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Review Article

Advances in covalent organic frameworks for photocatalytic CO_2 reduction: Strategies and future perspectives

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ABSTRACT

The rapid depletion of fossil fuels and increasing emissions of greenhouse gases, particularly CO_2, have amplified global energy and environmental challenges. Converting CO_2 into valuable fuels through photocatalytic processes offers a sustainable solution to these issues, especially by utilizing solar energy to drive CO_2 reduction into energy-dense compounds. Covalent organic frameworks (COFs), a unique class of crystalline and porous organic polymers, have emerged as promising photocatalysts due to their structural stability, tunable porosity, and adaptable functionality. These properties enable COFs to support various catalytic sites, both metallic and non-metallic, facilitating selective and efficient CO_2 reduction. This review systematically examines the intrinsic properties of COFs, the synthetic methods used to optimize their structures, and the functional modifications that enhance their photocatalytic capabilities. We explore how COFs with metal and non-metal active sites, as well as hybrid COF catalysts, advance photocatalytic CO_2 reduction and analyze the driving forces behind CO_2 reduction reaction (CO_2RR). Finally, we summarize recent breakthroughs and offer perspectives on future research directions in COF material synthesis, functional modifications, and mechanistic studies to further improve CO_2 reduction efficiency and sustainability.

KEYWORDS

CO_2 reduction, photocatalysis, three-dimensional (3D) covalent organic frameworks (COFs), two-dimensional (2D)-COFs, hybrid-COFs

1 Introduction

Covalent organic frameworks (COFs) materials are a novel class of crystalline organic porous polymers formed by the expansion of organic monomers in two-dimensional (2D) or three-dimensional (3D) space through covalent bonds [1–8]. In 2005, Yaghi et al. [5] first synthesized two crystalline organic porous materials, COF-1 and COF-5, initiating the research on covalent organic framework materials. By designing the organic monomers that make up COFs, precise control of material structure and function can be achieved. Thanks to the topological design theory of reticular chemistry, COFs have developed rapidly in recent years [9–12]. So far, the bonding methods of COFs have evolved from the initial B–O bond to C=N bond [13], and further to various types of connections such as C–O bond and C=C bond [14]. In terms of spatial topology, COFs can be divided into two categories: two-dimensional COFs and three-dimensional COFs. Two-dimensional COFs are structurally similar to graphite, with organic monomers covalently connected within layers to form two-dimensional planes, and stacked between layers through π–π conjugation [12]. Three-dimensional COFs extend in the three-dimensional direction through covalent bonds of non-planar organic monomers, and have various types of topological structures, usually exhibiting interlaced structures [15–19].

COFs materials typically have high structural order, large specific surface area, and good thermal stability, and are widely used in fields such as gas storage and separation [20–22], catalysis [23–25], sensing [26], energy storage [21, 27] and optoelectronic conversion [28–30]. In recent years, with the deepening of research on COFs, it has been found that COFs can generate charge separation under illumination, and combined with their designable pore structure, COFs have become potential photocatalysts.

Photocatalysis utilizes light energy to drive chemical reactions, which is a green catalytic method with great research value. In recent years, a large number of photocatalysts suitable for different systems have been prepared. Usually, photocatalysts are divided into two types: homogeneous and heterogeneous. Compared with

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homogeneous photocatalysts, heterogeneous photocatalysts have advantages such as recyclability and reusability while maintaining high catalytic activity, which makes heterogeneous photocatalysts more promising for industrial applications.

However, current heterogeneous photocatalysts based on inorganic metal oxides and other systems still face some challenges, such as weak light absorption ability and poor charge separation ability. Recently developed COF materials possess unique advantages in photocatalysis: (1) structural designability. The absorption capacity and band structure of COFs can be finely adjusted by changing the monomer chemical structure; (2) easy to functionalize. COFs skeleton can be functionalized in two ways before and after preparation, making it convenient to introduce catalytic sites; (3) high specific surface area and good stability. This enables the catalytic sites on COFs to be effectively dispersed and fully exposed, and remain stable during the catalytic process.

The excellent characteristics of COFs endow them with superior photocatalytic performance compared to classical photocatalysts such as TiO_2, cadmium sulfide (CdS) [33, 34], graphitized carbon nitride (g-C_3N_4) [33, 35–41], and COF materials, making them excellent carriers for photocatalytic reduction reaction catalysts. Moreover, compared to inorganic nanomaterials, graphite C_3N_4, and metal-organic frameworks (MOFs) materials [37, 39, 40, 42], COFs exhibit the following advantages as photocatalysts for CO_2 reduction: (1) COFs typically have a larger specific surface area and abundant heteroatoms (N, O, S, etc.), and have higher adsorption capacity and selectivity for CO_2 compared to traditional inorganic semiconductor (SC) materials; (2) the framework structure of COFs materials is connected by covalent bonds, thus possessing stronger thermal and chemical stability, which makes COFs have excellent potential in the field of photocatalysis; (3) COFs have a regular crystal structure and regular molecular arrangement, which reduces the electron recombination phenomenon during the reaction process and improves the electron transfer efficiency; (4) the COFs structure is easy to design, modify, and adjust, making it possible to synthesize COFs with expected electronic structures, thereby realizing or testing researchers' ideas; (5) two dimensional COFs have a large number of conjugated π electrons, which endow COFs with good light absorption and conductivity [43]. In recent years, research has shown that COFs have great potential in the field of photocatalysis, among which the application of COFs in photocatalytic CO_2 reduction has considerable prospects.

This article mainly introduces the research progress of new COFs for photocatalytic CO_2 reduction in recent years, providing a systematic and in-depth analysis of the relationship between the design concepts and functions of each work, as well as their reference significance. It also looks forward to their application prospects in the field of photocatalysis, aiming to promote further development in this field.

2 Properties of covalent organic frameworks

COFs are a unique class of crystalline, porous materials sharing several design features with MOFs, including the ability to pre-define their structure, achieve periodic porosity, and maintain highly organized architectures. However, the primary difference lies in their chemistry: Unlike MOFs, which are constructed through coordination bonds between organic linkers and metal ions, COFs consist solely of organic monomers interconnected by strong covalent bonds [44]. This covalent linkage provides COFs with enhanced thermal and chemical resilience compared to MOFs [43]. The formation of COFs is guided by the spatial arrangement of monomers, resulting in either 2D or 3D porous structures [45]. 2D COFs are characterized by their extended planar architectures and π-conjugated systems, which facilitate efficient charge transport and separation. Their high surface area ensures ample active sites for CO_2 adsorption and activation, making them particularly suited for light-harvesting applications. Additionally, their inherent anisotropy allows for the customization of interlayer spacing, promoting selective molecular interactions. Conversely, 3D COFs possess robust, interconnected networks with three-dimensional porosity, which not only enhances CO_2 capture due to their superior pore accessibility but also provides enhanced stability in harsh operational conditions. Their well-defined channels enable better diffusion of reactants and products, minimizing transport limitations during the photocatalytic process. While 2D COFs excel in light absorption and charge mobility due to their conjugated layers, 3D COFs offer superior durability and structural versatility, which can accommodate a wider range of functional modifications. Therefore, the choice between 2D and 3D COFs largely depends on the specific requirements of the CO_2 reduction system, balancing between charge dynamics and stability. The wide variety of monomers allows for tailoring COF structures and porosity to meet specific needs. Functional groups or metal coordination sites can be integrated into COFs either during synthesis through functionalized linkers or afterward via post-synthetic modification. Additionally, heteroatoms like triazines and imines can be incorporated to create special microenvironments or serve as metal-binding or redox-active sites [46]. Distinct from MOFs, many COFs feature π-conjugated frameworks, which give them moderate electronic conductivity—an asset for catalytic applications. Their macroscopic structures can also be adjusted using templates or processing techniques such as 3D printing [47, 48]. Metal sites or other functional materials can be added to COFs, forming composites that expand their functionality. Furthermore, COFs can undergo pyrolysis to produce nanostructured porous carbons or carbon-metal composites. In summary, COFs present a highly versatile material class with promising potential for advancing research and applications across multiple fields.

3 Synthesis protocols of covalent organic framework

The solvothermal method is the most widely employed strategy for COF synthesis, valued for its ability to produce high-quality crystalline materials. In a typical solvothermal process, a Pyrex tube of a specific volume is loaded with the monomer reactants, catalyst, and solvent. This mixture is sonicated to ensure uniform dispersion, then flash-frozen and degassed using multiple freeze-pump-thaw cycles to remove any dissolved gases. After sealing the tube under vacuum, it is heated to a controlled temperature to drive the reaction over a set period. Once the reaction completes, the precipitated COF product is isolated by filtration or centrifugation, washed with suitable solvents to remove unreacted monomers or by-products, and finally vacuum dried. For further purification or solvent exchange, Soxhlet extraction may be applied [44, 49]. The product is then typically vacuum dried at 80–120 °C to achieve a stable, high-purity COF material. However, traditional solvothermal methods are often time-consuming and require significant amounts of organic solvents. In response, recent research has focused on developing more sustainable, efficient approaches for COF synthesis. Methods such as microwave-assisted synthesis, ionothermal synthesis, solid-phase synthesis, and interfacial synthesis offer faster reaction times

and lower environmental impact. Readers interested in an in-depth exploration of green COF synthesis methods can refer to recent comprehensive reviews. The synthesis methods and characteristics of COFs are summarized in Table 1 for easy reference [50]. While COFs demonstrate promising potential for photocatalytic CO_2 reduction, there are significant challenges that need to be addressed for practical applications. One critical issue is their stability under operational conditions. COFs are often prone to structural degradation when exposed to light, moisture, or reactive species during photocatalytic processes. Strategies to enhance their stability include the incorporation of robust linkages (e.g., imine-to-amine conversion or introducing boronate ester alternatives), functionalizing frameworks with hydrophobic groups, and employing composite materials that shield COFs from harsh conditions. These advancements are crucial for ensuring prolonged operational efficiency. Another major challenge is the scalability of COF synthesis. Traditional methods, such as solvothermal or ionothermal techniques, are often resource-intensive, requiring high temperatures, extended reaction times, and organic solvents, which limit the feasibility of large-scale production. Developing scalable synthetic methods, such as mechanochemical synthesis or green chemistry approaches, can mitigate these barriers. Additionally, improving control over crystallinity and porosity during large-scale synthesis remains a significant hurdle that must be overcome to ensure consistent material performance in real-world applications. By addressing these issues, future research can move closer to translating the impressive laboratory-scale performance of COFs into viable technologies for CO_2 reduction.

4 Covalent organic framework materials

4.1 Introduction to covalent organic framework materials

COFs are a type of crystalline porous organic polymer material formed by connecting and extending organic building units through covalent bonds. Usually, covalent bonds connecting organic molecules to form solids often result in disordered, amorphous structures [7]. Therefore, when designing and synthesizing COFs materials with crystalline structures, it is often necessary to experimentally find the equilibrium point between their dynamics and thermodynamics. The common methods for synthesizing COFs materials currently studied include solvothermal method, ionothermal method, microwave method, sonochemical method, mechanochemical method, and light-assisted method. Among them, solvothermal method is the simplest and most common method for synthesizing COFs.

Due to the diversity of geometric structures of organic molecules that make up COFs materials, as well as the rich building blocks and internal functional covalent bond types, COFs exhibit strong designability in crystal structure. Given appropriate conditions, researchers can accurately design theoretical structures such as the composition, pore size, and porosity of COFs. At the same time, the synthesized COFs crystal structure can be accurately characterized using techniques such as powder X-ray diffraction (PXRD), ^{13}C solid-state nuclear magnetic resonance (^{13}C SSNMR), Fourier transform infrared (FT-IR) spectroscopy, combined with theoretical simulations. This undoubtedly provides directional guidance for the theoretical structure design of COFs. So far, a large number of COFs with various composition structures have been reported in the literature, covering zero-dimensional (0D), one-dimensional (1D), 2D, and 3D structures [51]. Among them, the design synthesis of 2D and 3D structures is the most common and widely used. In 2003, Yaghi and O'Keeffe's research group proposed the theory of reticular chemistry structure (RCS). In this theory, based on the geometric structure and symmetry of organic monomer molecules, monomers can be divided into C_1, C_2, C_3, C_4, C_6, and T_d types, and T_d geometric structure is often used to design 3D COFs. Some common topological structures are shown in Fig. 1 [32, 52]. Mesh synthesis is different from organic synthesis and supramolecular assembly,

Table 1 COFs synthesis methods and characteristics

Method	Organic solvents	Operating conditions			Product Yield (%)	S_{BET}[a] ($m^2 \cdot g^{-1}$)	Morphology	Advantage	Disadvantage
		Temperature (°C)	Time (h)	Pressure					
Solvothermal	Abundant	70–150	72	Degassing and seal	70–94	500–3000	Powder	Widely used	Organic solvents
Mixed solvent based	About 50%	RT[b]/140	24–48	ATM[c]	46–88	100–1300	Powder	Good crystallinity	Abundant solvent
Solid phase/mechano chemistry	Few drops	RT	1–2	ATM	80–90	100	Powder	Large scale synthesis	Limited application
Mechano chemistry + thermal crystallization	Few drops	70–150	1–120	ATM/degassing and seal	70–90	300–3000	Powder	Improved crystallinity	Use of organic solvent
Solvent free heating	No	80	72	Seal	80	295	Powder	Solvent free	Liquid precursor
Electron beam irradiation	Certain amount	RT	160 s	Degassing and seal	90	735	Powder	Ultra-rapid	Reaction critically controlled
Vapor assisted	Little	RT/120	48–72	ATM	80	280–1000	Powder	COF film obtained	Low yield
Ionothermal	No	RT/140	72	ATM/degassing and seal	70–90	400–1300	Powder	Functional modification available	Not economy
Hydrothermal	No	RT/120	0.5–72	ATM/degassing and seal	70–95	300–1500	Powder	Large scale synthesis	Limited application
Micelle-assisted	Little	30	72	Deoxygenation	85–90	685	Powder	Nano-sized COF	Conditions needs optimization

[a]S_{BET}: surface area (Brunauer–Emmett–Teller). [b]RT: room temperature. [c]ATM: atmospheric pressure.

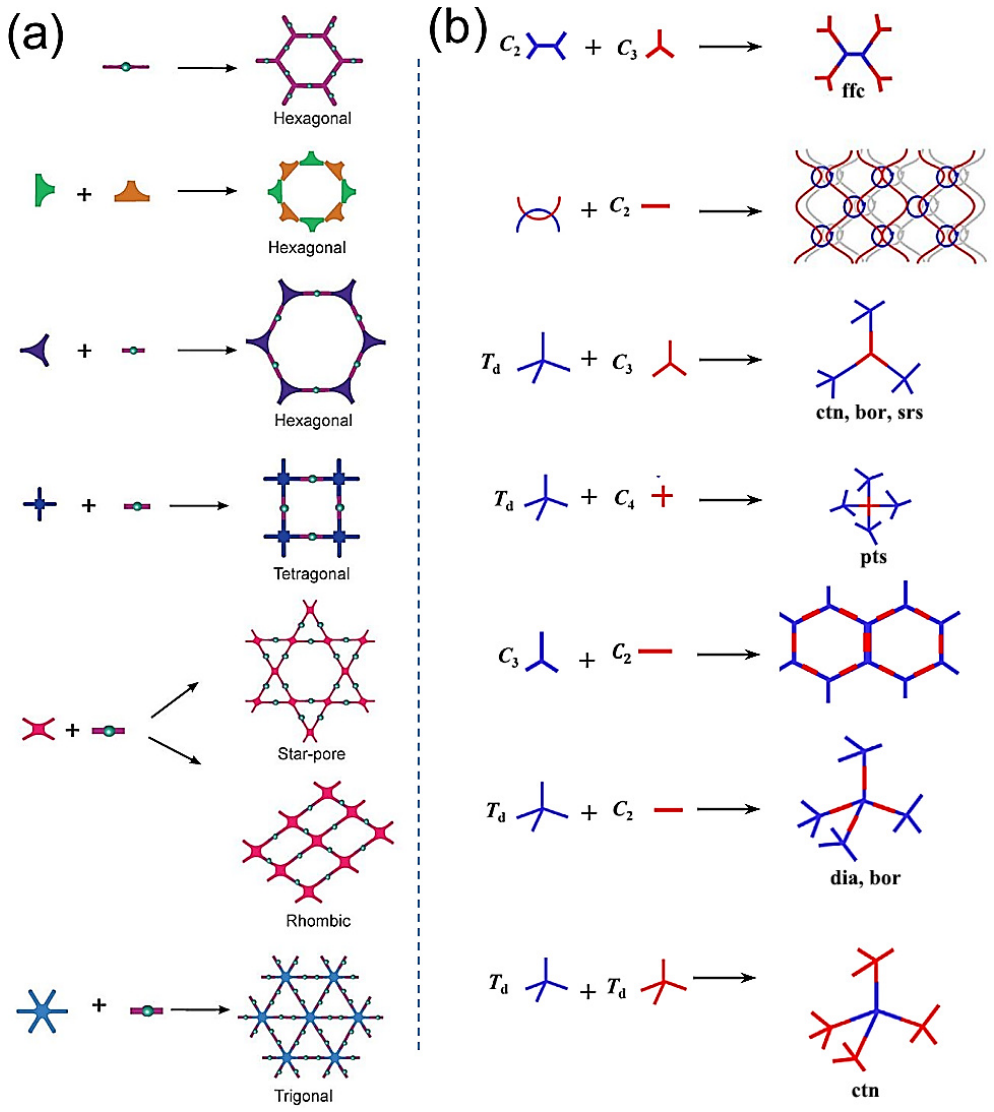

Figure 1 (a) Building monomers and commonly observed geometries of 2D COFs. Reproduced with permission from Ref. [31], © Lohse, M. S. et al. 2018. (b) 3D COFs. Reproduced with permission from Ref. [32], © Vardhan, H. et al. 2023.

and plays an indispensable role in the design of COFs. Through continuous exploration, researchers have been able to synthesize a variety of structural elements with special functions using mature organic chemistry methods [53, 54], and combine them with topology theory to covalently connect and orderly assemble them into crystalline COFs, further realizing the practical application of COFs materials [55].

4.2 Application of covalent organic framework materials in photocatalysis

In terms of the application of COFs, the following characteristics of COFs materials determine their enormous potential in the field of photocatalysis: (1) COFs often have a large specific surface area, providing them with great possibilities for loading a large number of catalytic active sites. Moreover, their enormous surface area allows the active sites to come into contact with reactant molecules more fully, which makes them highly efficient in catalysis; (2) the thickness of 2D COFs can be reduced to the nanometer or even sub-nanometer level, greatly reducing the migration distance of photo generated carriers, increasing the migration rate, and weakening the inherent recombination phenomenon of electron–hole pairs. In addition, not limited to 2D COFs, COFs with other structures can also provide a good platform for photo generated carriers [56]; (3) the framework structure formed by covalent bonding has higher chemical stability; (4) the extremely strong pre-designability of the structure endows COFs with opportunities for diverse applications in various catalytic fields, such as photocatalytic CO_2 reduction, hydrogen production [57], etc. The growing research interest in COF materials for photocatalytic CO_2 reduction is demonstrated by the annual publication trends shown in Fig. 2. At present, COFs have been

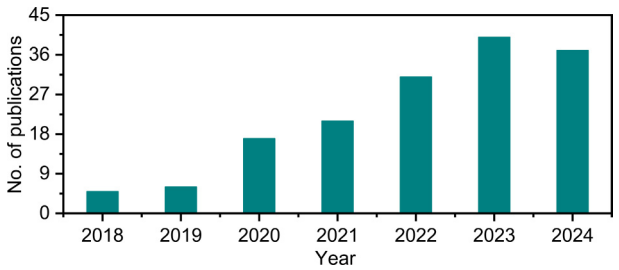

Figure 2 Annual publication trends from 2018 to November 2024, illustrating the increasing research interest in COF materials for photocatalytic CO_2 reduction. Data retrieved from the Scopus database using the keywords "COF materials", "CO_2 reduction", and "photocatalysis".

successfully applied in fields such as small molecule adsorption and separation [58, 59], sensing, photocatalysis [60, 61], energy storage, optoelectronic devices [62] and biomedicine [63]. The excellent performance of COFs materials combined with other materials has also attracted extensive research and attention [64].

5 Basic principles of photocatalytic CO_2 reduction

Artificial photosynthesis has become one of the most promising methods to address the increasingly severe environmental problems and energy crises caused by the combustion of fossil fuels. The most attractive method is to use inexhaustible solar energy as a driving force to reduce CO_2 into high-value chemical fuels (CO, HCOOH, HCHO, CH_3OH, CH_4, etc.). Exploring suitable photocatalysts is crucial for the effective implementation of this catalytic process.

Typically, photocatalytic processes involve three steps: light capture, electron hole separation, and redox reactions (Fig. 3). Furthermore, the photocatalytic CO_2 reduction reaction (CO_2RR) involves the following three processes: in the first stage, a photocatalyst with an appropriate bandgap width absorbs photons of a certain energy (i.e. when hv > bandgap energy (E_g)), and the ground state electrons absorb energy and transition from lowest unoccupied molecular orbital (LUMO) to highest occupied molecular orbital (HOMO), while the electron transition leads to the formation of electron–hole pairs (e^-–h^+) with a certain energy. In the second stage, photo generated electrons and holes are separated from each other and transferred to the active sites on the catalyst surface for further reduction and oxidation reactions. In the third stage, electrons and protons are injected into the active site to adsorb the substrate CO_2 molecules, thereby catalyzing the reduction reaction of CO_2 molecules on the catalyst surface [65].

Based on the reduction mechanism of photocatalytic CO_2, it is generally believed that efficient photocatalysts for photocatalytic CO_2 reduction need to possess several characteristics: (1) suitable energy bands combined with strong light absorption ability to achieve efficient utilization of solar energy; (2) strong chemical adsorption capacity for CO_2; (3) sufficient and rapidly separable photo generated electron–hole pairs to ensure the continuity and efficiency of the reaction under the action of the catalyst; (4) the removability of active sites with side reactions to be achieved through rational design to suppress side reactions and achieve high selectivity.

Based on the above discussions, it can be concluded that the structural characteristics of COFs materials make them potential excellent photocatalysts. A well-designed structure can achieve both suitable energy bands and sufficient active sites, thereby efficiently completing photocatalytic CO_2 reduction reactions.

6 COFs for photocatalytic CO_2 reduction

As mentioned above, many characteristics of COFs enable them to have the ability and potential to match the requirements of photocatalytic CO_2 reduction. Therefore, the application research of COFs in the field of photocatalysis has developed rapidly [68]. This article will introduce the research progress of COFs in the field of photocatalytic CO_2 reduction in recent years in chronological order.

In the research of COFs used in the field of photocatalytic CO_2 reduction, the first issue that needs to be addressed is how to overcome the problem of insufficient catalytic active sites in pure organic materials. Here, we can take advantage of the inherent structural characteristics of COFs to further design and synthesize COFs with efficient active sites. This type of research is also a challenging and attractive topic.

6.1 COFs introduce metal site catalysis

Rhenium complexes are an excellent class of homogeneous CO_2 reduction photocatalysts [69–71]. Cao et al. [72] synthesized a covalent triazine framework (CTF) containing pyridine (py), and anchored $Re(CO)_3Cl$ complex using pyridine nitrogen atoms in the organic framework to obtain a photocatalyst ReCTFpy with CO_2 reduction ability. ReCTFpy has high stability, strong CO_2 adsorption ability, and good photoactivity. Under visible light irradiation, triethanolamine acts as a hole sacrificial agent, and the rate of CO_2 reduction to CO is 353.05 $\mu mol \cdot g^{-1} \cdot h^{-1}$ with high selectivity. Due to the coordination effect of pyridine in ReCTFpy, the leaching of $Re(CO)_3Cl$ can be effectively avoided, resulting in excellent recyclability. Similarly, in 2018, Huang et al. [67] used 2D

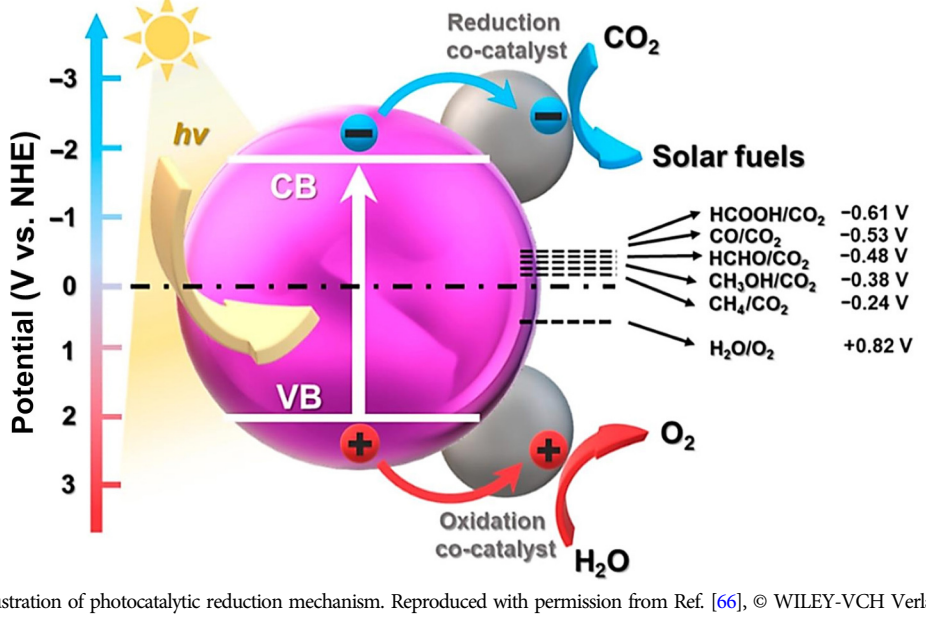

Figure 3 Schematic illustration of photocatalytic reduction mechanism. Reproduced with permission from Ref. [66], © WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim 2018.

triazine conjugated COFs with photoactivity as the basic framework, and introduced trimethyl chloride (bipyridine (bpy)) rhenium complex ($Re(bpy)(CO)_3Cl$) as the CO_2 reduction catalytic active site through post modification method, thus obtaining a heterogeneous COFs photocatalyst that can be used for CO_2 photocatalytic reduction (hereinafter referred to as Re-COF, Fig. 4). The test results show that using triethanolamine (TEOA) as a sacrificial agent, Re-COF can effectively reduce CO_2 to CO (15 $mmol \cdot g^{-1}$) under Xe lamp (cut-off wavelength = 420 nm) irradiation, and has high selectivity (98%) and persistence (> 20 h), with better activity than homogeneous Re catalyst. More importantly, this work combines *in-situ* testing and time-resolved absorption spectroscopy to reveal key intermediate species involved in CO_2 reduction.

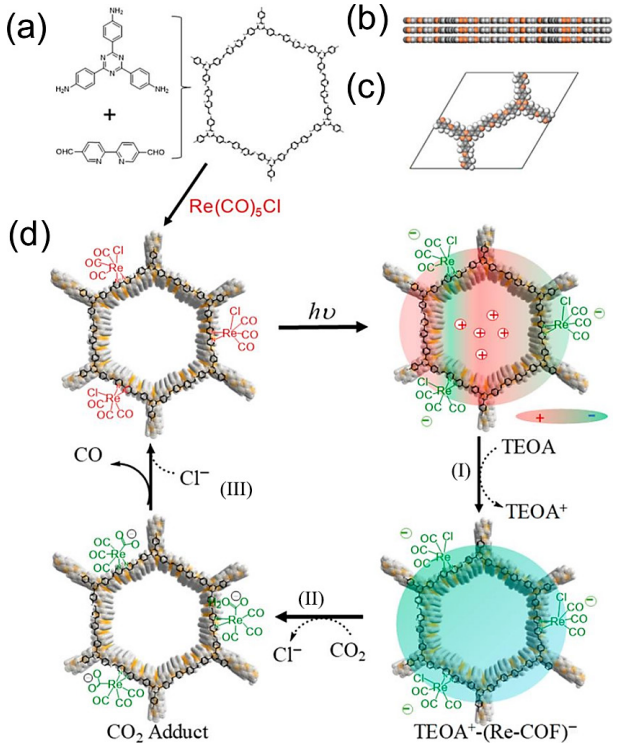

Figure 4 (a) Synthesis of COF, (b) side view of prepared COF, (c) unit cell block of COF and (d) proposed photocatalytic mechanism. Reproduced with permission from Ref. [67], © American Chemical Society 2018.

In addition, through transient electron absorption spectroscopy/X-ray absorption spectroscopy analysis, this work demonstrates the occurrence of rapid intermolecular charge transfer (ICT) from excited COFs to Re components in COFs structures through energy transfer (ET) processes. This work not only demonstrates the potential of COFs as a new generation photocatalyst for solar energy conversion, but also provides unprecedented insights into the mechanism of light driven carbon dioxide reduction. 2,2'-Bipyridine based COF chelates $Ni(ClO_4)_2$ through pyridine units in COF to form NiTpBpy COF containing single atom Ni sites [73]. Using $Ru(bpy)_3Cl_2$ as a photosensitizer, triethanolamine as a hole sacrificial agent, and NiTpBpy COF as a co-catalyst, the rate of CO_2 photocatalytic reduction to CO can reach 811.4 $\mu mol \cdot g^{-1} \cdot h^{-1}$, with a selectivity of 96%. In the NiTpBpy COF system, COF can not only serve as a carrier for CO_2 catalytic sites, but also the ketone groups in its structure promote the stability of intermediates and improve the reduction efficiency of CO_2.

Oxygen atoms can also serve as anchoring sites for metals. Lu et al. [74] synthesized 2,6-diaminoanthraquinone-2,4,6-triformylphloroglucinol (DQTP) COF using 2,6-diaminoanthraquinone as a monomer, in which the interlayer quinone oxygen atoms have appropriate distances, providing a feasible coordination environment for anchoring transition metal catalytic sites. It is interesting that by introducing different metal catalytic sites, CO_2 can be selectively reduced to different products. DQTP COF coordinates with Zn(II), Co(II), and Ni(II) to form DQTP-COF-M (M = Co, Ni, Zn) photocatalyst. Using $Ru(bpy)_3Cl_2$ as a photosensitizer and triethanolamine as a hole sacrificial agent, CO_2 was reduced under visible light. The reduction product of DQTP COF-Co was CO, and the reaction rate was 1020 $\mu mol \cdot g^{-1} \cdot h^{-1}$. When the coordinated metal ion changes to Zn, the reduction product of DQTP COF-Zn is HCOOH, with a reaction rate of 152.5 $\mu mol \cdot g^{-1} \cdot h^{-1}$ and a selectivity greater than 90%. The authors believe that during the reduction process, electron rich coordination environments tend to form CO, while electron deficient coordination environments tend to form HCOOH. Co(II), as a good π-bond donor, is beneficial for converting CO_2 to CO. Zn(II) is a poor π-bond donor, so its reaction product is mainly HCOOH. DQTP COF-Ni, which is between the two, produces almost equal amounts of CO and HCOOH in its photocatalytic CO_2 reduction reaction product.

Metalloporphyrins are excellent catalytic sites for CO_2 reduction, and introducing metalloporphyrins into COF frameworks is also an important strategy for synthesizing CO_2 photocatalytic catalysts. Lu et al. [75] synthesized TTFCOF-Zn ("TTF" stands for tetrathiafulvalene) using electron deficient Zn metalloporphyrin and electron rich tetrathiafulvalene. The porphyrin and tetrathiafulvalene in COF form a donor–acceptor (D–A) structure, which can effectively enhance the separation ability of photogenerated charges. Under visible light irradiation, without adding any sacrificial agents or photosensitizers, TTFCOF-Zn can reduce CO_2 to CO in aqueous solutions with a yield of 0.2055 $\mu mol \cdot g^{-1} \cdot h^{-1}$, but the selectivity can reach 100%, and the catalyst still maintains good catalytic activity after 5 cycles of use.

The morphology of the catalyst also has a significant impact on its performance. Nanosizing block shaped catalysts can expose more catalytic sites, thereby improving catalytic activity. Lu et al. [75] synthesized COF-367-Co nanosheets (NSs) containing porphyrin using 5,10,15,20-tetra (para-aminophenyl) cobalt porphyrin and 4,4'-biphenylaldehyde as monomers 2,4,6-trimethylbenzaldehyde (TBA) can be introduced into the edge of COF-367-Co nanosheets through imine exchange reaction 2,4,6-trimethylbenzene, with high steric hindrance hinders the axial stacking of COF two-dimensional layers promoting the growth of COF nanosheets along the plane direction, resulting in ultra-thin two-dimensional COF nanosheets. Ultra-thin two-dimensional COF nanosheets can effectively expose the catalytic sites of metalloporphyrin cobalt, shortening the distance for photo generated charge carriers to migrate to the catalytic sites. Under visible light irradiation, using $Ru(bpy)_3Cl_2$ as the photosensitizer and ascorbic acid as the hole sacrificial agent, COF-367-Co ultra-thin two-dimensional nanosheets reduce CO_2 to CO at a rate of 10,162 $\mu mol \cdot g^{-1} \cdot h^{-1}$ with a selectivity of 78%.

The above research indicates that metal modification of COFs materials to increase their active sites is an effective way to design COFs for efficient photocatalytic CO_2 reduction catalysts. On this basis, in 2019, Lan et al. [74] reported a series of transition metal modified COFs that can be used for heterogeneous photocatalytic CO_2 reduction reactions. By coordinating and loading different types of open metal active sites onto the COFs structural

framework, a series of DQTP-COF-M (M = Co, Ni, Zn) catalysts were obtained, and it was found that different metal centers have a significant impact on the catalytic activity and selectivity of CO_2 reduction products (CO or formic acid) (Fig. 5). Among them, DQTP-COF-Co has a high CO production of 1.02 × 10^3 μmol·g^{-1}·h^{-1}, while DQTP-COF-Zn has a high selectivity for formic acid generation (90% higher than CO). This work emphasizes the enormous potential of using stable COFs as substrates to anchor metal rich active sites for heterogeneous CO_2 reduction.

The practical application of COFs is not only limited by their catalytic ability, but also by the difficulties in large-scale synthesis that urgently need to be solved. In response to this challenge, in 2019, Liu et al. [56] proposed a scalable and universal bottom-up method, which achieved large-scale (> 100 mg) and high-yield (> 55%) synthesis of ultra-thin (< 2.1 nm) imine based COF NSs (including COF-366 NSs, COF-367 NSs, COF-367-Co NSs, 1,3,5-tris(4-aminophenyl)benzene (TAPB)-1,3,5-tris(4-formylphenyl)benzene (TFPB) COF NSs, and TAPB-4,4'-biphenyldialdehyde (BPDA) COF NSs) (Fig. 6). Among them, ultra-thin COF-367-Co NSs are efficient heterogeneous photocatalysts that promote CO_2-CO conversion, with a CO production rate of up to 10 162 μmol·g^{-1}·h^{-1} and a selectivity of 78% under visible light irradiation in aqueous solution. This material is comparable to the most advanced visible light driven heterogeneous catalysts reported so far.

With the continuous deepening of research in the field of COFs photocatalytic CO_2 reduction, various COFs materials that have been further developed to achieve efficient catalytic performance by increasing the active sites of COFs materials have been reported. In 2019, Wu et al. [76] proposed a CTF based photocatalyst. The nitrogen rich triazine groups in CTF contribute to the adsorption of CO_2, while their periodic pore structure facilitates the regulation of CO_2 and electronic media. In this work, the authors found that fixing cobalt on CTF can significantly improve its photocatalytic activity, reaching 44 times the original CTF activity, and the maximum CO production rate of Co/CTF obtained can reach 50 μmol·g^{-1}·h^{-1}. The results indicate that CTF not only serves as a carrier for active Co species, but also connects photosensitizers with cobalt catalytic sites, thereby effectively transferring photoexcited electrons.

In 2019, Zou et al. [73] designed a COFs material loaded with a single Ni site (NiTpBpy). Under visible light irradiation, the COFs can activate CO_2 molecules while transferring electrons from the photosensitizer to Ni sites to produce CO (Fig. 7). Among them, NiTpBpy showed good activity, with a CO production rate of

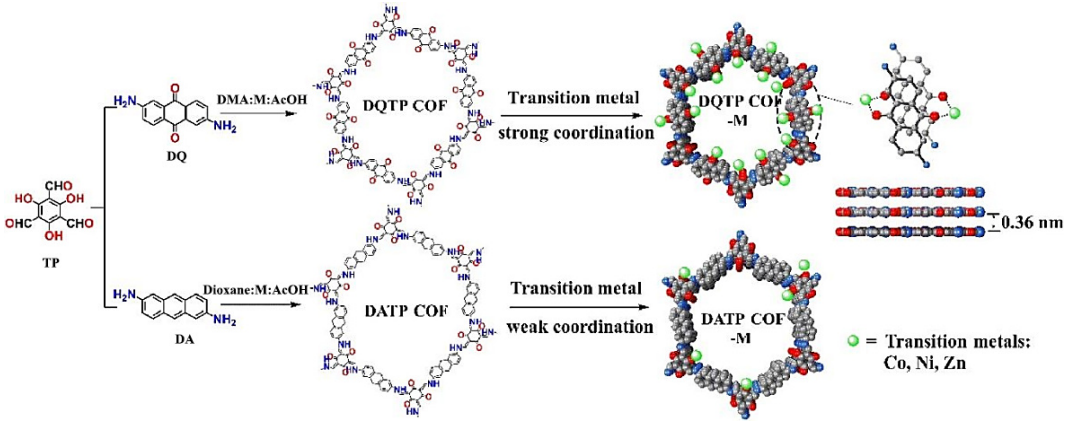

Figure 5 Synthesis of COFs and their depicted geometries. Reproduced with permission from Ref. [74], © Elsevier B.V. 2019.

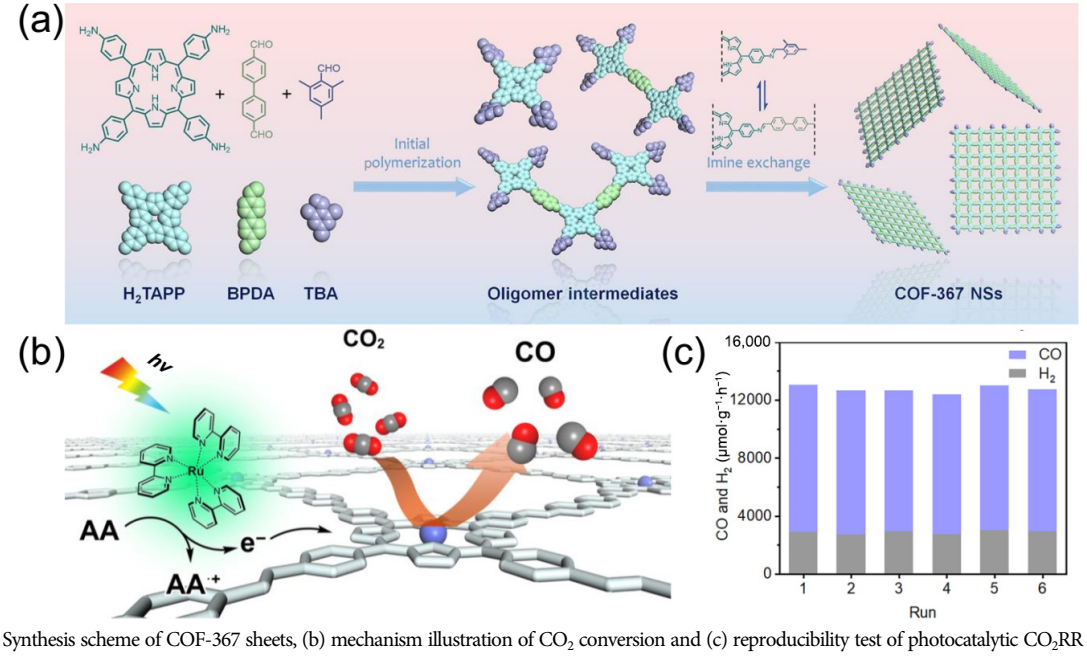

Figure 6 (a) Synthesis scheme of COF-367 sheets, (b) mechanism illustration of CO_2 conversion and (c) reproducibility test of photocatalytic CO_2RR over COF-367. Reproduced with permission from Ref. [56], © American Chemical Society 2019.

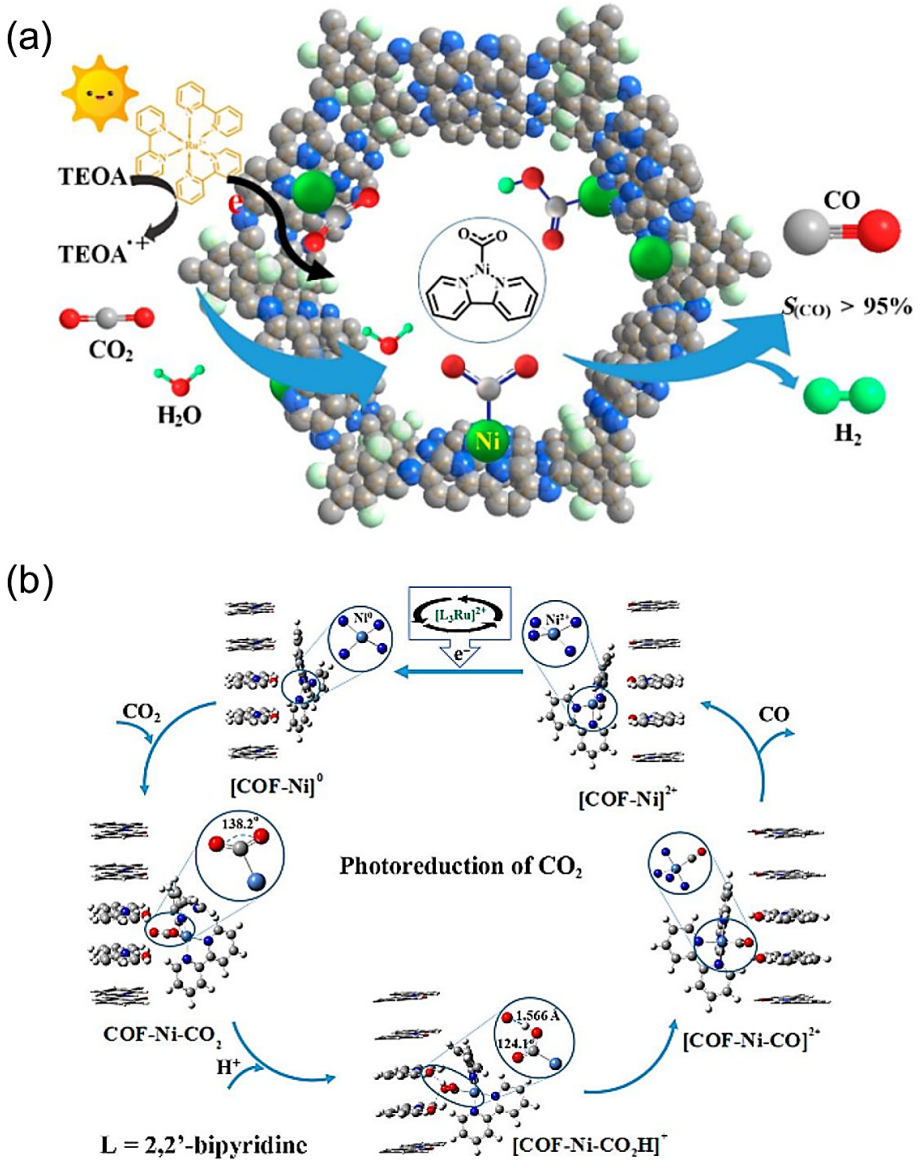

Figure 7 (a) Schematic illustration of photocatalytic CO_2 reduction over NiTpBpy and (b) proposed mechanism of CO_2 reduction over NiTpBpy. Reproduced with permission from Ref. [73], © American Chemical Society 2019.

4057 μmol·g^{-1} obtained in the 5 h reaction, and a CO selectivity of 96%, avoiding the side reaction of hydrogen production. More importantly, when the CO_2 partial pressure is reduced to 0.1 atm, the selectivity of CO products for photocatalysis using these COFs remains at 76%. Theoretical calculations and experimental results indicate that the synergistic effect of single nickel catalytic sites and TpBpy endows these COFs with excellent catalytic activity and selectivity. TpBpy not only adsorbs CO_2 molecules and provides Ni catalytic sites, but also promotes CO_2 activation while inhibiting competitive hydrogen production.

As mentioned earlier, researchers have developed numerous COFs to enhance photocatalytic CO_2 reduction performance by chelating and coordinating single metal sites, but often the binding ability of the bi-pyridine units used is insufficient to stabilize the active metal centers. In the photocatalytic CO_2 reduction process, even in the presence of excess bi-pyridine units, inevitable metal leaching phenomena can be observed. Porphyrin units are an ideal substitute for bi-pyridine units due to their strong chelating and coordinating ability with metal ions.

In 2020, Wang et al. [77] proposed the use of porphyrin tetrastyrene based COF (MP-TPE-COF), where M = H_2, Co, and Ni; TPE = 4, 4', 4'', 4''' -(ethane-1,1,2,2-tetrayl) tetrabenzaldehyde was used for photocatalytic CO_2 reduction (Fig. 8). By utilizing the high performance of metalloporphyrin units in selective adsorption, activation, and conversion of CO_2, as well as carrier separation and electron transfer, CoP-TPE-COF achieved a CO generation rate of 2414 μmol·g^{-1}·h^{-1} under visible light irradiation, with a selectivity of 61% for H_2, while NiP-TPE-COF achieved a CO generation rate of 525 μmol·g^{-1}·h^{-1} with a selectivity of 93%. This work provides molecular level insights into the mechanism of photocatalytic CO_2 reduction and can be extended to various COFs based catalytic materials for solar energy conversion and other applications.

At present, most COFs still rely on photosensitizers and sacrificial agents to achieve their efficient photocatalytic efficiency, which greatly reduces the economic value of COFs as photocatalysts. To solve the above problems, exploratory research on COFs photocatalysts that do not rely on photosensitizers and sacrificial agents has gradually developed. In 2019, Lu et al. [75] synthesized a series of crystalline porphyrin tetrathiafulvalene

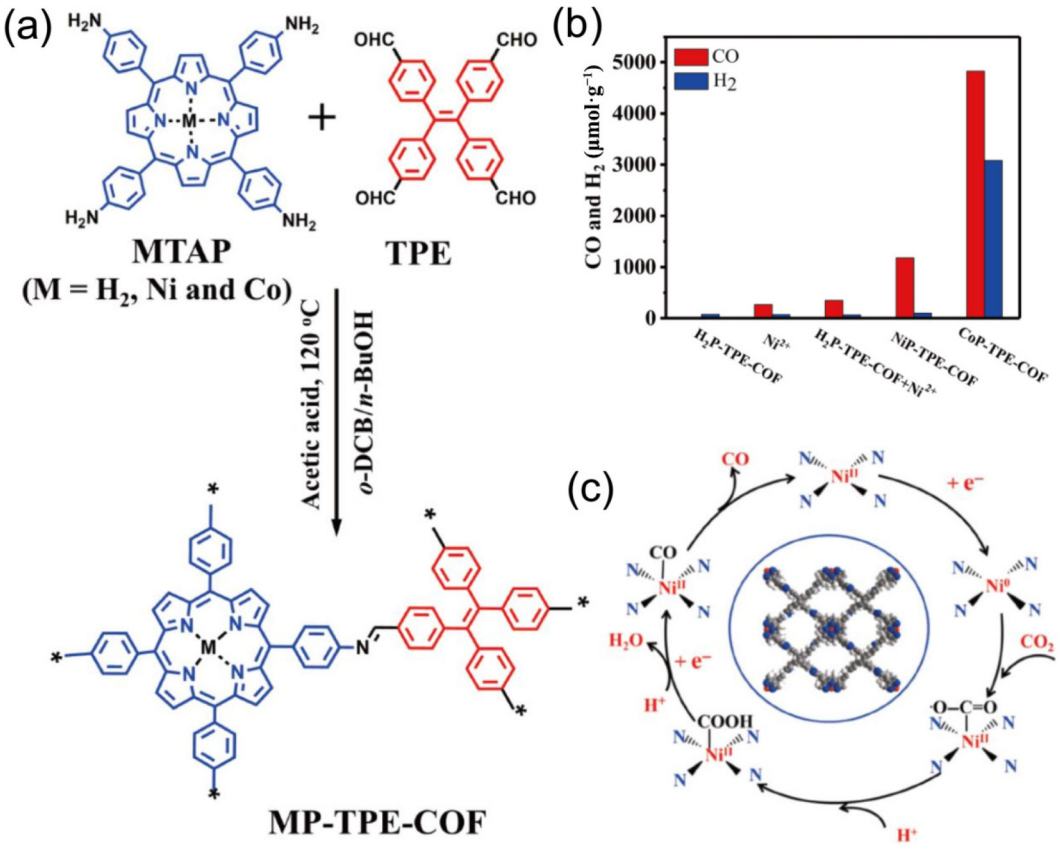

Figure 8 (a) Synthesis of COF, (b) concentration of reduction products against deferent COFs and (c) proposed photocatalytic CO_2 reduction mechanism over prepared COF. Reproduced with permission from Ref. [77], © Science China Press and Springer-Verlag GmbH Germany, part of Springer Nature 2020.

COF materials that can achieve efficient photocatalytic CO_2 reduction without additional photosensitizers, sacrificial agents, and noble metal co catalysts (Fig. 9). The COFs facilitate the transfer of effective photo generated electrons from tetrathiafulvalene to porphyrin via covalent bonds, resulting in the separation of electrons and holes for CO_2 reduction and water oxidation. In addition, by adjusting the band structure of TTCOFs, it was found that the maximum CO production obtained by photocatalytic CO_2 reduction of TTCOF-Zn was 12.33 μmol, with a selectivity of about 100%. At the same time, water was oxidized to oxygen as a sacrificial agent. This work provides a new approach for designing efficient artificial crystalline photocatalysts.

In order to achieve more efficient CO_2 reduction reaction in water, Lan et al. [78] proposed a strategy in 2020 to covalently link COFs with semiconductors, thereby creating a stable organic–inorganic Z-scheme heterojunction for artificial photosynthesis (Fig. 10). Based on this strategy, the project has been combined into a series of COF semiconductor Z-scheme photocatalysts. This type of catalyst combines water oxidation active semiconductors (TiO_2, Bi_2WO_6, α-Fe_2O_3) with CO_2 reduction COFs (COF-316/318), exhibiting high CO_2-CO conversion efficiency (reaching 69.67 $\mu mol \cdot g^{-1} \cdot h^{-1}$ without the addition of photosensitizers and sacrificial agents). This work is the first to achieve covalent bonding of COF/inorganic semiconductor assembly into Z-scheme for artificial photosynthesis.

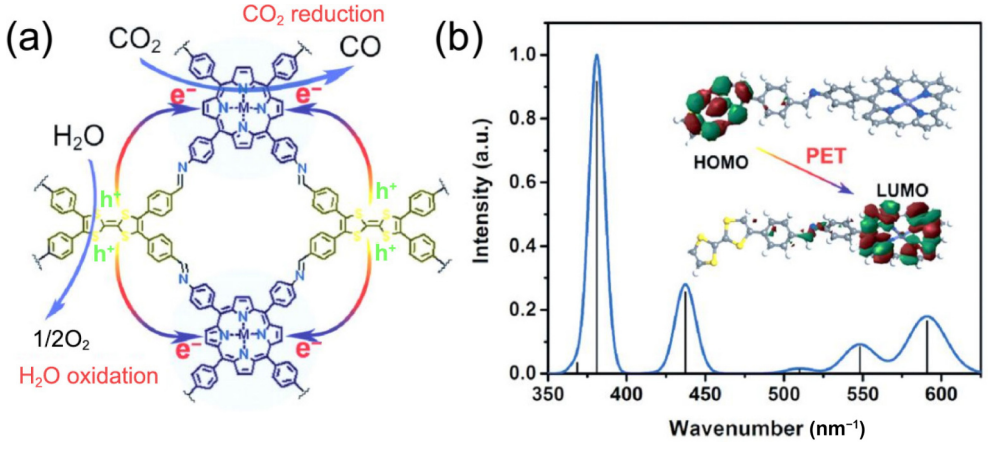

Figure 9 (a) Schematic illustration of CO_2RR mechanism over TTCOF-M (M = 2H, Zn, Ni, Cu) and (b) theoretical simulation ultraviolet/visible (UV/Vis) diffuse reflectance spectroscopy (DRS) inset with photoinduced electron transfer (PET) geometry. Reproduced with permission from Ref. [75], © Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim 2019.

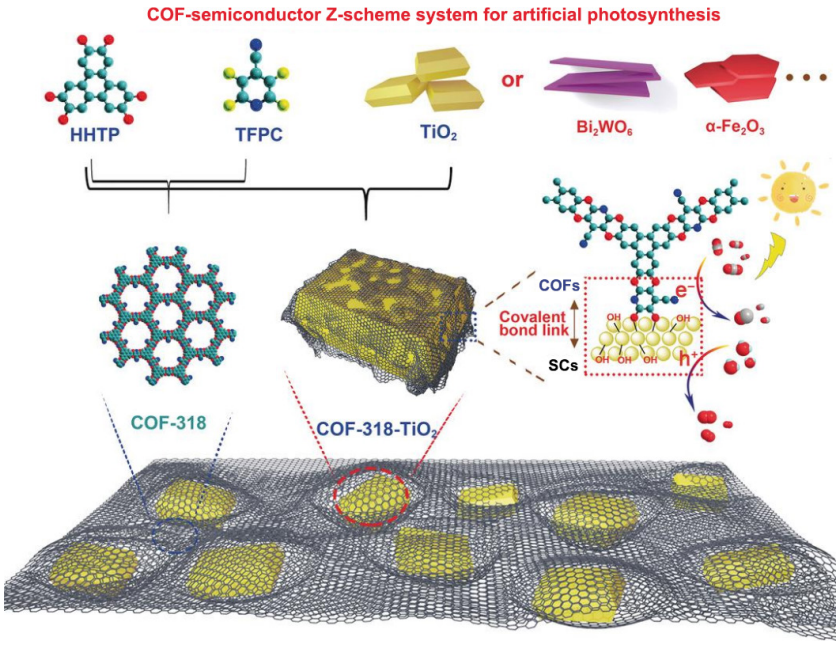

Figure 10 Schematic illustration of synthesis of COF-318 SCs. Reproduced with permission from Ref. [78], © Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim 2020.

Furthermore, Lan's research group [79] first proposed a method of loading polyoxometalates (POMs) into vacant COFs nanopores in 2021 and explored its application in artificial photosynthesis (Fig. 11). Among them, TCOF-POM showed the highest CO yield (37.25 μmol·g^{-1}·h^{-1}). Mechanism studies have shown that CO_2 reduction and H_2O oxidation reactions can occur on POM and COF, respectively, demonstrating the application prospects of COF POMs functional materials in the field of photocatalysis.

Changing the morphology and structure of COFs can also significantly affect their catalytic performance, such as the ultra-thin COF nanosheet structure being advantageous for catalytic reactions. In 2020, Cooper's research group [80] synthesized a series of covalent organic framework nanosheets (CONs) by embedding a single cobalt site and used them to catalyze CO_2 reduction reactions. Among them, a partially fluorinated and cobalt loaded CON produced 10.1 μmol of CO under visible light irradiation for more than 6 h (turnover number (TON) = 28.1), with a selectivity of 76%. Under the presence of iridium photosensitizer and irradiation with 420 nm light, its external quantum efficiency (EQE) reaches 6.6%. In this case, the COFs material itself does not seem to act as a photocatalyst, but rather as a semiconductor carrier that transfers the charge carriers generated in the photosensitizer to the cobalt center, which is the active site. This study found that ultra-thin CONs perform better than their corresponding bulk materials in most cases, indicating that this is a general strategy for improving the photocatalytic activity of COFs materials.

In the field of COFs photocatalytic CO_2 reduction, researchers have found that not only the number of active sites and light absorption capacity have an impact on the photocatalytic performance of COFs materials, but also their crystallinity and porosity cannot be ignored. In 2020, Cooper et al. [81] combined a molecular catalyst, a rhenium complex [Re(bpy)(CO)$_3$Cl], with COF to obtain a heterogeneous catalyst with strong visible light absorption ability and high CO_2 binding affinity. This COF can catalyze the reduction of CO_2 to CO under visible light irradiation, with a CO production rate of 1040 μmol·g^{-1}·h^{-1} and a selectivity of 81%; with the addition of photosensitizer, the CO efflux rate can reach 1400 μmol·g^{-1}·h^{-1}, with a selectivity of 86%. This study indicates that the crystallinity of COFs is beneficial for their photocatalytic performance in the process of carbon dioxide reduction. Crystallinity and porosity seem to be important in these materials, as amorphous, low porosity analogues exhibit almost no photocatalytic activity.

To increase the active sites of COFs, various metal ions are used to modify COFs to improve their photocatalytic performance, but the principles and further development of such methods still need to be explored. The latest research shows that not only the type of metal, but also the spin state of metal ions have an impact on its performance. Figure 12 illustrates the impact of spin state transitions on the photocatalytic performance of COFs, specifically COF-367-Co, as reported by Jiang's group in 2020 [82]. By incorporating Co(II) at the porphyrin center of COF-367-Co and subsequently oxidizing it to Co(III) under ambient conditions, the researchers effectively controlled the spin state of the Co center without altering the framework structure. This manipulation allowed them to investigate how the spin state affects the photocatalytic reduction of CO_2.

The Co(II) spin state (S = 1, 2) in COF-367-Co(II) exhibited moderate activity and selectivity for the reduction of CO_2 to CO and methane. In contrast, the Co(III) spin state (S = 0) in COF-367-Co(III) demonstrated significantly higher activity and selectivity for the production of formic acid, while showing reduced selectivity for CO and methane formation. This indicates that the spin state transition directly influences the pathway of CO_2 reduction. Using density functional theory (DFT) calculations, the research group revealed that COF-367-Co(III) has a higher charge separation efficiency than COF-367-Co(II), a critical factor contributing to its superior photocatalytic activity. These findings suggest that the spin state of the metal center in COFs plays a pivotal role in modulating their photocatalytic performance.

This study not only underscores the importance of spin state manipulation as a novel strategy for enhancing photocatalysis but also represents the first report of its kind. The insights gained provide a foundation for future research into the role of spin states in other COF-based systems.

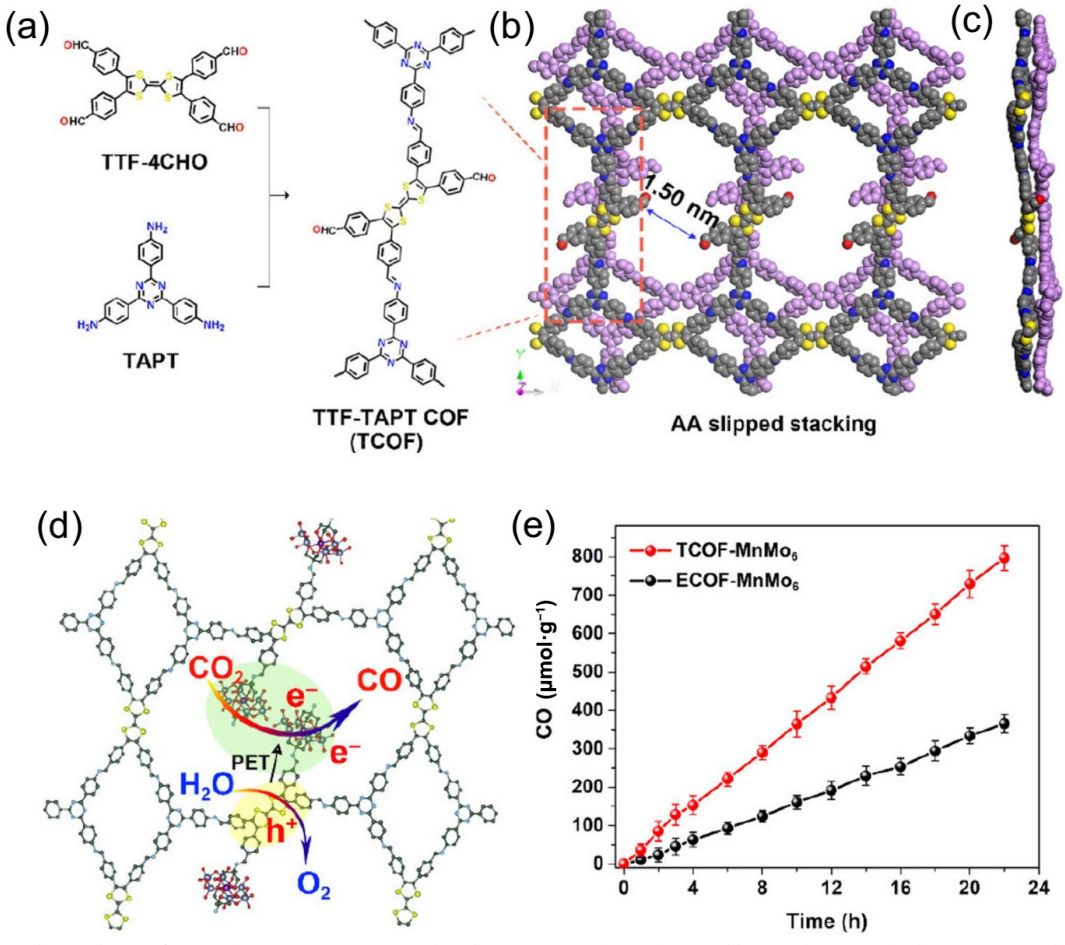

Figure 11 (a) Synthesis scheme of TCOF (TTF-2,4,6-tris(4-aminophenyl)-1,3,5-triazine (TAPT) COF abbreviated as TCOF), (b) tope view and (c) side view of TCOF, (d) schematic illustration and mechanism of CO_2 reduction over TCOF-$MnMo_6$ and (e) CO_2 conversion performance to CO against time intervals. Reproduced with permission from Ref. [79], © American Chemical Society 2022.

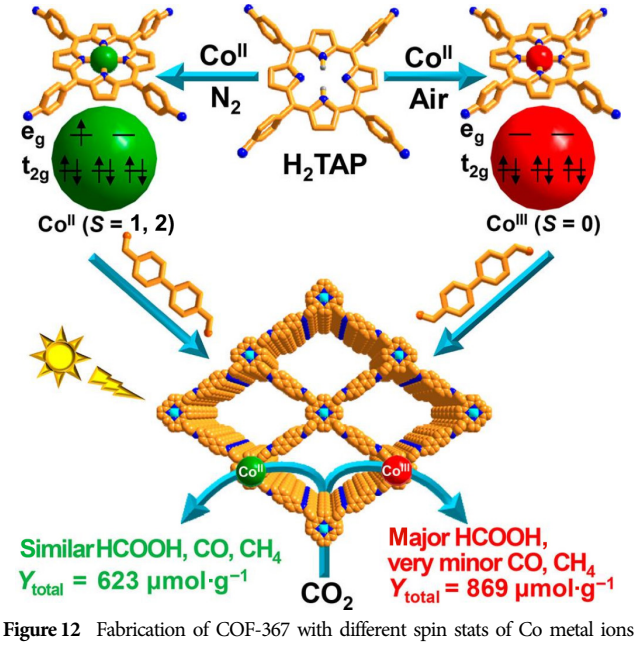

Figure 12 Fabrication of COF-367 with different spin stats of Co metal ions representing different production rates for CO_2RR products. Reproduced with permission from Ref. [82], © American Chemical Society 2020.

6.2 COFs introduce non-metallic site catalysis

In addition to using metals as catalytic sites for CO_2 reduction, nitrogen atoms in the COFs framework can directly serve as CO_2 catalytic sites, which can achieve a completely metal independent heterogeneous photocatalytic system. Zhu et al. [83] synthesized azine-linked 2D COF (ACOF-1) and N_3-COF by condensation of 1,3,5-triaoylbenzene (TFB) and 2,4,6-tris(4-bromophenyl)-1,3,5-triazine (N_3-Ald) with hydrazine, respectively. Through comparative experiments, it was found that the triazine units in COFs not only enhance the light absorption capacity, but also contribute to the adsorption of CO_2 and serve as catalytic sites. The electron deficient triazine in N_3-COF can effectively stabilize the negatively charged intermediates in the catalytic process. N_3-COF can reduce CO_2 to methanol in aqueous solutions under visible light irradiation without using any sacrificial agents, with a reaction rate of 0.57 $\mu mol \cdot g^{-1} \cdot h^{-1}$. Its catalytic activity is higher than that of ACOF-1 without triazine ring.

Heterojunction COFs based on donor acceptor structures can further enhance catalytic activity. To this end, Kong's research group [84] utilized the Schiff base reaction of carbazole triazine based D–A monomers to construct a novel D–A COF with suitable band structure, strong visible light capture ability, and abundant nitrogen sites, namely CT-COF (Fig. 13). In this structure, the carbazole group is electron rich and has good hole transport ability, while the triazine group has a high electron affinity, resulting in overall high electron mobility of COFs. CT-COF, as a non-metallic photocatalyst, can reduce CO_2 to CO by using gaseous water as an electron donor under visible light irradiation and without the assistance of the catalyst. Under the

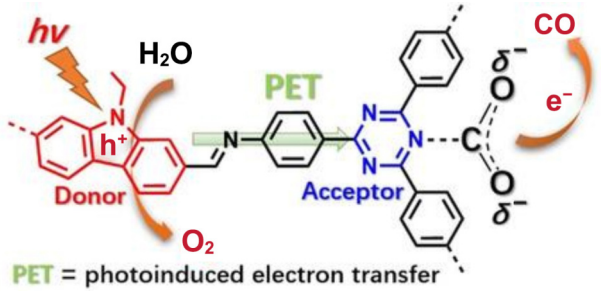

Figure 13 Proposed electron donor and acceptor pathway of photocatalytic COF. Reproduced with permission from Ref. [84], © Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim 2020.

same conditions, the CO production rate of this material (102.7 μmol·g^{-1}·h^{-1}) is 68.5 times that of g-C_3N_4. *In-situ* FT-IR analysis indicates that CT-COF can adsorb and activate carbon dioxide and water molecules, and *COOH species may be a key intermediate. DFT calculations indicate that the nitrogen atom in the triazine ring may be a photocatalytic active site.

The use of COF to form heterojunction structures with inorganic semiconductors can also effectively enhance photocatalytic activity. Lan et al. [78] synthesized COF-318 using 2,3,6,7,11-hexahydroxyphenanthrene and 2,3,5,6-tetrafluoro-4-pyridinonitrile as monomers, and covalently connected it with inorganic semiconductors TiO_2, Bi_2WO_6, and α-Fe_2O_3 to form a Z-type heterojunction catalyst. Both pyridine nitrogen and nitrile nitrogen in monomer pyridine nitrile can serve as CO_2 catalytic sites. Simultaneously utilizing the Z-type heterojunction composed of COF and inorganic semiconductor can effectively improve the separation efficiency of photo generated electrons and holes, and suppress carrier recombination. Under visible light irradiation, COF-318/TiO_2 can reduce CO_2 to CO at a rate of 69.67 μmol·g^{-1}·h^{-1} in aqueous solutions without the addition of other co-catalysts.

Although there have been many reports on the use of COFs photocatalysts to reduce CO_2, the quantum efficiency of photocatalysis is still difficult to compare with other systems, and it is difficult to obtain more valuable hydrocarbon products such as ethane and ethylene through COFs photocatalysis. Table 2 presents the performance data of COFs for photocatalytic CO_2 reduction.

In the development process of COFs photocatalysis, some researchers have also explored new ideas to enhance the photocatalytic performance of COFs, namely, to improve the electron–hole pairs in COFs and simultaneously increase their electron migration rate. The influence of the nano morphology of catalysts on photocatalytic performance has also been extensively studied. In 2021, Lan et al. [85] reported a MOF sacrificial *in-situ* acid etching (MSISAE) strategy, which can continuously synthesize core–shell, yolk shell, and hollow sphere nanocomposites based on COFs by adjusting the decomposition rate of MOF cores (Fig. 14). Among them, the design of egg yolk shells and hollow spheres endows COF materials with more exposed active sites, faster electron migration rates, and stronger light energy utilization efficiency. In the synthesized material, NH_2-MIL-125/TiO_2@COF-366-Ni-OH-acetic acid (HAc), the egg yolk shell material exhibits high photocatalytic CO_2-CO conversion efficiency in gas–solid mode. The MSISAE strategy developed in this study enables precise morphology design and control of multi-component hybrid composite materials based on COFs, paving the way for the development of multifunctional catalytic reactions with powerful superstructures.

On the basis of successfully introducing various single metal ions, the application of bimetallic nanoclusters (NCs) in COFs has also been successful. In 2021, Lu's research group [86] first loaded ultrafine bimetallic PdIn NCs with photosensitive N_3-COF confinement effect, and obtained a series of Pd_xIn_y@N_3-COF composite materials (Fig. 15). The test results indicate that PdIn@N_3-COF can be used for both photocatalytic CO_2 reduction and water oxidation, and has good alcohol production performance. The total yield within 24 h is 798 μmol·g^{-1} (74% methanol, 26% ethanol), which is 9.7 times higher than N_3-COF alone. This is also the first COF based photocatalyst for photocatalytic CO_2 reduction and water oxidation to produce ethanol.

6.3 Hybrid covalent organic framework catalysts

Recent studies have expanded the use of COFs as hosts for nanoparticles (NPs) and carbon dots, exploring their potential to enhance photocatalytic CO_2 reduction. Due to their unique microenvironments, COFs serve as excellent supports for noble metal nanoparticles, which are effective in reducing electron–hole recombination. For example, Zhu and collaborators incorporated varying amounts of Ru NPs into ketoamine-based COF (TpPa-1) and bipyridine-linked COF (TpBpy) via post-synthetic

Table 2 Representing photocatalytic CO_2RR performance of different COF materials

COFs	Co-catalyst	Condition	Light irradiation (nm)	Product (selectivity)	Activity (μmol·g^{-1}·h^{-1})	TON/TOF[a]	References
Re-CTF-py	Re	Solid–gas system	200–1100	CO	353.05	4.8/—	[72]
Re-COF	Re	TEOA/MeCN[b]	> 420	CO (98%)	750	48/—	[67]
Ni-TpBpy-COF	Ni/Ru(bpy)$_3$Cl$_2$	TEOA/MeCN/H_2O	> 420	CO (96%)	811.4	13.62/—	[73]
DQTP-COF-Co	Co/Ru(bpy)$_3$Cl$_2$	TEOA/MeCN	> 420	CO	1020	—/0.55 h^{-1}	[74]
DQTP-COF-Zn	Zn/Ru(bpy)$_3$Cl$_2$	TEOA/MeCN	> 420	HCOOH (90%)	152.5	—/0.08 h^{-1}	[74]
TTCOF-Zn	—	H_2O	420–800	CO (100%)	0.2055	—	[75]
COF-367-Co NSs	Ru(bpy)$_3$Cl$_2$	Ascorbic acid/ 0.1 mol·L^{-1} $KHCO_3$	> 420	CO (78%)	10,162	—	[56]
ACOF-1	—	H_2O	420–800	CH_3OH	0.36	—	[83]
N3-COF	—	H_2O	420–800	CH_3OH	0.57	—	[83]
CT-COF	—	H_2O	> 420	CO (98%)	102.7	—	[84]
COF-318/TiO_2	—	Solid–gas system	380–800	CO	69.67	—	[78]

[a]TOF: turnover frequency. [b]MeCN: acetonitrile.

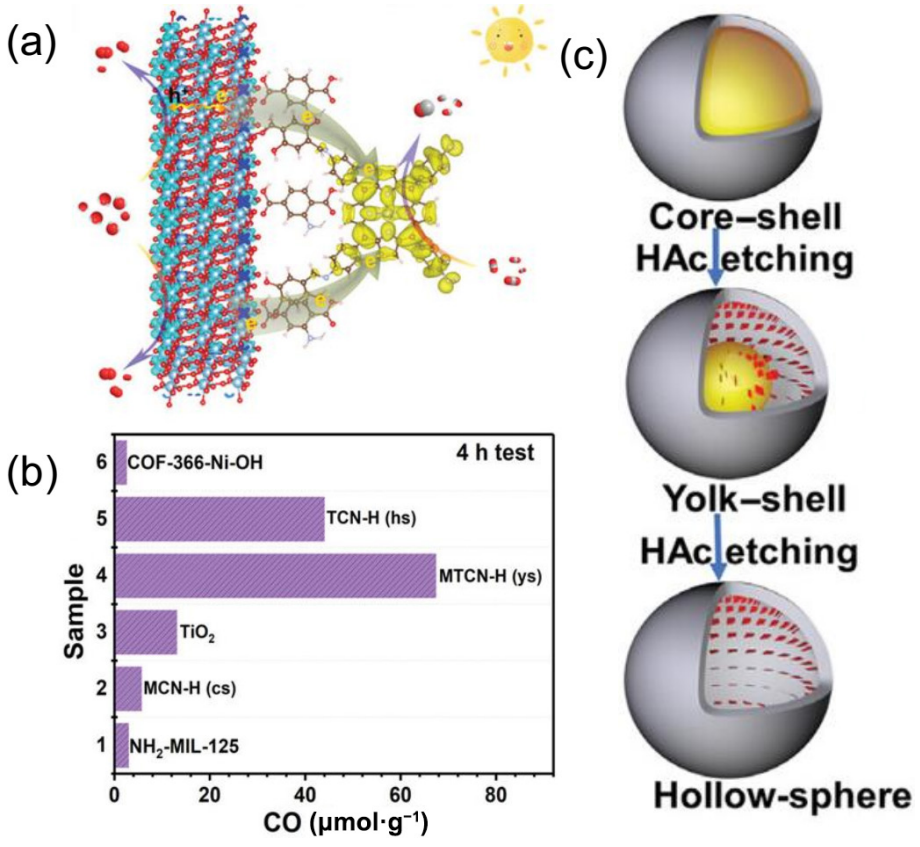

Figure 14 (a) Schematic illustration of CO_2 reduction along with H_2O oxidation, (b) CO_2RR performance of different COF based architectures and (c) COF derived architectures. Reproduced with permission from Ref. [85], © Wiley-VCH GmbH 2021.

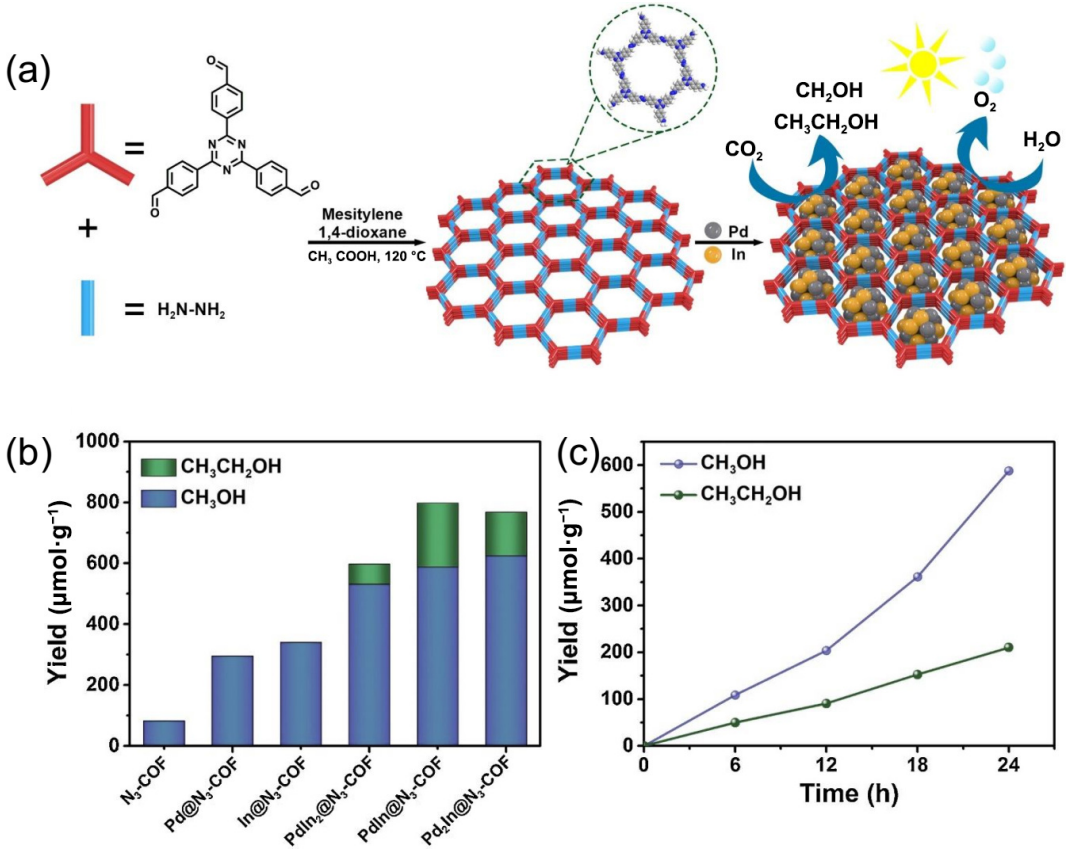

Figure 15 (a) Synthesis scheme of PdIn@N_3-COF, (b) CO_2RR performance of as-prepared indium based COFs and (c) CO_2RR yield against different time intervals. Reproduced with permission from Ref. [86], © Elsevier B.V. 2021.

modifications, resulting in Ru/TpPa-1 and Ru@TpBpy [43, 87]. Ru/TpPa-1 with 3.0 wt.% Ru achieved a peak HCOOH production rate of 108.8 μmol·g_{cat}^{-1}·h^{-1}, while Ru@TpBpy with 0.7 wt.% Ru yielded 172 μmol·g_{cat}^{-1}·h^{-1}, highlighting the importance of COF support properties. Semiconducting materials have also been integrated into COFs to enhance CO_2 reduction efficiency [78, 88]. While physically adsorbed NPs on COFs are less stable and may impact catalyst durability, chemically bonding NPs to COF hosts can improve stability. Lan and colleagues developed a covalently bonded organic–inorganic Z-scheme between semiconductors (TiO_2, Bi_2WO_6, α-Fe_2O_3) and COFs by synthesizing COFs in the presence of semiconductors, achieving a stable system for CO_2 reduction without photosensitizers, sacrificial agents, or co-catalysts. This COF-318-TiO_2 Z-scheme heterojunction produced CO at a rate of 69.67 μmol·g^{-1}·h^{-1}, surpassing physically mixed composites [78]. A similar Z-scheme hybrid of TiO_2 and a metalloporphyrin-block COF showed a CO production rate of 50.5 μmol·g^{-1}·h^{-1}, supporting the advantage of covalent bonding in facilitating charge transfer [78]. In an innovative study, Zhong and colleagues embedded metalloporphyrin-based carbon dots within COF cavities (M-PCD@TD-COF, with M = Ni, Co, or Fe; PCD: porphyrin carbon dots; TD: template-directed) for visible-light-driven CO_2 reduction [89]. This setup provided an advantageous microenvironment for CO_2 adsorption and activation at metalloporphyrin active sites, achieving a 98% selectivity for CO_2-to-CO conversion over H_2 generation. Additionally, these composite catalysts demonstrated high stability, maintaining catalytic performance over five cycles, marking them as promising COF-based materials for future development in photocatalysis. Table 3 provides a summary of the performance of both the aforementioned and recent COF catalysts in photocatalytic CO_2 reduction reactions.

7 Driving forces for CO_2RR

In previous discussions, electrochemical and photocatalytic CO_2 reduction were driven individually by either electrical energy or solar energy. A promising future direction in COF research is to integrate multiple energy sources, such as combining photocatalytic and electrocatalytic methods for CO_2 reduction. In this approach, photon energy can interact with light-responsive electrocatalysts, potentially altering the electrochemical reaction pathways and catalytic performance. Catalysts suited to these hybrid systems must exhibit stability under both photo-irradiation and electrical conditions, possess effective catalytic sites for CO_2 conversion, and show strong light absorption along with efficient photo-electron conversion. Lan et al. developed a series of robust dioxin-linked metallophthalocyanine-based 2D-COFs (MPc-TFPN-COF, where M = Ni, Co, Zn) tailored for these applications [49]. Their study revealed that an external light field could facilitate electron transfer to adsorbed CO_2 on phthalocyanine COFs, thereby enhancing CO_2 reduction efficiency. Quantitative analysis demonstrated that combining light and electrical energy significantly increased both the Faradaic efficiency (FE) for CO and the current density (j_{CO}) across a range of applied potentials (−0.6 to −1.2 V vs. reversible hydrogen electrode (RHE)). Under

Table 3 Summary of the performance of recent COF catalysts in photocatalytic CO_2 reduction

Catalysts	Light source	Wavelength (λ (nm))	Bandgap (eV)	Yield (μmol·g_{cat}^{-1}·h^{-1})	Selectivity	References
TFPG-DAAQ[a]	Blue LED light[b]	445	—	—	—	[90]
COF-367-Co(II)	Xe-lamp	380	1.03	48.6 HCOOH	FE = 96.5%	[82]
COF-367-Co(III)	Xe-lamp	380	1.10	93.00 HCOOH	FE = 97%	[82]
Zn-TTCOF	Visible light	800 ≥ λ ≥ 420	1.49	—	FE = 100%	[75]
COF-367-Co NSs	Xe-lamp	> 420	—	10,162 CO	FE = 78%	[56]
0.7 wt.% Ru@TpBpy	Xe-lamp	800 ≥ λ ≥ 420	—	172 HCOOH	—	[87]
Ru/TpPa-1	Xe-lamp, light filter	350	—	108.8 HCOOH	—	[43]
TpPa-1	Xe-lamp, light filter	350	—	32.4 HCOOH	—	[43]
1.5% TiO_2-INA@CuP-Ph COF[c]	Xe-lamp	—	2.60	50.5 CO	—	[91]
Ni-TpBpy	Visible light	—	—	811.4 CO	FE = 95%	[73]
Ni-PCD@TD-COF	Xe-lamp	> 420	1.69	478 CO	FE = 97%	[89]
COF-318-TiO_2	Simulated sunlight	800 ≥ λ ≥ 380	—	69.67 CO	—	[78]
CTF-BP[d]	Xe-lamp	> 420	—	7.81 CH_4, 4.60 CO	—	[92]
CTF	Xe-lamp	420	2.05	881.3 × 10^3 HCOOH	—	[93]
N3-COF	Xe-lamp	800 ≥ λ ≥ 420	2.60	0.57 CH_3OH	—	[83]
CT-COF	Visible light	> 420	2.04	102.5 CO	FE = 98%	[84]
TpBb-COF	Visible light	380	1.72	89.9 CO	FE = 99%	[94]
TpBD-$(CH_3)_2$[e]	Visible light	800 ≥ λ ≥ 420	2.17	108.3 HCOOH	—	[95]
Re-COF	Xe-lamp	420	—	—	FE = 98%	[67]
Mn-TTA-COF[f]	Xe-lamp	420	—	1700	—	[96]
Re-TpBpy-COF	Xe-lamp	> 390	—	—	—	[97]
Re-Bpy sp^2c-COF	Xe-lamp	> 420	—	1400 CO	FE = 85%	[81]
H-COF-Ni	Visible light	> 420	2.48	2847 CO	FE = 95%	[98]
Co-PI-COF	Xe-lamp	800 ≥ λ ≥ 420	0.56	50 HCOOH	—	[99]

[a]TFPG: 1,3,5-triformylphloroglucinol and DAAQ: 2,6-diaminoanthraquinone. [b]LED: light-emitting diode. [c]INA: isonicotinic. [d]BP: black phosphorus. [e]TpBD-$(CH_3)_2$: ketoenamine-based COFs. [f]TTA: 4,4',4''-(1,3,5-triazine-2,4,6-triyl) trianiline).

light conditions, NiPc-TFPN COF exhibited a rise in j_{CO} from 14.1 to 17.5 mA·cm^{-2} at −0.9 V, while the FE_{CO} approached ~ 100% within the potential range of −0.8 to −0.9 V, with the overpotential for peak FE_{CO} shifting positively by approximately 100 mV. These findings underscore the potential of this approach to enhance the efficiency and sustainability of COF-based catalysts for future applications.

Recent research introduced COFs as a promising support material in a photocatalyst-enzyme hybrid system for CO_2 reduction, providing an alternative strategy for enhanced performance (Fig. 16) [100]. In this study, a mesoporous olefin-linked COF (NKCOF-113) was utilized as a support to co-immobilize formate dehydrogenase (FDH) along with a Rh-based electron mediator. This COF-based catalyst achieved high selectivity in the photocatalytic transformation of CO_2 to formic acid. By incorporating both a metal complex and a biological enzyme into the COF structure, this approach facilitated an efficient cascade of chemical and biological catalysis, underscoring the significant potential of COF materials in CO_2 reduction applications.

8 Summary and future directions

8.1 Summary

In summary, this article systematically summarizes the design and synthesis of new COFs and their composite materials in recent years, as well as the latest research progress in the field of photocatalytic CO_2 reduction. This includes utilizing the structural characteristics of COFs to introduce different metal ions to provide active sites, increasing photosensitive functional groups to improve their utilization of visible light, and further coupling water oxidation with CO_2 reduction to achieve artificial photosynthesis. Based on the summary of the above work, we hope to promote further rapid development in this field. Looking ahead to future research directions, COFs, as a new type of crystalline porous material with high porosity, large surface area, low density, and other characteristics connected by covalent bonds, still have great potential in the field of photocatalytic CO_2 reduction. However, at present, this potential has not been fully realized, and the high performance of COFs catalysis mostly relies on photosensitizers and sacrificial agents, while some implementations that use COFs themselves as photosensitizers and catalysts often only exhibit low catalytic efficiency. Among them, further exploration of introducing suitable photosensitive functional groups to enhance their light absorption ability, embedding metal ions, and even designing bimetallic catalysts based on COFs to improve their internal electron migration rate, exploring new synthesis methods to obtain novel catalyst structures, establishing theoretical models, and exploring their catalytic principles have provided ideas and opened up their prospects for designing and preparing more efficient photocatalytic CO_2 reduction COFs based catalysts. Secondly, utilizing COFs to catalyze the reduction of CO_2 into high-value products such as C_{2+} (ethylene, ethane, propylene, propane, ethanol, acetic acid, etc.) is the next direction of development. In summary, the application research of COFs in the field of photocatalytic CO_2 photoreduction is still in the basic research stage, and further exploration is needed on how to achieve practical applications.

In recent years, research on COFs has achieved certain results, but it is still in a stage of rapid development. At the same time, there are still some challenges in the field of photocatalytic applications: (1) the large-scale and rapid synthesis of COFs with photocatalytic properties. At present, the methods for synthesizing high-quality COFs are cumbersome and time-consuming, which

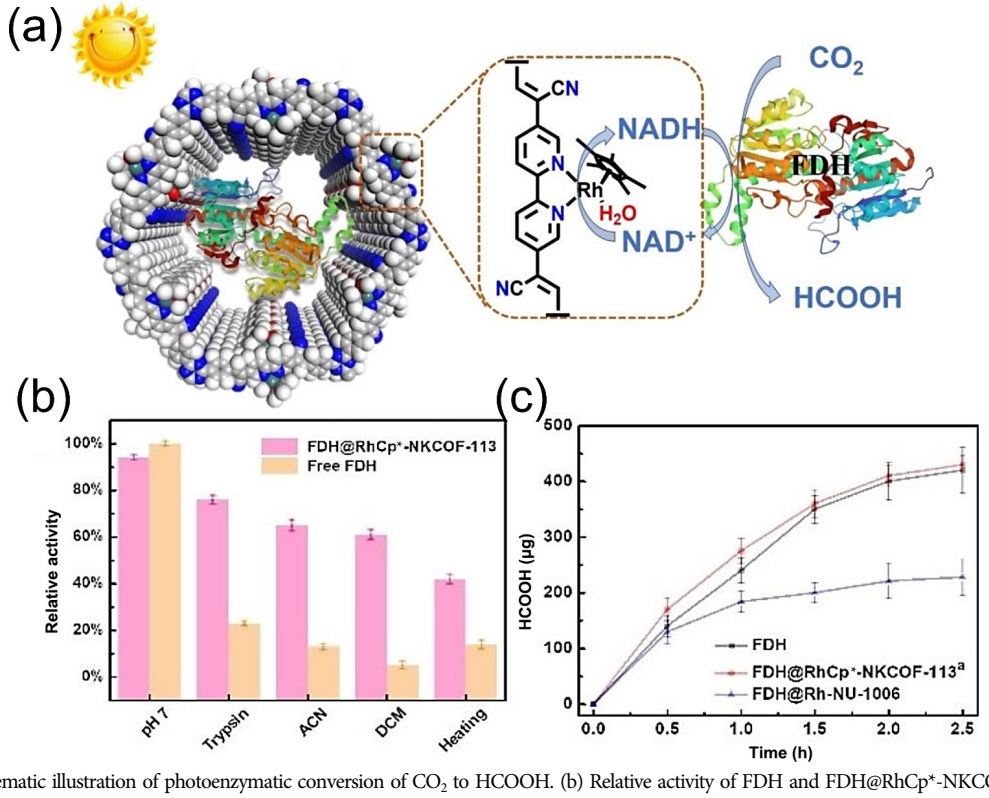

Figure 16 (a) Schematic illustration of photoenzymatic conversion of CO_2 to HCOOH. (b) Relative activity of FDH and FDH@RhCp*-NKCOF-113[a] after thermal treatment. (c) Visible-light-driven artificial photosynthesis of formic acid from CO_2 with different integration systems. Reproduced with permission from Ref. [100], © Wiley-VCH GmbH 2022.

hinders the exploration of their photocatalytic research and the progress of industrial applications; (2) due to the need for further exploration of the photocatalytic mechanism of COFs, designing corresponding COFs photocatalysts based on the requirements of catalytic reactions presents significant challenges; (3) at present, the cyclic use of photocatalytic COFs is limited, and developing highly stable COFs is an important test to expand their application scope; (4) the structure of photoactive COFs is unique. The formation of conjugated COFs skeleton through covalent bonding of absorbing monomers will effectively increase their light absorption, but suitable photoactive monomers are limited. Designing a reasonable photoactive monomer is an effective means to enhance the photosensitivity of COFs; (5) in the process of using COFs for photocatalysis, the vast majority require additional precious metal co-catalysts and sacrificial agents. Designing COFs photocatalysts that do not rely on co-catalysts and sacrificial agents is an important development direction; (6) the preparation of efficient and low-cost COFs photocatalytic devices provides an important approach to solving environmental pollution and energy crisis.

8.2 Future directions

(1) Focus on developing COFs with tailored pore structures, extended conjugation, and optimized functional groups to enhance CO_2 adsorption and activation. (2) Explore strategies such as integrating light-absorbing linkers, introducing heteroatoms, and incorporating plasmonic nanoparticles to improve light absorption and charge dynamics. (3) Investigate strategies to enhance the structural stability of COFs under operational conditions and develop scalable synthesis methods to transition from lab-scale to industrial applications. (4) Combine COFs with other materials like MOFs, metal oxides, or semiconductors to synergistically improve catalytic performance. (5) Study the effects of ionic liquids, deep eutectic solvents, and other innovative media to achieve higher efficiency and selectivity in CO_2 reduction.

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Declaration of conflicting interests

The authors declare no conflicting interests regarding the content of this article.

Data availability

All data needed to support the conclusions in the paper are presented in the manuscript. Additional data related to this paper may be requested from the corresponding author upon request.

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