

Review

Microenvironment Engineering: A Crucial Strategy for Enhancing C₂+ Products in CO₂ Photoreduction

Zekai Zhang ¹, Stéphane Abanades ² , Fengping Yu ^{3,*} and Hanfeng Lu ^{1,*}

¹ Institute of Chemical Reaction Engineering, College of Chemical Engineering, Zhejiang University of Technology, Chaowang Road 18, Hangzhou 310014, China; zzk@zjut.edu.cn

² Processes, Materials, and Solar Energy Laboratory, PROMES-CNRS (UPR 8521), National Center for Scientific Research (CNRS), 7 Rue du Four Solaire, 66120 Font-Romeu, France; stephane.abanades@promes.cnrs.fr

³ Zhejiang Zheneng Technology & Environmental Protection Group Co., Ltd., Huaxing Road 99, Hangzhou 310012, China

* Correspondence: yufengping@zjenergy.com.cn (F.Y.); luhf@zjut.edu.cn (H.L.)

Abstract

Photocatalytic CO₂ reduction to high-value-added C₂+ products is a practical route from an economic viewpoint for advancing the industrialization of CO₂ conversion. Despite significant progress in catalyst modification in recent years (such as defect engineering, heterostructure construction, and single-atom modification), the generation of C₂+ products still faces challenges due to the slow kinetics of multi-electron reactions and the high thermodynamic barrier for C-C coupling. Moreover, the severely imbalanced molar ratio of CO₂ to H₂O in the traditional liquid-phase reaction systems exacerbated the challenge to the unfavorable situation. This article summarizes various strategies to improve the yield of C₂+ products through the regulation of reaction environments, including: (1) increasing the partial pressure of CO₂ to enhance its solubility; (2) using alternative solvents like ionic liquids to reduce water content; (3) transitioning the reaction system from liquid phase to gas phase; (4) designing a three-phase (gas–liquid–solid) interface or floating photocatalysts to optimize reactant transfer and local concentration; (5) utilizing photo-thermal synergistic effects to enhance the reaction temperature and efficiency under concentrated light. It also discusses the role of different reactor designs in improving the reaction environment. Finally, it emphasizes that future research should pay more attention to the optimization of the reaction environment engineering in addition to catalyst design, providing new perspectives for achieving efficient and highly selective C₂+ products in CO₂ photoreduction.

Keywords: CO₂ photoreduction; solar fuel; CO₂ to H₂O molar ratio; reaction environment; C₂+ products



Academic Editor: Lenzi Giane Gonçalves

Received: 13 February 2026

Revised: 10 March 2026

Accepted: 16 March 2026

Published: 19 March 2026

Copyright: © 2026 by the authors.

Licensee MDPI, Basel, Switzerland.

This article is an open access article distributed under the terms and conditions of the [Creative Commons Attribution \(CC BY\)](https://creativecommons.org/licenses/by/4.0/) license.

1. Introduction

As a greenhouse gas, the atmospheric CO₂ level was primarily regulated by natural phenomena in the long history. However, since the 18th century, the utilization of fossil fuels has significantly increased CO₂ emissions and exacerbated the trend of global warming. Consequently, there is a growing need for human beings to actively participate in the carbon cycle process to help maintain the CO₂ balance [1]. Photocatalytic reduction in CO₂, mimicking plant photosynthesis, can transform CO₂ with H₂O into hydrocarbons with the aid of a photocatalyst and solar energy, which has given high expectations. Numerous studies have been reported in the past decades, and various significant progresses have

been achieved [2–6]. Unfortunately, a closer look reveals that many of these advances are not substantial enough. The solar energy conversion to chemical products efficiency is often much lower than that achieved by plant photosynthesis (0.4%), and the product yield is often at dozens of $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ [7–10]. In addition, these products are mainly C1 compounds with lower economic values, while today it is expected that the yield of C₂+ products is increased with higher economic value [11,12]. The efforts to mitigate one challenge just create conditions conducive to the emergence of another equally pressing issue. Given the considerable intellectual effort invested in this field, it is surprising that such challenges persist for a long period, although many complex problems have been successfully addressed.

Many researchers have recognized this issue and have published insightful reviews in recent years [13–16]. Wu et al. [17] considered that the high energy barrier of the C–C coupling process is the main challenge and summarized various strategies. A series of modification strategies, i.e., vacancy engineering, doping engineering, loading engineering, and heterojunction engineering, have been applied to construct charge-polarized active sites for enhancing C–C coupling efficiency. As noted by Zhu et al. [18], the intrinsic complexity of improving C₂+ selectivity stems from the multi-electron-coupled proton transfer steps and C–C coupling of reaction intermediates involved in the process. Meanwhile, the core factors governing C₂+ product selectivity have also been systematically summarized, which cover vacancy engineering, co-catalyst loading, doping engineering, as well as the surface plasmon resonance effect. Li et al. [19] investigated the potential pathways having important implications on improving the selectivity of C₂+ products. Band structure, fast charge separation and transfer of photoexcited carriers, and stabilizing the C1 intermediates play a key role in facilitating the C–C coupling, which is the rate-determining step for photocatalytic reduction in CO₂ to produce C₂+ products. Cui et al. [20] pinned down the key factors or parameters influencing the generation of C₂ products during CO₂ hydrogenation. The construction of different proportions of electron states on the surface of the employed catalysts, the creation of asymmetric double active sites, the creation of O vacancies, and surface defects with rich local electrons have been performed to increase C₂+ products. Meanwhile, all of them admitted the importance of modern characterization techniques for understanding the mechanism of C₂+ product formation.

These reviews highlight several important aspects. First, the formation mechanism of C₂+ products is not fully understood yet, while C–C coupling is considered to be one of the most critical steps for C₂+ product formation; second, research attention is more focused on photocatalysts but less on the reaction environment. While for a catalytic reaction process, both aspects are very important. It is necessary to consider the influence of reaction conditions or microreaction environment, especially the molar ratio of CO₂ to H₂O, on the reaction.

It is well known that the CO₂ photoreduction mimics nature's photosynthesis, including the reaction environment. The typical CO₂ photoreduction reaction environment at present is as follows: under room temperature and atmospheric pressure, a small amount of catalyst particles or a disk is placed into a vessel filled with liquid water, CO₂ gas is purged into the water with stirring, and the exit gas or retained liquid is analyzed after a period of reaction time. Meanwhile, it is a simple fact that the CO₂ photoreduction with H₂O is a two-reactant reaction. The CO₂ reduction rate equation can be written following the L-H mechanism [21],

$$-r_{\text{CO}_2} = k(T) \frac{K_I \sqrt{I}}{1 + K_I \sqrt{I}} \frac{P_{\text{H}_2\text{O}} P_{\text{CO}_2}}{\left(1 + K_{\text{H}_2\text{O}} P_{\text{H}_2\text{O}} + K_{\text{CO}_2} P_{\text{CO}_2}\right)^2} \quad (1)$$

where

I —light intensity;

$k(T)$ —rate constant;

K_I —light adsorption constant,

K_{H_2O} —adsorption constant of water;

K_{CO_2} —adsorption constant of CO_2 ;

P_{H_2O} —partial pressure of water vapor, kPa;

P_{CO_2} —partial pressure of CO_2 , kPa.

This equation represents a rate law with an influence of parameters on the reaction rate. The concentration and ratio of CO_2 and H_2O reactants may have a significant effect. When examining the typical environment of artificial photosynthesis, it appears that it cannot provide a suitable CO_2 to H_2O molar ratio. Clearly, the bubbled CO_2 in the liquid water is a typical dilute solution. For a 1 mol/L water solution, the ratio of solute to water is about 55.6. And for a real CO_2 solution, the situation is more extreme: the solubility of CO_2 is about 3.3 mmol/L at 25 °C and 0.1 MPa, so the molar fraction of CO_2 would decrease to

$$y_{CO_2} = \frac{C_{CO_2}}{C_{H_2O} + C_{CO_2}} = \frac{3.3 \times 10^{-3}}{55.6 + 3.3 \times 10^{-3}} = 5.9 \times 10^{-5} \quad (2)$$

where y_{CO_2} is the molar fraction of CO_2 in the system, and c represents concentration. An excessive amount of water in the system not only reduces the reaction rate of CO_2 photoreduction but also provides an overabundance of hydrogen atoms. The extremely low concentration of carbon atoms from dissolved CO_2 significantly reduces the collision probability between carbon-containing intermediates, thus strongly inhibiting the C-C coupling reaction and the subsequent formation of C_2+ products. The reaction chance between two carbon atoms to form C_2+ products is surely being suppressed. It is commendable that some researchers have made such progress in the reaction rate and C_2+ products under such unfavorable conditions. If the reaction conditions are optimized, further improvements may be expected. A. G. Variar [22] has summarized various operational parameters that may influence the CO_2 photoreduction process. Some of them can change the CO_2/H_2O molar ratio and reaction environment:

1. Increase the CO_2 solubility in the water;
2. Increase the CO_2 partial pressure;
3. Reduce the water content using other solvents, e.g., ion liquids;
4. Change the reaction phase into the gas phase, and even increase the temperature;
5. Remove water totally; it will change to CO_2 dissociation and yield pure CO.
6. Remove CO_2 totally, and it will change to water splitting and yield pure H_2 .

Based upon the classification, here we collected the main reports about C_2+ products production in the last decade (2015–2025). Before the detailed discussion, the following section briefly reviews the fundamental and representative results related to C_2+ products.

2. Fundamentals and Data Overview of C_2+ Products in the Literature

CO_2 photoreduction originates from the photosynthesis process in plants, which consists of the conversion of solar energy into chemical energy that can be utilized for intracellular biochemical reactions, a process that yields over 100 billion tons of dry biomass in diverse carbonaceous compounds each year [23]. As a cornerstone of terrestrial life, photosynthesis has been the subject of intensive research endeavors. These studies have aimed to decipher both the underlying mechanisms of its discrete sub-processes and the regulatory logic of the integrated photosynthetic pathway, thereby laying a solid

theoretical foundation for the development of CO₂ photoreduction in the name of artificial photosynthetic systems.

In essence, natural photosynthesis can be delineated into three core stages: (i) light-harvesting, where photon energy is captured and converted into energetic electrons and holes; (ii) charge transfer, during which these electrons drive the synthesis of chemical energy carriers and facilitate the release of molecular oxygen; and (iii) charge utilization, which stores the accumulated chemical energy in the form of stable carbon-containing compounds [17].

Inspired by this natural paradigm, artificial photosynthesis typically encompasses three critical steps: light harvesting, charge separation and migration, and catalytic reactions. In the initial light-harvesting phase, photocatalysts absorb incident photons with energy equal to or exceeding their bandgap, leading to the generation of electron–hole pairs [24–26]. Subsequently, the photogenerated electrons and holes migrate separately to the active sites on the surface of the photocatalyst particles. In the final catalytic step, the photogenerated electrons mediate the reduction of CO₂ into value-added carbon-based fuels, while the photogenerated holes oxidize water molecules to produce molecular oxygen.

Although the process can be emulated, artificial photosynthesis encounters difficulties in product activity and selectivity. Photosynthesis readily produces the big molecular sugars (Figure 1) and other multi-carbon compounds via the function of chlorophyll, while artificial photosynthesis often yields only C1 compounds from partially reduced product HCOOH to fully reduced product CH₄, etc. The common explanation is that the reduction in CO₂ is a complex process. Researchers have now only learned to generate electrons on the semiconductors based upon the photoelectron effect, while the mechanisms of using the electrons to yield multi-carbon products have not been well understood yet (Figure 2) [27]. A deeper knowledge is still waiting to be found in nature's photosynthesis.

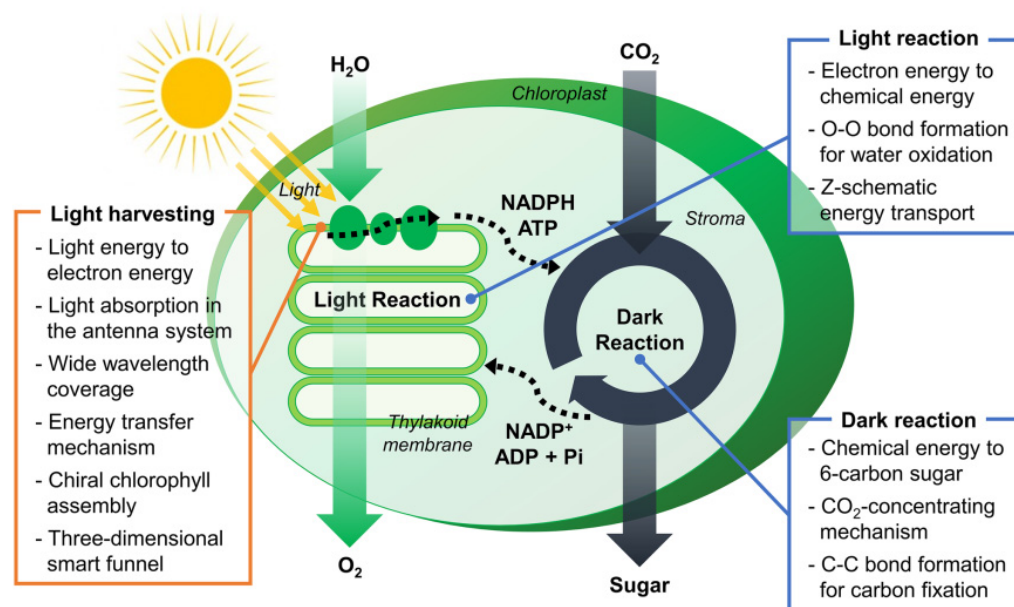


Figure 1. Schematic description of the biological photosynthesis and scientific lessons from three key processes (light harvesting, light reaction, and dark reaction) of the whole photosynthetic pathway. Ref. [23] Copyright 2020 Springer.

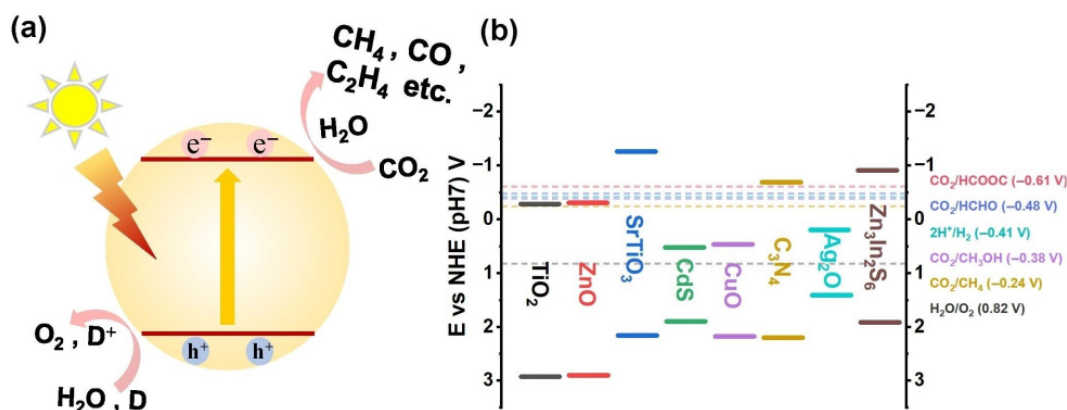


Figure 2. (a) Schematic of the photocatalytic mechanism. (b) VB and CB potentials of typical semiconductors and the potentials for some CO₂ reduction reaction (CO₂RR) and oxidation potential for H₂O. Ref. [24] Copyright 2025 Wiley.

In the very recent years, many researchers have succeeded in obtaining C₂+ products; representative examples are listed in Tables 1–4. Remarkable progress has been achieved in C₂+ product formation, especially when a reductant other than H₂O (C₂H₆ or H₂) is used. In 2020, the knowledge was still restricted to whatever factor that increases the accumulation of electrons and protons favors the formation of C₂+ products [28]. After 5 years, there is greater confidence in the formation mechanism, and the stability of the C1* intermediate and subsequent C-C coupling are recognized as the key steps [13–20]. Of course, searching for compatible catalysts and reaction conditions is still one of the breakthrough points in the following research.

Table 1. Data collection of C₂+ products formation in the gas phase.

Photocatalyst	C ₂ + Products	Products Rate [μmol·g ⁻¹ ·h ⁻¹]	Reaction Conditions	Ref.
MWCNTs/TiO ₂	69.7% CH ₃ CH ₂ OH	29.9	15 W UV lamp @ 365 nm, H ₂ O:CO ₂ = 5:1 (mol:mol), 5 h	[29]
15 wt% Cu/GO	CH ₃ CHO	3.88	halogen lamp, 100 mW/cm ² , moist CO ₂ , 2 h	[30]
Pt-G/defect-induced TiO ₂	22.9% C ₂ H ₆ (STF = 2.7%)	11	sun simulated light (100 mW/cm ²), moist CO ₂ , under continuous flow	[31]
Ni/TiO ₂ (IV)	100% CH ₃ CHO		300 W halogen lamp, moist CO ₂	[32]
Au/TiO ₂	27% C ₂ H ₆	/	Hg lamp @ 254 nm, 20 mW/cm ² , moist CO ₂	[33]
CuO _x @p-ZnO	C ₂ H ₄ 32.90%	2.7	300 W Xe lamp (100 mW cm ⁻²), 5 mg photocatalyst, water vapor saturated CO ₂ gas, 0.5 MPa	[34]
NiCo ₂ S ₄	C ₂ H ₄ 57.10%	13.42	a 300 W Xe lamp, 0.5 mL water with 100 kPa of CO ₂	[35]
V ₂ SAI ₄₀	C ₂ H ₄ 72.90%	44.3	300 W Xe arc lamp, ~4–5 mg photocatalyst, CO ₂ gas (ambient) + 0.4 mL H ₂ O	[36]
S _x CZ50	C ₂ H ₄ 12.10%	0.8	300 W Xe lamp (λ ≥ 420 nm), 20 mg photocatalyst, CO ₂ gas (80 kPa) + 2 mL H ₂ O	[37]

Table 1. Cont.

Photocatalyst	C ₂ + Products	Products Rate [$\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$]	Reaction Conditions	Ref.
C-In ₂ S ₃	C ₂ H ₄ 50%	472.7	300 W Xe lamp, CO ₂ was bubbled into the chamber with 0.1 mL water and reached 1 atm	[38]
Au–Cu alloy NPs	C ₂ H ₄ 11.90%	369.8	300 W Xenon-arc lamp with AM 1.5 G filter, 90 kPa CO ₂ + 0.15 mL H ₂ O	[39]
Au@TiO _x –Co(650)	C ₂ H ₆ 25.10%	58.65	a 300 W Xe lamp, water vapor bubbled with 0.12 MPa CO ₂	[40]
Bi ₂ WO ₄ /TiO ₂	C ₂ H ₆ 50.30%	6.1	a 300 W Xe lamp, CO ₂ and water vapor with a molar ratio of 7.25 (CO ₂ :H ₂ O)	[41]
Cu/TiO ₂	C ₂ H ₆ NA	267.60	a 300 W Xe lamp, 1.0 mL of H ₂ O and 1.0 MPa CO ₂ gas	[42]
Au ₂ /RP	C ₂ H ₆ 96%	1.32	a 300 W Xe lamp, CO ₂ and H ₂ O vapor generated by HCl + NaHCO ₃	[43]

N/A indicates that the data were not reported in the original paper.

Table 2. Data collection of C₂+ product formation in the liquid phase.

Photocatalyst	C ₂ + Products	Production Rate [$\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$]	Reaction Conditions	Ref.
LHCII/Rh:P25 TiO ₂	78.4% CH ₃ CHO + 5.9% CH ₃ OCHO	3.2	Xe lamp @362 mW/cm ² , aqueous dispersion CO ₂ saturated, 6 h	[44]
(200) oriented Cu ₂ O/G	CH ₃ CH ₂ OH	/	28.3 mW/cm ² lamp @ 254 nm, liquid-phase continuous flow under the Taylor regime	[45]
PtCu/TiO ₂ NTs	14.3% C ₂ H ₄ + 7.1% C ₂ H ₆	0.33 mL g ^{−1} h ^{−1} + 0.47 mL g ^{−1} h ^{−1}	100 mW/cm ² , CO ₂ (0.998% in N ₂) flow through H ₂ O	[46]
CdS/Cu-TNTs	31.1% C ₂ H ₄ + 17.9% C ₂ H ₆ + 1.3% C ₃ H ₆ + 0.5% C ₃ H ₈	$\mu\text{L g}^{-1} \text{h}^{-1}$ level	450 W Xe lamp ($\lambda > 420 \text{ nm}$), aqueous dispersion, CO ₂ saturated, 5 h	[47]
CuPd–MoO ₂	CH ₃ CH ₂ OH	130.4	300 W Xe lamp, aqueous dispersion CO ₂ saturated, 10 h	[48]
RP-BMO(21)	C ₂ H ₅ OH N/A	51.8	450 W Xe lamp ($\lambda \geq 400 \text{ nm}$), 5 mg photocatalyst in 20 mL H ₂ O (sat. CO ₂)	[49]
Au–CeO ₂	C ₂ H ₆ 93.10%	11.07	a 300 W Xe lamp, 5 mL water with 80 kPa of CO ₂	[50]
Cu–TiO ₂ /GO	CH ₃ CH ₂ OH	232.51	160 W Mercury lamp, CO ₂ bubble in water	[51]
AuCu/g-C ₃ N ₄	CH ₃ CH ₂ OH 93.10%	890	a 300 W Xe lamp, 100 mL water and 0.8 MPa CO ₂ , 160 °C	[52]

Table 2. Cont.

Photocatalyst	C ₂ + Products	Production Rate [$\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$]	Reaction Conditions	Ref.
STO/Cu@Ni/TiN	CH ₃ CH ₂ OH 79%	23.1	a 300 W Xe lamp, 10 mL water	[53]
Cu ₂ O/Pt/NH ₂ -MIL-125(Tl)	CH ₃ CH ₂ OH	239.49	a 300 W Xe lamp, 100 mL water and 0.1 MPa CO ₂	[54]
Cu/WO ₂	CH ₃ COOH 67%	2.87	a 300 W Xe lamp, 20 mL water and 0.1 MPa CO ₂	[55]
In ₂ O ₃ /InP	CH ₃ COOH 96%	9.67	a 300 W xenon lamp with a UVCUT-420 nm filter, 50 mg catalysts in 100 mL distilled water with 80 kPa CO ₂	[56]
WO ₃ •0.33H ₂ O	CH ₃ COOH 85%	9.4	a solar simulator (PEC-L11), 0.05g catalyst in 150 mL DI water with 50% CO ₂ at 4 °C	[57]
ZnGeO ₄	CH ₃ COOH 29.95%	12.7	a 300 W xenon lamp, 0.03 vol% CO ₂ / Ar mixture, 10 mg catalyst in 12 mL DI water	[58]
NiCo-TiO ₂	CH ₃ COOH 71%	22.6	/	[59]
Cu ₂ O/Ti n-type B	Methyl formate 4.00%, CH ₃ COOH 16.10%, Oxalic acid 1.40%	N/A	300 W Xe lamp (AM 1.5 G, 135 mW cm ⁻²) Water-saturated CO ₂ gas (atmospheric pressure)	[60]

Table 3. Data collection of C₂+ products formation in the liquid phase with additives.

Photocatalyst	C ₂ + Products	Production Rate ($\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$)	Reaction Conditions	Ref.
Pt/TaON	89.5% CH ₃ CH ₂ OH + 10.5% CH ₃ CHO	2.03 0.52	100 mW/m ² ($\lambda > 420$ nm), NaHCO ₃ aqueous solution CO ₂ saturated	[61]
Nafion/Pd-TiO ₂	6.4% C ₂ H ₆	/	300 W Xe lamp ($\lambda > 300$ nm), NaHCO ₃ aqueous dispersion CO ₂ saturated, 5 h	[62]
Au NPs	40% C ₂ H ₆		($\lambda > 488$ nm, 750 mW/cm ²), moist CO ₂ using isopropanol as sacrificial	[63]
AuPd/(101) TiO ₂	7% C ₂ H ₆ + 7% C ₂ H ₄	14.3	300 W Xe lamp, NaHCO ₃ aqueous dispersion with saturated CO ₂	[64]
TCNT2	C ₂ H ₅ OH 100%	87.7	300 W Xe lamp ($\lambda \geq 420$ nm) 100 mg photocatalyst in 100 mL 0.1 M KHCO ₃ + 0.1 M Na ₂ SO ₃ (sat. CO ₂)	[65]
Au/NT10	C ₂ H ₅ OH 13.60%	480	Solar simulator (150 mW cm ⁻²) 50 mg photocatalyst in 10 mL 10 wt.% TEOA + 60 mg NaHCO ₃ (sat. CO ₂)	[66]
2.5Cu/ZnV ₂ O ₄	C ₂ H ₅ OH 24.20%	1.58	300 W Xe lamp, 40 mg photocatalyst in 40 mL 0.1 M Na ₂ SO ₃ + 0.1 M NaOH (sat. CO ₂ , 0.2 MPa, 80 °C)	[67]
Bi@Bi ₂ MoO ₆	C ₂ H ₅ OH 92.50%	17.93	300 W Xe lamp, 50 mg photocatalyst in 30 mL 0.17 M NaHCO ₃ (sat. CO ₂)	[68]

Table 3. Cont.

Photocatalyst	C ₂ + Products	Production Rate (μmol·g ⁻¹ ·h ⁻¹)	Reaction Conditions	Ref.
PVP-coated Au NPs	C ₂ H ₆ 42.10%	N/A	300 W Xe lamp (λ ≥ 400 nm, 300 mW cm ⁻²) 10 vol% isopropanol (sat. CO ₂)	[69]
Au NPs	C ₂ H ₄ 16.00%, C ₂ H ₂ 14.80%, C ₂ H ₆ 13.50%, C ₂ H ₈ 8.40%	N/A	Laser (532 nm, 1 W cm ⁻²) 5 mol% EMM-BF ₄ (sat. CO ₂)	[70]
Cu scaffold/CsPbBr ₃	C ₂ H ₄ 34.20%	9.3	300 W Xe lamp (AM 1.5 G) 15 mL ethyl acetate + 10 μL H ₂ O + CO ₂ gas	[71]
CuAGS/PCN	C ₂ H ₄ 53.20%	30.51	300 W Xe lamp 45 mL water with 5 mL triethanolamine (TEOA) purged with CO ₂ gas for 1 h	[72]
NiAl-Fe-TCPP	C ₂ H ₄ 93.40%	24.7	300 W Xe lamp, [Ru(bpy) ₃]Cl ₂ ·6H ₂ O (0.005 mmol), LDHs (10 mg), and solvent [10 mL in total, CH ₃ CN/TEOA/H ₂ O = 3:1:1 (volume ratio)]	[73]
CsPbBr ₃	C ₂ H ₄	9.3	a 300 W Xe lamp, 5 mL of ethyl acetate solvent with 10 μL of purified water	[71]
Re-bpy/PTF(Cu)	C ₂ H ₄ 25%	73.2	a 300 W Xe lamp, 5 mL MeCN/TEOA (1/1) containing 10 mg of the as-obtained PTF(Cu) and 10 mg of the Re-bpy, 0.1MPa CO ₂	[74]
C@Fe ₂ C/TiO	C ₂ H ₄ NA	35.48	a 300 W Xe lamp, 90 mL water and 10 mL TEOA with 70 kPa of CO ₂	[75]
MoS ₂ @COF-15	C ₂ H ₆ 83.80%	56.2	a 300 W Xe lamp, [Ru(bpy) ₃]Cl ₂ ·6 H ₂ O(5.0 mg), acetonitrile (3.0 mL), water (1.0 mL), and triethanolamine (1.0 mL)	[76]
Zn-TC	C ₂ H ₆ 14.45%	10.27	a 300 W Xe lamp, 90 mL water and 10 mL TEOA, 80 kPa CO ₂	[77]

Table 4. Data collection of C₂+ products with reductants other than H₂O.

Photocatalyst	C ₂ + Products	Production Rate [μmol·g ⁻¹ ·h ⁻¹]	Reaction Conditions	Ref.
CoFeAl-LDH	35% C ₂ +	/	300 W Xe lamp, CO ₂ /H ₂ /Ar = 15/60/25, 0.18 MPa, 2 h	[78]
Pd/TiO ₂	C ₂ H ₄ 95.42%	230.5	300 W Xe lamp, CO ₂ /Ar and C ₂ H ₆ in a ratio of 1:1 (308 K, 0.2 MPa)	[79]
Ag/TiO ₂	C ₂ H ₄ NA	686	84.2 mW/cm ² Xenon lamp, CO ₂ /CH ₄ / Ar = 7.5/7.5/85 to 2 MPa	[80]
ZnGa ₂ O ₄	C ₂ H ₆ 53%	1315.3	a 300 W Xe lamp, 4 mL CH ₄ gas and a certain volume of oxygen	[81]

Table 4. Cont.

Photocatalyst	C ₂₊ Products	Production Rate [$\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$]	Reaction Conditions	Ref.
Au-ZnO/TiO ₂	C ₂ H ₆ 90%	5000	a 300 W Xe lamp, a total flowing rate of 70 mL min ^{−1} (gas ratio CH ₄ /air 69/1)	[82]
Na/Co@C	39.5% C ₂ H ₇ (C ₂ –C ₆) + 6.5% CH ₃ CH ₂ OH	/	1000 W Xe light 24 kW/cm ² , CO ₂ /N ₂ / H ₂ = 20/20/100 (2.8 bar)	[83]

In the listed examples in Tables 1–4, the catalyst systems cover a wide range, and the reaction environments are largely different. The results exhibit distinct performance in gas-phase or liquid-phase systems and liquid-phase systems with additives, while the replacement of H₂O with alternative reductants further reshapes the yield and selectivity of C₂₊ products. These differences are essentially the result of the synergistic effects of reaction microenvironment and catalysts.

Gas-phase systems (Table 1) are dominated by hydrocarbon C₂₊ products (C₂H₄, C₂H₆), with partial systems achieving ultra-high C₂₊ yield and specific selectivity: for example, C-In₂S₃ yields C₂H₄ at 472.7 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ with 50% selectivity, and Au–Cu alloy NPs reach a C₂H₄ yield of 369.8 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$, while Au₂/RP even achieves 96% C₂H₆ selectivity. The superiority in hydrocarbon production is attributed to the optimized CO₂/H₂O molar ratio (water exists in the form of trace vapor, avoiding H₂O excess), the enhanced mass transfer efficiency of gas-phase reactants on the catalyst surface, and the reduced competitive adsorption of H₂O on active sites, which facilitates the C–C coupling of carbon-containing intermediates and the formation of hydrocarbon products with low oxygen content. In contrast, liquid-phase systems (Table 2) are prone to generate oxygen-containing C₂₊ products (CH₃CH₂OH, CH₃COOH), with representative performances such as AuCu/g-C₃N₄ achieving an ethanol yield of 890 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ (93.10% selectivity) and In₂O₃/InP realizing 96% CH₃COOH selectivity. The liquid–water environment promotes the introduction of oxygen-containing functional groups, while the severe excess of H₂O in liquid-phase systems results in a very low CO₂/H₂O molar ratio, which may limit the collision probability of carbon-containing intermediates and thus restrict the further improvement of C₂₊ yield in most liquid-phase systems.

The introduction of additives in liquid-phase systems (Table 3) effectively modulates the reaction microenvironment, which can compensate for the defects of pure liquid–water systems in CO₂ solubility and thus vary the yield and selectivity of C₂₊ products. Common additives include inorganic salts (NaHCO₃, Na₂SO₃), organic sacrificial agents (TEOA, isopropanol), and organic solvents (ethyl acetate, acetonitrile). NaHCO₃ can increase the total carbon content in the solution and adjust the system pH to reduce the competitive adsorption of H₂O; TEOA and isopropanol act as sacrificial electron donors to inhibit the recombination of photogenerated electron-hole pairs. Ionic liquids and organic solvents (e.g., ethyl acetate) reduce the water content in the system, optimize the CO₂/H₂O molar ratio, and enhance CO₂ adsorption. Notably, the effect of additives on C₂₊ performance is not universal: some systems only improve the yield but not the selectivity, and some systems show limited promotion.

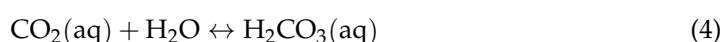
The performance is significantly higher than that of H₂O-based systems with the replacement of alternative reductants (Table 4). The alternative reductants mainly include H₂, C₂H₆, CH₄, etc., and the representative systems show ultra-high C₂₊ yields. Au-ZnO/TiO₂ achieves a C₂H₆ yield of 5000 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ with 90% selectivity, and ZnGa₂O₄ yields C₂H₆ at 1315.3 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ (53% selectivity). The fundamental reason is that alternative reductants avoid the dissociation step of H₂O and low CO₂ solubility in traditional systems;

meanwhile, the co-reaction of reductants with CO₂ reduction promotes the formation of C-C bonds and directly improves the selectivity of C₂₊ hydrocarbons. In addition, the mixed gas system optimizes the gas-phase mass transfer on the catalyst surface. However, the use of alternative reductants also has limitations: most reductants are fossil fuel-based small molecules (C₂H₆, CH₄), which deviate from the original goal of sustainable CO₂ conversion using solar energy and water.

In short, the reaction environment is a crucial factor determining the type of C₂₊ products, with gas-phase systems being superior for hydrocarbon production and liquid-phase systems for oxygen-containing product synthesis; additives can effectively optimize the liquid-phase microenvironment and improve C₂₊ yield/selectivity, but the effect is highly dependent on the cooperation of catalyst and additives; alternative reductants break through the performance bottleneck of H₂O-based systems and achieve ultra-high C₂₊ yield, but the sustainability and industrial feasibility need to be further improved. For the practical application of CO₂ photoreduction to C₂₊ products, future research should focus on the optimization of H₂O-based systems and developing green and sustainable sacrificial agents/additives to balance the yield efficiency of C₂₊ products and the sustainability of the reaction system.

3. Increase CO₂ Solubility in the Liquid Water

The limits of CO₂ solubility are familiar to researchers, while some have found that CO₂(aq) concentration significantly influences the formation rate of CO and its selectivity [84–86]. When the concentration of [CO₂(aq)] was low, the main process was not the CO₂ reduction but H₂O splitting. Reasonably, forming C₂₊ products would be even more difficult. Therefore, the researchers have attempted to change the situation by developing new methods to increase the CO₂ concentration in the water solution. The most convenient approach is to use some inorganic bases to adjust the pH. As it is known, part of the CO₂ in the water will form H₂CO₃, and decompose into CO₃^{2−} and HCO₃[−].



With the addition of OH[−], the equilibrium shifts to the right, producing more CO₃^{2−} and HCO₃[−], and thus dissolving more CO₂ and increasing total CO₂ content.

This seems like a perfect solution. However, there are still some problems remaining. In fact, it only guarantees the ion concentration. When the solution saturates, CO₂ will stop entering the solution. Thus, the most important point becomes: which species is the real reactant, CO₂, H₂CO₃, CO₃^{2−} or HCO₃[−]? If it is CO₂, the effect will be limited. Unfortunately, evidence suggests that molecular CO₂ is the primary reactant, which makes the dissolved carbonates less functional (Figure 3) and limits the strategy of increasing CO₂ solubility via pH adjustment [87,88]. Data in Table 2 also reflect this aspect: C₂₊ products do not show clear advantages in NaHCO₃ solution. Nonetheless, the group continued the study on the reaction conditions and formulated a general kinetic equation with CO₂ partial pressure and pH as variables, which is expected to generate more hydrocarbons [89].

$$R_{\text{CO}} = \frac{k_r k_a [\text{CO}_2(\text{aq})]}{(1 + \beta) \left\{ (k_d + k_r) \left(\frac{[\text{H}^+]}{K_b K_w} + 1 \right) + k_a [\text{CO}_2(\text{aq})] \right\}} \quad (7)$$

where

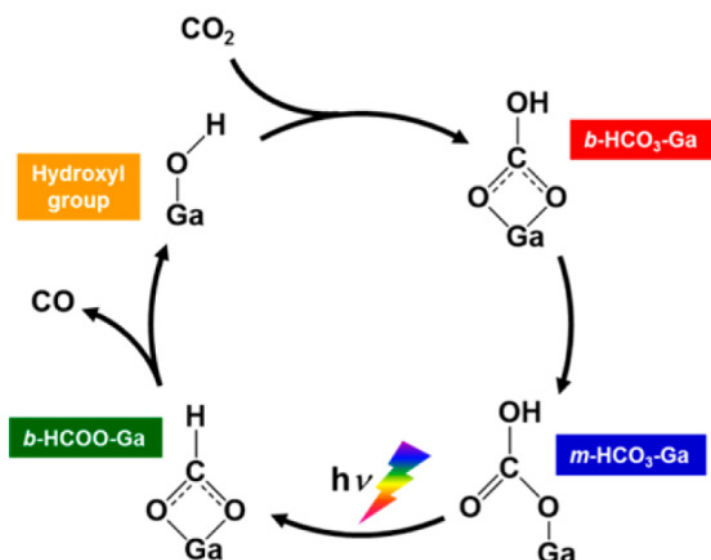


Figure 3. Proposed mechanism of the formation of intermediate species in the photocatalytic conversion of CO_2 by H_2O as the electron donor over $\text{ZnGa}_2\text{O}_4/\text{Ga}_2\text{O}_3$.

k_r —rate constant of the entire process;

k_a —rate constant of the adsorption;

k_d —rate constant of the desorption;

K_b —base dissociation constant;

K_w —water dissociation constant;

$[\text{CO}_2(\text{aq})]$ — CO_2 concentration in the liquid;

$[\text{H}^+]$ — H^+ concentration in the liquid;

$\beta = k_{\text{rev}} K_{\text{H,CO}} \alpha$, k_{rev} is a kinetic constant, $K_{\text{H,CO}}$, and α are Henry's constant of CO and the conversion coefficient from P_{CO} to R_{CO} .

Although adjusting the aqueous system pH with inorganic bases is a simple, low-cost approach to raise the CO_2 content by shifting the carbonic acid dissociation equilibrium, its practical effect on promoting C_{2+} production is severely limited by multiple critical factors, in addition to the core issue that molecular CO_2 is the primary reactant. Extremely high/low pH conditions easily damage the structural and catalytic stability of most photocatalysts, and even carbonate salt deposition on catalyst surfaces that cover active sites and block reactant mass transfer. Meanwhile, a large number of inorganic ions may be introduced and compete with molecular CO_2 . Furthermore, pH adjustment only increases bulk carbon content but cannot effectively elevate the local concentration of molecular CO_2 at the catalyst–liquid interface. The intrinsic low solubility of molecular CO_2 in water remains unaddressed. In total, pH adjustment alone cannot break the bottleneck of low C_{2+} yield in traditional liquid-phase systems and only acts as an auxiliary measure when combined with other microenvironment engineering strategies.

4. Increase CO_2 Partial Pressure in the Liquid Water

Based on the above kinetic equation, CO_2 partial pressure can influence the CO_2 photoreduction reaction rate. Increasing partial pressure becomes another way to increase CO_2 concentration in water, according to Henry's law.

The researcher who investigated the most about the CO_2 pressure effect on the CO_2 reduction is the group of Prof. I. Rossetti [90–94]. She summarized some problems about CO_2 photoreduction and then focused on the pressure effect. She designed a high-pressure reactor (Figure 4) in 2014 and then studied CO_2 photoreduction under high pressures. With some classic catalysts such as TiO_2 from the Degussa (now Evonik) company and some

TiO₂ with metal cocatalysts Au and Ag, they achieved a much higher yield at high pressure (1.8 MPa) than under normal conditions, as listed in Table 5. Those tests proved that high pressure is favorable for the formation of liquid reduction products, whereas intermediate pressure yields more gas-phase products. She also studied the influence of pH and adopted the addition of bases to make the reaction happen at a higher pH, suggesting that the process may proceed through a carbonate ion pathway [95].

Table 5. Collection data about increasing CO₂ partial pressure.

Catalyst	Results ($\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$)	Reaction Conditions	Ref.
P25	HCOOH 1859.31, HCHO 16,537.13, and CH ₃ OH 350.98	a 125 W medium-pressure Hg vapor lamp, NaOH was used to increase the pH, Na ₂ SO ₃ was used as hole scavenger, CO ₂ pressure 7 bar, constant temperature of 80 °C	[90]
Au/TiO ₂	CH ₄ 8.5–6.5 and H ₂ 2.3–2.7	a 125 W medium-pressure Hg vapor lamp, NH ₃ and HNO ₃ were used to adjust the pH, Na ₂ SO ₃ was used as hole scavenger, CO ₂ pressure 5–6 bar, constant temperature of 65 °C	[91]
Au/TiO ₂	CH ₃ OH 1350	a 125 W medium-pressure Hg vapor lamp, pH = 7, Na ₂ SO ₃ was used as hole scavenger, CO ₂ pressure 7 bar, constant temperature of 80 °C	
TiO ₂ -FSP	HCOOH 7433 and H ₂ 1613	a 125 W medium-pressure Hg vapor lamp, Na ₂ SO ₃ was used as a hole scavenger, constant temperature	[92]
TiO ₂	HCOOH 4499 and H ₂ 4000		
Ag/P25	HCOOH 20,000 and H ₂ 700	a 125 W medium-pressure Hg vapor lamp, NaOH was used to increase the pH, Na ₂ SO ₃ was used as hole scavenger, CO ₂ pressure 8–18 bar, constant temperature of 80 °C	[93]
C ₃ N ₄ -TE	HCOOH~16,000	a 125 W medium-pressure Hg vapor lamp, pH = 14, Na ₂ SO ₃ was used as hole scavenger, CO ₂ pressure 18 bar	[94]
<i>fac</i> -Re(bpy)CO ₃ Cl	CO 6.8 $\mu\text{mol}\cdot\text{h}^{-1}$	A 500 W Hg lamp, (0.10–2.45 MPa)CO ₂ charged with an Et ₃ N/DMF solution (9 mL, Et ₃ N 0.80 M)	[96]
<i>fac</i> -Re(bpy)(CO) ₃ P(O ^{<i>i</i>} Pr) ₃] ⁺	CO 24.1 $\mu\text{mol}\cdot\text{h}^{-1}$	A 500 W Hg lamp, (0.10–7.30 MPa)CO ₂ charged with a TEOA/DMF solution (9 mL, Et ₃ N 0.80 M)	[97]
ZIF-8/TiO ₂	15.6 CO	A 300 W Xe lamp, 3–5 bar CO ₂ , and water vapor circulation flow with the rates of 50, 100 mL/min, and pressure swing	[98]
Pd/TiO ₂	0.9–37 Σ C ₁	A 500 W Xe lamp, CO ₂ gas (0.12–0.80 MPa) in 120 mL water	[95]

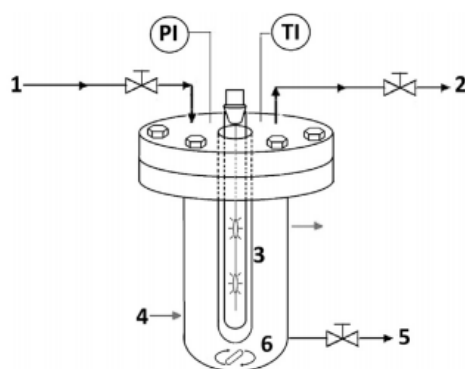
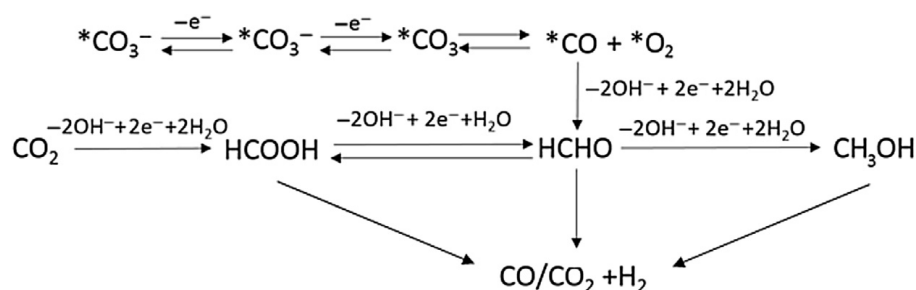


Figure 4. Sketch of the high-pressure photoreactor. 1: Pressure reducer, 2: sample valve for gas phase, 3: lamp, 4: double-walled thermostatic system, 5: sample valve for liquid phase, 6: magnetic stirrer. PI: pressure indicator; TI: temperature indicator. Ref. [98] Copyright 2017 Elsevier.

Increasing the reaction pressure means letting more CO₂ dissolve in the liquid phase, thereby changing the yield compared to the other data. By analyzing product distribution with reaction time, two parallel pathways were proposed: one involving chemical dissolution of CO₂ into carbonate (leading to aldehydes) and one involving physical dissolution of CO₂ in molecular form, as shown in Scheme 1.



Scheme 1. Parallel pathways for molecular CO₂ and carbonate photoreduction. * Indicate the species adsorbed on the photocatalyst surface.

Zhang et al. [99] explored how CO₂ pressure (ranging from 0 to 0.80 MPa) influences the photocatalytic conversion of CO₂ to fuels in environments containing both CO₂ and moisture. The findings indicated that at 0.80 MPa, the moisture involved in the reaction exhibited enhanced reactivity. In their opinion, this phenomenon was ascribed and limited to the efficient spatial separation of active sites: CO₂ reduction occurred on Pd nanoparticles, while water oxidation took place on the semiconductor surface.

Hori et al. [100] employed high-pressure CO₂ gas in the photocatalytic reduction of CO₂ to CO using a homogeneous catalyst, achieving a high CO production rate. They found that utilizing high-pressure CO₂ was more effective than adding an excess of Cl[−] ions. Specifically, when the CO₂ pressure was 1.36 MPa and triethanolamine (TEOA) served as the electron donor, the turnover number (TON) for CO generation reached 15.6–3.8 times higher than that in the atmospheric pressure system (i.e., 0.10 MPa).

Wang et al. [98] adopted pressure swing technology and evaluated the performance of a ZIF/TiO₂ composite catalyst under pressures between 0.3 and 0.5 MPa. The introduction of pressure fluctuations into the reaction system promoted the adsorption and desorption processes of both CO₂ and reaction products, which in turn enhanced the photoreduction efficiency of CO₂.

All these results confirm that the partial pressure of CO₂ has a clear effect on the reaction rate, though the products still seem to be limited to C1 compounds. However, it is also acceptable, as they also add inorganic bases to the solution.

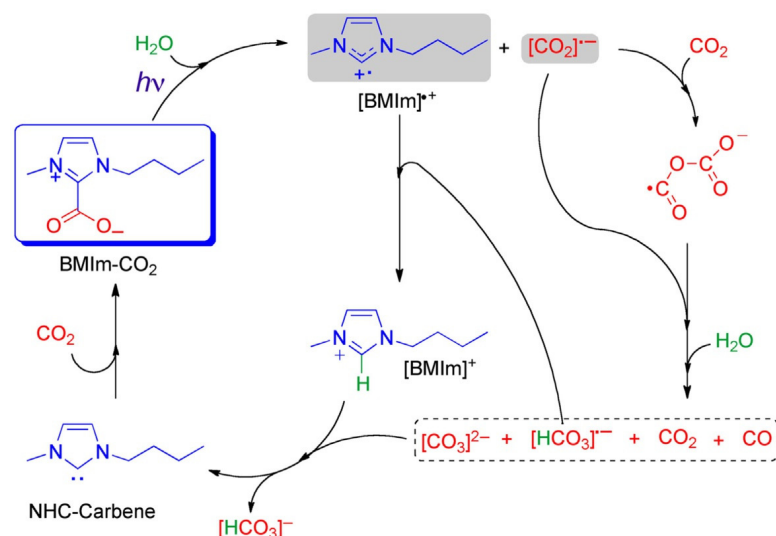
5. Reduce the Water in the Solution

To reduce the water composition in the liquid phase, some other reagents must be added, or the reaction environment must be changed. For example, the effects of water content in the feed gas on the methane production on Pt/TiO₂ (P25) have been investigated by Molins et al. [101]. A high H₂O ratio was found to be the most effective parameter for increasing the rate and lifetime of methane production on a Pt/TiO₂ photocatalyst, leading to significant enhancement in initial methane production rates, photocatalytic activity lifetimes, and total yields. This result may seem counter to the hypothesis. However, the story actually happened in the gas phase. Under this situation, the water content is less than CO₂, and there is an imbalance in another attitude.

Another effective approach is adding some other solvents to the water or even using the inert solvents as the main component with a lower content of water, such as ionic liquids (ILs). These ILs have been widely used in CO₂ capture due to their good CO₂ adsorption

ability. It is reasonable to extend their use in the CO₂ photoreduction reaction. Actually, ionic liquids have been used in both reverse water–gas shift (RWGS) and Fischer-Tropsch reactions, which are the advanced technological routes for producing C₂+ hydrocarbons from CO₂ conversion other than CO₂ photoreduction with water.

Qadir et al. [102] adopted a BMIm.CO₂ ionic liquid (IL) as the photocatalyst, and carried out a photocatalytic reaction in a quartz reactor fitted with a water-circulating jacket. Specifically, 3 mL of CO₂-saturated water was blended with a predetermined quantity of freshly synthesized IL. After purging the reactor with argon to remove air, CO₂ was introduced into the system using a pre-filled balloon. Through this approach, a CO yield of 134 $\mu\text{mol}\cdot\text{g}_{\text{IL}}^{-1}$ was achieved, and a distinct reaction mechanism was proposed in Scheme 2.



Scheme 2. Possible species involved in the CO₂ photoreduction driven by ILs. Ref. [102].

Yu et al. [70] demonstrated the green-light-induced synthesis of C1–C3 hydrocarbons from CO₂ and water over plasmonic gold nanoparticles (Au NPs) in an IL-based medium. Under optimized reaction conditions, various hydrocarbons, including methane, ethylene, acetylene, propane, and propene, were photosynthesized, with a total C₂+ selectivity of approximately 50%. They proposed that the IL exerts a synergistic effect by forming complexation interactions with CO₂, which prearranges CO₂ molecules to accept electrons from photoexcited Au NPs. The enhanced reactivity of CO₂ in the presence of IL eliminates the requirement for an externally applied potential or a sacrificial electron scavenger. Nevertheless, adjustments of the water content may also have contributed to the observed reaction outcomes.

An innovative strategy to reduce water content involves the utilization of supercritical fluids. Kuramochi et al. [103] explored the photocatalytic reduction in CO₂ to CO in single-phase, high-pressure mixtures of supercritical CO₂ and N,N-dimethylformamide (DMF), employing fac-ReCl(bpy)(CO)₃ as the catalyst and triethanolamine as the sacrificial electron donor. Their results revealed that the catalytic efficiency was significantly affected by both CO₂ and DMF concentrations. The turnover number (TON) for CO production rises linearly with increasing CO₂ pressure, reaching 60 at 17.8 MPa and 60 °C. The optimal TON of 62 was achieved under the conditions of 17.8 MPa CO₂, 60 °C, and a DMF concentration of 6.3 mol/L, demonstrating that possible improvements can be achieved through the use of high concentrations of CO₂ and reduced water content. The other two examples in Table 5 also used different solvents. These results indicate that reducing water content is worth investigating, and some of the studies have proved the potential for C₂+ products formation.

In general, the reports about adding additives are not very numerous; however, it is reasonable to believe that the design and use of suitable ionic liquids will gradually increase in the field, as research on ionic liquids is developing rapidly and seeking their application opportunities.

6. Move CO₂ Photoreduction into Gas Phase

6.1. CO₂ Photoreduction in Gas Phase

Compared to adjusting the CO₂ and water concentration in the liquid phase, it is more convenient to transfer the reaction into the gas phase. A classic gas–solid heterogeneous photocatalytic reaction would be more easily understood than a liquid–solid or even three-phase gas–liquid–solid heterogeneous photocatalytic reaction. The gas–solid phase photocatalytic reaction system is simple in composition, as no other solvents or sacrificial reagents are needed, and it is more convenient for the separation of products. From Table 1, the products also showed a tendency to form hydrocarbons rather than oxygen-containing components.

Yuan et al. [104] introduced 3,4-ethylenedioxythiophene (EDOT)-based conjugated trimers as visible-light-responsive photocatalysts for CO₂ conversion in the gas phase. By tuning the acceptor units, they achieved different aggregate states, which enabled them to modulate product selectivity, shifting from C1 to C2 products with high stability under continuous gas flow. 110.0 $\mu\text{mol}\cdot\text{g}^{-1}$ C₂H₆ was yielded as the primary product. *COOH was detected as the key intermediate for CO₂ reduction to CO, and the assembly of *COOH was considered as the key step to form C₂H₆.

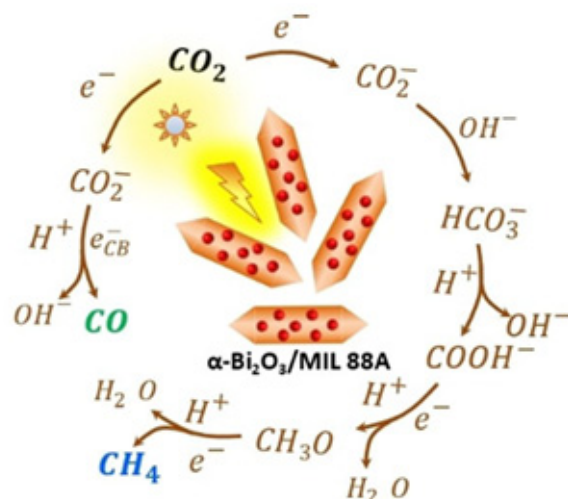
Thang et al. [105] reported that Ni single atoms (SAs) and surface oxygen vacancies (O_v) could regulate the CO₂ reduction pathway on the Bi₂WO₆ photocatalyst. Adsorption of H₂O and CO₂ readily forms CO₃^{2−} species on the O_v-rich catalyst. Optimally balancing Ni SAs and O_v lowers the energy barrier for the formation and dehydration of the key COOH intermediate, leading to favorable CO formation and desorption. Consequently, a superior CO production efficiency is reached, and a yield of 53.49 $\mu\text{mol}\cdot\text{g}^{-1}$ is achieved, surpassing previous reports on Bi₂WO₆-based catalysts for gas-phase CO₂ photoreduction.

Perovskite materials initially for photovoltaics are also introduced into this field. An S-scheme heterojunction based on Cs₃Sb_{0.5}Bi_{1.5}Cl₄Br₅ (CSBX) and bismuth-based organic framework (BOF) was constructed for efficient gas-phase CO₂ photoreduction [106]. Under simulated solar illumination, the heterostructure exhibited excellent photocatalytic performance without the addition of scavengers or cocatalysts, achieving CO and CH₄ yields of 135.22 and 13.52 $\mu\text{mol}\cdot\text{g}^{-1}$, respectively. In situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) measurements identified the key reaction intermediates (*COOH and CO), thereby revealing a plausible reaction pathway.

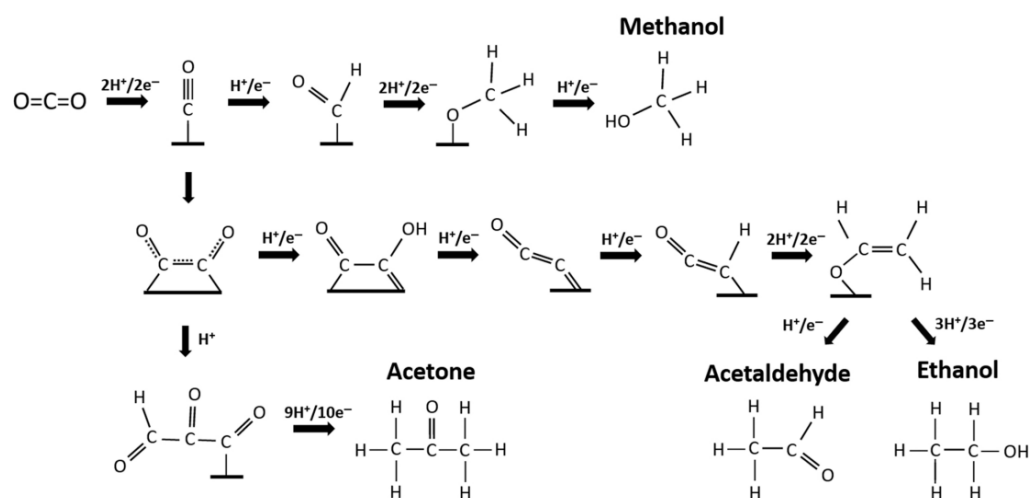
Ojha et al. [107] deposited discrete α -Bi₂O₃ nanospheres onto spindle-like hexagonal rod MIL88A to synthesize the α -Bi₂O₃/MIL88A heterostructure. This negatively charged heterostructure possesses visible-light-responsive activity and can efficiently reduce CO₂ in the presence of water without requiring sacrificial agents or noble metals. Compared with pristine MIL88A, the heterostructure enhanced CO₂ conversion efficiency, leading to a 1.5 times increase in CO production and a four times rise in CH₄ generation. Multiple in situ characterizations, including electron paramagnetic resonance (EPR) and DRIFTS, confirmed that the reaction proceeds via the pathway illustrated in Scheme 3.

ZDC (derived from carbon material with residual Co nanoparticles) and TiO₂ formed a ZDC/TiO₂ composite that was employed as a photocatalyst for gas-phase CO₂ reduction [108]. The ZDC photocatalyst tends to produce C₂ compounds (acetaldehyde), while the ZDC/TiO₂ composite shows high selectivity toward C₃ products (acetone). Based on the experimental results, the reaction mechanism was proposed as follows: CO₂ molecules

are first reduced to $^*\text{CO}$ intermediates at oxygen vacancies on TiO_2 . Due to the close interfacial contact between ZDC and black TiO_2 , the generated $^*\text{CO}$ intermediates are adsorbed on ZDC, where they are either further reduced to $^*\text{COH}$ or undergo C-C coupling with other $^*\text{CO}$ intermediates. Notably, the rate of CO production directly regulates the occurrence of CO dimerization, which is a key step for the formation of multi-carbon products (Scheme 4).



Scheme 3. Plausible reaction mechanism of the $\alpha\text{-Bi}_2\text{O}_3/\text{MIL88A}$ catalyst for the gas-phase photocatalytic CO_2 reduction reaction. Ref. [107].



Scheme 4. Proposed CO_2 reduction pathway in the gas phase on the catalyst ZDC/TiO_2 , Ref. [108].

In general, these studies show comparable results with those in the liquid phase. The CO_2 reduction in the gas phase is considered to follow a similar one- or two-electron reaction pathway in the liquid phase and first forms $^*\text{CO}_2$ and then the key intermediate $^*\text{COOH}$ to go through the remaining steps.

The most important difference between the reaction in the gas phase and the liquid phase might be the reactor system design. Unlike the liquid, the gas reactants do not have enough lifting force to distribute the solid catalyst powders uniformly in the reactor. The photocatalysts are often pressed into a disk shape and exhibit some characteristics of a fixed-bed reactor. However, for some more reasons, these gas-phase photoreactors do not switch to PBR type reactors completely.

Moustakas et al. [109] invented a high-purity gas–solid photoreactor system. A close-up view of the reaction chamber can be seen in Figure 5. It can be seen that the reactor is

still a tank-type reactor. The catalyst must be compressed into a flake shape to receive the light from the top round glass window. The gas flows through the upper surface of the catalyst, which hardly forms a plug flow in the reactor. It limits the volume efficiency of the tank reactor, resulting in significant mass transfer and bypassing effects between the gas reactants and the catalyst surface. As the catalyst bed is hardly likely to be improved, a very important research subject is the control of gas flow types and directions.

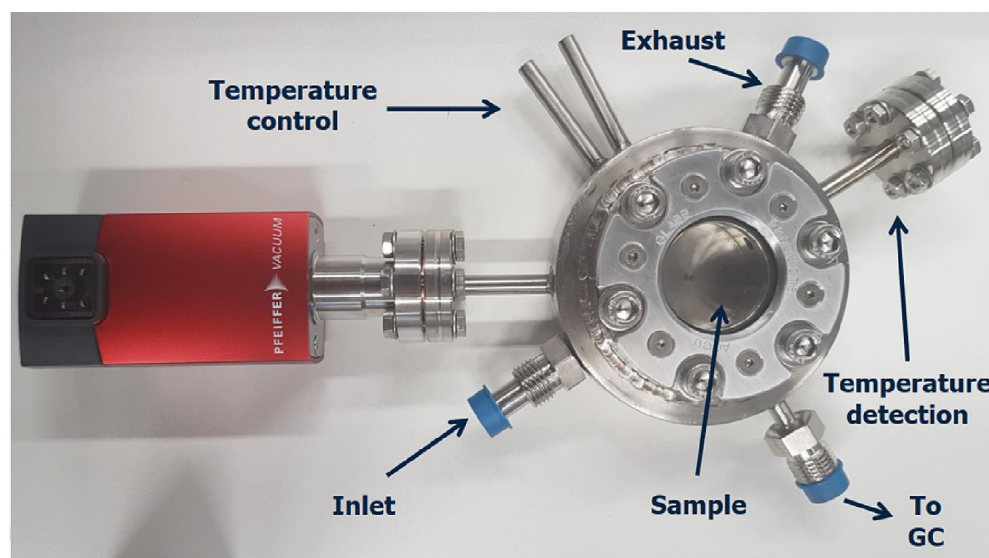


Figure 5. Close-up of the main body of the photoreactor. Ref. [109] Copyright 2023 Elsevier.

Gas flow direction also seems to promote better contact with the photocatalyst, as shown in Figure 6 by Sorcar et al. [110]. The catalyst was dispersed on a glass disk to form a bed. The reactant flow (water vapor-saturated CO_2) had to pass through the catalyst bed from the catalyst bed's upside to downside, and light was irradiated on the catalyst upside, improving the flow characteristic.

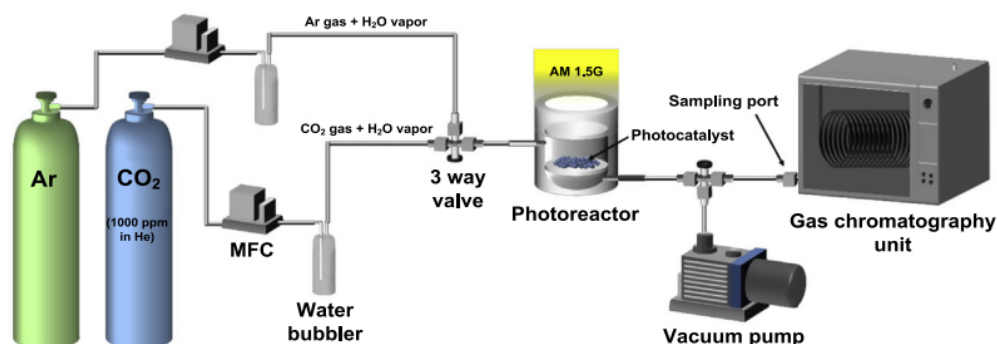


Figure 6. Experimental setup for photocatalytic CO_2 reduction. Ref. [110] Copyright 2017 Elsevier.

Another reactor to improve mass transfer and gas–solid contact is the thin film reactor. To increase the contact area and reduce the volume, a stick-shaped UV lamp was used instead of a round-shaped lamp [111]; correspondingly, the catalyst can be shaped into a long rectangular film, as shown in Figure 7. Compared to the round-shaped catalyst, the flow path of the reactants is clearly increased, and the performance is improved.

The ultimate design is the microchannel reactor, as shown in Figure 8 [112]. The catalyst films were fixed on the glass substrate, and a cover material, polydimethylsiloxane (PDMS), was put on top of the catalyst films to yield a closed environment. At the entrance and exit of the reactor, a gas distributor was arranged to distribute the gas evenly in

the reactor and fully contact the catalyst, and the light can irradiate the catalyst through the cover material. The CO_2 : H_2O ratio can be adjusted by controlling the feed flow temperature and flow rate through a mass flowmeter.

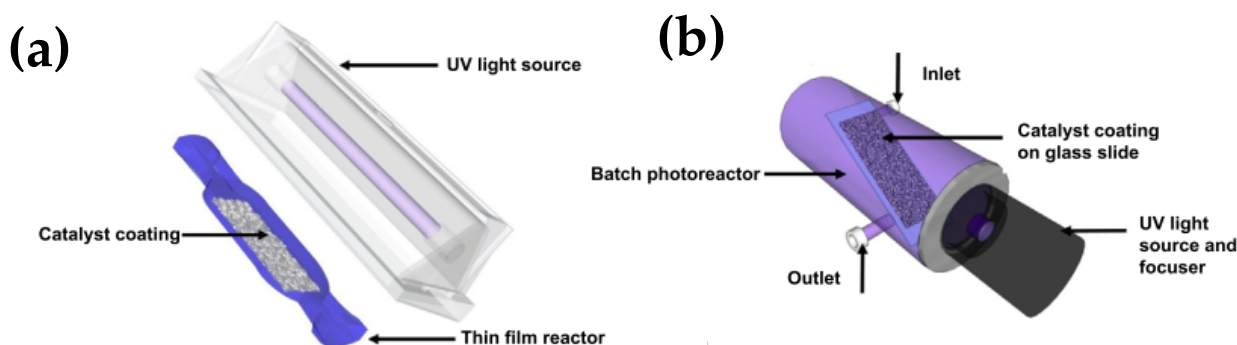


Figure 7. The film reactor diagram. Ref. [111] Copyright 2020 Elsevier.

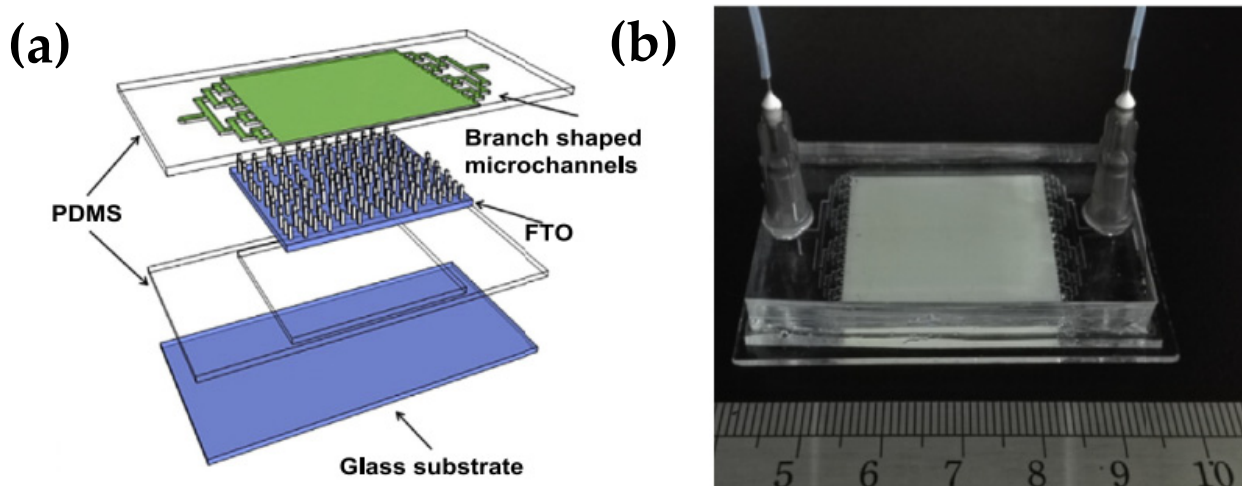


Figure 8. Design of the optofluidic planar microreactor and image of the microreactor. Ref. [112] Copyright 2017 Hydrogen Energy Publications LLC.

The reason for the design complexity of gas-phase photoreactors is that, unlike thermal-driven reactors, photoreactor design encounters the light input problem, i.e., one light source can only irradiate into the reactor in one axial or radial direction. Therefore, the photoreactor design must consider the interaction between the incident light and the catalyst to achieve an ideal configuration.

It can be figured out that a perfect candidate material for the light propagation, i.e., optical fiber, has the advantages of high light transmission efficiency and a large reaction surface area. Wu [113] fabricated the photocatalyst on the outer surface of a bunch of optical fibers and got an optical fiber reactor (Figure 9). As the catalysts are coated on the fiber, they will influence the light penetration through the side wall; therefore, the light source will be designed to enter the reactor from the ends of the fibers. It solves the problem of incident light direction, but brings the problem of light intensity, which will decrease with the transfer length prolonged in the fiber. Therefore, a concentrating light source is often used, as shown in Figure 10 [114]. Alternatively, fibers can be replaced with transparent or opaque tubes to form monoliths or honeycomb reactors. The dish concentrator enhances the incident light intensity. Therefore, a reflector concentrator is often used to introduce light from the side direction, as shown in Figure 11 [115]. The study integrated the honeycomb reactor design with a parabolic trough collector (PTC), which

remarkably enhanced light utilization efficiency, enlarged the light-harvesting region, and improved the photocatalytic performance for CO₂ reduction. When the diameter of the channel in the “honeycomb” was between 1.5 and 2.0 mm, it was more conducive to the reduction reaction.

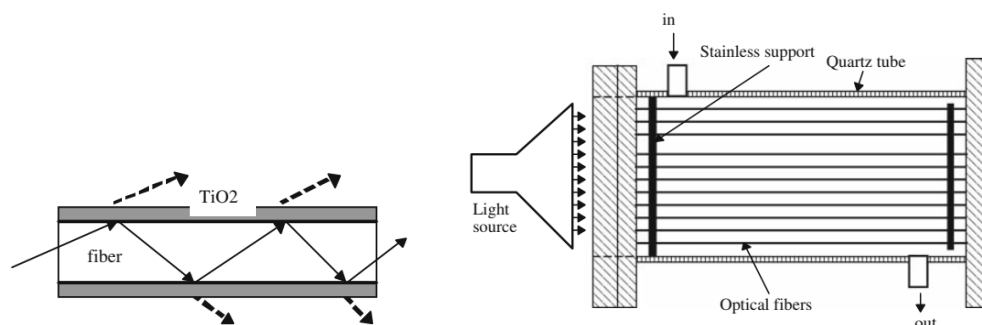


Figure 9. Schematic of optical-fiber photoreactor. Ref. [113] Copyright 2009 Springer.

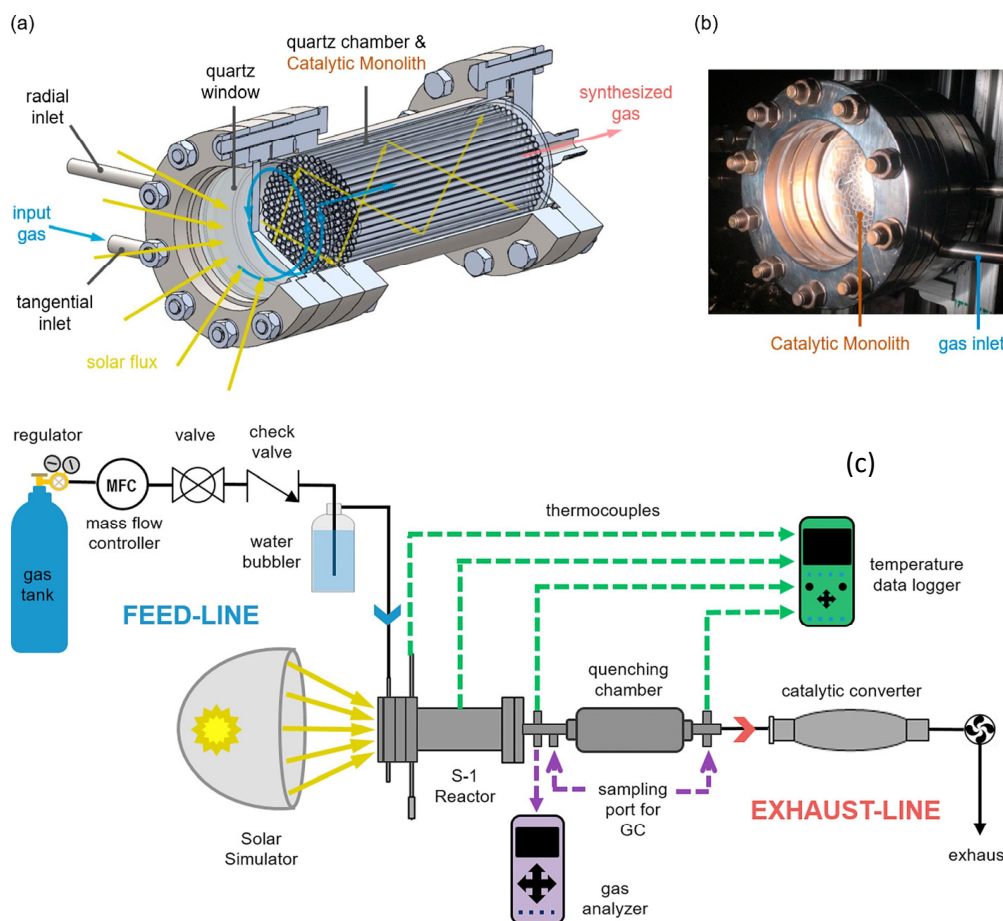


Figure 10. (a) The principal diagram of the reactor design, (b) the reactor model with designed components and schematic depiction of its operation, and (c) the schematic diagram of the experimental setup. Ref. [114] Copyright 2018 Elsevier.

In general, due to the light transfer property, it is not enough to only consider the reactive fluid characteristic alone to obtain an optimal photoreactor. It must effectively combine the reactants' flow with the light transfer property.

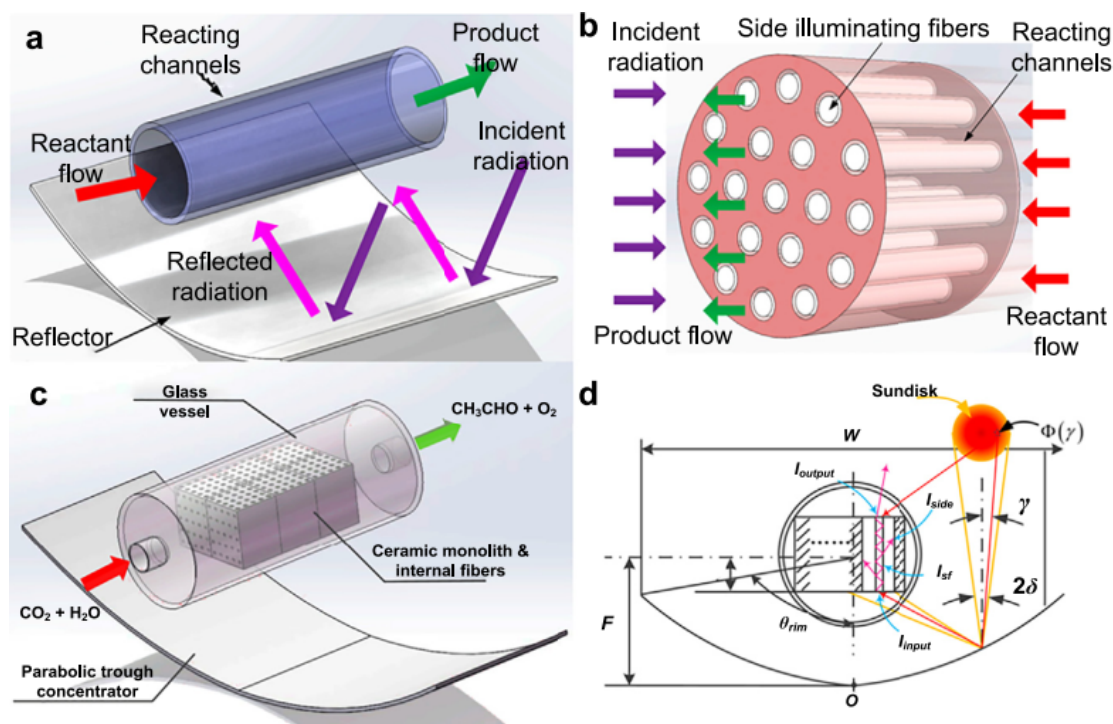


Figure 11. (a) Schematic diagram of a continuous reactor coupled with a reflector, (b) the optical fiber monolith reactors, (c) the optical fiber monolith reactors coupled with a parabolic trough concentrator system, and (d) transmission process diagram of rays. Ref. [115] Copyright 2021 MDPI.

6.2. Photothermal Catalytic Reduction in CO₂ with Water Vapor

In the previous section, we mentioned that concentrating technology can be used to increase the intensity of the incident light of photoreactors. In fact, the effect of concentrating light is not limited to this aspect. It actually brought some inconvenience to the researchers in the early decades, as concentrating light not only could increase the light intensity but also raise the temperature of the reaction system, which was considered to be unnecessary or even have a negative effect on the photocatalytic reactions, and thereby had to be removed to maintain the reaction system at a constant temperature [116,117]. Fortunately, this view has been changed in the very recent years with the emergence of photothermal catalysis [118,119].

Photothermal catalysis reappeared for the utilization of hot charge carriers, which are generated by localized surface plasmon resonance (LSPR) and have higher energies than those generated by direct photoexcitation. These high-energy carriers can deliver their energy to the surroundings and cause a temperature rise on the surface of the material. Together with the photo effect, it can generate the photo- and thermal co-functional catalysis while operating under moderate conditions [120]. Further, the content of photothermal catalysis was broadened soon by some other researchers [121]. Now, if a reaction involves light, heat, and catalytic conversion together, it can be regarded as photothermal catalysis [122]. The development of photothermal catalysis promotes the photothermal catalytic CO₂ reduction with H₂O by concentrating solar light technology [123]. Due to the increase in system temperature, the reaction basically takes place in the gas phase, and more water vapor can enter the gas phase than at normal temperature, which is conducive to the CO₂ and H₂O ratio.

Fang et al. [124] built an outdoor concentrating sunlight reaction system. Using a Fresnel lens with a 1 m diameter, the system got the high light intensity and temperature. Under the strengthened reaction conditions, the yield rates of hydrocarbon products were

greatly enhanced on the different photocatalysts [125–127]. Hundreds of $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ of C_2+ products were detected along with CH_4 (Table 6). The reasons for the high yield are rather complex, but the results are interesting. Mo et al. [128] investigated a (Ni, Fe)-N-CDSAC under concentrating light, while $\text{C}_2\text{H}_4\text{O}$ and $\text{C}_2\text{H}_5\text{OH}$ were detected in the products.

Table 6. Collection data of photothermal catalysis by concentrating light.

Photocatalyst		Reaction Conditions	Products	Yield ($\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$)	Ref.
Name	Mass				
TiO_2 (P25)	0.5 g	Real sunlight 0.1 MPa CO_2 at RT, 2.5 mL H_2O	CH_4 C_2H_4 C_2H_6	3157.2 511.6 1346.0	[124]
TiO_2 NTAs	0.01 g	Real sunlight 0.1 MPa CO_2 at RT, 2.5 mL H_2O	CH_4 C_2H_4 C_2H_6	861.1 100.8 53.3	[125]
Fe_2O_3	0.01 g	Real sunlight 0.1 MPa CO_2 at RT, 2.5 mL H_2O	CH_4 C_2H_4 C_2H_6	1281.11 85.46 55.08	[126]
$\text{Bi}_2\text{WO}_6/\text{WO}_3$	0.5 g	Real sunlight 0.1 MPa CO_2 at RT, 2.5 mL H_2O	CH_4 C_2H_4 C_2H_6	304.94 62.70 54.66	[127]
(Ni, Fe)-N-CDSAC	0.06 g	300 W Xe lamp, 5 mL/min CO_2 bubbled in 180 mL H_2O	CH_4 CO CH_3OH $\text{C}_2\text{H}_4\text{O}$ $\text{C}_2\text{H}_5\text{OH}$	135.35 86.16 59.81 ≈ 4.3 ≈ 9.2	[128]
NF@0.1%Ni@ CeO_2	-	Simulated solar light, 1200 mW/cm ²	CH_4	192.75 $\mu\text{mol}\cdot\text{cm}^{-2}\cdot\text{h}^{-1}$	[129]

Ren et al. [129] developed a CeO_2 -based catalyst with abundant oxygen vacancies, where single-atom Ni was immobilized on its surface sites, and realized efficient photothermal CO_2 reduction under concentrated light irradiation. The light intensity was elevated, leading to the catalyst surface temperature exceeding 300 °C. The high photon flux lowered the apparent activation energy required for CH_4 formation. Notably, the oxygen vacancy defects coordinated with single-atom Ni significantly facilitated the capture of charges and local phonons at the Ni d-impurity orbitals, thereby promoting more efficient H_2O activation. This catalyst achieved a CH_4 yield of 192.75 $\mu\text{mol}\cdot\text{cm}^{-2}\cdot\text{h}^{-1}$, accompanied by a solar-to-chemical conversion efficiency of 1.14%.

One challenge of photothermal catalysis is the stability of the photocatalyst under high temperature (and high light intensity), especially with water vapor. It naturally forms a hydrothermal environment, which makes it possible to reconstruct or transform the catalyst properties. There is little discussion mentioning this, but it is likely that the solution is in the tradeoff between the strong photothermal and classic mild conditions.

6.3. Move Reaction to Three-Phase or Using Floatable Catalyst

Many researchers have noticed the limitation of CO_2 supply during CO_2 photoreduction in aqueous solution and have given their solutions from different viewpoints. Bai et al. [130] invented a porous fixed-bed reactor (Figure 12). The main change is delivering CO_2 into the reactor by bubbling from the bottom of the reactor to pass through the porous catalyst disk. With the same catalyst system, Cu/Cd_{0.5}Zn_{0.5}, ~90% selectivity towards C_2+ products was obtained with a yield of 6.54 $\mu\text{mol}\cdot\text{h}^{-1}$ in the new reactor, while only 0.94 $\mu\text{mol}\cdot\text{h}^{-1}$ was achieved with a common suspension photocatalytic reactor. Their

research demonstrated that under the same CO_2 feed rate, the local CO_2 concentration in the porous fixed-bed photoreactor is significantly higher than that in the suspended photoreactor. The enhanced local CO_2 coverage, which originates from increased CO_2 supply and accumulation, promotes C-C coupling reactions and thus boosts the production of multi-carbon (C_2+) products.

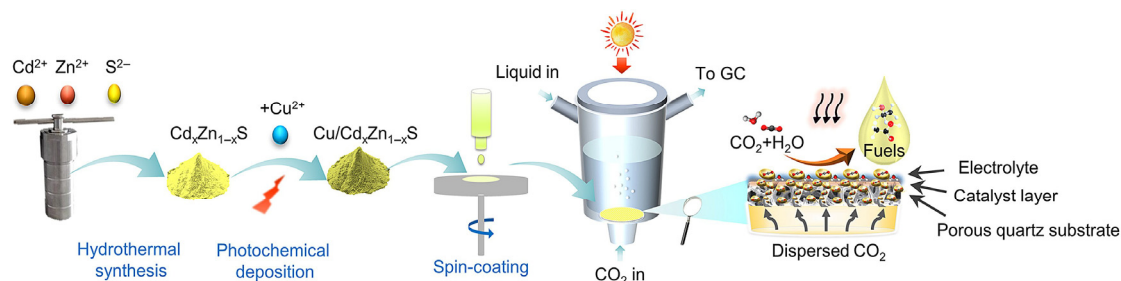


Figure 12. Schematic illustration presenting the synthesis of $\text{Cu/Cd}_{0.5}\text{Zn}_{0.5}$ photocatalyst and its integration in a photocatalytic reactor with a quartz gas dispenser. Ref. [130] Copyright 2022 Elsevier.

Huang et al. [131] constructed a triphasic interface on the photocatalyst surface by modifying it with a hydrophobic carbonaceous cocatalyst, enabling efficient contact between CO_2 (gas), catalyst (solid), and water (liquid), as illustrated in Figure 13. The modified photocatalyst exhibited remarkably improved CO_2 -to- CH_4 activity, with the CO_2 reduction reaction (CO_2RR) selectivity significantly increased from 61% to 97%. Studies confirmed that the hydrophobic cocatalyst exerts a pivotal role in regulating CO_2 reduction performance by enhancing the interfacial CO_2 concentration. Molecular dynamics simulations further revealed that the hydrophobic microenvironment is established by inhibiting the formation of hydrogen bonds on the surface of the carbonaceous cocatalyst. Overall, this strategy provides a universal approach to alleviate CO_2 mass transfer limitations and accelerate CO_2 reduction in aqueous systems.

In contrast to the catalyst construction-based solutions, Zhu et al. [132] designed a triphasic reactor from the perspective of optimizing heat and mass transfer processes by mimicking the lotus structure, as shown in Figure 14. Compared with traditional liquid–solid and gas–solid reaction systems, experimental and theoretical calculation results indicated that this system spontaneously optimizes the supply paths of gas and liquid through capillary action and evaporation phenomena, effectively adjusting the gas–liquid supply ratio near the catalyst surface. Using Bi- and Ti- co-doped $\text{g-C}_3\text{N}_4$ as a model catalyst, the performance was investigated under three reaction conditions: with sacrificial agents, without sacrificial agents, and coupled oxidation dual reactions. The results showed that the system exhibited a significant promoting effect in all three conditions: a reasonable reactant supply ratio was spontaneously formed near the catalyst, and the auxiliary solution could be easily supplemented. In the dual reaction coupling system, the efficiency reached 0.0458%, thus nearly 10 times higher than that of the liquid–solid phase reaction.

The design concept of the lotus-structured reaction system coincides with another category of catalyst or reactor design, namely floatable photocatalysis. Floatable photocatalysts refer to a type of photocatalytic material that can remain buoyant on the water surface for an extended period. They are mainly classified into two categories: supported photocatalysts and self-floatable photocatalysts [133,134].

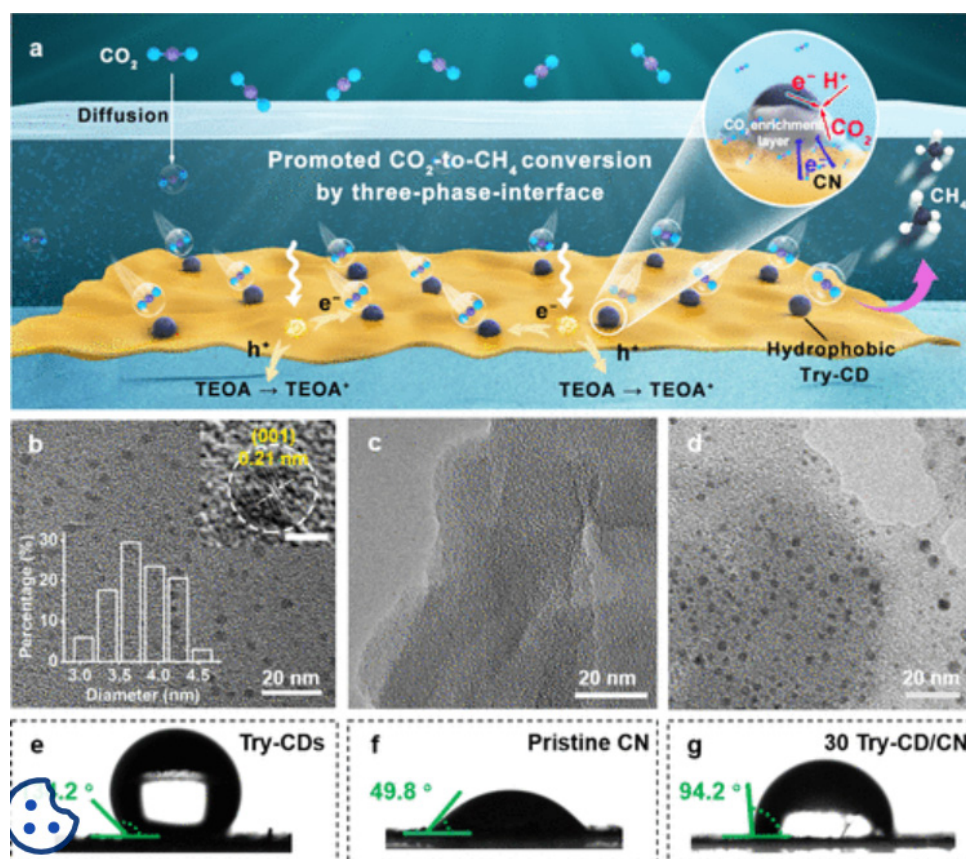


Figure 13. The anchor of the hydrophobic Try-CD cocatalyst on the CN nanosheet enables the efficient three-phase contact of CO₂ gas, catalyst, and TEOA solution. (a) Schematic illustration of the three-phase Try-CD/CN photocatalyst and the mechanism of three-phase photocatalysis. TEM images of (b) Try-CDs, (c) pristine CN, and (d) 30 Try-CD/CN. The size distribution and HRTEM image of Try-CDs are shown in the inset figure (the scale bar is 2 nm). Contact angle measurement of water on (e) Try-CDs, (f) pristine CN, and (g) 30 Try-CD/CN. Ref. [131] Copyright 2023 ACS Pub.

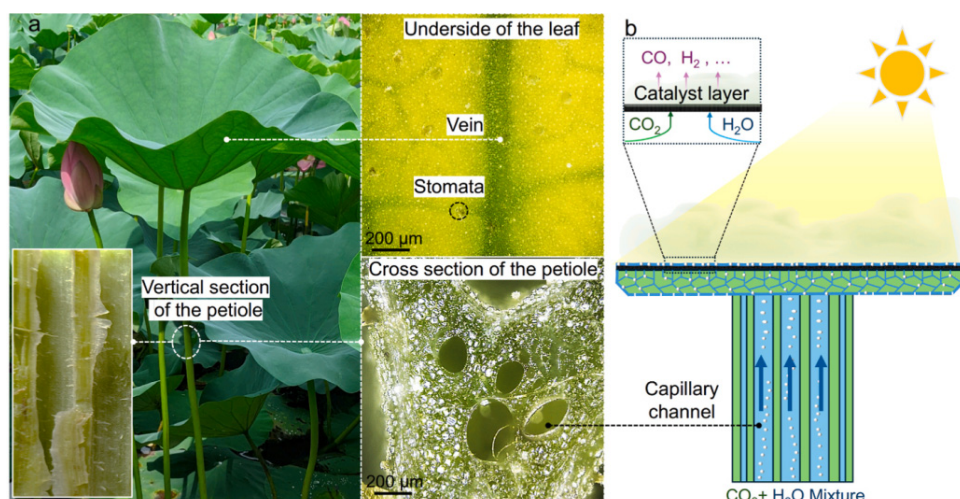


Figure 14. (a) Photo and cross-sectional images of lotus leaves and petioles, (b) mechanism diagram of the lotus-inspired reaction system. Ref. [132] Copyright 2023 Elsevier.

Xie et al. [135] developed a floating sheet as a high-performance photocatalytic CO₂ conversion system by integrating graphitic carbon nitride (CN) nanosheets onto a polytetrafluoroethylene (PTFE) fiber membrane, followed by oxygen (O) doping into CN (forming CN-O) via oxygen plasma treatment, as depicted in Figure 15. Under 0.25 MPa

CO_2 pressure in the reactor, the floatable CN-O/PTFE sheet exhibited weak wettability in water, facilitating the delivery of dissolved CO_2 to the surface of the CN-O photocatalyst. Consequently, the floating CN-O/PTFE system achieved an excellent photocatalytic CO_2 conversion rate of $102.3 \mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$, approximately 4.8 times higher than that of the conventional CN-powder dispersion system in water. Furthermore, the sheet displayed outstanding cycling stability, with no significant exfoliation of the catalytic layer or decline in CO_2 photoreduction activity after 20 consecutive cycles.

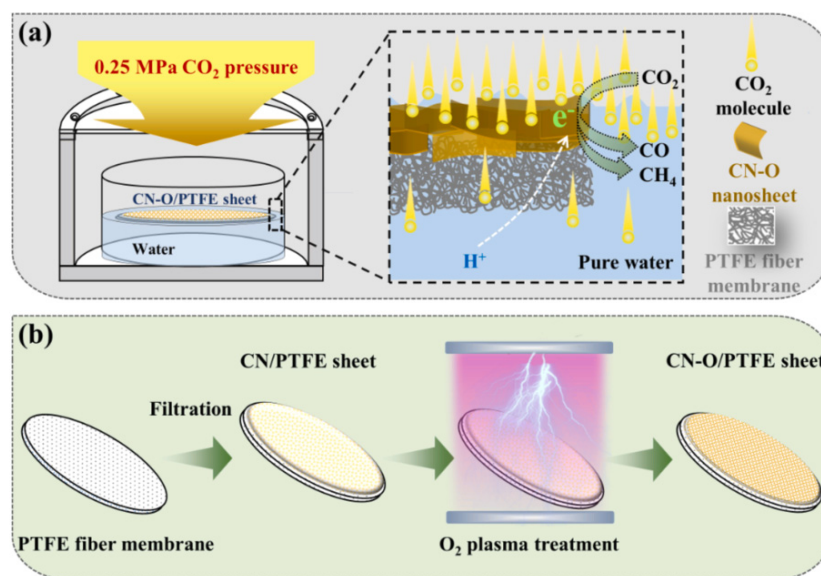


Figure 15. (a) Schematic illustration of the photocatalytic CO_2 conversion system utilizing a floating CN-O/PTFE sheet, which is slightly wetted in water. (b) Fabrication process of the CN-O/PTFE sheet. Ref. [135] Copyright 2025 Elsevier.

Wang et al. [136] filled ZnSnO_3 quantum dots (ZSO QDs) with self-floating poly(bismaleimide-co-divinylbenzene) porous microspheres (PBMs) to construct a polymer composite microreactor with an S-scheme heterojunction (ZSO QDs/AP-PBMs), as shown in Figure 16. The microreactor realizes efficient catalytic oxidation and degradation of antibiotic pollutants under light, and the CO_2 generated in this process is reduced to CO. The self-floating porous design effectively solves the problem of CO_2 adsorption and mass transfer in the gas–liquid–solid three-phase system, while the S-scheme heterostructure enhances charge carrier separation. As a result, ZSOQDs/AP-PBMs achieve complete degradation of LVX, providing up to $899.92 \mu\text{mol}\cdot\text{g}^{-1}$ of CO and $221.71 \mu\text{mol}\cdot\text{g}^{-1}$ of CH_4 .

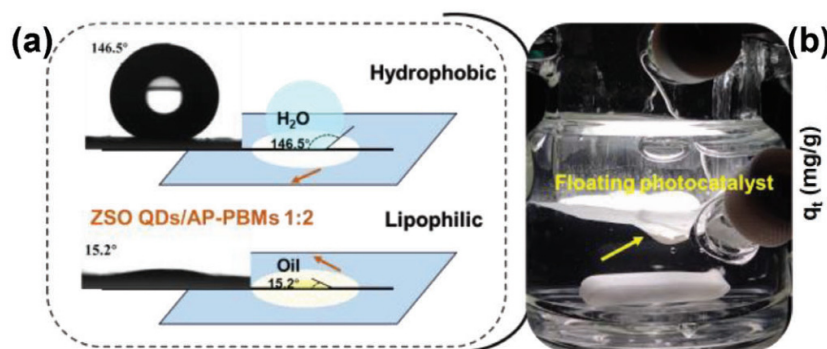


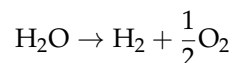
Figure 16. Schematic illustration of the synthesis of ZSO QDs/AP-PBMs. (a) Contact angles of water and oil on ZSO QDs/AP-PBMs 1:2 and photograph of the floating catalyst. (b) Adsorption capacity of ZSO QDs/AP-PBMs 1:2 for different pollutants. Ref. [136] Copyright 2025 Wiley.

Xie et al. [137] fabricated a floatable catalyst by depositing Cu₂O, Ag, and TiO₂ layers on a PTFE membrane support in a sequential manner. When this catalyst floats at the gas–water interface and is irradiated, oriented charge separation occurs across the membrane and at the triphasic (gas–water–solid) interface. Specifically, photogenerated electrons accumulate on the membrane side exposed to the gas phase, triggering gas–solid CO₂ reduction reactions. Meanwhile, photogenerated holes migrate to the membrane side immersed in water, promoting water–solid water oxidation. Compared with conventional gas–solid or water–solid systems, as well as triphasic systems based on catalysts without oriented charge separation, this design significantly enhances reaction performance: the production rates of CO₂ reduction and water oxidation to H₂O₂ are improved by up to 120-fold and 10-fold, respectively, while the selectivity of the two half-reactions is increased by a maximum of 105-fold and 2-fold.

The research of gas-phase and triphasic CO₂ photoreduction is changing from simple phase transformation and basic reactor design toward the catalyst structure, the reactor structure, the multiple cooperation between catalyst structure and reaction microenvironment, the photo/thermal catalytic synergy, etc. The core objective is to address key issues in gas-phase systems, such as low light utilization efficiency, uneven gas–solid mass transfer, and poor selectivity for C₂₊ products, achieving a synergistic breakthrough in improving the efficiency of product formation and engineering adaptation of gas-phase CO₂ photoreduction.

7. Remove H₂O or CO₂ Completely in One Step

As mentioned earlier, under extreme conditions, H₂O or CO₂ can be completely removed from the system, transforming the artificial photosynthesis into thermochemical CO₂ reduction or water splitting. The latter is commonly written as,



Meanwhile, the process often appears as solar thermochemical conversion via two-step redox cycling with metal oxide pairs [138,139].

1. O₂ generation (solar-driven reduction in the oxide): $\text{AO}_x \rightarrow \text{AO}_{x-\delta} + \frac{\delta}{2}\text{O}_2$ (T1, endothermic step).
2. CO generation (re-oxidation of the oxygen-deficient oxide): $\text{AO}_{x-\delta} + \delta\text{CO}_2 \rightarrow \text{AO}_x + \delta\text{CO}$ (T2 < T1, exothermic step).

The two-step reactions can reduce the two reactants to one in a single step and get rid of the ratio balance problem by means of losing the C₂₊ products' potential.

8. Conclusions and Perspectives

In summary, due to high economic value and closer resemblance to natural photosynthesis, studies aimed at producing C₂₊ products by artificial photosynthesis have begun and achieved notable results. To advance further, it is suggested that some attention may be paid to the following points:

- (1) It may be time to reconsider the basic reaction conditions for artificial photosynthesis. Artificial photosynthesis prided itself on having similar reaction conditions to natural photosynthesis in the past decades; however, artificial photosynthesis is a chemical process based on solar energy conversion and collection. Considering the properties of energy carriers, as shown in Figure 17. Photons and electrons can move much faster than molecules, which is helpful to the collection efficiency. Therefore, it may be better to collect (concentrate) light before the reaction to enhance storage efficiency. This

might also reflect in the adjacent field of electrocatalytic CO₂ reduction. In just a few years, the product generation efficiency of electrocatalysis has far surpassed that of artificial photosynthesis, which makes it closer to industrialization than natural temperature artificial photosynthesis. Many reasons may account for the rapid progress in electrocatalytic CO₂ reduction, but the ability to freely apply high-intensity current is likely one [140–142].

- (2) Temperature is another important factor; increasing the temperature has proved to be beneficial for the reaction and has already led to the generation of photothermal catalysis, or photothermal catalytic reduction in CO₂. Correspondingly, there are new demands for the catalyst system, and new guidelines for catalyst design must be developed. Especially for such a reaction, photothermal catalysis means creating an environment similar to a hydrothermal reaction, imposing excess requirements on the moisture-thermal stability of the photocatalysts.
- (3) Further, the catalytic performance depends not only on the intrinsic active sites but also on the surrounding microenvironment in heterogeneous reactions, which controls mass transfer, regional kinetics, and stability. Since most artificial photosynthesis studies are still conducted in the aqueous phase, creating and modulating a balanced gas–liquid phase reaction microenvironment should benefit the selectivity of C₂+ products, as reflected in the above-reported results in gas-phase and three-phase reactions.

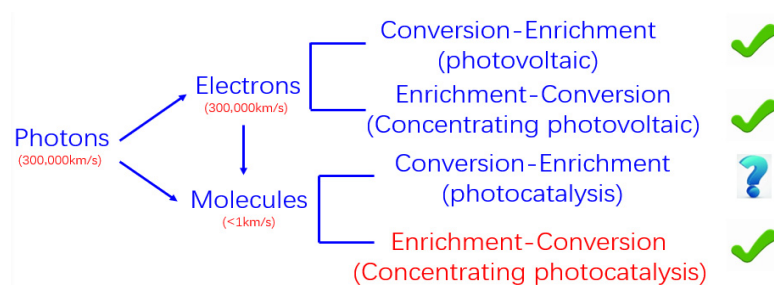


Figure 17. Comparing solar energy collection efficiency with different paths and sequences.

Funding: This research was funded by Zhejiang Zheneng Technology & Environmental Protection Group Co., Ltd. (KH-KJ-24-0070-W001).

Data Availability Statement: No new data were created or analyzed in this study.

Conflicts of Interest: Author Fengping Yu was employed by the Zhejiang Zheneng Technology & Environmental Protection Group Co., Ltd. The remaining authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest. The Zhejiang Zheneng Technology & Environmental Protection Group Co., Ltd. had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, or in the decision to publish the results.

References

- Shih, C.F.; Zhang, T.; Li, J.; Bai, C. Powering the Future with Liquid Sunshine. *Joule* **2018**, *2*, 1925–1949. [CrossRef]
- Li, X.; Yu, J.G.; Jaroniec, M.; Chen, X.B. Cocatalysts for Selective Photoreduction of CO₂ into Solar Fuels. *Chem. Rev.* **2019**, *119*, 3962–4179. [CrossRef]
- Inoue, T.; Fujishima, A.; Konishi, S.; Honda, K. Photoelectrocatalytic reduction of carbon dioxide in aqueous suspensions of semiconductor powders. *Nature* **1979**, *277*, 637–638. [CrossRef]
- Velty, A.; Corma, A. Advanced zeolite and ordered mesoporous silica-based catalysts for the conversion of CO₂ to chemicals and fuels. *Chem. Soc. Rev.* **2023**, *52*, 1773–1946. [CrossRef]
- Lee, J.; Chai, S.P.; Tan, L.L. Perovskite Paradigm Shift: A Green Revolution with Lead-Free Alternatives in Photocatalytic CO₂ Reduction. *ACS Energy Lett.* **2024**, *9*, 1932–1975. [CrossRef]

6. Habisreutinger, S.N.; Schmidt-Mende, L.; Stolarczyk, J.K. Photocatalytic Reduction of CO₂ on TiO₂ and Other Semiconductors. *Angew. Chem. Int. Ed.* **2013**, *52*, 7372–7408. [\[CrossRef\]](#)
7. Hisatomi, T.; Domen, K. Introductory lecture: Sunlight-driven water splitting and carbon dioxide reduction by heterogeneous semiconductor systems as key processes in artificial photosynthesis. *Faraday Discuss.* **2017**, *198*, 11–35. [\[CrossRef\]](#)
8. Teramura, K.; Tanaka, T. Necessary and sufficient conditions for the successful three-phase photocatalytic reduction of CO₂ by H₂O over heterogeneous photocatalysts. *Phys. Chem. Chem. Phys.* **2018**, *20*, 20733–20744. [\[CrossRef\]](#)
9. Zhang, B.; Sun, L. Artificial photosynthesis: Opportunities and challenges of molecular catalysts. *Chem. Soc. Rev.* **2019**, *48*, 2216–2264. [\[CrossRef\]](#)
10. Gong, E.; Ali, S.; Hiragond, C.B.; Kim, H.S.; Powar, N.S.; Kim, D.; Kim, H.; In, S.-I. Solar fuels: Research and development strategies to accelerate photocatalytic CO₂ conversion into hydrocarbon fuels. *Energy Environ. Sci.* **2022**, *15*, 880–937. [\[CrossRef\]](#)
11. Li, M.Q.; Han, Z.Q.; Hu, Q.Y.; Fan, W.Y.; Hu, H.; Qing, D.P.; Chen, Q.X.; Jiao, X.C.; Xie, Y. Recent progress in solar-driven CO₂ reduction to multicarbon products. *Chem. Soc. Rev.* **2024**, *53*, 9964–9975. [\[CrossRef\]](#)
12. Han, G.H.; Bang, J.; Park, G.; Choe, S.; Jang, Y.J.; Jang, H.W.; Kim, S.Y.; Ahn, S.H. Recent Advances in Electrochemical, Photochemical, and Photoelectrochemical Reduction of CO₂ to C₂+ Products. *Small* **2023**, *19*, 2205765. [\[CrossRef\]](#) [\[PubMed\]](#)
13. Ren, C.J.; Li, Q.; Ling, C.Y.; Wang, J.L. Mechanism-Guided Design of Photocatalysts for CO₂ Reduction toward Multicarbon Products. *J. Am. Chem. Soc.* **2023**, *145*, 28276. [\[CrossRef\]](#)
14. Shi, Q.C.; Zhang, B.Y.; Wu, Z.H.; Yang, D.; Wu, H.; Shi, J.F.; Jiang, Z.Y. Cascade Catalytic Systems for Converting CO₂ into C₂+ Products. *ChemSusChem* **2024**, *18*, e202401916. [\[CrossRef\]](#)
15. Chen, F.S.; Li, J.N.; Li, N.; Yang, X.; Liu, W.; Zhong, J.B.; Li, X.H. Noncopper Photocatalysts for Visible-Light-Driven Conversion of CO₂ into C₂+ Products. *Energy Environ. Mater.* **2026**, *9*, e70177. [\[CrossRef\]](#)
16. Zhou, H.X.; Hu, Y.B.; Zhang, Y.; Jiang, W.; Di, J. Rational design of materials for CO₂ photoreduction to yield C₂+ products. *Sep. Purif. Technol.* **2025**, *359*, 130549. [\[CrossRef\]](#)
17. Wu, Y.; Hu, Q.Y.; Chen, Q.X.; Jiao, X.C.; Xie, Y. Fundamentals and Challenges of Engineering Charge Polarized Active Sites for CO₂ Photoreduction toward C₂ Products. *Acc. Chem. Res.* **2023**, *56*, 2500–2513. [\[CrossRef\]](#)
18. Zhu, H.W.; Guo, R.T.; Liu, C.; Cui, H.F.; Liu, M.Y.; Pan, W.G. Recent Progress on Photocatalytic Reduction of CO₂ to C₂+ Products. *J. Mater. Chem. A* **2024**, *12*, 21677. [\[CrossRef\]](#)
19. Li, P.; Liu, Y.; Yan, D. Facts and Fictions About Photocatalytic CO₂ Reduction to C₂+ Products. *ChemSusChem* **2024**, *18*, e202401174. [\[CrossRef\]](#)
20. Cui, Y.Q.; Labidi, A.; Liang, X.X.; Huang, X.; Wang, J.Y.; Li, X.M.; Dong, Q.B.; Zhang, X.L.; Othman, S.I.; Allam, A.A.; et al. Pivotal Impact Factors in Photocatalytic Reduction of CO₂ to Value-Added C₁ and C₂ Products. *ChemSusChem* **2024**, *17*, e202400551. [\[CrossRef\]](#)
21. Zhang, Z.; Yan, W.; Wang, Y.; Cui, G.; Lu, H. Preparation, Activity and Mechanism of a Metallic Cu/TiO₂ Nanotube Array Catalyst by a Fast Solar Drying Method for Photothermal CO₂ Reduction under Concentrating Light. *Catal. Sci. Technol.* **2024**, *14*, 4187. [\[CrossRef\]](#)
22. Variar, A.G.; Ramyashree, M.S.; Ail, V.U.; Shanmuga, P.S.; Sudhakar, K.; Tahir, M. Influence of various operational parameters in enhancing photocatalytic reduction efficiency of carbon dioxide in a photoreactor: A review. *J. Ind. Eng. Chem.* **2021**, *99*, 19–47. [\[CrossRef\]](#)
23. Im, S.W.; Ha, H.; Yang, W.; Jang, J.H.; Kang, B.; Seo, D.H.; Seo, J.; Nam, K.T. Light polarization dependency existing in the biological photosystem and possible implications for artificial antenna systems. *Photosynth. Res.* **2020**, *143*, 205–220. [\[CrossRef\]](#)
24. Chen, L.Y.; Su, T.M.; Xie, X.L.; Luo, X.; Ji, H.B.; Qin, Z.Z. Fluorine-mediated defect site reconstruction on TiO₂ for enhanced photocatalytic CO₂ reduction. *J. Mater. Sci. Technol.* **2026**, *264*, 70–81. [\[CrossRef\]](#)
25. Li, C.; Lu, X.Y.; Chen, L.Y.; Xie, X.L.; Qin, Z.Z.; Ji, H.B.; Su, T.M. WO₃/BiOBr S-Scheme Heterojunction Photocatalyst for Enhanced Photocatalytic CO₂ Reduction. *Materials* **2024**, *17*, 3199. [\[CrossRef\]](#) [\[PubMed\]](#)
26. Yang, T.Y.; Sun, X.Y.; Dong, Y.M.; Zhang, J.W.; Jiang, X.X.; Zhu, Y.F. Activity Breakthrough in CO₂ Photoreduction to C₂H₆ via Accelerated Electron Accumulation from H₂O Photooxidation to H₂O₂. *Angew. Chem. Int. Ed.* **2026**, *65*, e21909. [\[CrossRef\]](#)
27. Liu, Q.; Yang, G.; Li, R.R.; Yang, X.W.; Duan, Y.N.; Chen, F.Y.; Shen, Z.R. Principal Design of C-C Coupling Pathway Towards Highly Selective C₂ Products Using Photocatalytic CO₂ Reduction: A Review. *Chem. Asian J.* **2025**, *20*, e202401379. [\[CrossRef\]](#)
28. Alberio, J.; Peng, Y.; García, H. Photocatalytic CO₂ Reduction to C₂+ Products. *ACS Catal.* **2020**, *10*, 5734. [\[CrossRef\]](#)
29. Xia, X.-H.; Jia, Z.-J.; Yu, Y.; Liang, Y.; Wang, Z.; Ma, L.-L. Preparation of multi-walled carbon nanotube supported TiO₂ and its photocatalytic activity in the reduction of CO₂ with H₂O. *Carbon* **2007**, *45*, 717–721. [\[CrossRef\]](#)
30. Shown, I.; Hsu, H.-C.; Chang, Y.-C.; Lin, C.-H.; Roy, P.K.; Ganguly, A.; Wang, C.-H.; Chang, J.-K.; Wu, C.-I.; Chen, L.-C.; et al. Highly Efficient Visible Light Photocatalytic Reduction of CO₂ to Hydrocarbon Fuels by Cu-Nanoparticle Decorated Graphene Oxide. *Nano Lett.* **2014**, *14*, 6097–6103. [\[CrossRef\]](#)

31. Sorcar, S.; Thompson, J.; Hwang, Y.; Park, Y.H.; Majima, T.; Grimes, C.A.; Durrant, J.R.; In, S.-I. High-rate solar-light photoconversion of CO₂ to fuel: Controllable transformation from C1 to C2 products. *Energy Environ. Sci.* **2018**, *11*, 3183–3193. [[CrossRef](#)]
32. Billo, T.; Fu, F.-Y.; Raghunath, P.; Shown, I.; Chen, W.-F.; Lien, H.-T.; Shen, T.-H.; Lee, J.-F.; Chan, T.-S.; Huang, K.-Y.; et al. Ni-Nanocluster Modified Black TiO₂ with Dual Active Sites for Selective Photocatalytic CO₂ Reduction. *Small* **2018**, *14*, 1702928. [[CrossRef](#)]
33. Gelle, A.; Jin, T.; de la Garza, L.; Price, G.D.; Besteiro, L.V.; Moores, A. Applications of Plasmon-Enhanced Nanocatalysis to Organic Transformations. *Chem. Rev.* **2020**, *120*, 986–1041. [[CrossRef](#)]
34. Wang, W.; Deng, C.; Xie, S.; Li, Y.; Zhang, W.; Sheng, H.; Chen, C.; Zhao, J. Photocatalytic C-C Coupling from Carbon Dioxide Reduction on Copper Oxide with Mixed-Valence Copper(I)/Copper(II). *J. Am. Chem. Soc.* **2021**, *143*, 2984–2993. [[CrossRef](#)]
35. Luo, X.; Qiao, L.; Zhang, S.; Li, Q.; Liao, Y.; Rao, S.; Liu, H.; Zhao, Y. S-vacancy-assisted dual-sites on NiCo₂S₄ for photoconversion of CO₂ to olefiant gas. *Appl. Surf. Sci.* **2022**, *601*, 154184. [[CrossRef](#)]
36. Gao, W.; Li, S.; He, H.; Li, X.; Cheng, Z.; Yang, Y.; Wang, J.; Shen, Q.; Wang, X.; Xiong, Y.; et al. Vacancy-defect modulated pathway of photoreduction of CO₂ on single atomically thin AgInP₂S₆ sheets into olefiant gas. *Nat. Commun.* **2021**, *12*, 4747. [[CrossRef](#)] [[PubMed](#)]
37. Tian, F.; Zhang, H.; Liu, S.; Wu, T.; Yu, J.; Wang, D.; Jin, X.; Peng, C. Visible-light-driven CO₂ reduction to ethylene on CdS: Enabled by structural relaxation-induced intermediate dimerization and enhanced by ZIF-8 coating. *Appl. Catal. B* **2021**, *285*, 119834. [[CrossRef](#)]
38. Wang, L.; Zhao, B.; Wang, C.; Sun, M.; Yu, Y.; Zhang, B. Thermally assisted photocatalytic conversion of CO₂-H₂O to C₂H₄ over carbon doped In₂S₃ nanosheets. *J. Mater. Chem. A* **2020**, *8*, 10175–10179. [[CrossRef](#)]
39. Yu, Y.; Dong, X.; Chen, P.; Geng, Q.; Wang, H.; Li, J.; Zhou, Y.; Dong, F. Synergistic Effect of Cu Single Atoms and Au–Cu Alloy Nanoparticles on TiO₂ for Efficient CO₂ Photoreduction. *ACS Nano* **2021**, *15*, 14453–14464. [[CrossRef](#)] [[PubMed](#)]
40. Fan, J.; Cheng, L.; Fan, J.; Wang, Q.; Gao, M.; Li, D.; Feng, J. Integrating Au@TiO_x and Co sites in a tandem photocatalyst for efficient C-C coupling synthesis of ethane. *J. CO₂ Util.* **2023**, *6*, 102333. [[CrossRef](#)]
41. Collado, L.; Gomez-Mendoza, M.; García-Tecedor, M.; Oropeza, F.; Reynal, A.; Durrant, J.; Serrano, D.; Shea, V. Towards the improvement of methane production in CO₂ photoreduction using Bi₂WO₆/TiO₂ heterostructures. *Appl. Catal. B* **2023**, *324*, 122206. [[CrossRef](#)]
42. Li, N.; Wang, B.; Si, Y.; Xue, F.; Zhou, J.; Lu, Y.; Liu, M.; Catal, A.C. Toward High-Value Hydrocarbon Generation by Photocatalytic Reduction of CO₂ in Water Vapor. *ACS Catal.* **2019**, *9*, 5590–5602. [[CrossRef](#)]
43. Ou, H.; Li, G.; Ren, W.; Pan, B.; Luo, G.; Hu, Z.; Wang, D.; Li, Y. Atomically Dispersed Au-Assisted C–C Coupling on Red Phosphorus for CO₂ Photoreduction to C₂H₆. *J. Am. Chem. Soc.* **2022**, *144*, 22075–22082. [[CrossRef](#)] [[PubMed](#)]
44. Lee, C.-W.; Kourounioti, R.A.; Wu, J.C.S.; Murchie, E.; Maroto-Valer, M.; Jensen, O.E.; Huang, C.-W.; Ruban, A. Photocatalytic conversion of CO₂ to hydrocarbons by light-harvesting complex assisted Rh-doped TiO₂ photocatalyst. *J. CO₂ Util.* **2014**, *5*, 33–40. [[CrossRef](#)]
45. Hurtado, L.; Natividad, R.; García, H. Photocatalytic activity of Cu₂O supported on multi layers graphene for CO₂ reduction by water under batch and continuous flow. *Catal. Commun.* **2016**, *84*, 30–35. [[CrossRef](#)]
46. Zhang, X.; Han, F.; Shi, B.; Farsinezhad, S.; Dechaine, G.P.; Shankar, K. Photocatalytic Conversion of Diluted CO₂ into Light Hydrocarbons Using Periodically Modulated Multiwalled Nanotube Arrays. *Angew. Chem. Int. Ed.* **2012**, *51*, 12732–12735. [[CrossRef](#)]
47. Park, H.; Ou, H.-H.; Colussi, A.J.; Hoffmann, M.R. Artificial Photosynthesis of C1-C3 Hydrocarbons from Water and CO₂ on Titanate Nanotubes Decorated with Nanoparticle Elemental Copper and CdS Quantum Dots. *J. Phys. Chem. A* **2015**, *119*, 4658–4666. [[CrossRef](#)]
48. Gao, P.P.; Wu, J.; Gong, X.X.; Wu, T.; Sun, S.M. Selective Reduction of Carbon Dioxide to Ethanol by CuPd–MoO₂: C–C Coupling Enhanced by Bimetallic Active Sites. *ACS Sustain. Chem. Eng.* **2025**, *13*, 14290–14300. [[CrossRef](#)]
49. Das, R.; Das, K.; Ray, B.; Vinod, C.P.; Peter, S.C. Green transformation of CO₂ to ethanol using water and sunlight by the combined effect of naturally abundant red phosphorus and Bi₂MoO₆. *Energy Environ. Sci.* **2022**, *15*, 1967–1976. [[CrossRef](#)]
50. Ji, J.; Li, R.; Zhang, H.; Duan, Y.; Liu, Q.; Wang, H.; Shen, Z. Highly selective photocatalytic reduction of CO₂ to ethane over Au–O–Ce sites at micro-interface. *Appl. Catal. B* **2023**, *321*, 122020. [[CrossRef](#)]
51. Lertthanaphol, N.; Pienutsa, K.; Chusri, K.; Sornsuchat, T.; Chanthara, P.; Seeharaj, P.; Kim-Lohsoontorn, P.; Srinives, S. One-Step Hydrothermal Synthesis of Precious Metal-Doped Titanium Dioxide–Graphene Oxide Composites for Photocatalytic Conversion of CO₂ to Ethanol. *ACS Omega* **2020**, *6*, 35769–35779. [[CrossRef](#)]
52. Li, P.; Liu, L.; An, W.; Wang, H.; Guo, H.; Liang, Y.; Cui, W. Ultrathin porous g-C₃N₄ nanosheets modified with AuCu alloy nanoparticles and C-C coupling photothermal catalytic reduction of CO₂ to ethanol. *Appl. Catal. B* **2020**, *266*, 118618. [[CrossRef](#)]
53. Yu, H.; Sun, C.; Xuan, Y.; Zhang, K.; Chang, K. Full solar spectrum driven plasmonic-assisted efficient photocatalytic CO₂ reduction to ethanol. *Chem. Eng. J.* **2022**, *430*, 132940. [[CrossRef](#)]

54. Jia, Q.; Zhou, J.; Gong, L.; Wang, L.; Ma, X.; Zhao, Y. Z-scheme heterostructure of Cu₂O/Pt/NH₂-MIL-125(Ti) for photocatalytic CO₂ reduction. *J. Mol. Catal.* **2022**, *530*, 112599. [\[CrossRef\]](#)
55. Zeng, D.; Wang, H.; Zhu, X.; Cao, H.; Zhou, Y.; Wang, W.; Zhang, L.; Wang, W. Single-atom copper modified hexagonal tungsten oxide for efficient photocatalytic CO₂ reduction to acetic acid. *Chem. Eng. J.* **2023**, *451*, 138801. [\[CrossRef\]](#)
56. Gong, S.; Niu, Y.; Liu, X.; Xu, C.; Chen, C.; Meyer, T.; Chen, Z. Selective CO₂ Photoreduction to Acetate at Asymmetric Ternary Bridging Sites. *ACS Nano* **2023**, *17*, 4922–4932. [\[CrossRef\]](#)
57. Sun, S.; Watanabe, M.; Wu, J.; An, Q.; Ishihara, T. Ultrathin WO₃-0.33H₂O Nanotubes for CO₂ Photoreduction to Acetate with High Selectivity. *J. Am. Chem. Soc.* **2018**, *140*, 6474–6482. [\[CrossRef\]](#)
58. Zhu, J.; Shao, W.; Li, X.; Jiao, X.; Zhu, J.; Sun, Y.; Xie, Y. Asymmetric Triple-Atom Sites Confined in Ternary Oxide Enabling Selective CO₂ Photothermal Reduction to Acetate. *J. Am. Chem. Soc.* **2021**, *143*, 18233–18241. [\[CrossRef\]](#)
59. Jia, G.; Sun, M.; Wang, Y.; Shi, Y.; Zhang, L.; Cui, X.; Huang, B.; Yu, J.C. Asymmetric Coupled Dual-Atom Sites for Selective Photoreduction of Carbon Dioxide to Acetic Acid. *Adv. Funct. Mater.* **2022**, *32*, 2206817. [\[CrossRef\]](#)
60. Giusi, D.; Ampelli, C.; Genovese, C.; Perathoner, S.; Centi, G. A novel gas flow-through photocatalytic reactor based on copper-functionalized nanomembranes for the photoreduction of CO₂ to C1-C2 carboxylic acids and C1-C3 alcohols. *Chem. Eng. J.* **2021**, *408*, 127250. [\[CrossRef\]](#)
61. Han, Q.; Zhou, Y.; Tang, L.; Li, P.; Tu, W.; Li, L.; Li, H.; Zou, Z. Synthesis of single-crystalline, porous TaON microspheres toward visible-light photocatalytic conversion of CO₂ into liquid hydrocarbon fuels. *RSC Adv.* **2016**, *6*, 90792–90796. [\[CrossRef\]](#)
62. Kim, W.; Seok, T.; Choi, W. Nafion layer-enhanced photosynthetic conversion of CO₂ into hydrocarbons on TiO₂ nanoparticles. *Energy Environ. Sci.* **2012**, *5*, 6066–6070. [\[CrossRef\]](#)
63. Yu, S.; Wilson, A.J.; Heo, J.; Jain, P.K. Plasmonic Control of Multi-Electron Transfer and C-C Coupling in Visible-Light-Driven CO₂ Reduction on Au Nanoparticles. *Nano Lett.* **2018**, *18*, 2189–2194. [\[CrossRef\]](#)
64. Chen, Q.; Chen, X.; Fang, M.; Chen, J.; Li, Y.; Xie, Z.; Kuang, Q.; Zheng, L. Photo-induced Au-Pd alloying at TiO₂ {101} facets enables robust CO₂ photocatalytic reduction into hydrocarbon fuels. *J. Mater. Chem. A* **2019**, *7*, 1334–1340. [\[CrossRef\]](#)
65. Wang, Y.; Jia, H.; Gong, H.; Zhou, L.; Qiu, Z.; Fang, X.; Du, T. Fabrication of trimodal porous silica/g-C₃N₄ nanotubes for efficient visible light photocatalytic reduction of CO₂ to ethanol. *Chem. Eng. J.* **2021**, *426*, 130877. [\[CrossRef\]](#)
66. Becerra, J.; Gopalakrishnan, V.N.; Quach, T.A.; Do, T.O. Enhancing CO₂ photoreduction over ZIF-based reticular materials by morphology control of Au plasmonic nanoparticles. *Sustain. Energy Fuels* **2022**, *6*, 449–457. [\[CrossRef\]](#)
67. Du, H.; Ma, Q.; Gao, X.; Zhao, T.S. Cu/ZnV₂O₄ Heterojunction Interface Promoted Methanol and Ethanol Generation from CO₂ and H₂O under UV-Vis Light Irradiation. *ACS Omega* **2022**, *7*, 7278–7286. [\[CrossRef\]](#) [\[PubMed\]](#)
68. Zhao, D.; Xuan, Y.; Zhang, K.; Liu, X. Highly Selective Production of Ethanol over Hierarchical Bi@Bi₂MoO₆ Composite via Bicarbonate-Assisted Photocatalytic CO₂ Reduction. *ChemSusChem* **2021**, *14*, 3293–3302. [\[CrossRef\]](#)
69. Bai, X.H.; Han, L.J.; Wang, Y.C.; Liu, T.X.; Li, Y.G.; Luo, Y.H.; Li, D.M.; Meng, Q.B. The flow-type artificial photosynthesis assisted by photothermal catalysis over Fe/Fe₃C nanocatalyst to convert CO₂ and H₂O into multi-hydrocarbons. *Nano Res.* **2025**, *18*, 94907966. [\[CrossRef\]](#)
70. Yu, S.; Jain, P.K. Plasmonic photosynthesis of C1–C3 hydrocarbons from carbon dioxide assisted by an ionic liquid. *Nat. Commun.* **2019**, *10*, 2022. [\[CrossRef\]](#)
71. Choi, B.N.; Seo, J.Y.; An, Z.; Yoo, P.J.; Chung, C.H. An in-situ spectroscopic study on the photochemical CO₂ reduction on CsPbBr₃ perovskite catalysts embedded in a porous copper scaffold. *Chem. Eng. J.* **2022**, *430*, 132807. [\[CrossRef\]](#)
72. Xie, W.; Li, K.; Liu, X.; Zhang, X.; Huang, H. P-Mediated Cu-N₄ Sites in Carbon Nitride Realizing CO₂ Photoreduction to C₂H₄ with Selectivity Modulation. *Adv. Mater.* **2022**, *35*, 2208132. [\[CrossRef\]](#)
73. Ning, C.; Yang, J.; Bai, S.; Chen, G.; Liu, G.; Shen, T.; Zheng, L.; Xu, S.; Kong, X.; Liu, B.; et al. An Efficient Intercalation Supramolecular Structure for Photocatalytic CO₂ Reduction to Ethylene Under Visible Light. *Adv. Funct. Mater.* **2023**, *33*, 2300365. [\[CrossRef\]](#)
74. Xu, R.; Si, D.; Zhao, S.; Wu, Q.; Wang, X.; Liu, T.; Zhao, H.; Cao, R.; Huang, Y. Tandem Photocatalysis of CO₂ to C₂H₄ via a Synergistic Rhenium-(I) Bipyridine/Copper-Porphyrinic Triazine Framework. *J. Am. Chem. Soc.* **2023**, *145*, 8261–8270. [\[CrossRef\]](#) [\[PubMed\]](#)
75. Hao, J.; Yang, D.; Wu, J.; Ni, B.; Wei, L.; Xu, Q.; Min, Y.; Li, H. Utilizing new metal phase nanocomposites deep photocatalytic conversion of CO₂ to C₂H₄. *Chem. Eng. J.* **2021**, *423*, 130190. [\[CrossRef\]](#)
76. Yang, X.; Lan, X.; Zhang, Y.; Li, H.; Bai, G. Rational design of MoS₂@COF hybrid composites promoting C-C coupling for photocatalytic CO₂ reduction to ethane. *Appl. Catal. B* **2023**, *325*, 122393. [\[CrossRef\]](#)
77. Ni, B.; Jiang, H.; Guo, W.; Xu, Q.; Min, Y. Tailoring the oxidation state of metallic TiO through Ti³⁺/Ti²⁺ regulation for photocatalytic conversion of CO₂ to C₂H₆. *Appl. Catal. B* **2022**, *307*, 121141. [\[CrossRef\]](#)
78. Chen, G.; Gao, R.; Zhao, Y.; Li, Z.; Waterhouse, G.I.N.; Shi, R.; Zhao, J.; Zhang, M.; Shang, L.; Sheng, G.; et al. Alumina-Supported CoFe Alloy Catalysts Derived from Layered-Double-Hydroxide Nanosheets for Efficient Photothermal CO₂ Hydrogenation to Hydrocarbons. *Adv. Mater.* **2018**, *30*, 1704663. [\[CrossRef\]](#)

79. Zhang, R.; Wang, H.; Tang, S.; Liu, C.; Dong, F.; Yue, H.; Liang, B. Photocatalytic Oxidative Dehydrogenation of Ethane Using CO₂ as a Soft Oxidant over Pd/TiO₂ Catalysts to C₂H₄ and Syngas. *ACS Catal.* **2018**, *8*, 9280–9286. [\[CrossRef\]](#)
80. Li, N.; Jiang, R.; Li, Y.; Zhou, J.; Ma, Q.; Shen, S.; Liu, M. Plasma-Assisted Photocatalysis of CH₄ and CO₂ into Ethylene. *ACS Sustain. Chem. Eng.* **2019**, *7*, 11455–11463. [\[CrossRef\]](#)
81. Chai, Y.; Tang, S.; Wang, Q.; Wu, Q.; Liang, J.; Li, L. Gold nanoparticles supported on ZnGa₂O₄ nanosheets as efficient photocatalysts for selective oxidation of methane to ethane under ambient conditions. *Appl. Catal. B* **2023**, *338*, 123012. [\[CrossRef\]](#)
82. Song, S.; Song, H.; Li, L.; Wang, S.; Chu, W.; Peng, K.; Meng, X.; Wang, Q.; Deng, B.; Liu, Q.; et al. A selective Au-ZnO/TiO₂ hybrid photocatalyst for oxidative coupling of methane to ethane with dioxygen. *Nat. Catal.* **2021**, *4*, 1032–1042. [\[CrossRef\]](#)
83. Liu, L.; Puga, A.V.; Cored, J.; Concepcion, P.; Pérez-Dieste, V.; García, H.; Corma, A. Sunlight-assisted hydrogenation of CO₂ into ethanol and C₂+ hydrocarbons by sodium-promoted Co@C nanocomposites. *Appl. Catal. B* **2018**, *235*, 186–196. [\[CrossRef\]](#)
84. Nguyen, V.C.; Nimbalkar, D.B.; Huong, V.H.; Lee, Y.L.; Teng, H.S. Elucidating the mechanism of photocatalytic reduction of bicarbonate (aqueous CO₂) into formate and other organics. *J. Colloid Interface Sci.* **2023**, *649*, 918–928. [\[CrossRef\]](#)
85. Zhong, H.; Fujii, K.; Nakano, Y.; Jin, F.M. Effect of CO₂ Bubbling into Aqueous Solutions Used for Electrochemical Reduction of CO₂ for Energy Conversion and Storage. *J. Phys. Chem. C* **2015**, *119*, 55–61. [\[CrossRef\]](#)
86. Yoshino, S.; Iwase, A.; Yamaguchi, Y.; Suzuki, T.M.; Morikawa, T.; Kudo, A. Photocatalytic CO₂ Reduction Using Water as an Electron Donor under Visible Light Irradiation by Z-Scheme and Photoelectrochemical Systems over (CuGa)_{0.5}ZnS₂ in the Presence of Basic Additives. *J. Am. Chem. Soc.* **2022**, *144*, 2323–2332. [\[CrossRef\]](#) [\[PubMed\]](#)
87. Teramura, K.; Hori, K.; Terao, Y.; Huang, Z.; Iguchi, S.; Wang, Z.; Asakura, H.; Hosokawa, S.; Tanaka, T. Which is an Intermediate Species for Photocatalytic Conversion of CO₂ by H₂O as the Electron Donor: CO₂ Molecule, Carbonic Acid, Bicarbonate, or Carbonate Ions? *J. Phys. Chem. C* **2017**, *121*, 8711–8721. [\[CrossRef\]](#)
88. Pang, R.; Teramura, K.; Asakura, H.; Hosokawa, S.; Tanaka, T. Role of Bicarbonate Ions in Aqueous Solution as a Carbon Source for Photocatalytic Conversion of CO₂ into CO. *ACS Appl. Energy Mater.* **2019**, *2*, 5397–5405. [\[CrossRef\]](#)
89. Morishita, M.; Asakura, H.; Hosokawa, S.; Tanaka, T.; Teramura, K. Kinetic Study of Heterogeneous Photocatalytic CO₂ Reduction: Development of a General Formula for Relations between Activity and Reaction Conditions. *ACS Catal.* **2023**, *13*, 6966–6973. [\[CrossRef\]](#)
90. Tommasi, M.; Conte, F.; Alam, M.I.; Ramis, G.; Rossetti, I. Highly Efficient and Effective Process Design for High-Pressure CO₂ Photoreduction over Supported Catalysts. *Energies* **2023**, *16*, 4990. [\[CrossRef\]](#)
91. Conte, F.; García-López, E.I.; Marci, G.; Bianchi, C.L.M.; Ramis, G.; Rossetti, I. Carbon Nitride-Based Catalysts for High Pressure CO₂ Photoreduction. *Catalysts* **2022**, *12*, 1628. [\[CrossRef\]](#)
92. Bahadori, E.; Tripodi, A.; Villa, A.; Pirola, C.; Prati, L.; Ramis, G.; Rossetti, I. High Pressure Photoreduction of CO₂: Effect of Catalyst Formulation, Hole Scavenger Addition and Operating Conditions. *Catalysts* **2018**, *8*, 430. [\[CrossRef\]](#)
93. Bahadori, E.; Tripodi, A.; Villa, A.; Pirola, C.; Prati, L.; Ramis, G.; Dimitratos, N.; Wang, D.; Rossetti, I. High pressure CO₂ photoreduction using Au/TiO₂: Unravelling the effect of co-catalysts and of titania polymorphs. *Catal. Sci. Technol.* **2019**, *9*, 2253. [\[CrossRef\]](#)
94. Rossetti, I.; Villa, A.; Compagnoni, M.; Prati, L.; Ramis, G.; Pirola, C.; Bianchi, C.L.; Wang, W.; Wang, D. CO₂ photoconversion to fuels under high pressure: Effect of TiO₂ phase and of unconventional reaction conditions. *Catal. Sci. Technol.* **2015**, *5*, 4481. [\[CrossRef\]](#)
95. Galli, F.; Compagnoni, M.; Vitali, D.; Pirola, C.; Bianchi, C.L.; Villa, A.; Prati, L.; Rossetti, I. CO₂ photoreduction at high pressure to both gas and liquid products over titanium dioxide. *Appl. Catal. B Environ.* **2017**, *200*, 386–391. [\[CrossRef\]](#)
96. Tang, X.L.; Chen, G.J.; Liu, H.L.; Fang, J. Affect of Pressure on Photoreduction of CO₂ to Acetaldehyde in Aqueous Suspensions of TiO₂. In Proceedings of the International Conference on Energy and Environment Technology, Guilin, China, 16–18 October 2009.
97. Devi, A.D.; Pushpavanam, S.; Singh, N.; Verma, J.; Pal, M.; Somnath, K.; Roy, C. Enhanced methane yield by photoreduction of CO₂ at moderate temperature and pressure using Pt coated, graphene oxide wrapped TiO₂ nanotubes. *Results Eng.* **2022**, *14*, 100441. [\[CrossRef\]](#)
98. Pipelzadeh, E.; Rudolph, V.; Hanson, G.; Noble, C.; Wang, L.Z. Photoreduction of CO₂ on ZIF-8/TiO₂ nanocomposites in a gaseous photoreactor under pressure swing. *Appl. Catal. B Environ.* **2017**, *218*, 672–678. [\[CrossRef\]](#)
99. Zhang, H.W.; Kawamura, S.; Tamba, M.; Kojima, T.; Yoshida, M.; Izumi, Y. Is water more reactive than H₂ in photocatalytic CO₂ conversion into fuels using semiconductor catalysts under high reaction pressures? *J. Catal.* **2017**, *352*, 452–465. [\[CrossRef\]](#)
100. Hori, H.; Takano, Y.; Koike, K.; Sasaki, Y. Efficient rhenium-catalyzed photochemical carbon dioxide reduction under high pressure. *Inorg. Chem. Commun.* **2003**, *6*, 300–303. [\[CrossRef\]](#)
101. Molins, F.; Küpper, K.; Schweers, E. Investigation of reaction condition effects on photocatalytic methane production over P25-TiO₂/Pt with CO₂ and H₂O gas. Applied and mechanistic implications. *ChemPhotoChem* **2020**, *4*, 526–534. [\[CrossRef\]](#)
102. Qadir, M.I.; Zannatta, M.; Gil, E.S.; Stassen, H.K.; Gonçalves, P.; Neto, B.A.; de Souza, P.E.; Dupont, J. Photocatalytic Reverse Semi-Combustion Driven by Ionic Liquids. *ChemSusChem* **2019**, *12*, 1011–1016. [\[CrossRef\]](#) [\[PubMed\]](#)

103. Kuramochi, Y.; Kamiya, M.; Ishida, H. Photocatalytic CO₂ Reduction in N,N-Dimethylacetamide/Water as an Alternative Solvent System. *Inorg. Chem.* **2014**, *53*, 3326–3332. [[CrossRef](#)]
104. Yuan, X.J.; Solé-Daura, A.; Li, C.; Díaz-Ruiz, M.; Liguori, N.; Biset-Peiró, M.; Murcia-López, S.; Luxa, J.; Sofer, Z.; Galán-Mascarós, J.R.; et al. Gas-Phase Photocatalytic CO₂ Reduction to Ethane via EDOT-Based Trimers. *ACS Catal.* **2025**, *15*, 6186–6198. [[CrossRef](#)]
105. Thang, N.Q.; Sabbah, A.; Putikam, R.; Huang, C.Y.; Lin, T.Y.; Hussien, M.K.; Wu, H.L.; Lin, M.-C.; Lee, C.-H.; Chen, K.H.; et al. Regulating COOH Intermediate via Rationally Constructed Surface-Active Sites of Bi₂WO₆ for Solar-Driven CO₂ -to-CO Production. *Adv. Funct. Mater.* **2025**, *35*, 2423751. [[CrossRef](#)]
106. Lee, J.; Waterhouse, G.I.N.; Mao, Y.; Wang, Z.; Zhu, E.; Low, J.; Chai, S.P.; Tan, L.L. Lead-free halide perovskites and Bi-BTC frameworks: Engineering S-scheme heterojunctions for photocatalytic CO₂ conversion. *Appl. Catal. B Environ. Energy* **2025**, *365*, 124942. [[CrossRef](#)]
107. Ojha, N.; Pant, K.K. Photocatalytic Synergy Between α -Bi₂O₃ Nanosphere and Spindle MIL-88A for Gas-Phase CO₂ Reduction. *ChemSusChem* **2025**, *18*, e202401260. [[CrossRef](#)]
108. Sung, P.-H.; Huang, C.-Y.; Lin, C.-Y.; Chung, P.-W.; Chang, Y.-C.; Chen, L.-C.; Chen, H.-Y.; Liao, C.-N.; Chiu, E.-L.; Wang, C.-Y. Photocatalytic CO₂ reduction for C2-C3 oxy-compounds on ZIF-67 derived carbon with TiO₂. *J. CO₂ Util.* **2022**, *58*, 101920. [[CrossRef](#)]
109. Moustakas, N.G.; Klahn, M.; Mei, B.T.; Pougin, A.; Dilla, M.; Poppel, T.; Ristig, S.; Strunk, J. A high-purity gas–solid photoreactor for reliable and reproducible photocatalytic CO₂ reduction measurements. *HardwareX* **2023**, *15*, e00448. [[CrossRef](#)] [[PubMed](#)]
110. Sorcar, S.; Hwang, Y.; Grimes, C.A.; In, S.-I. Highly enhanced and stable activity of defect-induced titania nanoparticles for solar light-driven CO₂ reduction into CH₄. *Mater. Today* **2017**, *20*, 507–515. [[CrossRef](#)]
111. Olivo, A.; Thompson, W.A.; Bay, E.R.B.; Ghedini, E.; Menegazzo, F.; Maroto-Valer, M.; Signoretto, M. Investigation of process parameters assessment via design of experiments for CO₂ photoreduction in two photoreactors. *J. CO₂ Util.* **2020**, *36*, 25–32. [[CrossRef](#)]
112. Cheng, M.; Yang, S.; Chen, R.; Zhu, X.; Liao, Q.; Huang, Y. Copper-decorated TiO₂ nanorod thin films in optofluidic planar reactors for efficient photocatalytic reduction of CO₂. *Int. J. Hydrogen Energy* **2017**, *42*, 9722–9732. [[CrossRef](#)]
113. Wu, J.C.S. Photocatalytic Reduction of Greenhouse Gas CO₂ to Fuel. *Catal. Surv. Asia* **2009**, *13*, 30–40. [[CrossRef](#)]
114. Bhatta, S.; Nagassou, D.; Mohsenian, S.; Trelles, J.P. Photo-thermochemical decomposition of carbon-dioxide in a direct solar receiver-reactor. *Sol. Energy* **2019**, *178*, 201–214.
115. Tong, K.; Chen, L.; Yang, L.; Du, X.; Yang, Y. Energy transport of photocatalytic carbon dioxide reduction in optical fiber honeycomb reactor coupled with trough concentrated solar power. *Catalysts* **2021**, *11*, 829. [[CrossRef](#)]
116. Rao, H.; Schmidt, L.C.; Bonin, J.; Robert, M. Visible-light-driven methane formation from CO₂ with a molecular iron catalyst. *Nature* **2017**, *548*, 74–77. [[CrossRef](#)]
117. Li, J.L.; Zhang, M.; Guan, Z.J.; Li, Q.Y.; He, C.Q.; Yang, J.J. Synergistic effect of surface and bulk single-electron-trapped oxygen vacancy of TiO₂ in the photocatalytic reduction of CO₂. *Appl. Catal. B Environ.* **2017**, *206*, 300–307. [[CrossRef](#)]
118. Robatjazi, H.; Zhao, H.; Swearer, D.F.; Hogan, N.J.; Zhou, L.; Alabastri, A.; McClain, M.J.; Nordlander, P.; Halas, N.J. Plasmon-induced selective carbon dioxide conversion on earth-abundant aluminum-cuprous oxide antenna-reactor nanoparticles. *Nat. Commun.* **2017**, *8*, 27. [[CrossRef](#)] [[PubMed](#)]
119. Li, Y.; Hao, J.; Song, H.; Zhang, F.; Bai, X.; Meng, X.; Zhang, H.; Wang, S.; Hu, Y.; Ye, J. Selective light absorber-assisted single nickel atom catalysts for ambient sunlight-driven CO₂ methanation. *Nat. Commun.* **2019**, *10*, 2359. [[CrossRef](#)] [[PubMed](#)]
120. Mateo, D.; Cerrillo, J.L.; Durini, S.; Gascon, J. Fundamentals and applications of photo-thermal catalysis. *Chem. Soc. Rev.* **2021**, *50*, 2173–2210. [[CrossRef](#)]
121. Ghoussou, M.; Xia, M.; Duchesne, P.N.; Segal, D.; Ozin, G. Principles of photothermal gas-phase heterogeneous CO₂ catalysis. *Energy Environ. Sci.* **2019**, *12*, 1122–1144. [[CrossRef](#)]
122. Song, C.; Wang, Z.; Yin, Z.; Xiao, D.; Ma, D. Principles and applications of photothermal catalysis. *Chem Catal.* **2022**, *2*, 53–83. [[CrossRef](#)]
123. Fu, Y.W.; Wang, Y.; Huang, J.; Lu, K.J.; Liu, M.C. Solar fuel production through concentrating light irradiation. *Green Energy Environ.* **2024**, *9*, 1550–1580. [[CrossRef](#)]
124. Fang, X.X.; Gao, Z.H.; Lu, H.F.; Zhang, Z.K. Boosting CO₂ photoreduction activity by large Fresnel lens concentrated solar light. *Catal. Commun.* **2019**, *125*, 48–51. [[CrossRef](#)]
125. Zhang, Z.K.; Wang, Y.; Cui, G.K.; Lu, H.F. Remarkable CO₂ photoreduction activity using TiO₂ nanotube arrays under favorable photothermal conditions driven by concentrated solar light. *Appl. Phys. Lett.* **2021**, *112*, 123906. [[CrossRef](#)]
126. Zhang, Z.K.; Gao, Z.H.; Liu, H.Y.; Abanades, S.; Lu, H.F. High photothermally active Fe₂O₃ film for CO₂ photoreduction with H₂O driven by solar light. *ACS Appl. Energy Mater.* **2019**, *2*, 8376–8380. [[CrossRef](#)]
127. Zhang, Z.K.; Zhang, D.; Lyu, L.; Cui, G.K.; Lu, H.F. In situ formation of Z-Scheme Bi₂WO₆/WO₃ heterojunctions for gas-phase CO₂ photoreduction with H₂O by photohydrothermal treatment. *Catalysts* **2022**, *12*, 1237.

128. Mo, S.P.; Zhao, X.Y.; Li, S.D.; Huang, L.L.; Zhao, X.; Ren, Q.M.; Zhang, M.Y.; Peng, R.S.; Zhang, Y.N.; Zhou, X.B.; et al. Non-interacting Ni and Fe dual-atom pair sites in N-doped carbon catalysts for efficient concentrating solar-driven photothermal CO₂ reduction. *Angew. Chem. Int. Ed.* **2023**, *60*, e202313868.
129. Ren, Y.Q.; Fu, Y.W.; Li, N.X.; You, C.J.; Huang, J.; Huang, K.; Sun, Z.K.; Zhou, J.C.; Si, Y.T.; Zhu, Y.H.; et al. Concentrated solar CO₂ reduction in H₂O vapour with >1% energy conversion efficiency. *Nat. Commun.* **2024**, *15*, 4675. [[CrossRef](#)] [[PubMed](#)]
130. Bai, S.J.; Qiu, H.R.; Song, M.M.; He, G.W.; Wang, F.; Liu, Y.; Guo, L.J. Porous fixed-bed photoreactor for boosting C-C coupling in photocatalytic CO₂ reduction. *eScience* **2022**, *2*, 428–437. [[CrossRef](#)]
131. Huang, Q.S.; Chu, C.C.; Li, Q.J.; Liu, Q.; Liu, X.R.; Sun, J.; Ni, B.-J.; Mao, S. Three-Phase Interface Construction on Hydrophobic Carbonaceous Catalysts for Highly Active and Selective Photocatalytic CO₂ Conversion. *ACS Catal.* **2023**, *13*, 11232–11243. [[CrossRef](#)]
132. Zhu, Q.B.; Xuan, Y.M.; Zhao, D.W.; Yu, H.T.; Wang, J.; Liu, X.L. A lotus-inspired triphase continuous CO₂ photo-thermal reduction system with wide applicability and tunable interface environment. *Mater. Today Energy* **2025**, *48*, 101777. [[CrossRef](#)]
133. Dai, L.L.; Li, B.L.; Li, Z.S.; Yu, C.L. Floatable photocatalysts: Design principles and application advances. *J. Environ. Chem. Eng.* **2024**, *12*, 113029. [[CrossRef](#)]
134. Maki, Y.; Ide, Y.; Okada, T. Water-floatable organosilica particles for TiO₂ photocatalysis. *Chem. Eng. J.* **2016**, *299*, 367–372. [[CrossRef](#)]
135. Xie, Z.H.; Yang, W. A robust floating oxygen-doped graphitic carbon nitride sheet for efficient photocatalytic CO₂ conversion. *Sep. Purif. Technol.* **2025**, *358*, 130420. [[CrossRef](#)]
136. Wang, M.M.; Zhang, Y.X.; Dong, S.H.; Li, N.J.; Xu, Q.F.; Li, H.; Lu, J.M.; Chen, D.Y. Self-Floating Polymer Microreactor for High-Efficiency Synergistic CO₂ Photoreduction and Antibiotic Degradation in One Photoredox Cycle. *Adv. Funct. Mater.* **2024**, *34*, 2408831. [[CrossRef](#)]
137. Xie, Y.G.; Wang, M.; Huang, Q.; Huang, Q.; Sheng, B.; Song, W.J.; Sheng, H.; Zhao, J.C. A floatable photocatalyst to synergistically promote CO₂ reduction and water oxidation by creating oriented charge separation across a tri-phase interface. *Energy Environ. Sci.* **2024**, *17*, 4725. [[CrossRef](#)]
138. Scheffe, J.R.; Steinfeld, A. Oxygen exchange materials for solar thermochemical splitting of H₂O and CO₂: A review. *Mater. Today* **2014**, *17*, 341–348. [[CrossRef](#)]
139. Agrafiotis, C.; Roeb, M.; Sattler, C. A review on solar thermal syngas production via redox pair-based water/carbon dioxide splitting thermochemical cycles. *Renew. Sust. Energy Rev.* **2015**, *42*, 254–285. [[CrossRef](#)]
140. Nitopi, S.; Bertheussen, E.; Scott, S.B.; Liu, X.Y.; Engstfeld, A.K.; Horch, S.; Segerluf, B.; Stephens, E.L.; Chan, K.; Hahn, C.; et al. Progress and Perspectives of Electrochemical CO₂ Reduction on Copper in Aqueous Electrolyte. *Chem. Rev.* **2019**, *119*, 7610–7672. [[CrossRef](#)] [[PubMed](#)]
141. Gao, D.F.; Arán-Ais, R.M.; Jeon, H.S.; Cuenya, B.R. Rational catalyst and electrolyte design for CO₂ electroreduction towards multicarbon products. *Nat. Catal.* **2019**, *2*, 198–210. [[CrossRef](#)]
142. Vasileff, A.; Xu, C.C.; Jiao, Y.; Zheng, Y.; Qiao, S.Z. Surface and Interface Engineering in Copper-Based Bimetallic Materials for Selective CO₂ Electroreduction. *Chem* **2018**, *4*, 1809–1831. [[CrossRef](#)]

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.