Recent progress in pristine MOF-based catalysts for electrochemical hydrogen evolution, oxygen evolution and oxygen reduction

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Among various kinds of materials that have been investigated as electrocatalysts for the hydrogen evolution reaction (HER), oxygen evolution reaction (OER) and oxygen reduction reaction (ORR), metal-organic frameworks (MOFs) have emerged as a promising material for electrocatalyzing these vital processes owing to their structural merits that integrate advantages of both homogeneous and heterogeneous catalysts; however there is still big room for their improvement in terms of inferior activity and poor conductivity, as well as the ambiguity of real active sites. In this review, advanced strategies with the aim of solving the activity and conductivity problems are summarized as microstructure engineering and conductivity improvement, respectively. The structural evolution of some MOFs and their real active species has also been discussed. Finally, perspectives on the development of MOF materials for HER, OER and ORR electrocatalysis are provided.

1. Introduction

The ever-increasing demands for exploring alternative energy resources and solving the severe environmental problems brought about by using traditional fossil fuels have stimulated worldwide concerns and endeavors on the development of clean, sustainable and renewable energy conversion and storage technologies. Among these energy technologies, water splitting, fuel cells and metal-air batteries have drawn most attention due to their high efficiency, reliability and environmental friendliness, the basis of which involves several important electrochemical oxidation and reduction reactions. As half-reactions, the hydrogen evolution reaction (HER), oxygen evolution reaction (OER) and oxygen reduction reaction (ORR) play crucial roles in the overall processes of the new technologies. To promote their practical use, electrocatalysts are usually required to lower the reaction energy barriers for the HER, OER and ORR. Currently, the well-recognized benchmark electrocatalysts are noble metal-based materials (Pt/C for the HER and ORR, and RuO2 and IrO2 for the OER) that exhibit high efficiency in catalyzing the above electrochemical reactions. However, the drawbacks of noble metal electrocatalysts are also ineluctable in terms of limited reserves, high cost and possible performance degradation during the potential cycling. Developing low cost electrocatalysts with high catalytic efficiency for the HER, OER and ORR has consequently become the big challenge that confronts researchers in recent years.

To date, various kinds of promising candidates have been investigated under extensive efforts, including Earth-abundant transition metal based compounds (metal oxides, metal sulfides, metal phosphides, metal hydroxides, etc.), nanocrystalline layered transition metal compounds (transition metal and compounds), carbon composites (doping with nitrogen, boron, sulfur, phosphorus, etc.), carbon composites (doping with nitrogen, boron, sulfur, phosphorus, etc.) and metal and compounds), carbon composites (doping with nitrogen, boron, sulfur, phosphorus, etc.), carbon composites (doping with nitrogen, boron, sulfur, phosphorus, etc.). As a unique source of both transition metals and carbon, metal-organic frameworks (MOFs) have recently attracted great attention and been considered as one of the most promising precursors for deriving efficient HER, OER and ORR electrocatalysts due to their tunable structural merits. MOFs are a class of porous and crystalline materials constructed by self-assembly from metal ions or clusters and organic linkers. The tailorable pore sizes, compositions and morphologies are invaluable properties for the fabrication of electrocatalysts with designed microstructures and can facilitate the subsequent screening of the as-synthesized materials. Nevertheless, using MOFs as precursors always involves a high temperature heat treatment, which not only leads to the collapse of the MOF crystalline structure, but also results in the loss of organic linkers due to volatilization and severe agglomeration of the metal centers, which greatly reduces the utilization of the well-defined MOF structure and readily accessible active sites for electrocatalysis. From a structural point of view, MOFs show advantages of both homogeneous and heterogeneous catalysts and can be directly used for electrocatalysis. Therefore, attention has recently been paid to pristine MOFs and their intrinsic poten-
tial as electrocatalysts. So far, many MOFs have been reported with superior catalytic performance for the HER, OER and ORR, revealing the bright future for the development of promising electrocatalysts based on MOFs. However, challenges still exist: (i) many MOFs show inferior activity due to the coordinatively saturated metal center and the small pore size in the structure. The former is unfavourable for the adsorption of reactants and intermediates and the sequential achievement of efficient catalysis, while the latter is detrimental to the fast mass permeability of MOFs during the catalytic reaction; (ii) most MOFs can be seen as the insulators or semiconductors that show poor charge conductivity, which greatly affects the progress of the catalytic reaction; and (iii) insufficient knowledge of the real active sites limits the optimal design of high-efficiency MOF-based electrocatalysts.

To solve the problems mentioned above, researchers have devoted great efforts to the preparation of desired MOF materials with high HER, OER or ORR activity, which has been realized via both experimental methods and theoretical calculations. The synthesis and exploration of MOF materials as electrocatalysts have already been systematically discussed in some early published reviews. In this review, we will mainly focus on the strategies that have been used for enhancing the electrocatalytic performance of pristine MOFs, which can be concluded as: (i) engineering microstructure based on the regulation of metal centers, linkers, dimensions, guest molecules, architectures, structures and composites to improve the intrinsic activity (section 2) and (ii) optimizing electron or proton conductivity, hybridizing or compositing with secondary conductive supports to improve MOF conductivity (section 3). Furthermore, the real active species in MOFs during the electrochemical process will also be discussed (section 4).

2. Microstructure engineering of MOFs for electrocatalyzing the HER, OER and ORR

2.1. Fundamentals

The reaction processes of the HER, OER and ORR in acidic and alkaline media are listed below (eqn (1)–(8)):

**HER:**
\[
2H^+ + 2e^- \rightarrow H_2 \quad \text{(acidic)}
\]
\[
2H_2O + 2e^- \rightarrow H_2 + 2OH^- \quad \text{(alkaline)}
\]

**OER:**
\[
2H_2O \rightarrow 4H^+ + O_2 + 4e^- \quad \text{(acidic)}
\]
\[
4OH^- \rightarrow 2H_2O + O_2 + 4e^- \quad \text{(alkaline)}
\]

**ORR:**
\[
O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \quad \text{(acidic)}
\]
\[
O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \quad \text{(alkaline)}
\]

The HER, a half reaction for water splitting, may happen through the Volmer (H^+ + e^- → H_{ads})–Tafel (H_{ads} + H^+ + e^- → H_2) or Volmer–Heyrovsky (2H_{ads} → H_2) mechanisms. The possible rate-controlling step can be determined by the value of the Tafel slope. No matter whether in the acidic or alkaline electrolyte, a proton is first adsorbed on an accessible catalytic site to form an adsorbed hydrogen (H_{ads}). Therefore, the HER rate strongly depends on the free energy of hydrogen adsorption (∆G_H^*), which should be neither too strong nor too weak to have an optimum ∆G_H^* close to 0. As an important process of fuel cells, the ORR is much more kinetically sluggish, which involves several elementary steps with multi-step electron transfer coupled or decoupled with proton transfer. To achieve high efficiency, the 4e^- pathway is preferred. The adsorption of formed OOH*, O* and OH* intermediates is critical to ORR kinetics and the step with the highest kinetic activation barrier is defined as the rate-determining step. On the catalyst surface, the active intermediate should be stable enough and the surrounding active centers need to possess strong buffer capability to facilitate proton transfer. As for the OER, it is the other half reaction of water splitting and its process is just inverse to that of the ORR.

2.2. Structure engineering strategies

Microstructure engineering is a direct and effective way to boost the intrinsic activity of MOFs, through which the electronic configurations and the binding energies toward the adsorption of rate-determining step intermediates can be optimized. The microstructure engineering of MOFs reported recently can be divided into the following aspects: bimetal/multimetal nodes, ligand-based regulation, metal center-based regulation, dimensional control, pore engineering, architectural design, partial structure transformation and MOF hybrid/composite (Fig. 1). The electrocatalytic performances of these pristine MOFs and MOF composites are summarized in Table 1. As indicated by the results, the successful utilization of MOF designable and adjustable characteristics can be an advantage in electrocatalysis.

2.2.1. Bimetal/multimetal nodes. The activity of pristine MOFs for electrocatalysis primarily originates from the coordinatively unsaturated metal nodes, which can be partially replaced by other metal elements with well-preserved MOF structural topology. Compared with the original monometallic MOFs, MOFs with bimetal and multimetal nodes are usually observed with improved catalytic activity due to the synergistic effect between different metal nodes. As confirmed by Zhou and co-workers, Fe^{2+} incorporated into a Co-MOF can weaken the chemical bond between the metal and the coordinated water molecule and modify the electronic state of Co centers to alter the Gibbs free energy of adsorbed intermediates, leading to the expedited electrochemical activation of the CoFe-MOF.

To construct such bimetallic/multimetallic MOFs, 3d transition metal ions (e.g., Fe^{2+}, Co^{2+}, Ni^{2+}, etc.) are widely used for their good electroactivity. Considering the stability of MOFs
in aqueous electrolytes, the MIL series attracts much attention. For example, a pioneering study reported by Li and co-workers explored a series of Fe/Ni MOFs based on the MIL-53 structure with modulated molar ratios of Fe/Ni as efficient OER catalysts. The high activity of these Fe/Ni MOFs can be further improved by forming trimetallic MOFs. The optimized Fe/Nil2.4/Co0.4-MIL-53 achieved a current density of 20 mA cm\(^{-2}\) at an overpotential of 236 mV with a small Tafel slope of 52.2 mV dec\(^{-1}\) (Fig. 2a and b).\(^{57}\) Similarly, the structures of MIL-88B,\(^ {58}\) MIL-100\(^ {59}\) and MIL-101\(^ {60}\) have been investigated as bimetallic MOFs as well with improved intrinsic electroactivity.

Besides the MIL series, the prototypical MOF of MOF-74 [M\(_2\)(DOBDC), M = Mg\(^{2+}\), Zn\(^{2+}\), Ni\(^{2+}\), Co\(^{2+}\), and Fe\(^{3+}\), H\(_4\)DOBDC = 2,5-dihydroxybenzenedicarboxylic acid] has also been studied with much interest. Its high density of open metal sites and favorable stability due to the fully coordinated oxygen of the H\(_4\)DOBDC linker are highly desirable for electrocatalysts. As reported by the Xu group in 2018,\(^{61}\) the mixed-node Co0.6Fe0.4-MOF-74 presented promising activity toward the OER with a low overpotential of 280 mV (at 10 mA cm\(^{-2}\) current density), a small Tafel slope of 56 mV dec\(^{-1}\) and a high faradaic efficiency of 91% for catalyzing the OER in 1.0 M KOH solution. That same year, another bimetallic MOF-74 with Ni and Fe as metal centers on Ni foam was reported by the same group.\(^ {62}\) The NiFe-MOF-74 composite showed enhanced OER performance with an overpotential of 223 mV at 10 mA cm\(^{-2}\). Ni and Fe were also chosen in the study of Chen’s group to construct the MOF-74 structure with H\(_4\)DOBDC.\(^ {63}\) An optimized Fe/Ni molar ratio of 3 : 1 was achieved to provide a small Tafel slope of 49 mV dec\(^{-1}\) and overpotentials of 270 and 287 mV to reach OER current densities of 50 and 100 mA cm\(^{-2}\) in 1.0 M KOH solution.

Since the Fe element has been widely utilized in the preparation of efficient electrocatalysts due to its recognized high catalytic activity, Fe-based MOF materials therefore have emerged as a promising kind of candidate. The trinuclear Fe\(_3\)(μ\(_3\)-O)(CH\(_3\)COO)\(_6\) cluster that can be replaced by a second atom to form the Fe\(_2\)M(μ\(_3\)-O)(CH\(_3\)COO)\(_6\) clusters appears to be an appealing component for building of the bimetallic MOF systems due to its high activity and stability that can be expected. Several bimetallic MOFs based on this trinuclear cluster have been adopted directly as electrocatalysts.\(^ {64}\) In the work reported by Wang and co-workers,\(^ {65}\) a series of bimetallic MOFs (NNU-22–24) assembled from Fe\(_2\)M(μ\(_3\)-O)(CH\(_3\)COO)\(_6\) solution.
## Table 1  Summary of pristine MOFs and MOF composites for electrocatalysis

<table>
<thead>
<tr>
<th>Strategy</th>
<th>MOF</th>
<th>Application</th>
<th>Conditions</th>
<th>Performance</th>
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<td></td>
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<td>1 M KOH</td>
<td>$E_{\text{overpotential}}$ ($E_{1/2}$) (mV)</td>
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<td>Co$<em>{0,9}$/Fe$</em>{0,4}$-MOF-74</td>
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<td><strong>Metal center-based regulation</strong></td>
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<td>MFC-MOFs (2 : 1)</td>
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<td>SnO$_2$ (15%) &amp; CTGU-14</td>
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<td>M–PCBN</td>
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<td></td>
<td>NSO-BDC (120 °C, 24 h)</td>
<td>OER</td>
<td>1 M KOH</td>
<td>$E_{10} = 507$</td>
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(H₂O)₃(Fe₂M, M = Co, Ni, Zn) clusters and biphenyl-3,4′,5-tricarboxylic acid (BPTC) ligands were used for catalyzing the OER, all of which showed better OER performance compared with a monometallic Fe-MOF (NNU-21) (Fig. 2c). The DFT calculations suggested that the introduction of a second metal can result in the d-band center close to the Fermi level and form a stronger binding interaction between the adsorbates and catalysts, thus improving the OER performance. Similar experimental and theoretical results were found by Zhou and co-workers when 4,4′,4″-benzene-1,3,5-triylhexabenzoic acid (H₆BHB) was used as the organic linker to construct the [NH₂(CH₃)₂][M₃(μ₃-OH)(H₂O)₃(BHB)] (M₃ = Co₃, Co₂Ni, CoNi₂, Ni₃) series of MOFs (CTGU-10a1-d1). They attributed the electronic change to the slight difference between Co–O and Ni–O bonds in the bimetallic MOF structures, which means that choosing specific metals or new ligands to cause heavier distortion can further improve the catalyzing performance of MOFs.

Recently, the concept of high entropy is introduced into MOFs. High entropy materials with multimetal components show enormous potential for further tuning positions in volcano plots. The Mu group synthesized a high entropy MOF material (HE-MOF) with five near-equimolar metal species (Mn²⁺, Fe³⁺, Co²⁺, Ni²⁺, Cu²⁺) and 1,4-benzedicarboxylic acid (H₂BDC) (Fig. 2d), which exhibits an overpotential of 245 mV at 10 mA cm⁻² and a Tafel slope of 54 mV dec⁻¹ for the OER in 1 M KOH solution. The high electrocatalytic activity of the HE-MOF was endowed by the synergetic effect from the multimetal nodes. This high entropy concept offers promising opportunities to tailor MOF materials and provide a new platform for future design and synthesis of MOF electrocatalysts.

2.2.2. Ligand-based regulation

2.2.2.1. Structure design of organic linkers. The catalytic activities of MOF materials are significantly influenced by their microstructures. As one of the two components building the MOF structures, the organic linkers can be regulated with the aim of improving activity for electrocatalysis. In this aspect, controllably tailoring organic linkers appears to be a promising way, which has been successfully carried out in several research studies. In the work reported by the Morris group in 2017, they incorporated a Ru-based complex of [Ru(TPY)(DCBPY)OH₂]²⁺ (TPY = 2,2′,6,2″-terpyridine, DCBPY = 5,5-dicarboxy-2,2'-bipyridine) into the MOF (UiO-67) backbone by substituting part of the original ligand (4,4′-biphenyldicarboxylic acid, BPDC). Due to the similar coordination mode and size of the DCBPY to BPDC, this Ru-based complex could participate in the in situ construction process of the MOF structure, bringing the Ru species into the MOF framework. Compared with UiO-67, the obtained Ru–UiO-67 exhibited increased electrocatalytic activity toward water oxidation. This work provides an idea for immobilizing atomic catalysts into a MOF scaffold taking advantage of both homogeneous WOCs and heterogeneous MOF platforms. The method of replacing original ligands with ligands containing functional groups was also reported by Xue and co-workers. They used 2-aminoterephthalic acid (H₂BDC-NH₂, B) to replace some of the terephthalic acid (H₂BDC, A) to bring –NH₂ groups into the MOF structure. AmB-MOF-FeCo1.6 with various molar ratios of A/B was synthesized and increased OER activity was observed. The optimized Am₂,B-MOF-FeCo1.6 showed superior OER performance (overpotential of 288 mV at 10 mA cm⁻² and Tafel slope of 39 mV dec⁻¹). Calculated DOS suggested that this activity improvement was attributed to the introduction of H₂BDC-NH₂, indicating that the electronic structure of the MOF can be adjusted via linker substitution to increase the intrinsic activity.

Rational design of the structures of organic linkers to involve more active sites is also an effective way adopted for...
obtaining highly electroactive MOFs. For example, Huang and co-workers used hexaiminohexaazatrinaphthalene (HAHATN) as a ligand to construct $\text{M}_2\{\text{M}_1\cdot\text{HAHATN}\}_2$ MOFs that possess an extra metallic center ($\text{M}\cdot\text{N}_2$) (Fig. 3a).

The optimal structure of $\text{Ni}_3\{\text{Ni}_3\cdot\text{HAHATN}\}_2$ exhibited a 115 mV overpotential at 10 mA cm$^{-2}$ and 45.6 mV dec$^{-1}$ Tafel slope for the HER in 0.1 M KOH solution. DFT calculations demonstrated that the metal atom in the $\text{M}\cdot\text{N}_2$ metallic center has a higher unsaturation degree than the main metal center of the MOF bonded with $\text{M}\cdot\text{N}_4$ linkage, which leads to a stronger ability to donate electrons for enhancing electroactivity. This design concept can be utilized for improving the activity of MOF materials with extra metallic centers for electrocatalysis.

2.2.2. Crystallinity control. In addition to the structure design concept of organic ligands, another idea for acquiring enhanced catalytic activity of the MOF is to remove some of the ligands that attach to metal atoms in the MOF structure to create coordinately unsaturated metal sites. Through this strategy, prototypical MOF materials that have been extensively studied but exhibit inferior activity toward electrocatalysis can be readily transformed to efficient catalysts by sacrificing a certain degree of crystallinity. For example, ZIF-67 is one of the most extensively studied MOF materials as the precursor for deriving an efficient carbon-based electrocatalyst. However, it is rarely used directly in electrocatalysis due to the fact that the Co centers of ZIF-67 are fully coordinated with N atoms from the 2-methylimidazole ligand (except for those on the surfaces) without accessible sites for electrocatalysis. Tao and coworkers successfully created unsaturated Co sites in ZIF-67 through dielectric barrier discharge plasma etching, and significant enhancement was brought in the OER catalytic activity of ZIF-67 (Fig. 3b and c).

Another way to enhance the electroactivity of MOFs is to functionalize their metal centers with a second metal through $\text{M}\cdot\text{O}^\cdot\text{M}'$ ($\text{M}$ = original metal center, $\text{M}'$ = the introduced metal center) interaction. Different from the bimetallic MOFs, the $\text{M}'$ would act as an extra active site rather than substituting the $\text{M}$ in the framework. The effectiveness of this strategy on the introduction of 3d metals has been demonstrated by a pioneering research study of Kung and co-workers, in which they used a Zr$_6$-based MOF (NU-1000) thin film that is grown on fluorine-doped tin oxide (FTO) conducting glass as the support and deposited Co$_2^+$ ions throughout the MOF film via self-limiting surface-mediated reaction chemistry. The Co$_2^+$ bound at aqua and hydroxo sites lining the

![Fig. 3](a) Synthetic diagram of conductive $\text{Ni}_3\{\text{Ni}_3\cdot\text{HAHATN}\}_2$ MOFs. Reproduced with permission from ref. 69. (b) Illustration of the preparation of ZIF-67 with created unsaturated metal sites and (c) its corresponding OER performance compared with the original ZIF-67. Reproduced with permission from ref. 70.)
channels of NU-1000, resulting in three-dimensional arrays of separated Co$_2^+$ in the MOF film (Co-AIM NU-1000). Compared with the NU-1000 film, the Co-AIM NU-1000 was confirmed to be a promising electrocatalyst for water oxidation. On the other hand, the strategy of metal center functionalization is also effective when the metal is non-3d metal, which cannot be introduced in the solid-solution manner as the preparation of bimetallic MOFs due to their very different size and coordination behaviors. Lately, the same group successfully functionalized the MOF NU-1000 with candidate catalysts-MoS$_x$ units via SIM (solothermal deposition in MOFs) of molybdenum (vi), followed by reaction with H$_2$S gas (Fig. 4a and b).

To overcome the problem of insulating nature of NU-1000 and probe the installed candidate electrocatalysts or contribute to desired electrochemical transformations, they introduced and examined three molecular-scale redox mediators (RMs), which were found to readily diffuse to the MOF-attached MoS$_x$ catalysts (MoS$_x$-SIM) and substantially boost overall catalytic rates. After this study, they carried out their work by exploring whether due to differing environments of the hexagonal mesopore and the channel-connecting micropore (c-pore) there are differing degrees of activity for hydrogen evolution.

They eliminated the installation of a single metal-atom catalyst in the c-pore of NU-1000 by preemptively blocking it via incorporating naphthalene dicarboxylate (NDC) in the c-pore, which caused subsequently installed Mo(SH)$_2$ units to be allocated to the mesopore only. As indicated by catalytic currents and direct assessment of TOFs for H$_2$, the catalytic activity of the sample with NDC incorporation (MoS$_x$-SIM–NDC–SALI) is lower than that of the NDC-free sample (MoS$_x$-SIM). It has a four-fold greater degree of catalytic activity for Mo(SH)$_2$ units sited in micropores vs. mesopores. They ascribed the difference to kinetically beneficial hydrogen-bond-networking across the narrow (<10 Å) micropores. In the work reported by Xu and coworkers, they incorporated oxide units of non-3d metals into a Co$^{II}$ imidazolate framework and prepared two isomorphous MOFs of [Co$_4$(MO$_4$)(EIM)$_6$] (M = Mo or W, HEIM = 2-ethylimidazole) with Co(EIM)$_5$(MO$_4$) units. The Mo-modulated framework (Co4Mo) showed drastically enhanced OER activity in different neutral media (in CO$_2$-saturated 0.5 M KHCO$_3$ solution: overpotential of 210 mV for 1 mA cm$^{-2}$; in phosphate buffer solution: overpotential of 388/490/570 mV for 2/10/22 mA cm$^{-2}$) compared to its counterpart (Co4W) and the original MOF (MAF-6-Co) (Fig. 4c–e). Spectroscopic characterization and computational results revealed that the non-3d metals modulated the electronic structure of Co for optimum reactant/product adsorption and tailored the energy of the rate-determining step to a more moderate value. However, research in this area is less performed at present. More efforts are still needed to further explore the potential of this strategy for enhancing the activity of MOF electrocatalysts.

2.2.4. Dimensional control. In a bulk MOF, the majority of metal sites are located inside the structure with limited accessibility to the reactants due to its micro-scale pore sizes and possible interference from the organic linkers. To solve such problems, thin 2D MOFs have been suggested according to the

Fig. 4  (a) The MoS$_x$-anchored Zr$_6$ node of the representative structure of MoS$_x$–SIM showing all the crystallographically distinct MoS$_x$ units (Mo1–Mo3) and (b) the framework viewed along the a-axis. Reproduced with permission from ref. 76. (c) Active-site structures of Co4Mo, Co4W, MAF-6–Co and their OER activities in comparison with RuO$_2$ in (d) 0.1 M PBS and (e) CO$_2$-saturated 0.5 M KHCO$_3$, respectively. Reproduced with permission from ref. 78.
following advantages: (i) the nanometer thickness will allow rapid mass transport and electron transfer; (ii) a much larger specific surface area can ensure a high percentage of exposed coordinatively unsaturated metal sites; (iii) identifiable surface atomic structures and bonding arrangements offer an ideal model system for exploring the structure–performance relationships. Thus, many efforts have been reported for the synthesis of thin 2D MOFs for electrocatalysis.

The synthesis of thin 2D MOFs can be achieved by top-down or bottom-up methods, which refers to the exfoliation of MOFs into layered structures and the direct synthesis from metal ions and organic linkers, respectively. As for the top-down method, the work reported by Huang and coworkers provides an instructive idea. They designed a pillared-layer MOF based on a catechol functionalized ligand, which is redox active and was selectively oxidized and removed to acquire the ultrathin 2D MOF (Fig. 5a). As confirmed by the electrochemical tests, the prepared sample (Fe:2D–Co–NS@Ni) showed a low overpotential of 211 mV at 10 mA cm$^{-2}$. In the study of Fei’s group, they exfoliated the synthesized bulk MOF material (TMOF-4) into 2D MOF nanosheets by surfactant sodium dodecyl sulfate in aqueous solution. The nanosheet structure effectively reduces the OER overpotential of 52 mV at 10 mA cm$^{-2}$, demonstrating the enhancement of catalytic activity after exfoliation and effectiveness of dimension control of MOF materials. Zhao and coworkers successfully acquired bimetallic MOF nanosheets (NiCo–UMOFNs) with a uniform thickness of approximately 3.1 nm through ultrasonication-assisted exfoliation. Compared with the bulk NiCo–MOFs, NiCo–UMOFNs exhibited significantly enhanced OER performance. Relevant partial density of states (PDOS) calculations suggested that the 3d e$_g$ states of coordinatively unsaturated metals in NiCo–UMOFNs are more filled than those of the fully coordinated metals in bulk NiCo–MOFs, indicating the important role played by coordinatively unsaturated metal centers in improving the catalytic activity. Although the top-down strategy is effective in the preparation of 2D MOFs, it is only applicable to limited MOF structures, and many bulk MOFs cannot be exfoliated due to their intrinsic structures. Meanwhile, the required treatment may give rise to unavoidable morphology damage and structural deterioration.

The bottom-up approach is more mild synthesis and shows advantage in the control of topological molecular architecture of 2D MOFs. To directly synthesize 2D MOFs, π-conjugated organic ligands that possess a rigid backbone (such as benzene-, triphenylene-, etc.) are always preferred due to their unique 2D features as well as improved electron transfer capacity. The bridging of square-planar metal ions with aromatic organic moieties is a promising path to bottom-up synthesis of conductive 2D MOFs. Recently, phthalocyanine (Pc)-based ligands have attracted much attention for constructing π-conjugated 2D MOFs since the MPc motif will play not only the role of connecting units, but also act as possible active sites for electrocatalysis. The Du group reported the first π-conjugated 2D MOF (NiPc–MOF) by using Pc as the building blocks and explored its performance toward the OER (Fig. 5b), the results of which confirmed the great potential of this Pc-based MOF as an efficient OER catalyst. Another Pc based 2D conjugated MOF was prepared by Zhong and co-workers by employing 2,3,9,10,16,17,23,24-octahydroxyphthalocyaninato copper (PcCu–(OH)$_8$) as the building blocks. In this work, Co was used as the metal centers to incorporate a molecular Co–Ox moiety into the final MOF structure (PcCu–O$_8$–Co), which had been verified by theoretical modeling and in situ Raman spectro-electrochemical studies to be the catalytic sites that substantially contributed to its good ORR.
activity. In addition to the Pce-based ligands, other organic linkers (such as hypoxanthine) have also been reported for building 2D MOFs with transition metals.\textsuperscript{84} Meanwhile, DFT calculations play an important role in structural design and offer possible directions for researchers, which may greatly expand the family of MOF electrocatalysts in the future.\textsuperscript{85,86}

Besides the microperspective of structural design, there are also effective bottom-up approaches that have been reported for obtaining 2D MOFs, such as introduction of modulators, self-sacrificial templates, \textit{etc.} In the modulator method, the selected modulator molecules usually possess similar functional groups to the organic linkers and can coordinate with the metal centers, which could inhibit the growth of certain crystal planes of MOFs, thus regulating the growth kinetics of MOFs. The Pang group used pyridine as a growth inhibitor during the synthesis of the 4,4′-bipyridine (BPY)-based MOF.\textsuperscript{87} The obtained bimetallic MOF nanoparticles (Ni\textsubscript{0.5}Co\textsubscript{1.5}-bp) showed well-defined 2D morphology and were applied directly as efficient OER electrocatalysts in 1.0 M KOH solution (overpotential of 256 mV at 10 mA cm\textsuperscript{−2} and small Tafel slope of 81.8 mV dec\textsuperscript{−1}). By this approach, more MOF materials, especially those composed of fully coordinated metal centers, may be explored as advanced electrocatalysts. With the intention to synthesize 2D MOFs, \textit{in situ} transformation of 2D templates to MOFs is another facile way that has been reported. Due to the lamellar structural features and abundant metal sources, the amorphous metal oxide nanosheets were utilized as a self-sacrificial template in the work reported by Zhuang and coworkers (Fig. 5c).\textsuperscript{88} They successfully prepared FeCo-MOF-74 nanosheets by confined ligand coordination of the Fe–Co oxide nanosheets. The acidic ligand H\textsubscript{4}DOBDC was conducive to leaching metal ions from metal oxide nanosheets and induced confined growth of MOF crystals into a 2D structure. With more extra coordinatively unsaturated metal sites compared to the bulk FeCo–MOF-74, the FeCo–MOF-74 nanosheets showed competitive activity for the OER and overall water splitting activity. Another ideal self-sacrificial template is layered double hydroxides (LDHs), which also come close to the central Co of [CoW\textsubscript{12}O\textsubscript{40}]\textsuperscript{6−} in alkaline medium. Other binary- or ternary-metal 2D MOF nanosheet arrays can be expected through this strategy with improved electrocatalytic activity.

2.2.5. Pore engineering. Due to their micro-sized pores and high surface area, a pristine MOF can also afford \textquotedblleft nanocages\textquotedblright for various applications in the fields of gas adsorption, separation, sensors, catalysis, and so forth. The \textquotedblleft nanocages\textquotedblright of MOFs could be taken better advantage of when MOFs are utilized directly as the HER, OER or ORR electrocatalyst. Pore engineering of MOFs, such as trapping active substances inside the pores as active sites accessible to reaction agents, thus has been considered as an important means to promote the catalytic activity and efficiency of MOFs.

The POM anion is considered as one kind of promising candidate for MOF pore engineering due to its intrinsic activity for catalysis. In the work reported by the Das group,\textsuperscript{84} Keggin-type POM anions [CoW\textsubscript{12}O\textsubscript{40}]\textsuperscript{1−} have been encapsulated inside the cavity of ZIF-8 by \textit{in situ} synthesis. The POM@ZIF-8 host–guest composite can perform water oxidation for a prolonged time period in neutral pH, while the pure POM and ZIF-8 showed little activity. They presumed that water molecules got associated with the Keggin surface (mostly, by hydrogen bond formation) during the water oxidation process as they cannot come close to the central Co of [CoW\textsubscript{12}O\textsubscript{40}]\textsuperscript{1−}, which allowed facile electron transport between Keggin and water molecules. Recently, a cobalt-trisubstituted silicotungstic Keggin POM [SiW\textsubscript{6}Co\textsubscript{3}(H\textsubscript{2}O)\textsubscript{3}O\textsubscript{17}]\textsuperscript{10−} (SiW\textsubscript{6}Co\textsubscript{3}) was loaded into the nanocages of the ZIF-8/ZIF-67 structure by Abdelkader-Fernández and co-workers via a similar \textit{in situ} synthetic strategy (Fig. 6a).\textsuperscript{95} The enhanced OER performance of the SiW\textsubscript{6}Co\textsubscript{3}@ZIF-67 nanocomposite compared with pristine ZIF-67 (2-times-higher current density values, reducing the overpotential by \textasciitilde 110 mV and Tafel slope by \textasciitilde 21%) was suggested emerging from ZIF–POM bidirectional synergy that had modified the intrinsic electrochemical behavior and thus promoted the OER electrocatalytic activity. This bidirectional synergy was not seen for the SiW\textsubscript{6}Co\textsubscript{3}@ZIF-8 nanocomposite, confirming the decisive role of Co\textsuperscript{2+} nodes in the ZIF-67 skeletons. In addition to POM anions, metals/metal alloys are also well recognized efficient electrocatalysts and can be used for pore engineering of MOFs. In the reported work of the Chen group,\textsuperscript{96} they immobilized Pd nanoclusters in the pores of
MOF-74–Co through a post-impregnation method (Fig. 6b). The obtained Pd@MOF-74–Co material exhibited both HER and ORR electrocatalytic performances in acidic and alkaline solutions, respectively. This pore engineering strategy not only promoted the activity of MOF-74–Co, but also stabilized Pd nanoclusters and lowered their dosage at the same time. Ding and coworkers encapsulated the noble metal alloyed nanoparticles (RhRu) in the cavities of an amino-functionalized MOF (UiO-66–NH₂) by post-impregnation and an in situ reduction method. The optimized hybrid (Rh50Ru50@UiO-66–NH₂) prepared showed high activity toward the HER over a wide pH range. From originally inactive UiO-66–NH₂ to the efficient electrocatalyst of Rh50Ru50@UiO-66–NH₂, the effectiveness of this pore engineering strategy was confirmed for improving the activity of MOFs. Another evidence was provided by the study of the Biradha group through a different idea. They utilized the uncoordinated ligands (with naked pyridine moieties) incorporated into the Cd–MOF (Cd–BNN) as the anchor sites of metal ions to prepare the Co(n) doped CoCd–MOF (CoCd–BNN). The presence of free pyridyl units within the network promotes the absorption of Co(n), which brought the change of the MOF from electrochemically inactive to active and significantly lowered the overpotential of the water oxidation process. Pore engineering of MOFs not only enhances the electroactivity of MOFs but also effectively protects the active species loaded in MOFs. Good and smart utilization of the guest–host interaction from this strategy may lead to the generation of high-performance MOF materials for electrocatalysis.

2.2.6. Architectural design. As discussed in the 2.4 section, the low-dimensional MOFs show advantages in exposing more active sites, promoting mass transport and reducing corresponding resistance in electrocatalysis. However, some problems cannot be avoided such as stacking or aggregation, which will reduce the available surfaces and sequentially decrease the activity expectation. One way to deal with such problems is to design hierarchical nanostructures of MOFs, which can well maintain the high surface area of low-dimensional MOFs, while offering ion transport pathways for rapid access to the active sites. Several research studies adopting this strategy have been reported very recently. In the work reported by Shinde and coworkers, Mn/Fe–hexaiminobenzene MOFs (Mn/Fe–HIB–MOF) with well-defined quintet-shelled hollow spheres were prepared (Fig. 7), which exhibited superior bifunctional oxygen electrocatalytic activity (half-wave potential of 0.883 V for the ORR and overpotential of 280 mV at 10 mA cm⁻² for the OER) and the highest lifetimes reported to date.

**Fig. 6** (a) ‘In situ’ methodology applied for the preparation of POM@ZIF nanocomposites. Reproduced with permission from ref. 95. (b) Synthetic process of Pd@MOF-74. Reproduced with permission from ref. 96.
for rechargeable Zn-air batteries (0.75 V voltage gap at 10 mA cm$^{-2}$ over 6000 cycles and 600 h of $\sim$65.24% efficiency at 25 mA cm$^{-2}$ over 3600 cycles). DFT calculations revealed that the electronic structures of the MOFs, with intrinsic conductivity and O$_2$ adsorption capability, facilitate their superior bifunctional performance. Zhou and co-workers presented a strategy for synthesizing hierarchical bimetallic MOF nanostructures by controlling the ratio of metal salts in the solvothermal synthesis of MOFs. The CTGU-10c2 (CoNi$_2$–MOF) nanobelts prepared exhibited competitive OER performances with an overpotential of 240 mV at 10 mA cm$^{-2}$ and a long-term stability of >50 h in an alkaline medium. DFT and experimental results indicated that the hierarchical nanobelt architecture played an important role in contributing to the final performance besides the unsaturated metal sites and coupling effect between Ni and Co. Some other MOF materials however can be readily grown into nanosheet 3D aggregates by a simple one-pot hydrothermal method, such as the nickel terephthalate MOF (Ni–MOF) used in the work of Zheng and co-workers. The thickness of these nanosheet 3D Ni–MOF aggregates could be adjusted by varying the synthesis time and the thinnest sample exhibited the most suitable OER catalytic activity (overpotential of 337 mV for 10 mA cm$^{-2}$ and Tafel slope of 29 mV dec$^{-1}$). Besides the pure phase of nanosheets, nanowires may also be integrated with nanosheets to derive the hierarchical nanostructure. The Jia group reported a hierarchical NiVFe–MOF composed of self-supported nanowires and nanosheets through substrate-assisted solvothermal growth. The MOF nanowires and nanosheets are tightly assembled with facile mass transfer and abundant exposure of active sites, resulting in enhanced OER activity (overpotential of 225 mV for 10 mA cm$^{-2}$ and 269 mV for 100 mA cm$^{-2}$, respectively). The studies mentioned above prove that the architectural design of the MOF materials shows great advantage in promoting the overall performance of MOF-based electrocatalysts mainly by reducing aggregation or stacking of the nanosized MOF, retaining the accessibility of active sites, allowing rapid transport of the electrolyte, etc. It is sure that more promising catalysts would be explored through this strategy in the near future.

2.2.7. Partial structure transformation. As mentioned at the beginning of this review, although converting MOFs to metal (compounds)/carbon electrocatalysts is benefiting from the conductive carbon scaffolds and homogeneity in the spatial distribution of active metal species, the total decomposition of MOFs usually led to the dramatic decrease of the surface area, damage of well-defined pore/channel structures, and less exposure of active sites, which would reduce the accessibility to the reactants and hardly taking full advantage of MOFs. To solve this problem and inherit the advantages of both pristine MOFs and MOF derivatives, a strategy of partial structure transformation in different atmospheres has been recently proposed by researchers. Wang and coworkers developed a controlled partial pyrolysis method. They heated the prepared trimetallic MOF NiCoFe-MOF-74 in a tube furnace under a N$_2$ atmosphere at 400 °C for 1 h to obtain semi-MOF derivatives (NiCo/Fe$_3$O$_4$/MOF-74) with nanoparticles of metal/metal oxide inside (Fig. 8a). It outperformed (overpotential of 238 mV at 10.0 mA cm$^{-2}$ and Tafel slope of 29 mV dec$^{-1}$) pristine NiCoFe–MOF-74 and the totally decomposed MOF deriva-
tives, demonstrating the effectiveness of this strategy. Motivated by the same goal of combining the merits of MOFs and MOF derivatives, He and coworkers performed partial sulfurization treatment on the prepared 2D Ni-BDC MOF in 2019. The partial sulfurization process transformed the surface MOF into NiS with the porous structure inside the MOF retained. The corresponding Ni-BDC@NiS composite displayed promoted electrochemical activity toward the OER with an overpotential of 330 mV at a current density of 20 mA cm\(^{-2}\). As indicated by the authors, it could be attributed to the synergistic effects from open active sites of Ni-BDC nanosheets and promote the electrical conductivity of NiS.

In the same year, another idea of designing transition metal phosphides/MOF hybrids was reported by partial phosphorization of the MOF, hoping to fabricate an efficient electrocatalyst that not only takes advantage of MOF’s well-defined porous structure but also possesses an optimal \(\Delta G_{H^*}\) for the HER. The partial phosphorization would create CoP species in the Co-MOF (based on imidazole) after reacting the pre-grown Co-MOF on carbon fiber paper with sodium hypophosphite (Fig. 8b). The produced CoP/Co-MOF hybrid showed pH-universal Pt-like activity with overpotentials of 27, 34, and 49 mV at 10 mA cm\(^{-2}\) in neutral, alkaline and acidic media, respectively. DFT calculations indicate that the enhanced HER performances came from the electron transfer from CoP to Co-MOF through N-P and N-Co bonds, which led to optimal \(\Delta G_{H_{1,0}}\) and \(\Delta G_{H^*}\). Another MOF material based on diaqua-bis (5-carboxy-1H-imidazole-4-carboxylate) (CoCu-MOF) has also been reported to be successfully partially phosphorized very recently, but through a two-step way. The first pyrolysis step thermally eliminated some functional groups to create a number of vacancy defects, which were converted to active CoP species in the second phosphorization step. Based on the defective MOF, the corresponding hybrid possessed a larger electrochemically-active surface area (ECSA) and a higher electron transfer rate, which efficiently promoted its OER activity (the overpotential was reduced by \(\sim\)700 mV at 10 mA cm\(^{-2}\)).

Besides the partial sulfurization and phosphorization, partial boronization has also been proposed for the synthesis of MOF electrocatalysts. Lately, the Wu group developed a room-temperature boronization method by simply immersing nickel zeolite imidazolate framework (Ni-ZIF) nanorods into ultrathin Ni-ZIF/Ni-B nanosheets. The formed abundant crystalline-amorphous phase boundaries were suggested by DFT calculations to provide an optimal adsorption energy change of the intermediates, which was confirmed by the experimental results. The Ni-ZIF/Ni-B nanosheets supported on nickel foam (Ni-ZIF/Ni-B@NF) required a small overpotential of 67 and 234 mV for the HER and OER at 10 mA cm\(^{-2}\) respectively under alkaline conditions and the electrolyzer needs a low cell voltage of 1.54 V at a current density of 10 mA cm\(^{-2}\) for overall water splitting.
This functionalization strategy of MOFs via partial pyrolysis, sulfurization, phosphorization, boronization, etc. can effectively enhance the electrocatalytic activity of MOFs by partial transformation of the MOF structure to corresponding metal compounds that can synergistically work with the retained MOF framework. It is a promising strategy and opens a new avenue for the design of new MOF-based materials for electrocatalysis.

2.2.8. MOF hybrid/composite. Mixing one component with a secondary phase is commonly adopted in catalyst synthesis with the aim to introduce synergistic effects (substrate-electrocatalyst, intra-molecular and inter-molecular) and further improve the catalytic functionalities, which is available to the construction of MOF-based electrocatalysts as well. The substrate-electrocatalyst synergistic effects will be discussed in section 3. The intra-molecular synergistic effect usually appears within an electrocatalyst that possesses more than one active components, such as the bimetallic/multimetallic MOFs mentioned at the beginning of this section. The inter-molecular synergistic effect will show up between well-mixed functional components due to the close contact, which will be mainly discussed in here.

MOF-involved hybridization and composition with a secondary functional phase, such as MOFs, covalent-organic frameworks (COFs), metal particles and metal oxides/sulfides, have been reported for the design and fabrication of MOF-based electrocatalysts. Rui and coworkers prepared H$_2$BDC-based MOF hybrids (Ni-MOF@Fe-MOF) by post-deposition of electrochemically inert Fe-MOF nanoparticles onto active 2D Ni-MOF nanosheets via a two-step synthesis at room temperature (Fig. 9a).

The optimal catalytic performance for the OER was achieved at a Ni/Fe atomic ratio of 3.5/1 (overpotential of 265 mV at a current density of 10 mA cm$^{-2}$), which was superior to that of the state-of-the-art IrO$_2$ catalysts (365 mV) and a simple mixture of both MOFs. The Fe-MOF is inert to drive the OER, whereas the hybridization with the Fe-MOF substantially decreased the overpotential of the Ni-MOF (370 mV) by about 100 mV, suggesting the synergistic interaction between Ni and Fe species. Besides the post-deposition, MOF/MOF composites may also be synthesized through one in situ step to produce the inter-molecular synergistic effects. As reported by the Lu group, well-mixed Fe- and Ni-MOFs based on the H$_2$BDC-NH$_2$ linker were grown on nickel foam in a one-step hydrothermal process. The optimal molar ratio of starting Fe/Ni salts of 2 : 1 (MFN-MOFs (2 : 1)) offered high activities toward the HER (overpotentials of 79 and 234 mV at 10 and 500 mA cm$^{-2}$, respectively) and OER (overpotentials of 235 and 294 mV at 50 and 500 mA cm$^{-2}$, respectively) in 1 M KOH. Low cell voltages of 1.495 V at 10 mA cm$^{-2}$ and 1.80 V at 500 mA cm$^{-2}$ and high stability (500 mA cm$^{-2}$ for over 100 h with 3.7% decay) were achieved for overall water splitting.

Fig. 9  (a) Schematic illustration of synthesis of Ni–MOF@Fe–MOF hybrid nanosheets. Reproduced with permission from ref. 107. (b) Schematic representation of the synthesis process of PCB, M-PCB, and M-PCBN. Reproduced with permission from ref. 116.
the utilization of active metal ion sites for catalyzing the HER and OER. A similar idea was also reported in the work of Zhou’s group, in which mixed Co- and Fe-BDC MOFs (MFC–MOFs (1:3)) were prepared, further confirming that the inter-molecular synergy could be designed and produced between MOFs to promote the activity of MOFs for electrocatalysis.

In addition to MOFs, COFs (a new class of crystalline and microporous materials that were constructed from organic components by covalent bonds) have also been considered as a promising candidate to combine with MOF materials for introducing inter-molecular synergistic effects. Cui and coworkers prepared a hybrid electrocatalyst comprising bimetallic CoCu-ZIF nanosheets and graphdiyne COF nanowires (CoCu-ZIF@GDY) that displayed an OER activity (overpotential of 250 mV at 10 mA cm\(^{-2}\)) which outperformed the individual CoCu-ZIF (300 mV) and COF (330 mV) in alkaline solution and at a low cell voltage of 1.52 V vs. RHE at 10 mA cm\(^{-2}\) for overall water splitting. These results demonstrated that hybridization with a COF could produce inter-molecular synergy and enhance the electrocatalytic activity of MOF materials.

Metal/metal alloy nanoparticles are also promising candidates for preparing MOF hybrids or composites for electrocatalysis due to the good conductivity and activity of metal/metal alloys. Noble metal Pt has been widely investigated for its high electrocatalytic performance, low dosage, uniform dispersion and stabilization of which may be achieved when combined with MOF materials. More importantly, the possible inter-molecular synergy between Pt nanoparticles and MOFs may greatly enhance the activity of MOF materials for electrocatalysis. This idea was carried out by Ye and coworkers via combining Pt quantum dots (Pt QDs) and Fe-H$_2$BDC MOF (Pt DQs@Fe-MOF) grown on Ni foam (low Pt content of 1.84 μg cm\(^{-2}\)). This exhibited good HER (overpotential of 33 mV and 191 mV for 10 and 100 mA cm\(^{-2}\)), OER (overpotential of 144 mV for 10 mA cm\(^{-2}\) and overall water splitting (1.47 V for 10 mA cm\(^{-2}\), stability over 100 h) performance in 1 M KOH. Zhang and coworkers confined Pt doped carbon (Pt/C) into a porphyrin-based MOF PCN-222 film by loading the glucose mixed H$_2$PtCl$_6$ and heating at 200 °C. Homogeneous and ultrafine Pt/C nanowires (Pt/CNWs) are formed in nanochannels of PCN-222 (Pt/CNW@PCN-222), which exhibited HER performance with an overpotential of ~115 mV at a current density of ~10 mA cm\(^{-2}\) under light irradiation in 1 M phosphate buffered saline (PBS) aqueous solution with 0.025 M Na$_2$SO$_3$. In addition to noble metals, transition metal alloys may also be a choice for preparing efficient MOF-based electrocatalysts. Ma and coworkers synthesized a Cu-Ni-MOF (MOF-74) encapsulating copper–nickel nanoparticles by \textit{in situ} etching copper–nickel spherical nanostructures as the precursors, through which better electrochemical behaviors than the copper–nickel nanoparticles and pure MOF-74 were achieved by the Ni-Cu@Cu-Ni-MOF toward the OER.

Besides metal/metal alloys, 3d transition-metal oxides that show promising OER activity and stability in alkaline solutions are also explored to synthesize MOF-based electrocatalysts. The integration of MOFs and metal oxides could promote electrical conductivity and robustness of MOFs and introduced the inter-molecular synergy simultaneously to further enhance the intrinsic activity of MOFs. In this regard, Tian and coworkers designed and synthesized a new microporous Co$_3$-based MOF and integrated it with SnO$_2$. The MOF/SnO$_2$ composite (SnO$_2$ (15%) & CTGU-14) exhibited an overpotential of 388 mV at 10 mA cm\(^{-2}\) for the OER in 0.1 M KOH solution, which was reduced by 66 mV compared with the pure MOF (overpotential of 454 mV at 10 mA cm\(^{-2}\)). This enhancement of OER activity was ascribed to the synergistic effects between the MOF and SnO$_2$. Similar synergistic effects were also demonstrated by the Wang group. After growing a Ni$_3$(HTTP)$_2$ (HTTP = 2,3,6,7,10,11-hexaiminotriphenylene) MOF on the surface of La$_0.6$Sr$_0.4$Co$_0.8$Fe$_0.2$O$_3$ perovskite oxide nanofibers, the prepared MOF/metal oxide composite [LSCF@Ni$_3$(HTTP)$_2$] showed greatly enhanced OER performance (overpotential of 272 mV) compared to the Ni$_3$(HTTP)$_2$ MOF (380 mV) and the perovskite oxide (345 mV). Lately, a study that combined the MOF with metal oxide nanoparticles was reported by the Zhou group. In the lattice of a monolayered Co–benzimidazolate MOF (PCB), they embedded ultra-fine CoFeO$_2$ nanoparticles to produce the metal–oxide–nanoparticle-embedded PCB (M-PCB), which was further exfoliated to form monolayered M-PCB nanosheets (M-PCBN) by ultrasonication (Fig. 9b). The created metal Co sites located at the CoFeO$_2$/MOF interfaces possessed a higher valence and changed 3d electronic configuration compared to the Co$_2$N$_x$ sites of the MOF, leading to an enhanced electrocatalytic OER performance (overpotential of 232 mV at 10 mA cm$^{-2}$).

In addition to the metal/metal alloy and metal oxides mentioned above, transition metal chalcogenides (especially sulfides) have also been considered and utilized to construct heterogeneous MOF-based electrocatalysts due to their low cost and good electronic conductivity. For example, Wang and coworker had recently integrated a Ni-BDC MOF with the Ni$_3$S$_2$/NiS hollow nanoparticles and explored its potential for catalyzing the OER. Nickel sulfides generally possess poor activity toward the OER, whereas their heterogeneous nanostructures with other species have demonstrated synergistically promoted kinetics and electron-reconfigured interfaces with superior performance to their single-component counterparts, which can be utilized to enhance the activity of MOFs as electrocatalysts. As revealed by the results, the prepared composite of MOF and Ni$_3$S$_2$/NiS nanoparticles (NiSO–BDC (120 °C, 24 h)) exhibited enhanced electrocatalytic performance for the OER (overpotential of 298 mV at 10 mA cm$^{-2}$ and Tafel slope of 58.6 mV dec$^{-1}$) in 1.0 M KOH compared to the pure MOF and Ni$_3$S$_2$/NiS nanoparticles.

These results point out the fact that incorporating a conductive/semiconductive phase into MOF materials is an effective way to introduce the inter-molecular synergy. The heterogeneous nanostructures can create new active sites at the interface, improve the electroconductivity of MOFs, accelerate the electron transfer between the catalysts and electrolyte, and thus increase the electrocatalytic performance of MOFs. More promising electrocatalysts based on MOF hybrid/composites can be expected through this strategy.
3. Improving conductivity of MOFs for electrocatalyzing the HER, OER and ORR

Although MOFs show great advantages as candidates for electrocatalysis, such as the atomically dispersed diverse metal centers and accessible accommodation spaces for electrolytes, very limited MOF materials have been studied directly as electrocatalysts because of their poor electrical conductivity. Therefore, improving the conductivity of MOFs has been considered as an important research direction in this area. To ameliorate the conductivity and the catalytic performance of MOFs, three main strategies have been investigated (Fig. 10): (i) designing and constructing electron conductive MOFs; (ii) utilizing and turning the proton conductivity of MOFs; (iii) hybridizing or compositing with secondary conductive supports. In this section, we will focus on these three strategies respectively and introduce related studies reported recently.

3.1. MOFs with electron conductivity

At present, MOFs based on triphenylene-derived ligands are the most studied electron conductive MOFs. The conductivity of the prepared MOFs can be flexibly modulated from $\sim 10^{-6}$ to $4 \times 10^4$ S cm$^{-1}$ by modifying the triphenylene ligands and using disparate metal ions. This class of MOFs have attracted considerable attention for electrocatalysis and several attempts have been made in the field.$^{118-122}$ To further increase the electrocatalytic activity of this kind of MOF, Li and coworkers very recently prepared bimetallic triphenylene-based 2D MOF ($\text{Fe}_2\text{Ni}_4$–HHTP,$^{56}$ HHTP = 2,3,6,7,10,11-hexahydroxytriphenylene) nanowire arrays on carbon cloth and utilized it as an OER electrocatalyst, showing 213 and 300 mV overpotentials at 10 and 150 mA cm$^{-2}$ respectively in 1 M KOH. The reason for this promising activity indicated by the DFT calculations was self-adaptable structure adjustment of Fe sites. It enabled the generation of additional hydrogen bonds between the OER intermediates and the adjacent layers, decreasing the free energy in the OER process. Further exploration of this MOF through structure designing or nanostructuring may produce more efficient catalysts for electrocatalysis.

With the aim to design and construct electron conductive MOFs, the 2D conjugated phthalocyanine based MOFs have also been considered as promising candidates with in-plane p-delocalization and weak out-of-plane p–p stacking to facilitate electron transfer capacity. Zhong and coworkers designed a cobalt bis(dihydroxy) linkage (Co–O$_4$) based 2D conjugated MOF constructed from Pccu-(OH)$_8$. The as-prepared MOF hybridized with carbon nanotubes displayed a competitive performance for the ORR ($E_{1/2} = 0.83$ V vs. RHE, $n = 3.93$, $j_L = 5.3$ mA cm$^{-2}$) and zinc-air batteries in alkaline media, suggesting that the optimization of the electronic structure of 2D MOFs is also important for developing efficient electrocatalysts toward the ORR in addition to the creation of active sites. This work points out the effectiveness of designing 2D conjugated phthalocyanine based conductive MOFs as electrocatalysts.

In addition to the M–O coordination-based MOFs, the MOFs that were constructed from Fe–N coordinate linkage...
have also been explored to date as electrocatalysts. For example, the Xu group investigated the potential of semiconducting iron triazoleate MOF (FeTa3) for catalyzing the ORR in 0.1 M KOH.124 The FeTa3 MOF with an intrinsic electrical conductivity of $\sigma = 9.5 \times 10^{-5}$ S cm$^{-1}$ was studied as the composite with conductive Ketjenblack carbon (KB), which showed an onset potential of 0.84 V and a half-wave potential of 0.64 V with stability up to 20,000 cycles. The N-Fe$^{III}$–OH$^{-}$ sites at the surface of the FeTa3 MOF were suggested to play the role of catalytically active sites. The performance of this Fe-N MOF might be inferior to that of the mentioned MOFs, whereas it offers more possibilities in future exploration of electron conductive MOFs for electrocatalysis.

3.2. MOFs with proton conductivity

Theoretically, the electrocatalysis processes involve not only electron transfer but also proton transfer. Thus, besides the electron conductive MOFs, the proton conductive MOFs are also promising candidates for further exploration as electrocatalysts. In the work reported by Hod and coworkers in 2015,124 also promising candidates for further exploration as electrocatalysts. Thus, besides the electron conductive MOFs, the proton conductive MOFs are also promising candidates for further exploration as electrocatalysts. In the work reported by Hod and coworkers in 2015,124 the hybrid electrocatalyst prepared via electrochemical deposition of the Ni–S on NU-1000 MOF film showed an overpotential of 238 mV (205 mV lower than MOF-free Ni–S) at 10 mA cm$^{-2}$ in 0.1 M HCl solution; however the MOF scaffold did not exert its co-catalytic effect by boosting the electroactive surface area of the deposited nickel sulfide. Instead, it served to modify the immediate environment for more favorable local proton delivery and/or transport. The aquo- and hydroxo-rich nodes of the MOF appeared to contribute in a manner that is reminiscent of organic acids or bases in proximity to metal-ion-based cofactors in enzymes that catalyze proton-coupled electron-transfer reactions. This work thus provides a new concept for utilization of pristine MOFs as catalysts for electrocatalysis.

Considering the advantages of MOFs in control of proton transfer, it is reasonable to propose a hypothesis that tuning the proton conductivity of MOFs may provide a convenient and efficient way to improve their electrocatalytic performances. According to this aim, Zhang and coworkers designed and synthesized two isostructural MOFs (FJU-82–Co/FJU-82–Zn) based on the same organic ligands but different metal centers.125 When applied to OER catalysis, the FJU-82–Co displayed a much lower overpotential (0.57 V) than FJU-82–Zn (1.17 V) at a current density of 1 mA cm$^{-2}$ in neutral buffer solution and a 127-fold higher proton conductivity than FJU-82–Zn at 60 °C and 98% RH. Since the metal sites were coordinatively unsaturated, the electrochemically active surface area of FJU-82–Co was 4.5 times lower than that of FJU-82–Zn, no free metallic ions were detected in the solution after the chronoamperometry test, the higher OER performance can be concluded mainly originating from the higher proton conductivity of FJU-82–Co. This work presents the influence of metal centers in MOF structures on proton transfer and corresponding OER performance. Other factors (such as organic ligands and guests of channels) and more MOF structures still need further exploration in this area, which might help to understand better the catalytic mechanism of MOF materials and perform more targeted design and synthesis of efficient MOF electrocatalysts.

3.3. Combination with a conductive support

At present, most pristine MOFs used as electrocatalysts possess low conductivity. One of the most critical procedures to apply them for electrocatalysis is to prepare the electrodes. There are mainly two ways, growing MOFs and casting MOFs or MOF composites (hybridized with a conductive support) on the electrode surface. Growing MOFs on a conductive support as an integrated electrode can greatly facilitate the electron transfer from the electrode to the catalyst, thus improving electrocatalytic performance of the MOF structure. For the casting method, conductive additives (such as carbon materials) can be used through simple physical mixing to better deliver the electroactivity of MOFs. Both ways have been confirmed effective for preparing the MOF decorated electrodes.

To prepare the integrated MOF/conductive support electrode, metal (alloy) foam is widely adopted due to its 3D macroporosity, relatively high specific surface area, and high mechanical strength and flexibility. The integrated nickel foam and MOFs can be applied directly as electrode materials without the casting step and addition of binder, and more importantly, favorable electrocatalytic performance usually can be expected as well from these composites due to the accelerated electron transport capability. For example, the Lin group grew the bimetallic FeNi–MIL-53 on Ni foam via an in situ solvothermal method,126 which displayed excellent OER performance (overpotentials of 233 mV and 245 mV at a current density of 50 and 100 mA cm$^{-2}$ respectively and small Tafel slope of 31.3 mV dec$^{-1}$) in 1 M KOH solution. Bimetallic FeNi–MIL-53 was also successfully synthesized on NiFe alloy foam by Cao and coworkers via using the NiFe alloy foam as both the metal sources and substrate.127 The as-prepared composite electrode required an overpotential of 253 mV to achieve a current density of 100 mA cm$^{-2}$ for the OER in alkaline electrolyte (1 M KOH) with a Tafel slope of 38.9 mV dec$^{-1}$. Laterly, Co and Fe were chosen as the metal centers to prepare the MIL-53 structure on Ni foam that displayed an OER performance of 262 mV overpotential at 100 mA cm$^{-2}$ and 69 mV dec$^{-1}$ Tafel slope.128 In addition to MIL-53, other materials in MIL series, such as MIL-88B, have also been reported grown on Ni foam as catalysts for electrocatalysis. The NH$_2$–MIL-88B (Fe$_2$Ni)/Ni foam composite prepared by the Lu group was demonstrated to be a highly efficient bifunctional electrocatalyst for overall water splitting,129 which exhibited overpotentials of 240 and 87 mV respectively for the OER and HER and cell voltage of 1.56 V for the overall water splitting at a current density of 10 mA cm$^{-2}$ in 1 M KOH solution. Without the NH$_2$–groups in the ligand, the MIL-88B (Fe$_2$Ni)/Ni foam was also reported with similar OER performance.130 Not only the MIL series, many other kinds of MOFs have also been reported in situ grown on Ni foam.62,111–114 Furthermore, Cu foam has also been used as a conductive substrate for growing MOFs as the electrocatalyst besides the Ni foam,135 which is confirmed
capable of enhancing the performance of the MOF as well as for the OER.

For the casting method, a carbon material is a popular kind of conductive additive to increase the conductivity of MOFs, which can not only facilitate their charge transfer, but also may guarantee the stability during the electrocatalysis processes. As indicated from the studies, carbon black could enhance the electrocatalytic activity of MOFs, as well as carbon paper. In the work reported by the Zhong group, reduced graphene oxide (rGO) was used to prepare the bimetallic CoNi-MOF/rGO composite, which required a 63 mV lower overpotential to achieve 10 mA cm\(^{-2}\) for the OER in 1.0 M KOH and showed 0.4 mA cm\(^{-2}\) higher diffusion limiting current density at 1600 rpm for the ORR in 0.1 M KOH than the CoNi-MOF, confirming the important role played by rGO. Similar results with simultaneously enhanced ORR and OER activity were also observed for ZnCo-ZIF after combining with graphene oxide (GO). To further increase the mass transfer during the electrocatalysis, three-dimensional (3D) carbon supports have been employed. Chen and coworkers constructed a Co-MOF on a 3D graphite foam via in situ synthesis. The resultant composite exhibited competitive ORR activity with an overpotential of 220 mV at 10 mA cm\(^{-2}\) in 1 M KOH solution that is much lower than that of Ir/C (380 mV). Afterwards, Xie and coworkers reported a study based on 3D rGO prepared via the freeze-drying technique, on which a Ni-MOF was mounted with the assistance of ultrasound. The OER performance of this hierarchical catalyst in 0.1 M KOH was superior to that of the pure Ni-MOF and 2D rGO/Ni-MOF composite with a greatly reduced overpotential of 60 and 40 mV at 10 mA cm\(^{-2}\), respectively. Lately, a new 3D carbon support of multi-channel carbon fibers (MCCF) was reported by Cheng and coworkers for the development of a MOF/carbon composite as a bifunctional oxygen electrocatalyst. The NiMn–MOF/MCCF composite was prepared via a hydrothermal growth and subsequent ligand exchange, which possessed outstanding ORR (half-wave potential of about 0.73 V vs. RHE) and OER (overpotential of 280 mV) performance than those of NiMn–MOFs + MCCF (0.64 V vs. RHE and 320 mV respectively), suggesting again the advantages of the 3D structure of carbon supports in the preparation of MOF/carbon composites for efficient electrocatalysis. Besides the widely used Ni foam and carbon materials as mentioned above, other conductive materials have also been utilized to increase the electroactivity of the MOF, such as metal nanowires. Wang and coworkers grew ZIF-67 on 1D Ag nanowires through in situ synthesis. For the OER, the ZIF-67/Ag nanowire composite exhibited an overpotential of 316 mV at 10 mA cm\(^{-2}\) in 0.1 M KOH solution, which is much lower than that of ZIF-67 (540 mV) and Ag nanowires (564 mV). For the ORR in the same electrolyte, the ZIF-67–Ag nanowire composite showed significantly improved activity as well with 0.852 V vs. RHE half-wave potential, superior to those of ZIF-67 (0.478 V vs. RHE) and Ag nanowires (0.626 vs. RHE), further demonstrating the effectiveness of introducing conductive supports in improving the charge transport and enhancing the electrocatalytic activity of MOFs.

As demonstrated by the above studies, improving the conductivity of MOFs is an effective way to deliver the intrinsic catalytic activity of MOFs and further promote the overall performance for electrocatalysis. Rational design of conductive MOFs and MOF composites will be highly desired in this strategy for the preparation of more efficient MOF electrocatalysts in the future.

4. Structural evolution of MOFs and the real active species

In addition to the activity, another important criterion for evaluating the efficiency of a catalyst is the stability. For electrocatalysts based on pristine MOFs, the stability is mainly related to structural evolution and stripping from the current collector. To avoid the stripping problems, a binder has widely been used (such as Nafion) in the literature to attach the catalysts on the electrode or directly growing the catalysts on the electrode, while there is still limited understanding about the mechanism and regularity of structural evolution of MOF catalysts. The structural evolution of MOFs has been pointed out by a handful of research studies. For example, Jiang and coworkers detected the in situ electrochemical conversion of the MOF (UTSA-16) to active CoO\(_x\) species during the OER process. Huang and coworkers mentioned the structure transformation of the 2D MOF to an amorphous intermediate phase after electrochemical aging and excluded the possibility to form CoO\(_x\) due to its much lower activity. Jayaramulu and coworkers proposed that the key active phase of exfoliated 2D Co–ZIF-9(III) was related to the reversible formation of cobalt oxyhydroxide N\(_x\)CoOOH species. However, the structural evolution mechanisms of MOFs are still unclear, making it difficult to identify the real active species. However, several pioneering studies have been reported exploring in this area.

In the study mentioned earlier, Rui and coworkers explored the real active species in the MOF/MOF hybrid (Ni-MOF@Fe-MOF) based on the ex situ transmission electron microscopy (TEM) and Raman spectra results. They found out that although the nanosheet morphology of the Ni-MOF@Fe-MOF could be maintained after cyclic voltammetry (CV) cycles in 1 M KOH solution, NIO domains (≈5 nm) were formed and uniformly distributed throughout the porous nanosheets with well-defined mesopores ranging from 5 to 10 nm. Solid evidence for the formation of Fe\(_2\)O\(_3\) nanograins in the Fe-MOF after CV cycles was obtained as well. Raman results confirmed the complete transformation of the Ni-MOF into NIO, rather than merely the superficial region, during which the chemical environment of Ni-based active centers remained unchanged (still bonded to six O atoms in NiO). They concluded that the real active species of the Ni-MOF@Fe-MOF catalyst for the OER should be the Ni–Fe oxides, the agglomeration of which was avoided due to the advantages of MOFs, thus achieving the improved performance compared with the pure Ni–Fe oxides.

The transformation of the MOF structure in alkaline medium might also be utilized to acquire efficient electrocata-
lysts. Li and coworkers transformed the as-prepared SURMOFs into electrocatalyst coatings by immersing them in 0.1 M KOH aqueous solution, which could be complete in a short period of 2 min indicated by the grazing incidence X-ray diffraction (GIXRD) characterization with the presence of new peaks corresponding to Ni(OH)₂ and Co(OH)₂ and/or some mixed metal hydroxide phase. Attenuated total reflectance infrared (ATR-IR) spectra and X-ray photoelectron spectroscopy (XPS) analysis revealed the formation of a nanocrystalline to amorphous mixed metal hydroxide material with some BDC present in the structure. It was mentioned that this situation could be related to layered double hydroxides intercalating organic linkers and thus might contribute to the enhancement of the electron/ion/mass transport of the SURMOF electrode.

To understand how to control the transformation of the MOF to the active catalytic phase, Bucci and coworkers used two MOF models that only differ in the substituent at the imidazole C2 position of the ligand (IFP-5 with a –Me; IFP-8 with an –OME). At pH 14, IFP-8 presented much lower overpotentials (319 mV) than IFP-5 (340 mV) at 10 mA cm⁻² toward the OER and was found with structure conversion and formation of the Co(O)OH phase (3–10 nm particles) after the OER process. As indicated by the further integrated ex situ spectroscopic study, the –R group could affect greatly the hydrolysis rate of the initial MOF framework in an alkaline environment, which would influence the formation of the Co(O)OH active phase that associated with the final electrochemical activity. Thus, it suggests us that the small change of the –R group at the MOF ligand could result in different electrocatalytic performances and controlling the rate of the hydrolysis of the MOF framework via regulation of the –R groups might a key feature to achieve high performances of MOFs in the future.

Lately, a potential-induced two-step reconstruction at the metal nodes inside the bimetallic NiCo-MOF-74 series during the OER was revealed by Zhao and coworkers. As suggested by operando X-ray absorption spectroscopy (XAS) and high-resolution TEM, a two-phase structural transition, Ni₉₅Co₃₀₂(OH)₂ and Ni₉₅Co₃₀₂OOH₀.₇₅, was formed under relatively low and high applied potentials, respectively. The highly active oxygen-vacant oxyhydroxide of V₀Ni₉₅Co₃₀₂OOH₀.₇₅ was transformed from the hydroxide of Ni₉₅Co₃₀₂(OH)₂ via Jahn–Teller distortion, which could be in turn converted from oxyhydroxide to hydroxide to NiCo–MOF-74 after the potential is removed and the catalyst placed in air. Furthermore, the ratio between Ni and Co was found to regulate this two-phase structural transition by tuning the phase transition potential of Ni–O and Co–O moieties, thereby leading to optimization of the catalytic activity. The principle of synchronous structural transformation was applied to a Ni₉₅Fe₃₀₂–MOF catalyst, and high OER activity was achieved (overpotential of 198 mV at 10 mA cm⁻²). These findings provide correlations between structural evolution and OER activity, which can help understand the catalytic mechanism in detail and may offer more insights into the design of highly active OER electrocatalysts based on MOFs in the future.

In addition to the above studies, a π–π interaction has also been proposed on the transformation process of MOFs during the OER with an unexplored formation mechanism. Although this structural evolution of MOFs has been suggested by many research studies, it is still a non-universal conclusion and cannot be assumed to happen on all the MOF materials applied for electrocatalysis. More substantial efforts are highly needed in this field to unveil the real active species and mechanism of electrocatalysis based on MOFs.

5. Summary and outlook

In summary, this review outlined the latest developments in exploring efficient electrocatalysts based on pristine MOFs. Due to the structural advantages, many MOFs have been reported so far directly used for electrocatalysis and excellent catalytic performances are observed for the HER/OER/ORR, which reveals the great potential of MOFs as electrocatalysts. At the same time, some drawbacks of MOFs, such as the inferior intrinsic activity and poor conductivity, gradually become prominent as well as the ambiguity of real active sites. With consideration of the inferior intrinsic activity, several advanced strategies have been summarized as microstructure engineering for MOFs, including the bimetal/multimetal nodes, ligand-based regulation, metal center-based regulation, dimensional control, pore engineering, architectural design, partial structure transformation and MOF hybrid/composite. Through microstructure engineering, the electronic configurations and the binding energies of the catalytic sites in MOFs toward the adsorption of rate-determining step intermediates can be optimized, thus boosting the intrinsic activity of MOFs. In terms of their poor conductivity, three main strategies are illustrated in this review, which have been widely adopted in the literature: designing and constructing electron conductive MOFs, utilizing and tuning the proton conductivity of MOFs, and hybridizing or compositing with secondary conductive supports. These various methods of microstructure engineering and conductivity improvement mentioned above have been demonstrated by different studies very effective for enhancing the electrocatalytic performance of MOF materials, resulting in numerous efficient MOF catalysts for the HER, ORR, and OER. On the other hand, to be the electrocatalysts, the stability of MOFs should be investigated as well with the key point to whether the coordination bond can be maintained during the electrocatalysis. The structural evolution of MOFs has been detected and suggested by a number of studies and a few of them have performed detailed analysis on the structure transformation of MOFs under electrocatalysis conditions and the formation mechanism of the new active phase, which have also been briefly described in this review.

Although the potential of pristine MOFs as electrocatalysts for the HER/OER/ORR has been universally recognized and tremendous advances have been achieved, there is still much room for further development: (i) despite the booming development of MOF materials in recent years, only a small pro-
portion of them have been explored for electrocatalysis. Deficient MOF precursors result in a limited type of active site, most of which are restricted to Co, Fe, Zn, Ni and Cr-based MOFs although their components are flexible, limiting the exploration of potentially more efficient active sites. Also, the inferior conductivity of MOFs hinders the transfer of charge and blocks the active sites to some extent. More efficient and reliable MOF materials (especially those with other active metal centers and high conductivity) are highly needed to be discovered. The simulation motivated design, synthesis and screening would facilitate this process; (ii) with the aim for future practical applications of these MOF electrocatalysts, further decrease in overpotentials is required, which can be realized via design and engineering of structure (such as controlling dispersion of active species, generating porous or hollow structures, and constructing hybrid architectures), morphology control (exposing more active sites, improving the accessibility of active species, and accelerating the mass transport during catalysis) and improvement of conductivity (exploring highly conductive MOF materials or combining with conductive components); (iii) besides the pure MOFs, interfaces and synergistic effects (including intra-molecular and inter-molecular) that can be introduced by combinations with other active species also play a very significant role in enhancing the catalytic performance of MOFs and their potentials, better advantage of which should be taken in the future; (iv) poor structural stability in aqueous solutions (acidic and alkaline) is a well-known issue for the practical applications of MOFs. Therefore, continuous study on the stability of MOFs is required in the electrolyte. Furthermore, the stability of MOFs undergoing redox processes is also an important point for researchers to dig further, which not only helps to understand better the real active sites and knows deeply the influence of structural factors and charge transfer on the structure evolution separately and in combination, but also provides insights for future design of more efficient catalysts based on MOFs; (v) researchers should see into the catalytic mechanisms behind the thermodynamics and kinetics and study their relationships with the MOF structure or structure evolution during the electrocatalysis. Then, the appealing goal of designing multifunctional MOF electrocatalysts would be more easily achieved with full utilization of the merits of MOF structures. Although there is still room for improvement, it has drawn a bright picture for the development of electrocatalysts based on pristine MOFs. We hope that this review will be a useful reference for the researchers that focus on this field. With full consideration of the issues mentioned above, more efficient MOF electrocatalysts can be expected in the future.

Author contributions
Lili Fan: Writing-original draft and Writing editing. Zixi Kang: Writing-review and editing. Mengfei Li: Table editing and Writing-review. Daofeng Sun: Conceptualization and supervision.

Conflicts of interest
There are no conflicts to declare.

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