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Covalent Organic Frameworks for Efficient Energy Electrocatalysis: Rational Design and Progress

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An efficient catalyst with a precisely designed and predictable structure is highly desired to optimize its performance and understand the mechanism beyond the catalytic activity. Covalent organic frameworks (COFs), as an emerging class of framework materials linked by strong covalent bonds, simultaneously allow precise structure design with predictable synthesis and show advantages of large surface areas, tunable pore sizes, and unique molecular architectures. Although the research on COF-based electrocatalysts is at an early age, significant progress has been made. Herein, the recent significant progress in the design and synthesis of COFs as highly efficient electrocatalysts for the oxygen reduction reaction (ORR), oxygen evolution reaction (OER), and hydrogen evolution reaction (HER) is summarized. Design principles for COFs as efficient electrocatalysts are discussed by considering essential factors for catalyzing the OER, ORR, and HER processes at the molecular level. Herein, a summary on the indepth understanding of the catalytic mechanism and kinetics limitations of COFs provides a general instruction for further exploring their vast potential for designing highly efficient electrocatalysts.

1. Introduction

Discovering and engineering electrocatalysts to speed up reactions with electrons and chemical species are crucial for a carbon-neutral economy.^[1] Metal–air batteries that reduce oxygen gas into hydroxide ions, also known as the oxygen reduction process (ORR), envision energy storage with superior energy density. The hydrogen and oxygen evolution reactions

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(HER and OER) by reducing protons and oxidizing hydroxide ions produce clean and renewable fuels (Figure 1a). The state-of-the-art electrocatalysts are noble metals (e.g., Pt) or their oxides (e.g., RuO₂ and IrO₂).^[2] Among them, Pt is the best electrocatalyst for the ORR and HER in both alkaline and acid media. whereas RuO₂ and IrO₂ dominate the landscape of OER.^[3] However, the disadvantages of noble metals, which include high price, scarcity, low selectivity, and poor long-term durability, have frustrated their large-scale application. Therefore, it is of great importance to develop cost-effective and highly efficient electrocatalysts from Earth-abundant materials as alternatives for noble-metal-based catalysts.^[2a,4]

Alternatives include transition-metal (TM) -based materials, such as layered metal hydroxides,^[5] perovskite oxides,^[6] TM oxides/nitrides/borides,^[7] metal alloys,^[8] and metal-free carbon nanomateri-

als (e.g., graphene,^[9] carbon nanotubes [CNTs],^[10] nanoporous carbon^[11]). Few of them achieve comparable catalytic performances as noble-metal-based catalysts.^[12] For instance, heteroatoms-doped metal-free carbon materials emerged as strong competitors for noble metals. These materials are usually prepared by traditional high-temperature carbonization and heteroatom doping processes, accompanied by challenges to precisely tune the density of active sites and accurately confirm the active sites.^[1c,13]

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Figure 1. a) A schematic illustration of an aqueous rechargeable metal-air battery and water electrolysis. b) Polarization curves of the typical ORR, OER, and HER in alkaline and acid media and their related mechanisms. Reproduced with permission.^[13] Copyright 2017, American Chemical Society.

To overcome these challenges, rational design and precise synthesis of electrocatalysts are highly desirable.

Covalent organic frameworks (COFs), an emerging class of framework materials linked by strong covalent bonds, are highly crystalline materials with large surface areas and tunable pore sizes, allowing for devolving highly ordered network structures with excellent mass transport ability.^[1c,14] Moreover, they have presented significant potentials for providing high precision in controlling metal or nonmetal heteroatom doping and locations of electrochemically active sites.^[15] A programmable COF electrocatalyst can be synthesized by choosing proper building blocks, linkage motifs, and synthesis routes.^[14,16] For example, Xiang et al. synthesized a class of 2D COFs incorporating metal (e.g., Fe, Co, Mn) macrocycles for catalyzing ORR.^[15a] These COF-based catalysts showed good catalytic activity, long-term stability, and immunity of any methanol-crossover/CO-poisoning effects in both alkaline and acid media. Although the field of COFs used for efficient electrocatalysis is still in its infancy, the prospect of COF electrocatalysts is undoubtedly attractive and much space remains to further improve their performances due to their structural diversity, framework tenability, and functional versatility.

Although COFs for efficient electrocatalysis have been summarized in some recent specialized reviews,^[17] a systematic and comprehensive review of recent advances and challenges of COF electrocatalysts for efficient energy electrocatalysis is still lacking. Herein, we review the development of COF-based electrocatalysts, focusing on fundamental and key factors of high efficiency for the OER, ORR, and HER, as well as the corresponding advantages of COFs as efficient electrocatalysts. Then, general design principles and the synthesis strategies of COF electrocatalysts will be discussed. Subsequently, the recent significant progresses in COF-based materials as single-functional electrocatalysts or bifunctional electrocatalysts are presented. Finally, we discuss the challenges and future perspectives of COF-based electrocatalysts for efficient electrocatalysis. In particular, the future directions for the development of metal-free intrinsic COFs without carbonization will be emphasized regarding the modulation of active sites and their densities at the molecular level.

2. Design Principles for Efficient COF Electrocatalysts

2.1. Key Factors for Designing Efficient Electrocatalysts

Multiple electrons are involved in ORR, OER, and HER reactions and they are often kinetically sluggish (Figure 1b). To overcome this, an electrocatalyst is required to reduce reaction energy barrier. At the same time, the charge and mass transfer have to be optimized to be highly conductive and have a large surface area. Practical applications also require long lifespan, thus demanding excellent durability of an electrocatalyst.

2.1.1. Low Reaction Energy Barrier

The reaction energy barrier mainly stems from the adsorption and desorption of intermediates (e.g., O*, OH*, OOH*, and H*) during the reactions. The ORR proceeds through the formation of OOH* from adsorbed O₂, followed by its further reduction to O* and OH*, whereas OER proceeds in the reverse direction. Typically, the ORR activity is limited by the OH* reduction step and O₂ reduction steps, and the OER activity is limited by the OOH* and O* formation steps.^[18] In this sense, the binding energies of these intermediates largely determine the reactivity of electrocatalysts. Surface properties of the electrocatalyst, such as surface functional groups, suspended bonds, and surface charge distribution, have direct impacts on the reaction energy barrier. For example, functional groups like the carbonyl group with high-density electron-donating capability can adsorb oxygen molecules and hence promote the ORR process.^[19] In contrast, an electron-withdrawing functional group, such as pyridinic-N, is favorable for the OER process.^[20] To modulate



the surface properties, heteroatom doping, surface vacancy engineering, and the introduction of metal catalytic units have proven to be powerful technologies by modulating the electronic properties of catalysts to adjust their electronic properties and/or chemical activities favorable for catalyzing.^[21] In addition, lattice oxygen and molecular sites on the catalyst surface play an important role in the electrocatalytic process by regulating the adsorption of intermediates, such as OH*, resulting in a lower reaction energy barrier.^[22] In short, the reaction energy barrier can be greatly reduced by the introduction of heteroatoms, surface vacancy engineering, and interfacial regulation.

2.1.2. Excellent Electrical Conductivity

Fast electron transport is essential for an electrocatalyst.^[23] With high conductivity, electrons can rapidly reach the active sites, thus facilitating the charge transfer processes and reducing electrochemical polarizations. The conductivity of a catalyst is determined by its band structure, carrier concentration, and mobility. Surface modifications, including surface dimensional confinement,^[24] incorporation with heteroatoms,^[25] and introduction of surface cations,^[26] have been applied to reduce the bandgap and enhance the carrier concentration. Moreover, complexing a highly conductive host material, such as CNTs and graphene, is another effective way to enhance the electrical conductivity of electrocatalysts via constructing an interfacial electron transfer channel.

2.1.3. Large Surface Area

Electrocatalysts with high specific surface areas provide sufficient active sites to participate in electrochemical reactions, allowing for efficient mass transfer, such as the rapid exchange of gases and adequate contact between catalysts and electrolytes.^[27] Normally, the limited reaction zone only involves a small number of active sites exposed to the triple-phase (gas/solid/electrolyte) interface, resulting in poor accessibility and inferior catalytic performance. Although numerous TM-based and metal-free porous carbon materials with high surface areas have been explored for efficient electrocatalysis, these electrocatalysts are usually fabricated through a high-temperature pyrolysis process.^[23a,28] The uncontrolled pyrolysis process will lead to the severe agglomeration of metal particles and the structural damage of the carbon matrix, which significantly reduces the reaction surface area and the density of exposed active sites. To improve reaction surface area, strategies involving defect engineering,^[29] surface heteroatom doping,^[30] and interface layer construction^[31] have been developed.

2.1.4. Superior Durability

The durability of electrocatalysts is a key issue for practical applications toward clean energy technologies. Usually, HER, ORR, and OER occur under severe chemical conditions, such as strong base (pH = 13) or acid (pH = 1) solutions and a high overpotential (>1 V vs standard hydrogen electrode). Therefore, the catalysts should be designed to resist electrochemical corrosion over a long time. In addition, the tolerance for any methanolcrossover or gas-poisoning effects is also critical for efficient electrocatalysts. In fuel cells, the presence of methanol or gas (e.g., CO) at the cathode can result in a significant poisoning effect and the deactivation of catalysts.

2.2. Advantages of COFs for Efficient Electrocatalysis

COFs, an emerging class of porous network polymers with crystalline frameworks, are built up by arranging individual building units, such as molecular building blocks containing aldehyde and amine functionalities, into highly ordered structures through covalent bonding.^[32] Simultaneously, a well-defined layered structure will form by π - π interactions that introduce the periodicity of open channels and pore structures. The ability to precisely design and control the heteroatom structure by choosing the organic building blocks and linkages provides a powerful technology to regulate the properties of targeted catalysts.^[33] Various coupling reactions, including boronic acid-based coupling, amino group-based coupling, alkynyl group-based coupling, bromine group-based coupling, and cyan group-based coupling (Figure 2), are available for precise design.^[34] For instance, Schiff base condensation has been profusely explored for the synthesis of COFs due to their high chemical stability, porosity, and crystallinity, which constitutes a majority of the COFs.^[35] Moreover, π -conjugated organic structures make COFs semiconducting materials.^[36] As a result, the conductivity and charge mobility can be simply tuned by common semiconductor engineer methods. For example, controlling dopants and modulating their surrounding environment will successfully modulate the electronic property.^[13]

COFs are highly porous with ultra-large surface areas (up to $4200 \text{ m}^2 \text{ g}^{-1}$).^[37] The periodic channels aid mass transfer, whereas well-defined and tunable pore sizes (up to 4.7 nm) allow for incorporating active molecules into their skeletons or channels, which is beneficial for electrochemical reactions.^[32,38] However, the dense stack of COF layers makes these channels too long to effectively exchange charges and chemical species.^[17d] In this regard, 2D COFs with a few atomic layers are of particularly interest for electrocatalysis applications.^[17b]

Moreover, COFs also possess a superior structural stability due to strong covalent bonds. Exceptional thermal stability (up to 600 °) has been demonstrated,^[17f] which makes postsynthetic modification that incorporates active sites into the porous and crystalline skeletons feasible. Strong covalent bonds also guarantee durability over long-term testing in harsh experimental conditions.

2.3. Design Principles for COF-Based Electrocatalysts

Pristine COFs show inferior electrocatalytic activities, which require proper modification and functionalization at the molecular level. Two main factors influence the catalytic performance: accessible active sites and intrinsic catalytic activity. The former one can be controlled by creating porous structures and engineering defects in materials. Building blocks with rigid aromatic moieties are able to generate extended porous nanostructures. Defects on a hierarchically porous structure function as additional accessible sites.





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Figure 2. The main types of coupling reactions closely related to the synthesis chemistry of COFs and representative illustrations of corresponding couplings. Reproduced with permission.^[34] Copyright 2013, Royal Society of Chemistry.

The latter factor, intrinsic activity, can be optimized by four standard protocols. First, the incorporation of heteroatoms using secondary structural units containing heteroatoms (e.g., N, P, S, etc.) creates positive charge accumulation on themselves and their neighboring carbon atoms, functioning as active centers within the COF skeleton for catalyzing ORR/OER/HER. It is worth noting that highly homogeneous loading and exact location control of heteroatoms within frameworks can be achieved by selecting the building units for COFs. Second, the incorporation of TM macrocyclic clusters, such as metalloporphyrin, metallophthalocyanine (MPc), and metallo-tetraazaannulene, accomplishes loading metal active sites onto COFs and the precise control of building in coordinating units at the molecular level. Moreover, metallic COFs can be further pyrolyzed into non-noble TM-nitrogen-carbon (M-N-C) hybrid materials. In this regard, the derived M-N-C possesses a synergistic effect among TMs, N species, and carbon moiety. Third, rich N heteroatoms with long pairs for metal coordination and tunable chemical environment in their ordered pore structures can support single-atom sites, allowing for precisely controlled environment around electrocatalytic active sites. Fourth, blending COFs and conductive supporting materials, such as graphene and CNTs, effectively improves the electron transfer, thus facilitating the catalytic process.^[39]

2.4. Computational Design of COF Electrocatalysts

Prior to the design and synthesis of COFs as efficient electrocatalysts, several important principles should be first established regarding the key parameters for oxygen electrochemical catalysts mentioned earlier. Although the catalytic capabilities of COFs have been proven, most of the COF-based catalysts are explored through numerous trial-and-error experiments. A rational design via computational approaches would be the best choice to reduce the research expense and time, as well as guide the development of efficient COF-based electrocatalysts. At this point, it is necessary to understand which intrinsic characteristics (termed descriptors) control the catalysis process and the

relationship between the structures and catalytic activity of COF-based catalysts as a function of the descriptor.

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The first-principle calculation is regarded as an effective approach to verify the molecular structures and catalytic activity of COF-based catalysts via density functional theory (DFT) techniques.^[40] Based on the first-principle calculation, several intrinsic activity descriptors have been proposed, such as the adsorption energy for TMs-based COF (TM-COFs, TM = Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, and Zn) catalysts and the electronegativity and electric affinity of dopants for metal-free carbonbased catalysts. These descriptors can result in a volcano relationship and give quantitative predictions for the best catalysts. For example, Lin et al. investigated the catalytic performance of TM-COFs for the ORR and OER.^[41] The free energies and overpotentials for ORR and OER elementary reactions were calculated by DFT calculations to predict the catalytic activities of TM-COFs. Two descriptors of adsorption energies $\Delta G^0_{OH^*}$ and $\Delta G^0_{O^*}$ – $\Delta G_{OH^*}^0$ were used to describe the catalytic behavior and resulted in a volcano diagram with Fe at the volcano summits (Figure 3a). Although these descriptors work reasonably well for the catalytic behaviors of TM-COFs, they are not related to the intrinsic properties of TM-COFs. Thus, it is inconvenient to use them for predictions of the catalytic properties.

To address this issue, Lin et al. proposed to use the crystal field stabilization energy (CFSE) as the descriptor for predicting ORR/ OER activities of the TM-COFs and established a volcano relationship between the CFSE and the catalytic activity toward OER and ORR.^[41] The CFSE is related to the *d*-orbital bonding of TMs and the energy determined by ligand architectures and the bonding structures with the Jahn–Teller effect.^[42] Using the new descriptor, they obtained the volcano plots for the four-electron pathway and two-electron pathway (Figure 3b–d). The mechanism map can be divided into two regimes, 2e⁻ transfer (CFSE > 0) and 4e⁻ transfer (CFSE < 0).^[41] In the volcano region, Fe-COF is identified to be the best catalyst for both ORR and OER.

In addition, DFT-based computational calculations are also applied for predicting the activity trends of HER electrocatalysts.^[43] Even though none of the reports related to predicting the activity of COF-based electrocatalysts toward HER, the relevant computational simulation will be beneficial for directing the proof-of-concept molecular design of efficient COF-based HER electrocatalysts. It was reported that the overall HER reaction kinetics on various surfaces are predominately determined by the change of Gibbs free energy (ΔG_{H^*}) .^[44] The interaction between hydrogen species (e.g., H*) and active centers plays a vital role in determining the chemical kinetics for the HER. Either too weak ($\Delta G_{H^*} > 0$) or too strong ($\Delta G_{H^*} < 0$) will greatly affect the HER process by showing poor activity. Remarkably, by correlating the experimentally measured exchange current density (*j*₀) and the computational simulated ΔG_{H^*} , a volcano plot can be obtained to predict the activity trends of various catalysts



Figure 3. a) Schematic of TM-COFs. The green, blue, deep gold, and silver colors represent C, N, TM, and H, respectively. b) Volcano plots of ORR overpotentials as a function of adsorption energy and reaction pathways. c) OER and ORR overpotentials as a function of CFSE for TM-COFs in the fourelectron pathway. d) ORR overpotentials as a function of CFSE and orbital configuration energy (CE) for TM and AM-COFs in 2e⁻/4e⁻ electron reactions. Reproduced with permission.^[41] Copyright 2017, Wiley-VCH.

toward HER. The ideal HER electrocatalyst should have ΔG_{H^*} of 0 eV and deliver the largest j_0 . As a result, the promising metal-free carbon-based materials demonstrated competitive properties as the new family of highly efficient HER catalysts.^[43]

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3. COF-Based Electrocatalysts for Efficient ORR

The electrocatalytic ORR plays an important role in clear energystorage and conversion devices, such as fuel cells and metal-air batteries.^[45] Due to the sluggish kinetics of the ORR process, the overall efficiency of the device depends on the activity of the cathodic ORR process. Therefore, the development of highly efficient ORR electrocatalysts is of great importance for the practical applications of these energy-storage and conversion devices. At present, the noble metal Pt is regarded as the best electrocatalyst for the ORR due to its high selectivity and activity. However, the large-scale applications of Pt-based catalysts are hampered by their scarcity, high cost, poor long-term durability, as well as low tolerance to the gas-poisoning or fuel-crossover effect. Therefore, the exploration of new catalysts with cost effectiveness, high selectivity and activity, and superior durability is essential. COFs with desirable properties, such as high porosity and specific surface area, tunable pore structure, and superior chemical stability, have been already explored as efficient electrocatalysts toward ORR.

3.1. Fundamental Principles of the ORR

'Generally, the ORR is a complicated multielectron transfer process and involves two possible pathways: a two-electron (2e⁻) pathway with the formation of H_2O_2 and a direct four-electron (4e⁻) transfer to produce H₂O or OH⁻ depending on the electrolyte.^[46] In acidic media, O₂ can be directly reduced to H₂O via a 4e⁻ process or can undergo a partial $2e^{-}$ process to form H_2O_2 , followed by a further reduction to form H₂O. In alkaline media, O₂ can be reduced through a direct 4e⁻ process to generate OH⁻ or by the two-step $2e^{-}$ process to form HO_{2}^{-} and then OH^{-} . Basically, the ORR paths are extremely complicated and surface sensitive, including the adsorption and dissociation of diverse intermediates, such as oxygenated (O*), hydroxyl (OH*), and superhydroxyl (OOH*) species on the catalyst surface.^[47] The * represents one catalytic active site on the catalyst surface. Accordingly, the selectivity of the 4e⁻ or 2e⁻ pathway depends on the adsorption energy of reactants and intermediates and their dissociation reaction barrier on the active surface.^[48] For the practical applications in energy-conversion technologies, the direct 4e⁻ process for the ORR is undoubtedly more efficient and highly desirable.

For the 4e⁻ process in alkaline media (similar in acid media, not shown here), there are two possible mechanisms proposed as follows, including the dissociative mechanism and associative mechanism.^[48] The dissociative mechanism can be described as the initial adsorption of O₂ on the catalyst surface, followed by the breaking of O–O bond and the formation of two adsorbed atomic O* species. Subsequently, the O* species interacts with hydrogen to produce OH* and are further converted to form the final product OH⁻.^[49] Alternatively, the ORR process can also be processed by the following associative mechanism: the adsorbed oxygen O₂* at the active centers first interacts with hydrogen to

form OOH*, followed by the breaking of O–O bond and the formation of O* and OH*. Finally, the O* and OH* interact with hydrogen to produce OH⁻. It can be induced that whether the reaction proceeds as a dissociative way or an associative way mainly depends on the initial O₂-dissociating energy barrier that determinates the breaking of the O–O bond.

From the above reaction mechanism, an ideal ORR electrocatalyst should have a high surface area with porous structures, excellent electrical conductivity, and low reaction energy barrier, providing fast reaction kinetics for catalyzing ORR. As for the evaluation of ORR electrocatalytic activity, the total electrode activity (e.g., limiting current density), the overpotential, and the electron transfer number are essential.

3.2. Efficient COF-Based Electrocatalysts for the ORR

COFs have drawn extensive interest as a new family of efficient ORR electrocatalysts due to their unique properties, including 1) large surface area, which provides sufficient active sites to participate in catalytic reactions, 2) intrinsic porous structures, which facilitate ion transportation and thus enhance the reaction rate, and 3) π -conjugated organic structures, which improve the transportation of charge carriers. Moreover, the robust frameworks of COFs provide a superior platform to achieve COF-based composites and derived materials with advantageous properties for efficient electrocatalysts. At this point, we focus in this section on the recent advances in the state-of-art COF-based electrocatalysts for the ORR, including pristine metal-free COFs, metal-free COF-derived carbons, heterometallic macrocycles-containing COFs and their derivatives, COF-supported single-atom catalysts (SACs), and COF-based nanohybrids (**Table 1**).

3.2.1. Pristine Metal-Free COFs for the ORR

COFs have been already explored as electrocatalysts due to their large surface area, tunable pore size, and unique molecular architecture. Generally, COFs in their pristine state are electroactive for the ORR and can directly serve as metal-free ORR electrocatalysts. For example, Hu and coworkers synthesized metal-free covalent triazine-based frameworks (CTFs) using an ionothermal method.^[50] The resultant CTFs possessed a high specific surface area of 782.44 m² g⁻¹ and a total pore volume of 0.42 cm³ g⁻¹, as well as a high content of pyridinic-N with a N/C atom ratio of 0.259. When explored as an ORR metal-free catalyst, the CTFs exhibited excellent electrocatalytic activity in alkaline media. The onset potential of CTFs is 0.0 V [vs saturated calomel electrode (SCE)], relative to that of the commercial Pt/C catalyst, and the transferred electron number was determined to be about 3.6, displaying a 4e⁻ transfer reaction. In addition, π -conjugated covalent organic radical frameworks (CORFs) have also been proven to be electroactive for ORR. Wu and coworkers synthesized the first π -conjugated CORF, PTM-CORF, using a stable polychlorotriphenylmethyl (PTM) radical (Figure 4a).^[51] The obtained PTM-CORF showed a small energy gap of 0.88 eV and a low-lying lowest unoccupied molecular orbital energy level of -4.72 eV, which were attributed to the strong electron-withdrawing feature of the PTM radical. As a result, the PTM-CORF displayed good electrocatalytic activity for the ORR with a half-

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Table 1. Summary of COF-based materials as electrocatalysts for the ORR in the literature.

COF-based electrocatalysts	Electrolyte	Loading [mg cm ⁻²]	^{a)} E _{onset} V versus RHE	^{b)} E _{1/2} V versus RHE	^{c)} $j_0 [mA cm^{-2}]$	Tafel slope [mV dec ⁻¹]	^{d)} N value	Ref.
CTFs	0.1 м КОН	-	0.0 versus SCE	_	-	_	3.6	[50]
PTM-CORF@C	0.1 м КОН	0.08	_	0.67	_	-	3.89	[51]
JUC-528	0.1 м КОН	0.034	0.82	0.70	-	65.9	3.81	[54]
JUC-527	0.1 м КОН	0.034	0.77	0.63	-	72.3	3.46	[54]
C-COP-4	0.1 м КОН	0.10	-	0.78	-	-	3.90	[15b]
POF-C-1000	0.1 м КОН	-	0.84	_	5.24	-	3.75	[56]
POF-C-800	0.1 м КОН	-	0.85	-	4.21	-	3.53	[56]
POF-DC-1000	0.1 м КОН	-	0.83	-	3.85	-	3.46	[56]
PA@TAPT-DHTA-COF ₁₀₀₀	0.1 м КОН	-	0.95	0.78	6.50	146	3.60-3.76	[57]
PA@TAPT- COF _{1000NH3}	0.1 м КОН	-	0.96	0.85	7.20	110	3.77-3.98	[57]
CoCOF-Py-rGO	0.1 м КОН	0.10	-	0.80	6.10	-	3.80	[58]
Co-POF	0.1 м КОН	0.14	0.84	0.765	4.72	61	3.7	[39a]
C-COP-P-Fe	0.1 м КОН	-	_	0.81	4.00	53	-	[59]
C-COP-P-Co	0.1 м КОН	0.20	0.98	-	4.20	-	3.82	[15a]
CoP-CMP800	0.1 м КОН	0.20	1.0	_	13.50	-	3.61	[15a]
	0.1 м КОН	0.60	0.85	0.78	4.60	-	3.86	[62]
COF-derived CoNCs800	0.5 м H ₂ SO ₄	0.60	0.74	0.64	4.84	-	3.94	-
	0.1 м КОН	0.20	0.905	0.807	4.72	-	3.98	[64]
FeSAs/PTF-600	0.5 м H ₂ SO ₄	0.20	0.80	0.70	4.40	-	3.90	-
	0.1 м КОН	-	1.01	0.87	5.51	62	3.88	[65]
COF _{BTC} -derived <i>pf</i> SAC-Fe-0.2	0.5 м HClO ₄	-	0.89	_	5.42	81	3.99	-
	0.1 м КОН	0.255	1.01	0.910	5.24	31.7	3.95	[66]

^{a)} E_{onset} represents the onset overpotential of electrocatalysts; ^{b)} $E_{1/2}$ is the half-wave potential; ^{c)} j_0 is the limiting current density, and; ^{d)}N stands for the transfer electron number.

wave potential of 0.671 V [vs reversible hydrogen electrode (RHE)] under alkaline media and an electron transfer number of 3.89.

COF electrocatalysts can be regarded in a simplified way as the active sites embedded within the porous organic framework (POF). Thus, a straightforward strategy to improve the performance of metal-free COF catalysts is to introduce the electrocatalytic active units into the framework.^[52] As a representative of active units, carbonyl compounds, such as quinone, carboxylates, anhydrides, and imides, undergo a revisable activity during the electrochemical processes, in which carbonyl groups can serve as electrochemically active centers for catalyzing the ORR process.^[53] In addition, π -electron-rich units, involving thiophene, phthalocyanine, and 2,6-diaminoanthraquinone, are other types of catalytic active units with enriched high carrier mobilities, being favorable for rapid electronic transportation and accessibility of active centers. For instance, Yao and coworkers reported the synthesis of two metal-free thiophene-sulfur COFs (JUC-527 and JUC-528) as efficient ORR catalysts (Figure 4b).^[54] JUC-528 was fabricated using bithiophene-sulfur structures with higher numbers of active centers, whereas JUC-527 was constructed with one thiophene-sulfur structure, possessing lower numbers of active centers. Without pyrolysis, both JUC-528 and JCU-527 exhibited a higher ORR catalytic activity than that of the

thiophene-free COF (termed PDA-TAPB-COF), indicating that thiophene–sulfur building blocks acted as active centers (Figure 4c). The pentacyclic thiophene-S building blocks were confirmed as efficient active centers for ORR via DFT calculations. Specifically, the two adjacent carbon atoms located at site-3 and site-5 of pentacyclic thiophene-S display lower overpotentials compared with PDA-TAPB-COF (Figure 4d), which represents the induced positive ORR catalytic capability by thiophene-S. As expected, JCU-528 with higher numbers of thiophene–sulfur structures displayed better ORR performance. This work not only sheds light on understanding and confirming the exact structure of the active center but also provides a new route to design and develop future high-performance electrocatalysts through the precise and controllable synthesis of active sites.

3.2.2. Metal-Free COF-Derived Carbons for the ORR

Although pristine metal-free COFs have been explored as ORR electrocatalysts, their catalytic performances are still unsatisfied due to their intrinsic poor conductive properties. Therefore, COFs consist of light elements (e.g., C, B, N, O, etc.), are more often carbonized into graphene-like carbon materials with the uniform distribution of heteroatom dopants in the carbon



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Figure 4. a) Schematic representation of the synthesis of PTM-CORF. Reproduced with permission.^[51] Copyright 2018, Wiley-VCH. b) Schematic of the synthesis routes of JUC-527 and JUC-528. The insets show their partial structures viewed normal and parallel to the ab plane (gray, yellow, and red spheres represent C, S, and N atoms, respectively). c) Linear sweep voltammetry (LSV) curves (at 1600 rpm) of PDA-TAPB-COF, JUC-527, and JUC-528 in O₂-saturated 0.1 M KOH electrolyte. d) Calculated free energy diagrams for metal-free thiophene-S COFs as compared with the thiophene-S-free COF. Reproduced with permission.^[54] Copyright 2020, American Chemical Society.

matrix, and render the COFs even better for catalyzing ORR. It should be noted that the introduction of heteroatom dopants (e.g., N) is commonly conducted either by in situ doping with the use of heteroatom-containing moieties or by postdoping of obtained carbon materials.^[55] However, it is still challenging to precisely control the distribution of dopants in the carbon matrix due to the uncontrollable pyrolysis process. In contrast, the pyrolysis of COFs provides an effective approach to control the type and distribution of heteroatom dopants in targeted carbon nanomaterials precisely, thus enhancing their catalytic activities.

Dai and coworkers reported the COF-derived metal-free ORR electrocatalysts for the first time.^[15b] A large class of COFs with N-rich building blocks were synthesized via the Ni-catalyzed Yamamoto reaction and subsequently carbonized to produce N-doped graphitic carbon materials. Through using various N-containing building units, four COF graphene derivatives with varied N-doping levels and porous structures were obtained (Figure 5a), in which the extracted locations of N-dopants were precisely controlled. The well-controlled N-doped holey graphitic carbon material demonstrated excellent electrochemical performances toward ORR in alkaline media (Figure 5b), such as a similar onset potential as the commercial Pt/C catalyst and half-wave potential of 0.78 V (vs RHE), comparable with that of Pt/C (0.8 V). Furthermore, the transferred electron number (*n*) per O_2 molecule is 3.90 at 0.55–0.70 V, suggesting closely four-electron transfer behavior for ORR (Figure 5c). This work is really a big breakthrough for precisely controlling the location of N-dopant heteroatoms and hole sizes in the N-doped graphitic structure, as well as showing promising potential for COFderived metal-free carbons as efficient ORR catalysts.

In another work, a COF-templated N-doped carbon was synthesized through a nanocasting method using N-enriched COFs as the self-sacrificing host template and furfuryl alcohol as the carbon precursor (Figure 5d).^[56] The resultant N-doped carbon (POF-C-1000) possessed a high N content of and a high surface area of 785 m² g⁻¹ and exhibited favorable electrocatalytic activity for the ORR with a higher onset potential (about 40 mV) than the commercially available Pt/C catalyst (Figure 5e,f).

To further increase the catalytic activity of COF-derived Ndoped carbon materials, the introduction of a second heteroatom such as P or S is regarded as an efficient way and has been explored. For instance, Jiang and coworkers used a templateassisted pyrolysis method to convert a conventional COF (TAPT-DHTA-COF) into carbon sheets (PA@ TAPT-DHTA-COF₁₀₀₀),^[57] as shown in **Figure 6a**. In this system, phytic acid (PA) not only serves as a template to strip the layered COFs to carbon sheets but also provides the phosphorous resource for P-doping. The resultant PA@ TAPT-DHTA-COF₁₀₀₀ exhibited excellent electrocatalytic activity for the ORR with an onset potential of 0.921 V (vs RHE), a half-wave potential of 0.751 V (vs RHE), and a limited current density of 6.5 mA cm⁻² (Figure 6b,c). Recently, N- and P-codoped nanohybrids were fabricated using N, P-containing COFs coated on CNTs as the



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Figure 5. a) Schematic representations of the synthesis of N-rich COP precursors through various monomers using nickel-catalyzed Yamamoto-type Ullmann cross-coupling reaction. b) LSV curves of COP graphitic electrodes and c) Rotating disk electrode (RDE) curves of C-COP-4 in O_2 -saturated 0.1 M KOH at a scan rate of 5 mV s⁻¹. The inset in (c) shows the Koutecky–Levich plots of C-COP-4 derived from RDE measurements. Reproduced with permission.^[15b] Copyright 2014, Wiley-VCH. d) Schematic representations of the synthesis of N-rich porous carbon material POF-C-1000 from a POF. e) Comparative cyclic Voltammetries (CVs) of Pt/C, POF-C-1000, POF-C-800, and POF-DC-1000 in oxygen-saturated 0.1 M KOH at a scan rate of 50 mV s⁻¹. b) Comparative LSV curves in 0.1 M KOH under oxygen bubbling at a scan rate of 10 mV s⁻¹ and an electrode-rotation speed of 1600 rpm. Reproduced with permission.^[56] Copyright 2013, Wiley-VCH.

carbon precursor (Figure 6d).^[58] Due to the active synergistic effect between graphitic-N and -P, the synthesized N- and P-codoped carbon materials exhibited a remarkable electrocatalytic performance with a half-wave potential of -0.162 V (vs Ag/AgCl) and high current density of 6.1 mA cm⁻² (Figure 6e,f), good stability, and excellent methanol tolerance for ORR in alkaline media.

3.2.3. Heterometallic Macrocycles-Containing COFs and Their Derivatives for the ORR

Considering that the uncontrollable pyrolysis process will cause the structure collapse and result in the elusive active sites, TM nitrogen-coordinated macrocycles, such as porphyrin and phthalocyanine, [^{30b,39a,59,60]} have been directly developed as efficient oxygen electrocatalysts without pyrolysis treatment. Taking the metal-porphyrin-based COF catalyst as an example, the TM ions with four coordinate nitrogen (TM-N₄) units serve as active sites for electrochemically catalyzing oxygen, where hydroxyl intermediates are absorbed and electrons are transferred.^[15,61] However, the adjacent porphyrin molecules tend to aggregate during electrochemical catalytic processes and thus affect the accessibility of these TM-N₄ active sites.

The introduction of porphyrin molecules into stable frameworks, such as COFs, is an effective strategy for further

design and optimization of coordinated porphyrin-based electrocatalysts. Favored by the unique framework of COFs (e.g., π -conjugated organic structures), the issues of the aggregation of small porphyrin molecules and low electronic conductivity can be addressed. Thus, heterometallic macrocycles-containing COFs are regarded as promising catalysts for the ORR.

Luo and coworkers first reported a reduced graphene oxide/ Co-porphyrin-based COF (CoCOF-Py-rGO) using pyridinefunctionalized reduced graphene oxide (rGO) as the building block (Figure 7a).^[39a] The presence of 4-styrylpyridine functional group on either side of rGO serves as the structural node to link Co-COF forming a unique 3D morphology. Thanks to the synergistic effect of the novel porous 3D architecture and good electronic properties of graphene, the resulting materials exhibited a high ORR activity with an onset potential of 0.84 V (vs RHE), a half-wave potential of 0.765 V, and much higher stability and methanol tolerance than those of Pt/C in alkaline solution (Figure 7b,c). Very recently, Zhang and coworkers designed and synthesized a series of COF electrocatalysts coordinated with various metal centers (M-POF, M = Mn, Fe, Co, Ni, Cu, or Zn) and further evaluated their ORR catalytic performances (Figure 7d).^[59] Among them, Co-POF demonstrated the best ORR electrocatalytic performance with the highest half-wave potential of 0.81 V (vs RHE) and the lowest Tafel slope of 53 mV dec^{-1} in alkaline media (Figure 7e,f). This work provides



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Figure 6. a) Schematic for the template synthesis of TAPT-DHTA-COF and PA@TAPT-DHTA-COF. b) CV curves of PA@TAPT-DHTA-COF₁₀₀₀ (blue) and PA@TAPT-DHTA-COF_{1000NH3} (red) at a scan rate of 100 mV s⁻¹ in N₂ (black) and O₂. c) Rotating ring-disk electrodes profiles of TAPT-DHTA-COF₁₀₀₀ (green), PA@TAPT-DHTA-COF₁₀₀₀ (blue), PA@TAPT-DHTA-COF_{1000NH3} (red), and Pt/C (black) electrodes in oxygen-saturated aqueous KOH solutions (0.1 M) at 1600 rpm. Reproduced with permission.^[57] Copyright 2018, Wiley-VCH. d) Illustration of the preparation of the N-, P-doped carbon derived from N-, P-containing COFs-coated CNTs. e) CV curves of T-N, P-CNT, 800-N-CNT, 800-N, and P-BC in N₂- and O₂-saturated 0.1 M KOH solution at a scan rate of 50 mV s⁻¹. f) LSV curves of 700-, 800-, 900-N, P-CNT, and Pt/C at a rotation rate of 1600 rpm. Reproduced with permission.^[58] Copyright 2017, American Chemical Society.

an instruction toward the further rational design of heterometallic porphyrin-based ORR electrocatalysts.

Apart from the alkaline media, ORR catalysts are also applied in acid media. Campidelli and coworkers synthesized a quintessential multi-walled carbon nanotubes (MWNT)/COF hybrid electrocatalyst by facile-templated polymerization of meso-tetraethynylporphyrin on the surface of MWNTs via Hay coupling.^[39b] During the reaction, the MWNT serves as the template for the formation of the COF adhesive layer. Due to the synergistic effect of π – π stacking interactions between the porphyrin-based COF and the MWNT, as well as covalent bonds between the porphyrins, the resultant MWNT/COF hybrid electrocatalysts exhibited superior electrocatalytic activities for the ORR in acid media with an electron transfer



Figure 7. a) Schematic illustration of the morphology-controlled synthesis of CoCOF-Py-rGO catalyst. b) Steady-state polarization curves of CoCOF-Py-rGO catalyst and c) steady-state current–potential responses on disk (lower-panel) and ring (upper-panel) electrodes. Reproduced with permission.^[39a] Copyright 2017, Royal Society of Chemistry. d) Schematic illustration of the fabrication procedure of various M-POFs electrocatalysts. e) *iR*-corrected LSV profiles of various M-COFs in O₂-saturated 0.1 M KOH at a scan rate of 10.0 mV s⁻¹ and f) corresponding Tafel plots. Reproduced with permission.^[59] Copyright 2019, Elsevier. g) Schematic representation of the synthesis for TM (Fe, Co, or Mn)-incorporated COF. h) LSV curves of metal-incorporated C-COP-P-M in O₂-saturated 0.1 M KOH at 1600 rpm. i) The comparison of electrochemical activities and electron transfer numbers for the TM-incorporated C-COP-P-M. Reproduced with permission.^[15a] Copyright 2014, Wiley-VCH.



number up to 3.93, revealing the complete reduction of oxygen into water.

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In addition to heterometallic-containing COFs directly used as ORR electrocatalysts, the pyrolysis of COFs containing N-rich TM macrocycles (e.g., metal-porphyrin complexes) has also been explored to obtain carbon-supported TM/nitrogen (M-N₄/C) materials (M = Co, Fe, Ni, Mn) for the ORR. For instance, Dai and coworkers synthesized a class of 2D COFs incorporated with TMs (TM, such as Fe, Co, Mn) using various N-containing porphyrin monomers (Figure 7g).^[15a] The resultant TM-incorporated COFs were further carbonized into COFderived M-N₄/C materials with uniform metal and nitrogen dopant distribution and found to exhibit efficient catalytic activities toward four-electron transfer in both alkaline and acid media, as well as free from any methanol-crossover/CO-poisoning effects. As a result, Fe-incorporated COF-derived carbon materials displayed a similar onset potential as the commercial Pt/C catalyst in both alkaline and acid media (Figure 7h). Moreover, the electron transfer number is close to 4 per O₂ molecule (Figure 7i), suggesting outstanding electrocatalytic activity for ORR. This study highlights that 2D COFs can be incorporated with the metal complex to form efficient electrocatalysts with precisely controlled locations of nitrogen and metal dopants.

Similar work was conducted by Müllen, Feng, and coworkers.^[62] They proposed a template-free pyrolysis of Co-COFs containing cobalt–nitrogen-coordinated complexes. The resultant Co–N-doped carbons displayed an outstanding catalytic performance toward ORR in both alkaline and acid media. In alkaline media, the doped carbons derived from Co-COFs exhibited a more-positive half-wave potential (-0.18 V vs Ag/AgCl), a high limiting current (\approx 4.62 mA cm⁻²), and almost a fourelectron transfer pathway, which are superior to Pt/C catalyst. In acid media, they also possessed excellent activities in terms of half-wave potential (\approx 0.64 V vs RHE), limiting current density (\approx 4.84 mA cm⁻²), and high electron transfer number (\approx 3.94) comparable with Pt/C. Therefore, the pyrolysis of TM-incorporated COFs is regarded as an effective strategy to obtain high-performance ORR electrocatalysts.

3.2.4. COF-Supported SACs and Nanohybrids for the ORR

COFs have abundant N heteroatoms with lone pairs for metal coordination and excellent mechanical robustness, making COFs suitable as promising platforms for supporting metal nanoparticles and SACs.^[63] Wang and coworkers reported an in situ strategy to anchor metal nanoparticles into N-doped carbon framework (MNCs) through the pyrolysis of MPc-based conjugated microporous polymers (MPc-CMPs) (**Figure 8**a).^[64] Various metal nanoparticles, such as Co, Fe, and Cu, were uniformly anchored into the porous N-doped carbon skeleton.



Figure 8. a) Schematic representation of the synthesis route of MPc-based CMPs (MPc-CMPs) and metal nanoparticles/MNCs. Reproduced with permission.^[64] Copyright 2017, Royal Society of Chemistry. b) Schematic illustration of the formation of FeSAs/PTF. c,d) High-angle annular dark-field (HAADF)-scanning transmission electron microscopy (STEM) image and enlarged image of FeSAs/PTF-600. e) LSVs of FeSAs/PTF-600, FeNPs/ PTF-600, and PTF-600 without metal load. Reproduced with permission.^[65] Copyright 2018, American Chemical Society. f) Schematic representation of the synthesis route of the *p*[SAC-Fe catalyst. g) Simulated structures of COFBTC and *p*[SAC-Fe according to the Fe K-edge extended X-ray absorption fine structure analysis result. h) HAADF-STEM of *p*[SAC-Fe-0.2. i) Tafel plots of graphene, *p*[SAC-Fe-0.2, and Pt/C. j) LSV curves of *p*[SAC-Fe-0.2 at different rotation speeds. Inset: The corresponding *K*–*L* plots and electron transfer number. Reproduced with permission.^[66] Copyright 2011, American Association for the Advancement of Science.





Benefiting from the unique structure, the resultant MNCs exhibited superior electrocatalytic activity with long-time durability and methanol tolerance for the ORR in both alkaline and acid media. This work reveals that COF-supported metal nanoparticles nanohybrids have great potential for efficient ORR electrocatalysts.

In addition, COF-supported SACs also possess high catalytic activity for the ORR. Cao, Huang, and coworkers reported a highly reactive and stable single-atom ORR catalyst (termed FeSAs/PTF) with high Fe loading up to 8.3 wt% by atomically dispersed Fe-N_x species on porous porphyrinic triazine-based frameworks (Figure 8b-d).^[65] Benefiting from the high density of single-atom Fe-N₄ active sites, the optimized catalyst FeSAs/ PTF-600 exhibited a highly efficient activity, methanol tolerance, and durability for the ORR in both alkaline and acidic media (Figure 8e). Recently, Peng, Shi, and Huo et al. developed a pyrolysis-free approach to synthesize high-activity SACs by assembling a fully π -conjugated iron phthalocyanine (FePc)-rich COF (COF_{BTC}) with graphene matrix via intermolecular interaction (Figure 8f-h).^[66] The optimized catalyst pfSAC-Fe-0.2 demonstrated a low Tafel slope of 31.7 mV and exceptional kinetic current density (25.86 mÅ cm^{-2}) for the ORR (Figure 8i,j), which is four times higher than the commercial Pt/C catalyst.

4. COF-Based Electrocatalysts for Efficient OER

OER occurs as an anodic reaction in water electrocatalysis and in the charging processes of rechargeable metal–air batteries. Different from the ORR, the OER not only involves a multielectron transfer process but also suffers from sluggish kinetics due to the large energy barriers in the complex procedures: 1) the breaking of four O–H bonds, 2) the removal of four electrons from water molecules, and 3) the formation of O–O bonds.^[67] Currently, RuO₂ and IrO₂ are regarded as the best electrocatalysts for the OER in both alkaline and acid media. Unfortunately, their limited availability, high cost, and poor durability hamper their commercial applications. Thus, there has been increasing demand in developing new OER electrocatalysts with low costs, high activity, and excellent durability for efficient water splitting with low energy. Numerous efforts have been devoted to exploring COFs-based materials as the efficient electrocatalysts for the OER, and remarkable achievements have been made in the last few years (**Table 2**). In this section, we focus on the fundamental principles of the OER and then summarize recent advances in COFs-based electrocatalysts for the OER.

4.1. Fundamental Principles of the OER

From the viewpoint of reaction pathway, the OER process is the reversed version to that of the ORR, in which O_2 is reduced to produce H_2O or OH^- , whereas H_2O is oxidized to form O_2 in the OER process.^[68] Different from the ORR, the proposed overall reaction pathways for the OER involve four discrete electron transfer steps, which are adsorption, electron transfer, chemical reaction, and desorption. The mechanism of OER is strongly sensitive to the structure of the electrode surface and very complex. In general, most of the OER reaction mechanisms involve the following two possible pathways: 1) the direct combination of two O* to produce O_2 or 2) the formation of OOH*, which further converts to O_2 .^[69]

For the evaluation of the OER catalytic performance, a series of important electrochemical parameters, including the

 Table 2. Summary of COF-based materials as electrocatalysts for the OER in the literature.

COF-based electrocatalysts	Electrolyte	Loading [mg cm ⁻²]	^{a)} η _{onset} , [mV vs RHE]	$^{ m b)}\eta_{j=10,}$ [mV vs RHE]	^{c)} <i>b</i> , [mV dec ⁻¹]	TOF, s ⁻¹ @300 mV	Ref.
COF-C ₄ N	1.0 м КОН	1.00	_	349	64	_	[74]
C4-SHz COF	1.0 м КОН	0.07	270	320	39	-	[75]
EPOP-600	1.0 м КОН	2.00	_	470	177	-	[77]
EPOP-700	1.0 м КОН	2.00	_	297	76	-	[77]
EPOP-800	1.0 м КОН	2.00	-	420	106	-	[77]
(CoP) _n -MWCNTs	1.0 м КОН	0.07	290	430	60.8	-	[39c]
Со-ТрВру	0.1 м PBS (pH 7.0)	-	_	400 @ 1 mA cm^{-2}	59	0.23	[79]
CoCMP	0.1 м КОН	-	340	$610@13 \text{ mA cm}^{-2}$	87	0.29	[60b]
macro-TpBpy-Co	0.1 м КОН	0.25	_	380	54	-	[80]
ТрВру-Со	0.1 м КОН	0.25	_	430	58	-	[80]
Co _{0.5} V _{0.5} @COF-SO ₃	1.0 м КОН	0.15	_	318	62	0.098	[81]
Ni _{0.5} Fe _{0.5} @COF-SO ₃	1.0 м КОН	0.15	_	308	83	0.1442	[82]
IISERP-COF ₃	1.0 м КОН	0.07	_	400	-	-	[84]
Ni ₃ N-IISERP-COF ₃	1.0 м КОН	0.07	200	230	79	0.52	[84]
CoP-2ph-CMP-800	1.0 м КОН	0.14	_	370	86	-	[85]
IISERP-COF1_RuO2@370	1.0 м КОН	-	_	210	65	0.103	[86]
IISERP-COF1_RuO ₂ @350	1.0 м КОН	-	_	217	67	-	[86]

 $^{a)}\eta_{onset}$ represents the onset overpotential; $^{b)}\eta_{j=10}$ is the overpotential required for the current density of 10 mA cm⁻², and; $^{c)}b$ is the Tafel slope.



overpotential needed for reaching a catalytic current density of 10 mA cm^{-2} , exchange current density, Tafel slope, and turnover frequency (TOF), have been established.^[70] These parameters are crucial and can provide valuable and insightful information that is beneficial for understanding the mechanism of the OER reaction. For example, the Tafel slope represents the rate-

4.2. Efficient COF-Based Electrocatalysts for the OER

slope, the better the performance of the OER catalysts.

determining step of the OER. The lower the value of the Tafel

Generally, the OER suffers from sluggish kinetics and large overpotentials. To facilitate its electrochemical kinetic, it is highly desired to exploit efficient electrocatalysts with sufficient surface areas and a high density of active sites to overcome the large overpotential. COFs as an emerging class of crystalline porous polymers possess a high accessible surface area, robust mechanical stability, and predesigned compositions, demonstrating the great potential for OER electrocatalysis. Moreover, the OER mechanism is unclear due to its sensitivity to the surface of the electrode and the complex system of electrocatalysts.^[71] Due to their unique molecular structures, COFs can be precisely designed with only desired elements, providing a simple but clear system to investigate the nature of active sites. In the following, significant progresses of the exploration of COFs as efficient OER electrocatalysts are presented, including pristine metal-free COFs and their derivatives, pyrolysis-free heterometallic macrocycles-containing COFs, and COF-supported metal nanoparticle hybrid materials.

4.2.1. Pristine Metal-Free COFs and Their Derivatives for the OER

Normally, pristine metal-free COFs possess relatively low electrocatalytic activity for the OER due to their inherent poor electrical conductivity and less-exposed active centers. It has been demonstrated that proper N-doped carbon stoichiometry and N-doped position within metal-free catalysts are essential for the OER activity.^[72] COFs with phenazine linkages contain porous graphene-like structures and N-enriched character similar to those of N-doped graphene, making them suitable for efficient OER electrocatalysts.^[73] Very recently, driven by DFT calculations, Zhang, Yang, and coworkers designed and fabricated a novel phenazine-linked 2D COF (COF-C₄N) by the solvothermal reaction of triphenylenehexamine (TPHA) and hexaketocyclohexane (HKH) (Figure 9a).^[74] Within DFT calculations, the designed $COF-C_4N$ possessed a higher electrocatalytic performance for the OER than the other two similar porous structures (h-C₂N and h-C₅N₂) due to its excellent crystallinity and stability, proper bandgap, and N-doped position (Figure 9c). Experimental analysis proved that COF-C₄N possesses highly ordered crystalline structures and super stabilities (Figure 9b). Benefiting from these unique features, COF–C₄N as a metal-free catalyst exhibited superior OER activity with a low overpotential of 349 mV at 10 mA cm⁻² and a Tafel slope of 64 mV dec^{-1} (Figure 9d). The C4 sites at the edge were demonstrated as potential active sites for the OER, resulting in low overpotential. This work is a big breakthrough in using pristine metalfree COFs as efficient OER electrocatalysts and provides a new way to further develop metal-free materials for efficient electrocatalysis.

Furthermore, Bhaumik and coworkers reported a new thiadiazole-based COF, termed C4-SHz COF, through the Schiff-base condensation reaction between 1,3,5-tris (4-formylphenyl)benzene (C4-CHO) and 2,5-dihydrazinyl-1,3,4-thiadiazole (SHz), as shown in Figure 9e.^[75] Through activation by the supercritical carbon dioxide treatment, the as-synthesized C4-SHz COF material showed the well-defined stacked framework (Figure 9f) and possessed superior properties such as a high specific surface area of 1224 m² g⁻¹, high porosity, and abundant active sites. When used as a metal-free OER electrocatalyst, the C4-SHz COF catalyst displayed outstanding OER activity and long-term durability, such as a low onset potential of



Figure 9. a) Schematic representation of the synthesis of $COF-C_4N$. b) Observed (red) and simulated (black) powder X-ray diffraction patterns of $COF-C_4N$. The insets show the AA stacking model of $COF-C_4N$. c) Absolute energy of the conduction band minimum and valence band maximum from PBE and HSE06 calculations and E^0 versus normal hydrogen electrode for h-C₂N, COF-C₄N, and h-C₅N₂. d) LSVs of various OER catalysts in N₂-saturated aqueous 1.0 M KOH solution. Reproduced with permission.^[74] Copyright 2019, American Chemical Society. e) Schematic presentation of the preparation of C4-SHz COF and f) switching from short- to long-range periodicity using supercritical carbon dioxide treatment. g) LSV polarization plots and h) Tafel plots of C4-SHz COF and IrO_2/C in 1 M KOH with a scan rate of 5 mV s⁻¹. Reproduced with permission.^[75] Copyright 2020, American Chemical Society.





270 mV, a low overpotential of 320 mV at the current density of 10 mA cm^{-2} (Figure 9g), and a Tafel slope of 39 mV dec⁻¹ (Figure 9h). This work also highlights the promising potential of a metal-free pristine COF electrocatalyst without pyrolysis treatment and conductive materials hybridization toward the OER.

Although metal-free carbon materials are usually applied as ORR catalysts, their OER catalytic activities are fairly low and rarely reported. The main reason is that the OER often occurs at high oxidation potentials and leads to unavoidable carbon corrosion, resulting in catalyst agglomeration and the formation of carbonates to block the active surface.^[76] Very recently, the pristine metal-free COFs are optimized using the postcarbonization process to increase the OER catalytic activity.^[77] As a result, an ethylene diamine-based porous COF was carbonized and explored as a metal-free electrocatalyst for the OER. Compared with pristine COFs, the COF-derived carbon material coated on carbon paper displayed significantly an enhanced OER catalytic activity in alkaline media with an onset potential of 1.527 V (vs RHE) and an overpotential of 297 mV at a current density of 10 mA cm^{-2} .^[77] Furthermore, even at a high current density of 300 mA cm^{-2} , the COF-derived carbon material showed a low overpotential of 580 mV and prolonged stability over 10 h, which is even better than some of the metal-based OER electrocatalysts.

4.2.2. Pyrolysis-Free Heterometallic Macrocycles-Containing COFs for the OER

As a promising candidate, TM-based electrocatalysts have been widely explored for catalyzing OER.^[7a,78] One of the advantages of COFs as efficient OER electrocatalysts is that they can be integrated with TM ions utilizing TM macrocyclic clusters, such as porphyrin and phthalocyanine. Among them, Co-based COFs have gained significant interest for OER electrocatalysts due to their stable redox states.^[39c,60b,79]

For the first time, Du and coworkers reported cobalt– porphyrin-based COF on multiwalled carbon nanotubes (defined as $(CoP)_n$ -MWCNTs) as a highly active electrocatalyst for OER (**Figure 10**a).^[39c] The combination of MWCNTs and cobalt–porphyrin networks (Figure 10b) can preserve the excellent electrical conductivity of CNTs as well as the high stability of assemblies in the catalyst. The resultant (CoP)_n-MWCNTs exhibited a low overpotential of only 290 mV at a catalytic current density of 1.0 mA cm⁻² (Figure 10c) and the lowest Tafel slope of 60.8 mV dec⁻¹. In another work, a bipyridine containing COF (TpBpy) was utilized as an OER catalyst by introducing active Co (II) ions into its porous framework (Figure 10d).^[79] Compared with pristine TpBpy, TpBpy containing Co ions



Figure 10. a) Molecular structure and b) TEM images of (CoP),-MWCNTs. c) LSV curves of (CoP),-MWCNTs and other catalysts in 1.0 M KOH. Reprinted with permission.^[39c] Copyright 2015, American Chemical Society. d) Schematic representation of the synthesis of TpBpy and Co-TpBpy. e) Comparative CV profiles of Co-TpBpy (red line) and as-synthesized TpBpy (black line) in phosphate buffer (pH: 7.0). f) LSV profile of Co-TpBpy before and after 1000 cycles. Reprinted with permission.^[79] Copyright 2016, American Chemical Society. g) Schematic representation of the synthesis of metal–organic CMPs: CoCMP and ZnCMP. h) LSV and i) the corresponding Tafel plot of CoCMP. Reproduced with permission.^[60b] Copyright 2018, Royal Society Chemistry.



showed an intense anodic wave at $\approx 1.63 \text{ V}$ versus RHE (Figure 10e), implying a marked difference in its OER activity. The obtained Co-TpBpy had a high accessible surface area of $450 \text{ m}^2 \text{g}^{-1}$ and exhibited outstanding catalytic performance in neutral pH conditions: retaining 94% of its OER activity even after 1000 cycles with a TOF of 0.23 S^{-1} and Faradaic efficiency of 95% (Figure 10f). The exceptional stability can be attributed to the synergetic effect of the inherent porosity and presence of coordinating units in the COF skeleton, which highlight the need for utilizing high surface catalyst support for designing robust OER catalysts. Similar work was reported by Singh and coworkers.^[60b] They designed a new N₄-coordinated Co²⁺-containing phthalocyanine-based COF through Schiff-base condensation reaction (Figure 10g). The obtained Co-COF (termed CoCMP) catalysts showed stable and efficient electrocatalytic activity toward the OER with an onset potential of 1.57 V (vs RHE), a low overpotential of 340 mV, and a Tafel slope of 87 mV dec $^{-1}$ (Figure 10i,j). Even after 1000 cycles, the Co-COF maintained a consistent electrocatalytic activity, demonstrating the superior durability without the leaching of Co ions.

In addition, porosity is a key concern in affecting the OER catalytic performance due to the requirement of fast mass transport. Hierarchical porous structures are highly desirable with small micropores for offering large reaction surface areas and large macropores for facilitating sufficient transportation to and from the catalyst surface. However, most of the reported COFs are designed and isolated as microcrystalline powders, only possessing the features of microporous or mesoporous structures. The introduction of hierarchical or secondary porosity is an effective way to achieve meso- or macroporous COFs with controllable porosity structures but yet challenging. As discussed in Section 3.1.5, Thomas and coworkers proposed a practical and efficient approach to prepare hierarchical porous COFs (termed macro-TpBpy) with interconnected macro-microporous structures using polystyrene spheres (PSs) as hard templates (**Figure 11**a).^[80] Importantly, the size of macropores within COFs can be tuned by modulating the size of PSs (Figure 11b-g). The capacity of fast mass and ion transport was confirmed by utilizing cobalt-coordinated COFs as an OER catalyst. The obtained cocoordinated COF catalysts (macro-TpBpy-Co) displayed superior OER performance, including a lower overpotential of 380 mV (vs RHE) at a current density of 10 mA cm⁻² and a lower Tafel slope of 54 mV dec⁻¹ compared with the original COF with only microporous structures. The enhanced activity can be attributed to the interconnected hierarchical pore structures, which allow fast mass transport and more accessible active sites. Notably, the PS templating method can be extended to obtain various macro-microporous imine-based COFs by modulating the corresponding amine linkers (Figure 11h,i), displaying their potential as a convenient route for the preparation of macro-microporous COFs with different functional groups for various applications.

To further improve metal-atom utilization efficiency and catalyst stability, bimetallic COFs with two active centers have been explored for the OER through selecting appropriate building blocks. Starting with a great contribution from Luo and



Figure 11. Scanning electron microscope (SEM) images of PSs and macro-TpBpy with macropore sizes of a,d) \approx 160 nm, b,e) \approx 320 nm, and c,f) \approx 360 nm. g) Schematic representation of the synthesis of macro-TpBpy-Co. h) OER polarization curves and i) corresponding Tafel plots for macro-TpBpy, macro-TpBpy-Co, TpBpy-Co, and a commercial RuO₂ catalyst. Reproduced with permission.^[80] Copyright 2019, American Chemical Society.





coworkers, flexible and robust Co/V-incorporated bimetallic COFs (defined as $Co_xV_{1-x}@COF-SO_3$) were synthesized and used as efficient OER electrocatalysts via a convenient and efficient cation-exchange strategy (**Figure 12a**).^[81] The obtained $Co_{0.5}V_{0.5}@COF-SO_3$ catalyst showed a morphology of the uniform nanofiber (Figure 12b). As a result, the optimized bimetallic $Co_{0.5}V_{0.5}@COF-SO_3$ exhibited the lowest Tafel slope of 62 mV dec⁻¹ and a high TOF value (0.098 s⁻¹) at the overpotential of 300 mV, all of which are superior to those of monometallic COFs (Figure 12c–e). The outstanding OER performance can be ascribed to the strong electronic effect of Co and V active sites,

maximizing the atom efficiency. Very recently, Luo and coworkers used the same strategy to synthesize pyrolysisfree Ni/Fe bimetallic COF (termed Ni_xFe_{1-x}@COF-SO₃) electrocatalysts for the OER (Figure 12f).^[82] The high-resolution transmission electron microscope (TEM) image determines the nanofiber network structure in Ni_{0.5}Fe_{0.5}@COF-SO₃ without detectable nanoparticles (Figure 12g). Due to the prominent electronic synergistic effect and the unique advantage of the COFs' structures, the optimized Ni_{0.5}Fe_{0.5}@COF-SO₃ catalyst showed a low Tafel slope of 83 mV dec⁻¹ and a high TOF value of 0.14 S⁻¹ at the overpotential of 300 mV (Figure 12h–j).



Figure 12. a) Schematic illustration of the preparation process of flexible and robust bimetallic-incorporated C_0V_{1-x} (COF-SO₃ catalysts. b) TEM image of $C_{0.5}V_{0.5}$ (COF-SO₃. c) LSV curves, d) TOF values versus overpotential, and e) Tafel slopes of C_0V_{1-x} (COF-SO₃. (x = 0, 0.2, 0.5, 0.8, 1) toward the OER. Reproduced with permission.^[81] Copyright 2020, Royal Society of Chemistry. f) Schematic illustration of the preparation process of bimetallic-incorporated Ni_xFe_{1-x} (COF-SO₃ catalysts. g) TEM image of Ni_{0.5}Fe_{0.5} (x = 0, 0.2, 0.5, 0.8, 1) toward the overpotential of 300 mV of Ni_xFe_{1-x} (COF-SO₃. (x = 0, 0.2, 0.5, 0.8, 1). Reproduced with permission.^[82] Copyright 2020, American Chemical Society.

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4.2.3. COF-Supported Metal Nanoparticle Hybrid Materials for the OER

Furthermore, pristine COFs can also directly serve as the support to introduce metal nanoparticles for OER electrocatalysis. Based on the OER mechanism, metal nanoparticles among the catalysts play a vital role in catalyzing OER, as they can coordinate and discharge H₂O or OH⁻ species.^[83] The size of nanoparticles and the electronic interaction between the host COFs and nanoparticles are vital to improve their OER electrocatalytic activities. For instance, the low-bandgap benzimidazole-based COF and the sp^3 N-rich flexible COF have been developed as the supports for loading Ni₃N and Co_xNi_y(OH)₂ nanoparticles, respectively.^[84] The resultant catalysts exhibited excellent OER catalytic performance with high activity and stability, which can be attributed to the synergistic interactions between the guest metal nanoparticles and COF supports.

To enhance the conductivity, metal-incorporated COFs as precursors have also been pyrolyzed into hybrid materials due to the uniform distribution of metal nanoparticles on the COF-derived carbon skeletons. Jia et al. reported a series of nitrogen-enriched porous carbons incorporating cobalt nanoparticles (defined as CoP-*n*ph-CMP-800, n = 2, 3, 4) derived from cobalt–porphyrinbased COF.^[85] Under optimal conditions, CoP-2ph-CMP-800 exhibited outstanding OER catalytic activities with a low overpotential of 370 mV at a catalytic current density of 10 mA cm⁻², as well as excellent stability. Recently, Kurungot, Vaidhyanathan, and coworkers developed a soft pyrolysis approach to prepare two composites consisting of small-sized RuO₂ nanoparticles (\approx 3–4 nm) and carbon derived from COFs.^[86] The COFs were utilized as a sacrificial reaction pot for the growth of RuO2 nanoparticles, resulting in the homogeneous dispersion of most of the nanoparticles within the interlayers of carbon skeletons. These two RuO₂@C composites displayed excellent OER catalytic performance with low overpotentials of 210 and 217 mV for IISERP-COF1_RuO₂@370 (composite I) and IISERP-COF1_RuO₂@350 (composite II), respectively.

5. COF-Based Electrocatalysts for Efficient HER

Hydrogen is considered as a promising renewable energy source to replace fossil fuels.^[87] The electrolysis of water provides an ideal approach for sustainable hydrogen generation. As an essential half reaction for achieving water electrolysis, the HER has gained great attention and has become a hotspot in clean energy conversion. To date, Pt-based catalysts possess the best catalytic performance toward HER, but high cost and poor stability hamper their large-scale practical applications. Although the TM-based catalysts show good catalytic activity for the HER, they still suffer from the metal corrosion and the deactivation caused by the leaching of metal ions.^[88] Therefore, the exploration of highly efficient electrocatalysts for the HER is of great importance and strongly urgent. COFs possess the appealing framework structures and unique electronic characteristics, showing great potential for developing highly efficient HER electrocatalysts (**Table 3**) and helping to gain more understanding of the HER mechanisms.

5.1. Fundamental Principles of the HER

Similar to the ORR and OER, the procedure of the HER is also a complex multistep reaction involving the adsorption, reduction, and desorption processes.^[89] In principle, the HER electrocatalytic process proceeds in two possible pathways as the Volmer-Heyrovsky pathway and the Volmer-Tafel pathway.^[89b] For instance, in acidic solutions, the Volmer step $(2 H^+ + 2e^- + * \rightarrow H^*)$ relates to the interaction between the hydrogen species (H⁺) and the active centers (*) on the surface of electrocatalysts and the formation of H*. Subsequently, the absorbed hydrogen species (H*) are bonded with H⁺ to produce H_2 molecules through a Heyrovsky step ($H^+ + e^- + H^* \rightarrow H_2$) or interact with another H* to generate H2 molecules in a Tafel step (2 H* \rightarrow H₂ + 2*). In alkaline solutions, the protons are in the form of H₂O molecules, in which the discharge species will be H₂O to form the adsorbed H* and H-O bonds with the releasing OH⁻ to the electrolyte.^[90]

Obviously, the selection of these pathways mainly depends on the properties of the electrocatalyst surface, so that the surface characteristics of the electrocatalysts play a crucial role in determining the electrocatalytic performance toward HER.^[91] In addition, the overall reaction of the HER is a rate-determining step, the rate measurements, as LSV is crucial to evaluate the HER catalytic performance. The Tafel slope calculated from LSV plots reveals the HER catalytic performance and pathway, gaining insightful understanding into the HER mechanism.

5.2. Efficient COF-Based Electrocatalysts for the HER

As discussed earlier, the essential properties of the electrocatalyst surface determine the reaction kinetics and the overpotential value of HER. COFs show fascinating framework structures with high porosity, sufficient surface area, and unique molecular structures, providing an excellent platform for designing highly efficient HER electrocatalysts. Generally, the activity of COFbased electrocatalysts originates from their intrinsic unit activity

Table 3. Summary of COF-based materials as electrocatalysts for the HER in the literature.

COF-based electrocatalysts	Electrolyte	Loading $[mg cm^{-2}]$	$\eta_{\rm onset} \; [{\rm mV} \; {\rm vs} \; {\rm RHE}]$	$\eta_{j=10}~[{ m mV}~{ m vs}~{ m RHE}]$	$b \; [mV dec^{-1}]$	Ref.
SB-PORPy-COF	0.5 м H ₂ SO ₄	0.285	50	380 @ 5 mA cm ⁻²	116	[93]
TpPAM-COF	0.5 м H ₂ SO ₄	-	-	250	106	[94]
CoP-2ph-CMP-800	1.0 м КОН	0.14	-	360	121	[85]
Cu @2DCCOF1	_	-	-	541	130	[95]
Ru@COF	1.5 м H ₂ SO ₄	0.305	159	212	75	[97]



and/or the number of exposed active sites (extrinsic factor). The former can be related to the dopants in COFs and synergic effect between the COF and matrix (e.g., graphene and CNT). As for the later one, there are several main factors that have to be considered including porosity, structural regularity, and functional moieties, which could increase the number of exposed active sites. Numerous efforts have been made to modulate these features by modifying the molecular architecture to explore highly efficient COF-based electrocatalysts toward HER. In the following sections, recent developments of COF-based electrocatalysts for efficiently catalyzing HER are summarized, including pristine metal-free COFs with heteroatoms dopants (e.g., N, P, or S) and COF-supported hybrids.

5.2.1. Pristine Metal-Free COFs for the HER

Over the past few decades, there has been increasing interest in exploring non-noble metal-based catalysts containing active TMs, such as Fe, Co, and Ni, for the HER.^[92] However, they suffer from the leaching of metal ions from the matrices, thereof

resulting in deactivation. Therefore, the development of metalfree electrocatalysts is regarded as a promising approach to address the earlier issues and should provide an ecofriendly way for hydrogen production.

Pradhan and Bhaumik et al. reported the first metal-free COFbased electrocatalysts for the HER. A quasi-2D COF (termed SB-PORPy-COF) was synthesized by the Schiff-base reaction through 5,10,15,20-tetrakis(4 aminophenyl)porphyrin (TAP) and 1,3,6,8-tetrakis (4-formylphenyl) pyrene (TFFPy) (Figure 13a,b).^[93] The obtained COF had a high surface area of $869 \text{ m}^2 \text{g}^{-1}$ and superior chemical and thermal stability. After drop casting on a glassy carbon (GC) electrode, SB-PORPv-COF showed a remarkable HER catalytic activity with a low onset overpotential of about 50 mV in acidic media (Figure 13c), which is the lowest overpotential reported for any type of COF. Moreover, no activity loss involving the onset potential and the current density at various potentials was observed after 500 cycles, demonstrating its good durability.

In another work, Pradhan, Bhaumik, and coworkers developed a porphyrin-based metal-free COF (TpPAM) as efficient



Figure 13. a) Schematic representation of the preparation of quasi-2D SB-PORPy-COF. b) AA stacking model structure of SB-PORPy-COF. c) Polarization curves for the hydrogen evolution reaction on bare GC (blue), Vulcan (red), and SB-PORPy-COF (black) electrodes. Reproduced with permission.^[93] Copyright 2017, American Chemical Society. d) Schematic diagram of the metal-free covalent organic polymer (TpPAM). e) LSV plots of TpPAM in its first and after 1000 cycles of test run. f) Volcano plot of logi₀ versus Δ GH* for model C (red circle) and TM-based catalysts (dark yellow circle). Reproduced with permission.^[94] Copyright 2017, American Chemical Society. g) Schematic representation of the synthesis of 2DCCOF1 film on the interface by Suzuki polymerization (Ar = aryl group; X = halide; B = boronic group). h) High-resolution transmission electron microscope (HRTEM) image (scale bar: 2 nm) and i) comparing the digital-zoomed HRTEM image and the view of the A–B–C... stacked structure. i) HER polarization curves of the bare copper electrode and the 2DCCOF1 electrode and j) the Tafel curve of 2DCCOF1. Reproduced with permission.^[95] Copyright 2018, Wiley-VCH.



HER electrocatalysts through a simple Schiff-base condensation between triformylphloroglucinol (Tp) and 5,10,15,20-tetra (4-aminophenyl)-21H,23H-porphyrin (PAM) (Figure 13d).^[94] The resultant TpPAM displayed superior catalytic activity for the HER, including a low overpotential of 250 mV at 10 mA cm^{-2} , a small Tafel slope of 106 mV dec^{-1} , a high Faradaic efficiency of 98%, and good durability with remaining 91% of the initial current density after 1000 cycles (Figure 13e). Furthermore, DFT theoretical calculations were carried out to investigate the high HER activity of TpPAM. As shown in the Volcano plot (Figure 13f), the $|\Delta G_{H^*}|$ (change of Gibbs free energy) value of the repeating unit of TpPAM is 0.08 eV, which is very close to that of the Pt catalyst (0.09 eV). Both the experimental results and DFT theoretical calculations suggest that metal-free COFs are promising as efficient HER electrocatalysis. Recently, free-standing 2D-conjugated COF films were also applied as metal-free catalysts for the HER. For instance, Li and coworkers synthesized a graphene-like 2DCCOF1 film through Suzuki polymerization on the water–toluene interface (Figure 13g–i).^[95] To explore its potential applications for HER electrocatalysis, the 2DCCOF1 film was deposited on a copper electrode. Compared with the bare copper electrode, the obtained 2DCCOF1 electrode exhibited a much stronger HER catalytic activity with an overpotential of 541 mV at a current density of 10 mA cm^{-2} and a Tafel slope of 130 mV dec^{-1} (Figure 13j,k), which are comparable with N- or P-doped graphene.

In addition, COFs are semiconductors and their bandgap can be altered by adjusting the degree of conjugation in the ligands. This provides the possibility for COFs as photocatalysts for photocatalytic hydrogen evolution. It has been reported that the functional groups in the backbone of COFs played an importance role in the overall photocatalytic hydrogen evolution. For example, Sun, Zhang, and coworkers synthesized a series of ketoenamine-based COFs using the same host framework (TpPa-COF) as the model system (**Figure 14**a).^[96] Three types of functional groups (-H, $-(CH_3)_2$, and $-NO_2$) were attached



Figure 14. a) Schematic illustration of the synthesis of TpPa-COF-X (X = -H, $-(CH_3)_2$, and $-NO_2$). b) UV-vis diffuse reflectance spectra curves and c) Mott–Schottky plots for TpPa-COF-X. d) The photocatalytic H_2 evolution activities and e) the photocatalytic stability of TpPa-COF-X. Reproduced with permission.^[96] Copyright 2019, Wiley-VCH. f) Digital photos of imine-linked COF and Ru@COF. g) TEM and h) HRTEM images of Ru@COF. i) LSV curves and j) Tafel curves of Ru@COF, bare RuCl₃, and COF. Reproduced with permission.^[97] Copyright 2019, Wiley-VCH. k) Schematic representation of the synthesis of TpPa-2 COF and CdS–COF hybrids. Reproduced with permission.^[98] Copyright 2019, Wiley-VCH.



in the backbone of TpPa-COF by selecting diverse building units, where TpPa-COF-(CH₃)₂ shows the strongest photoabsorption (Figure 14b). Mott–Schottky results demonstrated a remarkable characteristic of n-type semiconductors for all as-synthesized samples (Figure 14c). After the systematic investigation, TpPa-COF-(CH₃)₂ showed the best activity with the maximum photocatalytic activity of 8.33 mmol g⁻¹ h⁻¹ (Figure 14d). In contrast, TpPa-COF and TpPa-COF-NO₂ showed a relatively poor photocatalytic activity of 1.56 and 0.22 mmol g⁻¹ h⁻¹, respectively. Furthermore, TpPa-COF-(CH₃)₂ exhibited excellent stability without any structural damage for 30 h of irradiation (Figure 14e). The best photocatalytic H₂ production by TpPa-COF-(CH₃)₂ should be mainly attributed to the better electrondonating ability of –CH₃ groups compared with –H or –NO₂ groups, giving rise to the stronger conjugation effect and thereby improving the photocatalytic activity.

5.2.2. COF-Based Hybrids for the HER

In addition, COFs have crystalline porous structures and extensive π - π conjugation, making them ideal platforms for anchoring active metal nanoparticles and thus enhancing their catalytic activities. Das and coworkers designed and synthesized an imine-linked crystalline 2D COF through the condensation of benzene-1,3,5-tricarboxaldehyde and 3,4-diaminobenzohydrazide (Figure 14f).^[97] The as-prepared 2D COF served as an ideal support for the encapsulation of ruthenium (Ru) ions to generate Ru@COF (Figure 14g,h). The resulting Ru@COF exhibited high HER activity in acidic media with an onset overpotential of 159 mV and a small Tafel slope of 79 mV dec⁻¹, indicating fast rate and high catalytic activity for the HER (Figure 14i–j). The porous framework of 2D COF plays a vital role in enabling stability and catalytic efficiency.

Similarly, Banerjee and coworkers used a highly stable COF (TpPa-2) as a support matrix for anchoring CdS nanoparticles (Figure 14k).^[98] Benefiting from the large surface area of COFs, the CdS–COF hybrid materials showed enhanced photocatalytic H₂ evolution as compared with the bulk CdS. The optimized CdS–COF (90:10) displayed superior photocatalytic activity with H₂ production of 3678 μ mol h⁻¹ g⁻¹, which is up to 28 times higher than that of the bulk CdS. These two works reveal that COFs as catalytic support matrix can greatly improve the catalytic activities of loaded nanoparticles.

6. COF-Based Bifunctional Electrocatalysts for Bifunctional ORR/OER

ORR and OER are vital for clean energy conversion, especially for metal–air batteries.^[99] However, due to their sluggish kinetics, highly efficient electrocatalysts are generally applied to accelerate both the ORR and OER processes.^[100] Although Pt-based and Rubased materials show the best catalytic performance toward the ORR and the OER, respectively, the major obstacles are their high cost and scarcity.^[101] Therefore, it is demanded to develop bifunctional catalysts from Earth-abundant electroactive materials for the ORR and OER. To replace commonly used noble-metal-based electrocatalysts, COFs have also been explored as efficient bifunctional electrocatalysts for both the ORR and

OER, due to their superior advantages of cost effectiveness, good catalytic activity, and stability.

6.1. Fundamental Principles of Bifunctional ORR/OER Processes

Bifunctional ORR/OER processes involve sequential proton-coupled electron transfer reactions. In principle, there are four elementary reaction steps, in which ORR proceeds through the adsorption of O_2 and the formation of OOH*, followed by further reduction to O* and OH*, whereas the OER proceeds in the reverse direction.

Even though the ORR and OER processes are reverse, it is challenging to develop an advanced electrocatalyst for achieving a balanced reversibility.^[102] For example, Pt-based catalysts are the state-of-the-art catalysts toward ORR, whereas Pt is not a good candidate for the OER due to the formation of Pt oxides and deactivation under high potentials. The best catalysts for the OER are Ru- and Ir-based oxides due to their high activity and excellent durability, but they also cannot be used as bifunctional catalysts because of the poor activity for the ORR. An ideal bifunctional catalyst should be stable within a wide electrochemical potential window (0.6-1.9 V), which remains a great challenge. The wide potential window not only narrows down the scope of materials capable of catalyzing the ORR and OER processes but also introduces more complicated factors that make the catalytic activity inferior.^[103] In addition, the electrolyte media plays a crucial role in accelerating the catalytic process. Compared with the acidic media, the alkaline media is more suitable as it provides a relatively weaker corrosive environment and makes the catalysts more stable. In alkaline media, the hydroxide is oxidized to generate oxygen and water in the OER process, whereas oxygen and water are reduced to produce hydroxide or hydrogen peroxide through a 4e⁻ or 2e⁻ pathway for the ORR.

Commonly, the overpotential or potential gap is an important indicator for the evaluation of promising bifunctional catalysts.^[104] The potential gap (ΔE) can be calculated from the following equation.

$$\Delta E = E_{j=10} - E_{1/2} \tag{1}$$

where $E_{j=10}$ is the OER operating potential at a current density of 10 mA cm⁻², $E_{1/2}$ represents the half-wave potential in the ORR. The smaller the potential difference, the better the catalytic performance for both ORR and OER. To reach a low overpotential, the bifunctional electrocatalysts should have sufficient surface area and high porosity, as well as pore structures at the nanoscale, beneficial for more accessibility of catalytic active sites. In addition, the surface of catalysts should have high affinity for oxygen absorption, as both the ORR and OER involve oxygen. This can be conducted by the introduction of oxygen-containing groups or vacancies in lattice structures.

6.2. Efficient COF-Based Electrocatalysts for Bifunctional ORR/OER

COFs have crystalline porous structures that can be tuned and manipulated to optimize the surface properties, displaying great

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COF-based bifunctional electrocatalysts	Electrolyte	Loading [mg cm^{-2}]	^{a)} E _{1/2} [V vs RHE]	^{b)} E _{j=10} [V vs RHE]	$^{\rm c)}\Delta E~[V]$	<i>b</i> [mV dec ⁻¹] ORR&OER	Ref.
RM-COP-PA-900	0.1 м КОН	0.25	0.841	1.69	0.84	_	[105]
G@POF-Co	0.1 м КОН	0.10	0.81	0.43	0.85	46.9 & 161	[60a]
Co-POC	0.1 м КОН	0.10	0.83	0.47	0.87	53.5 & 139	[107]
PA@ TAPT-DHTA-COF _{1000NH3}	0.1 м КОН	-	0.85	1.94	-	110	[57]

Table 4. Summary of COF-based materials as bifunctional electrocatalysts for both ORR and OER in the literature.

^{a)} $E_{1/2}$ represents the half-wave potential in the ORR; ^{b)} $E_{j=10}$ is the OER operating potential at a current density of 10 mA cm⁻², and; ^{c)} ΔE is the potential gap between the ORR half-wave potential ($E_{1/2}$) and OER potential (at 10 mA cm⁻²) for evaluating the overall bifunctional activity.

potential as efficient bifunctional electrocatalysts for catalyzing the ORR and OER. As the field of COF-based catalysts for efficient electrocatalysis is still at the beginning, only a few works about COF-based materials as bifunctional electrocatalysts were investigated (**Table 4**). Herein, we summarize the recent significant progress on the use of COF-based materials as an advanced bifunctional electrocatalyst for both ORR and OER, including COF-derived metal-free carbons, COF-derived metal–carbon hybrids, and COF-supported SACs.

6.2.1. COF-Derived Metal-Free Carbons for Bifunctional ORR/ OER

Bifunctional catalysts are of great importance to accelerate both the ORR and OER processes in rechargeable metal–air batteries.^[102] As discussed earlier, heteroatoms-doped carbon materials derived from COFs have been explored as single-functional ORR or OER catalysts with outstanding catalytic performance. However, due to the wide range of the ORR/OER working potential, there remain several challenges to find a high-performance bifunctional catalyst with high catalytic activity and good stability, especially without sacrificing catalytic efficiency. The introduction of a second heteroatom, such as P or S, into N-doped carbon materials can improve the overall stability and change the surface electronic states, which enable the bifunctional activity.

For the first time, Xiang and coworkers synthesized N- and Pcodoped carbon materials (termed RM-COP-PA-900) derived from COFs through reaction milling and subsequent pyrolysis processes (Figure 15a).^[105] Benefiting from N and P codoping and the macroporous structure, the resultant material exhibited excellent bifunctional activity toward ORR and OER (Figure 15b, c), as well as superior durability and resistance to the crossover effect. The overall oxygen activity of RM-COP-PA-900 was evaluated by the potential difference (ΔE) with a value of 0.84 V. Moreover, Jiang and coworkers also synthesized 2D graphitic carbons with abundant N- and P-doped heteroatom catalytic edges using template carbonization.^[57] Using PA as a template, obtained carbons were used as bifunctional catalysts and achieved ultrahigh performance, including exceptional onset potential, half-wave potentials, high limiting current density, a low Tafel slope, and long-time stability in the ORR and OER processes.



Figure 15. a) Schematic illustration of the preparation process for RM-COP-PA-900 via an effective reaction milling process. The linear scan voltammogram (LSV) curves at an RDE (1600 rpm) in O₂-saturated 0.1 M KOH solution of a) Pt/C, RM-COP-900, and RM-COP-PA-900 for ORR and b) IrO₂, RM-COP-900, and RM-COP-PA-900 for ORR. Reproduced with permission.^[105] Copyright 2018, Elsevier. d) Schematic illustration of the one-pot synthesis of POF. The hydrogen, carbon, nitrogen, and oxygen atoms are marked with white, gray, blue, and red, respectively. e) SEM image of G@POF and f) 95% *iR*compensated ORR and OER LSV profiles of Pt/C, IrO₂, G, and G@POF-Co for bifunctional performance evaluation. Reproduced with permission.^[60a] Copyright 2019, Wiley-VCH.



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As mentioned earlier, cobalt-coordinated porphyrin-based COFs (Co-COF) show excellent electrocatalytic performance for both the ORR and the OER. It is reasonable that Co-COFs have great potential as bifunctional catalysts for OER and ORR. One big issue is that the pristine Co-COF suffers from poor electrical conductivity, which affects the catalytic efficiency. Fortunately, benefiting from the well-defined alignment of π -conjugated structures, COFs can grow on the similarly conjugated surface of conductive carbon scaffolds, such as CNTs or graphene.

Zhang and coworkers reported a cobalt-coordinated COF and graphene hybrid material (G@COF-Co) as bifunctional electrocatalysts for both OER and ORR (Figure 15d).^[60a] The pristine porphyrin-based COF showed a layered structure with an interlayer spacing of 0.39 nm. Using graphene as the template for hybridization, the COF layer was uniformly deposited on the surface of graphene due to the intermolecular π - π interaction between POF and graphene (Figure 15e). The resulting G@COF-Co demonstrated superior bifunctional reactivity toward the ORR with a half-wave potential of 0.81 V (vs RHE) and a low potential gap of 0.85 V between the ORR half-wave potential and the potential required at an OER current density of 10 mA cm^{-2} (Figure 15f). Sun, Li, and coworkers demonstrated a multifunctional electrochemical catalyst fabricated by pyrolysis of a bimetallic COF.^[106] The COF catalyst possesses abundant iron and cobalt nanoparticles embedded with standing carbon layers. Due to the integration of these features, the catalyst exhibited excellent electrocatalytic performances in the ORR and OER processes.

6.2.3. COF-Supported SACs for Bifunctional ORR/OER

Recently, SACs are regarded as efficient electrocatalysts due to their maximum atom efficiency. However, the fabrication of SACs is challenging, which requires extensive attempts of precursors with novel design principles. Due to their unique properties, COFs also demonstrate promising potential serving as precursors for fabricating single-atom M–N–C electrocatalysts (where M represents a TM atom) for both OER and ORR.

For instance, a cobalt-coordinated COF (termed Co-G@COF) with graphene hybridization was designed and fabricated as the pyrolysis precursor to obtain fabricated single-atom Co-N_x-C electrocatalysts (Figure 16).^[107] The as-prepared Co-G@COF showed a uniform contrast without any aggregated cobalt component (Figure 16a), but isolated cobalt single atoms are unambiguously observed in the carbon skeleton (Figure 16b). The obtained electrocatalyst exhibited outstanding bifunctional ORR/OER electrocatalytic properties, such as a small overpotential gap of 0.83 V comparable with noble-metal-based electrocatalysts (Figure 16c), rapid kinetics with reduced Tafel slopes (53.5 mV dec⁻¹ for ORR and 139 mV dec⁻¹ for OER, Figure 16d-f), and long-term durability. Such superior performance can be attributed to three factors: cobalt-coordinated porphyrin units, the 2D framework structure, and graphene hybridization.



Figure 16. Characterization and bifunctional oxygen electrocatalytic performance evaluation of the single-atom Co-COF electrocatalyst. a) TEM image and b) corresponding enlarged view of Co-COF. The bright dots highlighted with yellow circles in (c) mark the cobalt single atoms in Co-COF. c) 95% *iR*-compensated ORR LSV profiles and d) corresponding Tafel plots of Pt/C, Co-COF, and G electrocatalysts. e) 95% *iR*-compensated OER LSV profiles and f) corresponding Tafel plots of Ir/C, Co-COF, and G electrocatalysts. Reproduced with permission.^[107] Copyright 2019, Wiley-VCH.



7. Summary and Perspective

COFs have been rapidly developed over the past decade as promising electrocatalysts for efficient electrocatalysis in clean and renewable technologies. Combining the diversity of building blocks and flexible construction principles, COFs with predesigned compositions and properties can be achieved via the atomically precise selection of building units and predictable synthesis routes, providing outstanding platforms for the rational design of highly efficient electrocatalysts. Compared with traditional materials (e.g., polymer and MOFs) for efficient electrocatalysis, the COFs possess several inherent advantages, which include 1) precisely controllable molecular structures enabling the tailorable heteroatom incorporation and porous architectures for enhancing the catalytic performance, 2) exceptional thermal stability and abundant electronic character in the presence of conjugated π - π interactions, 3) functional moieties, such as functional groups and redox units, that can be introduced into COFs for further postsynthetic modifications, and 4) Incorporation with metal-porphyrin complexes/clusters for highly efficient electrocatalysts.

From the viewpoint of key parameters concerning the catalytic performance, design principles for COF-based electrocatalysts were established to increase the intrinsic activity and the content of active sites. Recent significant progress has been achieved in the design and synthesis of the COFs used as OER, ORR, or HER single-functional catalysts and bifunctional catalysts for both OER and ORR. Among them, pristine metal-free COFs, metal-free COF-derived carbons, heterometallic macrocyclescontaining COFs and their derivatives, and COF-supported SAC and nanohybrids were developed and showed superior catalytic properties with high activity, outstanding durability, and free from any methanol-crossover or gas-poisoning effects.

Although great progress has been made, some challenges or key issues for the development of COF-based electrocatalysts certainly have to be addressed. First of all, the activity of COF-based catalysts in acid media is rarely explored and their catalytic performance is unsatisfied compared with noble-metals catalysts. Considerable improvements are in demand for optimizing the catalytic performance, particularly for the ORR. Second, for practical applications in clean energy technologies, the stability of COF-based catalysts against harsh environmental conditions (e.g., strong acids and bases) needs further enhancement. For instance, under alkaline (6 M KOH, three days) or acidic (3 M HCl, 1 week) conditions, keto-type and hydrogen-bonding COFs suffer from the loss of crystallinity and porosity.^[108] In this regard, the synthesis of COFs with stable aromatic ring structures is highly recommended to endow high chemical stability. In addition, most COFs are synthesized as powders, and it is inconvenient for the integration into devices, such as fuel cells and metal-air batteries. The development of COFs with pellets or 2D film geometry will be beneficial for their future practical applications. Third, the role of COFs in the catalytic system is still not clear, especially the correlation between COF structures/compositions and the catalytic activities. It is of significant importance to verify the activity sites and chemical kinetic processes on the surface of COF architectures.

Until date, the field of COF-based catalysts for efficient electrocatalysis is still in its initial stage. To further explore the COFs as highly efficient electrocatalysts, we would like to list our perspectives and a few potential directions in this fascinating area as follows: 1) to make full use of their molecular structure features that allow for precisely integrating building units to achieve COFs with predesigned architectures and properties. For instance, the nanoarchitecture of COFs with precisely controlled conducting channels, uniform distribution and location of dopants, and highly ordered conjugated frameworks would be able to greatly enhance the catalytic performance; 2) to take advantage of the synergetic effect between multiheteroatoms or more than two types of metal ions, multitypes of heteroatom doping or metal ions could be introduced into the frameworks of COFs. This approach would significantly enhance the catalytic activities of the COF electrocatalysts and is worth further investigation; 3) to explore new metal-free intrinsic COFs without carbonization as efficient electrocatalysts with the aim of regularizing their active sites at the molecular or atomic level. Although COFderived carbon materials and heterometallic macrocyclescontaining COFs are regarded as efficient electrocatalysts, it is still hard to verify the precise structure acting as the active center and accurately tune the content of active centers to further improve catalytic performance due to the uncontrollable high-temperature pyrolysis or heteroatom doping process. The high-temperature pyrolysis process usually leads to undesirable structural damage or changes, which makes the investigation of the catalytic mechanism difficult. In this regard, the exploration of metal-free COF electrocatalysts with responsive active units through appropriate design and predictable synthesis routes can provide a possible, and even serve as an excellent, platform to investigate the nature of catalytic active centers in a simple and clear system with only desired elements. Moreover, by choosing tailorable building units, it is easy to optimize the content and distribution of active sites for more efficient catalysts. The introduction of single or multiactive units, such as pyrrole, thiophene, and 3,4-ethylene dioxythiophene, would be an effective strategy to achieve highly efficient COF electrocatalysts. These intrinsic COFs can be directly used as electrocatalysts without pyrolysis and provide a simple but desirable system for in-depth investigation of active sites, chemical kinetic processes, and reaction mechanisms; 4) last and more important, to fundamentally understand the details of the catalytic process and reaction mechanism and exact active sites. Therefore, a combination strategy of advanced characterization technologies and computational simulation would be greatly useful and highly desired.

In summary, even though a lot of challenges still remain, the recent significant achievements of COF-based electrocatalysts have shown promising potential to become a hot topic with extensive scientific significance. With deep understanding and more advanced technologies used to explore the mechanism and electrochemical kinetics, we do believe that COFs used as highly efficient electrocatalysts will show appealing properties for practical applications in the near future.

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Conflict of Interest

The authors declare no conflict of interest.

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