

Research Progress of Photocatalytic Reduction of Carbon Dioxide

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Abstract

The reduction of carbon dioxide (CO₂) into sustainable green solar fuels through photocatalysis is a promising solution to both environmental problems and the energy crisis. In this paper, the mechanism of photocatalytic CO₂ reduction is briefly introduced, and then the challenges of photocatalytic CO₂ reduction are analyzed from the aspects of light absorption, carrier separation and recombination, and CO₂ adsorption and activation. The corresponding strategies and the latest research progress are summarized, including the adjustment of band structure, cocatalyst load, heterojunction construction, MOFs material design, etc. Finally, the problems that remain unsolved and the obstacles to industrial application in the future are summarized.

Keywords

Photocatalysis; Carbon Dioxide Reduction; Band Structure; Cocatalyst; Heterojunction.

1. Introduction

With the development of industry, problems such as energy shortage and global warming have caused wide concern. It is estimated that due to excessive CO₂ emissions, the average temperature will rise by 1.9 °C after 80 years, which will bring a huge crisis to human survival. Scientists have proposed and implemented a variety of new technologies for CO₂ capture, storage and conversion. Among them, the conversion of CO₂ into high value-added chemical products and fuels can solve the problems of resource waste, environmental pollution and greenhouse effect caused by excessive CO₂ emissions, and is expected to realize the transition from a fossil fuel economy to a sustainable CO₂ economy. In particular, using sunlight as the only energy input, simulating photosynthesis in nature, and promoting the conversion of CO₂ into chemicals such as CO, CH₄, CH₃OH and HCOOH through photocatalysis will be a promising new green technology.

In recent years, a series of new photocatalysts have been reported for CO₂ reduction^[1,2], but most photocatalysts still cannot overcome the shortcomings of low energy conversion efficiency, uncontrollable product selectivity, and inability to completely inhibit competitive hydrogen evolution reactions^[3]. Therefore, the design of photocatalytic systems with high conversion efficiency and product selectivity still needs continuous research. On the other hand, many important advances have been made in the mechanism research of electrocatalytic CO₂ reduction and the development of high-performance electrodes. Among them, carbon monoxide (CO) and formic acid (HCOOH), represented by two electron transfer products, can be produced on suitable electrocatalysts with lower overpotential and higher Faraday efficiency^[4]. However, for multi-electron transfer products such as methane (CH₄) and ethanol (CH₃CH₂OH), electrocatalytic reduction reactions carried out directly on the bare electrode surface usually require large overpotential and exhibit low product selectivity.

Photocatalytic CO₂ reduction reaction (PECCO₂RR) combines the advantages of photocatalysis and electrocatalysis. The external bias can promote carrier separation and regulate the product type, and

the extra photovoltage reduces the energy consumption of the reaction, which has a good prospect. In this paper, the mechanism of photocatalytic CO₂ reduction is briefly introduced, and then the challenges of photocatalytic CO₂ reduction are analyzed from the aspects of light absorption, carrier separation and recombination, and CO₂ adsorption and activation. The corresponding strategies and the latest research progress are summarized, including the adjustment of band structure, the loading of cocatalyst, the construction of heterojunction, and the design of MOFs materials.

2. Mechanism of CO₂ Reduction

The total reaction of photocatalytic reduction is mainly divided into the following steps: photon absorption; Excitation, separation and migration of electron-hole pairs. Figure 1 shows a schematic diagram of photocatalytic reduction of CO₂ to produce hydrocarbons [5]. In the process of photocatalytic reaction, when the energy of light radiation is higher than its own band gap width, electrons will be excited from the valence band to the conduction band, so as to form holes with oxidation ability and electrons with reduction ability required for catalytic reaction. After the incident photon is absorbed and excited to produce an electron-hole pair, the electrons in the conduction band and the holes in the valence band migrate from the bulk phase to the catalyst surface. Subsequently, electrons react with H₂O to reduce CO₂ to hydrocarbons such as methanol, methane, formaldehyde, formic acid, etc. Photogenic holes with strong oxidation capacity oxidize H₂O and release O₂.

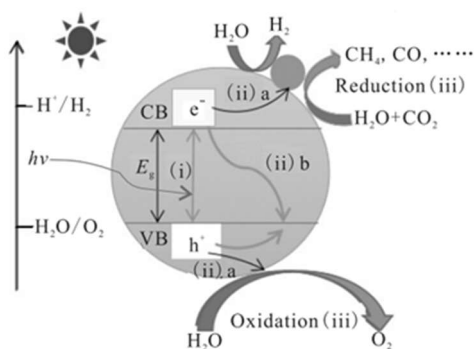


Figure 1. Photocatalytic reduction of CO₂ to hydrocarbons

The photoelectric catalytic system is generally composed of a working electrode, an opposite electrode and a reference electrode, and at least one of the working electrode and the opposite electrode is a photoelectrode. Taking the photoanode photocathode system as an example, the anode side of photocatalytic CO₂ reduction mainly consists of the following processes: a. The catalyst absorbs incident light larger than its band-gap width to produce electron-hole pairs, and electrons are transported to the cathode under the action of external bias. b. A hydrolysis reaction occurs on the anode to decompose H₂O into oxygen and protons, where the protons enter the cathode side through the proton exchange membrane. Correspondingly, the following reaction processes occur on the cathode side: a. On the photocathode, the catalyst absorbs photons to produce electron-hole pairs, and receives electrons and protons from the anode side through the external circuit and the proton exchange membrane; b. Electrons migrate to the active site on the catalyst surface to reduce CO₂ to the target product [5]. Since the whole reduction reaction is composed of the above several complex processes, there are problems and challenges in each step.

2.1 Light Absorption

The photoelectrode absorbs the incident light to produce an electron-hole pair as the beginning of a photocatalytic CO₂ reduction reaction. The absorbency of photoelectrode depends largely on the surface properties and band structure of catalyst. The surface reflectance of planar catalysts is relatively high, resulting in relatively poor light-trapping ability. Reasonable regulation of the surface

morphology of catalysts can effectively improve its light-absorbing ability^[6]. In addition, it is also an effective way to enhance the light absorption ability of catalysts by combining or doping appropriate elements with wide-band gap semiconductors and photosensitive materials to regulate the energy band structure^[6].

2.2 Carrier Separation and Recombination

The relatively low solar fuel conversion quantum yields achieved to date by most photocatalytic systems can be attributed primarily to electron-hole recombination, primarily non-radiative recombination. Therefore, slow recombination or fast separation of photoexcited carriers is the key to improve the reduction efficiency. The coulomb force between electrons and holes makes it very difficult to inhibit their recombination. In addition, the non-radiative relaxation of excited electrons to the ground state also leads to electron-hole recombination on the nanosecond scale. In contrast, electron transfer at semiconductor interfaces is typically two to three orders of magnitude slower than the electron-hole recombination rate. Therefore, the carrier dynamics of the semiconductor surface determines the rate of surface REDOX reaction, and the recombination of carriers has become one of the main limiting factors in the process of solar energy conversion. Carrier separation can be effectively promoted by constructing heterojunction or using the diffusion of elements to establish internal potential. In addition, the separation and transfer of electron-hole pairs are also facilitated by optimizing the carrier migration path and strengthening the conductivity.

2.3 Adsorption and Activation of CO₂

CO₂ is a thermodynamically stable molecule with a linear geometric structure, so its adsorption and activation on the catalyst surface also greatly affect the process of the reduction reaction. There are four key steps in this process: (i) the adsorption of CO₂ molecules on the catalyst surface; (ii) activation of CO₂ molecules to form partially charged CO₂-ion free radicals or intermediates; (iii) C = O bond dissociation to provide another chemical product after reaction with electrons and protons; (iv) desorption of newly formed products from the catalyst surface^[7]. For most metal oxides and sulfides, the C or O atoms of CO₂ form weak bonds with a single metal site through the hybridization of 2p and 3d orbitals, generating intermediates^[8]. In contrast to the highly stable C=O bonds of CO₂, the weaker M-O or M-C bonds are easily cleaved to form CO or more advanced hydrocarbons (after protonation). In addition, the binding properties of CO₂ molecules on the catalyst surface also determine the activity and selectivity of the catalytic reaction.

3. Strategies to Improve the Performance of Catalyst for CO₂ Reduction

3.1 Adjustment of Band Structure

The photocatalytic performance of semiconductors is closely related to the band structure (band gap, conduction band and valence band position), because the band gap determines the range of light absorption, and the photocatalytic REDOX potential requires appropriate conduction band and valence band position. So far, various strategies have been reported to adjust the electronic structure of photocatalysts, the most important of which is doping.

Taking TiO₂ as an example, the band structure of TiO₂ can be changed by element doping to generate visible light excitation and photoelectronic transition. TiO₂ bandgap width is generated by Ti's 3d track and O's 2p track affecting the position of conduction band and valence band^[9]. The doping of elements will affect the 3d orbital of Ti and the 2p orbital of O. Metal ions or non-metallic ions can enter the band gap as an "intermediate stage", which acts as a "springboard" to make the band gap become "narrow", causing the redshift of absorption wavelength, further expanding the light wave response range and generating visible light response. On the other hand, the doping of elements causes the covalent bond between Ti-O to break, resulting in certain defects in the crystal and the formation of oxygen vacancies. Low concentration of oxygen vacancies can strengthen carrier transport and photoelectron capture-release, inhibit electron-hole recombination, and increase the visible light response. However, if the crystal defect concentration is too large, the steady-state electron

concentration will be reduced, but the catalytic activity will be weakened. At present, there are four main doping types of element doping, which are transition metal element doping^[10], rare earth metal element doping^[11], non-metallic element doping^[12] and multi-component co-doping^[13].

3.2 Cocatalyst Load

The supported cocatalyst is the main means to accelerate the surface reaction, and very few semiconductors can achieve efficient CO₂ reduction by self-catalysis, so the cocatalyst is an indispensable part of the photocatalyst. The co-catalyst not only accelerates the extraction of photogenerated electrons or holes by forming heterojunctions, but also accelerates the multi-electron reaction by enriching electrons or holes, and improves the surface reaction kinetics by reducing the activation energy.

Recently, Dai et al.^[14] synthesized BiVO₄ photocatalyst (Ag-MnOx-BVO) modified with double cocatalyst Ag and MnOx by photodeposition method to address the inherent poor carrier separation ability of BiVO₄ photocatalyst in tetragonal zircon phase. This structure overcomes the limitations of fast recombination of photoelectrons with holes and slow charge transport in bulk phase photocatalysts, and is conducive to the directional separation of photogenerated carriers. The photocatalytic CO₂ reduction experiment showed that under full light irradiation, the Ag-MnOx-BVO samples modified with double cocatalyst showed higher CO₂ reduction activity than that supported by Ag or MnOx cocatalyst alone, and the CO production efficiency was 3.1 times that of pure BVO. Characterization such as photochemical testing and fluorescence testing also demonstrated that the increased activity was attributed to more efficient carrier separation and transport.

3.3 The Construction of Heterojunction

Constructing oxide-semiconductor heterojunctions with optimized band structures has many advantages. On the one hand, the appropriate heterostructure can adjust the band structure, so that it can make full use of light energy and increase the photogenerated carrier. On the other hand, an internal electric field is generated at the interface of the heterojunction, which promotes its transfer on the heterojunction to inhibit recombination, thus increasing the utilization rate of photogenerated electrons. In addition, since the properties of the surface and interface of the heterojunction profoundly affect the form and strength of the catalyst's adsorption of CO₂, this plays a crucial role in the selectivity of photocatalytic CO₂ reduction. For example, the additional active sites introduced by the co-catalyst are conducive to the adsorption and activation of CO₂, thereby improving the photoreduction efficiency of CO₂. Therefore, the construction of heterojunctions is expected to improve both quantum efficiency and product selectivity (Figure 2)^[15].

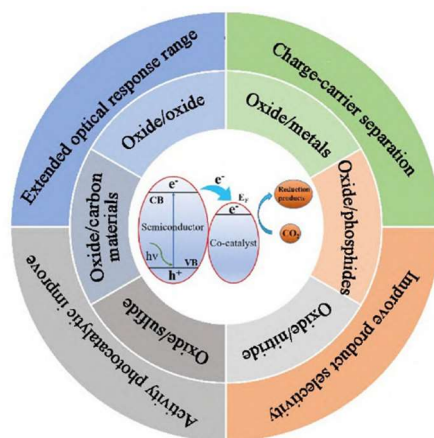


Figure 2. Heterostructure of oxide semiconductor

Zhu et al. [16] successfully developed a typical two-dimensional heterostructure by combining 2D g-C₃N₄ and Co₃O₄, and applied it to the photocatalytic CO₂ reduction reaction. Its charge transfer behavior and CO₂ reduction site. The introduction of narrow band gap Co₃O₄ can broaden the light absorption range, so that more sunlight can be responded to. In addition, the close contact between the two components effectively improves charge migration, and the specific exposed crystal face of Co₃O₄ allows photogenerated electrons to migrate through the interface to 2D g-C₃N₄, thereby increasing the surface charge density of the photocatalytic reaction. Therefore, the construction of 2D heterostructures can induce the efficient reduction of CO₂ to CO in the liquid-solid system with the addition of triethanolamine, the CO production is 419 μmol·g⁻¹·h⁻¹, and the selectivity is 89.4 %. This work fully demonstrates the important role and good prospect of rational design of photocatalysts based on heterogeneous structures to improve the performance of CO₂ photoreduction by optimizing synthesis methods and interface engineering.

3.4 Building MOFs

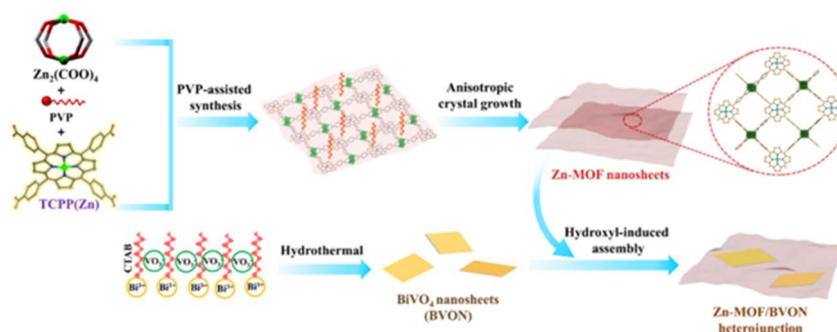


Figure 3. 2D/2D Zn-MOF/BVON heterojunction synthesis process diagram^[17]
PVP-polyvinylpyrrolidone; TCPP-5, 10, 15, 20-tetraketol (4-carboxyphenyl) porphyrin

Table 1. MoFs-based CO₂ conversion photocatalyst

Catalysis	Reduction efficiency	Photocurrent density /mA·cm ⁻²	Reaction condition	Reference
C-ZnZIF700	90.17 μmol·g ⁻¹ ·h ⁻¹ CH ₃ OH	—	0.1 mol/L KHCO ₃ , 2 V(vs. Ag/AgCl)	[18]
Cu/Cu ₂ O-Cu(BDC-NH ₂)	674 μmol·L ⁻¹ CH ₃ OH	2.5	300 W xenon arc lamp, 0.1 mol/L Na ₂ SO ₄ , +0.1 V	[19]
Cu ₃ (BTC) ₂ /Cu ₂ O	The efficiency of reduction to CO is 95 %	—	300 W Xenon lamp, 0.1 mol/L Tetrabutylammonium hexafluorophosphate	[20]
MOF to In ₂ O ₃ -x@C	The efficiency of reduction to HCOOH was 97 %	—	1 mol/L KOH, -1.0 V(vs. RHE)	[21]
Bi ₂ S ₃ /ZIF-8	The efficiency of reduction to formate was 74.2 %	16.1	300 W Xenon lamp, 0.7 V(vs. RHE)	[17]
NH ₂ -UiO-66@MIL-101	267.90 μmol·h ⁻¹ ·g ⁻¹ CO and 18.63 μmol·h ⁻¹ ·g ⁻¹ CH ₄	1.23	300 W Xenon lamp	[22]

Compared with traditional inorganic catalysts, MOFs photoelectrodes have the advantages of large surface area, versatility and easy structure regulation. Zhao et al.^[17] embedded ZIF-8 particles into Bi₂S₃ by in-situ synthesis method to prepare heterojunction MOF composite materials that could convert CO₂ into formate by photoelectric chemistry (Figure 3). Through the analysis of the catalytic properties of the composites with different Bi/Zn molar ratios, it was found that the catalyst with the Bi/Zn molar ratio of 1:10 had the highest photocatalytic performance, and there was no performance attenuation during the 12 h stability test. Table 1 summarizes the recently reported MOF-based photocatalysts for CO₂ conversion.

4. Conclusion

The technical challenge and difficulty of CO₂ resource utilization lies in how to efficiently and selectively convert it into high value-added products and realize large-scale commercial utilization. Photocatalytic CO₂ reduction technology combines the advantages of photocatalysis and electrocatalysis, which not only makes full use of environmentally friendly and clean solar energy as the driver, but also uses the characteristics of electrocatalysis to achieve the regulation of the product. In the past few decades, the photoelectric catalytic reduction of CO₂ system has been gradually developed and mature, and the shortcomings exposed in the early stage of research have gradually been improved. As we have summarized, the problems of limited light absorption, rapid recombination of carriers and poor CO₂ absorption in the photocatalytic reduction CO₂ system can be improved through the adjustment of catalyst band structure, the formation of supported cocatalyst and heterojunction, and the construction of MOFs-type materials. However, the resulting catalyst is still less active than for industrial applications. In addition, most scholars focus on the improvement of activity, and few studies focus on the improvement of catalyst stability, reactor design, product storage and separation, which are crucial for the eventual realization of large-scale industrial applications. Therefore, the future development of photocatalytic CO₂ reduction still needs more research and breakthroughs.

References

- [1] Dandan Li, M. Kassymova, et al. Photocatalytic CO₂ reduction over metal-organic framework-based materials[J]. *Coord. Chem. Rev.* 2020, 412: 213262.
- [2] Linxia Wang, Yali Dong, et al. Construction of NiO/g-C₃N₄ p-n heterojunctions for enhanced photocatalytic CO₂ reduction[J]. *J. Solid. State. Chem.* 2022, 308: 2169-2176.
- [3] Xiaoxia Chang, Tuo Wang, Jinlong Gong. CO₂ photo-reduction: insights into CO₂ activation and reaction on surfaces of photocatalysts[J]. *Energy Environ. Sci.* 2016, 9: 2177-2196.
- [4] Tingting Zheng, Kun Jiang, Haotian Wang. Recent advances in electrochemical CO₂-to-CO conversion on heterogeneous catalysts[J]. *Adv. Mater.* 2018, 48(30): 1802066.
- [5] Shunji Xie, Qinghong Zhang, et al. Photocatalytic and photoelectrocatalytic reduction of CO₂ using heterogeneous catalysts with controlled nanostructures[J]. *Chem. Commun.* 2016, 52(1): 35-39.
- [6] Pan Ding, Tianhao Jiang, et al. Photocathode engineering for efficient photoelectrochemical CO₂ reduction[J]. *Mater. Today Nano.* 2020, 10: 100077.
- [7] Weibin Chu, Qijing Zheng, et al. CO₂ photoreduction on metal oxide surface is driven by transient capture of hot electrons: Ab initio quantum dynamics simulation[J]. *J. Am. Chem. Soc.* 2020, 142(6): 3214-3221.
- [8] Xiaodong Li, Yongfu Sun, et al. Selective visible-light-driven photocatalytic CO₂ reduction to CH₄ mediated by atomically thin CuIn₅S₈ layers[J]. *Nat. Energy.* 2019, 4: 690-699.
- [9] Xuhan Zhang, Chenyu Xu, et al. Photothermal catalytic water splitting at diverse two-phase interfaces based on Cu-TiO₂. *ACS Appl. Energy Mater.* 2022, 5(4): 4564-4576.
- [10] Periyakaruppan Karuppasamy, Nagoorkani Ramzan Nilofar Nisha, et al. An investigation of transition metal doped TiO₂ photocatalysts for the enhanced photocatalytic decoloration of methylene blue dye under visible light irradiation[J]. *J. Environ. Chem. Eng.* 2021, 9(4): 105254.

- [11] Ju Li, Bingxian Chu, et al. Mechanism and DFT Study of degradation of organic pollutants on rare earth ions doped TiO₂ photocatalysts prepared by sol-hydrothermal synthesis[J]. Catal. Letters. 2022, 152(2): 489-502.
- [12] Elsayed T Helmy, Ahmed EL Nemr, et al. Photocatalytic degradation of textile dyeing wastewater under visible light irradiation using green synthesized mesoporous non-metal-doped TiO₂[J]. Bull. Mater. Sci. 2021, 44(1): 30.
- [13] Antonietta Mancuso, Olga Sacco, et al. Visible light active Fe-Pr co-doped TiO₂ for water pollutants degradation[J]. Catal. Today, 2021, 380: 93-104.
- [14] Dujuan Dai. Study on regulatory strategies and properties of BiVO₄-based photocatalysts[D]. Shandong: Shandong University, 2023.
- [15] Kai Li, Chao Teng, et al. Recent advances in TiO₂-based heterojunctions for photocatalytic CO₂ reduction with water oxidation: a review[J]. Front. Chem. 2021, 9, 637501.
- [16] Xingwang Zhu, Haiyan Ji, et al. A specifically exposed cobalt oxide/carbon nitride 2D heterostructure for carbon dioxide photoreduction[J]. Ind. Eng. Chem. Res. 2018, 57(51): 17394-17400.
- [17] Zhenlong Zhao, Ji Bian, et al. Construction of 2D ZnMOF/BiVO₄ S-scheme heterojunction for efficient photocatalytic CO₂ conversion under visible light irradiation[J]. Chinese J. Catal. 2022, 43(5): 1331-1340.
- [18] James W Maina, Cristina Pozo-gonzalo, et al. Tuning CO₂ conversion product selectivity of metal organic frameworks derived hybrid carbon photoelectrocatalytic reactors[J]. Carbon, 2019, 148: 80-90.
- [19] Beatriz Costa E Silva, Kallyni Irikura, et al. Effect of Cu(BDC-NH₂) MOF deposited on Cu/Cu₂O electrode and its better performance in photoelectrocatalytic reduction of CO₂[J]. J. Electroanal. Chem. 2021, 880: 114856.
- [20] Beatriz Costa E Silva, Kallyni Irikura, et al. Electrochemical preparation of Cu/Cu₂O-Cu(BDC) metalorganic framework electrodes for photoelectrocatalytic reduction of CO₂[J]. J. CO₂ Util. 2020, 42: 101299.
- [21] Chen Qiu, Kun Qian, et al. MOF-transformed In₂O₃-x@C nanocorn electrocatalyst for efficient CO₂ reduction to HCOOH[J]. Nanomicro Lett. 2022, 14(1): 167.
- [22] Nan Kong, Huiling Du, et al. Nano heterojunction of double MOFs for improved CO₂ photocatalytic reduction performance[J]. COLLOID SURFACE A. 2023, 663: 131005.