Critical Aspects of Metal–Organic Framework-Based Materials for Solar-Driven CO₂ Reduction into Valuable Fuels

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1. Introduction

With excess consumption of fossil fuels, as presented in Figure 1a, the annual carbon dioxide (CO₂) emission and global surface temperature are ever-increasing rapidly, which indicates that the “greenhouse effect” will increase profoundly if such a consumption of fossil fuels continues. There are two common strategies to mitigate the “greenhouse effect” through decreasing the concentration of CO₂ in the atmosphere. One solution is sequestering CO₂ in geological media through physical or chemical absorption. The other one is direct conversion of CO₂ into valuable fuels, such as CO, HCOOH, methanol, methane, ethane, etc. Such an economic pathway can not only reduce the atmospheric CO₂ concentration, but also provide significant chemical energy as substitutions to fossil fuels. Up to now, several energy sources with a large diversity of technical routes have been proposed to convert CO₂ into fuels, including thermochemical reduction, photochemical reduction, electrochemical reduction and biochemical reduction. Of those, solar energy outweighs the others given its pollution-free, inexhaustible, and cost-free nature. Hence, conversion of solar energy into chemical energy through photocatalytic CO₂ reduction is worth of investigating.

A typical process of CO₂ photoreduction involves three critical aspects. 1) Light absorption. Ultraviolet (UV) light accommodates high energy which readily excite photocatalysts, however, it only accounts for about 5% of the entire solar irradiance. Although inferred (IR) light accounts for more than a half, its low energy does not suffice to activate photocatalysts. Visible light, which accounts for about 43%, will be a sound and reliable source to be used for photocatalysis (Figure 1b). To obtain high solar energy conversion efficiency, a large number of visible-light responsive semiconductor materials have been investigated. 2) Carrier dynamics include carrier separation, migration, trap, etc. In general, light irradiation of a photocatalyst leads to the formation of photogenerated electron and hole pairs. Then they migrate toward the surface of the photocatalysts to participate in reduction and oxidation reactions, respectively. 3) Adsorption and activation of CO₂ molecules and reaction on the surface. In this process, CO₂ molecules are expected to be adsorbed on the surface of photocatalyst. Therefore, the capacity of uptake CO₂ is the key. Concentration of the adsorbed CO₂ on the surface of a photocatalyst and number of activated catalytic sites determine the efficiency of CO₂ reduction.
reduction process.\cite{12} In addition, some functional groups modified on the surface such as hydroxyl, amino, frustrated Lewis pairs (FLPs), could activate the adsorbed CO$_2$ molecules and decrease the reaction energy barrier, which will boost the efficiency of CO$_2$ reduction into fuels.\cite{13,14} A large number of inorganic semiconductors have been developed as inspired by the pioneering work led by Fujishima and co-workers in terms of employment of TiO$_2$ for solar-driven CO$_2$ reduction in 1979.\cite{15,16} In the recent years, significant advances have been achieved in expanding the visible-light absorption range and facilitating solar energy conversion efficiency.\cite{17–23} However, the performance of inorganic semiconductors remains unsatisfactory with respect to industrial applications, such as low capacity of CO$_2$ absorption, limited specific surface area, large bandgap, electron–hole recombination in nonporous\cite{24} and low photocatalytic CO$_2$ reduction selectivity of high value-added fuels. As such, it is of paramount significance to design and develop efficient and selective photocatalytic CO$_2$ reduction systems with possession of extended visible-light absorption ability, efficient photogenerated charge separation, excellent CO$_2$ molecular adsorption capacity, and abundant active CO$_2$ reduction sites.

In comparison with traditional porous/nonporous materials, metal–organic frameworks (MOFs), covalent–organic frameworks (COFs), and zeolites, recently have attracted considerable attention owing to low density, large surface area, high porosity, structural and compositional diversity, which holds great potential for a broad range of commercial aspects in physical, mechanical, acoustical, thermal, and electrical fields.\cite{25,26} Benefiting from these specialties, porous materials have been widely applied in catalysts, sensors, gas adsorption and separation, drug delivery, and environmental governance.\cite{27–38} In particular, solar-driven CO$_2$ reduction could be catalyzed by proper porous materials, owing to the tunable light absorption ability over broad range, the ameliorative carrier separation, the evenly distributed catalytic active site and the ideal catalytic platform for mechanism study of structure–activity relationships. In addition, the potential CO$_2$ capture capability of porous materials further endows their merits toward photocatalytic reduction of CO$_2$ into value-added fuels by concentrating CO$_2$ molecules at active sites.\cite{39}

To make a comprehensive understanding of rational design and development of more creative porous materials for solar-driven CO$_2$ reduction, it is necessary to provide a timely research progress report to capture the state-of-the-art progress in the field. Several reviews have focused on MOFs-based materials from the perspectives of categories of photocatalytic products, wide applications such as water splitting and cycloadition of CO$_2$.\cite{40–46} This report mainly summarized the state-of-the-art progress of MOFs-based photocatalytic systems for CO$_2$ reduction; together with COFs-based, zeolite-based, inorganic porous semiconductors or organic polymers photocatalyst. In this report, we highlight representative approaches for optimizing the performance of CO$_2$ photoreduction through using versatile porous materials and three main critical aspects will be discussed (Scheme 1). It includes the present fundamental of CO$_2$ photoreduction and the recent four types of photoactive porous materials applied in CO$_2$ reduction. Finally, challenges
and prospects of porous materials for photocatalytic CO₂ reduction are illustrated.

2. Fundamentals of Porous Materials for CO₂ Photoreduction

Photoreduction of CO₂ into chemical feedstocks is a promising solution to energy crisis and environmental problems. A typical process of photocatalysis includes three basic but critical principles. As shown in Figure 2a, semiconductor adsorbs sunlight of energy ≥Eₙ (bandgap) and generates electron–hole pairs simultaneously. Then photogenerated electrons transfer from valence band (VB) to conduction band (CB), leading to the separation of electron–hole pairs. Subsequently, the excited electrons and holes are transferred to the surface to take part in reduction reaction and oxidation reaction process, respectively. It is noted that CB potential of a semiconductor must satisfy the thermodynamic potential of different products. The main potentials of a range of CO₂ reduction products are listed in Table 1, which are referred the normal hydrogen electrode (NHE) at pH 7, namely E⁰ V versus NHE at pH 7.[47–49]

Porous materials exhibit a similar photocatalytic process to that of inorganic semiconductors. Taking MOFs as an example, compared with the inorganic semiconductors, the VB and CB of inorganic materials equal to the highest occupied molecular orbitals (HOMO) and the lowest unoccupied molecular orbitals (LUMO), respectively (Figure 2b). The following features make porous materials promising candidate for CO₂ photoreduction:[50,51] i) High CO₂ adsorption capacity makes the reaction site active to the adsorbed CO₂ molecules, thus facilitates the performance of photocatalytic reduction of CO₂. ii) The special porous structures have a pore confinement effect that will boost the catalysis process to a great degree. However, the performance of CO₂ photoreduction still suffers low efficiency owing to three key aspects: insufficient utilization of visible-light, negative electron–hole separation, and high inertness of active sites. Thus, in the next part, we summarize the existing strategies to improve the photocatalytic efficiency for CO₂ reduction through tackling those three critical challenges.

3. Three Critical Aspects of MOFs-Based Materials for CO₂ Photoreduction

MOFs, a typical category of porous materials and built up with organic ligands and metal ions of clusters, have been extensively explored for CO₂ photoreduction. Both the organic ligands and metal clusters can be a light harvest center owing to the metal complex like the inorganic semiconductor quantum dots (QDs), while the organic ligands can be considered antennae to harvest light.[52,53] Charge carrier separation and migration are vital for the reactions with the adsorbed molecules on the surface. Some sound strategies were introduced to ameliorate the charge carrier dynamics. Afterward, we discussed the correlation about the absorption of CO₂ coupled with the activity of CO₂ reduction.

3.1. Light Absorption

To expand the range of visible light absorption of MOFs materials, a number of strategies, such as amino-modified, photosensitizer-functionalized, electron-rich conjugated linkers, post synthetic modifications (PSMs), and post synthesis exchange (PSE) were postulated. For metal clusters, metals were replaced with nonferrous ones or doping other ones to generate light harvest center.
3.1.1. Amino-Functionalized CO₂ Reduction Photocatalysts

Since Garcia and co-workers reported the use of MOF-5 as a semiconductor to play charge-separation under light irradiation,[54] a number of publications regarding the semiconductor properties of MOFs have been explored.[55–57] However, most MOFs exhibit poor conductivity due to the mismatch between the orbitals of linker and metal, resulting in a short transfer distance. As above-mentioned, organic linker acts as antennae and transfers the generated electrons to metal clusters, namely linker-to-metal cluster charge transfer (LMCT), which provides a short-range transfer of photogenerated electrons. Therefore, it is crucial for the linker to produce photogenerated electrons and thus provide sufficient electrons to participate the photocatalysis process.

NH₂-functionalized linkers could greatly widen the range of optical absorption. Li and co-workers reported a visible light responsive NH₂-MIL-125(Ti) by a substitution of ligands NH₂-BDC for BDC linker of MIL-125(Ti),[58] which broadens the absorption edge from 350 nm for MIL-125(Ti) to 550 nm for NH₂-MIL-125(Ti) (Figure 3a). The formate evolution rate of NH₂-MIL-125(Ti) and MIL-125(Ti) was 16.28, ≈0 μmol h⁻¹ g⁻¹, respectively (Figure 3b). Later, the same group also explored the visible light responsive of NH₂-UiO-66 by substituting NH₂-BDC linkers for BDC linkers.[59] The absorption edge was increased to about 430 nm, which enhanced the photocatalytic activity (Figure 3c,d). It is noted that NH₂-UiO-66(Zr) with mixed linkers even shows an improved formate generation rate. Obviously, (NH₂)₂-BDC (DTA) partially replaces NH₂-BDC (ATA) in NH₂-UiO-66(Zr) leading to enhancement in light absorption and CO₂ absorption, which can improve the performance of photocatalytic reduction of CO₂ with MOFs. Similarly, Wang et al. reported that all three NH₂-functionalized Fe-based MOFs (NH₂-MIL-101(Fe), NH₂-MIL-53(Fe) and NH₂-MIL-88B(Fe)) exhibited higher photocatalytic activity.[60] However, these cases differ from above mentioned MIL-125 or UiO-66 with –NH₂-free modification. The NH₂-free Fe-based MOFs exhibit semiconductor likewise in the absence of LMCT and are able to produce formate form under visible-light irradiation.

![Figure 3](https://www.global-challenges.com)
Nevertheless, after −NH₂ modification, not only the light absorption edges of these Fe-based MOFs were extended to nearly 700 nm, but their flat band potentials became more negative than that of bare MOFs according to the Mott–Schottky analysis. The possible mechanism is that −NH₂ acts a photoexcited center, which facilitates photogenerated electrons to transfer to Fe center other than the direct photoexcitation of Fe–O clusters (Figure 3e).

Above-mentioned studies demonstrate that NH₂-functionalized MOFs are a promising option to extend visible-light range. However, most NH₂-functionalized MOFs exhibit light absorption limited to the range less than 550 nm. For instance, NH₂-MIL-125(Ti)[58] and NH₂-Uio-66(Zr)[59] expand the light absorption edge to nearly 550 and 450 nm, respectively. Therefore, some reports utilized conjugated molecules and amino groups together to further improve light responsive range of photocatalysts. By introducing functionalized conjugated ligand (H₂L = 2,2′-diamino-4,4′-stilbenedicarboxylic acid, H₂SDCA-NH₂) into porous UiO-type MOF, denoted as Zr-SDCA-NH₂,[61] Zr-SDCA-NH₂ illustrates a broad-band absorption edge at about 600 nm, respectively. Therefore, some reports utilized conjugated molecules and amino groups together to further improve light responsive range of photocatalysts. By introducing functionalized conjugated ligand (H₂L = 2,2′-diamino-4,4′-stilbenedicarboxylic acid, H₂SDCA-NH₂) into porous UiO-type MOF, denoted as Zr-SDCA-NH₂,[61] Zr-SDCA-NH₂ illustrates a broad-band absorption edge at about 600 nm, exhibiting a formate evolution rate of 96.2 µmol h⁻¹ mmol MOF⁻¹. This study provides a new platform for effectively improving light absorption of MOFs through employing molecular conjugation.

3.1.2. Electron-Rich Conjugated Linkers CO₂ Reduction Photocatalysts

Electron-rich conjugated linkers can improve the CO₂ absorption capacity, and increase the light response range.[62,63] Porphyrin-based ligand (H₂TCPP) is constructed from four pyrrole rings, exhibiting a near-planar 18 π-conjugated network, which may be beneficial for the porphyrin-based material for CO₂ capture and conversion. Robert and co-workers[64,65] reported an iron tetraphenylporphyrin complex modified with four triethylammonio groups, exhibiting excellent performance for converting CO₂ to CO or CH₄ and the mechanism was also proposed as depicted in Figure 4a. These investigations employed earth-abundant Fe-based materials with a cost-effective nature. Similarly, Sadeghi et al. prepared a H₂TCPP-based MOF (Zn/PMOF) for the photocatalytic conversion of CO₂ into CH₄ in the presence of H₂O vapor as a sacrificial agent.[66] The CH₄ production rate was 8.7 µmol h⁻¹ g⁻¹ and no by product was detected.

Anthracene-based linker also exhibits excellent light absorption for electron-rich conjugated structures. Su et al. reported that 4,4-(anthracene-9,10-diylbis (ethyne-2,1-diyl)) dibenzoic acid reacts with ZrCl₄ to form Zr-MOF NNU-28 ([Zr₆O₄(OH)₄(L)₆]·6DMF).[67] NNU-28 displays the highest formate production rate of 52.8 µmol g⁻¹ h⁻¹ in terms of Zr-MOFs, which is attributed to the role of anthracene-based ligand. In comparison with the organic ligand of H₂ATA, anthracene-based ligand serves as an antenna for light harvesting and participates in CO₂ reduction reaction by radical formation (Figure 4b). However, H₂ATA ligand shows no other extra contribution to the reaction, which provides a novel way to design visible-light responsive MOFs-based photocatalysts. Huang and co-workers[68] prepared porphyrin-based Al-PMOF coupled with Cu²⁺ and utilized it for photoreduction of CO₂ into CH₃OH.

![Figure 4](https://example.com/figure4.png)
achieving high CH$_3$OH formation rate of Al PMOF with Cu$^{2+}$ (262.6 ppm g$^{-1}$ h$^{-1}$). This work provides a new strategy for designing efficient porphyrin-based photocatalysts for capture and conversion of CO$_2$ into liquid fuels.

3.1.3. Photosensitizer-Functionalized CO$_2$ Reduction Photocatalysts

In addition to ligands, photosensitizer can also be modified to improve the photoresponse range of catalysts. The introduction of photosensitizers (Re I(CO)$_3$(bpy)X complexes with bpy = 2,2’-bipyridine and X = halide) into MOFs could harvest light and reaction centers. In general, 2,2’-bipyridine-5,5’-dicarboxylic acid (5,5’-dcbpy), 2,2’-bipyridine-4,4’-dicarboxylic acid (4,4’-dcbpy) and bpy units are ideal linkers for building photosensitizers given their promising coordination ability, which is analogue to a BPDC leaker with transition metal carbonyl complexes. Recently, a large number of research groups are exploring photosensitizer-functionalized MOFs as photocatalysts for CO$_2$ reduction, such as Ru–MOF (Y[Ir(ppy)$_2$(4,4’-dcbpy)]$_2$[OH]), Ir-CP ([Cd$_2$[Ru(4,4’-dcbpy)$_3$]·12H$_2$O]$_n$).[69,70] In 2011, Lin and co-workers reported visible-light responsive UiO-67 applied in CO$_2$ reduction under light irradiation.

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However, CO evolution rate was relatively low even under the conditions of sacrificial agent of triethylamine (TEA). Later, they also reported photosensitizing metal–organic layers (MOLs) (Hf$_{12}$-Ru, based on Hf$_{12}$ secondary building units (SBUs) and [Ru(bpy)$_3$]$^{2+}$ (bpy = 2,2’-bipyridine) derived dicarboxylate ligands) as a new 2D material. Combining with photosensitizer M(bpy)(CO)$_3$X (M = Re and X = Cl or M = Mn and X = Br), the complex exhibits efficient photocatalytic CO$_2$ to CO (Figure 5). These series of work demonstrate that incorporation of noble metal-based photosensitizers into MOFs as building blocks is a sound approach for photocatalytic CO$_2$ reduction.

3.1.4. Postsynthesis of Exchange (PSE) or Metal Doping CO$_2$ Reduction Photocatalysts

Apart from functionalized organic ligands, it is possible to enhance visible-light responsiveness and photocatalytic performance of MOFs via functionalization of metal centers. As mentioned before, metal clusters resemble inorganic semiconductor quantum dots and organic ligands play as antennae to harvest light. The methods of PSMs and PSEs represent typical doping methods in semiconductor-based photocatalysts, which may generate doped level or provide active photocatalytic sites to improve the overall efficiency of photocatalysis.[73,74] In 2015, Li and co-workers was the first to synthesize Ti-doping NH$_2$-UiO-66(Zr/Ti) by using PSE, which enhanced photocatalytic activity for CO$_2$ reduction and hydrogen production under visible light irradiation.[75] As shown in Figure 6a, the UV–vis spectra of Ti-doping indicate an enhanced visible light absorption at the wavelength of 400 to 600 nm, leading to a high formate evolution rate (Figure 6b). The possible mechanism is illustrated in...
Figure 6c. ATA generates photoelectrons under light irradiation, which are then transferred to Ti–Zr–O oxo–metal clusters. This work is the first example to improve photocatalytic performance by means of PSE, which provides a generic method to explore excellent MOF-based photocatalysts. However, HCOO\(^-\) evolution rate of Ti–Zr–O oxo–metal clusters needs further improvement compared pure NH\(_2\)-UiO-66(Zr).

Pure UiO-66(Zr) remains inactive for photocatalytic CO\(_2\) reduction up to date due to UV-responsive and inefficient electrons transfer from leaker to metal clusters. In 2015, Cohen et al. \cite{76} synthesized UiO-66-CAT (H\(_2\)BDC replaced by 2,3-dihydroxyterephthalic acid) and Cr-monocatecholato species UiO-66-CrCAT, Cr-monocatecholato species UiO-66-GaCAT through PSE (Figure 6d). The UV–vis spectra of the samples were shown in Figure 6e, UiO-66-CrACAT exhibited obvious visible light absorption because –OH increases HOMO level of H\(_2\)BDC.\cite{77,78} Photocatalytic performance reveals that UiO-66-CrACAT shows the highest formate evolution turnover number and presents a high stability. This work makes use of nonprecious metals (Cr) instead of noble metals (Ir, Pd) as dopants, providing a general way to develop more efficient catalysts.
3.2. Carrier Dynamics

The dynamics of charge carrier includes charge separation, migration, mobility, and diffusion length, which is one of the critical aspects in determining the efficiency of photocatalysis. In principle, photocatalytic reaction occurs only when photogenerated electrons are transferred to the surface. However, in many photocatalysts including porous materials or nonporous materials, the photogenerated electrons are recombination with holes. Only a small number of photoelectrons can participate in the process of photocatalysis. Therefore, it is extremely important to investigate the charge carrier dynamics. In this section, MOFs are coupled with other cocatalysts or semiconductors to form heterojunction or electron trapping sites, leading to efficient charge separation.

3.2.1. MOFs Coupled with Semiconductors as Photocatalysts

The acceleration of charge carrier separation and inhibition of harmful charge recombination is the key to improve the photocatalytic efficiency for photocatalytic CO$_2$ reduction.$^{[79]}$ MOFs coupled with other materials may form heterojunction or electron capture sites in composite materials, which enable photogenerated electrons transfer from one part to another, leading to effective charge separation and improved catalytic activity.

In 2013, Liu et al.$^{[80]}$ first synthesized the composites of Zn$_2$GeO$_4$ and ZIF-8 (zinc containing ZIFs) for efficient photocatalytic conversion of CO$_2$ into liquid CH$_3$OH, which is attributed to the efficiency carrier separation by forming heterojunction. Such a promising strategy is a key for investigating highly efficient photocatalysts to improve CO$_2$ reduction efficiency by the virtue of excellent adsorption property of MOFs in aqueous media. After that, Wang and co-workers systematically studied ZIF-9 coupled with semiconductors such as CdS$^{[81]}$ C$_3$N$_4$,$^{[82]}$ ameliorate the charge transfer in the CO$_2$ photoreduction process, which greatly improved the overall photocatalytic performance. Ye and co-workers synthesized Co-ZIF-9/TiO$_2$ nanocomposites for photocatalytic CO$_2$ reduction.$^{[83]}$ The results of transmission electron microscopy (TEM), and X-ray photoelectron spectroscopy (XPS) of the optimal sample show TiO$_2$ and ZIF-9 are very close with each other, leading to efficient separation of carrier. The highest photocurrent density of optimal further confirms the best carrier efficiency. This work presents that fabrication of Co-ZIF-9 with semiconductors to form a well-designed structure is vital to further improve the performance of CO$_2$ photoreduction.

Similarly, Li et al.$^{[84]}$ prepared core–shell-structured Cu$_3$(BTC)$_2$@TiO$_2$ (BTC = 1,3,5-benzenetricarboxylate) for photocatalyst in CO$_2$ reduction.$^{[84]}$ It was designed for photocatalytic reduction of CO$_2$ to CH$_4$ in the presence of water, which also acts as sacrificial donor. In the composite photocatalyst, a large surface area of MOF plays as core and provides adsorption and photoconversion to CO$_2$ molecules. Shell of the macroporous TiO$_2$ is a semiconductor for supplying photogenerated electrons, which is easy to be excited by light and easy to diffuse in a MOF based core. In order to examine the carrier dynamics of the samples, ultrafast transient absorption (TAS) was carried out. As shown in Figure 7a,b, the electrons were transferred from TiO$_2$ to the electrons trapping sites (Cu$_3$(BTC)$_2$) efficiently, leading to improvement in carrier separation.

Density functional theory (DFT) calculations presented that two photogenerated electrons transferred from TiO$_2$ to Cu$_3$(BTC)$_2$ leading to high adsorption energy of CO$_2$ and reducing $E_b$ from 776 eV for neutral state to 5.57 eV for charged with two electrons (Figure 7c,d), which facilitated the CO$_2$ adsorption by Cu$_3$(BTC)$_2$. Similarly, Crakea et al.$^{[85]}$ prepared TiO$_2$/NH$_2$-UiO-66 heterostructures via an in situ process.$^{[85]}$ The close contact between TiO$_2$ and NH$_2$-UiO-66 facilitated electron migration, and rendered high efficiency of electron hole separation. The efficient charge transfer was further confirmed by TAS spectroscopy.

Porphyrin-based semiconducting MOF PCN-222 was used in CO$_2$ photoreduction for the first time in 2015,$^{[86]}$ exhibiting higher activity than that of H$_2$TCPP leaker alone. As shown in Figure 7e,f, TA and photoluminescence spectra demonstrate that PCN-222 has a long-lived electron trap state, thus inhibits the electron–hole recombination and yields high efficiency of CO$_2$ photoreduction. PCN-222 exhibited much better activity than that of H2TCPP leaker alone. This work not only provides a new understanding of the carrier dynamics involved in MOFs, but also unveils the mechanism of charge-carrier transfer.

Recently, Zhang et al.$^{[87]}$ reported a MAPbI$_3$@PCN-221(Fe$_x$) composite for CO$_2$ photoreduction. As illustrated in Figure 7g,h, MAPbI$_3$ was encapsulated in the pores of PCN-221(Fe$_x$)$^{[87]}$ which is beneficial to the effective transfer of photogenerated electrons from the encapsulated MAPbI$_3$ QDs to Fe catalytic sites, leading to high charge separation efficiency. This current study provides a method to improve the stability of lead halide perovskite QDs in aqueous atmosphere.

Transition metal sulfides (TMSs) were widely studied for photoreduction of CO$_2$ in recent years owing to visible-light responsiveness, low cost and satisfactory performance.$^{[88,89]}$ A series of nanocomposites were prepared by incorporating different contents of UiO-66-NH$_2$ with solid-solution Cd$_{0.2}$Zn$_{0.8}$S for photocatalytic CO$_2$ reduction.$^{[90]}$ UV–vis spectrum reveals that the absorption edge of composites achieved slight red shift (Figure 7i), suggesting that composites are more responsive to sunlight. Of the as-synthesized samples, an optimal composite (CZS@UN20, 20 wt% of UiO-66-NH$_2$) exhibits the highest CH$_4$OH evolution rate of 6.8 µmol h$^{-1}$ g$^{-1}$ under visible-light irradiation, in which the CH$_4$OH production rate of pure Cd$_{0.2}$Zn$_{0.8}$S is only 2.0 µmol h$^{-1}$ g$^{-1}$. The remarkable enhancement in performance was mainly attributed to efficient charge carrier separation (Figure 7j). With visible-light irradiation, photogenerated electrons transferred from UiO-66-NH$_2$ to Cd$_{0.2}$Zn$_{0.8}$S since the LUMO potential of UiO-66-NH$_2$ was more negative than that of Cd$_{0.2}$Zn$_{0.8}$S, inhibiting the electron–hole recombination, thus achieved high activity of CO$_2$ photoreduction. This work offers a promising candidate to practical applications. Therefore, the heterojunction composite materials formed by MOF and semiconductor materials can effectively separate photogenerated carriers. However, due to the inherent defects on the surface of inorganic semiconductor cannot be well grafted tightly with MOFs, many literatures used this method to greatly improve the efficiency of photogenerated charge separation which needed to be verified.
Figure 7. a) Ultrafast transient absorption and b) photoexcited dynamics. c) The optimized structure of a CO₂ molecule adsorbed on Cu₃(BTC)₂. d) Change of band energy $E_B$ for CO₂ reduction after the addition of one or two-electron charge. Reproduced with permission.⁹⁴ Copyright 2014, Wiley-VCH. e–f) TA spectra and carrier dynamics of H₂TCPP, PCN-222. Reproduced with permission.⁹⁵ Copyright 2015, American Chemical Society. g,h) Schematic illustrations of encapsulated MAPbI₃@PCN-221(Fex). Reproduced with permission.⁹⁶ Copyright 2019, Wiley-VCH. i) UV–vis spectra of pure UiO-66-NH₂, Cd₀.₂Zn₀.₈S, and CZS@UN composites. j) Schematic depict of charge carrier separation of composites for CO₂ photoreduction. Reproduced with permission.⁹⁷ Copyright 2017, Elsevier.
Using likewise doping method to synthesize the so-called “multi-metal-site” catalysts, it is feasible to form doping energy levels in the metal cluster center, like inorganic semiconductors, which is not only conducive to light absorption, but also can provide the active site or acted as capture carrier center, so as to improve the overall efficiency of photocatalytic reduction of CO₂. However, up to now, there is no in-depth study at atomic level of polynuclear MOF to find out how the doping could generate defects in the structure, which is a hot spot in recent years but a difficult problem.

3.2.2. MOFs Coupled with Metal as Photocatalysts

Metal is utilized widely in photocatalysis as a light harvest center owing to their surface plasmon resonance (SPR) effect. Of those, double-shelled plasmonic Ag–TiO₂ hollow spheres are a good example for improving the activity of CO₂ photoreduction.[90] Similarly, MOFs are a category of materials with porous structures that are elegant host matrices in confining versatile functional guest species, such as metal nanoparticles (MNPs), to yield enhanced photocatalytic performance through a synergistic effect.[92] A recent report by Yaghi and co-workers presented such an attempt to the employment of MNPs/MOFs (Ag-nanocubes-MOF core–shell composites, Ag–Re₃-MOF) for photocatalytic reduction of CO₂.[93] Re(CO)₅(bpyd)Cl, a catalytic center, was attached to linkers to produce Re-UiO-67, followed by coating upon Ag nanocubes to yield Ag–Re-UiO-67 (Figure 8a,b). It is apparent that thickness of the Re complexes contributes greatly to the catalytic activity. As presented in Figure 8c,d, Re complexes with a thickness of 16 nm, i.e., Re₃-MOF-16 nm, plays the highest photocatalytic activity. Moreover, Ag–Re₃-MOF-16 nm retains the original SPR features, thus produces a strong electromagnetic filed to confine spatially photoactive Re metal sites in the shell, and consequently exhibits seven times higher enhancement in photocatalytic evolution activity of CO₂-to-CO than that of Re-UiO-67 under visible-light irradiation. This study shows that covalently attached active centers within interior MOFs can be spatially localized and increase their photocatalytic performance by electromagnetic field induced by plasmonic silver nanocubes.

In a following study, ultrafine Ag NPs were doped into Co-ZIF-9 (Ag@Co-ZIF-9) for photocatalytic reduction of CO₂ to CO under visible light in the presence of a photosensitizer.[94] The photocatalytic performance of composites was enhanced twofold from that of Co-ZIF-9, demonstrating doping with MNPs was an efficient way to enhance photocatalytic efficiency of MOFs.

In addition, it is well recognized that the separation efficiency of charge carriers is an important factor to photocatalytic activity of semiconductor photocatalysts. When a Schottky barrier was formed at the junction of semiconductor and noble metal, photogenerated electrons in the semiconductor of a CB can be transferred to adjacent noble metal center, thus improving the separation of photogenerated carriers and ultimately improving the photocatalytic performance.[94, 95] Therefore, doping precious metal, such as Pt and Au, into a semiconductor photocatalyst is a common method to suppress the recombination of photogenerated electrons and holes. Li and co-workers[95] studied the effects of different metal-doped M-NH₂-MIL-125(Ti) (M = Pt and Au) photocatalysts on CO₂ reduction. Compared with pure NH₂-MIL-125(Ti), Pt-doped exhibited a higher formate evolution rate while Au-doped exhibited lower formate production, indicating noble metal could influence the electron-trapping, which further changed the products. Interestingly, Au-NH₂-MIL-125 imposed a negative effect on photocatalytic formate production. To elucidate the mechanism of different photocatalytic activities, ESR and DFT calculations for M-NH₂-MIL-125 were carried out. Results indicate hydrogen could spill over from Pt to Ti atoms, leading to the formation of Ti⁺, which was considered as the active sites to produce formate. However, hydrogen spillover was difficult over Au-NH₂-MIL-125(Ti). Therefore, a negative effect on the photocatalytic formate generation was detected over Au-NH₂-MIL-125(Ti), indicating that the selection of an appropriate noble metal is key to the desired photocatalytic activity. This work illustrates that an effective Schottky barrier can be formed only if their Fermi band potential between noble metals and semiconductors are considered.

In addition to noble metal, nonprecious metal can also be incorporated with MOFs to photocatalytically reduce CO₂ in an efficient manner. In recent years, atomically dispersed catalysts such as so-called “single atoms anchored on matrix” which utilized maximum atom efficiency.[95] However, it is still challenging to fabricate practical and stable single atom catalysts owing to their high mobility in a catalytic process.[96] In this case, porous materials are a good candidate as matrix for providing coordination sites to anchor single metal atoms. Ye and co-workers synthesized atomic Co dispersion of active sites in MOF-525.[97] Co sites were incorporated into the porphyrin units to form MOF-525-Co and atomic Co was demonstrated by the Co K-edge extended X-ray absorption fine structure (EXAFS) and X-ray absorption near-edge structure (XANES) spectroscopy (Figure 8e–g). According to the energy transfer investigation coupled with the first principles calculation, photogenerated electrons could be effectively shifted to the reaction center Co “trap site,” which ameliorates charge separation, achieving CO evolution rate of 200.6 μmol g⁻¹ h⁻¹ and CH₄ production rate of 36.6 μmol g⁻¹ h⁻¹, 3.13-fold and 5.93-fold from that of pure MOF. This work provides a strategy that could take advantages of the coordination feature of porous materials to design MOF-based photocatalysts through efficient atomic doping for CO₂ reduction.

3.3. Adsorption/Activation and Reaction with CO₂

In general, a catalytic reaction requires the substrates adequately adsorbed on the surface of catalysts. Regarding photocatalytic CO₂ reduction, adsorption of CO₂ molecules on the surface of catalysts is a prerequisite owing to the low solubility of CO₂ in most liquid solutions. As shown in Scheme 2, three possible coordination structures of adsorbed CO₂ on the surface of a catalyst were proposed. Firstly, oxygen of CO₂ has a long pair of electrons that can coordinate with Lewis acid centers on the surface (Scheme 2a). Similarly, carbon in CO₂ acted as Lewis acid that could donated to Lewis base centers on the surface (Scheme 2b). In the third type, oxygen and carbon...
are mixed coordinated with surface Lewis acid and Lewis base centers, respectively (Scheme 2c). On one hand, MOF has multifunctional ligands that can be modified to form basic sites to activate inert CO₂ molecules. On the other hand, MOFs possess high porosity, large surface area and tunable structure such as replaced acidic leaker by basic leaker to adsorb more CO₂ molecules, thus facilitate photocatalysis. However, the concentration of CO₂ in atmosphere is quite low and to capture CO₂ from air will cost a lot of energy. Therefore, understanding how CO₂ uptake capacity of porous materials affects their photocatalytic CO₂ reduction is important for developing more efficient photocatalysts under low concentration of CO₂. It will be practical in industrial if flue gas can be directly used as CO₂ feedstocks.

Figure 8. a) Zr₆O₄(OH)₄(−CO₂)₁₂ secondary building units and the formation schematic of Re₆-MOF. b) Re₆-MOF coated on Ag nanocube. c) UV–vis spectra of Re₆-MOF, Ag nanocube, and Ag⊂Re₆-MOF. d) Photocatalytic CO₂-to-CO conversion activity of Re₆-MOFs (blue line), Ag⊂Re₆-MOF, Cuc⊂Re₆-MOF, and Ag⊂Re₆-MOFs with MOF thickness of 16 and 33 nm.[92] Reproduced with permission.[92] Copyright 2017, American Chemical Society. e) Schematic depicts of preparation of MOF-525-Co and f) Fourier transform magnitudes of the experimental Co K-edge EXAFS spectra of samples. g) Wavelet transform for the k³-weighted EXAFS signal of MOF-525-Co.[99] Reproduced with permission.[99] Copyright 2016, Wiley-VCH.
To understand the adsorption capacity of CO₂ and activation of inert CO₂ molecules, it is essential to unveil the relationships between the uptake capacity of CO₂ and performance. For instance, RuII-CO complex ([RuII(bpy)(terpy)(CO)(PF₆)₂] was synthesized using a PSE method with UiO-67 [101] (Figure 9a). As shown in Figure 9b, the photocatalytic activity decreases with decreasing partial pressure of CO₂, indicating that the photocatalytic activity was highly dependent on the concentration of CO₂. In contrast, catalytic performance of UiO-67/RuCO is close to that measured under 5% CO₂ atmosphere, which demonstrates that the composite could effectively adsorb CO₂ in dilute concentrations and use of synergy between the adsorptive sites and the catalytic active sites.

Recently, three isostructural MOFs including MAF-X27-Cl, MAF-X27-OH, MOF-74-Co were used for CO₂ photoreduction. [102] When the partial pressure was decreased to 0.1 atm, the photocatalytic activity of MAF-X27-Cl, MOF-74-Co decrease severely, while the MAF-X27-OH also exhibited a high CO TOF of 23 × 10⁻³ s⁻¹ (28 × 10⁻³ s⁻¹ at 1 atm). DFT simulations demonstrated that the m-OH of MAF-X27-OH was coordinated with the open Co sites, which stabilized the Co–CO₂ by hydrogen bonding, thus boosting the photocatalytic CO₂ reduction (Figure 9c,d). Very recently, Wang and co-workers synthesized...
UiO-66/TiO₂ composites which displayed high yields of CH₄ even at diluted CO₂ condition (≤2%), though the detailed mechanism was not clear yet.

Although many works tried to convert CO₂ at low concentrations, this filed is still at its early stage, suffering low durability and low selectivity of CO₂ reduction. Considering that, Lin and co-workers synthesized a monolayer Ni MOFs, namely Ni MOLs, for photoreduction in diluted CO₂, exhibiting CO generation rate of 12.5 µmol h⁻¹, with a high CO selectivity of 97.8%, much higher than that of Co MOLs (Figure 10a). To elucidate such a phenomenon, DFT calculations were carried out. As presented in Figure 10b, the active energy barrier COOH⁺ formation over Co MOLs was slightly smaller than that of Ni MOLs, indicating that Co MOLs were more favorable to COOH⁺ formation than Ni MOLs in kinetics, which was contrary to the performance results. As shown in Figure 10c, the adsorption energy of CO₂ on Ni MOLs is −200.11 kJ mol⁻¹, which was much stronger than that of the Co MOLs (−140.32 kJ mol⁻¹). Therefore, DFT results clearly demonstrated that the initial adsorption of CO₂ on MOLs was the crucial step of the reaction system. It was also validated that the selectivity of photocatalytic reduction of CO₂ is directly correlated with the binding affinity of CO₂ molecules.

Abovementioned relationships between CO₂ uptake capacity of MOFs photocatalyst and performance of CO₂ photoreduction are summarized as follows: Firstly, the activity of photocatalytic reaction is positively related to the concentration of CO₂. Secondly, some functional groups or a high diversity of metals in MOFs may activate CO₂ molecules and improve CO₂ uptake such as hydrogen bonding, thus improve photocatalytic activity. Thirdly, MOF-based materials combining with high CO₂ adsorption energies of catalysts enable high catalytic activity even in a diluted CO₂ atmosphere.

4. Recent Advances of Other Porous Materials for Photocatalytic CO₂ Reduction

In addition to MOF, other porous materials such as COFs-based, zeolite-based and inorganic/organic porous semiconductors are also used for photocatalytic reactions.

4.1. COF-Based Photocatalysts for CO₂ Reduction

Yaghi and co-workers first reported COF-1 via self-condensing with phenyl diboronic acid. As a new class of porous material, COFs provide a versatile platform for CO₂ photoreduction. COFs are formed by periodic organic building blocks through covalent bonds. The establishment of spiro-pyran (Ps) (i.e., extended π-conjugation) promotes effective separation of charge carrier.

COFs have a well adjustable structure. Organic compounds are combined into the original counterpart to form a multifunctional COF photocatalyst with a dual function of redox and oxide. This kind of close connection way makes photogenerated charge transfer rapidly and reduces instability of photocatalysis to a certain extent. In recent years, there are many ligands...
modified to achieve effective separation of photogenerated charges. Wisser et al. reported using chromophores as light harvest antenna (controlling HOMO) and Cp*Rh as catalytic sites (regulating LUMO), which realize the rapid transfer of photogenerated charge. This kind of unique structure of long-term stable perylene photosensitizer and the selective Rh-based catalyst Cp*Rh@PerBpyCMP made it possible for photoreduction of CO2 in several days. The yield of formate was about 65 mmol g cat⁻¹, which is the highest value obtained in heterogeneous photocatalysis. Wang and co-workers also reported a covalent triazine based framework (CTF) consisting of triphenylamine and triazine, which can be effectively used for photocatalytic reduction of CO2. The p-conjugated structure provides a channel for the migration and separation of photoexcited electrons, which improves the photocatalytic activity. The self-functionalized DA-CTFs method not only improves the photocatalytic activity of organic semiconductors, but also cast new sights upon the fabrication of photocatalysts.

Su and co-workers reported a pure TAPBB-COF (synthesized with TAPP [5,10,15,20-tetrakis(4-aminophenyl)-porphyrin] and 2,5-dibromo-1,4-benzenedialdehyde) for CO2 photoreduction in presence of water and without any additional co-reactants. By tuning the valence band of TAPBB-COF, the photocatalyst achieved a high CO evolution rate of 295.2 µmol g⁻¹ h⁻¹. This was the first work for photocatalytic CO2 reduction using COFs along without any sacrificial donor or co-catalysts. In comparison with pure COFs, metalized-COFs forming hybrid metal–complex systems often exhibited higher performance. Lan and co-workers synthesized the first metalized-COFs photocatalyst for CO2 photoreduction. As illustrated in Figure 11a, the as-synthesized DQTP-COF-Co(2,6-diaminoanthraquinone (DQ), (TP) 2,4,6-triformylphloroglucinol) exhibited excellent CO2 reduction activity coupled with photosensitizer Ru(bpy)₃Cl₂ and triethanolamine (TEOA) providing electron and protons, resulting in a high CO formation rate of 1020 µmol g⁻¹ h⁻¹.

Artificial photosynthesis is expected to use only H2O as electron sources in the absence of any additional sacrificial donor. To this end, Lan et al. developed a series of Z-scheme porphyrin–tetrathiafulvalene COFs (TTCOF-M, M = 2H, Zn, Ni, Cu) for photocatalytic CO2 reduction. In that composite, electron-deficient TAPP has good visible-light harvesting ability. Meanwhile, electron-rich tetrathiafulvalene (TTF) has demonstrated to be an excellent electron donor. Therefore, it is possible to combine TAPP and TTF to form a Z-scheme (TAPP and TTF act on the reduction site and oxidation site, respectively) to transfer photogenerated electrons from TTF to TAPP under visible light irradiation, and effectively separate electron holes (Figure 11b,c). As expected, TTCOF-Zn exhibited the highest CO evolution rate of 12.33 µmol after 60 h with nearly 100% selectivity and good stability. This is the first report of COF composites applied in the overall reaction of CO2 with H2O.

**Figure 11.** a) The photocatalytic schematic of DQTP-COF-M (M = Co, Zn). Reproduced with permission.[114] Copyright 2019, Elsevier. b) The mechanism of TTCOF-M CO2RR with H2O oxidation. c) DFT simulation UV/vis DRS of TTCOF-Zn and scheme of PET route under light excitation (inset). Reproduced with permission.[115] Copyright 2019, Wiley-VCH.
without any extra photosensitizer or sacrificial donor. However, the CO production rate surfs very slow. The possible reasons might be that the oxidation ability of TTF is relatively weak. Therefore, incorporated with much stronger oxidation ability material may be a good strategy for further improving photocatalytic performance.

Although many COFs were reported for CO₂ photoreduction, it is still worth to concern that a large enough 2D COF single-crystal is extremely difficult to be obtained. As a result, the actual structure of COFs is determined only by powder XRD and computational simulation, which limits the effective structure–activity relationship analysis of COFS.

4.2. Zeolite-Based Photocatalysts for CO₂ Reduction

Compared with traditional semiconductors, molecular sieves are intrinsic porous structure with high specific surface area and many active sites for photocatalysis. Anpo et al. took the lead in investigating a series of Titanium oxides anchored within zeolites. The highly dispersed TiO₂ within Y-zeolite cavities (Ti-oxide/zeolite) were synthesized by an ion-exchange method, achieving high selectivity to produce CH₄. The charge excited of the important intermediates (Ti⁺⁻O⁻)⁰ are generated under UV irradiation. The generated electrons were trapped into H⁺ and CO₂ to form H atoms and CO, then produced a series of carbon radicals. Finally, the reaction of these radicals produced CH₃OH and CH₄[^128]. Next year, Ti-MCM-41 and Ti-MCM-48 were investigated in CO₂ photoreduction[^122]. Bai and co-workers[^122] first investigated using Ti-MCM-41 photocatalysts in monoethanolamine (MEA) solution for methane production. The optimal photocatalyst of Ti-MCM-41(50) (50 denote Si/Ti molar ratio of 50) exhibited CH₄ yield of 62.42 µmol g⁻¹ of cat after 8 h of UV irradiation. However, monoethanolamine was used as sacrificial agent, which was not environmentally and energy saving. Other than parent molecule severs, the zeolite-based composites were also investigated in recent years. Cu–porphyrin impregnated mesoporous Ti-MCM-48 was investigated for the CO₂ reduction under visible light irradiation, exhibiting methanol yield of 85.88 µmol g⁻¹ L⁻¹[^123]. Yang and co-workers investigated the Pt/MgO loaded Ti-MCM-41 zeolite with different Si/Ti molar ratios for photocatalytic CO₂ reduction[^124]. The electrons and holes were photogenerated in TiO₂ tetrahedral units in molecular sieve under light irradiation, leading to form [Ti³⁺⁻O⁻]⁻ (Figure 12a). The high photocatalytic activity was achieved on Ti-MCM-41 because of synergistic effect. HZSM-5 zeolites were used in CO₂ photoreduction for the first time by Wang and co-workers[^125] [Fe₃⁺⁻O⁻²⁻] species could be excited by UV light to form an important intermediate, [Fe⁺⁻O⁻]⁰, achieving high photocatalytic activity (Figure 12b). Very recently, Jing and co-workers reported that composites of optimal Ag-modified 2D/2D hydroxylated g-C₃N₄/TS-1 exhibited sevenfold than that of 2D TS-1[^126] The enhanced photoactivity is attributed to the Z-scheme mechanism between hCN and TS-1, which greatly enhanced charge separation and extended range of visible-light absorption. This work presented a feasible design strategy to synthesize high efficiency TS-1 zeolite-based photocatalyst.

Although many zeolites have been used in photocatalytic CO₂ reduction, there are still many problems to be solved. For example, structure–activity relationship is still unclear. The overall yield is still very low. Much more novel molecular sieves need to be developed for photoreduction of CO₂.

4.3. Inorganic/Organic Porous Semiconductors

In addition to the classic porous materials for the CO₂ photoreduction, inorganic/organic porous materials were also discussed in this section[^127–132]. For the CO₂ reduction, an efficient photocatalyst should possess high uptake capacity of CO₂. Therefore, porous carbon materials, porous metal oxides, are discussed in this section. Wang et al.[^133] synthesized hybrid carbon@TiO₂ hollow sphere by utilizing a template of a carbon nanosphere. The optimal composites exhibited CH₄ evolution rate of 4.2 µmol g⁻¹ h⁻¹ and CH₃OH production rate of 4.2 µmol g⁻¹ h⁻¹. The enhanced photoactivity was attributed to the increased CO₂ uptake (0.64 mmol g⁻¹) and specific surface area (110 m² g⁻¹), together with enhancement light absorption due to the multiple reflections. When utilize water as electron sacrificial agent, hydrogen production is the main competitive reaction in the process of CO₂ reduction[^134,135]. In order to improve the selectivity of CO₂ reduction under the existence of water, covering a carbon layer on the photocatalyst will make more protons to participate in CO₂ reduction. In this case, Pan et al.[^136] reported wrapped a 5 nm thick carbon layer outside the In₂O₃, exhibited photoactivity of CO and CH₄ evolution rate of 126.6 and 27.9 µmol h⁻¹, respectively. The greatly enhancement performance was attributed to the improved chemisorption of CO₂, which increased the chance of proton capture by the CO₂⁻. In addition, Organic porous polymers such as C₃N₄, polymer and BN have been also explored in recent years[^137,138]. Yu and co-workers[^139] synthesized hierarchical porous O-doped g-C₃N₄ by heating, exfoliating, and curling-condensation of bulk g-C₃N₄. The methanol evolution rate is 0.88 µmol g⁻¹ h⁻¹, fivefold higher than that of bulk g-C₃N₄ (0.17 µmol g⁻¹ h⁻¹). The greatly enhanced photoactivity was mainly resulted from the porous g-C₃N₄ with higher specific surface area, enhanced light absorption, together with more exposed active edges. This work paved a novel way to design hierarchical porous nanostructures. However, the photocatalytic evolution rate needs to be improved.

Inorganic porous semiconductor ZnO was investigated by Long and co-workers[^140] ZnO forms 3D holes at high temperature, so that metal particles can be fixed to ZnO in the subsequent synthesis process, and this can make the metal particles evenly distributed. Utilization of the surface plasmon resonance (SPR) of noble metals, the as-prepared samples exhibited high yield of CH₄ and CO. Similarly, He and co-workers investigated the effect of defects in porous ZnO nanoplate on CO₂ photoreduction[^141]. In this work, defects in the porous ZnO accelerate separation of photogenerated carriers, resulting in greatly enhanced photocatalytic performance. However, the stability and photoactivity of the photocatalyst are desirable to improve. Furthermore, intermediate species for the CO₂ photoreduction on defective ZnO should be deep investigated. Chromium (Cr) doped mesoporous CeO₂ was synthesized via a nanocasting
The mesoporous structure could enhance the uptake capacity of CO$_2$, leading to high photocatalytic activity. However, it is still a challenge to synthesize porous inorganic semiconductors directly due to its inflexible tunability in structure. In the past few years, many porous semiconductors were derived from heating MOFs due to its intrinsic porous structure.\cite{143–145} Li and co-workers first reported the porous hierarchical TiO$_2$ derived from MIL-125(Ti) for photocatalytic CO$_2$ reduction.\cite{146} TiO$_2$ with high surface area modified with basic MgO, leading to high photocatalytic CO$_2$ reduction activity. Lou et al. synthesized a series of compounds with hierarchical structure such as In$_2$S$_3$-CdIn$_2$S$_4$ (Figure 12c,d) and sandwich-like ZnIn$_2$S$_4$-In$_2$O$_3$ based on MIL-68 as precursor. The hierarchical structure is benefit to light absorption through light scattering and reflection, reduce the free path of carrier diffusion, increase the reaction contact area with CO$_2$, thus greatly improves the efficiency of CO$_2$ photoreduction.\cite{147,148} Wang et al.\cite{149} synthesized porous polymer-TiO$_2$-graphene (HCP-TiO$_2$-FG) photocatalyst for the conversion of CO$_2$ under visible light irradiation (Figure 12e). This composite, with large surface area 988 m$^2$ g$^{-1}$ and CO$_2$ uptake capacity due to its porous structure, exhibited high CH$_4$ formation rate of 27.62 $\mu$mol g$^{-1}$ h$^{-1}$ without any sacrificial reagents or co-catalysts. This work provided a prototype of the combination of microporous organic polymers used in CO$_2$ photoreduction.

4.4. Comparison between Four Kinds of Porous Materials

Photocatalyst with high CO$_2$ uptake is a necessary condition for catalytic CO$_2$ conversion. Porous materials such as MOFs, COFs, molecule sieve and inorganic/organic porous materials have attracted considerable attentions in the CO$_2$ conversion field due to their high specific surface area and well-tailor structure.\cite{25} However, each kind of porous material has its advantages and disadvantages. For instance, MOFs exhibited large surface area and flexible tunability structure compared with inorganic porous materials but suffered poor water resistance. On the other hand, the inorganic porous material is so hardly decorated that it so difficult to study the structure–activity. With
regard to the molecule sieves, they possess uniform pore size, definite skeleton structure. However, just as MOFs, molecule sieves also suffer poor water resistance and unsuitable for high pressure adsorption. In recent years, COFs have attracted considerable attentions because of adjustable structure. However, the synthesis method is too complex and involves many organic compounds compared with inorganic porous material, which is not environmentally friendly. The advantages and disadvantages of different porous materials are summarized in Scheme 3.

5. Conclusions and Perspectives

The development of porous materials with high catalytic efficiency is an important research area given their diverse chemical structures and multitudinous applications (Table 2). This progress report summarizes the recent advances in MOFs-based materials for photocatalytic CO2 reduction from three critical photocatalytic aspects, say light absorption, carrier dynamics, and relationship between CO2 uptake capacity and activity. Owing to their intrinsic porosity and smooth implementation of function moieties, the catalytic performance can be improved fundamentally. As highlighted above, porous materials can be used as solid state photocatalysts that will harvest visible light and provide active catalytic centers simultaneously within a single structure. Their CO2 reduction performance can be enhanced by either tuning the building blocks for more efficient light absorber, adjusting the metal centers to improve adsorption capacity and catalytic activity, or a conjunction of both. In addition, a large number of porous materials allow them to couple with molecular catalysts, photosensitizer molecules, semiconductors or plasmonic metal clusters, thereby yielding novel, high surface area composite photocatalysts to present a higher catalytic activity. In particular, most porous materials have potential for CO2 capture capacities, which may promote their applications at low CO2 concentration conditions. Above all, porous materials hold their unique advantages in solar-driven CO2 reduction and all the synthetic strategies will offer the rational design of porous material-based photocatalysts with excellent catalytic performance.

Although great progress has been made, challenges remain toward commercialization of porous materials for solar-driven CO2 reduction.

1) Carrier dynamics includes carrier separation, lifetime, mobility, average diffusion free path, and other important factors. However, in terms of porous materials, rare work focuses on two key kinetic parameters, i.e., carrier mobility and average diffusion length. These two kinetic parameters determine the effective utilization of photogenerated charge, and then dominate the photocatalytic reaction rate.

2) Few studies were reported on the electron transfer mechanism between various ligands and metal clusters. More research is required to consider the band structure of different ligands and combine with high-throughput theoretical calculation to design porous photocatalytic materials with high carrier separation and fast mobility.

3) Regarding porous materials, there are few studies on the selectivity of photocatalytic reduction of CO2. Especially on the effect of pore size or pore volume on the activity and selectivity remains to be discussed. It is anticipated that there will

![Scheme 3. The advantages and disadvantages of four kinds of porous materials.](image-url)
be new insights of the selectivity of porous materials in the future.

4) At the present, there is a lot of research on the membrane formation of porous materials, such as the separation of gas by MOFs. Therefore, the membrane-forming characteristics of MOF can be used for catalytic reaction, which is conducive to the subsequent separation steps and can save a lot of separation cost.

5) Finally, most of the studies are still in the case of pure CO$_2$ and the need for electronic sacrificial agent or photosensitizer. Reaction with low concentration of CO$_2$ and water is more suitable for industrialization, energy saving and emission reduction. In addition, at present, the technology of photocatalytic CO$_2$ reaction device is still at the most basic stage, and more reaction device design is needed to further promote the industrialization process of photocatalytic CO$_2$.

| Photocatalysts | Reaction medium | Major product | Max rate evolution | Ref. |
|---------------|----------------|--------------|-------------------|------|
| NH$_2$-MIL-125(Ti) | MeCN/TEOA (5:1) | HCOO$^-$ | 8.14 µmol, 10 h | [58] |
| NH$_2$-UiO-66(Zr) | MeCN/TEOA (5:1) | HCOO$^-$ | 13.2 µmol, 10 h | [59] |
| Zr-SDCA-NH$_2$ | MeCN/TEOA (30:1) | HCOOH | 96.2 µmol h$^{-1}$ mmol$_{MOF}^{-1}$ | [61] |
| Zn/PMOF | Water (vapor) | CH$_4$ | 8.7 µmol h$^{-1}$ g$^{-1}$ | [66] |
| NNU-28 | MeCN/TEOA (30:1) | HCOOH | 52.8 µmol g$^{-1}$ h$^{-1}$ | [67] |
| Al-PMOF | 100 mL water + 1 mL TEA | CH$_3$OH | 262.6 ppm g$^{-1}$ h$^{-1}$ | [68] |
| UiO-67/Re(II)(dbpy) (CO)$_3$Cl | MeCN/TEA = 20:1 | CO | TON = 10.9 | [71] |
| Hf$_2$-Ru-Re[Ru(bpy)$_3$]$^+$ | 1.9 mL CH$_3$CN + 0.1 mL TEOA | CO | TON = 3849 | [72] |
| NH$_2$-UiO-66(Zr/Ti) | MeCN/TEOA (5:1) | HCOO$^-$ | 5.8 mmol mol$^{-1}$ | [75] |
| UiO-66-CrCAT | MeCN/TEOA (4:1) | HCOOH | 51.73 µmol, 6 h | [76] |
| ZIF-8/Zr$_2$GeO$_4$ | Na$_2$SO$_3$ | CH$_3$OH | 2.44 µmol g$^{-1}$ | [80] |
| Co-ZIF/g-C$_3$N$_4$ | MeCN:H$_2$O = 3:2 | CO | 20.8 µmol CO, 2 h | [81] |
| Co-ZIF-9/CdS | MeCN:H$_2$O = 3:2 | CO | 85.6 µmol, 3 h | [82] |
| Co-ZIF-9/TiO$_2$ | 3 mL water | CO | 8.79 µmol, 10 h | [83] |
| Cu$_3$(BTC)$_2$@TiO$_2$ | Water (vapor) | CH$_4$ | 2.64 µmol g$^{-1}$ h$^{-1}$ | [84] |
| NH$_2$-UiO-66/TiO$_2$ | CO$_2$/H$_2$ (1.5 v/v ratio) | CO | About 5 µmol g$^{-1}$ h$^{-1}$ | [85] |
| PCN-222 | MeCN/TEOA (10:1) | HCOO$^-$ | 30 µmol, 10 h | [86] |
| MAPbI$_3$@PCN-221(Fe$_{0.2}$) | MeCN/TEOA (v/v, 1:0.012) | CH$_4$ | 102.89 µmol g$^{-1}$ | [87] |
| Cd$_2$Zn$_5$S$_8$@UiO-66-NH$_2$ | 100 mL 0.1 m NaOH | CH$_3$OH | 6.8 µmol h$^{-1}$ g$^{-1}$ | [90] |
| Ag⊂Re$_3$-MOF-16 nm | MeCN/TEOA (20:1) | CO | TON = 0.1 | [92] |
| Ag@Co-ZIF-9 | MeCN/TEOA/H$_2$O = 4:1:1 (v/v) | CO | 28.4 µmol, 0.5 h | [93] |
| Pt/NH$_2$-MIL-125(Ti) | MeCN/TEOA (5:1) | HCOOH | 12.96 µmol, 8 h | [96] |
| MOF-525-Co | MeCN/TEOA (4:1) | CO | 200.6 µmol g$^{-1}$ h$^{-1}$ | [99] |
| Ni-MOLs | MeCN/TEOA/H$_2$O = 3:1:2 (v/v) | CO | 12.5 µmol h$^{-1}$ | [39] |
| DA-CTF | MeCN/TEOA (2:1) | CO | 9.3 µmol, 2 h | [112] |
| TAPBB-COF | 1 mL Water | CO | 295.2 µmol g$^{-1}$ | [113] |
| DQTP COF-Co/Zn | MeCN/TEOA = 4:1 | CO | 1.020 µmol h$^{-1}$ g$^{-1}$ | [114] |
| TTCOF-Zn | Water | CO | 12.33 µmol, 60 h | [115] |
| ex-Ti-oxide/Y-zeolite | Water | CH$_4$ | 10 µmol g$^{-1}$ h$^{-1}$ | [121] |
| Pt-loadedTi-MCM-48 | Water | CH$_4$ | 12 µmol g$^{-1}$ h$^{-1}$ | [121] |
| MgO/Ti-MCM-41 | Water | CH$_4$ | 157 ppm g$^{-1}$ h$^{-1}$ | [125] |
| HZSM-5 | Water | CO | 3.32 µmol h$^{-1}$ g$^{-1}$ | [126] |
| g-C$_3$N$_4$ nanotubes | MeCN/TEOA/H$_2$O = 3:1:2 (v/v) | CO | 103.6 µmol g$^{-1}$ h$^{-1}$ | [127] |
| CdS@BPC-700 | MeCN/TEOA/H$_2$O = 3:1:1 (v/v) | CO | 39.3 µmol g$^{-1}$ h$^{-1}$ | [128] |
| CdS/Mn$_2$O$_3$ | Water (vapor) | HCOOH | 1392.3 µmol g$^{-1}$ h$^{-1}$ | [129] |
| Cu$_3$(BTC)$_2$@TiO$_2$ | Water | C$_2$H$_6$ | 27 µmol g$^{-1}$ h$^{-1}$ | [140] |
| ZnIn$_2$Se$_3$-In$_2$O$_3$ | MeCN/TEOA/H$_2$O = 3:1:2 (v/v) | CO | 3073 µmol g$^{-1}$ h$^{-1}$ | [148] |
In conclusion, it remains far from optimal performance of porous materials for solar-driven CO₂ reduction. This progress report is expected to offer new viewpoints to promote the development of highly efficient CO₂ photoreduction systems.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

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