1. Introduction

Metal–organic frameworks (MOFs), also known as porous coordination polymers (PCPs), first defined by Yaghi and coworkers in 1995,[1,2] are a novel class of crystalline porous materials formed by the self-assembly of metal ions or clusters and organic ligands.

MOFs are of considerable interest from many perspectives due to ultrahigh specific surface area, adsorption/absorption capabilities, postsynthetic modifications, high porosity, and tunable pore sizes and have been explored for a myriad of applications, including gas sorption,[3] storage,[4–6] drug delivery,[7] luminescence,[8] sensor technology,[9,10] proton conduction,[11] and heterogeneous catalysis.[12,13] MOFs are composed of hard metal ions connected to redox-inactive organic ligands that are bound by hard oxygen or nitrogen atoms, causing the lack of low-energy pathways and free carriers for charge transport in MOFs. Therefore, most MOFs are inherently insulated (conductivity values lower than $10^{-10}$ S cm$^{-1}$), which largely limits their use in electrocatalytic systems. By imparting electrical conductivity to MOFs, their catalysis efficiency can be effectively improved.

Conductive MOFs have a relatively short history, namely, from their preparation to utilization only a short decade. For a long time, the electrical properties of MOFs have received less attention, while their potential as electrically conductive porous materials has just been taken into account recently.[14] According to different charge carriers, conductive MOFs can be classified into ionic conduction and electronic conduction. The earliest appearance of conductive MOFs can be traced back to 2009. Takaishi et al. reported the first electrically conductive MOFs, Cu[$\text{Cu(pdt)}_2$] ($\text{pdt}=2,3$-pyrazinedithiolate), which showed a high electrical conductivity of about $6 \times 10^{-4}$ S cm$^{-1}$ at 300 K.[15] In the same year, Sadakiyo et al. synthesized a MOF with high proton conductivity, namely, $\text{[NH}_4\text{]}_2\text{[adp]}[\text{Zn}_2\text{(ox)}_3\text{]}3\text{H}_2\text{O}$ (ox = oxalate, adp = adipic acid).[16] This is the first MOF example exhibiting a superprotonic conductivity of $10^{-2}$ S cm$^{-1}$ at ambient temperature. In 2010, Kobayashi et al. obtained Cu[$\text{Ni(pdt)}_2$] using the same method as Cu[$\text{Cu(pdt)}_2$]. The conductivity of Cu[$\text{Ni(pdt)}_2$] is $1 \times 10^{-8}$ S cm$^{-1}$ and its Brunauer–Emmett–Teller (BET) surface area is 385 m$^2$ g$^{-1}$, which is the first MOF that can take into account both high specific surface area and high conductivity.[17] Subsequently, a variety of conductive MOFs were synthesized.

Energy is indispensable in modern society. But traditional fossil energy sources such as coal, oil, and natural gas are nonrenewable and not environment friendly. So transforming our current energy system into a sustainable one is paramount. According to previous reports, both electrocatalysis and photocatalysis are effective for energy conversion and can satisfy the demands of green development.[18–20] Thus, seeking electrocatalysts with high conversion rates and efficiency could be a useful way to
mitigate environmental pollution and energy shortage. Conductive MOFs are considered as one of the ideal candidates for electrocatalysis due to their numerous active metal centers, large porosity, high conductivity, and structural rigidity which can facilitate surface contact and mass transfer. Recent years have witnessed a large number of high-performance conductive MOFs, and several even display activity comparable with that of the best heterogeneous catalysts. Although many advances in the synthesis of electrically conductive MOFs have been made, their utilization in electrocatalysis still faces a series of challenges, such as the instability of most MOFs, the control of MOF film thickness, and the construction of electrodes. To achieve a real breakthrough for conductive MOF-based electrocatalysts, a focused review of the general approaches taken toward achieving high conductivities in MOFs and the electrocatalytic application of the conductive MOFs is necessarily imminent.

In this review, we discuss a set of electrically conductive MOFs, including intrinsically conductive MOFs, guest-based conductive MOFs, and conductive MOF composites, as well as their utilization in the field of electrocatalysis. The scope of this review is limited to electrically conductive MOFs, while the ionic conduction of MOFs, which have been reviewed elsewhere, will be not discussed here. The purpose of this article is to provide a little guidance and inspiration to achieve the intriguing potential of electrically conductive MOFs in electrocatalysis. We hope this review can shed some light on the future development of this highly exciting area.

2. Conductive Mechanisms of MOFs

The conductivity ($\sigma$) of a conductive MOF is determined by the density ($n$) and mobility ($\mu$) of electrons ($e$) and holes ($h$). Therefore, to achieve high conductivity, it is essential to maximize both concentration and mobility of charge carriers (Equation (1))

$$\sigma = e(\mu_e n_e + \mu_h n_h)$$

Most MOFs are intrinsically insulated due to the high barriers for charge transfer and the lack of free charge carriers. The materials with high concentrations of loosely bound charge carriers generally have high charge densities. The sources of charge carriers can originate from the metal ions, organic ligands, or guest molecules. And the pathways for charge transport can be briefly classified into two categories (Figure 1a): redox hopping transport and band transport. In the former, charge carriers are localized at specific sites with discrete energy levels, and hop between neighboring sites. In the latter, the delocalized charge carriers can transport via continuous coordination or covalent bonds in MOFs. Both hopping transport and bond transport require a good spatial and energy overlap between orbitals of appropriate symmetry. Improving the charge transfer pathways by increasing orbital overlap enhances the charge mobility.

In general, there are two different design considerations in the synthesis of electronically conductive MOFs: 1) “through-bond” approach and 2) “through-space” approach (Figure 1b). Through-bond mechanism relies on improving covalent bonding between metals and ligands to achieve the high charge transfer in MOFs, while through-space mechanism harnesses noncovalent interactions between organic fragments.

3. Synthetic Strategies for Conductive MOFs

The field of conductive MOFs has witnessed a fast growth in the past 10 years. Many novel synthetic strategies have been developed to impart conductivity to MOFs at various levels. Using specific ligands and metal nodes to form long-range delocalized electrons for charge mobility is a rational choice to construct conductive MOFs. In addition, integrating guest molecules into MOFs or mixing MOFs with electrical conductors is also an intriguing strategy to tailor the scale of conductivity. According to different design strategies, conductive MOFs can be divided into three types: intrinsically conductive MOFs, guest-based conductive MOFs, and conductive MOF composites.

Figure 1. Schematics of two charge-transport a) mechanisms and b) approaches, in MOFs. Reproduced with permission. Copyright 2019, Royal Society of Chemistry.
3.1. Intrinsically Conductive MOFs

For intrinsically conductive MOFs, the conductivity is the inherent property of MOFs, rather than being induced by augmentations such as the exchange of guest molecules or conduction through the framework pores. Intrinsically conductive MOFs usually contain redox-active metal ions or ligands, or conjugated organic ligands that can generate charge transport pathways upon coordination with their metal ion counterparts. They are conductive due to their favorable spatial and energetic overlap between the metal and ligand orbitals as well as noncovalent interactions. A deliberate selection of metal ions and ligands can allow the synthesis of conductive MOFs.

3.1.1. Mixed-Valence Metal Ions and Ligands

The redox behavior of metal cations inside MOFs could provide a pathway for electrons. A vast number of conductive MOFs have been obtained by using metal ions with tunable valences as nodes. For instance, the first conductive MOF, which contains the donor Cu(I) and acceptor [CuII[pdt]2]−, is definitive evidence of the importance of the mixing valence.[15] A mixed-valence Cu(I)—Cu(II) framework was also reported by Okubo et al., which possesses low activation energy for charge transfer.[27] Similarly, the 3D framework [CuII CuI(DCTP)2(NO3)]·1.5DMF (DCTP = 4′-(3,5-dicarboxyphenyl)-4,2′,6′,4′′-terpyridine) also shows semiconducting behavior.[28]

In addition, the conductive MOFs with mixed-valence iron ions have also been reported. Sun et al. systematically studied 20 MOFs with four different topologies, in which iron ion as the redox metal center endows the best electrical properties.[26] They proved that mixed-valence FeII/FeIII increases the charge density and promotes charge delocalization, which leads to the high conductivity. In addition, the correlation between introduction of mixed-valence FeII/FeIII and increased conductivity has also been confirmed in FeII(BDT)_3 (BDT = benzene-1,4-ditrazolate).[30] The conductivity of as-synthesized material was largely improved after 30 days in air, which is ascribed to the partial oxidation of FeII centers to FeIII in the framework.

Mixed-valence ligands are also adopted to synthesize intrinsically conductive MOFs. Due to the partial oxidation of ligands in the synthesis, the resulting MOFs contain mixed-valent linkers, which may lead to high carrier density, thereby making MOFs conductive. Specific examples are a series of MOFs built with tetaoxolene ligands, such as dihydroxybenzoquinonate (dhbq) and chloranilate (ClIII dhbq). In 2015, Darago et al. synthesized [FeII(dhbq)]_2− using dhbq as ligand.[31] The electrical conductivity of the as-synthesized material is up to 0.16 S cm−1. The charge hopping between dhbq– and dhbq2− centers accounts for its high conductivity. In 2017, the Harris group reported the conductivity of the Fe-chloranilate framework.[32] Due to the electron transfer of the FeII ions to the ligands, the ligands in the framework are in mixed valency (ClII dhbq–, ClIII dhbq2−). It shows a high conductivity of 1.4(7) × 10−2 S cm−1. When all ligands are converted to the ClIII dhbq2− radical state, the conductivity decreases to 5.1(3) × 10−4 S cm−1. The relatively low conductivity (1.5(3) × 10−9 S cm−1) of [ZnII(ClII dhbq)]2− also illustrates that mixed valency plays an important role in the conductivity.

3.1.2. Infinite 1D/2D Metal–Sulfur Chains

The conductivity of MOFs could be realized by forming infinite 1D/2D metal—sulfur chains. Sun et al. reported a sulfur-substituted Mn-MOF-74 analogue MnIII(DSBDC) (DSBDC = 2,5-disulphydryl-benzene-1,4-dicarboxylic acid) with infinite 1D Mn−S zigzag chains along the crystal α axis, as shown in Figure 2a.[33] This material remains permanently porous, with a BET surface area of 978 m2 g−1. They subsequently reported its electrical conductivity of 2.5 × 10−12 S cm−1, which is about one order of magnitude higher than that of MnII(DOBDC) (DOBDC = 2,5-dihydroxybenzene-1,4-dicarboxylic acid) (3.9 × 10−13 S cm−1).[34] The result indicates that (−Mn−S−)∞ chain is more effective than (−Mn−O−)∞ chain in charge transfer, which may be attributed to the better energy matching between the frontier orbitals of the thiolate and the metal, thus increasing the conductivity of MnIII(DSBDC). They also studied the conductive difference of Fe and Mn analogues and found that the conductivity of FeII(DSBDC) (3.9 × 10−6 S cm−1)
is about 1 million-fold higher than that of Mn$_2$(DSBDC), and also much higher than that of Fe$_2$(DOBDC) (3.2×10$^{-7}$ S cm$^{-1}$). The higher conductivity of the Fe-MOF is ascribed to the substitution of d$^5$ Mn$^{II}$ by d$^6$ Fe$^{II}$ centers, which introduces high-energy, loosely bound minority-spin carriers. Recently reported [Cu$_2$(Hmma)(mma)][NH$_4$] (Hmma = 6-mercaptanonic acid) shows a high conductivity up to ≈11 S cm$^{-1}$, which is originated from the integration of the 2D (─Cu─S─)$_n$ plane in the structure (Figure 2b).[35] Infinite metal-sulfur chain is again invoked to explain the higher conductivity.

3.1.3. π-Interactions

According to the “through-space” approach, the efficient charge transport can also occur in MOFs through noncovalent interactions, particularly π−π stacking. Frameworks based on the well-known electron donor tetrathiafulvalene (TTF) constitute a large portion of MOFs designed following this principle. In 2012, Narayan et al. synthesized Zn$_2$(TTFTB) using tetrathiafulvalene-tetrabenzoate (H$_4$TTFTB) and Zn$^{2+}$, whose charge mobility is commensurate with some best organic semiconductors.[36] As shown in Figure 3a,b, the material possesses both columnar stacks of TTF and permanent pores lined by benzoate linkers, and a relatively close intermolecular S···S contact of 3.80(2) Å is found between neighboring TTF moieties, which is similar to the range of intermolecular S···S distances found in TTF-TCNQ (TCNQ = 7,7,8,8-tetracyano-9,9-dioxoquinodimethane) and other conductive charge-transfer salts. Park et al. in 2015 fabricated a series of isostructural M$_2$(TTFTB) with M = Mn, Co, Zn, and Cd.[37] All four MOFs contain infinite 1D π−π stacked helical TTF and their electrical conductivities range from 10$^{-6}$ to 10$^{-4}$ S cm$^{-1}$, which coincides with the size change of the metal cations. Cd$_2$(TTFTB) has the largest cation size and shows the highest conductivity of 2.86 × 10$^{-4}$ S cm$^{-1}$, while the conductivities of Zn$_2$(TFTB) and Co$_2$(TTFTB) are only 3.95 × 10$^{-6}$ and 1.49 × 10$^{-5}$ S cm$^{-1}$, respectively. The authors proved that their electrical conductivities are determined by the S···S distances between neighboring TTF moieties (Figure 3c). As the cation radius increases, the S···S distance decreases from 3.77 Å for Co$_2$(TTFTB) to 3.65 Å for Cd$_2$(TTFTB), resulting in better orbital overlap and higher conductivity. In 2018, Xie and Dincă reported several electrically conductive MOFs based on H$_4$TTFTB and lanthanide ions.[38] They confirmed that the S···S contacts between ligands provide possible charge transport pathways in the materials. Later, they synthesized three TTFTB-MOFs based on tetrathiafulvalene linker

Figure 3. a) Side view of a helical TTF stack and b) top view of the benzoate-lined infinite pores in Zn$_2$(TTFTB). Reproduced with permission.[36] Copyright 2012, American Chemical Society. c) Correlation between S···S distance and electrical conductivity in M$_2$(TTFTB) (M = Mn, Co, Zn, and Cd). Reproduced with permission.[37] Copyright 2015, American Chemical Society. d) Correlation between S···S distance and electrical conductivity (batch and average values) in La$_4$(HTTFTB)$_4$ (1), La(HTTFTB) (2), and La$_4$(TTFTB)$_3$ (3). Reproduced with permission.[39] Copyright 2019, Royal Society of Chemistry.
and La\(^{3+}\) and further demonstrated that long S—S distances between adjacent ligands lead to low electrical conductivities (Figure 3d).\(^{[39]}\)

The conductivity of MOFs through π—π stacking has also been demonstrated in non-TTF frameworks. A family of MOFs composed of Ln\(^{3+}\) (Ln = La, Nd, Ho, Yb) and 2,3,6,7,10,11-hexahydroxytriphenylene (H\(_6\)HHTP) were successfully prepared by Skorupskii et al.\(^{[40]}\) As shown in Figure 4a, extremely close π—π stacking (3.002—3.068 Å) can be found in these materials, so they display the high conductivity up to 0.05 S cm\(^{-1}\) (for HoHHTP). Chen et al. reported a zigzag stacked stacking has also \(^{[51]}\) 3.42 Å between neighboring ligands. Cd(DPNDI)\(^{π}\) In© 2021 The Authors. Advanced Energy and Sustainability Research

© 2014, National Academy of Sciences.

π

In

www.advenergysustres.com

1,4,5,8-naphthalenetetracarboxylate),\(^{[47]}\) Cd(DPNDI) (DPNDI = N,N’-di(4-pyridyl)-1,4,5,8-naphthalenetetracarboxdiimide),\(^{[44]}\) Cu(DPNDI)\(^{2+}\) and Cd\(^{2+}\)(TPDAP)\(^{3+}\) (TPDAP = 2,5,8-tri(4-pyridyl)1,3-diazaphenalenal).\(^{[46]}\) In addition to the formation of π-stacked pathways, MOFs with extended 2D π-conjugated and graphene-like structures have also aroused considerable interest owing to their good charge transport. A great quantity of 2D π-conjugated MOFs with amazing electrical conductivity values has been reported. In 2012, Hmadedh et al. obtained two kinds of 2D porous extended frameworks by linking H\(_6\)HHTP with Co(II) and Ni(II) ions, and named them metal-catecholates (M-CATs).\(^{[47]}\) The structure of Co-CAT-1 is shown in Figure 5a. Although the electrical properties of Co-CAT-1 and Ni-CAT-1 have not been reported, Cu-CAT-1 microcrystalline material has been confirmed to display high electrical conductivity. Later, 2D MOFs, Ni\(_3\)(HITP)\(^2+\) (HITP = hexaaminotriphenylene) and Cu\(_3\)(HITP)\(^2_2\), were both reported to have strong π-conjugation within their structures and exhibit brilliant conductivities (2 and 0.2 S cm\(^{-1}\), respectively) (Figure 5b,c).\(^{[48,49]}\) Several examples of 2D conductive MOFs based on hexaaminobenzene (HAB) have also been reported.\(^{[50–53]}\) In 2017, Lahiri et al. first published a report on 2D coordination polymers based on this linker, but no data on conductivity.\(^{[51]}\) Subsequently, two groups demonstrated that both Ni-HAB and Cu-HAB display impressive conductivities (Figure 5d).\(^{[52,53]}\) In addition, 2D MOFs constructed with benzenehexathiol (BHT), 1,2,5,6,9,10-triphenylenethiahexal (TTTh), and phthalocyanine (Pc) have also been carefully studied by researchers.\(^{[54–59]}\)

3.2. Guest-Based Conductive MOFs

The structures of MOFs derived from connected metal ions and linkers endow them with a large number of available pores, which present both a challenge and an opportunity with respect to conductivity. The incorporation of guest molecules into the inherent porosity is one of the most frequently adopted strategies to improve the conductivity of MOFs. These guest molecules, which can be introduced during the preparation of MOFs or by postsynthetic modification (PSM), can interconnect with the secondary building units (SBUs) of MOFs, thus generating redox active sites inside the network. Redox-active molecules, metal oxides, metal nanoclusters, cationic species, and conducting polymers are the widely used dopants in recent years.

3.2.1. Redox-Active Molecules

Redox-active guest molecules can significantly enhance the conductivity by inducing free charge carriers within the MOF.

![Figure 4](https://www.advancedsciencenews.com)

**Figure 4.** a) Electrical conductivity of LnHHTP. Reproduced with permission.\(^{[40]}\) Copyright 2020, Nature Publishing Group. b) Three In(III)-based isomeric MOFs: (I) In-IA-1D, (II) In-IA-2D-1, and (III) In-IA-2D-2. Reproduced with permission.\(^{[42]}\) Copyright 2014, National Academy of Sciences.
frameworks through guest-framework charge-transfer interactions. Different redox-active molecules that have been proposed over the years include iodine, TCNQ, and ferrocene. Such strategy has been extensively used to fabricate conductive MOFs by many researchers.

In 2010, Zeng et al. prepared a nonconductive, noninterpenetrated double-walled MOF $\text{Zn}_3(\text{DL-lac})_2(\text{pybz})_2$ ($\text{pybz} = 4$-pyridylbenzoate, $\text{DL-lac} = \text{lactate anion}$) with 1D square channels. As shown in Figure 6, the material was first desolvated by heating under vacuum and then immersed in a cyclohexane solution of $\text{I}_2$. It shows a conductivity of $3.42 \times 10^{-3} \text{S cm}^{-1}$ along the direction of the channels, which is about 440 times greater than that of a solid $\text{I}_2$ sample. At the same time, iodine treatment greatly decreased the crystallinity and surface area of the material. The pristine MOF, whose conductivity is limited, is used as a templating host for organizing the $\text{I}_2$ molecules and gets them involved in donor—acceptor interactions with the aromatic walls, thereby improving the electrical conductivity. In addition, $\text{Cu}_6(\text{pybz})_6(\text{OH})_2$, $\text{Co}_4(\text{NDC})_3$ ($\text{NDC} = \text{naphthalene-2,6-dicarboxylate}$), and $\text{Eu}_4(\text{BPT})_4$ ($\text{BPT} = \text{biphenyl-3,4',5-tricarboxylate}$) treated with iodine also show enhanced conductivity.$^{[61-63]}$

TCNQ is a redox-active molecule with high level of electron affinity and can act as the bridging species between the metal ions of the frameworks and result in conductive pathways inside the MOFs. In 2013, Talin et al. realized the regulation of conductivity of MOFs by soaking thin films of $\text{Cu}_4(\text{BTC})_2$ (also known as HKUST-1, $\text{BTC} = \text{benzene-1,3,5-tricarboxylate}$) in a saturated solution of TCNQ (Figure 7a).$^{[64]}$ The electrical conductivity of TCNQ-doped HKUST-1 surges to $7 \times 10^{-3} \text{S cm}^{-1}$ from $1 \times 10^{-8} \text{S cm}^{-1}$ recorded for the undoped material. And the authors proposed that the conducting regions are formed in the MOFs by TCNQ bridging the copper paddlewheel SBUs. Higher conductivity in TCNQ@$\text{Cu}_4(\text{BTC})_2$ compared with the pristine MOF has also been corroborated by other reports.$^{[65-67]}$ Furthermore, TCNQ incorporation was reported to increase the conductivity of MOF films via charge transfer between TCNQ and the frameworks for $[\text{Cu}(\text{TPyP})\text{Cu}_3(\text{O}_2\text{CCH}_3)_4]$ ($\text{TPyP} = 5,10,15,20$-tetra-$4$-pyridyl-$21\text{H},23\text{H}$-$\text{porphine}$) and $\text{Cu}_2(\text{TATAB})_3$ (TATAB = 4,4′,4″-((1,3,5-triazine-2,4,6-triyl)tribenzoate)).$^{[68,69]}$ In addition, ferrocene is also capable of constructing conductive MOFs, as the oxidation of ferrocene in MOFs can induce charge transfer in the nanochannels of the skeletons.$^{[70,71]}$

3.2.2. Metallic Species

Metallic species such as metal nanoclusters, metal oxides, and cationic molecules can be easily assembled into the pores of MOFs. In 2015, Han et al. incorporated silver nanocrystals (AgNCs) into the cavities of a Rb-based γ-cyclodextrin MOF (Rb-CD-MOF) by immersing single crystals of Rb-CD-MOF
into a CH$_3$CN solution of AgNO$_3$[72] Under high power light (1.48 W cm$^{-2}$), the conductivity of the blank MOF increases from $\approx$10$^{-12}$ to $\approx$2 $\times$ 10$^{-11}$ S cm$^{-1}$, while AgNC@Rb-CD-MOF surges about four orders of magnitude, from $\approx$2 $\times$ 10$^{-11}$ to 2.15 $\times$ 10$^{-7}$ S cm$^{-1}$. The authors proposed that the light-assisted tunneling between these AgNCs provides a charge transport network, which can transfer electrons into MOFs.

Figure 6. The structure of Zn$_3$(D,L-lac)$_2$(pybz)$_2$ with (I) DMF molecules inside the channels, (II) the symmetric channels after desolvation, and (III) ordered I$_2$ molecules filled along the channels. Reproduced with permission.[60] Copyright 2010, American Chemical Society.

Figure 7. a) TCNQ-doped Cu$_3$(BTC)$_2$. Reproduced with permission.[64] Copyright 2014, American Association for the Advancement of Science. b) NiCB@NU-1000. Reproduced with permission.[73] Copyright 2018, American Chemical Society. c) MV$^{2+}$-doped BMOF. Reproduced with permission.[75] Copyright 2016, Royal Society of Chemistry. d) Synthesis of MIL-101(Cr) $\supset$ PEDOT. Reproduced with permission.[78] Copyright 2016, American Chemical Society. e) Synthesis of conductive polymer/MOF composite. Reproduced with permission.[81] Copyright 2017, American Chemical Society.
Later, the metallocarborane molecule, nickel (IV) bis(dicarboxylide) (NiCB), was incorporated into MOF channels as the guest. A study by Kung et al. displayed that NiCB was selectively loaded in the micropores of NU-1000 while leaving the mesopores unoccupied, as shown in Figure 7b. By modifying, the conductivity of NU-1000 MOF increases from undetectable to 2.7 × 10⁻⁷ S cm⁻¹. UV—vis spectroscopy data revealed charge transfer between the pyrene-based linker and NiCB, which endows the material with electrical conductivity. In addition, the effects of tetratin(IV)oxy clusters doping on the conductivity of NU-1000 have also been investigated. By installing tetratin(IV)oxy clusters, NU-1000 obtains a significant improvement in conductivity, with the value as high as 1.8 × 10⁻⁷ S cm⁻¹.

Guo et al. demonstrated that cationic methyl viologen (MV²⁺) species can also be used to prepare conductive MOFs (Figure 7c). They soaked films of a pillared paddlewheel MOF with an electron-rich pyridyl- and dipyrrolidyl-substituted naphthalene diimide (NDI) ligand in a solution of MV²⁺, resulting in an enhanced conductivity, from 6 × 10⁻⁰ to 2.3 × 10⁻⁵ S cm⁻¹.

### 3.2.3. Conducting Polymers

The guest-promoted approach is not limited to small species, and large conducting polymers have also been reported to increase the conductivity by polymerization in the pores of MOFs. For MOFs-polymer assemblies, the conductivity of the resulted MOFs is higher than either of the pristine components. Enhanced transport properties in MOFs-polymer materials have been attributed to charge transfer interactions between polymer chains surrounded by π-donor ligands, as well as high degrees of order and orientation in the polymers.

Several common conducting polymers such as polyaniline, poly-3,4-ethylenedioxythiophene (PEDOT), polythiophene, and polypyrrole have been intercalated into different MOFs to improve their conductivities. For instance, Le Ouay et al. obtained a conductive porous composite material composed of Cr-MIL-101 and PEDOT, which was prepared by the polymerization of EDOT monomer in the cavities of MOFs with the catalysis of I₂ (Figure 7d). The conductivity of MIL-101(Cr)∶PEDOT is 1.1 × 10⁻⁵ S cm⁻¹, much higher than that of native Cr-MIL-101(10⁻¹¹ S cm⁻¹).

Recently, Mohmeyer et al. reported that the composite of Zr-bzpdc-MOF and PEDOT also exhibits good conductivity. Similarly, NU-1000 is given conductivity through the incorporation of a designed pentathiophene derivative by solvent-assisted ligand incorporation, as shown in Figure 7e.

### 3.3. Conductive MOF Composites

Hybridization of MOFs with carbon-based materials (like carbon nanotubes (CNTs), graphene oxide, graphene, quantum dots) is a valuable strategy to render or facilitate conductivity in the resulting composites. Furthermore, the growth of MOF nanostructures (nanosheets, nanorods, nanowires, etc.) onto conductive substrates is another way to allow the extension of the electrochemical applications of MOFs.

#### 3.3.1. MOF-Carbon Composites

Goswami et al. reported that the conductivity of C₆₀@NU-901 (Figure 8a) has been greatly improved by physically encapsulating an excellent electron acceptor, C₆₀, into the channels of NU-901, from unmeasurable to 10⁻¹³ S cm⁻¹. The diameter...
of C_{60} (≈7 Å) is well suited for encapsulation in NU-901 with pore aperture of 12 Å. Such remarkable conductivity enhancement is attributed to efficient charge-transfer interactions with pyrene moieties and C_{60} acting as π-donor and acceptor.

Graphene and graphene oxide have also been developed to construct conductive MOFs composites due to their wonderful electron mobility. For example, a hybrid material of graphene-like oxidized carbon nanoparticles and insulating HKUST-1 exhibits a tunable electrical conductivity.\(^{[91]}\) Preliminary electrical measurements showed that the direct-current conductivity in the samples improves greatly with the increase in carbonaceous layer content. The authors estimated that the order of the conductivity could increase to 10^{-4} S cm^{-1} when the carbon percentage is 40%. Furthermore, the sample of RGO/ZIF-8 (RGO = reduced graphene oxide, 20 wt%) displays a conductivity of 0.64 S cm^{-1}, which is the highest among all 3D microporous MOFs, while the GO/ZIF-8 is nonconductive due to the insulating properties of both GO and ZIF-8 (Figure 8b).\(^{[92]}\)

**3.3.2. MOF-Conductive Substrate Composites**

MOF-conductive substrate composites are in situ synthesized on conductive substrates without binder materials, and they have been widely used in electrocatalytic reactions due to the ability of conductive substrates to enhance the conductivity of loaded MOF samples. Although no conductivity data are available in most reports, MOF-conductive substrate composites usually exhibit extraordinary activity for electrochemical reactions. One of the most commonly conductive substrates is nickel foam (NF).\(^{[91-97]}\) For example, Sun et al. reported a binder-free 3D electrode, MIL-53(FeNi)/NF, which shows high current density (50 Ma cm^{-2}) at an overpotential of 233 mV, a Tafel slope of 31.3 mV decade^{-1}, and remarkable stability for oxygen evolution reaction (OER).\(^{[94]}\) Similarly, the Co-MOF nanoarrays grown on NF displays extraordinary OER catalytic activity and superior stability.\(^{[95]}\) An interfacial engineering approach which allows preferred chelation of carbosyl groups in the ligands with the metal interlayers was used to synthesize the electrocatalytic materials. Nickel—iron foam (NFF) is also an ideal substrate material due to its high air permeability and high specific surface area. Cao et al. prepared a self-supporting MOF-based nanocomposite electrode (NiFe—NFF) by using the NiFe alloy foam as the semisacrificial template.\(^{[98]}\) As shown in Figure 9, NFF was used as both metal sources and substrate. The results show that the bimetallic MOF composite NiFe—NFF possesses remarkable electrocatalytic OER activity with required overpotentials of 227 and 253 mV to achieve current densities of 10 and 100 mA cm^{-2}, respectively. Lin et al. synthesized Ni-MOF/Ni/CC by in situ growth of ultrathin and ultralong Ni-MOF nanowire arrays on highly rough and conductive scaffolds of porous Ni/CC.\(^{[99]}\) The resultant composite has an amazing water oxidation activity and durability with a \(\eta_{90}\) of 240 mV at the end of a constant current electrolysis for 32 h. In addition, according to previous reports, fluorine tin oxide (FTO) has also been used to construct conducting MOFs composites.\(^{[100,101]}\)

**4. Conductive MOFs for Electrocatalysis**

One of the most appealing applications of conductive MOFs is as electrocatalysts due to their uniform active sites, high porosity, and enhanced conductivity. In addition to the intrinsic electrical conductivity, the morphology of MOFs plays a significantly important role in electrocatalysis. Particularly, constructing the thin 2D nanostructures of MOFs could greatly expose the active sites and further enhance electrical conductivity due to the nano-sized thickness, opening up an opportunity to break through the bottleneck of MOF-based electrocatalysis. Moreover, the stability of conductive MOFs in electrocatalysis (strong acidic/alkaline solutions) is also a crucial factor. Although many conductive MOFs have been synthesized, the research on their electrocatalytic applications is obviously lagging behind. In this section, we briefly summarize some successful examples of conductive MOFs used as electrocatalysts for the most important electrochemical reactions, including hydrogen evolution reaction.
(HER), OER, oxygen reduction reaction (ORR), and CO₂ reduction reaction (CO₂RR).

### 4.1. HER

Metal-dithiolene-based MOFs have been extensively studied as promising electrocatalysts for HER. For example, Ni-THT, Co-BHT, and Co-ThT have been reported to display remarkable electrocatalytic activities for HER.\(^{57,58}\) The thin-film Ni-THT samples were prepared through an air—liquid interface process (the Langmuir—Blodgett method). The Tafel slope of Ni-THT is 80.5 mV decade\(^{-1}\) and the overpotential is 333 mV at 10 mA cm\(^{-2}\). Both Co-BHT and Co-ThT exhibit impressive stability under acidic conditions and the Tafel slopes are between 149 and 189 mV decade\(^{-1}\) at pH = 1.3 and a current density of 10 mA cm\(^{-2}\). The overpotentials are 340 and 530 mV, respectively, at pH = 1.3 and a current density of 10 mA cm\(^{-2}\). In 2017, a report showed that Cu-BHT nanoparticles have good activity and stability for HER with a Tafel slope of \(\approx 95\) mV decade\(^{-1}\) and an overpotential of 450 mV at 10 mA cm\(^{-2}\) under optimized conditions.\(^{102}\) Downes and Marinescu reported a series of metal-dithiolene-based MOFs using benzene-1,2,4,5-tetrathiolate (BTT) and benzene-1,2,4,5-tetraselenolate (BTSe) as ligands and all of them can be used as good hydrogen-evolution electrocatalysts.\(^{103-105}\) In 2018, the same group reported the evaluation of the HER activity of Co-BHT, Ni-BHT, and Fe-BHT.\(^{106}\) The reaction was conducted in an acidic aqueous solution (pH = 1.3) and the overpotentials of BHT-based MOFs follow the order of Fe-BHT (405 mV) > Ni-BHT (331 mV) > Co-BHT (185 mV). The lower overpotential of optimized Co-BHT should benefit from its improved charge transfer properties. They also studied the effect of film thickness on H₂ production and found that as the film thickness was increased, the overpotential initially decreases because thinner films correspond to higher bulk catalyst loadings for layered materials, so more accessible active sites can be realized. But when increased to a certain thickness, electrons and protons had poor diffusion in the thick film, which inhibited HER activity. In addition, metal-dithiolene-diamine MOFs have also been investigated as electrocatalysts toward HER.\(^{107}\)

Polyyoxometalate-based MOFs (POMOFs) also show outstanding electrocatalytic efficiency for HER. In 2011, Nohra et al. prepared three novel POMOFs under hydrothermal conditions and used them for HER.\(^{108}\) They found that POMOF-based electrodes exhibit higher activity than platinum with a hydrogen yield of more than 95% and a turnover number of \(1.2 \times 10^5\) after 5 h. In 2015, another POMOF (NENU-500) with good tolerance to acidic and alkaline media was found to play superior HER performance.\(^{109}\) It shows an onset overpotential of 180 mV and a Tafel slope of 96 mV decade\(^{-1}\). Moreover, the electrocatalytic activity of NENU-500 was maintained after 2000 cycles.

### 4.2. OER

For OER, multimetallic MOFs generally present higher electrical conductivity and better electrocatalytic activity compared with monometallic MOFs. A typical example is NiFe-MOF which consists of 2,6-naphthalenedicarboxyligands and metal—oxygen (MO₅ = Fe or Ni) nodes.\(^{110}\) The NiFe-MOF grown on nickel foam (NiFe-MOF/NF) was tested in 0.1 M KOH electrolyte, which delivers a lower overpotential (240 mV at 10 mA cm\(^{-2}\)) compared with Ni-MOF/NF (296 mV), Fe-MOF/NF (354 mV), NF (370 mV), NiFe-MOF powder loaded on NF (bulk NiFe-MOF, 318 mV), calcined NiFe-MOF (336 mV), and NiFe-MOF on a glass carbon macroelectrode (406 mV). NiFe-MOF/NF electrode also shows a relatively small Tafel slope of 34 mV decade\(^{-1}\) and robust operation for 20,000 s with no detectable activity decay, while the bulk NiFe-MOF displays a Tafel slope of 56 mV decade\(^{-1}\) (Figure 10a,b). The authors found that the 2D NiFe-MOF nanosheets have higher electrical conductivity (\(1 \pm 0.2 \times 10^{-3} \text{ S cm}^{-1}\) than its bulk counterpart (\(1 \pm 0.5 \times 10^{-8} \text{ S cm}^{-1}\)), which improves the charge transport during electrolysis and results in the higher catalytic activity. Furthermore, the NiFe-MOF is also highly active for electrochemically generating hydrogen from water. In 2019, Li et al. studied the embedding of ultrathin NiFe MOF nanosheets into 3D ordered macroporous hydroxides and the well-designed composite shows brilliant electrocatalytic activity for OER.\(^{111}\) In 2017, a thermal-, water-, and alkaline-stable hybrid MOF ([Fe₃(μ₃-O)(bdc)]₃[Co(η₅-na)(L)₃]_x) (Fe₃-Co₂, H₃bdc = 1,4-benzenedicarboxylic acid, Hna = nicotinic acid, L* = terminal ligand) achieves significant electrocatalytic activity for OER at pH = 13 with an overpotential of 225 mV at 10.0 mA cm\(^{-2}\).\(^{112}\) They found that the OER performance of Fe₃-Co₂@GC is much better than those of Fe₁@GC, Fe₃-Fe₁@GC, and Co₁-Fe₁@GC, as shown in Figure 10c. As shown in Figure 10d, they also explored the impact of electrode substrate and tested the OER performance of Fe₃-Co₂ coated on Cu foam and Ni foam. The result shows that the Ni substrate gives the best OER performance for Fe₃-Co₂. In another work by Zhang et al., MAF-X27-OH ([Co₃(μ₃-OH)(bbta)]) (H₃bbta = 1H,5H-benzo[1,2-d,4,5-4′,5′]bistriazol) was also reported to be an efficient electrocatalyst for oxygen evolution due to its open metal sites and hydroxide ligands.\(^{113}\) The overpotential is 292 mV at 10.0 mA cm\(^{-2}\) in 1.0 M KOH solution. In 2016, Zhao et al. reported 2D ultrathin Ni-Co bimetallic MOF nanosheets (NiCo-UMOFNs, 3.1 nm) for electrocatalytic oxygen evolution in alkaline conditions.\(^{114}\) Owing to the ultrathin nanosheet structure, the high percentages of coordinatively unsaturated metal sites, and the coupling effect between Co and Ni ions, NiCo-UMOFNs display extraordinarily high electrocatalytic oxygen evolution activity than those of bulky and monometal counterparts. In recent years, many similar examples have been reported.\(^{115-119}\)

Porphyрин-based MOFs are also used for OER. For example, \([\text{Pd}_2(\text{H}_2\text{TCPP})]_{4}\text{DMF}\cdot\text{H}_2\text{O}\) (H₂TCPP = 5,10,15,20-tetra(carboxylphenyl)porphyrin) was investigated as an OER catalyst, which possesses both gas adsorption properties and electrocatalytic activity for OER.\(^{120}\) In 2016, the films of PCN-224-Ni constructed by nickel(II) porphyrin linkers were found to perform activity for oxygen evolution at near neutral pH.\(^{121}\) Other MOF-based electrocatalysts for OER have also been reported.\(^{122-125}\)

### 4.3. ORR

The first report on the use of MOFs as electrocatalysts for ORR is Cu-BTC \{(Cu₃(BTC)₂)\}.\(^{126}\) However, Cu-BTC is structurally unstable in aqueous media. A water-stable MOF, copper...
(II)-2,2'-bipyridinebenzene-1,3,5-tricarboxylate (Cu-bipy-BTC, bipy = 2,2'-bipyridine) was thus prepared and can catalyze the ORR with almost 4e⁻/C₀ transfer pathway. Subsequently, another Cu-MOF was reported to be used as ORR electrocatalyst. The MOF layer on RGO immobilized glassy carbon electrode can catalyze the ORR through a 2–4 electrons reduction pathway. As an intrinsically conductive MOF, Ni₃(HITP)₂ has been demonstrated as a well-defined, tunable oxygen reduction electrocatalyst. Its catalytic activity for ORR is competitive with the most active nonplatinum group metal electrocatalysts. Transition metal porphyrins are found to be highly efficient molecular catalysts for ORR. Accordingly, PCN-223-Fe, which is constructed from Zr₆-oxo clusters and Fe(III) porphyrin linkers, has been observed to catalyze ORR through the nearly 4e⁻/C₀ pathway with high selectivity.

Composite materials composed of MOFs and conductive supports are demonstrated to facilitate the ORR. In 2012, a graphene-metalloporphyrin MOF composite was fabricated and used for ORR. It was found that the addition of pyridine-functionalized graphene enhanced the electrochemical charge transfer rate of iron-porphyrin; thus, the hybrid MOF shows an improved catalytic activity and facile 4-electron ORR. Co-MOF@CNTs was reported to be a superior bifunctional electrocatalyst due to the synergistic catalysis of Co(II), organic ligands, and CNTs. It shows outstanding stability and notable OER and ORR catalytic activities, which are comparable with RuO₂ and 20 wt% Pt/C catalysts, respectively.

4.4. CO₂RR

Reducing carbon dioxide to valuable chemicals has always been a hot issue. The most commonly used catalysts for CO₂RR are Cu-based MOFs. For instance, the uniform Cu₃(BTC)₂ film, supported on glassy carbon electrode, was tested for CO₂RR in CO₂ saturated DMF solution in the presence of supporting electrolyte. The major product oxalic acid (H₂C₂O₄) was obtained with 90% purity and the Faradaic efficiency (FE) of 51%. Hinogami et al. also demonstrated the high selectivity of Cu-based MOFs. They prepared a copper rubeanine MOF (CR-MOF) to reduce CO₂ into HCOOH with the selectivity of more than 98%, while the Cu metal electrode generated a series of products, including formic acid, methane, ethylene, and ethane. In another report, the authors investigated four Cu-based metal–organic porous materials for CO₂RR, which have high efficiency for the production of methanol and ethanol in the liquid phase. It is due to their large surface areas, accessibilities of the electrodes as well as exposure of the Cu catalytic centers. MOFs based on metalloporphyrin are also perceived as efficient electrocatalysts for CO₂RR. As reported by Hod et al., Fe-porphyrin-based MOF-525 (Fe-MOF-525) can be utilized as a promising electrocatalyst for the reduction of CO₂ to produce a mixture of CO and H₂ with ≥100% FE. Similarly, a cobalt-porphyrin-based MOF, AL₂(OH)₂TCPP-Co, was used as an active catalyst for efficient and selective reduction.
of CO₂ to CO in an aqueous electrolyte. The selectivity for CO production exceeds 76% and the stability is more than 7 h with a turnover rate (TON) of 1400 per site. In situ spectroelectrochemical measurements showed that the majority of catalytic centers in this MOF are redox-accessible where Co(II) was reduced to Co(I) during catalysis. So it might be an effective method for electrochemical CO₂ reduction with excellent performance to integrate active species into MOFs. This was also confirmed by Wang et al., who reported the ZIF-8 doped with electrocatalytically active 1,10-phenanthroline. The experimental results indicate that the electron-donating nature of phenanthroline promotes electron transfer, which facilitates the formation of COOH, thus improving the activity and FE toward CO production.

5. Conclusions and Perspectives

Owing to myriad intriguing and desirable physicochemical properties, MOFs are potential for a wide range of applications, especially in catalysis. However, the lack of electrical conductivity largely restricts their adaptation as electrocatalysts. The emergence of conductive MOFs is a good solution to this problem. In recent years, many effective approaches have been successfully developed to engender conductivity of MOFs, which is beneficial to broaden their electrical applications. Mixed-valence metal ions or ligands, infinite 1D/2D metal—sulfur chains, and π-interactions can be used to synthesize intrinsically conductive MOFs. The introduction of redox-active molecules, metallic species as well as conducting polymers can construct guest-based conductive MOFs. Furthermore, MOF—carbon composites and MOF—conductive substrate composites also show considerable conductivity. Although these methods greatly enrich the library of conductive MOF, their application in electrocatalysis is still quite limited. The vulnerability of most MOF materials is a dominant factor. Therefore, improving the stability of electrocatalysts in strongly acidic and alkaline solutions to avoid hydrolysis and framework collapse is of vital importance to put conductive MOFs into practice. In addition, the thickness of MOF film also greatly influences the catalytic activity. The use of adhesives during electrode construction also hinders charge transfer and thus reduces electrocatalytic activity. So exploiting effective methods to optimize MOF deposition on the electrode or substrate is essential for their utilization in electrochemical fields.

As the shining stars in the field of materials science, though faced with a number of key challenges, a few successful examples of conductive MOFs with fantastic catalytic efficiency reveal their promising application of electrocatalysis. Given the great efforts and encouraging advances in the last few years, the field of conductive MOFs is growing, and more and more conductive MOFs are used in electrocatalysis, some even outperform the most active catalysts. We are confident that further development will constantly provide opportunity for conductive MOFs to be served as novel electrocatalysts.

Acknowledgements

The authors are grateful for the financial support of the National Natural Science Foundation of China (NSFC) (grant nos. 21901246, 21905278, and 21771179) and the National Science Foundation of Fujian Province (grant nos. 2019J05158 and 2020J01116).
[27] T. Okubo, H. Anma, N. Tanaka, K. Hiramoto, S. Seki, A. Saeki, M. Maekawa, T. Kuroda-Sowa, Chem. Commun. 2013, 49, 4316.

[28] Z.-L. Wu, C.-H. Wang, B. Zhao, J. Dong, F. Lu, W.-H. Wang, W.-C. Wang, G.-J. Wu, J.-Z. Cui, P. Cheng, Angew. Chem., Int. Ed. 2016, 55, 4938.

[29] L. Sun, C. H. Hendon, S. S. Park, Y. Tulkensky, R. Wan, F. Wang, A. Walsh, M. Dinca, Chem. Sci. 2017, 8, 4450.

[30] L. S. Xie, L. Sun, R. Wan, S. S. Park, J. A. DeGayner, C. H. Hendon, M. Dinç, J. Am. Chem. Soc. 2018, 140, 7411.

[31] L. E. Darago, M. L. Aubrey, C. J. Yu, M. I. Gonzalez, J. R. Long, J. Am. Chem. Soc. 2015, 137, 15703.

[32] J. A. DeGayner, I.-R. Jeon, L. Sun, M. Dinç, T. D. Harris, J. Am. Chem. Soc. 2017, 139, 4175.

[33] L. Sun, T. Miyakai, S. Seki, M. Dinç, J. Am. Chem. Soc. 2013, 135, 8185.

[34] L. Sun, C. H. Hendon, M. A. Minier, A. Walsh, M. Dinç, J. Am. Chem. Soc. 2015, 137, 6164.

[35] A. Pathak, J. W. Shen, M. Usman, L. F. Wei, S. Marenditta, Y. S. Chang, B. Sainbilge, C. M. Ngue, R. S. Chen, M. Hayashi, T. T. Luo, F. R. Chen, K. H. Chen, T. W. Tseng, L. C. Chen, K. L. Lu, Nat Commun 2019, 10, 1721.

[36] T. C. Narayan, T. Miyakai, S. Seki, M. Dinç, J. Am. Chem. Soc. 2012, 134, 12932.

[37] S. S. Park, E. R. Hontz, L. Sun, C. H. Hendon, A. Walsh, T. Van Voorhis, M. Dinç, J. Am. Chem. Soc. 2015, 137, 1774.

[38] L. S. Xie, M. Dinç, Isr. J. Chem. 2018, 58, 1119.

[39] L. S. Xie, E. V. Alexandrov, G. Skorupskii, D. M. Proserpio, M. Dinca, Chem. Sci. 2019, 10, 8558.

[40] G. Skorupskii, B. A. Trump, T. W. Kasel, C. M. Brown, C. H. Hendon, M. Dinca, Nat. Chem. 2020, 12, 131.

[41] D. Chen, H. Xing, Z. Su, C. Wang, Chem. Commun. 2016, 52, 2019.

[42] T. Panda, R. Banerjee, Proc. Natl. Acad. Sci., India, Sect. A Phys. Sci. 2014, 84, 331.

[43] G. Haider, M. Usman, T. P. Chen, P. Perumal, K. L. Lu, Y. F. Chen, ACS Nano 2016, 10, 8366.

[44] L. Qu, H. Iguchi, S. Takaishi, F. Habib, C. F. Leong, D. M. D’Alessandro, T. Yoshida, H. Abe, E. Nishibori, M. Yamashita, J. Am. Chem. Soc. 2019, 141, 6802.

[45] X. Kuang, S. Chen, L. Meng, J. Chen, X. Wu, G. Zhang, G. Zhong, T. Hu, Y. Li, C. Z. Lu, Chem. Commun. 2019, 55, 1643.

[46] J. Y. Koo, Y. Yakiyama, G. R. Lee, J. Lee, H. C. Choi, Y. Morita, M. Kawano, J. Am. Chem. Soc. 2016, 138, 1776.

[47] G. Hmadyeh, Z. Lu, Z. Liu, F. Gándara, H. Furukawa, S. Wan, V. Augustyn, R. Chang, L. Liao, F. Zhou, E. Perre, V. Ozolins, K. Suenga, X. Duan, B. B. Yang, Y. Yamamoto, O. Terasaki, O. M. Yaghhi, Chem. Mater. 2012, 24, 3511.

[48] D. Sheberla, L. Sun, M. A. Blood-Forsythe, S. Er, C. R. Wade, C. K. Brozek, A. Aspuru-Guzik, M. Dinca, J. Am. Chem. Soc. 2014, 136, 8859.

[49] M. G. Campbell, D. Sheberla, S. F. Liu, T. M. Swager, M. Dinca, Angew. Chem., Int. Ed. 2015, 54, 4349.

[50] J. Park, M. Lee, D. Feng, Z. Huang, A. C. Hinckley, A. Yakovenko, X. Zou, Y. Cui, Z. Bao, J. Am. Chem. Soc. 2018, 140, 10315.

[51] N. Lahiri, N. Lotfzadeh, R. Tschikawa, V. V. Deshpande, J. Louie, J. Am. Chem. Soc. 2017, 139, 19.

[52] D. Feng, T. Lei, M. R. Lukatskaya, J. Park, Z. Huang, M. Lee, L. Shaw, S. Chen, A. A. Yakovenko, A. Kulkarni, J. Xiao, K. Fredrickson, J. B. Tok, X. Zou, Y. Cui, Z. Bao, Nat. Energy 2018, 3, 30.

[53] J. H. Dow, L. Sun, Y. Ge, W. Li, C. H. Hendon, J. Li, S. Gul, J. Yano, E. A. Stach, M. Dinca, J. Am. Chem. Soc. 2017, 139, 13608.

[54] X. Huang, P. Sheng, Z. Tu, F. Zhang, J. Wang, H. Geng, Y. Zou, C. A. Di, Y. Yi, Y. Sun, W. Xu, D. Zhu, Nat Commun 2015, 6, 7408.

[55] T. Pal, T. Kambe, T. Kusamoto, M. L. Foo, R. Matsuo, R. Sakamoto, H. Nishihara, ChemPlusChem 2015, 80, 1255.
Li Liu is an M.S. candidate at Fujian Institute of Research on the Structure of Matter (FJIRSM), Chinese Academy of Sciences (CAS). She joined Professor Qi-Long Zhu’s group at FJIRSM-CAS in 2020. Her research interest is the design and synthesis of atomic catalysts for electrocatalysis.

Qiang Xu received his Ph.D. in 1994 from Osaka University. He worked as a director of AIST-Kyoto University ChEM-OIL and is currently a Chair Professor at Southern University of Science and Technology (SUSTech). His research interests include the chemistry of nanostructured materials and their applications, especially for catalysis and energy. He is on a number of editorial/advisory boards of journals, including EnergyChem (Editor-in-Chief), Coordination Chemistry Reviews (Associate Editor), Chem, Matter, Small Structures, Advanced Sustainable Systems, Chemistry — An Asian Journal, and ChemNanoMat. He is a Fellow of the Engineering Academy of Japan, European Academy of Sciences, and National Academy of Sciences, India.

Qi-Long Zhu is a professor at Fujian Institute of Research on the Structure of Matter (FJIRSM), Chinese Academy of Sciences (CAS). He received his Ph.D. degree in Physical Chemistry from FJIRSM-CAS in 2012. He then joined Professor Qiang Xu’s group at National Institute of Advanced Industrial Science and Technology (AIST, Japan) as the postdoctoral and JSPS (Japan Society for the Promotion of Science) fellow, before taking the current faculty position in 2017. He has published more than 120 papers in refereed journals. His group currently focuses on the development of nanostructured materials for catalytic and energy-related applications.