

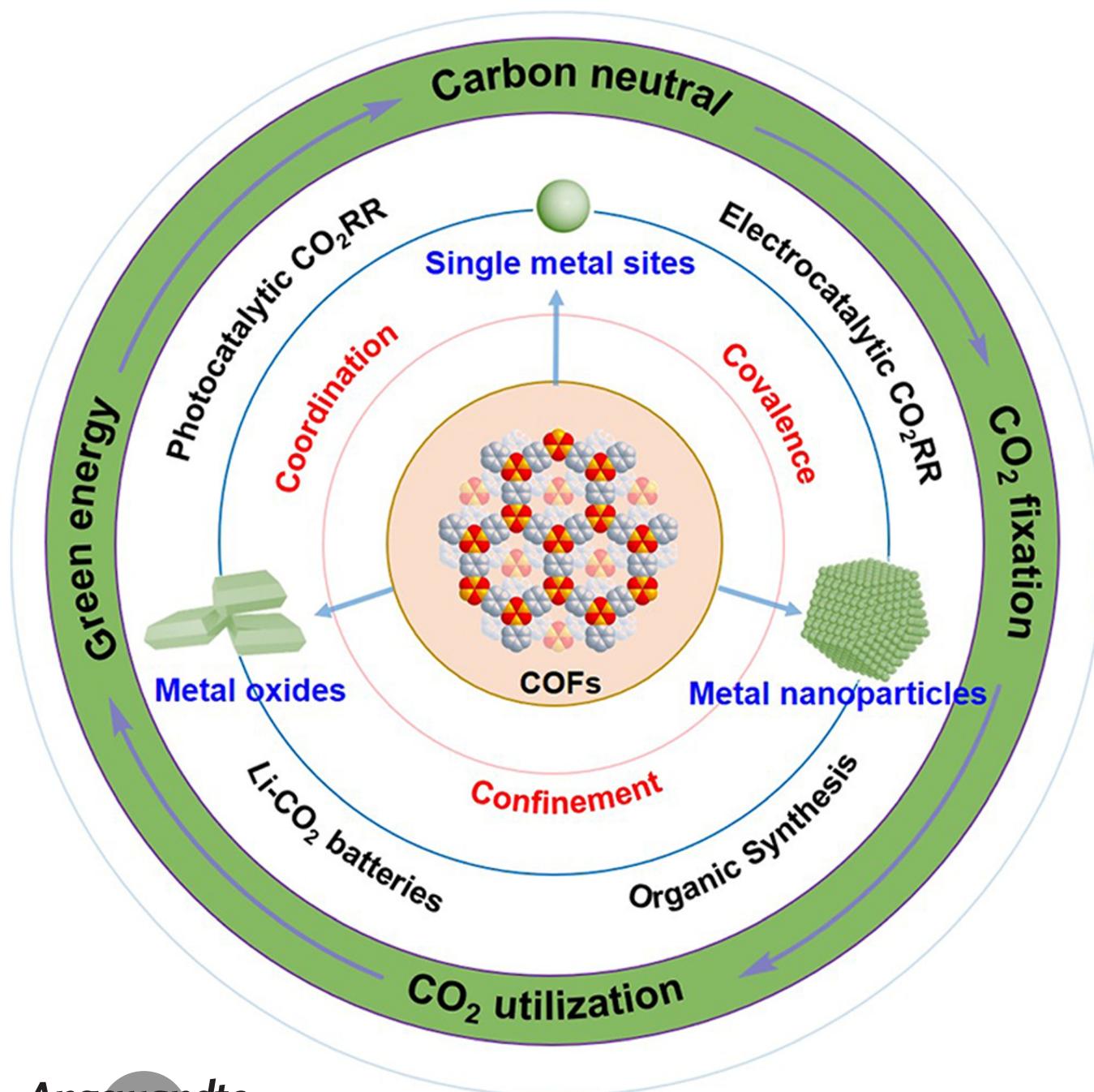
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Covalent Organic Framework Based Functional Materials: Important Catalysts for Efficient CO₂ Utilization

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As hot topics in the chemical conversion of CO₂, the photo-/electrocatalytic reduction of CO₂ and use of CO₂ as a supporter for energy storage have shown great potential for the utilization of CO₂. However, many obstacles still exist on the road to realizing highly efficient chemical CO₂ conversion, such as inefficient uptake/activation of CO₂ and mass transport in catalysts. Covalent organic frameworks (COFs), as a kind of porous material, have been widely explored as catalysts for the chemical conversion of CO₂ owing to their unique features. In particular, COF-based functional materials containing diverse active sites (such as single metal sites, metal nanoparticles, and metal oxides) offer great potential for realizing CO₂ conversion and energy storage. This Minireview discusses recent breakthroughs in the basic knowledge, mechanisms, and pathways of chemical CO₂ conversion strategies that use COF-based functional catalysts. In addition, the challenges and prospects of COF-based functional catalysts for the efficient utilization of CO₂ are also introduced.

1. Introduction

In recent years, the large-scale combustion of fossil fuels has been accompanied by an increasing release of excessive CO₂, which has led to energy depletion, environmental pollution, and the greenhouse phenomenon. All of these have seriously threatened the environment and sustainable development of mankind.^[1] In addition to reducing CO₂ emissions and CO₂ capture/storage, CO₂ utilization is considered to be a very important strategy in achieving carbon neutrality and complete the carbon cycle. In particular, as the main method of CO₂ utilization, the chemical conversion of CO₂ shows great potential to mitigate the above problem, with two research categories being hot topics in recent years. One approach is to develop the corresponding techniques (such as the photocatalytic and electrocatalytic reduction of CO₂) to transform CO₂ into useful chemical feedstocks such as carbon monoxide, methane, alcohols, and so on.^[2] Another approach is the direct utilization of CO₂ in the form of CO₂-based energy storage systems (such as Li-CO₂ batteries), which can not only fix CO₂ but also provide sustainable energy storage.^[3] However, many drawbacks such as the low efficiency of these approaches for the chemical conversion of CO₂ restrict their practical applications. In general, the efficiency of the photocatalytic or electrocatalytic CO₂ reduction reaction (CO₂RR) and Li-CO₂ batteries mainly depends on the physicochemical and photo-/electrochemical properties of the catalysts.^[4] Consequently, exploring highly efficient photo-/electrocatalysts and electrode catalysts has been a critical challenge for renewable energy conversion and storage.

So far, transition-metal complexes,^[5] inorganic semiconductors,^[6] metal-organic frameworks (MOFs),^[7] and the more recently developed covalent organic frameworks (COFs)^[8] have been used in the conversion and utilization of CO₂. In particular, as a burgeoning type of organic functional materials, COFs are assembled through covalent bonds and possess many excellent characteristics when used as photo-/electrocatalysts and electrode catalysts, such as:^[9] 1) the good chemical and thermodynamic stability of COFs ensures their robustness during the catalytic process; 2) their ease of modification and functionality are beneficial to the loading of various active sites, which enables the synthesis of COF-

based functional materials; 3) COFs are highly porous and have a large surface area, which can ensure the effective adsorption of CO₂ and rapid mass transfer; 4) the known chemical composition and structure of COFs can provide accurate structural models for further understanding the reaction mechanism. Therefore, COFs have promising application potential for the efficient chemical conversion of CO₂, especially in the photocatalytic or electrocatalytic CO₂RR and Li-CO₂ batteries (Scheme 1).^[10] However, some issues remain, such as the intrinsic COFs constructed from organic components always lack effective active sites, thus preventing exceptional performances when used as photo-/electrocatalysts and electrode catalysts.^[11] To solve this problem, an important strategy is to combine different active sites (such as single metal sites, metal nanoparticles, metal oxides, and so on) with COFs to form COF-based functional materials to enable the synergistic effects of the COFs and active sites. On investigation of the development of this field, it has been found that achieving the functionalization of COFs and designing COF-based functional materials with diverse active sites is still a hot topic of research. The general methods for the design and synthesis of functionalized COF materials include post-modification methods and bottom-up methods.

In recent years, several reviews have focused on the design and development of COF-based materials for energy storage and conversion.^[12] However, discussions are still lacking on

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the state-of-the-art progress in the field as well as knowledge about the active sites and active-site engineering in COF-based functional materials used for chemical CO₂ conversion, as well as the future development direction of this field. Therefore, in this Minireview, we will first briefly summarize catalytic mechanisms of the photocatalytic/electrocatalytic CO₂RR and Li-CO₂ batteries and the main challenges faced in these processes. After that, we will discuss recent efforts to meet these challenges by using COF-based functional materials modified with various active sites (mainly single metal sites, metal nanoparticles, and metal oxides). It should be noted that we categorize clusters in the field of NPs because of their similar mode of atomic assembly. Finally, we will propose and discuss the perspectives and challenges in the synthesis of COF-based functional materials as well as further potential strategies to realize CO₂ utilization. Overall, this Minireview emphasizes the pivotal strategies and developments of COF-based functional materials used for CO₂ utilization, as well as our understanding of active-site engineering for the design of high-performance catalysts,

hence establishing a bridge between COFs and CO₂ utilization.

2. Photocatalytic CO₂RR

CO₂, which is released in excess by human activities, has been recognized as one of the main greenhouse gases. Utilizing CO₂ as a carbon source by using photocatalysts to obtain useful chemical feedstocks is one of the tactics proposed to solve the energy crisis and global warming issues.^[9b,13] However, distinct from traditional thermocatalysts for the CO₂RR, photocatalysts should not only be excited by solar irradiation to obtain electron/hole pairs with oxidation and reduction ability, but also simultaneously reduce the activation energy for the CO₂RR. In addition, the photocatalytic CO₂RR is a multielectron transformation process which generates various reduction products at diverse redox potentials. As a result, it makes the selectivity and efficiency of the CO₂RR difficult to control. More importantly, protons can also be used as the electron acceptor to produce H₂ as



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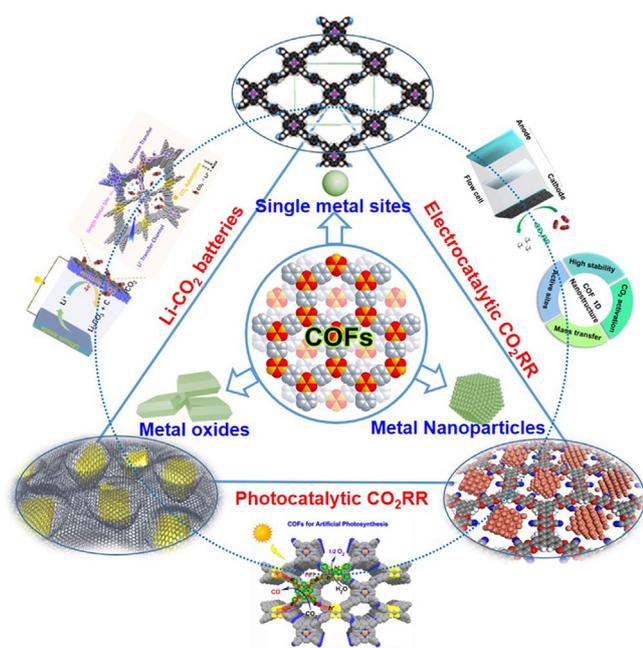
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Scheme 1. The synthesis of COF-based functional materials and chemical conversion of CO₂ using COF-based functional materials as catalysts.

a by-product, thereby lowering the selectivity of the CO₂RR.^[14] To overcome the above-mentioned issues, desirable photocatalysts for the CO₂RR should at least satisfy the following features: 1) have a suitable band gap structure; 2) have a high light absorption ability; 3) have effective separation and transmission of electron/hole pairs; 4) have a large quantity of adsorption and reaction sites. Fortunately, COF-based functional materials with different photocatalytic active sites can completely satisfy the above demands when they are used as photocatalysts in the CO₂RR, since they feature: 1) high tunability of the band structure and active sites through integration of various building blocks and active sites; 2) a high surface area and porous structure that offers enhanced accessibility of the substrate; 3) a high degree of conjugation and a suitable heterojunction structure which is instrumental for the separation and transport of electron/hole pairs; 4) various active sites which can be used for CO₂ uptake and activation. In this section, the photocatalytic structure–activity relationships of COF-based functional materials with multifarious photocatalytic active sites will be discussed.

2.1. Incorporation of Single Metal Sites into COFs for the Photocatalytic CO₂RR

Developing functional COFs with single metal active sites is a promising approach to improve the photoreduction of CO₂, since the metal centers in COF-based functional materials could play the role of both increasing the CO₂ uptake capacity and reducing the activation energy of the CO₂RR during photocatalysis. Single metal active sites can be incorporated into COFs through coordinate bonds such as through layer–layer coordination interactions, bipyridine

entities, and porphyrin units. For example, in 2019, Lan and co-workers first used layer–layer coordination interactions to develop three COF-based functional materials with metal-ion modification for the photocatalytic CO₂RR.^[16] The as-synthesized 2,6-diaminoanthraquinone-2,4,6-triformylphloroglucinol COF (denoted as DQTP-COF) containing an anthraquinone group was used to anchor diverse single metal ions, which acted as catalytic centers to allow the photoreduction of CO₂. It was found that the metal species (Co²⁺, Ni²⁺, and Zn²⁺) had a great effect on the photoreduction of CO₂. Ultimately, the DQTP-COF-Co catalyst showed an excellent CO production rate ($1.02 \times 10^3 \mu\text{mol h}^{-1} \text{g}^{-1}$), whereas DQTP-COF-Zn achieved superior selectivity for HCOOH formation ($152.5 \mu\text{mol h}^{-1} \text{g}^{-1}$). Similarly, 2,2'-bipyridine-based COFs containing single Ni active sites (termed Ni-TpBpy) were prepared by Zou and co-workers (Figure 1a).^[15] Impressively, Ni-TpBpy displayed excellent photocatalysis CO₂RR performances. In detail, a high CO production rate of $811 \mu\text{mol g}^{-1} \text{h}^{-1}$ and CO selectivity (96%) over H₂ were obtained in the presence of triethanolamine and Ru(bpy)₃Cl₂·6H₂O, as a result of the cooperative effects of COFs and single metal active site (Figure 1b,c). This study strongly emphasized the great potential of COFs for the preparation of single-site catalysts. Apart from metal ions, the conjunction of homogeneous metal complexes with 2,2'-bipyridine-based COFs is another strategy to obtain functional COFs with single metal active sites. Consequently, chemists have improved the photocatalytic CO₂RR performances of COF-based catalysts by loading Re(CO)₅Cl into various COFs, which has led to superior light absorption and electron-separation/migration capability.^[17]

The four nitrogen atoms in the porphyrin pocket can bind metal ions to form single active sites which display a good affinity to CO₂. Accordingly, a series of metalloporphyrin (MPor) based COFs have been prepared as catalysts for the photocatalytic reduction of CO₂ in recent years. For example,

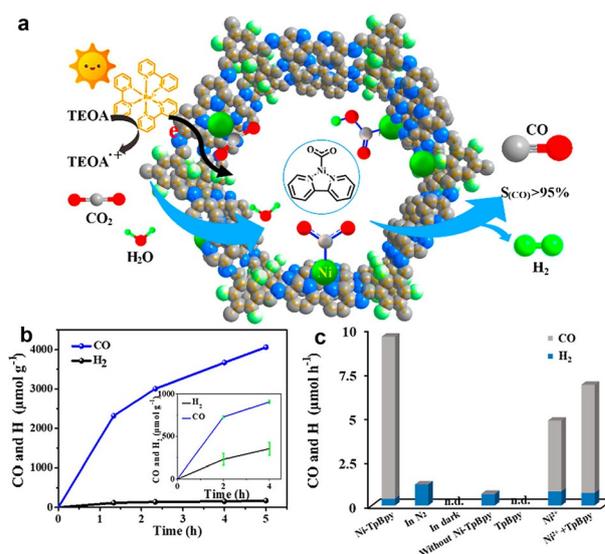


Figure 1. a) The photocatalytic CO₂RR over Ni-TpBpy. b,c) Photocatalytic performances of different samples. Reprinted with permission.^[15] Copyright 2019 American Chemical Society.

a series of porphyrin-tetrathiafulvalene-based COFs containing diverse single metal sites (denoted as TTCOF-M; M = H, Zn, Ni, Cu) were constructed by Lan and co-workers for the photoreduction of CO₂. Surprisingly, this catalytic system could achieve artificial photosynthesis without a photosensitizer or sacrificial agents. Of the four TTCOFs, TTCOF-Zn delivered the highest CO generation rate of about 2.1 μmol g⁻¹ h⁻¹ and an outstanding selectivity of nearly 100% (Figure 2 a,b). It is

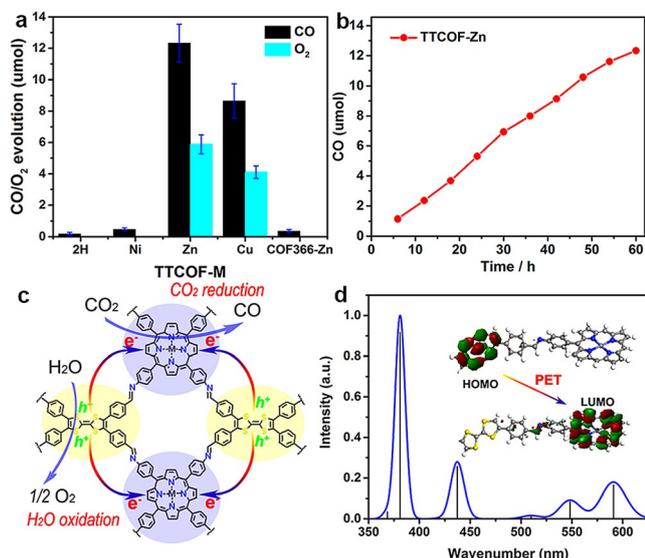


Figure 2. a,b) The photocatalytic CO₂ reduction properties of TTCOF-M. c,d) Schematic representation of the mechanism of TTCOF-M in artificial photosynthesis. Reprinted with permission.^[18] Copyright 2019 Wiley-VCH.

the first report of the use of porphyrin-based COFs with diverse single metal sites for the photocatalytic CO₂RR without photosensitizer and sacrificial agents.^[18] Furthermore, Lan and co-workers also proposed a mechanism for the photoinduced charge transfer, whereby electrons are transferred from the electron-rich tetrathiafulvalene (TTF) to the electron-deficient MPor on irradiation with visible light, which facilitates the separation and transmission of photo-generated carriers (Figure 2 c,d). The above-mentioned studies confirmed that COF-based functional materials composed of an electron-donor/acceptor skeleton can improve the photocatalytic CO₂RR. Lv et al. also synthesized a series of porphyrin-tetraphenylethene-based COFs (MP-TPE-COF; M = 2H, Co, and Ni) and used them as photocatalysts for the CO₂RR. These structures showed excellent catalytic efficiency for the photoreduction of CO₂ to CO (a generated rate of 2414 μmol g⁻¹ h⁻¹ with 61% selectivity for CoP-TPE-COF and a generated rate of 525 μmol g⁻¹ h⁻¹ with 93% selectivity for NiP-TPE-COF).^[19] These above studies suggested that the MPor units played key roles in the processes of CO₂ adsorption/activation and the separation of photogenerated carriers, thereby allowing the photoreduction of CO₂ to be adjusted in a flexible manner.

Photocatalytic CO₂RR performances are also correlated with the inherent spin state and the electronic structure of the metal ions in the porphyrin. In 2020, Gong et al. manipulated

the spin state of Co in COF-367 by changing the oxidation states of MPor, which led to a significantly enhanced activity for the photoreduction of CO₂.^[20] Various spin states led to diverse degrees of coupling between the Co-3d_{xz} or Co-3d_{yz} orbitals and the O-2p orbital, which would have an influence on the product species and photocatalytic activity. COF-367-Co^{III} demonstrated a boosted HCOOH yield rate of about 93 μmol g⁻¹ h⁻¹, with rates of CO and CH₄ generation of about 5.5 and 10.1 μmol g⁻¹ h⁻¹, respectively.

The strategy of exfoliating COFs into few-layer nano-sheets (NSs) has been proposed to further enhance the performance of COF-based single active site photocatalysts in the photocatalytic CO₂RR. It is recognized that an exfoliated two-dimensional (2D) COF-based photocatalyst will have a larger surface area and more accessible active sites than its bulk form. Therefore, it will have a higher utilization efficiency of the active sites for the adsorption and activation of CO₂. For example, ultrathin COF-367-Co NSs were designed and fabricated by Jiang and co-workers through a bottom-up strategy.^[21] These COF-367-Co NSs displayed excellent photocatalytic CO₂RR performances upon irradiation with visible light, delivering superior CO₂ photoreduction performances, such as a CO generation rate of 10672 μmol g⁻¹ h⁻¹ and high selectivity (about 78%), than COF-367-Co powder. The excellent photocatalytic performances were attributed to readily accessible active sites on the COF-367-Co NSs, which facilitate the CO₂ adsorption and photosensitization process. In addition, Wang et al. synthesized COF NSs loaded with a single Co site (denoted as Co-FPy-CON) and applied them to the photoreduction of CO₂ in the presence of an Ir-based complex as a photosensitizer.^[22] The Co-FPy-CON exhibited superior performances for the reduction of CO₂ to CO (CO yield of 10.1 μmol with a selectivity of 76%).

2.2. Incorporation of Metal Nanoparticles into COFs for the Photocatalytic CO₂RR

The loading of metal nanoparticles (NPs) onto COFs is deemed an excellent strategy to boost charge transportation while suppressing the recombination of electron/hole pairs in the photocatalytic process. This is due to the fact that metal NPs have higher electronegativity and, therefore, have the ability to enrich electrons and also act as active centers to efficiently utilize electrons. Nevertheless, metal NPs usually exhibit a strong agglomeration tendency in catalytic processes, which leads to a significant reduction of the catalytic activity. To this end, COFs possessing confined pores may be appropriate scaffolds to overcome the above issue. Thus, Huang et al. designed a method to encapsulate ultrafine PdIn NPs in an N₃-COF to solve the above problems, which led to a series of Pd_xIn_y@N₃-COF (x:y = 1:0, 0:1, 1:2, 1:1, 2:1) hybrids for the photoreduction of CO₂ to alcohols in water (Figure 3 a).^[23] The optimal total yield of CH₃OH (73%) and CH₃CH₂OH (26%) was 798 μmol g⁻¹ h⁻¹ for PdIn@N₃-COF, which was much superior to that of Pd@N₃-COF, In@N₃-COF, and N₃-COF (Figure 3 b,c). This study demonstrated that the synergistic effect of bimetallic NPs and the N₃-COF was

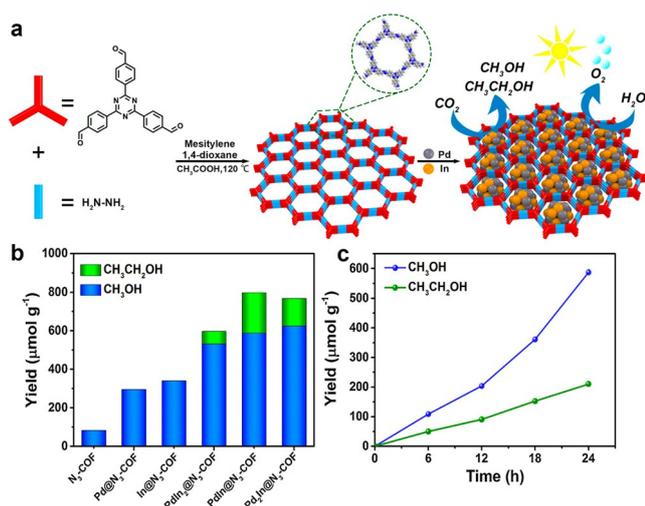


Figure 3. a) Schematic representation of the preparation of PdIn@N₃-COF. b) Photocatalytic performance of these samples for the CO₂RR. c) Time-dependent evolution curves of CH₃OH and CH₃CH₂OH using PdIn@N₃-COF as a photocatalyst. Reprinted with permission.^[23] Copyright 2019 Elsevier Inc.

crucial for stabilizing C₁ intermediates and C–C coupling. This study might guide the development of encapsulated bimetallic NPs as photosensitizing supports to realize the photocatalytic CO₂RR as well as enhance its activity.

In 2021, Guo et al. designed innovative ketoamine-based COF (TpPa-1) photocatalysts loaded with ruthenium (Ru) NPs (Ru/TpPa-1), which displayed exceptional catalytic CO₂RR performances.^[24] Indeed, all the Ru/TpPa-1 catalysts showed significant enhancements in the photocatalytic generation of HCOOH from CO₂ compared with TpPa-1, thus demonstrating the superior properties of these composites. In particular, it was found that 3.0 wt% Ru/TpPa-1 delivered a maximum HCOOH yield of 108.8 $\mu\text{mol}_{\text{cat}}^{-1}\text{h}^{-1}$. In addition, Fan and co-workers also used a bipyridine-linked TpBpy COF to anchor Ru NPs with high dispersion for the photocatalytic CO₂RR.^[25] In particular, 0.7 wt% Ru@TpBpy improved the photocatalytic conversion of CO₂ into HCOOH with a transformation rate of about 172 $\mu\text{mol g}^{-1}\text{h}^{-1}$. The above results indicated that COFs have huge potential as a scaffold for loading metal NPs with uniform dispersion through confinement effects, which could prompt the transfer of photogenerated electrons to the co-catalyst.

Polyoxometalates (POMs), a class of special metal nanoclusters, have also received much attention in terms of the photocatalytic CO₂RR. Recently, the Lan group proposed a general strategy for uniformly dispersing POMs in COFs by confining the POMs in the regular pores of the COFs through covalent bonds.^[26a] The obtained COF-POMs nanocomposites combined the merits of strong light absorption, fast electron transfer, and appropriate catalytic sites. The nanocomposites showed excellent performances in artificial photosynthesis. In particular, TCOF-MnMo₆ achieved the highest CO yield (37.25 $\mu\text{mol g}^{-1}\text{h}^{-1}$ with about 100% selectivity) in a gas–solid reaction system.

2.3. Incorporation of Metal Oxides into COFs for the Photocatalytic CO₂RR

A promising strategy has been designed to promote the efficiency of the photocatalytic CO₂ reduction, whereby COFs were integrated with metal oxides to form COF-based functional materials. In 2020, the Lan group first displayed that the electron–hole separation efficiency can be promoted through the construction of interfacial covalent bonds between COFs and metal oxides with a suitable electronic structure (Figure 4 a), whereby the COFs enabled the CO₂RR and the metal oxides offered active sites for the oxidation reaction of H₂O. One of the hybrid materials, COF-318-TiO₂ demonstrated a considerable improvement in CO₂ photo-reduction, with an optimal CO₂-to-CO transformation rate of about 69.67 $\mu\text{mol g}^{-1}\text{h}^{-1}$ and excellent selectivity under illumination (Figure 4 b,c).^[26b] Based on the methods proposed above, a large number of promising semiconductor candidates have the potential to be integrated into COFs to form multifunctional catalysts. These COF-metal oxide heterostructures display great potential in controlling the interfacial contacts, consequently leading to excellent photocatalytic activity. In addition, three-component COF-based functional materials, NH₂-MIL-125/TiO₂@COF-366-Ni-OH-HAc (yolk-shell; named MTCN-H (ys)), were also synthesized by the Lan group by a MOF-sacrificed in situ acid-etching method. MTCN-H (ys) exhibits high-efficient photocatalytic activity for the CO₂ to CO transformation.^[27]

3. Electrocatalytic CO₂RR

In general, the electrochemical CO₂RR process is similar to the photochemical CO₂RR, including of three main

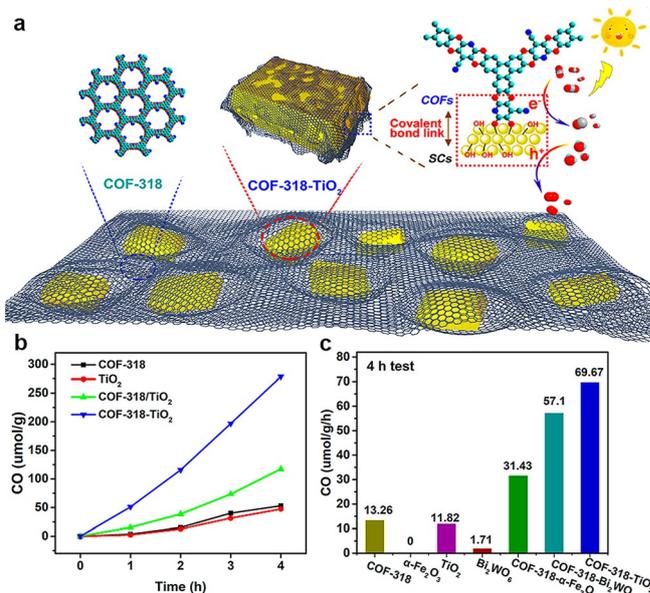


Figure 4. a) Schematic illustration of the mechanism of COF-318-TiO₂ in artificial photosynthesis. b,c) Photocatalytic performances of COF-318-TiO₂ as well as other control samples. Reprinted with permission.^[26b] Copyright 2020 Wiley-VCH.

aspects: 1) the fixation of CO₂, which interacts with active sites of catalytic materials; 2) the interaction among the adsorbed CO₂, electrons, and protons; and 3) the desorption of the final products. With crystalline and adjustable structures, COF-based functional materials with different active sites can be used in the electrochemical CO₂RR as a result of the following features: 1) the porous architecture provides high accessibility of the substrates; 2) the diverse active sites of COF-based functional materials facilitate the adsorption and activation of CO₂; and 3) electron transmission and mass-transfer properties can be adjusted through the selection of suitable building blocks and active sites. In this section, we shed light on the significance of COF-based functional materials in the electrocatalytic reduction of CO₂.

3.1. Incorporation of Single Metal Sites into COFs for the Electrocatalytic CO₂RR

3.1.1. Metalloporphyrin-Based COFs with Single Active Sites as Electrocatalysts for the CO₂RR

Metal-nitrogen-carbon (M-N-C) catalysts, particularly MPor-based single active site electrocatalysts, have displayed an ability to activate and reduce CO₂. For example, Lin et al. demonstrated a ground-breaking study with the design of two MPor-based COFs (COF-366-Co and COF-367-Co) as electrocatalysts for the CO₂RR (Figure 5a).^[28] The faradaic efficiency of CO (FE_{CO}) reached 90% at -0.55 V for COF-366-Co, which was superior to the molecular cobalt complex (Figure 5b). When the framework was expanded by replacing linking blocks, the obtained COF-367-Co with its higher surface area and pore width offers a much higher number of exposed single active sites. As a result, optimized CO₂RR properties were obtained with COF-367-Co (Figure 5c). In addition, this research group further explored the effect of the electronic character of single active sites on the CO₂ reduction activity by introducing diverse electron-withdrawing groups on metalloporphyrin-based COFs. Consequently, four COF-based functional materials with different groups were successfully synthesized and the effect on the electrocatalytic CO₂RR of electronically tuning the properties of the active sites investigated.^[29] The results showed that modification of the electronegative group of the framework would have an electron-withdrawing effect on the active sites, and its degree of influence was proportional to the electronegativity. This study offers an ideal platform for delivering excellent electrocatalytic activities through the construction of electronic functionality in COF-based functional materials.

Inspired by the electron-donating ability of the TTF monomer, a series of M-TTCOFs have been developed by the Lan group to improve the efficiency of electron transfer to the MPor. Compared with COF-336-Co (70.8%), the Co-TTCOFs exhibited a higher FE_{CO} (91.3%) at -0.7 V. As a type of 2D material, M-TTCOFs has the potential to be exfoliated into NSs and might provide great enhancements in the electroreduction of CO₂. Indeed, after exfoliation, a FE_{CO} value of over 90% at applied potentials between -0.6 and -0.9 V and nearly 100% at -0.8 V were achieved, which could be ascribed to the high surface area and good

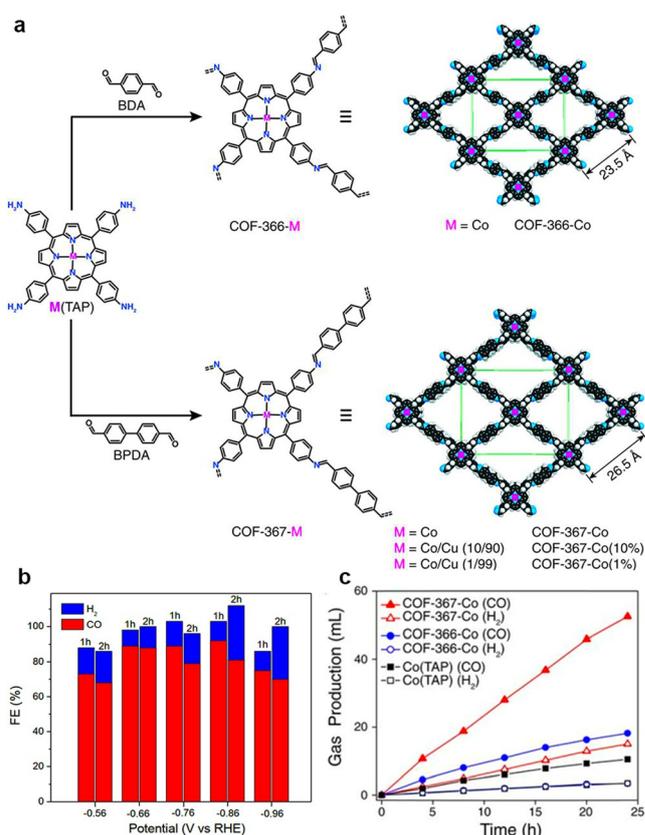


Figure 5. a) Preparation of COF-366-M and COF-367-M. b) The FE_{CO} values for COF-366-M. c) Long-cycle bulk electrolysis at -0.67 V, displaying the volume of CO obtained when using different samples as catalysts. Reprinted with permission.^[28] Copyright 2015 AAAS.

accessibility of the active sites.^[30] This work demonstrates that COFs can be engineered as efficient electrocatalysts by carefully regulating their structures and compositions.

Owing to the excellent activity of Co porphyrins for the electrocatalytic CO₂RR, a great number of investigations have been dedicated to the use of Co porphyrins as the monomer for the construction of COFs. Nevertheless, compared with iron, the abundance of cobalt in the earth's crust is relatively low. To design a more renewable catalytic system, Co can be substituted by Fe during the synthesis of MPor-based COFs. Accordingly, Cheung et al. designed an FeD-haTph-COF (containing 5,10,15,20-tetra-(4-aminophenyl)-porphyrin-Fe^{III} chloride (FeTAPPCl) and 2,5-dihydroxyterephthalaldehyde (Dha)) catalyst by a solvent-free method. The electrocatalyst displays an average FE_{CO} of 80% and a turnover frequency (TOF) of more than 600 h⁻¹ mol⁻¹.^[31]

However, most of the above-reported CO₂ reduction products, such as CO and HCOOH, are two-electron-transfer products. The highly efficient generation of higher value products by multiple proton-coupled electron transfer is still a scientific challenge for COF-based materials in the electrocatalytic CO₂RR. Consequently, in 2021, the Lan group synthesized ultrathin COF NSs (denoted as Cu-Tph-COF-Dct) by using a functional exfoliation agent. The obtained Cu-Tph-COF-Dct could serve as a powerful electrocatalyst in the CO₂RR to generate CH₄, which showed an FE value of about

80% with a current density of -220 mA cm^{-2} at -0.90 V . In contrast to Cu-Tph-COF-OH, the above electrocatalytic performances were improved substantially and also comparable to most Cu-based catalysts. The improved performances could be attributed to the immobilized functional exfoliation agent, which enhanced the CO_2 absorption/activation, stabilized the intermediates, and increased the CO concentration around the catalytic sites.^[32]

3.1.2. Metallophthalocyanine-Based COFs with Single Metal Sites as Electrocatalysts for the CO_2RR

Another kind of M-N-C catalyst, metallophthalocyanine (MPc), has also been integrated into COFs and also shown to possess an outstanding electrocatalytic CO_2RR performance. More recently, phenazine-linked Co-phthalocyanine COFs (CoPc-PDQ-COFs) were synthesized and used by Huang et al. as electrocatalysts for the CO_2RR .^[33] The phenazine linkage provided CoPc-PDQ-COF with both stability and conductivity, and the MPc link endowed CoPc-PDQ-COF with electrocatalytic activity. As a result, the CoPc-PDQ-COF delivered excellent efficiency (49.4 mA cm^{-2} at -0.66 V) and selectivity ($\text{FE}_{\text{CO}} = 96\%$ at -0.66 V) in the electroreduction of CO_2 to CO with an outstanding turnover number (TON; 320 000) and TOF ($11\,412 \text{ h}^{-1}$) as well as long-term durability (24 h). This study has clarified the guiding principle for designing MPc-based COFs to transform CO_2 into diverse value-added chemicals. In addition, a Ni-phthalocyanine-based COF, termed NiPc-COF, has also been constructed and applied by Zhang et al. as an effective catalyst for the electroreduction of CO_2 .^[34] The NiPc-COF displayed outstanding electrocatalytic properties for the generation of CO as a result of its excellent electron-transfer ability and highly accessible active sites.

Another new MPc linkage block, that is, tetraanhydrides of 2,3,9,10,16,17,23,24-octacarboxyphthalocyanine, were used by Han et al. for the construction of two new polyimide (PI) COFs, CoPc-PI-COF-1 and CoPc-PI-COF-2 (Figure 6a).^[35] As CoPc-PI-COFs-1 and CoPc-PI-COF-2 contain the same electroactive sites combined with analogous porosity and CO_2 uptake capacity, both of them could achieve $\text{FE}_{\text{CO}} = 87\text{--}97\%$ at a wide overpotential range from -0.6 to -0.9 V (Figure 6b). Nevertheless, in comparison to CoPc-PI-COF-2, CoPc-PI-COF-1 offered a higher j_{CO} value of -21.2 mA cm^{-2} at -0.90 V , which was attributed to its superior conductivity. CoPc-PI-COF-1 also exhibited a high TON and TOF, reaching up to 277 000 and 2.2 s^{-1} at -0.70 V (Figure 6c). These results not only showed that novel MPc-based COFs possessed outstanding chemical and thermal stability, but also provided an example of the design of reticular catalysts for the electrochemical CO_2RR . In the stacking arrangement of 2D COFs, especially for the framework containing conjugated linkages (such as MPor and MPc), the AA packing mode seemingly restricts the amount of exposed active sites to a certain extent. Porous three-dimensional (3D) COFs are anticipated to make a valuable contribution to addressing this issue by decreasing the aggregation of linkages and thus increasing the number of efficient catalytic sites for the electroreduction of CO_2 . Therefore, Han et al. further fab-

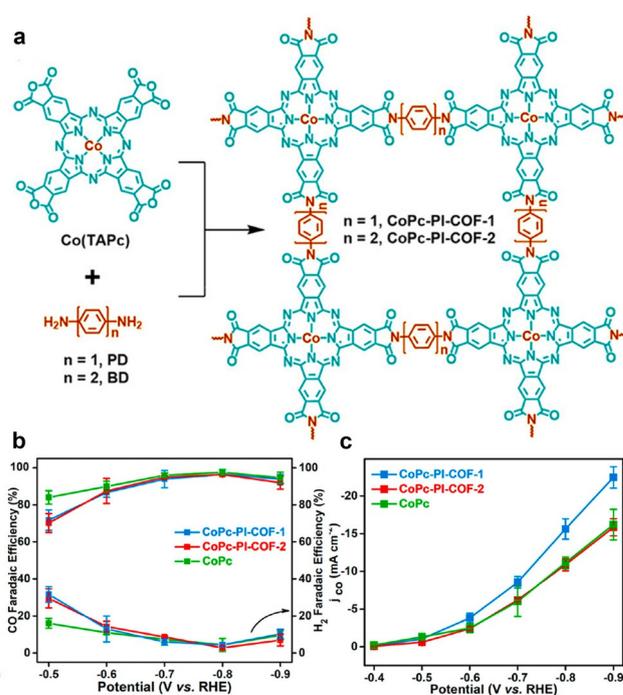


Figure 6. a) Schematic illustration of the formation of CoPc-PI-COF. b,c) Electrocatalytic performances of the samples. Reprinted with permission.^[35] Copyright 2021 American Chemical Society.

ricated 3D MPc-PI-COFs by a polymerization reaction.^[36] The unique 3D porous architecture of the MPc-based COFs guaranteed that about 32.7% of the total MPc subunits were exposed as active catalytic centers, thereby leading to outstanding CO_2 electroreduction properties, as shown by the higher j_{CO} value compared with that of the 2D COF.

To further enhance the electrocatalytic CO_2 performances of MPc-based COFs, bimetallic active sites were introduced into MPc-based COFs by Yue et al. The obtained bimetallic $\text{CuPcF}_8\text{-CoPc-COF}$ and $\text{CuPcF}_8\text{-CoNPc-COF}$ demonstrated positive effects in terms of enhancing their activity and stability. As a result of their robustness and rapid electron transfer, superior activity, selectivity, and higher stability were observed in these bimetallic COFs compared with the small MPc and monometallic COFs. Finally, an exceptionally high FE_{CO} value of 97% and a TOF of 2.87 s^{-1} were obtained for $\text{CuPcF}_8\text{-CoNPc-COF}$ in the electrochemical CO_2RR to generate CO.^[37]

Owing to the photosensitive 18π aromatic macrocyclic structure of the MPc linkage blocks, MPc-based COFs usually possess an efficient light-absorption capability. Many studies have proved that the external light field effect might have a significant influence on the electrocatalytic performance. In 2021, the Lan group successfully fabricated a series of ultrastable dioxin-linked MPc COFs (MPc-TFPN COF) and systematically studied their CO_2 electroreduction and photo-coupled electroreduction performance (Figure 7a,b). The NiPc/CoPc-TFPN COF delivered excellent electrocatalytic performances for the CO_2RR . FE_{CO} values of up to 99.8% and 96.1% were obtained for NiPc-TFPN and CoPc-TFPN,

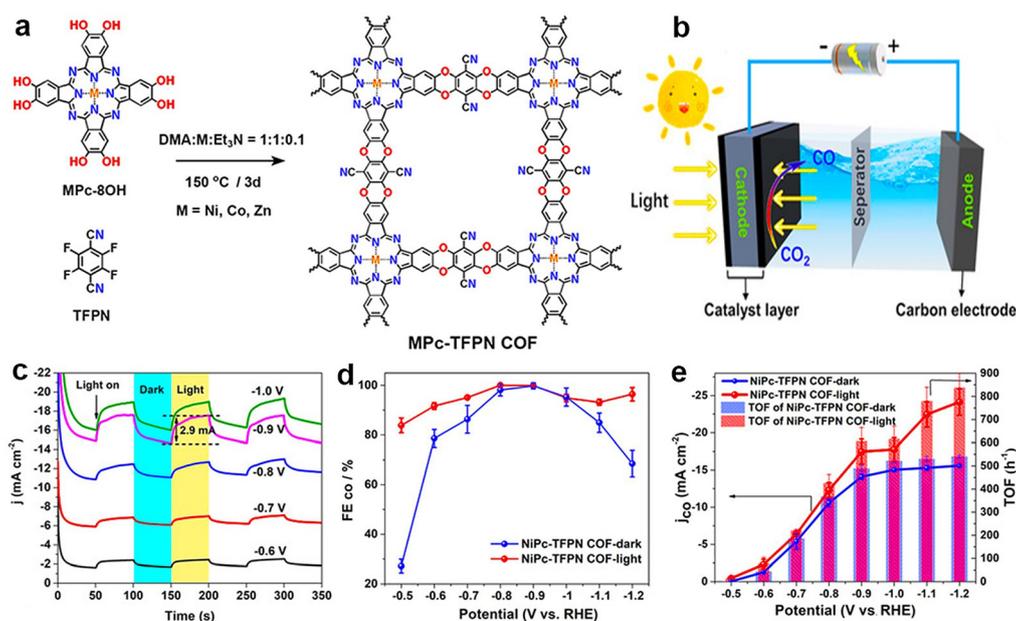


Figure 7. a) Schematic preparation of the MPc-TFPN COF. b) Illustration of photocoupled electrochemical tests. c) Photocurrent response of NiPc-TFPN COF. d, e) Plots of FE_{CO} , j_{CO} , and TOF values at applied potentials with or without light. Reprinted with permission.^[38] Copyright 2021 Wiley-VCH.

respectively, at -0.9 V. With additional illumination, NiPc-TFPN exhibited a higher activity ($FE_{CO} = 14.1 \text{ mA cm}^{-2}$ at -0.9 V) and selectivity ($FE_{CO} \approx 100\%$ at -0.9 V) compared to the dark conditions (Figure 7c–e). In addition, the TOF of NiPc/CoPc-TFPN COF was evidently increased over a wide potential range from -0.5 to -1.2 V (Figure 7e). This study first investigated the use of COFs as photoassisted electrocatalysts to enhance the electrocatalytic performance of the CO_2RR , and illustrated the potential of applying photosensitive COFs for the electrocatalytic CO_2RR .^[38]

3.1.3. Anthraquinone-Based COFs with Single Active Sites as Electrocatalysts for the CO_2RR

COF-based functional materials with MPor or MPc moieties have shown great potential in the electrocatalytic CO_2RR . Nevertheless, the obtained COF-based functional materials would not be cost-effective catalysts, since the synthesis or functionalization of the MPor or MPc monomers is cumbersome. Compared to these COF-based functional materials, COFs composed of 1,3,5-triformylphloroglucinol (TP) and anthraquinone-based monomers are less expensive. Bearing this idea in mind, in 2021, the Lan group prepared two anthraquinone-based COFs (AAn-COF and OH-AAn-COF) with adjustable 1D superstructures and post-modified them with different metal ions (Cu^{2+} , Co^{2+} , and Zn^{2+}) to study their electrocatalytic CO_2RR performances.^[39] AAn-COF-Cu and OH-AAn-COF-Cu displayed excellent FE_{CH_4} values of 77% at -0.9 V and 61% at -1.0 V, respectively, in a flow-cell mode reactor.

When reviewing the state-of-the-art applications of COF-based functional materials in the electrocatalytic CO_2RR , we found that except for MPor, MPc, and anthraquinone-based

COFs with single active sites, other COF-based functional materials (e.g. with incorporated metal nanoparticles or metal oxides in the COFs) are rarely reported for this catalytic reaction. Consequently, largely unexplored areas still exist in the field of electrocatalytic CO_2RR using COF-based functional materials, since: 1) the general strategy of incorporating diverse active sites into COFs is undeveloped; 2) the synergistic effect between the COFs and diverse active sites is unclear; 3) effective exposure of the active sites to enhance catalytic activity is unclear; and 4) great importance should be placed on mechanistic studies to guide the design of superior COF-based functional materials.

4. Li- CO_2 Batteries

At present, the generally recognized electrochemical mechanism of Li- CO_2 batteries involves the reaction: $4Li^+ + 4e^- + 3CO_2 \rightarrow 2Li_2CO_3 + C$.^[40] In view of this equation, ideal Li- CO_2 electrodes should satisfy the following requirements: 1) the capacity to store and uptake CO_2 ; 2) the space to limit the deposition of the discharged product; and 3) effective active sites to catalyze the decomposition of Li_2CO_3 . It is noteworthy that COF-based functional materials are suitable as cathode catalysts in Li- CO_2 batteries because of their structures and properties, including the ability for CO_2 capture, regular pores, and abundant catalytic sites.^[41] In this section, the application of COF-based functional materials with various electrocatalytic active sites for Li- CO_2 batteries and the design of active sites for the enhancement of the performances of Li- CO_2 batteries will be summarized.

4.1. Incorporation of Single Metal Active Sites into COFs for Li-CO₂ Batteries

In 2021, the Lan group synthesized a manganoporphyrin-based COF (TTCOF-Mn) and utilized it as an effectual cathode catalyst for Li-CO₂ batteries. TTCOF-Mn provides uniform nanopore channels for the CO₂ and Li⁺ ions to access the catalytic sites (single Mn^{II} sites), thereby enormously prompting the formation/decomposition of Li₂CO₃ during the discharge/charge process (Figure 8a).^[42] The as-obtained TTCOF-Mn cathode catalyst has a low terminal potential gap of 1.07 V at 100 mA g⁻¹. More importantly, the batteries exhibited exceptional stability when discharged/charged over 180 cycles at 300 mA g⁻¹ (Figure 8b,c). This was the first report of crystalline materials with a well-defined structure that discloses the catalytic sites and reaction mechanism of Li-CO₂ batteries.

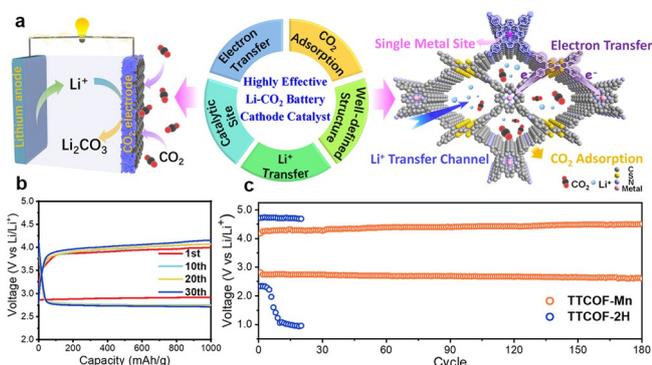


Figure 8. a) Schematic representation of the merits of using TTCOF-Mn as a cathode catalyst in Li-CO₂ batteries. b,c) Electrochemical properties of Li-CO₂ batteries with various COFs as cathode catalysts. Reprinted with permission.^[42] Copyright 2021 American Chemical Society.

4.2. Incorporation of Metal Nanoparticles into COFs for Li-CO₂ Batteries

Ru is one of the most extensively used noble metal catalysts and was considered capable of promoting the decomposition efficiency of the discharge products in Li-CO₂ batteries. Based on this, Li et al. designed COF-based functional materials (COF-Ru@CNT) as cathode catalysts for Li-CO₂ batteries. These materials were synthesized by integrating COFs with carbon nanotubes (CNTs) modified with Ru NPs (Figure 9a).^[43] COF-Ru@CNT with its well-tailored open channels could enrich CO₂ and improve the transportation of CO₂, electrons, and Li⁺ ions to the Ru nanoparticles. The Ru NPs in COF-Ru@CNT were considered as the catalysts responsible for CO₂ reduction and Li₂CO₃/C decomposition. The COF-Ru@CNT cathode could attain a high capacity of over 27 348 mAh g⁻¹ and sustain excellent cycle stability after 200 charge/discharge processes (Figure 9b,c).

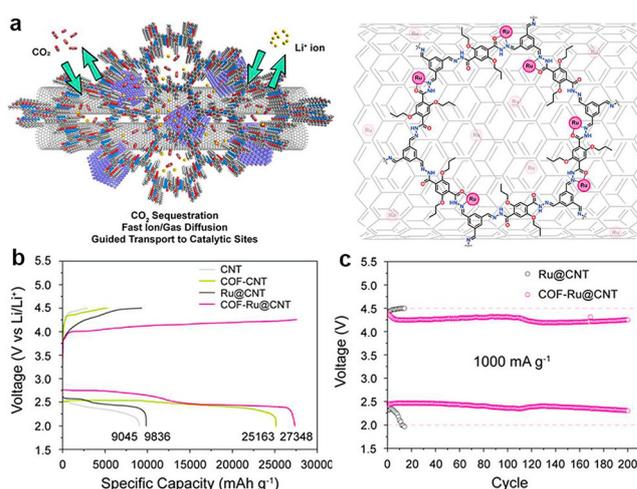


Figure 9. a) Illustration of the application of COF-Ru@CNT in Li-CO₂ batteries. b,c) Electrochemical properties of Li-CO₂ batteries with various COFs as cathode catalysts. Reprinted with permission.^[43] Copyright 2019 Wiley-VCH.

4.3. Incorporation of Metal Oxides into COFs for Li-CO₂ Batteries

MnO₂ is a common catalyst for the reduction of CO₂ and decomposition of Li₂CO₃/C in Li-CO₂ batteries. Consequently, the Lan group exfoliated quinone-based COFs by a chemical exfoliation method into ultrathin COFs NSs and obtained MnO₂/DQTP-COF-NS. The obtained samples were then applied as cathode catalyst materials in Li-CO₂ batteries. The MnO₂/DQTP-COF-NS-3 cathode could achieve a record discharge capacity of 42 802 mAh g⁻¹ at 200 mA g⁻¹. Furthermore, no apparent decline in the charging/discharging voltage was observed after 120 cycles.^[44] These excellent performances might stem from the intrinsic characters of the as-designed MnO₂/DQTP-COF-NS-3.

5. Conclusions and Perspectives

In the field of chemical CO₂ conversion, it is well-known that catalysts are the most important elements to convert efficiently between photoelectrical and chemical energy, and to realize renewable carbon cycles. COF-based functional materials are a family of crystalline materials that have the potential to simultaneously possess multiple features to achieve high performances. In this Minireview, we have summarized the fundamental aspects of diverse active sites in COF-based functional materials, providing novel insights into the design of the next-generation photo-/electrocatalysts for the utilization of CO₂. We also highlight recent advancements made in active site engineering in COF-based functional materials to improve or maximize their performances in the field of chemical CO₂ conversion, which mainly includes the photocatalytic or electrocatalytic CO₂RR and Li-CO₂ batteries. Some of the issues and challenges related to COF-based functional catalysts have been discussed and summarized. To maximize the application potential of COF-based

functional materials in the field of chemical CO₂ conversion, the following problems will need to be explored in depth.

Active sites: Firstly, incorporation of other kinds of active sites into COFs (such as organic functional groups, coordination compounds, and graphitic carbon nitride) and adjustment of the intrinsic structures to obtain superior substrate–catalyst interactions will be significant subjects for the development of high-performance COF-based photo-/electrocatalysts. Furthermore, exploration of innovative COF-based functional materials with electrostatic interactions, covalent bonds, and coordinate bonds etc. has been considered an effective way to regulate the electronic structure of materials to boost the performance of the photocatalytic or electrocatalytic CO₂RR as well as Li-CO₂ batteries.

Stability issues: Secondly, the stability issues of COF-based functional materials in reaction systems should also be considered. Decomposition of the structure or changes in the chemical constitution is likely to happen during the catalytic process. The components of COF-based functional materials are easy to modify under harsh conditions, such as light irradiation and high voltage. More importantly, it is indispensable to clarify the real active sites of catalysts in catalytic processes.

Optical activity and redox ability: Thirdly, for the photocatalytic process, the poor light absorption and oxidation capacities of COF-based functional catalysts still need to be further improved; many of the reported COF-based photocatalysts require an additional photosensitizer and electron donor to ensure continuous reaction, which cannot meet the requirements of green chemistry. In this respect, more desirable photocatalysts should be developed in the future. For the electrocatalytic process, many issues still remain to be solved for COF-based functional materials, such as: 1) weak electronic conductivity; 2) limited structural stability under special conditions; and 3) limited density of the effective active site. Furthermore, although COF-based functional materials have been successfully used for CO₂ photo-/electroreduction, the CO₂ reduction products are mostly CO/HCOOH, which arise from two electron and two proton transfer processes. Further explorations should focus on designing more efficient COF-based photo-/electrocatalysts to obtain value-added multicarbon products. On the other hand, based on the structure analysis and performance tests of the COF-based photo-/electrocatalysts, further rationalized design of the photo-/electrocatalytic devices will also be a useful approach to solve the above issues.

Catalytic coupling reaction: Fourthly, the previously reported catalytic systems for the photocatalytic CO₂RR with water or organic electron donors usually suffer from poor catalytic activity and cost-ineffective atom economy. Coupling the photocatalytic reduction of CO₂ with high value-added organic synthesis into one reaction system provides a novel way to collaboratively utilize photoexcited electrons and holes to fulfil the targets of a sustainable economy and green chemistry. The well-designed organic substrates could play the role of hole scavengers to be oxidized to value-added products, and also drive the protons and electrons to activate and reduce the CO₂ molecule, thereby enhancing the robustness and overall catalytic efficiency of the photocatalytic

CO₂RR systems. Similarly, previous studies on the electrolytic reduction of CO₂ mostly involve the oxygen evolution reaction (OER) at the anode. However, this anodic reaction requires a large proportion of the energy consumption and yields a product with little economic value. Consequently, the oxidation of anodic organic substrates of higher economic value is one of the promising alternatives to the OER, as it possesses a low thermodynamic potential.

Study of mechanisms: Finally, although much progress has been achieved with COF-based functional materials in the chemical conversion of CO₂, a comprehensive study of the mechanisms of the photo-/electrochemical CO₂RR and Li-CO₂ batteries, which is instructive for the rational construction of COF-based functional materials with effective active sites and better photo-/electrochemical performances, is still limited. Thus, a series of advanced in situ techniques, including in situ Fourier transform infrared spectroscopy, high-energy X-ray diffraction, X-ray absorption fine structure spectroscopy, and hard X-ray photoelectron spectroscopy, are urgently required to characterize and analyze in depth the relationship between the photo-/electrochemical activities and the chemical structures of the COF-based functional materials.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: CO₂ reduction · covalent organic frameworks · heterogeneous catalysis · Li-CO₂ batteries · photo-/electrocatalysis

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