Towards artificial photosynthesis: Sustainable hydrogen utilization for photocatalytic reduction of CO2 to high-value renewable fuels

Van-Huy Nguyen⁎, Ba-Son Nguyen, Zhong Jin, Mohammadreza Shokouhimehr, Ho Won Jang, Chechia Hu, Pardeep Singh, Pankaj Raizada, Wanxi Peng, Su Shiung Lam, Changlei Xia, Chinh Chien Nguyen⁎, Soo Young Kim⁎, Quyet Van Le⁎

Department for Management of Science and Technology Development, Ton Duc Thang University, Ho Chi Minh City, Vietnam
Faculty of Applied Sciences, Ton Duc Thang University, Ho Chi Minh City, Vietnam
Key Laboratory of Advanced Materials for Energy and Environmental Applications, Lac Hong University, Bien Hoa, Vietnam
Jiangsu Key Laboratory of Advanced Organic Materials, Key Laboratory of Mesoscopic Chemistry of MOE, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing, Jiangsu 210029, China
Department of Materials Science and Engineering, Research Institute of Advanced Materials, Seoul National University, Seoul 08826, Republic of Korea
Department of Chemical Engineering, R&D Center for Membrane Technology and Research Center for Circular Economy, Chung Yuan Christian University, Chungli Dist., Taoyuan City 32023, Taiwan
School of Chemistry, Faculty of Basic Sciences, Shoolini University, Solan Himachal Pradesh 172212, India
Henan Province Engineering Research Center for Biomass Value-added Products, School of Forestry, Henan Agricultural University, Zhengzhou, 450002, China
Pyrolysis Technology Research Group, Institute of Tropical Aquaculture and Fisheries (Akuatrop) & Institute of Tropical Biodiversity and Sustainable Development (Bio-D Tropika), Universiti Malaysia Terengganu, 21030 Kuala Terengganu, Terengganu, Malaysia
Co-Innovation Center of Efficient Processing and Utilization of Forestry Resources, College of Materials Science and Engineering, Nanjing Forestry University, Nanjing, Jiangsu 210037, China
Anhui Juke Graphene Technology Co., Ltd, Bishan, 233600, China
Institute of Research and Development, Duy Tan University, Da Nang 550000, Vietnam
Faculty of Environmental and Chemical Engineering, Duy Tan University, Da Nang 550000, Vietnam
Department of Materials Science and Engineering, Korea University, 145, Anam-ro Seongbuk-gu, Seoul 02841, Republic of Korea

HIGHLIGHTS
- Artificial photosynthesis for reduction of CO2 to renewable fuels was reviewed.
- Various photocatalysts and reaction parameters for photoreduction of CO2 were summarized and discussed.
- The CO2 photoreduction to mimic natural photosynthesis was proposed and verified successfully.

ARTICLE INFO
Keywords:
Artificial synthesis
Photocatalysts

ABSTRACT
Converting solar energy into fuel via photo-assisted water splitting to generate H2 or drive CO2 photoreduction is an attractive scientific and technological goal to address the increasing global demand for energy and to reduce the impact of energy production on climate change. Solar-driven hydrogenation of CO2 into value-added...
chemical products is one of the most promising strategies for reducing CO$_2$ and is anticipated to be a sustainable energy source shortly. In this study, we focus on the utilization of different sustainable H$_2$ sources for the photoreduction of CO$_2$ to value-added organic products. Various photocatalysts, photo reactor configurations, and reaction parameters for the photoreduction of CO$_2$ are discussed. For future research endeavors, a general approach for the photoreduction of CO$_2$ to mimic natural photosynthesis, in which the H$_2$ source is provided directly during the photocatalytic water splitting, is proposed and verified to generate value-added organic products successfully.

1. Introduction

With the significant increase in the levels of greenhouse gases, such as carbon dioxide (CO$_2$), in the atmosphere, considerable effort has been directed toward the development of methods for efficient CO$_2$ utilization. There is a wide range of literature on this topic [1,2]. Practically, CO$_2$ is a relatively inert and stable molecule ($\Delta G$ = –400 kJ·mol$^{-1}$) that requires a catalyst and input energy to be activated and converted into another chemical form [3-7]. CO$_2$ has attracted considerable attention as a C building block for generating high-value renewable solar fuels, and photocatalytic reduction (photoreduction) is a promising approach for storing solar energy and chemically reducing CO$_2$. In the recent few decades, many studies have been systematically examined and published on this subject [8-28]. However, the current conversion rate is unsatisfactory, emphasizing the need for further studies [1]. Many reducing substances can function as both H$_2$ sources and hole scavengers (also referred to as “electron donors”) for promoting CO$_2$ reduction (e.g., water (H$_2$O), H$_2$, methane (CH$_4$), and alcohols such as methanol (CH$_3$OH) and ethanol (C$_2$H$_5$OH)), leading to different high-value chemical products [29]. According to previous studies, C-free reductants, including H$_2$O and H$_2$, drive the generation of C$_1$ products, whereas C-containing reductants, such as CH$_4$, CH$_3$OH, and C$_2$H$_5$OH, yield C$_2$ and C$_3$ products [30]. The H$_2$ source can be simply obtained via photocatalytic or photoreductional water splitting [31-43]. To focus on the eco-friendly, renewable production of high-value chemicals from CO$_2$, C-free reductants, including H$_2$O and H$_2$, are investigated in this review.

The photoreduction of CO$_2$ with H$_2$O is of particular interest. Very early, Inoue et al. presented a potential approach for reducing CO$_2$ to organic compounds such as formic acid, formaldehyde, methyl alcohol, and methane using H$_2$O [44]. Subsequently, many studies were conducted on heterogeneous photocatalytic systems for elucidating the fundamental mechanisms, and inorganic semiconductor photocatalysts were engineered to capture light and accelerate the chemical reactions productively. Homogeneous photocatalytic systems have been used for the latter; however, molecular photosensitizers (dyes) could not provide a more realistic and robust concept [45].

According to the theoretical changes of the Gibbs free energy ($\Delta G_f^\circ$) for CO$_2$ reduction to generate hydrocarbons, such as CH$_3$OH and CH$_4$, the hydrogenation of CO$_2$ by H$_2$ to produce hydrocarbons (Eqs. (1) and (2)) is more feasible than the reduction of CO$_2$ by H$_2$O (Eqs. (3) and (4)) from a thermodynamic viewpoint [30].

\[
\begin{align*}
\text{CO}_2(g) + 3\text{H}_2(g) & \rightarrow \text{CH}_3\text{OH}(g) + \text{H}_2\text{O}(g) \quad \Delta G_f^\circ = 2.9 \text{ kJ mol}^{-1} \\
\text{CO}_2(g) + 4\text{H}_2(g) & \rightarrow \text{CH}_4(g) + 2\text{H}_2\text{O}(g) \quad \Delta G_f^\circ = -113.6 \text{ kJ mol}^{-1} \\
\text{CO}_2(g) + 2\text{H}_2\text{O}(g) & \rightarrow \text{CH}_3\text{OH}(g) + 3/2\text{O}_2(g) \quad \Delta G_f^\circ = 689 \text{ kJ mol}^{-1} \\
\text{CO}_2(g) + 2\text{H}_2\text{O}(g) & \rightarrow \text{CH}_4(g) + 2\text{O}_2(g) \quad \Delta G_f^\circ = 818.3 \text{ kJ mol}^{-1}
\end{align*}
\]

To learn this theory, photocatalytic reduction (photoreduction) of CO$_2$ by H$_2$ gas as a sacrificial electron donor under light irradiation has been proposed. This promising approach not only spontane ously hydrogenates CO$_2$ emission but also simultaneously transforms CO$_2$ into renewable organic compounds, such as methanol and hydrocarbons. Thampi et al. first reported photo-hydrogenation of CO$_2$ to CH$_4$ (49 µmol·g$_{cat}^{-1}$·h$^{-1}$) by H$_2$ over Ru/RuO$_2$/TiO$_2$ using a solar simulator (319 K; 80 mW·cm$^{-2}$) [46]. In addition to CH$_4$ [47-50], other products, such as carbon monoxide (CO) [47-62], ethane (C$_2$H$_6$) [47,50,54], and CH$_3$OH [60,61,63-65] have been obtained, depending on the photocatalytic materials and experimental conditions.

Artificial photosynthesis—another promising approach that was recently proposed—combines solar-driven water splitting and CO$_2$ reduction and is based on natural photosynthesis, as illustrated in Fig. 1. In this method, active H, which is directly produced from photocatalytic water splitting, is continuously used for the photoreduction of CO$_2$ to produce solar fuel in the same photocatalytic systems. Guan et al. first proposed mimicking the natural photosynthesis process by using hybrid photocatalysts [66]. In this regard, the active H, which was directly supplied via the sustainable photocatalytic water splitting, was continuously used for the photo-hydrogenation of CO$_2$ over hybrid photocatalysts to produce organic compounds.

Up to date, several review articles are covering structural engineering semiconductors, particular materials, their structure and applications for photoreduction of CO$_2$, such as sunlight-driven photocatalysts [13], crystal phase engineering on photocatalysts [67], metal-free-based materials [68], ultrathin structured photocatalysts...
cocatalysts [70], Bismuth-based photocatalysts [71]. Additionally, other reviews concentrate on tuning product selectivity [72], surface strategies for particulate photocatalysts [73], general aspects of light-driven C1 chemistry, including solar Fischer-Tropsch synthesis, the water-gas-shift reaction, CO2 hydrogenation, as well as methane and methanol conversion reactions [74]. Since the overall knowledge of chemical engineering for transforming the CO2 into value-added products using energy-efficient processes has significantly increased in the
last decade. To differentiate from these recent reviews, we focus on the utilization of different sustainable H2 sources for the photoreduction of CO2 to obtain value-added organic products. Various photocatalysts, photoreactor configurations, and reaction parameters for the photoreduction of CO2 are discussed. For future research endeavors, a general approach for the photoreduction of CO2 to mimic natural photosynthesis, in which the H2 source is provided directly during the photocatalytic water splitting, is proposed and verified to successfully generate value-added organic products.

2. Photo-hydrogenation of CO2 toward solar products

2.1. Understanding the roles and mechanism of H2 sources

The mechanism of CO2 photoreduction is complex. There has been intense debated regarding the roles of active H, including molecular H2 and atomic H+, in the photoreduction of CO2. Instead of molecular H2, atomic H+ has been proposed to photocatalyze CO2 reduction via the proton-coupled multi-electron transfer processes, as follows [75]:

\[
\text{CO}_2 + 2\text{H}^+ + 2e^- \rightarrow \text{HCOOH}
\]  

(5)
**CO**₂ + 2H⁺ + 2e⁻ → CO + H₂O (6)

**CO**₂ + 4H⁺ + 4e⁻ → HCHO + H₂O (7)

**CO**₂ + 6H⁺ + 6e⁻ → CH₃OH + H₂O (8)

**CO**₂ + 8H⁺ + 8e⁻ → CH₄ + 2H₂O (9)

Li et al. performed an isotope experiment in a D₂O, CO₂, and H₂ atmosphere with Ru/NaTaO₃ for verifying whether the H₂ source was water (D₂O) or H₂ in the products [49]. In the initial reaction, the H₂ in methane was mainly derived from water (D₂O), with CD₄ as the primary product. Other products, including CD₃H and CD₂H₂, were observed after several hours of the reaction. The results indicated that the active atomic H from the water source directly reduced CO₂ into solar products, while the molecular H₂ gas promoted the conversion of peroxide intermediates (O₂⁺) into the water, as shown in Fig. 2.

According to the proton-coupled multi-electron transfer concept, Chen et al. successfully fused *Halobacterium* purple membrane-derived vesicles (PMVs) onto the surface of Pd-deposited porous hollow TiO₂ NPs (Pd-HTNPs), which were then employed for CO₂ photoreduction, as shown in Fig. 3a [75]. As expected, a well-defined core–shell structure was observed (Fig. 3b and 3c). As shown in Fig. 3d, CH₄ and CO were detected. For CH₄, the production rate (56.4 µmol·g⁻¹·h⁻¹) and selectivity (95.2%) were high. In blank tests in the absence of the biohybrids (Pd-HTNPs@PMVs), light, or CO₂ (N₂ atmosphere), no catalytic performance was observed. The proton-coupled multi-electron transfer processes played an important role in the reduction of CO₂ into fuels and value-added chemicals, as shown in Fig. 3e.

As PtOₓ NPs have proven to be effective active sites for the direct splitting of water [76], PtOₓ NPs with a particle size of 2 nm were deposited on Bi₂WO₆ nanosheets (Fig. 4b), which were then applied for the photoreduction of CO₂ into hydrocarbons [77]. As expected, the product yield initially increased with the PtOₓ loading; the optimal CH₄ production rate (108.8 ppm·g⁻¹·h⁻¹) was observed at 0.5%PtOₓ (Fig. 4a). Wang et al. confirmed the role of the proton-coupled multi-electron transfer processes in accelerating CO₂ photoreduction, as shown in Fig. 4c.

In addition to the H₂ source from water, molecular H₂, or atomic H⁺ intermediates [78], the idea to use H₂-storage material to promote the photocatalytic reduction of CO₂ has received attention. Kang et al. reported that N₂H₄·H₂O, which had a high content of H₂ (7.9%), effectively worked as the H₂ source and electron donor over Au₃Cu@SrTiO₃/TiO₂ nanotube arrays [64]. Based on this system, CH₄ was the primary product (an evolution rate of 421.2 µmol·g⁻¹·h⁻¹), which accounted 60% of the total hydrocarbon products. Interestingly, N₂H₄·H₂O could generate a productive reductive atmosphere to protect and maintain the high stability of the Au₃Cu@SrTiO₃/TiO₂ nanotube.
arrays. As expected, the evolution rate of CH₄ still retained 87.6% of its original activity after five cycles of measurement during a 34 h test.

In summary, the concept of using H₂ source as reductants for CO₂ conversion might potentially impact solar fuel production. Many H₂ sources have been proposed, including water, molecular H₂, H₂-storage materials, or atomic H⁺ intermediates, which could offer advantages of enhancing photocatalytic activity and prolonging their performances. It believes that these feasible routes would bring promising concepts on designing reaction conditions and developing photocatalysts to potentially promote the efficiency of photo-reduction of CO₂.

2.2. Photocatalysts

Photon-assisted CO₂ hydrogenation has attracted increasing attention in recent years. This method can efficiently convert CO₂ into high-value chemicals (e.g., CO, CH₄, CH₃OH, C₂H₄). It has considerable potential to address current CO₂ issues because the use of H₂ as the reductant significantly enhances the product yield [51,79].

2.2.1. Reverse water-gas shift

To date, many candidates have been highlighted as potential photocatalysts for photocatalytic hydrogenation of CO₂ [26]. Typically, In₂O₃-based catalysts are a promising candidate for the photocatalytic hydrogenation of CO₂. Density functional theory (DFT) and time-dependent DFT calculations revealed that In₂O₃ containing O vacancies is favorable for the activation and hydrogenation of CO₂ [80,81]. Ghuman et al. reported that In₂O₃−x(OH)ₓ consisting of surface hydroxide groups, and O vacancies facilitated photoinduced CO₂-to-CO conversion. In₂O₃−x(OH)ₓ catalysts promote the heterolytic dissociation of H₂, which results in hydride- and proton-like H bonding to In atoms and the hydroxide group, respectively. Such as-formed species facilitate the interaction and electron transfer to the adsorbed CO₂ molecules [82]. In another study, He et al. prepared In₂O₃−x(OH)ₓ nanorods to catalyze the solar-driven RWGS reaction (CO₂ + H₂ → CO + H₂O) in a gas-phase medium. The In₂O₃−x(OH)ₓ nanorod superstructure prepared via a two-step synthesis process prolonged the lifetime of photogenerated charge carriers owing to interparticle charge transfer. Owing to the unique properties of In₂O₃−x(OH)ₓ and the nanorod superstructure comprising nanocrystals, the prepared In₂O₃−x(OH)ₓ catalyst exhibited a significant enhancement in the light-assisted RWGS reaction [83]. Recently, Wang et al. constructed an In₂O₃−x(OH)ₓ@Nb₂O₅ heterostructure, which exhibited a superior improvement in the photoinduced RWGS reaction, as illustrated in Fig. 5. This nanocomposite was prepared via a simple two-step synthesis process involving the preparation of In(OH)₃@Nb₂O₅, followed by calcination, to obtain an In₂O₃−x(OH)ₓ@Nb₂O₅ composite, as illustrated in Fig. 5a. The resulting heterostructure exhibited extraordinary performance in photocatalytic CO₂ reduction, as shown in Fig. 5b. The CO production rate was 44 times higher than that of pristine In₂O₃−x(OH)ₓ. This improvement was due to the presence of O vacancies and hydroxides, as well as the heterostructure-induced prolonged charge-carrier lifetimes, as shown in Fig. 5c. The O vacancies and hydroxides functioned as reservoirs for photoexcited electrons and holes, respectively, whereas the heterostructure encouraged charge separation, stabilizing the excited states.
The use of metal nanoparticle (NP)/metal oxide catalysts arouses concern as the crucial approach in the RWGS reaction because metals induce the dissociation of H₂, whereas metal oxides offer a medium for CO₂ adsorption and activation [85–87]. In this case, the irradiated light induces the generation of charge carriers, which can not only improve the dissociation of H₂ but also reduce the activation barrier, enhancing the selectivity [86,88,89]. For example, Upadhye et al. investigated the activity of an Au/TiO₂ nanocomposite for the RWGS reaction under visible light. The Au NP-incorporated TiO₂ enhanced the CO₂-to-CO performance owing to the decrease in the apparent activation energy from 47 to 35 kJ·mol⁻¹ under irradiation. This improvement was explained by localized surface plasmon resonance-induced Au NPs, which enhanced the reaction kinetics [90]. Jia et al. reported that a Pd/N₂O₅ nanocomposite was sufficient for the production of CO from CO₂ and H₂. The enhanced activity originated from the photothermal effect of Pd "nanoheaters" generating heat. Moreover, numerous H atoms, which resulted from the dissociation of H₂ on Pd nanocrystals and spillover to Nb₂O₅ nanorods and were associated with the in situ formation of O vacancies and/or the reduced Nb oxidation state, significantly promoted the reaction between CO₂ and H₂ to produce CO [91]. In another study, the Pd/H₃WO₄ bronze heterostructure was demonstrated as an efficient catalyst for the light-assisted RWGS reaction. This enhancement was due to the coexistence of Brønsted acid hydroxyls OH, W(V) sites, and O vacancies (Vₒ) occurred. These outstanding properties reduced the apparent activation energy, along with the light irradiation. Therefore, a large amount CO could be produced over Pd/H₃WO₄ [92]. In another study, by exploiting these features, Li et al. prepared a novel Cu-decorated nanowire Pd/H₃WO₄ bronze heterostructure, representing a step toward improving the RWGS reaction. As shown in Fig. 6a, the presence of Cu on Pd/WO₃ significantly increased the amount of CO produced in comparison with the sample prepared without Cu. Furthermore, the Cu-modified Pd/WO₃ exhibited significantly lower activation energy for the production of CO (32.2 kJ·mol⁻¹ in the dark and 29.3 kJ·mol⁻¹ under illumination), suggesting efficient CO₂-to-CO reduction over the Cu-modified Pd/WO₃, as shown in Fig. 6b. The Cu-modified Pd/WO₃ promoted the reduction of CO₂ via the formation of Cu-bound carbonyl intermediate, which was beneficial for the CO formation, as shown in Fig. 6c and 6d [93].

2.2.2. CO₂-to-CH₃OH conversion

The production of CH₃OH via CO₂ hydrogenation (CO₂ + 3H₂ → CH₃OH + H₂O) is a critical obstacle because of (i) the competing RWGS reaction, (ii) the exothermic nature of the methanol formation reaction, and (iii) the high activation barrier [94]. Thus, the efficiency of the reaction is limited. Motivated by these challenges, in 2018, Wang et al. performed an extraordinary investigation into the CO₂-to-CH₃OH conversion over In₂O₃₋ₓ(OH)ₓ rod-like nanocrystals. The CH₃OH product
was abundantly formed with the increasing hydrogenation temperature under light-assisted conditions. This was explained by the kinetic inhibition of the production of methanol at the low temperature and pressure, as shown in Fig. 7a–c. Notably, the amount of CH₃OH obtained via the hydrogenation approach was significantly higher than that for the best-known photocatalysts, indicating the potential of this method. Fig. 7d shows the reaction pathway for CH₃OH formation. Unique surface properties significantly impact the reaction pathway,

Fig. 9. (a) Schematic of the preparation of SA Ni/Y₂O₃ nanosheets; (b) aberration-corrected TEM image of the SA Ni/Y₂O₃ nanosheets; (c) schematic model of the SA Ni/Y₂O₃ nanosheets and the corresponding FT-EXAFS fitting curves for the SA Ni/Y₂O₃ nanosheets; (d) spatial temperature mapping obtained from the infrared camera under simulated solar light (1.0 kW·m⁻²), (e) temperature and CO₂ conversion over the SA Ni/Y₂O₃ nanosheets with respect to the light intensity; (f, g) solar flux and CO₂ conversion at different times of the day. Reproduced with permission from Ref. [109].
driving the formation of CH$_3$OH. In this case, the irradiation strengthens the surface frustrated Lewis pairs, improving the reactivity for H$_2$ activation and reducing the activation barrier [95].

The hydrogenation of CO$_2$ to CH$_3$OH is promising but rarely reported. Research in the field of catalysis is expended to grow significantly in the future, which can eventually lead to large-scale solar-driven CO$_2$-to-fuel production.

### 2.2.3. CO$_2$-to-methane (CH$_4$) conversion

Considering the potential solar fuel of methane (CH$_4$) and the environmental point of view of CO$_2$, photo-hydrogenation of CO$_2$ to CH$_4$ has been proposed as a viable approach to producing high-value chemicals, which can be used for chemical storage [96]. Solar-driven production of CH$_4$ from CO$_2$ and H$_2$ is promising because it is eco-friendly and inexpensive [50,97,98]. However, the performance of the CO$_2$-to-CH$_4$ reaction is limited, even though the reaction is thermodynamically favored (CO$_2$ + 4H$_2$ $\rightarrow$ CH$_4$ + 2H$_2$O; $\Delta$G$_{298K}$ = $-130.8$ kJ·mol$^{-1}$). This reaction involves an eight-electron process, which is a significant kinetic restriction [99,100]. Therefore, the catalysts play an essential role in driving the reaction and increasing the amount of CH$_4$ produced. In the past decade, considerable effort has been directed toward the investigation of robust catalysts for solar-driven CO$_2$-to-CH$_4$ hydrogenation [9,101–105]. The use of nanocomposites consisting of metal, metal oxide, and/or C-based materials is an attractive approach because the synergistic effects of the components significantly enhance the CO$_2$ adsorption, activation, and local thermal effect, facilitating the CH$_4$ formation. For instance, Ren et al. used Ru-anchored ultrathin layered double hydroxides (LDHs) to promote photothermal CO$_2$ methanation. The Ru-LDHs composite was a very active catalyst for the formation of CH$_4$ from CO$_2$ under light irradiation, owing to the efficient CO$_2$ and H$_2$ activation [103]. Mateo et al. recently prepared a RuO$_2$/SrTiO$_3$ heterostructure that significantly enhanced the generation of CH$_4$. The RuO$_2$-decorated SrTiO$_3$ exhibited high CH$_4$ production performance (up to 14.6 mmol·h$^{-1}$·g$^{-1}$ in the optimized condition), as shown in Fig. 8a and 8b. This nanocomposite had a high CO$_2$ adsorption capacity because of the SrTiO$_3$, and the local thermal effect at the Ru sites caused by charge separation and recombination was sufficient to drive the methanation reaction on the Ru NPs [102].

Recently, there are some candidates have been proposed for selective photoreduction of CO$_2$, which offer various advantages, including low-cost materials, high chemical/thermal stability. In typical, Barrio et al. recently reported the methanation of CO$_2$ using a Ni/g-C$_3$N$_4$ nanocomposite synthesized from supramolecular, followed by Ni$^{2+}$ impregnation and H$_2$ treatment. Fig. 8c shows the evolved CH$_4$ from various g-C$_3$N$_4$ and Ni/g-C$_3$N$_4$ samples, indicating the superior CH$_4$ formation over the Ni/g-C$_3$N$_4$ composite compared with the pristine g-C$_3$N$_4$. The optimized sample—Ni(25)/g-CN—produced CH$_4$ with a rate of 28 μmol·g$^{-1}$·h$^{-1}$, which was approximate $\sim$ 10.3 times higher than that of the g-CN sample [106]. This outstanding activity originated from the efficient charge-carrier separation and transportation from g-C$_3$N$_4$ to Ni NPs. The generated electrons easily migrated from g-CN to

![Fig. 10.](image-url)
Ni species, resulting in electron-rich reactive sites with an improved affinity for CO$_2$ and H$_2$. These advantages associated with the high reaction temperature improved the reactivity and methane formation, as shown in Fig. 8d [106]. In another study, Tahir et al. successfully designed montmorillonite (Mt) coupled with modified g-C$_3$N$_4$ (m-CN) 2D/2D hybrid composite [107], oxygen-defective OV-Ti$_3$AlC$_2$ with proton-rich functionalized carbon nitride (f-C$_3$N$_4$) [108], for CO$_2$ reduction to fuels. They found that the CO and CH$_4$ yield rate could reach to 253 and 165 µmol·g$^{-1}$·h$^{-1}$, respectively, over Mt/g-C$_3$N$_4$ photocatalyst. Photocatalytic conversion CO$_2$-to-CH$_4$ is a promising valuable source of renewable energy. Recently, the findings of metals free graphitic carbon nitride (g-C$_3$N$_4$), metal carbides compounds (MAX) materials, has opened a very bright future to develop non-noble metal catalysts for the light-driven methanation of CO$_2$.

Reducing the size of Ni species to a Ni cluster or a single atom (SA) is expected to result in extraordinary performance for CH$_4$ generation. In this aspect, the efficiency of Ni can be improved while reducing the amount of loaded Ni species. Li et al. recently prepared single Ni atom catalyst-anchored ultrathin amorphous Y$_2$O$_3$ nanosheets exhibiting a superior CO$_2$-to-CH$_4$ conversion ability. The preparation of the SA Ni/Y$_2$O$_3$ nanosheets involves three steps, as shown in Fig. 9a. Graphene oxide (GO) was utilized as a support for the Ni$^{2+}$ and Y$^{2+}$ ion adsorption caused by the interaction between metal ions and GO prior to the freeze-drying and calcination. The Ni SAs were uniformly decorated on the Y$_2$O$_3$ nanosheets, as shown in Fig. 9b. In the SA Ni-Y$_2$O$_3$ nanosheets (Fig. 9c), the Ni SAs formed Ni-O bonds with neighboring O atoms of Y$_2$O$_3$. These bonds stabilized the Ni SAs, restricting their aggregation into Ni NPs during the calcination step. The temperature under simulated solar light (1.0 kW·m$^{-2}$) was as high as ~ 255 °C (Fig. 9d). Furthermore, the temperature of the SA Ni/Y$_2$O$_3$ nanosheets under the assistance of a selective light absorber (AlN$_x$/Al foil) reached 285 °C under 1.0 kW·m$^{-2}$ when the gas inlet and outlet were encapsulated by thermal insulating covers, as shown in Fig. 9e. In this condition, the CO$_2$ conversion rate approached 90%, with very high CH$_4$ selectivity. These results indicate the extraordinary catalytic CO$_2$ methanation of the SA Ni-Y$_2$O$_3$ nanosheets. Fig. 9f and 9g show the solar flux and the CO$_2$ reduction performance concerning the irradiation time (time of day). The Ni/Y$_2$O$_3$ nanosheets exhibited superior CO$_2$ conversion under natural sunlight, suggesting that this composite is promising for solar-driven CO$_2$ methanation [109]. These results indicate the outstanding properties of materials containing SA catalysts. The preparation of single metal atom-supported metal oxides will be a popular research topic in the coming years. Various candidates for metal SA catalysts and numerous supports can be selected to promote CO$_2$ adsorption, activation, and reduction and enhance the product selectivity. Therefore, plenty of room will be waiting for the exploration of superior catalysts in this research field in the coming years.

Graphene-based catalysts have been sufficient for the preparation of highly active materials for the light-driven production of CH$_4$ from CO$_2$ and H$_2$. This is due to the unique properties of graphene, e.g., the extended π orbital, high thermal and electrical conductivities, and large specific surface area, which are beneficial for CO$_2$ adsorption and
reduction [101,110–112]. Therefore, the preparation of graphene-based composites has attracted research attention [113–115]. For instance, NiO/Ni NP-supported graphene exhibited a significant improvement in the CO₂ methanation performance compared with Ni NPs supported on large-surface area silica-alumina. Graphene facilitated the charge transfer from NiO/Ni to graphene sheets, while the high reaction temperature reduced the adsorption of H₂O molecules, which negatively affected the catalytic performance [104].

2.2.4. Hydrogenation of CO₂ into C₂+ products

The conversion of CO₂ into ethanol and C₂+ hydrocarbons is an attractive topic because of the higher value and energy density of C₂+ products compared with C₁ products [116–118]. However, the generation of C₂+ products is challenging, owing to the C–C coupling reaction. The intermediates should have the appropriate binding energy for binding to the catalyst surface to promote the C–C coupling reaction [117,119–121]. Therefore, the photocatalyst surface plays a crucial role in driving the reaction, leading to the formation of C₂+ with high selectivity. In 2018, Chen et al. reported the hydrogenation of CO₂ into high-value products via an alumina-supported CoFe alloy catalyst, which was fabricated via the hydrogenation of CoFeAl LDH nanosheets [121]. The optimum catalyst treated at 650 °C (denoted as CoFe-650) exhibited an evolved C₂+ product with high selectivity, along with a methane product, as shown in Fig. 10a. In this case, the formation of the CoFe alloy was considered as the primary factor driving the CO₂ hydrogenation that formed C₂+ hydrocarbons. DFT calculations (Fig. 10b) revealed that the CoFe surface provided a lower barrier to adsorbed CH₂ than the Co and Fe surfaces, indicating that the CoFe alloy promoted the C–C coupling reaction. This approach provides a novel pathway for the rational design of the hydrogenation of CO₂ into high-value chemical products, as shown in Fig. 10c [121].

In another study, Liu et al. found that a Na-Co@C nanocomposite had a robust capability for the photocatalytic production of C₂+ hydrocarbons and ethanol (Fig. 11a). In this case, UV light played an essential role in the generation of electrons, which were accumulated in C species. The electron-rich C species activated CO₂ into CO₂δ–, and CO₂ was dissociated into CO, driving the formation of ethanol. Importantly, the as-generated CO was stabilized by the C layer on the catalyst surface, while the Na affected the intermediate species, promoting the C–C formation. Such surface features are imperative for the formation of C₂+ products, as shown in Fig. 11a-c [122].

In the other approach, the use of Co-based catalysts appears to provide a pathway to obtain C₂+ products in light-assisted CO₂ hydrogenation. It is crucial to stabilize the CO intermediate on the catalyst surface to promote the C–C coupling reaction. Furthermore, the catalyst surface with a moderate amount of C₂+ products is beneficial for desorption, which can enhance the selectivity. In this context, Cu-based materials are potential candidates, as they have proven to be useful for hydrogenation and electrocatalytic CO₂ reduction [123–128].

Research on the production of C₂+ chemicals will become increasingly popular in the coming years. To date, various candidates, including CoFe-based catalysts, Na-Co@C nanocomposite, Co-based catalysts, Cu-based catalysts, and Cu-based materials, have been successfully prepared and demonstrated as a novel photocatalytic material platform to produce valuable chemicals and fuels from CO₂. From the present data, how to accumulate the charge carriers effectively and protons play a vital role to favor of the formation of C₂+ products. These investigations are expected to unveil the nature of photocatalysts and provide extraordinary materials for enhancing C₂+ production via photocatalytic hydrogenation of CO₂.
3. Photoreduction of CO2 for mimicking natural photosynthesis

Since the early pioneering work of Inoue et al. [44], the photo-hydrogenation of CO2 has received significant attention. However, in these studies, an electron donor (H2 gas) had to be continuously introduced to the reaction system. To mimic the natural photosynthesis in green plants, artificial photosynthesis using molecular H2 or atomic H+, which is directly produced by photocatalytic water splitting, for the photoreduction of CO2 has recently attracted increasing attention. Various promising photocatalytic semiconductor materials and fixed-bed photoreactor (385 mL in volume) is designed by Chen et al., which is applied for the photohydrogenation of CO2 in the presence of both H2O (liquid phase) and H2 (gas phase), as displayed in Fig. 12d [9]. Herein, the photocatalyst powder is evenly placed on a flat Teflon surface, which is fixed in the middle of the photoreactor. The advantages of bath-type photoreactor are simple construction and operation, low-cost for a large-scale photoreactor. However, it frequently causes undesired second reactions or decompositions. To minimize this drawback, flow reactors have been employed in various solar-driven CO2 hydrogenation studies and have achieved promising results. Fig. 12e shows a typical design of a capillary flow-type reactor. This configuration prolongs the reactant–catalytic surface interaction time, as the gas reactants travel through the capillary reactor [82]. Another advantage of the continuous flow-type could offer accurate control of the irradiation time, light irradiation via the flow rate.

In summary, several types of photoreactor have been proposed for photohydrogenation of CO2 to produce solar fuels. It is noting that some of the parameters and operating conditions, such as temperature, light distribution, reaction mode, and product separation, offer critical roles in promoting yield and selectivity to products. Although many efforts have been devoted to designing photoreactors, low surface-to-volume ratios, and inefficient light distribution are still the primary concerns. Therefore, further researches require special attention to upgrade the geometrical design of the radiation source to reaction space and improve the ratio of illuminated-light surface area to volume of photoreactor.

2.4. Influence of reaction mode on photocatalytic activity

Xiong et al. reported that the reaction mode (solid–liquid, solid–gas, and combined solid–liquid–gas, as shown in Fig. 13a) can influence the photocatalytic activity of Pt/TiO2. For example, the solid–liquid mode enhances the formation of H2 (H2: 47.3 µmol·gcat⁻¹·h⁻¹; CO: 0.03 µmol·gcat⁻¹·h⁻¹; CH4: 0.23 µmol·gcat⁻¹·h⁻¹), while the solid–gas mode promotes the reduction of CO2 (H2: 13.4 µmol·gcat⁻¹·h⁻¹; CO: 0.11 µmol·gcat⁻¹·h⁻¹; CH4: 0.73 µmol·gcat⁻¹·h⁻¹) [130]. As expected, combining the solid–liquid and solid–gas modes can significantly promote the photo-hydrogenation of CO2, yielding the highest CO and CH4 production rates (H2: 22.1 µmol·gcat⁻¹·h⁻¹; CO: 0.22 µmol·gcat⁻¹·h⁻¹; CH4: 1.1 µmol·gcat⁻¹·h⁻¹). In this mode, the H2 generated by the solid–liquid interaction interface promotes the photoreduction of CO2 through the solid–gas reaction. In another study, Chen et al. did a study on three types of reaction mode, including a gas-phase, a liquid-phase, and a gas–liquid-phases, correspondingly (as shown in Fig. 13b) [11]. They found that the combined gas–liquid phases showed a remarkable result (1.1 × 10⁻³% in quantum efficiency), whereas the efficiency levels of the gas- and liquid-phase systems were only 0.1 × 10⁻³% and 0.5 × 10⁻³%, respectively. The observation of efficiency enhancement might be contributed by the effective utilization of both H2 in the gas phase and the atomic H⁺ in the liquid phase. Although the experiments were carried out in different reaction modes (such as gas, liquid, gas–liquid phases), their photocatalytic mechanisms would not be changed [11]. However, the presence of photocatalysts in different reaction modes might boost reactions toward different reaction pathways.

2.3. Photoreactor design

It notes that the efficiency of photohydrogenation of CO2 is still relatively low. Hence, several factors, such as light distribution, reaction mode, product separation, and geometries of the reactor, have gained considerable attention. These factors lead to further design and develop novel photoreactors to enhance the photocatalytic hydrogenation of CO2 performances [8,11].

Two general types of reactors—batch- and flow-type—have been developed to perform the CO2 photohydrogenation reaction. Fig. 12a–c describes a typical batch-type reactor system for photocatalytic CO2 hydrogenation. This system consists of gas suppliers, reactors, and analyzer sections. It allows in situ product analysis, and the temperature can be controlled. Therefore, both thermal- and light-assisted hydrogenation of CO2 can be performed in this system [90,129]. Another
concepts to facilitate the production of solar fuels have been investigated.

In 2003, Guan et al. proposed the use of H2 from water splitting for the photo-hydrogenation of CO2 with hybrid photocatalysts under concentrated sunlight, as shown in Fig. 14a [66]. The photoreaction was conducted between 9:30 AM to 03:30 PM on sunny days (Oct. to Dec. 2001), which concentrated solar irradiation, providing effective photons and high thermal energy (average reaction temperature: 534–590 K; solar insolation: 3.73–6.06 kWh·m−2). In this system, the Pt/K2Ti6O13 and Fe-Cu-K/DAY (Fe-Cu-K/dealuminized Y-type zeolite) photocatalysts were cubic particles (approximately 0.5–2.0 μm, Fig. 14b) and rod-like crystallites (Fig. 14c), respectively. The role of the Pt/K2Ti6O13 photocatalyst was to split water into H2, and that of the Fe-Cu-K/DAY photocatalyst was to hydrogenate CO2 into organic compounds, including methane (CH4, 0.037–0.047 μmol·gcat−1·h−1), formic acid (HCOOH, 0–12.93 μmol·gcat−1·h−1), formaldehyde (HCHO, 0–3.43 μmol·gcat−1·h−1), methanol (CH3OH, 0–4.83 μmol·gcat−1·h−1), and ethanol (C2H5OH, 0–1.17 μmol·gcat−1·h−1). However, the yield of these products was not attractive and required further improvement.

Recently, a novel twin photoreactor, which was designed according to the Z-scheme concept, was proposed to mimic the natural photosynthesis process in green plants, as shown in Fig. 15 [131]. This photocatalytic reactor system is separated by a circular membrane that consists of two different photocatalytic materials—e.g., Pt/SrTiO3:Rh combined with Pt/CuAlGaO4, and WO3 [132], dual-function GaN:ZnO-Ni/NiO and Pt/WO3 [12], Pt/TiO2 and Cu/TiO2 [133], or Pt/CuAlGaO4 combined with Pt/SrTiO3:Rh and WO3 [10,134]—for CO2-hydrogenation/H2-generation and O2-generation, respectively, and integrates with different reversible shuttle redox mediators, e.g., IO3−/I− [12] or Fe2+/Fe3+ [10,132]. This concept has many advantages. First, the O2 and H2/solar products generated separately in the twin photoreactor via water splitting effectively hinder the backward reaction and...
oxidation of hydrocarbon products. Second, molecular H₂ and atomic H⁺, which are directly produced by the photocatalytic water splitting, are straightforwardly used for effective CO₂ hydrogenation.

Various experimental and theoretical studies on twin photoreactors for CO₂ have been conducted. Lee et al. reported that the performance of a dual-photocatalyst system in which Pt/SrTiO₃:Rh and Pt/CuAlGaO₄ were used as H₂-generation and CO₂-reduction photocatalysts, respectively, was more than twice that of a single-photocatalyst system[132]. Recently, Yu et al. proposed a dual-function GaN:ZnO-Ni/NiO photocatalyst with both CO₂-reduction and H₂-production capabilities [12]. Interestingly, the photoreduction quantum efficiency of the twin photoreactor was more than four times higher than that of a single photoreactor (an increase from 0.015% to 0.070%). In another approach, Chu et al. proposed a novel bubbling twin photoreactor on the basis of theoretical calculations [135]. The results indicated that the diffusion and mass transfer between the gas and liquid phases were significantly improved, resulting in a higher conversion efficiency compared to the traditional twin photoreactor.

To summarize, a combination of H₂O water splitting and CO₂ photohydrogenation in a Z-scheme system is successfully explored and adopted by using the novel twin photoreactor system to mimic the natural photosynthesis process in green plants. To date, various photocatalytic materials, which are integrated with different reversible shuttle redox mediators, perform significantly photoreduction quantum efficiency, selectivity for CO₂ reduction, diffusion, and mass transfer between the gas and liquid phases via twin photoreactor, in compared with single photoreactor. Currently, the bottleneck of this system is limited by the H₂-generating efficiency, leading to develop the novel H₂-photocatalysts further.

4. The prototype of an artificial leaf to mimic the unique structure of a leaf

The design of an artificial leaf that mimics the unique structure of a leaf has significant potential for the reduction of CO₂ emissions and the development of renewable fuels. Zhou et al. proposed a prototype artificial leaf for the photoreduction of CO₂ into hydrocarbon fuels, as shown in Fig. 16 [136]. The typical natural photosynthetic system (NPS) at multiple scales is depicted in Fig. 16a–c. At the macroscale, green leaves produce O₂, carbohydrates, and other C-rich products by splitting H₂O and reducing CO₂ in the presence of solar energy (Fig. 16a). At the microscale, the structures of the leaves function effectively to exchange gas, transport H₂O, and harvest solar light (Fig. 16b). At the nanoscale, CO₂ can efficiently diffuse throughout the mesophyll cells, where it may dissociate into carbohydrates and other C-rich products (Fig. 16c). By developing a special design for artificial leaves, which include perovskite titanates (ATiO₃, A = Sr, Ca, and Pb), an artificial photosynthetic system (APS) that mimics real leaves and employs only renewable resources, such as solar light and water, for photoreduction of CO₂ into hydrocarbon fuels, was proposed, as shown in Fig. 16d–g [136,137].

However, the efficiency of the APS is relatively low, and further research is required. The overall design of artificial leaves should comprehensively consider the geometries of leaf for optimizing solar light harvesting, exchanging gas, transporting H₂O, photocatalytic materials (type, morphology, composition, and support). Meanwhile,
special attention should also focus on enhancing durability and extend the lifetime of modularized artificial leaf units for the potential industrialization.

5. Hybrid photoelectrochemical biological approach for solar-chemical conversion

One promising approach that was recently proposed is the development of a hybrid photoelectrochemical biological system in which photocatalytic materials are combined to drive water splitting and microbial fixation of CO₂ into biomass and liquid fuels, as shown in Fig. 17a [138]. This sustainable concept uses only sustainable electrical and/or solar inputs to sustainably generate H₂ from water, and then, the H₂ is used with microorganisms to transform CO₂ into high-value chemicals.

In typical, Nichols et al. reported an electrochemical cell that contains two chambers: cathodic and anodic chambers (Fig. 17b) [139]. In the cathodic chamber, the p-InP cathode electrochemically generated H₂, which was subsequently used in situ by *Methanosarcina barkeri* to reduce CO₂ to CH₄. In the anodic chamber, O₂ was produced separately to prevent harmful potential by reactive O species. The conversion rate (in situ generations of H₂ at the cathode) reached 86%, followed by an H₂-driven reduction of carbon dioxide to methane by the *Methanosarcina barkeri* biocatalyst. As shown in Fig. 17c, Torella et al. designed a bioelectrochemical cell [140] containing a cobalt phosphate (CoPi) anode and a nickel molybdenum zinc (NiMoZn) cathode to generate O₂ and H₂ via water splitting. H₂ was used to efficiently convert CO₂ via the Calvin cycle into biomass in wild-type *Ralstonia eutropha* H16 and to isopropanol in an engineered strain of *Ralstonia eutropha*, Re2133-pEG12. The solar-to-biomass yields and the isopropanol reached 3.2% and 216 mg L⁻¹, respectively. However, this approach is a temporary solution owing to its limitations, including the low solubility, low mass transfer rate, and safety issues of the generated H₂ in the microbial cultures. For reducing the toxicity to the bacterium, Liu et al. proposed a hybrid bioelectrochemical system for CO₂ fixation (as shown Fig. 17d) [141], which could effectively minimize the generation of toxically reactive O species. The *R. eutropha* hybrid system achieved ηEC values of 9.7%, 7.6%, and 7.1% for biomass, bioplastic, and liquid fuels (C₂, C₃, C₄, and C₅ alcohols), respectively. Another approach is to electrochemically produce formate, instead of H₂ and then convert it into...
biofuels (isobutanol, 3-methyl-1-butanol, etc.) via a biological pathway (Fig. 17e) [142].

A concept of a hybrid photoelectrochemical biological system, which uses electrical and/or solar inputs to sustainably generate H₂ from water, and then, the H₂ is used with microorganisms to transform CO₂ into high-value chemicals, represents a significant breakthrough. However, this approach still requires further studies to enhance the efficiency of achieving sustainable solar-to-chemical energy conversion.

6. Conclusions and future perspectives

In conclusion, the conversion of CO₂ into valuable chemicals and renewable fuels associated with H₂ utilization has emerged as a main-stream approach to address the overwhelming CO₂ pollution. This research field can grow significantly in the future. In this review, four promising approaches for light-driven CO₂ reduction were identified: (i) the development of robust catalysts for light-assisted CO₂ hydrogenation, (ii) the mimicking of natural photosynthesis, (iii) the preparation of an artificial leaf, and (iv) the use of hybrid bioinorganic systems.

The hydrogenation of CO₂ has proven to be an efficient method of reducing CO₂. The selection of materials significantly affects the outcomes. This review identified the following critical reactions: RWGS, CO₂-to-CH₃OH, methanation (CO₂-to-CH₄), and CO₂-to-C₂⁺ conversion. The preparation of novel and inexpensive materials to increase the efficiency of each type of reaction is imperative. Research on the generation of C₂⁺ products, which are very high-value chemicals, is still in an early stage. The synthesis of extraordinary catalysts that reduce the working temperature and enhance the selectivity will facilitate the practical reduction of CO₂.

Mimicking natural photosynthesis is another outstanding route for converting CO₂ into high-value chemicals. In this method, a photocatalytic system is employed, and the reaction medium (e.g., solid-liquid, solid-gas, combined systems) and material designs significantly affect the conversion efficiencies. It is expected that innovative reactor designs and extra-dimensional materials will lead to enhancements in the CO₂ conversion performance with regard to conversion and selectivity. A reactor design that has outstanding properties and overcomes the limitations of current designs is highly needed. Additionally, the development of active and durable photocatalysts with a strong reduction capability will help to fill the current large gap in CO₂ conversion and inspire research on high-performance and low-cost materials for solar-driven CO₂ reduction.

The preparation of an artificial leaf is also an intensive approach to convert CO₂ owing to the unique structure of the leaf, which can promote light-harvesting, mass transfer, and gas diffusion. Notably, the integrated technique plays a crucial role in the preparation of an efficient leaf, and the use of efficient catalysts promotes the reduction reaction. It is believed that new techniques, e.g., three-dimensional printing, will lead to the development of leaves with unique structures for CO₂ conversion.

Hybrid photoelectrochemical biological systems have considerable potential for efficient solar-driven CO₂-to-fuel conversion. The critical issues regarding the solubility, mass transfer, and safety can be considered as the primary obstacles to be addressed. Solving these problems will present an excellent opportunity for the large-scale production of renewable solar fuels from CO₂. We believe that our review provides a roadmap for the future solar-driven CO₂ reduction into high-value chemicals.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This work is funded by the Creative Materials Discovery Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Science and ICT [grant number 2017M3D1A1039379], the Basic Research Laboratory of the NRF funded by the Korean government [grant number 2018R1A4A1022647] and the Korea Research Fellowship Program through the NRF funded by the Ministry of Science and ICT [grant number 2020H1D3A1A04081409].

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.cej.2020.126184.

References


