Photocatalytic conversion of carbon dioxide: From products to design the catalysts

Zhiyan Fu[a,b], Qi Yang[a,b,*], Zhan Liu[d], Fei Chen[c], Fubing Yao[a,b], Ting Xie[a,b], Yu Zhong[d], Dongbo Wang[a,b,*], Jing Li[a,b], Xiaoming Li[a,b], Guangming Zeng[a,b]

[a] College of Environmental Science and Engineering, Hunan University, Changsha, 410082, China
[b] Key Laboratory of Environmental Biology and Pollution Control, Hunan University, Ministry of Education, Changsha, 410082, China
[c] CAS Key Laboratory of Urban Pollutant Conversion, Department of Chemistry, University of Science & Technology of China, Hefei, 230026, China
[d] Key Laboratory of Water Pollution Control Technology, Hunan Research Academy of Environmental Sciences, Changsha, 410004, China

ARTICLE INFO

ABSTRACT

The emissions of carbon dioxide (CO$_2$) from the combustion of hydrocarbon fuels have brought increasingly serious global warming. Photocatalytic conversion of CO$_2$ to the renewable fuels or valuable chemicals is proposed as an effective solution to simultaneously achieve the reduction of CO$_2$ emission, the use of sustainable solar energy and the harvest of products with high added-value. Various products such as methane (CH$_4$), methanol (CH$_3$OH), carbon monoxide (CO) have been gained through the photocatalytic conversion of CO$_2$. This review systematically summarized the research progress of photocatalytic conversion of CO$_2$ from the product selectivity point of view. Particularly, the common strategies to covert CO$_2$ into the desired target products, including the surface modification of catalyst, the control of reaction conditions, the selection of incident light source, are completely discusses. Finally, the challenges and prospects in achieving efficient, stable and selective CO$_2$ photoconversion are pointed out.

1. Introduction

With the rapid development of economy and society, the demand of fossil fuels increasingly rises. Currently, the global energy consumption is about 15 TW (1.5 × 10^{10} KW), and it is estimated that it may achieve to 23 TW and 45 TW by 2050 and 2100, respectively [1]. Excessive use of fossil fuels not only brings great energy crisis, but also discharges plenty of greenhouse gases carbon dioxide (CO$_2$) into the atmosphere. The continuous increasing emission of CO$_2$ makes global warming become a widespread concern in the recent years [2]. The gradual rise in global temperature has brought a variety of problems, including ice melting at the Earth's pole, sea level rising and irregular global precipitation [3]. So, it is very urgent to explore an attractive and promising solution for the conversion and utilization of CO$_2$ [4].

The main methods to decrease the emission of CO$_2$ include the capture and storage of CO$_2$, chemical reduction and utilization of CO$_2$, and biological fixation of CO$_2$ [5,6]. However, capture and storage of CO$_2$ is not economically worth, simultaneously, the potential leakage of CO$_2$ is one of the problems. With the reduction of global vegetation coverage, the CO$_2$ fixation by green plants also becomes not feasible. During the past decade, more and more researches begin to focus on

artificial reduction of CO$_2$ [7], including electrochemical, bioelectrochemical, thermochemical, photocatalytic methods. Electrochemical reduction of CO$_2$ is achieved in solution, relying on an electrochemical cell as an energy input to reduce CO$_2$ at the cathode. However, the additional electricity is essential, which increases the cost of this technology. Meanwhile, the hydrogen evolution reaction accompanying with electrochemical reduction of CO$_2$ also has a great influence on the purity of the product. Bioelectrochemistry reduction is a novel technology for CO$_2$ reduction, where the microorganisms are as the catalysts. Because of the requirement of microorganisms for living environment, bioelectrochemistry reduction of CO$_2$ can only carry out under specific experimental conditions and its conversion of CO$_2$ is very low, which limits its development in practical. In the thermochemical reduction of CO$_2$, higher temperature is needed, which not only increases the energy consumption, but also requires that the catalysts for CO$_2$ reduction must maintain its activity at high temperature. Compared with these methods, photocatalytic conversion of CO$_2$, especially using solar energy is more promising, environmentally friendly and energy-efficient, because this process is substantial non–pollution and does not require extra energy [8].

Except for mitigating the global greenhouse effect, photocatalytic

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Table 1
Photocatalytic reduction of CO_2 by some common catalysts.

Catalyst	Synthesis method	Light source	Main Products	Ref
Ga_2O_3	Mixing-precipitation and calcined at 1073 K for 6 hours.	200 W Hg-Xe lamp	CO	[12]
MgO	Hydrated in distilled water and calcined at 873 K for 3 hours.	500 W ultra-high-pressure Hg lamp	CO and H_2	[13]
$BiVO_4$	Microwave assisted hydrothermal method.	300 W Xe arc lamp	CH_3CH_2OH	[22]
$NaNbO_3$	Hydrothermal reaction and high temperature heating.	300 W Xe arc lamp	CH_4	[23]
$InVO_4$	Solid-state reaction method.	500 W halogen lamp	CH_3OH	[24]
$NiO/InVO_4$	Incipient-wetness impregnation method.	500 W halogen lamp	CH_3OH	[24]
$NiO\text{-}InNbO_4$	Solid-state reaction method and water bath drying reaction.	500 W halogen lamp	CH_3OH	[25]
$Co_3O_4\text{-}InNbO_4$	Incipient-wetness impregnation method.	500 W halogen lamp	CH_3OH	[25]
$NiO/InTaO_4$	Aqueous sol-gel method.	Circular fluorescent lamps	CH_3OH	[26]
ZnO	/	125 W high pressure Hg lamp	CH_4 and formic derivatives	[27]
Au-ZnO	Hydrothermal synthesis.	532 nm green laser illumination	CH_4 and CO	[28]
ZrO_2	Calcined at 773 K for 5 hours after hydrothermal synthesis.	500 W ultrahigh-pressure Hg lamp	H_2, CH_4 and CO	[29]
Ag/TiO_2	Sol-gel process controlled.	UV 8 W Hg lamp	CH_4 and CH_3OH	[30]
$CuO\text{-}TiO_2$	Calcined at 723 K for 6 hours after hydrothermal synthesis.	250 W high pressure Hg lamp	$HCOOCH_3$	[31]
rGO-CuO	Hydrothermal reduction.	20 W white cold LED flood light	CH_3OH	[32]
$NiO\text{-}In_2O_3/TiO_2$	Modified sol-gel method.	200 W Hg reflector lamp	CO	[33]
$g\text{-}C_3N_4/(Cu/TiO_2)$	Wet impregnation-reduction method.	Pen-Ray Hg gas lamp	CH_3OH and HCOOH	[34]
WO_3	/	Light-emitting diode	CH_3OH, H_2, CO and CH_4	[35]

conversion of CO_2 also relieves the growing energy crisis, through producing valuable compounds with higher energy, such as methanol (CH_3OH) and methane (CH_4) [8], CO_2 is very stable and is difficult to react with other substances. The bond enthalpy of C=O in CO_2 is 805 kJ·mol^{-1} [9], which is much higher than that of C − C (336 kJ·mol^{-1}), C − O (327 kJ·mol^{-1}) and C−H (411 kJ·mol^{-1}), respectively [10]. In order to reduce CO_2 more effectively, the kinetics inertia and thermodynamics energy barrier should be overcome [1]. Suitable catalyst is the better solution. Many semiconductor photocatalysts have been applied to promote the reduction of CO_2 into liquid or gas products, such as TiO_2 [11], Ga_2O_3 [12], MgO [13], [Re(bpy) $(CO)_3\{P(OEt)_3\}]^+(1^+)$ [14], $g\text{-}C_3N_4$ [15] and some common catalysts used in photocatalytic conversion of CO_2 are listed in Table 1. Among them, TiO_2 is the most frequently used because of its comparatively stability, non-toxicity, and low cost [16]. However, the photocatalytic activity of TiO_2 is lower. So researchers have developed many alternative with higher photocatalytic activity of CO_2 reduction, such as $Pt^{2+}\text{-}P^0/TiO_2$ [17], $N\text{-}TiO_2\text{-}001/GR$ [18], Pt-loaded $g\text{-}C_3N_4$ [19], dye/ $TiO_2/Re(I)$ [20] and graphene oxide-CdS [21].

In 1979, Inoue and Fujishima et al. [36] reported that there was electrical bias in a variety of semiconductors under 500 W Xe or Hg lamps. Therefore, when different photocatalysts are used in the CO_2 conversion, different products are gained, such as CH_4 [37], CH_3OH [38], carbon monoxide (CO) [39], formic acid (HCOOH) [40], formaldehyde (HCHO) [40]. The photocatalysts play a very important role in the product selectivity of CO_2 reduction. In order to reduce the separation cost of products, lots of the researches have been conducted on the production of a single product under visible light. However, the selectivity of reduced product is very complicated, it also has a great connection with the reaction systems and routes [41]. So, not only the features of catalyst have a significant effect on the product, but also the reaction conditions including light intensity, reaction system, pH, temperature and pressure have great influence on the kinds of products. There are some unanswered questions in the product selectivity during the photocatalytic reduction of CO_2.

This review highlights the recent advances in photocatalytic reduction of CO_2 in the view of the selection of corresponding catalysts from the major catalytic products. Firstly, the photocatalytic reduction mechanism of CO_2 is briefly elaborated. Then, the criteria for suitable catalyst and optimal conditions of the reaction system are discussed in term of the product selectivity. Finally, the future research directions were prospected.

2. Photocatalytic reduction of CO_2

Photocatalytic reduction of CO_2 is similar to the process of photosynthesis for green plants. The photocatalysts play the role of green plants to convert CO_2 into fuel using ultraviolet (UV) or visible light in the photocatalytic reduction of CO_2 and the principle is illustrated in Fig.1. Typically, this reaction can be divided into four steps: Firstly, the catalyst is activated by the UV or visible light from sunlight or an illuminated light source. Subsequently, the electrons in the valence band (VB) leap into the conduction band (CB), simultaneously, the holes are left in the VB and form the negative- electron (e^-) and positive-hole (h^+) pairs, which respectively act as the reductants and oxidants for reducing and oxidizing the substances. Thirdly, the generated electron-hole pairs separate and transport to the surface of catalysts. Finally, CO_2 is reduced by the negative-electron and generates the corresponding products such as CH_4, CH_3OH, and CO [42].

In general, the photocatalytic activity and product selectivity of photocatalytic CO_2 reduction are greatly related to the reaction system and the photocatalysts [36]. As shown in Fig.2, photocatalytic CO_2 reduction can yield a wide variety of products. Among these products,
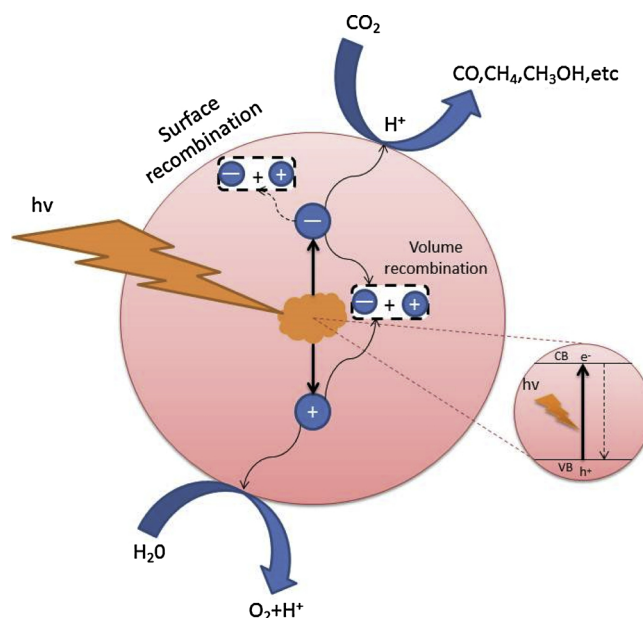

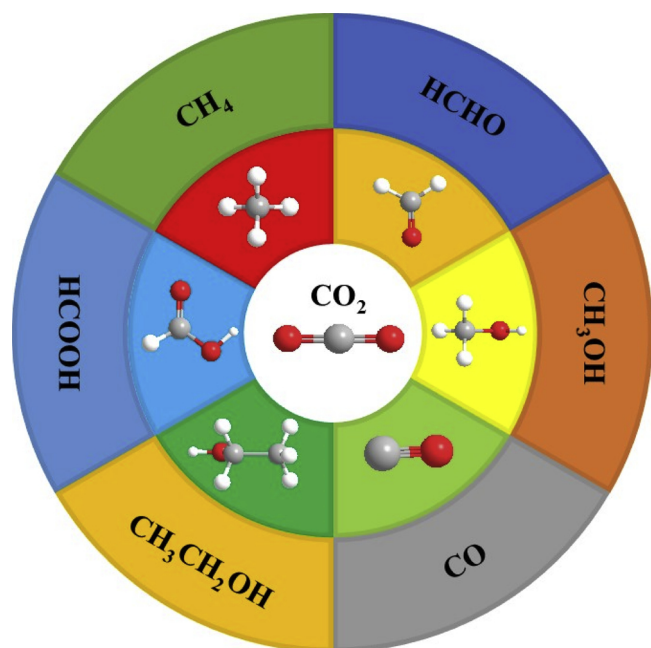**Fig. 1.** Schematic diagram of photocatalytic CO_2 reduction.

Fig. 2. Main products of CO₂ reduction.

the most common are CH₃OH and CH₄, while HCOOH, CO, HCHO, ethanol (CH₃CH₂OH), and elemental carbon also are detected [43]. The photocatalytic CO₂ reduction mainly is performed in gas or liquid phase system. It has been reported that CO and CH₄ are the main products in the gas phase system. However, the main products in the liquid phase system include CH₃OH, CH₃COOH, and HCOOH [24,26,34]. Moreover, a series of methods pointed to the photocatalysts have been developed to promote the photocatalytic activity and product selectivity of photocatalytic CO₂ reduction, such as the modification of catalysts and the construction of heterojunction [11,19]. Many reports demonstrated that the modification of catalyst by metals could promote the reduction of CO₂ to CH₄ due to the increasing surface electron density of the catalyst after doping the metal species [44,45]. In theory, CO formation is superior to CH₄ during the reaction because more electrons are required to generate CH₄ [46]. But the formation of CO can be suppressed by the increasing electron density due to the metal doping or other promoter. The surface electron density can also be boosted by constructing a heterojunction. For example, Park et al. [47] confirmed that
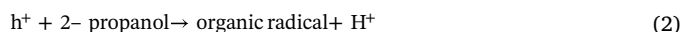
Cu$_x$O-TiO₂ had inherent p-n heterojunction, which offers the excellent light absorption and rapid charge separation to the catalysts, enhancing the selectivity for CH₄ generation (221.63 ppm ·g⁻¹ h⁻¹). Xiang et al. [48] also found that the CuO supported on the surface of NaTaO₃ nanocube could enhance the CO₂ adsorption and the reaction activity of CO₂ reduction, and the maximum CH₃OH yield of 335.93 μmol·g⁻¹·h⁻¹ was obtained.

3. Selectivity to products

The photocatalytic CO₂ reduction is a sequence of proton-coupled two-electron reactions. Based on the above discussion, a wide range of reduction products including CO, HCOOH, HCHO, CH₃OH and CH₃CH₂OH are observed during this process. Some main catalysts and their product selectivity in photocatalytic reduction of CO₂ are listed in Table 2.

3.1. Methane (CH₄)

The photocatalytic reduction of CO₂ into CH₄ has attracted most interesting because the physical and chemical properties of CH₄ are more stable and this reaction can occur at a lower potential from a thermodynamic point of view [7]. TiO₂ are the most common photocatalyst and some cases reported in literatures are listed in Table 3. In preliminary stage of photocatalytic CO₂ reduction, the catalysis process usually carried out under UV light. For example, Dey and his collaborators [67] found that the methanation of CO₂ under UV₃₅₀ in the TiO₂ suspension system was pronounced with the 2-propanol as a hole scavenger. In the oxygen-saturated system, however, the lower yield of CH₄ was observed due to the competition effects of O₂. It could be speculated that the CH₄ production was greatly related to the concentrations of O₂ and the hole scavenger (2-propanol) according to the following mechanism [67].

$$TiO_2 \xrightarrow{hv} e^- + h^+ \tag{1}$$

$$h^+ + 2-\ propanol \rightarrow organic\ radical + H^+ \tag{2}$$

$$CO_2 + 8H^+ + 8e^- \rightarrow 2H_2O + CH_4 \tag{3}$$

$$e^- + O_2 \rightarrow O_2^- \tag{4}$$

Tan et al. [72] reported that the transformation of CO₂ to CH₄ with TiO₂ pellets as the catalysts was significantly affected by the wavelength of UV. The total yield of CH₄ decreased from 200 ppm to less

Table 2
Main catalysts and their product selectivity in photocatalytic reduction of CO₂.

Catalyst	Main Products	Productivity	Enhanced mechanism	Ref
TiO₂-SiO₂	CH₄	2.42 μmol·g⁻¹	Hydrophobicity modification of composite photocatalyst	[49]
Ti₃₀Si₇₀MCM-41	CH₄	1.900 μmol·g$_{cat}$⁻¹· L⁻¹	Sensitization of photosensitizer	[50]
Ag-MgO-TiO₂	CH₄	37.18 μmol·g$_{cat}$⁻¹· L⁻¹	Strong local electric field of surface plasmon resonance to CO₂ reduction	[51]
Cu₂ZnSnS₄-ZnO	CH₄	138.90 μmol·g⁻¹· L⁻¹	Inherent direct Z scheme heterojunction	[52]
V$_o$-rich Pt/Ga₂O₃	CO	21.0 μmol·h⁻¹	Efficient separation of photoelectron-hole pairs on Pt/Ga₂O₃ led by V$_o$	[53]
Bi₄O₅I₂	CO	19.82 μmol·h⁻¹·g⁻¹	High lifetime of charge carrier and more electrons in the reaction	[54]
g-C₃N₄/Bi₂WO₆	CO	5.19 μmol·g⁻¹·h⁻¹	Band regulation and photosensitization	[55]
Fe₂O₃/Cu₂O	CO	5.0 μmol·g$_{cat}$⁻¹	p-n heterojunction between monomer interfaces	[56]
Cu/TiO₂	CH₃OH	1.8 μmol·cm⁻²·h⁻¹	Deposition of Cu nanoparticles	[57]
SnO₂ NRs/Fe₂O₃ NTs	CH₃OH	2.05 mmol·L⁻¹·cm⁻²	Matching band between SnO₂ NR and Fe₂O₃	[58]
Cu-promoted In₂O₃/TiO₂	CH₄/ CH₃OH	181 μmol·g⁻¹·h⁻¹ / 68 μmol·g⁻¹·h⁻¹	Doping of Cu	[59]
Sulfur-doped g-C₃N₄	CH₃OH	1.12 μmol·g⁻¹	Doping of S	[60]
ZnPc/TiO₂	HCOOH	978.6 μmol·g$_{cat}$⁻¹	Loading of ZnPc	[61]
Ru (II) multinuclear complexes	HCOOH	TOF$_{HCOOH}$ =11.6 min⁻¹	[Ru(bpy)₃]²⁺supramolecular redox sensitizer	[62]
Ru₂-Ru(CO)	HCOOH	TOF$_{HCOOH}$ = 44.9 min⁻¹	Photosensitizer unit with high effective state	[63]
Bi₂WO₆	CH₃OH/C₂H₅OH	56.5 μmol·g$_{cat}$⁻¹/20.5 μmol·g$_{cat}$⁻¹	Introduction of conductive polymers (polyaniline, polypyrrole, and polythiophene)	[64]
GO-TiO₂ Composite	CH₃OH/ C₂H₅OH	47.0 μmol·g⁻¹·h⁻¹/144.7 μmol·g⁻¹·h⁻¹	Synergistic interaction of interface electron transfer between constituent phases	[65]
Bi₂S₃	HC(O)OCH₃	300.94 μmol·g⁻¹	Special hierarchical structure, good air permeability and high light ability	[66]

Table 3
Application of TiO_2 in photocatalytic reduction of CO_2.

Photocatalyst	Reaction conditions	Light source	Productivity (μmol h^{-1} g$_{cat}^{-1}$)	Ref
TiO_2 (anatase, -325 mesh)	In the presence of a 2-propanol hole scavenger, the rate of CO_2 methanation is greatly increased.	Rayonet photoreactor	6.00	[67]
TiO_2 (Degussa P-25)	High pressure and hole scavengers can effectively accelerate the CO_2 methanation.	Xe lamp (4.2 kW, Ushio Electronics)	0.43	[68]
TiO_2	/	Hg lamp (365 nm)	18.75	[69]
TiO_2 nanoparticles	A significant amount of CH_4 can be obtained using a mixture of H_2O/H_2 reducing agents.	500 W Hg lamp (365 nm)	36.20	[59]
Commercial P25	/	Energy-saving daylight bulb	0.02	[37]
TiO_2	The production of CH_4 was increased by mesoporous TiO_2 nanoparticles and H_2O vapors.	500 W Hg flash lamp (365 nm)	30.85	[70]
TiO_2 nanocrystals	/	300 W Xe lamp (300 nm < λ < 400 nm, 20.5 mW cm^{-2})	1.58	[71]

than 100 ppm with the UV wavelength switching from UVC (253.7 nm) to UVA (365 nm). This result should be attributed to the lower photonic energy for UVA lamp (3.0 W) compared to UVC lamp (4.8 W). Meanwhile, the reforming photocatalytic experiment confirmed that the higher absorption capacity of catalyst also was the reason of better expected CH_4 yields.

The photoconversion route of CO_2 to CH_4 on TiO_2 is illustrated in Fig.3 [73]. The CO_2 is firstly adsorbed onto the surface of TiO_2 and then receives electrons from the CB under UV radiation. The CO_2 reacts with acidic protons to form a formyl HC˙O group. Then the formyl HC•O groups convert to glyoxal HOC˙HCHO in acidic solution. Subsequently, glyoxal accepts the protons and electrons, and then reacts with a sacrificial hole scavenger (such as formate, CH_3OH, and HCHO) to form acetaldehyde. Finally, the generated acetaldehyde releases the water and concurrently splits to CO and CH_4 through photolysis. Based on the above mechanism, acidic protons play important role in the photocatalytic conversion of CO_2 by TiO_2.

The pure TiO_2 catalyst exhibits poor ability to the photo-conversion of CO_2 and selectivity for the product due to the deficiency of itself property, such as the wide band gap and fast charge recombination. To solve these drawbacks, doping the modifier (Cu, Ni, Bi, *etc.*) with higher reduction potential and catalytic activity on TiO_2 had been adopted [45]. Compared with pure TiO_2 catalyst, the yield of CH_4 on Ni-doped TiO_2 nanoparticles significantly increased, which should be attributed that the band gap of TiO_2 narrowed with the doping of Ni [74]. When the nickel content was 0.1 mol%, the maximum CH_4 yield of 14 μmol·g$_{cat}^{-1}$ was obtained during 1 h. However, the improvement got worse with the further increase of nickel content as illustrated in Fig.4. Excessive nickel doping can cause the blockage of pores in TiO_2, resulting in the decrease in surface area of catalyst and the increase in electron-hole recombination. Recently, the photocatalysts doped with bismuth (Bi) have received increasing attention because the Bi as a semimetal element possesses the ability of hole trapping and depleting in the absence of a sacrificial agent. Meanwhile, the Bi-TiO_2 had better adsorption capacity of CO_2 than pure TiO_2, which plays a very important role in the rapid progress of the reaction [69]. After doping Bi, the absorption band gap increased from 1.0 eV of TiO_2 to 2.82 eV of Bi-TiO_2 (5.0 mol%). So the photoexcitation rate of the composite catalyst was faster than that of pure TiO_2, consequently, the photoexcited electrons were transferred efficiently to CO_2 molecules. Simultaneously, the holes in the valence band of Bi-TiO_2 could be captured by water and converted into ˙OH and ˙H, which reacted with the CO radicals formed from the reduction of CO_2^- over Bi-TiO_2 to produce CH_4.

Since the band gap of single catalyst is wider, the light utilization rate is lower and the recombination of charge carriers is faster. Many scholars begin to explore the composite catalyst or optimize the photoreaction conditions to achieve more perfect photo-conversion of CO_2 even under visible light. Tan et al [37] supported the noble metal (Pt, Pd, Ag and Au) nanoparticles on reduced graphene oxide (rGO)/TiO_2, and a very desirable catalytic effect to reduce CO_2 under visible light was obtained. The formation of ternary composites is believed to play a key role in obtaining high-efficiency photocatalytic performance, in which the graphene has a special zero band gap and the existence of Ti-O-C bonds between rGO and TiO_2 nanoribbons gives rGO/TiO_2 a better ability to separate photoinduced carriers and inhibit electron/hole pair recombination [75]. At shown in Fig.5, the Fermi level of TiO_2 is higher than that of Pt, Pd, Ag and Au [76]. Therefore, the photogenerated valence band holes remain on the TiO_2, and the photoexcited electrons are transferred from the conduction band to the metal particles. Meanwhile, the rGO/TiO_2 doped with a noble metal constructs a broad π–π conjugation system with excellent electron conductivity. The energy levels are facilitated to the transfer of photogenerated electrons from the conduction band of TiO_2 to the rGO sheets, thereby the separation of charge carriers is more effective. At the same time, a Schottky barrier is formed at the interface of TiO_2 and a noble metal, which is an electron trap and can hinder the electron-hole recombination.
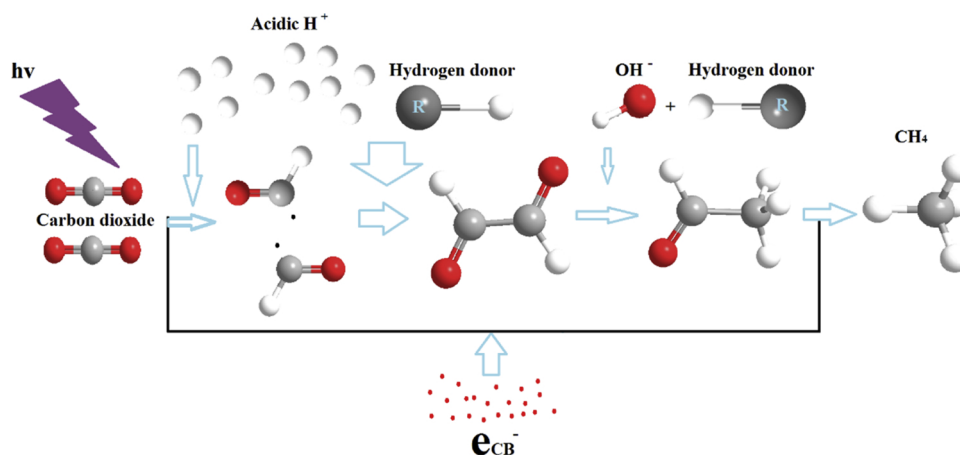
Fig. 3. Reduction of CO_2 molecules to methane.

3.2. Methanol (CH₃OH)

The photocatalytic conversation of CO_2 into CH_3OH was firstly observed by Inoue et al. with a mercury arc lamp as the light source [36]. There are two types reaction system for the reduction of CO_2 to CH_3OH including CO_2/H_2 mixture ($CO_2 + 3H_2 = CH_3OH + H_2O$, $\Delta H_{298K} = -90.7\,kJ\cdot mol^{-1}$) and CO_2/H_2O mixture ($CO_2 + 2H_2O = CH_3OH + \frac{3}{2}O_2$, $\Delta H_{298K} = -727\,kJ\cdot mol^{-1}$) [77,78]. The side reaction ($CO_2 + H_2 = CO + H_2O$) will occur during the conversation process in the CO_2/H_2 mixture system, which can consume hydrogen and produce a large amount of water, leading to the decrease of CH_3OH yield and even the deactivation of catalysts [79]. In addition, a series of by-products such as CH_3CH_2OH and other hydrocarbons are produced. Therefore, the photocatalytic conversation of CO_2 into CH_3OH mainly carries out in the CO_2/H_2O mixture system.

Anpo et al. [80] reported that higher photoactivity and excellent CH_3OH selectivity was achieved using the highly dispersed tetrahedral Ti-oxide species of ex-Ti-oxide/Y-zeolite catalyst in the CO_2/H_2O mixture system. The charge transfers excited state of the tetrahedral Ti-oxide species plays an important role in the formation of CH_3OH under UV irradiation. In addition, the Ti-mesoporous molecular sieve

exhibited higher photocatalytic activity and achieved higher CH_3OH yield than the powdered TiO_2 catalysts. Tseng et al. [81] demonstrated that CO_2 was more favorable to be reduced into CH_3OH on Cu/TiO_2 photocatalyst in NaOH solution and other by-products (*i.e.*, CH_4, HCOOH and other hydrocarbons) were not detected. This is because the alkaline solution dissolved more CO than the neutral water. The high concentration of OH^- in NaOH solution acted as the strong hole-scavengers, thereby reducing the recombination of electron-hole pairs. Shioya et al. [82] also found that Ti-containing mesoporous silica thin film showed the excellent selectivity to form CH_3OH and CH_4 with CO and O_2 as minor products under UV irradiation. They thought the small amounts of surface OH groups on the catalysts were more favorable to the highest selectivity for the formation of CH_3OH.

It has been reported that loading CuO on the surface of $NaTaO_3$ could serve as the catalyst for CO_2 reduction and CuO played photocatalytic sites for selective conversion of CO_2 to CH_3OH, and the reaction mechanism is showed in Fig.6 [48]. Xiang et al. [48] investigated the effect of the CuO loading amount on the photocatalytic activity of CO_2 conversation. Increasing CuO content improved the photocatalytic activity when the CuO loading was below the optimal amount (2 wt%). These results should be attributed that the CuO nanoparticles afforded
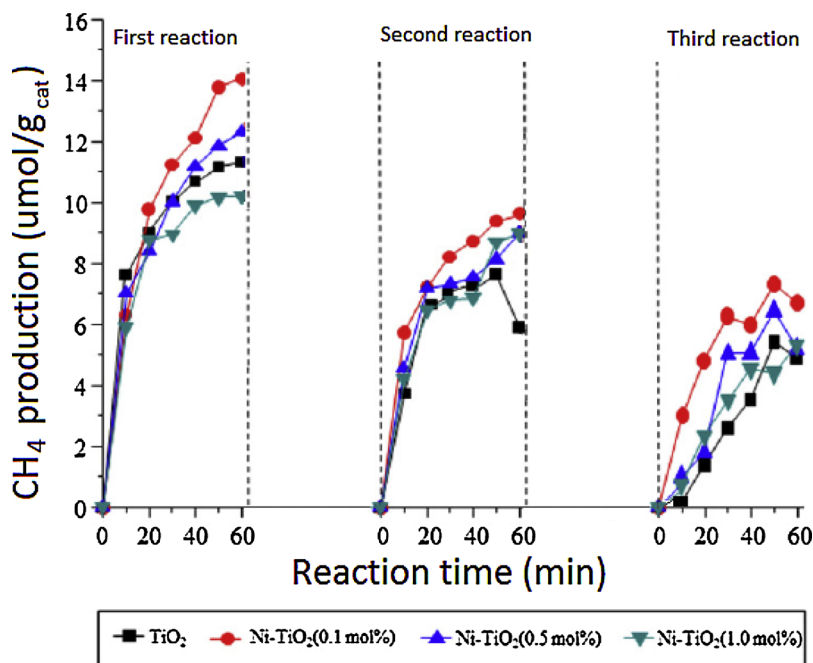

Fig. 4. CO_2 reduction by TiO_2 and TiO_2 doped with different proportions of nickel [73].
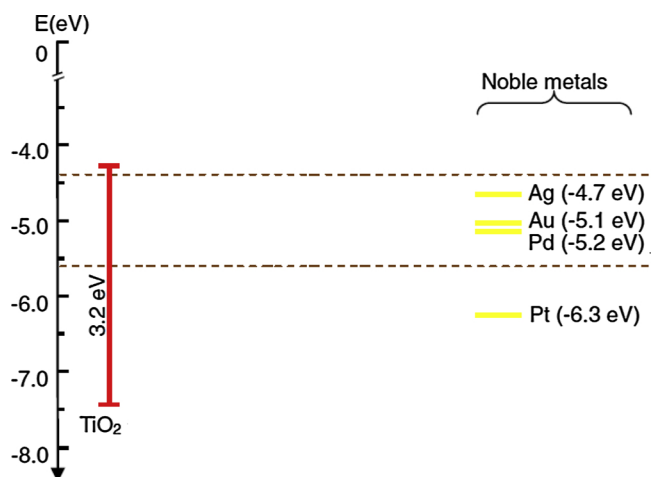
Fig. 5. The energy band positions of Pt, Pd, Ag and Au, including the conduction band and valence band of the TiO₂.

more photocatalytic activity sites and could decrease the recombination of photogenerated e^--h^+ pairs. However, the photocatalytic activity reduced due to the aggregation of CuO nanoparticles when the CuO content exceeded 2 wt%. In addition, the co-doping of TiO₂ with non-metal and metal elements has also been investigated to improve the photocatalytic activity for CO₂ reduction and selectivity for CH₃OH generation. The Cu-C co-modified TiO₂ (Cu-C/TiO₂) had been successfully synthesized by sonicated sol-gel method and used in photo-conversation of CO₂ into CH₃OH [83]. It was found that as-prepared photocatalyst obtained the maximum CH₃OH yields of 2593 and 885 µmol·g^{-1} after 5 h of illumination under UV and natural sunlight, respectively, which were much higher than those of C/TiO₂ and commercial TiO₂ (P25). The significant improvement of photocatalytic ability suggested that the C-doping could reduce the optical band-gap energy for TiO₂ activation and the Cu-modification could prevent the recombination of e^--h^+ pairs. Cu acts as a reduction site in the composite and it effectively promotes the reaction toward the direction of CH₃OH production. Because Cu^{2+} has a lower redox potential and unfilled 3d shell, the electrons can be captured by Cu^{2+} on the surface of TiO₂ [83]. The Cu^{2+} absorbs the photo-excited conduction band (CB) electrons (e_{CB}^-) and is reduced to cuprous (Cu$^+$), and then the Cu$^+$ lose electrons by converting hydrogen ions into hydrogen radicals, which makes the Cu$^+$ oxidize again to Cu^{2+} [83]. This process can successfully decrease the recombination rate of electron holes, and eventually the hydrogen radicals are combined with CO₂ to be converted into CH₃OH through Cu$^+$ substance as a reactive site. Except for doping metal elements as the reduction sites, modification of photocatalyst through combining two different catalysts to form a heterojunction structure is also a very effective method to enhance the photocatalytic reduction of CO₂. Li et al. [84] reported that modifying TiO₂ nanotubes

(TNTs) by CdS (or Bi₂S₃) to form the heterostructure photocatalyst not only enhanced the visible light absorbance, but also improved the photocatalytic activity for the reduction CO₂ to CH₃OH compared with single TNTs. The heterojunction formed between the two composites can promote the separation of e^- and h^+, prevent the charge-carrier recombination, and prolong the lifetime of photocarriers in the photocatalyst. Liu et al. [85] prepared ordered mesoporous g-C₃N₄ nanosheets supported on CdIn₂S₄ nanocomposites (CdIn₂S₄/mpg-C₃N₄) via a hard-template combinated with hydrothermal method. The CH₃OH production rate from CO₂ photoreduction over CdIn₂S₄/mpg-C₃N₄ (mpg-C₃N₄ 20 wt%) under visible-light irradiation was 42.7 µmol·g^{-1}·h^{-1}, which was 1.8 times than that of the pure CdIn₂S₄. This improvement is due to the better CO₂ adsorption and the improved separation and transfer of photogenerated e^--h^+ pairs at the close interface of photocatalysts heterojunctions. The mechanism of CO₂ reduction by photocatalyst composite with heterojunction structure can be summarized as Fig.7. Taking the CO₂ photo-reduction over CdIn₂S₄/mpg-C₃N₄ for example, the VB potential of mpg-C₃N₄ (+1.48 eV) is greater than that of CdIn₂S₄ (+1.50 eV), while CB potential of CdIn₂S₄ (−0.82 eV) is lower than that of mpg-C₃N₄ (-1.22 eV), resulting that the photogenerated e^- from the CB of mpg-C₃N₄ can easily migrate to CdIn₂S₄ and simultaneously the produced h^+ in VB of CdIn₂S₄ transfer to the mpg-C₃N₄ surface. Thought this way, the recombination of photogenerated e^--h^+ is inhibited, thereby the activity of photocatalyst for CO₂ reduction is enhanced. Moreover, the activated h^+ on the VB can oxidize H₂O to generate ·OH radicals and release O₂ and H$^+$. The H$^+$ and the photogenerated e^- reduce the CO₂ into CH₃OH.

The CO₂ can be effectively converted to CH₃OH under visible light, which is another major breakthrough because it achieves the utilization of natural abundant solar radiation. The CO₂ photo-conversion under visible light provides great prospects for the development of large-scale solar energy conversion facilities. Gondal et al. [86] reported that CO₂ could be reduced to CH₃OH using g-C₃N₄ photocatalyst under natural light. Kavil et al. [83] also demonstrated that the CO₂ could be converted into CH₃OH over Cu-C/TiO₂ catalyst under UV light or natural light. The production rate of CH₃OH in natural light was considerable and reached 885 µmol·g^{-1}, but it was obviously lower than that in UV light (2593 µmol·g^{-1}) since the photon flux and the spectral characteristics of incident light are the key factors to determine the CH₃OH yields [86]. However, it is also reasonable because the proportion of UV light in natural light is only about 4%. Adekoya and co-workers [34] compared the CO₂ photoreduction by g-C₃N₄/(Cu/TiO₂) nanocomposite under visible light and UV light and found that although the CH₃OH yield using UV light was initially higher than that of visible light, the higher CH₃OH yield was ultimately obtained under visible light. They thought that the g-C₃N₄/(Cu/TiO₂) nanocomposite might be oxidized under UV light, while the photocatalysts maintained higher stability under visible light. Therefore, considering both the products yield and the service life of catalyst, it is more effective and efficient for the photoreduction of CO₂ into CH₃OH under visible light using g-C₃N₄/(Cu/TiO₂) nanocomposite.
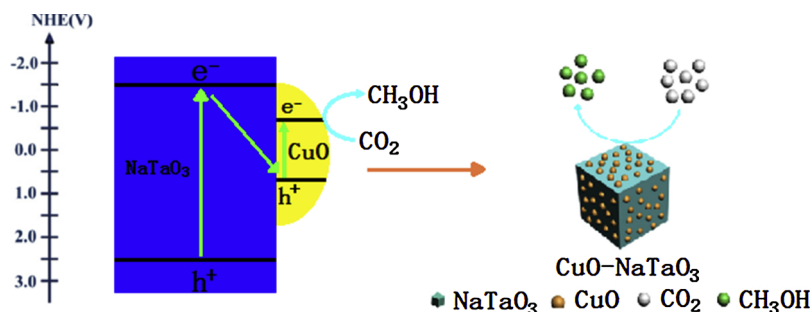

Fig. 6. CO₂ reduction to methanol on the reductive site of CuO-doped NaTaO₃ catalyst [47].
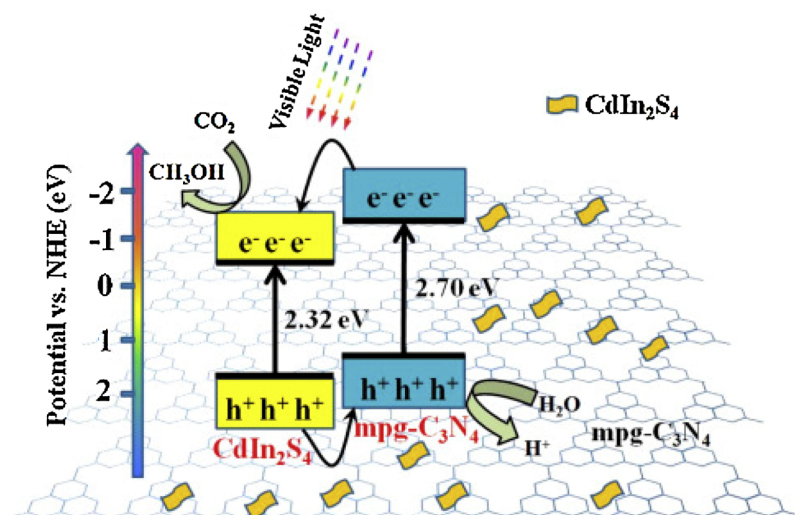
Fig. 7. The mechanism of CO_2 photoreduction by a heterojunction photocatalyst [47].

3.3. Carbon monoxide (CO)

Based on the reaction kinetic, the photoreduction of CO_2 to carbon monoxide (CO) is easier than the generation of CH_4 and CH_3OH because the formation of latter two products requires more electrons [87]. Beigi et al. [88] prepared a CdS-TiO_2 nanocomposite by hydrothermal method, which can reduce CO_2 to CO and CH_4 under UV–vis and visible light. They found that the activity of CdS-TiO_2 was related to the CdS content and the size of nanoparticles, and the optimal weight ratio CdS and average crystal size was 45% and 13 nm, respectively. Under UV–vis light, CO was the major product and its concentration was still growing after 8 h irradiation, whereas CH_4 yield maintained at the lower level. It is reported that the highly reactive H˙ radicals play the important role in the photoreduction of CO_2 to produce CH_4 [89]. Generally, the amount of H• radicals generated from water decreased when the gaseous water in the reaction system decreased, so CH_4 production was less than CO. However, the photocatalytic reduction of CO_2 in water by $Na_2Ti_6O_{13}$ nanoparticles can achieve CO as the main product and the H_2 and O_2 as by-products, the selectivity for the CO production increased to 60% when the photocatalytic reaction was carried out in the basic aqueous solution of Na_2CO_3 [90]. The crystal composition and size of $Na_2Ti_6O_{13}$ had a great influence on the photocatalytic efficiency. The thick rod-like structure with suitable aspect ratio of 3.2 could maintain a good balance for both reductive and oxidative reactions, resulting in the highest CO production rate.

In recent years, the application of heterogeneous photocatalysts has become a hot topic. Many kinds of Ag-modified heterogeneous photocatalysts have been investigated to effectively reduce CO_2 to CO, such as Ag-loaded $ALa_4Ti_4O_{15}$ (A = Ca, Sr and Ba) [91], Ag-loaded Ga_2O_3 [92], Ag modified $CaTiO_3$ [93]. The redox potential of CO_2 conversion to CO (-0.12 V, *vs.* SHE) is lower than the redox potential of protons (0.0 V, *vs.* SHE) [94]. Therefore, the reaction between CO_2 and excited electrons (Eq. (5)) should be prior to the oxidation of H_2O (Eq. (7)) and generation of H_2 (Eq (6)) [90]. Wang et al. [95] discovered the high rate of H_2 generation and the low rate of CO evolution using bare Ca_2O_3. It should be ascribed to the presence of a large amount of active sites on catalyst for H^+ reduction. However, the selectivity for CO evolution reached 100% over Ag-loaded Zn-modified Ga_2O_3 catalyst. As shown in Fig.8, Zn modification can form a $ZnGa_2O_4$ layer and a heterojunction with Ga_2O_3, which has a special function to eliminate the active sites for H^+ reduction and suppress the evolution of H_2. Meanwhile, the Ag-loaded catalyst provides an appropriate active site to promote CO_2 conversion. Similarly, the Ag-modified $La_2Ti_2O_7$ catalyst with a layered perovskite structure also displayed excellent activity for
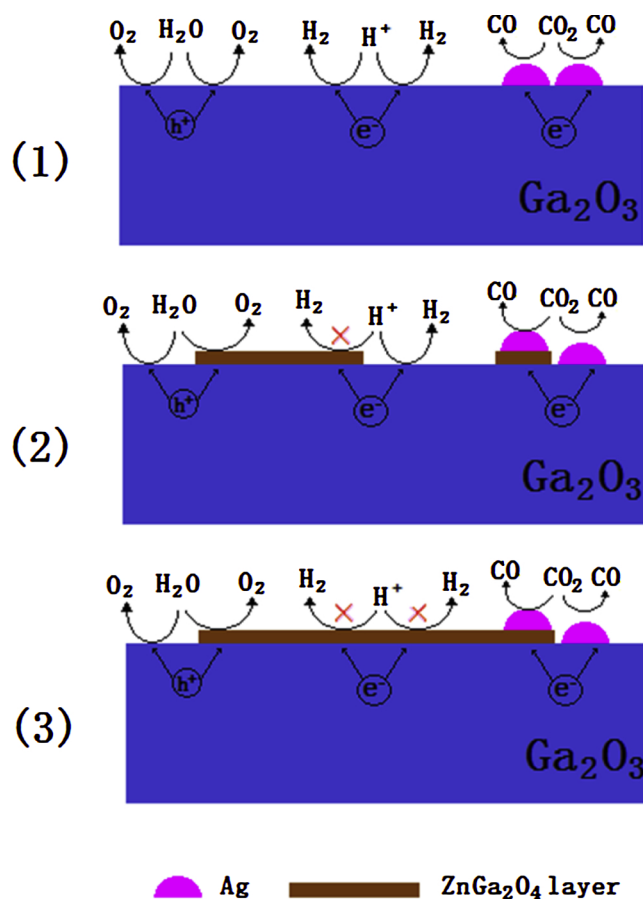

Fig. 8. The mechanism of photocatalytic CO_2 conversion over Ag-loaded Ga_2O_3 (1), Ag and low- content Zn loaded Ga_2O_3 (2), and Ag and high-content Zn loaded Ga_2O_3 (3) [94].

converting CO_2 to CO under UV light irradiation [96]. Tang et al. [97] studied the photoreduction of CO_2 to CO over alkali and alkaline earth metal ions (Mg^{2+}, Na^+, K^+) exchanged hydrogen titanate nanotubes (H-TNTs) in simulated sunlight. It was found that CO and CH_4 were the primary products with neglectable hydrocarbons. The ion-exchange between H^+ and alkali or alkaline earth metal ions could enhance the CO_2 adsorption and improve the photogenerated e^--h^+ pair formation, separation, and transformation, resulting in a higher CO_2-to-fuel

efficiency. It is also reported that TiO_2 with a thin overlayer of a basic oxide (*i.e.*, MgO, CaO, SrO, BaO) had an improved adsorption capacity of CO_2 [98]. The lattice parameter of these metal oxides can adjust the interaction between CO_2 and the surface of catalyst, thereby increasing the photocatalytic reduction of CO_2 to CO.

$$CO_2 + 2H^+ + 2e^- = CO + H_2O \qquad (5)$$

$$2H^+ + 2e^- = H_2 \qquad (6)$$

$$H_2O + 2h^+ = \frac{1}{2}O_2 + 2H^+ \qquad (7)$$

3.4. Other products

Some other organic products, such as HCOOH and HCHO are also produced during the photoreduction of CO_2. The $Ba_3Li_2Ti_8O_{20}$ can reduce CO_2 to HCHO under visible-light irradiation, but the incorporation of CuO particles can further increase the production of HCHO. The highest HCHO yield reached $50.0\,\mu mol \cdot g^{-1} \cdot h^{-1}$ when the CuO content was 2 w% [99]. The improvement should be attributed to the n–p heterostructure between the n-type $Ba_3Li_2Ti_8O_{20}$ and the p-type CuO interface, which facilitated the photogenerated e^--h^+ pairs separation and the protons accumulation for conversation CO_2 into HCHO. Khodadadimoghaddam [100] studied the photoreduction of CO_2 to HCHO over different semiconductor colloids including FeS, FeS/FeS_2, NiO and TiO_2 under UV radiation. Among these photocatalysts, TiO_2 exhibited the highest HCHO conversion ability. The maximum HCHO concentration for TiO_2 was 720 ppm, which was 1.89 times that of pure NiO. Meanwhile, the CO_3^- could promote the generation of HCHO, but decreasing the pH value and sulfide concentration of the mixture was not favorable to the generation of HCHO [100].

HCOOH is also a very common product in the photocatalytic reduction of CO_2 [101,102]. Zhang et al. [103] researched the reduction of CO_2 to HCOOH and CH_3OH under visible light using graphene- TiO_2. The results demonstrated that pH showed great influence on the catalytic efficiency. When the pH was 8, the better selectivity of HCOOH was achieved and reached 90%. Graphene can improve the catalytic activity due to its large surface area. The photocatalytic activity of graphene-TiO_2 was greatly affected by the content of graphene loading and the best catalytic result was gained with the 8.5% graphene loading. But excessive graphene might hinder the visible light to the catalytic surface, leading to the deterioration of reduction efficiency. It has been reported that $BiYO_3$ doped with different amounts of Cu could be as the highly-efficient photocatalyst for reduction of CO_2 to HCOOH under visible light irradiation [104]. The doping Cu can not only replace Bi^{3+} in $BiYO_3$ lattice and then form oxygen vacancies to capture electrons and inhibit e^--h^+ recombination, but also reduce the size of composite catalyst, increase the surface area and decrease the resistance of surface charge transfer.

The ethanol (CH_3CH_2OH) is another main product in the photocatalytic reduction of CO_2. Liu and his co-workers [22] found that CO_2 could be successfully converted to CH_3CH_2OH in water under high intensity visible light irradiation with $BiVO_4$ as the photocatalyst. The CH_3CH_2OH conversion was related to the construction of $BiVO_4$ and the intensity of light irradiation. The monoclinic $BiVO_4$ showed higher photocatalytic activity for CH_3CH_2OH generation than tetragonal $BiVO_4$ because CO_3^{2-} was anchored to the Bi^{3+} site via a weak Bi-O bond so that the catalysts could effectively accept the photogenerated e-. Moreover, the intensity of light irradiation acted as a significant role for CH_3CH_2OH generation since CH_3OH and CH_3CH_2OH were produced in comparable rates as a 36 W fluorescent lamp was applied. The increase of visible-light irradiation time and the extension of irradiation light into UV region can all increase the CH_3CH_2OH production rate. Generally, the photogenerated e- and protons increased with the increasing intensity and irradiation time of the light, which lead a large amount of C1 intermediates anchored on the surface of $BiVO_4$,

facilitating the generation of CH_3CH_2OH. The higher selectivity to produce the CH_3CH_2OH can be attributed that the interaction between photoelectrons and protons in water is difficult to form H_2 [105]. The conducting polymers (polyaniline, polypyrrole and polythiophene) modified Bi_2WO_6 also can reduce CO_2 to CH_3CH_2OH under visible light ($\lambda \geq 420$ nm) in the presence of water [64]. Among them, polythiophene modified Bi_2WO_6 (PTh/Bi_2WO_6) exhibited the best photocatalytic performance and the CH_3CH_2OH yield was $20.5\,\mu mol \cdot g_{cat}^{-1}$ in 4 h due to the narrow band gap and good charge mobility of polythiophene. The potential of CO_2 converted into CH_4 or CO is -0.24 eV and -0.53 eV, which are more negative than the CB of Bi_2WO_6 (0.24 eV). Hence, there was no CH_4 and CO production in this photoreduction CO_2 system.

4. Conclusions and perspective

With the global climate change and energy crisis intensifying, exploring suitable ways to solve these problems has become the focus of global research. The conversion of CO_2 to energetic hydrocarbons in visible light or UV light over the corresponding photocatalyst has been successfully achieved under experimental conditions, which has been proven to be a cost-effective technology to simultaneously solve above two problems. The choice of catalyst is very important to achieve the prefect and high-efficiency photoreduction of CO_2, because the conversion efficiency of solar energy to chemical fuels depends on the light absorption ability, the separation of the photoelectron/hole carrier and the surface reaction power of the photocatalysts. Simultaneously, the selective formation of desired products is affected by the VB/CB position and the redox sites of the photocatalyst. The catalytic performance of bare photocatalysts as well as the selectivity to the specific product can be obviously improved by the modification of photocatalysts, including material-doping, sensitization and heterojunction construction. TiO_2 for its high activity, good stability and non-toxic becomes the most frequently-used catalyst. However, new types of composite catalysts are gradually becoming the hotspot because of their lower oxidation potential and excellent surface structure.

CO_2 is a chemically stable molecule. The reduction of CO_2 involves up to eight electrons, the C=O bond breakage (bond energy is $805\,kJ \cdot mol^{-1}$) and the formation of the C–H bond, which requires very harsh conditions (such as high temperature and pressure). It needs a large amount of energy input to the reduction of CO_2, which limits the extensive application of this technique in practical. So, the photocatalytic reduction of CO_2 to fuel is still only in the experimental stage and far from the level of practical application. The current average productivity of fuel is about $100\,\mu mol \cdot g_{cat}^{-1} \cdot h^{-1}$ under sunlight. Meanwhile, the weak surface CO_2 adsorption and poor stability of photocatalyst, and the lower utilization of solar energy all make the conversion of CO_2 into fuel fairly low efficiency. Meanwhile, the reduction products are usually impure for the poor selectivity of catalysts, so the separation and purification of reduction products in the CO_2 photocatalytic system is also very difficult. Therefore, improving the performance of existing photocatalysts and finding more suitable photocatalysts for CO_2 reduction is particularly important.

There are massive researches focusing on the improvement of CO_2 photoreduction efficiency, while trying to enhance the selectivity of catalyst to produce the desired products. The most important issue in the photoreduction of CO_2 is to increase the output of products. Nowadays, the yield obtained under the Laboratory conditions is not enough to meet the requirements in practical production. In general, photocatalytic reduction of CO_2 is not selective and the reduction product are typically a mixture of multiple organics. The selectivity of product can be achieved by doping the metal oxides, adjusting the photocatalyst surface to be hydrophobic, controlling the reaction conditions such as pH, temperature, pressure and coexistence ion. In order to further improve the catalytic performance and selectivity, the future research should focus on the effective optimization of surface properties

of the catalyst, such as augmenting surface area, increasing surface load or selecting the co-doping element. Meanwhile, the light source is also very important. In practical, the photo-reduction of CO_2 under UV light is expensive due to huge energy for the UV excitation, so recent researches are gradually transferring to the visible light (solar light), the free unlimited energy source. However, in order to achieve the similar reduction performance of CO_2 in visible light to UV, it puts forward high requirements to improve the characteristic of catalyst, which will also become a hot development and research direction in the future. Meanwhile, it is worthwhile to explore efficient and simple technology to separate and purify the reduction products. If this problem can be solved, the research on photo-reduction of CO_2 can focus on the yield of products instead of the selectivity. To establish the coupling system of catalytic water decomposition and CO_2 reduction using solar light is a novel challenge. In this process, the water is decomposed to produce hydrogen and oxygen by solar photolysis, and the hydrogen and CO_2 are transformed to organic fuel through catalytic reaction. Along with the development of research, we have a more thorough understanding of the reaction mechanism, the development of new reaction systems, and the behavior of photogenerated carriers, the design of high efficiency, high selectivity and multi-functional catalytic materials will certainly become the subject.

Conflict of interest

Article Title: Photocatalytic Conversion of Carbon Dioxide: From Products to Design the Catalysts

Authors: Zhiyan Fu, Qi Yang, Zhan Liu, Fei Chen, Fubing Yao, Ting Xie, Yu Zhong, Dongbo Wang, Jing Li, Xiaoming Li, Guangming Zeng

All authors of this manuscript have directly participated in planning, execution, and analysis of this study.

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Acknowledgments

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