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Towards artificial photosynthesis: Sustainable hydrogen utilization for photocatalytic reduction of CO_2 to high-value renewable fuels

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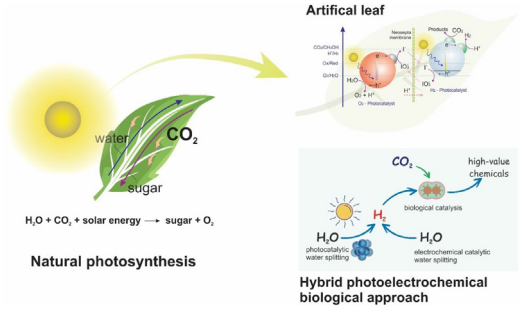
HIGHLIGHTS

- Artificial photosynthesis for reduction of CO_2 to renewable fuels was reviewed.
- Various photocatalysts and reaction parameters for photoreduction of CO_2 were summarized and discussed.
- The CO_2 photoreduction to mimic natural photosynthesis was proposed and verified successfully.

GRAPHICAL ABSTRACT



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ABSTRACT

Converting solar energy into fuel via photo-assisted water splitting to generate H_2 or drive CO_2 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 CO_2 into value-added

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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, photoreactor 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 (ΔG° = –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 scavenges (also referred to as "electron donors") for promoting CO_2 reduction (e.g., water (H_2O), H_2, methane (CH_4), and alcohols such as methanol (CH_3OH) and ethanol (C_2H_5OH)), leading to different high-value chemical products [29]. According to previous studies, C-free reductants, such as H_2O and H_2, drive the generation of C_1 products, whereas C-containing reductants, such as CH_4, CH_3OH, and C_2H_5OH, yield C_2 and C_3 products [30]. The H_2 source can be simply obtained via electrocatalytic or photocatalytic water splitting [31–43]. To focus on the eco-friendly, renewable production of high-value chemicals from CO_2, C-free reductants, including H_2O and H_2, are investigated in this review.

The photoreduction of CO_2 with H_2O 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_2O [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 (ΔG_r°) for CO_2 reduction to generate hydrocarbons, such as CH_3OH 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_2O (Eqs. (3) and (4)) from a thermodynamic viewpoint [30].

$$CO_{2,(g)} + 3H_{2,(g)} \rightarrow CH_3OH_{(g)} + H_2O_{(g)}\ \Delta G_r^\circ = 2.9\ \text{kJ·mol}^{-1} \quad (1)$$

$$CO_{2,(g)} + 4H_{2,(g)} \rightarrow CH_{4\ (g)} + 2H_2O_{(g)}\ \Delta G_r^\circ = -113.6\ \text{kJ·mol}^{-1} \quad (2)$$

$$CO_{2,(g)} + 2H_2O_{(g)} \rightarrow CH_3OH + 3/2O_{2,(g)}\ \Delta G_r^\circ = 689\ \text{kJ·mol}^{-1} \quad (3)$$

$$CO_{2,(g)} + 2H_2O_{(g)} \rightarrow CH_4 + 2O_{2,(g)}\ \Delta G_r^\circ = 818.3\ \text{kJ·mol}^{-1} \quad (4)$$

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 spontaneously 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/RuOx/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_2H_6) [47,50,54], and CH_3OH [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

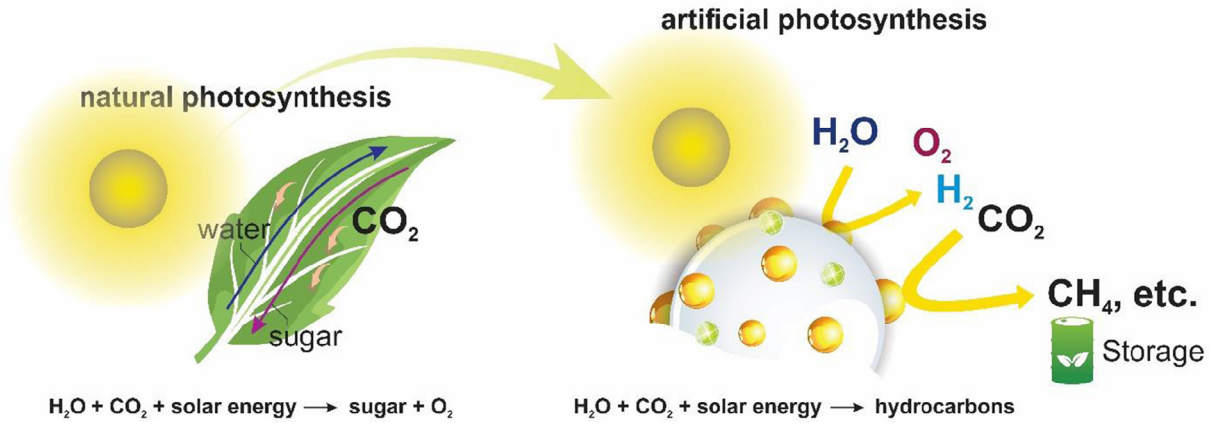

Fig. 1. Conversion of solar energy: natural leaf and mimicking photosynthesis in artificial systems via photocatalysis.

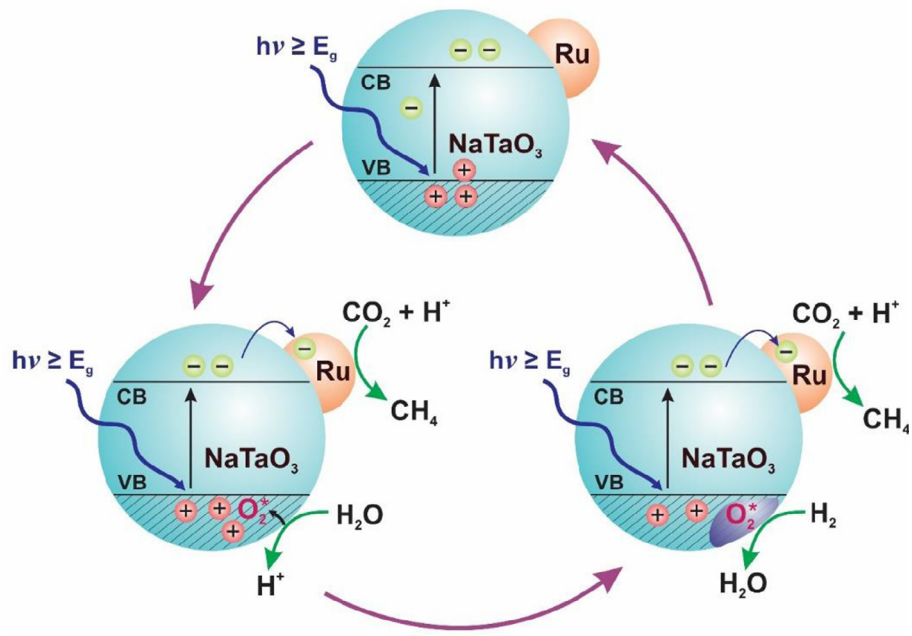

Fig. 2. Photoreduction of CO_2 over $Ru/NaTaO_3$ in the presence of H_2O and H_2. Reproduced with permission from Ref. [49].

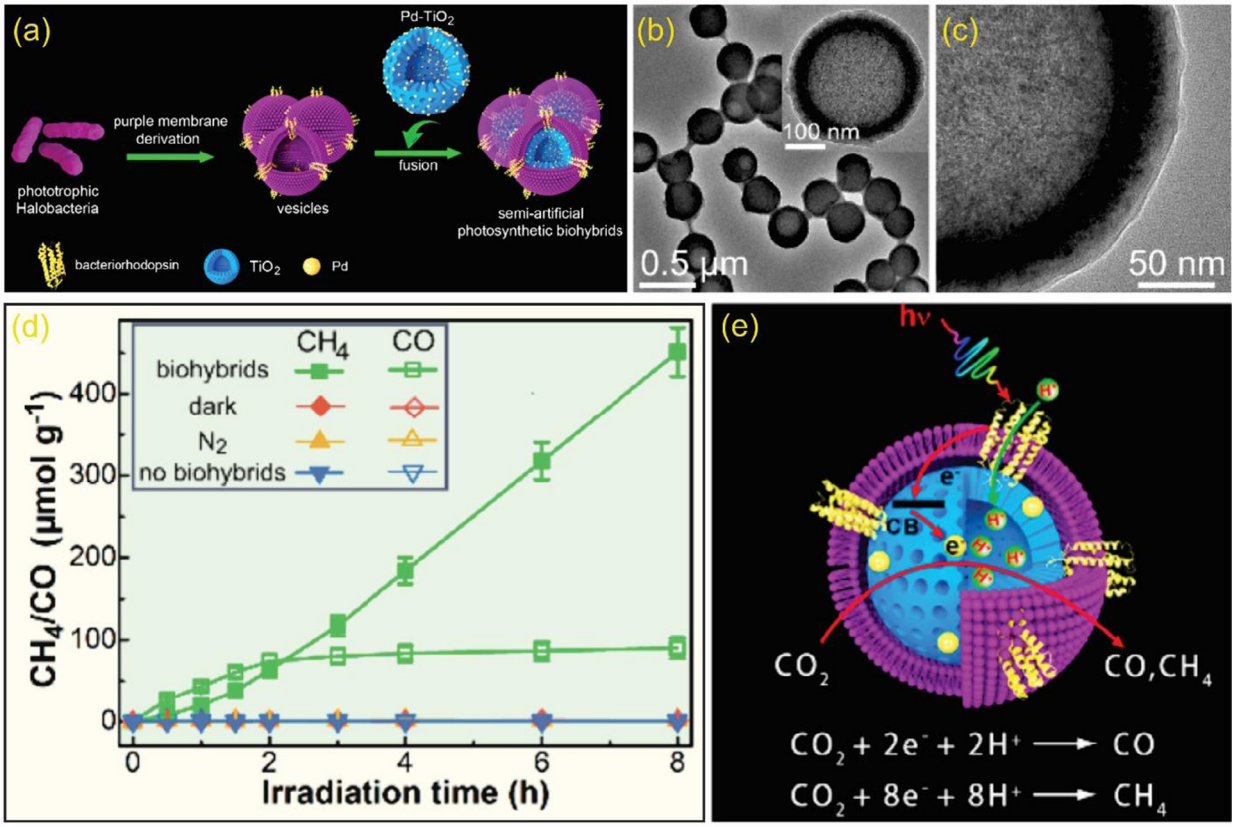

Fig. 3. (a) Preparation of Halobacterium purple membrane-derived vesicles with Pd-deposited hollow porous TiO_2 NPs (Pd-HTNPs@PMVs). (b, c) Magnified transmission electron microscopy (TEM) image showing the edge of a single Pd-HTNPs@PMVs. (d) Photocatalytic CH_4 and CO formation over the biohybrids (Pd-HTNPs@PMVs) under different conditions. (e) Proposed process of photoreduction of CO_2 by Pd-HTNPs@PMVs. Reproduced with permission from Ref. [75]. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

[69], 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, CO_2 hydrogenation, as well as methane and methanol conversion reactions [74]. Since the overall knowledge of chemical engineering for transforming the CO_2 into value-added products using energy-efficient processes has significantly increased in the

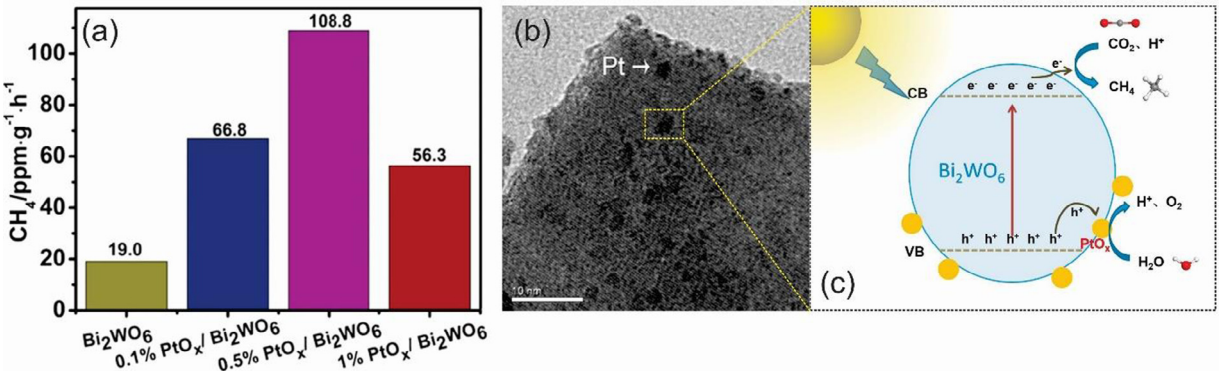

Fig. 4. (a) CH_4 production rate with respect to the loading amount (wt.%) of PtO_x. (b) TEM image of 0.5%PtO_x/Bi_2WO_6. (c) Proposed mechanism over PtO_x/Bi_2WO_6. Reproduced with permission from Ref. [77].

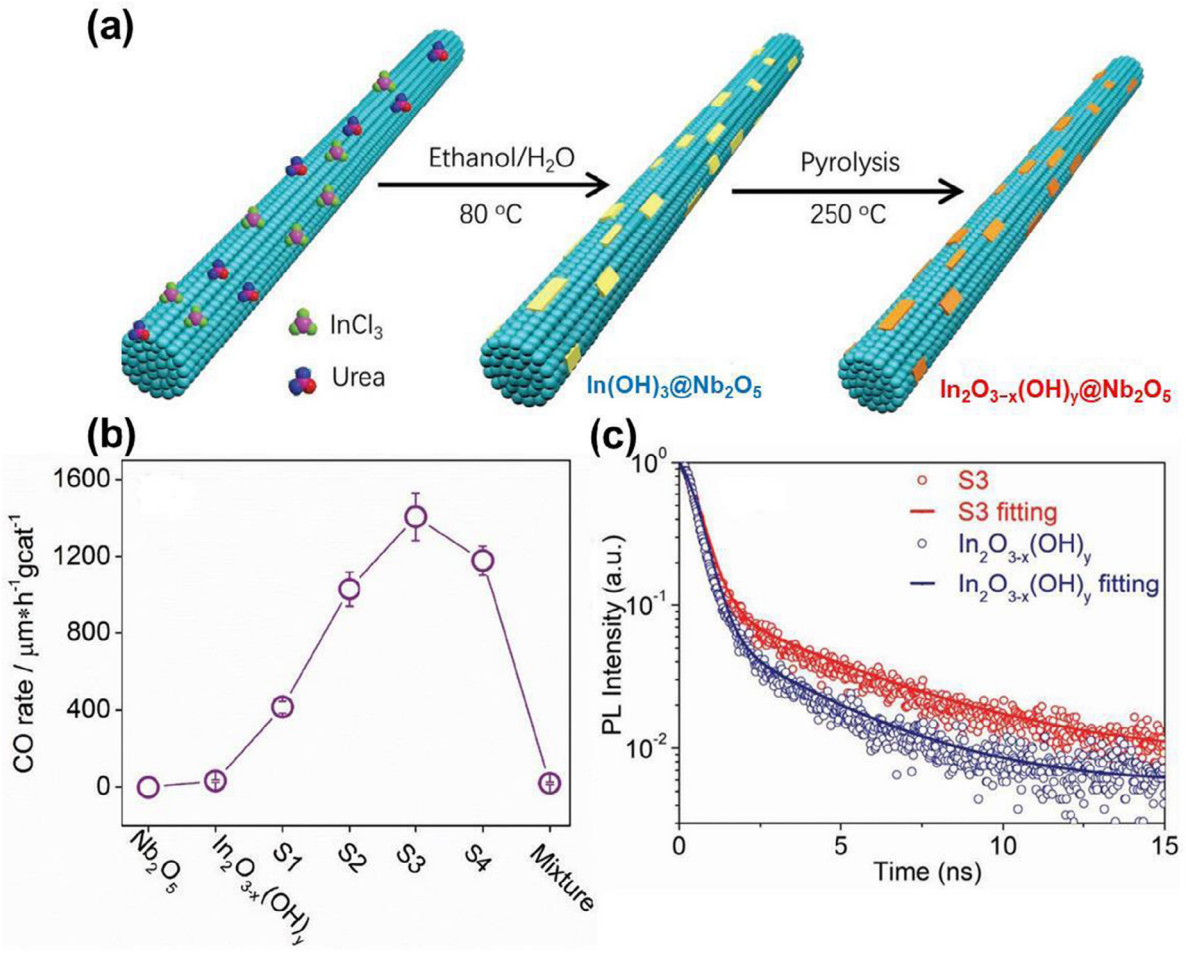

Fig. 5. (a) Schematic of the $In_2O_{3-x}(OH)_y@Nb_2O_5$ composite; (b) CO production rates for various samples; (c) fluorescence decay temporal profiles measured and fit for the optimized $In_2O_{3-x}(OH)_y@Nb_2O_5$ composite and pristine $In_2O_{3-x}(OH)$. Reproduced with permission from Ref. [84].

last decade. To differentiate from these recent reviews, we focus on the utilization of different sustainable H_2 sources for the photoreduction of CO_2 to obtain value-added organic products. Various photocatalysts, photoreactor 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 successfully generate value-added organic products.

2. Photo-hydrogenation of CO_2 toward solar products

2.1. Understanding the roles and mechanism of H_2 sources

The mechanism of CO_2 photoreduction is complex. There has been intense debated regarding the roles of active H, including molecular H_2 and atomic H^+, in the photoreduction of CO_2. Instead of molecular H_2, atomic H^+ has been proposed to photocatalyze CO_2 reduction via the proton-coupled multi-electron transfer processes, as follows [75]:

$$CO_2 + 2H^+ + 2e^- \rightarrow HCOOH \quad (5)$$

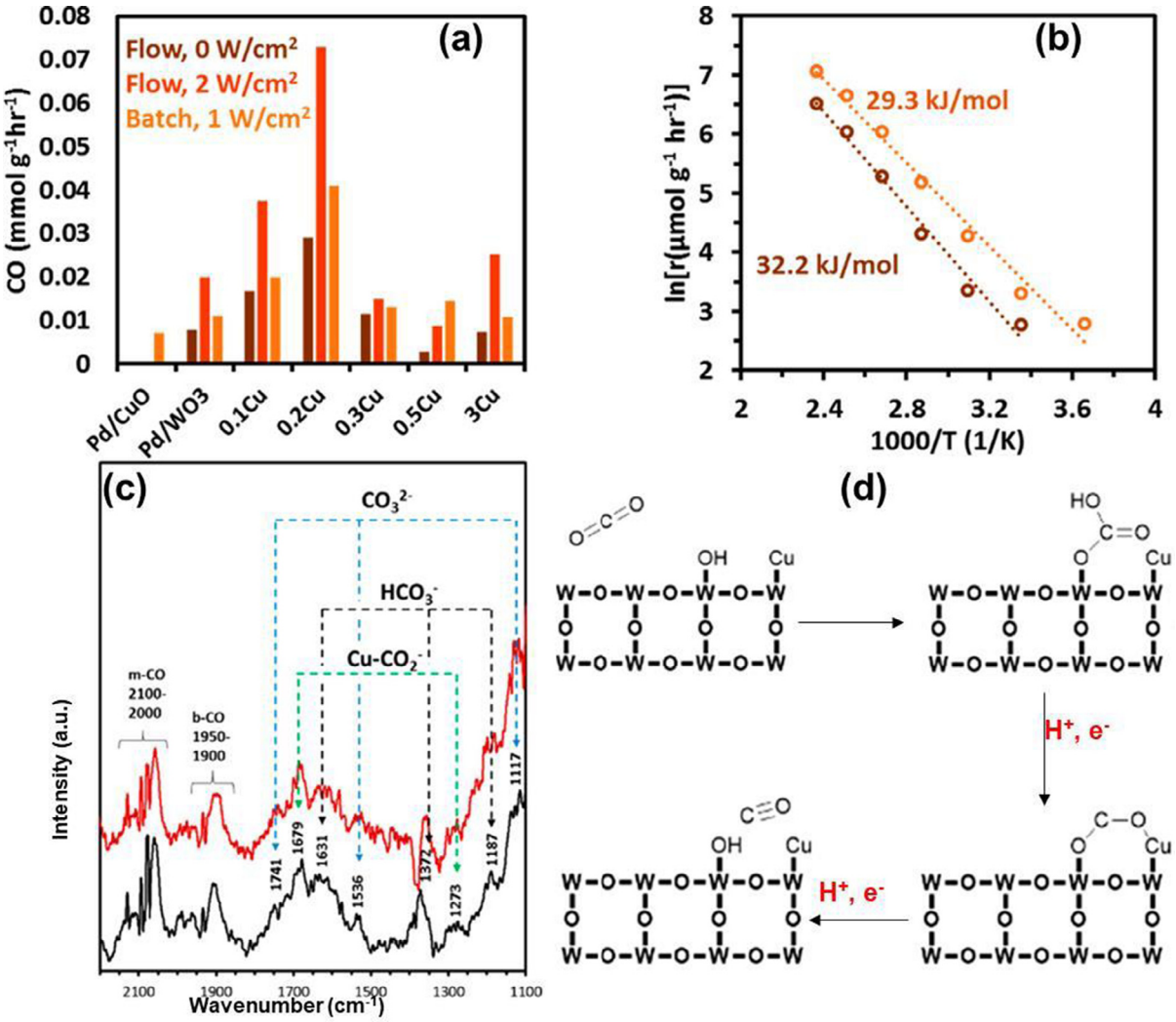

Fig. 6. (a) Light-assisted RWGS reaction for various samples; (b) Arrhenius plot for sample 0.2Cu in the dark (brown) and under illumination (orange); (c) DRIFTS of sample 0.2Cu in the dark (black) and under illumination (red); (d) proposed reaction pathway of CO formation over Cu-decorated Pd/WO_3. Reproduced with permission from Ref. [93] (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

$$CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O \quad (6)$$

$$CO_2 + 4H^+ + 4e^- \rightarrow HCHO + H_2O \quad (7)$$

$$CO_2 + 6H^+ + 6e^- \rightarrow CH_3OH + H_2O \quad (8)$$

$$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2\,H_2O \quad (9)$$

Li et al. performed an isotope experiment in a D_2O, CO_2, and H_2 atmosphere with Ru/$NaTaO_3$ for verifying whether the H_2 source was water (D_2O) or H_2 in the products [49]. In the initial reaction, the H_2 in methane was mainly derived from water (D_2O), with CD_4 as the primary product. Other products, including CD_3H and CD_2H_2, were observed after several hours of the reaction. The results indicated that the active atomic H from the water source directly reduced CO_2 into solar products, while the molecular H_2 gas promoted the conversion of peroxide intermediates (O_2*) 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 TiO_2 NPs (Pd-HTNPs), which were then employed for CO_2 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, CH_4 and CO were detected. For CH_4, the production rate (56.4 $\mu mol \cdot g_{cat}^{-1} \cdot h^{-1}$) and selectivity (95.2%) were high. In blank tests in the absence of the biohybrids (Pd-HTNPs@PMVs), light, or CO_2 (N_2 atmosphere), no catalytic performance was observed. The proton-coupled multi-electron transfer processes played an important role in the reduction of CO_2 into fuels and value-added chemicals, as shown in Fig. 3e.

As PtO_x NPs have proven to be effective active sites for the direct splitting of water [76], PtO_x NPs with a particle size of 2 nm were deposited on Bi_2WO_6 nanosheets (Fig. 4b), which were then applied for the photoreduction of CO_2 into hydrocarbons [77]. As expected, the product yield initially increased with the PtO_x loading; the optimal CH_4 production rate (108.8 $ppm \cdot g^{-1} \cdot h^{-1}$) was observed at 0.5%$PtO_x$ (Fig. 4a). Wang et al. confirmed the role of the proton-coupled multi-electron transfer processes in accelerating CO_2 photoreduction, as shown in Fig. 4c.

In addition to the H_2 source from water, molecular H_2, or atomic H^+ intermediates [78], the idea to use H_2-storage material to promote the photocatalytic reduction of CO_2 has received attention. Kang et al. reported that $N_2H_4 \cdot H_2O$, which had a high content of H_2 (7.9%), effectively worked as the H_2 source and electron donor over Au_3Cu@$SrTiO_3/TiO_2$ nanotube arrays [64]. Based on this system, CH_4 was the primary product (an evolution rate of 421.2 $\mu mol \cdot g^{-1} \cdot h^{-1}$), which accounted 60% of the total hydrocarbon products. Interestingly, $N_2H_4 \cdot H_2O$ could generate a productive reductive atmosphere to protect and maintain the high stability of the Au_3Cu@$SrTiO_3/TiO_2$ nanotube

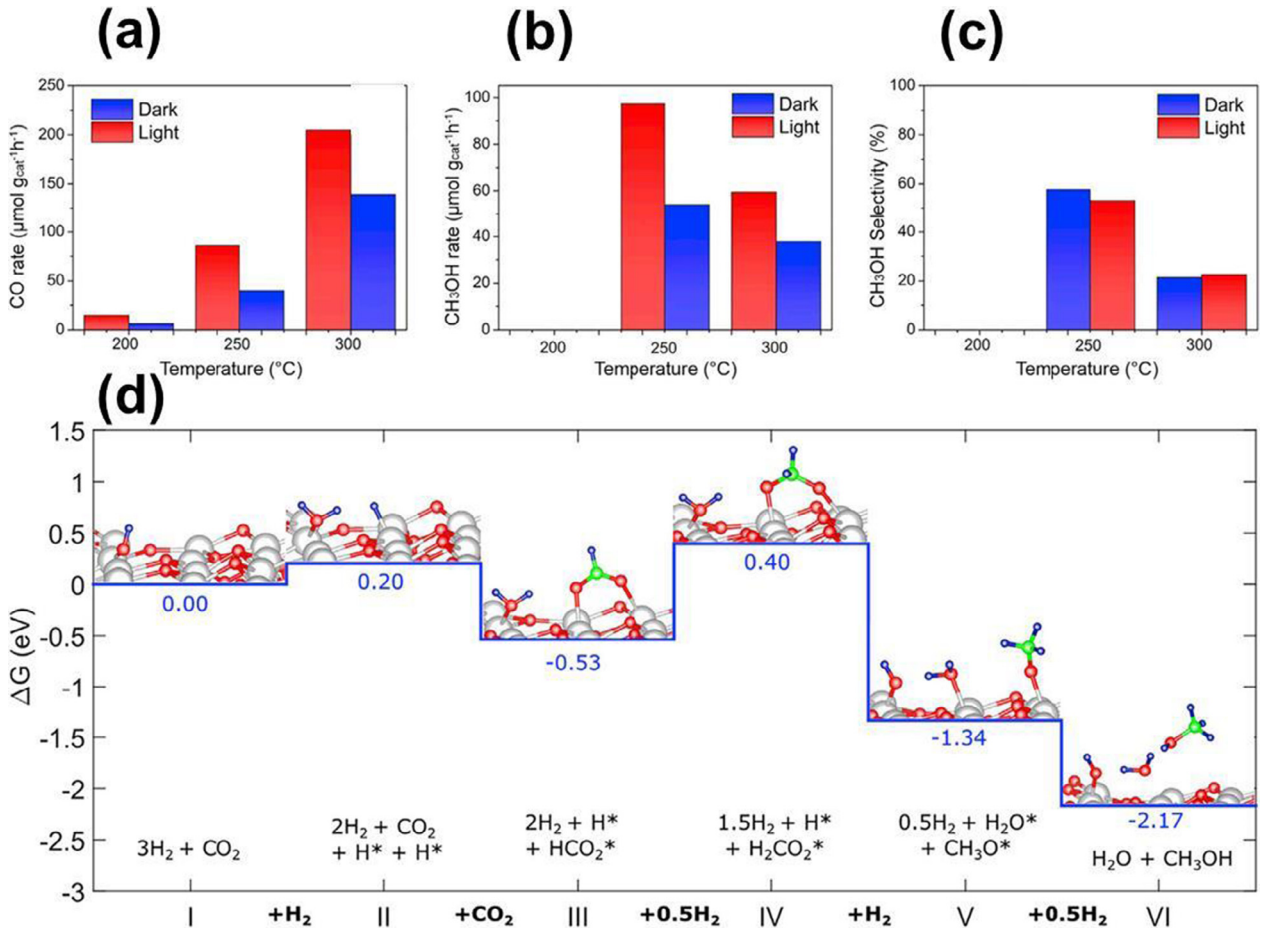

Fig. 7. Production of (a) CO and (b) CH_3OH at three different temperatures; (c) CH_3OH selectivity; (d) reaction pathway for CO_2-to-CH_3OH conversion. Reproduced with permission from Ref. [95].

arrays. As expected, the evolution rate of CH_4 still retained 87.6% of its original activity after five cycles of measurement during a 34 h test.

In summary, the concept of using H_2 source as reductants for CO_2 conversion might potentially impact solar fuel production. Many H_2 sources have been proposed, including water, molecular H_2, H_2-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 photoreduction of CO_2.

2.2. Photocatalysts

Photon-assisted CO_2 hydrogenation has attracted increasing attention in recent years. This method can efficiently convert CO_2 into high-value chemicals (e.g., CO, CH_4, CH_3OH, C_2H_4). It has considerable potential to address current CO_2 issues because the use of H_2 as the reductant significantly enhances the product yield [51,79]. In this section, the materials employed for four types of CO_2 conversion reactions—CO_2-to-CO (reverse water–gas shift, RWGS), CO_2-to-CH_3OH, CO_2-to-CH_4 (methanation reaction), and CO_2-to-C_{2+} (hydrogenation reaction)—are discussed in detail.

2.2.1. Reverse water–gas shift

To date, many candidates have been highlighted as potential photocatalysts for photocatalytic hydrogenation of CO_2 [26]. Typically, In_2O_3-based catalysts are a promising candidate for the photocatalytic hydrogenation of CO_2. Density functional theory (DFT) and time-dependent DFT calculations revealed that In_2O_3 containing O vacancies is favorable for the activation and hydrogenation of CO_2 [80,81]. Ghuman et al. reported that $In_2O_{3-x}(OH)_y$ consisting of surface hydroxide groups, and O vacancies facilitated photoinduced CO_2-to-CO conversion. $In_2O_{3-x}(OH)_y$ catalysts promote the heterolytic dissociation of H_2, 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 CO_2 molecules [82]. In another study, He et al. prepared $In_2O_{3-x}(OH)_y$ nanorods to catalyze the solar-driven RWGS reaction ($CO_2 + H_2 \rightarrow CO + H_2O$) in a gas-phase medium. The $In_2O_{3-x}(OH)_y$ 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 $In_2O_{3-x}(OH)_y$ and the nanorod superstructure comprising nanocrystals, the prepared $In_2O_{3-x}(OH)_y$ catalyst exhibited a significant enhancement in the light-assisted RWGS reaction [83]. Recently, Wang et al. constructed an $In_2O_{3-x}(OH)_y$@Nb_2O_5 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 $In(OH)_3$@Nb_2O_5, followed by calcination, to obtain an $In_2O_{3-x}(OH)_y$@Nb_2O_5 composite, as illustrated in Fig. 5a. The resulting heterostructure exhibited extraordinary performance in photocatalytic CO_2 reduction, as shown in Fig. 5b. The CO production rate was 44 times higher than that of pristine $In_2O_{3-x}(OH)_y$. 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

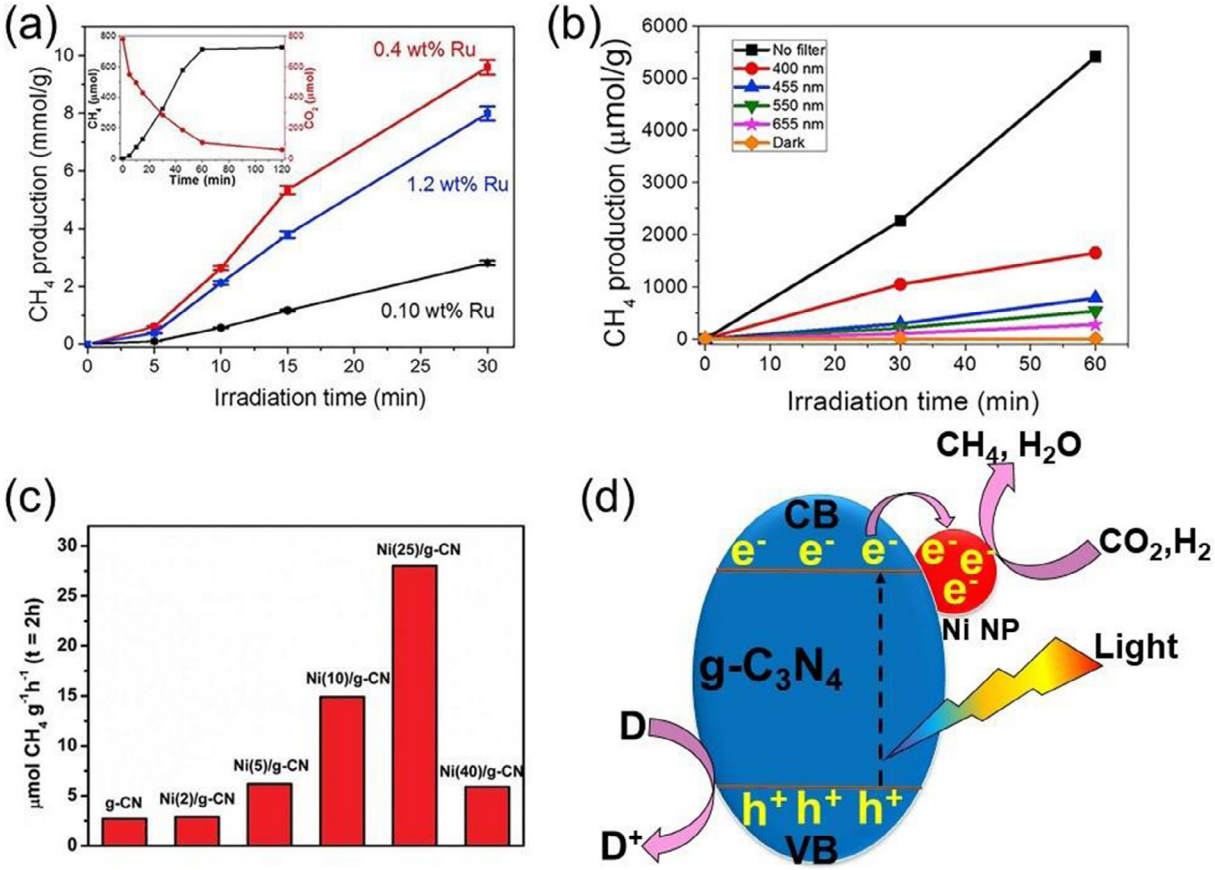

Fig. 8. Evolved CH_4 over various $RuO_2/SrTiO_3$ nanocomposites. (a) Different amounts of loaded Ru under the following conditions: a testing temperature of 150 °C, 1080-W·m^{-2} illumination, and partial pressures of 1.05 and 0.25 bar for H_2 and CO_2, respectively. The inset shows the CO_2 and CH_4 production (mmol) for the sample with 0.4 wt% Ru at 150 °C; 1000 W·m^{-2} was applied using a 300-W Xe lamp. (b) Different illumination conditions. Reprinted with permission from Ref. [102]; Copyright 2019, Elsevier. (c) Photocatalytic CH_4 formation of various Ni/g-C_3N_4 samples under the following conditions: a temperature of 150 °C, 1080-W·m^{-2} illumination, and partial pressures of 1.05 and 0.25 bar for H_2 and CO_2, respectively. Adapted with permission from Ref. [106]; Copyright 2019, Willey. (d) Proposed formation of CH_4 over Ni/g-C_3N_4 with the assistance of light and heat.

[84].

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 H_2, whereas metal oxides offer a medium for CO_2 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 H_2 but also reduce the activation barrier, enhancing the selectivity [86,88,89]. For example, Upadhye et al. investigated the activity of an Au/TiO_2 nanocomposite for the RWGS reaction under visible light. The Au NP-incorporated TiO_2 enhanced the CO_2-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/N_2O_5 nanocomposite was sufficient for the production of CO from CO_2 and H_2. The enhanced activity originated from the photothermal effect of Pd "nanoheaters" generating heat. Moreover, numerous H atoms, which resulted from the dissociation of H_2 on Pd nanocrystals and spillover to Nb_2O_5 nanorods and were associated with the *in situ* formation of O vacancies and/or the reduced Nb oxidation state, significantly promoted the reaction between CO_2 and H_2 to produce CO [91]. In another study, the Pd/H_yWO_{3-x} 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 (V_o), which were achieved by a hydrogenation process. Notably, the Pd NPs decorated on WO_3 significantly contributed to the formation of the defective structure of WO_3 because they facilitated the dissociation of H_2 via spillover of H to the WO_3 surface. Consequently, numerous modifications, such as Brønsted acid hydroxyls OH, W(V) sites, and O vacancies (V_o), occurred. These outstanding properties reduced the apparent activation energy, along with the light irradiation. Therefore, a large amount CO could be produced over Pd/H_yWO_{3-x} [92]. In another study, by exploiting these features, Li et al. prepared a novel Cu-decorated nanowire Pd/H_yWO_{3-x} bronze heterostructure, representing a step toward improving the RWGS reaction. As shown in Fig. 6a, the presence of Cu on Pd/WO_3 significantly increased the amount of CO produced in comparison with the sample prepared without Cu. Furthermore, the Cu-modified Pd/WO_3 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 CO_2-to-CO reduction over the Cu-modified Pd/WO_3, as shown in Fig. 6b. The Cu-modified Pd/WO_3 promoted the reduction of CO_2 via the formation of Cu-bound carboxylate intermediates, which was beneficial for the CO formation, as shown in Fig. 6c and 6d [93].

2.2.2. CO_2-to-CH_3OH conversion

The production of CH_3OH via CO_2 hydrogenation ($CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$) 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 CO_2-to-CH_3OH conversion over $In_2O_{3-x}(OH)_y$ rod-like nanocrystals. The CH_3OH product

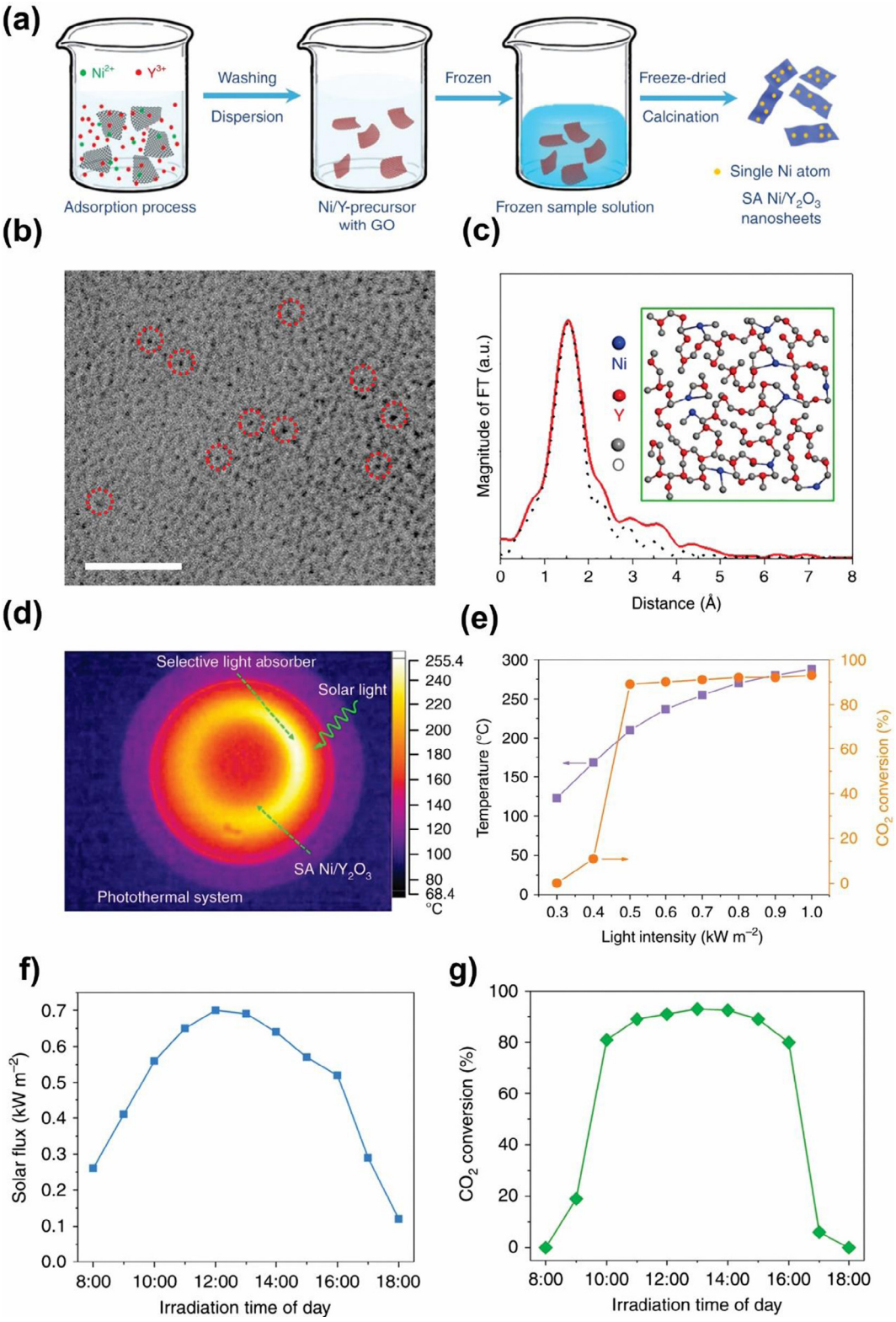

Fig. 9. (a) Schematic of the preparation of SA Ni/Y_2O_3 nanosheets; (b) aberration-corrected TEM image of the SA Ni/Y_2O_3 nanosheets; (c) schematic model of the SA Ni/Y_2O_3 nanosheets and the corresponding FT-EXAFS fitting curves for the SA Ni/Y_2O_3 nanosheets; (d) spatial temperature mapping obtained from the infrared camera under simulated solar light (1.0 $kW{\cdot}m^{-2}$), (e) temperature and CO_2 conversion over the SA Ni/Y_2O_3 nanosheets with respect to the light intensity; (f, g) solar flux and CO_2 conversion at different times of the day. Reproduced with permission from Ref. [109].

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 CH_3OH 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 CH_3OH formation. Unique surface properties significantly impact the reaction pathway,

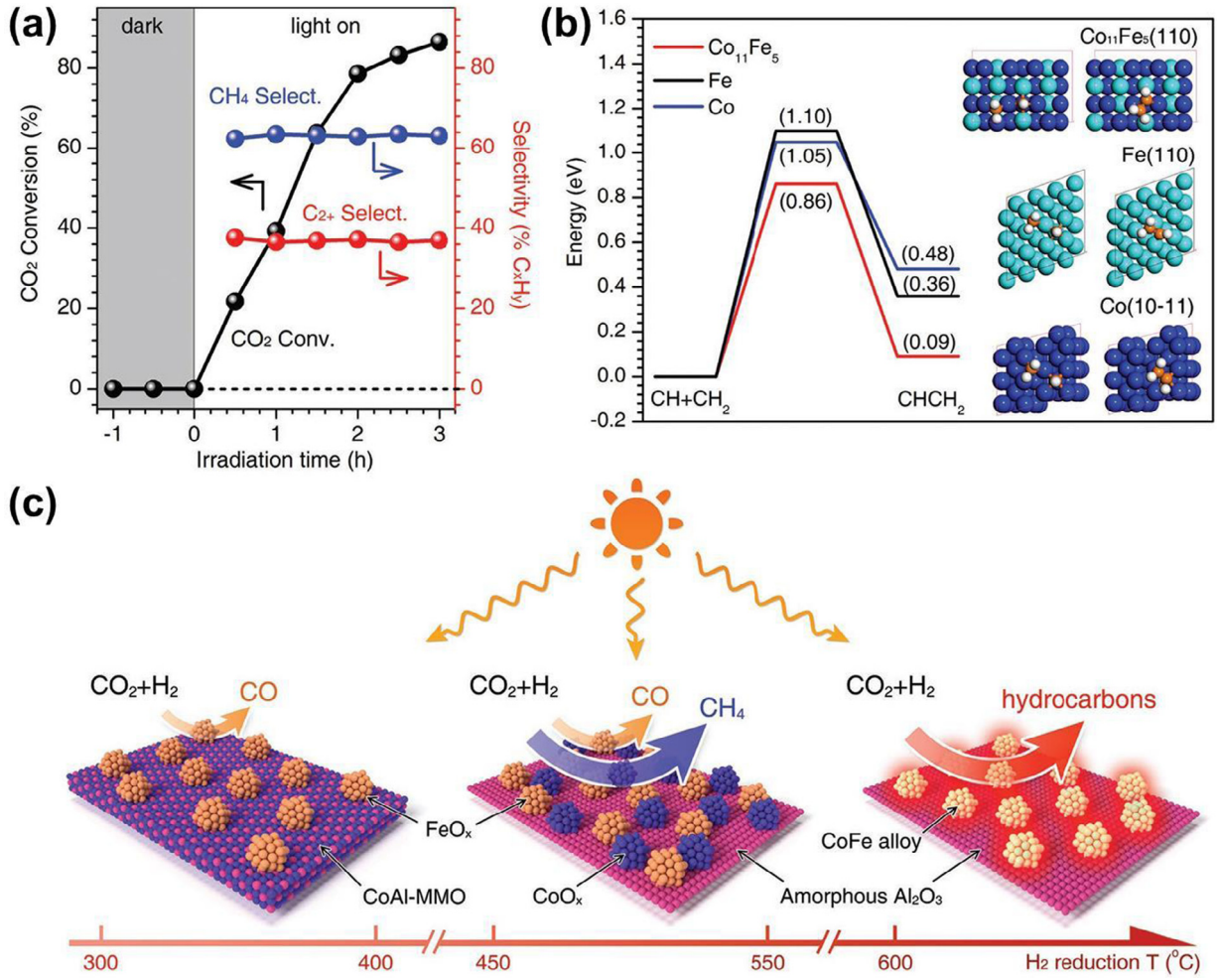

Fig. 10. (a) CO_2 conversion associated with the CH_4 and C_{2+} selectivity of the CoFe-650 sample under ultraviolet (UV)–visible irradiation; (b) DFT calculations for $Co_{11}Fe_5$ (1 1 0), compared with Co (10–11), and Fe (1 1 0) configurations for the C–C coupling; (c) schematic of various samples treated at different H_2 reduction temperatures toward the selectivity of CO and hydrocarbons. Reproduced with permission from Ref. [121]

driving the formation of CH_3OH. 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_3OH 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 ($CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$; $\Delta G_{298K} = -130.8$ 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_3N_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_3N_4 and Ni/g-C_3N_4 samples, indicating the superior CH_4 formation over the Ni/g-C_3N_4 composite compared with the pristine g-C_3N_4. The optimized sample—Ni(25)/g-CN—produced CH_4 with a rate of 28 μmol·g^{-1}·h^{-1}, which was approximate ~ 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_3N_4 to Ni NPs. The generated electrons easily migrated from g-CN to

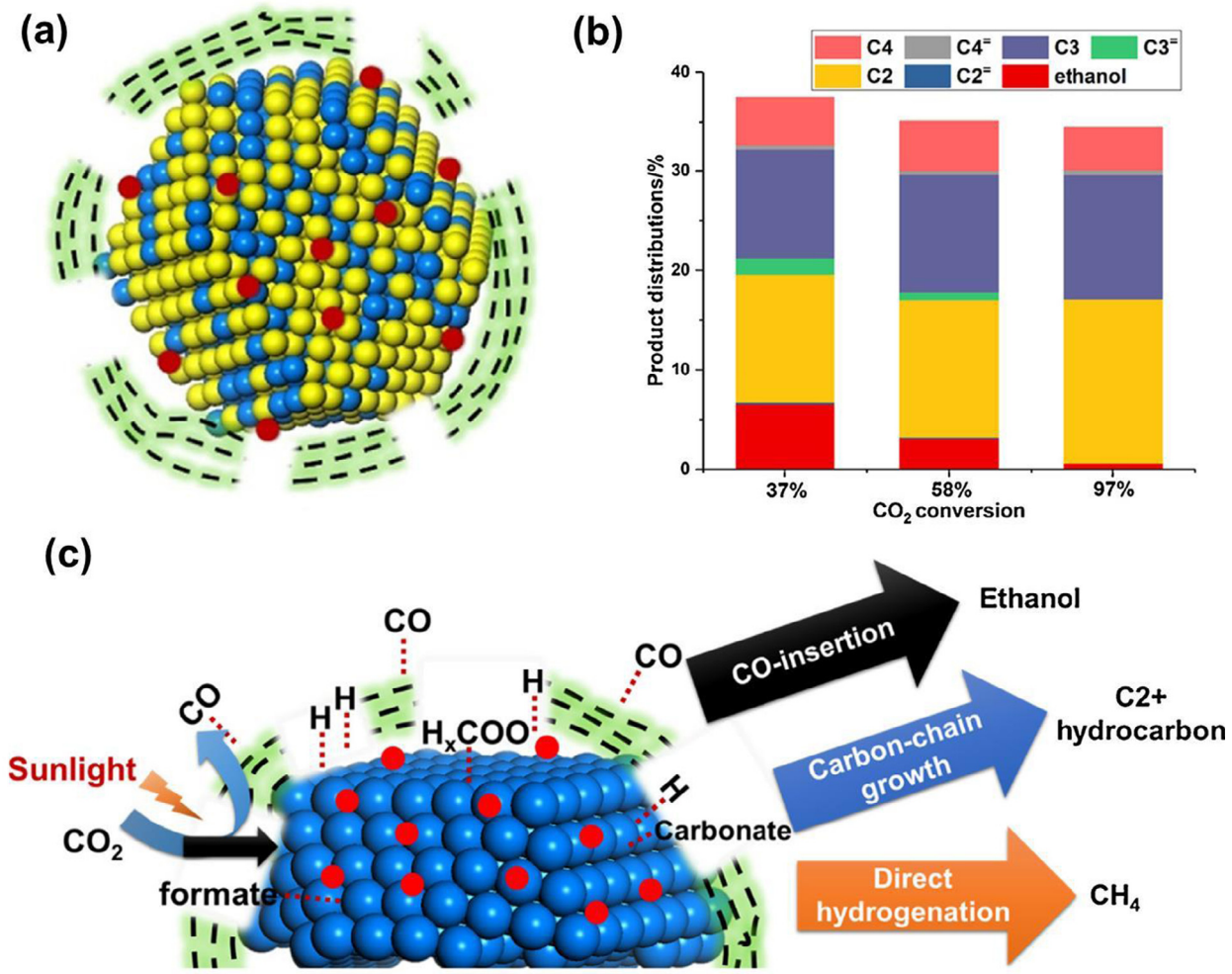

Fig. 11. (a) Schematic of the Na-Co@C structure; (b) selectivity of C_{2+} products under the photothermal condition over Na-Co@C at different CO_2 conversion rates; (c) schematic of the formation of CH_4 and C_{2+}. Reproduced with permission from Ref. [122].

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_3N_4 (m-CN) 2D/2D hybrid composite [107], oxygen-defective OV-Ti_3AlC_2 with proton-rich functionalized carbon nitride (f-C_3N_4) [108], for CO_2 reduction to fuels. They found that the CO and CH_4 yield rate could reach to 253 and 165 $\mu mol \cdot g^{-1} \cdot h^{-1}$, respectively, over Mt/g-C_3N_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_3N_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_2O_3 nanosheets exhibiting a superior CO_2-to-CH_4 conversion ability. The preparation of the SA Ni/Y_2O_3 nanosheet composites involved 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_2O_3 nanosheets, as shown in Fig. 9b. In the SA Ni-Y_2O_3 nanosheets (Fig. 9c), the Ni SAs formed Ni-O bonds with neighboring O atoms of Y_2O_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 $kW \cdot m^{-2}$) was as high as ~ 255 °C (Fig. 9d). Furthermore, the temperature of the SA Ni/Y_2O_3 nanosheets under the assistance of a selective light absorber (AlN_x/Al foil) reached 285 °C under 1.0 $kW \cdot m^{-2}$ 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_2O_3 nanosheets. Fig. 9f and 9 g show the solar flux and the CO_2 reduction performance concerning the irradiation time (time of day). The Ni/Y_2O_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

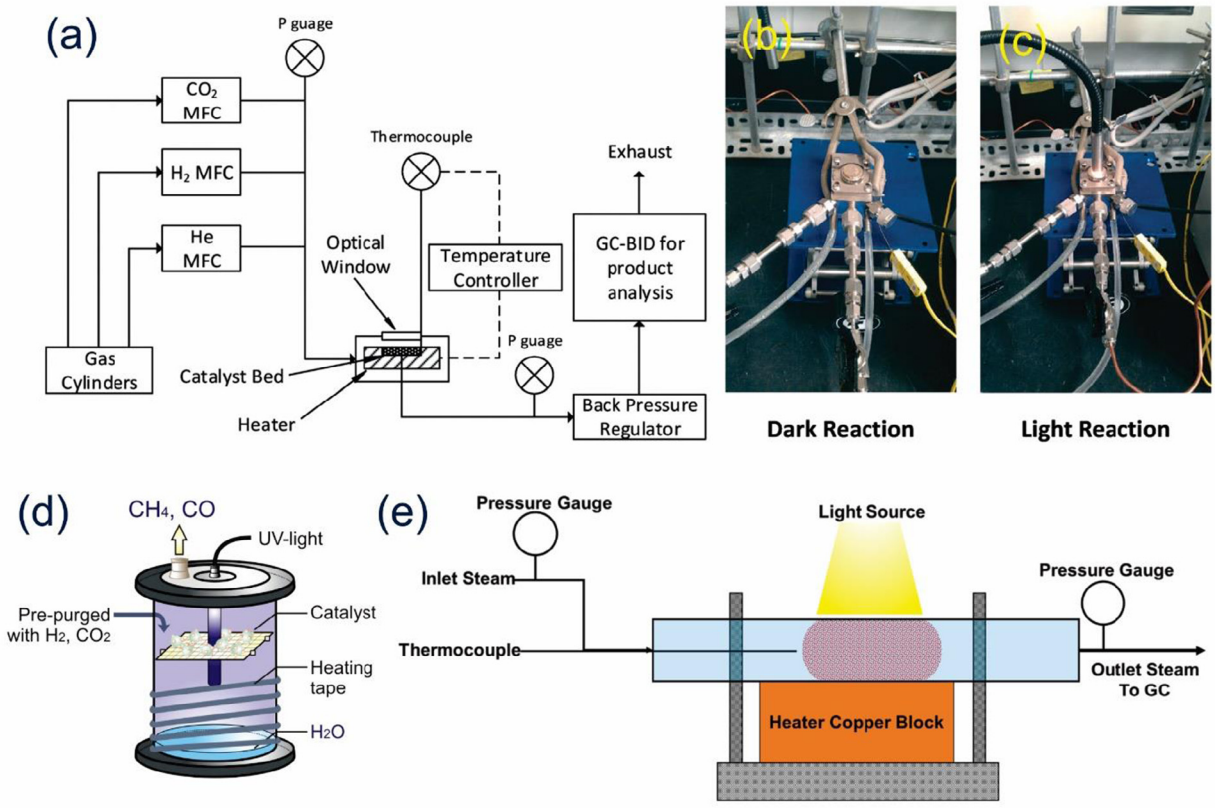

Fig. 12. (a) Schematic of a typical batch-type reactor; (b, c) corresponding photographs captured under dark and light conditions. Reproduced with permission from Ref. [90]. (d) Fixed-bed photoreactor Reproduced with permission from Ref. [9]. (e) Illustration of a flow reactor. Reproduced with permission from Ref. [82].

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 CO_2 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 H_2O molecules, which negatively affected the catalytic performance [104].

2.2.4. Hydrogenation of CO_2 into C_{2+} products

The conversion of CO_2 into ethanol and C_{2+} hydrocarbons is an attractive topic because of the higher value and energy density of C_{2+} products compared with C_1 products [116–118]. However, the generation of C_{2+} 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 C_{2+} with high selectivity. In 2018, Chen et al. reported the hydrogenation of CO_2 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 C_{2+} 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 CO_2 hydrogenation that formed C_{2+} hydrocarbons. DFT calculations (Fig. 10b) revealed that the CoFe surface provided a lower barrier to adsorbed CH-CH_2 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 CO_2 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 C_{2+} 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 CO_2 into $CO_2^{\delta-}$, and CO_2 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 C_{2+} 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 C_{2+} products in light-assisted CO_2 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 C_{2+} 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 CO_2 reduction [123–128].

Research on the production of C_{2+} 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, have been successfully prepared and demonstrated as a novel photocatalytic material platform to produce valuable chemicals and fuels from CO_2. From the present data, how to accumulate the charge carriers effectively and protons play a vital role to favor of the formation of C_{2+} products. These investigations are expected to unveil the nature of photocatalysts and provide extraordinary materials for enhancing C_{2+} production via photocatalytic hydrogenation of CO_2.

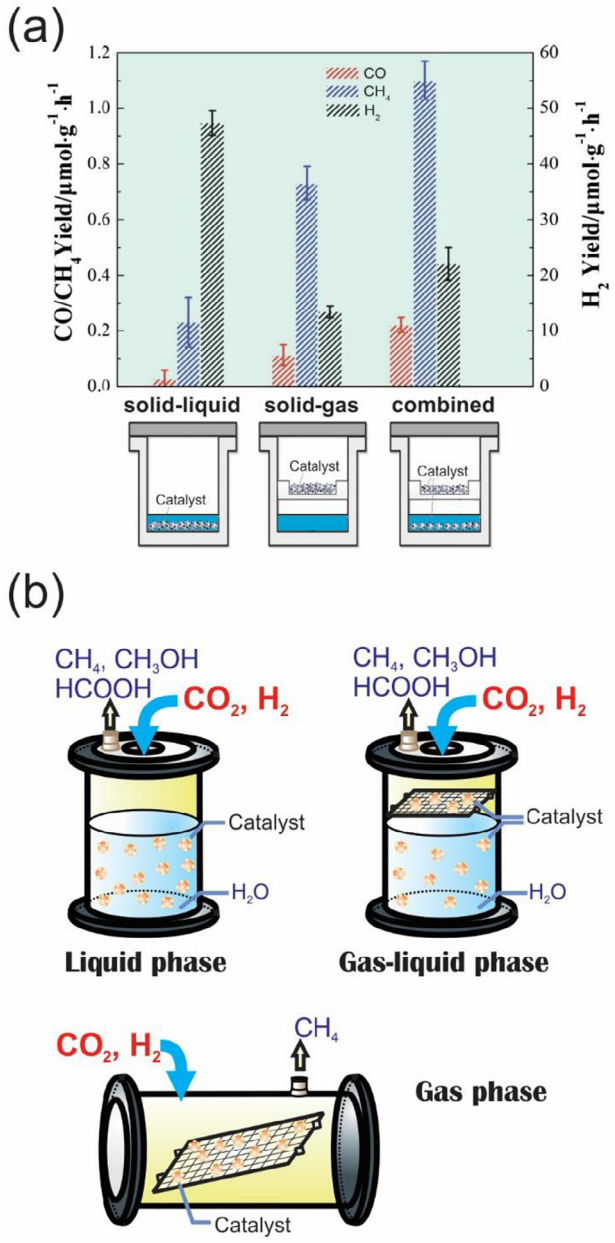

Fig. 13. (a) Photocatalytic hydrogenation/reduction of CO_2 over the Pt/TiO_2 photocatalyst with different reaction modes. Reproduced with permission from Ref. [130]. Three reaction modes were conducted for CO_2 photo-hydrogenation. Reproduced with permission from Ref. [11].

2.3. Photoreactor design

It notes that the efficiency of photohydrogenation of CO_2 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 CO_2 performances [8,11].

Two general types of reactors—batch- and flow-type—have been developed to perform the CO_2 photohydrogenation reaction. Fig. 12a–c describes a typical batch-type reactor system for photocatalytic CO_2 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 CO_2 can be performed in this system [90,129]. Another fixed-bed photoreactor (385 mL in volume) is designed by Chen et al., which is applied for the photohydrogenation of CO_2 in the presence of both H_2O (liquid phase) and H_2 (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 CO_2 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 CO_2 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/TiO_2. For example, the solid–liquid mode enhances the formation of H_2 (H_2: 47.3 $\mu mol \cdot g_{cat}^{-1} \cdot h^{-1}$; CO: 0.03 $\mu mol \cdot g_{cat}^{-1} \cdot h^{-1}$; CH_4: 0.23 $\mu mol \cdot g_{cat}^{-1} \cdot h^{-1}$), while the solid–gas mode promotes the reduction of CO_2 (H_2: 13.4 $\mu mol \cdot g_{cat}^{-1} \cdot h^{-1}$; CO: 0.11 $\mu mol \cdot g_{cat}^{-1} \cdot h^{-1}$; CH_4: 0.73 $\mu mol \cdot g_{cat}^{-1} \cdot h^{-1}$) [130]. As expected, combining the solid–liquid and solid–gas modes can significantly promote the photo-hydrogenation of CO_2, yielding the highest CO and CH_4 production rates (H_2: 22.1 $\mu mol \cdot g_{cat}^{-1} \cdot h^{-1}$; CO: 0.22 $\mu mol \cdot g_{cat}^{-1} \cdot h^{-1}$; CH_4: 1.1 $\mu mol \cdot g_{cat}^{-1} \cdot h^{-1}$). In this mode, the H_2 generated by the solid–liquid interface reaction promotes the photoreduction of CO_2 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 H_2 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.

3. Photoreduction of CO_2 for mimicking natural photosynthesis

Since the early pioneering work of Inoue et al. [44], the photo-hydrogenation of CO_2 has received significant attention. However, in these studies, an electron donor (H_2 gas) had to be continuously introduced to the reaction system. To mimic the natural photosynthesis in green plants, artificial photosynthesis using molecular H_2 or atomic H^+, which is directly produced by photocatalytic water splitting, for the photoreduction of CO_2 has recently attracted increasing attention. Various promising photocatalytic semiconductor materials and

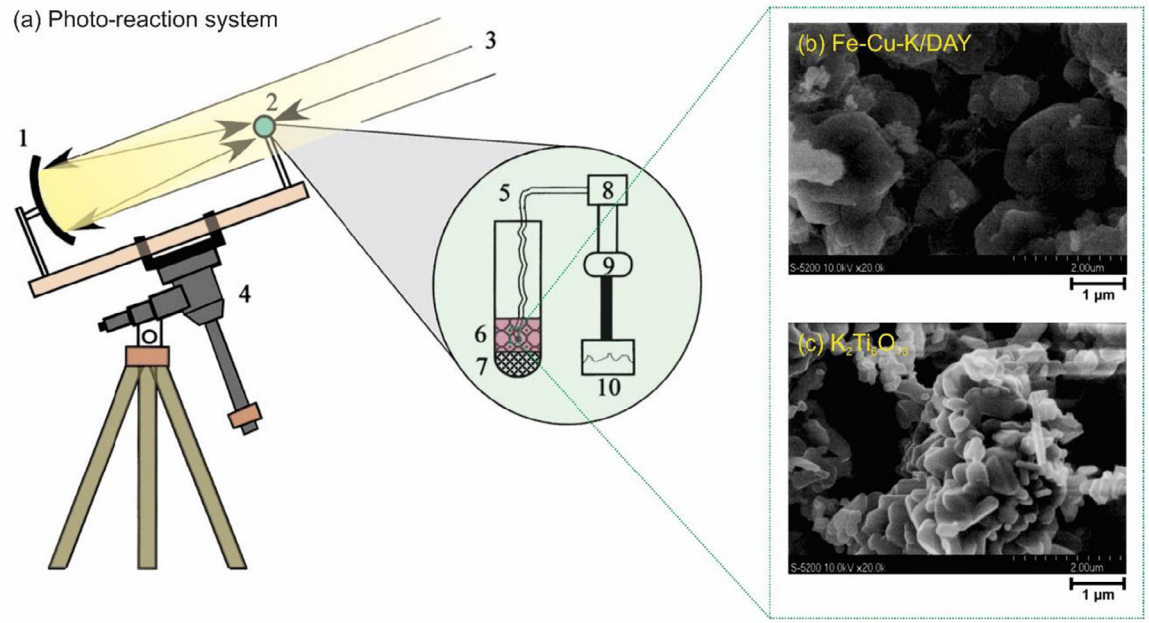

Fig. 14. (a) Experimental setup for the photo-hydrogenation of CO_2 using a concentrated sunlight system: (1) concave mirror; (2) reaction cell; (3) sunlight; (4) GPD-type equatorial mount; (5) thermocouple; (6) photocatalysts; (7) quartz wool; (8) temperature compensator; (9) NR-1000 data-acquisition system; (10) laptop computer. Scanning electron microscopy images of the (b) Fe-Cu-K/DAY photocatalyst and (c) $K_2Ti_6O_{13}$ photocatalyst. Reproduced with permission from Ref. [66].

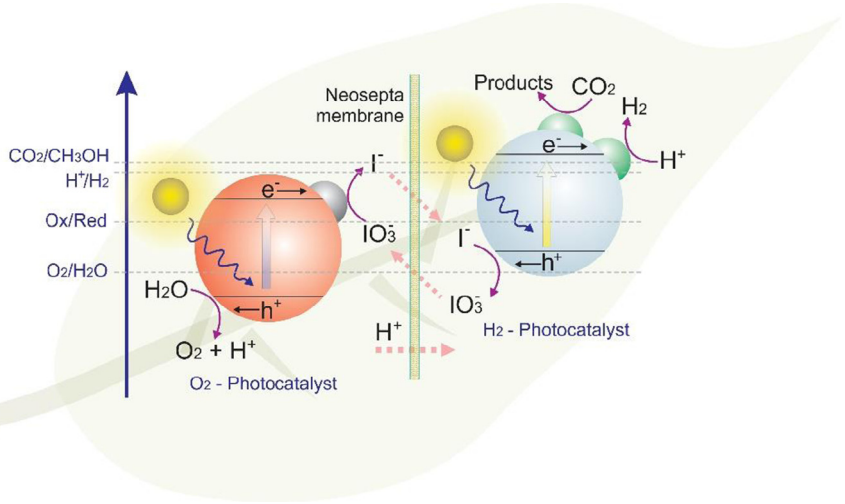

Fig. 15. Combination of H_2O water splitting and CO_2 photo-hydrogenation in a Z-scheme system to mimic the natural photosynthesis process in green plants. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

concepts to facilitate the production of solar fuels have been investigated.

In 2003, Guan et al. proposed the use of H_2 from water splitting for the photo-hydrogenation of CO_2 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 $kWh{\cdot}m^{-2}$). In this system, the $Pt/K_2Ti_6O_{13}$ 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 $Pt/K_2Ti_6O_{13}$ photocatalyst was to split water into H_2, and that of the Fe-Cu-K/DAY photocatalyst was to hydrogenate CO_2 into organic compounds, including methane (CH_4, 0.037–0.047 $\mu mol{\cdot}g_{cat}^{-1}{\cdot}h^{-1}$), formic acid (HCOOH, 0–12.93 $\mu mol{\cdot}g_{cat}^{-1}{\cdot}h^{-1}$), formaldehyde (HCHO, 0–3.43 $\mu mol{\cdot}g_{cat}^{-1}{\cdot}h^{-1}$), methanol ($CH_3OH$, 0–4.83 $\mu mol{\cdot}g_{cat}^{-1}{\cdot}h^{-1}$), and ethanol ($C_2H_5OH$, 0–1.17 $\mu mol{\cdot}g_{cat}^{-1}{\cdot}h^{-1}$). 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., $Pt/SrTiO_3$:Rh combined with $Pt/CuAlGaO_4$, and WO_3 [132], dual-function GaN:ZnO-Ni/NiO and Pt/WO_3 [12], Pt/TiO_2 and Cu/TiO_2 [133], or $Pt/CuAlGaO_4$ combined with $Pt/SrTiO_3$:Rh and WO_3 [10,134]—for CO_2-hydrogenation/H_2-generation and O_2-generation, respectively, and integrates with different reversible shuttle redox mediators, e.g., IO_3^-/I^- [12] or Fe^{2+}/Fe^{3+} [10,132]. This concept has many advantages. First, the O_2 and H_2/solar products generated separately in the twin photoreactor via water splitting effectively hinder the backward reaction and

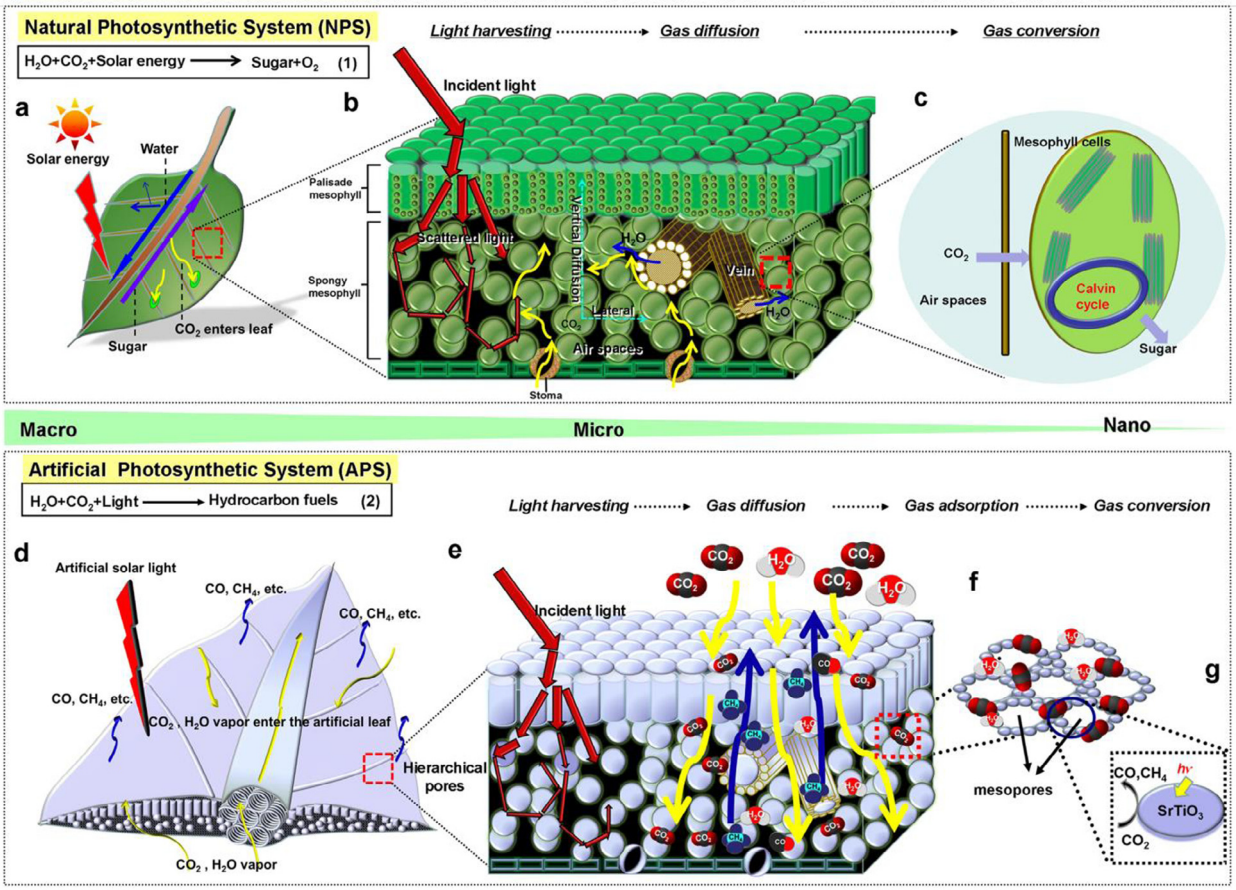

Fig. 16. Schematics of the NPS and APS: (a) Green leaf at the macroscale. (b) Light harvesting and gas diffusion in the NPS at the microscale. (c) Gas conversion at the nanoscale. (d) Artificial leaf at the macroscale. (e) Light harvesting and gas diffusion in the APS at the microscale. (f) Gas adsorption in the APS at the nanoscale. (g) Gas conversion in the APS at the nanoscale. Reproduced with permission from Ref. [136]. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

oxidation of hydrocarbon products. Second, molecular H_2 and atomic H^+, which are directly produced by the photocatalytic water splitting, are straightforwardly used for effective CO_2 hydrogenation.

Various experimental and theoretical studies on twin photoreactors for CO_2 have been conducted. Lee et al. reported that the performance of a dual-photocatalyst system in which Pt/$SrTiO_3$:Rh and Pt/$CuAlGaO_4$ were used as H_2-generation and CO_2-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 CO_2-reduction and H_2-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 H_2O water splitting and CO_2 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 CO_2 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 H_2-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 CO_2 emissions and the development of renewable fuels. Zhou et al. proposed a prototype artificial leaf for the photoreduction of CO_2 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 O_2, carbohydrates, and other C-rich products by splitting H_2O and reducing CO_2 in the presence of solar energy (Fig. 16a). At the microscale, the structures of the leaves function effectively to exchange gas, transport H_2O, and harvest solar light (Fig. 16b). At the nanoscale, CO_2 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 ($ATiO_3$, 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 CO_2 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 H_2O, photocatalytic materials (type, morphology, composition, and support). Meanwhile,

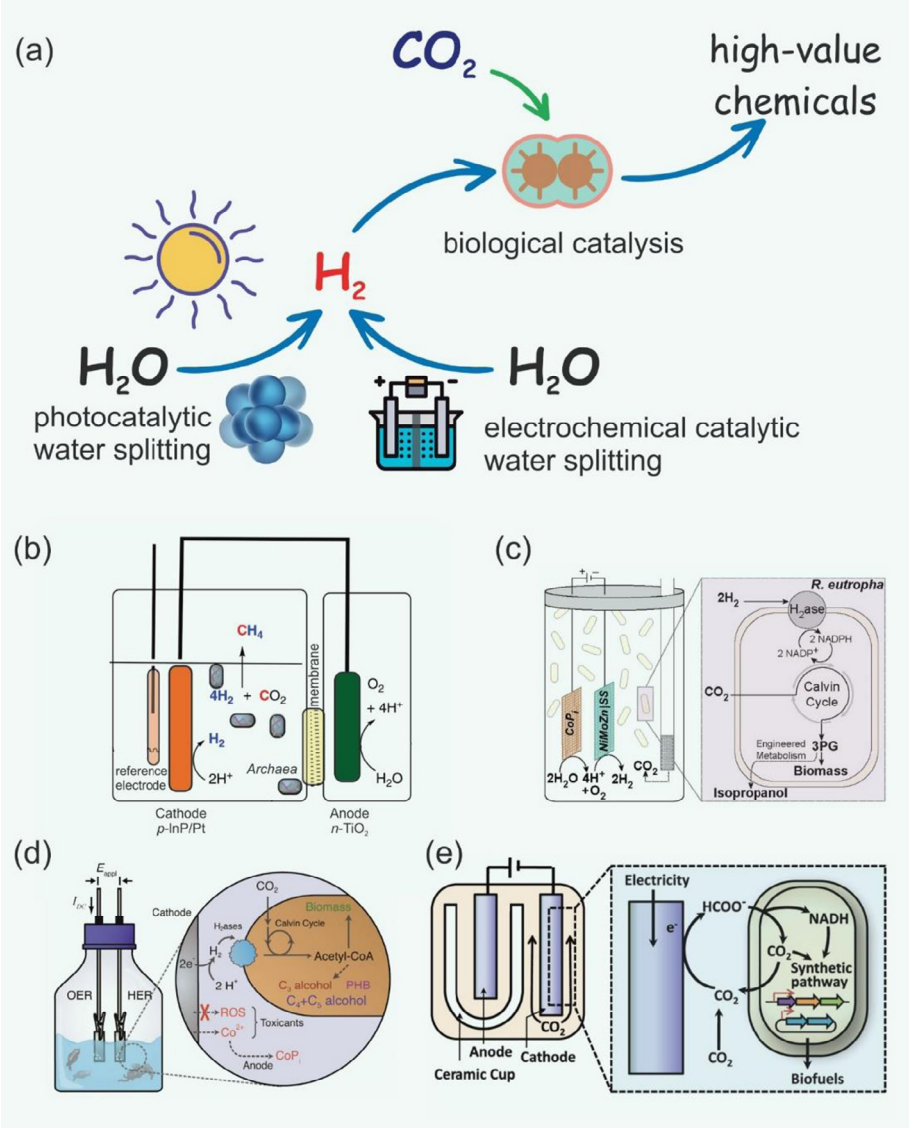

Fig. 17. (a) Hybrid photoelectrochemical biological approach for solar-to-chemical conversion. (b) Schematic of the generalized electrolytic setup, showing the *in situ* generation of H_2 at the cathode followed by H_2-driven reduction of carbon dioxide to methane by the M. barkeri biocatalyst. (c) Bioelectrochemical cell for CO_2 fixation. Reproduced with permission from Ref. [140]. (d) Hybrid bioelectrochemical system to convert CO_2 into higher alcohols. Reproduced with permission from Ref. [141]. (e) Integrated electromicrobial process for CO_2 fixation. Reproduced with permission from Ref. [142].

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-to-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 CO_2 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 H_2 from water, and then, the H_2 is used with microorganisms to transform CO_2 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 H_2, which was subsequently used *in situ* by *Methanosarcina barkeri* to reduce CO_2 to CH_4. In the anodic chamber, O_2 was produced separately to prevent harmful potential by reactive O species. The conversion rate (*in situ* generations of H_2 at the cathode) reached 86%, followed by an H_2-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 O_2 and H_2 via water splitting. H_2 was used to efficiently convert CO_2 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 $mg \cdot L^{-1}$, 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 H_2 in the microbial cultures. For reducing the toxicity to the bacterium, Liu et al. proposed a hybrid bioelectrochemical system for CO_2 fixation (as shown Fig. 17d) [141], which could effectively minimize the generation of toxically reactive O species. The *R. eutropha* hybrid system achieved η_{SCE} values of 9.7%, 7.6%, and 7.1% for biomass, bioplastic, and liquid fuels (C3, C4, and C5 alcohols), respectively. Another approach is to electrochemically produce formate, instead of H_2 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 H_2 from water, and then, the H_2 is used with microorganisms to transform CO_2 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 CO_2 into valuable chemicals and renewable fuels associated with H_2 utilization has emerged as a mainstream approach to address the overwhelming CO_2 pollution. This research field can grow significantly in the future. In this review, four promising approaches for light-driven CO_2 reduction were identified: (i) the development of robust catalysts for light-assisted CO_2 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 CO_2 has proven to be an efficient method of reducing CO_2. The selection of materials significantly affects the outcomes. This review identified the following critical reactions: RWGS, CO_2-to-CH_3OH, methanation (CO_2-to-CH_4), and CO_2-to-C_{2+} conversion. The preparation of novel and inexpensive materials to increase the efficiency of each type of reaction is imperative. Research on the generation of C_{2+} 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 CO_2.

Mimicking natural photosynthesis is another outstanding route for converting CO_2 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 extraordinary materials will lead to enhancements in the CO_2 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 CO_2 conversion and inspire research on high-performance and low-cost materials for solar-driven CO_2 reduction.

The preparation of an artificial leaf is also an intensive approach to convert CO_2 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 CO_2 conversion.

Hybrid photoelectrochemical biological systems have considerable potential for efficient solar-driven CO_2-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 CO_2. We believe that our review provides a roadmap for the future solar-driven CO_2 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.

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Appendix A. Supplementary data

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

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