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# Progress in photocatalytic reduction of $CO_2$ to CO by MOF materials

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**Abstract:**

By harnessing the power of photocatalysis, there is a promising pathway to develop sustainable carbon cycles, which can significantly reduce our reliance on fossil fuels and advance the goal of sustainable energy development. MOFs, with their ordered porous structures, have shown tremendous potential in photocatalytic $CO_2$ reduction. These materials are characterized by their excellent structural tunability, large surface areas, and outstanding $CO_2$ capture capabilities, making them ideal candidates for photocatalytic reactions. In the context of $CO_2$ reduction, the photocatalytic performance of MOFs is critically influenced by their light absorption properties, material design, and $CO_2$ capture efficiency. In recent years, researchers have made significant progress in exploring and developing MOF materials specifically for reducing $CO_2$ to carbon monoxide (CO). This paper reviews some of the most representative MOF materials in this domain, discussing their performance, advantages, and the challenges they face in practical applications. By synthesizing these research outcomes, we can gain a deeper understanding of the operational mechanisms of MOFs, providing valuable insights and guidance for future research directions.

**Keywords:** Photocatalysis; MOF materials; $CO_2$ reduction.

## 1. Introduction

In recent decades, the enormous consumption of fossil fuels has resulted in excessive $CO_2$ emissions, thereby precipitating severe environmental issues. $CO_2$ plays a pivotal role in amplifying the greenhouse effect in the atmosphere. To address this issue, countries worldwide are actively seeking effective strategies for emission reduction and carbon management strategies to mitigate the adverse environmental impacts of $CO_2$ emissions. Driven by the goal of carbon neutrality, converting carbon dioxide into recyclable fuels has become a promising solution [1]. Nevertheless, despite its enormous potential, $CO_2$ conversion is hampered by its exceptionally stable chemical structure, which makes the reduction process remarkably difficult. Photocatalytic $CO_2$ reduction requires substantial energy input and involves intricate reaction processes, including electron transfer and the generation and separation of intermediate products [2,3]. Therefore, these challenges underscore the critical importance of optimizing catalyst design and reaction conditions to achieve efficient $CO_2$ reduction.

In this context, MOFs have demonstrated remarkable advantages in photocatalytic $CO_2$ reduction because of the unique structural characteristics [4]. MOFs offer a high degree of design flexibility, allowing for precise tuning of their structure and functionality through the adjustment of metal nodes and organic ligands. Moreover, the high porosity and synergistic effects of multiple active sites in MOFs provide abundant reaction sites, enhancing the efficiency of photocatalytic reactions. Consequently, MOFs have been extensively studied and have made impressive strides in photocatalytic $CO_2$ reduction. This paper, therefore, focuses on summarizing the current states of research on MOFs for the conversion of $CO_2$ to CO. It explores the performance of various MOF materials in $CO_2$ reduction and discusses the challenges they face in practical applications. By reviewing these advancements, researchers can gain a better understanding of the mechanisms at play in MOF-mediated $CO_2$ conversion, providing valuable insights for future research.

## 2. Photocatalytic Mechanism

In a photocatalytic reaction, the photocatalytic material is activated by incident light, causing photogenerated electrons to transition from HOMO to LUMO under light irradiation. Under the action of electric field potential, the photogenerated electron-hole pair reacts with the adsorbed $CO_2$ at the catalytic active site effectively splitting and transferring to the surface of the photocatalytic material [5]. As shown in Figure 1, photogenerated electrons with strong reducing ability reduce $CO_2$ to CO, HCOOH, $CH_3OH$, $CH_4$, and other products [6]. Generally, MOFs are composed of organic ligands and metal clusters [7]. The structural tunability allows for the adjustment of optical and electronic properties, specifically the HOMO and LUMO energy levels [8]. This tunability enables the optimization of photocatalytic performance through the reasonable catalyst design.

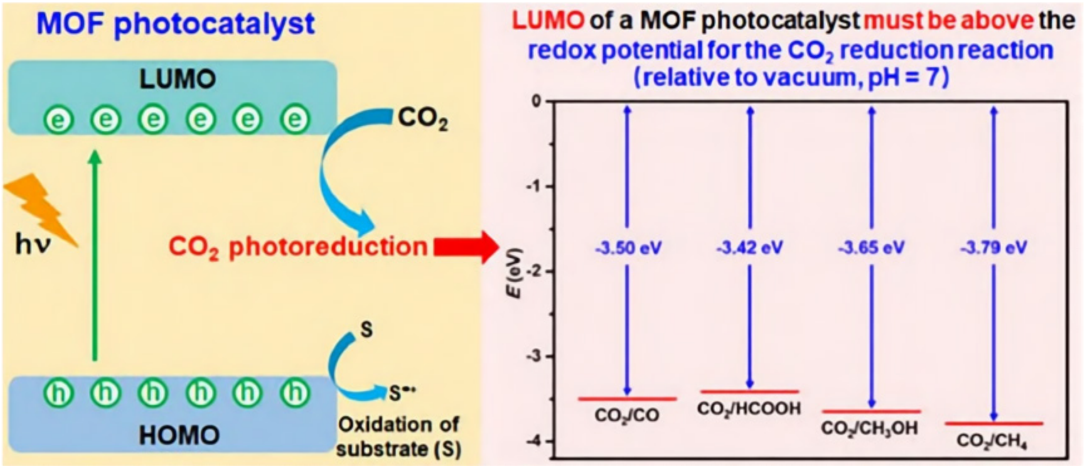

**Fig. 1 Schematic diagram of the photocatalytic reduction of $CO_2$ by MOFs and redox potentials of different fuel products [6]**

## 3. MOFs photocatalytic reduction

### 3.1 As photocatalyst

By modifying the ligands and metal clusters of MOF, it is possible to effectively reduce the HOMO-LUMO bandgap, thereby extending the material's range of light absorption [9]. Introducing functional photosensitive ligands, electron-rich conjugated ligands, and metal-based ligands is a key methodology to enhance the photocatalytic $CO_2$ reduction performance. Functional photosensitive ligands improve light absorption capabilities, electron-rich conjugated ligands enhance electron migration efficiency, and metal-based ligands provide the necessary active centers. The strategic combination of these ligands can optimize the photocatalytic performance of MOFs and improve their activity and selectivity. The kinetic barriers to this pathway are relatively low compared to other processes that form complex organic compounds because the photoreduction of $CO_2$ to CO is a two-electron process [10]. Therefore, by optimizing the catalyst design, the reduction of $CO_2$ can be achieved more easily.

Using MOF as a photocatalyst in catalytic reactions means that MOF acts as both a light-absorbing and catalytic part. In such MOFs, organic ligands are generally metalloporphyrins and metallobipyridine complexes. In the reaction,

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the organic ligand absorbs light and is excited, and electrons transition from HOMO to LUMO [11], which in turn are transferred to metal ions in metal ligands or molecular complexes (LMCT) for catalytic reduction of $CO_2$.

Zr-based UiO-MOFs, characterized by their strong Zr-O bonds, are among the most stable MOF materials. Additionally, the transition metal complexes within these MOFs can generate long-lived charge-separated excited states, making them effective components for absorbing light in solar energy conversion. In 2011, Lin et al. [12] combined the catalytically active dicarboxylic acid functional group complexes $H_2L_1$-$H_2L_6$ with a porous $Zr_6O_4(OH)_4(BPDC)_6$ to form MOFs1~6 that can be used as photocatalytically active catalysts. MOF4 is formed by introducing $[Re^I(CO)_3(dcbpy)Cl]$ into the backbone as a ligand. The photocatalytic $CO_2$ reduction process demonstrated that this catalyst is highly selective in the conversion of carbon dioxide to carbon monoxide in saturated carbon dioxide acetonitrile solutions, as illustrated in Figure 2. This study highlights the potential to create efficient heterogeneous catalysts for solar energy applications.

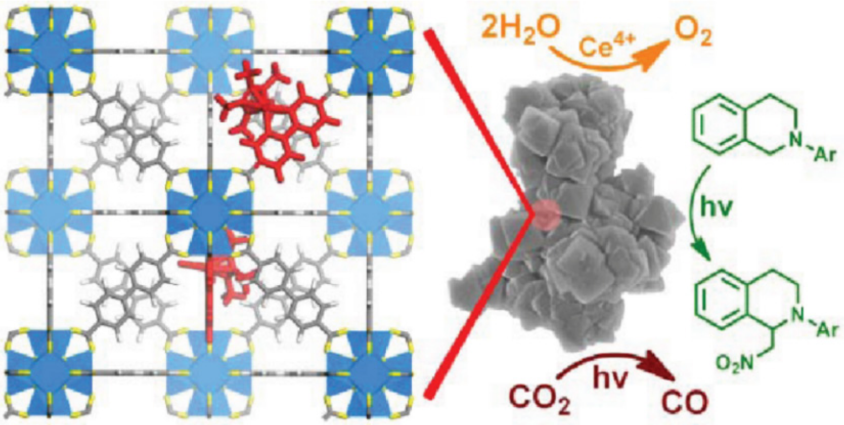

**Fig. 2 Schematic diagram of mixed ligand strategy for UiO-67 MOF photocatalytic $CO_2$ reduction process [12]**

In 2016, Ryu et al. [13] introduced amino ($–NH_2$) as a chemical functional group into Re-MOF, forming Re-MOF-$NH_2$(X%), which is formed by the covalent linkage of $Re^I(CO)_3(BPYDC)(Cl)$ with a Zr-based MOF of UiO-67 type structure. Experimental results indicate that Re-MOF-$NH_2$ (33%) exhibits the highest photocatalytic performance. With the assistance of triethanolamine, this newly synthesized MOF catalyst achieves 100% selectivity in converting $CO_2$ to CO. Additionally, its photocatalytic conversion rate is three times greater than that of the Re-MOF without the $–NH_2$ group, as depicted in Figure 3. In Metal-Organic Frameworks (MOFs), $–NH_2$ (amino) functional groups play a crucial role. Firstly, the $–NH_2$ groups modify the Re–CO (rhenium-carbonyl) bond length, which in turn adjusts the chemical properties of the catalyst. This modification significantly influences the electronic structure of the catalyst, leading to more efficient electron transfer during the catalytic reaction. Furthermore, the $–NH_2$ groups enhance the intermolecular stability between carbonate and $CO_2$ molecules. This increased stability improves $CO_2$ adsorption, thereby boosting the activity in the photocatalytic process. These enhancements contribute to higher catalytic efficiency and selectivity in photocatalytic $CO_2$ reduction. This is a typical example of modifying ligands in MOFs to improve photocatalytic performance.

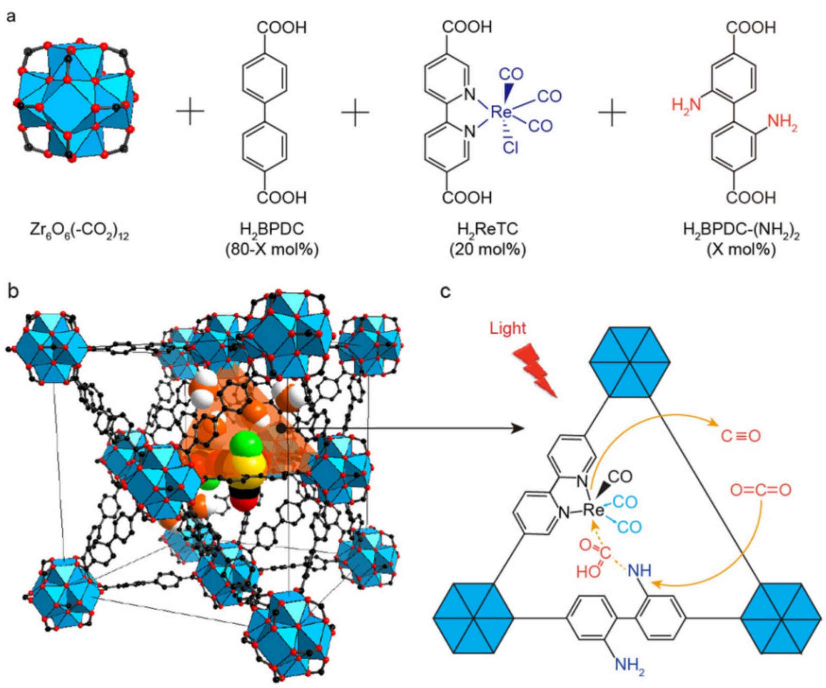

**Fig. 3 a) Structure of Re-MOF-$NH_2$(X%), b) Schematic of $CO_2$ conversion to CO by Re-MOF-$NH_2$(X%) [13]**

Other studies have further demonstrated how transition metals influence the activation performance of photocatalytic reduction. In 2022, Huang et al. [14] designed and synthesized an artificial photosynthesis crystalline catalyst RO-4, consisting of a reduced {Cu8} cluster linked by a bridge oxygen link and an oxidized $\{PMo_8V_6O_{42}\}$ cluster, as shown in Figure 4. The reduction of $CO_2$ occurs on the $\{Cu_8\}$ cluster, while the oxidation of H2O takes place on the $\{PMo_8V_6O_{42}\}$ cluster. The experimental results show that the RO-4 compounds exhibit higher CO yields (selectivity > 99.5%) than CuL and $\{PMo_8V_6O_{42}\}$, which is contributed to the advantage of faster transfer of photogenerated electrons facilitated by bridging oxygen, and the photogenerated electrons are effectively separated at the reduction site and the oxidation site. The durability of photocatalyst was assessed experimentally and the yield of CO produced rose nearly linearly under continuous light irradiation.

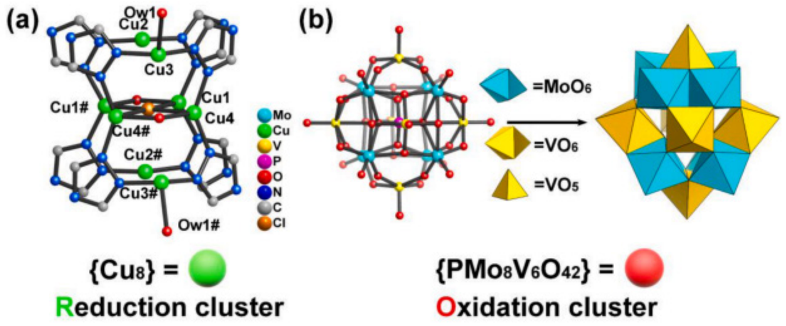

**Fig. 4 (a) The structure of $\{Cu_8\}$, (b) The coordination environment of $\{PMo_8V_6O_{42}\}$ node [14]**

## 3.2 As co-catalyst

The use of MOF as a co-catalyst in catalytic reaction means that MOF only serves as the catalytic part, and the light-absorbing part is generally a metal complex (terpyridine ruthenium/iridium, etc.) or a semiconductor (metal-semiconductor, organic semiconductor). In this system, metal complexes or semiconductors may have little catalytic activity, but the activity of the reaction system is greatly increased by the addition of MOFs [15], so such MOFs are often referred to as cocatalysts.

### 3.2.1 Metal complexes are used as a light-absorbing part of the MOF co-catalyst

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The porous nature of MOFs enhances $CO_2$ capture, and their metal complexes serve as effective light-absorbing components in MOF catalysts. Research indicates that the catalytic activity of metal centers and the adjacent μ-$OH^-$ ligand can significantly improve the stability of the photocatalyst for $CO_2$ reduction. In 2018, Zhang et al. [16] six Co-based MOFs with varying coordination environments and investigated the photocatalytic performance under identical conditions. When $CO_2$ pressure decreases, as shown in Figure 5, the TOF of the μ-$OH^-$ ligand adjacent to the Co center decreases by only 20%, whereas other MOFs experience at least a 90% drop. This is because the μ-$OH^-$ ligand stabilizes the initial Co- $CO_2$ adduct through strong hydrogen bonds and also provides protons to aid in C-O bond cleavage.

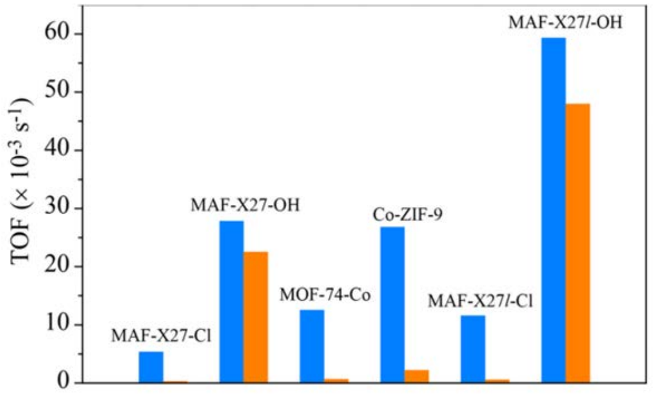

**Fig. 5 TOF values under 1.0 atm (blue) and 0.1 atm (orange) [16]**

MOF catalysts often exhibit reduced catalytic activity in an aqueous environment. In 2019, Liao et al. [17] demonstrated that incorporating a hydrophobic methylene group around the metal center of MOFs can enhance their catalytic activity for $CO_2$ reduction, as shown in Figure 6. Using $[Ru(phen)_3]Cl_2$ (where phen = 1,10-phenanthroline) as a photosensitizer, $CH_3CN/H_2O$ as a mixed solvent, and TEOA as a sacrificial agent, it was observed that MCF-55-Ni outperformed porphyrin-based MOF-525-Ni and MOF-525-Co in catalytic activity under the same experimental conditions. Crystal engineering methods are thus crucial for designing catalysts with high activity and stability.

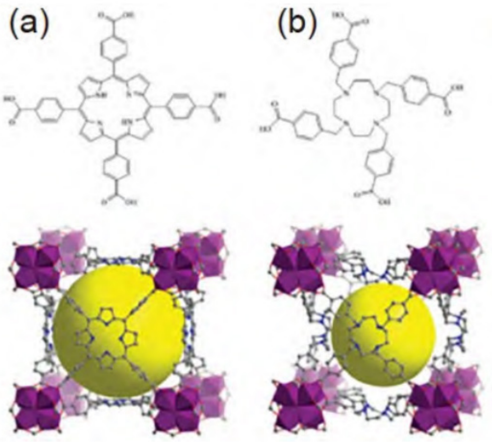

**Fig. 6 Ligand and cubic cage structure of a) MOF-525; b) MCF-55 [17]**

### 3.2.2 Metal semiconductors are used as MOF cocatalysts for light-absorbing fractions

In 2014, Wang et al. [18] established a non-precious metal photocatalytic $CO_2$ reduction system using semiconductor CdS as a photosensitizer, Co-ZIF-9 as a catalyst, and TEOA as a sacrificial agent. Fluorescence emission spectroscopy revealed that the fluorescence intensity of CdS decreased significantly when Co-ZIF-9 was introduced into the reaction system, as shown in Figure 7. This decrease is attributed to the rapid transfer of photogenerated electrons from CdS to Co-ZIF-9, which facilitates the catalytic reduction of $CO_2$. This electron transfer process greatly enhances the utilization of photogenerated charges, and thereby improves the catalytic capacity of $CO_2$ reduction system.

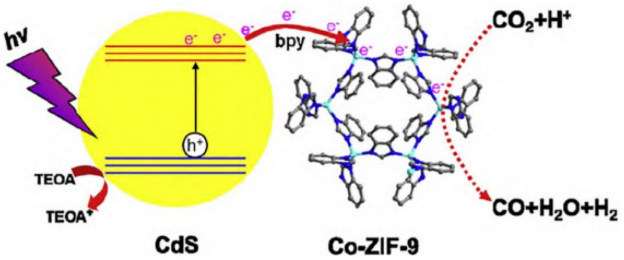

**Fig. 7 Mechanism for the photocatalytic reduction of Co-ZIF-9 system [18]**

### 3.3 As photosensitizer

Organic molecules with large conjugated structures have absorption in a wide range of wavelength bands, and when their HOMO and LUMO are suitable, they can participate in $CO_2$ reduction reactions as photosensitizers. When coordination groups such as –COOH, –OH, and $–NH_2$ are introduced into the structure of these organic molecules, the MOFs formed by them and inorganic ligands can act as photosensitizers, and this strategy of forming MOFs from organic molecules can recycle photosensitizers and reduce pollution and waste.

In 2018, Gao et al. [19] employed Zn-MOF as a semiconductor photosensitizer and used $[Co_2(OH)L](ClO_4)_3$ or ZIF-67 as cocatalysts for efficient, stable, and selective photocatalytic $CO_2$ reduction. $CO_2$ can be effectively reduced to CO under visible light using this MOF/ZIF system, as shown in Figure 9, marking its first application for $CO_2$ reduction. Photoelectrochemical impedance and photoluminescence studies revealed that the enhanced photocatalytic performance is attributed to the improved charge transport capability of the Zn-MOF nanosheets, as well as more efficient charge separation and longer lifetime of photogenerated charge carriers. It was demonstrated that the use of Zn-MOF nanosheets as photosensitizers resulted in higher photocatalytic activity and selectivity for CO compared with bulk Zn-MOF.

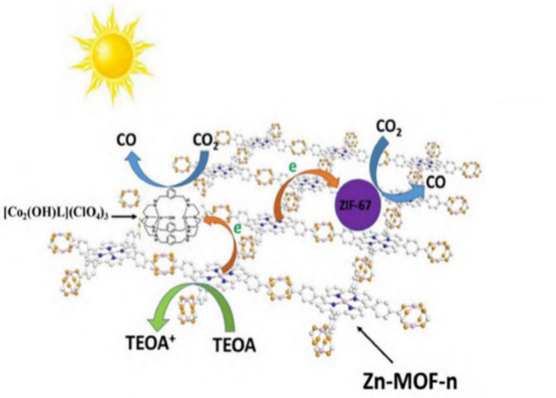

Fig. 9 Photocatalytic system of $CO_2$ reduction with a photosensitive MOF, Zn-MOF-n [20]

## 4. Conclusion

With the advancement of functionalized photocatalytic materials, the photocatalytic reduction of $CO_2$ has become a prominent research focus. Structurally well-defined MOFs offer valuable models for exploring various $CO_2$ conversion strategies. This review refers to recent progresses in MOF materials for photocatalytic $CO_2$ reduction to CO, discusses their roles as photocatalysts or co-catalysts, and highlights innovative strategies to enhance light absorption and carbon dioxide conversion, such as metal substitution, ligand modification, ligand mixing, and the introduction of polyacidic groups. Despite significant progress in this field over the past decade, it remains in its early stages, with many challenges yet to be addressed. Most MOF-based catalytic systems still require auxiliary catalysts or electron sacrificial agents, which, while improving performance, can also lead to environmental contamination or depletion of active sites, reducing material efficiency. Although well-defined MOFs facilitate mechanistic understanding, further study of $CO_2$ conversion mechanisms in MOF-based catalysts is necessary. Advanced characterization techniques and interdisciplinary collaboration are essential for deeper insights. Current research indicates that MOFs are promising materials for photocatalytic $CO_2$ reduction. This paper anticipates that through continuous technological innovation and in-depth mechanistic research, MOF catalysts are poised to have a pivotal impact in achieving efficient $CO_2$ reduction and environmental protection.

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