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MOF electrocatalysts in CO_2 conversion: critical analysis of research trends, challenges and prospects

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Achieving sustainable energy and a clean environment is a strong driving force behind the exploration of the electrocatalytic potential of MOFs for CO_2 conversion. The growing interest in the application of MOFs as electrocatalysts for CO_2RR has been attributed to their high surface area and excellent catalytic properties. MOFs have been deployed in their pristine form as catalysts, as porous cavity supports for the incorporation of catalytic active material, or as precursors to obtain single-atom catalysts, showing that they can reduce CO_2 into CO, formic acid and even hydrocarbons and alcohols. Despite these advantages and promising early results, they still have several challenges to overcome, such as poor electrical conductivity, stability and selectivity, and high overpotential, which would limit their practical application as electrocatalysts for CO_2 reduction. In this review, various strategies to improve the electrocatalytic performance of MOFs are highlighted and directions that future studies in this field may take identified.

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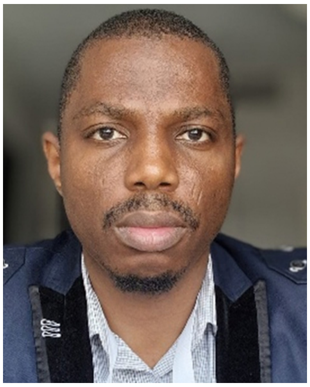

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1. Introduction

Right from the start of industrialization to the present time, global energy demand has skyrocketed due to the attendant increase in the human population.[1,2] An effort to sustain this ever-increasing population and economic growth has resulted in an over-dependence on hydrocarbon-based fossil fuels such as petroleum, natural gas and coal which still account for over 80% of world energy consumption.[3] This is in addition to the fact that the long-term availability of fossil fuels may not be guaranteed which could plunge the world into an energy crisis. However, the use of fossil fuels has been associated with global climate change which has been identified as the root cause of various environmental disasters ravaging the world in recent times.[4] Pertinent among these environmental problems are increased atmospheric CO_2 level which is being projected to reach 450 ppm by 2050 and a rising global average temperature which is promoting extreme weather events and negatively impacting our ecosystem.[5] The concern of continuous environmental disaster and the anticipated energy crisis has necessitated the urgent need to revolutionize technologies aimed at developing sustainable, clean and renewable energy to replace the use of fossil fuels.

To tackle this problem, various CO_2 capture and utilization technologies have been implemented.[6] However, CO_2 capture technology does not just consume a great deal of energy and financial resource, but its sustainability over a long period of time cannot be guaranteed. For this reason, the electrochemical CO_2 reduction reaction (CO_2RR) has been suggested as a promising CO_2 utilization technology to convert waste CO_2 streams into useful chemicals.[7] Unlike other chemical processes, electrochemical CO_2 reduction can be performed at ambient temperature using green renewable energy sources and water as a source of the protons making the overall operation a carbon neutral process.[8] However, so far the electrochemical reduction of CO_2 still suffers from high overpotential (large energy requirement) and poor product selectivity, making the practical application of electrochemical CO_2 reduction still unfeasible from the industrial point of view. The high overpotential and poor product selectivity are the result of non-ideal adsorption energies of key reaction intermediates.[9] The low faradaic efficiencies are due to the competition with the hydrogen evolution reaction (HER), which takes place in the same potential window as CO_2 reduction.[10]

Materials such as transition metals, noble metals, nanoporous carbon, oxides, sulfides and phosphides are notable state-of-the-art electrocatalysts for various electrochemical systems.[11–13] Despite the exceptional catalytic performance of these materials in some electrochemical systems, high cost, coupled with the scarcity of noble metals and the propensity to be poisoned of precious metal catalysts on exposure to some chemical compounds, has severely hindered their large-scale commercialization.[14] Therefore, the focus of 21st-century researchers is to develop nanostructured porous electrocatalysts featuring, high activities, low cost, ease of synthesis, and widespread availability. In the past decades, electrocatalytic porous functional materials such as zeolitic materials, mesoporous silica, metal–organic frameworks, *etc.*, have been the subject of intense research in the literature.[14–16] Among the numerous porous materials available in the literature, metal–organic frameworks (MOFs) as electrocatalysts have captured the attention of a wide variety of research scientists.

MOFs are a specific class of materials constructed by joining metal-containing units, termed secondary building units (SBUs), with organic linkers using strong bonds to create open crystalline frameworks with permanent porosity.[17] The early foundations of metal–organic frameworks (MOFs) can be traced back to the establishment of coordination chemistry by Swiss chemist Alfred Werner in 1893.[18] Werner proposed the arrangement of coordination complexes as structures comprising a central metal atom surrounded by organic or inorganic ligands, laying the groundwork for future developments. Over the following decades, research into porous supramolecular architectures gradually progressed, eventually leading to the creation of novel hybrid porous crystalline structures in the 1990s.[19] These structures, formed by the coordination of inorganic metal centres with organic linkers, marked a significant milestone. The term "metal–organic framework" (MOF) was introduced in 1995 by Yaghi's group, whose pioneering work on the topic was first published in Nature.[20] This was followed by the synthesis of MOF-5, the first known porous MOF with permanent porosity in 1999 which was also reported in

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Nature.[21] Since these important discoveries, the number of known MOF structures and published papers concerning MOFs has increased astronomically, attributed to the ever-expanding potential applications resulting from their unique properties and ease of synthesis.[22]

In this review, our discussion starts by investigating the numerous opportunities and challenges in the electrocatalytic application of metal–organic frameworks (MOFs) in CO_2 reduction. Attention is focused toward addressing the conductivity and stability problems, and how MOF electrode preparation methods can affect the electrocatalytic performance of MOFs in respect of the CO_2RR. We include a critical view on the lack of consensus on the normalization of catalytic activity—and some practices that can be considered to be incorrect—and the repetitive lack of information regarding *post-mortem* analysis of the MOFs. Finally, recent progress in utilizing MOFs as electrocatalysts in CO_2 reduction is explored, and we briefly summarize the findings and proposed future outlook for this research field. It is anticipated that this review will serve as useful reference for scientists in chemistry and materials science and interdisciplinary researchers who are interested in electrocatalytic application of MOFs in CO_2 reduction.

2. MOFS as electrocatalysts for CO_2 reduction

The growing interest in the application of MOFs as homogeneous and heterogeneous electrocatalysts in the CO_2 reduction reaction has been attributed to their promising catalytic properties.[23–26] The exceptionally high surface area of MOFs provides plentiful catalytic active sites for surface-related reactions such as adsorption/desorption, insertion/de-insertion, surface redox reactions and heterogeneous catalysis.[27] The large pore volume commonly exhibited by MOFs facilitates mass transport of selected substrates to the active sites as well as providing a platform for loading guest species.[27] Catalytically active sites, and an understanding of where they originate from, are essential in MOF catalytic applications (Fig. 1). For pristine MOFs, catalytically active sites are often associated with coordinatively unsaturated metal sites, which act as Lewis acids, and dangling acid/base sites from the organic linkers.[28]

Secondly, the porous nature of MOFs makes it possible in practice to modify them post-synthetically with various catalytically active species, such as molecular catalysts, metal-based nanoparticles (NPs), enzymes, *etc.*, which can create structural defects within the MOFs for efficient catalysis. Thirdly, the catalytically active sites of MOFs can be exposed to chemical/thermal treatment to obtain porous materials, including metal-based compounds, porous carbons and their composites. These MOF derivatives are promising candidates for catalytic application because of their exceptionally large surface area, tunable structures/composites and highly dispersed active sites. An interesting attribute of MOF-derived materials is their ability to retain, to a certain degree, the morphological architecture of the pristine MOF, which upon doping with heteroatoms, can improve the conductivity and the degree of graphitization, resulting in better performance in electrocatalytic applications.[28–30] Based on these merits—tunable porosity, high surface area and modifiable active sites—the electrocatalytic application of MOF-based nanocomposites has become the subject of intense discussion in recent years.[31–35] However, their role as electrocatalysts remains limited by critical challenges that hinder industrial viability. While MOFs provide well-defined catalytic sites, including coordinatively unsaturated metal centres and redox-active ligands, their inherently poor electrical conductivity severely limits charge transfer, requiring additional modifications such as guest-molecule doping or hybridization with conductive supports.

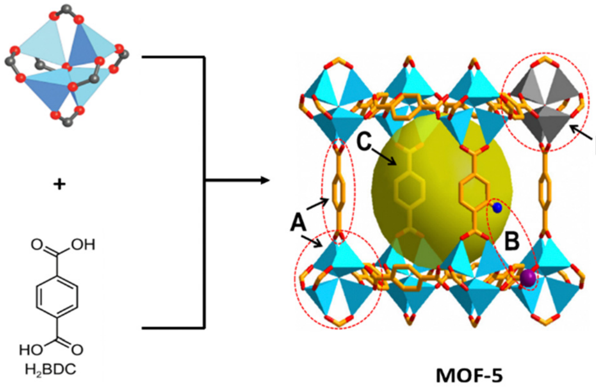

Fig. 1 Metal–organic framework catalyst structure where: (A) is the connecting site for metal clusters and linkers in pristine MOFs, (B) is a site for grafting metal/non-metals in MOFs by modification, (C) is a site for encapsulated species in MOF composites and (D) represents sites generated in MOF derivatives upon thermal/chemical conversion.[28] Copyright 2019, Elsevier.

Stability is another major limitation. Many MOFs degrade in electrochemical environments, particularly in aqueous bicarbonate electrolytes, leading to metal leaching or framework collapse. Strategies such as robust metal–ligand combinations and post-synthetic modifications improve durability but add complexity and cost. Moreover, while 2D MOFs, nanocages and defect engineering enhance active site accessibility, these modifications do not at present fully resolve conductivity and stability issues.

Despite their theoretical promise, MOFs in the CO_2RR largely serve as precursors or support materials rather than standalone catalysts. The field must shift toward MOF-derived materials or radically rethink MOF design to address fundamental limitations. Without breakthroughs in conductivity and stability, MOFs will remain an academic curiosity rather than a scalable CO_2RR solution.

2.1. Addressing conductivity challenges in MOFs

Based on the literature reports so far, conductivity in MOFs can range from 10^{-10} to 10^3 S cm^{-1} [36,37] which is still, unfortunately, far below the electrical conductivity requirement for industrial application in an electrochemical system. The poor electrical conductivity of MOFs has been linked to: (i) the insulating character of the organic ligands, attributable to the lack of free charge carriers; and (ii) poor overlap between π orbitals of the organic ligands and the d orbitals of the metal ions, which present a barrier for charge transfer.[8] Conductivity has become an important indicator to measure the suitability of MOFs for electrochemical application.[38] Since electrical conductivity (σ) in MOFs is dictated by the amount of charge density (n) and mobility (μ) of electrons (e) and holes (h), it is essential to maximize both charge density and mobility of charge carriers (eqn (I)) to achieve high conductivity.

$$\sigma = e(\mu_e n_e + \mu_h n_h) \qquad \text{(I)}$$

The general requirement for constructing MOFs with high conductivity is to select building blocks with loosely bound charge carriers, otherwise regarded as materials with high charge density. The metal ions, organic ligands or guest molecules in a MOF could serve as sources of charge carriers. Facile charge migration is required for efficient MOF electrocatalysts; otherwise, the reaction would only occur at the catalytic centres in direct proximity to the electrode. Pathways for charge mobility within a MOFmaterial can be described by two important processes, namely: redox hopping and band transport.[39]

In redox hopping, the charge carriers (such as redox centres) are usually localized at specific sites within the framework which often results in charge hopping between neighbouring sites in MOFs. However, in order to maintain electroneutrality during charge hopping, a counter ion usually must diffuse through the MOF structure, thereby limiting the charge transport.[39] Therefore, charge transport *via* redox hopping is evaluated based on diffusion phenomena where the measurable diffusion coefficient D_e ($\text{cm}^2\ \text{s}^{-1}$) for an electron-hopping mechanism in MOFs is related to total redox-active linker concentration C_P^0, the electron-exchange rate constant k_e (s^{-1}) and average hopping distance d *via* the following equation:[40]

$$D_e = \frac{k_e}{6} C_P^0 d^2 \qquad \text{(II)}$$

Hence to optimize charge transport *via* redox hopping, a MOF must be designed in such a way that its pore size is sufficiently large enough to allow smooth diffusion of the counter ion thereby enhancing MOF conductivity. One strategy to improve charge transport is *via* post-synthetic incorporation of guest redox molecules into the frameworks.[41,42] These guest molecules form charge transport pathways through guest to guest or guest to framework interactions. Iodine, redox-active molecules and some macromolecules or clusters are popular guest molecules that can be incorporated into the pores of MOFs to improve their conductivities.[42] For example Kobayashi *et al.* reported a significant increase in conductivity of $\text{Cu[Ni(pdt)}_2]$ from 10^{-8} to 10^{-4} S cm^{-1} after I_2 vapor treatment.[43] The authors attributed the increase in conductivity to the partial oxidation of the $\text{Cu[Ni(pdt)}_2]$ framework induced by I_2 doping. Talin *et al.* also reported that conductivity of a $\text{Cu}_3(\text{BTC})_2$ MOF thin film improved drastically from *ca.* 10^{-8} S cm^{-1} to 0.07 S cm^{-1} when the MOF was infiltrated with tetracyanoquinodimethane (TCNQ) which is a redox-active molecule (Fig. 2).[44] Based on spectroscopic data and first principles modelling, the authors claimed that conductivity arose from TCNQ guest molecules bridging the binuclear copper paddlewheels in the framework, leading to strong electronic coupling between the dimeric Cu subunits. Unfortunately, the disadvantage of this strategy is the blockage of pore channels resulting in the reduction of the surface area which is a key property for electrocatalysis.[42] Therefore, care must be taken to choose MOF and guest molecule to minimize these effects. Another early example of this strategy was reported by Kung *et al.*, where their findings shows a great improvement in conductivity of NU-1000 from 9.1×10^{-12} S cm^{-1} to 2.7×10^{-7} S cm^{-1} after loading nickel bis(dicarbollide) into the micropores of the MOF.[45] In more recent findings by Xin *et al.*, the electrocatalytic activity of MOF-545-Co for the CO_2RR was greatly enhanced after the incorporation of cobaltocene which acts as a potential donor and carrier to enhance the electron density within the MOF structure.[46] While the pristine MOF-545-Co FE_{CO} was 55% at −0.8 V *vs.* RHE, the presence of the guest molecule is reported to improve the FE_{CO} up to 97% at −0.7 V *vs.* RHE. This was

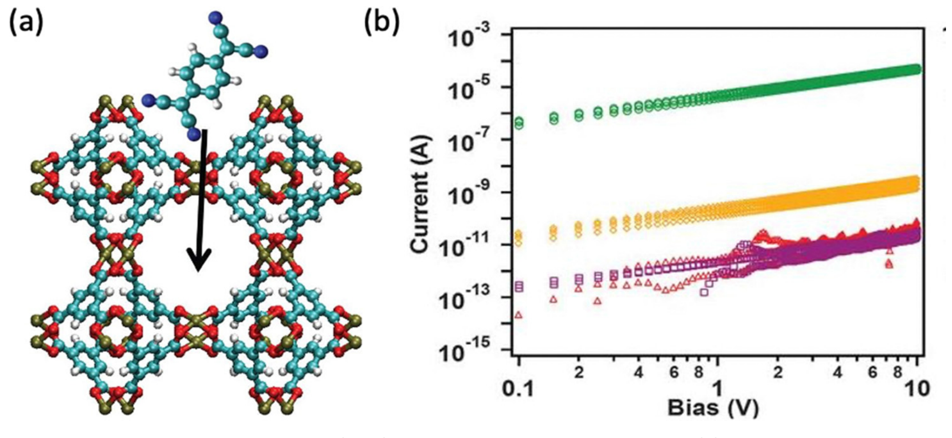

Fig. 2 (a) Fabrication of electrically conductive $\text{TCNQ@Cu}_3(\text{BTC})_2$ *via* post-synthetic incorporation (b) *I–V* curve showing the electrical conductivity of pristine $\text{Cu}_3(\text{BTC})_2$ (red), and after infiltration with TCNQ (green), F4-TCNQ (gold) and H4-TCNQ (purple). Reproduced with permission from Talin *et al.*[44] Copyright from The American Association for the Advancement of Science, 2014.

attributed to the increased conductivity which plays a crucial role in enhancing the electrocatalytic activity of the MOF.

The second and more efficient process that can be used in obtaining high charge transport and enhance conductivity in MOFs is through band transport.[38] This is achieved by increasing the extent of delocalization between the framework components by introducing mixed valent states in the node/linker, donor–acceptor type interactions, π–π stacking or π-conjugation into the framework which could lead to improved charge propagation.[47] Carefully selecting atoms with diffuse frontier orbitals, such as softer transition metal ions (Fe, Mn, Co, Ni and Cu) and linkers containing nitrogen or sulfur can result in construction of highly delocalized MOF frameworks.[48] Sun *et al.*, demonstrated that when a linker 2,5-dihydroxybenzene-1,4-dicarboxylic acid was replaced with 2,5-disulfhydrylbenzene-1,4-dicarboxylic acid in the construction of a Mn-MOF, infinite 1D metal–sulfur chains were created within the framework, prompting charge delocalization and resulting in a dramatic increase in conductivity.[49] The presence of extended π–π-stacking or π-conjugation in MOFs destined for electrocatalysis have been shown to create a pathway for the efficient delocalization of charge carriers within the framework.[50] The strategy of extended π–π-stacking was implemented by some researchers to design MOFs with functionalized TTF (tetrathiafulvalene) derivatives, with the π–π stacking of TTF moieties resulting in the formation of highly conductive charge transport columns within the framework, leading to improved conductivity.[51–53] In a similar strategy, incorporation of in-plane π-conjugation into MOF frameworks has been discovered to induce charge delocalization in 2D MOFs.[54–56] Of particular interest is the work of Zhu *et al.* where they reported that 2D MOF Cu-BHT (BHT = benzenehexathiol) displays great charge delocalization due to extended 2D π-conjugation, prompting conductivity as high as 1580 S cm^{-1} at room temperature (Fig. 3).[36] Overall, findings have shown that π-conjugation and π–π stacking strategies have resulted in the largest increase in conductivity.[37,57]

The reports on conductive MOFs for electrocatalysis have thus been encouraging so far. However, opportunities still abound in developing conductive MOFs with optimal electrocatalytic performance by carefully selecting ligand, metal centre and guest molecule that will promote redox hopping and/or band transport within the MOFs. It is important to notice that the vast majority of the reports, if not all, have provided information on the conductivity of pristine or post-synthetic modified MOF catalysts, however, information on the conductivity of the catalyst after the electrochemical experiments is missing. Such information is key to understanding the changes in MOFs under operating conditions, in particular with regard to stability and changes in the product selectivity.

It is important to note that the correlation between the conductivity and stability of metal–organic frameworks (MOFs) and their performance in the CO_2 reduction reaction (CO_2RR) is a critical aspect for their practical application as electrocatalysts. Conductivity in MOFs, whether achieved *via* redox hopping, band transport or guest-promoted pathways, is essential for efficient electron transfer during electrocatalysis. Enhanced electrical conductivity reduces charge transfer resistance, facilitating the activation of CO_2 and stabilizing key reaction intermediates, thus improving faradaic efficiency and product selectivity. Stability, on the other hand, ensures that MOFs maintain their structural integrity and catalytic activity over extended operational periods. However, many MOFs suffer from degradation under electrochemical conditions due to framework dissolution, ligand hydrolysis, or metal node leaching. It is also important to mention that strategies such as post-synthetic modification, incorporation of conductive linkers, and hybridization with conductive supports have been explored to enhance simultaneously conductivity and stability. The challenge remains in designing MOFs that balance high

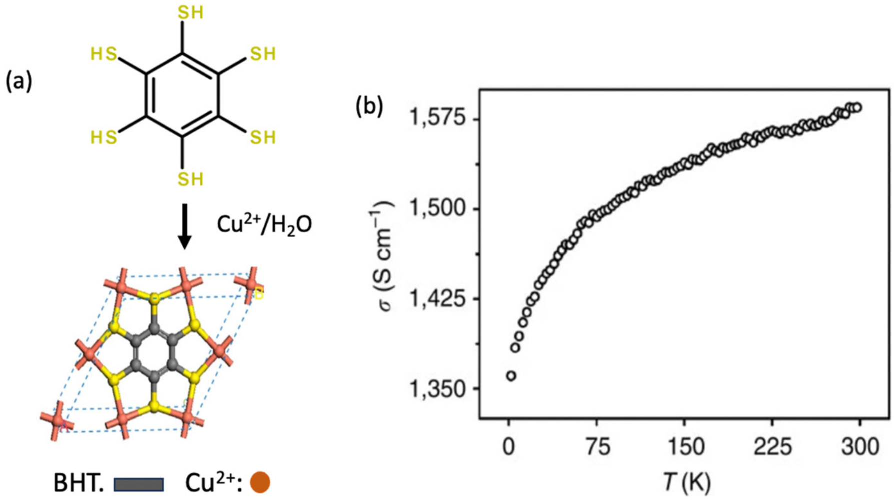

Fig. 3 (a) Electrically conductive Cu-BHT 2D MOFs designed by π-conjugation (b) electrical conductivity measurement of Cu-BHT film as a function of temperature ranging from 2 to 300 K. Reproduced with permission from Zhu *et al.*[36] Copyright Springer Nature, 2015.

electrical conductivity with robust chemical stability, ensuring their long-term viability for CO_2RR applications.

2.2. Addressing chemical stability challenges in MOFs

Stability of MOFs during electrochemical operation is another crucial factor for their use in electrocatalytic applications.[58] During electrocatalysis, the voltage applied induces diffusion of ions/molecules onto the MOF's surface to establish an electrical double layer (EDL) (Fig. 4(a)). This charged MOF surface creates a concentration gradient of ions (H^+ in this case), causing the local pH in the EDL to drift to higher or low values resulting in complete or partial destruction of the MOF structure (Fig. 4(b) and (c)).[59] Therefore, one of the main challenges to overcome in the CO_2RR on MOFs is to deliver materials that are stable in neutral and strongly alkaline media. Additionally, during potential cycling (Fig. 4(d)) chemical gradients of cation/anion at the MOFs electrochemical interface can result in degradation of the metal nodes and organic linkers (Fig. 4(e)) resulting on transformation of the MOFs into metal oxides, hydroxides or oxyhydroxides during catalysis.[58,60,61]

While it might be challenging to address both the chemical and electrochemical stability of MOFs without some form of trade off, research has progressed over the years on how to improve MOF stability in electrocatalytic applications.[63,64] There remain questions which are still the subject of discussion regarding the role of MOFs during electrocatalysis: are MOFs the real catalysts? Or are the MOFs merely the precursors to active phases produced during electrochemical treatment? It is therefore important to understand the reactivity of MOFs in the chemical and electrochemical environment, and confirm, either *in situ* or *post mortem*, their chemical and structural integrity in order to design and construct stable MOFs for electrocatalytic application. The chemical environment of MOFs during electrochemical reaction comprises water, counter ions, reactants and products from electrocatalysis, as well a flow of electrons owing to the applied potential. Generally, water has the tendency to interact with metal-linker coordination sites, prompting the decomposition of the framework, producing hydrated/hydroxide metal species (in basic electrolytes) and/or protonated linkers (in acidic electrolytes) that further diffuse into the electrolyte.[65,66] Aside from hydrolysis of MOFs, the effect of counter ions has also been documented to be destructive. For example, phosphate-buffered (PB) solution contains PO_4^{3-} anions (hard Lewis base) which can strongly interact with high valency metal ions. An example of this effect has been found when using the UiO-66 framework, which disintegrates within a few minutes in PB solution as a result of the strong interaction of PO_4^{3-} anions with the Zr^{4+}

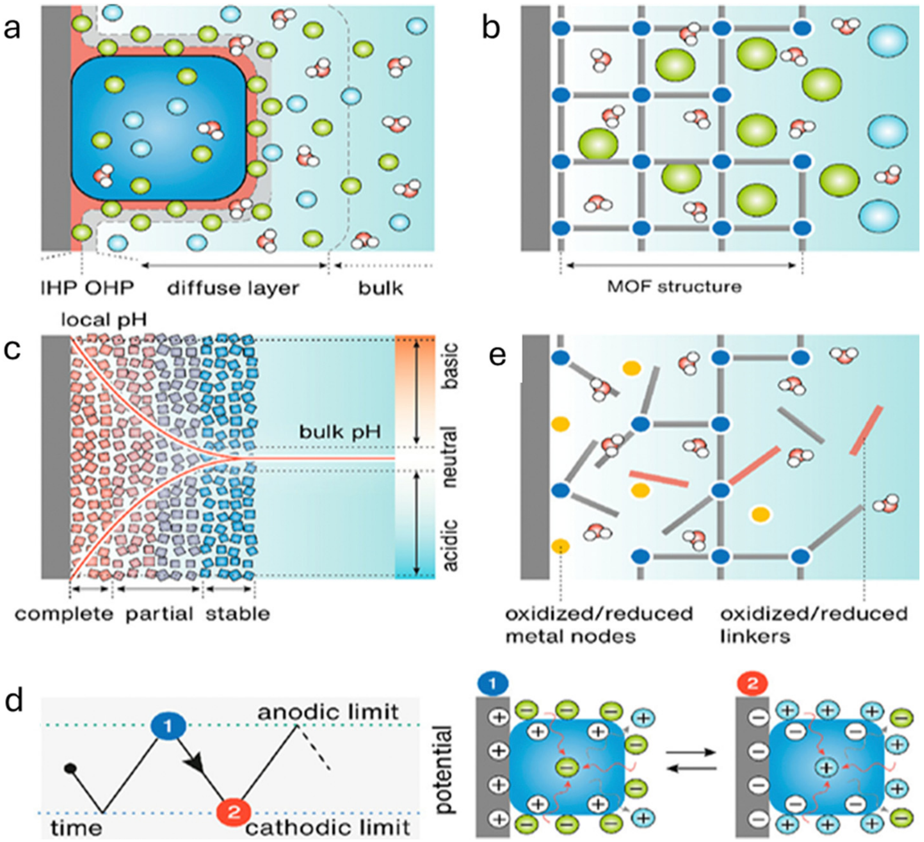

Fig. 4 (a) Established EDL structure on the surface of a MOF particle. (b) Diffusion of ions/molecules into a MOF framework in the established EDL. (c) Cross-sectional illustration of a MOF-coated electrode in neutral electrolyte. (d) EDL formation and ion diffusion on the surface or inside the pores of MOFs (right) due to the dynamic potential sweeping (left). (e) Structural destruction of MOFs due to the redox reaction of metal nodes and/or organic linkers. Reproduced with permission from Zheng *et al.*[62] Copyright American Chemical Society, 2021.

nodes of the UiO-66 framework.[67] Zeolitic imidazolate frameworks (ZIFs) are a class of porous materials characterized by their zeolite-like topology and imidazolate linkers. Mirsaidov's group demonstrated the lack of stability of ZIF-8 in Co^{2+}-containing solution resulting in the formation of $ZnCo(OH)_x$.[68] The products from electrocatalysis have not been given much attention as a possible cause of instability of MOFs. For example, it has been shown that nanobubbles can be generated at the active sites during gas evolution reactions which can pose both mechanical and chemical challenges to the structural integrity of MOFs.[69,70] Other products, such as formate/CH_3OH from the CO_2 reduction reaction (CO_2RR) and NH_4^+ from the nitrogen reduction reaction (NRR), may pose a similar threat.[62]

Due to the poor stability, some MOFs could show poor performance upon exposure to moisture which can attack the metal centre within the framework, causing decomposition and phase transformation of the MOF. Some reports have anticipated that the bond strength between the metal cation and the organic ligands is one of the main criteria that influences stability.[71–74] Therefore, the chemical stability of a MOF can be intrinsically improved by judicious selection of metal nodes and design of linkers.[75] *De novo* synthesis of MOFs by linking carboxylate-based ligands (hard bases) with high-valent metal ions (hard acids) has been explored in search of MOFs with improved stability. Based on the Hard–Soft Acid–Base Principle (HSAB) principle, high-valent metals with high charge density (hard acids), such as Zr^{4+}, Cr^{3+}, Al^{3+}, Fe^{3+}, *etc.*, tend to form strong coordination bonds with O donor ligands (hard bases) (Fig. 5) thereby presenting MOFs with good chemical stability.[76–79] Interestingly, the strong coordination bonds and the low pK_a of carboxylate linkers endow the high-valent metal ion-containing MOFs with a good level of stability in acid.

On the other hand, low-valent metal ions, including Zn^{2+}, Co^{2+}, Ni^{2+}, Fe^{2+} and Ag^+, which are considered as soft acids can form strong coordination bonds with suitable N-containing linkers (soft bases) (Fig. 6) producing a highly stable MOFs.[80–82] The high pK_a of azoles and the strong coordination bonds usually bestows remarkable stability in basic solutions on these MOFs. Generally speaking, MOFs built from high-valent metal ions and carboxylate ligands tend to be stable in acids and decompose in basic solutions while MOFs constructed using low-valent metals and azolate linkers tend to be stable under alkaline conditions while being readily hydrolysed by acids.[83] The introduction of hydrophobic/rigid ligands, and phosphonate/carboxyphosphonate ligands into MOF synthesis has also been suggested as a way to improve MOF stability.[84,85] Surface hydrophobicity prevents the adsorption of water into pores and/or the condensation of water around the metal clusters, which enhances the MOF stability in the presence of water. Phosphonate/carboxyphosphonate MOFs have been shown to exhibit robust structural tolerance in harsh chemical environments,[86] which has been attributed to the stronger metal–ligand bonds formed when the three oxygen atoms from phosphonic acid coordinate to metal ions compared to the corresponding carboxylate MOFs.

The challenge of electrochemical stability can be approached by optimizing the various electrocatalyst parameters. For example non-aqueous electrolytes such as tetrabutylammonium hexafluorophosphate ($TBAPF_6$) in acetonitrile or DMF, have been used as substitutes in studying the catalytic activity of MOFs that are unstable in aqueous electrolytes.[87] The implementation of organic solvents as electrolytes can also be linked to their ability to increase the solubility of CO_2 which can, as a result, reduce mass transport limitations.[88] In addition, the low proton concentration inhibits the competing process of the hydrogen evolution reaction which is prevalent in aqueous electrolyte. Nevertheless, aqueous electrolytes remain the electrolytes of choice as water is a green and abundant solvent that can be used in large scale processes.[89] Therefore, the use of catalytically active MOFs stable in the

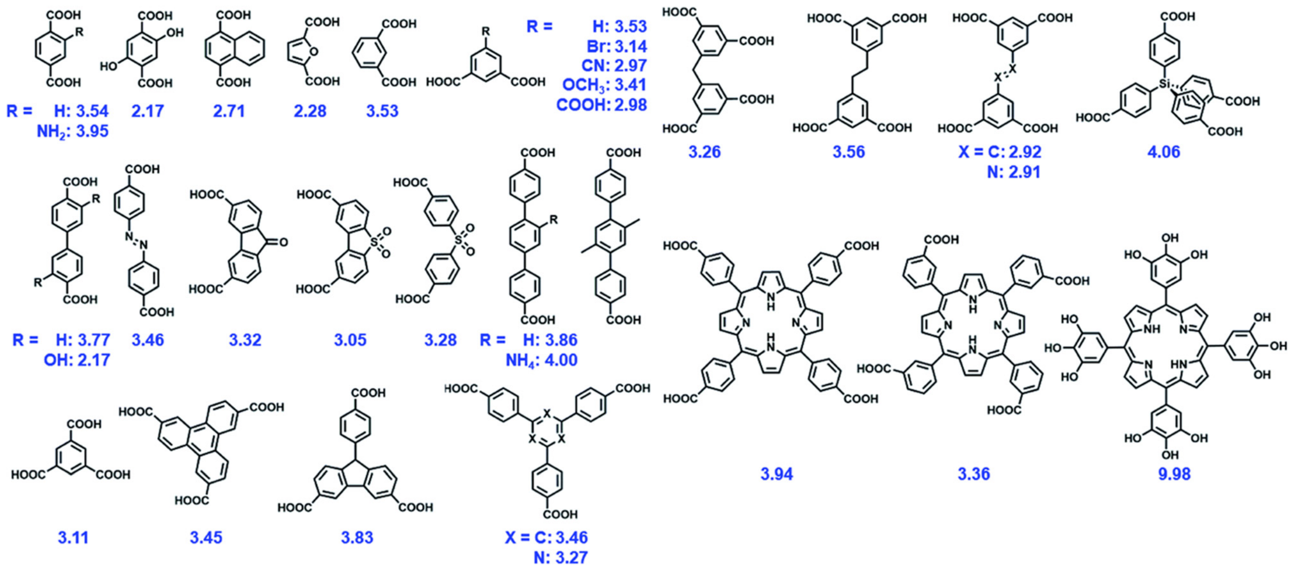

Fig. 5 Some representative O donor ligands, with their pK_as. Reproduced with permission from Ding *et al.*[63] Copyright Royal Society of Chemistry, 2019.

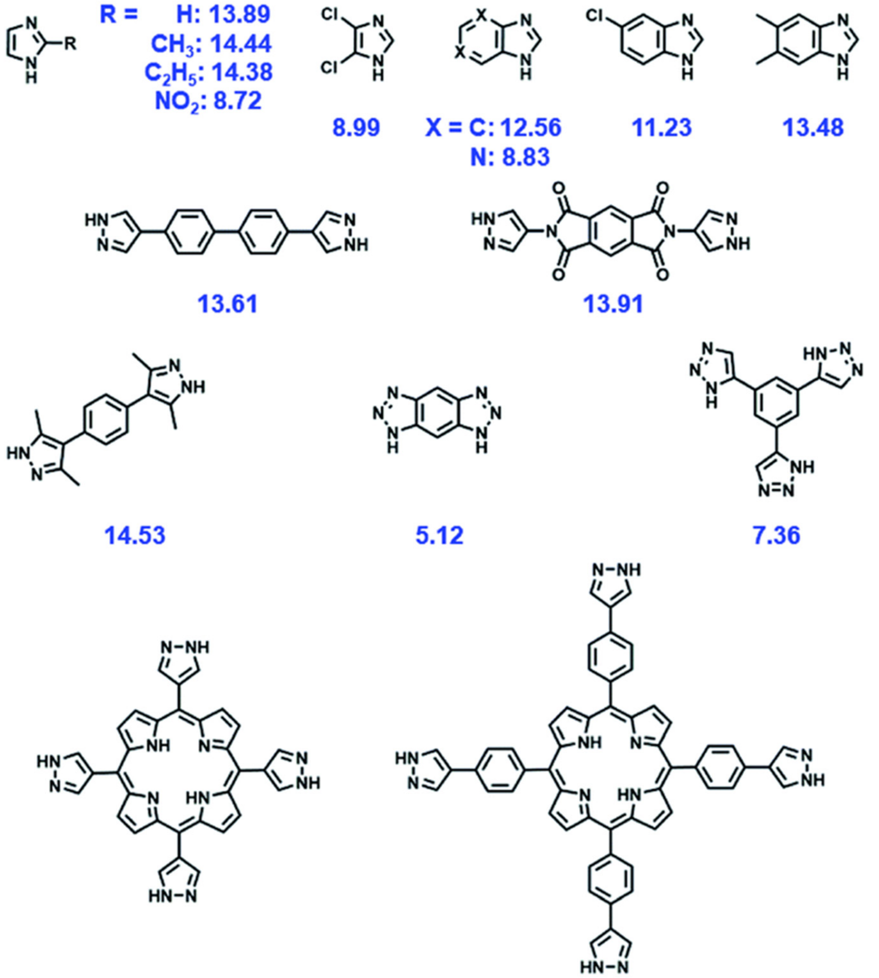

Fig. 6 Some representative N donor ligands, with their pK_as. Reproduced with permission from Ding *et al.*[63] Copyright Royal Society of Chemistry, 2019.

presence of bicarbonate ions is necessary for future applications. MOFs constructed with nitrogen-containing linkers such as ZIFs have been found to be highly stable in water over a wide pH range and this family of MOFs has consistently shown promising activity towards the CO_2RR in aqueous electrolytes.[80,90,91] On a final note, MOFs under electrochemical conditions must meet two additional stability requirements: (i) maintaining physical attachment to the electrode surface, and (ii) remaining structurally intact under reducing and/or oxidizing conditions during electron flow through the framework.[83] The likelihood of meeting the first stability challenge—the potential for delamination or generally loss of MOF from an electrode surface—depends to a large degree on how the electrode is prepared. The second stability issue of resisting degradation under electron flow while in the presence of substrate is a much more MOF-specific challenge. MOFs constructed from ligands that are able to give reversible electrochemical responses are often considered to be stable under electrochemical conditions. However, a significant number of reports have not performed adequate and exhaustive characterization of the MOF after electrochemical experiments. It should be expected and common practice to evaluate the structural and compositional integrity of the MOF catalyst after electrochemical experiments including: high-resolution scanning transmission electron microscopy (HR-STEM), energy-dispersive X-ray spectroscopy (EDX) and, if possible, *in situ* X-ray absorption spectroscopy XAS experiments to confirm the oxidation state and coordination of the metal centres. Numerous electrochemically stable MOFs have been successfully built from ligands based on a naphthalene diimide core,[92–94] a moiety that seems to be stable when reduced. For more in-depth discussion, readers are directed to a recent review by Liu *et al.*[95] Future studies focusing on the structural evolution of MOFs under CO_2RR conditions are fundamental to establish structure–activity correlations and to understand the different effects that contribute to the stability of MOF-based catalysts.

2.3. Addressing the product selectivity in MOFs

Achieving precise control over product selectivity in the CO_2 reduction reaction (CO_2RR) on MOF-based electrodes is essential for optimizing their practical applications in carbon-neutral fuel and chemicals production. While MOFs inherently offer tunable catalytic environments, their effectiveness in selectively generating desired products depends on a combination of structural modifications, electronic tuning and reaction environment optimization. However, as observed in other CO_2RR catalysts, product selectivity is highly sensitive to mass transport phenomena, including CO_2 diffusion, intermediate adsorption, and proton availability at the electrode interface.[96–98] The interplay between catalyst structure and reaction conditions must be carefully controlled to mitigate transport limitations that could otherwise lead to competing side reactions, such as hydrogen evolution. Additionally, the intrinsic porosity of MOFs plays a crucial role in governing mass transport, as pore size and connectivity dictate the diffusion of CO_2 molecules and reaction intermediates to active sites. While highly porous MOFs offer increased surface area and active site accessibility, excessive porosity or narrow pore channels can hinder CO_2 diffusion, leading to local variations in reactant concentration and altering selectivity.

Regulating the selectivity of products in the CO_2RR process on MOF electrodes requires a combination of material design and reaction environment optimization. One of the most effective strategies involves tailoring the organic ligands that coordinate with the metal centres. The choice of ligands influences the electronic properties and coordination environment, which in turn affects the binding strength of CO_2 and its reaction intermediates.[2] For example, 2-methylimidazole coordinated to Zn^{2+} in ZIFs has been shown to favor CO_2 reduction to CO, while other ligands may steer the reaction toward formate or hydrocarbons.[91]

Another powerful approach is doping MOFs with electron-donating molecules, such as 1,10-phenanthroline or metallocenes.[90] These additives enhance CO_2 adsorption and reduce the Gibbs free energy barrier for key reaction steps, making it easier to direct the reaction pathway toward a specific product. Similarly, structural modifications to MOFs can significantly impact selectivity. By reducing MOFs to 2D nanosheets, a larger proportion of active metal sites are exposed, improving electron transfer and influencing reaction intermediates.[99,100] Introducing strain or defects further modifies the electronic structure, fine-tuning the catalytic behaviour and favouring certain products over others.

The way MOFs are integrated into electrodes also plays a crucial role in selectivity. Growing MOFs directly on conductive substrates improves charge transfer efficiency, ensuring more effective electron flow to the catalytic sites. Additionally, combining MOFs with conductive additives such as carbon black or graphene oxide further enhances charge transport and helps control product distribution. However, mass transport limitations in porous MOFs must be carefully managed, as restricted CO_2 diffusion within the framework can lead to selectivity shifts, favouring hydrogen evolution over CO_2RR. Pore engineering strategies, such as optimizing pore size distribution or introducing hierarchical porosity, can help balance CO_2 diffusion rates and reactant accessibility, preventing local reactant depletion or oversaturation, both of which affect selectivity. Studies have shown that using imidazolium-based ionic liquids in electrolytes can promote the formation of methane,[101] while other electrolytes may favor CO or formic acid production.[102–104]

Finally, the construction of heterogeneous MOF structures, such as MOF heterostructures or composites with metal oxides, introduces synergistic effects that influence reaction pathways. By carefully designing these hybrid systems, it is possible to steer CO_2 reduction toward higher-value products like hydrocarbons or alcohols. Together, these strategies offer a comprehensive approach to improving product selectivity in CO_2 reduction on MOF electrodes, opening new possibilities for efficient and sustainable carbon conversion.

3. Assessing the performance of various methods of MOF electrocatalyst preparation

Electrochemical evaluation of MOFs requires interfacing the MOF with an electrode. Finding an effective method of preparing MOF-modified electrodes play an important role in the attachment of the MOF catalyst to the electrode and by extension determines the MOF electrochemical response, specifically regarding the rate of electron transfer between the electrode and the first MOF layer as well as how much of the bulk MOF is electrochemically accessible.[83] The type of MOF-electrode attachment can also have a large impact on the strength of mechanical adhesion, with poor adhesion resulting in delamination.[83,105] Two approaches have generally been adopted in preparing MOF-modified electrodes for the CO_2RR and other applications. The first entails immobilizing the MOF on a conductive substrate *via* physical interactions or through the formation of chemical bonds between the substrate and the MOF. The second method involves synthesizing MOFs directly on the electrodes. MOFs for electrochemical studies are generally prepared by four methods: drop-casting, direct solvothermal growth on a bare electrode surface, self-assembled monolayer deposition on the electrode surface or electrochemical methods. Each of these methods has different characteristics of mechanical stability, preparation time, and ease of electron transfer between the MOF and conductive electrode substrate. Despite the diversity of synthetic approaches used for preparing MOF-modified electrodes, some of them, like direct growth on conductive substrates are yet to be fully explored for preparing MOF electrodes for the CO_2RR unlike other electrochemical reactions such as the OER and ORR.[106]

3.1. Drop casting

Drop casting is one of the facile methods for immobilizing MOFs on a conductive electrode for electrochemical studies. In this case, a catalyst ink is usually prepared by dispersing (typically by sonication) MOF powder into a solvent or solvent mixture. The electrode is either left to dry in open air or oven dried at 60 °C, leaving behind a thin film of the MOF dispersed on the electrode for electrochemical analysis (Fig. 7(a)). Additives such as carbon black and graphite can be added to the catalyst ink to increase the MOF electrical conductivity,[107–109]

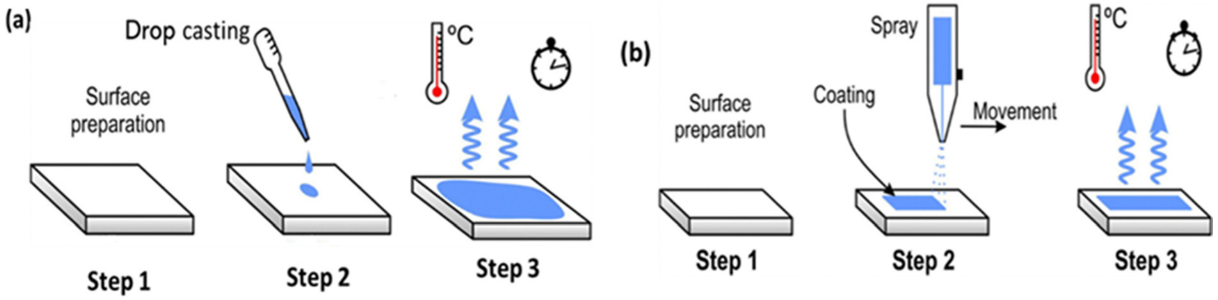

Fig. 7 MOF-based electrode construction by (a) drop casting (b) spray coating methods.

while polymeric binders such as Nafion can be added to improve catalyst immobilization on the electrode.[110] However, it is also possible for the electrochemical system to be contaminated by these additives, thereby increasing resistance and possibly blocking some MOF active sites, leading to a decrease of the desired catalytic activity or even change in selectivity.[111] Common working electrode substrates, where the drop casting takes place, include glassy carbon (GC), carbon paper and fluorine-doped tin oxide (FTO).[90,100,110,112–114] However, despite the simplicity of this method of preparing MOF electrodes, controlling the resulting films' thickness and morphology is challenging.[83] As a result of their poor stability, MOF films prepared by drop casting can only be used as electrodes for fundamental studies and are not suitable for use in electrolysers. Alternatively, MOF-based gas diffusion electrodes (GDEs) prepared by airbrushing catalyst ink on porous carbon paper have been proposed to overcome the above challenges (Fig. 7(b)).[115,116] In GDEs, since CO_2 gas is fed directly on one side of the electrode, the possible hindrance caused by the low solubility of CO_2 in the electrolyte is reduced. The work of Albo *et al.*[117] and Sikdar *et al.*[115] have used MOF-based GDEs in the CO_2RR with some promising results in terms of high selectivity towards hydrocarbon formation.

3.2. Direct solvothermal synthesis

In this method, direct growth of MOFs on conductive substrates is achieved by placing the electrode in a solvothermal reactor with the standard MOF precursors and heating for the reaction to take place (Fig. 8).[83,118] The direct solvothermal synthesis method has a significant advantage over drop casting which is that the resulting MOF is directly attached to the electrode surface without the need for extra additives that might interfere with the electrochemical performance. During synthesis, the rugosity of the surface of the electrode itself provides nucleation sites for MOF crystallization. To achieve effective MOF binding, the electrode is usually pre-treated in dilute linker, creating a monolayer, which provides the binding sites for the first secondary building unit (SBU) layer and subsequently initiate further growth.[119] Similarly to the drop casting method, GC, FTO glass and metal foams are commonly used as electrode substrates.

Before a MOF is grown on a carbon electrode, the electrode is usually pre-treated to create functional groups such as carboxylate groups that facilitate nucleation and subsequent MOF growth. As for FTO and ITO substrates, the metal oxides of the electrode provide centres for the nucleation of MOF precursors, facilitating MOF growth on the FTO and ITO, resulting in a uniform MOF thin film of nanocrystals.[120] The main drawback of these substrates, apart from the cost, is their reduced conductivity when compared with carbon electrodes.[8]

3.3. Liquid phase epitaxy (LPE)

The liquid phase epitaxy method for the preparation of MOF electrodes was first proposed by Shekhah *et al.*[121] The first step of the method involves the pre-coating of the substrate with self-assembled monolayers (SAMs) of organic molecules bearing carboxylate or pyridine moieties, which later will serve as nucleation sites.[122] Then the substrate is immersed sequentially into different solutions of MOF precursors in a layer-by-layer fashion, producing a highly orientated and homogeneous MOF thin film directly over the support (Fig. 9).[118] This strategy

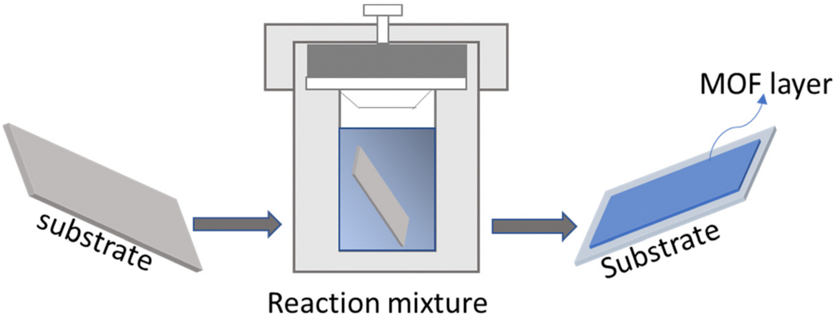

Fig. 8 MOF-based electrode construction by direct solvothermal growth.

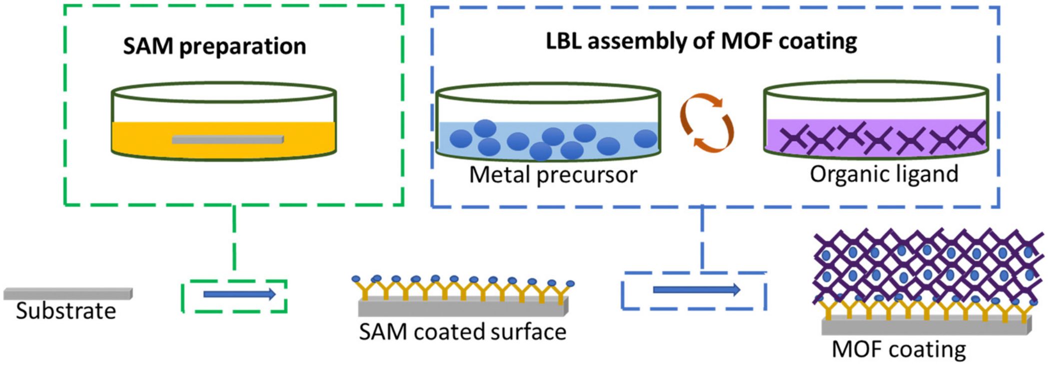

Fig. 9 MOF-based electrode construction by liquid phase epitaxy (LPE).

is also known as SURMOF (surface-bound metal–organic framework) in the literature.

Although this technique has useful advantages like control of orientation, tunable thickness and strong adhesion to the substrate surface,[123,124] the resulting SAM could also constitute an insulating layer between the electrode surface and the MOF, resulting in an increase of the electrical resistance, thus diminishing the electrochemical performance of the MOF-modified electrode.[125] Since its inception over a decade ago, there has been extensive research work on surface-mounted metal–organic frameworks (SURMOFs) and related epitaxial growth methods,[126,127] however, few SURMOFs prepared by LPE have been tested as electrocatalysts.[124] This, however, is a synthesis method that could be further explored since the strong bond between the MOF and the substrate could be advantageous for long-term electrolysis. It may also be possible to leverage the highly oriented nature of SURMOFs to tune their morphology and thickness in order to promote mass and charge transport through the MOF and possibly enhance catalytic performance.

3.4. Electrochemical synthesis

Two approaches have been identified for preparing MOF thin films on substrates for electrochemical application: direct and indirect electrosynthesis. With direct electrosynthesis, the process can be anodic or cathodic. On the other hand, electrophoretic deposition is a popular indirect electrosynthesis method used in depositing MOF thin films on conductive substrates (Fig. 10). The characteristics of these methods are summarized in Table 1.

The first MOF synthesized by anodic dissolution was HKUST-1. In this method, a potential of 12–19 V was applied for 150 min to a Cu anode which oxidized to Cu^{2+} ions in a BTC linker containing solution (Fig. 10). The chemical reaction between the Cu ions and the BTC linker resulted in the formation of an HKUST-1 layer on the electrode surface.[129] Since its first deployment for HKUST-1 synthesis, many other MOFs have been produced using electrochemical synthesis.[132–136] Dinca *et al.* reported the first MOF synthesized by cathodic deposition producing $Zn_4O(BDC)_3$ (MOF-5).[137] The synthesis was carried out by immersing FTO electrode in MOF-5 precursors and $(NBu_4)PF_6$ as conducting electrolyte (Fig. 11). As a constant cathodic potential of −1.6 V was applied for 15 min at a current density of −6.6 mA cm^{-2}, the probase (P) became reduced to a base equivalent (B) which increased the local pH near the electrode surface.[138] This change in pH induced deprotonation

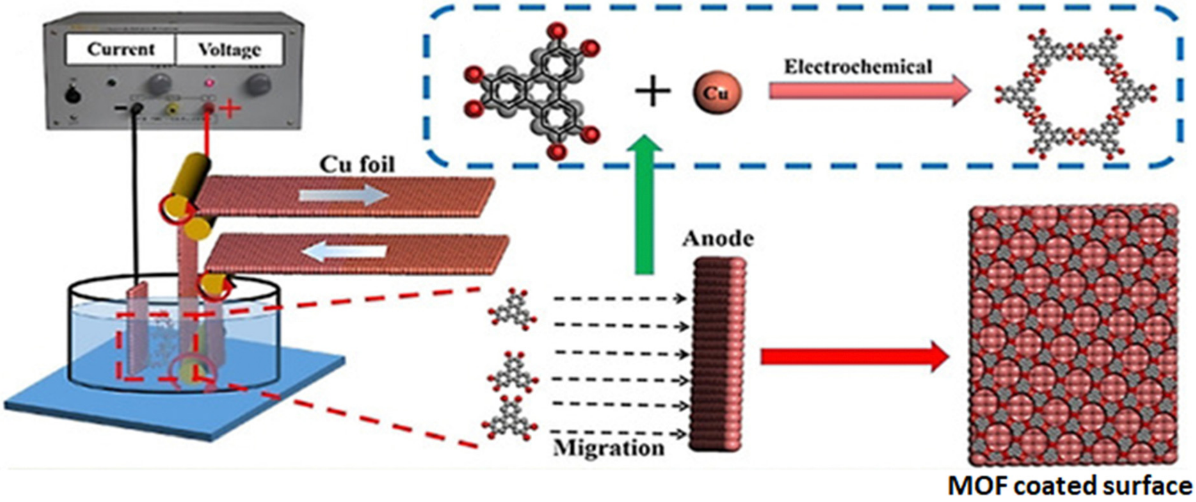

Fig. 10 MOF-based electrode construction by electrophoretic deposition. Reproduced from Liu *et al.*[128] Copyright 2021, Wiley-VCH.

Table 1 Summary of electrochemical synthesis methods

Direct electrosynthesis		Indirect electrosynthesis
Anodic electrosynthesis	Cathodic electrosynthesis	Electrophoretic deposition
• Anode electrode is immersed in an electrolyte which contains the ligand	• Anode and cathode electrodes are immersed in an electrolyte which contains MOF precursors	• Two similar electrodes acting as the anode and the cathode are immersed in a cell containing MOF suspension and supporting electrolyte
• As potential is applied, electrode (metal) is oxidized to metal ions	• MOFs are formed directly on the cathode electrode surface by an electrochemical reaction[129]	• After applying a potential, the MOF diffuses into the electrolyte and becomes deposited onto the oppositely biased electrode surface depending on the partial charges on the MOF (Fig. 13)[130]
• Metal ions react with ligand to form a thin-film MOF on the anode electrode surface	• The electrodes merely act as a source of electrons and surface for nucleation and MOF growth	
• MOF properties are independent of the metal precursor since no metal salts are used[131]	• MOFs are generated at lower potential (1.5–10 V) and within few minutes at room temperature	• Higher applied potential and longer time (typically 50–100 V during 1–3 h) are required to produce MOF films
• Different metal oxidation states can be generated at different potentials which lead to a better control over the MOF properties[129]	• Two different electrodes act as anode and cathode	• Longer deposition time is advantageous as it allows control of MOF electrode properties *e.g.* MOF film thickness and particle–particle connectivity at FTO surfaces[130]
• MOFs are generated at high potential (12–19 V) and longer time		

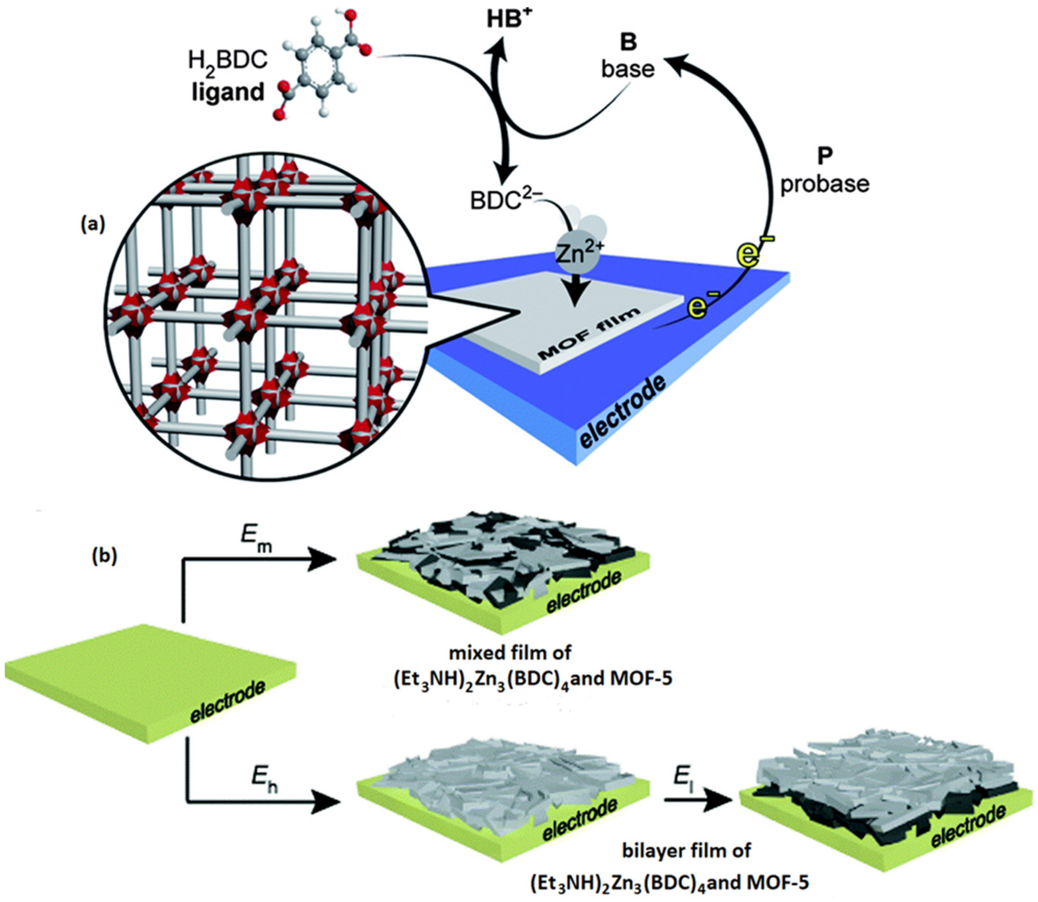

Fig. 11 (a) General scheme for the cathodically induced electrochemical deposition of MOFs, involving the reduction of probase (P), the generation of base equivalents (B), the deprotonation of ligands (H_2BDC), and MOF crystallization from BDC^{2-} and metal ions (Zn^{2+}). (b) Schematic illustration of the formation of a biphasic mixed film. Reproduced from Li *et al.*[138] Copyright 2014, Royal Society of Chemistry.

of the ligand (H_2BDC), which further coordinated with metal ions and eventually triggered precipitation of MOF-5 crystals.

It has been proposed that electrochemical synthesis has the potential to produce more CO_2RR efficient MOF-modified electrodes. For example, Kang *et al.*[139] synthesized MFM-300

Table 2 Summary of MOF-based electrode preparation methods, highlighting their key characteristics and associated considerations for CO_2RR applications

Method	Characteristics	Remarks
Drop casting	Simple, fast, limited control over film thickness	Prone to delamination, poor stability
Gas diffusion electrode (GDE)	Improved CO_2 mass transport, better selectivity	Improved dispersion on the support
Solvothermal growth on electrode	Strong adhesion, high crystallinity	Ensures better electron transfer and durability
Electrophoretic deposition	Uniform coverage, good mechanical stability	Enables precise control over film thickness, enhanced conductivity
Thermal treatment (MOF-derived catalysts)	Generates defect-rich, conductive structures	Improved conductivity, but may alter active sites
Electrochemical synthesis	Direct deposition, controlled morphology	Improved stability

on indium foil electrodes by immersing in a solution containing the organic linker and supporting electrolyte, and the MOF-modified electrode system was found to be catalytically active for the CO_2RR, exhibiting a current density of 46.1 mA cm^{-2} at applied potential of -2.15 V *vs.* Ag/Ag^+, demonstrating an faradaic efficiency of 99.1% for the formation of formic acid. Similarly, Hod *et al.*[125] deployed the electrophoretic deposition method to obtain a Fe–porphyrin MOF thin film on an FTO electrode which showed unprecedented catalytic activity towards the CO_2RR, generating a mixture of CO and H_2 at 100% faradaic efficiency. However, despite these promising results, not many MOF catalysts for the CO_2RR prepared by electrochemical synthesis have been reported, and this is an apparently promising path that remains largely unexplored.

Table 2 provides a concise summary of the various MOF-based electrode preparation methods discussed in the manuscript. It highlights their key characteristics and associated remarks, offering a comparative perspective on their advantages and limitations for CO_2RR applications.

4. Critical review of activity metrics for benchmarking electrocatalyst performance

The unprecedented growth witnessed in the field of MOFs has resulted in a rise in papers directly using MOFs in electrocatalysis.[140,141] Despite the increasing number of reports, a standardized method for determining the electrocatalytic performance and true electrochemical surface area of MOFs has not been fully established.[142] Many researchers on MOF electrocatalysts summarize and compare their results, however, the comparison of different experimental data from different laboratories remains problematic owing to a lack of standardization in the measurement procedure and reference system.[143,144] Therefore, a correct and convenient activity metric that can reasonably normalize the electrocatalytic performance is needed, to provide a basis for comparing the performance of different catalysts.

Several activity metrics have been utilized to report selectivity and electrocatalytic activity. One commonly used metric for selectivity is faradaic efficiency, which is defined as the fraction of faradaic charge utilized to produce a given product. Despite its utility in describing selectivity, faradaic efficiency is problematic when comparing catalysts with different activities. As an example, one might conclude that a catalyst that produces a specific product more selectively is also more active in producing that product. However, it is possible for selectivity toward a product to increase without increase in production rates of that product. Therefore, true differences between two catalysts can be obscured if they are only compared on the basis of faradaic efficiencies.[145] The rate of product generation, which is proportional to its partial current density, is a much less ambiguous descriptor of catalytic activity.

As for electrocatalytic activity, the most important activity metric used to benchmark the performance of a catalyst is exchange current density (j_0).[146] However, this must be normalized to provide a common ground for comparing the performance of catalysts. Normalized current densities may be described as: (i) geometric activity *i.e.* the current density normalized to the geometric area of electrode (mA $cm_{geo}{}^{-2}$), (ii) specific area activity *i.e.* the current per surface area of electrocatalyst (mA $cm_{catalyst}{}^{-2}$) and (iii) mass activity *i.e.* the current per loading mass of electrocatalysts (A $g_{catalyst}{}^{-1}$).

In geometric normalization, the current is normalized to the geometric area of electrode. However, geometric activity does not necessarily reflect a catalyst's intrinsic activity. The geometric activity fails to consider that the electrocatalytic reaction is a surface process, where only the surface active sites participate in the reaction.[147] On the other hand, the geometric activity is largely dominated by the loading mass of catalysts. It has been commonly observed that with more catalyst loading, the overpotential to reach the given geometric surface area normalized current density (i_{geo}) certainly becomes smaller.[148,149] Most electrocatalysts studied these days are nanostructured and have a large surface area with very high roughness factors, thus current normalization based on the geometrical area of the electrode is not appropriate and should ideally be avoided.[150]

Since electrocatalysis is a surface reaction where the adsorption/desorption of reactants/products take place only at the surface of the catalyst, the intrinsic electrocatalytic activity is best described using specific activity which is defined as the current divided by the surface area of the catalyst (mA cm^{-2} catalyst).[151] Specific activity is estimated by normalizing the current density by either the number of catalyst active sites or electrochemically active surface area.[147] While normalization to the number of active sites is the preferable metric,[142,152,153] in heterogeneous systems such as MOFs, it can be difficult to identify what actually the active site is. Extensive and detailed *in situ* spectroscopic studies will be required for such electrocatalysts. Therefore, normalizing the measured activity by the electrochemically active surface area is a more rational way to normalize catalytic activity.[144] Previous reports have proposed that the electrochemically active surface area (ECSA) of the catalyst can be determined by measuring the double-layer capacitance of the electrode–electrolyte interface. The double layer capacitance can be measured by conducting cyclic voltammetry (CV) in a potential range where no faradaic processes occur, typically a 100 mV window centred at the open circuit potential (OCP). In this potential region, any measured current can be ascribed to the non-faradaic process of charging the electrochemical double layer. The obtained C_{dl} is divided by the specific capacitance (C_{s}) of the material studied, which is not usually determined as part of the same experiment but taken from literature sources.[142] Unfortunately, poor practice of this method has led to misuse of the specific capacitance of the material. To determine the specific capacitance of a material, the C_{dl} of the material should be measured on an electrode with a well defined geometrical area in order to obtain a value of C cm^{-2}. As this is not usually the case, researchers are commonly tempted to use a generic value of C_{s} which inevitably causes a major error in the calculation of the ECSA.

Mass activity may serve as a reasonable parameter for evaluating intrinsic performance of different electrode materials in bulk chemical processes, such as lithium ion battery reactions, where the Li^+ diffuses deeply into the material and the original micro-structure cracks on charge/discharge cycles.[154] However, for the surface chemistry processes such as electrocatalysis, where the reaction occurs only at/near the surface of the electrode, the mass activity does not represent the intrinsic activity.[151] The definition of mass activity assumes that all atoms within each particle are electrocatalytic active sites, which is in conflict with the fact that the bulk atoms do not contribute to the electrocatalytic process. As a result, the mass activity is largely dependent on the particle size (or equivalently, surface area of catalyst), which reflects the fraction of surface atoms. Usually, catalysts of smaller particle size give higher mass activity, because smaller sized particles possess a larger ratio of surface atoms to the total atoms per mass and give a larger number of electrocatalytic active sites. As the particle size is decreased, most of the catalyst surface becomes active and the normalization by mass becomes more accurate. In addition, normalizing the catalytic activity per unit mass of catalyst could provide the end-users with a cost of operation. In this regard, the normalization can also be done per weight of the metal centre *e.g.*, Cu, Ni or Zn.

Many claims have been made regarding the performance of MOF electrocatalysts for the $\mathrm{CO_2RR}$ which have been subject to criticism, especially by more experienced electrochemists. It is argued that comparing the activity metric of one MOF catalyst to another without recourse to a method of normalization is not only misleading but can result in over-rating catalyst performance. A survey of MOF electrocatalysts for the $\mathrm{CO_2RR}$ has been carried out in an effort to identify the method of current normalization and expose errors in comparison of the electrocatalytic activities of different MOFs (Tables 3–5). First, some authors failed to clearly present the method they used to normalize their current, as they compared the activity metric of their catalyst with other catalysts from different laboratories, for example,[112,155,156] presenting the performance of their MOF electrocatalyst for $\mathrm{CO_2}$ reduction with no clear idea of the type of surface area used in normalizing the catalyst current. Misinformation of this sort has made it impossible to compare the performance of these catalysts objectively with other MOF electrocatalysts for $\mathrm{CO_2}$ reduction.

In another scenario, some reports have wrongly compared the catalytic activity of MOF electrocatalysts normalized by geometrical area with other reports whose catalytic activity was normalized by ECSA, and *vice versa*.[102,124,125,161,169,177–179] In addition to reports on MOFs catalyst normalized per geometrical area, information on the number of active sites per catalyst loading were not stated in most cases, making it difficult to make a comparative judgement of the activity of the catalysts. For instance, it has been claimed that polyoxometalate-based MOFs (PMOFs) show excellent catalytic activity towards the $\mathrm{CO_2RR}$, however, the catalyst was normalized by geometrical area and quantitative information on the active site loading per surface area was not provided as the entire catalyst cannot be assumed to be active toward $\mathrm{CO_2}$ reduction.[104]

5. Recent progress in utilizing MOFs for electrocatalysts for $\mathrm{CO_2}$ reduction

5.1. Pristine MOFs as electrocatalysts for $\mathrm{CO_2}$ reduction

The use of pristine MOFs in catalysing $\mathrm{CO_2}$ reduction was pioneered by Hinogami *et al.*,[102] who reported the use of a Cu rubeanate framework (CR-MOF) containing coordinatively unsaturated metal sites as catalyst for the $\mathrm{CO_2RR}$ to formic acid at 98% selectivity and 30% faradaic efficiency. Kumar *et al.*[112] reported the electrochemical conversion of $\mathrm{CO_2}$ to oxalic acid ($\mathrm{H_2C_2O_4}$) at 90% selectivity, 51% faradaic efficiency on a $\mathrm{Cu_3(BTC)_2}$ (1,3,5-benzenetricarboxylic acid [BTC]) thin film catalyst deposited on a glassy carbon electrode (Fig. 12). In Fig. 12(a), the cyclic voltammogram shows distinct reversible oxidation and reduction of Cu(II) to Cu(I) at 0.14 and 0.02 V *vs.* SCE, respectively. A reduction peak at 0.5 V *vs.* SCE and a sharp oxidation peak at 0.102 V *vs.* SCE indicate the presence of the Cu(0) to Cu(I) redox couple. $\mathrm{Cu_3(BTC)_2}$ exhibited a cyclic voltammetric response indicative of copper being in the $\mathrm{Cu^{2+}}$ ionic state, whereas Cu electrodes in 0.1 M KCl solution did not exhibit such behaviour (Fig. 12(a) inset). Fig. 12(b) shows the redox activities of a GCE and $\mathrm{Cu_3(BTC)_2}$ coated GCE in electrolyte without $\mathrm{CO_2}$ bubbling (1 and 3) and in $\mathrm{CO_2}$-saturated 0.01 M TBATFB/DMF (2 and 4), indicating that the direct reduction potential of $\mathrm{CO_2}$ starts at a potential more positive

Table 3 Summary of pristine MOF materials as electrocatalysts for CO_2 reduction

Electrocatalyst	Synthetic method	Electrode potential	FE (%)	Peak j_{total} (mA cm^{-2})	Current normalization	Main product	Electrolyte	Ref.
CR-MOF	Solution self-assembly	−0.78	98	~7.1	GSA	HCOOH	0.5 M $KHCO_3$	102
HKUST-1	Room temperature synthesis	−2.5 *vs.* Ag/Ag^+	51	19	N/A	Oxalic acid	0.01 M TBATFB in DMF	112
$Al_2(OH)_2$TCPP-Co	Microwave	−0.7 V *vs.* RHE	76	~1	N/A	CO	0.5 M $KHCO_3$	103
Fe_MOF-525	Electrophoretic deposition	−1.3 *vs.* NHE	50	4	GSA	CO	1 M $TBATF_6$ in DMF	125
Cu_2(CuTCPP)	Vigorous stirring at temperature of 85 °C	−1.55 V *vs.* Ag/Ag^+	68.4	1.0	GSA	Acetate	CH_3CN with 1 M H_2O and 0.5 M $EMIMBF_4$	100
Cu_2(CuTCPP)	Vigorous stirring at temperature of 85 °C	−1.40 V to −1.65 V	38.8% to 85.2%	3.5	GSA	Formate	CH_3CN with 1 M H_2O and 0.5 M $EMIMBF_4$	100
HKUST-1	Electrophoretic deposition	−2.2 *vs.* Ag/Ag^+	80	3	ECSA	CH_4	$BMIMBF_4$	157
HKUST-1	Solvent-free synthesis by oven heating	−0.9 *vs.* Ag/Ag^+	15.9	10	GSA	CH_3OH and C_2H_5OH	0.5 M $KHCO_3$	158
ZIF-8	Room temperature synthesis under vigorous stirring	−1.14 *vs.* SCE	65	~3	N/A	CO	0.5 M NaCl	155

Table 4 Summary of MOF composite as electrocatalytic for CO_2 reduction

Electrocatalyst	Synthetic method	Electrode potential	FE (%)	Peak j_{total} (mA cm^{-2})	Current normalization	Main product	Electrolyte	Ref.
Ligand doped ZIF-8	Room temperature synthesis	−1.2 V *vs.* RHE	90	10.1	N/A	CO	0.1 M $KHCO_3$	156
Cu^{II}/ade-MOFs	Room temperature synthesis	−1.4 V *vs.* RHE	45	8.5	ECSA	C_2H_4	0.1 M $KHCO_3$	159
Cu^{II}/ade-MOFs	Room temperature synthesis	−1.4 V *vs.* RHE	50	15	ECSA	CH_4	0.1 M $KHCO_3$	159
2D c-MOF	Solvothermal synthesis	−0.7 V *vs.* RHE	88	8	N/A	CO	0.1 M $KHCO_3$	160
Re-SURMOF/FTO	Liquid-phase epitaxy	−1.6 V *vs.* NHE	93 ± 5	>2	N/A	CO	0.1 M TBAH in CH_3CN + 5% CF_3CH_2OH	124
M-PMOF	Hydrothermal	−0.8 V *vs.* RHE	98.7	38.9	GSA	CO	0.5 M $KHCO_3$	104
FeTCPP-UiO-66	Thermal treatment	0.45	100	1.3	ECSA	CO	0.1 M $KHCO_3$	161
Cu_2O@Cu-MOF	Hydrothermal	−1.71	63.2	−14	ECSA	CH_4	0.1 M $KHCO_3$	162
Cu-SIM NU-1000	Heat treatment	−0.82	28	−1.2	GSA	$HCOO^-$	0.1 M $NaClO_4$	163
Ag_2O/layered ZIF composite	Refluxed at high temperature	−1.2 V *vs.* RHE	80.5	26	ECSA	CO	0.25 M K_2SO_4	164
TCPP(Co)/Zr-BTB	Thermal treatment	−0.769 *vs.* RHE	85.1	6	GSA	CO	0.5 M $KHCO_3$	165
PCN-222(Fe)	Thermal treatment	1.2	91	−0.6	GSA	CO	0.5 M $KHCO_3$	107
HKUST-1 mediate Cu	Thermal treatment	−1.07 V *vs.* RHE	45	262	GSA	C_2H_4	1 M KOH	166

Table 5 Summary of MOF-derived materials as electrocatalytic for CO_2 reduction

Electrocatalyst	Electrode potential	FE (%)	Peak j_{total} (mA cm^{-2})	Current normalization	Main product	Electrolyte	Ref.
OD Cu/C-1000(Cu-based HKUST-1)	−0.1 V *vs.* RHE	45.2–71.2	~8.9	GSA	CH_3OH and C_2H_5OH	0.1 M $KHCO_3$	167
ZIF/MWCNT	−0.86 V *vs.* RHE	100	7.7	ECSA	CO	0.1 M $NaHCO_3$	168
ZIF-8 to Ni SAs/N-C	−1.0 V *vs.* RHE	71.9	10.48	GSA	CO	0.5 M $KHCO_3$	169
Co/Zn ZIFs derived Co-N_2	−0.8 V *vs.* RHE	94.7	18.1	N/A	CO	0.5 M $KHCO_3$	170
C-AFC©ZIF-8	−0.43 V *vs.* RHE	93	2.8	N/A	CO	0.1 M $KHCO_3$	171
Ni SAs/NCNTs	−1.0 V *vs.* RHE	95	57.1	GSA	CO	0.5 M $KHCO_3$	172
ZIF-8 derived NC	−0.5 V *vs.* RHE	95.4	1	N/A	CO	0.5 M $KHCO_3$	173
ZIF-8 derived NC	−0.93 *vs.* RHE	78	1.1	N/A	CO	0.1 M $KHCO_3$	174
ZIF-8 derived Fe–N–C	−0.6 V *vs.* RHE	91	17.8	N/A	CO	0.5 M $KHCO_3$	175
ZIF-8 derived Fe-N	−0.4 *vs.* RHE	90	6.8	GSA	CO	0.5 M $NaHCO_3$	176

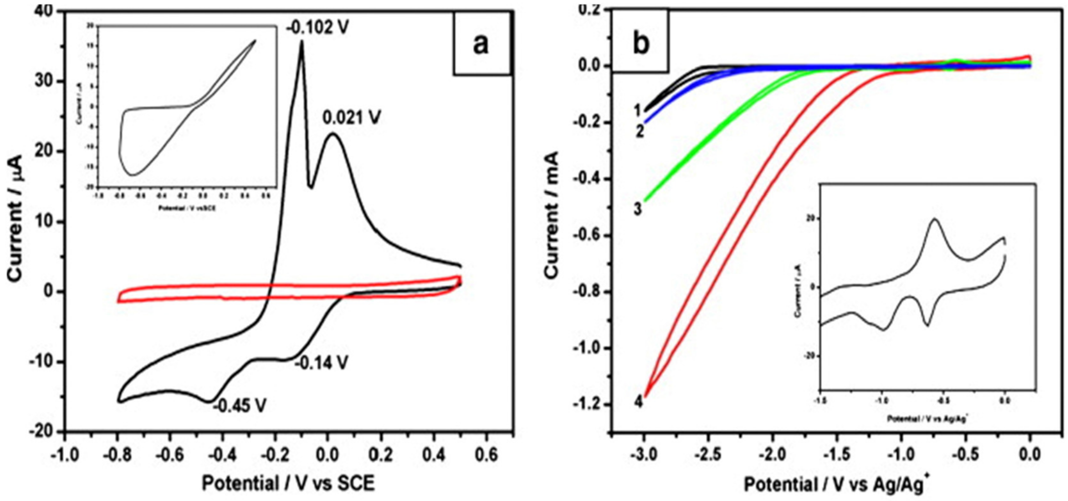

Fig. 12 (a) CV readings of $Cu_3(BTC)$ + GCE (b) CV scan showing redox activities of (1) GCE, (2) GCE in presence of CO_2, (3) $Cu_3(BTC)_2$ + GCE and (4) $Cu_3(BTC)_2$ + GCE in CO_2-saturated 0.01 M TBATFB/DMF. Reproduced from Kumar *et al.*[112] Copyright 2012, Elsevier.

on a $Cu_3(BTC)_2$ coated GC electrode (−1.12 V *vs.* Ag/Ag^+) than a bare GC electrode (−1.75 V *vs.* Ag/Ag^+), and also showing that cathodic evolution current density is increased from 2.27 mA cm^{-2} to 19.22 mA cm^{-2}. These two pioneering studies have proven the importance of nature and density of active site (metal centre) and the electronic environment (ligand) in deciding the product selectivity and efficiency.

In situ growth of MOFs into a thin layer has been recently explored to control MOF thickness which can enhance mass and charge transfer, thereby promoting higher catalytic activity towards CO_2 reduction. Kornienko *et al.*[103] demonstrated this idea by synthesizing a thin-film of cobalt–porphyrin MOF ($Al_2(OH)_2$TCPP-Co) *via* atomic layer deposition (ALD) on a transparent conducting fluorine-doped tin oxide (FTO) support. An analysis of this MOF's voltammogram trace showed that it displayed an enhanced current density under CO_2-saturated solutions relative to argon-saturated solutions and an irreversible catalyst peak, producing CO and H_2, with selectivity for CO reaching up to 76% at −0.7 V *vs.* RHE (Fig. 13(a) and (c)). The stability of the MOF catalyst was tested over an extended period of 7 h at −0.7 V *vs.* RHE in CO_2-saturated aqueous bicarbonate buffer, reaching a stable current density after several minutes, generating 16 mL of CO with estimated turnover number of 1400 (Fig. 13(d)). According to the author, the thin-layer configuration of $Al_2(OH)_2$TCPP-Co MOF was observed to enhance the reduction of CO_2 to CO. In another finding by Wu *et al.*,[100] layering of copper porphyrin MOF (Cu_2(CuTCPP) into nanosheets was reported to enhance the catalytic conversion of CO_2 into formate (FE = 68.4% at −1.55 V) and acetate (Fig. 14). Furthermore, spectroscopic studies showed that Cu_2(CuTCPP) was converted into copper clusters (CuO, Cu_2O and Cu_4O_3) which in turn catalysed the transformation of CO_2 to formate and acetate.

The choice of electrolyte has also been shown to enhance performance and product selectivity of catalytic MOFs toward the CO_2RR. For instance, Kang *et al.*[157] observed that ionic liquids (ILs) used as the electrolyte were able to influence the selective conversion of CO_2 to CH_4 using Zn-MOF catalyst. Imidazolium based ILs can interact with CO_2 by physical absorption,[180] thereby serving as both robust electrolytes and CO_2 activation promoters.[181] The cyclic voltammetry profile shows that the CO_2 reduction activities of Zn-MOF in CO_2-saturated saturated IL 1-butyl-3-methylimidazolium tetrafluoroborate ($BMIMBF_4$) gives a current density of 3 mA cm^{-2} at

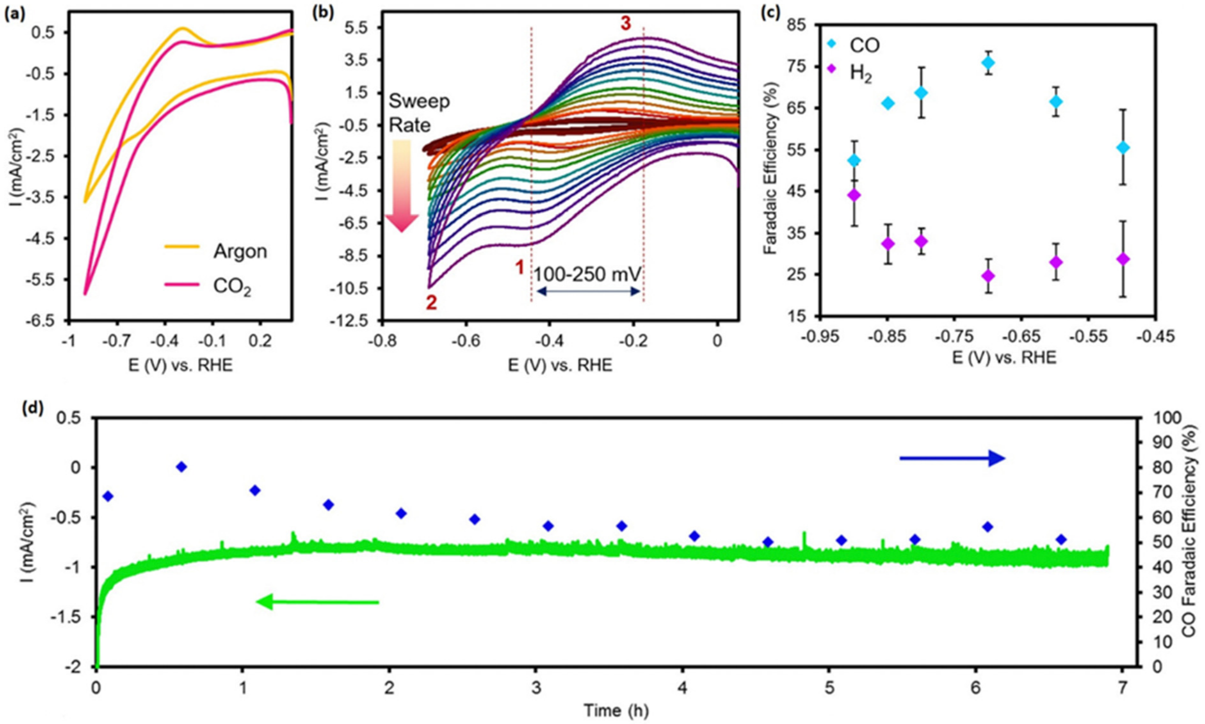

Fig. 13 (a) CV scan of the $Al_2(OH)_2$TCPP-Co MOF catalyst showing a current increase in a CO_2 environment relative to an argon-saturated environment. (b) Varying scan rate with corresponding redox potentials (c) plot of the faradaic efficiency at the potential range of −0.5 to 0.9 V *vs.* RHE; (d) MOF stability test with corresponding FE measurement. Reproduced from Kornienko *et al.*[103] Copyright 2015, American Chemical Society.

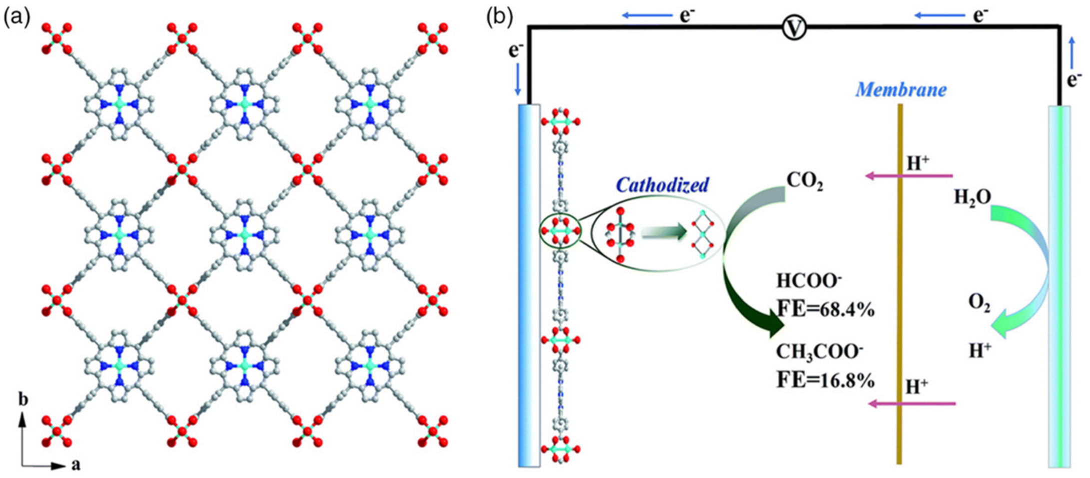

Fig. 14 (a) Crystal structure of Cu_2(CuTCPP) MOF nanosheets; (b) schematic of electrochemical system showing electrocatalytic reduction of CO_2 on Cu_2(CuTCPP) nanosheets. Reproduced with permission from Wu *et al.*[100] Copyright 2019, Royal Society of Chemistry.

reduction peak of about −2.2 V *vs.* Ag/Ag^+ while the current density of the N_2-saturated system was negligible (Fig. 15(a)). After 2 h of electrolysis, CH_4 was the dominant product (FE = 80% at −2.2 V *vs.* Ag/Ag^+), showing no decrease in current density with time, suggesting that the Zn-MOF electrode and the IL were stable (Fig. 15(b) and (c)).

Downsizing the dimensionality of MOFs into 2D nanosheets destined for catalytic application can increase their surface area thereby exposing more metal active sites and improve electrical conductivity by decreasing the electron transfer distance from the ultrathin nanosheets to the current collector of the electrodes.[182] The use of 2D MOFs as electrocatalysts for the CO_2RR was demonstrated by Yang *et al.*[159] where they attributed the significant catalytic activity and product affinity of their Cu-MOF nanosheets to the cathodized restructuring of the framework. Similarly, Zhang *et al.*[165] showed that using 2D

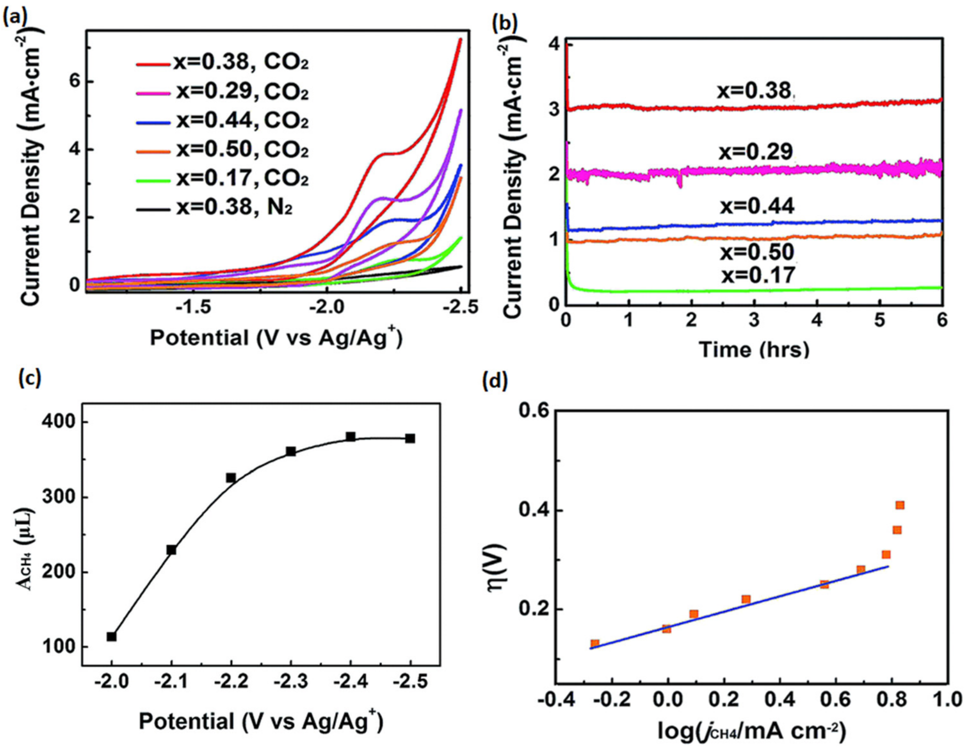

Fig. 15 (a) CV scans in CO_2-saturated and (b) stability test of different Zn-MOF/CP cathodes. (c) Amount of CH_4 (A_{CH_4}, volume at standard temperature and pressure) generated in 2 h under different potentials. (d) Tafel plot for CH_4 of the Zn-MOF/CP cathode using Zn-MOF synthesized at x = 0.38. Reproduced from Kang *et al.*[157] Copyright 2016, Wiley.

porphyrin-based MOF (TCPP(Co)/Zr-BTB) to catalyse the CO_2RR resulted in the production of CO with satisfactory faradaic efficiency and selectivity.

5.2. MOF composites as electrocatalysts for CO_2 reduction

Another strategy to obtain catalytically active MOFs is by incorporating catalytic/electrically conducting molecules which can be achieved either *via in situ* synthesis or post-synthetic modification.[141] Since an *in situ* synthesis strategy is very difficult to achieve owing to kinetic and steric challenges, and the chemical effect that guest species may have on the reaction mixture, post synthetic modification has been more explored to incorporate molecules such as metal ions, metal nanoparticles or organic linker-based functional groups into the framework.[183] Findings reveal that doping of MOF ligands could improve their electron-donating ability thus affecting their electrocatalytic activity towards the CO_2RR.[6] For example, Dou *et al.*[156] found that doping ZIF-8 (zeolitic imidazolate framework) with 1,10-phenanthroline molecules enhanced the charge transfer ability of the MOF, thereby promoting the catalytic conversion of CO_2 into CO (FE_{CO} = 90.47% and j_{CO} = 10 mA cm^{-2} at the −1.1 V *vs.* RHE) compared to pristine ZIF-8 (FE_{CO} = 50%) (Fig. 16).

Functionalizing the metal component of MOFs (active sites) with catalytic metals/NPs can create more coordinatively unsaturated sites (CUSs) within MOFs thereby boosting catalytic activities for the CO_2RR.[141] Feng *et al.*[160] demonstrated this strategy by using a MOF constructed from zinc-bis(dihydroxy) complex as node and copper–phthalocyanine as ligand to drive the CO_2RR producing syngas. *In situ* XAS was able to confirm that ZnO_4 being the active sites was responsible for the CO_2RR while CuN_4 act as supports to promote proton and electron transport. In this system, the authors claim that the CuN_4 might be responsible for drawing electrons and H_2O to produce protons which are reduced to molecular H_2. On the other hand, the adsorbed CO_2 on ZnO_4 complexes is reduced to *COOH by coupling with protons/electrons from the CuN_4 sites and electrode/electrolyte, releasing CO as the final product (Fig. 17). The possibility of having dual metallic sites in a catalyst is highly desirable, considering the overall effect it will have on electrocatalytic performance towards the CO_2RR. However, this strategy has not been widely explored and therefore presents exciting opportunities for further research.

It has been suggested that incorporating conductive materials (*e.g.* carbon black or graphene oxides) or catalytic species into MOFs *via* guest–host interaction is a plausible way to improve the performance in MOFs.[141] Ye *et al.*[124] adopted this strategy to enhance the catalytic performance of HKUST-1 MOF by grafting into its framework a catalytically active carboxylate-based complex-$ReL(CO)_3Cl$ (L = 2,2′-bipyridine-5,5′-dicarboxylic acid) (Fig. 18). The author reported that a thin film of this catalyst on FTO achieved selectivity towards CO formation of up 93 ± 5%, in comparison to just Re-linkers as catalysts. According to the authors, the higher % FE_{CO} of this Re-SURMOF was attributed to its highly oriented structure on the electrode surface.

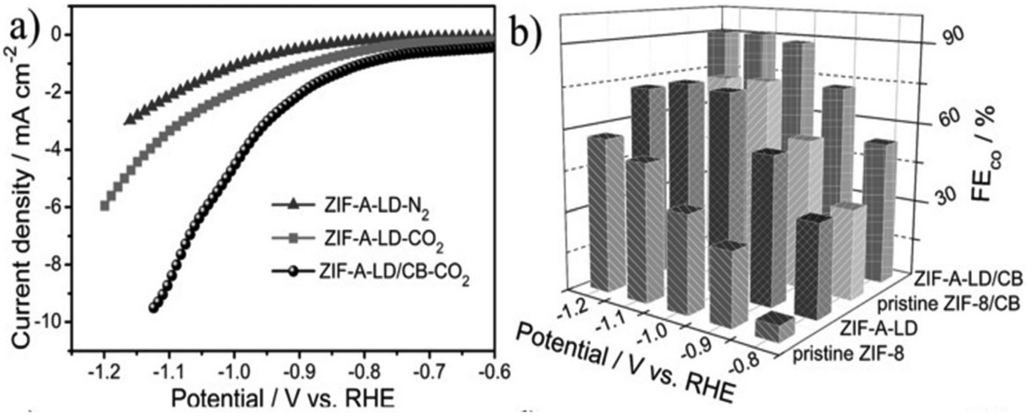

Fig. 16 (a) LSV curves of ZIF-8 activated and 1,10-phenanthroline ligand doped product (ZIF-A-LD) in N_2- and CO_2-saturated 0.1 M $KHCO_3$ solution in comparison with ZIF-A-LD/CB (b) FE_{CO}. Reproduced from Dou *et al.*[156] Copyright 2019, Wiley.

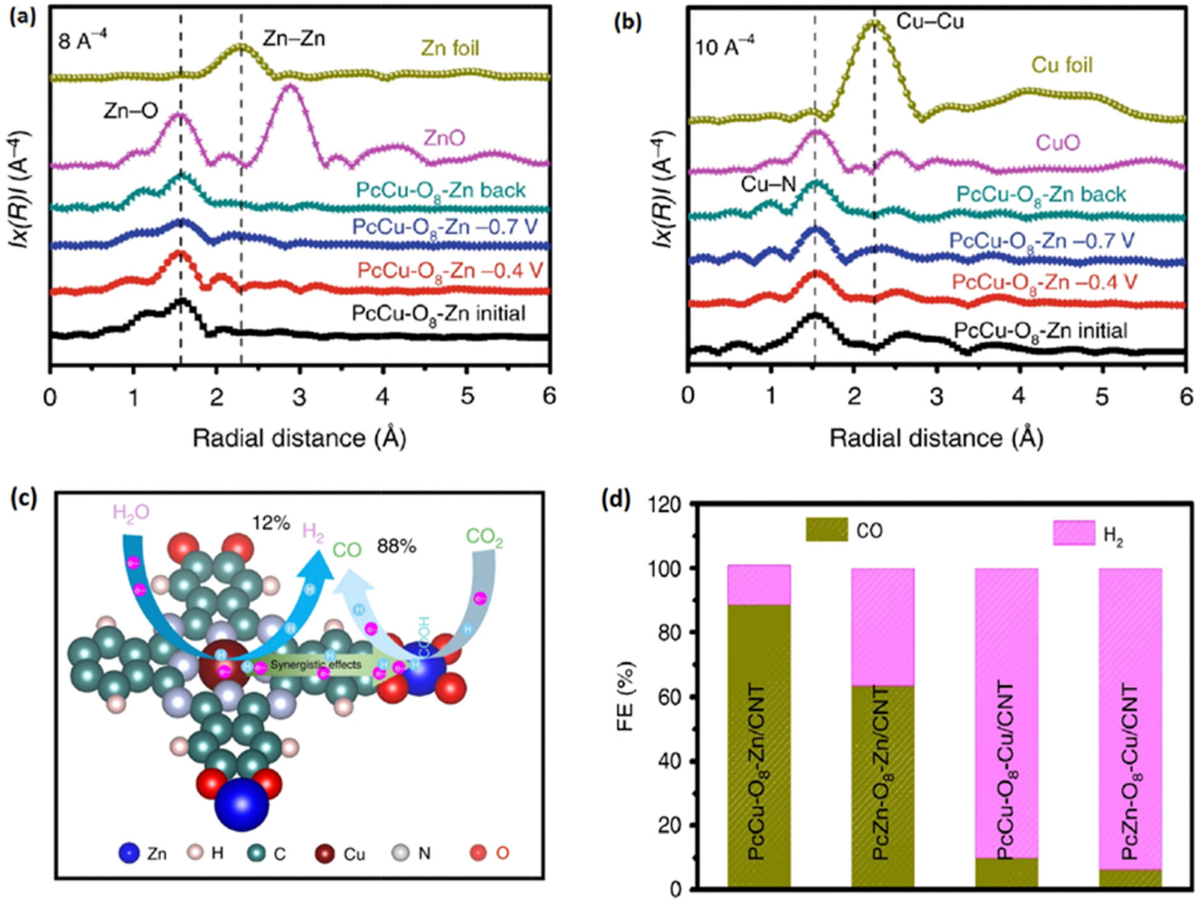

Fig. 17 (a) Zn K-edge Fourier transform EXAFS spectra of Zn foil, ZnO and PcCu-O_8-Zn samples. (b) Cu K-edge Fourier transform EXAFS spectra of Cu foil, CuO and PcCu-O_8-Zn samples (c) schematic HER and CO_2RR reaction processes for PcCu-O_8-Zn (d) faradaic efficiency of CO and H_2 for PcCu-O_8-Zn/CNT, PcCu-O_8-Cu/CNT, PcZn-O_8-Zn/CNT and PcZn-O_8-Cu/CNT at −0.7 V *vs.* RHE. Reproduced from Feng *et al.*[160] Copyright 2020, SpringerNature.

Wang *et al.*[104] proposed the implementation of a polyoxometalate MOF (PMOF) catalyst prepared from reduced polyoxometalates (POMs) and metalloporphyrin (M-TCPP). Among the metal polyoxometalate MOFs tested, Co-PMOF exhibited superior performance (99% FE_{CO} at 38.9 mA cm^{-2}) over metal polyoxometalate MOFs. The performance of this Co-PMOF

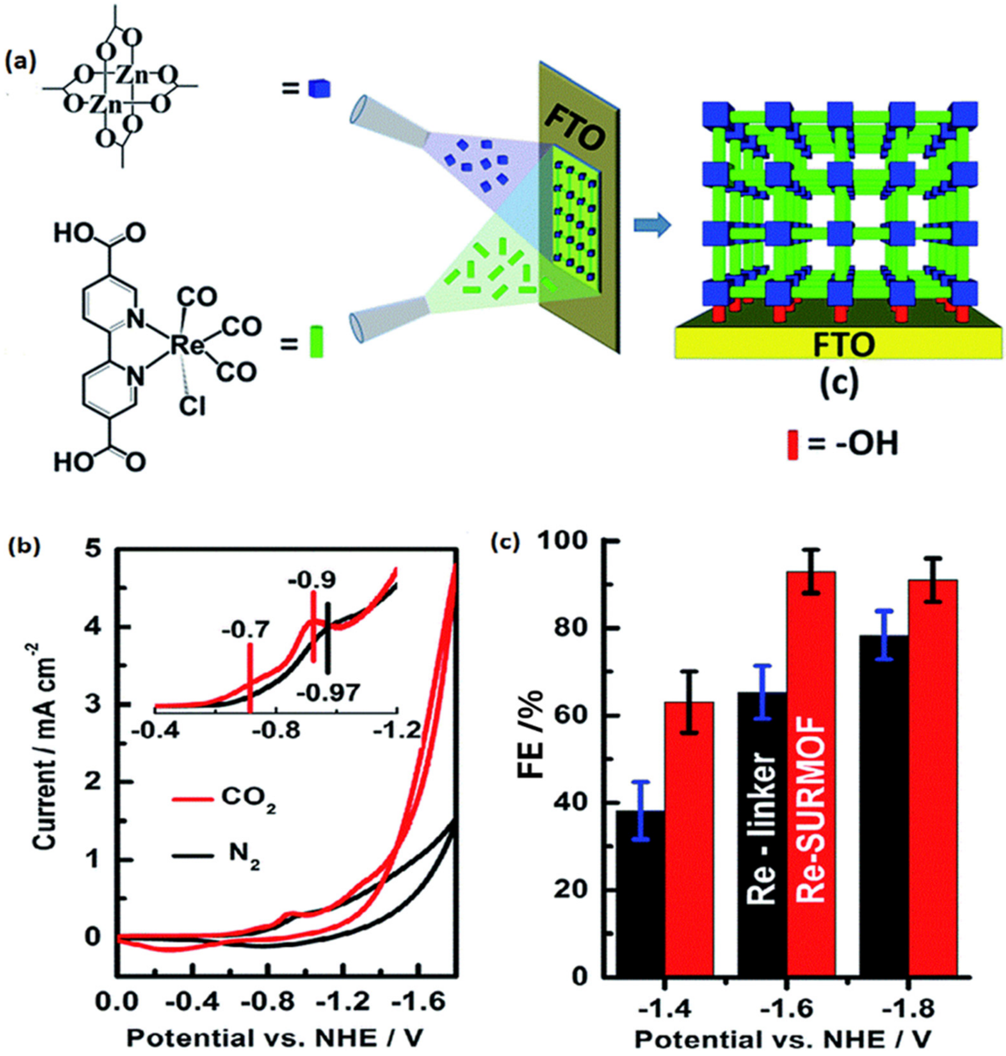

Fig. 18 (a) Schematic description of the preparation of a Re-SURMOF on fluorine-doped titanium oxide (FTO) electrode (b) CV scan and (c) FE of the Re-SURMOF and Re-linker at different applied potentials. Reproduced from Ye *et al.*[124] Copyright 2016, Royal Society of Chemistry.

was attributed to synergistic cooperation between Co-porphyrin and POMs.

It is important to note again the lack of standards in the normalization process of electrochemical activities as described in Section 1.4. While comparisons in catalytic activity are made across different experiments and materials, those comparisons, on occasion "benchmarking" using geometrical areas, surface areas measured from BET curves or electrochemical surface areas from capacitive curves, are often not only unreliable but also misleading.

5.3. MOF-derived materials as electrocatalysts for CO_2 reduction

Despite the popularity of research on the use of pristine MOFs as electrocatalysts for the CO_2RR, lack of electrical conductivity and structural stability are still major issues for most MOFs,[8] and have cast doubt in the minds of many among the electrochemical community on the use of MOFs as electrocatalysts. While significant amount of reports on MOFs electrocatalysts claim to exhibit long term stability, few, if any, of these works, have performed an appropriate post-reaction analysis of the catalyst to justify these claims.[184] A few reports have suggested that upon exposure of the MOF or MOF-composite to electrochemical conditions, the integrity of the MOF may be compromised resulting in the "segregation" of the metal centre and the formation of active metal clusters supported on organic matrix.[58] With this in mind, some groups have proposed the use of MOFs as sacrificial "templates" to generate more stable carbon-supported catalysts for efficient CO_2 reduction. MOFs, upon calcination/pyrolysis at various temperatures, can generate carbon-derived metal catalysts with inherited porosity and surface area. These MOF-derived materials are claimed to possess improved physicochemical and electrocatalytic properties including large surface area, better electronic conductivity (in comparison to MOFs), evenly dispersed single-atom active sites, clusters or NPs.[185] One example of this strategy is given by Zhao *et al.*[167] who pyrolysed HKUST-1 to produce an oxide-derived Cu/carbon (OD Cu/C) catalyst. During the CO_2RR, the

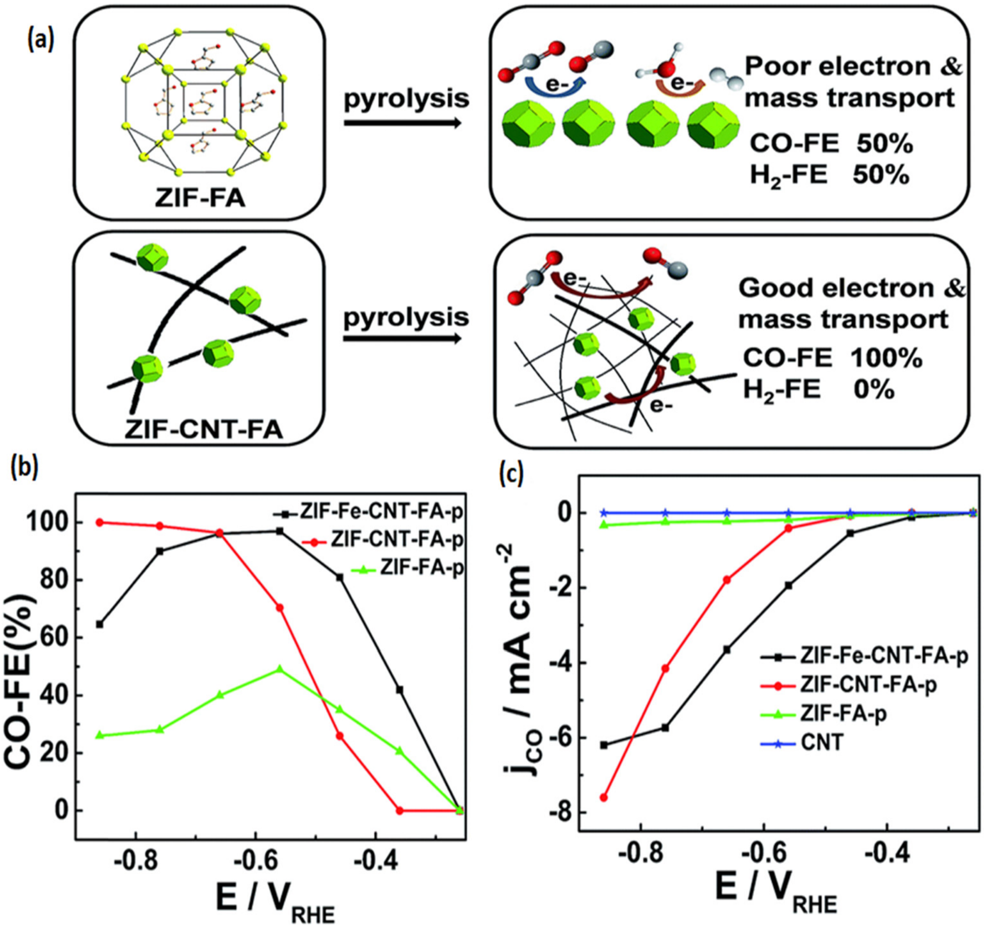

Fig. 19 (a) Schematic showing the pyrolysis of ZIFs on multi-walled carbon nanotubes (MWCNT) which aid interparticle conductivity and enhance the mass transport in CO_2RR. (b) $FE_{(CO)}$ and (d) partial CO current for different catalysts at different applied potentials. Reproduced with permission from Guo *et al.*[168] Copyright 2017, Royal Society of Chemistry.

OD Cu/C showed formation of alcohols at potentials as low as −0.1 V *vs.* RHE. The improvement in selectivity and activity of this catalyst was linked to the mutual interaction between the matrix of porous carbon and the highly dispersed copper. Nitrogen-doped carbon materials (N-Cs) obtained from pyrolysis of MOFs have been described as electrocatalyst materials with good electrical conductivity and sufficient mesoporous surface for effective transport.[183] The work of Guo *et al.*[168] demonstrated the effectiveness of using hybrid material obtained from pyrolysis of zeolitic imidazolate frameworks (ZIFs) and multi-walled carbon nanotubes (MWCNTs) to catalyse the CO_2RR, producing CO at almost 100% efficiency, overpotential of 740 mV and a current density of 7.7 mA cm^{-2} (Fig. 19). Upon adding Fe into the composite, higher FE_{CO} of 97% was observed at low overpotentials. The excellent CO_2RR activities of this material were attributed to synergistic cooperation between the inherent active sites in the hybrid material and the carbon nanotube (CNT) support which promotes electron and mass transport.

Promising electrocatalytic performance exhibited by MOF-derived catalysts has frequently been ascribed to "single atom catalysts" (SACs),[186] through direct evidence that the active sites are in fact single atoms is generally lacking. Zhao *et al.*[169] reported Ni-single atoms dispersed in nitrogen-doped porous carbon (Ni-SAs/N–C) prepared from ZIF-8 as precursor. Ni-SAs/N–C successfully catalysed CO_2 to CO at 71.9% faradaic efficiency, current density of 10.48 mA cm^{-2}, overpotential of 0.89 V and high TOF of 5273 h^{-1}, performing better than Ni foam and Ni NPs (Fig. 20). The clearly improved CO_2 reduction performance of Ni SAs/N–C may be attributed to the increased number of surface-active sites, lower adsorption energy of CO over active sites, and improved electronic conductivity.[187] In a similar report, Wang *et al.*[170] used ZIF-8 as sacrificial template to obtained a cobalt metal catalyst anchored on nitrogen-doped carbon (Co-SAs/N_x–C) which performed excellently catalysing CO_2 to CO, achieving FE of 94%, high current density of 18.1 mA cm^{-2} and TOF of 18 200 h^{-1}. In comparison to the work of Zhao *et al.*, it was reported that regulating the coordination number of the dispersed metal species obtained from ZIF-8 can enhance its CO_2RR activity. Some relevant works[171–176] have also demonstrated the use of the pyrolysis approach to obtain metal–N–C catalyst materials which have shown promising performance towards CO_2 reduction in terms of selectivity and activity.

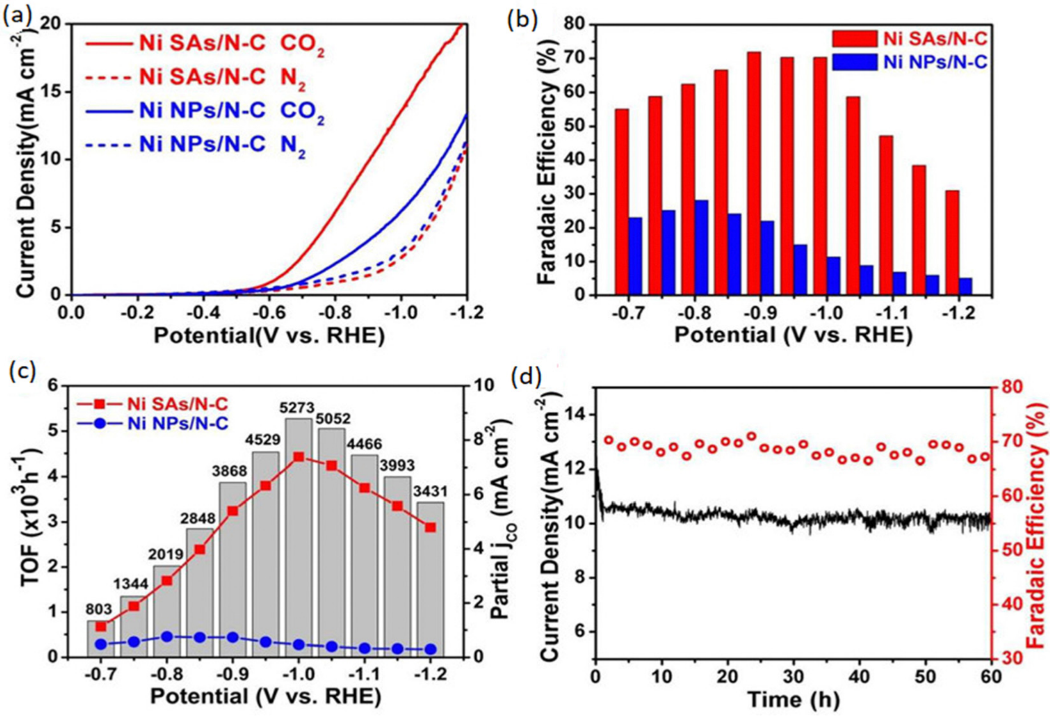

Fig. 20 (a) LSV curves in the N_2-saturated (dotted line) or CO_2-saturated (solid line) 0.5 M $KHCO_3$ electrolyte at a scan rate of 10 mV s^{-1}. (b) FEs of CO and (c) partial CO current density plots and TOFs of Ni SAs/N–C and Ni NPs/N–C at different applied potentials. (d) Stability of Ni SAs/N–C at a potential of −1.0 V *vs.* RHE for Ni SAs/N–C during 60 h. Reproduced from Zhao *et al.*[169] Copyright 2017, American Chemistry Society.

6. Summary and future outlook

Achieving sustainable energy and a clean environment is the driving force behind a rapid surge of interest in the electrocatalytic potential of MOFs for CO_2 conversion fuelled by their excellent properties. In the last decade, the drive to obtain a highly competitive, viable and cost-effective alternative catalyst for the CO_2RR has created unprecedented efforts to harness electrocatalytic potential of MOFs. Despite this development, there are still some challenges preventing the industrial application of MOFs as electrocatalysts for CO_2 reduction.

Fig. 21 provides a comparative analysis of the CO_2RR performance across pristine MOFs, MOF composites, and MOF-derived materials, highlighting key parameters such as faradaic efficiency, overpotential, current density, stability and conductivity. This visualization underscores the fundamental trade-offs between these material classes, demonstrating how MOF modifications and derivatization significantly enhance catalytic activity and durability. While pristine MOFs benefit from high surface areas and tunable active sites, their poor conductivity and limited stability hinder their practical application. MOF composites offer improved charge transport and catalytic synergy, while MOF-derived materials, particularly carbonized or metal-based derivatives, exhibit the highest conductivity and long-term stability. This comparison reinforces the need for continued material innovation, particularly in optimizing conductivity and structural integrity, to unlock the full potential of MOF-based catalysts for CO_2 electroreduction.

One key issue underlying the poor performance of MOFs compared to conventional inorganic catalysts is electrical conductivity. Therefore, building electrical conductivity into MOFs can push their limit, in terms of electrocatalytic performance, beyond the current catalysts. The general requirement for constructing MOFs with high conductivity is to select building blocks with loosely bound charge carriers that are capable of creating conducting pathways for charge transport *via* redox hopping and/or band transport. Carefully selecting building components which include mixed-valence metal ions, ligands with conjugated double bonds or nitrogen- or sulfur-containing ligands, can lead to the fabrication of MOFs with higher intrinsic conductivity. Taking advantage of the porosity, a guest-based conductive MOF can be built by way of incorporating conducting materials such as metallic species, redox-active molecules, or conductive polymers into the MOF framework.

Another major issue hindering the electrocatalytic performance of MOFs is stability, as many MOFs collapse into metal oxides/clusters during electrochemical reaction.[58] Because the metal–carbon bond in most MOFs is rather weak, they easily become degraded, losing their structural integrity, thereby limiting their operability in electrocatalysis. A few measures have been suggested to address MOF stability problems, such as *de novo* synthesis of MOFs by linking carboxylate-based ligands (hard bases) with high-valent metal ions (hard acids) or linking azolate ligands (soft bases) with low-valent metal ions (soft acids). The introduction of hydrophobic/rigid ligands, and phosphonate/carboxyphosphonate ligands into

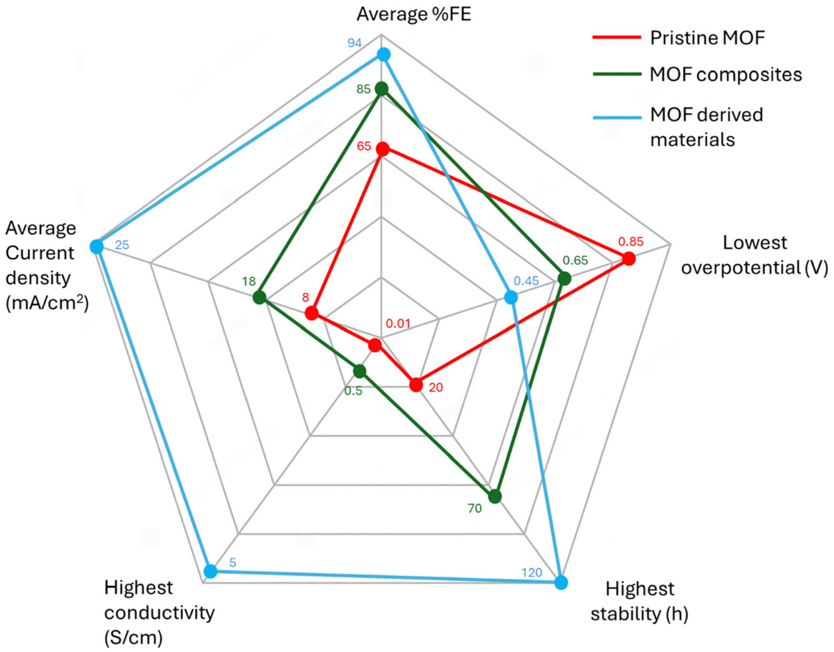

Fig. 21 Summary of the overall performance metrics of the three types of MOF discussed in the review.

MOF synthesis have also been suggested as a way to improve MOF stability.

The stability of MOFs can also be affected by the strength of their attachment to the electrode surface. Finding an effective method for preparing MOF-modified electrodes could play an important role in creating a strong attachment of the MOF catalyst to the electrode and by extension enhance the MOF electrochemical response. Drop casting is one facile method for immobilizing MOFs on conductive electrodes for electrochemical studies, however, the ease of delamination of the catalyst from the substrate during electrochemical studies is a major drawback. Additionally, controlling the resulting MOF film's thickness and morphology is challenging. As a result, it is highly desirable to use alternative preparation methods such as direct solvothermal synthesis, electrochemical synthesis *etc.*, which result in strong chemical bonds between the MOF and the substrate.

Having strong MOF attachment to the electrode surface is not sufficient to assure long-term stability as the supporting electrolyte and current flow can also affect the MOF structure. Considerable attention should be paid to the stability of the MOF in aqueous electrolytes and in the presence of bicarbonate ions, which is the preferred medium to carry out CO_2 electrolysis. Therefore, the development of stable MOFs which will be tolerant to electrochemical environments is vital for future CO_2RR electrocatalysis applications.

To complement the stability of MOFs, studies of catalytic performance should be accompanied by extensive material characterization, either during or after reaction, to ensure the MOF structure is maintained under reaction conditions. The method of catalyst normalization is crucial in rating and benchmarking the performance of catalysts, as comparing the activities without due consideration of the method of normalization is not only misleading but can lead to overrating or underrating the catalyst performance. While some authors failed to clearly present the method used in normalizing their current, others erroneously compared the activity metric of MOF electrocatalysts normalized geometrically to those normalized electrochemically. It is therefore necessary to be cautious in comparing the performance of catalysts without taking into account the method of catalyst normalization.

In addition, to confirm the stability of the materials, further *post mortem* analysis should be performed. Post-reaction analysis techniques play a crucial role in understanding the active sites and reaction mechanisms of electrocatalysts, particularly for CO_2RR. For instance, *in situ* X-ray absorption spectroscopy (XAS) has been widely used to monitor the oxidation state and coordination environment of metal centres during CO_2RR, providing insights into the dynamic transformations of catalysts, such as the reduction of Cu oxides into metallic Cu species, which directly influences product selectivity.[188] High-resolution transmission electron microscopy (HRTEM) has been instrumental in visualizing structural changes at the atomic level, as seen in the formation of defect-rich structures in carbon-supported single-atom catalysts, which enhance CO_2 adsorption and conversion efficiency.[188,189] Similarly, operando Raman spectroscopy has been used to track reaction intermediates in metal–nitrogen–carbon (M–N–C) catalysts, revealing the role of nitrogen coordination in stabilizing CO_2RR intermediates.[190] These techniques have been successfully applied to transition metal oxides, single-atom catalysts and bimetallic systems, but remain underutilized in MOF-based electrocatalysis. Implementing these methods in MOF-based CO_2RR research would provide real-time insights into MOF stability, electronic structure evolution, and potential catalyst degradation, paving the way for the rational design of highly selective and stable MOF-based CO_2RR electrocatalysts.

An overview of research on MOFs as electrocatalysts reveals that they have been deployed in pristine form as catalysts, as porous supports for the incorporation of catalytically active material or as precursors for dispersed metal catalysts, showing that they can reduce CO_2 into CO, formic acid and even hydrocarbons and alcohols. Several strategies have been attempted to improve the catalytic performance of MOFs for the CO_2RR.

In situ MOF growth into a thin layer has been reported to control MOF thickness which can enhance mass and charge transfer. Downsizing the dimensionality of MOFs into 2D nanosheets can increase the exposure of metal active sites and improve electrical conductivity by decreasing the electron transfer distance from the ultrathin nanosheets to the current collector of the electrodes. Compositing MOFs with conductive materials (such as carbon black or graphene oxides) or catalytic species *via* guest–host interaction has been demonstrated as a plausible means of inducing catalytic activity in MOFs.

Research involving the use of different MOF morphologies such as ultrathin 2D nanosheets, nanocages and nanowires for CO_2 reduction remains a tiny subset of the total and therefore channelling effort in this direction could yield results in producing efficient electrocatalysts that can promote mass transport and electronic transfer during electrocatalysis.

For the development of optimal catalysts, future studies should explore the tunability of MOFs to understand the role of the active metal centres, pore size or substituents on the linkers. Furthermore, theoretical studies can help understand the effect of metal centre and linker on the strength of interaction between the catalysts and reaction intermediates. This information is essential to elucidate and understand the reaction mechanisms, identify the rate-limiting step and to predict optimal active sites.

Additionally, using MOFs with multi-metal sites present an opportunity for further tuning their catalytic properties. Although, MOF-derived dispersed metal catalysts have recently emerged as a new frontier in catalysis science and have attracted extensive research attention due to their excellent activities toward CO_2 reduction, there remains a need to devise more efficient routes for the synthesis of catalysts having flexible structures and active sites, and for much better characterization of the latter.

Author contributions

All authors have contributed substantially and given approval to the final version of the manuscript.

Data availability

We would like to confirm that no primary research results, software or code have been included in this work, and no new data were generated or analysed as part of this review.

Conflicts of interest

The authors declare that they have no competing financial interests or personal relationships that could have influenced, or appeared to influence, the contents of this paper.

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