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Design and fabrication of semiconductor photocatalyst for photocatalytic reduction of CO₂ to solar fuel

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The shortage of fossil fuels and the disastrous pollution of the environment have led to an increasing interest in artificial photosynthesis. The photocatalytic conversion of CO₂ into solar fuel is believed to be one of the best methods to overcome both the energy crisis and environmental problems. It is of significant importance to efficiently manage the surface reactions and the photo-generated charge carriers to maximize the activity and selectivity of semiconductor photocatalysts for photoconversion of CO₂ and H₂O to solar fuel. To date, a variety of strategies have been developed to boost their photocatalytic activity and selectivity for CO₂ photoreduction. Based on the analysis of limited factors in improving the photocatalytic efficiency and selectivity, this review attempts to summarize these strategies and their corresponding design principles, including increased visible-light excitation, promoted charge transfer and separation, enhanced adsorption and activation of CO₂, accelerated CO₂ reduction kinetics and suppressed undesirable reaction. Furthermore, we not only provide a summary of the recent progress in the rational design and fabrication of highly active and selective photocatalysts for the photoreduction of CO₂, but also offer some fundamental insights into designing highly efficient photocatalysts for water splitting or pollutant degradation.

INTRODUCTION

The shortage of the energy supply and the problem of disastrous environmental pollution have been recognized as two main challenges in the near future [1]. It is a better way to efficiently and inexpensively convert solar energy into chemical fuels by developing an artificial photosynthetic (APS) system because solar fuels are high density energy carriers with long-term storage capacity. The most important and challenging reactions in APS—the photocatalytic water splitting into H₂ and O₂ (water reduction and oxidation) [2–4] and photoreduction of CO₂ to solar fuel, such as CH₄ and CH₃OH [5,6] have been extensively studied since the photocatalytic water splitting on TiO₂ electrodes was discovered by Honda and Fujishima in 1972 [7]. The photocatalytic reduction of CO₂ by means of solar energy has attracted growing attention in the recent years, which is also believed to be one of the best methods to overcome both global warming and energy crisis [8]. However, it is also generally thought that photocatalytic CO_2 reduction is a more complex and difficult process than H_2 production due to preferential H_2 production and low selectivity for the carbon species produced [9,10]. The progress achieved in the photoreduction of CO_2 is still far behind that in water splitting for a few decades because of the low efficiency and selectivity, and limited photocatalysts [11,12]. Therefore, there is an urgent need for artificial photosynthesis research to focus on the formidable challenge of converting CO_2 and water into valuable hydrocarbons or liquid fuels.

Up to now, many different heterogeneous [4,13,14] and homogeneous [15] photocatalysts have been extensively studied in the different fields of photocatalysis over the past decades. Extensive research has been underway to develop highly heterogeneous photocatalysts for the application of semiconductor photocatalysis because heterogeneous systems have more advantages and a wider range of potential applications than the homogeneous systems [2,13,16]. From the viewpoint of searching for suitable photocatalysts, a number of reviews about various TiO₂ and non-TiO₂ heterogeneous semiconductor photocatalyst materials used in the fields of photocatalytic reduction of CO₂ have been available [17-19]. However, most of them only focus on the review of various kinds of semiconductor photocatalysts, there are few reviews about the design strategies for the fabrication of highly efficient photocatalysts [20]. Besides continuous fabrication of new visible-light-driven photocatalysts, it is also a very important topic to enhance the selectivity, stability and activity of existing photocatalysts for CO₂ photoreduction. Furthermore, it is clear that photo-generated charge carriers and surface reactions play very important roles in enhancing the overall efficiency for CO₂ photoreduction. Thus, it is also significant to efficiently manage the photo-generated charge carriers and surface reactions of semiconductor photocatalysts to maximize the activity and selectivity for conversion of solar energy and CO₂ to fuel. Any processes consuming photo-gener-

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ated electrons and undesirable reactions will decrease the overall efficiency, which should be weakened or completely avoided. In addition, the kinetic challenges are great owing to the complex multi-electron reduction processes of CO₂ [21,22]. Thus, increasing the kinetics of CO₂ reduction is a critical step to enhance the overall efficiency. Therefore, this review will focus on the design of highly selective and efficient semiconductor photocatalysts for CO, photoreduction through a rational management of photo-generated charge carriers and surface reactions. Various strategies and their corresponding design principles are summarized here, including increased visible-light excitation, promoted charge transfer and separation, enhanced adsorption and activation of CO₂, accelerated CO₂ reduction kinetics and suppressed undesirable reaction. This review not only differs from the previous reviews focusing on the summarization of various photocatalysts for CO₂ photoreduction, but also is different from the reviews about the typical design strategies applied in the water splitting and organic pollutants degradation due to the complexity of the carbon species from CO₂ reduction [23,24]. It may open a new opportunity for designing highly effective photocatalysts for both CO₂ reduction and water splitting.

FUNDAMENTALS OF PHOTOCATALYTIC CO₂ REDUCTION

Thermodynamics of photocatalytic CO, reduction

The free energy ΔG^0 and the standard redox potential ΔE^0 of the multi-electron water splitting (Equation (1)) and CO_2 reduction (Equation (2–6)) are listed in Equation (1–6) [25]. The ΔG^0 values of all the reactions are highly positive, and make CO_2 reduction a highly endothermic process which is much more difficult to proceed at ambient temperature. The ΔG^0 values also indicate that the CO_2 reduction reactions can store more energy than the water splitting reaction [25,26].

$$H_2O(l) \rightarrow H_2(g) + 1/2O_2(g),$$

ΔG0 = 237 kJ/mol, ΔE0 = 1.23 V. (1)

 $CO_2(g) \rightarrow CO(g) + 1/2O_2(g),$

$$\Delta G^0 = 257 \text{ kJ/mol}, \Delta E^0 = 1.33 \text{ V.}$$

$$CO_2(g) + H_2O(l) \rightarrow \text{HCOOH}(l) + 1/2O_2(g),$$
(2)

$$\Delta G^0 = 286 \text{ kJ/mol, } \Delta E^0 = 1.48 \text{ V.}$$
(3)

$$CO_2(g) + H_2O(l) \rightarrow HCHO(l) + O_2(g),$$

$$\Delta G^{0} = 522 \text{ kJ/mol}, \Delta E^{0} = 1.35 \text{ V.}$$
(4)
$$CO_{2}(g) + 2H_{2}O(l) \rightarrow CH_{3}OH(l) + 3/2O_{2}(g),$$

$$\Delta G^{0} = 703 \text{ kJ/mol}, \Delta E^{0} = 1.21 \text{ V.}$$

$$CO_{2}(g) + 2H_{2}O(l) \Rightarrow CH_{4}(g) + 2O_{2}(g),$$
(5)

$$\Delta G^0 = 818 \text{ kJ/mol}, \Delta E^0 = 1.06 \text{ V}.$$
 (6)

For reduction of CO₂, the reaction by one electron to form CO_2^- radical is highly unfavorable due to the higher reduction potential of -1.9 V vs. normal hydrogen electrode (NHE). In addition, a large kinetic "overvoltage" for the one-electron reduction was required because of the structural differences between linear CO₂ and bent CO₂ [15,26,27]. In contrast, the multi-electronic processes are more favorable, which require much less energy for per electron transfer as compared to mono-electron process. The standard reduction potentials of CO₂ for the half-cell reactions are summarized in Table 1 (at pH 7 in aqueous solution vs. NHE) [15,22,26-30]. Fig. 1 shows a Latimer-Frost diagram for the multi-electron, multi-proton reduction of CO₂ in aqueous solution at pH 7 [31]. As depicted in Fig. 1, the slope derived from each blue dashed line represents the standard redox potential of the corresponding multi-electron CO₂ reduction reaction. It can be clearly seen from Table 1 and Fig. 1 that proton-assisted, multi-electron approach to CO₂ reduction lowers the thermodynamic barrier significantly [31]. Furthermore, every

Table 1 Reduction potentials of CO₂

Reaction	<i>E</i> ⁰ (V) <i>vs.</i> NHE at pH 7
Reduction potentials of CO ₂	
$2H^+ + 2e^- \rightarrow H_2$	-0.41
$CO_2 + e^- \rightarrow CO_2^-$	-1.9
$\rm CO_2 + 2H^+ + 2e^- \rightarrow \rm HCO_2H$	-0.61
$CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O$	-0.53
$\mathrm{CO_2} + 4\mathrm{H^+} + 4\mathrm{e^-} \rightarrow \mathrm{C} + 2\mathrm{H_2O}$	-0.2
$\mathrm{CO_2} + 4\mathrm{H^+} + 4\mathrm{e^-} \! \rightarrow \mathrm{HCHO} + \mathrm{H_2O}$	-0.48
$\mathrm{CO}_2 + 6\mathrm{H}^+ + 6\mathrm{e}^- \rightarrow \mathrm{CH}_3\mathrm{OH} + \mathrm{H}_2\mathrm{O}$	-0.38
$\text{CO}_2 + 8\text{H}^+ + 8\text{e}^- \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}$	-0.24
$2\text{CO}_2 + 8\text{H}_2\text{O} + 12\text{e}^- \rightarrow \text{C}_2\text{H}_4 + 12\text{OH}^-$	-0.34
$2\text{CO}_2 + 9\text{H}_2\text{O} + 12\text{e}^- \rightarrow \text{C}_2\text{H}_5\text{OH} + 12\text{OH}^-$	-0.33
$3\text{CO}_2 + 13\text{H}_2\text{O} + 18\text{e}^- \rightarrow \text{C}_3\text{H}_7\text{OH} + 18\text{OH}^-$	-0.32
Reduction potentials of H_2CO_3	
$2H^+ + 2e^- \rightarrow H_2$	-0.41
$2H_2CO_3 + 2H^+ + 2e^- \rightarrow H_2C_2O_4 + 2H_2O$	-0.8
$H_2CO_3 + 2H^+ + 2e^- \rightarrow HCOOH + H_2O$	-0.576
$\rm H_{2}\rm CO_{3} + 4\rm H^{+} + 4e^{-} \rightarrow \rm HCHO + 2\rm H_{2}\rm O$	-0.46
$H_2CO_3 + 6H^+ + 6e^- \rightarrow CH_3OH + 2H_2O$	-0.366
$\mathrm{H_2CO_3} + 4\mathrm{H^+} + 4\mathrm{e^-} \rightarrow \mathrm{C} + 3\mathrm{H_2O}$	-0.182
Reduction potentials of CO ₃ ²⁻	
$2H^+ + 2e^- \rightarrow H_2$	-0.41
$2CO_3^{2-} + 4H^+ + 2e^- \Rightarrow C_2O_4^{2-} + 2H_2O$	0.07
$\text{CO}_3^{2-} + 3\text{H}^+ + 2\text{e}^- \Rightarrow \text{HCOO}^- + \text{H}_2\text{O}$	-0.099
$\mathrm{CO}_3^{2-} + 6\mathrm{H}^+ + 4\mathrm{e}^- \! \rightarrow \mathrm{HCHO} + 2\mathrm{H_2O}$	-0.213
$\mathrm{CO}_3^{2-} + 8\mathrm{H}^+ + 6\mathrm{e}^- \rightarrow \mathrm{CH}_3\mathrm{OH} + 2\mathrm{H}_2\mathrm{O}$	-0.201
$CO_{3}^{2-} + 6H^{+} + 4e^{-} \rightarrow C + 3H_{2}O$	0.065



Figure 1 Latimer–Frost diagram for the multi-electron, multi-proton reduction of CO, in aqueous solution at pH 7.

step necessary for converting CO_2 to CO, then to H_2CO , then to hydrocarbons or alcohols also has low kinetic barriers [31,32]. Therefore, in comparison with the mono-electron process, proton-assisted multielectron transfer is an alternative and more favorable pathway to reduce CO_2 .

 $\rm H_2CO_3$ and the carbonate ions in the solution can be reduced to a number of products, such as CH_3OH, HCOOH, and HCHO, through multi-electron transfer processes. The potentials calculated for H_2CO_3 and CO_3^{2-} are also listed in Table 1, respectively [28,29]. When comparing them, it is clear that the route of methanol formation from H_2CO_3 or CO_3^{2-} is more thermodynamically favorable than that from CO_3.

Because of high stability and low energy grade of CO_2 , the chemical transformations of CO_2 are thermodynamically highly unfavorable. As a consequence, a large input of energy is required to drive the desired transformations.

Moreover, the use of catalysts is necessary owing to its inertness [27,33]. Therefore, the reduction reaction of CO₂ is quite challenging. So far, thermochemical, electrochemical, photoelectrochemical (PEC), and photochemical reductions of CO₂ into hydrocarbon fuels with the help of catalysts have been extensively studied [33-35]. Without producing more CO₂, economical and environment-friendly reduction of CO₂ to value added chemicals is highly desired, which is possible only if renewable energy, such as solar energy, is used as the energy source. Among them, development of APS systems, such as PEC or photochemical reduction of CO₂ into solar fuel, is one of the ultimate goals in the reduction of CO, [36]. For example, in 1978, Halmann [6] first found that CO, was photoelectrochemically reduced to CH₃OH on a *p*-type GaP electrode. In the second year, Inoue et al. [5] first reported that formic acid, formaldehyde, and methyl alcohol could be produced through the photocatalytic reduction of CO₂ in aqueous suspensions of semiconductors such as TiO₂, ZnO, CdS, GaP and SiC. Through APS systems, solar energy and CO, are directly transformed and stored as chemical energy such as CH₃OH. Consequently, the photoreduction of CO₂ to solar fuel is particularly interesting and amazing, and has been extensively studied in the past decades.

It is well known that the photocatalytic properties of semiconductor mainly come from the formation of photogenerated charge carriers (holes and electrons) which occur upon the absorption of photons with energy equal to or greater than the band gap energy (E_g) separating the valence band (VB) from the conduction band (CB) (Fig. 2) [37,38]. The photogenerated holes in the VB diffuse to the semiconductor surface and react with water to produce O₂ or form hydroxyl radicals (•OH). Then, hydroxyl radicals further oxidize nearby organic molecules on the semicon-



Figure 2 Processes involved in photocatalytic CO_2 reduction over a heterogeneous photocatalyst. CRC, CO_2 reduction co-catalysts; WOC, water oxidation co-catalysts.

ductor surface [37,38]. Meanwhile, electrons in the CB participate in reduction processes, which typically react with water to produce H₂ or with CO₂ to produce fuel [4,37,38]. To achieve CO₂ photoreduction, a good photocatalyst must have suitable band positions (VB and CB) and E_{g} . In other words, the bottoms of CB must be located at a more negative potential than the reduction potentials of CO₂, whereas the tops of the valence bands must be positioned more positively than the oxidation potential of H₂O to O₂, the redox reaction can proceed under irradiation at an energy equivalent to or greater than the band gap of the semiconductor photocatalyst [16]. Importantly, the yields of products from CO₂ reduction increase as the CB becomes more negative with respect to the redox potential of a certain reaction of CO₂ reduction, which has been demonstrated by the pioneering report in 1979 [5].

Based on this principle, it is easily found that many candidate materials with suitable CB positions are suitable for photocatalytic reduction of CO₂. Several potential semiconductors (e.g., TiO₂ [19,39], ZnO [5,40-43], ZnS [36,44-47], SrTiO₃ [11,48-50], SiC [5,51-53], Cu₂O [54-57], CdS [5,58-63], GaP [5,64], TaON [65-68], C₃N₄ [69-71], BiVO₄ [72-76] and Ta₃N₅ [77-80]) are listed in Fig. 3. Among them, TiO₂ is the most studied photocatalyst for CO₂ reduction because it is cheap, nontoxic, made up of abundant elements, and resistant to photocorrosion. However, its poor visible light absorption ability should be enhanced. Meanwhile, Cu₂O, CdS, GaP, TaON, C₃N₄ and Ta₃N₅ are good candidates for photocatalytic reduction of CO, under visible light irradiation. However, their weak photostability should be improved. The photocatalysts with more negative CB levels (in the right side of Fig. 3) seem to be better choices for the photocatalytic reduction of CO₂.

Process and mechanism of photocatalytic CO₂ reduction

Process of photocatalytic CO₂ reduction

In addition to suitable $E_{\rm g}$ and CB potentials, there are many other factors influencing the overall efficiency of photocatalytic CO₂ reduction, such as photocatalytic process and CO₂ reduction kinetics. Typical processes of photocatalytic CO₂ reduction over a semiconductor photocatalyst are illustrated in Fig. 2. They include the excitation, transport, separation, the elctrocatalytic reduction of CO₂ and water oxidation.

The first step (1) in Fig. 2 is the excitation of photo-generated electron-hole pairs in the bulk of semiconductor particles by absorbing photon energy greater than the band gap energy of a material. Therefore, to increase the excitation efficiency of electron-hole pairs by visible light, a photocatalyst should have a much narrower band gap (E_g < 3.0 eV or λ > 415 nm). From the viewpoint of visible light utilization, it should be an efficient strategy to develop visible-light-driven photocatalysts.

The second step (2) in Fig. 2 shows the separation of excited electrons and holes and their migration to the surface for the desired chemical reaction. As a competitive process, the bulk charge recombination, step (3), is an important deactivation process because the number of excited charge carriers significantly decreases by generating phonons or heat. To enhance the overall efficiency, it is of significant importance to improve transfer of photo-generated charge carriers to surface and inhibit their recombination in the bulk. Clearly, the structural and electronic properties of a photocatalyst have significant effects on these two steps. Thus, any strategy beneficial to the charge separation and transport, such as fabrication of nano-structured semicon-



Figure 3 Band positions of some semiconductor photocatalysts and the redox potentials of CO, reduction at pH 7 in aqueous solution.

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ductor, semiconductor heterojunctions or semiconductor/ nano-carbon heterojunctions, should be taken into account to maximize the utilization rate of photo-generated charge carriers.

Once the photogenerated electrons reach the surface, the step (4) will occur. The process (4) is the electrocatalytic reduction of CO₂ by photo-generated electrons trapped in the CO₂ reduction co-catalysts (CRC) or the surface active sites. This process is usually a multi-electron and multi-step process involving a cascade of reactions, electron and proton transfer, C-O bond breaking, C-H/C-C bond formation and a multitude of products [81-86]. In most cases, the CRC should be loaded on the surface of semiconductors to achieve a highly efficient and selective reduction of CO₂ to specific products. During the photocatalytic reduction of CO₂, the formation of stable products requires at least two electrons, because some of products or intermediates are unstable or difficult to detect and quantify. Accordingly, the multistep mechanism is very complex. Any efficient strategy that promotes CO₂ reduction kinetics should be considered to be a possible way to boost the efficiency, such as developing mesoporous photocatalysts and loading CRC.

Meanwhile, the step (5) will also occur when the photogenerated holes reach the surface. The step (5) represents the electrocatalytic oxidation of water by the photogenerated holes trapped in the water oxidation co-catalysts (WOC) or the surface active sites. Improving water oxidation can promote the separation of photo-generated charge carriers on the surface of semiconductors, thus leading to the enhancement in activity for CO₂ photoreduction. In addition, the process (6), surface charge recombination, will occur if there are no enough active sites or co-catalysts on the surface of semiconductors. Apparently, the surface charge recombination should also be avoided because it is also ineffective for photocatalytic CO₂ reduction process, whereas the surface trapping should be enhanced by improving surface properties of the photocatalysts such as surface reaction sites, surface states and morphology.

In addition, the processes (7) and (8) in Fig. 2 represent the electrocatalytic H_2 evolution by trapped photo-generated electrons in CO₂ reduction co-catalysts and the electrocatalytic oxidation of reduction products by water oxidation co-catalysts, respectively. In the processes (7), the H_2 evolution will greatly decrease the utilization rates of photo-generated electrons for CO₂ reduction. In the processes (8), the oxidation of CO₂ reduction products by photo-generated holes is harmful for both water oxidation and CO₂ reduction. Clearly, these two processes are the unfavorable ones, because they could significantly reduce the quantum yield of photocatalysts for CO₂ photoreduction. Thus, to design highly efficient photocatalysts for photocatalytic CO_2 reduction, these factors should be comprehensively considered and the effective strategies should also be developed to avoid or decrease these unfavorable processes.

Mechanism and kinetics of photocatalytic CO, reduction

One famous mechanism based on the formation of CO_{2}^{-} radical anion was first suggested by Anpo et al. [86]. In terms of this mechanism, the adsorbed CO₂ molecule was activated by a one-electron reduction, leading to the formation of surface-bound CO₂ radical anion. Then, the CO₂ radical anion was selectively reduced to CO (or HCOOH), CH₂OH, CH₃OH and CH₄ by the photo-generated electrons, $H^{\scriptscriptstyle +},$ hydrogen radical (H^{\bullet}) and OH radical (OH^{\bullet}) [5,17,83-85]. Although the COO₂ radicals and CO₂ reduction intermediates during the processes of CO₂ reduction have been identified by different spectroscopy [86-88], the one-electron reduction of CO₂ is thermodynamically unfavorable due to the highly negative electrochemical reduction potential (-1.9 V vs. NHE) of the anion radical CO₂ and the low CB potential of semiconductors. Therefore, most favorable reaction pathways consisting of a multiple electron transfer have been also reported.

The two-electron, two-proton reaction pathway is one typical multiple-electron reaction mechanism, which was first proposed by Inoue and co-workers [5] based on small amounts of formic acid, formaldehyde, methyl alcohol, and methane produced by photoreduction of CO_2 . A multi-step reduction process of conversion of CO_2 to methane can be described using Equation (7).

$$CO_{2} \xrightarrow{+2e^{-}} HCO_{2}H \xrightarrow{+2e^{-}} H_{2}CO \xrightarrow{+2e^{-}} H_{2}CO \xrightarrow{+2e^{-}} H_{2}H^{+} \rightarrow CH_{3}OH \xrightarrow{+2e^{-}} CH_{4}, \qquad (7)$$

$$CO_2 + 2e^- + H^+ \rightarrow HCOO^-.$$
(8)

A similar route involving surface formate species as the primary intermediate has been also proposed by Wu et al. [89] on the basis of *in-situ* IR spectroscopic studies. The bicarbonate, carbonate, formate, formaldehyde and methoxy species on TiO₂ surface were observed from IR absorption bands. A concerted two-electron and one-proton transfer (see Equation (8)) to adsorbed CO_2 molecules on the TiO₂ surface was also demonstrated by Dimitrijevic et al. [90] using low temperature electron paramagnetic resonance (EPR) measurements. The formation of H atoms and OH. radicals in addition to methyl (•CH₂) and methoxy (•CH₂O) radicals on the surface was also observed by the electron spin resonance (ESR) results. Then the reaction of methoxyl radical with H₂O can lead to the formation of methanol. However, it appears clearly that methanol or formic acid as intermediates in the formation of hydrocarbons on Ti-SBA-15 is impossible because added methanol or formic acid does not enhance the concentration of hydrocarbons. While, added formaldehyde can increase the photoconversion of CO₂ to hydrocarbon products [91]. Meanwhile, Frei and coworkers [92,93] demonstrated that formic acid is the primary 2-electron reduction product of CO₂ at the excited Ti centers of Ti silicalite molecular sieve using methanol as electron donor, while CO is the single-photon, 2-electron-transfer reduction product of CO₂ at framework Ti centers with H₂O acting as an electron donor. Moreover, methyl formate was also mainly produced for photocatalytic reduction of CO₂ over some other photocatalysts (such as Bi₂S₃ [94], CuO-TiO₂ [95], Ni-doped ZnS [96] and Ag Loaded SrTiO₃ [49]) in methanol solution. Therefore, the two-electron, two-proton reaction steps from methanol or formic acid to hydrocarbons on most semiconductors seem to be impossible in many systems.

A hypothesis, the CO would react with atomic hydrogen to form hydrocarbons, was also proposed by Varghese *et al.* [97]. The possible reactions are seen in Equation (9–14):

$$H_2O + 2h^+ \rightarrow 1/2O_2 + 2H^+,$$
 (9)

$$H_2O + h^+ \rightarrow {}^{\bullet}OH + H^+, \qquad (10)$$

$$\mathrm{H}^{+} + \mathrm{e}^{-} \rightarrow \mathrm{H}^{\bullet}, \qquad (11)$$

$$\mathrm{H}^{\bullet} + \mathrm{H}^{\bullet} \to \mathrm{H}_{2}, \tag{12}$$

$$2CO_2 + 4e^- \rightarrow 2CO + O_2, \tag{13}$$

$$CO + 6e^{-} + 6H^{+} \rightarrow CH_{4} + H_{2}O.$$
 (14)

However, the validity of this hypothesis need to be further verified. Meanwhile, another reaction mechanism through the formation of CO in the initial stages followed by its conversion to formaldehyde, then to other hydrocarbon products was proposed by Yang *et al.* [91]. Importantly, it also showed that formaldehyde is extremely reactive over Ti-SBA-15 and that the formation of C_2 and $>C_2$ hydrocarbons could be also explained through this mechanism.

Recently, a mechanism involving dimerization of surface C, species was proposed as a possible route for the formation of C₂ hydrocarbon products [98,99]. Interestingly, Shkrob et al. [87] recently reported a glyoxal cycle for CO₂ fixation. In addition to methane, this cycle generates complicated organic molecules, such as glycolaldehyde, acetaldehyde, and methylformate, which were observed in product analyses. This cycle can be regarded as one of the simplest realizations of multistep, photosynthetic fixation of atmospheric carbon in prebiotic nature [87]. Therefore, the glyoxal cycle accounts for several known byproducts, such as methanol, formate, formaldehyde, acetaldehyde, and methylformate, which provides a new idea to study the mechanisms for photocatalytic reduction of CO₂. Thus, it is clear that the products for CO₂ photoreduction in aqueous medium exist in both the gas and liquid phases. However, most researchers only measured one or two of reduction

products in liquid phase and ignored the analysis of products in gas phase, which was not beneficial for a detailed study on the mechanism of CO₂ photoreduction and the selectivity of products. Therefore, in addition to the measurements of products in liquid phase, it is also important to analyze the reduction products in the gas for CO₂ photoreduction in aqueous medium [83,100,101]. Special attention should also be focused on the photocatalytic reduction of CO₂ to C_x ($x \ge 2$) organic compounds, which is also promising and has received far less attention than analogous systems leading to C₁ products [84,98,99].

Furthermore, the kinetic equations based on different mechanisms were developed for modeling the photocatalytic reduction of CO₂. A Langmuir–Hinshelwood type kinetic equation was first developed for modeling the photocatalytic reduction of carbonate by the UV/TiO₂ process in aqueous solution [102]. The results indicate that the photocatalytic reduction rate of carbonate is adsorption-controlled [102]. Meanwhile, a one-site Langmuir–Hinshewood (L–H) kinetic model was further applied to simulate the photoreduction rate of CO₂ to CO (or H₂) and CH₄ using H₂O over TiO₂ [102–105]. In addition, Anpo's mechanism, wherein CO is proposed as the primary intermediate, was well supported by this kinetic model [102–104].

In summary, the complex photocatalytic processes and kinetics of CO₂ reduction on semiconductors lead to a very low efficiency of CO₂ photoreduction. It is clear that the reduction potentials of CO₂ to CH₃OH and CH₄ products are thermodynamically more feasible than that required to reduce protons to H₂. However, the kinetics of CO₂ reduction is unfavorable due to the multi-electron reduction processes. At this point, the kinetic challenges are great, and thus the improvements of kinetics of CO₂ reduction play important roles in enhancing the overall efficiency. Meanwhile, the complex photocatalytic processes, including excitation, transport, separation, adsorption and activation of CO₂, CO₂ reduction kinetics and water oxidation have also important impacts on the overall efficiency of CO₂ reduction. Therefore, the control of photocatalytic processes and kinetics of CO₂ reduction is rather critical to enhance the overall efficiency, which is strongly dependent on the bulk and surface properties of photocatalysts and can be improved by rational design and fabrication of photocatalysts [16,106,107].

All factors influencing the efficiency of photocatalytic CO_2 reduction, including charge excitation and transport, adsorption and activation of CO_2 , CO_2 reduction kinetics and undesirable reaction are summarized in Fig. 4. As shown in Fig. 4, to achieve a high efficiency and selectivity, the corresponding engineering strategies including increased visible-light excitation, improved charge transfer and separation, enhanced adsorption and activation of



Figure 4 Factors influencing photocatalytic efficiency and corresponding design strategies for highly efficient photocatalysts used in the photocatalytic reduction of CO₂.

 CO_2 , accelerated CO_2 reduction kinetics and suppressed undesirable reaction, can be used to manage photo-generated charges and enhance the overall efficiency, which will be discussed in detail in the following sections.

STRATEGIES FOR DESIGN AND FABRICATION OF PHOTOCATALYSTS FOR CO, REDUCTION

Increased visible-light excitation

As described above, the process (1) in Fig. 2 is strongly dependent on the band gap of a semiconductor photocatalyst. The low visible light absorption is a key factor affecting the photocatalytic efficiency of many wide band gap semiconductors. This is because the wide band gap makes semiconductors active only in ultraviolet region of the solar spectrum (about a 4% of the total sunlight energy), and limits utilization of light in visible region (about 48% of the total sunlight energy). Therefore, many efforts have been made to search for the visible-light-driven photocatalysts. One typical strategy is to exploit new single-phase visible-light-driven photocatalysts (e.g., CdS [60,63,108], C₂N₄ [69,109,110], WO₂ [111,112], CaFe₂O₄ [113,114], La-CoO₂ [115], BiVO₄ [116,117], Bi₂WO₄ [118,119], Fe₂V₄O₁₃ [120] and $InTaO_{4}$ [121–124]), which have proven to be active for photocatalytic reduction of CO₂ in visible region. The other typical strategy is to make the wide band gap semiconductors active in visible region through a suitable modification. As shown in Fig. 5, there are generally five strategies to develop visible-light-driven photocatalysts from wide band gap semiconductors: impurity doping, introduction of structural defects, sensitization, surface plasmon resonance (SPR) effect and solid solution, all of which have been applied in the fields of photocatalytic reduction of $\rm CO_2$.

Impurity doping

The first strategy is to tune the electronic properties and visible-light response of semiconductor nanocrystals via an impurity doping, which can introduce a localized electronic states (LS) into the band gap of a wide band gap semiconductor, thus achieving a two-step photoexcitation by the low-energy visible-light photons [125]. On the one hand, nonmetal ion doping such as nitrogen and iodine can lead to an obvious red shift in optical response and an significant enhancement in the visible light activity of wide band gap semiconductors, although there is still a lively debates about the causes for red-shifts of the absorption edges [126]. For example, Li et al. [127] reported that nitrogen-doped mesoporous TiO, samples displayed good visible-light absorption and enhanced activity for CO₂ photoreduction to methane by water in gas phase under visible-light irradiation. It was believed that the mesoporous structure and N-doping were responsible for inhibiting the recombination of photogenerated electrons and holes and improving visible light absorption, respectively, thus leading to an improved photoactivity. The mesoporous nitrogen doped Ta₂O₅ exhibits excellent photocatalytic activity for hydrogen evolution and CO₂ reduction (modified with ruthenium-complex) under visible-light irradiation due to their larger surface area, enhanced visible light absorption and controlled morphology [128]. Similar results were observed for nitrogen-doped InTaO, photocatalysts, which showed a 2-fold increase in the yield of methanol compared to the undoped one [124]. In addition to N-doped TiO₂, iodine-doped TiO₂ (I-TiO₂) nanoporticles (NPs) demonstrated significant enhancements in



Figure 5 Typical strategies for increasing visible-light excitation.

 CO_2 photoreduction to CO compared with undoped TiO₂ under both visible and UV-vis irradiations. The possible reasons are the synergistic effects of slightly increased surface area, enhanced visible light absorption, and improved charge separation owing to the iodine doping [129]. The further enhancements in CO₂ photoreduction to CO were also achieved by copper and iodine co-modified TiO₂ NPs (Cu-I-TiO₂) [130].

On the other hand, metal ion doping can also create the impurity levels in the forbidden band of wide-band gap semiconductors, which can also enhance their absorption for visible light. Furthermore, the doped metal ion can also perform as electron traps and active sites for highly selective CO₂ photoreduction. It is well known that TiO₂ doped with copper shows good selectivity for CH₃OH from the reduction of CO₂, which will be discussed below [55,131– 133]. Besides Cu, other metal-ion doping such as Ce [134], Mn [135], Ru [83,136], Ni [96,137], In [105], Fe [89], Ag [89,132], Au [136,138], Mg [139] and their co-doping with Cu or N have also been reported for photocatalytic reduction of CO₂ and exhibit enhanced photocatalytic activities for the reduction of CO₂. Generally, a metal cation doping of TiO₂ not only creates oxygen vacancies and new active sites for the reaction, but also introduces localized mid-gap states which contribute to charge separation and the absorption of visible light [39]. In addition, self-doped Ti³⁺ is also an effective strategy to enhance the photocatalytic activity of TiO₂ under visible light, which deserves more attention in photocatalytic reduction of CO₂ [140]. It should be noted that the excess amount of dopants as recombination centers can also lead to a greatly decreased activity for CO₂ photoreduction. Thus, it is rather important to optimize dopant concentration to achieve the highest activity for CO₂ photoreduction.

Introduction of structural defects

The second effective strategy to enhance the visible light activity of wide band gap photocatalysts is to introduce defects (such as oxygen vacancies) on the surface of semiconductor substrates, which can effectively tailor their electronic structure, thus leading to an enhanced visible light absorption, improved charge transport and separation and increased active sites for adsorption and reduction of CO₂ [141,142]. The previous results showed that the oxygen vacancies on the surface of semiconductors play important roles in the photocatalytic reduction of CO₂ under visible light. Liu et al. [143] first systematically studied the photoreduction of CO₂ with H₂O on defect-free and defective TiO₂ anatase, rutile, and brookite nanocrystals, respectively. It was found that the activity of the defective brookite (He-pretreated samples) was enhanced by a factor of 10.3 for CO production and 8.2 for CH₄ produc-

tion. The photocatalytic activities for CO₂ reduction over un-pretreated samples follow the order anatase > brookite > rutile. The enhancement in the production of CO and CH₄ from CO₂ photoreduction was primarily attributed to the creation of oxygen vacancies and Ti³⁺ on the surface [143]. A H₂-pretreated Cu/TiO₂ exhibited a 10-fold and 189-fold enhancement in the photoreduction of CO₂ to CO and CH₄, respectively [144]. The existence of Cu^+/Cu^0 couples and the formation of surface defect sites (such as oxygen vacancies and Ti³⁺) in the H₂-pretreated Cu/TiO₂ can greatly improve CO, adsorption, charge transfer and trapping at the active sites of the adsorbed CO₂ thus leading to the significant enhancement in the activity for CO₂ production [144]. The existence of oxide vacancies on the surface of Bi₆Mo₂O₁₅ sub-microwires enhanced the photocatalytic activity toward the photoreduction of CO₂ into CH₄ through capturing photo-generated electrons at the surface [145]. Recently, it was also reported that a highly selective photoreduction of CO₂ to CO was achieved over defective CeO, nanorods under ambient conditions (CO,, 400 ppm) due to the synergistic effects of local strain and surface oxygen vacancies [146]. More interestingly, the ultrathin $W_{18}O_{49}$ nanowires with diameters below 1 nm also exhibited very high activity for CO₂ photoreduction to methane which was several hundred times higher than that of commercial WO₃ due to the presence of a large number of oxygen vacancies [141].

Similar results were obtained in the metal sulfide semiconductors. The quantized ZnS crystallites with low density of surface defects are indispensable for effective CO_2 reduction owing to stabilization of the electron-hole pair against recombination and elimination of electron deactivation by surface traps [36]. The surface sulfur vacancies on CdS-DMF surface formed by reaction with the excess Cd^{2+} added in the systems can act as adsorptive sites for the CO_2 molecule and increase the photocatalytic activity for reduction of CO_2 to CO [58]. Meanwhile, the surface sulfur vacancies on the surface of ZnS-DMF(ClO_4) formed by addition of excess Zn^{2+} result in the change in the product distribution without losing photocatalytic activity [46].

In addition, the location of defects and the relative concentration ratio of bulk defects to surface defects in photocatalysts have also profound effects on their electronic properties and photocatalytic activities [147,148]. Therefore, the density and location of defects should be paid more attention for the application of CO_2 photoreduction in future studies.

Sensitization

The third effective strategy is to sensitize wide band gap semiconductors using dye and quantum dots (QDs) with visible-light activity. Clearly, the sensitizers as the absorb-

ing species not only improve the sunlight harvesting due to their low band gap, but also inhibit the electron-hole recombination owing to the efficient charge separation by the semiconductor/sensitizer interface. Recently, dye-sensitized TiO₂ has also been reported in the photoreduction of CO₂ to fuels with H₂O. The formation rate of formic acid, methanol and formaldehyde on zinc-phthalocyanine (ZnPc) or CoPc sensitized TiO₂ are much higher than those of TiO₂ and physically absorbed CoPc(or ZnPc)/TiO₂ [149–151]. Recently, it was found that the graphene oxide (GO)-immobilized CoPc photocatalyst exhibited higher photocatalytic activity and selectivity for the photocatalytic reduction of CO₂ to methanol by using water as a solvent and triethylamine as the sacrificial donor. Importantly, the photocatalyst also showed good photostability during the reaction [152]. A new copper(I) dye-sensitized TiO_{2}^{-} based photocatalyst exhibits impressive effectiveness for the selective photoreduction of CO₂ to CH₄ under visible light [153]. Furthermore, full absorption of visible light of N_3 -dye along with efficient charge transfer in N_3 dye-TiO₂ system gives rise to the superior photoreduction of the resulting dye-adsorbed catalyst [154]. However, the improvement of efficiency and long-term stability of dye-sensitized photocatalysts is still a great challenge for their practical applications. Meanwhile, a series of CdSe QD-sensitized Pt/TiO₂ hetero-structures yield 48 ppm g⁻¹ h⁻¹ of CH₄ and 3.3 ppm g^{-1} h⁻¹ of CH₃OH (vapor) for photocatalytic reduction of CO₂ in the presence of H₂O under visible light irradiation ($\lambda > 420$ nm) [155]. The PbS QDs enhance CO, photoreduction rates over TiO₂ by a factor of 5 in comparison with un-sensitized photocatalysts under broad band illumination (UV-NIR) [156]. The activity of CdS (or Bi₂S₂) QD-sensitized TiO₂ nanotubes for photocatalytic reduction of CO₂ to CH₂OH was about 1.6 (or 2.2) times higher than that of TiO, nanotubes due to enhanced visible-light absorption and improved charge separation [63]. It was also reported that 23.2% AgBr sensitized TiO, exhibited relatively high activity and selectivity for methane and methanol production under visible light irradiation. The highly efficient photocatalytic activity of AgBr/TiO₂ is attributed to its strong absorption in the visible-light region and the improved transfer and separation of photo-excited electrons and holes [157]. Moreover, a new composite photocatalyst based on overlapping energy states of TiO₂ and copper indium sulfide (CIS) QDs was exploited, exhibiting the highest selectivity for ethane (> 70%) and a higher efficiency of converting ultraviolet radiation into fuels (4.3%) using concentrated sunlight (> 4 Sun illumination) [158]. In addition, a new class of green QDs, silicon and carbon QDs [159-162], were expected to apply in designing the QD-sensitized photocatalysts for photocatalytic reduction of CO₂.

Surface plasmon resonance (SPR) effect

The forth effective strategy is to use the localized surface plasmon resonance (SPR) effect, which refers to the collective oscillation of the conduction electrons in noble metal NPs (i.e., Au and Ag) under visible light irradiation [163]. Thus, the plasmonic noble metal NPS can serve as an alternative type of sensitizer to enhance the visible-light absorption of photocatalysts due to SPR effects. In recent years, the interesting SPR effects have also been reported in the photoreduction of CO₂ under visible light irradiation [138,164,165]. For instance, Zhang et al. [164] reported that the co-decoration of Au and Pt NPs with sizes of 5-12 nm on TiO₂ nanofibers could remarkably enhance their photocatalytic activity and selectivity for CO₂ reduction to CH₄. It was believed that the synergy of surface electron trapping of Pt and SPR of Au NPs greatly improve the charge separation of photoexcited TiO₂ (as illustrated in Fig. 6), thus leading to a significant enhancement in the activity of photocatalytic CO2 reduction [164]. A 24-fold enhancement in activity and selectivity for photoreduction of CO₂ to CH₄ with water vapor was also observed because of the intense local electromagnetic fields created by the surface plasmons of Au NPs on TiO₂ [138].

Besides good selectivity of plasmonic Au for CH_4 production, the plasmonic Ag NPs have also attracted much attention due to their excellent selectivity for methanol in liquid phase system. The methanol yields of CO₂ photore-duction over the plasmonic-shaped AgCl:Ag and AgBr:Ag are 188.68 and 108.696 µmol g⁻¹, under visible-light irradiation, respectively, due to the SPR of Ag NPs [166]. The 2.5% Ag/TiO₂ exhibited the best activity for photocatalytic reduction of CO₂ to methanol due to the SPR effects, which was 9.4 times higher than that of pure TiO₂ [167]. Furthermore, the CH₄ yield over plasmonic Ag NPs/TiO₂ nanorods was almost 5 times higher than that of undecorated



Figure 6 Schematic diagram of photocatalytic process for CO₂ reduction on the Au/Pt/TiO, nanofibers.

 TiO_2 nanorods in gas phase system, which was correlated with the SPR effect and structure of TiO₂ nanorods [168].

In addition, it was reported that the Cu-TiO₂ nanorod films showed about twice the rate observed with pure titania films due to better separation of photogenerated electrons and holes and mild SPR effects [169]. Since Au and Ag are noble metals, in future studies, more attention should be placed on plasmonic Cu NPs or alloy plasmonic NPs with better selectivity for CO₂ reduction [170–173].

Solid solution

The fifth effective strategy is solid solution, which can be formed through adding a narrow band gap semiconductor (for example, Ag₂O, Cu₂O, Fe₂O₃, Cr₂O₃, CuO and so on) into a wide band gap semiconductor. Both the band gap and position can be continuously adjusted by varying the ratio of the compositions of the narrow and the wide band gap semiconductors in the solid solution. Thus, the electronic structures and the photocatalytic performances of a semiconductor can be efficiently optimized. Recently, many researchers have revealed that solid solutions exhibited relatively high activity and selectivity for photocatalytic reduction CO₂ to methanol, methane or ethanol under visible light. The multicomponent metal oxides (e.g., CuGa, Fe₂O₂ [174]), metal sulfides (e.g., solid solutions of ZnS-CdS microcrystals [45] and $Cu_{v}Ag_{v}In_{z}Zn_{k}S_{m}$ [175]) and oxynitrides (e.g., zinc germanium oxynitride [176]) exhibited high activity for the photoreduction of CO₂ under visible light irradiation. For instance, the yellow Zn_{1,7}GeN_{1,8}O solid solution, synthesized by the nitridation of the wideband-gap Zn₂GeO₄, exhibits high activity for photocatalytic reduction CO₂ into CH₄ with H₂O at room temperature under visible light irradiation. The reported photonic yield for $Zn_{12}GeN_{18}O$ at 420 nm was 0.024% [177]. The further research showed that CH₄ evolution over mesoporous zinc germanium oxynitride nitrided over a 10-h period is about 26.8 ppm g⁻¹, which is even higher than that of commercial nitrogen-doped TiO₂ (22.1 ppm g⁻¹) under visible light [176]. The $(Ga_{1-x}Zn_x)(N_{1-x}O_x)$ solid solutions with a band gap of 2.2–2.7 eV exhibited a high visible-light activity for photocatalytic conversion of CO, and H₂O into hydrocarbon fuel [178]. A high activity in converting CO₂ and H₂O into CH₄ and O₂ was achieved over zinc gallogermanate solid solution synthesized by introducing Zn₂GeO₄ into ZnGa₂O₄, due to improved hole mobility, enhanced water oxidation ability and effectively narrowed band gap [179]. Importantly, this zinc gallogermanate solid was prepared by a hydrothermal ion exchange reaction, which is beneficial to its surface area enhancement.

So far, most of these oxides are synthesized by high temperature solid state reaction with very low surface area. The preparation of high surface area photocatalysts with mesoporous structures is still a great challenge. Thus, to further boost the photocatalytic activities, it is highly desired to prepare mesoporous photocatalysts with high crystallinity by soft chemistry routes.

Promoted charge transfer/separation

As mentioned above, the process (3) and (6) account for the bulk and surface recombination of photo-generated electron-hole pairs, respectively. Obviously, the above two processes are detrimental to photocatalytic efficiency enhancement of a semiconductor photocatalyst due to the decreased utilization rate of carriers for desired photoreactions. Meanwhile, the process (2) represents the charge transfer to the surface without recombination, which is dependent on the crystal structure, crystallinity and particle size of a semiconductor photocatalyst. Thus, the issue of photo-generated charge transfer and separation has become another key factor strongly affecting the efficiency of photocatalysis process. So far, a number of strategies have been employed to promote the transfer and separation of the photo-induced electrons and holes. Here, three dominant strategies including nanostructured photocatalysts, semiconductor heterojunctions and semiconductor/nano-carbon heterojunctions will be discussed in detail.

Nanostructured photocatalysts

An efficient strategy for accelerating the transfer and separation of the photo-induced carriers is to construct nanostructured photocatalysts. As is known, the nano-architectures (e.g., physical dimensions, sizes, shapes and porous structures) of semiconductors have profound impacts on their photocatalytic performances. Generally, semiconductor nanomaterials have several advantages over their bulk counterparts for solar fuel generation due to the following reasons: higher surface-to-volume ratio, higher optical absorption, shorter charge migration length, stronger redox power and tunable electronic structure [180]. Furthermore, the photo-generated charges can also be efficiently separated to avoid bulk/surface charge recombination and transfer to the separated active sites on the surface of the photocatalysts. The relevant nanostructures including 0D nanocrystals, 1D nanowires/rods, 2D nanosheets and 3D hierarchical architectures have been widely investigated, which will also be discussed in detail in this section.

First, the construction of 0D nanocrystal photocatalysts has also become a widely accepted strategy to enhance the photocatalytic activities for CO_2 reduction because of the nanosized and quantum size effects. Kocí *et al.* [100] studied the photoreduction of CO_2 by water upon pure TiO₂ anatase particles with a crystallite diameters ranging from 4.5 to 29 nm. Methane and methanol were the main reduction products. The optimum particle size corresponding to the highest yields of both products was 14 nm. The observed optimum particle size is a result of competing effects of specific surface area, charge-carrier dynamics and light absorption efficiency [100]. Liu et al. [181] studied the photocatalytic reduction of CO₂ in various kinds of solvents using TiO₂ nanocrystals embedded in SiO₂ (Q-TiO₂/ SiO₂) with an average diameter of 5.3 nm. Apart from TiO₂ [143,181–183], other semiconductor NPs such as ZnS [36,46], CdS [62,184] and silicon [185] nanocrystals have also been found to exhibit better photocatalytic activities for the reduction of CO₂. Consequently, with regard to the application of nanocrystalline semiconductors, it is important to obtain the optimal particle size for maximizing their photocatalytic efficiency for CO₂ photoreduction. In addition, to prevent agglomeration of these particles, they should be capped with polymers or anchored on a stable support [2].

Second, there are many reports about the application of 1D nanostructures in photocatalytic reduction of CO₂ due to the shortened distance for charges to diffuse to the semiconductor/electrolyte interface and improved transport properties of charge carriers. TiO, nanotubes [63,97,186-191], nanofibers [192] and nanorods [168,169,193] exhibited a much better photocatalytic activity for CO₂ reduction than P25 or TiO, NPs. For instance, Fu et al. [192] demonstrated that the TiO₂ nanofibers with a 2-h solvothermal treatment exhibited the highest activity for photocatalytic reduction of CO_2 to CH_4 , which was about 6 and 25 times higher than those of TiO₂ nanofibers without solvothermal treatment and P25, respectively, due to the enhanced CO₂ adsorption capacity and the improved charge separation. Moreover, NaNbO₃ nanowires [194], Zn₂ GeO₄ nanoribbons [195] and nanorods [196] synthesized using a hydrothermal/solvothermal route showed much better photocatalytic activity for the conversion of CO₂ to CO or CH₄ than the corresponding samples prepared by a high-temperature solid state reaction. In addition, the surface area value and

the activity of HNb_3O_8 nanobelts prepared by hydrothermal synthesis increased six and twenty times, respectively, in comparison with those of HNb_3O_8 particles prepared by solid state reaction [197].

Third, there is an increasing interest in developing 2D nanosheet-based semiconductors with dominant high-energy facets for the application in photocatalytic reduction of CO₂ because of their facet-dependent properties. Among them, TiO_2 nanosheets with exposed (100), (010), (101) or (001) facets were the most widely investigated photocatalysts in this field [172,198-201]. For instance, the anatase TiO₂ ultrathin nanosheets with 95% exposed (100) facets showed a 5 times higher photocatalytic activity for reduction of CO_2 to CH_4 than TiO_2 cuboids with 53% exposed (100) facets [198]. The anatase TiO₂ single crystals and mesocrystals with dominant (101) facets exhibited a much superior activity towards CH₄ generation from photoreduction of CO2, in comparison with solid crystals [199]. The anatase TiO₂ (010) facets demonstrated a higher photocatalytic reduction efficiency of CO₂ to CH₄ than (001) facets due to its larger CO₂ adsorbed amount and longer charge lifetime [200]. More interestingly, Yu and coworkers [201] reported that the highest activity of TiO₂ nanosheet for photoreduction of CO₂ to CH₄ can be achieved at an optimal ratio of the exposed (101) and (001) facets (45:55). This is attributed to the synergistic effect of an electron overflow and surface heterojunction between the co-exposed (101) and (001) facets of anatase (Fig. 7). Importantly, the concept of surface heterojunction was first proposed in terms of the density functional theory (DFT) calculations, which may provide a new strategy for designing sufficiently efficient photocatalysts [201].

In addition, $ZnGa_2O_4$ nanocube with the exposed (100) or (110) facets [202,203], Bi_2WO_6 square nanoplates with the exposed (001) surface [118], BiOCl nanoplates with oxygen vacancies [204], nanoplate-textured Zn_2SnO_4 with the exposed (100) surface [205] and WO₃ nanosheets with



Figure 7 An overflow effect and hetero-facet junction between (101) and (001) facets in anatase.

the exposed (001) surface [111] were successively reported. These nanoplate/nanosheet photocatalysts exhibit enhanced performance for photocatalytic reduction of CO_2 into CH_4 in the presence of water vapor due to the improved separation of photo-generated electron and hole pairs. However, so far, the photocatalytic selectivity on different facets of various semiconductors has not been studied systemically for the photoreduction of CO_2 . Thus, it is still very interesting to identify optimal ratio and the selectivity of different facets for CO_2 photoreduction. In addition, much attention should be also paid to the simple and efficient methods to prepare nanosheets such as liquid exfoliation of layered materials [206].

Finally, it is known that 3D hierarchical semiconductor architectures assembled by nanoscaled building blocks generally display unique properties (such as the optical, electronic, and photocatalytic performances), which are distinguished from those of the mono-morphological structures. Thus, the 3D hierarchical semiconductor architectures have been widely applied in the CO₂ photoreduction due to their increased specific areas and adsorption of CO₂, as well as improved light harvesting and interfacial charge separation [94,119,207]. For example, Bi, WO, hierarchical microspheres with hollow interiors synthesized via a facile anion exchange method display an excellent photoactivity for reduction of CO₂ to methanol (32.6 μ mol g⁻¹), which is 25.5 times higher than that of Bi₂WO₆ prepared by solid state reaction (1.28 μ mol g⁻¹) under the same conditions [119]. The significantly enhanced activity can be attributed to the improved surface area and high CO₂ adsorption capacity. Bi₂S₃ microspheres also showed the higher activity for photocatalytic reduction of CO₂ to methyl formate in methanol due to their special hierarchical structure, good permeability and high light-harvesting capacity, as compared with Bi_2S_3 NPs [94].

Semiconductor heterojunctions

Coupling semiconductors has also turned out to be another effective design strategy for improving their photocatalytic activity because better photo-generated charge transfer and separation can be achieved in the interface region between two different phases (or semiconductors) in close contact. In coupled semiconductors, the electric-field-assisted charge transport from one particle to the other via interfaces between the semiconductors with matching band potentials can be achieved, which can greatly improve the electron-hole separation, increase the lifetime of the charge carrier, and enhance the interfacial charge transfer efficiency to adsorbed substrate. Constructing heterophase junctions (homojunctions) and heterojunctions are two main strategies used in designing the coupled photocatalysts.

So far, TiO₂-based heterophase junction has been well

developed in the photocatalytic reduction of CO₂. The bicrystalline anatase-brookite composite displays the strongest absorption in the visible-light region and on which the highest CH₃OH yield from CO₂ photoreduction is 3.4 times higher than that on P25 or anatase catalyst in an aqueous system due to its unique electrical band structures and efficient transfer of electrons from brookite to anatase [208]. Similarly, the bicrystalline mixture with a composition of 75% anatase and 25% brookite also showed the highest photocatalytic activity for CO₂ photoreduction to CO and CH₄ in the presence of water vapor, as compared with pure anatase, brookite, and P25 [209]. The rutile TiO, nanoparticle modified anatase TiO, nanorods showed high photocatalytic activity for CO₂ reduction to CH₄, which was almost two times higher than that of pure anatase TiO₂ nanorods [193]. A sputtered mixed-phase film (70% anatase, 30% rutile) deposited at low angle exhibited a strong red shift and the highest methane yield from the photoreduction of CO₂ compared to TiO₂ fabricated under other sputtering conditions and commercial standard Degussa P25 under UV irradiation [210]. Li et al. [211] modified the commercial anatase TiO₂ with the rutile by a low-temperature hydrothermal method and found that mixed-phase TiO₂ nanocomposites sintered in air at 773 K exhibited a much greater rate of methane formation than Degussa P25. In addition, compared with cubic and orthorhombic NaNbO₃, the activity of mixed-phase NaNbO₃ is enhanced by 30% and 200% in reducing CO₂ into CH₄, respectively, due to improved the charge separation by surface-junctions (Fig. 8) [212].

Since the wide band gap of TiO_2 -based heterophase junctions limits their practical applications under visible light irradiation, the design of visible-light-driven photocatalysts with heterophase junctions has attracted much attention in recent years. Many visible-light-driven homojunctions (i.e., one-dimensional $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ nanorod



Figure 8 Proposed electron transfer in NaNbO₃-based junctions and the surface photocatalytic reactions.

homojunctions [213], a tungsten-doped BiVO₄ homojunctions [214], alpha-/gamma-Bi₂O₃ [215] homojunctions, and p–n Cu₂O [216] homojunctions) have been reported recently, and all of them exhibited much higher photocatalytic activity or photovoltaic efficiency than the pure phase. However, there have been no reports about the application of visible-light-driven homojunctions in the CO₂ photocatalytic reduction. Therefore, it is of great interest and worth noticing at this point that the heterophase junctions based on visible-light-driven semiconductors might have potential applications in the CO₂ photoreduction under visible light irradiation.

Up to now, there are also many hetero-structured semiconductor systems applied in the fields of photochemical reduction of CO₂. Among them, TiO₂-based semiconductor composites have been extensively studied. The ordered mesoporous CeO2-TiO2 composites exhibited excellent photocatalytic activity in the reduction of CO₂ with H₂O to CH₄ and CO under simulated solar irradiation, which were about ten and three times higher than that of commercial P25, respectively, due to the enhanced separation of photogenerated electrons and holes [217]. TiO₂/ZnO composites showed much higher performance in the photoreduction of CO_2 into CH_4 , which was about six times higher than that of commercial P25. The enhancement in CO₂ reduction performance of the hybrid TiO₂/ZnO composites was probably resulted from a faster diffusion transport of photogenerated electrons, decrease of electron-hole recombination rate and increase of specific surface areas [41]. 1.0 wt% CuO-loaded TiO₂ showed the highest photocatalytic reduction activity of CO₂ to methyl formate in methanol solution, which was about two times higher than that of TiO₂ [95]. The methane production rate over hetero-structured CuO-TiO_{2-x}N_x hollow nanocubes was 2.5 times faster than that of Degussa P25 TiO₂ when measured under the same conditions [218]. In addition, the CH₄ production yield of optimal In_2O_3 -g-C₃N₄ hybrids with 10 wt% In_2O_3 (76.7 ppm) is three to four times higher than that of pure $g-C_3N_4$ or In_2O_3 , due to effective charge separation and longer lifetime of the photogenerated charge carriers [219]. The hetero-structured Bi₂S₃/CdS [60] and Cu₂O/SiC [52] photocatalysts have been used to photoreduction of CO₂ to CH,OH under visible-light irradiation. In contrast to the single semiconductor, the hetero-structured photocatalysts showed a 2- or 3-fold enhancement in the photoactivity for CO₂ reduction. It can be mainly ascribed to the improved charge separation. However, challenges still remain in the further promotion of electron transfer between two semiconductors. In future studies, it is of great interest to construct the core/shell structured [220-222] and two-dimensional layered heterojunction systems [223] because of the larger contact area and better surface passivation effects.

Semiconductor/nano-carbon heterojunctions

Another strategy for improving charge separation is coupling semiconductor with nano-carbon materials, which can greatly enhance the collection and transfer of photogenerated electrons and reduce the charge recombination due to the excellent properties of nano-carbon materials. Among carbon-based supports, carbon nanotubes (CNT) and graphene are excellent candidates due to their outstanding properties. CNT possesses many unique properties such as a large electron-storage capacity, good electron conductivity, good chemical stability, excellent mechanical strength, a large specific surface area (> 150 m² g⁻¹), and mesoporous character which favors the diffusion of reacting species [224-226]. Consequently, as a good support for semiconductors, CNT has been widely used to construct semiconductor-CNT nanocomposite photocatalysts in the past few years [227,228]. However, there are very restricted reports on semiconductor-CNT nanocomposite photocatalysts for photocatalytic CO₂ reduction. The multi-walled CNTs (MWCNTs) supported TiO₂ composite catalysts prepared by the sol-gel method lead to the main formation of C₂H₅OH, while HCOOH is found to be the major product on the sample prepared by the hydrothermal method [229]. Chai and his coworkers [230,231] reported that the CNT@ Ni/TiO₂ and MWCNT/TiO₂ core-shell nanocomposites showed excellent photocatalytic activity towards CH₄ synthesis as compared to TiO₂ and Ni/TiO₂ under visible light illumination, on which the maximum yields of $\mathrm{CH}_{\!_4}$ were 0.145 and 0.17 $\mu mol~g_{_{cat}}^{^{-1}}~h^{^{-1}}\text{, respectively.}$

Graphene, a single layer of graphite, possesses a unique twodimensional structure, high conductivity (~5,000 W m⁻¹ K⁻¹), superior electron mobility (200,000 cm² V⁻¹ s⁻¹), and extremely high specific surface area (~2,600 m² g⁻¹), and can be produced on a large scale at low cost [232–234]. Since the pioneering studies by Kamat and coworkers [235,236], semiconductor/graphene-based nanocomposites have attracted a lot of attention in different fields due to their good electron conductivity, large specific surface area and high adsorption [222,237–240].

There were a large number of reports about the semiconductor-graphene nanocomposite photocatalysts for $\rm CO_2$ photoreduction. Interestingly, the graphene oxide can be directly applied as a promising photocatalyst for $\rm CO_2$ to methanol conversion. The largest conversion rate of photocatalytic $\rm CO_2$ to methanol on modified graphene oxide is 0.172 µmol g_{cat}⁻¹ h⁻¹ under visible light, which is 6-fold higher than that of pure TiO₂ [241]. The nanocomposites based on the less defective solvent-exfoliated graphene exhibit a significantly larger enhancement in $\rm CO_2$ photoreduction, especially under visible light [242]. The rates of CO and $\rm CH_4$ formations over the Ti_{0.91}O₂-graphene hollow spheres were 8.91 and 1.14 µmol g⁻¹ h⁻¹, respectively,

which was about 5 times higher than that over the $Ti_{0,0}O_{2}$ [243]. Meanwhile, the TiO₂-graphene 2D sandwich-like hybrid nanosheets were also synthesized by a one-step hydrothermal method in a binary ethylenediamine (En)/ H₂O solvent. The results showed that the synergistic effect of the surface-Ti³⁺ abundant TiO₂ and graphene favors the generation of C_2H_4 , and the yield of the C_2H_4 increases with increasing the content of incorporated graphene [244]. In addition, the hierarchically mesostructured TiO₂/graphitic carbon composite photocatalyst exhibited considerably higher activity in the photocatalytic reduction of CO₂ with H₂O than a mesostructured anatase TiO₂ prepared by a solgel method [245]. The NiO_x-Ta₂O₅-rGO (reduced graphene oxide) containing 1 wt% graphene (G1.0) displayed the highest activity for photoreduction of CO₂ to CH₃OH, which was 3.4 times higher than that of corresponding photocatalyst without graphene (G0) under the same conditions, due to promoted electron transfer and collecting characteristics of rGO [246]. The photocatalytic activity of graphene-WO₃ (GW) nanobelt composites is higher than that of graphene oxide (GO), WO₃ and P25 TiO₂ because of the elevated conduction band of WO₃ [247]. In another example, Cu₂O/rGO composites exhibit a high activity for CO₂ photoreduction to CO, which is about 6 and 50 times higher than that of the optimized Cu₂O and Cu₂O/RuO₂ junction, respectively. The enhanced activity is attributed to the efficient charge separation and transfer and the protection function of rGO [248]. Similarly, the CH₄-production rate of a rGO-CdS nanorod composite photocatalyst was increased 10-fold compared with that of the pure CdS nanorods, which was even better than that of an optimized Pt-CdS nanorod photocatalyst under the same reaction conditions [108]. The rGO sheets in the composites not only promote the surface trapping and efficient separation of photo-generated charge carriers as an electron acceptor and transporter (as presented in Fig. 9), but also



Figure 9 Schematic illustration of the charge transfer and separation in the RGO-CdS nanorod system under visible-light irradiation.

enhance the adsorption and activation of CO_2 molecules, thus boosting the photocatalytic efficiency of the composite photocatalysts.

In addition, it is worth noticing that the defects of graphene in carbon/TiO₂ nanocomposite photocatalysts also play a significant role in the photocatalytic reduction of CO₂. Liang *et al.* [242] demonstrated that the less defective solvent-exfoliated graphene (SEG) resulted in a larger enhancement in the activity for photoreduction of CO₂ to CH₄, compared to the solvent-reduced graphene oxide (SRGO). It was found that the optimized graphene/TiO₂ nanocomposites exhibit approximately 7-fold improvements in the photoreduction of CO₂ compared with TiO₂ alone under visible illumination [242].

Enhanced adsorption and activation of CO,

Effective adsorption and activation of CO_2 is a key step for improving the efficiency for CO_2 reduction. The adsorption and photoinduced activation of CO_2 on stoichiometric and oxygen-deficient TiO₂ surfaces have been theoretically [39,81,249,250] and experimentally studied [251,252]. Recently, some interesting results have been reported through the quantum chemical calculations. Several CO_2 adsorption sites on the predominant anatase TiO₂ (101) surface and on nanoclusters can be identified using first-principles calculations [39,249,253]. Thus, to well understand the key factors affecting adsorption and photoinduced activation of CO_2 , a combination of experimental and computational studies is also highly expected.

Increased surface area for CO₂ adsorption

For TiO₂, it is clear that the adsorption isotherms of CO₂ on pure and nitrogen modified TiO₂ photocatalysts can be well described by the Freundlich adsorption equation [63,254], which indicates that adsorption of CO₂ onto TiO₂ photocatalysts is a favorable physical process. Therefore, the enhancement in adsorption capacity of TiO₂ photocatalyst for CO₂ can be realized through increasing its surface area.

In recent years, it was widely reported that most metal-organic frameworks (MOFs) with super-high surface areas exhibit excellent adsorption capacity for CO₂ [255,256]. Interestingly, MOFs are also a class of potential semiconductors [257], which could be also directly applied in the photocatalytic CO₂ reduction as photocatalysts [258–261]. For example, Fu *et al.* [259] reported that a photoactive Ti-containing metal-organic framework, NH₂-MIL-125(Ti), exhibited a good photocatalytic activity for reduction of CO₂ to formate anion under visible light irradiation. The Re complexes derivatized UiO-67 served as an active catalyst for photocatalytic CO₂ reduction to CO with a total turnover number (TON) of 10.9, which was three times higher than that of the homogeneous Re complexes [260].

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Wang *et al.* [262,263] demonstrated that a cobalt-containing zeolitic imidazolate framework (Co-ZIF-9) as a robust MOF co-catalyst could achieve the photocatalytic conversion of CO₂ to CO by using a Ru-based dye or CdS as the light harvester. It was suggested that the Co-ZIF-9 could not only promote the CO₂ capture and reduction catalysis, but also play a crucial role in improving electron transfers in the light harvester system [262,263]. Thus, it is naturally expected that MOFs as good supports can greatly promote the activity of a photocatalyst for CO₂ photoreduction to fuels due to their excellent adsorption capacity and photocatalytic reduction the activity for CO₂. Recently, it

was first verified that the addition of 25 wt% ZIF-8 to Zn- $_2$ GeO₄ nanorods could achieve a 3.8-fold enhancement in adsorption capacity for CO₂ dissolved in water and a 62% enhancement in photocatalytic activity for the reduction of CO₂ to CH₃OH [264]. Therefore, as molecularly tunable and recyclable photocatalysts in CO₂ reduction, MOFs deserve more attention. However, the instability of MOFs in some conditions should be improved for their practical applications.

Increased basic sites for CO₂ adsorption

Apart from increasing the surface area for CO₂ adsorption, another widely selected strategy to maximize adsorption of acidic CO₂ molecules is to introduce functional basic groups (or basic sites) on the material surface of porous materials [255,256,265]. For example, the amine-functionalization of TiO₂ NPs exhibited significantly enhanced activities for photoreduction of CO₂ into methane and CO due to improved chemisorption and activation of CO₂ and charge transfer from excited TiO₂ [266]. At this regard, it is expected that mesoporous C₃N₄ photocatalyst should have excellent adsorption selectivity and capacity for CO₂ because of rich nitrogen-containing groups on the surface of C_3N_4 [70]. However, so far, there are few reports about the CO₂ adsorption and photoreduction on C_3N_4 [69,109,110,267]. Thus, more efforts should focus on the adsorption and photocatalytic reduction CO₂ on mesoporous g-C₃N₄ photocatalysts in future studies. Furthermore, the nitrogen-doped carbon nanotubes (CNTs) or graphene have been extensively used as an efficient electrocatalyst for hydrogen or oxygen evolution [268-270], because nitrogen impurities can function as catalytic sites. Interestingly, the nitrogen-containing sites are also potential active sites for CO₂ adsorption. Thus, it is highly expected the promising nitrogen-doped CNTs or graphene can be deeply studied and applied in photocatalytic reduction of CO₂ due to the synergistic effect of their good electron conductivity and potential adsorption ability for CO₂.

In addition, the loading of basic sites on the surface of photocatalysts can also be achieved using the solid basic

(hydro)oxides such as NaOH, MgO and ZrO₂. Ye and coworkers [271] demonstrated that the surface modification of TiO, with NaOH could greatly enhance the CO, adsorption, activation, thus leading to highly effective photoreduction of CO₂ into CH₄ without loading any noble metal co-catalysts. Kohno et al. [272,273] reported that the photocatalytic reduction of CO₂ to CO can be achieved over MgO. However, the mechanism of the photoreduction of CO₂ on MgO cannot be explained by the conventional band theory because MgO is not a semiconductor [272]. Thus, a new concept for photocatalytic reduction of CO₂ over an insulating material was proposed. It is believed that a CO radical can form by activating CO, adsorbed on MgO under photoirradiation. Then it was reduced to the surface bidentate formate by H_{2} or CH_{4} in the dark. The surface bidentate formate as photoactive species can further reduce CO₂ in the gas phase to CO under photoirradiation. The mechanism can also be used to explain the photocatalytic reduction of CO₂ over ZrO₂ [274]. Recently, the addition of MgO modifier onto TiO₂ [275–277] was found to be capable of significantly enhancing the activity for photocatalytic reduction of CO₂. The proposed mechanisms of the MgO layers and Pt NPs over TiO₂ for photocatalytic reduction of CO, in the presence of H₂O were shown in Fig. 10. Clearly, the MgO layers on TiO₂ surfaces not only enhance the adsorption of CO₂ as basic sites, but also can capture the holes and promote charge separation. More importantly, it also can inhibit the reoxidation of products owing to avoiding direct contact of products and TiO, [276]. In addition to MgO, ZrO, [278], Ga,O, [279] and layered double hydroxides [280-282] also have great potentials to function as modifiers to enhance the activities for photocatalytic reduction of CO₂ over semiconductor photocatalysts.

Important factors affecting CO, activation

The surface oxygen vacancies play very important roles in governing the adsorption, activation and dissociation of



Figure 10 Proposed mechanisms of the MgO layers and Pt NPs over TiO, for photocatalytic reduction of CO, in the presence of H,O.

 CO_2 , which provide not only an electronic charge (Ti³⁺) but also the sites for the adsorption of oxygen atoms from CO₂ [283]. It was even demonstrated that CO_2^- species, generated upon an electron attachment to CO₂, are spontaneously dissociated into CO on defective Cu(I)/TiO_{2-x} at room temperature even in the dark [283]. Indrakanti et al. [249] performed the excited-state ab initio calculations of CO₂ adsorbed on clusters from the (010), (101), and (001) anatase surface planes. The calculated results indicated that oxygen vacancies may act as the active sites for CO₂ photoreduction, whereas the activation of CO₂ can't be achieved on the stoichiometric TiO₂ surfaces. Meanwhile, the adsorption of CO₂ and temperature programmed desorption (TPD) experiments also demonstrated that chemical adsorption of CO₂ can be improved through increasing the oxygen vacancy in SrTiO₃, which would lower the activation barrier of CO₂ and favor the photoreduction of CO₂ to hydrocarbon fuels [284]. It is expected that the oxygen vacancies, and the adsorption and activation of CO₂ on the defective surface of a given photocatalyst can be experimentally investigated in detail, which may provide necessary information for designing highly efficient photocatalysts.

It is also clear that the polarity and dielectric constant of solvents, acid-base properties of supports and the hydrophobic-hydrophilic nature of catalysts have significant influences on the activation of CO₂, the stability of CO_{2}^{-} radical anion and the catalytic activity and selectivity [59,84,181,285]. For example, through loading TiO₂/Pd, CuO/ZnO and Li₂O-TiO₂ on the supports of magnesium oxide, aluminium oxide and silicon dioxide, it was found that the conversion of CO_2 to C_1-C_3 compounds took place preferentially on basic oxide supported systems, and acidic oxide supported catalysts showed more selectivity to C₁ compounds [84]. Consequently, the acidic oxide such as SiO₂ was generally used to obtain the C₁ compounds in most studies. The formation of CH₄ and CH₃OH from CO₂ photoreduction with gaseous and liquid water was observed over Ru-TiO₂/SiO₂ [83] and TiO₂-containing porous SiO₂ thin film [286], respectively. It is also evident that the selective formation of CH₃OH from CO₂ photoreduction with gaseous water increases rapidly with decreasing the surface concentration of hydroxyl groups [286]. Very recently, it was reported that the selectivity for photoreduction of CO₂ can be tailored by controlling the band structure of a $g-C_3N_4$ photocatalyst [287]. Thus, it is clear that the band structure, surface state and sites (e.g., the chemistry of CO₂ adsorption, oxygen vacancies, isolated Ti-species, acidbase properties and the hydrophobic-hydrophilic nature) played very crucial roles in the photoinduced activation of CO₂ [39,88,288–290].

Meanwhile, the water vapor adsorption can be also tuned through managing the surface area and pore struc-

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ture of porous materials [291-293]. It is worth noticing that the SiO₂-pillared HNb₃O₈ photocatalysts also exhibit a 6-fold enhancement in the photocatalytic activity for CO₂ reduction due to increased adsorption ability for water vapor molecules on SiO₂ [294]. However, an excess amount of H₂O will suppress the reaction. The optimum mole ratio of H₂O/CO₂ for CO₂ photoreduction over highly dispersed TiO₂ anchored on porous Vycor glass was found to be about 5 [295]. Recently, efficient high-rate sunlight-driven conversion of diluted CO₂ into light hydrocarbons in gas phase was also achieved by coupling coaxial Cu-Pt bimetallic coatings with these TiO, nanotube arrays as catalysts at room temperature [188]. Therefore, for the photocatalytic reduction of CO₂ by water vapor, control of CO₂ and H₂O adsorption capacity of photocatalysts and the ratio of H₂O to CO₂ is of great importance to optimize the photocatalytic activity and selectivity in future studies.

Accelerated CO, reduction kinetics

Developing mesoporous photocatalysts

Developing mesoporous semiconductor photocatalysts has become a popular strategy to effectively increase the active sites, surface area and light harvesting. The mesoporous structure can also facilitate access of reactants to the surface active sites and improve multiple scattering. All these factors can subsequently maximize the activity for photoreduction of CO₂. Typically, the micro/mesoporous Zn₂GeO₄ with crystalline pore-walls [296] and mesoporous zinc germanium oxynitride [176] exhibited much higher activities for CO₂ photoreduction (about 2.5–5.0 times) than the corresponding samples obtained by a solid state reaction, respectively, due to the increased surface area and improved pore structure. The mesoporous ZnGa₂O₄ prepared by a reactive templating route at room temperature also exhibited a higher activity (CH₄: 5.3 ppm h⁻¹) than ZnGa₂O₄ (CH₄: trace) obtained by a solid state reaction [297]. The indium hydroxide $(In(OH)_{2})$ sample with mesoporous structure is about 20 times higher in efficiency for the photoreduction of CO₂ to CH₄ than that of sample without mesoporous structure [298]. With respect to the bulk NPs, the porous gallium oxide exhibits the enhanced photocatalytic activity of conversion of CO_2 into CH_4 , which is mainly due to the 300% higher CO₂ adsorption capacity, as well as the 200% increased surface area [299]. For mesoporous graphitic C_3N_4 , it was revealed that the photoactivity for CO₂ reduction to formic acid was strongly dependent on its specific surface area and crystallinity rather than the pore size and the volume [300]. Similarly, the enhancements of photocatalytic performance for CO₂ reduction over mesoporous composites (CeO₂-TiO₂ [217] and TiO₂/ZnO [41]) were also observed in a different group. However, the direct synthesis of highly crystalline mesoporous transition-metal oxides that are thermally stable and well-ordered remains a major challenge [301]. Another challenge is to prepare multimetallic oxide mesoporous materials and their oxynitride. Particular emphasis should be placed on preparing these kinds of active materials by soft chemical methods for the application of photoreduction of CO_2 under visible-light irradiation.

Meanwhile, as another effective strategy to develop mesoporous photocatalysts, constructing isolated centers in zeolite matrices (or loading photocatalyst NPs onto zeolites or mesoporous molecular sieves) has also been widely investigated. Zeolites exhibit unique nanoscaled porous structures and ion exchange properties. Zeolites are often employed as organizational media or supports for entrapped or adsorbed transition-metal catalysts and photocatalysts [302]. Therefore, zeolites have been widely utilized in the design of efficient photocatalytic systems for CO₂ photoreduction. So far, the highly dispersed Ti-oxides in silica matrices are one of the best performing photocatalysts in direct CO, reduction to hydrocarbons, pioneered by Anpo and his co-workers in the 1990s [303]. The titanium oxide anchored on Y-zeolite exhibits the highest photocatalytic activity and the highest selectivity for the formation of CH. and CH₃OH, whereas CO is formed as a main product on the titanium oxide anchored on ZSM-5 [295]. It is clear that the activity and selectivity of photocatalysts for different products strongly depend on the chemical nature of the supports. Yet, the microporous structure of zeolites is not beneficial for the improvement of photocatalytic activity. Thus, a variety of mesoporous molecular sieves (MCM-41, MCM-48, KIT-6, FSM-16 and SBA-15) are also applied in photocatalytic CO₂ reduction [285,290,295,304-309]. Ti-MCM-41 and Ti-MCM-48 mesoporous zeolite catalysts exhibited high photocatalytic reactivity for the reduction of CO₂ with H₂O at 328 K to produce CH₄ and CH₃OH in the gas phase. Especially Ti-MCM-48 with a large pore size and three-dimensional channels exhibited the highest reactivity for CH₄ production, which was almost ten times higher than that of bulk TiO₂ [304]. The further results showed that the dispersed TiO₂ within mesoporous FSM-16 and SBA-15 exhibited much higher photocatalytic activities for CO₂ reduction than other supports. Furthermore, Ti-containing Ti-KIT-6, Ti-FSM-16 and Ti-SBA-15 prepared by hydrothermal synthesis also showed very high yields in methane or/and methanol, respectively. In particular, the photocatalytic reaction yields of the Ti-SBA-15 catalyst for CH₄ formation under UV light are over 240 times higher than those of the TiO_2 catalyst and the yields for CH_3OH formation increase remarkably over 4000 times [290,310]. More recently, a new photocatalyst, Ti-TUD-1, showed a 30% increase in the total hydrocarbons produced by CO₂

photoreduction, as compared with Ti-SBA-15 [311]. In a word, highly dispersed titanium oxide in mesoporous silica materials (KIT-6, FSM-16, SBA-15 and TUD-1) leads to relatively high yield in CH₄ or/and CH₃OH, which is a promising candidate for CO₂ photoreduction.

Recently, much attention has been directed at monolayered zeolites [312] and zeolite nanosheets [313–315] which can increase the external to internal surface ratio and thus can enhance the catalytic activity. However, this kind of layered zeolite nanosheets has not been used in photocatalysts. Maybe zeolite nanosheets can provide a new strategy for designing highly efficient photocatalysts for photocatalytic reduction of CO_2 .

Loading CO, reduction co-catalysts

It is generally believed that the co-catalysts can extract the photogenerated charge carriers from semiconductors, provide reaction sites, lower the electrochemical overpotentials associated with the multielectron water oxidation and CO_2 reduction reactions, and decrease the activation energy for gas evolution [316,317]. Another function is to provide a junction/interface between the co-catalyst and the semiconductor to enhance electron–hole separation or charge transport [317,318].

For photoreduction of CO₂, the loaded co-catalysts could serve as electron traps to enhance the separation of the photogenerated electron-hole pairs and hence improve the photocatalytic activity and selectivity for CO₂ reduction. Generally, Pd, Pt and Au can selectively reduce CO, into CH₄ products. Ishitani *et al.* [136] first systematically studied the photoreduction of CO₂ on a series of metal-deposited TiO₂ and found that depositing metals (Pd, Rh, Pt, Au, Cu₂O, etc.) on TiO₂ photocatalysts can greatly boost their photocatalytic activities for CO₂ reduction to CH₄ (in decreasing order). The addition of Pt onto the highly dispersed titanium oxide catalysts promotes the charge separation which leads to an increase in the formation of CH₄ in place of CH₃OH [305]. Pt NP/TiO₂ nanotube composite greatly promoted the photocatalytic conversion of CO₂ and water vapor into methane due to a large number of active reduction sites from the homogeneous distribution of metal co-catalyst NPs over the TiO₂ nanotube array surface [186]. A unique one-dimensional (1D) structure of TiO₂ single crystals coated with ultrafine Pt NPs (NPs, 0.5–2.0 nm) exhibited extremely high CO₂ photoreduction efficiency with selective formation of methane (the maximum CH₄ yield of 1361 µmol g_{cat}^{-1} h⁻¹) [319]. A similar result was also observed on the Pt-C₃N₄ system [201]. The highest yield of CH4 was obtained on the g-C3N4 loaded by about 1 wt% Pt. Here, Pt NPs not only improve the transfer of photogenerated electrons and the activity for photocatalytic reduction of CO, as a co-catalyst, but also promote

the oxidation of reduction products (as shown in Fig. 11) [201]. The loading of Pd (> 0.5 wt %) on TiO₂ can suppress the CO formation and promote the CH₄ formation [320].

In addition, it is worth noticing that the bimetallic co-catalysts systems (Cu and Pt) exhibited better activities for CO₂ reduction than single metallic co-catalysts systems. For example, a hydrocarbon production rate of 111 ppm cm⁻² h⁻¹, or $\approx 160 \ \mu L \ g^{-1} \ h^{-1}$), is obtained when the nitrogen-doped TiO₂ nanotube array samples are loaded with both Cu and Pt NPs. It was pointed out that this rate was at least 20 times higher than that in the previously published reports [97]. The mechanisms for photocatalystic CO₂ conversion to fuels over this composite photocatalyst were illustrated in Fig. 12. In another example, a bimetallic co-catalyst of Cu_{0.33}-Pt_{0.67} was loaded on the double-walled TiO₂ nanotube for the photoreduction of diluted CO₂ to CH₄ (1% in N₂), an average hydrocarbon production rate of 6.1 mmol m⁻² h⁻¹ was realized under AM 1.5 one-sun



Figure 11 Schematic illustration of CO_2 photoreduction in the Pt/g- C_3N_4 system under visible light irradiation.



Figure 12 Mechanisms for photocatalytic CO_2 conversion to fuels using nitrogen-doped TiO_2 nanotube arrays loaded with Cu and Pt co-catalyst NPs.

illumination [321]. However, the enhancement mechanism of bimetallic co-catalysts is still unclear. Thus, a deeper understanding and investigation of these bimetallic co-catalysts might be needed for their further application in this field.

Meanwhile, Au and Ag-loaded TiO₂ photocatalysts have also been widely studied. For a leaf-architectured artificial photosynthetic system of SrTiO₃, Au exhibits the best performance as a suitable co-catalyst for both CO and CH₄ selectivity [11]. The nanoscale TiO₂ particles embedded in the hydrophilic cavities of Nafion membrane films significantly improved photoconversion of CO₂ to methanol when coated with silver [322]. Ag co-catalyst-loaded ALa₄ Ti₄O₁₅ (A = Ca, Sr, and Ba) photocatalysts showed better activities for CO₂ reduction to CO and HCOOH without any sacrificial reagents [323].

Furthermore, RuO₂ has also proved to be a good co-catalyst for CO₂ photoreduction. The maximum CH₃OH yield observed was about 118.5 µmol g⁻¹ h⁻¹ in the presence of RuO₂/Cu_xAg_yIn_zZn_kS_m photocatalysts under H₂ atmosphere [175]. The generation rate of CH₄ over meso-ZnGa₂O₄ could be significantly enhanced by loading 1 wt% RuO₂ as co-catalyst to improve separation of the photogenerated electron–hole pairs [297]. The rate of CH₄ generation over the Zn₂GeO₄ nanoribbons could also be significantly enhanced by loading of Pt or RuO₂ and especially by co-loading of Pt and RuO₂ as co-catalysts [195].

Besides noble metal co-catalysts mentioned above, it is indispensable to search for cheap, earth-abundant and highly efficient co-catalysts for photocatalytic reduction of CO₂ [324]. Generally, the first-row transition metals such as Co, Ni, Mn, Fe and Cu, have been recognized as good candidates for practical applications [325,326]. For example, copper as an earth-abundant co-catalyst has been extensively used in the photoreduction of CO₂. In most cases, the active species on Cu-loaded TiO, is Cu₂O, which not only greatly enhances the photochemical production of CH₃OH, CO and CH₄ from the CO₂ and gaseous H₂O system [54,86,327], but also greatly improves the photocatalytic activity for CO₂ reduction to methanol in liquid phase. The copper cluster is an effective electron trapper, and able to reduce the recombination of electron-hole pairs [55,133]. However, higher Cu loading gave a lower rate of methanol yield because of the masking effect of Cu₂O clusters on the TiO₂ surface [132,133]. Consequently, it is generally believed that CO₂ can be selectively reduced to methanol in an aqueous solution under light irradiation due to the Cu₂O or CuO species on the TiO₂ surface [54,55,131,133,218,308,328].

In addition, NiO NPs were also usually loaded on different semiconductors as a co-catalyst to enhance their photocatalytic activity for CO_2 reduction. The NiO_x co-cat-

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alysts loaded on the surface of $InTaO_4$ can slightly increase the methanol yield from CO_2 reduction [121–123]. Thus, to further enhance the activity for CO_2 reduction, core/ shell Ni/NiO co-catalysts were also constructed and used in the photocatalytic conversion of CO_2 [122,246,329]. In particular, the methanol yield over the Ni@NiO core/shell structure-modified nitrogen-doped InTaO₄ photocatalyst is about three times higher than that of pure InTaO₄. It is believed that the co-catalyst loading not only dramatically enhances absorbance, but also efficiently avoids electronhole recombination [124].

Unfortunately, the molecular O_2 and H_2 had not been quantitatively measured in these reports. It is very important to detect the molecular O_2 and H_2 for the Nibase co-catalysts systems because NiO_x is also an efficient co-catalyst for photocatalytic hydrogen generation from water splitting. Therefore, it is suggested that the molecular O_2 and H_2 should also be detected when the NiO and core/ shell Ni/NiO co-catalysts were used for the photocatalytic reduction of CO_2 .

However, nowadays, there were seldom reports on the photocatalytic reduction of CO_2 by loading two different co-catalysts for water oxidation and CO_2 reduction. Therefore, special attention should be given in future studies to the systems with two separated co-catalysts for water oxidation and CO_2 reduction [330].

Improving water oxidation kinetics

Generally, to increase the photocatalytic activities of semiconductors and prevent the oxidation of the reduction products in liquid phase, some highly efficient electron-donor sacrificial agents including EDTA, Na₂SO₃, acetonitrile, dichloromethane, iso-propyl alcohol, alcohols and amines were also widely used in many photocatalytic reduction systems. It can be expected that these electron donors will not compete with CO_2 in the trapping of the electrons in the CB since they are more difficult to be reduced as compared to water. For instance, Richardson *et al.* [12] also demonstrated a very interesting concept using a tertiary amine as an recycling electron donor to combine CO_2 photoreducton with water splitting for improving the overall efficiency.

However, water is not a real electron donor in the presence of sacrificial reagents. In theory, the oxygen-evolution half-reaction is an important part of the process of CO_2 photoreduction [331–335], as improvements of water oxidation must be favorable for the efficient separation of the photo-generated carriers and the enhancement in the photocatalytic activity for the reduction of CO_2 . Especially, the water oxidation reaction is an important bottleneck for both photocatalytic H₂ production and CO_2 reduction because this reaction is considerably more difficult and com-

plicated. It requires a four-electron oxidation of two water molecules coupled to the removal of four protons to form a relatively weak oxygen-oxygen bond [336,337]. Although it is well accepted that the CO₂ photoreduction process (the reduction half-reaction) is accomplished by O₂ and H₂O₂ formation, which comes from the oxidation of water (the oxidation half-reaction) [5,89,92,338], or water splitting [90,143,252,339], many researchers only measured the products from the reduction of CO₂ and always ingored the measurement of the products $(O_2 \text{ and } H_2)$ from water splitting reaction. The evolution rate of O₂ from the photoreduction of CO₂ with H₂O was first studied by Ogura et al. [340]. In particular, water oxidation products (O_2) were also detected during the photoreduction of CO₂ over ZrO₂ [341], KCaSrTa₅O₁₅ [342], KTaO₃ [343] and ALa₄Ti₄O₁₅ (A = Ca, Sr, and Ba [323]) photocatalysts in water. Importantly, evolution of $(H_2 + CO)$ and O_2 in a stoichiometric amount (2:1 in a molar ratio) was observed in the absence of sacrificial reagents, further indicating that water could function as a reducing reagent (an electron donor) for the CO₂ reduction [323]. Consequently, it is of great significance to examine the amounts of oxygen from the CO₂ photoreduction with H₂O in future studies. In particular, to identify who is the real electron donor, it is quite necessary that the molecular O2 should be also quantitatively measured during the photocatalytic reduction of CO₂ [59,117,181,344]. To some extent, O₂ should be especially carefully checked whether they do not form really or may be not detected, remaining adsorbed on the photocatalyst.

Meanwhile, when the photocatalytic reduction of CO_2 is performed in the gas phase with controlled proportion of water vapor as a reductant agent, the photocatalytic activity of semiconductor for CO_2 reduction is much higher than that observed in liquid phase. Therefore, for these reasons, the photocatalytic reduction of CO_2 in the gas phase without using any sacrificial reagent seems to be more promising than that in liquid phase.

So far, there are seldom reports on the application of cobalt-based co-catalysts in the photocatalytic reduction of CO_2 . Recently, Lin *et al.* [109] verified that the introduced cobalt oxide (COO_x) NPs on carbon nitride as reductive and oxidative promoters can improve the photocatalytic activity toward CO_2 -to-CO conversion due to the acceleration in the oxidative partner reaction, charge-carrier separation and transfer kinetics. Therefore, loading oxygen-evolution co-catalysts such as Co-Pi, CO_3O_4 and $Fe_{100-y-z}Co_yNi_zO_x$ [345–349] may provide a strategy for improvement of the photocatalytic performance for the reduction of CO_2 . Importantly, they not only can enhance the kinetics of water oxidation and suppress the recombination of photo-generated charge carriers, but also can increase the stability of semiconductors.

Suppressed undesirable reaction

Inhibited hydrogen evolution

Selective reduction of CO₂ is another major challenge in the photocatalytic reduction of CO₂ in aqueous solutions because the hydrogen evolution via water reduction is the main competing reaction, which can greatly decrease the efficiency and selectivity for CO₂ reduction. During CO₂ photocatalytic reduction, hydrogen evolution as the side reactions of the photoreduction of CO₂ also usually exists in the systems. The kinetics for CO₂ reduction is unfavorable due to the multi-electron reduction processes, while H₂ evolution generally predominates when thermodynamic conditions for both processes are satisfied [21,22]. Therefore, it is of immense importance to couple CO₂ reduction with water splitting, which is beneficial for finding the rate-determining steps and improving the efficiency and selectivity of CO₂ photoreduction in aqueous solutions. In a certain sense, suppressing the reduction of H₂O to H₂ (a competitive reaction with the reduction of CO₂) can enhance the efficiency and selectivity of CO₂ photoreduction.

Recently, considerable attention has been drawn to this issue. Wang and his coworkers [344] founded that a coreshell structured Pt@Cu₂O co-catalyst on P25 can significantly promote the photoreduction of CO₂ with H₂O to CH₄ and CO and suppress the reduction of H₂O to H₂. The selectivity for CO₂ reduction reached 85%. It was proposed that the Cu₂O shell was capable of providing sites for the preferential activation and conversion of CO₂ molecules in the presence of H₂O and suppressing the reduction of H₂O to H₂, while the Pt core extracts the photo-generated electrons from TiO₂ (Fig. 13).



Figure 13 Mechanism of a core-shell structured Pt@Cu₂O co-catalyst on TiO, for photocatalytic reduction of CO₂.



Figure 14 Degradation profiles of the standard hydrocarbons over the prepared samples. The concentrations were recorded every 15 min for the duration of 2 h. Reproduced with permission [311]. Copyright 2014, American Chemical Society.

Inhibited products oxidation

It is a great challenge to separate oxidation and reduction processes on the surface of semiconductor NPs, because many intermediate products of CO₂ reduction cycle adsorbed on the surface could be oxidized, which will reduce overall yield of hydrocarbons and the photocatalytic efficiency [90,350]. The research from the Mul's group [91] demonstrated that the backward reaction, i.e., oxidation of hydrocarbons back to CO₂ and water, proceeds to a significant extent due to the existence of the oxygen from the splitting of water. The further results revealed the importance of evaluating hydrocarbon oxidation in explaining performance of catalysts designed for CO₂ reduction [311]. As displayed in Fig. 14, it is clear that methane only slowly degraded over the catalytic systems within 120 min of illumination whereas the other hydrocarbons (i.e., ethane and propane) were easily degraded, in particular over the Ti-1-Cr-1 sample. Interestingly, the products from CO₂ photoreduction as electron donors are even employed to improve the evolution rate of hydrogen in water splitting, further indicating the reduction product oxidation also exist in the liquid phase [351]. Therefore, it is still a great challenge to minimize hydrocarbon oxidation in process conditions needed for CO₂ reduction.

For CO₂ reduction by water vapor, the control of water vapor pressure appears the challenge, since it is not only the hydrocarbon oxidant but also the reductant for activating CO₂. For CO₂ reduction by liquid water, it is still a challenge to physical separation of oxidation and reduction sites. A thin Nafion layer on Pd-deposited TiO₂ NPs [352] and a proton conducting Nafion membrane [322,353–355] have been used to inhibit the reoxidation of the reduction products and enhance the photosynthetic conversion of

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Figure 15 Scheme of the PEC device for CO_2 reduction to fuels and H_2 production. Reproduced with permission [356]. Copyright 2010, RSC Publishing.

CO₂ to corresponding products (mainly methane, ethane, methanol and formic acid) in an aqueous suspension or gas phase. In addition, the PEC conversion of CO₂ to fuel appears to be more promising among various other routes owing to the ability of separating the two half-reactions to avoid reverse processes [17]. For example, to avoid the oxidation of obtained products, the physical separation of the two reactions of water oxidation and CO₂ reduction in a photoanode and cathode, respectively, can be achieved in a newly-designed PEC reactor (as presented in Fig. 15) [356]. Similarly, in another system of PEC reduction of CO₂ into chemicals, Pt-rGO and Pt modified TiO, nanotubes (Pt-TNT) performed as cathode and photoanode catalysts, respectively. As a consequence, the separated Pt-rGO exhibited an outstanding activity for CO₂ reduction due to its enhanced adsorption capacity for CO₂ and suppressed oxidation of products [357]. Furthermore, a bifunctionalized TiO₂ film containing a dye-sensitized zone and a catalysis zone as cathode exhibited highly efficient conversion of CO₂ to formic acid, formaldehyde, and methanol through the electron transfer at the CB of TiO, under visible light [358]. Importantly, the oxidation of obtained products was prevented via the anode in separated solution. In addition, in Izumi's group, the photocatalytic water oxidation and photocatalytic reduction of CO₂ were successfully integrated in reverse photofuel cells [281,359]. In this new reactor, the oxidation of products from photoreduction of CO_2 can be avoided due to the separate water oxidation and CO₂ reduction, thus leading to an enhanced activity for photoreduction of CO₂[18]. Therefore, it is interesting to carry out the photocatalytic reduction of CO₂ using a PEC cell.

CONCLUSION AND PROSPECTIVE

In summary, this review highlights the design and fabrica-

tion of semiconductor photocatalysts for enhancing photocatalytic efficiency and selectivity of converting CO_2 into useful fuels. Although some significant advances have been achieved in the recent years, the selectivity and yields of the desired products are still rather low and at this point is far from practical application. Therefore, many problems such as the underlying mechanisms of CO_2 photoreduction, the lack of highly efficient photocatalyst and appropriate non-noble metal co-catalyst for special carbonaceous product still need to be clarified in the future.

From our review, it is clear that every step in photocatalysis processes including charge excitation, separation, transport, adsorption and activation of CO_2 , CO_2 reduction kinetics and undesirable reactions has significant influences on the overall efficiency of photocatalytic CO_2 reduction. In addition to the photocatalytic properties, adsorption and activation of CO_2 , the development of CO_2 reduction electrocatalyst and the suppression of products oxidation are very important to achieve a maximum efficiency. Thus, all the factors should be taken into account and optimized carefully when designing and fabricating multifunctional semiconductor photocatalysts for CO_2 reduction.

Especially, the oxidation of water and products should be also paid more attention in future studies. In photocatalytic systems using semiconductor particles as photocatalysts, it is still a challenge to physical separation of oxidation and reduction sites. A PEC cell seems to be a good choice for the photoreduction of CO_2 in water solution due to the physical separation of water oxidation and CO_2 reduction. The typical strategies in this review can also be used in designing photocathode or photoanode for PEC reduction of CO_2 . One possibility for PEC cell is the use of multijunction systems coupling with suitable protective layers or co-catalyst.

The mechanism needs to be deeply investigated in future studies, which still significantly limits the development of the CO₂ photo-reduction. The finding of the ratedetermining steps in CO₂ photoreduction is favorable for the design and fabrication of highly efficient and selective photocatalysts. Thus, an in-depth study to understand the surface transformations at the molecular level during CO₂ reduction, including adsorption/desorption of CO₂, surface chemistry and reaction, intermediate products, as well as the role of adsorbed water and carbonates during the reaction is needed in order to reveal the reaction mechanism [90]. To get accurate production yields of the photocatalytic conversion of CO₂, it was essentially important to use isotope labeling of ¹³CO₂ as a reactant, which can determine whether the products were derived from CO₂ and not from carbon impurity intermediates [18,320,360]. In addition, the blank tests and different control experiments are highly needed in future studies.

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Meanwhile, almost all known non-oxide and many oxide semiconductors suffer from photocorrosion in aqueous electrolytes, which is one of the most fundamental problems that limit the lifetime of all photocatalysts. Therefore, the photostability of the semiconductor should be fundamentally improved to prevent corrosion in the practical application [2,8]. Nanostructured wide-bandgap oxide semiconductor (TiO₂ and titanate mostly) or carbon material coating, surface passivation and co-catalyst loading, have proved to be effective strategies for reducing the photocorrosion of unstable semiconductors.

In a word, all results indicate that the photocatalytic conversion of CO_2 into valuable energy-bearing fuels is still in its infancy, and that breakthroughs for bringing this technology to reality can occur when all these problems and strategies above have been taken into consideration and the photocatalytic system has been well designed.

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Conflict of interest The authors declare that they have no conflict of interest.



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中文摘要 近年来,严重的化石燃料短缺以及环境污染问题使得人工光合作用引起了科研工作者的广泛关注,光催化转换CO₁成为有价值的太阳能燃料被认为是解决能源危机以及环境问题的最好的方法之一.有效地控制半导体表面的催化反应以及光生载流子是制备高活性以及高选择性半导体CO₂还原光催化剂的关键因素,至今,研究人员已经提出了许多策略来增强光催化转换CO₁的活性以及选择性.本文在分析提高光催化效率和选择性限制因素的基础上,尝试从几个不同方面总结了近些年来提高光催化CO₂还原效率的方法以及它们的设计原理,包括增强半导体可见光响应、促进光生电子空穴分离、提高CO₂的吸附和活化、加速CO₂还原的动力学以及抑制不良反应等方面.因此,本文不仅系统地总结了近年来高活性高选择性光催化CO₂还原光催化剂的设计进展,而且为高效光解水产氢和污染物降解光催化剂的设计提供了重要参考.

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