Metal-organic frameworks for photo/electrocatalysis

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Abstract: Metal-organic frameworks (MOFs), constructed from metal clusters/ions and organic ligands, are ideal materials for photo/electrocatalysis, mainly due to the advantages of large surface areas, high porosity and easily tunable optical and electronic structures. In this comprehensive review, we summarize the recent and important advances on MOF-based photo/electrocatalysts including pristine MOFs, MOF composites and MOF-derivatives. The novel strategies to improve the photo/electrocatalytic performances are highlighted. Finally, we also discuss and outline the current challenges and future development of MOFs for photo/electrocatalysis.

1. Introduction

The depletion of fossil fuels and environmental pollution are the main challenges that the human society are facing. The demand for energy is highly dependent on fossil fuels, leading to air pollution and the increase of CO\(_2\) concentration in the atmosphere which causes the global warming. To solve these problems, scientists are seeking for sustainable and clean energy sources to replace fossil fuels.\(^1\) Renewable energy conversion and storage systems, including solar energy, wind energy, hydropower, fuel cells and electrochemical systems have received extensive attentions due to their environment benignity and effectiveness to reduce pollution and the greenhouse gas emission. The capture and catalytic conversion of CO\(_2\) into valuable chemicals is another promising approach to reduce the level of CO\(_2\) in the atmosphere.\(^2\) The catalytic conversion of various abundant energy into chemical energy via photo/electrocatalysis is recognized as a highlydisable approach to fulfill the requirement of sustainable development and therefore has attracted tremendous research interest in the past several decades.\(^3\)

Natural photosynthesis of green plants and certain other organisms transforms solar energy into chemical energy with high efficiency.\(^4\) During photosynthesis of plants, light is harvested and utilized to convert water and CO\(_2\) into O\(_2\) and energy-rich carbohydrates.\(^5\) In the photosynthesis reaction center, the chlorophyll pigment arrays in chloroplasts serve as light harvesting antenna and the catalytic water splitting reactions are performed by the reaction center composed of Mn\(_3\)O\(_4\) cubane cluster in photosystem II.\(^6\) Inspired by the photosynthesis process, photocatalysis, including photocatalytic water splitting, CO\(_2\) reduction reaction (CO\(_2\)RR), \(N_2\) reduction reaction (NRR), pollution degradation, and organic transformation, is considered as the most promising technology for the utilization of abundant solar energy to resolve global energy crisis and pollution problems.\(^7\)

Numerous semiconductors with low-cost, highly stable and environment-friendly characteristics such as TiO\(_2\), graphitic carbon nitride (g-C\(_3\)N\(_4\)) and metal sulfides etc. have been reported to be promising photocatalysts for various photoredox reactions.\(^8\)

Electrocatalysis, including electrocatalytic H\(_2\) evolution reaction (HER), O\(_2\) evolution reaction (OER), oxygen reduction reaction (ORR), CO\(_2\)RR, NRR and electroorganic synthesis etc., is another promising approach for the conversion of various energy into chemical energy via chemical bond formation, especially when the reaction is driven by electricity generated by solar, wind and other renewable energy resources.\(^9\) The particular attraction of electrocatalysis bases on the high transformation efficiency (up to 100% Faradaic efficiencies (FEs)) compared with the low quantum yield of photocatalysis, and the simple control of the reaction through modulating the applied electrical potential. The advanced electrochemical energy conversion devices such as fuel cells, electrolytic cells and metal-air batteries have the advantages of high efficiency, high energy density and without harmful emission. These electrochemical systems are expected to produce green energy under operation conditions, in which HER, OER and ORR reactions are involved. The high-activation barriers of these reactions lead to large overpotential, limiting both the efficiency and conversion rate. The electrocatalytic water splitting process including HER and OER to produce clean hydrogen energy, is hindered by the sluggish reaction kinetics of OER. Both the CO\(_2\)RR and NRR reactions suffer the low selectivity and FE. Till now, most of the benchmark catalysts for electrocatalysis are noble metal-based materials, such as Pt, IrO\(_2\) and RuO\(_2\), limiting the large-scale applications due to their high cost and scarcity. Thus, it is highly desirable to develop earth-abundant materials as highly efficient electrocatalysts.

Metal-organic frameworks (MOFs), constructed from metal clusters/ions and organic ligands, are a new type of porous materials with high surface areas (up to 10,000 m\(^2\) g\(^{-1}\)), large pore volume and tunable pore size distribution (from 3 to 100 Å).\(^10\) MOFs have shown promising applications in gas storage and separation,\(^11\) luminescence,\(^12\) magnetism,\(^13\) biology and...
MOFs possess good recyclability to improve economic benefits and easier recyclability compared with their molecular counterparts. (2) The porous structure and large surface areas of MOFs are beneficial for increasing active sites and accelerating mass transport (such as reactant, product and electrolyte), thus improving the photo/electrocatalytic performance. (3) The optical and electronic structure of MOFs can be easily modulated via metal ions-doping or functionalization of organic ligands without changing the crystalline structure of MOFs. (4) More than one functional sites can be integrated into one MOF, making MOFs to act as bifunctional or multifunctional materials for catalysis, such as photocatalytic or electrocatalytic bifunctional overall water splitting. (5) The pore size and pore environment of MOFs are tunable, making the improvement of the selectivity of aimed products possible, especially for catalytic organic synthesis reactions. (6) The morphology of MOFs is controllable. Various nanostructures such as 1D nanorods, 2D ultrathin nanosheets, hollow nanocrystals can be facilely synthesized. Specific morphologies such as ultrathin nanosheets are critical for the improvement of photo/electrocatalytic activity, which will expose more active sites, boost charge transfer and also benefit devices fabrications. (7) Functional molecules or clusters with high photo/electro-activity can be easily introduced into the backbones or pores of MOFs, increasing the catalytic activity. (8) MOFs can be easily composed with other functional materials by either into the large pores or on surface. Compared with each component, MOF nanocomposites have the advantages of increased intrinsic activity, enhanced conductivity and charge transfer process, minimized aggregation of the nanomaterials and possible synergistic interfacial effect to improve the catalytic activity. To overcome the low conductivity and weak stability in the electrolyte, the pyrolysis of MOFs to their derivatives (such as carbon materials, oxides, sulfides, phosphides with unique structures and single atom) have also been extensively studied. Meanwhile, the stable MOF-derivatives can not only enhance the ability to cope with complex working environments (e.g. acidic, alkaline and neutral), but also possess good recyclability to improve economic benefits.

In the past several years, it has been witnessed significant growth of MOFs for photo/electrocatalysis (Fig. 1). Though some reviews focus on MOFs for photocatalysis or electrocatalysis were published, an overall summary that covers all these rapid developing fields is still lack, and a timely summary of these fast-growing fields is highly desirable for better understanding of the structure-property relationship and strategic guidelines to develop better MOF-based photo/electrocatalysts. In this comprehensive review, we will focus on recent development of MOF-based photo/electrocatalysts including pristine MOFs, MOF composites and MOF-derivatives. We summarized the latest advances in the design and architecture of MOFs for photo/electrocatalysis and highlighted novel strategies to improve the photo/electrocatalytic activities. Finally, the current challenges and future development of MOF-based materials for photo/electrocatalysis are briefly discussed and outlined.

2. MOFs and MOF-derivatives for photocatalysis
Photocatalysis is an environmentally-friendly way to convert solar energy into chemical energy, such as photocatalytic water splitting, photoreduction of CO₂, photocatalysis of organic synthesis and photodegradation of contaminants. Efficient photocatalysts usually feature with (i) appropriate band gap, (ii) distribution more active sites, (iii) efficient carrier separation and charge transfer. To develop such photocatalysts, numerous materials were investigated ranging...
from traditional semiconductor systems to organic compounds, including TiO$_2$, CdS, MOFs and their composites.\textsuperscript{[36]} Traditional semiconductor catalysts suffer from limited band gap, low charge separation efficiency and low catalytic activity. Subsequently, a lot of research have been proposed to address these issues, such as doping with C/N materials to change band gap and modifying with precious metal cocatalyst on material surface to promote efficient charge separation.\textsuperscript{[37]} However, the lacking of definite structure of these materials leads to further research on the reaction mechanism being limited.

MOFs emerged as a kind of novel photocatalyst, due to the high specific surface area, clear active sites and tunable structural components.\textsuperscript{[38]} Intrinsic pores and ultra-high specific surface area facilitate the adsorption of reactant molecules, which provides more opportunities for access to active sites; clear active sites are beneficial to further study of photocatalytic reaction mechanism; regulatable ligand and metal active center are conducive to extending light absorption region, and investigating the effects of different metal activities to guide the development of highly efficient photocatalysts. In the section of MOF-based photocatalysis, we will introduce the charge transfer mechanism, the strategies of improving photocatalytic performance, and the application of photocatalysis (including photocatalytic water splitting, photoreduction of CO$_2$, photocatalytic organic synthesis, photocatalytic degradation of pollutants, etc.).

### 2.1 MOFs as photoresponsive semiconductor

More than a decade ago, theoretical calculations demonstrated that the MOFs (such as IR-MOFs) can be regarded as semiconductors with large band gap.\textsuperscript{[39]} Generally, for MOFs, highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) were utilized to describe the energy levels to distinguish from periodic semiconductor.\textsuperscript{[40]} The HOMO-LUMO bands are mainly controlled by the C sp$^3$ state of the linker molecules. Because the HOMO band is dominated by conjugation of organic ligands, the bandgaps of MOFs could be modulated by various ligands. Under illumination, the organic linkers of MOFs were generally assigned to harvest light and to be photoexcited, further to activate the metal nodes or metal cluster through from linker-to-metal charge transfer (LMCT).\textsuperscript{[40-41]} Such semiconductor-like behavior of MOFs provided the platform and new opportunity for photocatalytic reaction.

In 2010, García and co-workers first utilized the Uio-66 and Uio-66-NH$_2$ as photocatalysts toward H$_2$ generation by water splitting due to the excellent water stability of the two MOFs.\textsuperscript{[42]} It is demonstrated that the absorption wavelength of MOF will be red-shifted with the modification of ligand by amino group. The long-lived charge separation, about 300 μs, were recorded by laser flash photolysis, illustrating the photoresponsive behaviors of MOF semiconductor. Furthermore, the semiconducting mechanism under illumination, could be explicated by MIL-125(Ti) series. When the MIL-125-NH$_2$ was used for CO$_2$ reduction, the electron spin resonance (ESR) experiments revealed that the transfer path of photogenerated electrons from ligand to the Ti$^{4+}$ induces by O atom of 2-aminoterephthalate (ATA) group.\textsuperscript{[43]} As a result, the Ti$^{3+}$ of Ti–O cluster was formed by transferring electron to Ti$^{4+}$ through LMCT (Fig. 2A). In addition, compared with pristine MIL-125, the MIL-125-NH$_2$ exhibited excellent performance attributed to the –NH$_2$ functionalization, extending the light adsorption from ultraviolet (UV) to visible light. Inspired the development, organic ligands were rationally designed and synthesized toward photocatalytic reaction, considering the importance on the integration of additional groups. The band gaps will be changed owing to the contribution of 2p electrons, when functional groups (−NH$_2$, −CH$_2$, −OH, or −Cl) were induced. Similar modification by the −NH$_2$, MIL-125-NH$_2$ could be utilized for photocatalytic oxidation of amines to imines under O$_2$ atmosphere.\textsuperscript{[44]} In this reaction, the Ti$^{3+}$ ions were formed through LMCT, and the resulting Ti$^{3+}$ further reacted with O$_2$ molecules to form superoxide radical anion (O$_2^-$), while the as-formed Ti$^{3+}$ ions were oxidized back to Ti$^{4+}$ ions (Fig. 2B). Meanwhile, amine served as the electron donor to provide the electron, and then formed the carbon centered free radical through deprotonation. Next, the aldehydes were generated by the reaction between the O$_2$ and carbon centered free radical, followed by occurring aldmine condensation on aldehydes via nuclear attack by unreacted amine.

The study of ligand-to-ligand charge transfer (LLCT) within MOFs is not extensive and in-depth enough, as it is difficult to control multiple factors at the same time. It demanded a mixed ligand coordination system, in which the coordination between metal ion and electron donor (D) as well as electron acceptor (A) must preclude the M-A or M-D separation and D-A combination (Fig. 2C).\textsuperscript{[45]} Some LLCT within MOFs were presented, such as [MnL(bpa)(H$_2$O)$_n$]$_2$NiH$_2$O, [MnL(bpe)$_3$(bpy)$_n$]$_2$NiH$_2$O and [MnL(4,4′-bpy)(H$_2$O)$_n$]$_2$nCH$_3$CN (L = dimethylthiotetrafluorvalenecarboxylate, bpa = 1,2-bis(4-pyridyl)ethane, bpe = 1,2-bis(4-pyridyl)-ethene and 4,4′-bpy = 4,4′-bipyridine).\textsuperscript{[46]} Theoretical calculations and ESR experiments revealed that the charge transfers from L ligand to the other ligand. However, these LLCT light-responsive MOFs have not continued to be used for photocatalysis. Another LLCT light-responsive Bi-MOF (Bi-mna) was presented for decomposition of organic dyes Rhodamine B and methylene blue.\textsuperscript{[47]} The LLCT occurred from Bi–S to Bi–O, in which Bi atom served as the bridge between two ligands. Compared with LMCT, LLCT within MOFs for photocatalytic reactions are not often observed and reported (Fig. 2D).

Metal to ligand charge transfer (MLCT) is common in ligands with low-level π antibonding empty orbits, especially in complexes formed by aromatic ligands, such as photosensitive Ru-based and Ir-based complex compounds.\textsuperscript{[47]} Integration of these photosensitive molecules to MOFs can improve the ability for sensitizing electron transfer, and the energy band structure can be facilely regulated. By using photoactive Ru(II)-bpy as building blocks, Lin and co-workers presented microscale Ru-based MOFs which displayed “antenna”-like behaviors with efficient charge transfer efficiency (>98%).\textsuperscript{[48]} MLCT excitations extended the light adsorption and underwent rapid energy migration in crystal, which showed promising photochemical performance (Fig. 2E). Such
The main advantage of MOFs over other materials is that their assembled structure permits the combination of a variety of transition metals, organic linkers and structural arrangements. Building blocks and pre-designed organic ligands can be selected to make target MOFs have better photocatalytic performance. In order to obtain highly efficient photocatalytic MOF-based materials, the primary request is harvesting light to be photoexcited and further to transfer electrons. The proportion of visible light to total solar radiation energy is much higher than that of UV light. To utilize solar energy efficiently, photocatalytic reaction is preferred to perform under natural light or visible light. Therefore, a great deal of investigations focused on extending light absorption range and intensity of MOF materials. In particular, the use of –NH₂ groups and macrocyclic conjugated ligands as linkers will extend the adsorption region from UV to visible light. In order to improve the catalytic activity of Uio-66 to produce H₂, García and co-workers presented an analogous MOF (Uio-66-NH₂) with –NH₂ modification of BDC ligand. –NH₂ served as auxochrome group in BDC ligand can make K band (n–π*) redshift, giving rise to an intense absorption region from 300 to 440 nm. Therefore, under visible light, compared with pristine Uio-66, Uio-66-NH₂ exhibited more excellent performance due to the enhanced light harvesting. Similar functionalized MIL-125-NH₂ was reported for photoreduction of CO₂ into HCOOH. Light harvesting can be solved by using porphyrin derivatives as organic linkers, since porphyrin rings have 26 π electrons which are highly conjugated leading to the highly photosensitive properties. Chen et al. presented a series of porphyrin-based Zr-MOFs, ZrPP-n-M (M = H₂, Zn, Cu, Fe, Co, n = 1, 2), toward photoreduction of CO₂ under visible light irradiation (Fig. 3). Among these M-ZrPP-n crystal materials, ZrPP-1-Co exhibited the best photocatalytic activity for CO₂ conversion, splitting CO₂ into CO with high selectivity of 96.4% without cocatalyst. Similarly, PCN-222 was used for photoreduction of CO₂ into HCOOH under visible light region.

Fig. 2 (A) Proposed mechanism for the photocatalytic CO₂RR over MIL-125-NH₂ under visible light irradiation. Copyright (2012) Wiley-VCH. (B) Proposed mechanism of the photocatalytic amine oxidation over MIL-125-NH₂. Copyright (2014) Elsevier. (C) Sketch map of the possible electron-transfer mechanism in the MOF with MLCT interaction. Copyright (2016) American Chemical Society. (D) (a) Calculated electron localization function (ELF) plots for Bi-mna. (b) Fukui function F’(ı) and F’(r) for Bi-mna. The isosurface value is 0.0015 e Å⁻². Bi purple, C brown, O red, N gray, H pink. Copyright (2015) Wiley-VCH. (E) (a) Schematic representation of a light-harvesting MOF microcrystal. The MLCT excited states undergo rapid intraframework energy migration to carry out electron transfer quenching at the MOF/solution interface. (b) Chemical structures of the photocative MOF building blocks and reductive (TMDB) and oxidative (BQ) quenchers. Copyright (2011) American Chemical Society.

Fig. 3 (A) The structure of ZrPP-n. (a) ZrIV-pyrogallate coordination chain. (b) Structure of ZrPP-1. (c) Structure of ZrPP-2. (d) Augmented rod-like rib topology of ZrPP-n, where the green rods and blue squares represent ZrIV-pyrogallic pillars and porphyrinic nodes. C black, O red, N blue, Zr Green, metal (in porphyrin core) yellow, all H atoms are not depicted for clarity. (B) UV–vis diffuse-reflectance spectroscopy (DRS) of ZrPP-1-Co and mixture of ZrIV-pyrogallate chain and THPP-Co, with their absorption onsets tagged by A and B, respectively. (C) Time courses of CO obtained from CO₂ photoreduction with catalysts of ZrPP-1-M under visible light irradiation. Copyright (2017) Wiley-VCH.

Besides the design of ligands, metal ions or metal clusters can also be used as visible light collection centers. For example, Fe(III)-based MOFs consisting of Fe₃O₄–μ₄-O clusters can be served as photocatalysts for various photocatalytic reactions. Under visible light irradiation, MIL-88B(Fe) and MIL-101(Fe) were used for degradation of Rhodamine 6G in aqueous solution by Laurier et al. Because the linker was
insensitive to visible light, the Fe$_3$μ$_3$-oxo cluster was responsible for harvesting the visible light and acting as photocatalytic sites. Subsequently, Ye and co-workers combined Fe$_3$μ$_3$-oxo clusters and –NH$_2$ functionalized ligands to prepare NH$_2$-MIL-88B(Fe), NH$_2$-MIL-53(Fe) and NH$_2$-MIL-101(Fe) toward photoreduction of Cr(VI) under visible light.\textsuperscript{[56]} It was demonstrated that such a combination strategy contributed to photocatalytic activity for Cr(VI) degradation, which was owing to the improved light-adsorption sites and efficient charge transfer via LMCT. MOFs are excellent photocatalytic platform, as the light harvesting efficiency can be flexibly modulated by ligand and metal cluster.

### 2.2.2 Active sites

Ligands are mainly responsible for collecting light in photocatalysis, while metals or clusters are usually acting as active sites for photocatalysis. In addition to the traditional stable Zr-MOFs or Ti-MOFs,\textsuperscript{[55]} novel MOF materials based on other metals and metal clusters were gradually used for photocatalysis and showed good performance. Recently, Wang et al. presented three stable MOFs, MOF-Ni, MOF-Co, and MOF-Cu, for photoreduction of CO$_2$\textsuperscript{[56]} MOF-Ni showed a high selectivity of 97.7% for splitting CO$_2$ into CO due to the strong binding between Ni and CO$_2$ while high energy barrier for H$_2$ evolution. It was demonstrated that Ni(II) ion was a good active site for CO$_2$ reduction. Introducing other highly active metals into MOFs is also a good way to increase the numbers of active sites and promote photocatalytic activity. Very recently, catalytic active Co(II) centers were anchored into the Zr-based MOF modified with thiol groups for metal insertion via post-synthetic exchange (PSE).\textsuperscript{[57]} The resulting MOF material (denoted as Zr-DMBD@Co MOF) was modified by Co-thiolate units, which exhibited high photocatalytic activity (TON = 97941) and high selectivity (98% for CO) toward CO$_2$ conversion under visible light irradiation. In addition, modification of different metals in porphyrin centers as active sites also promotes photocatalytic activity, due to adding new active center and further greatly boosting separation efficiency of the photogenerated electrons and holes in porphyrin sections. In 2016, Ye and co-workers realized modular optimization within MOFs through incorporating single atoms into porphyrin center (Fig. 4A).\textsuperscript{[60]} MOF-525, MOF-525-Zn and MOF-525-Co were used for photocatalytic CO$_2$RR under visible light irradiation, and the MOF-525-Co exhibited highest activity toward CO generation (200.6 μmol g$^{-1}$ h$^{-1}$) than that of MOF-525 and MOF-525-Zn (Fig. 4B-C). The enhanced diversity in activity for two catalysts was attributed to the different charge separation efficiencies caused by different metal locating porphyrin center. Therefore, different active sites dispersion in MOF exhibited photocatalytic activity because of the energy transfer from ligand to the lower energy center at Co or Zn “trap site” (Fig. 4D-E). In fact, the electron trapping effect promotes the charge separation efficiency. Apparent embodiment of the different catalytic active sites exhibited diversity.

### 2.2.3 Charge separation

Efficient charge separation and long lifetime of charge separation are critical for photocatalytic reaction, as the recombination of charges will hinder the smooth migration of charges and abate catalytic activity. A large number of studies on promoting electron-hole separation and extending charge separation lifetime were devoted to developing efficient MOF photocatalysts,\textsuperscript{[59]} such as the introduction of other metals as intermediaries,\textsuperscript{[60]} the integration of photosensitive dyes into MOF frameworks,\textsuperscript{[49]} doping with metal nanoparticles (NPs)\textsuperscript{[61]} and composing of other semiconductors.\textsuperscript{[62]} Ti-substituted NH$_2$-UiO-66(Zr/Ti) was synthesized by a post-synthetic exchange method, exhibiting a reinforced activity for both HER and CO$_2$RR under irradiation.\textsuperscript{[66]} ESR experiments and density functional theory (DFT) calculations showed that the enhanced photocatalytic activity was attributed to the efficient electron transfer from ligand to Zr$^{4+}$ ion through mediator at Ti section. The integration of photosensitive dyes into MOF frameworks also can greatly promote charge separation and lengthen charge separation time. Recently, Kong and co-workers designed and synthesized an Eu-Ru(phen)$_3$-MOF (phen = phenanthroline) by combing Ru(phen)$_3$ with dinuclear Eu(III), and the developed MOF can convert CO$_2$ into HCOOH at the rate of 321.9 μmol h$^{-1}$ mmol$_{MOF}^{-1}$ (Fig. 5).\textsuperscript{[51]} The results of UV-vis absorption and time-resolved photoluminescence (PL) revealed that the electrons transfer from ligand to Eu$_2$ oxoclusters due to quenching effect after Eu$_2$ coordination (Fig. 5A-B).

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*Fig. 4* (A) View of the 3D network of MOF-525-Co featuring a highly porous framework and incorporated active sites. (B-C) Time dependent CO and CH$_4$ evolution over MOF-525-Co (green), MOF-525-Zn (orange), MOF-525 (purple) photocatalysts, and H$_2$TCPP ligand (pink). (D) The optimized structure for CO$_2$ adsorption on a porphyrin-Co unit. (E) The C=O bond length-dependent CO$_2$ activation energy barrier. Key: charged with one electron (orange), neutral state (green). Copyright (2016) Wiley-VCH.\textsuperscript{[148]}
Furthermore, Ultrafast transient absorption and electron paramagnetic resonance (EPR) experiments coupling with fitting the kinetics detected the electron transfer time of 1.2 ns (Fig. 5C-D). The Ru(phen)_3 ligand effectively promoted the charge separation and electrons transfer to clusters, further improving charge separation lifetime (Fig. 5F). In addition, Lin’s group has been committed to photocatalytic reactions in photosensitive ligand-integrated MOFs. They have successfully integrated the Ir/Ru/Re complex into UiO-67 toward photocatalytic OER, CO₂RR, and organic photocatalysis.[69] Similarly, Kitagawa’s group integrated the [Ru(H₂bpydc)(terpy)(CO)]PF₆ and Ru(phen)_3 into UiO-67 by PSE method.[64] The developed MOF was used for photoreduction of CO₂, and the HCOOH was the main product.

![Fig. 5](image-url) (A) Normalized UV-vis spectra of Eu-Ru(phen)_3-MOF and H₂L in DMF. Inset: Emission luminescence spectra of Eu-Ru(phen)_3-MOF and H₂L (λex = 465 nm). (B) Normalized luminescence decay traces of Eu-Ru(phen)_3-MOF and H₂L over the first 50 ns (λem = 377 nm). Inset: Decay transients measured at 630 nm (λex = 465 nm). (C) Transient absorption spectra of Eu-Ru(phen)_3-MOF and H₂L at various time delays, and (D) Corresponding kinetic traces at 604 nm. (E) Time profiles of HCOO⁺ catalyzed by Eu-Ru(phen)_3-MOF or H₂L or without catalyst under visible light. (F) Schematic light-induced dynamics of Eu-Ru(phen)_3-MOF based on the initial excitation of the Ru photo-center and the pathways of electron transfer from Ru to catalytic Eu₃ oxo-cluster center. Copyright (2018) Nature Publishing Group.[64]

The above examples are all methods that directly change the building elements of MOF to promote charge separation and increase separation lifetime. Compounds of other substances can achieve the same purpose. Noble-metal NPs were loaded on MOFs, which not only had the surface plasmonic effect, but also had the cocatalytic effect.[65] On the one hand, under visible light illumination, the hot electrons can be injected into MOF from the photoexcited noble-metal NPs, thus the extra photogenerated electrons will enhance photocatalytic activity. On the other hand, the excited NPs can induce electrostatic field near nanoparticles, which will increase charge distance, and prolong carrier lifetime along with low recombination probability. Choi et al. covalently attached Re-based complex into UiO-67 and loaded Ag nanocubes into MOF (Ag⊂Re₃-MOF) (Fig. 6).[64] The enhancement of near-surface electric field of photoactive Re centers on Ag nanocubes, results in a 7-fold increase for CO₂ to CO conversion along with a long-term stability about 48 h under visible light. In addition to loading with noble-metal NPs, other semiconductor materials have also been doped into MOFs, including metal oxides sulfide-based semiconductor and g-C₃N₄ etc. Most of semiconductor materials combined with MOFs, which can form Schottky junction to prolong charge separation lifetime. Semiconductor TiO₂ was accurately positioned in the different pores of MIL-101 and its derivatives. The TiO₂ units was photoexcited to provide photogenerated electrons which efficiently transfer to the catalytic metal clusters in MOFs for photoreduction of CO₂.[66] Cu₂O was encapsulated in Cu₃(BTC)₂ (BTC=1,3,5-benzene tricarboxylate) used for photocatalytic CO₂ reduction.[67] The MOFs not only suppresses the Cu₂O corrosion, but also promotes the charge separation and CO₂ uptake. CdS coupled with Co-ZIF-9 was applied for photocatalytic CO₂RR,[68] and ZnIn₂S₄ was dispersed on MIL-125-NH₂ toward photocatalytic HER.[69] g-C₃N₄ is not only a visible light collector due to its conjugated polymeric characteristic, but also can promote efficiently charge separation. g-C₃N₄ nanosheets were combined with UiO-66, such a hybrid showed enhanced photocatalytic performance on CO₂ to CO conversion due to prolonging of charge separation lifetime.[70]

![Fig. 6](image-url) Structures of Re₃-MOF and Ag⊂Re₃-MOF for plasmon-enhanced photocatalytic CO₂RR. (A) Zr₆O₆(H₂O)₆(BTC)₄ secondary building units are combined with BPDC and ReTC linkers to form Re₃-MOF. The structure of Re₃-MOF identified from single-crystal X-ray diffraction is shown. The 12-coordinated Zr-based metal clusters are interconnected by 21 BPDC and 3 ReTC linkers in a face-centered cubic array. Atom labeling scheme: C, black; O, red; Zr, blue polyhedra; Re, yellow; Cl, green; H atoms are omitted for clarity. (B) Re₃-MOF coated on a Ag nanocube for enhanced photocatalytic conversion of CO₂. Copyright (2017) American Chemical Society.[64]

### 2.3 MOFs for photocatalytic water splitting

#### 2.3.1 Photocatalytic HER

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Porous MOFs can provide additional photoexcited possibility through integrating the light harvesting moiety into organic ligands, and the catalytic metal ions. Such advantages make MOFs as good candidates for photocatalytic HER. The Zr-MOFs were widely developed for H\(_2\) evolution by photocatalytic water splitting, due to their high chemical stability in different solvents and excellent mechanical stability. Garcia and co-workers first utilized UiO-66 and UiO-66-NH\(_2\) for photocatalytic HER under UV or visible light in 2010, while methanol served as sacrificial electron donor.\(^{[42]}\) Compared with UiO-66, UiO-66-NH\(_2\) had a better catalytic performance due to the integration of –NH\(_2\) group, extending the region of absorption wavelength and promoting charge separation. When Pt nanoparticles was added as cocatalyst into the photocatalytic reduction system, the total amount of H\(_2\) generation accelerated evidently up to 2.4 mL (UiO-66/Pt) and 2.8 mL (UiO-66-NH\(_2\)/Pt) after 3 hours of illumination. In addition, a series of spectroscopic results revealed that the two Zr-MOFs have the veritable precondition of semiconductors due to the long-lived charge separation time. This work opened up a new path for developing MOFs as semiconductors for photocatalytic HER.

### 2.3.1.1 Doping with precious metal

After that, a lot of excellent work based on MOFs as photocatalyst has emerged. When mixing MOF with precious metals and creating a Schottky barrier at the border, the photoexcited electrons can transfer from MOFs to the precious metals in the conduction band (CB).\(^{[71]}\) As a result, loading precious metals (eg. Pt, Au and Pd) into MOFs, which efficiently promoted separation of photogenerated electron-hole pairs, suppressed the recombination of photogenerated electron-hole and prolonged the carrier lifetime.\(^{[72]}\) In 2012, Lin and co-workers utilized Pt-deposited Zr-MOF for HER. Pt NPs were loaded into the channels of UiO MOFs which assembled by photosensitive Ir-based molecular (L1 and L2) and Zr\(_2\)(O\(_2\)OH)\(_6\).\(^{[73]}\) Higher Pt loading was observed in MOF 2 than MOF 1 as MOF 2 has a larger cavity structure and a higher Ir-complexes enrichment. Such two Pt@MOF assemblies showed outstanding performance for H\(_2\) generation with triethylamine (TEA) as electron donor in photocatalytic water splitting. After 48 h illumination, the Ir-based TONs of 3400 and 7000 for H\(_2\) generation were recorded, which were assigned to Pt@1 and Pt@2, respectively. While control groups of homogeneous K\(_2\)PtCl\(_4\)/[Ir(ppy)\(_2\)(bpy)]Cl exhibited lower TONs of 1500 and 2200, respectively. Such excellent photocatalytic activity gave the credit to efficient electron transfer from the photoexcited Ir-complexes to Pt NPs. The Pt NPs accelerated the H\(_2\) generation, and slowed down the degradation of unstable Ir-based molecular compounds. Such a method can greatly enhance the photocatalytic performance of MOF-based materials.

In 2016, to increase the photogenerated electron-hole separation efficiency, Pt NPs of ca. 3 nm were encapsulated inside of UiO-66-NH\(_2\) (Pt@UiO-66-NH\(_2\)) or attached on UiO-66-NH\(_2\) surface (Pt/UiO-66-NH\(_2\)) by Xiao et al.\(^{[74]}\) Both Pt-loading UiO-66-NH\(_2\) catalysts exhibited more excellent photocatalytic performance for HER compared with the pristine UiO-66-NH\(_2\), notably Pt@UiO-66-NH\(_2\) (Fig. 7A). In that case, the dramatically difference depends mainly on the position of Pt-loading. Pt@ UiO-66-NH\(_2\) showed outstanding cyclic performance and stability due to the encapsulation of Pt NPs into UiO-66-NH\(_2\), while the activity for Pt/UiO-66-NH\(_2\) was gradually losing owing to the Pt NPs attachments were easier to leach and aggregate. As a result of greatly shortening the electron-transfer distance to promote electron-hole separation by Pt@UiO-66-NH\(_2\), Pt@UiO-66-NH\(_2\) catalyst exhibited excellent photocatalytic activity for HER. In 2018, Jiang and co-workers also loaded Au into two types of MIL-125 surface, denoted as Pt@MIL-125/Au and Pt/MIL-125/Au (Fig. 7B).\(^{[61]}\) Plasmonic effect and Schottky junction electron trapping greatly extended the adsorption wavelength to visible light and accelerated electron-hole separation in Au-decorated Pt-MIL-125. Therefore, Pt@MOF/Au exhibited a better photocatalytic performance for HER by water splitting, far exceed the Pt/MIL-125/Au and MIL-125/Au.

![Fig. 7](A) Schematic illustration for the synthesis of Pt@UiO-66-NH\(_2\) and Pt/UiO-66-NH\(_2\) with the photocatalytic HER process over Pt@UiO-66-NH\(_2\) being highlighted. Copyright (2016) Wiley-VCH.\(^{[74]}\) (B) Schematic illustration showing the synthesis of Pt@MIL-125/Au and the corresponding Pt/MIL-125/Au and MIL-125/Au analogues. Copyright (2018) Wiley-VCH.\(^{[61]}\)
2.3.1.2 Decorating with non-noble metal
The high cost of precious metals makes it impossible to apply them on a large scale. Therefore, MOFs decorated with non-noble metals are also documented. Nasalevich et al. proposed an ingenious strategy (ship-in-a-bottle) to synthesize the Co@MOF photocatalyst toward HER.\[20] L[12] was firstly encapsulated in MIL-125-NH₂ and then CoBr₂ was added to construct Co@MOF. Compared with the pristine Ti-MOF, a 20-fold improvement for H₂ generation rate was achieved due to the encapsulation of the Co-based molecular active site into MIL-125-NH₂. Co-based molecule complex ([Co²⁺(TPA)Cl][Cl]), TPA = tris(2-pyridylmethyl)amine) was successfully encapsulated into MIL-125-NH₂ by the similar strategy.\[76] ESR results revealed that the efficient photoelectrons directly transfer from NH₂-BDC to the [Co²⁺(TPA)Cl][Cl], while hardly flow to the Ti-O clusters. Compared with pristine MOF (17 μmol g⁻¹ h⁻¹), the host Co-based complex greatly boosted H₂ generation rate (553 μmol g⁻¹ h⁻¹).

2.3.1.3 Loading with metal oxides
Metal oxide loading on MOFs for photocatalytic HER has also gradually attracted researchers’ interest. Two main methods were commonly observed for photocatalytic HER by water splitting: (1) attaching metal oxide on the surface of the MOF, (2) forming core-shell structure between metal oxide and MOFs. In 2018, Shen et al. prepared a series of UiO-66-NH₂-based complex decorated with NiO NPs, which was denoted by U6N-NiO.\[77] When the complex embedded with 10 wt% NiO, the H₂ generation rate greatly increased to 2561.32 μmol h⁻¹ g⁻¹ with eosin Y as the photosensitizer and triethanolamine (TEOA) as the electron donor by visible-light-driven. The rate has been enhanced 5 folds than that of pristine MOF and 23 folds than that of U6N-NiO (10 wt% NiO) without photosensitizer. It is demonstrated that high efficiency comes from both photoexcited eosin Y and organic ligand. The efficient photogenerated electron-hole pairs separation stems from cascadic band structure that electrons transfer to a more negative CB of NiO with high concentration of electrons along with the excellent dispersion of NiO NPs on the MOF surface. In 2018, Zhang et al. prepared the core-shell material (MIL-125-NH₂@TiO₂) by corroding MOF from outer to inner.\[78] A great deal of linker defects and oxygen vacancies were created to accelerate mass/charge transfer and offer more active sites by the pyrolysis method. As a result, compared with pristine MOF, 70 folds enhancement was caused by MIL-125-NH₂@TiO₂ core-shell material for HER.

2.3.1.4 Combining with metal sulfides
CdS is a common semiconductor photocatalyst, and is widely employed for photocatalytic water splitting for H₂ generation owing to more negative flat-band potential than reduction potential of H₂. However, the fast recombination of photogenerated electrons and holes leads to low quantum efficiency of solar light absorption. Also, the photocatalytic stability of CdS semiconductor is poor. Therefore, it is necessary to combine or deposit with other materials in order to give full play to their good properties. In early years (2013), CdS NPs were first embedded on MOFs by Wang and co-workers with greatly enhanced photocatalytic efficiency. Due to the large specific surface area of MIL-101(Cr) and good dispersion of CdS NPs, the more active sites and photoexcited location were caused.\[79] After that, CdS NPs also could be grown on UiO-66[80] and MIL-125[81] using hydrothermal method in situ. In addition, other sulfides loading MOFs also showed excellent photocatalytic performance for HER, such as Cd₀.₆Zn₀.₄S@UiO-66-NH₂[82] and ZnIn₂S₄@MIL-125-NH₂[83].

2.3.1.5 Doping with metal phosphides
Given the unique structural and electronic properties of transition-metal phosphides (TMPs) (e.g. Co₃P, Ni₃P, etc.), they have been considered as promising noble-metal-alternative cocatalysts for photocatalytic HER. However, the large size, small interface contact with semiconductors and easy agglomerate are still challenging issues. In recent years, Sun and co-workers first time reported the fabrication of the MOF (UiO-66-NH₂) doped with monodisperse, small-size, and noble-metal-free TMPs for photocatalytic H₂ production.\[84] TMPs@MOF composites exhibited significantly enhanced H₂ production rates. Thermodynamic and kinetic studies demonstrate that the doping of TMPs can greatly accelerate the linker-to-cluster charge transfer, which promote charge separation and reduction the activation energy of H₂ production.

2.3.1.6 Introducing with carbon-containing materials
In recent years, carbon-containing materials, such as g-C₃N₄ and reduced graphene oxide (RGO), are gradually introduced into MOFs due to their good photoelectrochemical properties.\[85] g-C₃N₄ is a planar pi-conjugated non-metallic semiconductor with medium band gap. Introducing g-C₃N₄ into MOFs can effectively promote the separation and transmission of photogenerated electrons and holes, prolong the lifetime of electrons and holes, and improve the photocatalytic performance. Recently, Zhou et al. synthesized the composite catalyst of CFB/ MIL-125-NH₂ (CFBM) by covalent bonds, utilizing the g-C₃N₄ functionalized by benzoic acid (CFB) and MIL-125-NH₂.\[81] As a result, CFBM exhibited a high H₂ generation rate of 1.123 mmol h⁻¹ g⁻¹, which caused an enhancement about 6 folds than that of the pristine MOF. Graphene is composed of a 2D carbon atom layer, which has flexible structure, good optical and electrical properties. Cao and co-workers introduced the RGO into CdS@NU-1000 to prepare the composite of CdS@NU-1000/RGO toward photocatalytic water splitting for HER.\[86]
2.3.1.7 Hybridizing with covalent organic frameworks (COFs)

Porous COFs have attracted attention in photocatalytic water splitting for H2 generation attributed to the high stability, large surface areas and porosity. Integrating the COF into MOFs can combine the advantages of both, and design high stable and porous hybrid materials with light absorption locations and active sites. Recently, Lan and co-workers designed and prepared the MOF/COF complex for HER under visible light. Uio-66-NH2 was anchored onto TpPa-1-COF by covalent bonds. The Uio-66-NH2/TpPa-1-COF exhibited outstanding photocatalytic activity of HER (23.41 mmol g⁻¹ h⁻¹), which is 20 folds higher than that of pristine COF (Fig. 8).

2.3.2 Photocatalytic OER

Both OER and HER are half reaction in water splitting. In general, it is sluggish for OER in kinetic, due to the high overpotential, high energy barrier and the rate determining step involving multiple electrons participation. Therefore, compared with HER in photocatalytic water splitting, the development of OER is relatively limited, which is also more restricted than hydrogen production in the field of MOFs.

In 2011, three iridium-based MOF photocatalysts were prepared via incorporating three iridium-based complexes into Uio-67 respectively, and were used to photocatalytic OER by Lin and co-workers. Compared with pristine MOF and homogeneous catalyst, the three modified MOF photocatalysts have high stability and catalytic activity, when the cerium ammonium nitrate served as an oxidant. Subsequently, in 2012, they synthesized two stable Uio-MOFs with elongated dicarboxylate ligands based on the Ir complexes. The detailed kinetic investigations of Ce⁴⁺-driven and MOF-catalyzed in OER were carried out by diffuse-reflectance UV-vis absorption, luminescence, X-ray photoelectron and IR spectra. Moreover, they established the diffusion reaction model for MOF-catalyzed OER.

In addition to the incorporation of noble metal complexes into MOF, non-noble metal complexes have also been introduced into MOF for OER. In 2013, Das and co-workers successfully encapsulated the [(Mn(tpy))₃(μ-O)]²⁺ (tpy = 2,2':6',2″-terpyridine), denoting by MnTD, into the MIL-101(Cr) cage for OER. Such a simple method greatly improved the sustainability of catalysis with minimized degradation of side-reactions. In MIL-101(Cr), the cage is too small to migrate to the adjacent cage for the catalyst, while the cavity itself is enough to provide catalytic environment for active sites. Therefore, the catalyst molecule can be detained in the cage.

In the cage, its function is similar to that of a homogeneous system, but it can be separated from the accumulation of catalysts. Compared with homogeneous catalyst, this cage encapsulation catalyst caused the 20 times enhancement of TON in OER with good sustainability.

In 2016, Su and co-workers employed three Fe-based MOFs, MIL-101(Fe), MIL-88B(Fe) and MIL-53(Fe), as photocatalysts for OER. Among them, MIL-101(Fe) showed high photocatalytic activity for OER when Na₂S₂O₇ served as the electron acceptor and [Ru(bpy)]₃²⁺ acted as the sensitizer under visible light. [Ru(bpy)]₃²⁺ was transformed to [Ru(bpy)]₂⁺ under photocexcitation and the photogenerated electrons transferred to S₂O₇²⁻, generating the SO₄²⁻ and SO₃²⁻. As the oxidation potential of SO₄²⁻ is higher than that of [Ru(bpy)]₂⁺ ([E (SO₄²⁻//SO₃²⁻) = +2.40 V vs. Ag/AgCl], [E (Ru(bpy)]₂⁺//Ru(bpy)]³⁺) = +1.12 V vs. Ag/AgCl), which is a strong oxidant can convert [Ru(bpy)]₂⁺ into [Ru(bpy)]³⁺. The catalyst provided the electrons for accumulated [Ru(bpy)]³⁺. Finally, the generated holes of catalyst were consumed by water which was oxidized to generate O₂.

2.3.3 Photocatalytic overall water splitting

Photocatalytic water splitting is a carbon-free and sustainable alternative to fossil fuels. Through the combination of HER and OER, overall water splitting aim to light fuel conversion. In 2017, An et al. developed a Al-based MOF (Al-ATA-Ni) for photocatalytic overall water splitting. They selected amino-modified ligand to construct the MOF, and aimed to incorporate Ni⁴⁺ into the pore via the coordination of amino groups and Ni⁴⁺ ions (Fig. 9A-B). Compared with the O₂ evolution rate of 16.5 mmol h⁻¹ for Al-ATA MOF without Ni⁴⁺ incorporation, the Al-ATA-Ni MOF exhibited much higher O₂ evolution rate of 155 mmol h⁻¹. The Al-ATA-Ni MOF also showed excellent performance for HER at a rate of 36.0 mmol h⁻¹, while the Al-ATA MOF kept silent for HER. The attenuation of light absorption intensity between 450-650 nm of the resulting MOF, may be due to the d-d transition of the Ni⁴⁺ ions in an octahedral environment (Fig. 9B). However, it is demonstrated that Al-ATA-Ni MOF is more conducive to enhancing electron-hole separation via the PL and UV-vis diffuse reflectance spectra.

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In 2018, Li and co-workers employed the Cd-TBAPy MOF as the bifunctional catalyst for photo-reduction and oxidation of water (Fig. 9C)\cite{22} Cd-TBAPy MOF showed wide adsorption region from UV to visible light attributed to the organic ligand. It is demonstrated that the Cd-TBAPy is an n-type semiconductor via the analysis of Mott-Schottky measurement. Combination of Mott-Schottky measurement and UV-vis analysis, the bandgap, CB and VB were recorded at 2.15 eV, ~0.05 eV and 2.10 eV. After loading Pt cocatalyst, the H$_2$ generation rate is about 4.3 µmol h$^{-1}$ by Cd-TBAPy catalyst. After loading CoPi cocatalyst, the Cd-TBAPy exhibited high oxygen evolution rate of 81.7 µmol h$^{-1}$ by Cd-TBAPy catalyst.

Table 1. MOF catalysts for photocatalytic CO$_2$RR.

<table>
<thead>
<tr>
<th>MOF catalyst</th>
<th>Main product</th>
<th>Illumination range</th>
<th>Catalytic activity</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>UiO-66-NH$_2$</td>
<td>HCOO$^-$</td>
<td>Visible</td>
<td>13.2 µmol</td>
<td>[95]</td>
</tr>
<tr>
<td>NH$_2$-UiO-66(Zr/Ti)-120-16</td>
<td>HCOO$^-$</td>
<td>Visible</td>
<td>3.4 mmol h$^{-1}$</td>
<td>26</td>
</tr>
<tr>
<td>NH$_2$-UiO-66(Zr)</td>
<td>HCOO$^-$</td>
<td>Visible</td>
<td>5.8 mmol h$^{-1}$</td>
<td>26</td>
</tr>
<tr>
<td>MIL-125</td>
<td>HCOO$^-$</td>
<td>UV</td>
<td>4.28 µmol g$^{-1}$ h$^{-1}$</td>
<td>[43]</td>
</tr>
<tr>
<td>MIL-125-NH$_2$</td>
<td>HCOO$^-$</td>
<td>Visible</td>
<td>16.28 µmol g$^{-1}$ h$^{-1}$</td>
<td>[43]</td>
</tr>
<tr>
<td>MIL-101(Fe)</td>
<td>HCOO$^-$</td>
<td>Visible</td>
<td>147.5 µmol g$^{-1}$ h$^{-1}$</td>
<td>[53c]</td>
</tr>
</tbody>
</table>

2.4 MOFs for photocatalytic CO$_2$RR

2.4.1 Ligand candidate

MOFs have exhibited great potential for photoreduction of CO$_2$ due to its modifiable ligands, high CO$_2$ adsorption and clear metal active sites.\cite{36d,53b} By modifying the ligand with –NH$_2$, –NHX, or directly using photosensitive molecules as ligands to construct MOF, the absorbance range of MOF can be extended and the absorbance performance can be improved. The porous structure of MOF is usually tunable, which has a certain adsorption capacity for CO$_2$. MOFs with well-defined structure, is more conducive to clarifying the catalytic active sites and further studying the catalytic mechanism. The summary of MOF catalysts for photocatalytic CO$_2$RR is shown in Table 1.

In view of the facile availability, unique connection angle-mode, and a wide range of functional groups of Isophthalic acid (IPA), Wang and co-workers first reported the Ti-IPA MOF (MIP-208) that combines the as-prepared Ti$_6$ oxoclusters and in situ acetylation of the 5-NH$_2$-IPA linker.\cite{93} MIP-208 was utilized as a cocatalyst to participate in photoreduction of CO$_2$ cooperating with ruthenium oxide, resulting in easily capturing and reducing of CO$_2$. It will open up a new path in photoreduction of CO$_2$ by emerging functionalized ligands, different active metals and photosensitive compounds into MOFs. Cheng and co-workers focused on the facet regulation based on NH$_2$-MIL-125(Ti) for improving the photocatalytic activity.\cite{94} The different exposed facets of NH$_2$-MIL-125(Ti) ((001), (111), and co-exposed (001) and (111) facets) were successfully prepared with various morphologies. The (111) facets exhibit a large specific surface area, which provide a superior CO$_2$ uptake and more active sites for the CO$_2$ reduction.

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<table>
<thead>
<tr>
<th>Material</th>
<th>HCOO⁻</th>
<th>Visible</th>
<th>Productivity (µmol g⁻¹ h⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH₃-MIL-101(Fe)</td>
<td>HCOO⁻</td>
<td>Visible</td>
<td>445</td>
</tr>
<tr>
<td>MIL-53(Fe)</td>
<td>HCOO⁻</td>
<td>Visible</td>
<td>74.25</td>
</tr>
<tr>
<td>NH₃-MIL-53(Fe)</td>
<td>HCOO⁻</td>
<td>Visible</td>
<td>116.25</td>
</tr>
<tr>
<td>MIL-88(Fe)</td>
<td>HCOO⁻</td>
<td>Visible</td>
<td>22.5</td>
</tr>
<tr>
<td>NH₃-MIL-88(Fe)</td>
<td>HCOO⁻</td>
<td>Visible</td>
<td>75</td>
</tr>
<tr>
<td>PCN-222</td>
<td>HCOO⁻</td>
<td>Visible</td>
<td>60</td>
</tr>
<tr>
<td>MOF-525</td>
<td>CO</td>
<td>Visible</td>
<td>64.02</td>
</tr>
<tr>
<td>MOF-525-Zn</td>
<td>CO</td>
<td>Visible</td>
<td>111.7</td>
</tr>
<tr>
<td>MOF-525-Co</td>
<td>CO</td>
<td>Visible</td>
<td>200.6</td>
</tr>
<tr>
<td>ZrPP-1-Co</td>
<td>CO</td>
<td>Visible</td>
<td>210</td>
</tr>
<tr>
<td>ZrPP-1-Fe</td>
<td>CO</td>
<td>Visible</td>
<td>61.8</td>
</tr>
<tr>
<td>ZrPP-1-Cu</td>
<td>CO</td>
<td>Visible</td>
<td>40.4</td>
</tr>
<tr>
<td>NNU-13</td>
<td>CH₄</td>
<td>Visible</td>
<td>704</td>
</tr>
<tr>
<td>NNU-14</td>
<td>CH₄</td>
<td>Visible</td>
<td>25</td>
</tr>
<tr>
<td>NNU-28</td>
<td>HCOO⁻</td>
<td>Visible</td>
<td>12</td>
</tr>
<tr>
<td>Co-ZIF-9</td>
<td>CO</td>
<td>Visible</td>
<td>52.8 12</td>
</tr>
<tr>
<td>Al-PMOF</td>
<td>CH₃OH</td>
<td>Visible</td>
<td>41.8</td>
</tr>
<tr>
<td>Al PMOF embedded Cu²⁺</td>
<td>CH₃OH</td>
<td>Visible</td>
<td>37.5</td>
</tr>
<tr>
<td>Eu-Ru(phen)₃-MOF</td>
<td>HCOO⁻</td>
<td>Visible</td>
<td>262.6</td>
</tr>
<tr>
<td>UiO-66-Cr³⁺CAT</td>
<td>HCOO⁻</td>
<td>Visible</td>
<td>321.9 90</td>
</tr>
<tr>
<td>UiO-66-Ga³⁺CAT</td>
<td>HCOO⁻</td>
<td>Visible</td>
<td>1724.3 88</td>
</tr>
<tr>
<td>UiO-67-Re(5,5′-dcbpy)(CO)₃Cl</td>
<td>CO</td>
<td>Visible</td>
<td>TON = 5</td>
</tr>
<tr>
<td>Y[Ir(ppy)₂(4,4′-dcbpy)]₃(OH)</td>
<td>HCOO⁻</td>
<td>Visible</td>
<td>118.8</td>
</tr>
<tr>
<td>(Cd₃)[Ru(5,5′-dcbpy)₂]₂(Me₂NH₂)ₙ</td>
<td>HCOO⁻</td>
<td>Visible</td>
<td>67.5</td>
</tr>
<tr>
<td>(Cd[Ru(ppy)(4,4′-dcbpy)]₂ 3H₂O)n</td>
<td>HCOO⁻</td>
<td>Visible</td>
<td>67.5</td>
</tr>
<tr>
<td>UiO-67-Cp*Rh(5,5′-dcbpy)Cl₂(10%)</td>
<td>HCOO⁻</td>
<td>Visible</td>
<td>464</td>
</tr>
<tr>
<td>MOF-253-Ru(5,5′-dcbpy)(CO)₂Cl₂</td>
<td>CO</td>
<td>Visible</td>
<td>46.5</td>
</tr>
<tr>
<td>Ag⊂Re₂-MOF-16 nm</td>
<td>CO</td>
<td>Visible</td>
<td>16.8</td>
</tr>
<tr>
<td>Pt/MIL-125-NH₂</td>
<td>HCOO⁻</td>
<td>Visible</td>
<td>32.4</td>
</tr>
<tr>
<td>Au/MIL-125-NH₂</td>
<td>HCOO⁻</td>
<td>Visible</td>
<td>16.3</td>
</tr>
<tr>
<td>Cu₃(BTC)₂@TiO₂</td>
<td>CH₄</td>
<td>UV</td>
<td>2.64</td>
</tr>
</tbody>
</table>

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Introducing photosensitive molecules into MOF for photocatalytic CO$_2$RR can also improve the light absorption range and intensity, and promote charge separation. As we all know, Re(CO)$_3$(bpy)X complexes were good photosensitizers and were widely used in photoreduction of CO$_2$. Instead of bpy ligand, fac-ReBr(CO)$_3$(4,4’-dcbpy) (dcbpy = 2-phenylpyridine-5,40-dicarboxylic acid) was successfully entrapped into the cages of the MIL-101-NH$_2$(Al) for CO$_2$ conversion under visible light, which is a sensible strategy designed by Stanley’s group for the integration of molecular photosensitizers into MOF. Some of the works have focused on photosensitized ligands such as porphyrins and their derivatives to construct MOF toward photoreduction of CO$_2$. [23, 52, 58] Jiang and co-workers utilized PCN-222 as a photocatalyst for converting CO$_2$ into HCOOH (60 µmol g$^{-1}$ h$^{-1}$) with 100% selectivity under visible light. [23] Compared with porphyrin ligand, detrimental electron-hole recombination was greatly inhibited in PCN-222 owing to the deep electron trap state, which demonstrated the relationship between the electron-hole separation efficiency and the photocatalytic activity. In addition, ZrPP-n-M ($n$ = 1, 2, M = H$_2$, Zn, Cu, Fe, Co) have been successfully synthesized and further utilized in CO$_2$ photoreduction, and the ZrPP-1-Co exhibited much higher CO generation rate of 14 µmol g$^{-1}$ h$^{-1}$ than other ZrPP-n-M MOFs. [52] Similarly, atomic dispersion of active sites (Co or Zn) in MOF-525, and the Co-MOF-525 exhibited relatively good performance for CO$_2$ photoreduction. [58]

### 2.4.2 Metal/metal oxygen clusters

As the secondary building unit, metal/metal oxygen clusters are not only important components of MOFs, but also play an indispensable role in the elaboration of the photocatalysis mechanism. Ti–O, Zr–O, Fe–O and polyoxometalates (POMs) are common metal oxygen cluster-based MOFs for the photoreduction of CO$_2$. MIL-125(Ti) series are the main representative of the Ti–O clusters. The Zr–O clusters mainly contain UiO-66 series and porphyrin-based Zr-MOF. The Fe–O clusters include MIL-101(Fe), MIL-88(Fe) and MIL-53(Fe) series. POMs mainly concern the reductive Zn-ε-Keggin based MOFs. In addition, other non-noble metals also exhibited relatively effective photocatalysts, such as Co-based MOFs. In MIL-125-NH$_2$ photoreduction system, it was important to detect the valence changes in the reaction process by EPR experiments, and to propose a reasonable photocatalytic mechanism. [43] Under the irradiation of visible light, the excited photoelectrons were transferred from the organic ligand to the Ti–O cluster, while the electron holes were consumed by sacrificial agents (TEOA). Ti$^{4+}$ was reduced to Ti$^{3+}$, and the CO$_2$ was reduced into HCOOH on Ti$^{3+}$. Li and co-workers utilized the post-synthetic exchange method to synthesize Ti-substituted NH$_2$- UiO-66(Zr/Ti) for enhancing photocatalytic performance in CO$_2$ reduction (CO$_2$ to HCOOH). [60] DFT calculations and ESR results showed that electrons tend to transfer to Ti$^{4+}$ than that to Zr$^{4+}$ when the part of Zr$^{4+}$ was replaced by Ti$^{4+}$. Ti$^{4+}$ was reduced to Ti$^{3+}$ in excited (Ti$^{3+}$/Zr$^{4+}$)–O cluster, thus the Ti$^{3+}$ can further provide electrons to Zr$^{4+}$ to form Ti$^{4+}$–O–Zr$^{4+}$. The electron transfer mechanism is similar to previously reported Fe-doped SrTiO$_3$ and zeolite-anchored bimetallic assemblies. Such incorporation of the second metal is conducive to promoting the interfacial charge transfer from organic ligand to clusters, which is contributed to photocatalytic activity. Most of the excitation and transfer of electrons in MOFs correspond to LMCT mechanism, but the mechanism of synergistic light response between ligands and metal clusters are observed in the MOFs constructed by Fe–O clusters, such as NH$_2$-MIL-53(Fe), NH$_2$-MIL-88B(Fe) and NH$_2$-MIL-101(Fe). Fe–O clusters can be directly excited by visible light, leading to that electron was induced from O$^{2-}$ to Fe$^{3+}$. Besides of the direct excitation, Fe center accepted the electron from the excited ligand modified by –NH$_2$. Thus, these Fe-based MOFs with amine modification can significantly enhance their catalytic performance for CO$_2$ photoreduction (CO$_2$ to HCOOH) owing to the synergistic effect of dual excitation routes.

MOFs constructed by these high-valent metal oxygen clusters was widely used for the photoreduction of CO$_2$. The main products are two-electron products, such as HCOOH or CO. Recently, Lan and co-workers found that incorporating reductive POM (Zn-ε-Keggin) into porphyrin-based MOF can boost eight-electron products (CH$_4$) in photoreduction of CO$_2$ (Fig. 10). [86] Given that eight Mo$^7$ atoms can theoretically provide 8 electrons to accomplish the multi-electrons transformation process of CO$_2$ into CH$_4$, NNU-13 and NNU-14 were synthesized and used for CO$_2$ photoreduction with the high selectivity of CH$_4$ over 96%. DFT calculations revealed that the photo-excited electrons more easily transfer from TCPP linker to Zn-ε-Keggin unit. Such a sensible approach, assembling strong reductive cluster into photosensitive

<table>
<thead>
<tr>
<th>TiO$_2$-Co-ZIF-9</th>
<th>CO</th>
<th>UV-visible</th>
<th>8.8 µmol g$^{-1}$ h$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_4$</td>
<td></td>
<td>UV-visible</td>
<td>2.0 µmol g$^{-1}$ h$^{-1}$</td>
</tr>
<tr>
<td>CdS- Co-ZIF-9</td>
<td>CO</td>
<td>Visible</td>
<td>TON = 12.6</td>
</tr>
<tr>
<td>CdS- Co-MOF-74</td>
<td>CO</td>
<td>Visible</td>
<td>TON = 9.9</td>
</tr>
<tr>
<td>CdS- Mn-MOF-74</td>
<td>CO</td>
<td>Visible</td>
<td>TON = 0.3</td>
</tr>
<tr>
<td>CdS-Zn-ZIF-8</td>
<td>CO</td>
<td>Visible</td>
<td>TON = 0.2</td>
</tr>
<tr>
<td>CdS-Uio-66-NH$_2$</td>
<td>CO</td>
<td>Visible</td>
<td>TON = 0.1</td>
</tr>
<tr>
<td>Zn$_2$GeO$_4$Zn-ZIF-8</td>
<td>CH$_3$OH</td>
<td></td>
<td>0.22 µmol g$^{-1}$ h$^{-1}$</td>
</tr>
<tr>
<td>Cd$<em>2$Zn$</em>{0.5}$UiO-66-NH$_2$ (20%)</td>
<td>CH$_3$OH</td>
<td>Visible</td>
<td>6.8 µmol g$^{-1}$ h$^{-1}$</td>
</tr>
<tr>
<td>g-C$_3$N$_4$:Co-ZIF-9</td>
<td>CO</td>
<td>Visible</td>
<td>495 µmol g$^{-1}$ h$^{-1}$</td>
</tr>
<tr>
<td>CNNS-Uio-66(2Zr)</td>
<td>CO</td>
<td>Visible</td>
<td>2.9 µmol g$^{-1}$ h$^{-1}$</td>
</tr>
</tbody>
</table>
architecture, could inspire to develop more reductive MOF or other materials for selective photoreduction of CO₂ into CH₄ or other high-valued hydrocarbons.

Wang et al. demonstrated that the active metal center can cooperate with μ-OH of ligand to promote the CO₂ photoreduction.⁹¹ At 1.0 atm, the MOFs with μ-OH ligands neighboring the open Co catalytic centers exhibited high CO selectivity (98.2%) and TOF (0.059 s⁻¹). Combination of isotope tracing experiments and periodic DFT calculations revealed that the μ-OH ligands act as the strong hydrogen-bonding donors to stabilize the initial Co-CO₂ adduct and serve as local proton sources to accelerate the C–O bond breaking.

2.5 MOFs for photocatalytic organic transformation

Under light irradiation, photocatalysts can be photoexcited to generate electron-hole, which provides the platform for reduction (reacting with electrons) and oxidation (reacting with holes) of organic molecules, offering a new methodology for the synthesis of fine chemicals. In 2011, Lin and co-workers developed two modified UiO-67 (MOF 5 and MOF 6) by incorporation of [Ir(ppy)₂(dcbpy)]Cl₂ (H₂L₃) and [Ru(’ppy)₂(dcbpy)]Cl₂ (H₂L₄)⁹⁰. The two MOFs were served as photocatalysts toward Aza-Henry reactions with tetrahydroisoquinoline as the amine substrate in CH₂N₂O₂ solvent under visible light. The catalytic conversion efficiency of the two MOF catalysts can reach up to 97% after 12 h, which is comparable to that of homogeneous catalysts. Moreover, the catalysts also exhibited excellent cyclic stability compared with homogenous catalysts. Then, they also found that the MOF 6 exhibited excellent performance for photocatalytic aerobic amine coupling reactions and photocatalytic aerobic oxidation of thioanisole. The cyclic experiments revealed that there was no loss of activity and no deterioration of the MOF frameworks.

Chiral MOFs showed promise as heterogeneous asymmetric catalysts, as the chiral active sites can be immobilized into the porous MOF framework. The strategy was adopted by Wu et al. in 2012.²¹ The organocatalyst L- or D-pyrrolidin-2-ylimidazole (PYI) were incorporated into the frameworks as well as containing the tri phenylamine photoredox group, denoting as Zn-PYI1 and Zn-PYI2 respectively. Catalytic activities of Zn-PYI1 and Zn-PYI2 toward light-driven asymmetric α-alkylation of aliphatic aldehydes were evaluated. In these MOFs, the triphenylamine was excited and induced the photogenerated electrons transport, acting as an active intermediate for α-alkylation (Fig. 11A). Meanwhile, the chiral PYI served as the cooperative active sites of α-alkylation, driving asymmetric catalysis with excellent stereoselectivity (Fig. 11B). Such a collaborative strategy, integration of chiral active sites and photosensitive ligands into MOF frameworks, is essential for enantioselective photocatalysis. Another similar strategy was developed for heterogeneous asymmetric photocatalysis by Tang and co-workers in 2017, establishing the tunable MOF frameworks by chiral photoredox ligands and various metal ions.²⁴ The resulting MOFs, S(R)-Ti-MOF, S(R)-Zn-MOF and S(R)-Zr-MOF, exhibited efficient photocatalytic activity for α-alkylation of aldehydes due to the synergistic effect of photoredox chiral ligand and metal ions (Fig. 11C). Compared with pristine S(R)-HL, these MOFs showed enhancement for catalytic activity at 25 W illumination under visible light (Fig. 11D). For Ti-MOF, LUMO and HOMO were located at Ti d-orbital and organic linker respectively, accessing to an effective overlap. When the ligand was excited under visible light, the photogenerated electrons transferred from ligand to Ti⁴⁺ species giving rise to Ti³⁺ as active site. Therefore, the Ti-MOF exhibited a superior photocatalytic active for α-alkylation of aldehydes. For Zn-MOF, the weak adsorption of visible light led to much lower conversion than Ti-MOF. Binding energy of d orbital in Zr is too low to overlap with π* orbital of ligand efficiently, resulting in relatively low transformation for the organic reaction.

MOFs were also applied for organic oxidation reaction. The photocatalytic activity of UiO-66-NH₃ was evaluated by oxidation of hexyl alcohol, cyclohexanol, cyclohexane and benzyl alcohol.²¹⁴ Recently, Xiao et al. developed Cu@UiO-66 and Cu/Cu@UiO-66 for oxidation of aromatic alcohols under visible light.²¹⁵ Cu@UiO-66 was prepared by the encapsulation of Cu quantum dots (QDs) into UiO-66 cages via double-solvent approach (DSA). The advanced double-solvent approach (ADSA) was adopted to synthesize Cu@ UiO-66 by encapsulating the QDs and simultaneously load Cu NPs. 0.1%Cu/Cu@UiO-66 exhibited high photocatalytic activity for

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conversion aromatic alcohols into aldehydes due to the cooperation of plasmonic effect and Schottky junction. The work on the oxidation of aromatic alcohols to aldehydes has also been reported by Jiang’s Group. They prepared Pt/PCN-224(M) (M = Zn, Ni, Co, Mn, 2H) composites by loading the Pt nanocrystals to porphyrin-based MOFs, PCN-224(M).\textsuperscript{[116]} The Pt/PCN-224(M) exhibited excellent photocatalytic activity for oxidation of aromatic alcohols under O\textsubscript{2} atmosphere, thanks to the combination of singlet oxygen production and photothermal effect. In addition, the hot electrons transferred from plasmonic Pt into MOF, reducing the electron density of Pt surface. The oxidation reaction can be modulated via competition between plasmonic and Schottky junction. They also developed the Pt/PCN-777 and Pt/MOF-808 as photocatalysts for selective benzylamine oxidation along with the generation of H\textsubscript{2} fuel.\textsuperscript{[117]} Such coupled reactions showed great potential of combining H\textsubscript{2} evolution with organic transformation to produce high value chemicals. The similar work about oxidation of benzylamine was documented by Zhang and co-workers.\textsuperscript{[118]} The bipyridyl-containing Cd-MOFs were used as photocatalysts toward oxidation of benzylamine, and exhibited high selectivity for converting benzylamine into N-benzylbenzaldimine.

2.6 MOFs for photocatalytic contaminant degradation
Photocatalysis is an efficient and alternative method for the degradation of contaminant by solar energy. MOFs have high porosity, tunable scale and modulated semiconducting functions, which is a good platform for photocatalytic contaminant degradation. MOFs have been used for degradation of organic dyes, aromatic molecules, Cr(VI) and other contaminants. In photocatalytic degradation of organic dyes, the performance of photocatalysis is usually evaluated by the time of color change, because light-induced active substances attack weak organic bonds of dyes making dyes colorless in this process.\textsuperscript{[119]} Three common organic dyes were frequently reported to evaluate the MOF photocatalytic performance, including Rhodamine family, Methyl Orange and Methyl Blue. In 2013, Roeffaers’s group utilized Fe(III)-based MOFs toward the degradation of Rhodamine 6G. It is demonstrated that Fe\textsubscript{3+}-μ\textsubscript{3}-oxo clusters of MOFs are crucial for photocatalytic degradation of Rhodamine 6G, which unveiled the prelude in the study of photocatalysis of Fe-based MOF.\textsuperscript{[54]} Subsequently, MIL-53(Fe) served as a photocatalyst for photocatalytic degradation of Rhodamine B cooperating with H\textsubscript{2}O\textsubscript{2} under visible light.\textsuperscript{[120]} In such a synergistic system, the degradation rate enhanced 4.3-folds than that of the system without H\textsubscript{2}O\textsubscript{2} due to the activation of H\textsubscript{2}O\textsubscript{2} by MIL-53(Fe).
results of transient photocurrent responses and hydroxyl radicals (·OH) detection revealed that the H₂O₂ can be activated by MIL-53(Fe) to generate ·OH undergoing two pathways. Under visible light irradiation, photogenerated electrons transferred from the excited state of MIL-53(Fe) to H₂O₂, giving rise to ·OH. Further, the ·OH was used to degrade organic dyes.

Aromatic compounds are relatively stable, not easy to decompose, and have strong toxicity, which will cause serious environmental pollution and great harm to human body. In the participation of H₂O₂, the benzene was oxidized to phenol under visible light irradiation using the MIL-100(Fe) and MIL-68(Fe) as catalysts. Fe-O clusters were photoexcited to generate photoelectrons that were captured by H₂O₂ to form ·OH radicals via a Fenton-like reaction. The ·OH radicals attacked the benzene ring to generate the corresponding radicals, and then formed phenol with the electrons transfer and the proton release. Phenol needs to be further degraded into less toxic products. In 2007, MOF-5 was employed to photodegrade phenol and N, N, N', N'-tetramethyl-p-phenylenediamine to a less toxic compound under visible light. Under photoexcitation, MOF-5 served as a semiconductor with a band gap of 3.4 eV, and the charge separation lifetime is up to 30 μs. Interestingly, it was demonstrated that the bulky phenol substrate showed an enhanced degradation rate compared with phenol. In addition, a dicarboxyl-functionalized Fe³⁺-salen complex was incorporated into two heterometallic-organic frameworks, denoted as [Zn₂(Fe-L)₂(μ₂-O)(H₂O)₂]·4DMF·4 H₂O and [Cd₂(Fe-L)₂(μ₂-O)(H₂O)₂]·2DMF·H₂O (H₄L=1,2-cyclohexanediamino-N,N'-bis(3-methyl-5-carboxysalicylidene), which was employed for photocatalytic degradation of 2-chlorophenol under visible light. When tert-butyl alcohol (TBA) as ·OH radical scavenger was added into the photocatalytic system, the degradation activities dramatically decreased about 44% for [Zn₂(Fe-L)₂(μ₂-O)(H₂O)₂]·4DMF·4 H₂O and 19% for [Cd₂(Fe-L)₂(μ₂-O)(H₂O)₂]·2DMF·H₂O. The ·OH quenching results revealed that the degradation process of 2-chlorophenol predominantly involved the attacking by ·OH radicals when the above resulting MOFs sever as photocatalysts. The central [salen-Fe³⁺] was coordinated by H₂O to form [salen-Fe³⁺-OH] species, which was attacked by hydrogen peroxide from the axial site of the Fe³⁺ center giving rise to [salen-Fe³⁺OOH] species. The [salen-Fe³⁺OOH] was photoexcited, forming [salen-Fe³⁺OOH]* under visible light irradiation. Subsequently, ·OH radical species and [salen-Fe(V)=O] were emerged by breaking O-O bond. Finally, 2-chlorophenol was degraded by the generated ·OH radicals immediately.

Cr(VI) has strong migration ability and toxicity, thus reducing it to Cr(III) is an environmentally friendly strategy to remove Cr(VI) pollutants from wastewater. MIL-88B(Fe) served as photocatalyst toward degradation of Cr(VI) into Cr(III) under visible light irradiation, which was recorded by monitoring the decolorization of diphenylcarbazide (DPC)-Cr(VI) complex solution through UV-vis absorption spectroscopy. UV-vis spectra revealed that Cr(VI) was almost completely degraded by MIL-88B(Fe) after 45 minutes irradiation. It was demonstrated that the lower the pH solution led to the better degradation activity. In addition, compared with MIL-88B(Fe), UiO-66-NH₂ and MIL-125-NH₂, NH₂-MIL-88B(Fe) exhibited the best photocatalytic performance on the degradation of Cr(VI), which was attributed to two light harvesting sections including both amino ligands and Fe=O clusters. Other MOFs also can be used for the photocatalytic reduction of Cr(VI) under visible light, such as MIL-68(In) and MIL-68(In)-NH₂. Mott-Schottky results and degradation results suggested that MIL-68(In)-NH₂ is a promising photocatalyst toward the reduction of Cr(VI) due to the relatively high CB.

2.7 MOF-derivatives for photocatalysis

Although MOFs possess huge potential in photocatalysis due to their unique properties, the moisture sensitivity and instable coordination bond between metal clusters and organic ligands, hinder the development of MOFs for photocatalysis. For example, the reaction environment (wide pH solution) significantly affects the stability of MOFs and the low electrical conductivity of MOFs limits the application in catalytic reactions. It is worth noting that MOF-derivatives inherit the superior properties of pristine MOFs with outstanding stability. In recent years, MOF-derivatives have been widely developed for various photocatalytic reactions such as photocatalytic water splitting, CO₂RR and contaminant degradation. As promising photocatalysts, MOF-derivatives possess unique advantages, for example, the high porosity can promote the charge carriers with the substrates access to active sites and inhibit the volume recombination of electrons and holes. Here, we summarize the remarkable application of MOF-derivatives in photocatalysis in the last several years (Table 2).

Table 2. Recent remarkable summary of the MOF-derivatives for photocatalysis.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>MOF precursor</th>
<th>Reaction</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO/ZnS</td>
<td>MOF-5</td>
<td>HER</td>
<td>[127]</td>
</tr>
<tr>
<td>CdS/ZIF</td>
<td>Zn/Co ZIFs</td>
<td>HER</td>
<td>[128]</td>
</tr>
<tr>
<td>Cu-TiO₂/C</td>
<td>HKUST-1</td>
<td>HER</td>
<td>[129]</td>
</tr>
<tr>
<td>Ni/g-C₃N₄</td>
<td>Ni-based MOF</td>
<td>HER</td>
<td>[130]</td>
</tr>
<tr>
<td>MOC-16@CZIF</td>
<td>ZIF-8</td>
<td>HER</td>
<td>[131]</td>
</tr>
<tr>
<td>TiO₂</td>
<td>MIL-125-NH₂</td>
<td>HER</td>
<td>[132]</td>
</tr>
<tr>
<td>g-C₃N₄/α-Fe₃O₄</td>
<td>g-C₃N₄/MIL-100</td>
<td>HER</td>
<td>[133]</td>
</tr>
<tr>
<td>CuₓCo₂₋ₓS₄@MoS₂</td>
<td>Cu/Co MOF</td>
<td>HER</td>
<td>[134]</td>
</tr>
<tr>
<td>Cu/TiO₂</td>
<td>Cu-MOF</td>
<td>HER</td>
<td>[135]</td>
</tr>
<tr>
<td>Co₁₁Te₆C₃C</td>
<td>ZIF-67</td>
<td>CO₂RR</td>
<td>[136]</td>
</tr>
</tbody>
</table>

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PMMeCoCC-1200 Co-MOF74 CO₂RR [137]
Co₂O₃ HoMSSs ZIF-67 CO₂RR [138]
CoO₀.₅ NS ZIF-67 CO₂RR [139]
MWCNT@MOF-derived MIL-68(In) Photodegradation of tetracycline (TC) [140]
In₀.₇S₃ magnetic carbon-αFe/Fe₃O₄ Zn-doped MIL-53(Fe) Photodegradation of TC [141]
CoO/C MOF-5 Photodegradation of TC [142]
M₅S₉O₃@C M-MOF (M = Co, Zn, Cu, Ni) Photodegradation of TC [143]
HKUST-1-P-300 HKUST-1 Photodegradation of phenol [144]

2.7.1 Photocatalytic HER

Semiconductor nanostructures as photocatalysts for HER have caused considerable attention. The semiconductor structure derived from MOFs effectively improves the activity and stability of the catalyst in photocatalytic hydrogen production.²¹²⁵[a, 128, 145] Zhao and co-workers developed a MOF-templated strategy to fabricate heterostructured ZnO/ZnS with excellent photocatalytic HER activity.²¹²⁷ The heterostructured ZnO/ZnS can be adjusted to enhance photocatalytic activity and visible-light absorption through controlled calcination of host-guest MOF-5 and thioacetamide. The nanoscale ZnS@C exhibited an excellent light absorption capability and charge separation efficiency with enhanced photocatalytic HER activity (435 μmol g⁻¹ h⁻¹) and recoverability. Recently, Chen and co-workers designed a novel MOF-derived photocatalyst decorated with CdS nanoparticles via annealing the N-containing MOF.²¹²⁸ The economic CdS/Zn₃O₃·O₄(CdS/ZCO) nanohybrid showed outstanding catalytic activity and excellent stability for hydrogen production. When the optimized loading of CdS nanoparticles reached 30%, the hydrogen evolution rate reached to 3978.6 μmol g⁻¹ h⁻¹ with sacrificial agent, and the hydrogen evolution efficiency of CdS/ZCO is four times higher than that of CdS/Co₃O₄ or CdS nanospheres.

2.7.2 Photocatalytic CO₂RR

Owing to the high thermodynamic stability of the linear CO₂ molecule, MOF-derivatives have been considered as functional photocatalysts to improve the energy conversion efficiency of CO₂ photoreduction.²¹³⁰⁻¹⁴⁰ Wang and co-workers reported a sequential templating approach (STA) to prepare the Co₃O₄ dodecahedron with hollow multi-shelled structures (HoMSSs).²¹³⁸ The Co₃O₄ nanocrystals well inherited the topologic arrangement of Co atom in ZIF-67, increasing the exposure of (111) facets, which possesses high activity for CO₂ photoreduction. In addition, quadruple-shelled (QSS) Co₃O₄ HoMSSs exhibited 3 and 5 times higher catalytic activity than Co₃O₄ HoMSSs without facet control and Co₃O₄ nanoparticles, respectively. Recently, Su et al. fabricated hollow nickel hydroxide nanocages (Ni(OH)₃-NCs) derived from ZIF-8 via ion-assisted etching protocol.²¹⁴⁷ The optimal cavernous structure with thin walls significantly improved light harvest, which promote multiple light reflection and scattering, static charge transfer and facilitate the coherent energy flow. the optimized structure of Ni(OH)₃-NCS-2 achieved a remarkable CO evolution rate of 1.44 × 10⁵ μmol g⁻¹·cat⁻¹·h⁻¹ and a desirable CO selectivity of 96.1%.

2.7.3 Photocatalytic degradation of dyes

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3. MOFs and MOF-derivatives for electrocatalysis

Electrocatalysis is an efficient method for converting electrical energy into chemical energy, such as electrocatalytic water splitting, ORR, CO₂RR, NRR and electroorganic synthesis. Efficient electrocatalysts possess the advantages of (i) favorable electrical conductivity, (ii) more active sites, (iii) excellent charge transfer and carrier separation. Currently, traditional commercial precious metal electrocatalysts suffer from expensive price, rare reserves and poor stability. Thus, a large number of materials have been developed to avoid these issues, such as transition metal composites, semiconductive composites and carbon composites. As a new generation of electrocatalysts, MOFs possess the features with ultrahigh surface areas, definite structure and clear active sites, which are beneficial to investigate the electrocatalytic reaction mechanism (the adsorption and separation of carrier, mass transfer and active sites access, etc.). In following section, we will introduce the mechanism for energy-related MOF-based electrocatalysts, the strategies of improving electrocatalytic performance and the applications of electrocatalysis of MOF-based materials (including electrocatalytic water splitting, ORR, CO₂RR, NRR, etc.).

3.1 Mechanism and criteria for energy-related electrocatalysts

The cathodic HER is the simplest electrocatalytic reaction, which involves a central intermediate and a two-electron transfer. The basic step can be depicted by Volmer-Heyrovsky mechanism or Volmer-Tafel mechanism, as shown in the following reaction (equation (1) to (5)).

Volmer step (120 mV dec⁻¹):

\[ \text{H}_2\text{O} + e^- \rightarrow H^* + \text{OH}^- \] (alkaline solutions)

\[ \text{H}_2\text{O}^+ + e^- \rightarrow H^* + \text{H}_2\text{O} \] (acidic solutions)

Heyrovsky step (40 mV dec⁻¹):

\[ H^* + \text{H}_2\text{O} + e^- \rightarrow \text{H}_2 + \text{OH}^- \] (alkaline solutions)

\[ H^* + H^+ + e^- \rightarrow H_2 \] (acidic solutions)

Tafel step (30 mV dec⁻¹):

\[ H^* + H^* \rightarrow H_2 \] (alkaline/acidic solutions)

The rate of the reaction is highly related to the Gibbs' free energy for hydrogen evolution ($\Delta G_{\text{H}_2}$). A volcano relationship (Fig. 13A) revealed the Sabatier principle: If the binding between $H^*$ and catalysts is too strong, the Volmer step (adsorption) will be limited. On the contrary, if the binding is too weak, the Heyrovsky/Tafel (desorption) will limit the overall reaction. Controlling the binding energy of catalytic reaction intermediates is the key to improving activity. Theoretical research has shown that the activity trend is based on hydrogen adsorption (H_{ad}) of active sites in acidic environment while the trend is controlled by three crucial descriptors in alkaline environment: (a) The H_{ad} on the electrocatalyst surface, (b) the prevention from the adsorption of hydroxyl (OH_{ad}), and (c) the energy for $\text{H}_2\text{O}$ dissociation. As shown in the HER volcano plot, platinum (Pt) possesses optimal binding energy ($\Delta G_{\text{H}_2} \approx 0$) with only negligible overpotential in acidic environment.

OER in acidic or alkaline environment is a complex four-electron process and involves several intermediates (OH*, O* and OOH*) on the catalyst surface (Equations (6)-(15), E⁰ represents thermodynamic potential). Many different reaction mechanisms have been proposed for heterogeneous OER electrocatalysis, such as oxide path, electrochemical metal peroxide path, electrochemical oxide path and lattice O participated mechanism. The most difficult step in OER is to form OOH* on the metal surface by decomposing water on the adsorbed O* and this formation is an uphill at the equilibrium potential (1.23 V vs. RHE) for OER. The voltage above 1.23 V to motivate OER is defined as overpotential.

\[ 2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4e^- \] (alkaline solutions)

\[ 4\text{OH}^- \rightarrow \text{O}_2 + 2\text{H}_2\text{O} + 4e^- \] (alkaline solutions)

Proposed mechanism based on DFT calculations in acidic solutions:

\[ 2\text{H}_2\text{O} \rightarrow \text{OH}^* + \text{H}^* + e^- \] (8)

\[ \text{OH}^* \rightarrow \text{O}^* + \text{H}^+ + e^- \] (9)

\[ \text{O}^* + \text{H}_2\text{O} \rightarrow \text{OOH}^* + \text{H}^+ + e^- \] (10)

\[ \text{OOH}^* \rightarrow \text{O}_2 + \text{H}^+ + e^- \] (11)

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Proposed mechanism based on DFT calculations in alkaline solutions:

\[ \text{OH}^- \rightarrow \text{OH}^* + e^- \]  
\[ \text{OH}^- + \text{OH}^* \rightarrow \text{O}^* + \text{H}_2\text{O} + e^- \]  
\[ \text{O}^* + \text{OH}^- \rightarrow \text{OOH}^* + e^- \]  
\[ \text{OOH}^* + \text{OH}^- \rightarrow \text{O}_2 + \text{H}_2\text{O} + e^- \]  

For metal-based catalysts, the oxygen adsorption energy can often be used as a single descriptor to draw a volcano plot (Fig. 13B). It can be observed that the state-of-art IrO$_2$ is an active OER catalyst while IrO$_2$ still binds oxygen too strong. Therefore, achieving stabilization of OOH$^*$ and OH$^*$ is crucial for designing catalysts. In addition, except for adsorption energy, some other descriptors such as d-band center and e$_g$ filling degree can also be utilized to evaluate the OER catalytic activities. While for metal oxides, \( \Delta G_{\text{OOH}} \) is hampered by associative/dissociate mechanism when the metal binds oxygen too weak.

ORR is a core half-reaction in electrochemical energy devices such as electrolyte membrane fuel cells (PEMFCs) and metal-air batteries. Various intermediates including O*, OH* and OO H* species could be generated during ORR. Oxygen is generally reduced by two ways during ORR process, including a direct four-proton-electron pathway (Equations (16)-(17)) to generate HO$_2$-species (HOOH or OH-) and indirect two-proton-electron two pathways (Equations (18)-(19)) to generate hydrogen peroxide. The direct reduction route is highly efficient for application since H$_2$O$_2$ reduces the energy conversion efficiency and accelerates the electrolyte degradation in PEMFCs. Direct four-proton-electron pathway:

\[ \text{O}_2 + 2\text{H}_2\text{O} + 4e^- \rightarrow 4\text{OH}^- \] (alkaline solutions)  
\[ \text{O}_2 + 4\text{H}^+ + 4e^- \rightarrow 2\text{H}_2\text{O} \] (acidic solutions)  

Indirect two-proton-electron pathway:

\[ \text{O}_2 + \text{H}_2\text{O} + 2e^- \rightarrow \text{HO}_2^- + \text{OH}^- \] (alkaline solutions)  
\[ \text{O}_2 + 2\text{H}^+ + 2e^- \rightarrow 2\text{H}_2\text{O} \] (acidic solutions)  

Two possible mechanisms including associative mechanism and dissociation mechanism are proposed in the following steps (in acidic solutions):

**Associative:**

\[ \text{O}_2 + \ast \rightarrow \text{O}_2\ast \]  
\[ \text{O}_2\ast + \text{H}^+ + e^- \rightarrow \text{OOH}^* \]  
\[ \text{OOH}^* + \text{H}^+ + e^- \rightarrow \text{O}^* + \text{H}_2\text{O} \]  
\[ \text{O}^* + \text{H}^+ + e^- \rightarrow \text{OH}^* \]  
\[ \text{OH}^* + \text{H}^+ + e^- \rightarrow \text{H}_2\text{O} + \ast \]  

**Dissociative:**

\[ \text{O}_2 + 2\ast \rightarrow 2\text{O}^* \]  
\[ 2\text{O}^* + 2\text{H}^+ + 2e^- \rightarrow 2\text{HO}_2 \]  

In most instances, the rate of overall ORR is determined by the following steps: (a) the first electron transfer to the adsorbed O$_2$ molecules at the surface of electrocatalysts, (b) \( \text{O}_2 \) hydration, and (c) the desorption of H$_2$O. A theoretical ORR activity volcano plot was established using \( \Delta E_0 \) as a descriptor, where Pt is near the top (Fig. 13C). As illustrated in the ORR volcano plot, when the metal binds oxygen too strong, the property will be limited by the proton-electron transfer between intimate O* and OH*. On the contrary, the activity is hampered by associative/dissociate mechanism when the metal binds oxygen too weak.

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products.\textsuperscript{[165]} DFT calculation was conducted to provide theoretical guidance and a volcano plot was drawn as shown in Fig. 13D.\textsuperscript{[162]} The DFT calculations suggested that if the metal binds CO* too strong, the overpotential of CO2RR will be limited by the protonation of CO* to CHO*. On the other hand, the protonation of CO to CHO* will be the determined reaction.\textsuperscript{[162]}

Electrocatalytic NRR (2N₂ + 6H₂O → 4NH₃ + 3O₂) possesses high efficiency and has the ability to occur under moderate conditions. The detailed reactions at both cathode and anode are presented (Equations (33)-(36)).

Cathodic reaction:

\begin{align*}
N₂ + 6H₂O + 6e^- &\rightarrow 2NH₃ + 6OH^- \quad \text{(alkaline solutions)} \\
N₂ + 6H^+ + 6e^- &\rightarrow 2NH₃ \quad \text{(acidic solutions)}
\end{align*}

Anodic reaction:

\begin{align*}
4OH^- &\rightarrow 2H₂O + O₂ + 4e^- \quad \text{(alkaline solutions)} \\
2H₂O &\rightarrow O₂ + 4H^+ + 4e^- \quad \text{(acidic solutions)}
\end{align*}

When the metal binds N too strong, the catalytic activity is limited by the protonation of NH* to NH₂* or the evolution of NH₂* as NH₃. On the other hand, when metal binds N too weak, the reductive adsorption of N₂ to N₂H* is limited in the first step.\textsuperscript{[166]} Furthermore, the HER can be a major competing reaction during NRR for the electrocatalysts near the top of the volcano. It is worth highlighting that limiting the supply of proton and electron can suppress HER therefore motivate Table 3. Summary of benchmark MOF electrocatalysts for HER.

![Table 3. Summary of benchmark MOF electrocatalysts for HER.](image)

3.2 Electrocatalytic water splitting

3.2.1 Electrocatalytic HER

The electrocatalytic water splitting is a clean and efficient method to generate H₂. Pt is the most efficient electrocatalyst in both acidic and alkaline conditions. Yet, the high cost and scarcity of noble metals limit its practical applications. So, it is highly desirable to develop non-noble metals-based catalysts for HER. Enzymes such as hydrogenases and nitrogenases which can produce hydrogen contain Ni-Fe and Fe-Mo active sites for catalysis. Inspired by nature and DFT calculations (volcano plots in Fig. 13A), Co, Fe, Ni and Mo-based homogenous and heterogeneous electrocatalysts were developed for efficient HER. Yet, the drawbacks such as large overpotentials and low stability hindered their electrocatalytic applications. Most of the MOFs are constructed from transition metals which are earth-abundant. The pore environments and electronic structures of MOFs could be systematically modulated. Also, MOFs could be easily functionalized with HER active components such as inorganic nanoparticles or molecules. All these merits as well as their intrinsic activity make MOFs promising electrocatalysts for HER. Though, there are only limited reports of MOFs for HER reaction (Table 3) and the development of MOFs for HER application is still at its early stage.
POMs, a rich family of soluble metal-oxygen anion clusters of early transition metals in high oxidation states (Mo^{V,VI}, W^{VI,V,V}), have reversible multivalence reduction/oxidation states, which are active HER molecular catalytist.\[184\] POM could be used as building blocks to form porous POM-based MOFs (POMOMFs).\[185]\ The first report of MOFs for electrocatalytic HER was reported by Nohera et al. in 2011 by introducing POMs into MOFs to construct POMOMFs.\[28\] The 3D electroactive POMOF (TBA)$_4$[PMo$_8$V$_4$O$_{36}$(OH)$_2$Zn$_2$][C$_6$H$_4$(COO)$_2$]$_{36}$H$_2$O (ε(trim)$_{4/3}$) was fabricated by using Zn-modified ε-Keggin POM as building blocks and connecting with trimesic acid likers. The HER activity of ε(trim)$_{4/3}$ was studied in pH = 1 electrolyte that contains 1 M of alkali cations (Li$^+$, Na$^+$, K$^+$). ε(trim)$_{4/3}$-based electrode demonstrated higher HER active than Pt and a TON as high as 1.2×10$^4$ after 5 h was achieved. The excellent activity of this POMOF for HER were mainly attributed to the unique 3D open framework structures and the confinement effect of electroactive POMs into the pores of MOFs. Since then, a series of POM-based MOFs were developed for efficient HER catalysis.\[168-169, 186\] Later, Qin et al. synthesized two novel 3D POMOMFs (TBA)$_4$[PMo$_8$Mo$_4$O$_{36}$(OH)$_2$Zn$_2$][BTB]$_{4/3}$xGuest (NENU-500) and (TBA)$_4$[PMo$_8$Mo$_4$O$_{36}$(OH)$_2$Zn$_2$][BPT] (NENU-501) by using Zn-modified ε-Keggin POM and tri-carboxylate acids BTB and BPT.\[186\] In both NENU-500 and NENU-501, the electroactive ε-Keggin POM moiety connects with organic ligands as node directly, which will expose more accessible active sites. The HER activities of NENU-500 and NENU-501, as well as ε(trim)$_{4/3}$, ε(trim)$_{5}$, and HKUST-1 for comparison, were investigated in 0.5 M H$_2$SO$_4$ solution. In all the MOFs studied, NENU-500 demonstrated the best HER activity, with an overpotential of 237 mV at 10 mA cm$^{-2}$, which is much larger than that of MOS 1. MOS 1 also demonstrated high stability and good durability in electrocatalysis under acid conditions. The results indicated that metal dithiolen-based 2D MOFs are promising HER electrocatalysts. Yet, the different performance between BHT and THT ligands-based MOS 1 and MOS 2 were not elucidated.

Later, Feng's group reported the synthesis of nanosheet layer of 2D MOF H$_2$[Ni$_2$(THT)$_2$] (THT-Ni) by using Langmuir-Blodgett method, as shown in Fig. 14A. THT-Ni is isostructural with MOS 2 and the lateral dimensions of the fabricated nanosheet are several millimeters with thickness of about 0.7-0.9 nm. Due to the sufficient exposure of Ni-dithiolene moieties in 2D MOF, THT-Ni demonstrated high HER activity, with an overpotential of 333 mV at 10 mA cm$^{-2}$, which is 190 mV lower than that of MOS 1. MOS 1 also demonstrated high stability and good durability in electrocatalysis under acid conditions. The results indicated that metal dithiolene-based 2D MOFs are promising HER electrocatalysts. Yet, the different performance between BHT and THT ligands-based MOS 1 and MOS 2 were not elucidated.

Zhang et al. reported two novel POM-encapsulated MOFs with 1D nanotube-like channels (metal-organic nanotube frameworks, MONT)\[169\] By using Dawson-type POMs as templates, the coordination assembly of Cu$^{II}$ dithiolene diamine (M-N) coordination bonds-based planar 2D MOFs reported POMOMFs. The main drawbacks for MOFs as HER electrocatalysts are their poor conductivity. Metal dithiolene (M-S) or metal-diamine (M-N) coordination bonds-based planar 2D MOFs demonstrate good electroconductivity, which have potential applications for electrocatalysis.\[187\] Clough et al. synthesized two isoreticular 2D MOFs H$_2$[Co$_2$(BHT)$_2$] (MOS 1) and H$_2$[Co$_2$(THT)$_2$] (MOS 2) with high HER activity.\[170\] isoreticular MOS 1 displayed an overpotential of 340 mA at 10 mA cm$^{-2}$ and a TOF (at 550 mA) of 0.113 s$^{-1}$ in 0.05 M H$_2$SO$_4$ solution (pH = 1.3). While MOS 2 displayed poorer electroactivity with an overpotential of 530 mA at 10 mA cm$^{-2}$, which is 190 mA lower than that of MOS 1. MOS 1 also demonstrated high stability and good durability in electrocatalysis under acid conditions. The results indicated that metal dithiolene-based 2D MOFs are promising HER electrocatalysts. Yet, the different performance between BHT and THT ligands-based MOS 1 and MOS 2 were not elucidated.

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improves the H₂ adsorption ability of Co atoms, making synergistic improvement of HER activity. Further composition of CoS₂N₂ with graphene would further improve the electron transfer process and show much better HER activity (η₁₀0 = 230 mV).

The integration of MOFs with materials with high conductivity such as graphene (oxide), carbon nanotubes (CNTs) and acetylene black (AB) is another efficient approach to improve the electroconductivity and electron transfer capability, thus enhancing the electrocatalytic activity. Jahan et al. reported a composite made from the assembly of Cu-based MOF and GO (GO/Cu-MOF) which showed good electrocatalytic performance. The synthesized pure Cu-MOF showed an overpotential (at 30 mA cm⁻²) of 369 mV with a Tafel slope of 135 mV dec⁻¹ in 0.5 M H₂SO₄ solution. When this MOF is assembled with graphene oxide (with 8 wt% GO), the HER performance was obviously improved, with an overpotential (at 30 mA cm⁻²) of 209 mV with a low Tafel slope of 84 mV dec⁻¹. The unique porous scaffold structure, synergistic interactions between the GO and MOF and improved electron transfer lead to the enhanced HER activity and good stability.

Fig. 14 (A) Synthesis of a 2D MOF THT-Ni single-layer sheet by using the Langmuir–Blodgett method at an air/water interface. (B) HER polarization plots of the THT-Ni electrode in 0.5 M H₂SO₄. The inset shows the corresponding Tafel plot. aqueous solution. Copyright (2015) Wiley-VCH. [172] (C) Schematic synthesis of single-layer 2D MOFs THTA-Co and THAT-Ni. (D) HER polarization plots of THTA-Co, THAT-Ni and THTA-Co in 0.5 M H₂SO₄. Copyright (2017) Wiley-VCH. [172]

Wu et al. reported the combination of a Co-MOF (CTGU-S) with conductive AB to get a new MOF composite (AB/CTGU-S) with superior HER activity. CTGU-S is 2D structure with one H₂O molecule coordinated to Co atom. The onset potential, overpotential (η₁₀₀) and Tafel slope of pure CTGU-5 electrocatalyst are 298 mV, 388 mV and 125 mV dec⁻¹ respectively. When the stoichiometric ratio between CTGU-5 and AB is 1:4 [AB/CTGU-S(1:4)], the composite exhibited superior HER properties, with an onset potential of 18 mV, an overpotential (η₁₀₀) of 44 mV and a low Tafel slope of 45 mV dec⁻¹ in 0.5 M H₂SO₄ solution. The composites of CTGU-5 with graphene/CTGU-5 (with 6 wt% graphene) also showed good HER activity with an overpotential (η₁₀₀) of 91 mV and a Tafel slope of 88 mV dec⁻¹. The unique 2D structure of CTGU-5 and the interactions between MOFs and conductive materials to improve the electron transfer of electrode contribute the high HER activities.

The large porosity and easy functionalization of MOFs makes them ideal platforms to host or compose with various HER active catalysts, such as metal sulfides, metal phosphides and precious metals to generate synergistic enhancement for HER activity. MOF scaffolds can improve the catalytic active sites, facilitate the electron transfer and mass transport, thereby boosting the electrocatalytic activities of electrodes. Hod et al. reported a high HER active composite by utilizing a mesoporous and highly stable Zr-based MOF NU-1000 film as scaffolds for the deposition of Ni₅S₇ electrocatalyst (Fig. 15A) [177]. As shown in Fig. 15B-C, The fabricated Ni₅S₇/NU-1000 electrode showed an overpotential (η₁₀₀) of 238 mV in 0.1 M HCl solution, which is 402 mV and 322 mV lower than that of NU-1000 film and Ni₅S₇ film, respectively. The Tafel slope of Ni₅S₇/NU-1000 electrode is 120 mV dec⁻¹, indicating a Volmer-Tafel reaction mechanism. Though NU-1000 have mesopores and large surface areas, the scaffold does not improve the electroactive surface areas of Ni-S. Instead, this MOF scaffold changes the environment of Ni-S, making the electrocatalytic electrode more favorable for proton transport. Later, Dai et al. anchored molybdenum polysulfide (MoS₃) on Zr-MOF UiO-66-NH₂ via one-pot solvothermal method to get a new MOF/metal sulfide composite MoS₃/UiO-66-NH₂ [178]. The optimized component of MoS₃/UiO-66-NH₂ nanocomposites showed high HER activity and excellent durability in 0.5 M H₂SO₄ solution, with an overpotential (η₁₀₀) of 200 mV and a low Tafel slope of 59 mV dec⁻¹. The electrode had a TOF of 1.28 s⁻¹ at η = 200 mV. Wang et al. fabricated MoS₂-based nanohybrid for HER by combing Cu-MOF HKUST-1 with MoS₂ nanosheets (Fig. 21C) [179]. Compared with pure MoS₂, the MoS₂/HKUST-1 nanocomposite exhibited enhanced HER activity and stability in acidic condition (0.5 M H₂SO₄ solution) with an overpotential (η₁₀₀) of 300 mV and Tafel slope of 69 mV dec⁻¹ (Fig. 15D).

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While most MOFs and composites are reported to show good HER performance in acidic solutions, the applications of MOFs for HER in basic solutions were not well studied, which is mainly because the HER kinetics in alkaline conditions are more sluggish and complex. Recently, Qiao’s group synthesized a new 2D hybrid nanosheets combing MOF Co-BDC and MoS$_2$ nanosheet via a facile sonication-assisted method, as shown in Fig. 16A.\cite{180}

The Co-BDC/MoS$_2$ electrocatalyst showed excellent HER activity in 1 M KOH solution, with an overpotential ($\eta_{10}$) of 248 mV and Tafel slope of 86 mV dec$^{-1}$. While the overpotentials ($\eta_{10}$) of Co-BDC and MoS$_2$ are 529 mV and 349 mV, respectively (Fig. 16B-C). Also, the hybrid nanosheet showed quite high stability for 15 h at a constant current density of 10 mA cm$^{-2}$. The decoration of Co-BDC on semiconducting 2H-MoS$_2$ phase leads to the partial phase transfer to metallic 1T-MoS$_2$, which is more active for HER. The interfacial interactions between Co-BDC and MoS$_2$ not only improved the intrinsic activity, but also made synergistic effect by reducing the sluggish water dissociation step in alkaline HER, paving the way for interface engineering of MOF composites for improved electrocatalytic performance.

Transition metal phosphides (TMPs) are a new type of advantageous HER electrocatalysts. The incorporation of TMPs and MOFs represents promising MOF composites for highly active HER catalysts. Liu et al. reported the doping of CoP into a Co-based MOFs to generate CoP/Co-MOF composites with superior pH-universal HER activity and high stability.\cite{181} CoP/Co-MOF exhibited an overpotential ($\eta_{10}$) of 27 mV, 49 mV and 34 mV in 0.5 M H$_2$SO$_4$, 1.0 M PBS (pH = 7) and 1.0 M KOH solutions, respectively. Experimental and DFT calculations revealed that the electron transfer from CoP to MOFs results to the optimized adsorption energy of hydrogen ($\triangle G_{\text{H,ads}}$) and water molecules ($\triangle G_{\text{H2O,ads}}$). Also, the unique porous structure of Co-MOFs contributes significantly to the remarkable HER activity of CoP/Co-MOF in different pH conditions.

Plasmonic noble metal nanoparticle can generate localized surface plasmon resonance (LSPR) driven by incident light, could provide metal nanoparticles several unique benefits, such as enhanced local electromagnetic fields and efficient charge-carrier separation.\cite{188} The resulting hot-electron injection can reduce the activation barrier of a chemical reaction by electronically or vibrationally exciting the adsorbed atoms or molecules, and was found recently can accelerate the
It’s expected that the LSPR effect can be applied in MOFs to improve the electrocatalytic activity. Wang et al. reported the composites of bimetallic MOF nanosheets (CoFe-MOFNs) and Au nanorods (Au/CoFe-MOFNs) can dramatically improve the HER activity under light illumination, as shown in Fig. 17. The Au/CoFe-MOFNs composite showed an onset potential of 228 mV, an overpotential (η10) of about 435 mV and a Tafel slope of 115 mV dec⁻¹ under dark condition at 0.1 M KOH. When irradiated with light of wavelength at 808 nm, the Au/CoFe-MOFNs composite demonstrated improved HER activity, with an onset potential of 135 mV, an overpotential (η10) of about 292 mV and a Tafel slope of 94 mV dec⁻¹ (Fig. 17B-C). Mechanism studies revealed that the enhancement of HER performance was mainly contributed from the LSPR effect that injects hot electrons from Au nanorods to CoFe-MOFNs, affording decreased activation energy for HER. This work provided a new approach to utilize solar energy to boost the electrocatalytic activity.

**3.2.2 Electro catalytic OER**

OER is the key process for fuel cells, water splitting electrolyzers and metal-air batteries. Most of the OER activity catalysts such as metal oxides are not stable in acids, so OER performances are usually investigated in strong alkaline solutions. Currently, the most efficient OER catalysts are precious metal-based IrO₂/RuO₂, which seriously suffer from the high cost, and poor operation stability. Hence, it’s highly desirable to develop earth-abundant OER catalysts with low overpotential, high mass activity and high durability.

MOFs especially metal-oxo nodes-based MOFs have been demonstrated to display promising OER activity. At the early stage, MOFs for OER are mainly based on a trial-and-error approach without a rational guidance and a clear relationship of structure-activity. Some MOFs, such as Prussian Blue-type MOFs, UTSA-76, Co-ZIF-9, ZIF-67 etc. were reported to show OER activity. Yet, their performances are not satisfactory. In the last several years, MOFs for OER catalysis are the most fantastic and fast-growing field in MOF electrocatalysts based on rational design strategies. There are three distinctive approaches to efficiently improve OER activity of catalysts: (1) improving the intrinsic activity of catalysts; (2) increasing the number of active sites via porosity or morphology control; (3) enhancing electron conductivity/charge transfer by composing. In this section, we mainly focus on summarizing the strategies to improve the OER activity of MOFs (Table 4).

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**3.2.2.1 Improving the intrinsic activity**

The coordination environments of MOFs could be modulated, thus changing the electronic structures of metal nodes and intrinsic activity of MOFs. Lu et al. prepared OER active MOF [Co₂(μ-OH)₂(BBTA)] (MAF-X27-OH) with both open metal sites and hydroxide ligands via a postsynthetic ion exchange approach of [Co₂(μ-Cl)₂(BBTA)] (MAF-X27-Cl) (Fig. 18A-B). The bridge Cl⁻ ligand of MAF-X27-Cl could be successfully replaced by OH⁻ ligand to get MAF-X27-OH by immersing MAF-X27-Cl into 1.0 M KOH solution for 24 h at RT. MAF-X27-OH coated on Cu foil exhibited an outstanding OER activity, with an overpotential (η10) of 292 mV, a Tafel slope of 88 mV dec⁻¹ in 1.0 M KOH solution (Fig. 18C). The TOF is up to 0.25 s⁻¹ at an overpotential of 400 mV and the FE is almost 100%. Controlled experiments at pH = 7 and isotope tracing experiments demonstrated that the OH⁻ ligands were involved in the OER process and it played a critical role in improved activity.

By using a modular and stepwise synthesis strategy, Shen et al. successfully introduced the paddle-wheel type cluster Co₃(RCDO)₄ with open metal sites and high catalytic activity into MOFs (Fig. 18D). After two-step postsynthetic modifications, an outstanding OER catalyst [(Fe₃(μ-O)(BOC)(CO₂)₄)(Co₂(NA)(L)₄)₃] (Fe₃-Co₂ or MCF-49) was fabricated, which otherwise can’t be synthesized directly. MCF-49 coated on GC electrode showed high OER activity, with an overpotential (η10) of 283 mV, a low Tafel slope of 43 mV dec⁻¹ and a TOF of 0.27 s⁻¹ at an overpotential of 300 mV in 0.1 M KOH solution (Fig. 18E-F). While for the pure Fe-based MOF precursors Fe₃-Fe and Fe₃ they showed very poor OER performance at the same condition. The OER performance of MCF-49 could be further improved when utilizing Nickel foams (NFs) as substrates, with an outstanding overpotential (η10) of 225 mV, a Tafel slope of 48 mV dec⁻¹, and a high TOF of 1.82 s⁻¹ at overpotential of 300 mV. The results confirmed that the introduced paddle-wheel type Co₂ cluster with special coordination environment of Co atoms contributed to the high OER performance.
While MOF catalysts for OER mainly perform at strong alkaline conditions, in which most MOFs are not stable. The development of OER catalysts in benign neutral media is much eco-friendly and practically useful. Xu et al. reported a cobalt imidazolate framework-based catalyst by introduction of high valence non-3d metal Mo (Fig. 19A). The [Co₄(MoO₄)(EIM)₆] (Co₄Mo) catalyst showed much better OER activity than RuO₂ and Co(EIM)₂ in neutral PBS solution (pH = 7), with an onset potential of 1.50 V, an overpotential (ŋ₁₀) of 490 mV, and a Tafel slope of 144 mV dec⁻¹ (Fig. 19B-D). The combination of experimental results and theoretical calculations revealed that the introducing of non-3d metals can modulate the oxidation state and electronic structure of Co. Correspondingly, the energy of OER rate-determining step and the reactant/product adsorption energy were optimized, resulting to the greatly improved OER performances.

The introduction of coordinatively unsaturated metal sites (CUMSs) have been proved to be an efficient approach to enhance the OER activity of MOFs. Plasma treatment can partially destroy the coordination geometry of metal nodes in MOFs to generate unsaturated metal sites, which could act as active sites for improving the OER performance. Tao et al. reported the treatment of MOFs with dielectric barrier discharge (DBD) plasma to create CUMSs with enhanced OER performance for the first time. Some ligands of ZIF-67 are removed via plasma treatment for several minutes to generate abundant coordinatively unsaturated Co atoms in ZIF-67 (CUMSs-ZIF-67). CUMSs-ZIF-67 showed significantly enhanced OER activity compared to pristine ZIF-67 in 1.0 M KOH solution, with an overpotential (ŋ₁₀) of 330 mV, a Tafel slope of 53.7 mV dec⁻¹, and a TOF of 0.462 s⁻¹ at an overpotential of 300 mV. While the overpotential (ŋ₁₀), Tafel slope and TOF of pristine ZIF-67 are 400 mV, 74.9 mV dec⁻¹, and 0.043 s⁻¹, respectively. The specific activity of CUMSs-ZIF-67 at potential of 1.55 V demonstrated a current of 37.35 mA m⁻² (normalized by the BET surface) compared to that of pristine ZIF-67 (3.34 mA m⁻²), indicating the good intrinsic activity of the CUMSs. DFT calculations indicated that the plasma induced CUMSs in ZIF-67 with excellent adsorption of reactant are the active sites for improved OER performances. This work provided a new route to generate unsaturated metal sites for modification of MOFs as superior OER electrocatalysts. Later, Guo et al. treated Co/Fe-based Prussian blue analogues with air plasma (Co-PBA-plasma-2h). The low-temperature air plasma contains highly reactive oxygen species, which can mildly etch the ligands in Co-PBA and react with the coordinatively unsaturated Co sites while keep the framework structure (Fig. 20A). XPS and FTIR spectra confirmed the introduction of oxygen binding to metal cations and the valence states of Co ions are increased via air plasma treatment. The plasma treated catalyst Co-PBA-plasma-2h demonstrated improved OER activity compared with pristine Co-PBA. The overpotential (ŋ₁₀) and Tafel slope of Co-PBA-plasma-2h are 274 mV, 53 mV dec⁻¹ respectively, compared with that of Co-PBA (ŋ₁₀ of 334 mV and Tafel slope of 74.9 mV dec⁻¹) (Fig. 20B-C). Remarkably, Co-PBA-plasma-2h showed
only a low overpotential of 330 mV at high current density of 100 mA cm\(^{-2}\) and a FE of near 100%.

The crystal structure, making MOFs ideal platforms to study the doping strategies to improve the OER activity. Based on this strategy, a series of bimetal/multimetal-based MOFs have been reported to show superior OER activities, resulting from the synergistic effect between different metals that can modulate the electronic structures of active sites to optimize the free energy of adsorbed intermediates.\(^{[29, 203]}\) Wang et al. synthesized a series of bimetal MOFs based on \(\text{Fe}_2\text{M}([\mu_3-O](\text{CH}_3\text{COO})_6(\text{H}_2\text{O})_3)\) (\(\text{M} = \text{Fe}, \text{Co}, \text{Ni}, \text{Zn}\)) clusters.\(^{[29]}\) The trinuclear clusters were bridged by diphenyl-3,4',5-tricarboxylic acid (BPTC) to get four stable isostructural MOFs \(\text{Fe}_3\text{BPTC} (\text{NNU-21}), \text{Fe}_2\text{Co-BPTC} (\text{NNU-22}), \text{Fe}_2\text{Ni-BPTC} (\text{NNU-23})\) and \(\text{Fe}_2\text{Zn-BPTC} (\text{NNU-24})\). All the heterometallic MOFs showed a better OER performance than the monometallic \(\text{Fe}_3\text{BPTC} (\text{NNU-21})\), and \(\text{Fe}_2\text{Ni-BPTC} (\text{NNU-23})\) showed the best OER performance, with an overpotential \(\eta_{10}\) of 365 mV, a Tafel slope of 72.2 mV dec\(^{-1}\), and a TOF of 0.03 s\(^{-1}\) at an overpotential of 400 mV in 0.1 M KOH solution (Fig. 21B). Also, NNU-23 had the largest electrochemical double-layer capacitance \(\text{C}_{\text{dl}}\) (5.10 mF cm\(^{-2}\)), which is much larger than that of NNU-21 (2.48 mF cm\(^{-2}\)), indicating the large electrochemical active surface area (ECSA) of bimetallic MOFs. DFT calculations revealed that the introduction of heteroatoms into \(\text{Fe}_3\) cluster can efficiently strengthen the adsorption of O* intermediate species, thus improving the OER activity. Further investigation of the partial density of states (DOS) of metal atoms in \(\text{Fe}_2\text{M}\) clusters demonstrated that the d-band center of \(\text{Fe}_2\text{Co}, \text{Fe}_2\text{Ni}\), and \(\text{Fe}_2\text{Zn}\) cluster are much closer to the Fermi level than that of \(\text{Fe}_3\) cluster, which leads to stronger binding interactions between the adsorbates and catalysts and essentially contributes to the improvement of OER performance of heterometallic clusters. Later, Li et al. prepared a series of trimetallic MOFs (\(\text{Fe}/\text{Ni}/\text{Co(Mn)}\)-MIL-53) with high OER activity and stability, in which the molar ratios of different metals can be precisely modulated.\(^{[203e]}\) The \(\text{Fe}/\text{Ni}\)-based bimetallic MIL-53 exhibited better OER activity than monometallic \(\text{Fe}-\text{MIL-53}\) with an overpotential \(\eta_{10}\) of 255 mV, a Tafel slope of 37.8 mV dec\(^{-1}\) for \(\text{Fe}/\text{Ni}_{1.6}\)-MIL-53 in 1.0 M KOH, in which Ni was recognized as the active center for OER while Fe could tune the intrinsic activity of catalysts. Further introducing of small amount of third metal Co or Mn into \(\text{Fe}/\text{Ni-MIL-53}\), the resulting trimetallic MOFs \(\text{Fe}/\text{Ni}/\text{Co(Mn)}\)-MIL-53 showed improved OER activity as compared with the bimetallic \(\text{Fe}/\text{Ni-MIL-53}\). The optimized trimetallic MOF \(\text{Fe}/\text{Ni}_{2.4}/\text{Co}_{0.4}\)-MIL-53 can reach a low overpotential \(\eta_{10}\) of 219 mV, and a Tafel slope of 53.5 mV dec\(^{-1}\). The synergistic effect in different metal ions was confirmed via XPS spectra. Compared with bimetallic MOFs, the Ni 2p\(_{3/2}\) in trimetallic MOFs is shifted to higher binding energy (ca. 0.4 eV), indicating the third metal doping can efficiently modify the coordination environment of the Ni active centers. Because of the synergistic effects of mixed metals, the modulation of electronic properties of the active centers is crucial for promoting the OER activity.

In electrocatalysis, doping is an efficient approach to improve the electrocatalytic performance, because the dopant can alter the electron distribution and also improve the electrical conductivity. One of the most advantage for MOFs is part of the metal clusters can be replaced without changing

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Not only the metal ions, the organic ligands also can be easily replaced in MOFs without changing the framework structure, in which their conductivity, pore size, and active centers can be simultaneously modulated. Xue et al. prepared a heterogeneity MOF A₄Bₓ-MOF-FeCo₁.₆ (A = terephthalic, B = 2-aminoterphthalic) by modulating the molar ratio of A/B [Fig. 22A]. The optimized A₄.₇B-MOF-FeCo₁.₆ MOF showed a low overpotential (η₁₀) of 288 mV, a small Tafel slope of 39 mV dec⁻¹ and a TOF of 0.46 s⁻¹ at an overpotential of 300 mV in 1.0 M KOH solution, exceeding the OER performance of A-MOF-FeCo₁.₆ and B-MOF-FeCo₁.₆ (Fig. 22B-C). Experimental and DFT calculations revealed that not only the synergistic effects of bimetals, but also the synergistic effects of mixed linkers can efficiently modulate the electronic structure of intrinsic catalytic center, improving the OER activity.

### 3.2.2.2 Increasing the active sites via morphology control

The morphology of electrocatalysts plays an important role in electrochemical performance. The ideal morphological structures can increase the number of active sites, allow superior electron transfer and provide channels for the diffusion of reactants and products, efficiently improving the electrocatalytic activities. Ultrathin 2D nanomaterials, including graphene, MoS₂, layered double hydroxides (LDHs) etc. have exhibited outstanding electrocatalytic activities due to their unique shape, high surface-to-volume ratios and exposure of more active sites on the surface. Compared with the 3D counterparts, 2D MOF ultrathin nanosheets demonstrate considerable advantages for efficient electrocatalysis. For example, the nanometer thicknesses allow the superior electron transfer, rapid mass transport and fast permeation of gas/liquid molecules, rendering enhanced performance in electrocatalysis. Moreover, the high density of exposed catalytic active surfaces, with coordinatively unsaturated metal sites improves the catalytic activity. Also, the 2D morphology is preferred to form films and increase the contact area between MOFs nanosheet and the substrate. Till now, most of the superior active OER MOF catalysts are 2D nanosheet structures, especially MOF nanosheets coated on porous conductive substrates.
NiCo-UMOFNs on glassy-carbon electrodes demonstrated an overpotential (\(\eta_{10}\)) of 250 mV, a small Tafel slope of 42 mV dec\(^{-1}\) and a TOF of 0.86 s\(^{-1}\) at an overpotential of 300 mV in 1.0 M KOH solution (Fig. 23B-C). The overpotential (\(\eta_{10}\)) of NiCo-UMOFNs was much smaller than that of bulk NiCo-MOFs (317 mV), Ni-UMOFNs (321 mV), Co-UMOFNs (371 mV), and commercial RuO\(_2\) (279 mV) at the same conditions. When NiCo-UMOFNs was loaded on conductive Cu foam, the electrode showed further enhanced OER activity with an ultralow overpotential (\(\eta_{10}\)) of 189 mV.

XAS analysis and DFT calculations revealed that the high OER activity of NiCo-UMOFNs compared with bulk NiCo-MOFs is mainly resulted from the coordinatively unsaturated metal sites on the exposed surface of ultrathin nanosheets. Also, the electronic coupling effect between unsaturated Co and Ni benefits the improvement of OER activity. This work demonstrated a new ultrathinning MOF strategy for improving OER activity.

Fig. 23 (A) Crystal structure of NiCo-UMOFNs. (B) LSV plots and (C) Tafel slopes of NiCo-UMOFNs, Ni-UMOFNs, Co-UMOFNs, RuO\(_2\) and bulk NiCo-MOFs in O\(_2\)-saturated 1.0 M KOH solution. Copyright (2016) Nature Publishing Group. (D) Illustration of synthesis of ultrathin MOF nanosheets and their utilization for OER. Copyright (2019) Wiley-VCH. (E) Schematic illustration of the exfoliation of a pillared-layer MOF and selective pillar removal. Copyright (2018) Wiley-VCH.

The large-scale synthesis of MOF ultrathin nanosheets is still a challenging task. Li et al. developed a method for large-scale and bottom-up synthesis of bimetallic MOF nanosheets for efficient OER (Fig. 23D).\(^{206a}\) The bimetallic MOF nanosheet NiM-BDC-NS (M = Fe, Al, Co, Mn, Zn and Cd) with a thickness of only several layers at large scale were prepared by a simple solvothermal method. All the MOF nanosheets were OER active, in which NiFe-BDC-NS demonstrated the best OER performance, with an overpotential (\(\eta_{10}\)) of 221 mV and a Tafel slope of 56 mV dec\(^{-1}\) in 1.0 M KOH solution. The increased active sites of the ultrathin nanosheets and the synergistic effects in mixed metals contributed to the outstanding OER activity of MOF nanosheets. Huang et al. reported a new electrochemical/chemical exfoliation strategy for synthesizing MOF ultrathin nanosheet with outstanding OER activity and stability (Fig. 23E).\(^{206c}\) A redox active pillar ligand 2,3-dihydroxy-1,4-benzenedicarboxylic acid (H\(_4\)DHBDC) was utilized to construct a pillared-layer Co-based MOF (MCF-13 or 3D-Co). When MCF-13 was applied as OER catalysts in 0.1 M KOH solution, an in situ oxidation of the pillar ligands occurred, and a new 2D MOF ultrathin nanosheet was obtained (named as MCF-12 or 2D-Co-NS). 2D-Co-NS showed a low overpotential (\(\eta_{10}\)) of 211 mV, a small Tafel slope of 46 mV dec\(^{-1}\) and a high TOF of 30 s\(^{-1}\) at an overpotential of 300 mV in 0.1 M KOH solution.

Recently, Liu’s group grew NiFe-NPC nanosheet arrays on porous NFs via simple solvothermal method and then treated the sample with UV light to get lattice-strained MOF arrays for outstanding OER activity (Fig. 24A).\(^{207}\) The interlayer spacing distance of lattice-strained NiFe-MOF is enlarged by about 0.2-0.5 Å based on the UV light treatment time as confirmed via HRTEM. The enlargement of 0.5 Å corresponds to the lattice expansion ratio of 4.3%, and the MOF is denoted as NiFe-NPC-4.3%. XPS spectroscopy indicated that the valence state of Ni is between +2 and +3, which is higher than the valence state in pristine NiFe-NPC (+2), indicating the lattice-strain modulation can redistribute the atomic and electronic configurations of Ni sites in NiFe-NPC. NiFe-NPC-4.3% exhibited the best OER activity with an overpotential of 210 mV at a high current density of 200 mA cm\(^{-2}\) and a Tafel slope of 68 mV dec\(^{-1}\) in 0.1 M KOH solution.
MOFs can be easily composed with conductive materials or OER active catalysts to significantly enhance the OER performance.\cite{208b} Zhao et al. combined 2D MOF nanosheets (CoBDC) with electrically conductive Ti$_3$C$_2$T$_x$ (the MXene phase) nanosheets to obtain a MOF composite (Ti$_3$C$_2$T$_x$/CoBDC) with outstanding OER activity (Fig. 25A).\cite{208a} The Ti$_3$C$_2$T$_x$/CoBDC nanocomposite was fabricated via an interdiffusion reaction-assisted process. Ti$_3$C$_2$T$_x$/CoBDC exhibited improved OER performance compared with CoBDC nanosheets and Ti$_3$C$_2$T$_x$ nanosheets, with an overpotential ($\eta_{10}$) of 410 mV and a small Tafel slope of 48.2 mV dec$^{-1}$ in 0.1 M KOH solution (Fig. 25B-C). In the nanocomposite, CoBDC provided large active surface area, while the electrically conductive Ti$_3$C$_2$T$_x$ boosted the charge transfer process across the hetero-interface, making a synergistic effect to improve the OER activity.

![Fig. 25](image_url) (A) Illustration of fabrication of Ti$_3$C$_2$T$_x$/CoBDC hybrid for OER. (B) LSV plots and (C) Tafel slopes of Ti$_3$C$_2$T$_x$/CoBDC, IrO$_2$, and Ti$_3$C$_2$T$_x$/CoBDC hybrid in N$_2$-saturated 0.1 M KOH. Copyright (2017) American Chemical Society.

### Table 4. Summary of benchmark MOF electrocatalysts for OER.

<table>
<thead>
<tr>
<th>MOFs</th>
<th>Electrolyte</th>
<th>Substrate</th>
<th>$E_{\text{onset}}$ (V vs. RHE)</th>
<th>$\eta_{10}$ (mV)</th>
<th>Tafel slope (mV dec$^{-1}$)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>UTSA-16</td>
<td>1.0 M KOH</td>
<td>GC</td>
<td>1.60</td>
<td>408</td>
<td>77</td>
<td>[193]</td>
</tr>
<tr>
<td>Co-ZIF-9</td>
<td>0.1 M KOH</td>
<td>GC</td>
<td>1.47</td>
<td>510@1 mA cm$^{-2}$</td>
<td>93</td>
<td>[194]</td>
</tr>
<tr>
<td>FeTPyP-Co</td>
<td>0.1 M KOH</td>
<td>GC</td>
<td>1.47</td>
<td>351@1 mA cm$^{-2}$</td>
<td>128</td>
<td>[196a]</td>
</tr>
<tr>
<td>Co-WOC-1</td>
<td>0.1 M KOH</td>
<td>GC</td>
<td>1.47</td>
<td>390@1 mA cm$^{-2}$</td>
<td>64</td>
<td>[198]</td>
</tr>
<tr>
<td>MAF-X27-OH</td>
<td>1.0 M KOH</td>
<td>GC</td>
<td>1.55</td>
<td>387</td>
<td>66</td>
<td>[199]</td>
</tr>
<tr>
<td>MCF-49</td>
<td>0.1 M KOH</td>
<td>GC</td>
<td>1.46</td>
<td>283</td>
<td>43</td>
<td>[199]</td>
</tr>
<tr>
<td></td>
<td>0.1 M KOH</td>
<td>NF</td>
<td>1.43</td>
<td>225</td>
<td>48</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.1 M PBS</td>
<td>GC</td>
<td>1.53</td>
<td>431@2 mA cm$^{-2}$</td>
<td>134</td>
<td></td>
</tr>
<tr>
<td>ZIF-67</td>
<td>1.0 M KOH</td>
<td>GC</td>
<td>1.60</td>
<td>400</td>
<td>74.9</td>
<td>[195]</td>
</tr>
<tr>
<td>CUMS-ZIF-67</td>
<td>1.0 M KOH</td>
<td>GC</td>
<td>1.60</td>
<td>320</td>
<td>53.7</td>
<td>[195]</td>
</tr>
<tr>
<td>Co-PBA</td>
<td>1.0 M KOH</td>
<td>GC</td>
<td>1.60</td>
<td>334</td>
<td>67</td>
<td>[202a]</td>
</tr>
<tr>
<td>Co-PBA-plasma-2h</td>
<td>1.0 M KOH</td>
<td>NF</td>
<td>1.60</td>
<td>274</td>
<td>53</td>
<td>[202a]</td>
</tr>
<tr>
<td>P-Phy-CoFe</td>
<td>0.5 M K Bi</td>
<td>GC</td>
<td>1.54</td>
<td>265</td>
<td>36.1</td>
<td>[200]</td>
</tr>
<tr>
<td>MAF-48</td>
<td>1.0 M PBS</td>
<td>GC</td>
<td>1.54</td>
<td>352</td>
<td>71</td>
<td>[201]</td>
</tr>
<tr>
<td>MAF-69-Mo</td>
<td>CO$_2$-0.5 M KHCO$_3$</td>
<td>GC</td>
<td>1.54</td>
<td>456</td>
<td>219</td>
<td>[201]</td>
</tr>
</tbody>
</table>

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3.2.3 Bifunctional electrocatalysts for water splitting

Water splitting process \((2\text{H}_2\text{O} \rightarrow 2\text{H}_2 + \text{O}_2)\) involves two half reactions: HER at the cathode and OER at the anode which require multiple electron transfer, leading to large overpotentials. A cell voltage of 1.8-2.0 V is needed for commercial electrolyzers, which is much higher than the theoretical minimum value of 1.23 V for water splitting. The benchmark catalysts are Pt and its alloys for the HER and Ir/Ru oxides for the OER, which are all precious metal-based materials. But the cost and scarcity of these catalysts limited their large-scale applications. For practical overall water splitting, both the HER and OER catalysts are performed in the same electrolyte (usually strong acidic or basic solutions). Low-cost bifunctional electrocatalysts that can perform both HER and OER in the same electrolyte is highly imperative, which can reduce the overpotential, cut the cost and simplify the operating system. A large number of transition metal-based catalysts have been investigated as outstanding bifunctional electrocatalysts for overall water splitting. Though MOFs are well studied for HER and OER catalysis, the applications of MOFs for overall water splitting are still rare (Table 5). The cell voltage at 10 mA cm\(^{-2}\) of water electrolyzer cell and the

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One exciting example was reported by Duan et al. by assembling ultrathin bimetal MOF (NiFe-MOF) nanosheet array on porous NFs with superior electrocatalytic water splitting performances (Fig. 26).\textsuperscript{[30]} The bimetal MOF electrodes demonstrated a HER overpotential ($\eta_{10}$) of 134 mV, with a high TOF of 2.8 s$^{-1}$ at 400 mV in 0.1 M KOH solution. For OER performance, an overpotential ($\eta_{10}$) of 240 mV, with a low Tafel slope of 34 mV dec$^{-1}$ and a TOF of 3.8 s$^{-1}$ at 400 mV. To investigate the overall water splitting performance, a two-electrode cell was built by using NiFe-NPC nanosheet loaded NFs as both the cathode and the anode, where H$_2$ and O$_2$ were generated, respectively. The electrocatalytic cell reached a voltage of 1.55 V at the current density of 10 mA cm$^{-2}$, which is smaller than that of cells using the benchmark precious metal-based IrO$_2$ anodes and Pt/C cathodes (1.62 V at 10 mA cm$^{-2}$). The in situ growth of NiFe-NPC nanosheet on NFs avoided the using of binders that usually needed to adhere the electrocatalysts on the electrode, leading to enhanced catalyst-substrate contact and efficient electron transport. Also, the unique hierarchical architecture of MOF nanosheet arrays on NFs contributed to highly exposed active molecular metal sites, thus improving electrical conductivity and effective mass transport of gas products and electrolyte, resulting in the unexpected high electrocatalytic activity.

Most of the MOFs catalysts for HER and OER are investigated at low current densities (smaller than 100 mA cm$^{-2}$), which are not practical for large-scale and industrial applications.\textsuperscript{[216]} So, it’s quite desirable to develop electrocatalysts that can perform good activity and stability at high current densities such as 500 mA cm$^{-2}$ for practical water electrolyzers. Lin et al. deposited bimetal-based MOFs with BDC ligands (FeNi-BDC-DMF) on porous NFs substrate directly without binders.\textsuperscript{[214]} The obtained FeNi-BDC-DMF/NF electrode demonstrated outstanding electrocatalytic activity for overall water splitting due to the hierarchical synergistic effects between MOFs and conductive NFs substrate. The electrode exhibited an overpotential ($\eta_{10}$) of 160 mV and a Tafel slope of 96.2 mV dec$^{-1}$ for HER, and a low overpotential (at 60 mA cm$^{-2}$) of 227 mV and a Tafel slope of 37.4 mV dec$^{-1}$ for OER in 1.0 M KOH solution. Low cell voltages of 1.58 V and 1.90 V at a current density of 10 mA cm$^{-2}$ and 400 mA cm$^{-2}$ were obtained by using FeNi-BDC-DMF/NF as both the anode and the cathode.

Raja et al. grew bimetallic Fe and Ni-based MOFs (MNF-MOFs) onto conductive NFs as highly efficient bifunctional catalysts for overall water splitting at high current densities. The MFN-MOFs/NF electrode showed overpotentials of 235 mV and 294 mV at 50 and 500 mA cm$^{-2}$ for OER, and overpotentials of 79 mV and 234 mV at 10 and 500 mA cm$^{-2}$ for HER in 1 M KOH solution, respectively. The electrolytic cell reached a voltage of 1.495 V and 1.80 V at the current density of 10 mA cm$^{-2}$ and 500 mA cm$^{-2}$ respectively.
or metal atoms dopants is an efficient way to increase the active sites by tuning the electronic structure of catalysts.\textsuperscript{[219]} Whereas the porosity and specific surface area are key factors in determining the density of exposed above-mentioned active sites on the surface of the catalyst. Thus, increasing porosity and surface area of the catalysts is beneficial for their ORR activity. Other than the above two points, several aspects should be considered such as the interface compatibility, the mass and electron transfer ability which are all related to the electrocatalytic performance of an ORR catalyst.\textsuperscript{[220]}

With the mentioned theory-guided strategy, to some extent, it’s accessible to design non-noble ORR catalysts rationally. MOFs hold great expect as non-noble catalysts due to its tunable composition/structures. The large surface area and high porosity that is the typical features of MOFs are beneficial to the sufficient exposure of active sites and good transport properties of ORR-relevant species. Therefore, here we set our sights on MOFs ORR electrocatalysts and present some relevant research progress nowadays (Table 6).

**Table 6. Summary of benchmark MOF electrocatalysts for ORR reactions.**

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>$E_{\text{onset}}$ (V vs. RHE)</th>
<th>$E_{1/2}$ (V vs. RHE)</th>
<th>TS (mV dec$^{-1}$)</th>
<th>The transfer number</th>
<th>Electrolyte</th>
<th>Substrate</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Cu$_2$(OH)(bpy)$_2$(BTC)$_2$]</td>
<td>0.5</td>
<td>–</td>
<td>–</td>
<td>3.8</td>
<td>0.1 M PB</td>
<td>GC-RDE</td>
<td>[221]</td>
</tr>
<tr>
<td>Pccu-O$_8$-Co</td>
<td>–</td>
<td>0.83</td>
<td>61</td>
<td>3.93</td>
<td>0.1 M KOH</td>
<td>GC-RDE</td>
<td>[33]</td>
</tr>
<tr>
<td>Co-Al-PMOF</td>
<td>0.75</td>
<td>0.55$^{\text{al}}$</td>
<td>–</td>
<td>2.9</td>
<td>0.1 M H$_2$SO$_4$</td>
<td>GC-RDE</td>
<td>[222]</td>
</tr>
<tr>
<td>Ni-CAT</td>
<td>–</td>
<td>0.236</td>
<td>–</td>
<td>3.7</td>
<td>0.1 M KClO$_4$ and 0.02 M PBS</td>
<td>GC-RDE</td>
<td>[223]</td>
</tr>
<tr>
<td>Ni$_3$(tha)$_2$</td>
<td>0.82</td>
<td>0.67$^{\text{al}}$</td>
<td>128</td>
<td>2.25</td>
<td>0.1 M KOH</td>
<td>GC-RDE</td>
<td>[224]</td>
</tr>
<tr>
<td>Co$<em>{0.27}$Ni$</em>{0.73}$-CAT</td>
<td>0.47</td>
<td>0.34</td>
<td>104</td>
<td>3.94</td>
<td>0.1 M NaClO$_4$ and 0.02 M PBS</td>
<td>GC-RDE</td>
<td>[225]</td>
</tr>
<tr>
<td>PolyCuDAB-CB</td>
<td>0.862</td>
<td>0.76</td>
<td>–</td>
<td>3.57</td>
<td>0.1 M KOH</td>
<td>GC-RDE</td>
<td>[226]</td>
</tr>
<tr>
<td>(Fe-P)$_n$ MOF</td>
<td>0.70</td>
<td>0.57$^{\text{al}}$</td>
<td>–</td>
<td>1.93</td>
<td>0.1 M KOH</td>
<td>GC-RDE</td>
<td>[227]</td>
</tr>
<tr>
<td>Cu-BTC</td>
<td>0.71</td>
<td>0.56$^{\text{al}}$</td>
<td>–</td>
<td>1.74</td>
<td>0.1 M KOH</td>
<td>GC-RDE</td>
<td>[228]</td>
</tr>
<tr>
<td>E-MnO$_2$/MOF(Fe)CuSi(28 wt%@Cu-BTC</td>
<td>0.84</td>
<td>0.64</td>
<td>117</td>
<td>3.8</td>
<td>0.1 M KOH</td>
<td>GC-RDE</td>
<td>[229]</td>
</tr>
<tr>
<td>(G-dye-FeP)$_n$</td>
<td>0.93</td>
<td>0.78$^{\text{al}}$</td>
<td>–</td>
<td>3.82</td>
<td>0.1 M KOH</td>
<td>GC-RDE</td>
<td>[227]</td>
</tr>
<tr>
<td>NiFe-NPC-4.3%</td>
<td>0.92</td>
<td>0.83</td>
<td>70</td>
<td>3.8</td>
<td>0.1 M KOH</td>
<td>GC-RDE</td>
<td>[207]</td>
</tr>
</tbody>
</table>

**3.3.1 Metalloporphyrin catalysts**

In nature, metalloporphyrin plays a key role in various proteins and enzymes for O$_2$ binding, transport, and storage, electron transfer, O$_2$ activation and utilization, and peroxide management and degradation\textsuperscript{[233]} It has been proved that the structural arrangement of the porphyrins can greatly influence the ORR performance.\textsuperscript{[232]} By adjusting the pore shape and polarity as well as the relative arrangement of porphyrins,
Lions et al. reported a [Al$_2$(OH)$_3$(Co(TCPP))] (Co-Al-PMOF) catalyst which is the porphyrin metalated analog of [Al$_2$(OH)$_3$(H$_2$TCPP)] (H$_2$-Al-PMOF) as shown in Fig. 27A.\cite{222} The obtained samples possess microporous characters and a large BET surface area of 1150 m$^2$ g$^{-1}$. Besides, Co-Al-PMOF displayed a further enhanced ORR activity. In an O$_2$-saturated 0.1 M H$_2$SO$_4$, the Co-Al-PMOF exhibited an $E_{\text{onset}}$ of 0.75 V while the $E_{\text{onset}}$ of H$_2$-Al-PMOF and the discrete complex [Co(TCPP)] (CoTCP, insoluble and used as heterogeneous catalyst) are 0.72 V and 0.75 V, respectively. These results clarified that the use of ORR-active complexes as building blocks is available to develop higher electroactive ORR catalysts. The enhanced ORR activity can be attributed to the increased porosity of the extended framework.

Zhong et al. constructed a copper phthalocyanine based 2D conjugated MOF with cobalt bis(dihydroxy) complexes (Co-O$_2$) as linkages (PcCu-O$_2$-Co) through a solvothermal method, as shown in Fig. 27B.\cite{234} Thanks to the high coverage of electrochemically active Co centers, high conductivity and highly ordered porous structure, PcCu-O$_2$-Co 2D MOF mixed with carbon nanotubes exhibited a superior ORR activity (Fig. 27C). It exhibited a half-wave potential ($E_{1/2}$) of 0.83 V in an O$_2$-saturated 0.1 M KOH, and the equivalent transfer number (n value) was calculated to be 3.93, which is the record value among the reported intrinsic MOF electrocatalysts. Their work elucidated that optimizing the architecture and electronic structure of 2D MOF is an effective way to enhance the ORR electroactivity.

3.3.2 Conductive MOFs catalysts

Although MOFs have been considered as the promising materials for electrocatalytic applications, the majority of MOFs cannot be used directly in electrocatalytic applications because they are typically electrical insulators. Recently, some conductive MOFs have been developed as oxygen reduction catalysts.\cite{226,233} Among them, conductive 2D conjugated MOFs with unique 2D structure, enhanced electron transport capability, high utilization of exposed active sites and the inherent merits of traditional MOF attracted a lot of attention.\cite{234} For example, Miner et al. reported a Ni$_3$[hexaminotriphenylene]$_2$, (Ni$_3$ (HITP)$_2$) 2D MOF as an ORR electrocatalyst (Fig. 28A).\cite{33} Ni$_3$(HITP)$_2$ exhibited outstanding oxygen reduction activity and was comparable to most of the non-platinum group metal electrocatalysts. In Fig. 28B, the catalyst reduced oxygen with an onset potential of 0.82 V in an O$_2$-saturated 0.1 M KOH aqueous solution. Notably, Ni$_3$(HITP)$_2$ also possessed excellent stability that it retained 88% of its initial current density over 8 h at 0.77 V and underwent no visible morphological degradation during prolonged electrochemical cycling. The notable ORR activity may be resulted from the defined active sites (Ni-Ni) as well as the 2D porous structure of Ni$_3$(HITP)$_2$ which is able to increase the density and facilitate easy access to the catalytic active sites. Thus Miner et al. drew the conclusion that a well-defined, intrinsically conductive MOF is available to be a powerful platform for the development of tunable ORR electrocatalysts.

Recently, conductive 2D hexagonal MOF layers (called M-CAT; M = Co, Ni or Cu) have been widely used in the electrocatalysis, which were constructed by the hydrothermal reaction between 2,3,6,7,10,11-hexahydroxytriphenylene (HHTP) and a divalent metal ion, such as Co$^{2+}$, Ni$^{2+}$ or Cu$^{2+}$.\cite{235} However, most research has been regarded on the material preparation related to the monometallic M-CATs and their electrochemical utilization. Yoon et al. put forward a strategy for the property enhancement via mixing the metal components (Fig. 28C).\cite{235} Importantly, compared to their monometallic counterparts, Co-CAT and Ni-CAT, the Co$_{0.20}$Ni$_{0.33}$-CATs catalyst displayed obviously enhanced ORR activities. In the O$_2$-saturated 0.1 M NaClO$_4$ and 0.02 M PBS electrolyte solutions, the acquired bimetallic Co$_{0.20}$Ni$_{0.33}$-CATs exhibited an onset potential and half-wave potentials of 0.46 V and 0.34 V, respectively. And the electron transfer number of Co$_{0.20}$Ni$_{0.33}$-CAT was found to be 3.95. The enhanced ORR activity was attributed to the well-defined Co-Ni mixed active sites.
activity may be attributed to the abundant active sites of CO<sub>0.27</sub>Ni<sub>0.33</sub>-CATs and the high conductivity of two monometallic M-CATS.

Fig. 28  (A) Scheme of 2D layered structure of Ni<sub>x</sub>(HITP);  (B) Polarization curves of Ni<sub>x</sub>(HITP) in N<sub>2</sub>- and O<sub>2</sub>-saturated 0.1 M KOH. Copyright (2016) Nature Publishing Group.  (C) Schematic illustration of the construction of bimetallic 2D Co,Ni<sub>y</sub>-CATs. Copyright (2019) Wiley-VCH.

3.3.3 MOFs composite catalysts

It has been reported that modifying the interface properties of the ORR catalysts is able to exert synergistic functions to the ORR. Especially, constructing graphene, metal sulfide composites and other hierarchical structures are deemed as efficient ways. In the consideration of improving the ORR activity, Cho et al. reported a new method for fabricating various amounts of CuS nanoparticles (nano-CuS) in/on a 3D Cu-MOF, [Cu<sub>x</sub>(BTC)₂·(H₂O)₃].[238] The electrical conductivity and the porosity of the composites can be tuned by the amount of nano-CuS. As the content of nano-CuS increases, the electrical conductivity of the modified Cu-MOF increases exponentially by up to 10<sup>5</sup>-fold while its porosity decreases. In the present composite materials, the CuS(28 wt%)@Cu-BTC exhibits the best ORR activity with an onset potential of 0.91 V, a quasi-four-electron transfer pathway (n=3.82) and a kinetic current density of 11.3 mA cm<sup>-2</sup> at 0.55 V. The enhanced ORR activity is due to the synergistic effect of the two different materials that plays a key role in terms of conductivity and porosity, respectively.

Among 2D materials, graphene which possesses unique structure and brilliant electron-conductivity, has drawn a great deal of attention. Not only can it be modified to be a metal-free catalyst, but also can be a support for developing graphene-based composite catalysts. Jahan et al. prepared electrocatalytically active graphene-porphyrin MOF composites as ORR catalysts by the combination of (Fe-P)ₙ MOF and RGO sheets that are functionalized with donor-π-acceptor dye (G-dye).[227] The obtained catalyst (G-dye-FeP)ₙ MOF exhibited a higher ORR activity and stability. In 0.1 M KOH solution saturated with O₂, the (G-dye 50%-FeP)ₙ MOF displayed the best ORR activity as well as high 4e⁻ selectivity. Apart from the activity, the durability of the (G-dye 50%-FeP)ₙ is also superior, it exhibits a very slow attenuation after a 39% loss in its initial current density at a constant voltage of −0.23 V in alkaline media. These superiorities can be explained by the unique structure of the hybrid in which G-dye interconnects with the Fe-MOF in a 3-D manner and the synergistic effect between them that afforded better ORR activity.

3.3.4 Other MOFs catalysts

In addition to the three types described above, inducing lattice strain in the structure also can enhance the electroactivity of the catalysts towards ORR. Cheng et al. developed lattice-strained transition metal MOF materials by an additional UV light treatment for both the enhancement of OER and ORR.[207] The sample that treated 12 h of UV irradiation (NiFe-NPC-4.3%) exhibited the best ORR activity with an onset potential of 0.92 V, a half-wave potential of 0.83 V as well as a Tafel slope of 70 mV dec<sup>−1</sup>, which are superior to these of commercial Pt/C (a half-wave potential of 0.81 V and a Tafel slope of 76 mV dec<sup>−1</sup>). The electron transfer number of the 4.3%-MOF was estimated to be 3.8, indicating an efficient 4e⁻ dominated ORR pathway. The ORR improvement was attributed to the redistribution of atomic and electronic configurations of Ni sites in NiFe-NPC via lattice-strain modulation. Their work shed light to a new avenue to construct efficient and low-cost materials for oxygen catalysis. Meanwhile, it can deepen our understanding of the operating mechanism.

3.4 Electrocatalytic CO₂RR

CO₂RR is one of the most promising approaches to reduce the greenhouse gas CO₂ into valuable chemicals, such as CO, CH₄, C₂H₄, HCOOH, oxalic acid and alcohols.[2, 212] Yet, the essential chemical inertness of CO₂ and the participation of multiple electrons lead to high thermodynamic and kinetic energy barriers for CO₂RR and often low conversion efficiency and poor selectivity toward aimed chemicals. MOFs can be designed to have open metal sites, embedded electro-active molecules, functionalized ligands, specific heteroatoms and tunable porosity. Also, the large BET surface area of MOFs enables strong adsorption ability of CO₂ molecules and fast mass transport, which are quite essential for CO₂RR. In the past several years, MOFs have been investigated to be promising CO₂RR electrocatalysts with high FE and selectivity (Table 7).[3, 238]

<table>
<thead>
<tr>
<th>Electrocatalysts</th>
<th>Main product</th>
<th>Peak FE (%)</th>
<th>Potential (V)</th>
<th>TOF (s&lt;sup&gt;−1&lt;/sup&gt;)</th>
<th>Electrolyte</th>
<th>substrate</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CR-MOF</td>
<td>HCOOH</td>
<td>30</td>
<td>−1.20 SHE</td>
<td>–</td>
<td>0.5 M KHCO₃</td>
<td>CP</td>
<td>[239]</td>
</tr>
</tbody>
</table>

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Cu-BTC Oxalic acid 51 $-2.2$ SHE $-$ 0.01 M TBATFM/DMF GC [240]
Cu-BTC ethanol 10.3 $-0.70$ SHE 0.02 0.5 M KHCO$_3$ CP [241]
CuAdeAce MeOH 1.2 $-1.55$ SHE 0.002 0.5 M KHCO$_3$ CP [241]
HKUST-1 CH$_4$ 27 $-1.16$ RHE $-$ 0.5 M KHCO$_3$ GC [242]

Al$_2$(OH)$_3$ CO $76 -0.7$ RHE 0.056 0.5 M K$_2$CO$_3$ Carbon disk [243]

Table 1: Electrochemical performances of different catalysts.

Cu is one of the most promising metallic CO$_2$RR catalysts to convert CO$_2$ to valuable hydrocarbons such as CH$_4$, C$_2$H$_4$ and ethanol.[248] Yet, Cu showed poor selectivity for specific carbon products.[259] The molecular size refinement effect in MOF pores may be beneficial to improve the catalytic selectivity of CO$_2$RR. Cu-MOFs, especially Cu$_2$(COO)$_4$ paddle-wheel cluster-based MOFs that possess open metal sites, are promising electrocatalysts for CO$_2$RR.[239-240] In 2012, Cu-MOFs CRM-MOF [259] and Cu-BTC (HKUST-1) [240] were reported to convert CO$_2$ into HCOOH (FE = 30%) and oxalic acid (FE = 51%) via electrocatalysis respectively, which represent the first examples of MOFs for CO$_2$RR applications. Later, Albo et al. systematically studied the CO$_2$RR activity of two Cu-MOFs (HKUST-1 and CuAdeAce) and two Cu-based metal organic aerogels (MOAs) supported on gas diffusion electrodes.[241] HKUST-1 contains Cu paddle-wheel clusters with open metal sites which act as adsorption sites for CO$_2$. While CuAdeAce is based on dicycloputter paddle-wheel units similar to HKUST-1 but without uncoordinated metal sites. Both HKUST-1 and CuAdeAce are active for CO$_2$RR in CO$_2$ saturated 0.5 M KHCO$_3$ aqueous solutions. Recently, Yi and co-workers proposed the in situ synthesis of Cu$_2$O(111) quantum dots on porous conductive Cu-based MOFs (CuHHTP) to stable key reaction intermediates, which enhance the sluggish kinetics and achieve the high selectivity of CH$_4$ in CO$_2$RR.[240] The Cu$_2$O quantum dots transformed by Partial Cu$^{2+}$ centers in CuHHTP, exposed sole (111) crystalline planes and liberated hydroxyl groups from the uncoordinated HHTP ligand. Thus, the obtained Cu$_2$O@CuHHTP exhibited a high Faradaic efficiency of $73\%$ and a partial current density of $10.8$ mA cm$^{-2}$. Stability is still one issue needs to be addressed for Cu-MOFs, since most Cu-MOFs are not stable in water. In situ and operando characterization techniques are advanced powerful tools to examine the local coordination environment changes of catalysts during reaction conditions, identify the real active sites and illustrate the catalytic mechanism. Recently, Weng et al. investigated the CO$_2$RR performance of Cu-MOF HKUST-1 and identified the active sites via in situ and operando X-ray absorption spectroscopy (XAS) as shown in Fig. 29A.[242] HKUST-1 can transform CO$_2$ into methanol with high FE of $27\%$ at a reduction potential of $-1.16$ V vs. RHE in CO$_2$ saturated 0.5 M KHCO$_3$ aqueous solutions (Fig. 29B). After CO$_2$RR, the SEM characterization demonstrated that the submicron-sized morphology of HKUST-1 changed to dendritic nanostructures. PXRD patterns showed the coexistence of Cu$_2$O and Cu. In situ and operando EXAFS characterization revealed that at the reduction potential of $-1.06$ V, the EXAFS spectra of HKUST-1 was similar to that of the Cu metal, indicating the formation of Cu metal. When the electrode potential was back to 0.64 V, the EXAFS spectra confirmed the existence of Cu$_2$O, suggesting the metallic Cu originated from HKUST-1 was oxidized to form Cu$_2$O. Thus, the in situ generated Cu nanomaterials were the real catalytic active sites for CO$_2$RR in HKUST-1.

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Metal (Co, Fe, Ni etc.) porphyrin molecular compounds with M–N₄ coordination environment were proven to demonstrate high activity for CO₂RR.[261] Inspired by the M-porphyrin molecules, M-porphyrin based MOFs were investigated as potential catalysts for CO₂RR.[31, 243-246] Kornienko et al. reported a Co-porphyrin based MOF Al₂(ΟH)₄TCP-Co that demonstrated high CO₂RR activity for reduction of CO₂ to CO.[248] The MOF thin film was deposited onto conductive carbon disk electrodes via atomic layer deposition (ALD) method. Al₂(ΟH)₄TCP-Co electrode with optimized thickness showed excellent CO₂RR activity, with high FE of 76% for CO at a reduction potential of −0.70 V vs. RHE and a high TOF of 0.056 s⁻¹ in CO₂ saturated 0.5 M K₂CO₃ aqueous solutions. In situ spectroelectrochemical measurements revealed that the reduced Co(I) from Co(II) is the active site for CO₂RR. Later, Hod et al. synthesized Fe-porphyrin based MOF (Fe-MOF-S25) thin films on FTO substrates via electrochemical deposition method for CO₂RR.[244] Fe-MOF-S25 film electrode showed CO₂RR activity for converting of CO₂ to CO with a FE of 50% at a reduction potential of −0.70 V vs. RHE and a TOF of 0.018 s⁻¹ in CO₂ saturated 0.1 M TBAPF₆ acetoniolite electrolyle. However, the electrocatalytic stability of Fe-MOF-S25 film electrode was not good, as after electrocatalysis for 5 h, the MOF was found to degrade. Dong et al. synthesized Fe-porphyrin MOF PCN-222(Fe) as CO₂RR catalyst.[245] The PCN-222(Fe)/carbon black electrode exhibited high CO₂RR activity for the conversion of CO₂ to CO with a high FE of 91% at a reduction potential of −0.60 V vs. RHE and a TOF of 0.014 s⁻¹ in CO₂ saturated 0.5 M K₂CO₃ aqueous solutions. PCN-222(Fe) also demonstrated high catalytic stability, as confirmed via PXRD without loss of crystallinity after 10 h of electrolysis. Recently, Wu et al. designed a Cu paddle-wheel cluster-based Cu-porphyrin MOF nanosheet [Cu₆(Cu-TCP)] deposited on conductive FTO substrates for CO₂RR.[246] The Cu₆(Cu-TCP) electrode showed outstanding activity for formate production with a FE of 68.4% and a superior TOF of 0.566 s⁻¹ at a reduction potential of −1.55 V vs. Ag/AgCl in CO₂ saturated 0.5 M EMIMBF₆ acetoniolite electrolye. Due to the instability of Cu paddle-wheel clusters, Cu₆(Cu-TCP) was decomposed into Cu and Cu₂O as confirmed via PXRD and XPS analysis after catalysis. The Cu₂O/Cu-porphyrin complex composite was believed to mainly contribute to the CO₂RR performance.

Lan and colleagues combined reductive Zn-ε-Keggin POM and M-porphyrin to form POM-metalloporphyrin MOFs (M-PMOF, M = Co, Fe, Ni, Zn) for highly selective CO₂RR.[31] The introducing of POMs benefited the electron collecting and donating, and the electron mobility in MOFs. All the M-PMOFs were CO₂RR active for converting CO₂ to CO, among which Co-PMOF demonstrated the best catalytic activity. Co-PMOF electrode showed an ultrahigh FE of 98.7% for CO at a reduction potential of −0.80 V vs. RHE and a high TOF of 0.46 s⁻¹ in CO₂ saturated 0.5 M KHCO₃ aqueous solutions. Also, Co-POMF showed high catalytic stability with negligible decay in activity after 36 h. DFT calculations revealed that the excellent CO₂RR performance was attributed from synergistic effects of reductive POMs and Co-porphyrin while the Co centers in the porphyrin species were the active sites for CO₂RR. This work demonstrated that POM-based MOFs could be promising catalysts for CO₂RR. It should be noted that POM-based MOFs exhibited outstanding HER activity, which acts a competing reaction for CO₂RR. The HER process should be avoided via rational design in the synthesis of POM-MOFs for CO₂RR applications.

Except the metal active sites in MOFs, the organic ligands may also act as catalytic centers. Zn(II) has a fully occupied 3d orbital, thus Zn-MOFs are ideal platforms to study the role of ligands in electrocatalysis. Recently, Zn-based MOFs have also been investigated for CO₂RR.[248-250, 262] Jiang et al. systematically investigated the CO₂RR performances of Zn-ZIFs (ZIF-8, ZIF-108, ZIF-7 and SIM-1) with the same SOD (sodalite) topology but different organic ligands (Fig. 30A).[249] All the four ZIFs are CO₂RR active for converting CO₂ to CO in CO₂ saturated 0.25 M K₂SO₄ aqueous solutions, among which ZIF-8 showed the highest CO₂RR performance, with a high FE of 81% for CO at a reduction potential of −1.10 V vs. RHE. While the FEs for ZIF-7, ZIF-108 and SIM-1 are 23.8%, 63.5% and 66.6%, respectively (Fig. 30B). The morphology and the Zn/N ratio in ZIF-8 after CO₂RR showed no change, indicating the strong stability of ZIF-8 in CO₂RR. In Fig. 30C-D, in situ XAS characterization and DFT calculations revealed that the sp² C atoms of the imidazolate ligands in ZIFs are the real active sites for CO₂RR. This work presented the first report of ligands as active sites for CO₂RR in MOFs, pointing out a new strategy to improve the CO₂RR activity of MOFs by tuning the organic ligands. Followed this work, Dou et al. proposed a new strategy of ligand doping to boost the CO₂RR performances of MOFs (Fig. 30E-F).[250] 1,10-phenanthroline, a strong electron-donating ligand was introduced to the vacant Zn sites of thermal activated ZIF-8 (ZIF-8-A-LD) as efficient CO₂RR electrocatalysts shown in Fig. 30E. Raman, EPR and XANES spectra confirmed the charge transfer from phenanthroline to Zn centers and imidazole ligands. ZIF-8-A-LD with 20 wt% of carbon-black to improve the conductivity was deposited on carbon paper (CP) electrode and CO₂ saturated 0.1 M KHCO₃ aqueous solutions was used as the electrolyte. CPE showed that ZIF-8-A-LD with optimized doping amount of phenanthroline exhibited quite high FE (90.57%) for CO at a reduction potential of −1.10 V vs. RHE. While the pristine ZIF-8...
Several nanoparticles such as Ag, Ag$_{2}$O, Cu and Cu$_2$O have been combined with MOFs to form MOF composites with improved CO$_2$RR activity. Kung et al. embedded Cu nanoparticles into a Zr-MOF (NU-1000) thin film via a solvothermal deposition of single site Cu(II) into MOFs followed by electrochemical reduction to metallic Cu nanoparticles in the channels of NU-1000. The obtained Cu@NU-1000 composites electrode demonstrated high CO$_2$RR activity, with a FE of 28% for HCOOH at a reduction potential of $-0.82$ V vs. RHE in CO$_2$ saturated 0.1 M NaClO$_4$ aqueous solutions. Both the morphology and crystallinity of the composites remained unchanged after CO$_2$RR, indicating its high electrocatalytic stability.

Recently, Guntern et al. developed a new approach to synthesize metal nanocrystals (NCs)/MOF hybrids as efficient CO$_2$RR catalysts. Ag NCs were first coated with Al$_2$O$_3$ via ALD method on glassy carbon substrate and then treated with TCPP ligands by converting the Al$_2$O$_3$ into Al-based MOF (Al-PMOF), and the final Ag@Al-PMOF hybrid thin films were formed. The Ag@Al-PMOF electrode showed excellent CO$_2$RR performance, with a FE of 55.8% for CO at a reduction potential of $-1.1$ V vs. RHE and a TOF of 0.14 s$^{-1}$ in CO$_2$ saturated 0.1 M KHCO$_3$ aqueous solutions, which is much larger than that of Ag NCs (FE of 25% for CO). The synergistic electronic coupling effects in the interface of Ag and Al-PMOF contributed to the enhanced CO$_2$RR performance. As confirmed via XPS and UV spectra, the charge transfer from Al-PMOF to Ag NCs led to the electron enrichment of the Ag within the hybrids. Not only the catalytic activity, but also the catalytic stability was improved by the composition of Ag NCs and MOFs. The bare Ag NCs suffered serious sintering after CO$_2$RR, while for Ag@Al-PMOF, the sintering was strongly inhibited during CO$_2$RR. This approach was also applied to fabricate other electrochemically active NC/MOF composites. Cu nanocubes@Al-PMOF, Au nanorods@Al-PMOF and Au nanospheres@Al-PMOF were facilely prepared and demonstrated CO$_2$RR activity.

### 3.5 Electrocatalytic NRR

NH$_3$, one of the most important industrial chemicals, is produced by the reduction of N$_2$ via century-old Haber-Bosch process, consuming half of the global H$_2$ production and 1-2% of global energy. The electrocatalytic reduction of N$_2$ to NH$_3$ at mild conditions is a promising alternative for the Haber-Bosch process and have attracted tremendous attentions in the past few years. Yet, the inertness of N$_2$ with strong N≡N bond (941 kJ mol$^{-1}$) and low solubility of N$_2$ in water significantly limit the NRR performance. Also, the potential window between HER and NRR is quite narrow, making HER more preferred for most electrocatalysts and seriously reducing the NRR selectivity. The ambient ammonia contamination during experiments is another issue that should be addressed, which would affect the reproducibility and even result in misleading conclusions. Though numerous catalysts have been investigated to exhibit NRR activity, the low catalytic activity and ultralow selectivity making them far from practical applications. Till now, there are only three reports of MOFs and MOF composites for NRR.

Zhao et al. reported the first application of MOFs for NRR by using MIL-100(Fe), ZIF-67 and HKUST-1 as catalysts. All the three MOFs showed excellent NRR activity for the electrochemical synthesis of NH$_3$ by using pure N$_2$ and water as raw materials at a potential of 1.2 V, ambient pressure and 90 °C in 2 M KOH solution. Among the MOFs, MIL-100(Fe)

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**Fig. 30** (A) Molecular structures of various ZIF catalysts. (B) Faradaic efficiencies of various ZIF catalysts. (C) Calculated free energy diagrams of various ZIF catalysts for CO$_2$RR. (D) Calculated free energy diagrams of various ZIF catalysts for HER. Copyright (2018) Elsevier. (E) The fabrication of phenanthroline-doped ZIF-8. (F) Free energy diagrams for CO$_2$RR on the sp$^2$ C atom sites. Copyright (2019) Wiley-VCH.
exhibited the best NRR activity, with a high NH₃ formation rate of 2.12×10⁻⁹ mol s⁻¹ cm⁻² and an FE of 1.43%. The stability of the MOFs at these conditions were not studied in this work and no control experiments were performed to avoid the ambient ammonia contamination during experiments.

One promising strategy to improve NRR efficiency and selectivity is to suppress the competitive HER reaction at the catalyst surface. Lee et al. coated Ag-Au alloy NRR catalyst surface with a superhydrophobic MOF layer (ZIF-71) to inhibit HER and improve NRR activity, as shown in Fig. 31A. The obtained Ag-Au@ZIF composite exhibited both excellent NRR selectivity and improved FE. The NRR investigation was performed at 298 K and 1 bar at an applied potential of −2.9 V vs. Ag/AgCl for 6 h. The electrolyte is a dry THF solution containing 0.2 M LiCF₃SO₃ and 1 volume % ethanol. The Ag-Au@ZIF electrode showed a NH₃ formation rate of about 1×10⁻¹¹ mol s⁻¹ cm⁻² and a high FE of 18 ± 4%, which are 4-fold and 2-fold superior to Ag-Au electrode without ZIF encapsulation, respectively (Fig. 31B-C). The hydrophobic interior of ZIF can block the entrance of water for impeding HER and also accumulate N₂ and other reactant molecules at catalytic active sites, leading to efficiently improved NRR performance. Recently, Yang et al. coated nanoporous gold (NPG) with hydrophobic ZIF-8 nanocomposite with high NRR performance, as shown in Fig. 31D. In the nanocomposite, NPG was the catalytic active site for NRR, and ZIF-8 shell can suppress HER and accelerate the reactant diffusion. The NRR investigation was performed at 298 K and 1 bar at an applied potential of −6 V vs. RHE for 2 h. The NPG@ZIF-8 electrode displayed a high FE of 44% and selectivity of 98% for NH₃, and a NH₃ formation rate of about 0.36×10⁻⁹ mol s⁻¹ cm⁻², which are superior to NPG and traditional Au nanoparticles (Fig. 31E). Also, the nanocomposite electrode showed high electrochemical stability, without obvious drop of electrocatalytic activity after 20 h test (Fig. 31F). In the nanocomposite, ZIF-8 showed no NRR activity, and performed to inhibit HER due to its hydrophobic interior. Both the works above indicated that the strategy by coating NRR catalysts with hydrophobic MOFs to suppress HER can construct promising NRR electrocatalysts for practical applications.

### 3.6 Electroorganic synthesis

Electroorganic synthesis has risen as a new mild, environmentally friendly and large-scale transformation method that use electricity for redox transformations. With proper potential bias, organic starting materials can generate highly reactive intermediates at the electrode surface by gain or loss electrons. The reactivity and chemoselectivity of electrochemical reactions can be precisely controlled by regulating the applied potential, making electroorganic synthesis one of the most promising approaches to synthesize some complex organic molecules.

There are some advantages of MOFs for electroorganic synthesis, for example, the large porosity is beneficial for mass transfer, and the tunable pore structures make the improvement of chemoselectivity or even chiral selectivity possible. Yet, the main drawback of MOFs for electroorganic synthesis is the low conductivity of most MOFs. Compared with vast reports of MOFs for electrocatalytic water splitting,
ORR and CO₂RR applications, there are only several reports of MOFs to electroorganic synthesis applications. Much more studies are needed in this promising field. Yang et al. fabricated a nanocomposite by decorating 2D ultrathin MOF nanosheets of Hf₄(μ₂-OH)₂(μ₂-OH)₃(μ₁-OH)₂(HCO₃)₂(NTB)₂ also called metal-organic layers (MOL) onto conductive multiwalled CNTs (CNT/MOL) to improve the conductivity of MOFs in electrocatalysis (Fig. 32A). Then CNT/MOL was modified with TEMPO-OPO₂H (CNT/MOL-TEMPO-OPO₂⁻) and loaded on a macroporous reticulated vitreous carbon (RVC, 100 PPI) electrode to act as an efficient electrocatalyst for electrochemical acceptorless dehydrogenation of N-heterocycles to obtain quinoline or indole derivatives. The monolayer structure of MOL can accelerate the diffusivity of organic substrates and afford high densities of active sites, and CNT can efficiently improve the conductivity of catalyst. CNT/MOL-TEMPO-OPO₂⁻ electrode exhibited excellent electrocatalytic performance for the acceptorless dehydrogenation of N-heterocycles in a mixed solvent of CH₃CN/H₂O (9/1) containing 0.5 M Bu₂NBF₄ at room temperature. When use 1,2,3,4-tetrahydroquinidine as the organic substrate, the desired quinaldine product was synthesized with a high yield of 79% at a constant current of 7 mA. The electrode could be used for three times without loss of activity, indicating the strong stability of CNT/MOL-TEMPO-OPO₂⁻ catalyst. Control experiments confirmed the TEMPO moiety anchored on CNT/MOL was the active sites for electroorganic synthesis.

3.7 Other electrocatalytic applications

Except for the afore-mentioned OER, HER, ORR, CO₂RR and NRR, some other electrocatalytic reactions motivated by MOFs have also been reported, including the synthesis of chemical substances, energy conversion, degradation of organic pollutants and sensing (Table 8). For example, direct alcohol fuel cells have recently attracted great interest for electronic devices. Wu and co-workers achieved a novel 3D MOF [Ni₄(OH)₆(tatb)₂]₃⁻(bpe)₂ (CTGU-15) based on the cubane [M₄(OH)₆] (M = Ni, Co) clusters via facile solvothermal method. The obtained CTGU-15 was studied as an electrocatalyst for methanol oxidation reaction (MOR). The CTGU-15 possessed large BET surface area (3537 m² g⁻¹) and showed well-defined bi-micropores features at 0.86 nm and 1.51 nm. Moreover, the CTGU-15 exhibited an excellent stability in alkaline media (0.1 M KOH), which was suitable for alkaline MOR. Compare with the pure Ni-MOF electrocatalyst, the optimized KB/CTGU-15 (1:2) presented an outstanding electrocatalytic MOR activity with a large mass specific current density (527 mA mg⁻¹) and superior peak current density of 29.8 mA cm⁻² at a potential of 0.6 V.

Guo et al. reported a new approach to improve the conductivity and selectivity for electroorganic synthesis by incorporating ion electrocatalyst (TEMPO-SO₃⁻) into charged MOFs [MIL-101(Cr)-HIMBr] (Fig. 32B). The ionic MIL-101(Cr)-HIMBr was obtained by introducing ionic liquid group (HIMBr) into porous MIL-101(Cr) via post-functionalization method, leading to markedly improved electrical conductivity and accelerating electron transfer compared with pristine MIL-101(Cr). Then the catalytic active TEMPO-SO₃⁻ ions were trapped in the charged pores by ion exchange with the Br⁻ ions in MIL-101(Cr)-HIMBr to obtain the hybrid electrocatalyst TEMPO-SO₃⁻@MIL-101(Cr)-HIM. TEMPO-SO₃⁻@MIL-101(Cr)-HIM was coated onto a carbon plate as the working electrode, and the electrocatalytic oxidative self-coupling of benzylamine reaction was performed at a constant potential of 1.0 V vs. Ag/AgCl in 0.1 M BuNB₄ acetonitrile solution. After catalytic reaction for 3 h, benzylamine was fully converted to imine with >99.9% conversion and a high selectivity of 94.9%. While the homogeneous catalyst TEMPO-SO₃H by using carbon plate as working electrode only showed a low selectivity (61.3%) of self-coupling imine product with formation of large amount byproducts under identical conditions. TEMPO-SO₃⁻@MIL-101(Cr)-HIM electrode also demonstrated high catalytic stability, with almost no performance drop after six recycling runs. The cationic pores of MIL-101(Cr)-HIM prevented the leaching of TEMPO-SO₃⁻ active sites, and the unique pore structure can prevent the degradation of the oxidative intermediates, thus resulting to the improvement of catalytic selectivity and stability.

![Fig. 32](image-url) (A) CNT/MOL-TEMPO-OPO₂⁻ for electrochemical acceptorless dehydrogenation of N-Heterocycles. Copyright (2019) Wiley-VCH. (B) Schematic representation of the synthetic procedures for MIL-101(Cr)-HIMBr for electrocatalytic oxidative self-coupling of benzylamine. Copyright (2019) Wiley-VCH.
Yang et al. constructed a 2D MOL with multiwalled CNT as an electrocatalyst for selective alcohol oxidation reaction.\textsuperscript{[275]} The MOLs were assembled by 4,4',4″-nitriilotribenzoate and Hf_{6}({\mu}_{5}-O)_{4}({\mu}_{2}-OH)(HCO_{2})_{6} to form a 2D network, which existed in the form of wrinkle ultra-thin film (0.3 \times 0.3 \mu m^{2}). The composite structure of CNT/MOL dramatically enhanced the conductivity of MOLs from 1.6 \times 10^{-2} S m^{-1} to 3.65 S m^{-1}. After further modification with 4-carboxy-2,2,6,6-tetramethylpiperidine (TEMPO), the catalyst was loaded on a microporous RVC electrode. An electrocatalytic oxidation current could be observed at 0.34 V with high selectivity (100\%) and FE (97\%). The only products for benzyl alcohol are benzaldehyde and H_{2}. Further research revealed that the kinetic measurements of catalysis exhibited a Langmuir-type dependence of density on the concentration of substrate.

Nitrite is an important class of food additives and its concentration is vital for controlling food quality. Kung and co-workers grew MOF-525 on graphene nanoribbons (GNR) and the thin film MOF-525/GNR can not only catalyze nitrite oxidation reaction, but also be utilized as a nitrite sensor.\textsuperscript{[276]} Nitrogen adsorption-desorption curves revealed the porous characteristic of the composite (1535 m^{2} g^{-1}). CV curves demonstrated that the existence of MOF-525 was required to achieve better catalytic performance than the GNR. Furthermore, MOF-525/GNR thin film was assembled as an amperometric nitrite sensor with a high sensitivity of 93.8 A mM^{-1} cm^{-2}, a low limit of detection (LOD) of 0.75 \mu M and a wide linear range of 100-2500 \mu M.

Glucose is the most widely distributed and most important monosaccharide in nature. Electrocatalytic glucose oxidation has a wide range of applications, such as sensors and bio-fuel cells. Co_{2}(OH)_{4}pta is a 2D ultrathin network, where the coordination mode of central cobalt ion has both six- and five-coordinated position.\textsuperscript{[277]} The 2D Co-MOF (2.041 nm of thickness) had a large specific surface area and good catalytic activities for glucose oxidation reaction. The CV curves showed a couple of redox peaks in the range of 0.2 V to 0.5 V, corresponding to the Co(III)/Co(II) couple. The ultrathin 2D structure provided abundant active sites, shorter particle transport path and high electron conductivity. Based on the above results, Co_{2}(OH)_{4}pta was used to develop an amperometric glucose sensor and a superior selectivity (219.67 \mu A mM^{-1} cm^{-2}) was obtained, together with a LOD of 0.25 \mu M and a linear range of 0.5-8065.5 \mu M.

### Table 8. Summary of MOFs for other electrocatalytic applications.

<table>
<thead>
<tr>
<th>Type of catalysis</th>
<th>Catalysts</th>
<th>Substrate</th>
<th>Electrolyte</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alcohol oxidation</td>
<td>[Ni_{4}(OH)<em>{4}(tatb)</em>{2}]^{4+/-}</td>
<td>GCE</td>
<td>0.1 M KOH</td>
<td>[274]</td>
</tr>
<tr>
<td></td>
<td>Pt/NPC-900</td>
<td>GCE</td>
<td>0.5 M H_{2}SO_{4}</td>
<td>[278]</td>
</tr>
<tr>
<td></td>
<td>Co-MOF-71@GO</td>
<td>GCE</td>
<td>1.0 M KOH</td>
<td>[279]</td>
</tr>
<tr>
<td></td>
<td>Cu(II)-bpy-BTC</td>
<td>Carbon rod</td>
<td>0.1 M KOH</td>
<td>[281]</td>
</tr>
<tr>
<td>Glucose oxidation</td>
<td>CNT/MOL</td>
<td>RVC</td>
<td>0.02 M H_{3}PO_{4}</td>
<td>[275]</td>
</tr>
<tr>
<td></td>
<td>[(HOC,H_{2})_{2}dtocCu]</td>
<td>GCE</td>
<td>0.5 M H_{2}SO_{4}</td>
<td>[282]</td>
</tr>
<tr>
<td></td>
<td>Co_{2}(OH)_{4}pta</td>
<td>GCE</td>
<td>0.1 M NaOH</td>
<td>[277]</td>
</tr>
<tr>
<td></td>
<td>[Cu_{2}(BTC)_{2}]</td>
<td>GCE</td>
<td>0.1 M NaOH</td>
<td>[283]</td>
</tr>
<tr>
<td>Nitrite oxidation</td>
<td>MOF-525/GNR</td>
<td>ITO</td>
<td>0.1 M KCl</td>
<td>[276]</td>
</tr>
<tr>
<td></td>
<td>Au/Cu-MOF/CPE</td>
<td>Carbon paste</td>
<td>0.1 M phosphate buffer solution</td>
<td>[284]</td>
</tr>
<tr>
<td></td>
<td>Co(TCPP)</td>
<td>FTO</td>
<td>0.1 M LiClO_{4}/ DMF</td>
<td>[285]</td>
</tr>
<tr>
<td>Hydrazine oxidation</td>
<td>Co-MOF–MPC-2</td>
<td>GCE</td>
<td>0.1 M NaOH</td>
<td>[286]</td>
</tr>
<tr>
<td>Nitrophenols oxidation</td>
<td>Ag@MOF-S(Zn)</td>
<td>GCE</td>
<td>0.1 M KCl</td>
<td>[287]</td>
</tr>
<tr>
<td>Acetaminophen oxidation</td>
<td>Au/ZIF-L</td>
<td>GCE</td>
<td>0.1 M phosphate buffer solution</td>
<td>[288]</td>
</tr>
<tr>
<td>Cysteine oxidation</td>
<td>Au-SiO_{2}@Cu-MOF</td>
<td>GCE</td>
<td>0.1 M phosphate buffer solution</td>
<td>[290]</td>
</tr>
<tr>
<td>Peroxide oxidation</td>
<td>Cu-bpy-BTC</td>
<td>GCE</td>
<td>0.1 M phosphate buffer solution</td>
<td>[291]</td>
</tr>
<tr>
<td></td>
<td>[Cu(adp)<a href="H_%7B2%7DO">bib</a>]_{n}</td>
<td>GCE</td>
<td>0.1 M NaOH</td>
<td>[292]</td>
</tr>
</tbody>
</table>

### 3.8 MOF-derivatives for electrocatalysis

In view of the highly adjustable structure and compositional characteristics of MOFs, their derivatives have been considered to be the most promising alternative to electrocatalytic materials.\textsuperscript{[293]} Through rigorous control of the experimental process, as well as rational modification/post-treatment, the pristine MOFs present as promising templates/precursors to fabricate outstanding catalysts with compositional properties and desirable structures after controlled thermal/chemical treatment.\textsuperscript{[294]} MOF-derivatives not only inherit the dominant features of MOF precursors (large specific surface, high porosity and compositional diversity), but also transform MOFs to carbon/metal-based nanomaterials with more stable structures and richer active sites. Since the first acquisition of MOF-derivatives from pyrolysis MOF reported by Xu et al. in 2008, subsequently, the exploration of MOF-derived materials presented explosive developments.
growth, especially as catalysts for electrocatalysis.\textsuperscript{[293a]} Although few earlier reviews reported the applications of MOFs derivatives. For example, Jiang’s group reviewed MOF-derived porous materials for catalysis.\textsuperscript{[18a, 125a]} Moreover, Xu’s group has paid attention to the development of MOF-derivatives in the field of energy applications.\textsuperscript{[294b, 295]} Here, we summarize the remarkable application of MOF-derivatives in electrocatalysis recently (Table 9).

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>MOF precursor</th>
<th>Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co-Fe-P</td>
<td>MIL-88B</td>
<td>HER</td>
</tr>
<tr>
<td>CoPS-N/C</td>
<td>ZIF-67</td>
<td>HER</td>
</tr>
<tr>
<td>CuP@NPPC</td>
<td>Cu-NPMOF</td>
<td>HER</td>
</tr>
<tr>
<td>CoP/NCNWs</td>
<td>Co-MOF</td>
<td>HER</td>
</tr>
<tr>
<td>Cs@CNC NAs/CC</td>
<td>ZIF-67 NAs</td>
<td>HER</td>
</tr>
<tr>
<td>CoOx/Co-Fe</td>
<td>ZIF-67</td>
<td>OER</td>
</tr>
<tr>
<td>FeNiP/C</td>
<td>BMM-10</td>
<td>OER</td>
</tr>
<tr>
<td>ZnCo-Fe</td>
<td>ZnCo MOF</td>
<td>OER</td>
</tr>
<tr>
<td>CoN/C</td>
<td>ZIF-67</td>
<td>OER</td>
</tr>
<tr>
<td>NiCoOOH-NiCoS</td>
<td>ZIF-67</td>
<td>OER</td>
</tr>
<tr>
<td>Ni3P/CoN-PCP</td>
<td>ZnCo-BMOF</td>
<td>HER/OER</td>
</tr>
<tr>
<td>CoS8/EC-MOF</td>
<td>Co-based MOF</td>
<td>HER/OER</td>
</tr>
<tr>
<td>Co/NBC</td>
<td>BIF-82-Co</td>
<td>HER/OER</td>
</tr>
<tr>
<td>N-CNTs</td>
<td>ZIF-67 with N-Cdot</td>
<td>ORR</td>
</tr>
<tr>
<td>H-MOFP-Np-C</td>
<td>ZIF-8</td>
<td>ORR</td>
</tr>
<tr>
<td>Co-Zn-N-C</td>
<td>Zn-Co-MOF</td>
<td>ORR</td>
</tr>
<tr>
<td>Fe-N-C</td>
<td>Fe-ZIF-8</td>
<td>ORR</td>
</tr>
<tr>
<td>FeSAs-N/C-x</td>
<td>FePc-x@ZIF-8</td>
<td>ORR</td>
</tr>
<tr>
<td>Co-Fe</td>
<td>CoFe-BM0F</td>
<td>ORR</td>
</tr>
</tbody>
</table>

### 3.8.1 MOF-derivatives

Up to now, a large number of MOF-derivatives with different morphologies and structures have been widely prepared, such as polyhedral and core-shell structures of nanoparticles, nanorods, nanotubes, nanosheets, arrays and so on. In addition, the investigation of MOF-derivatives with various composition features (e.g. porous carbon, metal compounds and composites) were also underway, in order to explore the complex transformation mechanism and influence conditions like annealing temperature and atmospheres for MOF-derivatives fabrication.

#### 3.8.1.1 The strategies of MOF-derivatives

In recent years, tremendous efforts have been devoted to studying various strategies for preparation of MOF-derivatives due to the diversity of composition and structural tunability of pristine MOFs.\textsuperscript{[323]} Apart from a large number of direct carbonization strategies, other strategies (such as direct oxidation and direct sulfidation) have also been used to develop MOF-derivatives. For example, Castillo-Blas and co-workers developed a series of new MOFs with different arrangements (up to four different metal elements) and programed the composition of multimetal oxides via direct oxidation in air.\textsuperscript{[325]} Owing to the distribution of multiple metal cations at specific locations when construct MOFs, it is possible to prepare a multi-metal oxide with a novel composition by facile oxidizing the code selected metal ratio MOFs. The adjustable new oxides presented an enhancement of ORR activity, and the activity approached to commercial Pt/C. Meanwhile, Yilmaz et al. developed a feasible strategy to reconstruct Zn-Co coordinated Co-Mo disulfide, which derived from bimetallic (Co, Zn) MOFs by doping heteroatoms and functionalizing ligands.\textsuperscript{[326]} The Zn-N coordinated cobalt-molybdenum disulfide (MoS-CoS-Zn) was fabricated through successively sulfidation of CoS-Zn-MOF to CoS-Zn followed by two steps of solvothermal transformation. The MoS-CoS-Zn achieved distinct HER activity compared to MoS and MoS-CoS hybrid.

Recently, single-atom catalysts (SACs) have caused widespread concern thanks to their special catalytic properties. Owing to the advantage of highly ordered arrangements of metal sites, ordered pore structure and chemical stability, MOFs represent as ideal templates to fabricate carbon-supported SACs.\textsuperscript{[327]} For example, Deng et al. reported a novel metal-organic gaseous doping strategy to prepare embedding single Fe atoms N-doped carbon polyhedron catalysts.\textsuperscript{[328]} The single Fe atoms catalyst was
obtained by the pyrolysis of as-optimized ZIF-8 precursor. The Fe–N₅ sites synergy the porous structure of ZIF-8, resulting in an outstanding ORR activity and stability in both acidic and alkaline media. Jiao and co-workers proposed a novel dual protection strategy to fabricate high-contented single-atom Fe-implanted N-doped porous carbon (FeSA-N-C) by nanocasting SiO₂ in porphyrinic MOFs. The SiO₂ in MOFs created the thermally stable FeN₄/SiO₂ interfaces to provide the addition protection. The FeSA-N-C exhibited excellent catalytic activity and durability for ORR in both alkaline and acidic media because of high-density single-atom Fe sites. Recently, Hou and co-workers reported an overhang-eave structure decorated with iron single atom sites (Fe/OES) by silica-mediated MOF-templated (SMMT) strategy. The overhang-eave design provided three-phase exchange spots, which are favourable to the transport of ORR-relevant species and to maximize the exposure of single-atom active sites.

3.8.1.2 Structural design of MOF-derivatives

In view of the key role of nanostructure structure/morphology in catalytic applications, MOF-derivatives possess the stable structures that facilitate the transportation of mass/electron and the unique morphology is desirable for high exposure of active sites. Various synthetic strategies have been proposed to synthesize MOFs with different structures/morphologies, and the MOFs were further converted to various types of MOF-derivatives (0D, 1D, 2D and 3D) through controlled self-templating and external-templating methods.

Through reasonable controlling of the synthesis conditions, the morphology of the MOF precursors can be well inherited after chemical/thermal conversion. Therefore, MOF nanocrystals with high thermal stability can be used to fabricate MOF-derived polyhedral/hollow nanoparticles. For example, Chen and co-workers proposed a simple and straight method to synthesize yolk-shell Co@C-N nanoreactor with highly efficient, controllable and recyclable properties. As shown in Fig. 33A, the multi-yolk@shell nanostuctures was obtained through direct pyrolysis of hollow Zn/Co-ZIF precursors. Compared to the single metal MOF-derivatives, bimetal MOF-derived polyhedral structures owned more active sites and better facile mass dispersion. Xiong et al. designed a series of bimetallic MOF-derived carbon nanocomposite embedded with Co-Fe alloys via a facile host-guest method. The nanocomposite possessed a high specific surface and uniformly distributed bimetallic nanoparticles, which are favorable toward ORR.

Given the high exposure of active sites, stable structure and abundant channels/space for electron/mass transport, controlled synthesis of 1D MOF-derivatives have made rapid development in catalytic applications. Xie et al. reported a Co@CoNₓ/N-doped carbon tubes hybrid (Co@CoNₓ/NCT hybrid) derived from ZIF-67 via facile and economical one-step pyrolysis with urea. The urea not only served as nitrogen and carbon sources, but also promoted the growth of carbon tube. Recently, Xu and co-workers proposed a nitrogen-doped carbon nanotubes encapsulated with Co nanoparticles through direct pyrolysis of GO-wrapped ZIF-67. The fabrication is shown in Fig. 33B. The addition of triethylamine (TEA) can accelerate the crystallization of ZIF-67, and owing to the pining effect of RGO sheet, the N-CNTs are bonded with both sides of RGO sheet seamlessly.

In recent years, in view of the favorable electron transport, abundant active sites and short ion diffusion pathway, 2D materials are widely applied in various catalysts. The self-templating and external-templating methods are usually used to fabricate 2D MOF-derivatives. Recently, Zheng and co-workers presented a rational strategy to fabricate the N-doped carbon nanosheets with high loading of single/paired Fe atoms via carbonization of 2D bimetal MOF precursor (Fig. 34A).
The g-\(\text{C}_3\text{N}_4\) provides a nitrogen source for the catalyst and promotes the formation of Fe single atoms. The 2D carbon structure and the single/paired Fe atoms are favorable for OER catalysis. Compare to self-templating, external-templating is the process of growing the MOF in situ on the external template and then maintaining the morphology. Zhong and co-workers presented a 2D sandwich-like N-doped porous carbon nanosheets through the growing of ZIF on the surface of GO.\[338\] The N-doped porous carbon nanosheets were obtained through annealing the MOF/GO nanosheets, and exhibited excellent catalytic performance for ORR.

The 3D structure of the MOF-derivatives possesses the advantages of easy mass transfer/dispersion, high electrolyte permeability and high electron transfer rate. The 3D MOF-derivatives with different morphologies can be controllably synthesized by rational design of the structure and composition of MOF precursors.\[234a, 339\] For example, Sun and co-workers reported a series of urchin-like nanotube structures catalysts anchored with hierarchical single cobalt atom (UNT Co SAs/N-C) derived from well-aligned 3D hollow urchin-like ZIF-superstructures (UNT ZIF-67) (Fig. 34B).\[340\] The as-prepared UNT Co SAs/N-C catalysts manifest superior functionality for both ORR/OER. Zhou et al. developed a facile strategy to synthesis a series of nanoarrays constructed with metal oxide/carbon (MOx/C, M = Co, Ni, and Cu).\[341\] Among them, the array of nanosheets can expose more active sites with high conductivity, high catalytic activity and long-term durability.

**3.8.1.3 Compositional design of MOF-derivatives**

Apart from the effects of structure/morphology, the components of MOF-derivatives also play an important role in various catalytic applications. Through chemical treatment and pyrolysis in different atmospheres, active sites or active materials can be introduced during the conversion of the original MOF to MOF-derived materials, such as heteroatom doping (N, P, S and B), metal compounds doping (sulfides, phosphides selenides etc.) and single-atom catalysts. Metal-free carbon catalysts with defect structure and the introduced heteroatoms are widely investigated in catalytic applications, since the doping of heteroatoms can tune the optoelectronic properties and provide active sites.\[342\] MOF-derivatives can limit the active sites to permeable carbon and effectively improve the catalytic performance.\[343\] Recently, Zhang and co-workers reported N, P, S co-doped carbon hollow polyhedron derived from ZIF-8.\[344\] The ZIF-8 precursor was coated with poly(cyclotriphosphazene-co-4,4′-sulfonyldiphenol), which provided N, P, S atoms and Zn was evaporated at high temperature, thus causing the porous structure.

Metal compounds have shown great potential in electrocatalytic applications and MOF-derived functional metal compounds have been extensively studied since MOF is a promising template/precursor. Deng et al. developed a MOF-derived carbon nanorods encapsulated bismuth oxides by a facile in-situ oxide method for the efficient CO\(_2\) electroreduction.\[345\] The preparation process of MOF-derived oxide encapsulated in in-situ carbon is shown in Fig. 35A. The strategy also can be extended to prepare MOF-derivatives encapsulated with other metal compounds. As shown in Fig. 35B, Pan and co-workers proposed a novel pyrolysis-oxidation-phosphating strategy to fabricate hollow polyhedron anchored with CoP nanoparticles in N-doped CNT (NCNHP), which was derived from core-shell ZIF-8@ZIF-67.\[346\] The CoP/NCNHP hybrid exhibited superior electrocatalytic performances for electrocatalytic overall water splitting due to the synergistic effects between NCNHP and CoP NPs.

**3.8.2 Electrocatalytic water Splitting**

Electrochemical water splitting is one of the most promising large-scale and commercial hydrogen production methods. In recent years, the development of MOF-derivatives as electrocatalysts to promoting water splitting have been extensively studied.\[347\] Transition metal phosphides possess excellent HER performance. Chen and co-workers presented Co-incorporating FeP nanotubes (Co-Fe-P) derived from MIL-88B MOFs.\[348\] The Co, Fe, and P atoms were uniformly dispersed on Co-Fe-P nanotubes with hollow interior, and the synergistic effect caused by the substitution of Co atoms provides rich active sites and improved HER performance over a wide pH range with the overpotentials of 66, 86 and 138.
mV@10 mA cm$^{-2}$ in 0.5 M H$_2$SO$_4$, 1.0 M KOH and 1.0 M PBS, respectively. Meanwhile, transition metal phosphosulfides also exhibited the potential for HER. Li et al. reported the ternary pyrite-type cobalt phosphosulphide (CoPS-N/C) anchored to nitrogen-doped carbon, which was fabricated by carbonization and phosphosulfurization of ZIF-67. The CoPS nanoparticles was anchored on the inherent polyhedron of ZIF-67 and the catalysts exhibited outstanding HER activity in both acidic and alkaline conditions, achieving a small overpotential of $-80$ and $-148$ mV@10 mA cm$^{-2}$ in 0.5 M H$_2$SO$_4$ and 1.0 M KOH, respectively.

Reducing the energy barrier of OER is also an effective way to promote the electrocatalytic activity. MOF-derivatives have been considered as promising electrocatalysts to overcome the kinetic barriers of OER to replace precious metal catalysts (RuO$_2$ and IrO$_2$). Recently, 2D MOF-derivatives with intriguing physicochemical properties are attracting increasing attention for OER. Lin and co-workers proposed a topology-guided bottom-up strategy of a novel hexagonal 2D MOF nanoplate. The morphology can be modified into nanoplates through a substitution-suppression under the inhibition and modulation of pyridine. The obtained N-doped Ni@carbon composite after pyrolysis treatment exhibit the superior OER performance (a small overpotential of 307 mV@10 mA cm$^{-2}$) Tian et al. presented a novel strategy to convert bulk MOFs into ultrathin metal oxyhydroxide nanosheets for efficient OER through electric-field assisted hydrolysis. The MOF-derived ultrathin nanosheets achieve high OER activity (a low overpotential of 231 mV@10 mA cm$^{-2}$) and small Tafel slope of 42 mV dec$^{-1}$). The work provides new ideas for preparation of novel MOF derivatives for OER. Furthermore, the 3D structure stacked by 2D nanosheets can also effectively improve the OER performance. Li and co-workers prepared the interconnected nanoarrays embedded with Co–Ni bimetallic metaphosphate nanoparticles (Co$_{2-x}$Ni$_x$P$_4$O$_{12}$) through a mild phosphorylating process of CoNi-ZIF. The Co$_{2-x}$Ni$_x$P$_4$O$_{12}$-C exhibited excellent OER activity ($\eta = 230$ mV @10 mA cm$^{-2}$) and long term stability in 1M KOH, which can be attributed to the adsorption sites on the doping Ni site and the morphology integrity of the interconnected metaphosphate nanoarrays.

In view of the cost effect of electrolytic water splitting in practical applications, the catalysts possess both HER and OER activity to overall water splitting are expected. Liu et al. presented a universal vapor-phase strategy to fabricate echinops-like Co-based MOF (EC-MOF), which was well-aligned on conductive carbon cloth (Fig. 36). Since the electron transfer between active Co$_3$S$_4$ species and EC-MOF provides a more optimized adsorption performance for Co, the Co$_3$S$_4$/EC-MOF hybrid performed much enhanced electrocatalytic performance with overpotentials of 84 and 226 mV@10 mA cm$^{-2}$ for both HER and OER, resulting in highly efficient overall water splitting, and the system afforded a cell voltage of 1.55 V@10 mA cm$^{-2}$ which is lower than that of commercial Pt/C-IrO$_2$ (1.61 V) (Fig. 436 B-D).

### 3.8.3 Electrocatalytic ORR

Pt-based catalysts, despite their excellent ORR properties, hinder the development of large-scale commercialization due to their high cost and poor durability. As cathode catalysts for ORR, MOF-derivatives possess hierarchical pores, high active sites density and excellent conductivity, especially, potential rich N-C or M-N-C (M refer to Co, Fe, etc.) active sites play a vital role in improving ORR performance. Niu and co-workers reported an efficient N-doped CNTs (N-CNTs) derived from MOFs with N-doped carbon dots (N-Cdots) for ORR. The N-Cdots not only provide hydroxyl and amine groups, which is beneficial to the formation of N-CNTs, but also induce

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the graphitic structure and extra nitrogen to extend the ORR activity for N-CNTs. Thus, the N-CNTs showed a positive onset potential (0.88 V vs. RHE) and a low Tafel slope (~81 mV dec⁻¹). Extensive studies of M-N-C materials have shown that they have outstanding ORR activity and stability, and M-N-C materials are promising substitutes for Pt/C catalysts. Ang et al. developed a versatile strategy to prepare hollow N-doped carbon capsules. One or more atomically metals (H-M-N-C and H-M₂₅₉₁-N₄-C, respectively, M = Co, Fe or Ni) were dispersed to study the relationship between catalyst composition and electrocatalytic activity for ORR. The catalyst was fabricated through annealing the core-shell (ZIF core and a metal-tannic acid coordination polymer shell) precursors to obtain N-doped carbon support dispersed with Fe-N₄ active sites in 3D interconnected mesopores, which improved the ORR activity of Fe@MNC-1. The optimized Fe@MNC-1 exhibited a larger positive half-wave potential of 0.88 V in alkaline media compare to that of 20 wt% commercial Pt/C catalyst (0.85 V). Recently, single atom M-N-C catalysts have attracted widespread attention and the M-N₄ sites near the N-bonding environment plays a key role in the catalytic performance of the ORR. Jiang et al. fabricated a series of Fe-N-C nanoarchitectures with atomically dispersed Fe-N₄ sites through precisely atomic-level control method. The Fe-N₄ sites possessed well-defined single-atom sites and were dispersed on 3D hierarchically porous carbon. Adjustable grading of micro-mesoporous structures and the exposure of Fe-N₄ single sites make a significant contribution to ORR activity. The catalyst containing 0.2 wt% of transition metal (Fe SAs-N/C-20) exhibited excellent ORR performance (E₁/₂ = 0.915 V vs. RHE), which was significantly higher than that of commercial Pt (E₁/₂ = 0.85 V) in 0.1 M KOH. In particular, the atomic utilization is enhanced by 10 times compared with most previous reports.

3.8.4 Electrocatalytic CO₂RR

Efficient electrocatalytic CO₂RR not only reduce greenhouse effect, but also convert CO₂ to value-added products. However, the high overpotential of electron transfer from electrocatalysts to CO₂ and the competition of side reactions seriously impede the high energy efficiency and scalability for CO₂RR. Over the past decades, MOF-derivatives have been considered as potential catalysts for CO₂RR due to their promising activity sites and adjustable structures. Wang et al. prepared a series of atomically dispersed Co catalysts derived from bimetallic Co/Zn ZIFs, which possessed different nitrogen coordination numbers. The obtained catalyst with two coordinate nitrogen atoms exhibited a high CO formation FE (94%) and high selectivity. The synergistic interactions based on various molecules and their interfaces of plenary single-atomic structures can significantly promote the CO₂RR process. Later, Ren et al. developed an efficient nitrogenated carbon catalysts anchored with isolated diatomic Ni-Fe sites for CO₂RR. Based on mechanism research, the structural change of bimetal nitrogen sites effectively reduces the reaction energy barrier, resulting in superior CO₂RR activity. The Ni/Fe-N-C showed an outstanding FE for CO (up to 98%) and robust durability. Gu and co-workers developed a catalyst dispersed with single-atom Fe sites, which presented ultrahigh activity for CO₂RR. The single-atom Fe catalyst (Fe₃⁴-N-C) was fabricated via annealing the Fe-doped ZIF-8 under N₂ at 900 °C. They found the discrete Fe³⁺ ions possessed more activity compare to Fe²⁺ sites, resulting to faster adsorption for CO₂ and weaker absorption for CO. Thus, Fe₃⁴-N-C exhibited superior CO₂RR performance that only required an overpotential of 80 mV to produce CO and the current density reached 94 mA cm⁻² at a low overpotential of 340 mV.

3.8.5 Other electrocatalytic reactions

In addition to the above electrocatalytic reactions (ORR, HER, OER and CO₂RR), MOF-derivatives have also been applied to other catalytic reactions (such as NRR and MOR). Given the promising and environmental-friendly method of electrochemical NNR for sustainable ammonia production, the development of MOF-derivatives for efficient NRR has
attracted increasing attention.[357] Liu et al. successfully synthesized the N-doped porous carbon (NPC) derived from nitrogen-rich ZIF-8 as cost-effective NRR catalysts.[320] Through adjusting the N content and species, the N$_2$ chemical adsorption and Ni/N cleavage significantly enhanced, resulting in high activity of the optimized NPC for NRR. They found that the contents of pyridinic and pyrrolic N were crucial for promoting ammonia production on NPC by theory calculation. Geng and co-workers presented nitrogen-doped carbon distributed with Ru single atoms (Ru SAs/N-C) as N$_2$ reduction catalysts.[321] The obtained Ru SAs/N-C derived from ZIF-8 exhibited a record-high activity for N$_2$ electrochemical reduction, which achieved a FE of 29.6% for NH$_3$ production and a high ammonia production rate of 120.9 μg h$^{-1}$ mg$_{cat.}^{-1}$. Recently, Luo et al. reported a nitrogen-doped carbon/Co$_3$O$_4$ nanocomposites (Co$_3$O$_4$@NCs) derived from ZIF-67 with core-shell structures, which exhibited an outstanding NRR performance with a FE of 8.5% at $–0.2$ V vs RHE and a high NH$_3$ yield of 42.58 μg h$^{-1}$ mg$_{cat.}^{-1}$. Owing to the simplicity, high energy conversion efficiency and renewable fuel, direct methanol fuel cell (DMFCs) has been attracted as promising power source for energy demand in future.[358] Recently, Rezaee and Shahrokhiyan reported a fabrication of 3D ultrathin nanoporous carbon composite embedded with petal-like NiCo/NiO-CoO metal/metal oxides.[322] The nanoporous carbon composite is synthesized through direct carbonization of the as-designed bimetallic MOFs. The obtained NiCo/NiO-CoO/NPCC exhibited excellent electrocatalytic MOR performance with a small $E_{\text{onset}}$ of 0.32 V compare to Ni/NiO/NPCC ($E_{\text{onset}} = 0.38$ V) and Co/CoO/NPCC ($E_{\text{onset}} = 0.43$ V), which can be attributed to the fast ion/electron transfer offered by enlarged specific surface of unique ultrathin petal-like structure.

### 4. Summary and perspective

In summary, the recent progress of MOF-based materials, including pristine MOFs, MOF composites and MOF-derivatives for photo/electrocatalysis is comprehensively reviewed. The novel strategies to improve the photo/electrocatalytic activities are discussed and highlighted. The vast developments in the past several years have proven that MOFs are promising photo/electrocatalysts to resolve the energy and environmental problems. Though tremendous achievements have been realized, MOF-based photo/electrocatalysts still face some challenges which need to be addressed. The main drawbacks of MOFs for photo/electrocatalysis are their low stability and low conductivity, hampering their photo/electrocatalytic activities. Highly stable MOFs with improved conductivity are crucial for high catalytic activity and long-term durability. Also, the low cost, facile and large-scale synthesis of MOFs with high catalytic activities is everlasting targets for large scale industry applications. What’s more, the build-up of structure-property relationship of MOFs for photo/electrocatalysis is highly eager. A deep insight of the catalytic mechanism and reaction pathways can predict and modulate the activity and selectivity, guiding the rational design of highly efficient photo/electrocatalysts of MOFs. Advanced in situ and operando techniques are needed to investigate the real active sites and reaction pathways.

The semiconductor-like behavior is the most important characteristic for MOF photocatalysts. The bandgaps of MOFs can be modulated via metal-doping, ligand functionalization and forming composite with other materials to improve the light harvesting efficiency. The location of HOMO and LUMO levels to match the redox potential is prior considerations for some photochemical reaction. The study and understanding of systematic control of the band structure of MOFs is particularly important but still lack. Also, most MOF photocatalysts suffer from low conversion efficiency, especially for photocatalytic CO$_2$ reduction and organic synthesis, so a trade-off between efficiency and selectivity should be concerned, and MOFs photocatalysts with both high efficiency and selectivity need to be explored.

Noble metal materials are usually utilized to improve the photocatalytic activities of MOFs, such as using noble metal Pt as cocatalyst, or using Ru/Ir-based molecules as light harvesting component. Yet, the scarcity and high price of noble metal materials limit their practical applications. The replacement of noble metals with earth-abundant elements as cocatalysts or light harvesting components without loss of high efficiency is highly important. Also, for most photocatalytic reactions such as HER, OER and CO$_2$RR, only half reduction or oxidation reactions can be utilized and sacrificial agents as electron donor or accept are needed. It is highly desirable to integrate the reduction reaction and oxidation reaction together to avoid the usage of sacrificial agents. For practical applications by using natural sunlight, the use of sacrificial agents is not feasible. The photocatalytic overall water splitting process only use H$_2$O as the reactants, and in the natural photosynthesis of plants, the photocatalytic CO$_2$RR only involves H$_2$O and CO$_2$ to produce carbohydrates and O$_2$. Yet, MOFs for photocatalytic reactions without sacrificial agents were rarely investigated and reported. The artificial photosynthesis to mimic the photosynthesis with high efficiency and selectivity for carbohydrates is still a formidable but also promising task.

For large scale and industrial applications, the electrocatalysis should be performed at large current density (usually 200-500 mA cm$^{-2}$) with high efficiency and stability. Yet, the electrocatalytic performances of MOFs at large current density is still rare and the stability of MOFs in these conditions need more studies. The electrochemical reactions are performed in electrolyte, which usually need strong acidic or basic conditions that are harmful to environments and the stability of catalysts. More attentions need to be paid to the development of efficient MOFs electrocatalysts working at environmentally benign and neutral pH electrolyte, or even solid electrolyte. Electrocatalytic pollution degradation and electroorganic synthesis possess much higher conversion efficiency compared with photocatalytic reactions, and are more promising when utilize electricity generated by clean solar energy. Yet, the studies of electrocatalytic pollution degradation and electroorganic synthesis are quite limited and on the early stage. 2D ultrathin MOFs are very promising electrocatalysts with superior activity and efficiency, due to...
the high density of coordinatively unsaturated metal sites, superior electron transfer, rapid mass transport and fast permeation of gas/liquid molecules. Yet, the development of facile and large-scale synthesis of 2D MOFs in multigram quantities is still lacking. MOF-derivatives have the advantages to surpass the low stability and low conductivity issues of pristine MOFs, and have demonstrated superior photo/electrocatalytic activities. Yet, the lacked knowledge of transformation mechanism from MOFs to MOF-derivatives hampers the precise control of fine structures. By using in situ and operando techniques to monitor the synthesis process can help to establish a better understanding of the formation mechanism of MOF-derivatives, guiding the accurate control of the structure and active sites of MOF-derivatives toward aimed photo/electrocatalysis. Single-atom catalysts derived from MOFs have caused widespread concern for their superior photo/electrocatalytic performance. Yet, MOF-based single-atom catalysts is still on the early stage, and more experimental and theoretical studies should be launched for a better understanding of the formation process of single-atom catalysts and revealing the catalytic mechanism on the active sites at an atomic level. Also, new strategies for the facile and low-cost synthesis of MOF-based single-atom catalysts should be explored.

By integrating various MOF-based photo/electrocatalysis together, it is possible to build a sustainable system with low carbon or even carbon-neutral energy cycle. H₂O, CO₂ and N₂ can be converted to high value-added compounds via electrocatalysis driven by renewable energy or photocatalysis. ORR and OER catalysts-driven metal-air battery can drive the electrocatalytic water splitting process, and the generated H₂ and O₂ are used to generate clean electricity in fuel cells via hydrogen oxidation reaction (HOR) and ORR reactions, forming a self-powered system. All the system involved photo/electrocatalysis is able to be realized via MOFs with high stability and catalytic efficiency to make sustainable pathways for the production of high value fuels and chemicals. There is no doubt that MOF-based photo/electrocatalysts will continue to trigger much increasing research in the future. We believe that low-cost, stable and efficient MOF-based photo/electrocatalysts combined with other emerging applications such as gas storage and separation, will present a bright future for creating global-scale sustainable energy system.

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Abbreviations
4,4′-bpy, 4,4′-bipyridine; AB, acetylene black; ALD, atomic layer deposition; ATA, 2-aminoterephthalate; BTBA, benzo-(1,2-d,4,5-d′)bistriazole; BDC, 1,4-bicarboxybenzene; bib, 1,4-bisimidazolebenzene; bpa,1,2-bis(4-pyridyl)ethane; bpe,1,2-bis(4-pyridyl)-ethene; bpy, 2,2′-bipyridine; BHT, benzenehexamthiol; BPDC, biphenyl-3,4′,5-tricarboxylic acid; BPT, [1,1′-biphenyl]-3,4′,5-tricarboxylate; BPTC, biphenyl-3,4′,5-tricarboxylic acid; BTB, benzene tribenzoate; BTC, 1,3,5-benzenetricarboxylate; CF, carbon foam; CNTs, carbon nanotubes; CO₂RR, CO₂ reduction reaction; CP, carbon paper; CPE, constant potential electrolysis; CV, cyclic voltammograms; dcbpy, 2-phenylpyridine-5,40-dicarboxylic acid; DFT, density functional theory; dtao, dithiooxamidato; ECSA, electrochemical active surface area; EIM, 2-ethylimidazolide; EMIMBF₄, 1-ethyl-3-methylimidazolium tetra-fluoroborate; EPR, electron paramagnetic resonance; ESR, electron spin resonance; FE, Faradaic efficiency; FTO, Fluorine-doped tin oxide; GC, glassy carbon; GC-RDE, rotating glassy carbon disk electrode; GDE, gas diffusion electrodes; H₂bpydc, 2,2′-bipyridine-5,5′-dicarboxylic acid; HER, hydrogen evolution reaction; HHTP, 2,3,6,7,10,11-hexahydroxytriphenylene; HIM, hexane imidazolium; HTP, hexaiminotriphenylene; HOMO, highest occupied molecular orbital; ITO, Indium tin oxide; LLCT, ligand-to-ligand charge transfer (LLCT); LMCT, ligand-to-metal charge transfer; LUMO, lowest unoccupied molecular orbital; maa, mercaptoacetic acid; MLCT, metal to ligand charge transfer; mna, 2-mercaptonicotinic acid; MOF, metal-organic layers; MOR, methanol oxidation reaction; NA, nicotinic acid; NFs, Nickel foams; NHE, normal hydrogen electrode; NPs, nanoparticles; NPC, 2,6-naphthalenedicarboxylic acid; NRR, N₂ reduction reaction; NTB, 4,4′,4″-nitrotriphenylenebazoate; OER, oxygen evolution reaction; ORR, oxygen reduction reaction; PBS, phosphate buffer solution; phen, phenanthroline; PL, photoluminescence; POM, polyoxometalate; ppy, 2-phenylpyridine; PSE, post-synthetic exchange; pta, p-thiophenic acid; PYI, pyrroloidin-2-ylimidazole; Ptza, 5-(2-pyrazinyl)tetracazol; RDE, rotating ring disk electrode; RVC, reticulated vitreous carbon; SHE, standard hydrogen electrode; tattb, 4,4′,4″-s-triazine-2,4,6-tribenzoic acid; TBA, tetrabutylammonium; TBAPF₆, tetrabutylammonium hexafluorophosphate; TBAPy, 1,3,6,8-tetraakis(p-benzoic acid)pyrene; TBATFB, tetrabutylammonium tetrafluoroborate; TC, tetracycline; TCPP, 4,4′,4″-(porphyrin-5,10,15,20-tetrayl)tetrabenzoate; TEOA, triethanolamine; terpy, 2,2′,6′,2′′-terpyridine; Trim, trimesate; THA, triphenylethenehexahmine; THF, tetrahydrofuran; TOF, turnover frequency; TON, turnover number; TPA, tris(2-pyridylmethyl)amine; TTH, triphenylethanolthiol; Tpy, 2,2′,6′,2′′-terpyridine.

Conflicts of interest
There are no conflicts to declare.

References

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This review summarizes the recent and important advances on MOF-based photo/electrocatalysts including pristine MOFs, MOF composites and MOF-derivatives. The novel strategies to improve the photo/electrocatalytic performances are highlighted.

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