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Mechanisms and Structural Regulation of Metal–Organic Framework Materials for Photocatalytic CO_2 Reduction

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Abstract. Photocatalytic CO_2 reduction can convert CO_2 into high-value chemicals and fuels such as CO, HCOOH, CH_3OH, and CH_4 by utilizing solar energy, representing an important pathway for carbon resource utilization. Metal-organic frameworks (MOFs), with their tunable metal nodes, organic linkers, and regular pore structures, exhibit unique advantages in CO_2 enrichment, light absorption, charge transport, and stabilization of key intermediates. This review focuses on the mechanisms and structural regulation of MOFs for photocatalytic CO_2 reduction. It first introduces the fundamental processes of photogenerated carrier generation and migration, CO_2 adsorption and activation, proton-coupled electron transfer, and product formation. It then summarizes representative MOF systems based on Zr, Fe, and Ti, as well as the performance characteristics of composites with metal nanoparticles, molecular catalysts, and semiconductors. On this basis, it further analyzes the influence mechanisms of metal-node regulation, linker functionalization, defect engineering, pore-microenvironment modulation, and heterointerface construction on light absorption, charge separation, intermediate adsorption, and product selectivity. Existing studies indicate that the photocatalytic performance of MOFs depends on the synergistic matching of their electronic structure, active sites, and local reaction microenvironment. Future efforts should address challenges including photogenerated charge recombination, structural stability, and selectivity in multi-electron reactions, while combining in situ characterization and theoretical calculations to deepen the understanding of real active sites and reaction pathways, thereby providing a theoretical basis for the rational design of efficient and stable MOF photocatalysts and CO_2 resource utilization.

Keywords: metal-organic frameworks, photocatalysis, carbon dioxide reduction

1. Introduction

With the continuous growth of global industrialization and energy demand, the massive consumption of fossil fuels has led to a steady increase in anthropogenic carbon dioxide (CO_2) emissions. The International Energy Agency (IEA), in its Global Energy Review 2026, noted that global energy-related CO_2 emissions reached approximately 38.4 billion tonnes in 2025, setting a new historical record [1]. Meanwhile, records from the NOAA Mauna Loa Observatory in Hawaii show that atmospheric CO_2 concentrations continue to rise, reaching 431.44 ppm in June 2026, an increase of more than 50% over the pre-industrial level of approximately 280 ppm [2]. The IPCC

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Sixth Assessment Report estimates that the best estimate of global surface warming caused by human activities from 1850–1900 to 2010–2019 is approximately 1.07 °C [3, 4]. Therefore, alongside the transition to a low-carbon energy structure, converting CO_2 from a greenhouse gas into a valuable carbon resource is of great significance for achieving a circular carbon economy and sustainable energy development.

CO_2 can be converted into CO, HCOOH, CH_3OH, CH_4, and higher-carbon-number products through different proton-coupled multi-electron-transfer processes [5, 6]. Among these, CO serves as an important feedstock for Fischer–Tropsch synthesis and carbonylation reactions, HCOOH has potential for chemical hydrogen storage, CH_3OH functions both as a fuel and a basic chemical raw material, and CH_4 has a well-established energy-utilization system [5, 7]. However, the CO_2 molecule possesses a highly stable linear structure and a strong C=O bond; its activation requires a high energy barrier, particularly for the formation of initial activated species such as $CO_2^{\cdot -}$, which demands a strong reduction driving force [5, 6]. In addition, CO_2 reduction involves a complex network of multi-electron/multi-proton reactions, and different intermediates may further yield various C_1 or even C_2^+ products [6, 8]; in aqueous systems, the hydrogen evolution reaction also competes with CO_2 reduction for photogenerated electrons [5, 8]. Consequently, promoting CO_2 adsorption and activation, lowering the formation barriers of key intermediates, and regulating electron-transfer pathways to achieve high activity and product selectivity remain the core scientific challenges in CO_2 catalytic conversion.

Among the various CO_2 conversion technologies, photocatalysis can harness light energy to excite catalytic materials and generate high-energy electrons, enabling CO_2 reduction under relatively mild conditions and providing an important route for the conversion of solar to chemical energy [7, 9]. A typical photocatalytic process comprises a sequence of steps: light absorption, photogenerated carrier generation and separation, carrier migration to the reaction interface, and surface redox reactions; a low efficiency in any one step limits the overall performance [10, 11]. Conventional wide-band-gap semiconductors such as TiO_2 respond mainly to ultraviolet light, with limited visible-light utilization; although g-C_3N_4 absorbs part of the visible spectrum, it still suffers from a restricted light-absorption range and rapid carrier recombination [10, 12]. At the same time, the adsorption and polarization capabilities of CO_2 on conventional semiconductor surfaces are generally limited, and the chemical environment of active sites is difficult to tune finely [5, 13]; competition among multiple reduction pathways and the hydrogen-evolution side reaction further constrains the selectivity toward target products [14, 15]. Therefore, relying solely on band-gap engineering of conventional semiconductors cannot simultaneously solve the multiple problems of light harvesting, charge separation, CO_2 enrichment/activation, and selective catalysis, which has driven the development of novel photocatalytic materials with designable pores and well-defined active sites.

Metal–organic frameworks (MOFs) are constructed from metal ions or metal clusters and organic linkers through coordination interactions, combining the catalytic properties of inorganic nodes with the structural tunability of organic linkers [13, 16]. Their highly porous structures and large specific surface areas enhance the local concentration of CO_2 near the catalyst, while tunable pore sizes and pore microenvironments facilitate interactions between substrates and active sites and stabilize specific reaction intermediates [16, 17]. More importantly, both the metal nodes and organic linkers of MOFs can be designed independently: varying the metal center and its coordination environment modulates CO_2 binding and activation; introducing amino, porphyrin, or other conjugated photosensitizing linkers improves visible-light absorption and tunes the charge-transfer process between linkers and metal nodes [13]. Thus, MOFs provide a unique platform for the synergistic

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regulation within a single structure of "light absorption – charge separation – CO_2 adsorption – catalytic conversion."

However, the use of MOFs for photocatalytic CO_2 reduction still faces several key limitations. On the one hand, not all MOFs possess good intrinsic photoresponse and charge-transport capabilities; localized electronic structures and weak long-range carrier migration may lead to a high electron–hole recombination probability [13, 18]. On the other hand, some MOFs may undergo coordination-bond cleavage, linker degradation, or metal-node reconstruction under the action of water, light, or reaction intermediates, compromising long-term stability [5]. Furthermore, in multi-electron reduction processes, it remains difficult to precisely match the binding strength between active sites and key intermediates, and pronounced pathway competition still exists among products such as CO, HCOOH, CH_3OH, and CH_4 [6, 8]. Therefore, recent research has gradually shifted from the mere construction of MOF materials toward multi-scale structural design involving linker functionalization, metal-node regulation, defect engineering, heterostructure construction, and active-center incorporation, aiming to synergistically improve light absorption, charge transport, and catalytic selectivity [15, 18, 19].

Based on this, this review focuses on MOF materials for the photocatalytic reduction of CO_2. It first analyzes the fundamental reaction processes of photocatalytic CO_2 reduction and the mechanisms of photogenerated charge transfer and CO_2 activation in MOF systems. It then reviews the structural characteristics and structure–activity relationships of representative MOF photocatalytic systems, with particular emphasis on performance-enhancement strategies including linker engineering, metal-node regulation, defect construction, and composite-structure design, in order to provide a theoretical reference for the rational design of highly active, selective, and stable MOF photocatalysts and for solar-driven CO_2 resource utilization.

2. Mechanisms of photocatalytic CO_2 reduction over MOFs

Photocatalytic CO_2 reduction is a continuous reaction composed of light absorption, carrier generation and separation, carrier migration, CO_2 adsorption and activation, surface proton-coupled electron transfer, and product desorption. Upon illumination, the catalytic material absorbs photons satisfying the electronic-transition condition, promoting electrons from the ground state to an excited state and generating electrons and holes with redox capability [10, 12]. Subsequently, the photogenerated carriers must migrate to the corresponding active centers before recombination: electrons participate in CO_2 reduction, while holes maintain charge balance by oxidizing H_2O or other electron donors [10, 20]. CO_2 arriving at the reaction interface is first captured by active sites and undergoes polarization and structural bending through electron injection, coordination, or local electric fields, forming key adsorbed intermediates such as $*CO_2$, *COOH, and *OCHO [5, 13]. On this basis, successive proton-coupled electron transfer drives C–O bond cleavage, C–H bond formation, and, when necessary, C–C coupling, ultimately yielding different reduction products [5, 8]. Therefore, the overall photocatalytic efficiency is determined not by a single step alone, but by the kinetic matching among photogenerated-charge generation and transport and surface chemical reactions.

Compared with the relatively continuous band structure of conventional inorganic semiconductors, the photophysical processes of MOFs are closely related to the electronic coupling between their metal nodes and organic linkers. In many photoactive MOFs, the organic linker first assumes the light-harvesting function; after photoexcitation, a linker-localized excited state is formed, and electrons can then migrate through coordination bonds to the metal node or to catalytic centers near the node, giving rise to a ligand-to-metal charge-transfer (LMCT) process. In some

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systems, metal-to-ligand charge transfer (MLCT), interligand charge transfer, or node-localized excitation may also occur. Different charge-transfer modes determine the final accumulation position of photogenerated electrons and their reducing power. Therefore, MOFs cannot be simply equated with the "valence band–conduction band" model of conventional semiconductors; their electronic structure is better described in terms of the linker frontier orbitals, metal-node energy levels, and the coupling between them. Variations in metal type, coordination environment, and linker conjugation can all readjust the excited-state lifetime and charge-migration direction, thereby affecting the number of effective electrons that reach CO_2-reduction sites [21].

After photogenerated electrons arrive at the catalytic center, CO_2 adsorption and activation become the key link connecting photophysical processes and surface chemical reactions. Open metal sites, coordinatively unsaturated nodes, and polar groups such as $–NH_2$ and –OH on the pore walls of MOFs can enhance CO_2 enrichment through Lewis acid–base interactions, electrostatic interactions, or hydrogen bonding, and alter its local electronic environment. The transformation of CO_2 from a linear molecule to a bent adsorbed configuration usually indicates that it has acquired a certain degree of electronic activation; it can then follow different pathways to generate intermediates such as *COOH or *OCHO. The *COOH pathway is usually closely associated with CO formation, whereas *OCHO is often related to HCOOH formation, but the specific reaction pathway still depends on the composition of the active center, the adsorption free energy of intermediates, and the interfacial proton source. It can thus be seen that MOF pores do not merely serve to "store CO_2"; their confined environment also participates in reaction-kinetics regulation by tuning the local concentration, reactant orientation, proton transport, and intermediate stability [22].

The further reduction of CO_2 involves different numbers of electron and proton transfers. Among typical C1 products, CO and HCOOH generally correspond to two-electron/two-proton reduction processes, CH_3OH requires six electrons/six protons, and complete reduction to CH_4 involves eight electrons/eight protons. As the degree of electron transfer deepens, intermediates may undergo successive transformations such as *CO, *CHO, $*CH_2O$, and $*CH_3O$; if adjacent active centers can stabilize two carbon-containing intermediates and lower the C–C coupling barrier, C_2H_4, C_2H_5OH, and other multi-carbon products may be formed. Therefore, product selectivity is essentially determined by the generation of key intermediates, their adsorption stability, further hydrogenation capability, and the final desorption process. For example, when CO is weakly bound to the active center it desorbs more readily to yield CO, whereas a moderate enhancement of CO adsorption may promote its continued protonation; however, excessively strong binding may cause intermediates to occupy active sites, thereby inhibiting the catalytic cycle [5, 8, 13].

The structural advantages of MOFs are precisely reflected in their ability to regulate the above reaction steps at a molecular scale. Metal nodes and their coordination environments can alter the binding strength of CO_2 and key intermediates and determine the electron-enrichment position; organic linkers tune light absorption, excited-state energy levels, and charge-transfer behavior through conjugated structures and substituents, while also modifying the local proton-supply environment; pore size, polarity, and hydrogen-bonding networks can regulate the local CO_2 concentration, intermediate configuration, and proton-migration processes [13, 14, 18, 20]. These three aspects are not independent of one another; rather, they jointly determine the complete reaction chain of "light absorption – charge separation and migration – CO_2 activation – intermediate transformation – product desorption." Therefore, the essence of MOF photocatalytic CO_2 reduction performance lies in the synergistic matching of its electronic structure, active centers, and pore microenvironment, which also provides a theoretical basis for subsequent performance optimization

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through metal-node regulation, linker engineering, defect engineering, and heterostructure construction.

3. Representative MOF photocatalytic systems and composite design

Different metal nodes endow MOFs with differentiated electronic structures, chemical stability, and catalytic behavior; therefore, the performance of a single MOF system is often jointly controlled by the node type and linker structure. Zr-based MOFs are most representatively exemplified by the UiO-66 series, whose $Zr_6O_4(OH)_4$ clusters form strong coordination bonds with carboxylate linkers, conferring good thermal and hydrolytic stability. The light-response capability of unmodified UiO-66 is limited, whereas the introduction of electron-donating groups such as $–NH_2$ can extend visible-light absorption by shifting the linker frontier-orbital energy levels and promote linker-to-node charge transfer. Its advantages mainly lie in framework stability and the ease of tuning defects and functional groups, but the effective charge-migration distance in single-component systems is long, limiting deep reduction reactions [23]. Fe-based MOFs such as MIL-101(Fe) exploit Fe–O clusters to participate in photoinduced electron transfer; the Fe^{3+}/Fe^{2+} redox couple facilitates the formation of metal centers with reducing activity, so they exhibit good visible-light response, but their structural stability and the persistence of metal sites during reaction still require attention [23]. Among Ti-based MOFs, MIL-125(Ti) and its aminated derivative NH_2-MIL-125(Ti) display characteristic ligand-to-Ti-oxo-cluster charge transfer; amino functionalization markedly improves visible-light absorption and enriches photogenerated electrons at Ti centers [23]. Overall, Zr-, Fe-, and Ti-based MOFs differ in stability, visible-light response, and photoinduced charge transfer, and their performance entails no absolute superiority or inferiority but rather depends on the matching among light absorption, electron lifetime, active sites, and the reaction system.

When a single MOF struggles to simultaneously satisfy the demands of efficient light harvesting and highly active catalytic sites, the introduction of metal nanoparticles, single atoms, or molecular catalytic centers becomes an important performance-enhancement strategy. Metal components can be loaded on the MOF external surface or confined within pores or near nodes, thereby forming highly dispersed active centers. Compared with conventional supports, the regular pores of MOFs can restrict nanoparticle migration and aggregation, while linker functional groups or defect sites can form strong anchoring interactions with metals, improving the stability of active components [24]. Ag and Au can exploit localized surface plasmon resonance to enhance visible-light response and generate hot electrons, whereas metal centers such as Pt, Ni, and Co can participate in the adsorption of key intermediates and subsequent protonation. More importantly, metal–MOF interfaces can redistribute electrons, making it easier for photogenerated electrons to migrate from the photosensitive framework to catalytic sites, thereby improving the utilization efficiency of effective charge [24].

In addition to inorganic metal components, immobilizing molecular catalysts within MOF pores is also an important approach to achieving selectivity control. Porphyrins, phthalocyanines, and complexes of Re, Ru, etc. possess well-defined photosensitizing or catalytic centers, but homogeneous systems often suffer from difficulties in recovery, molecular aggregation, and insufficient stability. MOFs can spatially isolate these molecular sites through covalent linkage, coordination immobilization, or pore encapsulation, preserving their molecular catalytic characteristics while suppressing deactivation by aggregation [25]. At the same time, the ordered framework can shorten the spatial distance between photosensitizing units and catalytic centers, enabling excited-state electrons to migrate along a preset path [25]. If the pore walls further introduce functional groups capable of hydrogen bonding or tuning local polarity, the

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microenvironment around key intermediates can be altered, thereby influencing the tendency to form CO, HCOOH, or more deeply reduced products [25]. Therefore, the core of such systems is not simply to increase the number of active components, but to construct an artificial reaction microenvironment with a well-defined electron-migration pathway through spatial isolation and interfacial coupling.

Further constructing heterostructures by combining MOFs with TiO_2, g-C_3N_4, $ZnIn_2S_4$, and other semiconductors can exploit the complementary advantages of the two materials in light absorption and charge transport. After compounding, the energy-level difference and Fermi-level re-equilibration at the interface can create a directed charge-migration driving force, thereby reducing bulk-recombination probability [26]. Depending on the specific band alignment and interfacial charge-transfer mode, such systems can exhibit type-II, Z-scheme, or S-scheme charge-transfer mechanisms. Compared with simple physical mixing, an effective heterojunction requires a close interface between the two phases so that photogenerated carriers can complete cross-interface transfer on a short timescale [26]. The semiconductor component enhances visible-light absorption and provides additional electron-transport channels, while the MOF offers highly dispersed reaction sites and a local CO_2-enrichment environment, thereby achieving synergy among light harvesting, carrier separation, and surface reactions [27].

In summary, single MOFs constructed from different metal nodes establish the basic photochemical characteristics of the material, the introduction of metals or molecular catalysts further strengthens active centers, and MOF/semiconductor heterostructures primarily improve the spatial separation and utilization efficiency of photogenerated carriers. These three types of systems reflect a development trend in MOF photocatalytic materials from "composition selection" toward "multi-component synergy," and also indicate that the key to constructing high-performance CO_2 photoreduction systems lies not in simply increasing material complexity, but in establishing reasonable interfacial electron coupling, active-site distribution, and reaction microenvironment, thereby providing a material basis for the refined structural regulation of nodes, linkers, defects, and interfaces in subsequent stages.

4. Structural regulation strategies for photocatalytic CO_2 reduction over MOFs

Metal nodes are crucial structural units connecting photogenerated charge transport and surface catalytic reactions in MOFs; their elemental composition, valence state, and local coordination environment directly influence the electron-enrichment capability and the adsorption strength of key intermediates. By changing the node metal, one can tune the formation and subsequent transformation of intermediates such as *COOH, *OCHO, and *CO, thereby affecting product distribution. For example, under suitable local structures Cu centers have the potential to stabilize carbon-containing intermediates and promote C–C coupling, while transition-metal sites such as Fe and Co often display pronounced CO_2-activation and two-electron-reduction capabilities, but the specific selectivity still depends on the coordination environment and reaction conditions. Compared with single-metal nodes, introducing a second metal can construct bimetallic active centers with asymmetric electronic properties, lowering the barrier of specific reaction steps by tuning the local charge density and intermediate adsorption configuration. If the two metal sites are spatially close enough, they may separately undertake CO_2 activation, electron supply, or intermediate stabilization, thereby achieving synergistic catalysis. Therefore, the core of bimetallic-node design is not simply to increase the variety of metals, but to establish atomically defined active sites with clear functional division [28].

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Corresponding to node engineering, linker regulation primarily acts on light absorption, electronic coupling, and the local reaction environment. Introducing electron-donating groups such as $–NH_2$ onto aromatic linkers shifts the frontier-orbital energy levels and moves the absorption edge into the visible region; extending the π-conjugation system or introducing photosensitive structures such as porphyrins and heterocycles enhances the excited-state delocalization and electron coupling between linkers and nodes. At the same time, polar sites such as $–NH_2$, –OH, and N-heterocycles can strengthen interactions between CO_2, proton donors, and the pore walls. It is worth noting that linker modification does not become more beneficial as the degree of substitution increases. Excessive functionalization may reduce the effective pore volume, increase diffusion resistance, or even alter the framework topology and local flexibility; an overly strong electron-donating ability of the linker may also cause a mismatch between the excited-state energy level and the catalytic center. Therefore, linker engineering essentially requires a balance among light harvesting, charge transfer, substrate mass transport, and structural stability [29].

Without changing the main topology, defect engineering can further tune the local coordination structure of MOFs. Common missing-linker, missing-node, or coordinatively unsaturated sites expose metal centers that were originally occupied by linkers, increasing the likelihood of contact between CO_2 and active centers while altering the electron density of neighboring atoms. In some MOFs containing variable-valence metals, defects may also be accompanied by valence rearrangement or the formation of oxygen-defect-related electronic states, thereby providing additional charge-capture and -migration channels. However, an excessively high defect concentration weakens the connectivity of inter-node connections, causing pore-structure distortion or even framework destabilization; thus, their catalytic effect usually exhibits an optimal concentration window. Compared with defect quantity, the location of defects and their surrounding chemical environment are equally important: if an active defect site is adjacent to pore-wall functional groups capable of hydrogen bonding, it can simultaneously promote CO_2 adsorption and proton-coupled electron transfer, making the local reaction environment more favorable for the generation of specific intermediates [30].

The pore microenvironment provides further spatial regulation for the node and defect sites described above. By tuning pore size, polarity, and hydrophilicity/hydrophobicity, one can regulate the relative concentrations of CO_2, H_2O, and reaction intermediates near active centers. Moderate confinement helps to enrich substrates locally and stabilizes specific adsorption configurations through hydrogen bonding, electrostatic interactions, or van der Waals interactions; however, pores that are too small increase mass-transport resistance, so pore design must simultaneously consider substrate enrichment and product diffusion. Particularly in photocatalytic systems involving water, the local hydrophilic/hydrophobic environment may also alter the competitive adsorption between CO_2 and protons, thereby influencing the competition between CO_2 reduction and the hydrogen-evolution reaction. Thus, pores are not merely passive mass-transport spaces, but nanoreactors capable of actively modifying the reactant composition and intermediate stability [30].

When node, linker, and defect regulation within a single framework still cannot achieve efficient charge utilization, interfacial engineering can further reconstruct the spatial-migration pathways of photogenerated carriers. After a MOF forms a close heterointerface with another photoactive component, the energy-level difference and interfacial charge redistribution between the two phases can generate a directed migration driving force. Depending on the electronic structure and the actual charge-transfer pathway, the interface may exhibit different mechanisms such as type II, Z-scheme, or S-scheme. The key to a high-quality interface lies in shortening the cross-interface transport distance and reducing ineffective traps, rather than simply expanding the contact area; constructing

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strong interfacial coupling through in situ growth, coordination-bond linkage, or crystal-face matching is generally more favorable for rapid charge transfer than physical mixing. In addition, introducing metal or molecular catalytic sites near the interface can enable electron separation and surface reactions to occur continuously in space, reducing charge losses during migration [27].

In summary, structural optimization of MOF photocatalytic CO_2 reduction can be summarized into four levels: regulation of the node electronic structure, tuning of the linker optoelectronic properties, construction of defects and the pore microenvironment, and heterointerface engineering. These strategies are not independent of one another; rather, they jointly influence photogenerated-carrier generation and migration, key-intermediate stabilization, and competing reaction pathways. Therefore, the design of high-performance MOFs should evolve from optimization of a single structural parameter toward multi-scale synergistic regulation, achieving a match between photophysical processes and surface catalytic kinetics while maintaining framework stability and effective mass transport, thereby improving CO_2-reduction activity and target-product selectivity.

5. Conclusions and perspectives

This review has systematically summarized the reaction mechanisms, representative material systems, and structural-regulation strategies of MOF materials for photocatalytic CO_2 reduction. Benefiting from tunable metal nodes, organic linkers, and pore microenvironments, MOFs exhibit unique advantages in CO_2 enrichment, photogenerated-charge transport, and stabilization of key intermediates; however, their performance is still constrained by factors such as a limited light-absorption range, rapid charge recombination, and insufficient long-term stability. Through node regulation, linker functionalization, defect engineering, and heterointerface construction, light harvesting, charge migration, and product selectivity can be synergistically improved to a certain extent. Future research should further integrate in situ spectroscopy, transient characterization, and theoretical calculations to identify the evolution of real active sites and key intermediates, and to achieve synergistic optimization among structural stability, interfacial charge dynamics, and reaction selectivity, thereby driving MOF photocatalytic CO_2 reduction from performance improvement toward mechanism clarification, high efficiency and stability, and practical application.

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