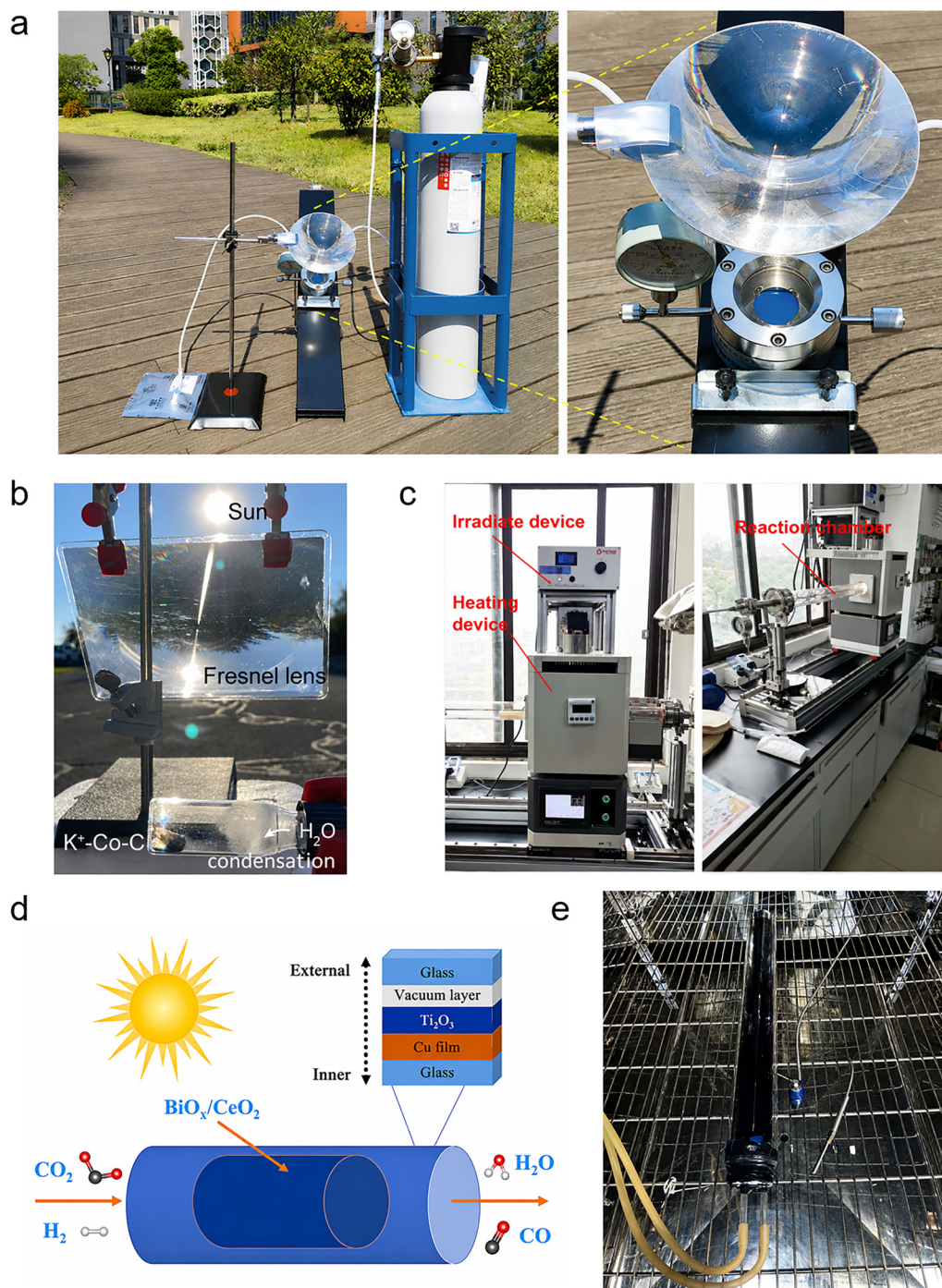


Fig. 9 Representative real-world reactor configurations for photothermal CO₂ hydrogenation. (a) Outdoor solar-driven photothermal reactor equipped with a solar concentrator for direct utilization of natural sunlight. Adapted from ref. 95 with permission from Wiley-VCH, copyright 2024. (b) Batch photothermal reactor using a Fresnel lens to concentrate natural sunlight onto the catalyst. Adapted from ref. 135 with permission from Wiley-VCH, copyright 2023. (c) Laboratory-scale photothermal reactor system equipped with irradiation and external heating devices. Adapted from ref. 35 with permission from Royal Society of Chemistry, copyright 2026. (d) Schematic illustration of a Ti₂O₃-based photothermal system for solar-driven CO₂ hydrogenation via the RWGS reaction. Adapted from ref. 136 with permission from the Royal Society of Chemistry, copyright 2022. (e) Photograph of the corresponding Ti₂O₃-based photothermal reactor setup. Adapted from ref. 136 with permission from the Royal Society of Chemistry, copyright 2022.

dielectric SiO₂ spacer, and a Ni/SiO₂ cermet photothermal layer to simultaneously achieve high solar absorption and suppressed thermal radiation (Fig. 8b and 9a).⁹⁵ The multilayer architecture exhibited a solar absorptivity of 0.86 while maintaining

an ultralow emissivity below 0.08 at 300 °C, thereby substantially reducing radiative heat losses and increasing local photothermal temperatures. As a result, the reactor achieved an exceptional CO₂ conversion rate of 516.9 mmol g_{cat}⁻¹ h⁻¹ under a relatively mild

irradiation intensity of only 0.8 W cm^{-2} , together with nearly 90% CO selectivity and excellent operational stability. Heat-balance analysis further revealed that reducing emissivity fundamentally altered the heat dissipation pathway, decreasing radiative losses to less than 20% of the total heat loss while maintaining efficient thermal confinement around the catalytic surface. This work demonstrates that engineering selective solar absorbers to regulate heat flow and suppress thermal radiation represents an effective reactor-level strategy for improving solar energy utilization and photothermal catalytic performance.

Hierarchical porous architectures provide another effective reactor engineering strategy for simultaneously regulating light harvesting, heat transfer, and mass transport within photothermal catalytic systems (Fig. 8c and 9b). Wang and co-workers developed a lotus-pod-inspired hierarchical porous carbon architecture that integrates photothermal energy conversion with efficient gas diffusion for solar-driven RWGS reactions.¹³⁵ The interconnected porous framework promotes multiple light scattering and photon trapping, facilitating rapid photothermal heating while simultaneously providing continuous transport pathways for reactants and products. Such a confined porous architecture effectively shortens diffusion distances and accelerates heat distribution throughout the catalyst bed, thereby improving the coupling between photon absorption, thermal transport, and catalytic reaction. Benefiting from these structural advantages, the system achieved a record-high CO production rate of $758 \text{ mmol g}_{\text{cat}}^{-1} \text{ h}^{-1}$ with 99.8% CO selectivity under Xe lamp irradiation at ambient pressure. Moreover, the reactor maintained efficient CO production under natural winter sunlight, demonstrating excellent solar adaptability under practical operating conditions. This work highlights that bio-inspired hierarchical porous architectures can simultaneously optimize optical, thermal, and mass-transfer processes, providing an effective reactor-level strategy for intensifying photothermal CO₂ conversion.

Additive manufacturing provides a versatile reactor engineering strategy for constructing customized photothermal reactors with precisely controlled macrostructures (Fig. 8d and 9c). Li and co-workers integrated vat photopolymerization (VPP) with photothermal catalysis to fabricate 3D-printed cordierite monolithic reactors featuring programmable pore architectures.³⁵ Compared with conventional extruded monoliths, the printed reactors offered precise control over channel geometry, pore dimensions, and transport pathways, enabling systematic optimization of reactor-scale photon, heat, and mass transport. By reducing both transverse and longitudinal pore sizes, the optimized monolithic architecture enhanced multiple light reflection, improved heat distribution, and increased the effective reactive surface area, thereby promoting more efficient photothermal energy utilization. Under photothermal conditions ($200 \text{ }^{\circ}\text{C}$, $\text{H}_2/\text{CO}_2 = 4:1$), the optimized reactor achieved CO and CH₄ production rates of 67.42 and $25.5 \text{ mmol g}^{-1} \text{ h}^{-1}$, respectively. Numerical simulations further revealed that tailored macrostructures increase internal light absorption, improve temperature uniformity, and accelerate reactant diffusion through coordinated regulation of optical

and thermal transport. Compared with conventional packed-bed configurations, the monolithic architecture also offers lower pressure drop, more uniform irradiation, and enhanced gas-flow management, highlighting the advantages of programmable reactor architectures for scalable solar-driven CO₂ hydrogenation.

A distinctive example of reactor microenvironment engineering is the liquid out/gas in concept (LOGIC) photothermal reactor developed for methanol synthesis (Fig. 8e).⁸⁹ Unlike conventional photothermal reactors, the LOGIC design spatially separates the illuminated catalyst bed from the condensation zone. Under light irradiation, only the catalyst bed is heated to drive CO₂ hydrogenation, whereas the remaining reactor volume remains sufficiently cool to continuously condense CH₃OH and H₂O products. This *in situ* product removal decreases their partial pressures and continuously shifts the reaction equilibrium toward methanol formation. Benefiting from this thermodynamic regulation, the reactor achieved an exceptional CO₂ conversion of 98% with 86% CH₃OH selectivity under purely light-driven operation. Moreover, 9.0 g of condensed liquid products, including 5.3 g CH₃OH and 3.7 g H₂O, were collected during xenon-lamp irradiation. Compared with conventional thermocatalytic methanol synthesis, where CO₂ conversion is typically limited to below 30% near $250 \text{ }^{\circ}\text{C}$ because of equilibrium constraints, the LOGIC reactor effectively overcomes this limitation through reactor-level equilibrium engineering rather than catalyst modification. This work highlights that reactor design can actively regulate the local thermodynamic environment and product evolution, providing an effective strategy for overcoming equilibrium limitations in photothermal CO₂ hydrogenation.

Another representative approach is the integration of efficient solar-thermal conversion with the catalytic reaction system (Fig. 9d and e). Kang and co-workers developed a Ti₂O₃-based photothermal system in which the Ti₂O₃ layer absorbs broadband solar irradiation and converts it into thermal energy to drive the RWGS reaction over BiO_x/CeO₂.¹³⁶ Under 1 and 3 suns irradiation, the system reached approximately 314 and $470 \text{ }^{\circ}\text{C}$, respectively, enabling CO production rates of 1.01 and $31.00 \text{ mmol g}^{-1} \text{ h}^{-1}$. More importantly, the schematic configuration and corresponding experimental setup shown in Fig. 9d and e demonstrate the practical integration of solar absorption, thermal conversion, and catalytic reaction within a compact photothermal system. This work illustrates that integrating photothermal energy conversion directly into the reaction system provides an effective route to enhance solar energy utilization and drive CO₂ hydrogenation under relatively mild solar irradiation.

Collectively, these representative reactor systems demonstrate that, despite employing different engineering strategies, practical photothermal reactors share a common objective: regulating the local reaction microenvironment through coordinated control of light harvesting, heat transfer, and mass transport. Such reactor-level regulation complements catalyst design by improving solar energy utilization and creating favorable conditions for selective C₁ production. These advances

establish reactor engineering as an essential component of efficient photothermal CO₂ hydrogenation systems.¹³⁷

5. Conclusions and outlook

5.1 Concluding remarks

Photothermal CO₂ hydrogenation has emerged as a promising route for solar-driven C₁ fuel production by integrating light harvesting with catalytic hydrogenation. Rather than simply combining photochemical and thermochemical processes, photothermal catalysis operates through the coordinated regulation of photon absorption, localized heat generation, interfacial electronic structure, and surface reaction kinetics. This unique coupling enables broader solar-spectrum utilization and provides additional opportunities to manipulate reaction pathways beyond those accessible in conventional thermocatalysis or photocatalysis.

A central conclusion emerging from this review is that product selectivity is ultimately governed by regulation of the local reaction microenvironment. Across different catalyst systems, efficient CO, CH₄, and CH₃OH production relies on the coordinated control of CO₂ activation, H₂ dissociation, intermediate evolution, hydrogen transfer, and product desorption. These processes are simultaneously influenced by catalyst composition, defect chemistry, metal-support interactions, localized photothermal heating, and reactor operating conditions. Consequently, catalyst optimization should not be considered solely at the active-site level but within the broader context of coupled light–heat–mass transport processes.

Recent advances further demonstrate that reactor engineering has become an indispensable component of photothermal CO₂ hydrogenation. Continuous-flow operation, light and thermal management, structured reactor architectures, and reactor-level microenvironment regulation not only improve solar energy utilization and transport efficiency but also directly influence reaction pathways and product selectivity. Together, these developments indicate a clear transition from catalyst-centered optimization toward integrated catalyst–reactor co-design, providing a practical framework for efficient solar-driven CO₂ hydrogenation.

5.2 Future perspectives

Despite substantial progress, several fundamental and technological challenges remain before photothermal CO₂ hydrogenation can be translated into practical solar-fuel production.

First, a deeper mechanistic understanding of photothermal catalysis is still required. Although localized heating is recognized as the dominant driving force in many systems, the respective contributions of thermal and non-thermal effects remain difficult to quantify because catalyst surfaces experience highly dynamic and spatially heterogeneous temperature fields under illumination. Future studies should integrate *operando* spectroscopy, spatially resolved temperature characterization, isotope-labeling experiments, and multiscale simulations to establish quantitative relationships between photon excitation,

local heating, intermediate evolution, and catalytic performance, thereby identifying the elementary steps governed by photochemical and thermally driven processes. Such mechanistic insights will help distinguish genuine photothermal synergy from purely thermal enhancement and provide a foundation for the rational design of next-generation photothermal catalysts and reactors.

Second, future catalyst design should move beyond maximizing activity toward precise regulation of reaction microenvironments. Rather than independently optimizing active sites or defect concentrations, greater attention should be devoted to coordinating light harvesting, heat generation, hydrogen transfer, intermediate stabilization, and mass transport across multiple length scales. Establishing such multiscale regulation strategies will be essential for simultaneously improving activity, selectivity, stability, and solar energy utilization.

Third, catalyst development and reactor engineering should be considered as an integrated design problem rather than independent optimization processes. Future photothermal reactors should be designed together with catalyst architectures to coordinate photon distribution, thermal management, gas-flow characteristics, and catalyst geometry. Emerging technologies such as structured reactors, additive manufacturing, digital reactor design, and artificial-intelligence-assisted optimization may provide new opportunities for developing scalable photothermal systems with improved energy efficiency and operational stability.

Finally, practical implementation will require integrating photothermal CO₂ hydrogenation with renewable hydrogen production, direct air capture, and continuous solar-driven operation. Beyond catalyst performance alone, future studies should increasingly consider long-term outdoor stability, intermittent solar irradiation, techno-economic analysis, and life-cycle assessment to evaluate practical feasibility. Addressing these challenges will accelerate the transition of photothermal CO₂ hydrogenation from laboratory demonstrations toward sustainable solar-fuel technologies.

In summary, photothermal CO₂ hydrogenation is evolving from a catalyst-centered research field into an integrated energy-conversion platform in which catalyst design, reaction microenvironment regulation, and reactor engineering are closely coupled. Continued advances across these interconnected aspects are expected to provide new opportunities for efficient solar-driven CO₂ utilization and practical carbon-neutral C₁ fuel production.

Conflicts of interest

The authors declare no competing financial interest.

Data availability

No primary research results, software or code have been included and no new data were generated or analysed as part of this review.

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