

Review

Solar-Driven CO₂ Conversion: A Review of Long-Chain Products

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Abstract

The solar-driven conversion of CO₂ into long-chain (C₃₊) products offers a sustainable pathway to mitigate climate change, produce carbon-neutral fuels and value-added chemicals. Over the past few decades, significant advances have been achieved in CO₂ photoreduction; however, most systems still favor C₁ products (CO, CH₄) or C₂ intermediates. However, the synthesis of C₃₊ products poses a formidable challenge due to the complex multi-electron transfer steps required for C–C bond formation. This review provides a concise overview of recent progress in solar-driven photocatalytic and photothermal CO₂ reduction, with a specific focus on the formation of C₃₊ products. The fundamental principles are discussed, including the critical role of C–C coupling mechanisms and the stepwise reaction pathways for C₃₊ products. It highlights how the extended carbon chain length significantly increases the complexity and reduces selectivity, with the suppression of side reactions being a primary research objective. Key catalytic strategies, such as the use of copper-based materials, are examined for their unique ability to facilitate these demanding transformations. Finally, the major challenges are outlined, and a future outlook for this field is provided, with an emphasis on the need for advanced catalyst design and in situ characterization to unlock the potential of solar fuels.

Keywords: photocatalysis; photothermal; long-chain products; CO₂ conversion

1. Introduction

Climate change is widely recognized as one of the most significant challenges of the twenty-first century [1]. The continuous increase in greenhouse gases, particularly carbon dioxide (CO₂), has led to a substantial warming of the Earth [2,3]. By December 2020, atmospheric CO₂ concentration had risen to 414.02 ppm, up from ~270 ppm in the early 1800s, surpassing the 350 ppm threshold commonly cited as the upper limit for a stable climate system [4]. Rising CO₂ levels are strongly linked to more frequent heatwaves, droughts, floods, and other climate-related extremes [5]. The urgency of addressing climate change has therefore never been greater [6]. At the same time, global energy demand continues to grow, driven by population growth, industrial expansion, and urbanization [7]. This creates a dual crisis: the need to limit carbon emissions while meeting rising energy demands.

Renewable energy technologies, such as solar photovoltaics, wind turbines, and hydropower, have expanded rapidly over the last decade [8]. They now contribute significantly to the global electricity mix, but their deployment alone is insufficient to achieve carbon neutrality [9]. Renewables face challenges related to intermittency, grid integration, and storage [10]. The mismatch between energy generation and consumption results in



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curtailment in some regions and reliance on fossil fuel backup in others [11]. These issues highlight the importance of developing strategies that can not only harvest renewable energy but also store it in a stable and transportable form [12]. This is where solar-driven CO₂ conversion becomes strategically important.

Solar energy is the most abundant renewable resource available on Earth [13]. Every hour, more solar energy reaches surface of the Earth than the entire global population consumes in a year [14]. However, sunlight is intermittent and diffuse, which limits its direct use [15]. Converting solar energy into chemical energy provides a pathway to overcome these challenges [16]. Solar-driven CO₂ conversion utilizes sunlight to power the transformation of CO₂, a waste greenhouse gas, into valuable products [17]. These products can serve as fuels, such as hydrocarbons and alcohols, or as chemical feedstocks for plastics, lubricants, and specialty chemicals [18]. The dual benefit of reducing CO₂ emissions while generating carbon-neutral fuels makes this approach highly attractive for sustainable development [19].

Over the past two decades, several approaches to solar-driven CO₂ conversion have been investigated [20,21]. These include particulate photocatalysis (PC) [22], photoelectrochemical (PEC) devices [23,24], photovoltaic-electrochemical (PV-EC) coupling [25], and photothermal (PT) catalysis [26]. Each method has strengths and weaknesses [27–30]. PEC and PV-EC technologies have achieved relatively high solar-to-fuel efficiencies in laboratory demonstrations, especially for C₁ products such as carbon monoxide [31–33]. However, this review will focus on photocatalysis and photothermal catalysis. These two routes are particularly promising because of their conceptual simplicity, scalability, and ability to directly utilize solar energy without complex device integration [34].

Photocatalysis relies on semiconductor materials that absorb light and generate electron-hole pairs [35]. The electrons reduce CO₂, while the holes oxidize water or other sacrificial agents [36]. This simple design has inspired a vast amount of research since the first reports in the 1970s [37]. Early studies suffered from low efficiencies and poor selectivity, but rapid advances in materials science have led to significant improvements [38]. Cocatalyst loading has been shown to facilitate charge separation and lower activation barriers [39]. Defect engineering and heterojunction formation enhance light absorption and extend charge lifetimes [40]. More recently, single-atom catalysts and plasmonic nanostructures have been employed to stabilize reaction intermediates and promote multi-carbon coupling [41,42]. Despite these advances, challenges remain in achieving both high activity and high selectivity under sunlight, especially for long-chain products [43].

Photothermal catalysis, in contrast, operates primarily by converting light into heat [44]. Materials such as plasmonic metals, black absorbers, and oxides efficiently capture sunlight and generate localized heating [45]. This heat accelerates surface reactions, enabling catalytic transformations at relatively low bulk temperatures [46]. In some cases, photothermal systems also produce energetic charge carriers that can directly participate in reactions [47]. The combination of thermal and non-thermal effects gives photothermal catalysis unique advantages [48]. It can reach high turnover frequencies and enable tandem processes such as the reverse water-gas shift (RWGS) reaction followed by Fischer-Tropsch (FT) synthesis [49,50]. These processes are particularly suited for producing long-chain products because they mimic conventional thermocatalytic routes, with the added efficiency gains from solar input [51,52].

The production of C₁ products such as CO, CH₄, CH₃OH, and HCOOH has been extensively demonstrated in both photocatalytic and photothermal systems [53–55]. These molecules are valuable, but they suffer from limitations. Their energy density is relatively low, and they are often incompatible with existing energy infrastructure [56]. Long-chain (C₃₊) hydrocarbons and oxygenates such as higher alcohols, ketones, and carboxylic acids

are more desirable. They possess higher volumetric energy densities, are easier to store and transport, and can be used directly in modern engines, pipelines, and refineries [57,58]. They also serve as essential precursors in the production of polymers, detergents, and lubricants [59,60]. Economically, these molecules have greater market value compared to C_1 or C_2 products [58,61]. From a climate perspective, their direct production from CO_2 offers a clear route to carbon-neutral drop-in fuels.

However, producing C_{3+} products from CO_2 is extremely challenging [62]. It requires C–C coupling reactions that involve multiple proton and electron transfers [63]. For example, intermediates such as $^*CO$, $^*CHO$, and $^*CH_2$ must be stabilized long enough to undergo dimerization or insertion reactions [64]. This stabilization must occur without triggering unwanted hydrogen evolution or over-hydrogenation to methane [65]. In photocatalysis, strategies such as creating oxygen vacancies (O_V s), constructing heterojunctions, and designing bifunctional active sites are being developed to guide these complex transformations [66,67]. In photothermal catalysis, tandem reaction schemes have been proposed where CO is first generated from CO_2 and then converted into C_{3+} products under FT-like conditions [68,69]. Both routes face hurdles in maintaining stability, suppressing side reactions, and scaling the systems beyond laboratory settings [70,71].

C_{3+} hydrocarbons and oxygenates represent the most promising product class for solar-driven CO_2 conversion, but they are also the most difficult to obtain selectively [72,73]. Photocatalysis and photothermal catalysis are two of the most direct and scalable approaches to achieve this transformation [74,75]. They take advantage of abundant solar energy and offer pathways that can, in principle, be integrated with existing CO_2 capture and utilization frameworks [76,77]. By focusing on these two methods, this review aims to consolidate the state of the art, highlight the main advances in catalyst design and reaction engineering, and identify the remaining barriers.

The scope of this review is to critically examine photocatalytic and photothermal strategies for converting CO_2 into long-chain hydrocarbons and oxygenates. It will first discuss the fundamental mechanisms of light absorption, charge generation, and surface activation relevant to both methods. This review focuses specifically on catalyst design principles that enable C_{3+} product formation. It highlights mechanistic features, active-site architectures, and structure–function relationships uniquely relevant to long-chain hydrocarbons and oxygenates. Finally, it will present an outlook on durability, efficiency metrics, and integration with renewable hydrogen and CO_2 capture systems. By consolidating recent works, particularly from the period 2020–2025, this review seeks to provide a roadmap for developing selective, scalable, and economically viable solar-driven routes to long-chain products.

2. Fundamentals of Long-Chain Hydrocarbon Formation

The solar-driven conversion of CO_2 into C_{3+} products is a complex, multi-step process [68,78]. Several factors, such as light harvesting, charge or heat management, and surface reaction pathways, require strict control in this process [79,80]. The fundamental difference between photocatalytic and photothermal approaches lies in how they activate CO_2 and drive C–C coupling reactions [81]. A clear understanding of these mechanisms is vital to enable rational catalyst development and to surmount the current limitations in selectivity and efficiency for the formation of C_{3+} products.

2.1. Photocatalytic CO_2 Conversion

Semiconductor catalysts play a crucial role in photocatalytic systems [82]. They absorb photons with energy equal to or greater than their bandgap, generating electron–hole pairs [83]. The photogenerated electrons reduce CO_2 , while holes oxidize water or other

sacrificial agents [17]. For C_{3+} products formation, the process requires: (1) Efficient absorption under ultraviolet and visible light to maximize solar utilization; (2) Effective charge separation to prevent recombination losses; (3) CO_2 activation via adsorption at active sites of catalyst, often involving O_V s or metal- CO_2 complexes; (4) Multi-electron/proton transfer steps enabling C-C coupling, typically through intermediates such as $^*CO$, $^*CHO$, or $^*CH_2$ [35,70]. To illustrate the fundamental steps of solar-driven CO_2 valorization via semiconductor-based systems, the general photocatalytic mechanism for C_{3+} product formation is summarized in Figure 1a.

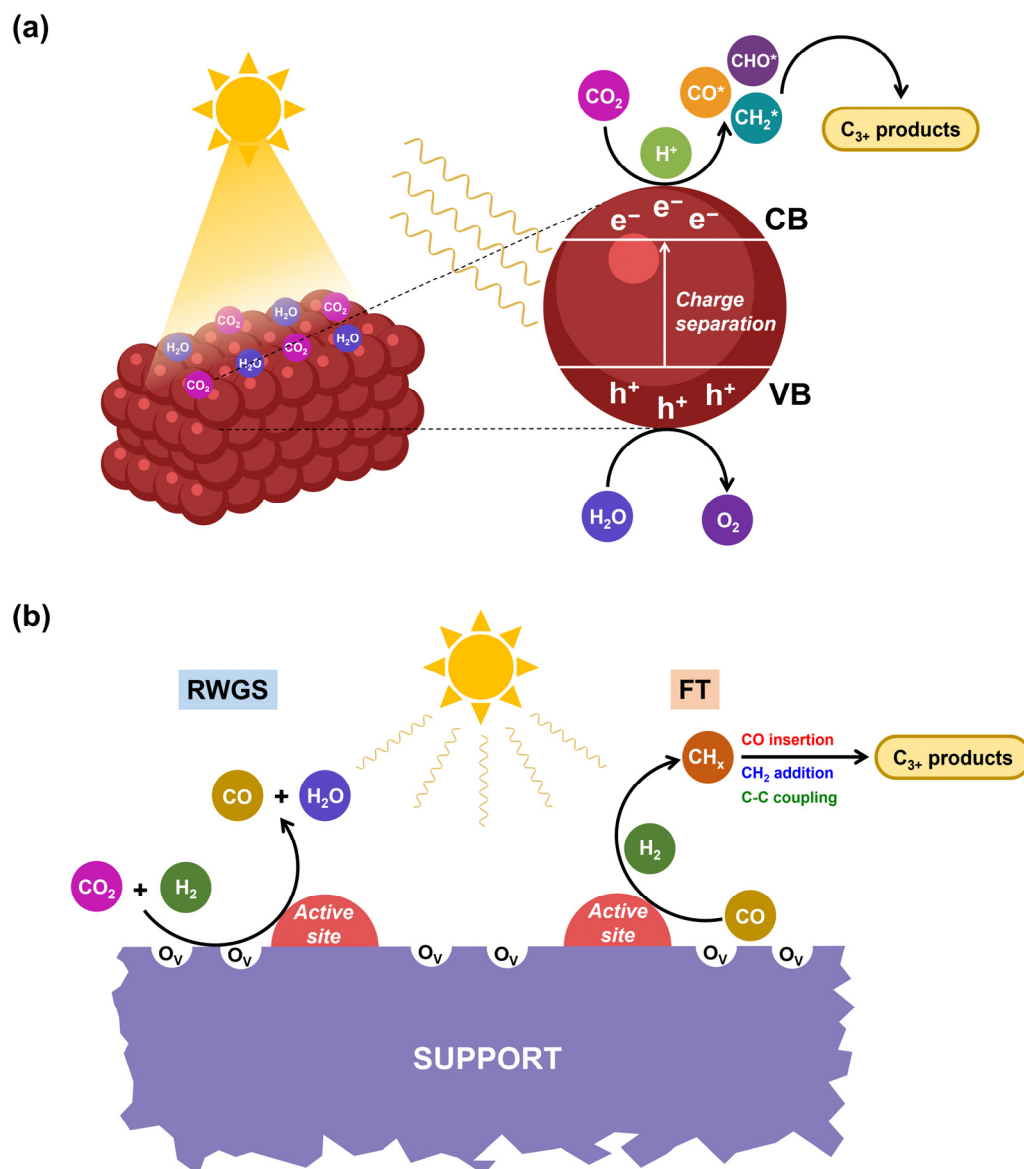


Figure 1. (a) Photocatalytic mechanism for solar-driven CO_2 conversion to C_{3+} products. (b) Photothermal RWGS-FT tandem mechanism for CO_2 hydrogenation to C_{3+} products.

Strategies such as heterojunction engineering, defect modulation, and the incorporation of ionic liquid interfaces have been widely recognized for their ability to stabilize key intermediates and regulate selectivity toward higher-order C_{3+} products [84–86]. Notably, significant progress has been made with layered double hydroxide based photocatalysts and semiconductor–metal heterojunction architectures [87]. Such progress demonstrates superior charge-separation efficiencies and enhanced multi-carbon product selectivity.

These advancements collectively highlight promising design principles for advancing solar-to-fuel conversion technologies.

2.2. Photothermal CO₂ Conversion

Photothermal catalysis combines light absorption with localized heating, enabling reaction rates and selectivity beyond those achievable by purely thermal or photocatalytic routes [46].

Key principles of photothermal CO₂ conversion include: (1) Plasmonic enhancement: Noble metal nanoparticles (e.g., Au, Ag, Cu) generate hot carriers and intense local heating upon light excitation, lowering activation barriers for CO₂ hydrogenation. (2) Non-plasmonic photothermal effects: Transition metal carbides, nitrides, and black semiconductors absorb broadband sunlight and convert it to heat efficiently. (3) Synergistic light–heat interactions: Localized heating accelerates surface reactions, while photogenerated carriers participate in redox steps, facilitating C–C bond formation [80,88,89].

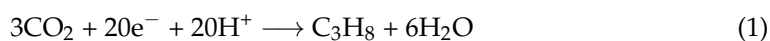
Recent studies emphasize that photothermal RWGS combined with FT tandem systems can yield C₃₊ products with high selectivity, especially when using broadband absorbers and continuous-flow reactors [90–92]. Catalyst design strategies (such as bifunctional active sites, surface defect engineering, and cocatalyst coupling) are critical for enhancing C₃₊ yields [93]. To demonstrate the integrated thermochemical and photonic effects in light-assisted CO₂ hydrogenation, Figure 1b presents the tandem photothermal RWGS–FT pathway toward C₃₊ products.

3. Catalytic System and Strategies for Long-Chain Hydrocarbon Selectivity

3.1. Active Site Engineering and Asymmetric Coordination

This strategy focuses on creating local chemical environments that facilitate multi-step coupling and lower activation barriers for C–C bond formation, with representative catalytic performances summarized in Table 1.

Single-atom/vacancy synergy: The use of Cu single atoms anchored on vacancy-rich TiO₂, which enables room-temperature propane formation under visible light irradiation [94]. The Cu–Ti–VO/Ti_{0.91}O₂–SL catalyst operates via a tandem mechanism in which the TiO₂ matrix reduces CO₂ to CO, while the Cu–Ti–VO sites drive sequential C₁–C₁ and C₁–C₂ coupling steps through stabilized *CHOCO and *CH₂OCOCO intermediates. These intermediates undergo exergonic coupling and subsequent hydrogenation to yield propane. The synergy between Cu single atoms and OVs is essential: it enables strong electronic interactions, lowers intermediate energy levels, and makes multicarbon formation thermodynamically favorable at room temperature (Figure 2a). The proposed tandem catalytic mechanism delineates the reaction pathway as follows:



Although the overall conversion rate remained modest under mild operating conditions, the system demonstrated selective propane formation solely from solar input, underscoring the promise of defect-engineered photocatalysts. Specifically, the Cu–Ti–VO/Ti_{0.91}O₂–SL photocatalytic system demonstrates efficient CO₂ conversion to C₂₊ hydrocarbons at ambient conditions, achieving an electron-based selectivity of 64.8% toward propane and a product-based selectivity of 32.4% (Figure 2b).

Recent advances in solar-driven CO₂ conversion have demonstrated that propane synthesis can be achieved through integrated light–heat strategies and electronic structure engineering. Unlike conventional thermocatalytic bifunctional systems, these approaches

exploit photonic energy to accelerate multi-electron transfer and stabilize key intermediates for C–C coupling.

Asymmetric triple-atom sites: Oxygen-vacancy-rich CuWO_4 engineered via H_2 -spillover creates asymmetric $\text{Cu}-\text{Cu}^{\delta+}-\text{W}^{\delta+}$ triple-atom sites to synthesize propionic acid (Figure 2c) [95]. O_Vs serve a dual purpose: they act as electron-trapping sites that prolong the lifetime of photogenerated charge carriers, thereby facilitating continuous proton-coupled electron transfer (PCET), and they induce the formation of charge-asymmetric active sites by injecting additional electrons into neighboring metal atoms. The reaction mechanism involves a multi-step C–C coupling relay: first, CO_2 is reduced to $^*\text{CO}$ intermediates, which are strongly adsorbed by suboxide $\text{Cu}^{\delta+}$ species. The asymmetric $\text{Cu}-\text{Cu}^{\delta+}$ pairs then trigger the initial C_1-C_1 coupling to form a $^*\text{CC}$ intermediate, which is further protonated into $^*\text{CH}_2\text{CH}_3$. Finally, subsequent C_2-C_1 bonding occurs as the $^*\text{CH}_2\text{CH}_3$ species adsorbed on Cu atoms reacts with $^*\text{COOH}$ adsorbed on adjacent $\text{W}^{\delta+}$ sites, leading to the formation and desorption of propionic acid. Under simulated solar light and aqueous CO_2 , this catalyst achieved a production rate of $86.46 \mu\text{mol} \cdot \text{g}_{\text{cat}}^{-1} \cdot \text{h}^{-1}$ with an electron selectivity of 89.27% (Figure 2d).

Topological active centers: Single-atom Cu sites on Kagome-lattice COFs (BTA-COF-Cu) represent a breakthrough in integrating atomic-level active centers with tailored topologies [96]. The Kagome lattice provides a high surface area and efficient charge transport channels, while isolated Cu sites serve as catalytic centers for CO_2 activation and intermediate coupling. Under visible light, BTA-COF-Cu achieved $6.55 \mu\text{mol} \cdot \text{g}_{\text{cat}}^{-1}$ of propene without additional cocatalysts, marking the first report of propene generation in such systems. The Kagome lattice provides ordered channels that accelerate charge migration and stabilize key intermediates, while the Cu single atoms, coordinated to bipyridine N sites, serve as highly active centers that adsorb and hydrogenate $^*\text{CO}$, $^*\text{CHO}$, and $^*\text{CHOCO}$ species. In situ DRIFTS confirms the generation of $^*\text{COOH}$, $^*\text{CO}$, $^*\text{CHO}$, and $^*\text{CHOCO}$ intermediates, indicating a stepwise reduction pathway followed by two C–C coupling events to yield propene. The Cu sites lower the energy barriers for both coupling steps and enhance electron transfer from the COF backbone, enabling efficient visible-light-driven conversion of CO_2 to propene.

Multi-site cascade architectures: Complementary work on ZIF-67-derived carbon interfaced with oxygen-deficient TiO_2 demonstrated acetone selectivity in gas-phase photoreduction [97]. Under AM 1.5 illumination at $\sim 50^\circ\text{C}$, the composite catalyst produced $3.406 \mu\text{mol}$ of acetone in 6 h with 51.8% selectivity and an apparent quantum efficiency of 0.154. In the ZDC/T composite, acetone originates from a synergistic C–C coupling pathway enabled by Co–N–C active sites and oxygen-deficient TiO_2 . The ZDC framework provides pyridinic/pyrrolic N sites and highly dispersed Co nanoparticles, which strongly adsorb and activate CO_2 to $^*\text{COOH}$ and $^*\text{CO}$ intermediates. Simultaneously, black TiO_2 with abundant O_Vs enhances CO_2 dissociation, accelerates electron transfer, and supplies additional $^*\text{CH}_x$ species through photoreduction. On ZDC/T, these intermediates undergo sequential hydrogenation to methanol, followed by homolytic C–C coupling between CH_3 radicals and carbonyl-containing intermediates (e.g., $^*\text{CO}$ or $^*\text{CHO}$), forming a C_3 backbone. The stabilized $^*\text{CH}_3$ and $^*\text{CO}$ species at the Co–N–C/ TiO_2 interface then couple to yield acetone as the dominant C_3 product. The TiO_2 component prevents Co aggregation and preserves N-doped carbon sites, maintaining a high density of dual active centers essential for C_3 formation.

Frustrated Lewis pairs (FLP): Ag-modified CeO_2 with stabilized O_Vs and Ag–O– Ce^{3+} atomic interfaces promotes visible-light-driven CO_2 reduction to acetone [98]. At an optimal Ag loading of 0.3 wt%, the system exhibited high selectivity for acetone formation. The selective formation of acetone on Ag/ CeO_2 arises from the synergistic interaction between

atomically dispersed Ag species and surface O_V s, which together create a frustrated Lewis pair, like Ag–O–Ce³⁺ interface. The Ag sites stabilize surface O_V s and promote electron transfer from Ce³⁺ defect sites to Ag, enhancing charge separation and enabling strong, simultaneous adsorption of $^*COOH$ and $^*CH_3$ intermediates. O_V s activate CO_2 to form $^*COOH$, while Ag sites preferentially stabilize $^*CH_3$ generated from H_2O -derived protons. The proximity of these co-adsorbed intermediates on the Ag–O–Ce³⁺ interface facilitates C–C coupling between CO and CH_3 , followed by further hydrogenation and rearrangement to yield acetone. This cooperative mechanism of O_V s-driven CO_2 activation, Ag-assisted $^*CH_3$ stabilization, and interface-enabled C–C coupling explains the high selectivity of Ag/CeO₂ toward C₃ ketone formation under visible light.

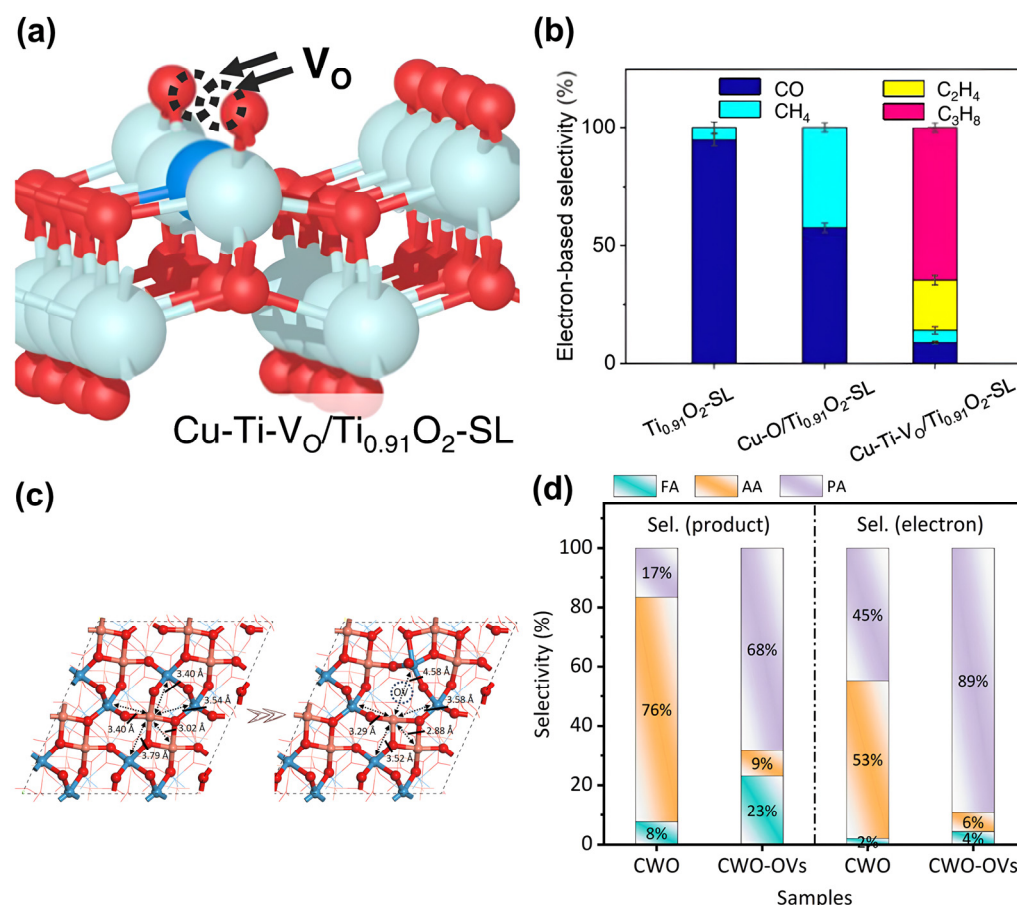


Figure 2. (a) Atomic structure model showing the configuration of constituent elements (color code: light blue = Ti, blue = Cu, red = O). (b) Electron-based selectivity of Ti_{0.91}O₂-SL, Cu-O/Ti_{0.91}O₂-SL, and Cu-Ti-V_O/Ti_{0.91}O₂-SL catalysts [94]. Copyright © 2023 The Author(s). (c) Surface atom arrangements of optimized CWO and CWO-OV_s structures. (d) Distribution of photoreduction products and corresponding electron selectivity over CWO and CWO-OV_s systems [95]. Copyright © 2025 Wiley-VCH GmbH. Note: V_O denotes oxygen vacancies, and the numerical values in (c) represent atomic distances in Å.

3.2. Interfacial Engineering and Heterojunction Design

Directing charge flow through high-potential junctions or toward specific facets is critical for supplying the massive reducing power required for C₃ synthesis. Interfacial modification and the construction of heterojunctions are key strategies for directing charge flow toward multi-carbon pathways, with representative performance metrics for these systems detailed in Table 1.

Facet-dependent compatibility: Recent breakthroughs have shown that facet engineering and interfacial optimization can significantly enhance photocatalytic CO₂-to-butanol conversion. For example, CeO₂/Cu₂O heterostructures with controlled facet orientations have been employed to probe the role of interfacial compatibility in directing multi-carbon pathways [99]. Cu₂O crystals were synthesized with distinct facets ((100), (111), and mixed (100 + 111)) and coupled with CeO₂ (111) to form Z-scheme heterojunctions. Among these, the CeO₂/Cu₂O (100) composite exhibited the most efficient charge separation and transfer, as confirmed by ESR and photocurrent measurements. DFT calculations revealed that electron transfer from Cu₂O (100) to CeO₂ reached 4.091 e[−], significantly higher than the 0.822 e[−] observed for the CeO₂/Cu₂O (111) interface, confirming superior interfacial compatibility.

This optimized heterostructure achieved a remarkable butanol yield of 34 μmol.g_{cat}^{−1}.h^{−1} with a selectivity of 59%, representing an ~87-fold improvement over CeO₂/Cu₂O (111). The C₂–C₄ selectivity exceeded 75%, indicating a strong preference for multi-carbon products. In contrast, composites with mixed or (111) facets primarily produced CO, highlighting the critical role of facet orientation in determining product distribution.

Mechanistic investigations using in situ DRIFTS and isotopic labeling confirmed that butanol forms through an aldol condensation pathway, involving intermediates such as acetone, crotonaldehyde, and 3-hydroxybutanal. The Z-scheme heterojunction between CeO₂ and Cu₂O (100) facilitates spatial charge separation, enabling CO₂ reduction on Cu₂O and water oxidation on CeO₂ without the need for sacrificial agents. This architecture not only extends the redox potential window but also suppresses electron–hole recombination, thereby promoting the multi-electron transfer steps required for higher-order C–C coupling.

Z-Scheme potential regulation: A direct Z-scheme WO₃/ZnS heterojunction offers another promising route to C₃ hydrocarbon formation [100]. Under UV–Vis irradiation and water vapor, the optimized WO₃/ZnS composite achieved propane yields of 101.4 μmol.g_{cat}^{−1}.h^{−1} and propene yields of 16.7 μmol.g_{cat}^{−1}.h^{−1} at 80 °C. This enhanced performance is primarily attributed to the efficient separation and fast transfer of photo-generated charge carriers to CO₂ molecules adsorbed on basic active sites of the direct Z-scheme WO₃/ZnS photocatalyst. Under UV–Vis irradiation, the heterojunction synergistically combines the high CO₂ adsorption capacity and negative CB potential of ZnS with the visible-light activity of WO₃, resulting in an optimal CB potential of −1.81 V vs. NHE for the W_{5%}Z composite. This high reduction potential provides the necessary thermodynamic driving force to facilitate the complex multielectron and multiproton transfer required for C–C bond formation. The mechanism involves the reduction of CO₂ using H⁺ ions provided by simultaneous water oxidation, where the optimal crystallite size of approximately 7.1 nm and an intimate interfacial junction enable the high-rate production of C₃ hydrocarbons. Although the process achieves significant selectivity for propane at lower temperatures, the reaction eventually faces deactivation due to surface fouling from coke depositions, which is attributed to the formation of high-molecular-weight hydrocarbons that fail to desorb or to a local deficit of protons at higher temperatures.

2D–2D heterostructure platforms: A 2D–2D heterostructure of Cu-doped sodium dititanate nanosheets and graphene oxide (CTGN) exhibited exceptional photoactivity under UV–vis light [101]. This catalyst produced acetone and isopropanol at rates of 113 and 171 μmol.g_{cat}^{−1}.h^{−1} (Figure 3a), respectively, along with methanol and ethanol. In the CTGN heterostructure, copper-doped sodium dititanate nanosheets intimately interfaced with graphene oxide create a 2D–2D charge-separation platform that stabilizes key carbon-based radicals during CO₂ photoreduction (Figure 3b). Under illumination, efficient electron–hole separation at the nanosheet–graphene junction generates abundant photoelectrons that reduce CO₂ to *CO₂[−]. These radicals react with protons and addi-

tional electrons provided by the simultaneous water dissociation to produce liquid fuels via multi-electron reduction pathways. Specifically, isopropanol is synthesized via an eighteen-electron/eighteen-proton reduction, while acetone formation proceeds through a sixteen-electron/sixteen-proton pathway. The high efficiency of these C₃ couplings is enabled by the 2D–2D heterostructure, which directs charge flow along short paths and reduces recombination, while the copper dopants and graphene oxide interfaces provide critical active sites to stabilize intermediates and house reactive radicals.

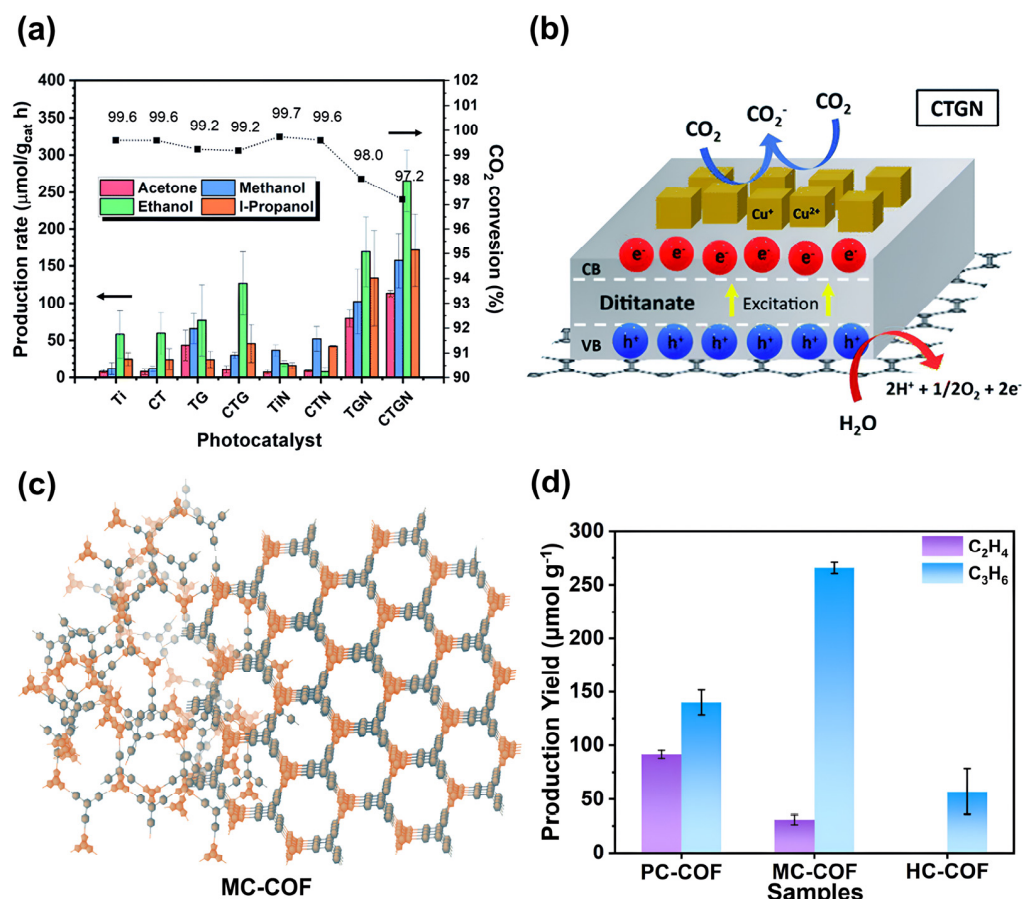


Figure 3. (a) The mechanism of electron transfer in CO₂ photoreduction using CTGN; (b) Photocatalytic performances of different catalysts including Ti, CT, TG, CTG, TiN, CTN, TGN, and CTGN [101]. Copyright © 2022 The Author(s). (c) Structure of MC-COF; (d) Cumulative production of C₂H₄ and C₃H₆ from CO₂ photoreduction over HC-COF, MC-COF, and PC-COF catalysts [102]. Copyright © 2025 American Chemical Society.

3.3. Electronic Structure and Dimensionality Control

Modulating internal order and electronic states suppresses carrier recombination, maintaining the high electron concentrations needed for long-chain growth, as summarized in Table 1.

Order–disorder modulation: Order–disorder modulated COFs (MC-COF) further highlighted the role of structural heterogeneity in optimizing photocatalytic performance [102]. A moderately ordered–disordered framework that forms in-plane heterojunctions exhibited superior visible-light absorption, significantly accelerated the migration of photogenerated carriers to catalytic centers on the triazine rings and imine bonds, and prolonged carrier lifetimes, enabling efficient multi-electron transfer (Figure 3c). MC-COF delivered 265.8 μmol.g_{cat}^{−1} of propene (Figure 3d) with an electron selectivity of 33.58%, surpassing highly ordered and fully disordered analogs. The mechanism proceeds through an exother-

mic reduction of $^*\text{CO}$ to form $^*\text{CHO}$. With the aid of a CuI cocatalyst, a critical $\text{C}_1\text{--C}_1$ coupling occurs between $^*\text{CHO}$ and escaping $^*\text{CO}$ to generate a $^*\text{CHOCO}$ intermediate. This species undergoes PCET to form $^*\text{CH}_2\text{OCO}$, which then undergoes a $\text{C}_1\text{--C}_2$ coupling with another $^*\text{CO}$ molecule to produce the key $^*\text{CH}_2\text{OCOCO}$ intermediate. Following a multistep PCET process to form $^*\text{CH}_2\text{OCOHCH}_2\text{OH}$, the subsequent transformation into stable $^*\text{CH}_2\text{OCOHCH}_2$ via proton-coupled reduction and water elimination is identified as the potential determining step.

Topological surface states (TSSs): Topological semimetal OsCoTe_2 introduces an electronic-structure-driven strategy for propane formation [103]. The 1T phase of OsCoTe_2 exhibits non-trivial TSSs that enhance carrier mobility and suppress recombination. Under visible light in $\text{MeCN}/\text{H}_2\text{O}$ mixtures, this catalyst achieved an electron-based selectivity of 71.2% for propane ($10.3 \mu\text{mol.g}_{\text{cat}}^{-1}.\text{h}^{-1}$) and 84.7% for total C_{2+} hydrocarbons. This high performance originates from a synergistic Os–Te–Co electron-bridging mechanism that accelerates C–C coupling and stabilizes key multicarbon intermediates. Under illumination, electrons flow from Os to Co through Te atoms, creating an electron-rich Co center and an electron-deficient Os center. This redistribution enhances $^*\text{CO}$ adsorption and promotes the sequential formation of $^*\text{CH}_3$, $^*\text{CHOCO}$, and $^*\text{CH}_2\text{OCOCO}$ intermediates, which are essential for $\text{C}_1\text{--C}_1$ and $\text{C}_1\text{--C}_2$ coupling. The TSSs of 1T- OsCoTe_2 further increase carrier mobility and maintain stable active sites, lowering reaction barriers and suppressing competing hydrogen evolution. As a result, the Os–Te–Co framework provides fast charge transfer, strong intermediate stabilization, and efficient multistep hydrogenation, enabling selective conversion of CO_2 to propane with high electron-based selectivity.

Donor–acceptor frameworks: Fluorinated donor– π –acceptor COFs (DF-TP-COF) introduce a dual-functional strategy that combines electronic structure tuning and interfacial engineering [104]. Multiple fluorination locks π -conjugated units into coplanar configurations via hydrogen bonding, accelerating charge migration, while surface hydrophobicity enhances CO_2 adsorption and three-phase contact (Figure 4a). DF-TP-COF achieved $22.3 \mu\text{mol.g}_{\text{cat}}^{-1}.\text{h}^{-1}$ of propene (Figure 4b) under visible light without cocatalysts, outperforming its monofluorinated and nonfluorinated counterparts by 18.1-fold and 1.5-fold, respectively. Strong intramolecular $\text{F}\cdots\text{H}$ hydrogen bonding locks the π -acceptor units into a coplanar configuration, improving electron transfer and stabilizing key intermediates such as $^*\text{CO}$, $^*\text{CHO}$, and $^*\text{CH}_x$ species. Simultaneously, the hydrophobic surface suppresses water adsorption, ensuring efficient proton availability and promoting C–C coupling toward ethene and ultimately propene. This dual electronic–interfacial regulation enables DF-TP-COF to selectively drive multielectron CO_2 reduction to propene under visible light.

3.4. Microenvironment and Radical Modulation

Regulating the local concentration of protons and reactive radicals allows catalysts to bypass traditional scaling relations that limit chain growth, with comparative results from representative studies listed in Table 1.

Proton-trapping enzyme-like clefts: Bridge-position engineered COFs (DA-COF) demonstrated that structural modulation can significantly influence proton-coupled electron transfer [105]. By introducing an anthraquinone-based donor–acceptor configuration and an enzyme-like cleft (Figure 4c), DA-COF facilitated efficient proton trapping and accelerated charge migration. Under visible light ($\lambda \geq 420 \text{ nm}$), DA-COF achieved a remarkable propene yield of $270.5 \mu\text{mol.g}_{\text{cat}}^{-1}$ (Figure 4d) with an electron selectivity of 30.95%, outperforming its counterpart DP-COF, which produced no detectable propene. Propene formation on DA-COF originates from its neighbor-bridged anthraquinone units, which create an enzyme-like cleft that traps protons and stabilizes reduced CH_x intermediates needed for C–C coupling. This bridging also forms an internal donor–acceptor pathway

that accelerates charge separation, prolongs carrier lifetimes, and suppresses recombination, enabling the multi-electron, multi-proton steps required for propene formation. Under visible light, anthraquinone groups undergo electron-coupled hydrogenation, supplying protons and electrons that drive sequential CO₂ reduction and C₁–C₂ coupling, while CuI co-catalyst lowers the C–C coupling barrier. As a result, DA-COF supports efficient propene generation, whereas DP-COF lacks this proton-capturing microenvironment.

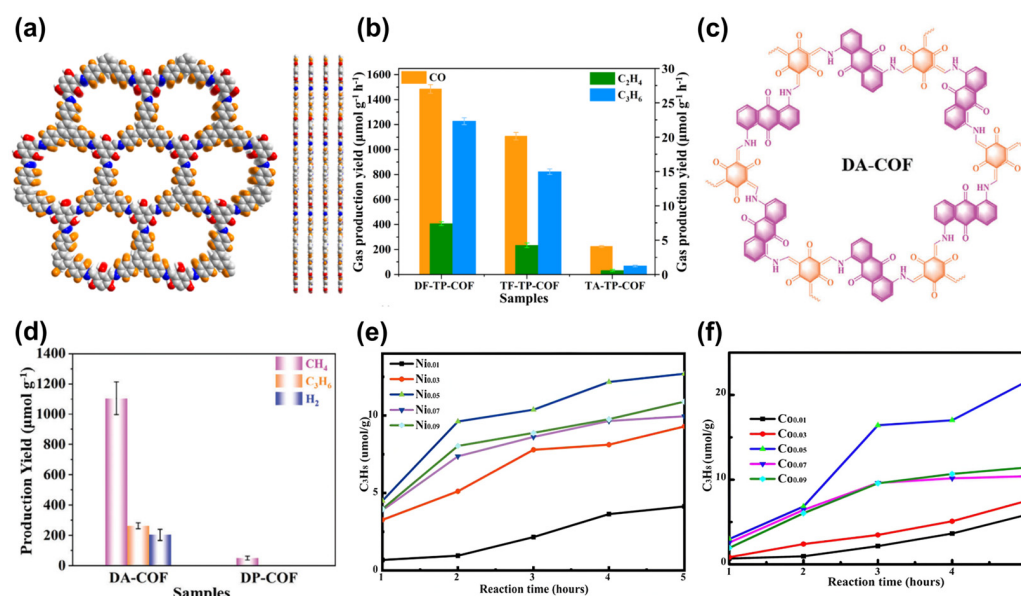


Figure 4. (a) Modeled 2D crystal frameworks of DF-TP-COF catalysts; (b) CO₂ photoreduction performance of TA-TP-COF, TF-TP-COF, and DF-TP-COF toward CO, C₂H₄, and C₃H₆ production [104]. Copyright © 2025 American Chemical Society. (c) Molecule structure of DA-COF; (d) Photocatalytic CO₂ reduction profiles of DA-COF and DP-COF over time [105]. Copyright © 2024 Wiley-VCH GmbH. (e) Photothermal CO₂ hydrogenation to propane on BZCY532 catalysts with different Ni dopant concentrations; (f) Effect of Co doping on C₃H₈ formation over BZCY532 catalysts under photothermal coupling [106]. Copyright © 2020 The Author(s).

Protonic conductivity for multi-proton transfer: Proton-conducting perovskite catalyst BaZr_{0.5}Ce_{0.3}Y_{0.2}O_{3-δ} (BZCY532) represents a notable photothermal route [106]. Under UV irradiation combined with moderate heating (350 °C), BZCY532 selectively produced methane, ethane, and propane, with propane yields of 3.22 μmol.g_{cat}⁻¹ after 5 h. The formation of propane over the BZCY532 proton conductor occurs through a complex photothermal catalytic process involving a 20-electron and 20-proton reduction of CO₂. Specifically, under UV irradiation and at high temperatures (350 °C), the catalyst generates photogenerated electrons and protons via water splitting, which are rapidly transferred owing to the high proton conductivity of BZCY532. The mechanism follows a carbene pathway, in which CO₂ is first reduced to CO, which is then converted to *CH₃ radicals. BZCY532 facilitates the stabilization of these *CH₃ intermediates on its surface, which is critical for promoting the C–C and C–C–C coupling reactions necessary for long-chain hydrocarbon formation rather than simple methane production. The introduction of Ni or Co dopants further enhances this efficiency by creating surface O_Vs that act as active sites for CO₂ adsorption and intermediate stabilization, thereby increasing the selectivity and yield of propane (Figure 4e,f).

Radical-mediated tandem pathways: Lamellar BiVO₄ synthesized via microwave-assisted methods also demonstrated acetone formation alongside methanol under UV-vis irradiation [107]. The optimal condition for acetone production was achieved at 140 °C for 10 min, yielding 30 μmol.g_{cat}⁻¹ after 240 min of photocatalysis. Acetone formation

on BiVO₄ arises from a tandem pathway in which CO₂ is first photoreduced to methanol, followed by radical-mediated C–C coupling. Under UV–vis irradiation, BiVO₄ generates electron–hole pairs that reduce CO₂ to *CO₂[−] and subsequently to CH₃OH. At longer irradiation times, methanol undergoes homolytic cleavage on the BiVO₄ surface, especially when Bi₂O₃ is present, to form *CH₃ and *OH radicals. These *CH₃ radicals then couple with *CO₂[−]-derived intermediates, enabling a C₂–C₁ coupling step that produces acetone. Thus, acetone formation is not a direct CO₂ reduction product but a secondary reaction driven by methanol-derived radicals and CO₂ reduction intermediates, facilitated by defect-rich BiVO₄/Bi₂O₃ junctions that enhance charge separation and radical stability.

Photothermal strategies further expand the product scope. Pt nanoparticles supported on GaN and prepared via surface organometallic chemistry combine H₂ activation with photoexcited charge transfer [108]. Under mild conditions (60 °C, 1 bar, λ > 320 nm), this system produced acetone at 53 μmol.g_{cat}^{−1}.h^{−1} and isopropanol at 113 μmol.g_{cat}^{−1}.h^{−1}, alongside methanol and ethanol. The photothermal formation of acetone and isopropanol over the Pt/GaN catalyst is driven by the synergistic interaction between highly dispersed 0.9 nm platinum nanoparticles and the gallium nitride support under visible-light irradiation at mild temperatures. The mechanism initiates with the photochemical activation of CO₂ on the GaN surface to form a bent species, which is subsequently hydrogenated to a formate intermediate. While standard hydrogenation typically leads to methanol, acetone production is proposed to occur via a methyl insertion step into the formate intermediate, a process facilitated by the presence of methyl species, as evidenced by methane gas byproducts. Isopropanol is then produced as the direct hydrogenation product of the synthesized acetone. Efficient C–C coupling and subsequent reduction are enabled by the superior ability of Pt nanoparticles to activate H₂, combined with the broad redox potential of GaN, which allows the system to selectively generate C₂₊ oxygenates over C₁ products common in traditional thermal catalysis.

Recent studies demonstrate that both photocatalytic and photothermal routes can effectively convert CO₂ into C₃₊ hydrocarbons and oxygenates by precisely controlling light absorption, charge transfer, and interfacial coupling. Advances such as defect engineering, heterojunction design, and single-atom catalysis have improved CO₂ activation and C–C coupling efficiency under mild conditions. Photocatalytic systems achieve selective propane and propene formation under visible light, while photothermal catalysts integrate heat and photon energy to broaden the product scope to include alcohols. Despite remaining challenges in activity and efficiency, these developments highlight the growing potential of light-driven strategies for producing long-chain fuels and chemicals, paving the way toward sustainable, solar-powered carbon conversion.

Table 1. Summary of representative photocatalytic and photothermal systems for solar-driven CO₂ conversion to C₃₊ products.

Product	Catalyst	Synthesis Method	Light Source	Rate (μmol.g _{cat} ^{−1} .h ^{−1})	Selectivity (%)	Reference
Propane	Cu–Ti–V ₂ O ₇ /Ti _{0.91} O ₂ -SL	Acid exchange, colloidal exfoliation, metal precursor adsorption, and rapid thermal treatment	300 W Xe lamp	13.8	64.8	[94]
	BZCY532 (Ni/Co-doped)	Conventional solid-state reaction	300 W Xe lamp	21.3 (Co-doped)		[106]
	1T-OsCoTe ₂	Solid-state reaction under vacuum	300 W Xe lamp (100 mW cm ^{−2})	10.28	71.2	[103]
Propane-Propene	WO ₃ /ZnS	Hydrothermal	300 W Xe lamp (150 mW cm ^{−2})	101.4 (C ₃ H ₈) 16.7 (C ₃ H ₆)		[100]

Table 1. Cont.

Product	Catalyst	Synthesis Method	Light Source	Rate ($\mu\text{mol.g}_{\text{cat}}^{-1}.\text{h}^{-1}$)	Selectivity (%)	Reference
Propene	DA-COF	Solvothermal	300 W Xe lamp *	270.5	30.95	[105]
	MC-COF	Solvothermal	Xe lamp with 420 cut-off filter *	265.8	33.58	[102]
	BTA-COF-Cu	Solvothermal, metalation	300 W Xe lamp	6.55		[96]
	DF-TP-COF	Solvothermal	300 W Xe lamp *	22.3	6.70	[104]
Propionic acid	CWO-O _V s	H ₂ -spillover	300 W Xe lamp *	86.46	89.27	[95]
Acetone	Ag/CeO ₂	Hydrothermal, surface coordination, reduction	Xe lamp (300 mW cm ⁻² with UV-cut 420)	1.0		[98]
	BiVO ₄	Microwave-assisted solvothermal	125 W lamp	1.5		[107]
	ZDC/T	Hydrothermal, coordination-driven self-assembly	150 W AM 1.5 solar simulator, 100 mW.cm ⁻²	3.406 μmol in 6 h	51.8	[97]
Acetone-isopropanol	CTGN	Hydrothermal	Mercury lamp (160 W)	113 (acetone) 171 (isopropanol)		[101]
	Pt/GaN	Surface organometallic chemistry	300 W Xe lamp	53 (acetone) 113 (isopropanol)		[108]
Butanol	CeO ₂ /Cu ₂ O	Hydrothermal, in situ growth	Simulated solar light (100 mW cm ⁻²)	34	59	[99]

* This information is taken from Supplementary Information of respective references.

4. Key Challenges and Future Perspectives

4.1. Challenges

Despite notable advances, the selective formation of C₃₊ hydrocarbons and oxygenates from CO₂ remains one of the most demanding goals in solar-driven catalysis. A central challenge arises from the intrinsic difficulty of stabilizing the reactive intermediates required for dual C–C coupling. Unlike C₁ or C₂ pathways, which involve only one coupling step, C₃₊ formation requires the sequential generation and preservation of species such as *CHOCO, *CH₂OCO, and *CH₂OCOCO. These intermediates are short-lived and often desorb, over-hydrogenate, or undergo side reactions before coupling can occur. For example, the Cu–Ti–VO/TiO₂–SL system only achieves propane formation when *CHOCO and *CH₂OCO coexist at Cu–Ti–VO sites, yet the overall rate remains extremely low because maintaining these intermediates at room temperature is kinetically challenging [94]. Similar limitations appear in COF-based catalysts, where the second C–C coupling step frequently becomes the rate-determining barrier, underscoring the mechanistic complexity unique to C₃₊ chemistry [96,102,104,105].

A second major obstacle is the structural instability of the active sites required for long-chain formation. Many of the most promising C₃₊-selective catalysts rely on O_Vs, single-atom sites, or asymmetric multi-metal motifs, all of which are highly dynamic under illumination and heat. Vacancy-rich CuWO₄ gradually loses its Cu–Cu^{δ+}–W^{δ+} asymmetry as vacancies heal during aqueous operation, while Ag/CeO₂ suffers from Ag aggregation and Ce³⁺ re-oxidation, both of which shift selectivity away from acetone [95,98]. Photothermal systems such as Pt/GaN and BZCY532 experience surface reconstruction, vacancy loss, or nanoparticle sintering under elevated temperatures [106,108]. Because C₃₊ formation requires long reaction sequences, even subtle structural changes can redirect

the mechanism toward C_1 or C_2 products, making stability a disproportionately severe challenge for long-chain pathways.

Competition with hydrogen evolution and over-hydrogenation further complicates C_{3+} selectivity. Multi-carbon formation requires a delicate balance between $^*CO$, $^*CHO$, and $^*CH_x$ intermediates, yet many catalysts, especially Cu-based and photothermal systems, favor HER or rapid hydrogenation to methane. In WO_3/ZnS , proton deficiency at elevated temperatures suppresses the hydrogenation steps needed for C_3 formation, while in $OsCoTe_2$, strong $^*CO$ adsorption risks poisoning unless hydrogenation is precisely controlled [100,103]. COF systems also struggle with proton management, leading to incomplete coupling or premature termination at C_2 [96,102,104,105]. These competing pathways are far more problematic for C_{3+} products because the reaction sequence is longer and more sensitive to proton availability.

Finally, a significant mechanistic knowledge gap persists. While C_1 and C_2 pathways are relatively well understood, the formation and evolution of C_{3+} intermediates remain poorly resolved. Only a few systems, such as Cu–Ti–VO/TiO₂-SL, MC-COF, and CuWO₄, have provided operando evidence for intermediates like $^*CHOCO$ or $^*CH_2OCOCO$ [94,95,102]. The roles of dual-site cooperativity, vacancy dynamics, and photothermal gradients remain unclear, and the kinetics of the second C–C coupling step are still largely unknown. Without deeper mechanistic insight, catalyst development for C_{3+} products remains empirical and difficult to generalize.

4.2. Future Perspectives

Future progress in solar-driven C_{3+} formation will depend on integrating mechanistic understanding with rational catalyst design. One promising direction is the deliberate engineering of dual-site or asymmetric active centers that can simultaneously stabilize C_1 and C_2 intermediates. Systems, such as Ag–O–Ce³⁺, Cu–Cu^{δ+}–W^{δ+}, and Cu–Ti–VO demonstrate that frustrated Lewis pairs, multi-metal ensembles, and single atom/cluster interfaces can create the charge asymmetry needed to stabilize $^*CHOCO$ and $^*CH_2OCOCO$ while suppressing over-hydrogenation [94,95,98]. Designing catalysts that intentionally incorporate such motifs, whether through heterometallic interfaces, vacancy modulation, or COF based donor–acceptor channels, may provide a path toward more reliable C_{3+} selectivity.

Stabilizing vacancies and single-atom sites under operating conditions is another essential direction. Strategies such as aliovalent doping, lattice confinement, covalent anchoring of single atoms, and the use of photothermal resistant supports (e.g., nitrides, carbides) could prevent vacancy healing, metal aggregation, and surface reconstruction. These approaches are particularly important for photothermal systems, where high temperatures accelerate structural degradation.

Controlling proton and electron flux is equally critical. C_{3+} formation requires precise PCET management, and future catalysts should incorporate features that regulate proton availability and charge migration. Proton trapping clefts in DA-COF, hydrophobic surface engineering in DF-TP-COF, plasmonic hot carrier injection in $OsCoTe_2$, and photothermal modulation of local temperature all represent promising strategies for suppressing HER and promoting selective C–C coupling [103–105].

A deeper mechanistic understanding of C_{3+} formation requires experimental tools capable of tracking charge carriers, surface intermediates, and active-site dynamics under realistic reaction conditions. While conventional steady-state characterization provides valuable structural information, it cannot capture the ultrafast and transient processes that govern multi-electron C–C coupling. Recent advances in time-resolved, in situ, and operando spectroscopies now offer powerful capabilities for probing these processes with unprecedented temporal and spatial resolution.

Time-resolved X-ray spectroscopies, including X-ray absorption, X-ray emission, and X-ray scattering, provide direct insight into oxidation-state changes, coordination environments, and structural rearrangements occurring during photocatalysis. With femtosecond to nanosecond resolution, these techniques can track the formation and decay of photoexcited charge carriers and identify transient metal–ligand configurations that stabilize key intermediates. Their ability to probe buried interfaces makes them particularly valuable for studying heterojunctions and photothermal catalysts, where subsurface vacancy migration and metal–support interactions strongly influence C_{3+} selectivity [109,110].

Complementary information is provided by time-resolved optical spectroscopies, such as transient infrared, transient absorption, and time-resolved Raman. These techniques directly monitor vibrational and electronic signatures of surface-bound intermediates, enabling real-time tracking of $^*CO$, $^*CHO$, $^*CH_2$, $^*CHOCO$, and $^*CH_2OCOCO$ species under working conditions [111–113]. As C_{3+} formation requires the sequential stabilization of multiple intermediates, transient infrared and transient absorption are uniquely suited to identifying the rate-determining steps and mapping the evolution of $C_1 \rightarrow C_2 \rightarrow C_3$ intermediates.

Time-resolved electron paramagnetic resonance provides an additional dimension of mechanistic insight by detecting spin-state changes associated with trapped electrons, radical intermediates, and metal-center redox cycling [114]. This is particularly important for systems such as Cu-based catalysts, COFs, and vacancy-rich oxides, where spin-polarized states play a central role in directing C–C coupling pathways.

Together, these techniques form a complementary toolbox for elucidating the dynamic processes that govern C_{3+} selectivity. Categorizing and integrating these methods into future studies will enable researchers to correlate active-site structure with intermediate evolution, identify transient species that are inaccessible by steady-state measurements, and ultimately design photocatalytic and photothermal systems with improved long-chain product selectivity.

5. Conclusions

Solar-driven photocatalytic and photothermal CO_2 conversion represents one of the most promising strategies for achieving carbon neutrality through direct solar energy utilization. Significant advances have been made in the past few years, with notable progress in C_{3+} product formation, defect-engineered catalysts, and bifunctional oxide–zeolite systems that enable complex C–C coupling. Photocatalytic systems have demonstrated controllable selectivity through vacancy engineering, heterojunction formation, and single-atom site engineering, while photothermal systems have shown that light-induced heating and hot-carrier effects can accelerate tandem RWGS–FT pathways toward higher hydrocarbons. However, the field remains at an early stage of development. Fundamental kinetic and thermodynamic constraints still limit the selective formation of C_{3+} products, and the gap between laboratory demonstrations and scalable implementation remains wide. Continued innovation in catalyst architecture, mechanistic understanding, and device integration is required to achieve practical solar-to-fuel efficiencies. Looking ahead, combining material innovation with system-level engineering (including advanced photothermal reactors, persistent photocatalytic systems, and hybrid solar–electrochemical setups) will be crucial. By bridging molecular-level control and process-scale design, solar-driven CO_2 conversion can evolve from scientific discovery to a cornerstone technology for sustainable fuel and chemical production.

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Abbreviations

The following abbreviations are used in this manuscript:

PC	Particulate photocatalysis
PEC	Photoelectro-chemical
PV-EC	Photovoltaic-electrochemical
PT	Photothermal
RWGS	Reverse water–gas shift
FT	Fischer–Tropsch
O _{Vs}	Oxygen vacancies
BZCY532	Perovskite catalyst BaZr _{0.5} Ce _{0.3} Y _{0.2} O _{3–δ}
TSSs	Topological surface states
COFs	Covalent organic frameworks
CTGN	Cu-doped titanate nanosheets coupled with graphene oxide
PA	Propionic acid
CWO-O _{Vs}	CuWO ₄ -based photocatalysts with engineered O _{Vs}

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