

Methods to Make Conductive Covalent Organic Frameworks for Electrocatalytic Applications

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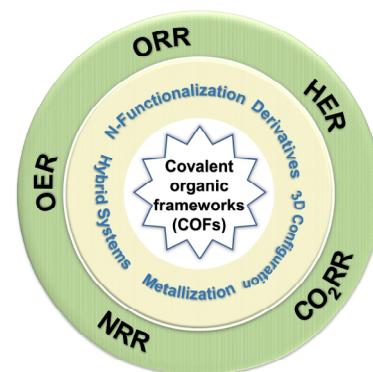
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ABSTRACT Covalent organic frameworks (COFs) represent a new class of crystalline organic polymer materials with the characteristics of high specific surface area, uniform pore distribution, high porosity, low density, devisable chain structures and good structural stability. These collective features play an important role in creating highly efficient electrocatalysts for energy conversion and fuel generation. Recent years have witnessed considerable advances in COF-based electrocatalysts for major electrocatalytic reactions such as oxygen reduction, oxygen evolution, hydrogen evolution, and reduction of carbon dioxide and nitrogen. However, it has been widely accepted that the poor electrical conductivity of most pristine COFs limits the further progress in electrocatalytic field. In this review, recent structural engineering strategies are summarized toward improving the electrical conductivity of COFs for achieving high performance. The researches of conductive COFs and their derivatives are described in detail. The structure-activity relationship between molecular structures of COFs and their electrocatalytic performance is emphasized. Lastly, current challenges and future perspectives on fabricating COFs as promising electrocatalysts are discussed. The purpose of this review is to provide guidelines for the preparation of highly efficient COF-based electrocatalytic materials with a view to replacing the commercially available noble metal-based electrocatalysts.

Keywords: COFs, electrocatalyst, electrocatalytic reactions, engineering strategies, electrical conductivity



1 INTRODUCTION

In the past decades, excessive exploitation and use of non-renewable fossil fuels have resulted in serious environmental pollutions.^[1-3] In addition, with annual increasing demand of energy, the available life of fossil fuels is not optimistic.^[4] Therefore, it is urgent to find clean and sustainable energy, and develop efficient energy storage and conversion technologies. At present, various promising energy conversion technologies have been developed to deal with the raising energy and environmental issues, including fuel cells, metal-air batteries, electrolysis of water (H₂O), carbon dioxide (CO₂) and many other small molecules.^[5-9] In particular, the electrolytic processes exhibit the advantages of simple operation, high efficiency, only requiring mild temperature and pressure, environmental friendliness and easy integrating with electrical grids as driven renewable energy.^[2] While a series of electrochemical reactions involved in the electrolysis are commonly thermodynamically sluggish, it is therefore of primary importance to have a deep understanding of those reactions for facilitating the exploration of efficient electrocatalysts, thereby promoting the efficiency of such energy storage and conversion technology.

Typically, hydrogen (H₂) is one critical energy carrier with high energy density without outputting any contamination. Electrolysis of water for H₂ production consists of cathodic hydrogen evolution reaction (HER) and coupled anodic oxygen evolution reaction (OER), whereas low temperature proton exchange mem-

brane fuel cells consume hydrogen through cathodic oxygen reduction reaction (ORR) and coupled anodic hydrogen oxidation reaction (HOR).^[10-12] Generally, compared with HER and HOR, both processes of OER and ORR exhibit much slower kinetics as they involves four electron (4e⁻) transfer and multiple elemental steps producing reactive oxygen species, which are the main obstacle in corresponding electrochemical energy devices.^[13-17] Therefore, searching for suitable electrocatalysts to facilitate the kinetically determined reactions of OER or ORR is of great importance. Currently, noble metals (e.g., Pt, Ir and Ru) have been used as electrocatalysts for OER and ORR, while is suffering from the scarcity of those noble metals.^[18-20]

Massive consumption of fossil fuels leads to the emission of a large amount of greenhouse gas CO₂, which has caused serious environmental problems.^[21-25] Electrochemical CO₂ reduction reaction (CO₂RR) in aqueous media is potential to reduce the content of atmospheric CO₂, and further produce valuable chemical species.^[26-32] However, there also remain some challenges for wide application of such a technology. Due to its high electronic conjugation, a lot of energy needs to be taken to break the molecular structure of CO₂.^[33-35] The products of CO₂RR are various including CO, CH₃OH, HCOOH, CH₄, C₂H₄, etc. It lacks very efficient strategies to control the electrocatalytic selectivity so as to obtain a specific product, especially for C_{2/2+} species.^[36-40] Additionally, as a competitive reaction, HER occurs simultaneously with CO₂RR because of its close standard reduction potential, which leads to some waste of energy.^[41] Nitrogen

(N₂) is another inert molecule with high thermal stability, and is recognized as the main raw material for ammonia (NH₃) production, which can relieve the dependence on carbon based energy.^[42,43] Compared to conventional Haber-Bosch process for NH₃ production with the disadvantages of high cost, high energy consumption and CO₂ emission,^[44] electrochemical N₂ reduction reaction (NRR) can operate at mild conditions with few CO₂ emission.^[9,45] Similar to the case of CO₂RR, the inherent thermal stability of N₂ and the accompanying competitive HER make the electrochemical NRR have low reaction activity and selectivity, making it difficult to meet the needs of practical applications.^[46,47] In brief, developing highly efficient and selective CO₂RR or NRR electrocatalyst is also of great significance.

COFs represent a new class of crystalline organic polymer materials with periodic frameworks and ordered pores linked by strong covalent bonds.^[48-51] Since COF-1 was first reported in 2005,^[52] these crystalline porous materials have received wide attention. Over the past decade, a series of new COFs have been designed, which enables them multiple functions. Owing to their high specific surface area, uniform pore distribution, high porosity, low density and good structural stability, COFs show various potential applications in sensing, gas adsorption and separation, catalysis, energy storage, photoelectric devices, and so on.^[48,53-57] In this context, well-defined COFs are demonstrated to act as potential electrocatalysts, showing superior electrocatalytic performance in various electrochemical energy conversion related reactions. By comparison with other types of electrocatalysts, COFs have higher adsorption, diffusion, and activation capacity for substrates. Numerous studies have confirmed that reasonably designed molecular catalysts can achieve high electrocatalytic efficiency.^[50] Interestingly, specific structural units and high stability of framework help COFs possess both features of traditional molecular catalysts and heterogeneous catalysts. Therefore, using COFs is expected to bring new opportunities for the design of highly efficient electrocatalysts. It has been accepted that COF-based materials have the following advantages,^[54,58] (1) Different secondary building blocks can accurately control the specific structures and functions of synthesized COFs, thereby providing abundant active sites; (2) To control the second units also enables systematically tuning the active sites for model study of structure-activity relationship and optimization of electrocatalytic performance; (3) Large conjugate in COFs is conducive for electron transport, which is beneficial for many electrocatalytic reactions; (4) Designable and ordered porous structures can control the adsorption and transport of specific substrates of target reactions. However, for electrochemical application, some COFs have insufficient electrical conductivity to degrade performance possibly because of the insufficient electronic conjugation, lacking of appropriate electron relays inside the frameworks or electrical resistance between layers.^[10,59,60] This requires continuous efforts to design high-performed COF-based electrocatalysts via engineering strategies.

Earlier reviews were generally concerned on the design of functional COFs for various applications. However, in this review, we focus on the COFs as efficient electrocatalysts for major and key reactions (ORR, OER, HER, CO₂RR and NRR) emerging in

the energy conversion and storage processes. Note that this review gives a description of the engineering strategies of making conductive and active frameworks based on (a) nitrogen functionalization, (b) metallization, (c) hybridization with carbon supports and (d) pyrolytic derivation. Finally, the challenges and prospects for future direction of development of COFs as electrocatalysts are proposed.

2 STRATEGIES FOR MAKING CONDUCTIVE FRAMEWORKS OF COFS

Nitrogen Functionalization. Metal-free COFs generally have relatively low density of active sites, low redox activity and poor conductivity compared to other common metal-based electrocatalysts. These COFs thus are not very intrinsically active.^[59,61] While to construct metal-free COFs with high surface area improves the accessibility of the active site. In the meantime, to increase N contents of COFs is capable of enhancing the efficiency of electron transfer, as well as redox activity via adding appropriate functional groups.

Recently, a novel nitrogen-rich thiadiazole-based COF (C4-SHz COF) has been obtained via the reaction between 1,3,5-tris-(4-formylphenyl) benzene and 2,5-dihydrazinyl-1,3,4-thiadiazole (Figure 1).^[62] Such a structure presents very high specific surface area (1224 m² g⁻¹), high pore volume (1.12 cc g⁻¹), and abundant active sites. Toward the electrocatalysis of OER, this as-synthesized COF exhibited lower overpotential of 320 mV at current density of 10 mA cm⁻² than the commercial catalyst IrO₂/C. In addition, lower Tafel slope (39 mV dec⁻¹) was achieved in C4-SHz COF than that in IrO₂/C (57 mV dec⁻¹). The boosted activity of C4-SHz COF was further demonstrated by achieving the mass activity of 286 A g⁻¹, specific activity of 0.011 mA cm⁻², electrochemically active surface area (ECSA) of 68.75 cm² and roughness factor of 968.30 due to the abundant surface N atoms, high surface area and fast electron transfer from N atoms to the active C atoms.

In addition, phenazine-linked 2D COF (COF-C₄N) with a highly conjugated basal plane and improved structural stability was achieved by solvothermal reaction of triphenylenehexamine (TPHA) and hexaketocyclohexane (HKH).^[63] Compared to *h*-C₂N with similar structure but less nitrogen content, COF-C₄N

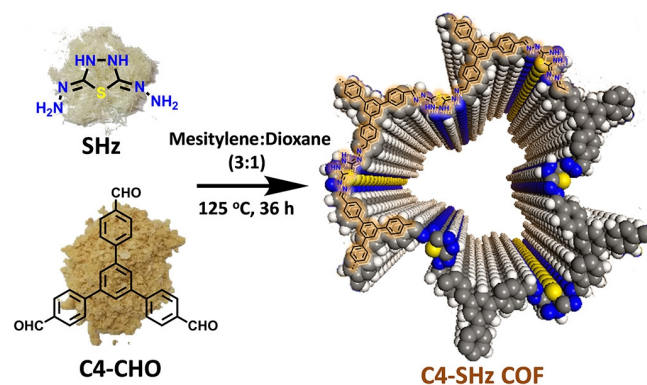


Figure 1. Schematic presentation of the C4-SHz COF proposed structure. Reprinted with permission from ref. [62]. Copyright 2020, American Chemical Society.

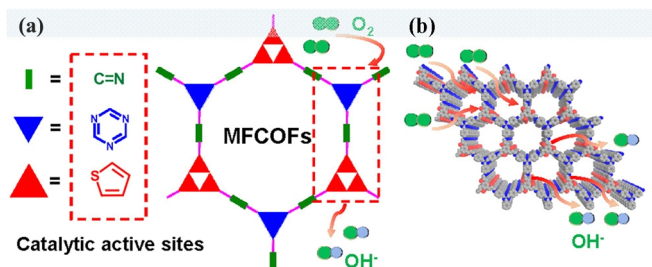


Figure 2. Schematic diagram of the (a) tandem synthetic procedure of the MFCOFs and (b) ORR process induced by BTT-TAT-COF. Reprinted with permission from ref. [64]. Copyright 2022, Elsevier.

achieved lower overpotential of 349 mV at 10 mA cm⁻² (vs. 546 mV for *h*-C₂N), lower Tafel slope of 64 mV dec⁻¹ (vs. 184 mV dec⁻¹ for *h*-C₂N) and larger electrochemical double layer capacitance (Cdl) value of 5.01 mF cm⁻² (vs. 2.03 mF cm⁻² for *h*-C₂N) in OER. Combining density functional theoretical (DFT) calculation with experimental evidence, it revealed that due to more nitrogen contents in COF-C₄N, the band gap of COF-C₄N was smaller than that of *h*-C₂N, which was helpful for lower adsorption free energy of the OOH* intermediate.

Moreover, BTT-TAT-COF was obtained by integrating benzo-[1,2-b':3,4-b':5,6-b'']trithiophene-2,5,8-tricarbaldehyde (BTT) into triazine-COF (TAT) (Figure 2).^[64] Compared to BTT-TAPB-COF based on 1,3,5-tris(4-aminophenyl) benzene and BTT, BTT-TAT-COF exhibited lower overpotential of 1.10 eV (vs. 1.39 eV for BTT-TAPB-COF), lower Tafel slope of 71.0 mV dec⁻¹ (vs. 85.9 mV dec⁻¹ for BTT-TAPB-COF), higher mass activity of 15.23 A g⁻¹ (vs. 9.28 A g⁻¹ for BTT-TAPB-COF) and higher Cdl of 13.7 mF cm⁻² (vs. 9.0 mF cm⁻² for BTT-TAPB-COF) in ORR. These results demonstrated that the incorporation of triazine-N units was helpful for electron transferring and thus enhanced the catalytic performance of BTT-TAT-COF. DFT calculations revealed that the gap between the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) of BTT-TAT-COF (3.27 eV) was lower than that of BTT-TAPB-COF (3.51 eV).

From above examples, it can be known that N-doping can adjust the energy band structure of COFs and polarize with neighboring carbon atoms, thereby enhancing the adsorption of reactive molecules and substrates, regulating their semiconductive properties and expanding their electrochemical capacitance. The high N content can probably result in low BET due to steric hindrance, while low N content would limit their performance in electrocatalysis. Thereafter, reasonably controlling the N content into COF is very necessary.

Metallization. Metal species usually have rich redox states to be more electrochemically active than non-metal species.^[65] To incorporate metal sites into pristine COFs is applied for improved electrocatalytic performance. Mechanistic insights suggest that with incorporation of metal sites, both intrinsic electrocatalytic activity and electron transfer/transport efficiency of COFs are improved.^[66]

Chang et al. connected cobalt porphyrin as secondary

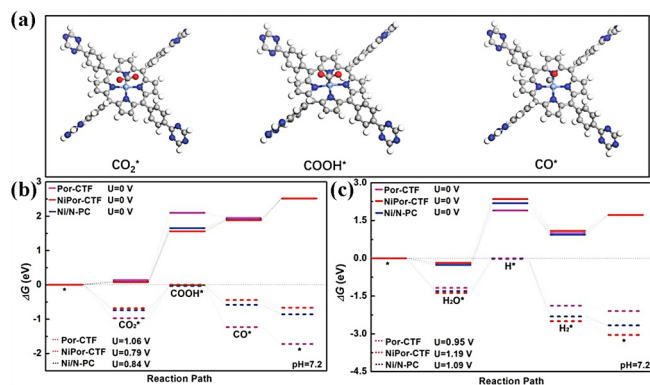


Figure 3. (a) The DFT-calculated representative models: NiPor-CTF with CO₂, COOH, and CO adsorbed. (b) Schematic Gibbs free energy profile for the CO₂RR pathway on the three models with a pH of 7.2. (c) Schematic Gibbs free energy profile for the HER pathway on the three models with a pH of 7.2. Reprinted with permission from ref. [69]. Copyright 2019, Wiley-VCH.

structural units into COF linked by imine bonds for CO₂RR.^[58] Owing to π -conjugate systems and short interlayer distances, the model COF (COF-366-Co) exhibited high carrier mobility and conductivity, whose Faradaic efficiency (FE) reached 90% at -0.67 V versus reversible hydrogen electrode (RHE) for CO₂RR. Additionally, the catalytic performance of cobalt porphyrin can be influenced by introducing different functional groups into the COF structure. In particular, COF-366-F-Co showed improved current density of 65 mA mg⁻¹ than initial COF-366-Co (45 mA mg⁻¹).^[67] The introduction of electronegative groups near porphyrin can induce the porphyrin molecules to be more inclined to absorb electrons. Similarly, iron porphyrin embedded COF represented another classical catalyst for CO₂RR. One example is termed as FeDhaTph-COF, which exhibited a high (turnover frequency) TOF above 600 h⁻¹mol⁻¹ and FE of 80% for CO production.^[68] Porphyrin-COF functionalized with Ni sites (NiPor-CTF) was further developed to show high activity of the conversion reduction of CO₂ into CO with a FE above 90% over the range of -0.6 to -0.9 V (vs. RHE).^[69] Moreover, NiPor-CTF showed higher Cdl (15 mF cm⁻²), lower Tafel slope (120 mV dec⁻¹) and lower charge transfer resistant (93.8 Ω) than Por-CTF (6.3 mF cm⁻², 316 mV dec⁻¹, and 110.2 Ω , respectively). DFT calculations demonstrated that on the Ni sites, the barrier of the transformation from CO₂* to COOH* intermediate was significantly decreased by 0.382 eV compared to 2.334 eV of Por-CTF, which was rate determining for CO₂RR (Figure 3). Meanwhile, the free energy of the side reaction HER for NiPor-CTF was increased to 2.550 eV compared with that for Por-CTF (2.115 eV).

Besides, a porphyrin-based COF (TT-Por(Co)-COF) containing donor-acceptor (D-A) heterojunctions was demonstrated to show higher FE_{CO} of 91.4% at -0.6 V (vs. RHE) and larger partial current density of 7.28 mA cm⁻² at -0.7 V (vs. RHE) for CO production compared with COF-366-Co in aqueous solution.^[70] Thieno[3,2-b]thiophene-2,5-dicarbaldehyde (TT) moieties acting as the electron donor facilitate the electron transfer from them to the Co sites.

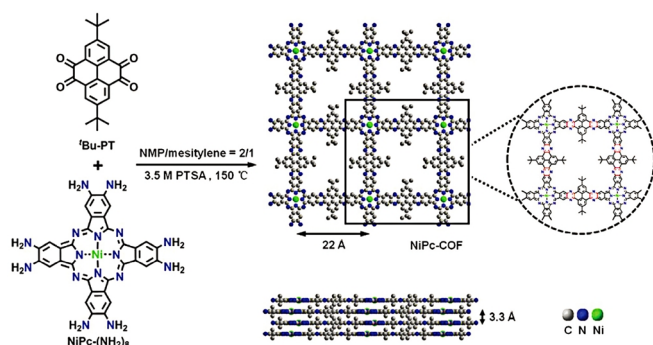


Figure 4. Schematic illustration for the synthesis of 2D conductive NiPc-COF with top and side views of the slipped AA stacking structure. Reprinted with permission from ref. [72]. Copyright 2020, Wiley-VCH.

Moreover, a couple of tetraphenyl-*p*-phenylenediamine (TPPDA) and metalloporphyrin-based COFs (TPPDA-MPor-COFs, M = Co and Ni) were applied towards CO₂RR.^[71] The as-synthesized TPPDA-CoPor-COF showed high FEs of 87-90% ranging from -0.6 to -0.9 V (vs. RHE) for CO production, while TPPDA-NiPor-COF showed lower FE_{CO} (60-76% in -0.7 to -0.9 V). Note that exfoliated TPPDA-CoPor-COF nanosheets (TPPDA-CoPor-COF-NSs) showed even much better electrocatalytic performance with FE of CO production above 90% over a wider potential range (-0.7 to -0.9 V) and maximum *j*_{CO} up to 29.2 mA cm⁻² at -1.0 V. DFT calculations indicated that TPPDA-CoPor-COF exhibited higher LUMO level relative to the CoPor monomer (-2.29 eV vs. -2.42 eV), suggesting the higher reducibility of TPPDA-CoPor-COF with the integration of TPPDA block.

Apart from metalloporphyrins, complexes of metalophthalocyanine (MPc) have also been recognized as a type of second structural unit for constructing electrocatalytically active metalized COFs. For instance, a 2D Ni-phthalocyanine-based COF (NiPc-COF) was synthesized for highly efficient CO₂RR (Figure 4).^[72] The MPc clearly has higher conjugated degree than the above porphyrin. Correspondingly, the derived COFs are more conjugated to exhibit improved intrinsic conductivity. This makes metal sites very redox active and effectively involved into the electrochemical reactions. As a result, in an aqueous solution, the as-obtained 2D NiPc-COF exhibited very high FE for CO production (> 93%) ranging from -0.6 to -1.1 V (vs. RHE). Ni-N₄ structures were considered as active sites for CO₂RR and the covalent pyrazine linkage was critical, as it endowed the resulting framework with stability and conductivity. After making 2D COF into nanosheets, the maximum FE of the 2D NiPc-COF nanosheets is as high as 99.1% at -0.9 V with the partial current density up to 35 mA cm⁻² at -1.1 V.

Metal sites anchored in phthalocyanines-pyrazine-COFs exhibited multifunction for catalyzing HER, OER and ORR, attributing to a synergistic effect between metal sites and COFs skeletons where the nitrogen in pyrazines is highly active for HER, while the transition metals (TM) and phthalocyanines are active for the ORR/OER.^[73] Particularly, Mn- and Cr-COFs were deemed to have extremely low overpotentials of -0.014 V/0.44 V/0.31 V and -0.239 V/0.35 V/0.29 V for HER/OER/ORR, re-

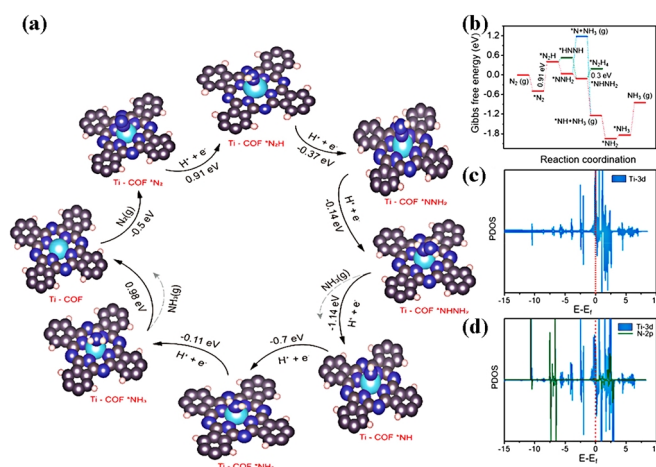


Figure 5. (a) Schematic diagram of a possible reaction mechanism for electrochemical reduction of N₂ to NH₃ on Ti-COF. (b) Free energy diagrams of possible N₂ fixation pathways on Ti-COF. (c) PDOS of Ti(3d) before N₂ adsorption on Ti-COF. (d) PDOS of Ti(3d) and *N₂(2p) after N₂ adsorption on Ti-COF. Reprinted with permission from ref. [75]. Copyright 2022, American Chemical Society.

spectively, which were comparable or even superior to those of the state-of-the-art noble catalysts. Besides, toward the NRR application, 2D metal-based COFs were constructed by linking octaamino-derived TM-phthalocyanine with pyrenetetraone.^[74] Among all these metal-based COFs, the Mo sites exhibited the highest electrocatalytic performance by affording a very low overpotential of 0.16 V for NH₃ production because the Mo based COF exhibited excellent electrical conductivity, large spin moment on the Mo sites and appropriate adsorption capacity toward N₂.

Moreover, it was demonstrated that the introduction of ordered N-coordinated metal sites into a quasi-phthalocyanine conjugated COF can further promote the NRR performance.^[75] On the abundant N-coordinated metal sites, the activation of inert N₂ molecule could be enhanced with suppressing the competitive HER. Among Cu-COF, Co-COF and the pristine COF, Ti-COF possessed the highest electrocatalytic activity and selectivity with a high NH₃ yield of 26.89 μg h⁻¹ mg_{cat}⁻¹ and a FE of 34.62%. Importantly, the Ti-COF showed much inferior catalytic activity for HER with a much higher overpotential than other COFs. DFT calculations verified that the reduced energy barrier on Ti center was beneficial for the activation of N₂ and N₂ derived intermediates (Figure 5).

Cobalt-pyrimidine-modified COF (Co@COF-Pyr) was designed to exhibit remarkable performance for electrocatalytic OER with overpotential of 450 mV at 10 mA cm⁻² in 1 M KOH.^[76] Notably, due to its uniformly dispersed cobalt sites on the surface of COF, Co@COF-Pyr exhibited higher TOF of Co@COF-Pyr, 0.1 s⁻¹, at the overpotential of 370 mV than most reported OER catalysts. The as-prepared COF also possessed excellent stability where the performance can be remained after 1000 cyclic voltammetry sweeps. Moreover, a tetrazole-functionalized β-ketoenamine-linked COF anchoring cobalt ion (COF-TpDb-TZ-

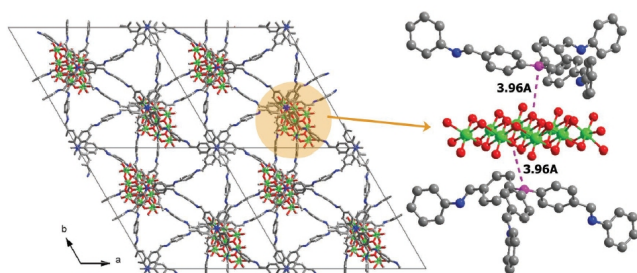


Figure 6. DFT-optimized model structure of a $\text{Ni}(\text{OH})_2$ sheet within the COF. Reprinted with permission from ref. [79]. Copyright 2016, Wiley-VCH.

Co) displayed a higher OER activity by a lower overpotential of 390 mV at 10 mA cm^{-2} compared to the above pristine COF.^[77] Distinctly, the Cdl and electrochemically active surface area of COF-TpDb-TZ-Co were 1.74 mF cm^{-2} and 43.5 cm^2 , respectively. A composite consisting of metallic Ni_3N nanoparticles and benzimidazole COF was reported as an excellent OER electrocatalyst with a near-record low overpotential of 230 mV at 10 mA cm^{-2} , which was attributed to some synergistic effects between the above two components.^[78] Furthermore, the ECSA and Cdl were estimated to be 1.21 cm^2 and $3.63 \times 10^{-5} \text{ F cm}^{-2}$ for the composite, respectively. DFT calculations revealed that the COF can confine the Ni_3N nanoparticles, and thus a low band gap character (1.49 eV) can be obtained due to the synergy between the conductive Ni_3N nanoparticles and the π -conjugated COF. This allowed good electron transport within the periodic structure of COF, making the loaded Ni_3N nanoparticles highly accessible.

It has been accepted that traditional COFs are made from rigid, planar aromatic building blocks with π -stacking to form stable porous materials. Distinctively, a COF was synthesized based on highly flexible tetrahedral sp^3 N atoms, and was applied for electrocatalytic water splitting.^[79] The existence of sp^3 N atoms enabled the structure to generate mesopores to confine very small ($< 2 \text{ nm}$) $\text{Co}_x\text{Ni}_y(\text{OH})_2$ NPs. This composite showed exceptional activity toward OER by affording an overpotential of 258 mV at 10 mA cm^{-2} , as well as outstanding kinetics of Tafel slope of 38.9 mV dec^{-1} . The part of $\text{Ni}(\text{OH})_2$ NPs of the composite was claimed as the active sites, and the corresponding DFT calculations indicated that the $\text{Ni}(\text{OH})_2$ NPs was sandwiched between the two sp^3 N atoms of neighboring layers (Figure 6). This possibly resulted in a synergistic interaction between the support and nanoparticle, and enhanced the OER performance.

Cu-Tph-COF-Dct, functionalized by 2,4-diamino-6-cholo-1,3,5-triazine (Dct), was constructed as a CO_2RR electrocatalyst.^[80] The obtained Cu-Tph-COF-Dct showed superior FE toward CH_4 production ($\sim 80\%$) with a very large current density of 220.0 mA cm^{-2} at -0.9 V (vs. RHE). The FE was almost two-folds higher than the case of the unmodified COF. The corresponding DFT calculations revealed that such significantly boosted performance can be attributed to the immobilized Dct groups. The presence of Dct clearly strengthened the adsorption and activation of CO_2 on the Cu based active sites, and they further enriched the CO concentration around the Cu sites during electrocatalysis, which endowed an enhanced catalytic activity towards

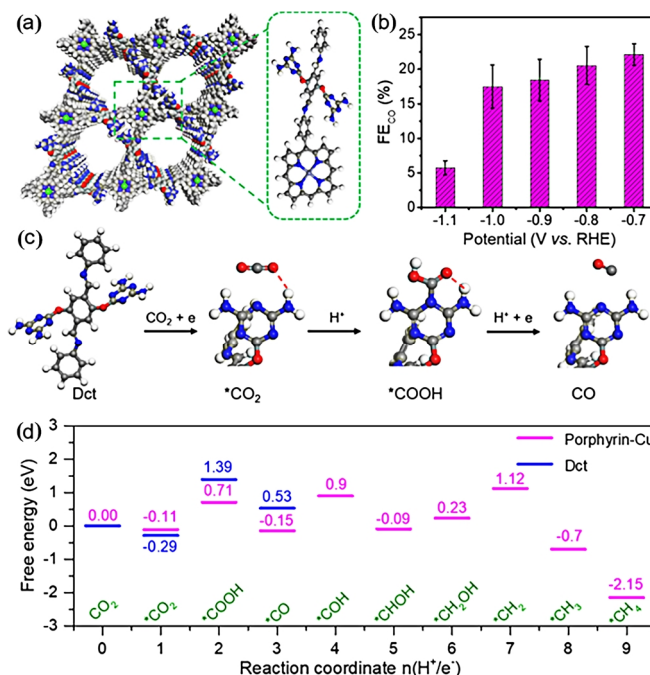


Figure 7. Mechanism and DFT calculations. (a) Schematic diagram of DFT calculation units. (b) FE for CO recorded at different potentials on Tph-COF-Dct. (c) The CO_2 -to-CO conversion reactive pathway and intermediate architectures over Dct molecule of Cu@Tph@COF@Dct . (d) Free energy profiles for CO_2 -to-CO and CO_2 -to- CH_4 reaction pathway on Dct and porphyrin-Cu, respectively. Reprinted with permission from ref. [81]. Copyright 2021, Wiley-VCH.

CH_4 production (Figure 7). A Ni site decorated COF (Ni@COF-TPP-CB[6]) was constructed by clicking perpropargyloxy cucurbit[6]uril (CB[6]) to tetraphenylporphyrin (TPP-4 N_3).^[81] It claimed that the free carbonyl groups of CB[6] can coordinate with water molecules and facilitate the HER reaction. Notably, 12%Ni@COF-TPP-CB[6] catalyst exhibited good durability for HER and produced $18.7 \text{ mmol g}^{-1} \text{ h}^{-1}$ of H_2 at FE of 85%.

To design bifunctional COFs electrocatalysts both effective for ORR and OER is meaningful for metal-air batteries recently emerged. For the purpose, Co nanoparticles (NPs) were incorporated into pyridine-linked triazine COF (Co NP-PTCOF) to show the bifunctions in the alkaline condition.^[82] As for ORR, CoNP-PTCOF exhibited an overpotential of 0.45 V (vs. RHE) at 10 mA cm^{-2} (E_{10}) in OER, which is comparable to that of commercial RuO_2 (0.4 V). Besides, the E_{10} value of CoNP-PTCOF was much lower than that of PTCOF ($E_{10} = 0.6 \text{ V}$). Moreover, CoNP-PTCOF showed a much larger ECSA than PTCOF, Pt/C, and RuO_2 . A combination of experimental evidence and DFT calculations indicated that charge transfer occurred from the Co NP to the carbon framework. It thus facilitated the adsorption and desorption of oxygen intermediates on the Co based active sites, resulting in the p -band center of CoNP-PTCOF downshift.

Bimetallic polyphthalocyanine COFs were constructed based on dioxin linking, which were realized through a nucleophilic aromatic substitution between octahydroxylphthalocyanine and

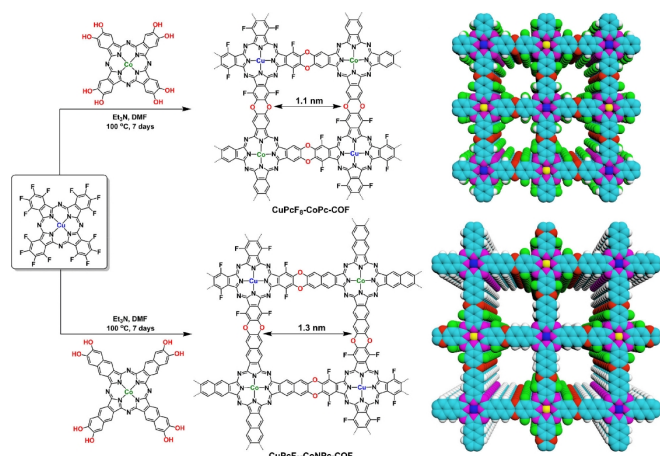


Figure 8. Schematic representation for the synthesis of CuPcF₈-CoPc-COF and CuPcF₈-CoNPc-COF under typical solvothermal conditions. Reprinted with permission from ref. [83]. Copyright 2021, American Chemical Society.

hexadecafluorophthalocyanine (Figure 8).^[83] Note that CuPcF₈-CoNPc-COF showed a faradaic efficiency of 97% for electrocatalytic CO₂ to CO and an exceptionally high turnover frequency of 2.87 s⁻¹, which constituted the new record values for COF-based CO₂RR electrocatalysts. The excellent catalytic performance can be attributed to its more hydrophobic surfaces, high porosity and electrical conductivity.

Taking the advantage of the high specific surface areas, COFs are ideal to load noble metals serving as efficient active sites, which can decrease the cost of electrocatalysts. For instance, Ru@COF-1 was prepared by the complexation of triazine-cored sp² C atoms conjugated COFs with Ru ions (Figure 9),^[84] and was applied for the electrocatalysis of HER. Because the triazine moieties of COF-1 can be protonated to enhance the conductivity of electrocatalyst, the overpotential on Ru@COF-1 was about 200 mV at 10 mA cm⁻², which is lower than that of pure RuCl₃ (260 mV at 10 mA cm⁻²). After 1000 CV cycles, the HER performance of Ru@COF-1 was remained, which was ascribed to the structural stability of sp² C atoms conjugated COF-1 and strong coordinating bonds between COF-1 and Ru ions. DFT calculations showed that some Ru-N₂Cl₂ moieties contained in Ru@COF-1 are the major contributors to HER performance.

In addition, COF-2,2'-bpy-Re was prepared by the treatment of COF-2,2'-bpy (2,2'-bpy-5,5'-diamine as a building block) with Re(CO)₅Cl via a post-metalation synthetic route.^[85] Toward CO₂RR, high FE_{CO} of 81% at -2.8 V (vs. RHE) was achieved by such a modified COF. Moreover, COF-bpyTPP was obtained from free-base porphyrin and bipyridine-dialdehyde via solvothermal method, and then was applied to support Pt NPs (6.09 wt%) with an average size of 2.95 nm. It showed superior HER performance to the commercial 10 wt% Pt/C in the alkaline conditions,^[86] producing 13 times more amount of hydrogen gas at the same potentials with almost 100% FE.

The introduction of metals can accelerate electron transport and enhance adsorption of reactive molecules for COFs, thus

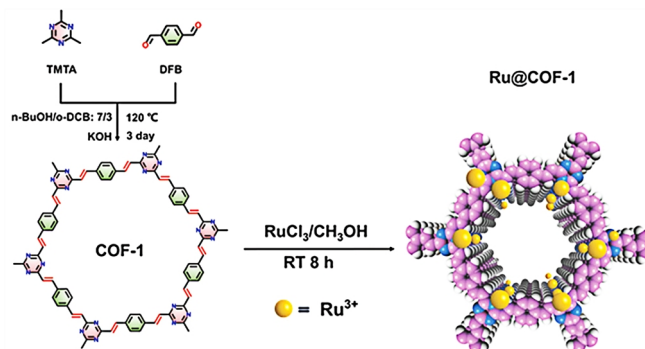


Figure 9. Synthetic routes to COF-1 and Ru@COF-1. Reprinted with permission from ref. [84]. Copyright 2022, Wiley-VCH.

enhancing their conductivity and promoting their catalytic performance. However, the synthesis of metal-COFs was mainly based on metalloporphyrins-, metallophthalocyanine- and post-treatment. Therefore, developing COFs based on new metal building blocks is urgent.

Hybridization with Carbon Supports. As stated above, the efficiency of interfacial electron transfer is one of the most parameters to determine the kinetics of electrochemical reactions. However, most pristine COFs have poor electron conductivity due to their relatively wide band gaps compared to the common carbon-based conductors.^[87] It mainly limits the interfacial electron transfer. To address the issue, those pristine COFs simply have hybridization with highly conductive carbonaceous materials, such as graphene and carbon nanotubes.^[88] It has been accepted that such carbonaceous materials can have strong π - π interaction with the pristine COFs. It thus results in clear electron donating-accepting behavior with COFs commonly functioning as acceptors. This can not only improve the electron transfer ability of COFs, but also tune the electronic structures of COFs to improve their intrinsic activities for certain reactions.^[89-91]

For example, multiwalled carbon nanotubes (MWCNTs) were served to support multilayer covalent cobalt porphyrin framework to show high OER activity.^[88] The resultant (CoP)_n-MWCNTs achieved 1.0 mA cm⁻² with an applied potential of 290 mV in an alkaline solution of pH 13.6. For comparison, the mixture of cobalt porphyrin and MWCNTs required a higher overpotential of 350 mV. Moreover, (CoP)_n-MWCNTs exhibited a Tafel slope of 60.8 mV dec⁻¹ in 1.0 M KOH, which was a very low value for molecular OER catalysts. Similarly, for the CO₂RR application, another MWCNT-Por-COF composite was prepared by mixing the reaction system of Por-COF with quantitative NH₂-MWCNT (Figure 10).^[92] The obtained composite possessed covalent bonds between MWCNT and Por-COF, and was further coordinated with transition metals. Note that the covalently bonded MWCNT-Por-COF-Co exhibited higher FE_{CO} (99.3%) at -0.6 V (vs. RHE) than non-covalently connected MWCNT-Por-COF-Co (76.8%) and the mixture of NH₂-MWCNT and Por-COF-Co (46.3%). In addition, MWCNT-Por-COF-Co displayed much higher current density of 18.77 mA cm⁻² than Por-COF-Co (0.05 mA cm⁻²) with its Tafel slope calculated to be 319 mV dec⁻¹. This

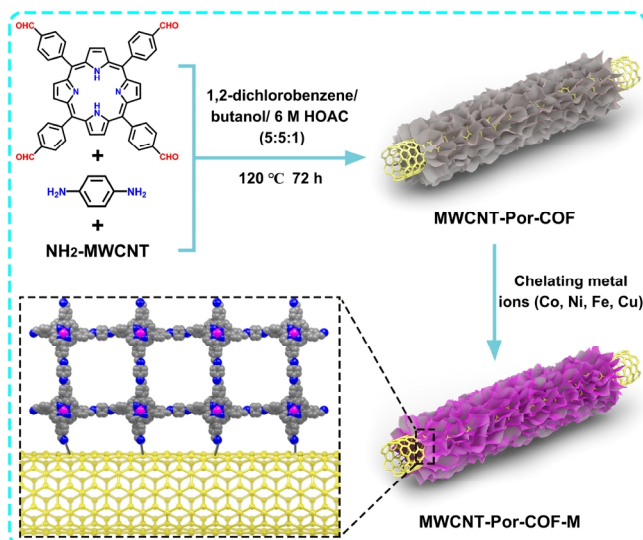


Figure 10. Schematic diagram of the synthetic process of MWCNT-Por-COF-M (M: Co, Ni, Fe, Cu) composite materials. Re-printed with permission from ref. [92]. Copyright 2022, Elsevier.

superior performance was due to that the existence of covalent connection can facilitate the electron transfer from MWCNT to the porphyrin plane of Por-COF-Co. Moreover, COF-366-(OMe)₂-Co@CNT was prepared by an assembly of Co(TAPP) and 2,5-dimethoxyterephthalaldehyde in the presence of amino-functionalized CNTs (Figure 11).^[93] The COF-366-(OMe)₂-Co@CNT exhibited higher FE_{CO} of 94% at -0.68 V (vs. RHE) than COF-366-Co@CNT (92%) and COF-366-Co (87%) due to its higher ability for electron transfer. In addition, it displayed smaller Tafel slope of 190 mV dec⁻¹ and larger Cdl value of 23 mF cm⁻² than COF-366-Co@CNT (235 mV dec⁻¹ and 16 mF cm⁻², respectively), indicating its higher intrinsic catalytic activity and faster kinetics.

Typically, the hybrid catalyst was obtained by in-situ growth of porphyrin-phthalaldehyde-COF on MWCNTs.^[94] The Co ions were coordinated with the porphyrin units to serve as active sites. Compared with the Tafel slope (137 mV dec⁻¹) and resistance (125 Ω) of COF-366-Co, COF-366-Co@CNT-0.4 (0.4 represented the mass ratio of COF monomers input over MWCNTs) was provided with the lower Tafel slope (62 mV dec⁻¹) and resistance (90 Ω), indicative of its highly facilitated kinetic process.

Construction of composites consisting of carbonaceous materials and COFs can improve the electron transfer ability of COFs and thus enhance their conductivity for electrochemical reactions. However, the composite is faced with the challenges of high cost and uncontrollable synthesis process.

3D COFs. Due to the face to face lamellar stacking, the active sites in the layers of 2D COFs may not be fully exposed to electrolytes and reactive molecules, usually resulting in low activity and current density.^[95] In contrast, three-dimensional (3D) COFs allow the building blocks to be well-separated, making their active sites completely exposed to the surface and accessible for substrates, thereby promoting their ability of electron transfer,

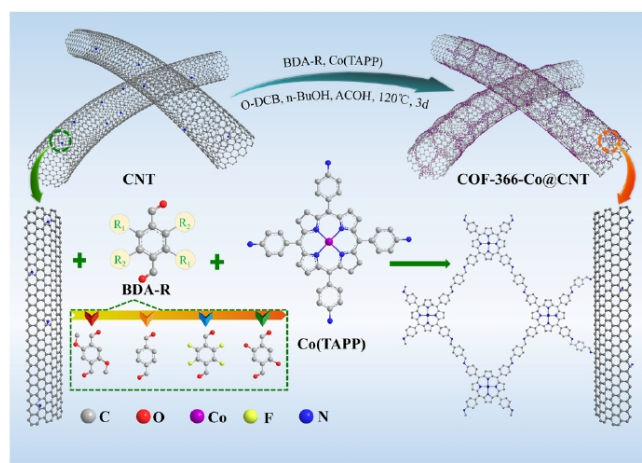


Figure 11. Schematic diagram for the construction of COF-based catalysts with isolated cobalt porphyrin units. Reprinted with permission from ref. [93]. Copyright 2020, American Chemical Society.

improving their conductivity and leading to enhanced electrocatalytic activity.^[96]

A porous 3D cobalt porphyrinic COF (3D-Por(Co/H)-COF) was synthesized by reacting tetra(4-formylphenyl)methane (TFPM) with Co-porphyrin and porphyrin.^[97] CO₂RR displayed higher FE_{CO} of 92.4% at -0.6 V (vs. RHE) and higher TOF of 4610 h⁻¹ at an applied potential of -1.1 V than 2D COF-366-Co (82.4% and 2500 h⁻¹, respectively). Moreover, the 3D COF showed higher CO partial current density of 15.5 mA cm⁻² at 1.1 V than COF-366-Co (13.2 mA cm⁻²). The excellent electrocatalytic activity of 3D-Por(Co/H)-COF was ascribed to the 3D structure, which was helpful to maximize the active sites and enhance electron transport by reducing the aggregation of molecular building blocks, thus making the Co-TAPP active sites exhibit high activity for CO₂RR.

Additionally, a 3D phthalocyanine COF (CoPc-PI-COF-3) through rigid imide bond connection was fabricated by dehydration of 2,3,9,10,16,17,23,24-octacarboxyphthalocyanine tetraanhydride (TAPc) and 1,3,5,7-tetra(4-aminophenyl)adamantine (TAPA) (Figure 12).^[98] Impressively, the unique 3D porous structure of CoPc-PI-COF-3 ensured 32.7% of the total metal phthalocyanine subunits as the active centers, which was higher than those for 2D COF electrocatalysts under similar conditions. Consequently, CoPc-PI-COF-3 electrode was demonstrated to exhibit partial CO current density of -31.7 mA cm⁻² at -0.90 V (vs. RHE), superior to that for almost all 2D Pc electrocatalysts reported previously.

Although 3D COFs can maximize active sites by spatially separating the building blocks to achieve higher catalytic performance than 2D COFs, it still remains a challenge to design and synthesize 3D COFs because of few available building blocks as well as the significantly increased difficulty in the crystallization and structure determination towards 3D systems.

Pyrolytic Derivation. In view of the relatively poor conductivity of COFs, pyrolysis is also applied to directly convert pristine

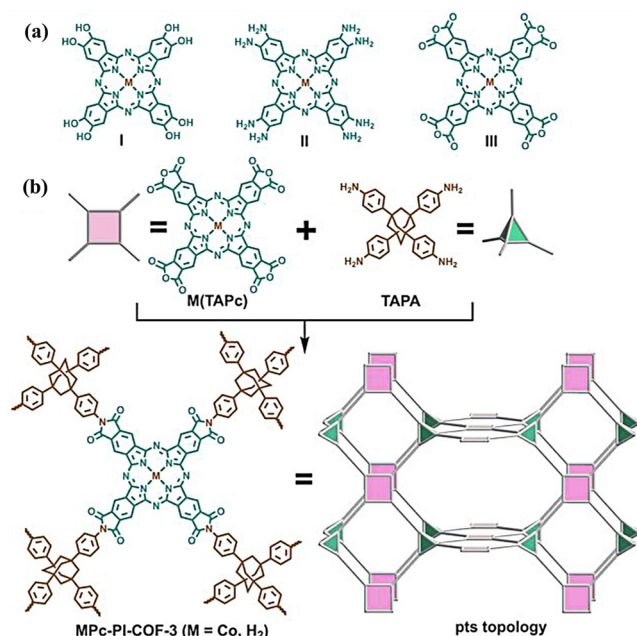


Figure 12. Synthesis of MPC-PI-COF-3 ($M = \text{Co}^{\text{II}}, \text{H}_2$). Reprinted with permission from ref. [98]. Copyright 2021, Wiley-VCH.

COFs into highly conductive graphitic carbonaceous materials. In the meantime, during pyrolysis, the non-metal atoms of COFs are generally turned into heteroatoms doped into graphitic skeleton. The metal atoms are converted into single atoms or clusters because of the confinement of COFs. These doped heteroatoms or single metal atoms/clusters have exhibited exceptional intrinsic activity upon the conductivity issue being addressed.^[99]

IISERP-COF1 was synthesized by reacting 4,4',4'-((1,3,5-triazine-2,4,6-triyl)tris(oxy))tribenzaldehyde and 1,4-phenylenediamine, and then was applied to mix with $\text{Ru}(\text{acac})_3$ solution to get the precursor. After soft pyrolysis of the precursor at 370 °C for 3 h under air, IISERP-COF1_ RuO_2 @370 was obtained for catalyzing OER.^[100] The resultant sample exhibited the lowest overpotential of 210 mV at 10 mA cm^{-2} among all the RuO_2 -based heterogeneous OER catalysts. Besides, the Tafel slope of IISERP-COF1_ RuO_2 @370 was calculated to be only 65 mV dec^{-1} , indicating the fast kinetics. The high catalytic activity arose from the uniformly dispersed RuO_2 nanoparticles in COF-derived carbon. Furthermore, small-sized (~3–4 nm) RuO_2 particles were anchored in N-rich framework, making themselves highly stable and recyclable without aggregation.

To achieve good ORR performance, a novel nitrogen doped porous carbonaceous material (HBY-COF-900) was prepared.^[101] Firstly, HBY-COF was synthesized by one-step polymerization of pyrrole with tetrakis(4-formyloxymethylene)methane in the presence of FeCl_2 . Secondly, HBY-COF-900 was obtained by heating HBY-COF to 900 °C at a rate of 3 °C/min. The synthesis resulted in Fe-N_4 as ORR active sites in HBY-COF-900, which displayed comparable onset potential to 20%Pt/C but higher CO tolerance.

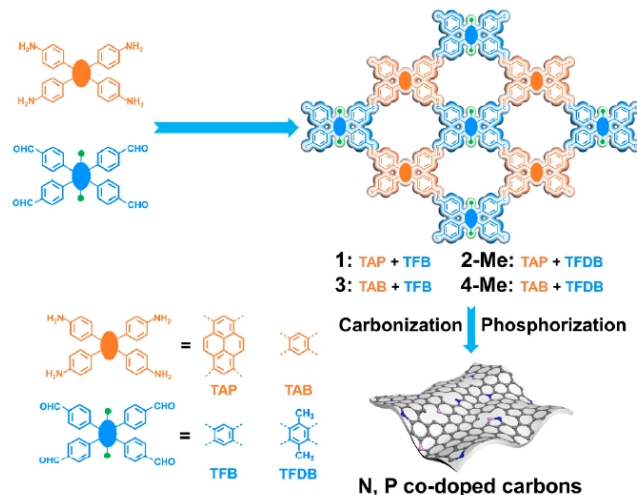


Figure 13. Schematic diagrams for the synthesis of 2D [4 + 4] COFs and their N, P codoped carbons. Reprinted with permission from ref. [102]. Copyright 2020, American Chemical Society.

In addition, porous carbons with N, P co-doping were rationally prepared by the pyrolysis of a series of 2D [4 + 4] (two different tetratopic building blocks) COFs as a bifunctional ORR/HER electrocatalyst (Figure 13).^[102] Na_2HPO_2 served as the phosphorus source to mix with COFs prior to pyrolysis. As for ORR, the obtained porous carbons exhibited a high half-wave potential of 0.81 V and a small Tafel slope of 70 mV dec^{-1} . Besides, a low overpotential of 0.26 V with excellent stability was achieved in HER.

A novel s-tetrazine based COF (TZA-COF) was prepared by the condensation of 1,3,5-tricyanobenzene (BzCN) and hydrazine,^[103] and used to form composites with reduced graphene oxide (rGO). The obtained hybrid composite was impregnated with Co NPs (TZA-COF-rGO-Co), and then further annealed to yield Co-encapsulated nitrogen doped graphitic carbon (Co@NC-600). For ORR, Co@NC-600 displayed higher onset potential (0.94 V) and half wave potentials (0.835 V) than TZA-COF (0.86 and 0.76 V, respectively) and TZA-COF-rGO-Co (0.88 and 0.81 V, respectively), which were comparable to those of the state-of-the art 20 wt% Pt/C.

ZIF-67 is commonly applied to synthesize oxygen based electrocatalysts by pyrolysis with the contained Co serving as active sites. However, the exposed Co sites can be leached under the harsh turnover conditions. To address such an issue, a COF layer was covered onto Co sites by the growth of a β -ketoenamine-linked 2,6-diaminoanthraquinone (DAAQ)-1,3,5-triformylphloroglucinol (TFP)-COF (DAAQ-TFP-COF), resulting in a core-shell hybrid.^[104] The COF shell was thermally converted into graphitic carbon for improving the interfacial electron transfer. Accordingly, compared to the commercial 20 wt% Pt/C catalyst, such a structure (GC@COF-NC) displayed comparable onset and half-wave potentials but superior long-term stability. After 5000 continuous cycles, the half-wave potential of GC@COF-NC only decreased by 9.1 mV, while 20 wt% Pt/C showed a significant decline with a negative shift of 36.7 mV.

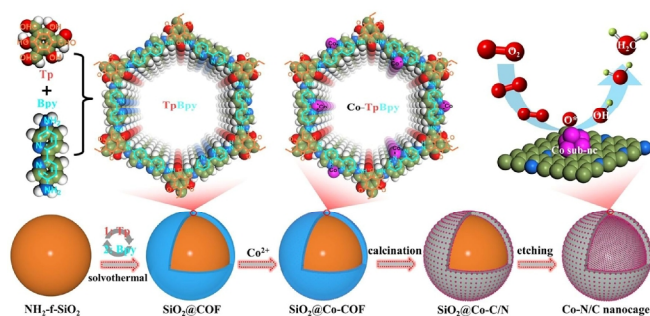


Figure 14. Schematic illustration for preparation of cobalt subnanoclusters dispersed N doped carbon nanocages for ORR. Reprinted with permission from ref. [105]. Copyright 2020, Elsevier.

For the same purpose, core-shell $\text{SiO}_2@\text{Co-TpBpy}$ was obtained by using NH_2 -functionalized silica (SiO_2) nanospheres as the core and cobalt-coordinated bipyridine-COF (Co-TpBpy) as the shell (Figure 14).^[105] After calcination at 800 °C and etching the SiO_2 template with KOH , Co subnanoclusters dispersed with N/C nanocages were obtained (Co-TpBpy-800 nanocages). They exhibited an onset potential of 0.91 V and a half-wave potential of 0.831 V, both better than those of most Co based ORR electrocatalysts in an alkaline solution. The subnanometer Co clusters coordinated with N atoms in the carbon nanocages were also verified to provide the ORR active sites by DFT calculations.

Although pyrolysis can improve the electron transfer process for COF-derivatives, the pyrolytic process normally brings about undesirable structural changes and even destruction of the original structures of COFs, and generates high costs derived from the high temperatures required for this process.

n CONCLUSIONS AND PERSPECTIVE

As an emerging type of framework materials, COFs exhibit the advantageous features of highly ordered organic structures and well-defined nanoscale pores, which can be assembled into extensive structures via systematic design of diverse building units at the molecular levels. Because of these advantages, COFs and their derivatives exhibit great potential in the application of electrocatalysis. In brief, the ordered porous structures make COFs tend to possess very large theoretical specific surface areas and thus can have very high-volume density of accessible active sites. The various designability of building units enables COFs with different functions for a variety of electrochemical reactions, as well as systematic tuning of intrinsic activities. Thanks to the linkages made of covalent bonds, the structures of COFs are highly stable and can be adapted to various electrocatalytic environments. This is however not available for analogous metal organic frameworks (MOFs) linked by coordination bonds. Although COFs have a significant potential role in electrocatalytic reactions, most of them are faced with the problems of insufficient electron conjugation capacity and inadequate electronic relays or interlayer resistance inside the framework, resulting in low conductivity and inferior electrocatalytic performance. Therefore, this review focuses on the recent

developments in strategies to construct COFs as efficient electrocatalysts.

In the meantime, we would like to list our perspectives on the key challenges and a few potential research directions in this fascinating area, including: (1) Due to low crystallization and phase purity, the specific surface areas of most COFs are far less than their theoretical values, resulting in failure to play potential role in the electrocatalysis of small molecules. At present, there is no effective method to fundamentally improve the crystallization of COFs, and obtaining 2D and 3D COFs with large single crystals is still of a great challenge. (2) Developing high-performance organic building blocks is of core significance to fabricate COFs with high electrocatalytic activity. There are extensive molecular catalysts having been recognized as intrinsically active for different target reactions, while many of them have not been applied in the heterogeneous electrocatalysis. For example, metal-based porphyrins or phthalocyanines embedded into the COF framework can significantly improve the catalytic activity of corresponding molecular catalysts.^[68,106] Through appropriate linkages, the assembly of COFs with these active molecular catalysts could be very promising. (3) It is clear that metal species play an important role in electrocatalysis. The presence of metal active sites can promote the adsorption capacity of reactive molecules, enhance the electron transfer capability and lower the reactivity barrier. Thus, the electrocatalytic efficiency can be greatly improved. However, current researches are mostly available for single metal, and few bimetallic COFs have been reported. Therefore, the design of different bimetallic COFs for electrocatalytic reactions to enhance their activity and selectivity and clarify the internal mechanism remains the focus of future development. (4) Currently, the synthesized COFs are mainly in the form of powders and laboratory-grade membrane, while large-scale production and device transformation of COFs are rarely reported due to that the secondary processing and molding of COFs is of great challenge. Therefore, controlling the morphologies of COFs in other ways such as crosslinking polymerization or substrate loading is of great concern. (5) Multi-component COFs have unique structures and abundant active sites, exhibiting higher catalytic performance than conventional two-component COFs in heterogeneous reactions.^[64,107] However, most of the multi-component syntheses of COFs are still based on unstable imine linkage, and thus developing new linkage multi-component COFs with crystallinity, porosity and structural stability is of desire.

In conclusion, although many challenges remain as above stated, COFs have been playing an increasingly important role in the field of electrocatalysis by taking advantages of their characteristics such as large specific surface area, ordered porosity, structural stability and systematic designability. This gradually drives COFs to become the new class of versatile electrocatalytic materials, which will further promote addressing current energy and environmental issues.

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n COMPETING INTERESTS

The authors declare no competing interests.

n ADDITIONAL INFORMATION

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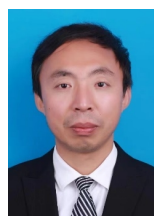
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