

Metal-organic frameworks (MOFs) for photoreduction of CO₂

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Abstract. In recent decades, human industrialisation has become increasingly advanced, and the quality of life has also improved. Subsequently, the excessive consumption of fossil fuels has caused a series of problems, for example, global environmental warming caused by excessive CO₂ emissions. Among numerous CO₂ reduction technologies, using solar energy as an energy source for the CO₂ photoreduction is considered one of the most prospective technologies. This method not only reduces the amount of CO₂, but also enables to converse CO₂ into other valuable chemicals, thereby achieving carbon cycling. Metal-organic frameworks (MOFs) are composed of metal ions and organic ligands as three-dimensional porous materials. MOFs have many advantages, including sizeable specific surface area, excellent CO₂ absorption capacity and modifiable pore structure, leading to broad application potential in photocatalytic reduction of CO₂. This article mainly introduces three aspects: functionalisation and modification of pure MOFs, MOF-based composite materials, and MOF-derived materials, which further improve the CO₂ photocatalytic efficiency of MOFs. Furthermore, it includes the analysis of reported examples, discussion and outlook on reaction mechanisms and challenges. At present, the main difficulties faced by MOFs-based photocatalysts lie in their economic feasibility and poor material stability. Therefore, this review aims to help stimulate in-depth research in this area as well as better exert the advantages of MOFs.

Keywords: Metal-Organic framework, CO₂ photoreduction, Composite material, MOFs synthesis.

1. Introduction

In recent decades, as the level of industrialisation has gradually risen, so has the standard of living. However, this progress has come at a cost. The overreliance on human demand for fossil fuels, substantial emissions of industrial gas waste and vehicle exhaust, has led to an escalation in carbon dioxide in the environment in the past few decades. As predicted, global energy consumption will increase by 0.5 times of the current level by 2040. At that time, fossil fuel resources will not be enough to supply the growing energy demand [1]. This has contributed to a range of environmental issues, including environmental warming, glacier melting, and sea level rising [2]. Consequently, the demand for new energy sources and pollution control is becoming increasingly urgent. Thus, methods of reducing CO₂ emissions and reusing it have become global research focus. Currently, the techniques for reducing CO₂ emissions are mainly categorised: CO₂ capture and storage [3] and CO₂ chemical

conversion and consumption [4]. However, capturing and storing CO₂ is not a long-term applicable solution; merely relocating the gas spatially. This method has also brought up practical challenges, such as possible leaks and storage costs [3]. Different from it, the CO₂ chemical conversion and consumption can reduce the CO₂ content and solve the environment crisis. At the same time, it can also convert CO₂ into valuable fuels or other organic substances, which can lead to the fuel recovery and solve the energy crisis. Therefore, this method has become one of the research hotspots worldwide.

Given the high stability of CO₂'s structure, breaking the C=O bonds requires substantial energy [5]. By the inspiration from natural photosynthesis, researchers have attempted to use clean, economical, and safe solar energy for CO₂ photoreduction. A significant breakthrough occurred in 1972 when Honda and Fujishima used a TiO₂ electrode to reduce CO₂ to CH₃OH and CHO by photocatalysis [6], demonstrating the feasibility of using photocatalysis to convert CO₂. Additionally, by varying the number of electrons and protons involved in the redox reaction process, it is practicable to obtain different valuable molecule chemical materials or fuel products, such as CO [7], CH₄ [8], HCOOH [9], CH₃OH [10] and, etc. As a result, this approach achieves a closed carbon cycle, offering promising avenues for further research and development [11].

Metal-organic frameworks (MOFs) generally refer to the periodic multidimensional skeleton structure formed by the metal ions and bridged organic ligands. They are porous solid materials included by organic-inorganic hybridisation. The earliest appearance of MOFs can be traced back to the research of Robson and Hoskins in 1989 [12]; they prepared the 3D network coordination compounds and inferred that they may have larger pores and holes than zeolite molecular sieve from which began the research boom of MOFs. However, the early synthesised MOFs' pore structure and skeleton is not very stable and easier to collapse. It was not until 1995 that Yaghi et al. reported a coordination compound with a stable pore structure prepared by the reaction of trimesic acid (BTC) and Cobalt (Co), and called it MOF [13], which made it possessed practical. With the rapid development of modern X-ray crystallisation, the original problems in crystal structure testing and structure analysis have been well solved, and the rapid growth of new crystal data has extensively promoted the research progress of MOFs.

Compared with traditional photocatalytic materials, MOFs have the following advantages: (1) The special pore structure of MOFs is conducive to CO₂ adsorption and enhances their catalytic performance. (2) The structure of MOFs can be functionalised and modified; (3) MOFs can be combined with other functional materials to form composite materials, maintaining the structural properties of MOFs while also possessing the excellent properties of additional materials, etc. [14, 15]. Therefore, they are used in catalysis, gas separation, storage and conversion, dye decomposition, etc. Among them, catalysis is one of the fastest-growing application fields of MOFs with the longest research time [16]. Recently, with more research, MOFs have shown the following advantages in photocatalysis and electrocatalysis. On the one hand, MOFs' high specific surface area and unique porous structure can make active sites evenly dispersed. Because its internal environment can be regulated by synthetic means, its light absorption range can also be adjusted, making the reaction easier. On the other hand, MOFs can remain stable in solution, even in moderately acidic or alkaline solutions [17]. In the reaction system, they can be simply separated so that they can be reused. Therefore, they have high economic and environmental benefits.

In the process of photocatalysis, as the photon energy is higher than or equal to the band gap of MOFs, firstly, MOFs can generate electrons with reducing ability and holes with oxidising ability after receiving photoexcitation. Secondly, the electron-hole pair moves to the surface of the catalyst [18]. During their movement, part of the electron-hole pairs will recombine, and the other part will reach the active site to participate in the photocatalytic reaction. Thus the CO₂ has been adsorbed and reduced. The more CO₂ is adsorbed, the more number of active sites of the photocatalyst can be contacted, which is also beneficial for the reduction reaction. The unsaturated coordination site of metal ions in MOFs can be used as the active site of catalytic reactions [19]. The organic ligand and large surface area are beneficial for loading catalytic active molecules and metal active components [20]. In the adsorption and separation of CO₂, MOFs have good CO₂ adsorption capacity and unique semiconductor behaviour [21]. It has a good application prospect in CO₂ photoreduction.

However, MOFs' visible light-capturing ability is weak, and the electron-hole recombination is relatively severe. The existing research directions for improve the efficiency of photoreduction are mainly divided into metal node modification and functional modification of organic ligands, embedded semiconductors, precious metal particles and other materials with light absorption ability, and prepared MOFs-derived materials. This paper is a review of the MOFs for photocatalytic CO₂ reduction. It discusses recent developments in photoactive MOFs and their application in CO₂ photoreduction reactions. This paper is composed of (1) functional modification of pure MOFs, (2) MOF-composite materials and (3) MOF-derived materials as photocatalysts. In addition to these, it also makes the prospects for future development.

2. Function modification of pure MOFs

MOFs have semiconductor-like properties, so that pure MOFs can be used as photocatalytic materials. The presence of organic ligands can stabilise and support the frame structure and can excite electrons under specific wavelengths of sunlight, then move electrons to the activated metal clusters to participate in the photocatalytic reactions [22,23], giving MOFs semiconductor properties. Reasonable modification of the frameworks of MOFs can effectively reduce the energy difference between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), thereby improving the light capture ability of MOFs and enhancing the catalytic performance of MOFs for photocatalyst CO₂ reduction. Common methods include introducing organic ligands with photosensitive functional groups, electron-rich conjugated systems, or metallising organic ligands of MOFs.

2.1. Amino-modified organic ligands

The unique structures of MOFs have led to widespread interest in their utilisation for photoreduction of CO₂ under visible light exposure. The amino group presently is the most extensively applied among the active functional groups. Its potent electron-donating capacity serves a dual purpose. On the one hand, acting as a weak base, it facilitates the adsorption of acidic gases like CO₂, thereby augmenting CO₂ adsorption capability. On the other hand, the incorporation of auxochrome groups causes a displacement of the absorption wavelength of MOFs towards the visible spectrum. This shift intensifies the absorption of light and consequently substantially elevates the catalytic proficiency of MOFs in CO₂ photoreduction. In organic ligand modifications, NH₂-MIL-125(Ti) and other amino-functionalised MOFs have shown promise in improving the photocatalytic ability for CO₂ reduction (MIL= Materials of Institute Lavoisier).

NH₂-MIL-125(Ti) is synthesised by introducing amino-functionalised organic ligands (such as H₂ATA) within the framework of MIL-125(Ti), considering its structure [24]. The process typically entails mixing a Ti precursor, such as titanium tetrachloride (TiCl₄), with a linker molecule containing amino groups, such as 2-aminoterephthalic acid (ATA). The mixture is then heated under appropriate conditions, allowing the Ti nodes and ATA linker to assemble and form the porous framework structure of NH₂-MIL-125(Ti). The resulting MOFs possess a substantial surface area and exhibits remarkable thermal stability, making it suitable for many prospective applications, such as gas separation and catalysis. The presence of amino groups does not compromise the structural stability of the parent MOF, leads to improvements in optical absorption and CO₂ adsorption, but affects the charge transfer within the metal cluster, making the NH₂-MIL-125(Ti) display a wide absorption range. The broadened absorption range allows the MOF to harness more visible light energy for photocatalytic processes. Then, the introduction of amino-functionalised ligands enhances the interaction between NH₂-MIL-125(Ti) and CO₂ molecules. The amino groups provide weak basic sites that can effectively interact with the acidic CO₂, leading to higher CO₂ adsorption capacity [25]. NH₂-MIL-125(Ti) demonstrates a significantly greater CO₂ uptake ability than unmodified MIL-125(Ti).

In addition to this, it exhibits enhanced photocatalytic ability for CO₂ reduction. When exposed to visible light, NH₂-MIL-125(Ti) can catalytic the reduction from absorbed CO₂ to HCOO⁻ with the presence of sacrificial agent like triethanolamine (TEOA) and triethylamine (TEA). The excited

electrons from the amino-functionalised ligands transfer to Ti(IV), reducing it to Ti(III), which plays an indispensable role in promoting CO₂ reduction (Figure 1). This is the first time that photoactive Ti-MOFs have been used for the CO₂ photoreduction. TEOA, as an electron donor, is essential for photocatalytic process, as it provides the necessary electrons for holes, simultaneously suppressing the recombination of electron-hole pairs in reducing Ti(IV) as well as subsequent CO₂ conversion [26].

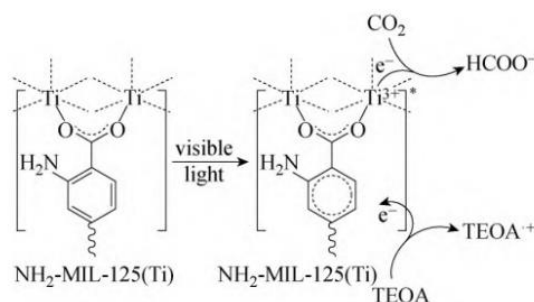


Figure 1. Under visible light irradiation, the speculated mechanism of NH₂-MIL-125(Ti) CO₂ photoreduction [24].

NH₂-UiO-66(Zr) refers to a variant of the Metal-organic Framework UiO-66(Zr) that has been functionalised with amino groups [24] (UiO=University of Oslo). ATA is used as a ligand during the synthesis process to achieve the functionalisation. ATA contains amino (NH₂) groups that can form coordination bonds with the zirconium ions present in UiO-66(Zr). These amino groups serve as anchor points for the attachment of the ligand to the metal nodes, leading to the NH₂-UiO-66(Zr). This modification has been shown to improve the MOF's photocatalytic activity and its light absorption capabilities.

A prominent benefit of NH₂-UiO-66(Zr) is its improved adsorption capacity for CO₂. This makes it particularly interesting for applications in CO₂ capture and sequestration. Moreover, this MOF demonstrates enhanced photocatalytic activity, which can convert the adsorbed CO₂ into formic acid, a useful industrial chemical. An interesting modification of NH₂-UiO-66(Zr) involves partially replacing ATA with 2,5-diaminoterephthalic acid (DTA) to create a mixed-ligand MOF [27]. This results in further enhancements in photocatalytic performance and spectral absorption range. The photocatalytic reaction mechanism of it is in Figure 2.

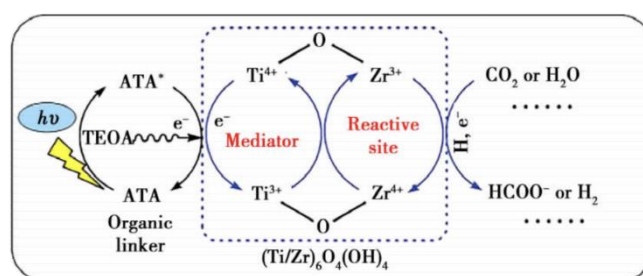


Figure 2. Photocatalytic reaction mechanism of NH₂-UiO-66(Zr/Ti) [27].

Furthermore, post-synthetic modification (PSM) of UiO-66(Zr) with a catechol-functionalised organic ligand (catbdc) and incorporation of Cr(III) and Ga(III) metal ions resulted in M(III)-monocatecholato functionalised MOFs with improved visible light absorption ability and electron transfer properties [27]. The modified MOFs showed higher photocatalytic activity for CO₂ reduction, with UiO-66-CrCAT demonstrating a high light responsiveness and formic acid yield. NH₂-UiO-66(Zr) also demonstrates higher catalytic ability than UiO-66(Zr) in various reactions, such as cross-aldol

condensation and jasminaldehyde synthesis [28]. This multi-catalytic activity is attributed to these MOFs' NH_2 groups and oxygen atoms.

Recently, as the abundant iron resources on Earth, Li et al. also studied the photocatalytic reduction from CO_2 to HCOO^- by three iron-based MOFs: $\text{NH}_2\text{-MIL-53(Fe)}$, $\text{NH}_2\text{-MIL-101(Fe)}$, and MIL-88B(Fe) [29]. They proposed that the dual excitation pathway present in the photocatalytic process is the main reason for the enhanced catalytic performance. Namely, electrons can be directly excited through Fe-O clusters. From O^{2-} to Fe^{3+} , the ligand can absorb light, generate electron transfer to Fe^{3+} reduce to Fe^{2+} , and undergo a CO_2 reduction reaction. The combined action of two excitation pathways significantly boosted the photocatalytic activity compared to the parent MOFs. Similarly, TEOA serves as an electron sacrificial agent to supplement the consumed electrons, enabling the catalytic reaction to continue. Additionally, Incorporating Ti into $\text{NH}_2\text{-UiO-66(Zr)}$ to create $\text{NH}_2\text{-UiO-66(Zr/Ti)}$ further enhances its photocatalytic ability. The addition of Ti facilitates metal-metal charge transfer and promotes charge transfer from the ligand to the Zr-O centre, thereby improving the photocatalytic reduction of CO_2 .

In conclusion, the functionalisation of MOFs with amino groups, incorporation of Ti or other substituents in bimetallic or modified MOFs, and the introduction of electron-withdrawing groups enhance their photocatalytic and catalytic activities. This expands their potential applications in CO_2 reduction and other reactions, positioning them as promising tools for addressing environmental challenges such as greenhouse gas emissions.

2.2. Porphyrin-modified organic ligand

Porphyrins are a class of macromolecular heterocyclic compounds with a nearly planar 18 π electron-rich structure. In natural photosynthesis, antenna light collection is accomplished through porphyrin-like pigments [30]. Porphyrin organic ligands are rigid, so porphyrin-based metal-organic frameworks generally have good stability. In addition, porphyrin is an important photosensitive compound due to its highly conjugated aromatic electron system, which can broaden the light absorption of MOFs to the entire visible light region, with high light absorption efficiency and intense interaction with CO_2 [31]. Therefore, it is widely used in CO_2 photocatalytic reduction reactions.

Liu et al. [32] reported on the first rhodium porphyrin metal-organic skeleton (Rh-PMOF-1). Firstly, they prepared the Rhodium porphyrin complex $\text{Rh(TCPPCO}_2\text{Me)Cl}$ (TCPP = tetrakis(4-carboxyphenyl)porphyrin) with ZrCl_4 , by hydrolyzing it, they obtained Rh(TCPP)Cl . Then, they put all the raw materials together in a glass vial, including Rh(TCPP)Cl , ZrCl_4 , benzoic acid, etc. After 48 hours at 120°C , they obtained the red crystals—— Rh-PMOF-1 . Their study revealed that the material had a greater adsorption ability for CO_2 at 298K compared to MOFs without porphyrin modification, which is conducive for enhancing the photocatalytic activity of MOFs. In addition, they also reported that the selective catalytic reduction rate of HCOO^- in this reaction is as high as 99%, which has good application prospects.

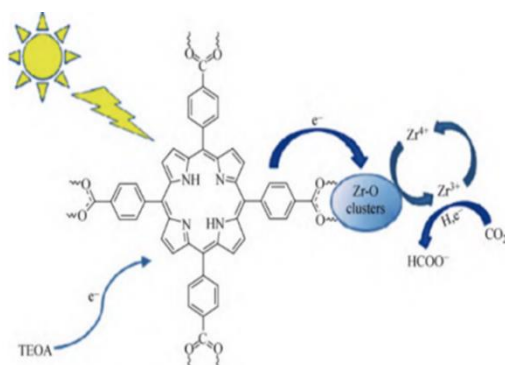


Figure 3. Photocatalytic mechanism of the double catalytic centres in Rh-PMOF-1 [33].

Based on experimental and theoretical results, it is inferred that there are dual catalytic centres in this reaction. As the “antenna”, the metal porphyrin ligand first captures photons to form an excited state,

generates photogenerated electrons and transfers them to the metal Zr_6O_8 cluster and the metal Rh porphyrin ring. Subsequently, a CO_2 reduction reaction is carried out (Figure 3). During the reaction, the sacrificial agent TEOA offers electrons to consume the holes for the reaction smoothly. In addition, the team also studied the application of bimetallic PMOF in this direction and reported a Cu Al/PMOF [33]. Liu et al. measured the adsorption capacity for CO_2 and proved it was much higher than that of Al/PMOF, resulting in a nearly seven times increase in the amount of methanol precipitated from the reaction. The results indicate that incorporating Cu ions is helpful in improving the adsorption capacity of photocatalysts for CO_2 . It is speculated that CO_2 can adsorb at the copper site, causing linear CO_2 molecules to bend, thereby reducing the reaction potential energy and enhancing the catalytic reaction efficiency.

Feng [34] synthesised a highly stable zirconium-based porphyrin PCN-222 (Porous Coordination Network), also known as MOF-545, using Fe-TCPP as the ligand and highly stable ZrCl_4 clusters as the nodes. Xu et al. [35], through a series of experiments, found that this material exhibits the visible light absorption ability of porphyrin ligands, coupled with its CO_2 adsorption capacity and high specific surface area, which can prominently enhance the photocatalytic efficiency of CO_2 reduction to HCOO^- . Their research speculates that the mechanism of this process is that the porphyrin ligand H_2TCPP serves as the light absorption centre, and the photogenerated electrons generated after absorption transition to the Zr-O cluster, which will reduce Zr(IV) to Zr(III) . At the same time, Zr(III) acts as a reducing agent, reducing CO_2 to HCOO^- (Figure 4). TEOA is also an electron sacrificial agent that participates in the reaction. In addition, the ultrafast transient absorption spectrum indicates that in PCN-222, the appearance of ultra-long lifetime electron trap states significantly suppressed the recombination of electrons and holes during the transfer to metal clusters, thereby improving the efficiency of CO_2 photoreduction.

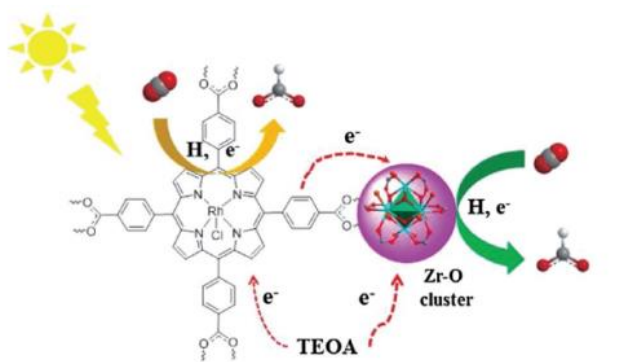


Figure 4. Photocatalytic mechanism of PCN-222 photoreduction CO_2 [34].

2.3. Metallising organic ligands

In recent years, transition metals have shown good catalytic activity for CO_2 photoreduction in homogeneous systems such as iron, copper, cobalt, manganese, etc. In addition, precious metal complexes such as rubidium and iridium have also been widely used as photosensitisers or homogeneous photocatalysts due to their good photoresponse ability [36-41]. The structure of MOFs has unique adjustability, which can be adjusted by fixing metal complexes into the MOFs framework, combining their advantages, thereby adjusting the function and structure of MOFs. After introducing metal complexes, the photocatalytic ability of MOFs can be enhanced, and the rapid deactivation of active centres can also be inhibited [42].

Elcheikh et al. [43] synthesised a novel Zr-based MOF, AUBM-4 (AUBM=American University of Beirut Materials), using bis(4'(4-carboxylphenyl) pyridinyl) Ru(II) complex as ligand. The preparation process of AUBM-4 material is summarised in Figure 5. This complex exhibits excellent absorbance of the metal complex Ru(II) , and the time-resolved photoluminescence (TRPL) spectrum results show that the recombination of AUBM-4 electron-hole pairs is effectively suppressed, resulting in a longer fluorescence lifetime. The density functional theory calculation (DFT) results indicate that the catalytic

centre of the CO₂ photoreduction reaction is most likely located on the complex ligand. After Ru absorbs light, it generates electron-hole pairs, and electrons move to the complex ligand to form free radical anions, thereby reducing the adsorbed CO₂ to HCOO⁻. The sacrificial agent TEOA will reduce the holes (Figure 6).

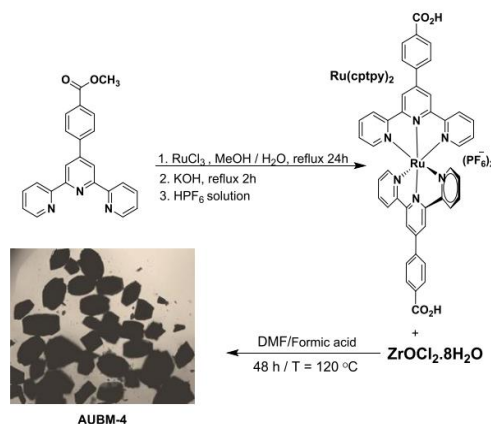


Figure 5. Process of synthesizing AUBM-4 through Ru(cptpy)₂ [43].

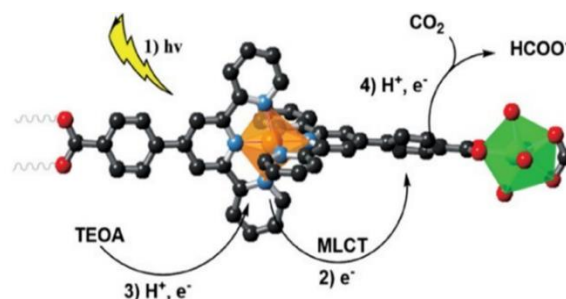


Figure 6. The mechanism of AUBM-4 catalyzed CO₂ photoreduction [43].

Although Ru and Ir complexes have quite ideal application prospects in photosensitisers (PSs), developing catalysts for non-noble metal complexes is another hot field of current research due to their limited reserves, expensive, and high toxicity. Feng et al. [44] reported that the multifunctional MOFs comprising Cu-PSs and Re-based CO₂ reduction catalyst (mPT-Cu/Re) were prepared. They used the Earth's most abundant Cu complex as PS-ligands and the Re complex as the active centre in the reaction. It shows an excellent catalytic performance for the reduction reaction from CO₂ to CO, with a turnover value (TON) of 95 times that of a homogeneous system under the same conditions. Cohen et al. [45] introduced Cr(III) and Ga(III) complexes into the UiO-66's framework through a post-synthesis strategy. This operation enhanced the modification of the metal complex and metallised the organic ligand, promoting the electron transfer process within the MOF and enhancing the photocatalytic ability.

Despite the above advantages, due to the poor stability and difficult separation of metal complexes in the catalytic process, they often cause environmental pollution and cannot achieve the recycling and reuse of photocatalysts, resulting in poor atomic economy. Therefore, this is also one of the problems that researchers need to work hard to solve and improve in the future.

3. MOF-based composite materials

The pure MOFs photocatalyst still needs to be improved, such as its poor response to visible light and easy-to-generate photogenerated electron-hole recombination. The improvement of photocatalytic CO₂ reduction efficiency depends on separating photogenerated charges and inhibiting charge recombination [46]. Therefore, to improve catalytic performance, MOFs can be combined with other materials to

quickly migrate photogenerated electrons within the composite material. The material produced by this method has the dual characteristics of the parent MOFs and the binding material. It can cause more efficient charge separation while improving the selectivity of photocatalysts. The commonly used method is to design MOF-based composite materials with high catalytic activity by combining MOFs with semiconductors, precious metals, etc [47].

3.1. Semiconductor-MOF composites

TiO₂, as a classic photocatalyst, has been extensively and deeply explored since its excellent CO₂ photoreduction activity was discovered in 1972 [6]. However, it still has some disadvantages, such as high electron-hole pair recombination rate and low CO₂ adsorption capacity. To improve the photocatalytic effect of TiO₂, researchers have proposed combining MOFs with TiO₂ for CO₂ photoreduction.

Wang et al. [48] modified ZIF-67 (Zeolitic Imidazolate Framework) with a multifunctional amorphous TiO₂ (a-TiO₂) layer using a hydrothermal and low-temperature calcination method. The resulting composite, ZIF-67@a-TiO₂, exhibited improved conversion efficiency and selectivity for CO₂ photoreduction under visible light. The a-TiO₂ layer facilitated light scattering, suppressed charge recombination, introduced mesoporous properties, and inhibited photocorrosion, enhancing performance and stability. TiO₂/HKUST-1 (Hong Kong University of Science and Technology-1) catalysts were prepared by functionalising TiO₂ nanocrystals with phosphonic acid (PHA) using a slow diffusion method. The resulting TiO₂/HKUST-1 nanocomposite demonstrated significantly higher photocatalytic efficiency for CO₂ reduction to CH₄ under sunlight than the individual components. Figure 7 [49] presents a schematic illustration of the mechanism involved in the reduction of CO₂. When the reaction system is exposed to visible light, the photosensitiser absorbs the light, leading to the generation of photogenerated electron-hole pairs and an excited state ([Ru(bpy)₃]^{2+*}). The presence of the ZIF-67@a-TiO₂ layer enhances the light capture capacity of the photosensitiser through multiple scattering effects. The photoinduced electrons are rapidly injected into the a-TiO₂ layer, where surface defects temporarily trap them. Subsequently, these electrons are transported to ZIF-67 and react with CO₂. The a-TiO₂ layer also acts as a blocking layer, impeding the reverse flow of electrons as well as reducing surface recombination, thus facilitating the acceleration of CO₂ reduction. Furthermore, the robust structure of the a-TiO₂ shell enhances the stability of the reduction process during cycling.

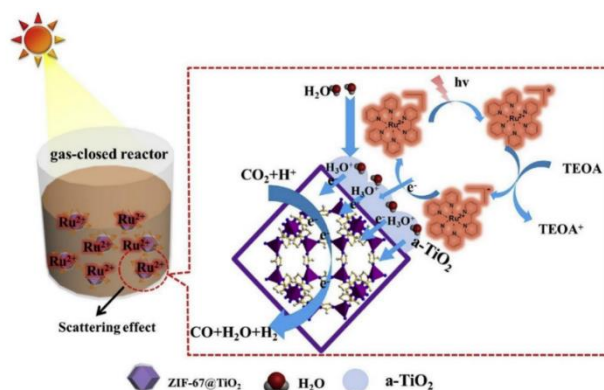


Figure 7. Schematic illustration of the CO₂ photoreduction mechanism by ZIF-67@a-TiO₂ [49].

Except for TiO₂, BiVO₄ is another highly regarded photocatalyst according to its exceptional photocatalytic activity. When subjected to light within the visible spectrum, BiVO₄ can generate electron-hole pairs, which are crucial in various photochemical reactions. BiVO₄'s optimal band-edge positions and appropriate bandgap contribute to its efficiency as a photocatalyst. To understand the impact of Cu on the photoactivity of the BiVO₄-Bi₂O₃ semiconductor, researchers investigated the CO₂ photoreduction catalyst by CuO [50]. They analysed the concentrations of the resulting products after a

2-hour photoreaction, setting the experimental conditions based on previous studies, including temperature, supporting electrolyte, pH, and reaction time. The findings, depicted in Figure 8, revealed variations in the concentrations of methanol and acetone, the products of CO₂ reduction, depending on the amount of Cu found within the BiVO₄-Bi₂O₃ photocatalyst. Interestingly, the types of molecules produced remained consistent across all cases. However, higher levels of copper doping (>1.0%) did not improve the photoactivity for CO₂ reduction. Instead, the concentrations of methanol and acetone decreased below the levels achieved with the unmodified BiVO₄-Bi₂O₃ semiconductor. This indicates that excessive copper doping may introduce recombination centres, leading to a decline in photocatalytic performance.

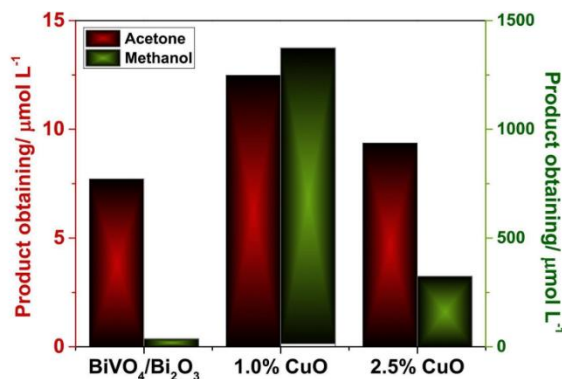


Figure 8. The chart of Acetone and methanol production from CO₂ photoreduction by using BiVO₄ and Cu-BiVO₄ photocatalysts [50].

3.2. Rare earth-MOF composites

Rare Earth Metal-Organic Frameworks (RE-MOFs) share several characteristics with other MOF families. Nevertheless, they also unveil distinct structures and attributes attributed to the distinctive characteristics of RE elements, such as their high coordination numbers and unique optical properties [51]. Endowed with favourable Lewis acid characteristics, RE compounds hold promise as catalysts. Mirroring other MOF families, RE-MOFs leverage consume CO₂ as a reactant, ingeniously adsorbing and subsequently converting it into valuable refined chemicals [52].

As per the IUPAC classification, the RE elements primarily encompass the 15 lanthanides positioned within the periodic table (Figure 9) [53]. The RE elements' concentration within their primary minerals seldom exceeds 10–15%, while their crustal abundance fluctuates from 0.5 to 60 parts per million. Notably, nearly all RE elements maintain a stable trivalent oxidation state (Ln³⁺), although certain RE elements also endure alternative oxidation states (e.g., Eu²⁺, Ce⁴⁺, Sm²⁺, Pr⁴⁺, Yb²⁺, and Tb⁴⁺) [54]. The preponderance of lanthanides existing in the trivalent oxidation state safeguards their heightened photostability, facilitating well-defined 4f to 4f transitions characterised by precise luminescence spectra spanning from ultraviolet-visible regions to near-infrared (NIR) regions [55].

Sc	Y	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
21 44.96	39 88.91	57 138.91	58 140.12	59 140.91	60 144.24	61 144.91	62 150.36	63 151.96	64 157.25	65 158.93	66 162.50	67 164.93	68 167.26	69 168.93	70 173.06	71 174.97

Figure 9. A periodic table which is introduced the rare-earth (RE) elements [53].

Due to constraints on f-f transitions between different configurations, the absorption effect of Ln^{3+} is weak [56]. However, it can be suppressed by integrating Ln^{3+} ions into the crystalline framework of MOFs. Within the coordination framework, the ligand acts as an antenna, absorbing photons to obtain energy [57]. Subsequent radiative transitions of absorbed photon energy (T_1) from the antennas to the emitting states of RE nodes, facilitated by ligand-metal charge transfer (LMCT) mechanisms, culminate in the emergence of well-defined, sharp, and narrow luminescent emissions characteristic of RE-MOFs [55, 58].

There are seven distinct synthesis methods for RE-MOFs, each characterised by unique features and requirements. These methods encompass both traditional and novel approaches, with one of them offering the ability to generate a wide array of RE-MOF sizes. One prominent technique is the solvo(hydro)thermal synthesis method [51], which employs electrical heating to precipitate RE-MOFs directly under autogenous pressure at varying temperatures (100-300°C). This approach requires hours to days for synthesis. Alternatively, microwave irradiation can be employed to grow RE-MOFs under autogenous pressure at lower temperatures (<180°C), resulting in synthesis times ranging from minutes to hours. This method offers the advantage of straightforward reaction conditions for controlling shape, size, or crystallinity, and it accelerates reactant reactivity, especially within a microwave oven. However, products may contain contaminants due to unreacted ionic elements, and energy consumption can be substantial.

Another method, the sonochemical synthesis, utilises ultrasonic waves to generate RE-MOFs of varying sizes through a simple or modulator-based technique. This method assembles RE-MOFs within minutes to hours using atmospheric-pressure, low-temperature (25-100°C) ultrasonic vapour-phase scattering. The resulting RE-MOFs exhibit high crystallinity in diverse forms like nanoparticles and nanotubes. Nonetheless, the quantitative yield is modest, and the increase in ultrasound frequency may compromise the thermodynamic stability of RE-MOFs [59, 60].

Extensive exploration into lanthanide chemistry has spotlighted the exceptional reactivity of the Eu(II) ion in reduction processes [61, 62]. A notable study by Kong et al. in 2018 [63] featured the Eu-Ru(phen)₃-MOF (phen = 1,10-phenanthroline). This remarkable structure entailed Ru(phen)₃-derived tricarboxylic acid linkers interconnecting binuclear nodes of Eu(III)-clusters. This distinctive configuration operated as a photocatalyst, deftly harnessing and channelling solar energy into chemical energy. Figure 10 shows the catalytic mechanism of photoreduction from CO₂ to HCOOH. The photoexcitation of metal ligands initiated the injection of electrons into nodes, engendering dinuclear {Eu(II)}₂ active sites that selectively executed CO₂ conversion through an impressive two-electron process, clocking a remarkable reduction rate. A standout feature is the self-assembled nature of the Eu-Ru(phen)₃ MOF, underscoring the prowess of selective CO₂ photoreduction within the Ln-MOF realm. Noteworthy is its superior photocatalytic activity when pitted against NH₂-MIL-125(Ti) [64], NH₂-UiO-66(Zr) [65], PCN-222 [66], and certain light-responsive semiconductors [67, 68]. This augmented efficacy owes its credit to the robust photosensitising and light-harvesting attributes of the Ru(phen)₃ group, particularly evident in the visible light spectrum.

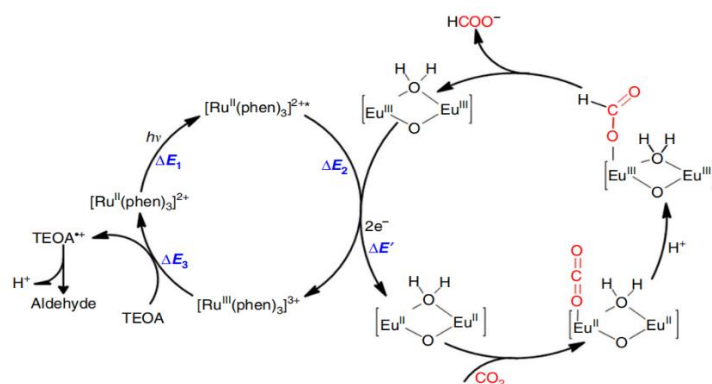


Figure 10. The catalytic mechanism of photoreduction from CO₂ to HCOOH [63].

The synthesis of this exceptional RE-MOF involves encapsulating $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, H_3L , 2-FBA, and DMF within a 20 mL Teflon-lined autoclave. This amalgamation is subjected to a 105°C temperature over a span of 70 hours in a preheated oven, and once cooled to room temperature, red block-shaped crystals emerge, yielding around 44%.

A pioneering study by He et al. in 2016 [69] brought forth the inaugural application of Ln-MOFs in photocatalytic CO_2 reduction. Gb-TCA (Trichloroacetic acid) was identified as a potent photosensitiser for light-driven H_2 evolution and CO_2 reduction. The well-suited microporous structure of Gb-TCA, optimised for selective CO_2 capture and conversion, exhibited superior attributes due to its finely tuned pore characteristics and high charge carrier mobility. Furthermore, the negative excited state potential of Gd-TCA proved pivotal in facilitating the reduction of $\text{Ni}(\text{Cyclam})\text{Cl}_2$, a well-regarded catalyst in electrochemical CO_2 reduction [70, 71, 72, 73]. Figure 11 shows the process of Gd-TCA photocatalytic reduction of CO_2 .

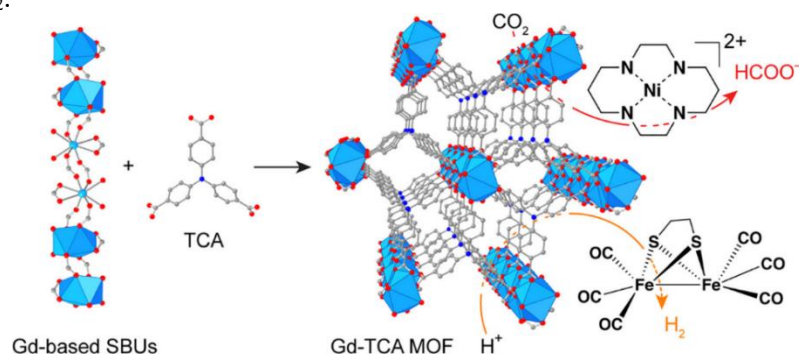


Figure 11. Catalytic process in the photocatalytic Gd-TCA system. Atom colors: Gb, blue polyhedra; O, red; C, gray; N, blue. H atoms are omitted for clarity [69].

The meticulous preparation of this extraordinary RE-MOF through a solvothermal reaction encompasses the dissolution of a blend of 4,4',4''-tricarboxytriphenylamine (H_3TCA) and $\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ within a DMF-ethanol mixture. This amalgamation is then exposed to a temperature of 100°C for a span of 3 days in an oven. The outcome comprises yellow block-shaped crystals, subsequently acquired via filtration and vacuum drying, yielding an impressive approximately 60%. The process of reducing carbon dioxide entails saturating the solution with CO_2 , followed by pH adjustment to 11.0 within a $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ mixture solvent at 25°C . Subsequently, the solution containing a Gd-TCA suspension, a redox catalyst, trace quantities of $\text{Ni}(\text{cyclam})\text{Cl}_2$, and Et_3N undergoes 12 hours of irradiation. In the presence of $\text{Ni}(\text{cyclam})\text{Cl}_2$, Gb-TCA catalyses the light-driven photocatalytic reduction of CO_2 , yielding HCOO^- [69].

4. MOF-derived materials

Through appropriate treatment, MOFs can be transformed into nanomaterials of related porous carbon, nitrogen-doped carbon, metal oxides, or other metal compounds. Compared with MOF materials, MOF-derived nanomaterials have higher catalytic activity due to their good organisational structure, dispersed metal centres, high porosity, and larger specific surface area, making them ideal carriers for multiphase catalytic materials [74].

Recently, due to its various structures and excellent adjustability, hollow architectures have been developed as effective photosensors for many applications in photoreactions, such as CO_2 photoreduction [75]. The hollow reduces the length of electron transitions to catalytic sites, accelerates the separation of electron-hole pairs and provides a large surface area and more catalytic active sites. By reason of their special structure, suitable bond energy, and adjustable optical properties, metal sulfides exhibit certain catalytic activity in light reactions [76]. Therefore, Wang et al. prepared a multidimensional In_2S_3 - CdIn_2S_4 nanotube with a heterogeneous structure [77]. They used MOF (MIL-68) as the reaction precursor, first prepared In_2S_3 nanosheets through a liquid phase substitution process, and then prepared In_2S_3 - CdIn_2S_4 through a cation exchange reaction (Figure 12 & Figure 13).

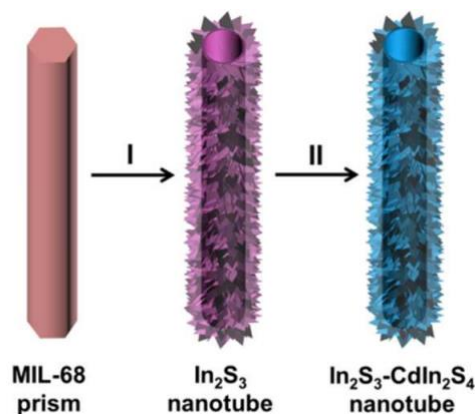


Figure 12. Schematic diagram of In₂S₃-CdIn₂S₄ nanotube preparation process. (I) liquid phase sulfidation, (II) cation exchange reaction [77].

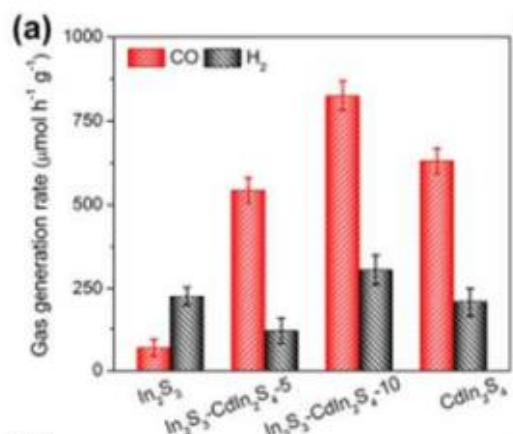


Figure 13. Comparison chart of catalytic production of CO through different catalysts [77].

Due to its unique heterostructure, it not only improves the separation and migration of photogenerated electron-hole pairs but inhibits their recombination. It promotes CO₂ adsorption ability as well as provides rich active sites for surface photocatalysis reactions. According to their experimental results, the pure In₂S₃ sample has a CO₂ reduction rate of only 68% μmol h⁻¹g⁻¹; when detecting In₂S₃-CdIn₂S₄, the performance of CO₂ reduction reaction significantly improved, reaching a maximum of 825 μmol h⁻¹g⁻¹, 12 times higher than In₂S₃ material. Therefore, the optimised In₂S₃-CdIn₂S₄ nanotubes exhibit significant CO₂ reduction performance under visible light exposure, with a high CO generation rate and excellent stability.

In another work, they used In-MIL-58 as a precursor for photocatalytic CO₂ conversion to CO, proposing a sandwich-shaped ZnIn₂S₄-In₂O₃ multidimensional tubular heterostructure with excellent performance and high stability [78]. This material is obtained by assembling ZnIn₂S₄ on the surfaces of In₂O₃ microtubules. This design has similar catalytic properties to In₂S₃-CdIn₂S₄ nanotubes and can also efficiently catalyse the photoreduction reaction from CO₂ to CO. According to experimental measurements, pure In₂O₃ has almost no catalytic activity for CO₂ photoreduction, and the reduction rate of CO₂ by a single ZnIn₂S₄ material is approximately 900-1300 μmol h⁻¹g⁻¹. However, with the emergence of the multidimensional catalyst ZnIn₂S₄-In₂O₃, this material exhibits the highest reduction rate for CO₂ reduction, approximately 3000 μmol h⁻¹g⁻¹ exhibits catalytic activity for up to eight hours.

In addition to metal sulfides, carbon nitride is also a nano-semiconductor material that can utilise visible light to catalyse reactions [79]. This material has the characteristics of a short bandgap, stable structure, and simple preparation. However, because of the good recombination of the electron-hole pair,

its catalytic activity could be better, which also limits its application in photocatalysis. Meng et al. first used a facile thermal polymerisation method to obtain the bulk g-C₃N₄. Then, they prepared ZIF-67 by Co(NO₃)₂·6H₂O and 2-methylimidazole as the raw material. Eventually, they mixed g-C₃N₄ with MOFs through stirring and ageing, and g-C₃N₄ was encapsulated in ZIF-67 composite photocatalyst, obtaining g-C₃N₄/ZIF-67 material (Figure 14 & figure 15) [80]. A heterojunction was successfully constructed between the two of them.

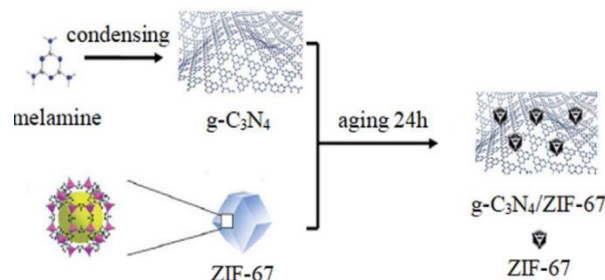


Figure 14. Schematic diagram of the synthetic process of the g-C₃N₄/ZIF-67 [78].

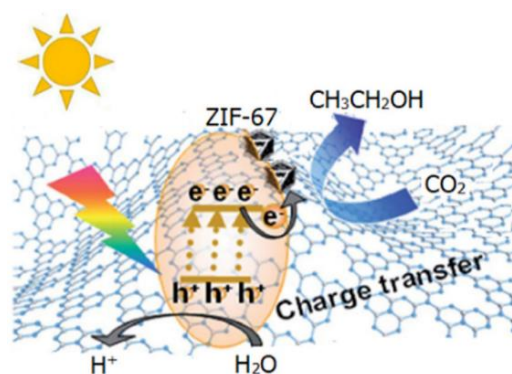


Figure 15. The mechanism of the photocatalytic process [78].

This design shortens the distance of charge transfer, accelerating electron transfer, enhancing the separation rate of electron-hole pairs, and greatly improving its catalytic efficiency. Therefore, the recovery rate and stability increase with the increase of concentration. The above research demonstrates the special advantages of MOF derivatives in photocatalytic CO₂ reduction.

5. Conclusion

MOFs are a new type of porous material with a unique structure that has broad application prospects. In recent years, due to the advantages such as high specific surface area, excellent structural adjustability, and high CO₂ adsorption capacity, the use of inexhaustible solar energy for CO₂ photoreduction has become one of the current research hotspots.

In this article, we discuss the improved MOF-based materials in CO₂ photoreduction from the above three aspects. Firstly, they can improve catalytic efficiency through synthetic modifying organic ligands. Common methods include introducing organic ligands with photosensitive functional groups and electron-rich systems and applying metal complexes as ligands. This way can broaden the light absorption of MOFs to the entire visible light region and has shown a significantly higher CO₂ adsorption ability than unmodified materials. Secondly, MOFs-based hybrid materials that consist of other semiconductors or transition metals would offer better photocatalytic ability. Their respective advantages can also be well preserved and reflected. Finally, MOFs can be converted into other related materials which have photocatalytic properties as raw materials. The derived materials have higher specific surface area and pore size, resulting in higher catalytic activity than MOFs. However, the preparation process is complex and cannot be widely adopted.

However, there are still many things that could be improved in the photoreduction of CO₂ in MOFs: (1) The utilisation rate of visible light in MOFs is still feeble, resulting in a lower reduction rate of CO₂ in photocatalytic reduction. There is still a certain distance from its application in industry and the environment; (2) Most MOFs still have poor stability and are susceptible to structural collapse after several catalytic cycles, resulting in a rapid decrease in activity; (3) In most of the reported examples of MOFs participating in the photoreduction of CO₂, organic sacrificial agents (such as TEOA, TEA) and organic solvents are still needed in the reaction system, which is undoubtedly an uneconomical and environmentally friendly measure. From these, future research on MOFs in CO₂ photocatalysis should focus on addressing the above issues by functionalising MOFs and combining them with functional materials to improve their catalytic selectivity and stability. In short, MOF materials have their unique advantages in photocatalytic applications and will definitely be used in more vigorous developments in photocatalysis in the future.

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