

Mini Review

Open Access



Research progress of photoelectrochemical conversion of CO₂ to C₂₊ products

Xia Jiang^{1,2}, Rui Chen^{1,2}, Yan-Xin Chen^{1,2,3,*} , Can-Zhong Lu^{1,2,3,*}

¹State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou 350002, Fujian, China.

²Xiamen Key Laboratory of Rare Earth Photoelectric Functional Materials, Xiamen Institute of Rare-earth Materials, Haixi Institutes, Chinese Academy of Sciences, Xiamen 361021, Fujian, China.

³Fujian Science & Technology Innovation Laboratory for Optoelectronic Information of China, Fuzhou 350108, Fujian, China.

***Correspondence to:** Prof. Yan-Xin Chen, Prof. Can-Zhong Lu, State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, 155 Yangqiao Road West, Fuzhou 350002, Fujian, China. E-mail: yanxinchen@fjirsm.ac.cn; czlu@fjirsm.ac.cn

How to cite this article: Jiang X, Chen R, Chen YX, Lu CZ. Research progress of photoelectrochemical conversion of CO₂ to C₂₊ products. *Chem Synth* 2024;4:46. <https://dx.doi.org/10.20517/cs.2024.03>

Received: 9 Jan 2024 **First Decision:** 20 May 2024 **Revised:** 29 May 2024 **Accepted:** 28 Jun 2024 **Published:** 8 Aug 2024

Academic Editors: Xiang-Dong Yao, Aicheng Chen **Copy Editor:** Dong-Li Li **Production Editor:** Dong-Li Li

Abstract

The reduction of CO₂ to C₂₊ products using photoelectrochemistry (PEC) is significant and highly challenging. However, systematic summaries on PEC CO₂ conversion into C₂₊ products are lacking. Therefore, this paper systematically reviews the current research status of the PEC CO₂ conversion for the preparation of C₂₊ products, including the pathways of C₂₊ products, the usage of catalysts and reactors, and methods for improving C₂₊ product selectivity. Besides, the deficiencies in current research are analyzed, and future developments are discussed.

Keywords: Photoelectrochemistry, C₂₊ products, CO₂ conversion

INTRODUCTION

The hazards of climate change to humans and the environment necessitate transitioning from our current fossil fuel economy to an economy based on renewable and carbon-neutral energy technologies. The urgency to reduce primary greenhouse gas (CO₂) emissions while continuing to provide fuel for the growing global population remains one of the most significant technological challenges of our time. Photoelectrochemical technology not only maximizes the advantages of photocatalysis and electrocatalysis,



© The Author(s) 2024. **Open Access** This article is licensed under a Creative Commons Attribution 4.0 International License (<https://creativecommons.org/licenses/by/4.0/>), which permits unrestricted use, sharing, adaptation, distribution and reproduction in any medium or format, for any purpose, even commercially, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made.



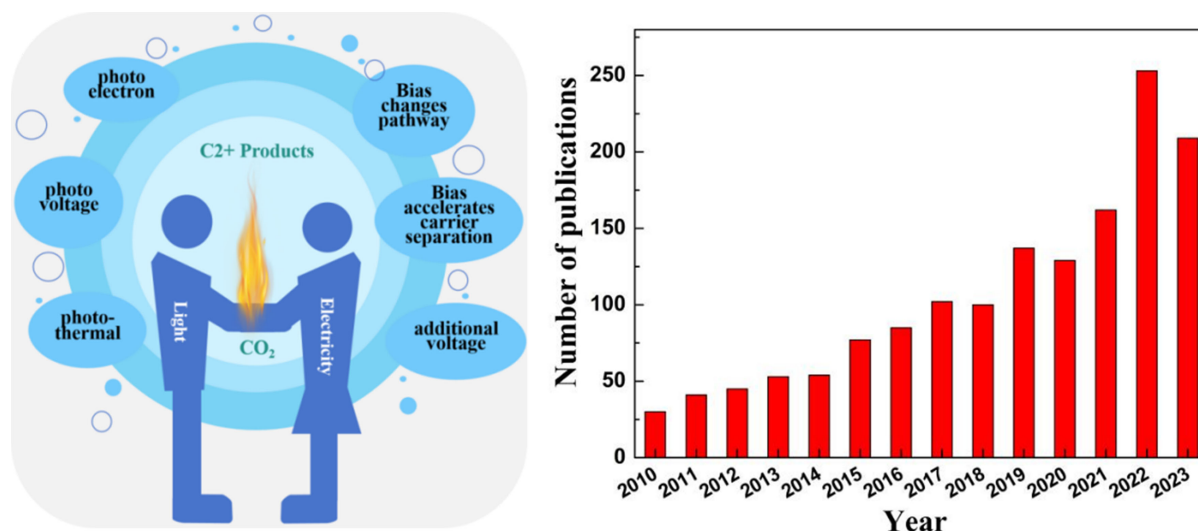


Figure 1. The role of light and electricity in photoelectrochemical CO₂ reduction and the number of publications on PEC CO₂ conversion were obtained using keyword search (photoelectric and CO₂). Data was extracted from the Web of Science in May 2024. PEC: Photoelectrochemistry.

but their synergy also sparks a different kind of brilliance. Utilizing photoelectrochemistry (PEC) technology to convert CO₂ into fuel represents a new, clean, and green approach to using CO₂ [1-3], which is increasingly attracting the interest of researchers [Figure 1]. Similar to other types of catalysis, the PEC conversion of CO₂ also involves multiple-step processes, resulting in a wide range of products such as C₁ (CO, CH₄, HCOOH, *etc.*) and C₂₊ products (C₂H₄, C₂H₆, CH₃COOH, *etc.*). Currently, most reported CO₂ conversion products are C₁ products because the generation of C₂₊ products involves a C-C coupling process, which is more difficult to obtain than C₁ products. But, compared with C₁ products, C₂₊ products have higher added value, and research on directly converting CO₂ into C₂₊ products holds significant significance. To date, several review articles have covered the overall research status on PEC CO₂ conversion [1-7], the influence of cocatalysts [8-10], the design of the PEC cathodes [11-15], the impact of PEC parameters [16,17], and the study of catalysts [18-20]. However, no individual summaries have been on converting CO₂ into C₂₊ products using the PEC technology. Hence, firstly, this paper aims to briefly introduce the basic principles of CO₂ conversion into C₂₊ products. Secondly, it summarizes the catalysts and reactor types reported thus far for obtaining C₂₊ products. Thirdly, it emphasizes the design strategies of catalysts currently available for generating or enhancing C₂₊ selectivity. Finally, it concludes with a summary of the current work and prospects for future research.

FUNDAMENTAL OF PHOTOELECTROCHEMICAL CO₂ REDUCTION

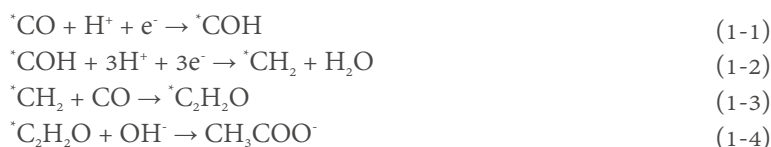
The PEC reduction of CO₂ involves light absorption, charge carrier transfer, CO₂ adsorption and activation, surface reactions, and product desorption. The energy input for PEC catalysis is provided by light and electricity. Light plays a role in generating high-energy photoelectrons for CO₂ reduction, generating photoelectric voltage to reduce energy consumption to some extent and lower economic costs, and producing heat to promote the progress of the reaction. Electricity plays a role in introducing an additional bias voltage to accelerate charge carrier separation and increase local charge density. By adjusting the bias voltage, the CO₂ reduction pathway can be altered to enhance selectivity.

Additionally, the supplementation of voltage can enable semiconductor materials that were originally not viable for photocatalytic CO₂ conversion to become feasible [Figure 1]. The synergistic effects of light and

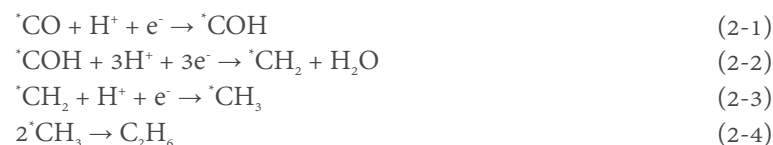
electricity can effectively reduce the activation energy for CO₂ reduction, but the study of the photoelectric synergistic effect is still lacking^[21,22]. Furthermore, the contribution and distinction between photogenerated and voltage-provided electrons have not yet been reported.

Based on current reports, the mechanism for converting CO₂ into C₂₊ involves first converting CO₂ into ^{*}CO intermediates, followed by the generation of various intermediates of C₂₊ products through C-C coupling and multi-proton-coupled electron transfer (PCET), as shown by the equations for different pathways (Route 1-6)^[23]. However, the competitive adsorption of ^{*}H_{ad} and ^{*}CO on monocomponent catalysts hinders the enhancement of PCET and C-C reaction kinetics. In order to break the linear scaling relationship between the adsorption of ^{*}H_{ad}/^{*}CO intermediates and improve water dissociation on auxiliary sites or CO₂-to-CO production, tandem catalysts consisting of multicomponents have been developed. These catalysts can achieve higher coverage of ^{*}H_{ad} and ^{*}CO, which is more conducive to the generation of C₂₊ products. However, to our knowledge, while there are detailed reports on achieving C₂₊ products through serial pathways in the electrocatalytic conversion of CO₂^[24], their application in the field of photoelectrocatalytic CO₂ conversion has not been observed.

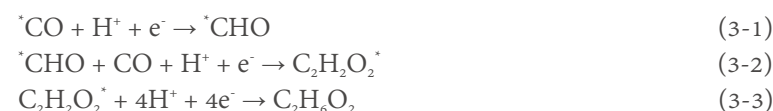
Route 1:



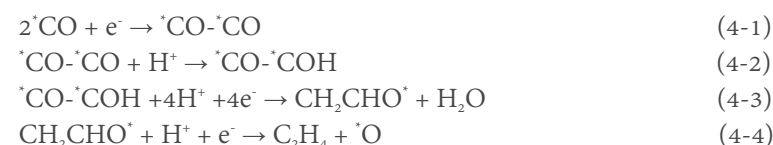
Route 2:



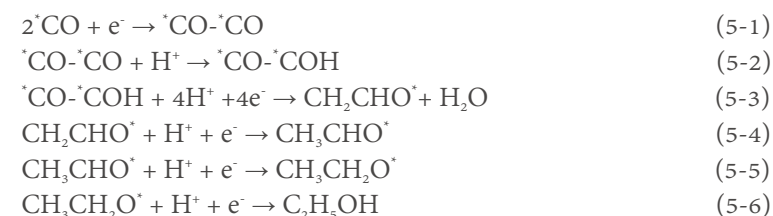
Route 3:



Route 4:



Route 5:



Route 6:



CATALYSTS AND REACTORS OF PHOTOELECTROCHEMICAL CO₂ UPGRADING TO C₂₊

Hitherto, catalyst research for the PEC conversion of CO₂ into C₂₊ products is focused on photocathodes, primarily using Cu-based catalysts^[21,24-29] [Table 1]. Cu-based species have a high binding affinity for ^{*}CO intermediates, making them active sites for CO₂ reduction and the generation of C₂₊ chemical species. However, the high energy barriers associated with C-C coupling and PCET processes still pose challenges for Cu-based catalysts regarding high overpotential and low selectivity towards C₂₊ products. In addition to Cu-based catalysts, reasonable structural design of some non-Cu-based catalysts enables higher selectivity towards C₂₊ products. Table 2 lists the selectivity of some non-Cu-based catalysts in photoelectrocatalytic CO₂ conversion. It shows that the non-Cu-based catalysts are mainly composite materials, including TiO₂, ZnO, WO₃, etc., with more negative potentials compared to Cu-based catalysts. Regardless of Cu-based or non-Cu-based catalysts, ethanol, acetic acid, and ethylene are the main C₂₊ products; the yield of C₂₊ products is relatively low (typically at the μmol level); the Faradaic efficiencies cover a wide range, and the faradaic efficiency for a single C₂₊ product can reach up to 80%. The selectivity of C₂₊ products is primarily enhanced by adjusting the synthesis process of materials, doping with heteroatoms, and compositing with other metals/metal oxides/non-metallic materials to alter the morphology, band structure, and local electron density of the electrode materials.

In addition to catalysts, the selection of reactors also significantly influences the generation of C₂₊ products. The light source, membrane characteristics, electrolyte, manufacturing materials, wall thickness, operational modes (batch or flow), heat exchange, phase requirements (gas-solid, liquid-solid, or gas-liquid-solid), CO₂ solubility, and flow characteristics of feed gases and electrolytes can affect catalytic performance^[54,55]. Currently, reactors used for CO₂ PEC conversion are primarily modified from electrochemical CO₂ reduction reactors and can be divided into H-type and flow electrolysis cells [Figure 2]^[56-58]. The H-type electrolysis cell is a relatively simple device that belongs to a batch reactor. It separates the anode and cathode using ion exchange membranes. However, its significant Ohmic resistance between the electrodes and limited CO₂ solubility have hindered its development. The low current density (< 100 mA·cm⁻²) achieved in H-type cells does not meet industrial requirements. Furthermore, alkaline electrolytes are more conducive to suppressing H₂ reduction and enhancing C-C coupling. However, alkaline electrolytes are not feasible in aqueous CO₂ reduction conducted in H-type electrolysis cells. Nevertheless, the gas diffusion electrode (GDE) of the flow electrolysis cell separates the CO₂ flow field from the liquid electrolyte, allowing the use of high-concentration alkaline electrolytes.

The flow electrolysis cell is a continuous operation reactor where gases and electrolytes can be continuously supplied to the electrolytic cell. GDEs are used as the electrodes, which greatly overcome the limitations of CO₂ solubility. However, a certain distance between the anode and cathode still exists, resulting in significant Ohmic resistance. The membrane-electrode reactor integrates the anode, cathode, and membrane assembly, significantly reducing the distance between the electrodes and exhibiting improved catalytic performance. However, it lacks a reference electrode, making it challenging to obtain accurate working electrode potentials. Although membrane-electrode reactors have found wide applications in

Table 1. Selected Cu-based catalyst for photoelectrochemical conversion of CO₂ to C₂₊.

Photoelectrode	Electrolyte	Light source	Potential	C ₂₊ products	Ref.
Cu@porphyrin-COFs	KHCO ₃ (0.5 M)	300 W Xenon lamp (200 mW·cm ⁻²)	-1.0 V vs. SCE	Ethanol + acetic acid + acetone (~27 μmol·h ⁻¹ ·cm ⁻²)	[30]
Zn _{0.2} :Co ₁ @Cu	KHCO ₃ (0.1 M), Eosin Y (0.01 M)	AM 1.5G (200 mW·cm ⁻²)	-0.4 V vs. SCE	Paraffin (325 μg·h ⁻¹)	[31]
CuBi ₂ O ₄ /TiO ₂ -NTs	NaHCO ₃ (0.1 M)	250 W Xenon lamp (200 mW·cm ⁻²)	-0.6 V vs. SCE	Ethanol (1.32 μmol·h ⁻¹) (FE 73%)	[32]
6 wt% Re-doped CuO/TiO ₂ -NTs	NaHCO ₃ (0.1 M)	300 W Xenon lamp	-0.5 V vs. SCE	Ethanol (1.9 μmol·h ⁻¹)	[33]
CZTS/CdS	KHCO ₃ (0.1 M)	AM 1.5G (100 mW·cm ⁻²)	-0.4 V vs. RHE	Ethanol (~2.5 μmol·h ⁻¹ ·cm ⁻²)	[34]
TiO ₂ -NT/GNR/Cu/Pd-Pt	Na ₂ SO ₄ (0.1 M)	150 W Xenon lamp	-0.7 V vs. Ag/AgCl	Ethanol (4.3 mmol·g ⁻¹ ·h ⁻¹ ·cm ⁻²)	[35]
GO/Cu _x O/Cu-BTC	KHCO ₃ (0.1 M), Na ₂ SO ₄ (0.1 M)	AM 1.5G (100 mW·cm ⁻²)	-0.5 V vs. Ag/AgCl	Ethanol (40.5 μmol·h ⁻¹ ·cm ⁻²)	[36]
Cu	KOH (1 M)	UV LED lights (365 nm, 100 mW·cm ⁻²)	-1.8 V vs. Ag/AgCl	Ethylene (4.7 μmol·s ⁻¹ ·m ⁻²) (FE 46.6%)	[37]
CuN _x /CuO	KHCO ₃ (0.1 M)	AM 1.5G (100 mW·cm ⁻²)	0.2V vs. RHE	Ethanol (13.7 μmol·h ⁻¹ ·cm ⁻²) (FE 15.2%)	[38]
CuO-CuFeO ₂	H ₂ O: triethanolamine (volume ratio of 9:1)	300 W Xenon lamp (100 mW·cm ⁻²)	-0.6 V vs. Ag/AgCl	Ethanol (FE 66.73%)	[39]
Cu/TiO ₂ /p-Si	CsHCO ₃ (0.1 M)	300 W Xenon lamp, AM 1.5G (100 mW·cm ⁻²)	-0.9 V vs. RHE	Ethylene (FE ~23%)	[40]

COFs: Covalent organic frameworks; SCE: saturated calomel electrode; FE: Faradaic efficiency; RHE: reversible hydrogen electrode; UV LED: ultraviolet light-emitting diode.

electrochemical CO₂ reduction, there are few reports on their use in photoelectrochemical CO₂ conversion^[37]. In addition, the state-of-the-art electrocatalytic CO₂ reduction performance achieved from flow electrolysis cells and membrane-electrode electrolyzers can almost produce CO and formic acid at industrial current densities. However, producing single high-value C₂₊ products, such as ethylene and ethanol, remains challenging. As for photoelectrochemical CO₂ reduction, the current densities used in the electrolytic cells have a significant gap compared to industrial current densities. It is worth mentioning that most of the recent research employs self-designed, assembled, or customized CO₂ photoelectrochemical reactors. No universally recognized standard exists for the configuration and operation of CO₂ electrolyzers. Different studies use distinct reactor structures, components, and catalysts, making it difficult to directly compare results and select optimal cathodic catalysts.

STRATEGIES TO IMPROVE THE SELECTIVITY OF C₂₊ PRODUCTS

The photoelectrochemical conversion of CO₂ into C₂₊ products is highly challenging. The entire process involves multiple aspects: absorption of light to obtain electron-hole pairs, followed by charge separation and transfer to the surface of the photocathode. At the same time, CO₂ adsorption is necessary for reducing CO₂ to form C₁ radicals and intermediates, and the stability of intermediates and C-C coupling is crucial. Moreover, the production of C₂₊ products requires more electrons compared to C₁ products. These processes indicate that improving light absorption, enhancing CO₂ adsorption capacity, increasing charge separation and transfer efficiency, and constructing suitable active sites are essential for obtaining high-content C₂₊ products. In addition, the reactor configuration, operating conditions, and electrode assembly also significantly influence catalytic performance. A continuous flow PEC reactor can produce more C₂-C₃ products compared to batch reactors^[58], and selecting an appropriate voltage is beneficial for the generation of C₂₊ products^[17]; appropriate electrode assembly can increase CO₂ adsorption, suppress hydrogen production, and facilitate C₂₊ product generation^[40]. However, there is a lack of research on the impact of reactor configuration, operating conditions, and electrode assembly on the obtained C₂₊ products. Besides,

Table 2. The selected non-Cu-based catalyst for photoelectrochemical conversion of CO₂ to C₂₊

Photoelectrode	Electrolyte ¹¹¹	Light source	Potential	C ₂₊ products	Ref.
Ti/TiO ₂ NT-ZIF-8	Ascorbic acid (0.2 M), sodium sulfate (0.1 M)	125 W high pressure mercury vapor lamp	0.1 V vs. Ag/AgCl (E _{app})	Ethanol (10.5 mmol·L ⁻¹)	[41]
CsPbBr ₃ /graphite (C)	KHCO ₃ (0.1 M)	-	-0.8 V vs. Ag/AgCl	Oxalic acid (3.44 × 10 ⁻⁵ mmol) (FE 44%)	[42]
Dye/Pd/N-TiO ₂	KHCO ₃ (0.1 M), Eosin Y (1 mM)	300 W Xenon lamp (200 mW·cm ⁻²)	-1.0 V	Ethanol (26.8 μmol·h ⁻¹ ·cm ⁻²) (FE 28.4%)	[43]
ZnO/Ni-30	KHCO ₃ (0.1 M), Eosin Y (1 mM)	300 W Xenon lamp (100 mW·cm ⁻²)	-0.6 V	Ethanol + acetic acid (12.5 μmol·h ⁻¹ ·cm ⁻²) (FE 100%)	[44]
Pd-TiO ₂ @ZnO	KHCO ₃ (0.1 M), Eosin Y (1 mM)	300 W Xenon lamp (200 mW·cm ⁻²)	-1.0 V	Ethanol + acetic acid (~30 μmol·h ⁻¹ ·cm ⁻²)	[45]
Bi ₂ WO ₆ /BiOCl	KHCO ₃ (0.1 M), Eosin Y (1 mM)	300 W Xenon lamp	-1.0 V	Ethanol (11.4 μmol·h ⁻¹ ·cm ⁻²) (FE 80%)	[46]
S-TiO ₂ @GS	KHCO ₃ (0.1 M), Eosin Y (1 mM)	300 W Xenon lamp (200 mW·cm ⁻²)	-0.9 V vs. SCE	Ethanol (20.7 μmol·h ⁻¹ ·cm ⁻²)	[47]
P-WO ₃	KHCO ₃ (0.1 M), Eosin Y (1 mM)	300 W Xenon lamp (200 mW·cm ⁻²)	-0.8 V vs. SCE	Acetic acid (4.7 μmol·L ⁻¹ ·h ⁻¹ ·cm ⁻²)	[48]
CdS/V ₅ -MoS ₂ -PS	KHCO ₃ (0.1 M), Na ₂ SO ₃ (0.1 M), Eosin Y (1 mM)	200 mW·cm ⁻²	-0.9 V vs. SCE	Ethanol + ethylene glycol (350 μmol·h ⁻¹ ·cm ⁻²) (FE 67%)	[49]
Pd@TiO ₂ /Ti ₃ CN	KHCO ₃ (0.1 M)	300 W Xenon lamp	-0.8 V	Ethanol (14 μmol·h ⁻¹ ·cm ⁻²)	[50]
Pd/R-TiO ₂ /TiN-30	KHCO ₃ (0.1 M), Eosin Y (1 mM)	300 W Xenon lamp (200 mW·cm ⁻²)	-0.8 V vs. SCE	Ethanol + acetic acid + glycolaldehyde (39.41 μmol·L ⁻¹ ·h ⁻¹ ·cm ⁻²) (FE 65.69%)	[51]
NiMoO ₄ /ZnO-3	Na ₂ SO ₃ (0.1 M)	Xenon lamp (100 mW·cm ⁻²)	-0.8 V vs. SCE	Ethanol + acetic acid + glycolaldehyde + ethylene glycol (29.2 μmol·h ⁻¹ ·cm ⁻²) (FE 72.6%)	[52]
Si@WO ₃ -NS	KHCO ₃ (0.1 M)	300 W Xenon lamp (100 mW·cm ⁻²)	-1.0 V vs. SCE	Acetone + ethanol + acetic acid + glycolaldehyde (~43 μmol·h ⁻¹ ·cm ⁻²) (FE 62.7%)	[53]

FE: Faradaic efficiency; SCE: saturated calomel electrode; NS: nanosheet.

the current yield of C₂₊ products from CO₂ conversion via photoelectrocatalysis is generally low (often below 50 μmol·cm⁻²·h⁻¹), with correspondingly low current densities (below 10 mA·cm⁻²); many studies do not report CO₂ conversion rates or product yields^[25]. According to the reaction process, conversion rates and yields can be enhanced by adjusting reactor and reaction parameters (such as applying pressure) and modifying the properties of the photoelectrode. Specifically, improving light absorption capacity (through morphology control and elemental doping, *etc.*), enhancing charge carrier separation (via auxiliary metal addition and defect or heterojunction construction, *etc.*), and promoting surface reactions (by depositing a thin bilayer of Sustainion/Nafion, *etc.*) can contribute to these enhancements^[4]. Therefore, this section mainly summarizes the research progress in improving the selectivity of C₂₊ products from four aspects: electrode material morphology design, adjustment of band structure, construction of heterojunctions, and design of active sites.

Morphology

The morphology significantly influences the selectivity of CO₂ PEC reduction products [Figure 3]. Current research suggests that C₂₊ products can be acquired by constructing specific spatial structures. Wang *et al.* found that three-dimensional (3D) nanorod-shaped zinc oxide exhibited the optimal spatial environment compared to amorphous block-, mushroom-, and ball cactus-like structures, facilitating C-C coupling to produce C₂ products (ethanol and acetic acid)^[44]. Furthermore, their research group discovered that porous PEC based on a 3D hierarchical structure of covalent organic frameworks (COFs) could effectively enhance

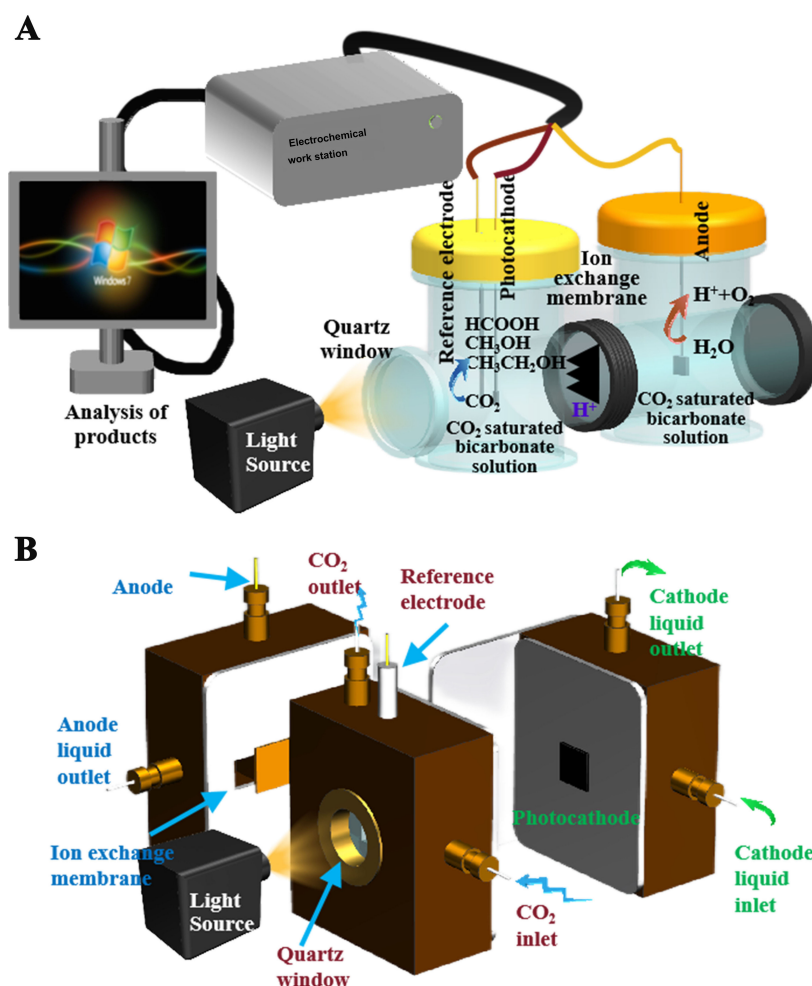


Figure 2. PEC reactor for CO₂ conversion (A) H-type cell (batch reactor)^[54], (B) flow cell (continuous reactor). PEC: Photoelectrochemistry.

CO₂ adsorption and the rate of C-C coupling to generate C₂₊ products^[30]. Hollow catalysts exhibited different selectivity on the inner and outer surfaces due to the increased collision probability of intermediates within the closed cavity, achieving a high selectivity of C₂₊ products (67.0%) on the inner surface^[49]. In addition, by simulating the morphology of thylakoids in plant cells, the Si@WO₃-nanosheet (NS) catalyst with a 2D-3D structure is advantageous for achieving C-C coupling^[53].

Band structure

The band structure of electrode materials significantly influences light utilization and the types of CO₂ reduction products. A narrower band gap is beneficial for broadening the absorption range of light. In contrast, adjustable conduction band positions facilitate the control of product selectivity [Figure 4]. The position of the conduction band is related to the reduction capability of the catalyst, playing a crucial role in the photoelectrocatalytic reduction of CO₂ and serving as a thermodynamic factor influencing the availability of C₂₊ products. Adjusting the conduction band to the appropriate position is beneficial for improving the acquisition of certain C₂₊ products. Han *et al.* achieved improved selectivity of CO₂ reduction products by depositing metals such as Pd, Pt, Ni, Au, *etc.*, to modulate the conduction band potentials of the TiO₂@ZnO/FTO^[45]. Besides doping with metals, doping with non-metals can alter the conduction band

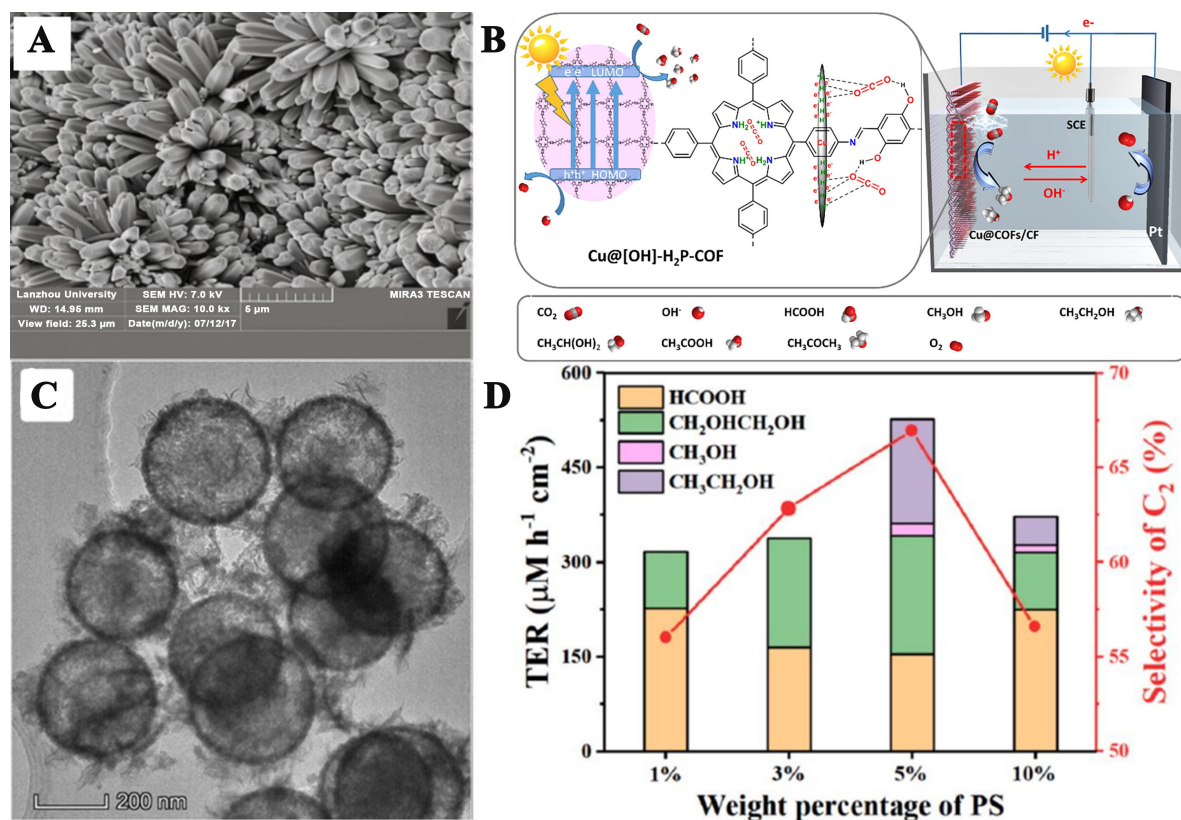


Figure 3. (A) SEM image of 3D nanorod ZnO^[44]. Copyright 2018 Springer; (B) COFs-based porous photoelectrochemical with 3D hierarchical structure for CO₂ reduction^[30]. Copyright 2020 Elsevier; (C) TEM image of CdS/V₅-MoS₂ and (D) catalytic performance of CdS/V₅-MoS₂-PS^[49]. Copyright 2023 Elsevier. SEM: Scanning electron microscopy; 3D: three-dimensional; COFs: covalent organic frameworks; TEM: transmission electron microscopy.

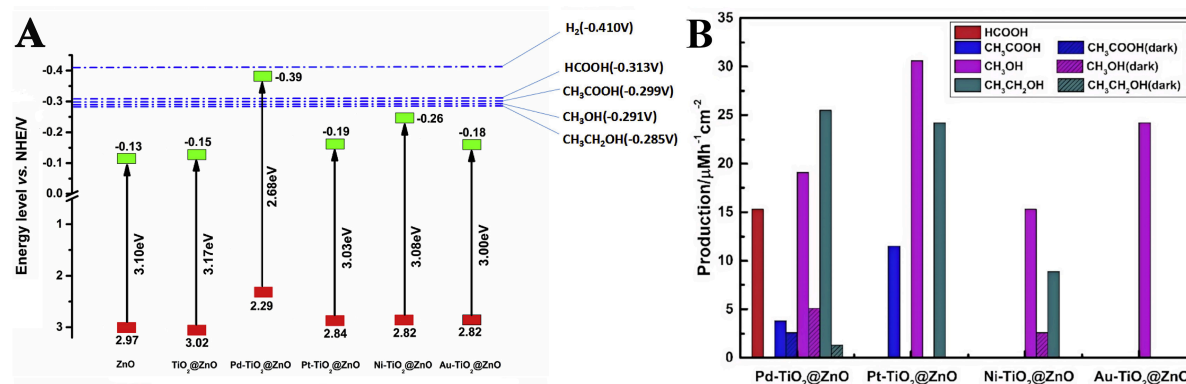


Figure 4. (A) Band structure of samples; (B) CO₂ PEC performance of the samples^[45]. Copyright 2018 Elsevier. PEC: Photoelectrochemistry.

position. Yu *et al.* designed and prepared a novel P-doped WO₃ catalyst where P doping elevated the conduction band position of the WO₃ electrode from -0.13 to -0.54 V [V vs. normal hydrogen electrode (NHE)], achieving an acetic acid yield of 4.7 μmol/(L·h·cm²) at a conduction band position of -0.38 V (V vs. NHE)^[48].

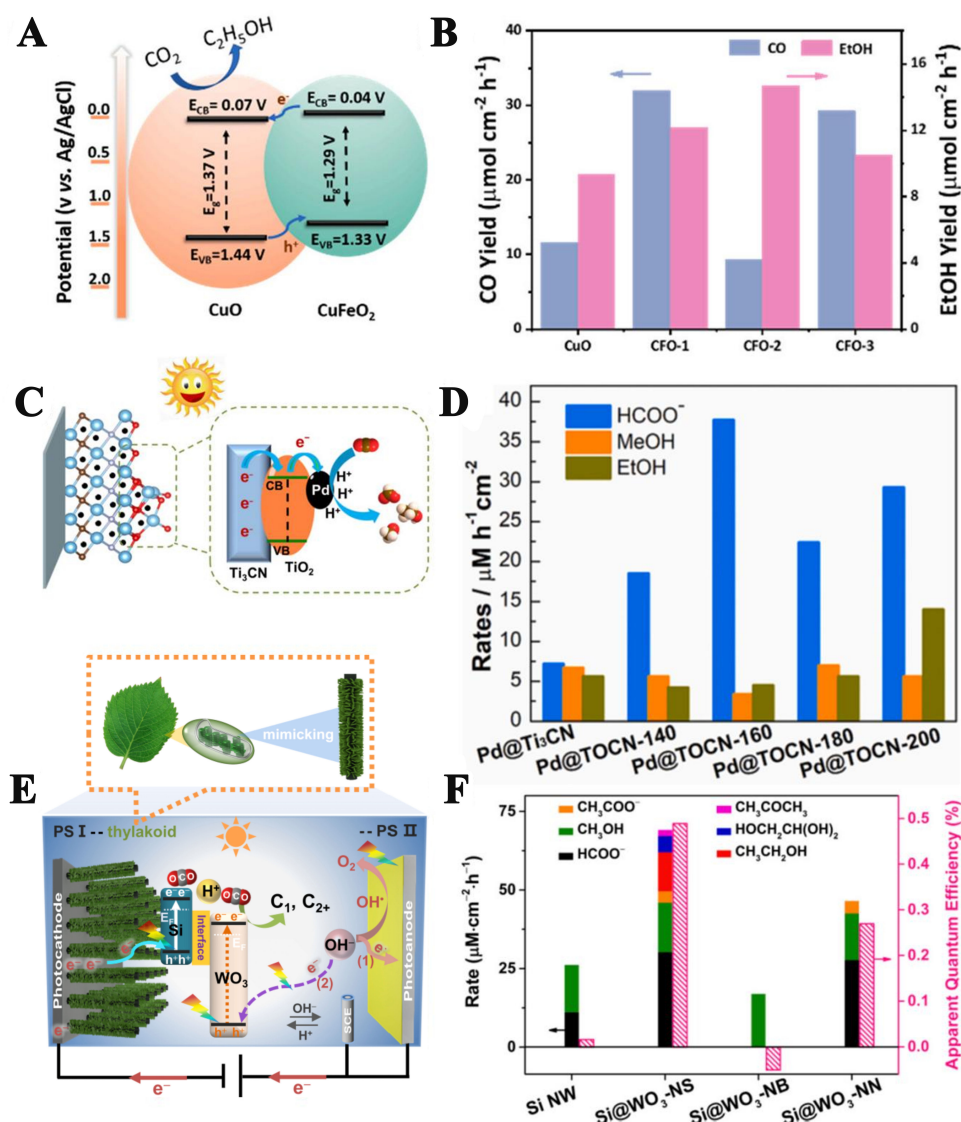


Figure 5. (A) Band structure of CuO-CuFeO₂; (B) CO₂ PEC performance of samples at -1.0 V vs. Ag/AgCl^[39]. Copyright 2023 Elsevier; (C) Band structure of Pd@TiO₂CN; (D) CO₂ PEC performance of samples^[50]. Copyright 2023 Elsevier; (E) Band structure of Si@WO₃ and (F) CO₂ PEC performance of samples^[53]. Copyright 2023 Elsevier. PEC: Photoelectrochemistry.

Heterojunction

The built-in electric field of heterojunctions facilitates carrier separation, accelerates charge transfer, and enhances the velocity of intermediates, resulting in a high probability of C-C coupling and, consequently, higher C₂₊ product yields^[31,53] [Figure 5]. Lu *et al.* constructed 0D/1D CuFeO₂/CuO nanowire heterojunction arrays. They achieved a higher Faradaic efficiency (66.73%) for ethanol production at -0.6 V vs. Ag/AgCl, mainly attributed to the rapid separation of photogenerated electrons and holes in the heterojunction material and the transfer of electrons from CuFeO₂ to CuO, enabling highly content of C₂₊ products (ethanol)^[39]. Xu *et al.* fabricated 2D TiO₂/Ti₃CN MXene heterojunctions, where the Pd@TOCN-200 photoelectrode exhibited the highest ethanol production rate (14 μM·cm⁻²·h⁻¹) due to the enhanced CO₂ adsorption and favorable C-C coupling environment provided by the 2D TiO₂/Ti₃CN heterojunction structure^[50].

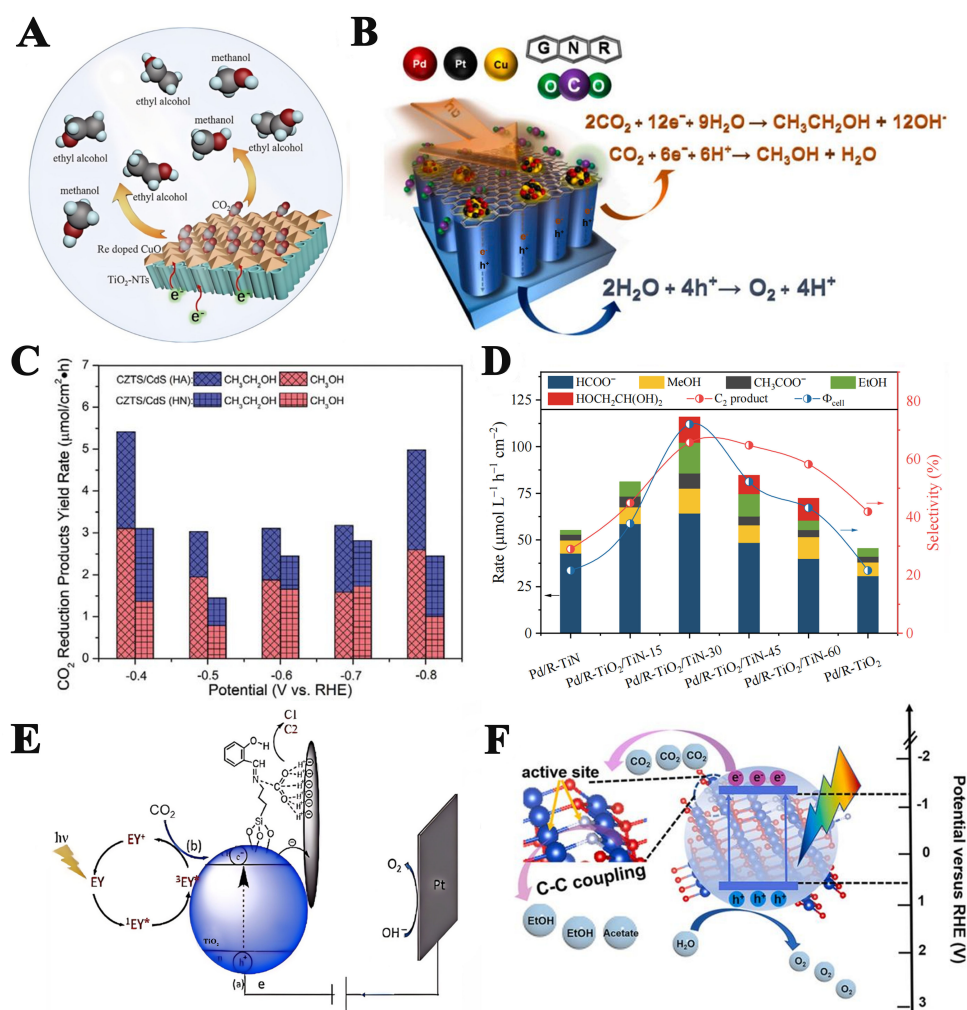


Figure 6. (A) Schematic mechanism of Re-doped CuO/TiO₂-NTs for CO₂ reduction^[33]. Copyright 2021 Elsevier; (B) The scheme for product generation of TiO₂-NT/GNR-metal electrodes^[35]. Copyright 2021 Elsevier; (C) The corresponding CO₂ conversion yields of CZTS/CdS (HA) and CZTS/CdS (HN)^[34]. Copyright 2021 Wiley; (D) CO₂ PEC performance of Pd/R-TiO₂/TiN-x^[51]. Copyright 2023 Elsevier; (E) Schematic mechanism of EY+S-TiO₂@GS for CO₂ reduction^[47]. Copyright 2020 Elsevier; and (F) Schematic mechanism of Cu_N/CuO for the CO₂ PEC reduction^[38]. Copyright 2022 Elsevier. PEC: Photoelectrochemistry.

Active site

The active site is a critical part of catalytic reactions and directly determines the distribution of products. They change product distribution by affecting the adsorption strength of products and intermediates and promote the coupling of *CO with *CO by adjusting the local electron density gradient, facilitating C-C coupling, and enhancing the acquisition of C₂₊ products. In the PEC CO₂ reduction reaction, active sites composed of multimetallic species^[31,33,35,36,52], oxygen vacancies/sulfur vacancies^[34,51], certain specific functional groups (such as adjacent imine groups)^[47], and metal-nonmetal junctions^[38] are favorable for CO₂ adsorption and C-C coupling, promoting the generation of C₂₊ products [Figure 6]. Among them, Lu *et al.* doped Re into CuO and combined it with Ti nanotubes. Under solar light and -0.5 V vs. saturated calomel electrode (SCE) conditions, the product was almost entirely ethanol (1.9 μM·h⁻¹). The above results were attributed to high-valence rhenium as an active site for hydrogenation reactions. Its doping promoted the alcoholization process and facilitated C-C coupling^[33]. Zhou *et al.* adjusted the surface sulfur vacancies of Cu₂ZnSnS₄ (CZTS)/CdS by annealing in different atmospheres, which were active sites for CO adsorption and followed C-C coupling. By rational tuning, they achieved higher ethanol selectivity^[34]. In addition,

Wang *et al.* introduced N into CuO to obtain Cu-N active components. These components possessed asymmetric d-p orbitals, which could reduce the activation energy of C-C coupling and induce local charge redistribution, thereby improving the material's conductivity. They achieved a 15.2% C₂ product selectivity in a water solution at 0.2 V vs. reversible hydrogen electrode (RHE)^[38].

CONCLUSION AND PROSPECTS

Currently, research on PEC conversion of CO₂ to C₂₊ products primarily focuses on developing photoelectrodes. The catalysts used are mainly Cu-based, and the major C₂₊ products obtained are ethanol, acetic acid, and ethylene. The involved reactors are predominantly flow reactors. Adjusting the catalyst morphology, band structure, and active sites can improve light absorption, enhance charge carrier transfer, strengthen CO₂/CO[•] adsorption, and provide a favorable C-C coupling environment, achieving high selectivity for C₂₊ products. Although some progress has been made in the research on PEC CO₂ conversion to C₂₊ products, there is currently limited reporting on products containing three or more carbon atoms. The types of catalysts used are also limited, and their yields are relatively low (typically at the level of μmol). The reactors used in studies are mostly self-designed, assembled, or customized. There is no recognized standard for the configuration and operation of CO₂ reactors, and it is difficult to selectively optimize cathode catalysts by directly comparing different research reports. The current density employed in electrolytic cells differs significantly from industrial-scale requirements, making industrialization challenging. The present reaction pathway is not yet clear, and there is still insufficient research on the specific reaction mechanisms involved in catalysts. Additionally, research on photoelectric synergies is lacking. Therefore, increasing efforts in reactor development and establishing design standards, exploring and developing cost-effective and high-performing catalysts, and conducting in-depth research to enhance catalytic performance and understand reaction mechanisms are the main directions for future investigations.

DECLARATIONS

Authors' contributions

Prepared and revised the manuscript: Jiang X, Chen R

Designed and revised the manuscript: Chen YX, Lu CZ

All authors contributed to the discussion and preparation of the manuscript.

Availability of data and materials

Not applicable.

Financial support and sponsorship

Authors are thankful for the financial support of the Natural Science Foundation of Fujian Province (2023H0046), the XMIREM autonomously deployment project (2023CX10, 2023GG01), the National Natural Science Foundation of China (22275185), the Major Research Project of Xiamen (3502Z20191015), and the Fujian Science & Technology Innovation Laboratory for Optoelectronic Information of China (2021ZR132, 2021ZZ115).

Conflicts of interest

All authors declared that there are no conflicts of interest.

Ethical approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

Copyright

© The Author(s) 2024.

REFERENCES

1. Zhou W, Guo JK, Shen S, et al. Progress in photoelectrocatalytic reduction of carbon dioxide. *Acta Phys Chim Sin* 2020;36:1906048. DOI
2. Tang B, Xiao FX. An overview of solar-driven photoelectrochemical CO₂ Conversion to chemical fuels. *ACS Catal* 2022;12:9023-57. DOI
3. Xu S, Shen Q, Zheng J, et al. Advances in biomimetic photoelectrocatalytic reduction of carbon dioxide (Adv. Sci. 31/2022). *Adv Sci* 2022;9:2270196. DOI PMC
4. Chen P, Zhang Y, Zhou Y, Dong F. Photoelectrocatalytic carbon dioxide reduction: fundamental, advances and challenges. *Nano Mater Sci* 2021;3:344-67. DOI
5. Zhang N, Long R, Gao C, Xiong Y. Recent progress on advanced design for photoelectrochemical reduction of CO₂ to fuels. *Sci China Mater* 2018;61:771-805. DOI
6. Ochedi FO, Liu D, Yu J, Hussain A, Liu Y. Photocatalytic, electrocatalytic and photoelectrocatalytic conversion of carbon dioxide: a review. *Environ Chem Lett* 2021;19:941-67. DOI
7. Kan M, Wang Q, Hao S, et al. System engineering enhances photoelectrochemical CO₂ reduction. *J Phys Chem C* 2022;126:1689-700. DOI
8. Chang X, Wang T, Yang P, Zhang G, Gong J. The development of cocatalysts for photoelectrochemical CO₂ reduction. *Adv Mater* 2019;31:e1804710. DOI PubMed
9. Dutta S, Patil R, Chongdar S, Bhaumik A. Dehydrogenase-functionalized interfaced materials in electroenzymatic and photoelectroenzymatic CO₂ reduction. *ACS Sustain Chem Eng* 2022;10:6141-56. DOI
10. Li Y, Li S, Huang H. Metal-enhanced strategies for photocatalytic and photoelectrochemical CO₂ reduction. *Chem Eng J* 2023;457:141179. DOI
11. Liu L, Zhang Y, Huang H. Junction engineering for photocatalytic and photoelectrocatalytic CO₂ reduction. *Solar RRL* 2021;5:2000430. DOI
12. Brillas E, Serrà A, Garcia-segura S. Biomimicry designs for photoelectrochemical systems: Strategies to improve light delivery efficiency. *Curr Opin Electrochem* 2021;26:100660. DOI
13. Devi P, Verma R, Singh JP. Advancement in electrochemical, photocatalytic, and photoelectrochemical CO₂ reduction: recent progress in the role of oxygen vacancies in catalyst design. *J CO₂ Util* 2022;65:102211. DOI
14. Putri LK, Ng BJ, Ong WJ, Chai SP, Mohamed AR. Toward excellence in photocathode engineering for photoelectrochemical CO₂ reduction: design rationales and current progress. *Adv Energy Mater* 2022;12:2201093. DOI
15. Li Y, Li S, Huang H. Defective photocathode: fundamentals, construction, and catalytic energy conversion. *Adv Funct Mater* 2023;33:2304925. DOI
16. Pawar AU, Kim CW, Nguyen-le M, Kang YS. General review on the components and parameters of photoelectrochemical system for CO₂ reduction with in situ analysis. *ACS Sustainable Chem Eng* 2019;7:7431-55. DOI
17. King AJ, Bui JC, Bell AT, Weber AZ. Establishing the role of operating potential and mass transfer in multicarbon product generation for photoelectrochemical CO₂ reduction cells using a Cu catalyst. *ACS Energy Lett* 2022;7:2694-700. DOI
18. Verma S, Yadav A. Emerging single-atom catalysts and nanomaterials for photoelectrochemical reduction of carbon dioxide to value-added products: a review of the current state-of-the-art and future perspectives. *Energy Fuels* 2023;37:5712-42. DOI
19. Hiragond CB, Kim J, Kim H, Bae D, In S. Elemental-doped catalysts for photoelectrochemical CO₂ conversion to solar fuels. *Solar RRL* 2024;8:2400022. DOI
20. Bienkowski K, Solarzka R, Trinh L, et al. Halide perovskites for photoelectrochemical water splitting and CO₂ reduction: challenges and opportunities. *ACS Catal* 2024;14:6603-22. DOI
21. Li CF, Guo RT, Zhang ZR, Wu T, Pan WG. Converting CO₂ into value-added products by Cu₂O-based catalysts: from photocatalysis, electrocatalysis to photoelectrocatalysis. *Small* 2023;19:e2207875. DOI PubMed
22. Zhang W, Jin Z, Chen Z. Rational-designed principles for electrochemical and photoelectrochemical upgrading of CO₂ to value-added chemicals. *Adv Sci* 2022;9:e2105204. DOI PubMed PMC
23. Zheng Y, Vasileff A, Zhou X, Jiao Y, Jaroniec M, Qiao SZ. Understanding the roadmap for electrochemical reduction of CO₂ to multi-carbon oxygenates and hydrocarbons on copper-based catalysts. *J Am Chem Soc* 2019;141:7646-59. DOI PubMed
24. Zheng W, Yang X, Li Z, et al. Designs of tandem catalysts and cascade catalytic systems for CO₂ upgrading. *Angew Chem Int Ed Engl*

- 2023;62:e202307283. DOI PubMed
25. Han GH, Bang J, Park G, et al. Recent advances in electrochemical, photochemical, and photoelectrochemical reduction of CO₂ to C₂₊ products. *Small* 2023;19:e2205765. DOI PubMed
26. Otgonbayar Z, Yoon CM, Oh WC. Photoelectrocatalytic CO₂ reduction with ternary nanocomposite of MXene (Ti₃C₂)-Cu₂O-Fe₃O₄: comprehensive utilization of electrolyte and light-wavelength. *Chem Eng J* 2023;464:142716. DOI
27. Landaeta E, Kadosh NI, Schultz ZD. Mechanistic study of plasmon-assisted *in situ* photoelectrochemical CO₂ reduction to acetate with a Ag/Cu₂O nanodendrite electrode. *ACS Catal* 2023;13:1638-48. DOI
28. Liang H, Li M, Li Z, Xie W, Zhang T, Wang Q. Photoelectrochemical CO₂ reduction with copper-based photocathodes. *J CO₂ Util* 2024;79:102639. DOI
29. Guo X, Wang C, Yang Z, Yang Y. Boosting C₂₊ production from photoelectrochemical CO₂ reduction on gallium doped Cu₂O. *Chem Eng J* 2023;471:144539. DOI
30. Wang B, Yang F, Dong Y, et al. Cu@porphyrin-COFs nanorods for efficiently photoelectrocatalytic reduction of CO₂. *Chem Eng J* 2020;396:125255. DOI
31. Wang J, Guan Y, Yu X, et al. Photoelectrocatalytic reduction of CO₂ to paraffin using p-n heterojunctions. *iScience* 2020;23:100768. DOI PubMed PMC
32. Cao H, Yu H, Lu Y, et al. Photoelectrocatalytic reduction of CO₂ over CuBi₂O₄/TiO₂-NTs under simulated solar irradiation. *ChemistrySelect* 2020;5:5137-45. DOI
33. Lu Y, Cao H, Xu S, et al. CO₂ photoelectroreduction with enhanced ethanol selectivity by high valence rhenium-doped copper oxide composite catalysts. *J Colloid Interface Sci* 2021;599:497-506. DOI PubMed
34. Zhou S, Sun K, Huang J, et al. Accelerating electron-transfer and tuning product selectivity through surficial vacancy engineering on CZTS/CdS for photoelectrochemical CO₂ reduction. *Small* 2021;17:e2100496. DOI
35. de Souza MKR, Cardoso EDSF, Fortunato GV, et al. Combination of Cu-Pt-Pd nanoparticles supported on graphene nanoribbons decorating the surface of TiO₂ nanotube applied for CO₂ photoelectrochemical reduction. *J Environ Chem Eng* 2021;9:105803. DOI
36. Nandal N, Prajapati PK, Abraham BM, Jain SL. CO₂ to ethanol: a selective photoelectrochemical conversion using a ternary composite consisting of graphene oxide/copper oxide and a copper-based metal-organic framework. *Electrochim Acta* 2022;404:139612. DOI
37. Merino-garcia I, Castro S, Irabien A, et al. Efficient photoelectrochemical conversion of CO₂ to ethylene and methanol using a Cu cathode and TiO₂ nanoparticles synthesized in supercritical medium as photoanode. *J Environ Chem Eng* 2022;10:107441. DOI
38. Wang K, Liu Y, Wang Q, et al. Asymmetric Cu-N sites on copper oxide photocathode for photoelectrochemical CO₂ reduction towards C₂ products. *Appl Catal B Environ* 2022;316:121616. DOI
39. Lu M, Jia D, Xue H, Tian J, Jiang T. 0D/1D CuFeO₂/CuO nanowire heterojunction arrays for improved photoelectrocatalytic reduction of CO₂ to ethanol. *J Alloys Compd* 2023;960:170626. DOI
40. Kim C, King AJ, Aloni S, Toma FM, Weber AZ, Bell AT. Codesign of an integrated metal-insulator-semiconductor photocathode for photoelectrochemical reduction of CO₂ to ethylene. *Energy Environ Sci* 2023;16:2968-76. DOI
41. Cardoso J, Stulp S, de Souza M, et al. The effective role of ascorbic acid in the photoelectrocatalytic reduction of CO₂ pre-concentrated on TiO₂ nanotubes modified by ZIF-8. *J Electroanal Chem* 2020;856:113384. DOI
42. Bergamini L, Sangiorgi N, Gondolini A, et al. CsPbBr₃/platinum and CsPbBr₃/graphite hybrid photoelectrodes for carbon dioxide conversion to oxalic acid. *Solar Energy* 2023;254:213-22. DOI
43. Zhang Y, Han B, Xu Y, et al. Artificial photosynthesis of alcohols by multi-functionalized semiconductor photocathodes. *ChemSusChem* 2017;10:1742-8. DOI
44. Wang J, Han B, Nie R, et al. Photoelectrocatalytic reduction of CO₂ to chemicals via ZnO@Nickel foam: controlling C-C coupling by ligand or morphology. *Top Catal* 2018;61:1563-73. DOI
45. Han B, Wang J, Yan C, et al. The photoelectrocatalytic CO₂ reduction on TiO₂@ZnO heterojunction by tuning the conduction band potential. *Electrochim Acta* 2018;285:23-9. DOI
46. Wang J, Wei Y, Yang B, Wang B, Chen J, Jing H. In situ grown heterojunction of Bi₂WO₆/BiOCl for efficient photoelectrocatalytic CO₂ reduction. *J Catal* 2019;377:209-17. DOI
47. Wang L, Wei Y, Fang R, et al. Photoelectrocatalytic CO₂ reduction to ethanol via graphite-supported and functionalized TiO₂ nanowires photocathode. *J Photochem Photobiol A Chem* 2020;391:112368. DOI
48. Yu X, Wei Y, Chen Y, Wang J, Jing H. P-doped WO₃ semiconductor with enhanced conduction band on highly efficient photoelectrocatalytic reduction of CO₂. *Chinese Sci Bull* 2020;66:825-32. DOI
49. Liu C, Xiao Y, Wan W, et al. Different behaviors on the external and inner surface of hollow CdS/V_s-MoS₂ heterojunctions in photoelectrocatalytic CO₂ reduction via SH-assisted mechanism. *Appl Catal B Environ* 2023;325:122394. DOI
50. Xu Y, Wang F, Lei S, et al. In situ grown two-dimensional TiO₂/Ti₃CN MXene heterojunction rich in Ti³⁺ species for highly efficient photoelectrocatalytic CO₂ reduction. *Chem Eng J* 2023;452:139392. DOI
51. Wei Y, Duan R, Zhang Q, et al. Photoelectrocatalytic reduction of CO₂ catalyzed by TiO₂/TiN nanotube heterojunction: nitrogen assisted active hydrogen mechanism. *Chinese J Catal* 2023;47:243-53. DOI
52. Cao Y, Wei Y, Wan W, et al. Photoelectrochemical reduction of CO₂ catalyzed by a 3D core-shell NiMoO₄@ZnO heterojunction with bicentre at the (111) plane and thermal electron assistance. *J Mater Chem A* 2023;11:4230-7. DOI
53. Wan W, Zhang Q, Wei Y, et al. p-n heterojunctions of Si@WO₃ mimicking thylakoid for photoelectrocatalytic CO₂ reduction to C₂₊ products - morphology control. *Chem Eng J* 2023;454:140122. DOI

54. Kumaravel V, Bartlett J, Pillai SC. Photoelectrochemical conversion of carbon dioxide (CO₂) into fuels and value-added products. *ACS Energy Lett* 2020;5:486-519. [DOI](#)
55. Chu S, Rashid RT, Pan Y, Wang X, Zhang H, Xiao R. The impact of flue gas impurities and concentrations on the photoelectrochemical CO₂ reduction. *J CO₂ Util* 2022;60:101993. [DOI](#)
56. Jiang X, Chen R, Chen YX, Lu CZ. Proton exchange membrane fuel cells: application for value-added chemical productions. *Chem Synth* 2024;4:6. [DOI](#)
57. Gao D, Wei P, Li H, Lin L, Wang G, Bao X. Designing electrolyzers for electrocatalytic CO₂ reduction. *Acta Phys Chim Sin* 2021;37:2009021. [DOI](#)
58. Castro S, Albo J, Irabien A. Photoelectrochemical reactors for CO₂ utilization. *ACS Sustainable Chem Eng* 2018;6:15877-94. [DOI](#)