

Insight on Reaction Pathways of Photocatalytic CO₂ Conversion

Yiou Wang, Enqi Chen, and Junwang Tang*

Cite This: *ACS Catal.* 2022, 12, 7300–7316

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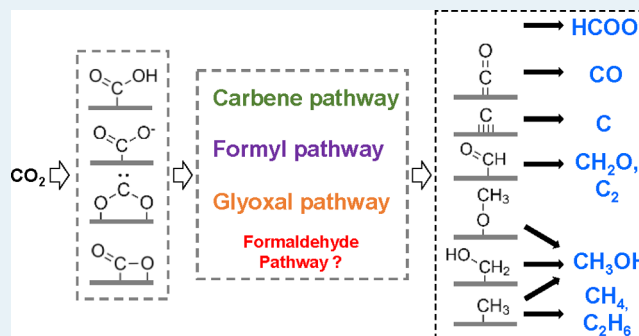
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ABSTRACT: Photocatalytic CO₂ conversion to value-added chemicals is a promising solution to mitigate the current energy and environmental issues but is a challenging process. The main obstacles include the inertness of CO₂ molecule, the sluggish multi-electron process, the unfavorable thermodynamics, and the selectivity control to preferable products. Furthermore, the lack of fundamental understanding of the reaction pathways accounts for the very moderate performance in the field. Therefore, in this Perspective, we attempt to discuss the possible reaction mechanisms toward all C₁ and C₂ value-added products, taking into account the experimental evidence and theoretical calculation on the surface adsorption, proton and electron transfer, and products desorption. Finally, the remaining challenges in the field, including mechanistic understanding, reactor design, economic consideration, and potential solutions, are critically discussed by us.

KEYWORDS: CO₂ conversion, photocatalysis, mechanism, reaction pathways, selectivity

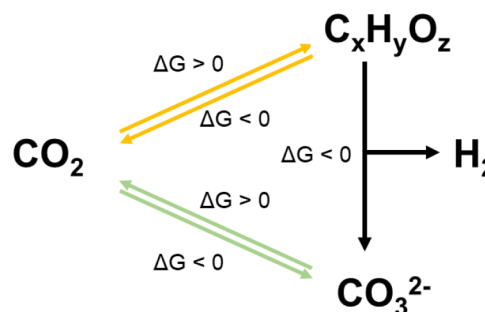


1. INTRODUCTION

The atmospheric CO₂ content has inevitably increased from 275 ppm to over 400 ppm since the industrial evolution, far exceeding its natural fluctuation (180–300 ppm) over the past 800 000 years because of an emission rate of more than 2 ppm per annum.^{1,2} The reactions emitting CO₂, such as the combustion of fossil fuels, could directly release heat and, in most cases, also produce water that is also a greenhouse gas in its vapor form.³ The IR-active CO₂ molecules trap the thermal radiation from the Earth's surface and the sunlight, raising the global temperature and subsequently liberating even more CO₂ by shifting the CO₂-carbonate dissolution equilibrium in the oceans.⁴ Once the natural carbon-cycle capacity is overwhelmed, an adverse process leads to dramatic climate change and other environmental issues, highlighting the urgent need for artificial approaches to maintain the carbon balance by capturing CO₂ for the carbon-neutral economy.⁵

The carbon on Earth simply moves between different reservoirs because of geological and geochemical processes as well as human activities, while the total carbon amount has remained constant (Scheme 1).⁶ The new technology for CO₂ utilization should at least be carbon-neutral either via exergonic pathways or endergonic ones but driven by renewable energy sources. Inspired by the fact that the majority of carbon on the Earth's surface is stored in the form of carbonates, scientists have developed thermodynamically favorable CO₂-to-carbonate mineralization technologies.⁷ Recently, the concept of converting a carbon-containing fuel into carbonates and carbon-free hydrogen was reported.⁸ Meanwhile, inspired by

Scheme 1. Illustration for the Natural Carbon Cycles Including CO₂ to Organic and Inorganic Pathways

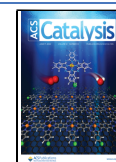


natural photosynthesis, scientists have also made significant progress in uphill reactions to fix CO₂ into high-value fuels with the input of energy from sunlight. Such sustainable solar fuels are attractive with a satisfactory density of energy stored in their chemical bonds (e.g., 20 MJ/kg for methanol), which are significantly higher than current batteries (~0.1–0.7 MJ/kg) and able to be released on demand without additional carbon emission.^{9–11} The storage of almost inexhaustible solar

Received: February 27, 2022

Revised: April 29, 2022

Published: June 3, 2022



energy in CO₂-reduction fuels will significantly contribute to balance the carbon-cycle and address the issues of carbon-neutral energy supply,¹¹ leading to the concept of the photocatalytic process for CO₂ reduction.

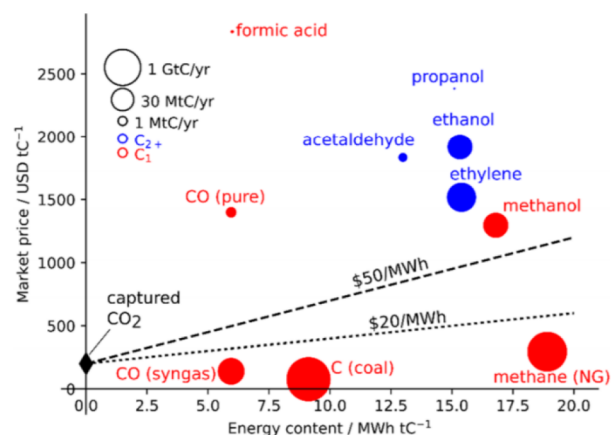
The earliest demonstration of photoassisted CO₂ reduction in water dates back to the late 1970s when the Pt-SrTiO₃ was used to convert gaseous water and CO₂ to methane, as reported by Hemminger et al., and many semiconductors (TiO₂, ZnO, CdS, GaP, and SiC) were also shown to reduce aqueous CO₂ to formic acid, formaldehyde, methanol, and methane by Inoue et al.^{12,13} Since then, many efforts have been devoted not only to improve the efficiency of CO₂ photoconversion or the related but also to tune the selectivity of a specific product.^{14,15} Moreover, the formation of C₂₊ products has attracted emerging attention because of their high value compared with their C₁ counterparts.^{16,17} Despite the advancement made in the past decades, the performance of CO₂ photoconversion is still unsatisfactory, far from the target 10% solar-to-fuel efficiency, because of a few intrinsic reasons.

- (1) The difficulty in activation of inert CO₂. Owing to the closed-shell electronic configuration, linear geometry, and D_{∞h} symmetry,¹⁸ it requires -1.9 V potential (vs NHE at pH 7) to activate CO₂ and to form an anion radical CO₂⁻, which the majority of semiconductors could hardly provide except for a few reports (e.g., poly *p*-phenylene in trimethylamine).^{19–22} A possible solution to lower the barrier to the reduction reaction is to adsorb CO₂ on the surface of catalysts and then reduce CO₂ together with protons, which usually requires the loading of active cocatalysts or the engineering of surficial defects such as oxygen vacancies.^{19,20,23,24}
- (2) The challenging multiple-electron kinetics. It is commonly believed that CO₂ reduction is a process via multi-proton and multi-electron transfer, lowering the CO₂ reduction potentials close to that of proton reduction, making it much more difficult than the two-electron proton reduction process to hydrogen.¹⁷ Except for some reports of molecular catalysts, it is challenging to validate whether the reactions proceed via a simultaneous multi-electron transport process or through a cascade of one-electron steps, where the first electron transfer seems to be the limiting step.^{25,26} Another question is whether the lifetime of the charge carriers matches that of the surface reactions of interest.
- (3) Unfavorable thermodynamics of CO₂ reduction by water. Opposite to the exothermal combustion of fuels, the production of solar fuels from CO₂ and water is endothermal (e.g., Gibbs free energy of 818.3 kJ/mol for CH₄ and 702.2 kJ/mol for CH₃OH).²⁷ Although using hydrogen instead of water could turn CO₂ reduction into exothermic reactions hence having demonstrated much-enhanced activity, these thermal catalytic processes usually proceed under higher temperatures (>150 °C) even promoted by light, requiring an additional step and energy for water electrolysis to hydrogen. Thus, hydrogenation systems and those using sacrificial hole scavengers will not be included in this Perspective as they are debatably sustainable to some extent. As the water oxidation half-reaction is very sluggish because of the four-hole chemistry and the likely oxidation of the reduction intermediates before the multi-electron carbon products are generated,²⁸ using water to reduce CO₂ to

valuable chemicals is exceptionally challenging. In short, to overcome the obstacles mentioned above for CO₂ photoreduction, besides the commonly existing issues for photocatalysis such as light-harvesting, one has to carefully tailor the photocatalysts, cocatalysts and the reaction conditions based on the fundamental understandings.

- (4) Selectivity toward preferable products. Various products could be obtained from CO₂ conversion while tuning the selectivity remains the major challenge. It should be noted that not all of the products are value-added chemicals if the cost of CO₂ capture is taken into consideration (Scheme 2).¹⁶ For example, the com-

Scheme 2. Market Price of CO₂ Recycling Products as a Function of Energy Content.^a Reproduced from Ref 16. Copyright 2019 American Chemical Society

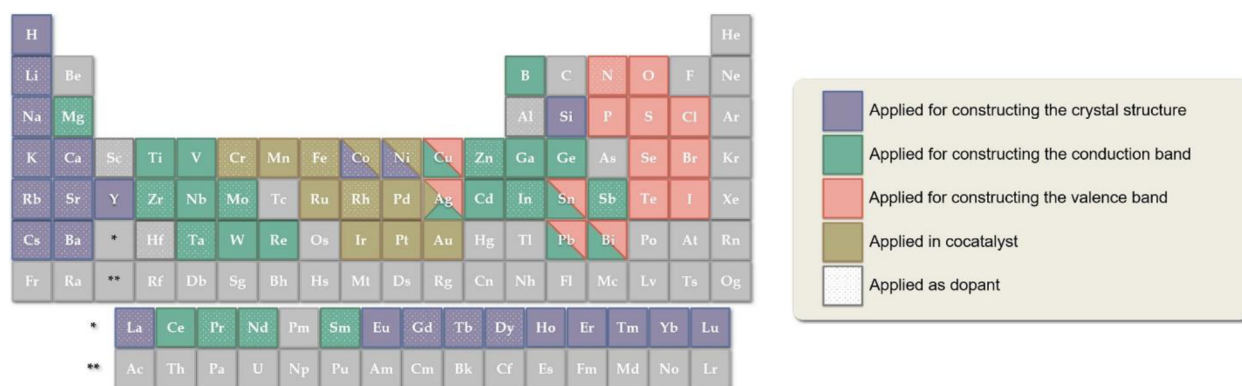


^aDotted lines represent minimum energy cost required for CO₂ capture and conversion based on the present commercially available technology.

monly observed CO (with low purity) and CH₄ are economically unfavorable due to their relatively low market price. The most profitable C₁ product is formic acid, which unfortunately has a low energy content. Methanol and C₂₊ products are more attractive because of their outstanding market price, market demand, and energy content. However, because of the lack of molecular-level understanding of reaction mechanisms, the selectivity control to preferable products is still challenging.

Apart from the four key factors as mentioned above, the core of CO₂ photoreduction lies in the selection of semiconductor photocatalysts. The progress of semiconductor photocatalyst development has been heavily summarized by many comprehensive reviews.^{20,27,29–31} Also, the strategies to design novel photocatalysts for CO₂ reduction resemble those for water splitting, which could be found in broad literatures (Scheme 3).^{32–34} For example, Li et al. summarized the selectivity for photocatalytic reduction of CO₂ over different cocatalysts.³¹ Briefly, Pd, Pt, or Au are more favorable for CH₄ production; Ag for CO, CH₄, or CH₃OH; Cu for hydrocarbons; and Cu₂O, RuO₂, or NiO_x for CH₃OH production. Therefore, complementary to these reviews on photocatalysts' development, here we aim to discuss the possible reaction pathways and mechanisms on the basis of our understandings in this Perspective, including how to design photocatalysts and

Scheme 3. Elements Used to Construct Photocatalysts for Photocatalytic Water Splitting and Their Roles.^a Reproduced from Ref 32. Copyright 2019 American Chemical Society



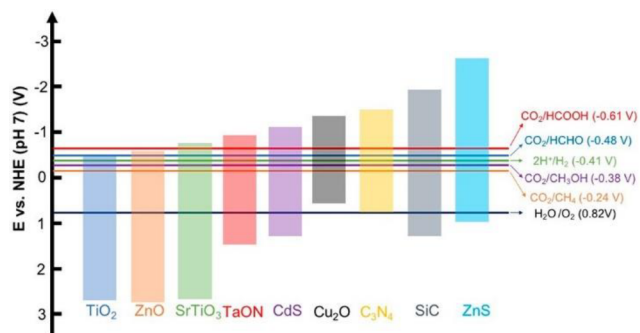
^aAlkali metals, alkaline earth metals, and some rare-earth ions usually do not directly contribute to the formation of bands and just construct crystals structure (e.g., as the A position of cations in perovskite). Most metal oxide photocatalysts are composed of metal cations with d^0 (Ti^{4+} , Zr^{4+} , Nb^{5+} , Ta^{5+} , V^{5+} , W^{6+} , and Ce^{4+}) or d^{10} (Zn^{2+} , In^{3+} , Ga^{3+} , Ge^{4+} , Sn^{4+} , and Sb^{5+}) configurations. The conduction bands for d^0 and d^{10} metal oxide photocatalysts typically consist of the d and sp orbitals of the metal cations, respectively. The valence band of semiconductors usually consists of the p orbitals of N, P, O, S, Se, Te, Cl, and so on. Cocatalysts elements include, for example, Cr, Mn, Fe, Ru, Rh, Pd, Ag, Ir, Pt, Au. Some elements have more than a single function.

how to obtain this fundamental information by spectroscopies, as well as the principles for various products. Furthermore, we propose challenges facing this field, such as the characterizations needed to validate and understand the experimental process and pathways to practical applications.

2. REACTION PATHWAYS AND POSSIBLE PRODUCTS

Scheme 4 lists the redox potential of various products from photocatalytic CO_2 conversion and the band alignment of a

Scheme 4. Band Alignments of a Few Representative Semiconductor Photocatalysts and the Related Redox Potentials to CO_2 Reduction Reactions to Different Products. Reproduced with Permission from Ref 17. Copyright 2020 American Chemical Society

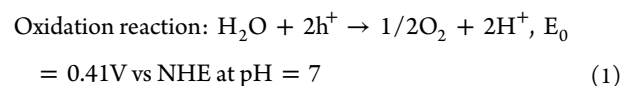


few representative photocatalysts.¹⁷ To determine the selectivity and efficiency of the process, gas chromatography coupled with mass spectrometry (GCMS) is commonly used to quantify the products, while for nonvolatile ionic formate or oxalate products, ion-exchange chromatography is necessary. Understanding the exact reaction mechanism of CO_2 photo-reduction relies on evidence from experimental and theoretical methods. Infrared spectroscopy (IR) is helpful for surface chemistry studies, and electron paramagnetic resonance (EPR) is an essential tool to reveal the mechanism via the detection of paramagnetic unpaired electrons of the intermediates. The charge carrier dynamics could be analyzed by transient

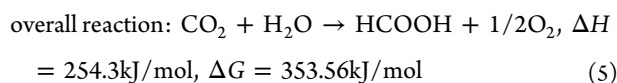
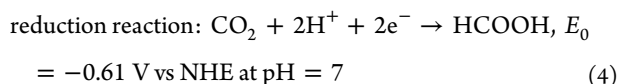
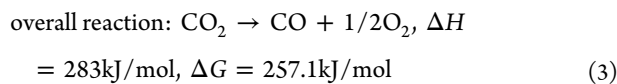
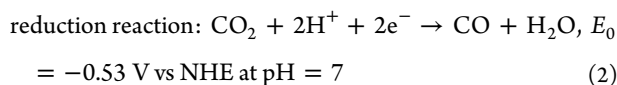
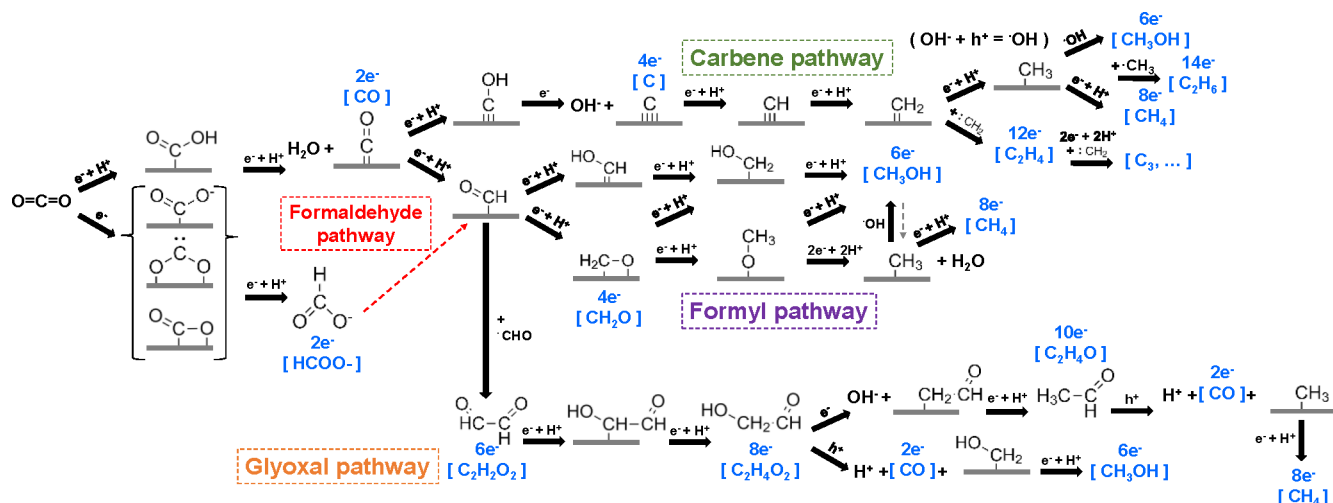
absorption measurements, together with modeling. Important information regarding adsorption and kinetics could also be provided by electrochemical measurements and theoretical computation.

In an earlier review, Habisreutinger et al. had summarized three possible mechanisms for the photocatalytic formation of five C_1 (CO , $HCOOH$, CH_2O , CH_3OH , CH_4) and some C_2 products from CO_2 on TiO_2 , namely the formaldehyde pathway, the carbene pathway, and the glyoxal pathway.¹⁴ These different possibilities start with the binding modes of CO_2 on the surface of catalysts, including oxygen coordination, carbon coordination, and side/mixed coordination.³⁵ On the basis of these, we proposed a comprehensive description of pathways (Scheme 5). The pathways are directed by whether the following reaction occurs via electron transfer, proton transfer (sometimes hydroxyl transfer) or concerted electron–proton transfer.¹⁶ An intermediate molecule in one pathway could be the final product of another pathway if it fast desorbs from the surface of the catalysts before further steps take place. Since the final products from the experiments are the most direct clues, we thus discuss the possible mechanistic details guided by respective products and the issues open to be elucidated.

As mentioned above, using water to reduce CO_2 is the ideal and sustainable process, which includes two half-reactions, water oxidation (eq 1) and multi-electron reduction of CO_2 . The following details all these reduction processes, involving the production of C_1 (e.g., formic acid, carbon monoxide, formaldehyde, carbon, methanol, and methane) and C_2 products (e.g., oxalic acid, acetic acid, acetaldehyde, ethanol, ethylene, ethane) by photocatalysis.



Pathways to C_1 Products. Two-Electron Reduction Process. The two-electron reduction process produces CO and $HCOOH$ on the basis of eqs 2–5, and $HCOOH$ production happens together with water oxidation (eq 1).

Scheme 5. Mechanistic Pathways of CO₂ Reduction to Commonly Observed C₁ and C₂ Products

Carbon monoxide plays a crucial role in the Fischer–Tropsch synthesis and carbonylation of alkenes, while formic acid is a necessary preservative and antibacterial agent in livestock feed.¹⁷ Regarding the numbers of electrons needed, CO and HCOOH are kinetically the most accessible products from CO₂, while thermodynamically, both are uphill reactions. Meanwhile, it should be noted that the minimal potential for CO₂ reduction decreases with the increase of the number of electrons involved in the products. For example, photocatalytic CO₂ conversion to CO or HCOOH requires slightly more negative potential than that to CH₄.

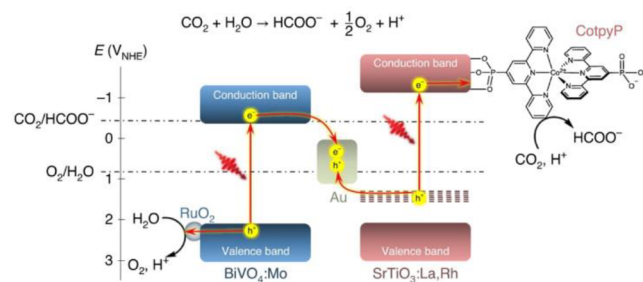
CO, as shown in Scheme 5, is a product, a byproduct or an intermediate in CO₂ reduction. In detail, CO is an intermediate in the carbene pathway after anchoring the C atom of CO₂ to the surface of the catalysts. One proton attacks the O atom in CO₂ to form COOH radicals in the presence of the first electron, followed by an immediate cleavage of the C–OH bond, which releases CO and water if not proceeding further.^{36,37} The selectivity of this process could be controlled by the binding strength of CO on the surface of a catalyst. CO can be a poison if it binds too strongly to the metal, while CO desorbs as a final product before further reduction occurs if the binding is too weak.³⁸ Studies have shown that the suitable binding energy of CO on the copper catalyst and the high coverage ensures the formation of more reduced products and inhibits the competitive hydrogen evolution.³⁹ In the glyoxal pathway, CO is a byproduct when the C₂ intermediates decarbonylate to form methanol or methane,⁴⁰ which agrees well with the literature that CO is commonly detected together

with methanol and methane products. The oxidation of organic products such as formaldehyde and methanol by photoholes also results in CO, which we observed.⁴¹ Such backward reactions convert the kinetically more challenging reduction products to a two-electron product CO, which can be mitigated by hindering the adsorption of the formaldehyde and methanol on the oxidation sites.^{41,42}

It should be noted that the selective conversion of captured CO₂ toward formic acid has been identified as one of the relatively profitable processes, although the market demand and the energy content are low (Scheme 2). Formate might be the most accessible product as all three binding modes can possibly lead to formate production (Scheme 5). Moreover, it only requires two electrons and one proton to form formate, and the breaking of the C–O bond does not occur during the formation of HCOOH. So far, the benchmark efficiency in a formate production system reaching a solar-to-formate conversion efficiency of 0.08 ± 0.01% on a Z-scheme system of SrTiO₃:La,Rh/Au/BiVO₄:Mo modified with molecular cocatalysts (Scheme 6).⁴³

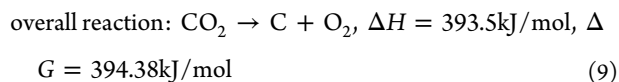
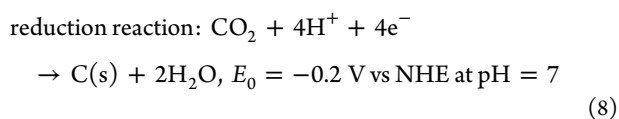
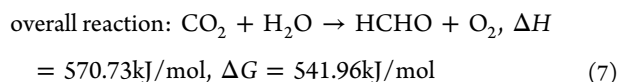
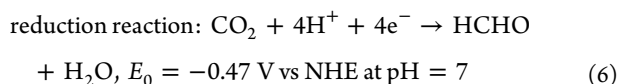
HCOOH has been previously proposed as an intermediate in the formaldehyde pathway via the surface adsorption involving O, including bidentate and monodentate O coordination or the mixed C–O coordination.⁴⁴ EPR studies by Shkrob et al. demonstrated that only when CO₂^{•−} radical is

Scheme 6. (a) An Energy Diagram Depicting the Photosynthetic CO₂RR Coupled with Water Oxidation. The Reduction Potentials Are Given versus the NHE at pH 6.7. Reproduced with Permission from Ref 43. Copyright 2020 Springer Nature Publishing AG



doubly bound through its oxygens to the metal ions at the surface can this radical be further reduced to formate. Otherwise, the reduction is stalled.⁴⁵ The bidentate binding of the CO₂ via both O atoms results in the proton attaching to the C atom in CO₂⁻ to form the formate HCOO radical, which further accepts one electron and proton to form HCOOH, being a favored reaction in water with a high dielectric constant.^{46,47} Regarding the further reduction of formic acid, Koci et al. showed the profiles of produced CH₄ and CH₃OH disagreed with the formaldehyde pathway, as CH₃OH is not observed as an intermediate of CH₄.⁴⁸ Hori et al. also suggested that formate is more likely the terminal product for electrochemical CO₂ reduction on copper except for systems with very high concentrations, high cathodic bias, and highly acidic or basic electrolytes.⁴⁹ Therefore, we did not wholly draw the proposed debatable formaldehyde pathway (gray dashed lines) in Scheme 5. Instead, we summarize a new formyl pathway from the literature discussed in detail below.

Four-Electron Reduction Process. The four-electron reduction process produces HCHO and C on the basis of eqs 6–9, while HCHO production requires water oxidation (eq 1).

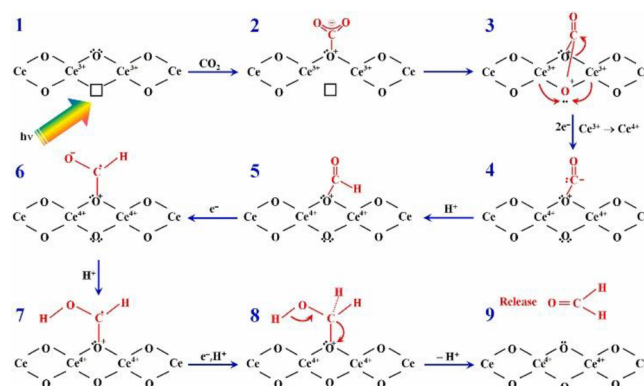


Formaldehyde is helpful for disinfection and is a precursor to more complex compounds in industry. In the proposed formyl pathway (Scheme 5), if the catalyst has moderate adsorption strength, the C-anchored CO intermediate can accept one electron while a proton attacks the C atom, forming the formyl intermediate (CHO), as shown in Scheme 5, which could further be converted to CH₂O with the other proton–electron pair.³⁸ By calculation of Gibbs free energy differences and the energy barriers, Cheng et al. showed that adding the proton to C (forming CHO) is preferable to adding to O (forming COH) on Cu (100), which leads to the reaction toward the formyl pathway over the carbene pathway.⁵⁰ Formaldehyde could then be formed after receiving another pair of electron and proton. If the formaldehyde is not desorbed, the path further leads to CH_x species that can produce methane, as observed experimentally.⁴⁴ Cheng et al. also calculated that although CH₂O has been detected as a product, the energy barrier of CH₂O formation is 0.47 eV higher than for CHO and hence is kinetically unfavorable.⁵⁰ In other words, reactions on Cu (100) should more likely have CHO as an intermediate. CH₂O is detectable as a product only if it is not strongly chemically bonded to the oxide surface. Nie et al. suggested that the COH intermediate more likely exists on Cu (111), since the CHO intermediate needs to overcome a significant energy barrier, blocking further reactions to produce

CH₃OH and CH₄ by calculation study.⁵¹ Therefore, it is concluded that the exposed surface facets dominate the products and pathways.

However, Park et al. proposed an oxygen vacancy mediated mechanism to release formaldehyde on an rGO-grafted NiO-CeO₂ sample (Scheme 7).⁵² The CeO₂ surface and CO₂⁻

Scheme 7. Photocatalytic CO₂ Reduction Process on NiO/CeO₂/rGO Hybrid Composite Photocatalyst^a Reproduced with Permission from Ref 52. Copyright 2021 Elsevier



^aReaction mechanism and pathways associated to photoactivation of CO₂ molecules at oxygen vacancy sites of CeO₂ surface and CO₂ reduction through proton-coupled electron transfer processes at different stages of reaction.

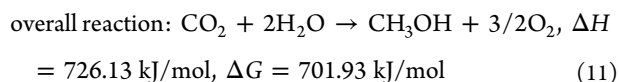
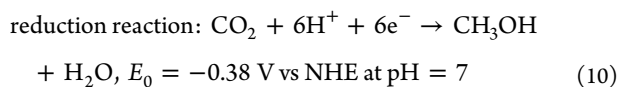
radicals were monitored by *in situ* X-ray absorption near edge structure (XANES), *in situ* attenuated total reflectance infrared (ATR-IR) and *in situ* EPR, and then a detailed description of the multistep CO₂ photoreduction process was illustrated. Briefly, CO₂ capture occurs at the oxygen site adjacent to oxygen vacancy. One O atom from the CO₂ molecule fills the vacancy site, and the C–O bond is broken. The formation of CHO, CHOH, and CH₂OH occurs through a few electron and proton transfer processes, and then formaldehyde is produced. The formation of oxygen vacancies is due to solar light illumination, which could be validated by *in situ* XANES spectroscopy. Hence the catalytic process is sustainable, and this also indicates that a combination of these characterization techniques can reveal the mechanism in a straightforward way.

Carbon could also be formed as a four-electron product in the carbene pathway. When the proton attacks the O atom of the adsorbed CO followed by eliminating one OH⁻ (or with another proton to eliminate one H₂O), carbon radicals are generated (Scheme 5).¹⁴ Such a process has been verified by the signals of the C residue on the surface detected by EPR spectroscopy.³⁶ DeWulf et al. also observed graphitic carbon species by X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES).⁵³ Such surface carbon product or intermediate could further be reduced to CH, CH₂, and CH₃ over relatively low barriers.

Besides, three theoretical models have been proposed to investigate the CO₂ reduction process via the formyl pathway, including implicit solvent models, explicit solvent models, and the H-shuttling model.¹⁶ In the implicit solvent model, a continuous description of the ions is included, whereas the explicit solvent model offers an atomistic-level picture of solvation and cation effects.⁵⁴ Furthermore, the H-shuttling model considers that water molecules shuttle the protons, and CHO radicals are formed via a direct transfer of H.⁵⁵ However,

on the Cu surface, explicit calculations concluded that all steps after the formation of CO radicals are proton–electron transfers. The inconsistencies in the explanation for CO₂ reduction pathways come from both different study methods and the intrinsic complexity of the reaction mechanism. Clearly, more efforts are required to clarify this ambiguous pathway, and the combination of state-of-the-art operando spectroscopies can provide a strong potential to acquire the solution to this.

Six-Electron Reduction Process. The six-electron reduction process produces CH₃OH on the basis of eqs 10 and 11, together with water oxidation (eq 1).



In the suggested “methanol economy” by Olah et al., methanol could be a crucial alternative to fossil fuels as it is a suitable energy-storage material, a fuel, and a feedstock to synthesize hydrocarbons and their products.⁵⁶ In the context of the “hydrogen economy”, methanol is also regarded as a promising liquid medium to store hydrogen safely and efficiently before use.⁵⁷ Methanol contains 40% more hydrogen mass density (kg H₂ per m³) as well as over 80% more volumetric energy density than liquid H₂. In contrast, the energy for compression and liquefaction of H₂ accounts for 10–15% and 30–40% of the energy contained, respectively.^{58–60} Methanol also has a suitable balance between market demand, market price, and energy content (Scheme 2). Therefore, photocatalytic CO₂ conversion by water to methanol with a high selectivity has attracted substantial attention. The reduction potential (−0.38 V vs NHE at pH = 7) is slightly more positive than proton reduction (−0.41 V vs NHE at pH = 7); hence, a large group of photocatalysts reported for hydrogen production could be applied. However, the 6-electron process of methanol generation requires an exceptionally prolonged lifetime of charge carriers for accumulation. Moreover, the oxidation of methanol with holes (~10 ns) on TiO₂ is kinetically much more favored over water oxidation (up to ~1 s), making the continuous production of methanol with high selectivity a significant challenge.⁴¹

In the carbene pathway, the C radicals continue to accept three electron–proton pairs, forming the methyl CH₃ radicals. Methanol could then be produced if the methyl CH₃ radical recombines with a hydroxyl radical (•OH).¹⁴ In this case, methanol is not intermediate to CH₄, and formaldehyde was not formed at all. Electrochemical studies also support that methanol could not be reduced to form methane.^{53,55} Instead, CH₃OH is a competitive product to CH₄, depending on a few factors such as the hydrophilicity of the surface and water amount.^{61,62} The kinetic model of such a mechanism agrees with the experiment results of methanol and methane production reported by Tan et al. and Koci et al. based on TiO₂.^{37,48} CO is commonly observed in experiments with methanol as the major product since CO is an intermediate in this mechanism.

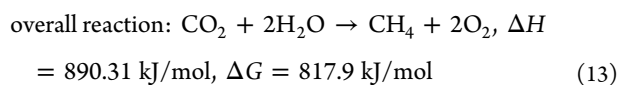
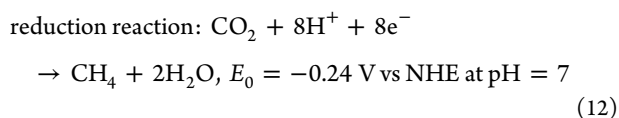
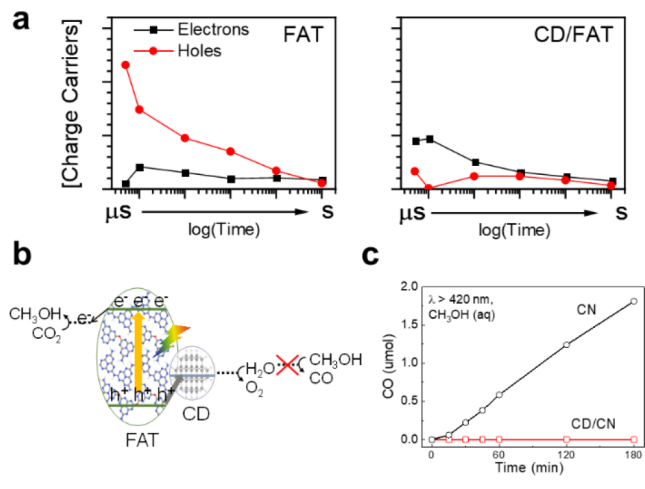
In another C-coordinated formyl pathway, the adsorbed CO was not dehydrated to C radicals but was attacked by

electron–proton pairs. Interestingly, despite the variety of proposed paths how the electron and protons are bought to the CO radical intermediate, namely, CHO/COH or CHOH/CH₂O, it seems that they eventually all lead to CH₂OH and CH₃O, as shown in Scheme 5, which possibly desorb as a CH₃OH, although not all the intermediates are evidenced by experiments.^{16,29} Lum et al. carried out an electroreduction experiment of C¹⁶O₂ in H₂¹⁸O on various Cu surfaces to identify the mechanism and found that CH₃OH was not ¹⁸O rich, and it was only detected on Cu (111).⁶³ This interesting experiment shows the face-dependent selectivity of CO₂ reduction and, more importantly, indicates that the O in CH₃OH comes from CO₂ at the beginning instead of water. This result suggests that the formyl pathway or glyoxal pathway is more likely for methanol production than the carbene pathway, where OH radicals might come from water. Cheng et al. reported that at low pH, the intermediate CHOH underwent the dehydrating process, which led to the formation of CH₃ radicals and then a higher selectivity to CH₄ over CH₃OH. In contrast, a high pH, more hydrophobic environment, weak hydrogen bonding solvent, or gaseous phase benefits the selectivity toward CH₃OH.⁵⁰ In fact, methanol is very often a competitive product to CH₄ in all the proposed pathways in Scheme 5, including the glyoxal pathway. It should be noted that the production of methanol is very challenging, as the final step of releasing methanol in both the carbene pathway and formyl pathway require hydroxyl radicals, and the glyoxal pathway involves photoholes, both of which are highly oxidative. The upper routine to methanol in the formyl pathway (Scheme 5), where the intermediates are continuously bonded via carbon to avoid the oxidation of intermediates, prefers to produce methanol with high selectivity.

The stable production of methanol not only relies on the sufficient transport of electron–proton pairs but also depends on whether the produced methanol could be protected from the strongly oxidative nature of photoholes. The backward reaction of methanol oxidation could be determined by the CO yield in the products. A strategy to avoid such an issue is to suppress the adsorption of the methanol on these oxidation sites and to promote the kinetically sluggish oxidation of water against methanol. One can know whether the holes oxidize water or methanol by measuring stoichiometry between reduction and oxidation products during CO₂ reduction. We have recently reported a unique hole-accepting carbon-dots cocatalyst (CD), where water instead of methanol selectively adsorbs (Scheme 8).⁴¹ Such CD prolongs the lifetime of charge carriers on pristine and oxygen-doped carbon nitride photocatalysts by 6–8 folds, resulting in the almost unity selectivity to methanol with stoichiometric oxygen production and internal quantum yields (IQYs) of 2–6% at 420 nm.^{42,64} A transient absorption spectroscopic investigation shows that extraction of holes by the CD is critical for the remarkable performance. Under visible light, methanol can be readily oxidized to CO by photoholes of carbon nitride (CN), while on the CD-decorated CN, no CO was detected, consistent with that methanol could not be readily adsorbed on the surface of CD where holes accumulate, and photooxidation of water occurs.

Eight-Electron Reduction Process. The eight-electron reduction process produces CH₄ on the basis of eqs 12 and 13, together with water oxidation (eq 1).

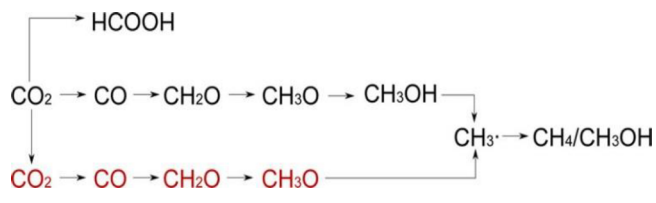
Scheme 8. (a) Charge Carrier Populations of Electrons and Holes Determined from Spectral Deconvolution of the TAS Spectra for FAT, CD/FAT, CN, and CD/CN samples. (b) Schematic Diagram of Photocatalytic CO₂ Reduction by the CD/FAT. (c) Methanol Oxidation Tests in the Presence of Light and CN, ^mCD/CN Catalysts. Reproduced with Permission from Refs 41, 42. Copyright 2020 Springer Nature Publishing AG. Copyright 2021 Wiley-VCH



Methane is not only fuel but also a precursor for syngas, hydrogen, and methanol via its reforming.⁶⁵ The methane production requires the least negative reduction potential but the most significant amount of electrons in C₁ products. As discussed above, the carbene pathway for methane formation is more plausible than the formaldehyde pathway (Scheme 5) via the acceptance of four electron–proton pairs on the C radicals (Scheme 5).¹⁴ In such a case, CO is an intermediate, and methanol is a competitive product. A low pH in an aqueous solution promotes the selectivity toward CH₄, which could also be beneficial via the modification of surface hydrophilicity by deposition of, for example, Pt NPs.⁵⁰ In the formyl pathway toward CH₃OH, the CH₃O intermediate is found using the explicit water model not to form CH₄ because of the significant barrier for proton–electron transfer from CH₃O to CH₄ + O.³⁵ The protonation of *CO to *CHO is the rate-determining step, which is followed by a series of proton–electron transfers to form *CHOH, *CH, *CH₂, *CH₃, and finally CH₄.³⁵

Surface oxygen vacancies are commonly used strategies to modify a photocatalyst. Ji et al. proposed a mechanism for the perfect and defective surfaces by theoretical calculation (Scheme 9). They found that a fast-hydrogenation path can occur at both the surface Ti atoms and the oxygen vacancies, while the oxygen vacancies are more active than the surface Ti atoms for the reaction. The fast-hydrogenation path at the oxygen vacancies combines the hydrogenation and deoxygenation paths.⁶⁶ This pathway agrees with the experimental results because CH₃OH and CH₄ often appear simultaneously

Scheme 9. Mechanism for the Photoreduction of CO₂ on the Perfect (Black) and Defective (Red) Surfaces. Reproduced from ref 66. Copyright 2016 American Chemical Society



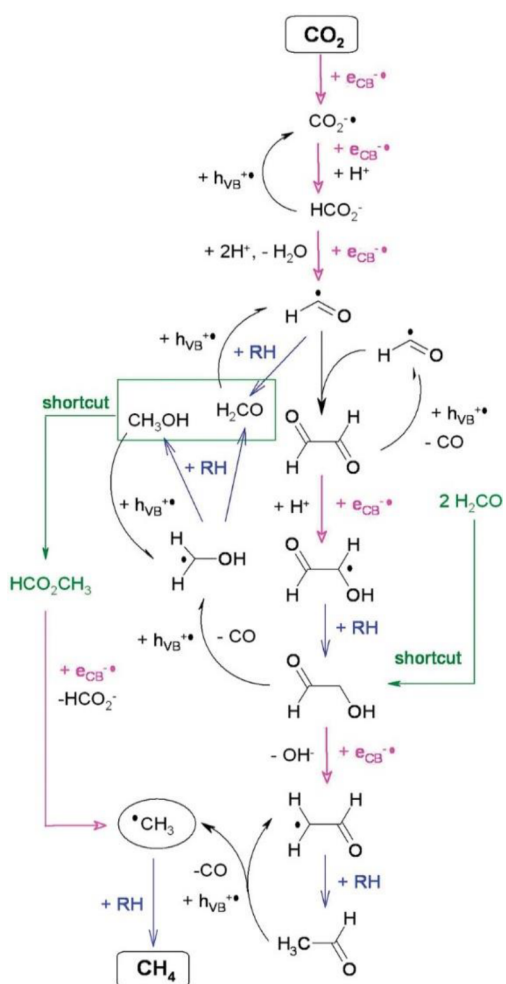
and explain the possible formation of formic acid and formaldehyde.

As discussed above, the existence of more active intermediates, including formaldehyde and methanol in the presence of highly oxidative photoholes, contradicts the formaldehyde pathway for CH₄ formation, in that one-electron reduction of these molecules in the reaction is energetically prohibitive.³⁸ Shkrob et al. found that reaction barriers for further reduction could be significantly lowered by joining two carbon atoms and proposed to follow the glyoxal (CHO)₂ pathway toward CH₄ involving a number of C₂ compounds (Scheme 10). In this pathway, the critical intermediate is the glyoxal (or ethanediol), produced from the dimerization of formyl radicals CHO radicals (Scheme 5).⁴⁰ Because of its π-conjugation, glyoxal is still a much more efficient electron acceptor than formaldehyde, which can be step-by-step reduced to glycolaldehyde (HOCHCHO), acetaldehyde (CH₂CHO), and acetaldehyde. These C₂ molecules can be further oxidized to an unstable acetyl radical, which undergoes decarboxylation to a methyl radical. The recombination of the methyl radical with a hydrogen atom forms CH₄. Formate, methanol, and formaldehyde are intermediates all formed in this pathway and serve as sacrificial hole scavengers. The glyoxal pathway will be further discussed later.

The representative examples of photocatalytic systems of CO₂ reduction to C₁ products have been summarized in Table 1. Considering the economic potential of the C₁ products such as formate/formic acid and methanol, the efficient systems for these products are of particular interest. For example, the highest solar-to-fuel efficiency of 0.08 ± 0.01% (solar-to-formate) measured under the solar simulator was achieved on the molecular cocatalyst coated on a Z-scheme particulate sheet (phosphonated Co(II) bis(terpyridine) and RuO₂ catalysts modified SrTiO₃: La, Rh/Au/ BiVO₄: Mo).⁴³ The benchmark system for CO₂ photoreduction to formic acid was based on a gas-permeable metal–organic framework (MOF) with an apparent quantum efficiency (AQE) of 15.76% at 420 nm, at the porous gas–solid interfaces with a near-unity selectivity.⁶⁷ Such a high quantum efficiency is also the highest among most systems for the C₁ products, suggesting that the metal–organic complexes play a significant role in CO₂ reduction. More examples of metal complex photocatalysts could be found in other reviews.²⁶ The highest internal quantum efficiency at 420 nm toward methanol was measured on carbon dots/oxygen-doped carbon nitride.⁴² The key to maintaining a reasonable efficiency of methanol is to mitigate overoxidation of methanol product to CO.

Pathways to C₂ Products. The direct photoconversion of CO₂ to C₂ products is more attractive because of their significantly higher market price and energy content per carbon compared with the C₁ products (except for methanol in

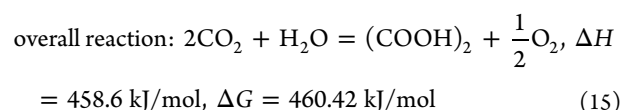
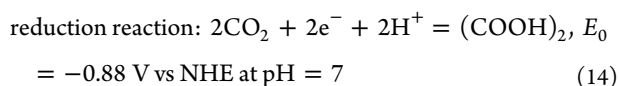
Scheme 10. "Glyoxal Cycle".^a Reproduced from Ref 40. Copyright 2012 American Chemical Society



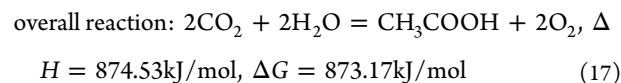
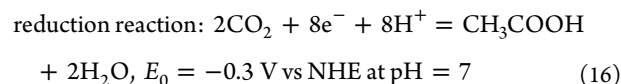
^aIn this scheme, RH stands for the generic (molecular or radical) donor of H atoms.

Scheme 2).¹⁶ The formation of the C–C bond by dimerization of C₁ intermediates on the surface of catalysts is the key to further producing C₂ products. For example, the pathways toward ethylene or ethane involve the coupling of carbene intermediates (CH₂, CH₃) in the carbene pathway while the dimerization of formyl (CHO) in the glyoxal pathway can result in a variety of C₁ and C₂ products (Scheme 5). These pathways mostly require multiple electrons and protons, which will be favorable on the surface with an increased density of charge carriers and protons. Also, the binding of intermediates on the surface of the catalysts must be sufficiently strong to reach the C₂ products instead of desorbing them early as C₁ products such as CO and CH₂O. C₁ products such as CO, CH₄, and CH₃OH can also be byproducts of these processes. All these processes again share the water oxidation half-reaction (eq 1). The following lists the chemical eqs (eqs 14–25) for C₂ products with 2 to 14 electrons, respectively.

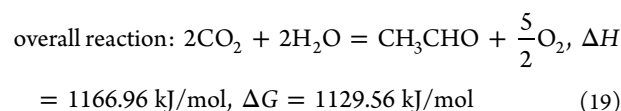
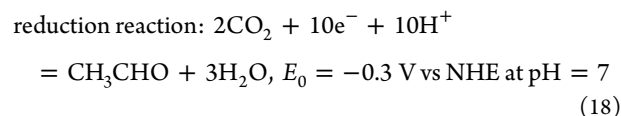
Two-Electron Reduction Process. The two-electron reduction process produces (COOH)₂ on the basis of eqs 14 and 15.



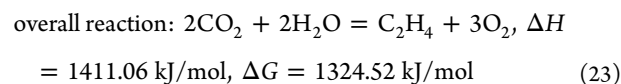
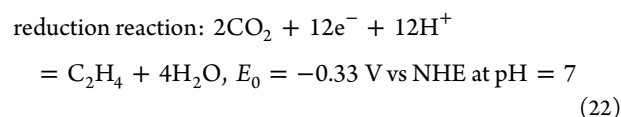
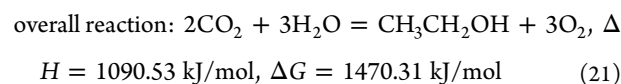
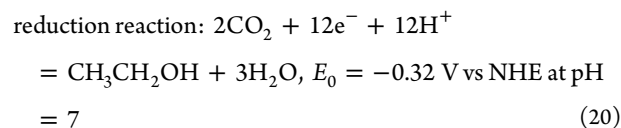
Eight-Electron Reduction Process. The eight-electron reduction process produces CH₃COOH on the basis of eqs 16 and 17.



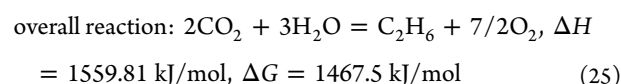
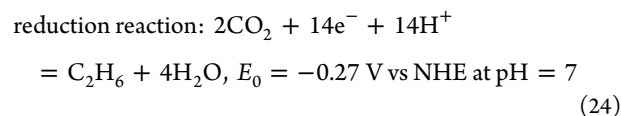
Ten-Electron Reduction Process. The 10-electron reduction process produces CH₃CHO on the basis of eqs 18 and 19.



Twelve-Electron Reduction Process. The 12-electron reduction process produces CH₃CH₂OH and C₂H₄ on the basis of eqs 20–23.



Fourteen-Electron Reduction Process. The 14-electron reduction process produces C₂H₆ on the basis of eqs 24 and 25.



Since the pathways to C₂ products are believed to involve both multi-electron coupled proton transfer and the C–C coupling processes, the reactions are generally more challenging, and fewer reports have achieved high selectivities.⁸⁰ Different from the reactions toward C₁ products, which are mostly proton-coupled one-carbon two-electron processes, the

Table 1. Representative Examples for Selective Photocatalytic CO₂ Reduction to C₁ Products

final product	electron transfer	catalyst	production rate	pressure and temperature	other conditions	selectivity	efficiency
CO	2	Au-MMT/TiO ₂ ⁶⁸	1223 μmol g ⁻¹ h ⁻¹	atm.; 100 °C	CO ₂ and H ₂ , UV-light	99%	∕
		Ru@Co ₃ O ₄ ⁶⁹	2003 μmol g ⁻¹ h ⁻¹	1 atm; 15 °C	30 mL acetone/nitrile/TEOA/H ₂ O = 3:1:1 (v/v/v), 300 W xenon lamp with a 420 nm cutoff filter	77%	EQE = 0.069%
HCOOH	2	Ru@g-C ₃ N ₄ ⁷⁰	181.25 μmol g ⁻¹ h ⁻¹	∕	400 W Hg lamp, 20 vol % TEOA in DMA,	64%	∕
		TiO ₂ /CsPbBr ₃ ⁷¹	9.02 μmol g ⁻¹ h ⁻¹	80 kPa; 10 °C	30 mL of acetonitrile, and 100 μL of water; 300 W Xe arc lamp	95%	∕
HCHO	4	photocatalyst sheet SrTiO ₃ :I ₄ , RhAuRuO ₂ -BiVO ₄ :Mo ⁴⁵	1.09 ± 0.12 μmol cm ⁻² h ⁻¹	atm.	CO ₂ , saturated 0.1 M KHCO ₃	97 ± 3%	solar-to-formate conversion efficiency of 0.08 ± 0.01%. AQY = 2.6% (420 ± 15 nm)
		single metal atom @ A-aUiO ⁶⁷	46.425 μmol g ⁻¹ h ⁻¹	r.t.	λ > 400 nm, 20 vol % TEOA in acetonitrile	∕	∕
CH ₃ OH	6	Pt and Cu @K ₂ Ti ₆ O ₁₃ particles ⁷³	3.42 μmol g ⁻¹ h ⁻¹	r.t.	particle-in-solution mode, and gas-membrane-gas mode	near unity	AQE = 2.51% (gas-liquid-solid reaction interface); AQE of 15.76% (porous gas-solid interfaces, 420 nm)
		Au NPs @TiO ₂ films ⁷⁴	1.36 μmol g ⁻¹ h ⁻¹	∕	300 W Xe lamp; H ₂ O and CO ₂	∕	∕
C	4	NiO/CeO ₂ /rGO ⁵²	421.09 μmol g ⁻¹ h ⁻¹	∕	254 nm UV	∕	∕
		reduced NiFe ₂ O ₄ ⁷⁵	∕	atm.; 80 °C	0.2 M NaHCO ₃ and 0.2 M Na ₂ SO ₃ solution	∕	solar to fuel conversion efficiency 0.775%
CH ₄	8	carbon dot/C ₃ N ₄ ⁴¹	13.9 ± 1.7 μmol g ⁻¹ h ⁻¹	atm.; r.t.	glass reactor	99.60%	IQY: 2.1% (420 nm), 0.7% (500 nm), 0.4% (600 nm)
		carbon nitride-like polymer (FAT) decorated with carbon dots ⁴²	24.2 μmol g ⁻¹ h ⁻¹	atm.	H ₂ O and CO ₂	100.00%	IQY: 5.9% at λ=420 nm
CH ₄	8	carbon nitride-Cds QD ⁷⁶	186.4 μmol g ⁻¹ h ⁻¹	∕	H ₂ O and CO ₂	73%	AQE = 0.91% (435 nm)
		BiVO ₄ /WO ₃ ⁷⁷	105 μmol g ⁻¹ h ⁻¹	∕	CO ₂ in 40 mL of KHCO ₃ (0.1M) and Na ₂ SO ₃ (0.1M)	99%	0.074% solar to methane efficiency
CH ₄	8	Ni@SiO ₂ -Al ₂ O ₃ ⁷⁸	4200 μmol g ⁻¹ h ⁻¹	150 °C	30 mL of 0.1 M NaOH, purged with high purity CO ₂ for 45 min	∕	∕
		CoDAC-3.5 with BV NSs ⁷⁹	19.5 μmol g ⁻¹ h ⁻¹	∕	H ₂ (14.5 mmol, 80 v/v %) and CO ₂ (3.63 mmol, 20 v/v %); 300 W Xe lamp, 1 KW/m ²	65%	AQY = 5.23% (400 nm)

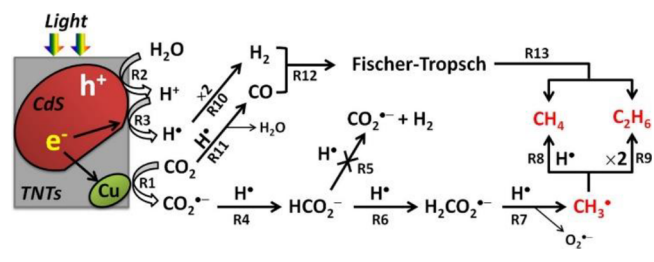
pathway to C₂ products proposed by Shkrob et al., namely the glyoxal pathway (Scheme 10), is a mainly one-electron two-carbon process through a glyoxal intermediate (e.g., on TiO₂) as evidenced by EPR.⁴⁰ The reason to postulate an alternative mechanism is that no evidence of one-electron reduction intermediate (e.g. formate, formaldehyde, or methanol) has been observed in EPR. As mentioned above, these intermediates are more likely to be oxidized than reduced. However, the glyoxal intermediate is a strong electron acceptor, which is more facile to be reduced than oxidized. Moreover, the glyoxal pathway can provide mechanisms for C₁ products such as CO, CH₄, methanol, formate and formaldehyde and explain the possible C₂ products observed, including acetaldehyde and methylformate.

As shown in Schemes 5 and 10, different from the de-OH⁻ step after receiving one proton in the carbene pathway, the crucial step in the glyoxal pathway is the dehydration step after getting three protons (or de-OH⁻ step after accepting two protons¹⁴), forming formyl radicals (HC*O). Then the formyl radicals dimerize to yield glyoxal, which is reduced to trans-ethan-1,2,-semidione (HO-C*H-CHO), glycolaldehyde (HO-CH₂-CHO), and vinoxyl (*CH₂-CHO) radicals. The vinoxyl radical could be further converted to acetaldehyde (CH₃CHO) or decarbonylized to *CH₂OH, which is the precursor for methanol (CH₃OH). The acetaldehyde could be further oxidized to acetic acid or undergo decarbonylation to form methyl radicals (*CH₃), which leads to the formation of methane (CH₄). These decarbonylation processes release carbon monoxide (CO). In this case, CO is a byproduct commonly observed in CH₄ and CH₃OH production.

The most distinct difference between the glyoxal cycle and other pathways is that the former involves not only proton-coupled electron transfer but also oxidation steps. Such pathways are not possible in the absence of holes, for example, at the cathode in the electrocatalytic system. However, the existence of holes results in the production of CO rather than C₂ products. Therefore, if one targets value-added C₂ products, the oxidative conditions should be mitigated. Another interesting difference is that the glyoxal pathway has some recycling steps where some of the intermediates (e.g., CH₃OH and CH₂O) serve as hole scavengers, hence replenishing the pool of formyl and hydroxymethyl radicals. Compared with C₁ products, glyoxal and methanol have the same required electrons with the number of 6, and the acetic acid and glycolaldehyde have the same electrons needed with the number of 8 as methane. The production of acetaldehyde and ethylene glycol need 10 electrons, while ethylene and ethanol need 12 electrons. It should be noted that the 10-electron product acetaldehyde is an intermediate for an 8-electron product CH₄ and a 2-electron product CO, which are much cheaper. It is not economically favorable to oxidize acetaldehyde to CH₄ and CO, considering the high numbers of demanded electrons and the low price of methane in the market. It is preferable to produce the C₂ products with those electrons. How CO₂ molecules bind on the surface of the catalysts usually determines the following steps for various possible products. In the pathways to C₂ products, C–C, C–O and single C bindings probably exist at the initial stages when forming glyoxal intermediates, and the coordination might rearrange to O–O binding during the reaction. However, it seems that a few binding modes and the following steps all can lead to products including glycolaldehyde, acetaldehyde, ethylene glycol, ethylene, and ethanol.⁸¹

Park et al. reported a CdS/(Cu-TNT: Na_xH_{2-x}Ti₃O₇) for photoconversion of CO₂ and water into C₁–C₃ hydrocarbons (e.g., CH₄, C₂H₆, C₃H₈, C₂H₄, C₃H₆) under visible light without the detection of CO or H₂ (Scheme 11).⁸² It could go

Scheme 11. Proposed Elementary Reaction Pathways of Photocatalytic CO₂ Conversion into Hydrocarbons. Reproduced from Ref 82. Copyright 2015 American Chemical Society



through an F–T process consuming hydrogen and CO. They also proposed that the bidentate binding of O=C=O to specific reactive surface sites reduced the energy barrier for conduction band electron transfer to CO₂. The formate radical eliminates an O₂*- radical, forming a methyl radical. The methyl radical (CH₃*), as observed by ESR, was trapped by the copper on the surface of TNTs and then self-reacts to produce ethane.⁸² This pathway indicates that the C–C coupling of methyl radicals on the surface of photocatalysts is crucial for the production of C₂₊ products such as ethane.

Regarding the C₂H₆ formation on the surface of Pt-graphene/defect-induced TiO₂, where CO₂ adsorption takes place upon abundant Ti³⁺/V_O sites through the O atom of CO₂.⁸³ An alkaline surface is favorable for C₂H₆ formation by significantly improving the activation and dissociation.⁸⁴ Electrons and holes accumulate on Ti³⁺ and graphene, respectively, with Pt accelerating electron extraction. Graphene scavenges water to supply sustained protons and benefits the stabilization of *CH₃, thus promoting C₂H₆ formation, although CH₄ is also a major product.

Hori et al. and Schouten et al. showed that Cu (111) leads to lower onset overpotentials for both CH₄ formation and C₂H₄ formation, while the dimerization of CO leads to C₂H₄ as the product on Cu (100).^{85,86} The dimerization of CO is followed by a few steps which are similar to the glyoxal pathway, except that the intermediate (CH₂CHO) changes from C-coordination to O-coordination. CH₂CHO* could further produce C₂H₄ or CH₃CH₂OH.⁴⁴ It should be noted that these reports are based on studies on the electrochemical reduction of CO₂, and the pathways to C₂ products have not been observed in photocatalytic research.

There is also a possibility that C₂ products can be produced via the carbene pathway (Scheme 5). In this pathway, another carbene radical might attack the formed CH₄ or CH₃OH to make C₂H₄ or C₂H₆.³¹ Other products, including C₃ and C₃₊, could also be obtained if more carbene radicals are involved in such a mechanism but are hardly reported.³¹ Kuhl et al. have proposed an enol-like intermediates pathway. However, how the enol (e.g., C₂H₄O₃, C₃H₆O₂) is formed on the surface of catalysts remains unclear.⁸⁷ Strategies that increase the density of charge carriers and protons, tune the surface adsorption/desorption, and modify the surface acidity and alkalinity are believed to promote the reaction toward C₂₊ products,

Table 2. Representative Examples for Selective Photocatalytic CO₂ Reduction to C₂ products

final product	electron transfer	catalyst	production rate	pressure and temperature	other conditions	selectivity	efficiency
CH ₃ COOH	8	partially reduced Co ₃ O ₄ nanosheets ⁸⁹ MoS ₂ ⁹⁰ 1% MgO@TiO ₂ ⁹¹ WO ₃ -0.33H ₂ O ⁹²	3 μmol g ⁻¹ h ⁻¹ 39.0 μmol g ⁻¹ h ⁻¹ 1.04 μmol L ⁻¹ g ⁻¹ h ⁻¹ 9.4 μmol g ⁻¹ h ⁻¹ 1814.7 μmol g ⁻¹ h ⁻¹	25 °C 0.1 MPa 25 °C 4 °C 10 °C	simulated air (0.03% CO ₂) H ₂ O and CO ₂ with visible light 100 mL 0.1 M NaOH with CO ₂ ; 253.7 nm (0.167 mW/cm ²) H ₂ O and CO ₂ (50% in Ar) 3 mL of 10% triethanolamine (TEOA)/acetonitrile (MeCN) solution with 0.3 mL of H ₂ O in a 60 mL sealed flat quartz reactor	92.50% 94.00% / 85% 98%	2.75% CO ₂ -to-CH ₃ COOH conversion ratio / / / quantum efficiency of 22.4% at 385 nm; QE of 13.3% at 420 nm
CH ₃ CHO	10	locally crystallized polymeric carbon nitride (PCN) ⁸⁸ bulk g-C ₃ N ₄ ⁹³ C-SnS ₂ ⁹⁴ Nb-doped TiO ₂ ⁹⁵	0.4 μmol h ⁻¹ 139 μmol g ⁻¹ h ⁻¹ 572 μmol g ⁻¹ h ⁻¹ 51.8 μmol g ⁻¹ h ⁻¹ 51 μmol g ⁻¹ h ⁻¹ 5.13 μmol g ⁻¹ h ⁻¹ 14.37 μmol g ⁻¹ h ⁻¹ 0.016 μmol h ⁻¹	0.06 MPa Atm.; 25 °C R.t. / r.t. 4 °C 4 °C, atm. atm.; r.t.	water vapor and CO ₂ UV-vis light source 300 W halogen lamp, gas flow reactor NaHCO ₃ solution (0.1 M, 45 mL) with triethanolamine (5 mL) as the sacrificial agent. water vapor NaHCO ₃ and CO ₂ , Xe lamp (450W) H ₂ O and CO ₂ H ₂ O and CO ₂ 0.1 M KHCO ₃ and CO ₂	/ / 98% / / / 56.1%	photochemical quantum efficiency: 0.7% / / AQE = 3.5% AQE = 0.0086% of PTh/Bi ₂ WO ₆ AQE = 0.00793% at 300 W Xe lamp with a 420 ± 15 nm band-pass filter AQE = 1.36% at 400 nm
C ₂ H ₄	12	red phosphorus decorated Bi ₂ MoO ₆ ⁹⁶ AgBr-Nitrogen doped graphene-g-C ₃ N ₄ ⁹⁷ conducting polymers modified Bi ₂ WO ₆ microspheres ⁹⁸ Bi ₂ MoO ₆ quantum dots in situ grown on reduced graphene ⁹⁹ C/Cu ₂ O mesoporous nanorods ¹⁰⁰ Cu/TiO ₂ powders ¹⁰¹	0.542 μL g ⁻¹ h ⁻¹ 0.048 μmol g ⁻¹ h ⁻¹ 17 μL g ⁻¹ h ⁻¹ 1 μmol h ⁻¹ 11 μmol g ⁻¹ h ⁻¹ 1 μmol g ⁻¹ h ⁻¹	28 kgf/cm ² pressured CO ₂ bubbling CO ₂ in H ₂ O at 60 °C, Atm. 20–25 °C and atm. atm.; r.t. atm.; r.t. 0.26 MPa, 40 °C	H ₂ O and CO ₂ H ₂ O and CO ₂ H ₂ O and CO ₂ , 450 W Xe lamp, 420 nm NaHCO ₃ aqueous dispersion CO ₂ saturated, pH 1, 300 W Xe lamp (λ > 300 nm), 5 h sun simulated light (100 mW/cm ²), moist CO ₂ , continuous flow 1 mL min ⁻¹ NaHCO ₃ aqueous dispersion CO ₂ saturated, 300 W Xe lamp	48.7% 5% / 6.4% 22.9% 7%	/ / / AQE = 2.7%
C ₂ H ₆	14	g-MWCNT@TiO ₂ core-shell nanocomposites ¹⁰² CdS/(Cu-TNTs) ⁸² Nafion/Pd-TiO ₂ ¹⁰³ Pr-C/defect-induced TiO ₂ ⁸³ AuPd/(101) TiO ₂ ¹⁰⁴	1 μmol h ⁻¹ 11 μmol g ⁻¹ h ⁻¹ 1 μmol g ⁻¹ h ⁻¹	atm.; r.t. atm.; r.t. atm.; r.t. 0.26 MPa, 40 °C	H ₂ O and CO ₂ , 450 W Xe lamp, 420 nm NaHCO ₃ aqueous dispersion CO ₂ saturated, pH 1, 300 W Xe lamp (λ > 300 nm), 5 h sun simulated light (100 mW/cm ²), moist CO ₂ , continuous flow 1 mL min ⁻¹ NaHCO ₃ aqueous dispersion CO ₂ saturated, 300 W Xe lamp	/ 6.4% 22.9% 7%	AQE = 2.7%

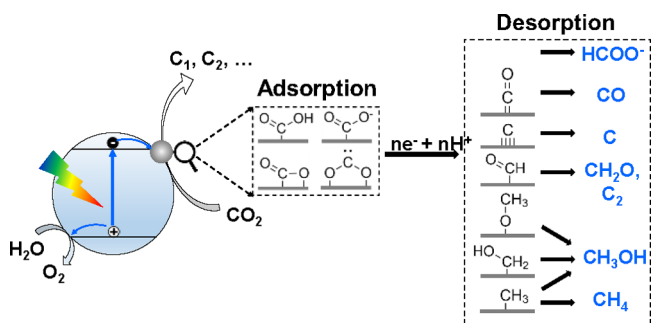
including using a larger number of photon flux and higher energy, cocatalysts, SPR effects and surface defects.¹⁷

Most of the C₂ products are valuable products. As summarized in Table 2, the benchmark quantum efficiency for C₂ products is 22.4% at 385 nm and 13.3% at 420 nm (CO₂ to acetaldehyde with a 98.3% selectivity) achieved on locally crystallized carbon nitride.⁸⁸ Liu et al. used DRIFT and theoretical calculation to prove that an amino-2-propanol-assisted hydrothermal treated carbon nitride had strong bonding with the *OCCHO group, which is favorable to a C–C coupling process and changes the reaction pathway to form CH₃CHO instead of HCHO. The highest quantum efficiency for ethanol was 3.5% on AgBr–N-doped carbon nitride. While the activity and selectivity for ethylene and ethane are generally much smaller, which might result from the large numbers of electrons needed for these products (12–14 electrons).

3. CHALLENGES AND OUTLOOK

We have discussed the detailed potential pathways toward various products, including the well-established carbene pathway, glyoxal pathway and a formyl pathway. The reaction pathway and consequently the product selectivity of photocatalytic CO₂ conversion highly depends on the surface chemistry of adsorption of CO₂ and desorption of intermediates on the surface of photo/cocatalysts, which has been thoroughly summarized in other reviews (Scheme 12).^{17,20,29,31,48,105} Other factors including crystal facets,

Scheme 12. Possible Adsorption of CO₂ and Desorption of Intermediates on the Surface of Cocatalysts in Photocatalytic CO₂ Reduction



surface poisoning phenomena, which are closely related with the bonding modes and strength as discussed above, could also influence the reactivity and selectivity.^{16,69,81}

The key facts of these pathways are summarized in Table 3 regarding different profiles of product distribution. For example, formate can be a promising product because it is both economically beneficial and kinetically easy to produce. However, CO exists in all the pathways. Based on the amount and production profile, the possible mechanism could be inferred. For example, if the amount of CO is minor compared with other main products, it is likely an intermediate or an oxidation product from, for example, methanol. If the amount of CO is comparable to methanol or methane, the reaction is most likely via the glyoxal pathway. Methanol and methane are always competitive products in these pathways, but methanol is more desired in the aspect of market price and transportation, providing its further oxidation could be mitigated. However, this is challenging because the final step of releasing methanol

in a few pathways involves photoholes or hydroxyl radicals, which are highly oxidative. Methane requires multi-electrons (8 e⁻), but its price is even below the cost of capturing CO₂. If the reaction goes through the glyoxal pathway, terminating the products at C₂ before the decarbonization is more meaningful, rather than the decomposition of the C₂ to unprofitable CO and CH₄. Another pathway to C₂₊ products via carbene coupling is promising as it has the potential to produce long-chain products.

Although substantial progress has been made in developing and understanding photocatalysts for solar fuel production from CO₂ and water, we believe there are at least four significant challenges to overcome in this field apart from the discovery of catalysts/cocatalysts, which have been extensively reviewed by others.^{16,17,27,29,31,105,106}

Validation of the Reactions. The first challenge is the confirmation of the products in CO₂ reduction reactions. In two studies, Yang et al. and Yui et al. observed ¹²C products (¹²CO and ¹²CH₄, respectively) even if ¹³CO₂ was used as the carbon source, indicating the carbon residues in the system could participate in the photoreactions hence should not be ignored. Therefore, the detection of all carbon-based products is not indeed proof of CO₂ reduction before the validation by control experiments. Control experiments in the CO₂ atmosphere and inert gas (e.g., Argon) might give some hints. While the direct evidence is the isotopic labeling experiments, which could be carried out in a GCMS,⁴¹ an IR system¹⁰⁷ or NMR⁴³ to distinguish the ¹³C labeled products. Hence it is crucial for all CO₂ reduction reactions.

Meanwhile, the oxidation products (e.g. oxygen) should also be scrutinized and calculated with the detected carbon products to verify whether the stoichiometry of proposed reactions is achieved. Besides, the performance reported by different groups critically depends on many specific details of the experimental setup and reaction conditions, such as the light source, the pH, cocatalyst selection and loading, the sample concentration, and the reactor design. To minimize such influences, the quantum yield (QY) together with the product generation rate is all required.

Mechanism to Generate High-Value-Added Products. The second challenge is to understand the production mechanism of high-value chemicals, especially C₂₊, via multi-electron processes since interfacial reactions such as CO₂ and multiproton reduction usually occur on a time scale of microseconds or longer.²⁸ As observed for CN_xH_y, such trapping leads to a severe loss of driving force and microsecond charge transfer rate.¹⁰⁸ To obtain a sufficient charge carrier lifetime without losing too much driving force for the interface redox reaction, nature uses a dual photocatalyst system instead of a single photocatalyst, allowing the realization of effective charge separation via a series of downhill charge transfers and overcome the inevitable back reaction.¹⁰⁹ There were reports on the Z-scheme CO₂ reduction systems, in which electrons and holes are generated on the spatially separated subsystems, thereby reducing the tendency of electron–hole recombination and allowing a longer lifetime and more significant accumulation of charge carriers to overcome the kinetic limitations.⁴³ The accurate determination of the time scale of the charge carrier relaxation and the excited state as well as the respective reaction intermediates at the surface will provide us with the information needed to design effective materials for the selective production of the high-value products. This

Table 3. Summary of Important Facts for the Diverse Products from Photocatalytic CO₂ Conversion by Three Proposed Pathways

products	remarks	carbene pathway	formyl pathway	glyoxal pathway
HCOO ⁻	high market price, one-step final product, no C–O breaking, accessible from various binding modes	×	×	×
CO	uneconomic if produced with H ₂ , while valuable if pure CO, may exist in all pathways	intermediate and final product if weak binding	intermediate, byproduct from e.g. methanol oxidation	intermediate, final byproduct to methanol or methane
C	uneconomic	intermediate and product	×	×
CH ₂ O		×	intermediate and product	intermediate and product
CH ₃ OH	high energy content, valuable liquid fuel	the final competitive product to methane	the final competitive product to methane	the final competitive product to methane, release with CO
CH ₄	high energy content but Uneconomic	the final competitive product to methanol	the final competitive product to methanol	the final competitive product to methanol, release with CO
C ₂ H ₄ , C ₂ H ₆	high energy content and high market price	product from carbene coupling	×	×
C ₂ H ₂ O ₂ , C ₂ H ₄ O ₂ , C ₂ H ₄ O	high energy content and high market price	×	×	intermediate and final product if not further decarbonised

information can be obtained by *in situ* spectroscopies such as IR, EPR, XPE, XANES, and theoretical calculation.

Practical Devices. The third challenge is to develop practical devices for photocatalytic CO₂ conversion. For simplicity and to focus on evaluating materials, a closed batch reactor is the most commonly used system in the literature despite its limitations. However, for potential large-scale use in the future, rationally designed reactors such as a flow system would be beneficial, in which the light distribution and mass flow need to be considered carefully.¹¹⁰ Only limited types of CO₂ conversion devices have been reported so far. Wang et al. reported a wireless and stand-alone photocatalyst sheet device for scalable solar formate production from carbon dioxide and water with the solar-to-formate efficiency of ~0.1% using a nature-mimicking Z-scheme architecture.⁴³ Recently, a modular 5 kW pilot-scale solar-thermal system was demonstrated to synthesize methanol from H₂O and CO₂ captured directly from the ambient air operated under actual conditions.¹¹¹ This large-scale reactor could be an exciting reference for practical CO₂ conversion, although the device was only used in thermal catalysis so far. In the broad field of photocatalysis, a water-splitting device extended to the scale of 100 m² was preliminarily validated very recently, reaching a solar to hydrogen efficiency (STH) of 0.76%,¹¹² which to some extent demonstrated the safe, large-scale photocatalytic water splitting and gas collection and separation. However, the overall process was summed up as energy negative. A continuous flow reactor for scalable organosynthesis was also tested.¹¹³ Another group of practical reactors for CO₂ photoreduction are the membrane reactors, which immobilize photocatalyst (nano)particles on the membrane substrates to replace a suspension.¹¹⁴ Although such systems might suffer from possible catalyst losses under long-term operation, they have the advantages such as no need to separate the catalyst from the solution and highly stable catalytic efficiency.¹¹⁵ The reported examples of such membrane reactors include C₃N₄ or TiO₂ on Nafion membrane,^{116,117} TiO₂ on carbon paper,¹¹⁸ TiO₂ and Cu–TiO₂ on zeolitic imidazolate framework (ZIF-8),¹¹⁹ and so on, which are good examples for the potential use in a flow system. Reactors under concentrated solar power also have been developed to obtain the high density of electron–hole pairs in the photocatalyst, and the catalyst can also be heated to high temperatures.^{73,120} We have also recently developed a flow-reactor for oxidative coupling of methane to

C₂ products and a multilayer device for methanol reforming.^{8,121} All these devices for the equivalent photocatalytic reactions might accelerate the development of efficient and scalable devices for practical CO₂ photoconversion, especially driven by the current global concern of the critical climate change.

Economic Considerations. The last challenge, closely connected to the third, is to take the cost of the reactant CO₂ into account, which is a limiting factor for scaling up but is often ignored. Most reports used CO₂ in significant excess without considering the cost of CO₂ capture processes or the conversion efficiency of CO₂. The approaches to directly capture CO₂ from the air include aqueous alkali capture (cost US \$97–134 tCO₂⁻¹ for 0.1 MPa CO₂, US \$116–168 tCO₂⁻¹ for 15.1 MPa CO₂), supported amine capture (cost ~ US \$90 tCO₂⁻¹) and the disruptive solid absorption (cost ~ US \$15–50 tCO₂⁻¹).^{64,122,123} Besides, other criteria such as carbon intensity (CI, the amount of net carbon by weight emitted per unit of fuel energy consumed) and the full-cycle time should also be considered.⁶⁰ An analysis by Nitopi et al. showed that products such as methane and CO (syngas) are not economically feasible because their market prices do not make up for the energy cost of CO₂ capture, although these products are commonly reported in the literature.¹⁶ Instead, more preferable C₁ products include methanol, formic acid, and CO (pure), while promising C₂₊ products are ethylene, ethanol, acetaldehyde, and propanol.¹⁶ The direct reduction of CO₂ from the air is a very high cost and challenging process since CO₂ only accounts for ~400 ppm in the atmosphere, and the existence of oxygen also tends to react with photoelectrons to form O₂⁻ competitively. A preliminary example is the photocatalytic CO₂ conversion directly from air with a ca. 98.35% selectivity to CH₃OH and ca. 4.32% conversion efficiency of CO₂ after 4 h reaction by selectively adsorbing CO₂ rather than O₂ on Rb_{0.33}WO₃ catalyst.¹²⁴ Clearly, this is promising, while the economic benefit is too early to assess. However, the development of routes for high value-added products could be promoted by the driving force from the market.

Overall, the photocatalytic efficiency of CO₂ to chemicals, in particular, the selectivity to the C₂ chemicals, remains moderate so far, and its economic and environmental feasibility should be evaluated carefully to avoid extra carbon emission. An in-depth understanding of the reaction pathway will enable

a precise design of the photocatalytic system, including the semiconductor, surface modification, defect engineering, cocatalyst loading, reaction conditions, and so on, toward preferable products. All these are at a very early stage at present, requiring multidisciplinary efforts and collaborations to overcome the barriers facing.

AUTHOR INFORMATION

Corresponding Author

Junwang Tang – Department of Chemical Engineering, University College London, London WC1E 7JE, U.K.;
orcid.org/0000-0002-2323-5510;
Email: junwang.tang@ucl.ac.uk

Authors

Yiou Wang – Department of Chemical Engineering, University College London, London WC1E 7JE, U.K.; Department of Physics, Ludwig-Maximilians-Universität München, 80539 Munich, Germany; Present Address: Advanced Research Institute for Multidisciplinary Sciences, Beijing Institute of Technology, No. 5 South Zhongguancun Street, Beijing 100081, China

Enqi Chen – Department of Chemical Engineering, University College London, London WC1E 7JE, U.K.

Complete contact information is available at:
<https://pubs.acs.org/10.1021/acscatal.2c01012>

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

All authors are thankful for UK EPSRC (EP/S018204/2), Leverhulme Trust (RPG-2017-122), Royal Society Newton Advanced Fellowship grant (NAF\R1\191163), and Royal Society Leverhulme Trust Senior Research Fellowship (SRF\R1\21000153). Y.W. thanks the Alexander von Humboldt Foundation for a fellowship.

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