

Optimizing CO₂ Photoreduction Through Metal-Organic Frameworks: The Impact of Metal Selection and Composite Structures

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ABSTRACT

The rising atmospheric carbon dioxide (CO₂) concentration poses significant environmental challenges, including global warming and associated climate change. Metal-organic frameworks (MOFs) have emerged as promising materials for addressing and mitigating CO₂ levels due to their high surface area, tunable pore sizes, and customizable metal nodes. This review focuses on the influence of metal selection and MOF composites on the efficiency and stability of MOFs in CO₂ photoreduction reactions. The findings underscore the potential of MOF-based catalysts in developing sustainable solutions for CO₂ reduction, offering a pathway to mitigate environmental impacts while advancing renewable energy technologies.

Keywords: Metal-organic Frameworks (MOFs); CO₂ reduction; Metal selection; MOF composites; Photocatalyst

INTRODUCTION

CO₂ is a major greenhouse gas contributing to global warming and an ongoing energy crisis (1-4). The concentration of CO₂ in the atmosphere continues to increase due to human activities, like burning fossil fuels and deforestation (2-4). This eventually results in an enhancement of the greenhouse effect (2, 3). As the global temperature increases, it threatens human and other species' habitation and can also result in severe

environmental consequences, including melting polar ice and rising sea levels (3, 5, 6). Avenues for CO₂ conversion are crucial for further investigation under these circumstances (2-4). CO₂ reduction is an excellent method for stabilizing atmospheric CO₂ levels and converting CO₂ to other valuable products (2, 4). By developing strategies for CO₂ photoreduction, researchers can harness reusable solar energy to drive reduction reactions (1-4). Furthermore, the use of MOFs-based catalysts to promote more efficient and sustainable CO₂ reduction systems shows great promise in addressing this environmental threat (2, 3).

In the late 1990s, a new class of porous materials, known as MOFs, were first described (7). Known for their unique and uniform molecular structure, high internal surface areas, ultrahigh porosity, and customizable

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functionalities, MOFs have garnered significant interest in the scientific community (8, 9). Various metals have been employed in the design of MOFs with different properties, which have been applied to diverse research areas (9). MOFs have already been utilized for many applications, including gas storage and capture, catalysis, and photoreduction reactions (10).

This paper will primarily focus on the applications of MOFs in CO₂ photoreduction. As global warming becomes more severe, investigating methods to capture CO₂ and convert it into high-value-added products becomes more crucial (2, 4). By utilizing light in conjunction with MOF-based catalysis for CO₂ photoreduction, researchers can achieve spatiotemporal reaction control under mild and highly efficient conditions, providing a new avenue for broadly applicable CO₂ conversion (10). This article review seeks to organize the recent advancement in this area, focusing on the impact of MOF metal selection on the efficiency, yield, and throughput of CO₂ photoreduction processes.

Introduction to Catalytic Photoreduction

Catalytic photoreduction refers to catalyst-driven reduction reactions in the presence of irradiation (11). Conventional inorganic catalysts, such as titanium dioxide (TiO₂), are commonly used in photoreduction reactions (12). Photoreduction methods are crucial for many environmental and energy-saving applications, such as the degradation of environmental pollutants, the generation of renewable energy sources, and the conversion of CO₂ into valuable chemicals and fuels (11, 13). Furthermore, photoreduction leverages the ability to harness light, one of the cleanest and most abundant energy sources, to drive chemical reactions that relieve environmental issues and contribute to sustainable energy solutions (2, 13).

The mechanism of catalytic MOF-driven photoreduction involves several key steps, as illustrated in the process of CO₂ reduction (11, 14). Initially, a photosensitizer, semiconductor, or molecular complex absorbs photons from light and is excited to a higher energy state (11, 15). The excited state of the catalyst is both a potent reductant and an oxidant (15). Electrons from the excited state are then captured by CO₂, the electron acceptor (2, 3, 7). This can reduce CO₂ to form products like carbon monoxide (CO), methane (CH₄), or methanol (2, 4). These compounds can be used off-cycle as energy sources for heating, electricity generation, and vehicle fuel (2). In the last step of the photoreduction cycle, the oxidized state of the catalyst can oxidize a sacrificial donor molecule, such as triethanolamine or ethanol, to regenerate the

resting state of the catalyst (15). Methods to enhance the overall efficiency of photoreduction, electron transfer rate in MOFs, MOF stability under extreme conditions, and MOF reactivity are areas of active development (1, 2, 4).

Principles of MOFs in Photoreduction

Development and Characterization of MOFs for Photoreduction. MOFs are a class of crystalline materials composed of metal nodes and organic ligands (16). On the microscale, MOFs' chemical structure is highly ordered, wherein the organic linker interconnects all of the metal nodes, generating a three-dimensional porous framework (15, 16). When MOFs absorb light, electrons in the organic linker can be excited and transferred to the metal nodes, or vice versa, and the metal nodes serve as the catalytic centers (15-17). Because of their uniform structure and large pore size, MOFs are commonly used in applications like storage, catalysis, and separation (8, 9, 16, 17). Metal nodes act as coordination centers, while the organic linkers determine the MOFs' overall structure and functionality (15-17). Adjusting either of these two components enables precise control of MOFs' overall physicochemical properties (16). By designing unique MOF structures and choosing metals with different coordination environments, MOFs can be selectively tuned for high internal surface areas and porosity (15, 16). These characteristics provide many active sites for reactivity and make MOFs particularly effective for many reactions and applications (3, 4, 16).

When target gases, like CO₂, pass through the pores in MOFs, the metal nodes can capture CO₂ and perform the reduction reaction (2, 4, 7). MOFs have several advantages over traditional catalysts in photoreduction reactions (12). One significant advantage is their structural versatility, which enables scientists to design highly efficient catalysts for specific photoreduction reactions (7, 9, 14). Compared to conventional photocatalysts, MOFs also tend to have higher thermal stability, which prevents them from decomposing under extreme reaction conditions; adjustable pore size, which allows them to capture greater amounts of the desired substrate; organic linkers with different functional groups, which results in broader redox properties and a greater wavelength range of absorbed light (2, 4, 8, 9). Due to their high surface area, tunable pore sizes, and customizable structure, the efficiency of CO₂ photoreduction is enhanced in MOFs versus in other photocatalysts (2, 9). By integrating various metals and functional groups into MOFs' structure, they can facilitate the adsorption of CO₂ and optimize the light absorption and electron transfer rate,

creating a conducive environment for photoreduction reactions (15, 16). The unique advantages of MOFs make them a promising material for addressing environmental challenges and advancing renewable energy technologies (1, 3). In recent years, the evolution of MOF applications has shifted from basic gas storage and separation to more complex catalytic processes, such as photoreduction and oxidation (1, 2, 4). The choice of metal nodes, organic linkers, and synthetic methods can significantly influence the efficiency of MOF-driven CO₂ photoreduction and other photoreduction processes (15, 16).

Metal Selection Governs MOF Properties and Performance. The selection of metals is crucial in determining the properties and performance of MOFs (15, 16). Types of metals commonly used in MOF synthesis are lanthanides and transition metals (18, 21). Due to these metals' different oxidation states and coordination sites, the distribution of electron density through the framework and the spatial arrangement of ligands are correspondingly influenced (10, 18, 20). Moreover, metal selection can affect the redox potential of MOFs, which determines their ability to facilitate redox reactions, as well as the catalytic sites' activity and selectivity (18, 20).

The metal's oxidation state can affect MOFs' coordination environment and reactivity (18, 20). Metals with multiple oxidation states tend to have greater reactivity in catalytic redox reactions, a property also observed in MOFs (18, 19, 21). For example, the first row of transition metals, like iron (Fe), copper (Cu), and nickel (Ni), are favored for their ability to switch between different oxidation states, which can manipulate the potentials of the conduction band and valence band, and facilitate various catalytic processes (20-25, 28-30). Other considerations in metal selection include the cost and availability of the metals, as well as the associated toxicity (10, 20, 21). Judicious metal selection is important for advancing the impact of MOFs for sustainable and efficient catalytic systems.

Lanthanides and Transition Metals in Photoreductive MOFs. The lanthanides, such as cerium (Ce) and lanthanum, are incorporated into MOFs to enhance their catalytic ability (18, 19). In different MOF structures, Ce-MOFs have been synthesized with surface areas ranging from 100 to 2000 m² g⁻¹ in the N₂ Brunauer-Emmett-Teller (BET) test, which estimates porous materials' pore surface area and size by filling the pores with N₂ (18). This broad range of surface areas facilitates better gas adsorption and reaction rates under catalytic conditions (18, 19). Additionally, lanthanide-based MOFs exhibit excellent thermal stability, capable of withstanding

temperatures above 500°C without significant degradation (11, 12, 18, 19). However, the disadvantages of lanthanide-based MOFs are their relatively high cost and limited availability, which hinders their application to large-scale reactions present in industrial settings (18). Despite these limitations, lanthanide-based MOFs are highly efficient in CO₂ photoreduction reactions due to their light absorption properties (19). The f-orbital lanthanide electrons extend the wavelength range of absorbed light into the visible light regime (18).

D-block transition metals such as Fe and Cu are also commonly used in MOF synthesis (10, 17-20). Transition metal-based MOFs share similar advantages to lanthanide-based MOFs (18, 20, 25). The metal nodes can capture photons from incident light, form a long-lived charge-separated state, and increase the reduction potential of the MOFs (20, 21, 24). In general, transition metal-based MOFs demonstrate excellent photoreductive performance (10, 20, 22, 23). By incorporating different metal nodes, the absorbed light wavelength range can span 200 nm to 1000 nm, i.e. from ultraviolet (UV) to infrared; and reaction chemoselectivity can reach 100% (21-23). The unique advantages of transition metal-based MOFs are their lower cost and higher availability (20, 22, 23). However, the applicability of transition metal-based MOFs can be limited due to lower water, temperature, and pH stability (21-23).

MOF Composites and Their Applications

Three prominent types of MOF composites, employed broadly in photoreduction and other catalytic processes, include MOFs/metal nanoparticles (NPs), MOFs/semiconductors, and MOFs/carbon materials (4).

MOF/Metal Nanoparticle (NP) Composites. MOF/NPs composites combine MOFs with metal NPs, such as nickel (Ni), iron (Fe), and silver (Ag) (4, 24-29). The porous structure in MOFs provides a channel space for NPs to attach (4, 24). Because of the low Fermi energy levels, which are the highest energy levels occupied by electrons, these NPs can act as an electron reservoir to improve the lifetime of charge carriers and enhance charge separation, increasing the efficiency of CO₂ photoreduction (26, 27, 29).

In 2018, Zhu reported that incorporating Ir^{III} and Ni^{II} NPs into Zr-MOFs significantly boosted electron and radical transfer rates (24). The MOFs achieved a turnover number (TON) of 38,500, an order of magnitude higher than its homogenous counterpart, indicating that this catalyst can be reused for at least five cycles without losing significant catalytic activity (24). Similarly, Cheng

incorporated Ag NPs into NH₂-MIL-125 to achieve maximum yields of CO and CH₄ that are 2.2 and 16.2 times higher, respectively, than seen for the NH₂-MIL-125 MOFs without Ag NPs (25). Moreover, this Ag-doped material achieved 90.5% CH₄ production selectivity (25). Due to the interband transition in d-bands, the electrons in photoexcited Ag NPs can more easily transfer to the CB and lead to more efficient charge transfer, resulting in higher catalytic activity (25). Finally, Chen synthesized Co-ZIF with different loadings of Ag NPs (26, 27). As the loading of Ag NPs increased, the selectivity for CO production also increased, while H₂ evolution experienced an obvious decrease (26, 27). The yield of CO was 28.4 μmol, twice that achieved by the native Co-ZIF without Ag NP doping (26, 27). The Ag NPs in this structure served as photocatalytic active sites for CO₂ reduction and as an electron trap, improving the efficiency of the MOFs in CO₂ photoreduction (26, 27). Additionally, Maina reported a catalytic system with MOFs with a membrane physical form (26, 28). By doping Cu ions and TiO₂ NPs into the ZIF-8 membrane, the yield of CO increased by 233%, and the yield of methanol increased by 70% over the native ZIF-8 membrane (26, 28). A further study showed that the amount of Cu-TiO₂ NPs doped on the ZIF-8 membrane correlated strongly with the yield of photocatalytic reduction of CO₂, suggesting a synergistic effect between the photoexcited NPs and the high CO₂ absorptivity of the MOFs (26, 28). On the other hand, Zheng utilized Fe NPs with different oxidation states in conjunction with Ni in bimetallic MOFs. With their unique Fe^{II}/Fe^{III}-Ni structure, the synthesized MOFs have a higher charge transfer rate between Fe and the photoactive Ni center (29). The rate of CO production from CO₂ reached 12.27 mmol g⁻¹ h⁻¹, which outperforms many other Ni-based MOFs (29). Even though the BET surface area of this MOF is only 10.26 m² g⁻¹, the intrinsic micropores in the structure enable high CO₂ adsorption around 51.72 cm³ g⁻¹ (29).

MOF/Semiconductor Composites. MOF/semiconductor composites involve the integration of semiconductors, such as titanium dioxide (TiO₂) or zinc oxide (ZnO), into MOFs (4, 32). By incorporating a semiconductor or designing semiconductive MOFs with facile photoexcitability, the CO₂ absorption ability of MOFs can be enhanced (4, 30-34). MOF/semiconductor composites can achieve excellent photocatalytic activity and high CO₂ reduction yield with efficient photoelectron transfer rate from the semiconductor structure to the organic structure (30-34).

Xiao's work demonstrated that Ni-Co bimetallic porphyrin-sensitized TiO₂ nanotube arrays exhibited

significantly enhanced photocatalytic activity for CO₂ reduction compared to the pure TiO₂ nanotubes, and one of the main reasons is the synergistic effect between the MOFs and semiconductor components (30). Compared to the bare TiO₂NTs, which can only harvest ultraviolet light below 400 nm, all of the newly synthesized bimetallic MOFs can absorb visible light from 400-700 nm, allowing the reaction to proceed under sunlight (30). By incorporating bimetallic porphyrin into MOFs, the light response range and photocatalytic properties are enhanced (30). Furthermore, Liao designed semiconductive amine-functionalized Co^{II}-MOFs, which demonstrated efficient H₂ production and suggested catalytic competence in the related process of CO₂ reduction (31). The catalyst showed thermal stability up to 430°C (31), and the BET indicated a pore surface of 343 m² g⁻¹, which contains both microporous and mesoporous features indicative of photocatalytic ability (31). The Co-MOF's UV-visible spectrum exhibits a broad peak around 560 nm not visible in the ligand's absorbance spectrum (31). This is due to the significant d-d transition adsorption of Co²⁺ (31). After testing Co-MOFs' catalytic behaviors under various conditions, the authors found that when the Co-MOFs were ground and soaked into the photosensitizer solution before the reaction, they achieved the highest yield of H₂ production, at 1102 μmol g⁻¹ h⁻¹; the authors thus propose a potential application of the Co-MOFs in CO₂ photoreduction (31).

Wang synthesized the UiO-66 MOF structure with Cu^{II} tetra(4-carboxyphenyl)porphyrin (CuTCPP) and further seeded TiO₂ on the MOF (32). The catalytic result showed that the CO production of these MOFs is 7 times higher than pure TiO₂ (32). The yield of CO reached 31.32 μmol g⁻¹ h⁻¹ under an Xe lamp, and CO₂ to CO photoreduction also proceeded under simulated solar light (32). By incorporating CuTCPP into the MOFs, both the absorption range and the energy transfer between ligand and metal can be improved (32). Targeting CO formation, Su designed an innovative structure by coupling Co-ZIF MOFs with CdS. In this structure, Co-ZIF acts as a co-catalyst to enhance CO₂ absorption, and CdS serves as the photocatalyst for CO₂ photoreduction (33, 34). Upon irradiation with visible light for 3 hours, this ZIF reduces CO₂ effectively (33, 34), resulting in an apparent quantum yield of 1.93% and an accumulated CO production of 85.6 μmol (33, 34). Furthermore, the catalytic activity of this ZIF is retained under longer irradiation times, suggestive of the MOF's structural stability (33, 34).

MOF/Carbon Material Composites. MOF/carbon material composites incorporate carbon materials, such

as graphene, into MOFs (4, 35, 36). By adding carbon materials, the electrical conductivity of MOFs can be improved and the active sites for catalytic reactions increased (35, 36). The ultimate goal of adding carbon materials is to increase MOFs' photocatalytic activity and stability (4, 35, 36).

Wang reinforced this principle by incorporating graphitic carbon nitride (g-C₃N₄) into ZIFs (35). In this noble metal-free photocatalytic system, this ZIF achieved a 0.9% apparent quantum yield and 35 TON (35). The authors tested the photoreduction activity of ZIF under various temperatures from 10°C to 60°C and found that the yield of CO initially increased, and then decreased at the higher end of the temperature range (35). The optimal temperature was found to be around 40°C owing to the variation of release/desorption of CO₂ from the reaction mixture under different temperatures (35). Furthermore, Cheng used 2D cobalt porphyrin-based MOFs/graphene (Co²⁺-PMOFs/GR) to design a sacrificial agent- and photosensitizer-free photocatalytic system (36). When the loading of graphene is 10% wt, the photocatalytic performance of Co-PMOFs/GR reaches its optimal point (36). The yield of CO and CH₄ from CO₂ reduction is 2.84 and 2.44 times higher, respectively, than seen in the pure cobalt-based MOFs (36). The increase in photocatalytic activity is due to the synergistic effect between the high light harvesting of the catalyst, high CO₂ absorption, and rapid charge transfer rate (36).

Summary. MOFs have many different composites that are currently being investigated (4, 25, 33, 36). Three types of MOF composites—MOF/NPs, MOF/semiconductors, and MOF/carbon materials—demonstrate the versatility and future potential of MOF catalysis for CO₂ photoreduction (4, 24-36). By combining MOFs with different materials, researchers can enhance the properties and photocatalytic performance of the composites, making them more suitable for industrial and batch-scale applications (4, 26, 33).

CONCLUSION

In the face of escalating environmental challenges, the reduction of atmospheric CO₂ is a critical barrier to sustainability. As an emerging material, MOFs represent a versatile and promising runway for catalytic CO₂ photoreduction. This review has explored the various aspects of MOFs, including metal selection, the significance of three types of MOF composites, and the photoreduction efficiency of CO₂ under each regime.

MOFs possess unique advantages in structure,

stability, and tunability. Due to their high surface area and customizable metal nodes, MOFs provide a remarkable platform for using renewable solar energy to control the process of photoreduction reactions, such as CO₂ reduction. By selecting different metals and/or incorporating them with different composites, MOFs' catalytic properties can be tuned and their CO₂ reduction efficiency can be improved with excellent selectivity for the desired product. As the demand for environmentally friendly technologies grows, the development of MOFs-based catalysts for CO₂ photoreduction offers a viable pathway to sustainable energy solutions. This review not only emphasizes the current advancements in the field but also foreshadows further innovation to enhance MOFs' photocatalytic performance. By harnessing the unique properties of MOFs, researchers can investigate more effective and sustainable solutions for CO₂ reduction and ultimately contribute to a cleaner and more habitable environment.

DECLARATION OF CONFLICT OF INTERESTS

The authors declare that there are no conflicts of interest regarding the publication of this article.

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