



Design and application of metal-organic framework-derived catalysts for oxygen reduction in energy conversion devices

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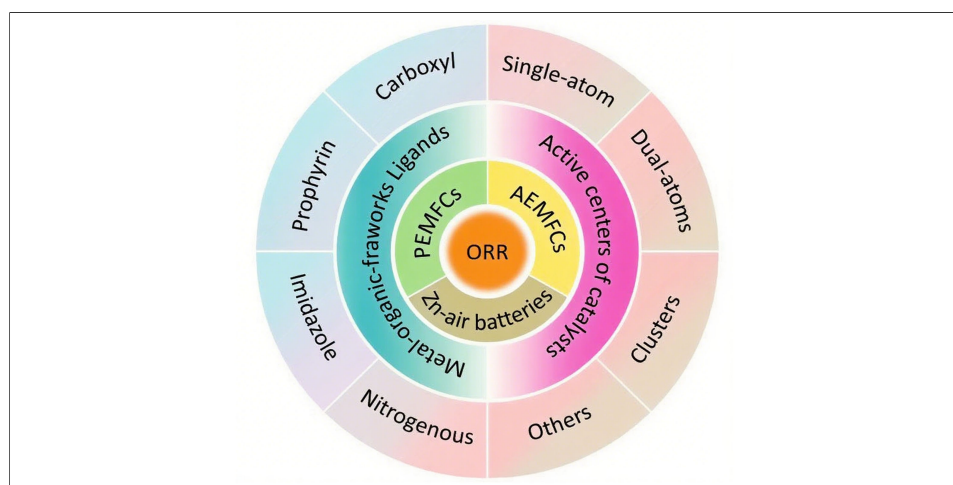
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Abstract

The oxygen reduction reaction (ORR) is a clean energy conversion process with the potential to address the current energy crisis and promote the adoption of clean energy sources. Developing high-activity catalysts is essential to accelerate the inherently slow ORR kinetics and improve overall efficiency. Atomic-level oxygen reduction catalysts can be prepared through pyrolysis and solvothermal synthesis, using metal-organic frameworks (MOFs) as precursors or templates. This approach preserves the structural advantages of MOFs while enabling precise, atomic-scale tuning of catalyst composition and structure, thereby optimizing their ORR catalytic performance. Advances in catalyst synthesis and characterization methods have improved the understanding of the dynamic evolution of active centers and ORR performance in real-world devices. This paper provides a comprehensive review of ORR mechanisms, describes MOF-derived ORR catalytic materials with distinct ligands, and classifies them by ligand type to elaborate on the role of

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ligands in catalyst derivation and their influence on ORR performance. It further discusses the tuning of various MOF-derived catalyst types—single-atom, dual-atom, and cluster configurations—through precise control of metal content and species, exploring the relationship between catalyst architecture and ORR activity. The challenges of real-time monitoring of MOF pyrolysis and of understanding dynamic metal coordination during catalytic processes are also discussed. Finally, it examines the future prospects and challenges of MOF-based catalysts for the ORR.

INTRODUCTION

Continuous economic progress has increasingly intensified the conflict between energy and environmental protection^[1–3]. Advanced clean energy conversion devices, such as fuel cells and Zn-air batteries (ZABs), are considered promising solutions to this challenge^[4–8]. However, the cathodic oxygen reduction reaction (ORR) on which these devices rely suffers from slow kinetics, necessitating the use of expensive platinum-group metal catalysts, which considerably increase application costs^[9–16]. Consequently, many researchers have sought low-cost, high-performance alternatives to precious metal catalysts^[17–21]. A major challenge in the development of such ORR catalysts is the precise regulation of active sites^[22,23]. Metal-organic frameworks (MOFs), with their well-defined and tunable structural architectures, have emerged as ideal precursors for these catalysts^[24].

MOFs are porous coordination polymers constructed from organic ligands and metal ions or clusters^[25]. Since the first MOF was reported in 1995, nearly three decades of research have produced tens of thousands of MOF structures, with novel frameworks continually emerging. In recent years, their exceptional properties and broad potential have been leveraged in various applications, including adsorption, separation, catalysis, sensing, and ionic conductivity. In catalysis, MOFs stand out for their unique advantages, including diverse metal centers, flexible structural design, and tunable organic ligands^[26–30]. These characteristics have drawn notable attention from scientists across multiple disciplines, reflecting a clear trend toward interdisciplinary research^[31–37]. Moreover, by tailoring pore types and sizes and modifying structural models, researchers have created a wide range of potential MOF configurations^[38–40]. MOFs have recently been employed as templates for synthesizing metal-nitrogen-carbon (M-N-C) catalysts and extensively studied for ORR applications^[41–45]. The individual components of MOFs play distinct roles during material derivation, enabling the creation of diverse new materials^[46–49]. For instance, some MOFs form stable single-atom materials after calcination, whereas others yield nanoparticles (NPs)^[50]. This morphological diversity is closely linked to the ligands and metal species in MOFs.

It is well known that most MOFs are nonconductive and require a treatment process to become ORR catalysts, involving changes to their ligands and metal coordination environment. However, no systematic summary exists on which MOFs ligands can be post-treated to obtain ORR catalysts, why some MOFs thermally decompose to form single-atom sites, dual-atom sites, nanoclusters and so on, and how these transformations influence ORR performance. This review aims to bridge the gap between MOF materials and ORR catalysts by summarizing recent applications of MOF-based catalysts for ORR from the perspectives of ligands and metals.

Advancing the applications of MOF-based materials requires a thorough understanding of the interplay between MOFs and their derivatives, as well as the correlation between the original MOF architecture and the properties of MOF-derived materials. To examine this relationship, this review first analyzes MOF ligands and metal/metal clusters, then summarizes recent progress on how MOF structures and their derivatives influence ORR and energy conversion devices. The discussion begins with MOF-derived ORR

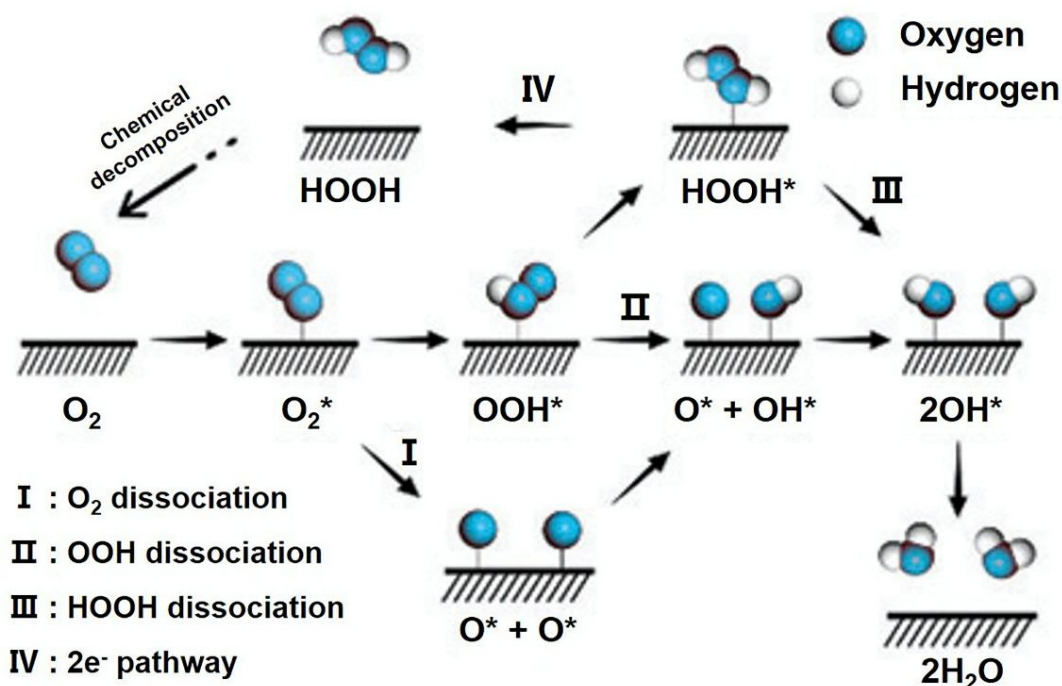


Figure 1. Molecular model of the oxygen reduction reaction process (reproduced with permission from Royal Society of Chemistry, copyright 2021)^[53].

catalytic materials categorized by ligand type, detailing their role in catalyst derivation and their influence on ORR performance. It then shifts to the modulation of MOF-derived catalyst architectures—single-atom, dual-atom, and cluster configurations—through precise control of metal content and species, followed by an exploration of the relationship between catalyst structure and ORR activity. For example, ligand design governs the formation of hierarchical pores, metal dispersion, and active-site configurations during pyrolysis; morphological tuning improves mass transport; and adjustments to the chemical environment can modulate electronic properties to enhance ORR kinetics. Building on these insights, the review presents a comprehensive summary of coordination-control strategies for MOF-based catalysts in ORR, highlighting how precise manipulation of metal-ligand interactions can stabilize single-atom sites and optimize their geometric and electronic structures for efficient oxygen activation. The article concludes with a discussion of future opportunities and challenges for MOF-based ORR catalysts.

FUNDAMENTALS OF THE OXYGEN REDUCTION REACTION

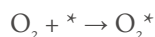
Mechanism of the oxygen reduction reaction

The electrocatalytic oxygen reduction process comprises two competing reactions: the 2e⁻ conversion process and the 4e⁻ conversion process^[51,52], which convert O₂ into H₂O₂ and O₂ into H₂O, respectively^[53] [Figure 1]. As the 2e⁻ transfer exhibits much lower energy conversion efficiency than the 4e⁻ transfer, the latter predominates in energy conversion devices^[54].

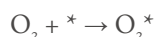
In the first stage of the ORR process, freely diffusing O₂ adsorbs onto the catalyst surface, forming adsorbed O₂*. Further reduction occurs via one of three main pathways: the dissociation pathway, the coalescence pathway, or the peroxide (secondary coalescence) pathway. In the dissociation pathway, the O-O bond is broken prior to electron and proton adsorption, forming two O* adsorption intermediates that are subsequently reduced to OH* and then to hydroxide anion (OH⁻) (steps 1 and 2). In the coalescence pathway, electrons and protons combine to form OOH* before O-O bond rupture; cleavage of the O-O bond

in OOH^* yields O^* and OH^* intermediates, which are further hydrogenated to form OH^- (steps 3-6). The peroxide pathway is a branch of the associative pathway, in which O_2 binds to the catalyst surface before O-O bond cleavage. The OOH^* intermediate is reduced to hydrogen peroxide at the active site (H_2O_2^*), which can desorb from the catalyst surface to produce H_2O_2 as the final product (steps 7-10). Alternatively, H_2O_2^* can undergo O-O bond cleavage and formation of the OH^* intermediate, which is ultimately reduced to OH^- . The detailed ORR reaction mechanisms are given below^[55]:

Dissociation pathway:



Coalescence pathway:



Peroxy pathway:

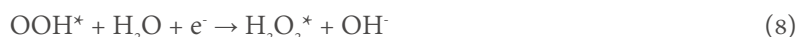
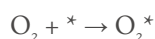


Figure 2A presents a volcano plot of the O-binding energy functions of different metals, and Figure 2B shows a volcano plot of the binding energy functions of O and OH. Clearly, Pt and Pd are the most effective metals for oxygen reduction catalysis. As demonstrated in Figure 2C, the mechanism underlying the calculated changes in oxygen reduction free energy and oxygen dissociation potential barrier is illustrated. The process and dissociation reaction schemes are identical [Figure 2D]. The binding mechanisms of Au (111) under low oxygen coverage and Pt (111) under high oxygen coverage exhibit lower free energy barriers than the dissociation mechanism. For Pt under low oxygen coverage, O_2 dissociation cannot be activated, and its dissociation mechanism-featuring the lowest barrier-dominates the process^[56].

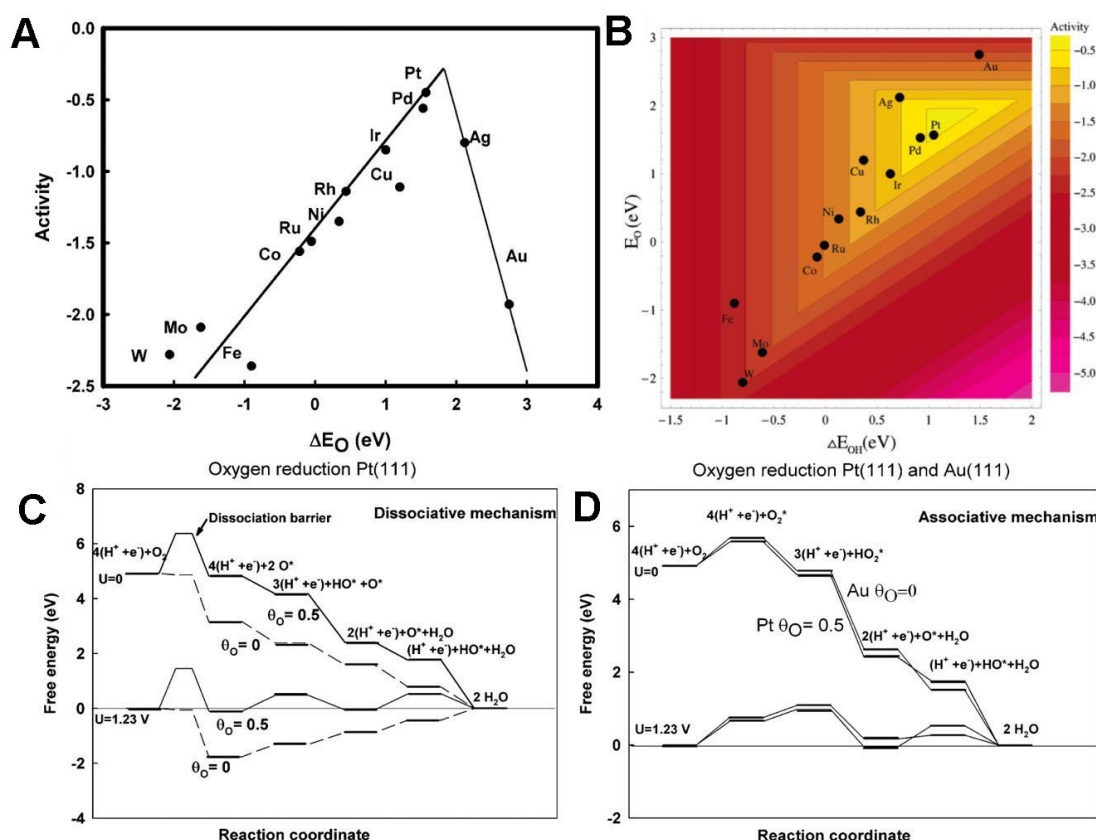


Figure 2. Function diagrams of (A) O binding energies and (B) O-OH binding energies for different metals; Free energy diagrams of (C) oxygen reduction under different potentials and oxygen coverages, including the oxygen dissociation potential barrier, and (D) the oxygen peroxidation mechanism under low oxygen coverage of Au (111) and 1/2 oxygen coverage of Pt (111). A-D reproduced with permission from the American Chemical Society, copyright 2004^[56].

Development of devices for the ORR

Traditional extraction of fossil fuels, including oil and coal, is depleting natural resources and degrading the environment. To address these issues, governments and businesses worldwide are investing in the advancement and integration of new energy sources^[57–59], accelerating the transition from traditional energy sources to clean and efficient alternatives. Hydrogen energy, in particular, has attracted increasing attention from the scientific community as a promising new energy source^[60–65], driving considerable research into hydrogen energy conversion devices such as proton exchange membrane fuel cells (PEMFCs) and anion-exchange membrane fuel cells (AEMFCs)^[66]. Metal-air batteries, particularly ZABs, have also drawn considerable attention as potential clean energy technologies^[67–70].

Proton-exchange membrane fuel cells

PEMFCs are considered a potentially viable power source for electric vehicles^[71,72]. A PEMFC comprises four primary components: a bipolar plate, a catalyst layer, a proton-exchange membrane, and a gas-diffusion layer [Figure 3A]^[73]. Of these, the catalyst layer plays the most critical role in determining maximum power density, while the other components are largely supportive. Significant improvements in catalyst activity and catalyst-layer design remain necessary^[74]. Commercial Pt/C catalysts, though widely used, are costly and insufficiently stable^[75], creating demand for efficient catalysts containing low Pt content or entirely without platinum group metals^[76]. Numerous M-N-C catalysts have exhibited performance comparable to Pt/C in rotating disk electrode (RDE) tests^[77]. However, the acidic operating environment in which PEMFCs operate diminishes catalyst effectiveness in membrane electrode evaluations and hinders industrial application. The

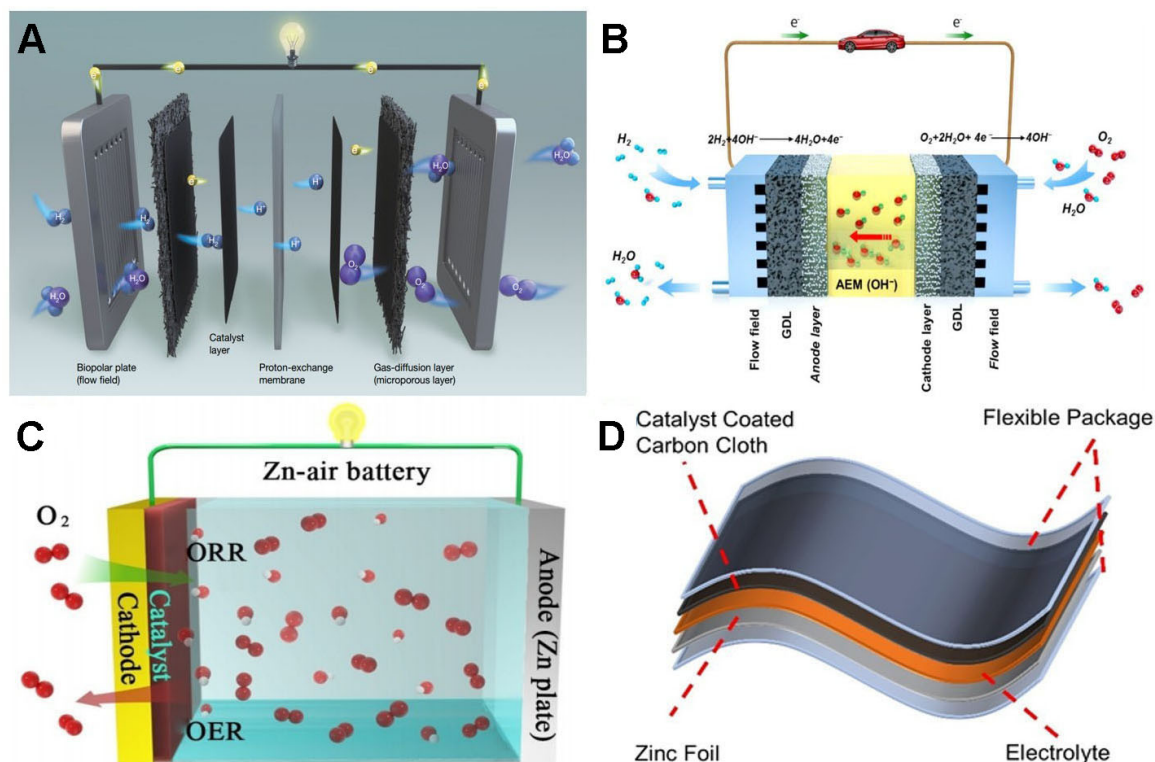


Figure 3. (A) Diagrams of the structure and working principle of proton-exchange membrane fuel cells (reproduced with permission from Springer Nature, copyright 2021)^[73]; Schematics of (B) an anion-exchange membrane fuel cell (reproduced with permission from Elsevier, copyright 2021)^[78], (C) a liquid Zn-air battery (reproduced with permission from Wiley-VCH, copyright 2023)^[88], and (D) a solid flexible Zn-air battery (reproduced with permission from Wiley-VCH, copyright 2023)^[90]. ORR: Oxygen reduction reaction; OER: oxygen evolution reaction; AEM: anion-exchange membrane.

replacement of precious metal catalysts remains a major challenge.

Anion-exchange membrane fuel cells

In AEMFCs, the proton exchange membrane of PEMFCs is replaced with an anion-exchange membrane [Figure 3B], thereby creating an alkaline working environment that reduces the leaching of transition metals^[78]. This significantly enhances the practicality of M-N-C catalysts and substantially lowers costs^[79]. However, AEMFCs require more expensive auxiliary components than PEMFCs. Even so, AEMFC catalysts are expected to offer enhanced performance at lower overall cost. The coordination structure of M-N-C catalysts is difficult to control, making it challenging to balance metal site density and reaction mass transfer resistance—an imbalance that largely influences catalytic performance^[80]. Furthermore, AEMFC efficiency and stability are marginally inferior to those of PEMFCs^[78]. Developing catalysts with stable coordination structures that optimize catalytic performance and stability remains a top priority.

Zn-air batteries

Metal-air batteries are clean energy storage devices that convert chemical energy into electrical energy through the oxidation reaction of metals inside the battery^[81,82]. Among them, ZABs are the most widely studied, offering high energy density, low production cost, and safe operation [Figure 3C]^[83,84]. They are suitable for extensive applications across diverse domains, such as large-scale energy storage, new energy vehicles, and portable devices^[85–87]. In ZABs, Zn plates serve as the anode and air as the cathode—an arrangement that is cost-effective, nontoxic, and environmentally friendly^[88]. Nevertheless, the conventional liquid electrolytes used in ZABs are inconvenient^[89], prompting the development of flexible ZABs with solid

electrolytes [Figure 3D]^[90]. In comparison with conventional ZABs, flexible ZAB designs offer superior safety and stability, and can operate at low temperatures. Regardless of type, ORR catalysts are fundamental to ZAB performance^[91]. The alkaline operating environment allows the use of transition metals as catalysts, offering a potential avenue for further cost reduction.

The requirements for ORR catalysts vary among energy conversion devices. PEMFCs, the only devices operating in an acidic environment, demand catalysts with high activity and stability under acidic conditions. AEMFCs and traditional ZABs require catalysts optimized for alkaline conditions. Flexible ZABs, as a distinct class, require catalysts with dual functionality for both the ORR and oxygen evolution reaction, which is essential for their unique charge-discharge cycles.

MOFS WITH DIFFERENT LIGAND-DERIVED CATALYSTS

The ligands in MOFs play a crucial role in constructing MOF topology and regulating crystal morphology. In addition to providing structural support, they determine pore dimensions and geometries, and enable the incorporation of functional moieties or chiral centers for post-modification-attributes of paramount importance in ORR catalyst derivation^[92]. Through the rational design of ligands and coordination modes, the performance characteristics of MOF-derived catalysts can be systematically modulated, facilitating the transition from fundamental research to practical applications^[93]. The most prevalent MOFs include the Materials Research Institute Lavoisier (MIL) and the University of Oslo (UiO) MOFs, which use carboxylic acids as organic ligands. Other MOF structures include PCN-224, featuring a porphyrin framework, and zeolite imidazole frameworks (ZIFs) with imidazole as the organic ligand. As the electrocatalytic ORR requires highly conductive catalyst materials, most MOF-derived catalysts must be calcined to improve graphitization and thereby enhance conductivity^[94]. In this process, MOFs prepared with different organic ligands can be used to tailor the catalyst microenvironment and catalytic performance.

Carboxyl ligand-based MOF-derived catalysts

Carboxylic ligands, with their abundant coordination oxygen sites and diverse coordination modes, form stable MOFs with various metal ions, providing numerous active sites for catalysis. In addition, carboxylic acid groups have a high negative charge density and strong coordination ability with metals, further enhancing catalytic activity. Common carboxylic acid ligands include isophthalic acid, p-phthalic acid, and trimesic acid. However, catalysts derived from the pyrolysis of carboxylate-ligand-based MOFs typically form NPs, as the carboxyl oxygen atoms stably coordinate with multiple metal centers, bridging them and promoting metal-particle aggregation during pyrolysis^[95].

Zhang *et al.* synthesized a polyCo-MOF precursor using terephthalic acid as the ligand [Figure 4A]^[96]. The hybrid precursor polyCo-MOF@MCA, obtained through the complexation of polyCo-MOF, melamine, and cyanuric acid, was pyrolyzed at varying temperatures to yield a series of catalysts. The catalyst CoO_x/Co@CN_y, produced by thermal decomposition at 700 °C, exhibited the highest 2e⁻ oxygen reduction activity. Experimental and computational analyses showed that CoO_x NPs and metal Co/CoO_x interfaces enhance H₂O₂ selectivity. In addition, CoO_x NPs with a high density of oxygen vacancies and lattice defects modulate O₂ adsorption and facilitate O-O bond cleavage, thereby increasing H₂O₂ activity and selectivity.

The high specific surface area and elevated space utilization of MOF-derived catalysts have also attracted considerable research interest. For example, Yang *et al.* synthesized a rod-shaped indium-based MIL-68-NH₂ using indium salts and 2-aminoterephthalic acid (NH₂-H₂BDC), with pyridine added to control MOF particle size [Figure 4B]^[97]. Thermal conversion transformed the MOF into a porous carbon-based material, yielding FePc@NCNS. During calcination, molten indium species evaporated, creating additional

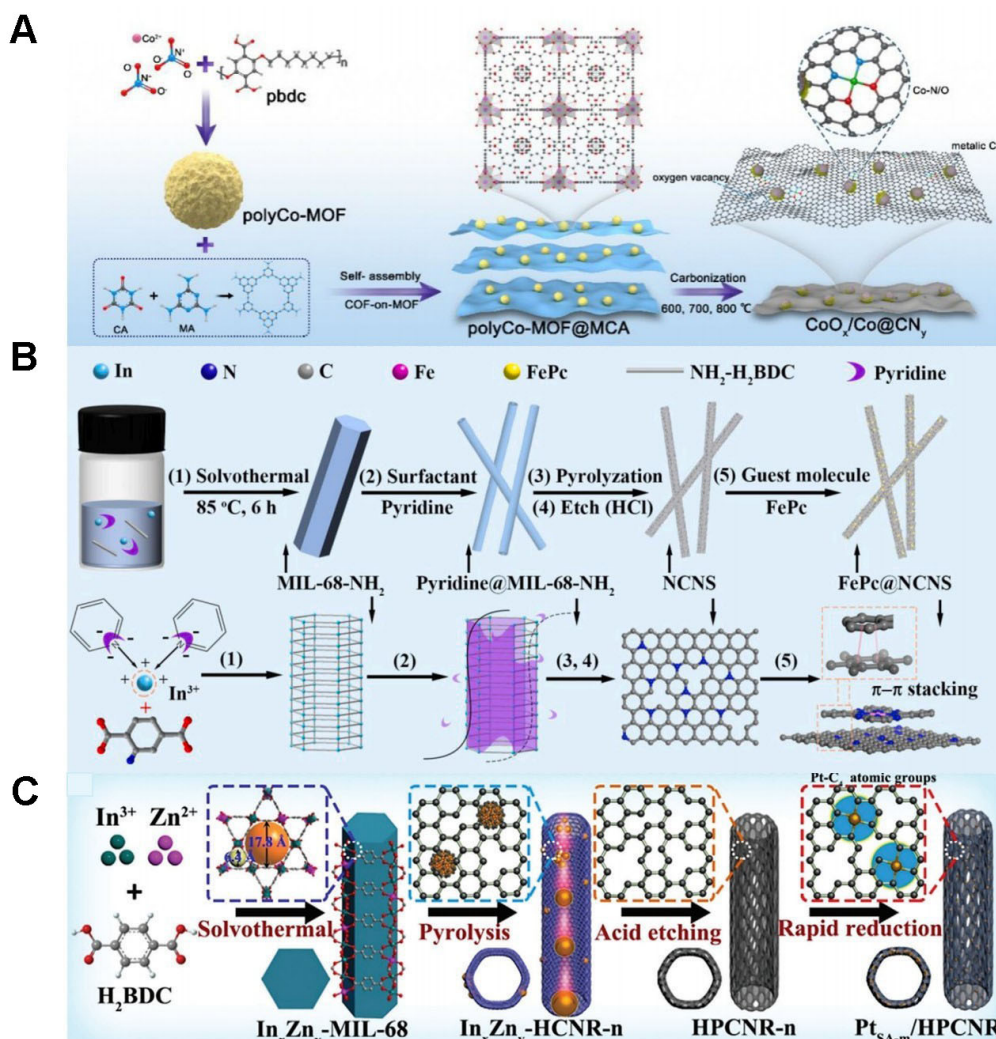


Figure 4. (A) Synthesis of $\text{CoO}_x/\text{Co}@\text{CN}_y$ hybrid materials (reproduced with permission from Elsevier, copyright 2023)^[96]; (B) preparation of $\text{FePc}@\text{NCNS}$ (reproduced with permission from Elsevier, copyright 2023)^[97]; (C) schematic of the $\text{Pt}_{\text{SA-m}}/\text{HPCNR}$ composite material (E-H reproduced with permission from Wiley-VCH, copyright 2023)^[98]. MOFs: Metal-organic frameworks; MIL: Materials Research Institute Lavoisier.

micropores and mesopores that facilitated FePc adsorption and the formation of stable nanocomposites. High-resolution transmission electron microscopy (HR-TEM) images of $\text{FePc}@\text{NCNS}$ revealed conspicuous black spots on the carbon layer, confirming successful FePc synthesis. In performance tests, $\text{FePc}@\text{NCNS}$ achieved an initial potential (E_{onset}) of 0.978 V and a half-wave voltage ($E_{1/2}$) of 0.904 V, outperforming Pt/C in ZAB testing.

Chai *et al.* developed hollow porous carbon nanorods (HPCNR-n) by controlling the pyrolysis of $\text{In}_x\text{Zn}_y\text{-MIL-68}$ hexagonal prisms [Figure 4C]^[98]. Pt single atoms were then anchored on the surface and interior of the HPCNR matrix via a rapid thermal reduction method, producing $\text{Pt}_{\text{SA-m}}/\text{HPCNR}$. During pyrolysis, Zn and In volatilized, enhancing the MOF structure, while detachment of carboxyl groups increased the surface area and generated additional active sites. The $\text{Pt}_{\text{SA-m}}/\text{HPCNR}$ catalyst showed high specific capacitance and good capacitance retention. By varying Pt content, three catalysts were obtained: $\text{Pt}_{\text{SA-1.74}}/\text{HPCNR}$, $\text{Pt}_{\text{SA-0.92}}/\text{HPCNR}$, and $\text{Pt}_{\text{NP-3.59}}/\text{HPCNR}$. Increasing Pt content led to the spontaneous formation of larger Pt NPs, with $\text{Pt}_{\text{SA-1.74}}/\text{HPCNR}$ showing the best performance.

A review of the literature shows that MOFs with carboxylic acid ligands exhibit distinctive behavior in the ORR process^[99–101]. This is attributed to the decarboxylation of carboxylic acid ligands during calcination, followed by carbonization of the organic rings to form a highly graphitized carbon support. Partial collapse of the MOF framework during decarboxylation creates a hierarchical pore structure in the carbon substrate, improving mass transfer and metal dispersion. However, the high oxygen content of carboxylic acid ligands can also promote the formation of metal oxide particles during carbonization.

Porphyrin-based MOF-derived catalysts

Porphyrins are derivatives of substituted porphyrin rings, consisting of four pyrrole units connected by methylene groups at the alpha position to form a macrocyclic conjugated structure. This configuration enables efficient electron transfer during electrochemical processes—an essential property for many applications. The ligand's central cavity also readily chelates transition metal ions, yielding a stable M-N₄ coordination mode. Upon pyrolysis of porphyrin-based MOFs, the hierarchical mesoporous/microporous structure is retained, while the M-N₄ moieties are transformed into atomically dispersed metal sites anchored within the carbon matrix. These isolated metal centers act as highly efficient catalytic active sites, minimizing metal-particle agglomeration and maximizing atom utilization.

PCN-224, composed of a Zr₆ cluster as the metal site and tetra(4-carboxyphenyl) porphyrin (H₂-TCPP) as the organic ligand, features a mesoporous structure with high periodicity, diverse topology, and numerous active defect sites, making it an attractive member of the MOF family. Zhang *et al.* synthesized PCN-224 using 3-mercaptopropionic acid (MA) to regulate crystal growth, adjusting the size by varying MA concentration, and obtained the corresponding MA_x-NC via pyrolysis [Figure 5A]^[102]. The catalytic efficacy is closely tied to the number of exposed active sites; MA₂-NC provided the optimal balance, delivering the best ORR performance. Subsequently, MA₂-NC was impregnated with Fe single atoms (SAs), producing a catalyst with excellent activity in alkaline and acidic electrolytes.

Multicore metal clusters, common in nature, catalyze small-molecule activation reactions involving multiple electron transfers. These clusters have frequently been integrated into the organized framework structures of MOFs, demonstrating considerable potential in this context. Liang *et al.* performed a reaction involving metal complexes of CoSO₄ and tetrakis(4-pyridyl) porphyrin (MTPyPP, M = Co, Cu, or Zn) in dimethylformamide to obtain Co₄-M-MOF [Co₄(SO₄)₄(CoTPyP)₂] [Figure 5B]^[103]. Single-crystal data showed that the Co^{II} at the center of the porphyrin macrocycle is coordinated via four Co-N bonds, indicating that metalloporphyrins can serve as connecting units in MOF synthesis. Replacing CoTPyP with CuTPyP or ZnTPyP yielded the corresponding Co₄-Cu-MOF and Co₄-Zn-MOF, confirming the versatility of this strategy. The electrocatalytic oxygen activity of Co₄(SO₄)₄ clusters was demonstrated by testing catalysts derived from different metalloporphyrin units, with results showing that the clusters substantially contributed to the observed activity of Co₄-M-MOFs.

Two-dimensional (2D) MOFs nanosheets are highly promising due to their high aspect ratio, which increases the distance between metal centers and exposes more active sites. Efficient synthesis of MOF nanosheets while preserving morphology, ensuring uniform distribution of active sites, and maintaining accessibility remains challenging. To address this, Li *et al.* prepared NTU-70 nanosheets with high aspect ratios using a surfactant-assisted bottom-up approach [Figure 5C]^[104]. The surfactants coordinate with metal ions, restricting axial growth and promoting the formation of 2D nanosheets. The resulting catalyst displayed a homogeneous distribution of Co atoms around the external regions of the Co clusters, along with notable ORR activity and enhanced durability.

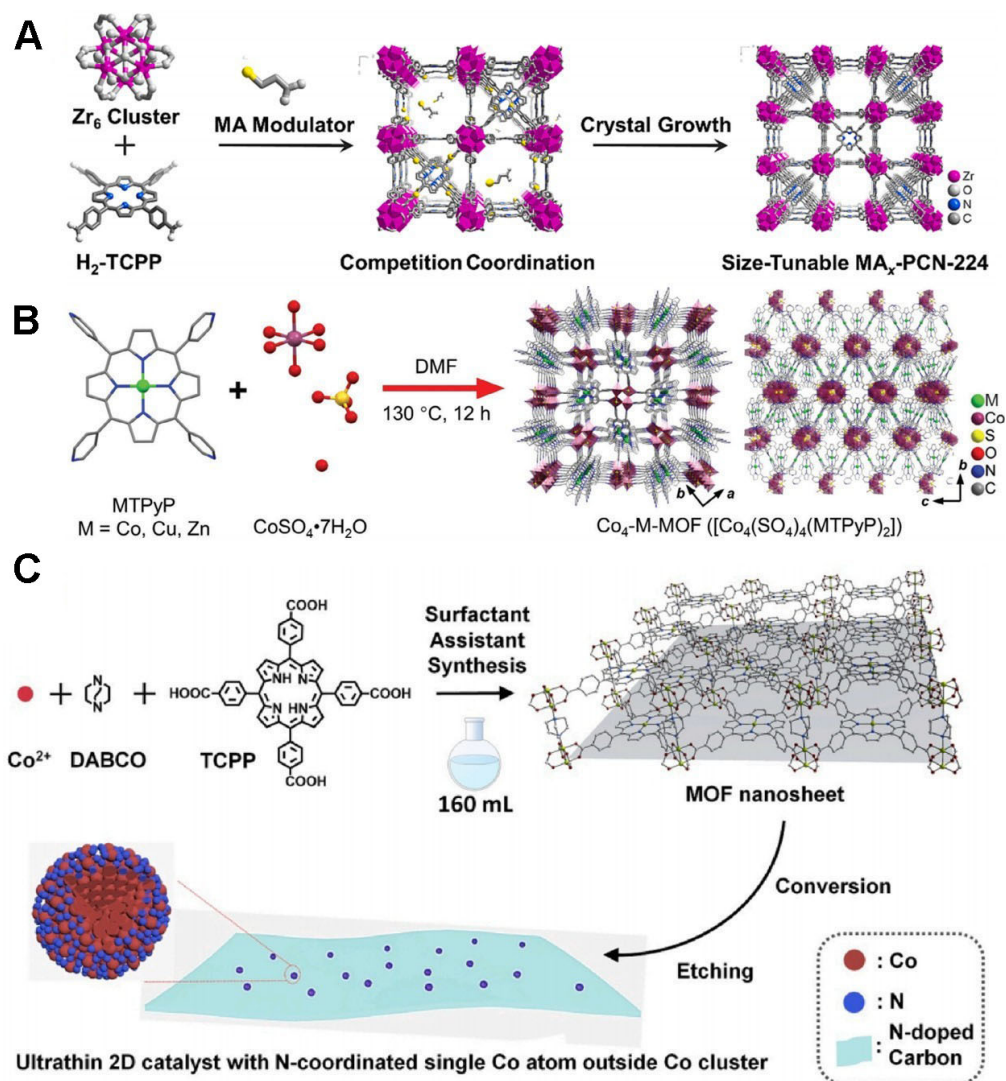


Figure 5. (A) Schematic of $\text{MA}_x\text{-PCN-224}$ (reproduced with permission from Elsevier, copyright 2024)^[102]; (B) synthesis and crystal structure of $\text{Co}_4\text{-M-MOFs}$ ($\text{M} = \text{Cu}, \text{Co}, \text{and Zn}$) (reproduced with permission from Wiley-VCH, copyright 2024)^[103]; (C) schematic of the Cu/NC catalyst (reproduced with permission from Elsevier, copyright 2021r)^[104]. DMF: Dimethylformamide; MOFs: metal-organic frameworks.

As noted above, porphyrin ligands possess a high density of pyrrole rings, which provide abundant N sources under high-temperature calcination, promoting the formation of M-N_x sites^[105,106]. The oxygen atoms in the porphyrin ring also favor the formation of metal oxides and the aggregation of NPs during calcination. Consequently, catalysts derived from these ligands typically contain NPs and single atoms.

Imidazole-based MOF-derived catalysts

ZIFs are MOFs synthesized with imidazole compounds as ligands. The imidazole moiety is a conjugated aromatic system with dual N coordination sites. The N atoms in the imidazole ring readily form stable M-N coordination bonds with transition metals, enabling homogeneous dispersion of metal ions within the MOF framework. In dimethylimidazole ligands, the nitrogen atoms restrict metal-atom migration through a “coordination capture” mechanism, mitigating agglomeration and producing atomically or near-atomically dispersed metal sites, thereby greatly enhancing atomic utilization efficiency. Upon pyrolysis, N atoms from the imidazole ligands remain in the carbon skeleton, yielding a highly N-doped carbon layer. Pyridinic- and pyrrolic-N species act as active sites directly involved in ORR processes (adsorption and activation of O_2),

while graphitic N modulates the carbon matrix's electronic structure, increasing charge density and thus electrical conductivity^[107]. The methyl groups ($-\text{CH}_3$) of dimethylimidazole provide a carbon source during pyrolysis and, through an “electronic induction effect”, fine-tune the electron cloud density of adjacent N atoms, optimizing their interaction with metal centers. These intrinsic structural features of imidazole-based MOFs are particularly advantageous for ORR applications^[108].

These characteristics are exemplified in the CoFe NC polypyrrole (PPy) catalyst developed by Nguyen *et al.* [Figure 6A]^[109]. The researchers combined ZIFs and PPy in a one-pot synthesis, producing a non-noble metal ORR catalyst in which the active components were uniformly distributed during MOF crystallization and pyrrole polymerization. The catalyst exhibited a multi-stage porous structure, a large surface area ($700 \text{ m}^2 \text{ g}^{-1}$), abundant Fe/Co- N_4 ZIF precursors, active centers, and a N-rich carbon matrix from polymer decomposition. In RDE tests, it achieved an $E_{1/2}$ of 0.915 V and demonstrated excellent durability, retaining 94.2% of its initial current capacity and strong methanol resistance over 20 h^[109]. When applied in an actual AEMFC system, the catalyst delivered a power density of 352 mW cm^{-2} , confirming that the MOF-polymer hybrid strategy can yield next-generation fuel cell catalysts with high efficiency, robust stability, and economic viability.

Using an ice-template co-assembly method driven by van der Waals forces, Yang *et al.*^[110] designed an advanced carbon superstructure with a customized atomic-scale metal configuration and optimized mass transfer performance for energy conversion applications. This bimetallic organic framework superstructure comprised ZIF-8 and ZIF-67 nanocubes [Figure 6B]. Cobalt monoatoms and NPs were then anchored onto a 2D N-doped rice nanoribbon, producing an excellent ORR electrocatalyst. After pyrolysis, the resulting catalyst contained synergistically combined atomically dispersed Co SAs and Co NPs. The 2D carbon nanobelts possessed a layered porous structure with interconnected hollow carbon nanocubes, increasing active-site exposure, enhancing mass transfer, and accelerating reaction kinetics. The optimized catalyst (CO/CNB-10) showed a higher $E_{1/2}$ (0.888 V) than commercial Pt/C, along with exceptional stability and methanol resistance. Integrated into a ZAB, it achieved a peak power density of 179 mW cm^{-2} , outperforming comparable Pt/C-based products.

Using a water-etching technique, Li *et al.*^[111] created missing-connector-type defects in leaf-like ZIF (ZIF-L) [Figure 6C]. Fe^{3+} was chemically anchored to coordination-unsaturated Zn-N_3 sites, forming an $\text{N}_3\text{-Zn-O-Fe}$ structure. During pyrolysis, Fe^{3+} replaced Zn^{2+} via metal exchange, producing an asymmetric Fe-N_3 configuration. Simultaneously, endogenous ZnO corroded the surrounding carbon matrix, generating carbon vacancies (CVs) that promoted directional construction of Fe-N_3 sites. The resulting $\text{Fe-N}_3/\text{CV}$ catalyst achieved excellent $E_{1/2}$ values in alkaline and acidic media (0.92 and 0.77 V, respectively). This linker-free auxiliary synthesis strategy demonstrates the versatility of multiple MOF precursors and iron sources and enables precise atomic-scale fabrication of high-performance M-N-C electrocatalysts for energy conversion applications.

Imidazole ligands have been shown to release a substantial N-sites during high-temperature calcination^[112,113]. Because of their low oxygen content, these MOFs tend to form metal particles rather than metal oxide particles. Additionally, Zn, a common metal used to form MOFs with imidazole ligands, has a low boiling point, leading to the creation of a substantial number of metal vacancies during calcination. These vacancies, in turn, facilitate the formation of M- N_x sites. Consequently, imidazole ligand-derived catalysts can be readily converted into single-atom catalysts.

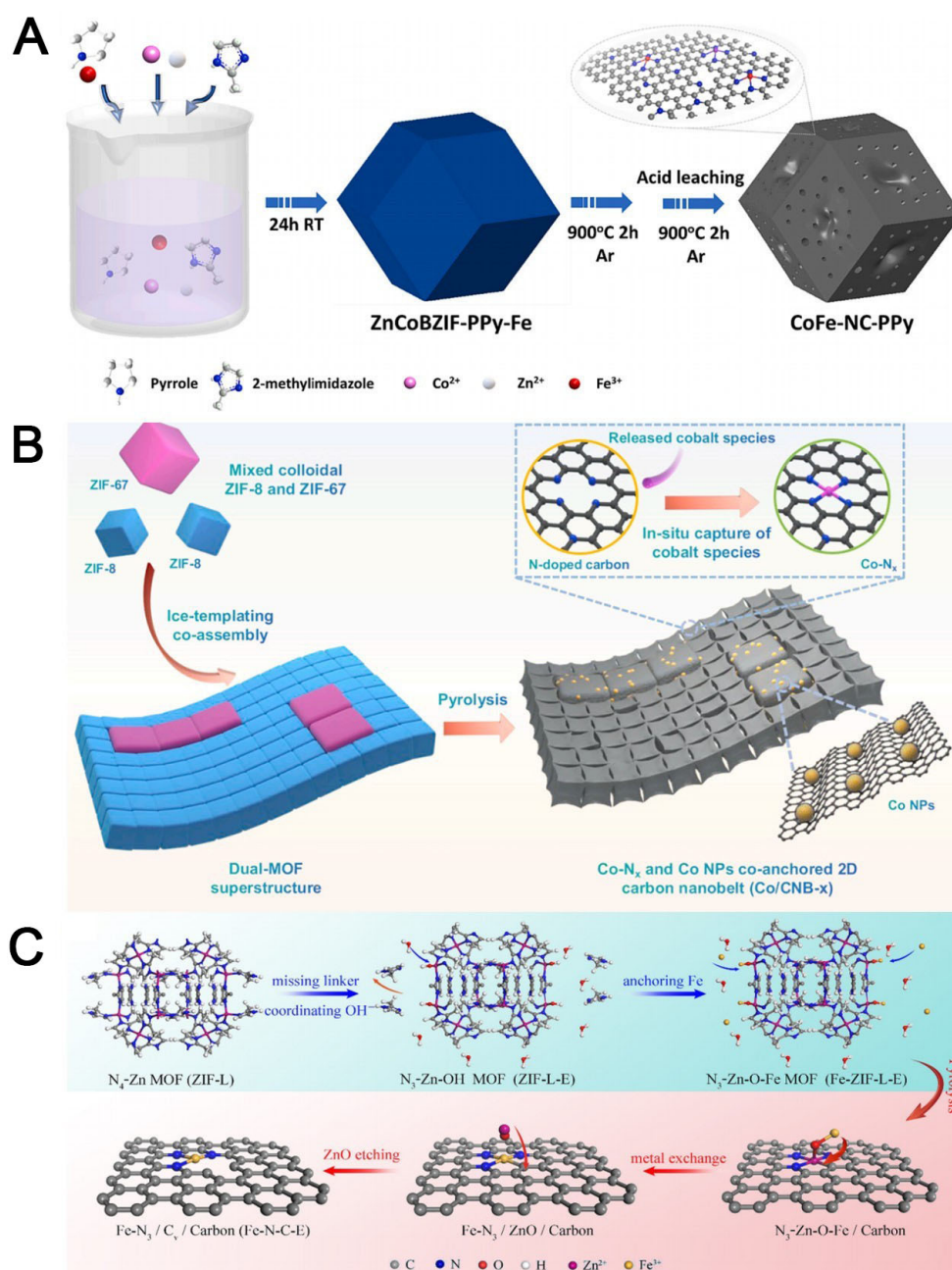


Figure 6. Synthetic procedures of (A) the CoFe-NC-PPy electrocatalyst (reproduced with permission from Elsevier, copyright 2024)^[109] and (B) the Co/CNB-x catalyst (reproduced with permission from Elsevier, copyright 2023)^[110]; (C) construction of Fe-N-C-E (Reproduced with permission from the Copyright 2024, American Chemical Society, copyright 2024)^[111]. N-C-E: Metal-nitrogen-carbon; ZIFs: zeolite imidazole frameworks; MOFs: metal-organic frameworks.

Nitrogenous heterocycle-based MOF-derived catalysts

Like the traditional ligands mentioned above, MOFs constructed from nitrogen-containing heterocyclic ligands possess unique ORR properties that are governed by ligand chemistry, metal node coordination, and structural porosity. Nitrogen-containing heterocyclic ligands coordinate with transition metals (Fe, Co, and Mn) to form catalytically active M-N_x sites mimicking the Fe-N_x centers of enzyme catalysts. Such active sites promote oxygen adsorption, O-O bond cleavage, and the four dominant electron transfer pathways. The electron-donating properties of nitrogen atoms have been shown to optimize the d-band electronic state in the metal center, thereby reducing the potential barrier of key steps such as *OH desorption, whereas the

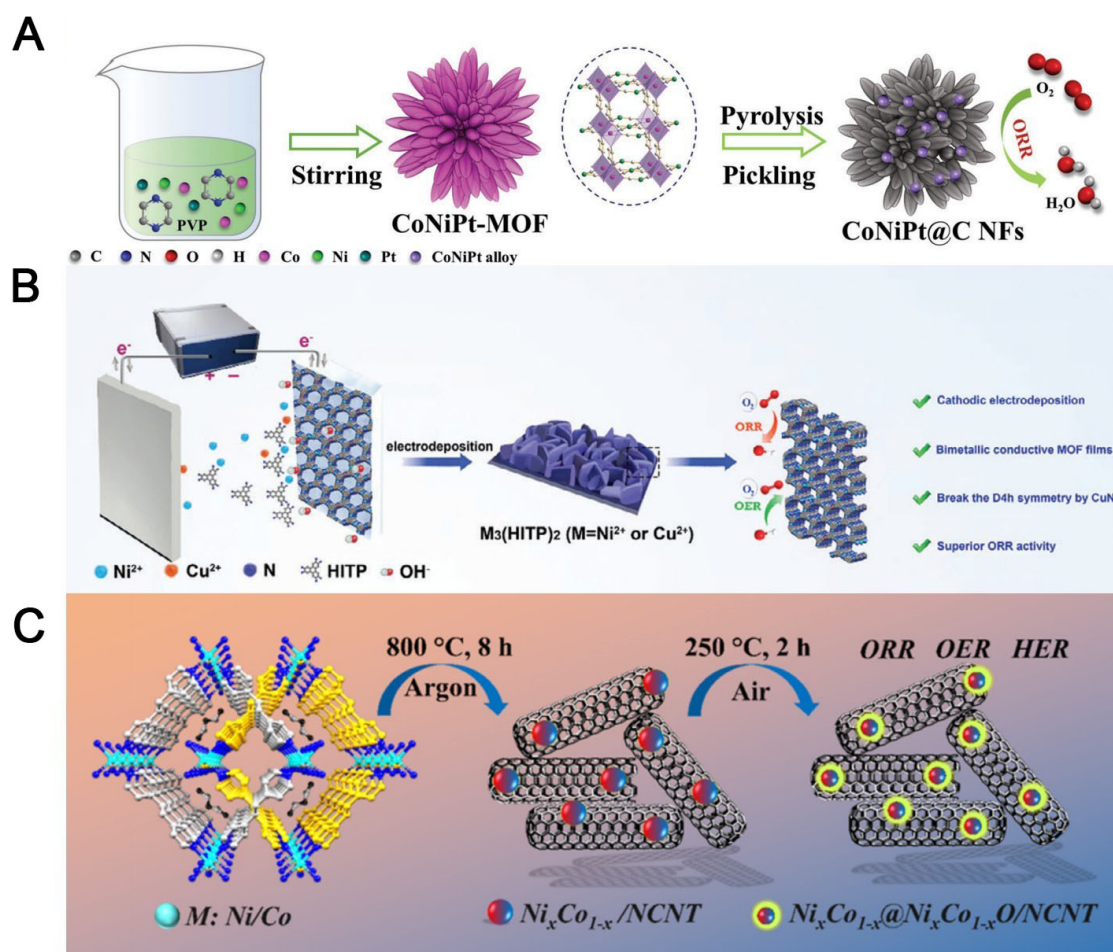


Figure 7. (A) Synthesis of CoNiPt@C NFs catalysts (reproduced with permission from Wiley-VCH, copyright 2023)^[115]; (B) electrochemical reaction scheme for the preparation of $M_3(HITP)_2$ thin film on a conductive substrate (reproduced with permission from Wiley-VCH, copyright 2024)^[116]; (C) schematic showing the two-step calcination process for preparing a $Ni_xCo_{1-x}@Ni_xCo_{1-x}O/NCNT$ catalyst on bimetallic MOF-1 (reproduced with permission from the American Chemical Society, copyright 2023)^[117]. MOFs: Metal-organic frameworks; ORR: oxygen reduction reaction; OER: oxygen evolution reaction; HER: hydrogen evolution reaction.

conjugated π -system in the ligand enhances charge delocalization and electron transfer dynamics. The enhanced stability of nitrogen-rich MOFs is attributed to robust m-n bonding. In addition, an N-doped carbon matrix, which cooperatively improves the conductivity and corrosion resistance of the MOFs, is embedded in the metal sites after pyrolysis^[114]. These materials effectively function over a wide range, spanning acidic to alkaline conditions. Protonated nitrogen sites stabilize the intermediates in acidic media, while the M- N_x centers directly drive the ORR in alkaline environments. The inherent challenges (low conductivity and durability) are overcome by hybrid or protective packaging strategies with conductive substrates.

Pan *et al.* synthesized Hofmann-type MOFs with pyrazine as the ligand [Figure 7A]^[115]. The pyrolysis process formed a nanoflower-like segregation alloy, which was subsequently loaded into nitrogen-doped porous carbon. By precisely modulating the pyrolysis and acid-treatment parameters, the researchers optimized the composition of CoNiPt@C NFs to 15%. The resulting catalyst exhibited a remarkable $E_{1/2}$ of 0.93 V under alkaline conditions. The hierarchical nanoflower structure exposed numerous active sites and accelerated the transmission of the intermediates, while the microstructure synergistically optimized the adsorption energy of the ORR intermediates. When integrated into ZABs with RuO_2 , the test performance is also superior to that of Pt/C-based catalysts.

Liu *et al.* developed high-performance bimetallic conductive MOF as electrocatalysts for the ORR process in ZABs [Figure 7B]^[116]. A room-temperature electrochemical cathodic deposition method yielded continuous 2D Ni/Cu-HITP MOF films without polymeric binders, circumventing the intrinsic conductivity limitations and aggregation issues of conventional MOFs. The E_{onset} of the optimized $\text{Ni}_{2.1}\text{Cu}_{0.9}(\text{HITP})_2$ reached 0.93 V. In aqueous ZABs, the catalyst delivered exceptional performance metrics (specific capacity = 706.2 mAh g⁻¹) and remarkable durability over 1,250 charge/discharge cycles. Besides enabling the effective design of binder-free conductive MOF electrodes, Liu *et al.*'s^[116] study provides fundamental insights into bimetallic coordination effects for advanced energy storage applications.

Jena *et al.* developed the triply-functional electrocatalyst $\text{Ni}_x\text{Co}_{1-x}@\text{Ni}_x\text{Co}_{1-x}\text{O}/\text{N-doped carbon nanotubes}$ (NCNTs) via pyrolysis followed by calcination of a bimetallic (Ni, Co) MOF [Figure 7C]. This catalyst, consisting of core-shell bimetallic NPs (with an $\text{Ni}_x\text{Co}_{1-x}$ alloy core and an $\text{Ni}_x\text{Co}_{1-x}\text{O}$ oxide shell) stabilized on the NCNTs, achieves superior electrocatalytic activities for multiple reactions^[117]. During the ORR process, the alloy core, oxide shell, N-doped carbon matrix, Co-to-Ni charge transfer, and oxygen vacancies synergistically yield an excellent half-wave potential ($E_{1/2} = 0.87$ V). Density functional theory (DFT) calculations clarified the roles of the Ni active center and Co-induced electron modulation. When implemented in a ZAB, the catalyst yielded a high specific capacity (746 mAh g⁻¹), a high power density (157 mW cm⁻²), and exceptional stability^[117].

As the core components of MOFs, ligands largely influence the active centers of the derived single-atom, nanocluster, or porous-carbon matrix catalysts. This impact is attributable to the chemical structure, electronic properties, and pyrolysis behavior of the ligands. A comprehensive review of the extant literature revealed that ligands with high nitrogen content (such as imidazole) provide more nitrogen coordination sites than other ligand types, facilitating the formation of single-atom catalysts, whereas ligands with elevated oxygen content (such as carboxylic acid) tend to form NP catalysts during the calcination process. Ligands with elevated nitrogen and oxygen contents (such as porphyrin ligands) tend to form catalysts with coexisting single atoms and NPs. The catalytic active center can be selectively regulated through ligand modification and design.

MOF-derived catalysts have demonstrated unique potential for the ORR. Some processes can yield kilogram-level catalysts and the catalytic performances of MOF-derived catalysts are comparable to those of commercial Pt/C catalysts. Furthermore, the effectiveness and reliability of MOF-derived catalysts have frequently been demonstrated in practical batteries. As MOFs can effectively catalyze chemical conversion reactions, nonprecious metal catalysts achieve comparable performance to their precious metal counterparts. This advancement promises high-performance, cost-effective applications in various fields of chemistry. Tables 1 and 2 report the catalytic performance data of MOF-based catalysts with different ligands and MOF-based catalysts used in different energy conversion devices, respectively. Remarkably, most of these catalysts outperform commercial Pt/C, underscoring their considerable promise in future applications. Catalysts derived from imidazole-based MOFs deliver the highest half-wave potential performance and ZABs are most commonly employed in energy conversion devices. Many catalysts for PEMFCs have reached or approached the 2025 target of the US Department of Energy (DOE).

MOF-DERIVED CATALYSTS WITH DIFFERENT ACTIVE CENTERS

Metal ions or clusters are integral components of MOF frameworks, as they support the formation of porous architectures and regulate their pore sizes and topological structures. The type of active center, existence form (e.g., single atoms, dual atoms, clusters, or NPs), and electronic structure of the metal species play decisive roles in the catalytic performance (e.g., activity, selectivity, stability) of a MOF-derived catalyst^[135].

Table 1. Summary of the reported performance data of MOF-based ORR electrocatalysts

Ligand	Catalyst	ORR condition	$E_{1/2}$ (V vs. RHE)	Ref.
Carboxylic	FePc@NCNS	Alkaline	0.904	[97]
	Co ₄ N@NCNT-900	Alkaline	0.875	[118]
	FePc@NC-1000	Alkaline	0.86	[119]
	Fe@NSC	Alkaline	0.87	[100]
	Fe _{0.05} -N@ MOF	Alkaline	0.86	[101]
	L/Fe-NC	Acid	0.82	[120]
	Fe/I-N-CR	Alkaline	0.915	[99]
Porphyrin	MA ₃ -NC(Fe)-2	Alkaline	0.824	[102]
	Co ₄ -Co-MOF	Alkaline	0.83	[103]
	Co@N-C700	Alkaline	0.78	[104]
	CuNC-1000	Alkaline	0.85	[121]
	CoNiFe _{0.08} -NC@p-NCNTs	Alkaline	0.811	[122]
	Co _{5A-AC} @SNC	Alkaline	0.86	[105]
Imidazole	CoFe-NC-PPy	Alkaline	0.915	[109]
	Co/CNB-10	Alkaline	0.888	[110]
	Fe-N-C-S	Alkaline	0.92	[111]
	Co-NCR	Alkaline	0.88	[123]
	FeCo@NC-II	Alkaline	0.907	[124]
	FeCu-HCNFs	Alkaline	0.884	[112]
	MOF CoTe ₂ /MnTe ₂	Alkaline	0.81	[125]
	CoNP@FeNC-0.05	Alkaline	0.85	[126]
Nitrogenous	15% CoNiPt@CNFs	Alkaline	0.93	[115]
	Ni _{2.1} Cu _{0.9} (HITP) ₂	Alkaline	0.76	[116]
	Ni _x Co _{1-x} @Ni _x Co _{1-x} O/NCNT	Alkaline	0.79	[117]
	Rbf-Ni-MOF	Alkaline	0.84	[127]
	Ni ₃ Fe-NCNTs-800	Alkaline	0.862	[128]

ORR: Oxygen reduction reaction; MOF: metal-organic framework.

First, metals are direct active centers in catalytic reactions and their atomic-level structures (e.g., coordination environment, valence state) dictate the reactant adsorption behavior and reaction pathways^[136,137]. Second, the d-band center, electron density, and orbital hybridization of metals and their ligands directly influence the catalytic properties. Finally, the strong interaction between the metal and the MOF-derived carbon matrix (typically containing heteroatoms such as N and O) affects the metal dispersion and electronic structures^[138].

MOF-derived single-atom catalysts

Owing to the porous nature of MOF materials, the types of metal catalysts derived from a given MOF are correlated with both the MOF itself and the metal content within its pores. The metal content in the MOFs and the reaction conditions can be controlled to obtain relatively pure single-atom catalysts (SACs), in which a single atom site is the active center of catalysis^[139–143]. Smaller metal particles are preferred for heterogeneous catalysis because they provide a higher proportion of surface atoms than larger particles, thereby improving both the atomic utilization efficiency and catalytic activity^[144]. The atomic utilization efficiency of SACs can potentially reach 100%, far exceeding the capabilities of traditional catalysts^[145,146]. Transition metal catalysts loaded on nitrogen-doped carbon supports, a subcategory of SACs, have demonstrated remarkable potential

Table 2. Reported performance data of MOF-based ORR electrocatalysts in different energy conversion devices

Device	Catalyst	Power density	Durability	Ref.
PEMFC	OP-Fe-NC	937 mW cm ⁻² (2 bar)	27.8% loss (240 h)	[129]
	Mn-N-C-HCl-800/1100	600 mW cm ⁻² (1 bar)	20% loss (16 h)	[130]
	CoMn/NC	970 mW cm ⁻² (1 bar)	Negligible loss (24 h)	[85]
	Fe-Al-RNC	1.05 W cm ⁻² (1.5 bar)	19.7% loss (100 h)	[131]
	Fe-AC-CVD	535 mW cm ⁻²	3.9% (30,000 cycles)	[18]
	700 CO ₂ Fe-NC	670 mW cm ⁻²	38.6% (100 cycles)	[132]
AEMFC	CoFe-NC-PPy	352 mW cm ⁻²	/	[109]
	Fe-NC-1000	149 mW cm ⁻²	/	[133]
ZAB	CoMn-N/S-C	203 mW cm ⁻²	350 h (5 mA cm ⁻²)	[85]
	Co-N-C/CNF	159 mW cm ⁻²	> 100 h (10 mA cm ⁻²)	[7]
	Co ₃ Fe ₇ /NC-50	248.1 mW cm ⁻²	1,000 h (5 mA cm ⁻²)	[40]
	Co@N-CNTs/NSs	142.3 mW cm ⁻²	421 cycles (5 mA cm ⁻²)	[89]
	Co/CNB-10	179 mW cm ⁻²	90 h (10 mA cm ⁻²)	[110]
	CoNiPt@C	172 mW cm ⁻²	70 h (10 mA cm ⁻²)	[115]
	Ni ₂₁ Cu _{0.9} (HTP) ₂	41.5 mW cm ⁻²	12,500 min (5 mA cm ⁻²)	[116]
	FeSAs-UNCNS	305.7 mW cm ⁻²	> 180 h (5 mA cm ⁻²)	[134]
	Fe _N -N-C	225 mW cm ⁻²	> 1,200 h (5 mA cm ⁻²)	[135]

ORR: Oxygen reduction reaction; MOF: metal-organic framework; PEMFC: proton exchange membrane fuel cell; AEMFC: anion-exchange membrane fuel cell; ZAB: Zn-air batterie.

for the ORR and are regarded as an optimal alternative to conventional Pt/C^[147,148].

MOF-derived Fe single-atom catalysts

The isolated Fe atoms in MOF-derived single-atom Fe catalysts derive from two sources: inherent Fe nodes within the MOF structure, and externally adsorbed Fe precursors. The latter are anchored on the porous MOFs architecture and subsequently transformed into isolated single atoms through postsynthetic treatments. By virtue of their elevated activity, minimal cost, and four-electron selectivity, Fe SACs have been extensively researched as potential alternatives to noble metal catalysts^[149,150]. For instance, Li *et al.* prepared OP-Fe-NC through chelate-assisted selective etching with xylenol orange and opening of the ZIF material [Figure 8A]^[129]. Interconnected openings in these carbon materials facilitate the diffusion and mass transfer of oxygen in the catalyst layer. High-angle annular dark field-scanning TEM (HAADF-STEM) revealed abundant iron sites on the carbon surface [Figure 8B]. The coordination around the single Fe site was analyzed by R-space fitting of the extended X-ray absorption fine structure (EXAFS) data [Figure 8C-E]. The OP-Fe-NC catalyst achieved a high $E_{1/2}$ (0.89 V) for the ORR under acidic conditions [Figure 8F]. Meanwhile, the H₂-O₂ fuel cell outperformed the Pt/C catalyst at different pressures [Figure 8G]. Finally, DFT calculations revealed the excellent properties of the catalyst in principle [Figure 8H-J].

To overcome the limitations of conventional microporous MOF-derived catalysts, Xie *et al.* pyrolyzed NH₂-MIL-101(Al) at varying temperatures, creating NC-MIL-101-T with optimized pore structures [Figure 9A and B]^[151]. After impregnating these supports with Fe(II)-phenanthroline complexes and performing a secondary pyrolysis, they obtained a catalyst rich in exposed FeN_x single-atom sites. The optimized Fe SAC-MIL-101-1000 exhibited exceptional ORR performance in alkaline media. The mesoporous architecture enhanced the mass transport and active site utilization, as evidenced by the superior performance of the catalyst in both aqueous and solid-state ZABs.

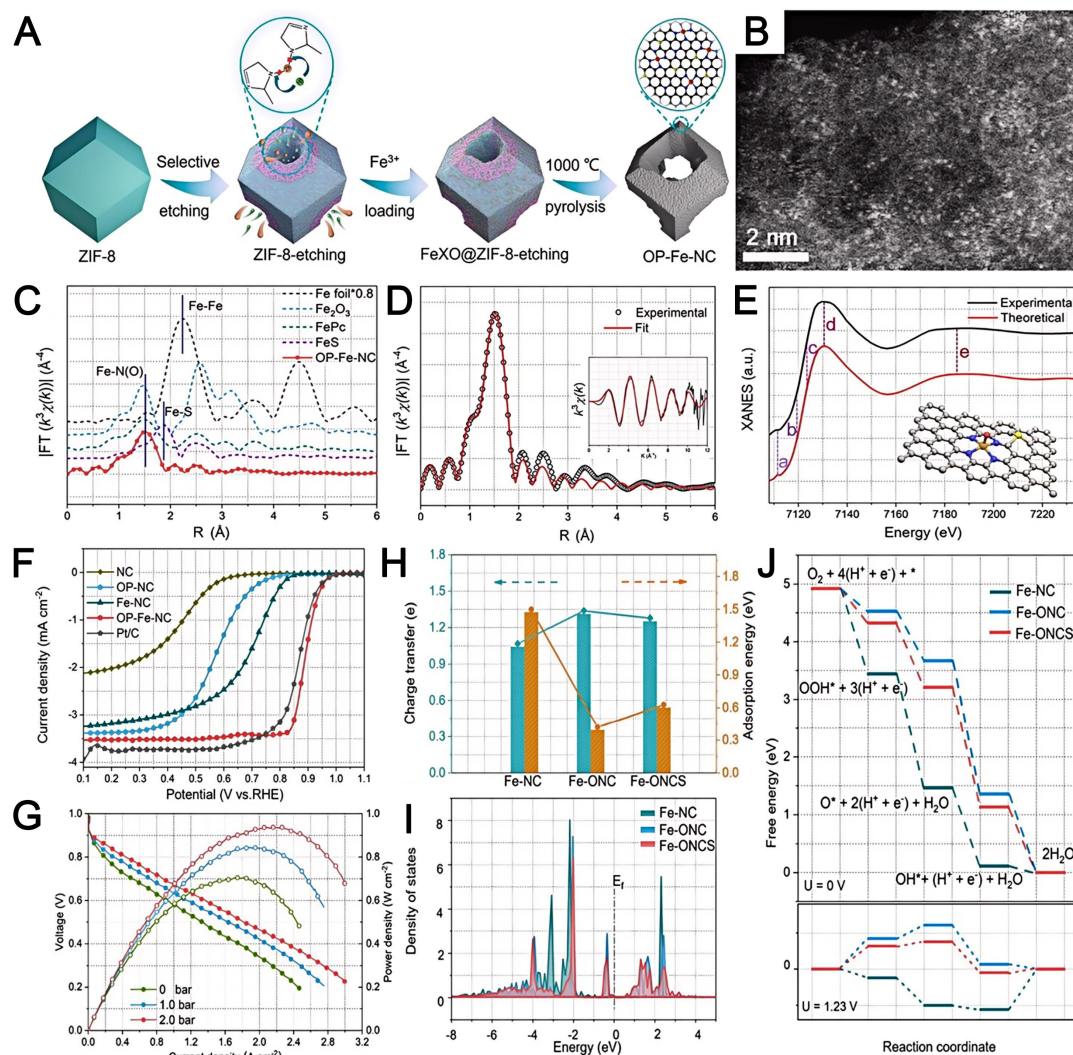


Figure 8. (A) Schematic and (B) HAADF-STEM image of OP-Fe-NC; (C) Fourier transformed EXAFS spectra of OP-Fe-NC catalysts; (D) corresponding quantitative fittings of the EXAFS spectra in R space. Inset shows the corresponding EXAFS fitting in K space; (E) Comparison between the experimental and theoretical X-ray absorption near-edge structure (XANES) spectra. Inset is a schematic of the interfacial model of OP-Fe-NC; (F) LSV curves; (G) polarization and power density curves of H₂-O₂ fuel cells with OP-Fe-NC and 20 wt% Pt/C; (H) Bader charge transfers and adsorption energies of the intermediates and (I) partial densities of states (PDOSs) of the Fe d bands in Fe-NC, Fe-ONC, and Fe-ONCS; (J) Gibbs free energy profiles of the ORR at U = 0 and 1.23 V (A-J reproduced with permission from the American Chemical Society, copyright 2023)^[129]. HAADF-STEM: High-angle annular dark field-scanning transmission electron microscopy; EXAFS: extended X-ray absorption fine structure; LSV: linear sweep voltammetry.

Xie *et al.* obtained a high-performance Fe SAC-MOF-5 from MOF-5-derived carbon for the ORR in PEMFCs [Figure 9C]^[152]. Pyrolysis of Zn-based MOF-5 with a three-dimensional microporous cubic structure yielded a highly porous carbon support with a Brunauer-Emmet-Teller specific surface area of 2,751 m² g⁻¹ and a large external surface area (1,651 m² g⁻¹). Applying a ligand-mediated approach, the authors anchored atomically dispersed FeN₄ sites (Fe loading 2.35 wt%) on the carbon matrix with no Fe aggregation [Figure 9D]. The Fe SAC-MOF-5 catalyst delivered a half-wave potential of 0.83 V. When incorporated into an H₂-O₂ PEMFC under 0.2 MPa, the peak power density reached 0.84 W cm⁻². This high performance was attributed to the hierarchical porosity of SAC-MOF-5, which simultaneously enables dense FeN₄-site formation and efficient mass transport. MOF-5-derived carbons were highlighted as superior supports that maximize the number of accessible active sites in SACs, providing insights for designing high-performance Platinum Group Metals (PGM)-free electrocatalysts through MOF precursor engineering.

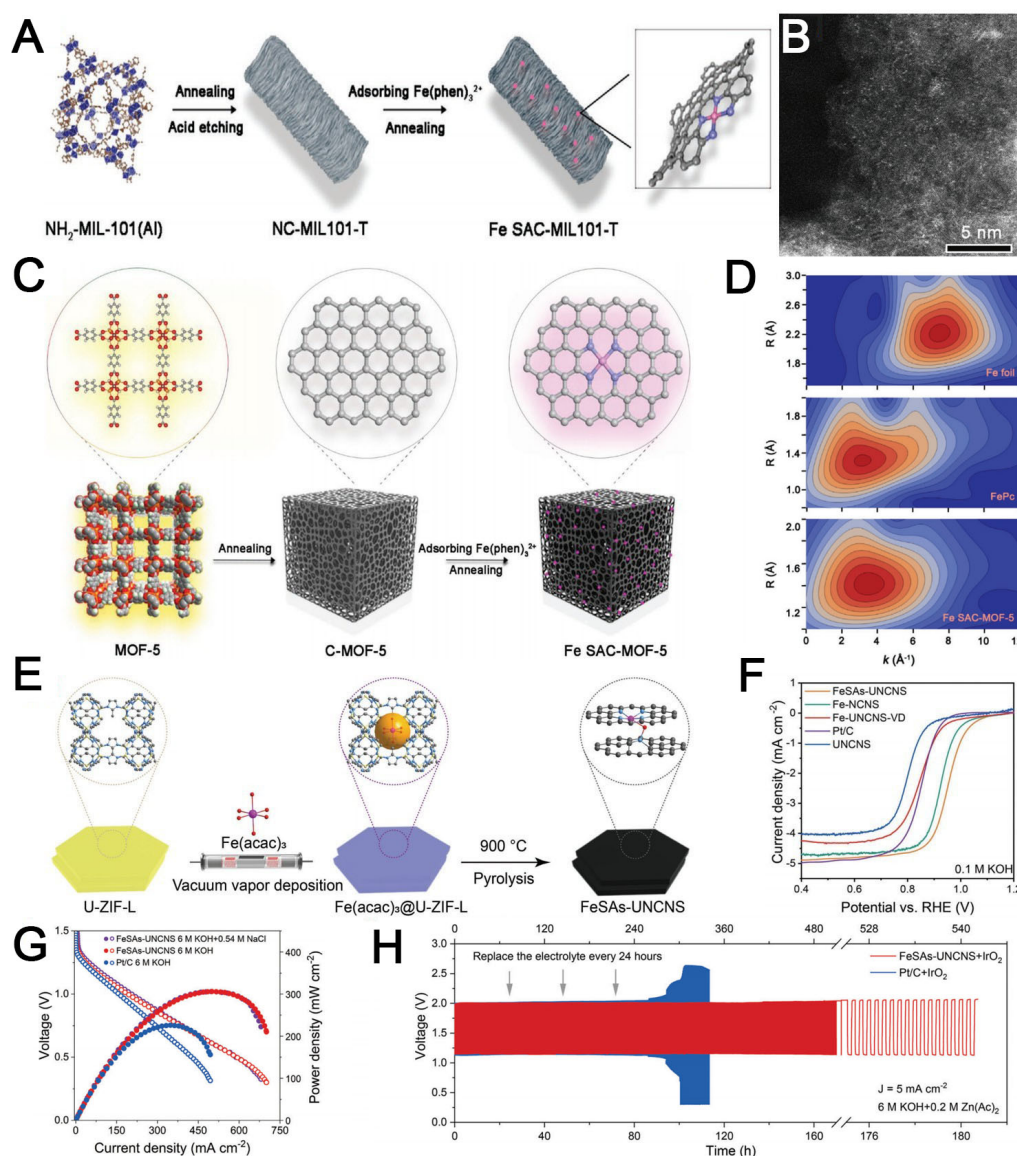


Figure 9. (A) Schematic of Fe SAC-MIL101-T and (B) aberration-corrected HAADF-STEM image of Fe SAC-MIL101-1000 (A and B reproduced with permission from Wiley-VCH, copyright 2021)^[151]; (C) synthesis of the Fe SAC-MOF-5 catalyst; (D) wavelet-transformed k^2 -weighted EXAFS spectra of Fe SAC-MOF-5, FePc, and Fe foil (C and D reproduced with permission from Wiley-VCH, copyright 2021)^[152]; (E) Synthetic scheme of FeSAs-UNCNS; (F) LSV curves recorded in an O₂-saturated 0.1 M KOH solution at a rotation speed of 1,600 rpm and a sweep rate of 10 mV s⁻¹; (G) polarization and power density curves of primary and simulated seawater-based Zn-air batteries (ZABs); (H) galvanostatic charge-discharge cycling curves of rechargeable ZABs at a current density of 5 mA cm⁻² (reproduced with permission from Wiley-VCH, copyright 2024)^[134]. HAADF-STEM: High-angle annular dark field-scanning transmission electron microscopy; EXAFS: extended X-ray absorption fine structure; SAC: single-atom catalyst; MIL: materials research institute lavoisier; MOF: metal-organic framework; UNCNS: ultrathin nitrogen-doped carbon nanosheets; LSV: linear sweep voltammetry.

Applying a novel vacuum-vapor deposition strategy, Yang *et al.* synthesized FeSAs-ultrathin nitrogen-doped carbon nanosheets (UNCNS) with densely accessible active sites in Fe-N₄O for high-performance ZABs [Figure 9E]^[134]. The iron salt is sublimated into the micropores of the ultrathin ZIF-L nanosheet precursors under vacuum conditions, effectively preventing iron aggregation while achieving high Fe loading (4.22 wt.%). The optimized catalyst demonstrated an exceptional $E_{1/2}$ of 0.951 V in alkaline media [Figure 9F]. When applied in ZABs, FeSAs-UNCNS achieved a power density of 306 mW cm⁻² and outstanding stability, outperforming commercial Pt/C and previously reported SACs [Figure 9G and H].

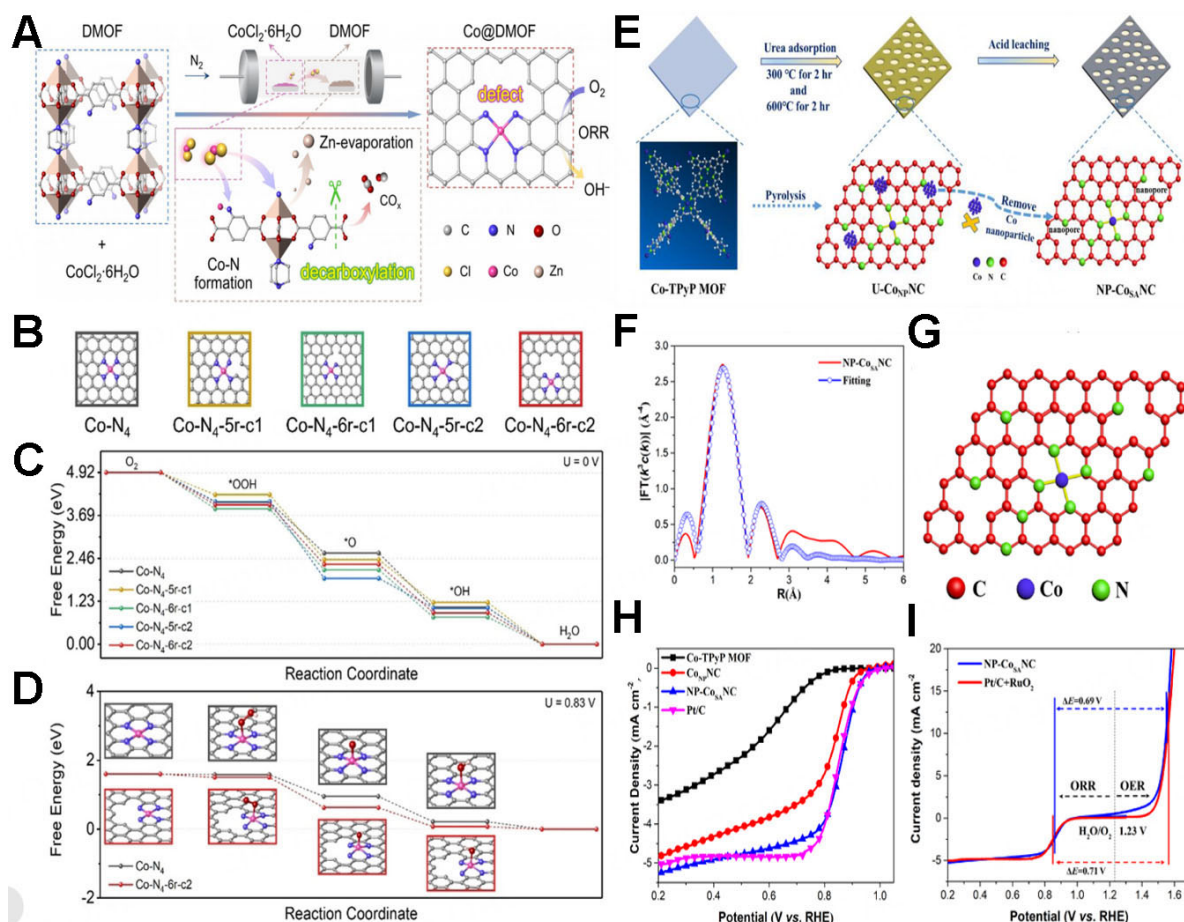


Figure 10. (A) Preparation and proposed formation mechanisms of Co@diamondized MOF; (B) five possible models of atomic Co-N_4 configurations with different defect degrees; free energy diagrams of the models in (B), calculated at (C) $U = 0 \text{ V}$ (vs. SHE) and (D) $U = 0.83 \text{ V}$ (A–D reproduced with permission from Wiley-VCH, copyright 2021) [153]; (E) Preparation, (F) EXAFS R-space fitting curve, and (G) model of CoN_4 configuration in NP-CoSA/NC; (H) LSV curves, (I) Overall polarization curves. (E–I reproduced with permission from Elsevier, copyright 2023) [154]. MOF: Metal-organic framework; EXAFS: extended X-ray absorption fine structure; LSV: linear sweep voltammetry.

MOF-derived Co single-atom catalysts

To enhance the intrinsic ORR activity of Co SACs, Yuan *et al.* introduced defects through decarboxylation of MOF-derived carbon supports [Figure 10A] [153]. Using a mixed-ligand carboxylate/amide MOF (DMOF) as a precursor, the researchers synthesized defect-rich Co SACs via pyrolysis coupled with gas-phase Co transport. The carboxylate groups were decarboxylated during the thermal treatment, generating abundant defects in the carbon matrix while maintaining the atomic Co-N_4 active sites. Consequently, Co@DMOF-900 outperformed the conventional ZIF-8-derived Co SACs in ORR catalysis. Despite possessing only one-fifth the Co content of ZIF-8-derived Co SACs, Co@DMOF-900 achieved an eight-fold increase in turnover frequency ($2.015 \text{ e}^- \text{ s}^{-1} \text{ site}^{-1}$) and a half-wave potential of 0.866 V . According to experimental characterization and DFT calculations, the defects near Co-N_4 weaken the adsorption free energy of *OOH , optimizing the reaction pathway [Figure 10B–D]. The optimized catalyst demonstrated exceptional stability in alkaline media and high performance in a ZAB (power density 158 mW cm^{-2} ; capacity 815 mAh g^{-1}).

Rong *et al.* derived a high-performance NP-CoSA/NC catalyst from a Co-TPyP MOF for ORR and ZAB applications [Figure 10E] [154]. By introducing urea as an additional nitrogen source during pyrolysis, they successfully inhibited cobalt aggregation while creating a nanoporous structure, achieving a high cobalt

loading (6.4 wt%) within atomically dispersed CoN_4C active sites across nitrogen-doped carbon [Figure 10F and G]. The optimized catalyst demonstrated excellent ORR performance with a half-wave potential of 0.86 V and a low ΔE (0.64 V), outperforming commercial Pt/C [Figure 10H and I]. DFT calculations showed that the defect-edge and nitrogen-rich CoN_4C configurations lower the energy barriers of the ORR intermediates from those of the conventional center-coordinated sites. In practical application evaluations, the catalyst performed remarkably well in both aqueous and flexible quasi-solid-state ZABs (with peak power densities of 158.1 and 48.2 mW cm^{-2} , respectively) and remained excellently stable during prolonged cycling.

Others

Qu *et al.* presented a gas-migration method that directly converts bulk copper into isolated Cu-SAs/N-C [Figure 11A]^[155]. Leveraging the ability of ammonia to form $\text{Cu}(\text{NH}_3)_x$ through Lewis acid-base interactions, this method extracts Cu atoms from the bulk metal foam and subsequently anchored them to defect-rich carbon supports derived from pyrolyzed ZIF-8 [Figure 11B–D], enabling the scalable production of thermally/chemically stable SACs with a high surface coverage (0.06 atoms nm^{-2}). The Cu-SAs/N-C delivered a half-wave potential of 0.895 V, surpassing that of commercial Pt/C (0.87 V), and remained exceptionally durable through 5,000 electrochemical cycles. Moreover, the strategy was generalizable to the synthesis of cobalt and nickel SACs (Co/Ni-SAs/N-C) [Figure 11E–G].

By engineering the coordination environment, Jia *et al.* precisely controlled the selectivity of Zn catalysts for the ORR pathway [Figure 11H]^[156]. They synthesized two distinct Zn single-atom catalysts— ZnO_3C (O/C-coordinated) and ZnN_4 (N-coordinated)—from MOFs precursors with different functional groups (benzene-1,4-dicarboxylic acid (BDC) *vs.* BDC- NH_2). DFT calculations clarified that ZnO_3C is the $2e^-$ pathway of H_2O_2 production, proceeding with near-zero overpotential and 90% Faraday efficiency under alkaline conditions; meanwhile, ZnN_4 promotes the $4e^-$ pathway for H_2O generation. The higher electronegativity of oxygen in ZnO_3C than in ZnN_4 modifies the electronic structure, lowering the d-band center of Zn, weakening the intermediate adsorption, and favoring the $2e^-$ ORR [Figure 11I and J].

The aqueous synthesis method of Chen *et al.* creates Mn-N-C catalysts for the ORR in PEMFCs [Figure 11K]^[130]. The authors replaced the traditional toxic organic solvents with a dilute HCl-assisted aqueous solution, synthesizing Mn-doped ZIF-8 precursors. The precursors were carbonized through a two-step pyrolysis strategy (800 °C followed by 1,100 °C), forming highly porous carbon structures with curved surface morphologies. The Mn-N-C catalysts achieved higher ORR activity ($E_{1/2} = 0.815$ V) and stability (14 mV loss after 30,000 potential cycles) than Fe-N-C catalysts and their peak power density reached 0.39 W cm^{-2} under practical H_2 -air conditions [Figure 11L]. DFT calculations revealed higher metal-leaching resistance in MnN_4 than in FeN_4 , which was attributed to the strong Mn-N coordination and reduced Fenton reaction activity in MnN_4 .

In summary, MOFs are ideal precursors for the synthesis and fine-tuning of SACs. In particular, they provide a designable coordination environment, multilevel porosity, and strong metal anchoring ability. For instance, the ligands in MOFs facilitate the formation of stable M-N/O sites, while the MOFs themselves provide both intrinsic metal sites and extrinsic metal sites introduced through their porous structures. In addition, the metal species are well isolated within the highly uniformly dispersed pores of MOFs, effectively preventing metal agglomeration. Subsequent modification of the skeleton can further enhance the activity and stability of defect engineering or heteroatom doping. Saccharides derived from pyrolytic MOFs (such as Fe-N-C materials^[5]) confer high conductivity and durability, achieving catalysts with performances approaching that of Pt/C in fuel cells. However, precise synthesis, long-term stability under harsh conditions, and scalable production are challenging tasks requiring advanced characterization, protective packaging, and template-free synthesis strategies. Future work should focus on clarifying the structure-activity relationship

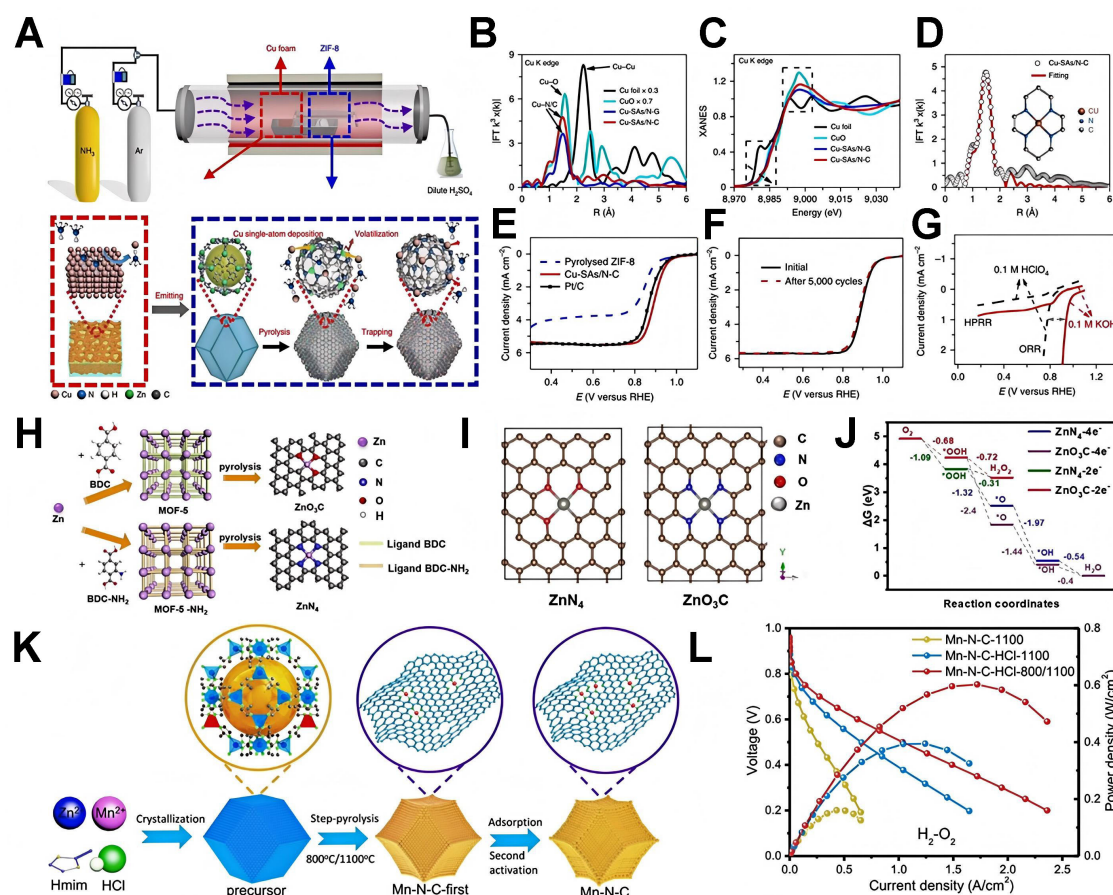


Figure 11. (A) Schematic and reaction mechanism of Cu-SAs/N-C; (B) K^3 -weighted $\chi(k)$ functions of EXAFS spectra; (C) copper K-edge XANES spectra of Cu-SAs/N-C; (D) EXAFS fitting curve of Cu-SAs/N-C. Inset shows the proposed Cu-N₄ coordination environment. LSV curves of (E) Pt/C, Cu-SAs/N-C and pyrolyzed ZIF-8 and (F) Cu-SAs/N-C before and after 5,000 cycles of accelerated durability testing; (G) Comparison between the HPRR and ORR. Reactions were performed in N₂-saturated electrolyte (3.5 mM H₂O₂) (A-G reproduced with permission from Springer Nature, copyright 2018) [155]; (H) Schematic showing the preparation process of ZnO₃C and ZnN₄ electrocatalysts; (I) optimized geometric model of Zn single atoms in ZnN₄ and ZnO₃C; (J) Free energy diagrams of the 2e⁻ and 4e⁻ ORR pathways on ZnO₃C and ZnN₄ at 0 V vs. RHE (H-J reproduced with permission from Wiley-VCH, copyright 2021) [156]; (K) Aqueous synthesis scheme of Mn-N-C catalysts and (L) fuel-cell performances of different catalysts under H₂-O₂ (K and L reproduced with permission from the American Chemical Society, copyright 2020) [130]. EXAFS: Extended X-ray absorption fine structure; SAs: single atoms; ZIF: zeolite imidazole frameworks; ORR: oxygen reduction reaction; XANES: X-ray absorption near-edge structure; HPRR: hydrogen peroxide reduction reaction.

through DFT simulations and on bimetallic site engineering to promote MOF-based SACs for sustainable energy applications.

MOF-based dual-atom catalysts

The synthesis of MOF-based dual-atom catalysts requires precise control over the metal content in the precursor MOFs, most of which are derived from the ZIF-8 system. One strategy leverages the porous nature of MOFs by adsorbing small molecules capable of chelating dual metal atoms prior to pyrolysis. By controlling pyrolysis conditions, the chelated metal pairs can be retained as isolated dual-atom sites. Chelation of identical metals produces homonuclear dual-atom configurations, while chelation of different metals yields heteronuclear sites. Alternatively, partial substitution of the original MOF metal nodes with a secondary metal can generate heteronuclear dual-atom sites after pyrolysis. This approach directly exploits the structural tunability of MOF nodes to preorganize the desired metal pairs.

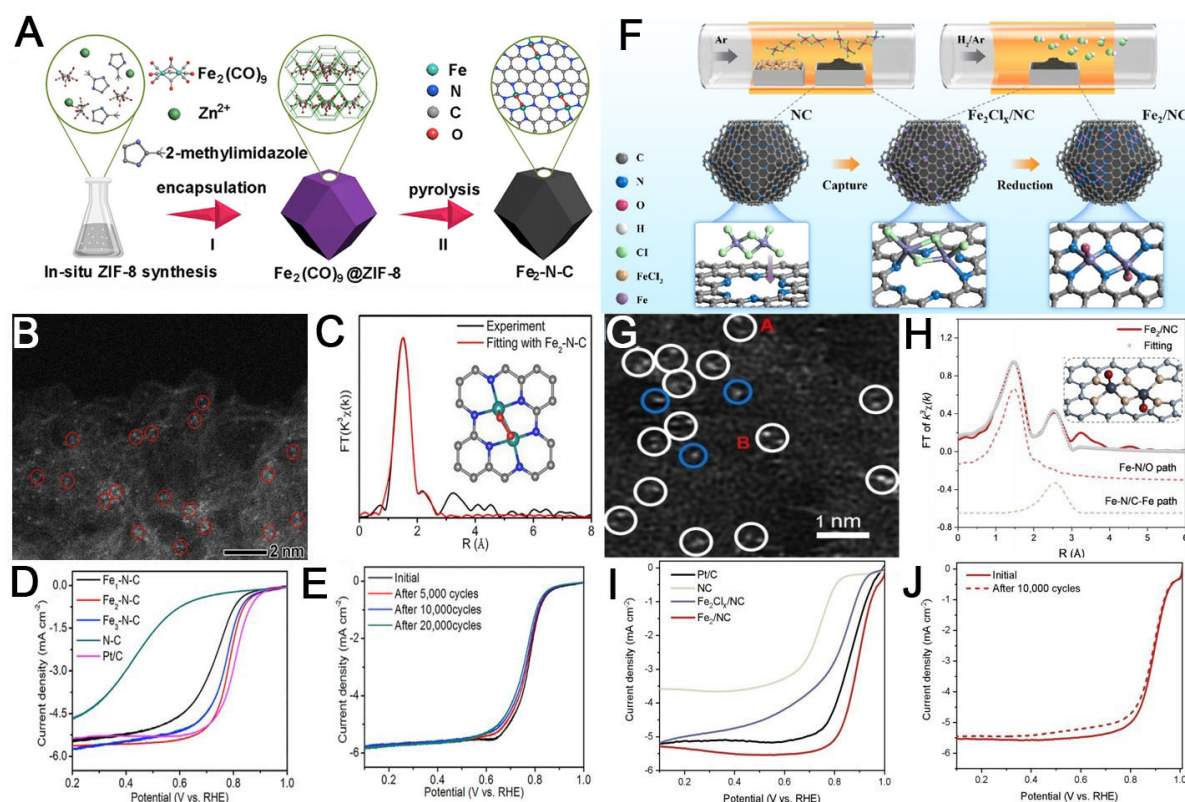


Figure 12. (A) Schematic showing the two-step synthesis of Fe₂-N-C; (B) HAADF-STEM images and (C) K³-weighted $\chi(k)$ function of the EXAFS spectra of Fe₂-N-C; (D) LSV curves in O₂-saturated 0.5 M H₂SO₄ solution at a sweep rate of 10 mV s⁻¹ and a rotation speed of 1,600 rpm; (E) durability test results of Fe₂-N-C after 5,000, 10,000 and 20,000 cycles (A-E reproduced with permission from Elsevier, copyright 2019) [158]; (F) Schematic showing the synthesis of the Fe₂/NC catalyst; (G) aberration-corrected HAADF-STEM image of Fe₂/NC (white circles delineate the diatomic Fe₂ sites); (H) corresponding EXAFS fitting curves of Fe₂/NC in R space; LSV curves of (I) NC, Fe₂Cl₆/NC, Fe₂/NC and Pt/C at 1,600 rpm in O₂-saturated 0.1 M KOH and (J) Fe₂/NC before and after the stability test (F-J reproduced with permission from Wiley-VHC, copyright 2024) [159]. HAADF-STEM: High-angle annular dark field-scanning transmission electron microscopy; EXAFS: extended X-ray absorption fine structure; LSV: linear sweep voltammetry.

Homologous dual-atom catalysts

Similar to the synthesis of SACs, controlling the metal content in MOF materials can yield relatively pure dual-atom catalysts [157]. Ye *et al.* developed a novel method to enhance ORR performance by precisely controlling Fe atoms anchored on nitrogen-doped carbon supports [Figure 12A] [158]. Fe-containing precursors were encapsulated within ZIF-8 and pyrolyzed, producing Fe clusters with specific atomic configurations. HAADF-STEM and X-ray Absorption Fine Structure (XAFS) analyses revealed that Fe₂ clusters exhibited optimal peroxo-like O₂ adsorption configurations and modulated the N-species distribution in the carbon matrix [Figure 12B and C]. Electrochemical tests showed that Fe₂-N-C achieved an $E_{1/2}$ of 0.78 V, approaching that of commercial Pt/C, with remarkable durability (only 20 mV decay after 20,000 cycles). Mechanistic studies indicated that Fe₂ clusters facilitated O₂ activation through enhanced electron transfer and optimized support properties [Figure 12D and E].

In another study, Yan *et al.* synthesized dual-atom Fe catalysts (Fe₂/NC) with a precisely controlled Fe-Fe distance of 0.3 nm from Fe₂Cl₆ vapor precursors [159]. Sublimation of FeCl₃ produced Fe₂Cl₆ dimers anchored on N-doped carbon supports. Subsequent hydrogen treatment removed chlorine ligands, yielding atomically dispersed Fe-Fe pairs with preserved structural features [Figure 12F]. Comparative experiments with a shorter Fe-Fe distance catalyst (Fe₂/NC-S, ~0.25 nm) confirmed the critical role of interatomic spacing in catalytic enhancement [Figure 12G and H]. The Fe₂/NC catalyst demonstrated outstanding ORR performance, with an $E_{1/2}$ of 0.90 V (vs. RHE) and superior stability over 10,000 cycles [Figure 12I and J].

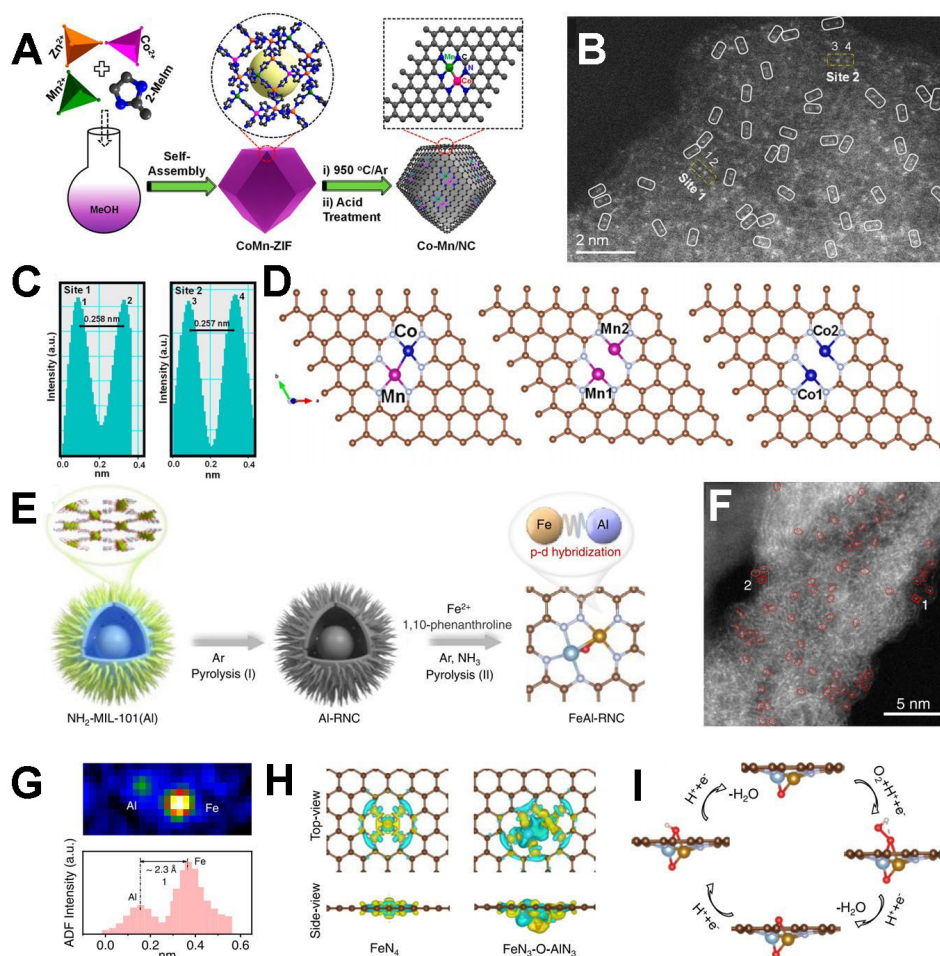


Figure 13. (A) Synthesis and (B) high-resolution HAADF-STEM image of the CoMn/NC catalyst; (C) intensity profiles obtained at sites 1 and 2 in (B); (D) optimized geometries of the CoN₃-MnN₃, MnN₃-MnN₃, and CoN₃-CoN₃ dual-atom catalyst models (A-D reproduced with permission from the American Chemical Society, copyright 2023)^[160]; (E) Synthesis and (F) aberration-corrected HAADF-STEM image of the FeAl-RNC catalyst; (G) intensity profile and corresponding colored raster graphic of the Fe-Al atomic pairs; (H) differential charge densities of FeN₄ and FeN₃-O-AlN₃ (top and side views); (I) schematic of the proposed ORR pathway of FeN₃-O-AlN₃ (E-I reproduced with permission from the American Chemical Society, copyright 2024)^[131]. HAADF-STEM: High-angle annular dark field-scanning transmission electron microscopy; ORR: oxygen reduction reaction.

Heterogeneous dual-atom catalysts

Similar to the synthesis of homologous dual-atom catalysts, heterogeneous dual-atom catalysts can be obtained by controlling the metal content and types in the MOF precursor, along with post-treatment conditions. As shown in Figure 13A, Dey et al. reported the synthesis of a dual single-atom catalyst featuring atomically isolated CoMn/NC, derived from Co/Mn-doped ZIF-8 via high-temperature calcination^[160]. HAADF-STEM, X-ray photoelectron spectroscopy (XPS), and synchrotron X-ray absorption spectroscopy (XAS) analyses confirmed the atomic dispersion of Co-Mn sites coordinated with nitrogen in a CoN₃-MnN₃ configuration [Figure 13B and C]. DFT calculations revealed that the Co-Mn dual sites facilitate O₂ activation through bridging adsorption, favoring an associative 4e⁻ ORR pathway over a dissociative mechanism owing to lower thermodynamic and kinetic barriers [Figure 13D]. CoN₃-MnN₃ exhibited exceptional ORR performance in alkaline and acidic electrolytes, achieving $E_{1/2}$ values of 0.89 V in 0.1 M KOH and 0.82 V in 0.5 M H₂SO₄. Furthermore, it demonstrated excellent durability and methanol tolerance, outperforming commercial Pt/C catalysts. In practical applications, the catalyst achieved peak power densities of 970 mW cm⁻² in PEMFCs and 176 mW cm⁻² in rechargeable ZABs, underscoring its potential in energy conversion technologies.

Additionally, Liu *et al.* developed FeAl-RNC with atomically dispersed Fe-Al dual-atom pairs [Figure 13E]^[131]. Leveraging p-d orbital hybridization between Al and Fe atoms, the catalyst modulates electron distribution around Fe sites, optimizing the adsorption strength of oxygen intermediates and markedly enhancing intrinsic ORR activity. Its unique rambutan-like structure, with abundant micropores and macropores, increases active-site exposure, improves mass transport, and boosts stability. Experimental results showed exceptional PEMFC performance under H₂-O₂ conditions, including high kinetic current density, peak power density, and durability-exceeding U.S. DOE 2025 targets. Theoretical calculations indicated that Fe-Al pairs lower the d-band energy of Fe and promote OH* desorption, clarifying the mechanism underlying the improved catalytic efficiency [Figure 13F-I].

MOF-based cluster catalysts

Owing to their porous architectures, MOF materials can yield different types of metal catalysts depending on their intrinsic properties and the metal loading within their pore structures. By systematically tuning the metal content, SACs, dual-atom catalysts, or metal cluster catalysts can be obtained.

Based on ZIFs, Wang *et al.* developed non-planar, nest-like [Fe₂S₂] cluster catalysts exhibiting structural similarity to plant-type ferredoxin [Figure 14A]^[161]. Aberration-corrected HAADF-STEM measurements revealed numerous paired bright spots, confirming the successful synthesis of Fe₂ clusters. EXAFS curve-fitting analysis [Figure 14B] further elucidated the fine structure of the Fe₂S₂ clusters. DFT calculations of the complete ORR reaction process indicated a notable difference in the adsorption mode of the second O atom when the first OH* was separated [Figure 14C]. This variation resulted in distinct deformations in the spatial structure of the active site, subsequently influencing its desorption behavior. Fe₂S₂@CN showed the highest relative $E_{1/2}$ (0.92 V) among the tested catalysts and exhibited exceptional stability [Figure 14D and E], highlighting its considerable potential in ORR catalysis.

Liu *et al.* synthesized Fe₂ clusters based on plant ferritin and encapsulated them within the cavities of ZIF-8 [Figure 14F]^[162]. These clusters featured a distinctive Fe₂N₆-S fine structure. The Fe 3d orbitals in Fe₂N₆ and Fe₂N₆-S exhibited pronounced orbital coupling [Figure 14G]. In FeN₄, OH* intermediates strongly adsorbed to the Fe site, hindering desorption and electron transfer. This step was identified as the rate-determining step of the overall reaction, resulting in a higher overpotential (0.70 V). By contrast, Fe₂N₆-S displayed the lowest overpotential (0.37 V) among the three catalysts calculated [Figure 14H].

Others

Several researchers have investigated the impacts of multiple catalytically active centers operating in concert on MOF substrates for ORR catalysis. For example, Wang *et al.* utilized Prussian blue as a self-assembly substrate on a carbon cloth [Figure 15A]^[163], synthesizing a catalyst Fe/Fe₃C@N-C with both Fe₃C and atomically dispersed Fe-N₄ active sites following calcination. All catalysts presented the peaks of Fe₃C in their X-ray diffraction (XRD) patterns [Figure 15B] and the (121) and (312) crystal planes of Fe₃C in their TEM images, confirming the formation of Fe₃C [Figure 15C]. Concurrently, a substantial quantity of iron single atoms (Fe-N₄ active sites) were identified in the HAADF-STEM images [Figure 15D]. The electron microscopy observations were corroborated by the EXAFS results. As the Fe/Fe₃C@N-doped C-700 catalyst performed excellently in RDE testing ($E_{1/2}$ = 0.903 V), it was installed as the cathode in a ZAB. The Fe/Fe₃C@N-doped C-700 achieved a higher power density and higher stability than various commercial precious metal catalysts, demonstrating its considerable application potential [Figure 15E-G].

IN SITU DETECTION OF MOF-DERIVED CATALYSTS

In situ monitoring methods, which capture real-time or quasi-real-time information under actual reaction

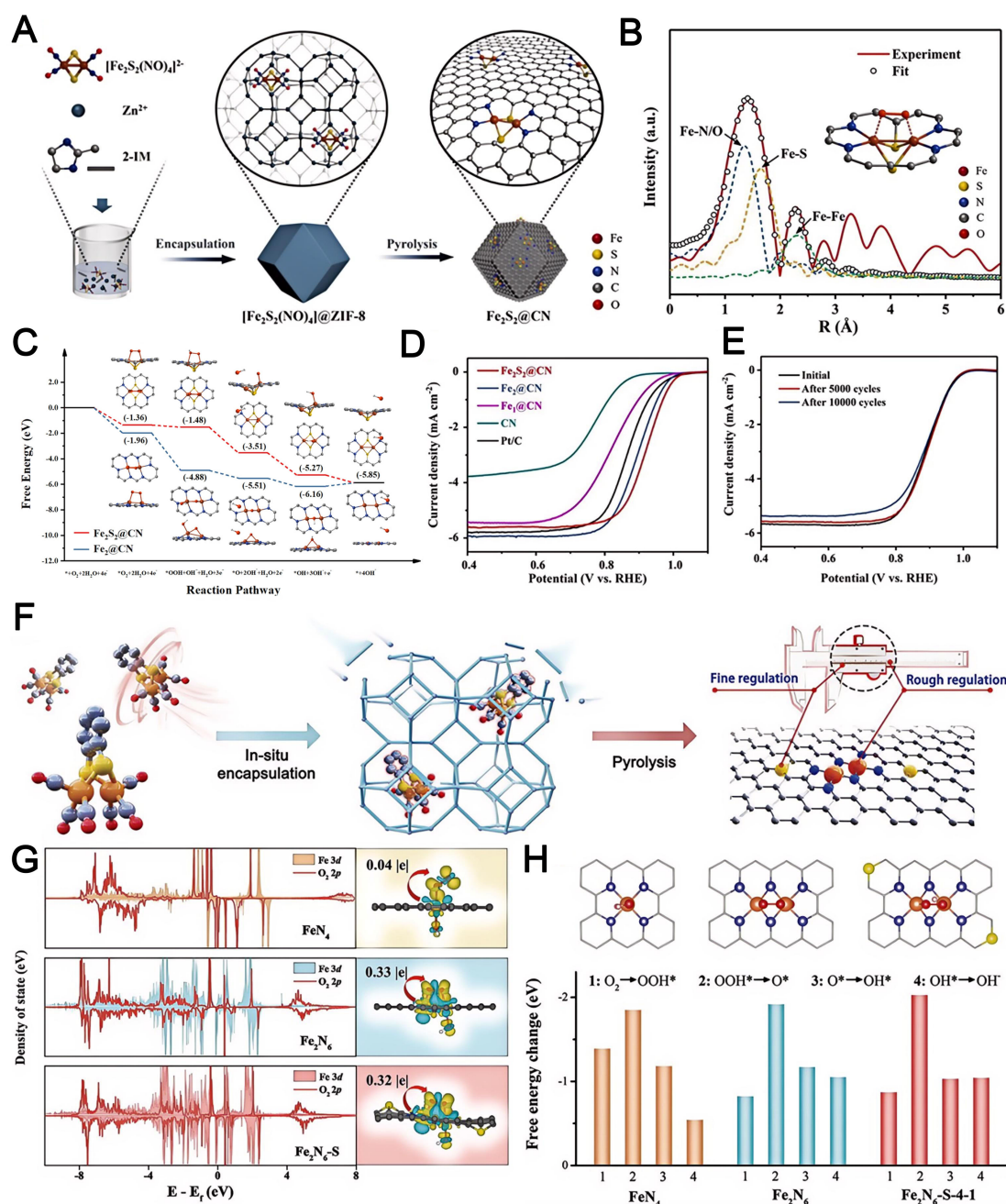


Figure 14. (A) Synthetic procedure of non-planar nest-like $[\text{Fe}_2\text{S}_2]$ cluster sites in the N-doped carbon plane; (B) corresponding Fe K-edge EXAFS fittings of $\text{Fe}_2\text{S}_2@\text{CN}$ and the optimized non-planar nest-like $[\text{Fe}_2\text{S}_2]$ cluster structure model (inset); (C) Free energy diagram of the ORR process, along with configurations of the corresponding adsorbed intermediates; (D) ORR polarization curves of $\text{Fe}_2\text{S}_2@\text{CN}$, $\text{Fe}_2@\text{CN}$, $\text{Fe}_1@\text{CN}$, CN and Pt/C; (E) ORR durability test results of $\text{Fe}_2\text{S}_2@\text{CN}$ after 5,000 and 10,000 cycles (A-E reproduced with permission from Wiley-VCH, copyright 2023)^[161]; (F) Schematic of a synthesis-targeted electrocatalyst; (G) PDOS profiles and corresponding differential charge densities of the samples; (H) free energy changes during each reaction step (F-H reproduced with permission from Wiley-VCH, copyright 2024)^[162]. ORR: Oxygen reduction reaction; EXAFS: extended X-ray absorption fine structure.

conditions, have revolutionized ORR research. By overcoming the limitations of traditional non-*in situ* characterization, they enable direct observation of the reaction mechanism, kinetic processes, catalyst structural evolution, and failure mechanisms in ORR^[164,165]. For instance, Liu *et al.* used *in situ* XAFS and *in situ* synchrotron radiation infrared spectroscopy (SRIR) to monitor changes in CR-Co/CINC catalysts during the ORR^[166]. *In situ* EXAFS and X-ray absorption near-edge structure (XANES) results indicated that during

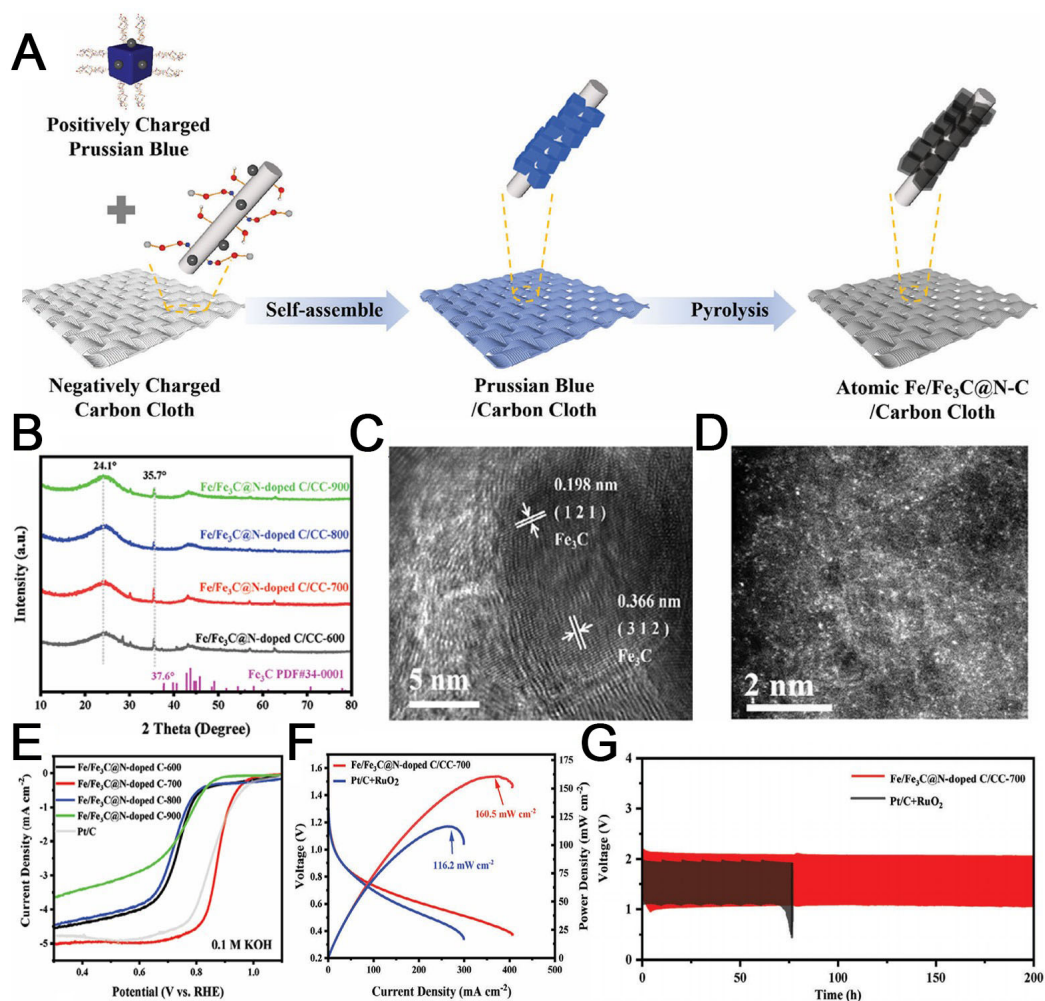


Figure 15. (A) Synthesis of the Fe/Fe₃C@N-C catalyst; (B) XRD patterns of the as-prepared samples; (C) TEM and (D) HAADF-STEM images of Fe/Fe₃C@N-C; (E) LSV curves of Fe/Fe₃C@N-C in O₂-saturated 0.1 M KOH; (F) discharge polarization curves and power density curves; (G) Galvanostatic cycling stability of the as-prepared samples under 10 mA cm⁻² charge and discharge conditions (A-G reproduced with permission from Wiley-VCH, copyright 2024)^[163]. HAADF-STEM: High-angle annular dark field-scanning transmission electron microscopy; XRD: X-ray diffraction.

the early reaction stage, the d-band electrons underwent rapid modulation as the fractured Cl-Co-N₄ moieties evolved into coordination-reduced Cl-Co-N₂ species [Figure 16A–C]. SRIR spectra during ORR showed only the absorption band of *O, indicating rapid cleavage of the O–O bond in *O and the dynamic evolution of OH intermediates on Cl-Co-N₂ sites [Figure 16D and E].

Similarly, Hu *et al.* employed *in situ* Raman spectroscopy to track structural changes in catalysts during ORR^[167]. Upon application of voltage, two peaks appeared in the Raman spectrum at 457 and 628 cm⁻¹, corresponding to Co–OH and Co–OOH, respectively. Among the catalysts studied, CoSe/Co/NC exhibited the fastest reaction rate, consistent with its outstanding ORR performance [Figure 16F–H].

Overall, these *in situ* characterization results provide detailed insights into catalyst transformations during ORR, deepening understanding of the reaction process and offering new concepts and approaches for designing advanced catalysts.

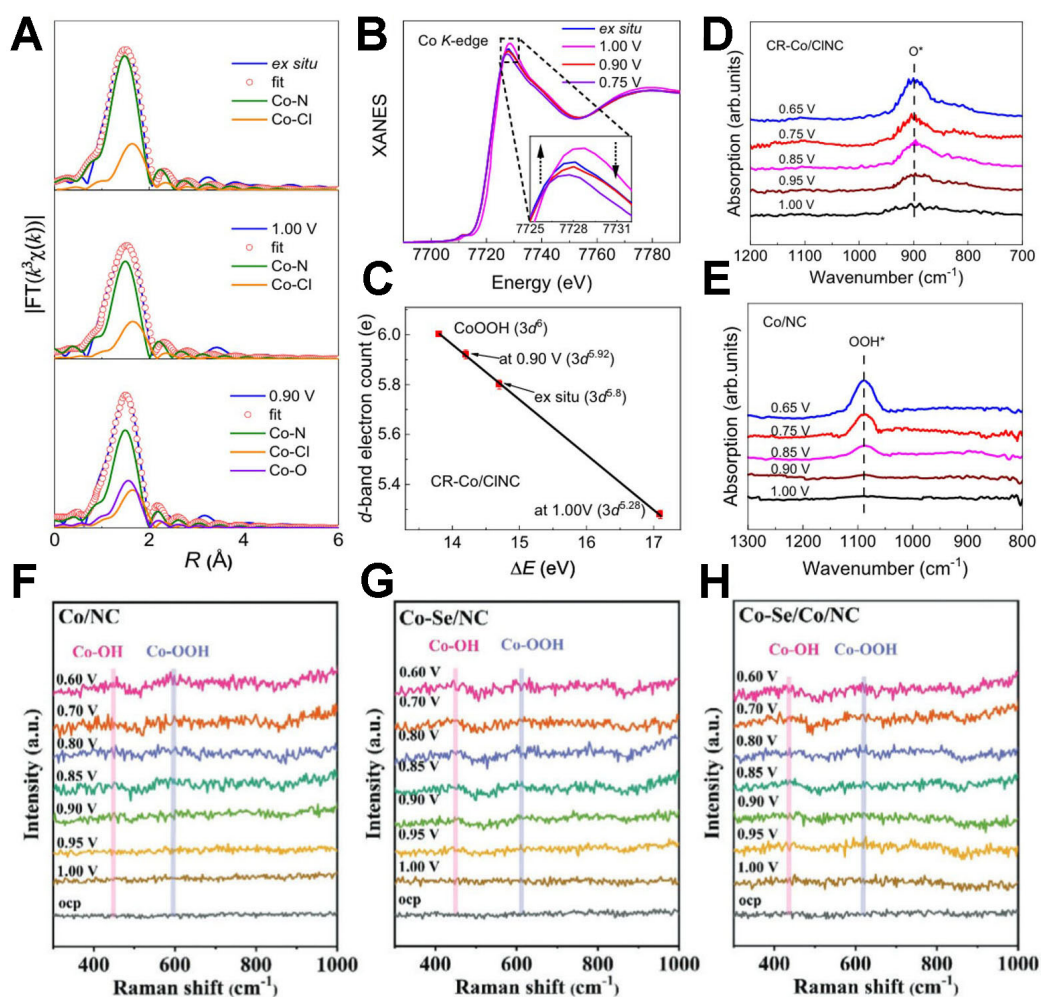


Figure 16. (A) Curve-fitting analysis of the EXAFS spectra of CR-Co/CINC, (B) XANES spectra of the Co K-edge of CR-Co/CINC recorded at different applied potentials during the ORR process; (C) fitted average formal d-band electron counts of Co in CR-Co/CINC under *ex situ*, 1.00 V, and 0.90 V conditions, determined from the absorption edges of the Co K-edge XANES spectra. *In situ* synchrotron radiation infrared spectra of (D) CR-Co/CINC and (E) Co/NC under various potentials (A–E reproduced with permission from Springer Nature, copyright 2024)^[166]. *In situ* Raman spectra of (F) Co/NC, (G) Co-Se/NC, and (H) Co-Se/Co/NC in 0.1 M KOH (F–H reproduced with permission from Wiley-VCH, copyright 2024)^[167]. EXAFS: Extended X-ray absorption fine structure; ORR: oxygen reduction reaction; XANES: X-ray absorption near-edge structure.

CONCLUSIONS AND PERSPECTIVES

In conclusion, the ORR stands as a cornerstone of clean energy conversion, and unlocking its full potential hinges on advancing high-performance catalysts to overcome its intrinsically sluggish kinetics. MOFs have emerged as versatile precursors and templates for the fabrication of atomically precise ORR catalysts: via pyrolysis or solvothermal synthesis, these materials retain the structural tunability of MOFs while enabling atomic-level control over catalyst composition and coordination environments, thereby delivering substantial improvements in ORR activity.

As described earlier, the rational selection of ligands—including porphyrins, imidazoles, and carboxylates—coupled with precise modulation of metal loading and species, yields a diverse array of active center architectures, spanning single-atom, dual-atom, and cluster configurations. This approach not only delineates the pivotal role of ligands in governing catalyst evolution but also elucidates the intricate interplay between coordination environment, active center geometry, intermediate adsorption, and ORR performance.

Notwithstanding these advances, critical challenges persist, notably the real-time monitoring of MOF pyrolysis dynamics and the *in-situ* characterization of metal coordination evolution under operational catalytic conditions. Looking ahead, the integration of cutting-edge *in-situ* characterization with first-principles calculations will deepen our mechanistic understanding of structure-activity relationships, while translating MOFs-derived ORR catalysts into practical devices such as zinc-air batteries and fuel cells will be instrumental in driving their commercial deployment. These efforts will not only underpin the transition to a low-carbon energy landscape but also provide a robust technical framework for addressing global energy challenges.

DECLARATIONS

Authors' contributions

Literature search and organization and manuscript drafting: Xu, D.; Jiang, J.

Administrative and software technical support: Liu, D.; Dou, Y.

Manuscript revision: Duan, J.; Zhuang, Z.

Supervision and suggestion: Wei, X.; Yang, J.

Project supervision: Liu, X.; Wang, D.

Availability of data and materials

Not applicable.

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Conflicts of interest

Wang, D. is an Associate Editor of the journal *Microstructures*. Wang, D. was not involved in any steps of editorial processing, notably including reviewer selection, manuscript handling, or decision making. The other authors declared that there are no conflicts of interest.

Ethical approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

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REFERENCES

1. Nie, Y.; Li, L.; Wei, Z. Recent advancements in Pt and Pt-free catalysts for oxygen reduction reaction. *Chem. Soc. Rev.* **2015**, *44*, 2168-201. [DOI](#)
2. Seh, Z. W.; Kibsgaard, J.; Dickens, C. F.; Chorkendorff, I.; Nørskov, J. K.; Jaramillo, T. F. Combining theory and experiment in electrocatalysis: insights into materials design. *Science* **2017**, *355*, eaad4998. [DOI PubMed](#)
3. Fei, H.; Dong, J.; Feng, Y.; et al. General synthesis and definitive structural identification of MN_4C_4 single-atom catalysts with tunable electrocatalytic activities. *Nat. Catal.* **2018**, *1*, 63-72. [DOI](#)
4. Wang, H.; Xu, S.; Tsai, C.; et al. Direct and continuous strain control of catalysts with tunable battery electrode materials. *Science* **2016**, *354*, 1031-6. [DOI](#)
5. Shao, M.; Chang, Q.; Dodelet, J. P.; Chenitz, R. Recent advances in electrocatalysts for oxygen reduction reaction. *Chem. Rev.* **2016**, *116*, 3594-657. [DOI PubMed](#)
6. Cui, H.; Liu, T.; Chen, Y.; et al. Dynamics of non-metal-regulated FeCo bimetal microenvironment on oxygen reduction reaction activity and intrinsic mechanism. *Nano. Res.* **2023**, *16*, 2199-208. [DOI](#)

7. Zhang, B.; Zhao, Y.; Li, L.; et al. Bead-like cobalt-nitrogen co-doped carbon nanocage/carbon nanofiber composite: a high-performance oxygen reduction electrocatalyst for zinc-air batteries. *Nano. Res.* **2023**, *16*, 545-54. DOI
8. Huang, Z.; Zhan, C.; Yuan, Y.; et al. Designing natural cell-inspired heme-spurred membrane electrode assembly for fuel cells. *J. Am. Chem. Soc.* **2025**, *147*, 22818-26. DOI
9. Chung, H. T.; Cullen, D. A.; Higgins, D.; et al. Direct atomic-level insight into the active sites of a high-performance PGM-free ORR catalyst. *Science* **2017**, *357*, 479-84. DOI
10. Chen, C.; Kang, Y.; Huo, Z.; et al. Highly crystalline multimetallic nanoframes with three-dimensional electrocatalytic surfaces. *Science* **2014**, *343*, 1339-43. DOI
11. Li, M.; Zhao, Z.; Cheng, T.; et al. Ultrafine jagged platinum nanowires enable ultrahigh mass activity for the oxygen reduction reaction. *Science* **2016**, *354*, 1414-9. DOI
12. Liu, G.; Shih, A. J.; Deng, H.; et al. Site-specific reactivity of stepped Pt surfaces driven by stress release. *Nature* **2024**, *626*, 1005-10. DOI
13. Ji, N.; Sheng, H.; Liu, S.; et al. Boosting oxygen reduction in acidic media through integration of Pt-Co alloy effect and strong interaction with carbon defects. *Nano. Res.* **2024**, *17*, 7900-8. DOI
14. Zhang, H.; Sun, Q.; He, Q.; et al. Single Cu atom dispersed on S,N-codoped nanocarbon derived from shrimp shells for highly-efficient oxygen reduction reaction. *Nano. Res.* **2022**, *15*, 5995-6000. DOI
15. Hu, Y.; Zhu, M.; Luo, X.; et al. Coplanar Pt/C nanomeshes with ultrastable oxygen reduction performance in fuel cells. *Angew. Chem. Int. Ed.* **2021**, *60*, 6533-8. DOI
16. Li, Q.; Zhang, D.; Wu, J.; et al. Cation-deficient perovskites greatly enhance the electrocatalytic activity for oxygen reduction reaction. *Adv. Mater.* **2024**, *36*, 2309266. DOI
17. Jiao, L.; Li, J.; Richard, L. L.; et al. Chemical vapour deposition of Fe-N-C oxygen reduction catalysts with full utilization of dense Fe-N₄ sites. *Nat. Mater.* **2021**, *20*, 1385-91. DOI
18. Liu, S.; Li, C.; Zachman, M. J.; et al. Atomically dispersed iron sites with a nitrogen-carbon coating as highly active and durable oxygen reduction catalysts for fuel cells. *Nat. Energy.* **2022**, *7*, 652-63. DOI
19. Stamenkovic, V. R.; Fowler, B.; Mun, B. S.; et al. Improved oxygen reduction activity on Pt₃Ni(111) via increased surface site availability. *Science* **2007**, *315*, 493-7. DOI
20. Yuan, Y.; Zheng, Y.; Luo, D.; et al. Recent progress on mechanisms, principles, and strategies for high-activity and high-stability non-PGM fuel cell catalyst design. *Carbon. Energy.* **2024**, *6*, e426. DOI
21. Chen, M. Strong metal-support interaction of Pt-based electrocatalysts with transition metal oxides/nitrides/carbides for oxygen reduction reaction. *Microstructures* **2023**, *3*, 2023025. DOI
22. Wang, X.; Li, Z.; Qu, Y.; et al. Review of metal catalysts for oxygen reduction reaction: from nanoscale engineering to atomic design. *Chem* **2019**, *5*, 1486-511. DOI
23. Tang, B.; Zhou, Y.; Ji, Q.; et al. A Janus dual-atom catalyst for electrocatalytic oxygen reduction and evolution. *Nat. Synth.* **2024**, *3*, 878-90. DOI
24. Ahmad, M.; Chen, J.; Liu, J.; et al. Metal-organic framework-based single-atom electro-/photocatalysts: synthesis, energy applications, and opportunities. *Carbon. Energy.* **2024**, *6*, e382. DOI
25. Kitagawa, S.; Kitaura, R.; Noro, S. Functional porous coordination polymers. *Angew. Chem. Int. Ed.* **2004**, *43*, 2334-75. DOI PubMed
26. Lee, J.; Farha, O. K.; Roberts, J.; Scheidt, K. A.; Nguyen, S. T.; Hupp, J. T. Metal-organic framework materials as catalysts. *Chem. Soc. Rev.* **2009**, *38*, 1450-9. DOI PubMed
27. Gao, Y.; Yang, C.; Sun, F.; et al. Ligand-Tuning metallic sites in molecular complexes for efficient water oxidation. *Angew. Chem. Int. Ed.* **2025**, *64*, e202415755. DOI
28. Sui, R.; Zhang, X.; Wang, X.; et al. Silver based single atom catalyst with heteroatom coordination environment as high performance oxygen reduction reaction catalyst. *Nano. Res.* **2022**, *15*, 7968-75. DOI
29. Liu, S.; Liu, M.; Li, X.; et al. Metal organic polymers with dual catalytic sites for oxygen reduction and oxygen evolution reactions. *Carbon. Energy.* **2023**, *5*, e303. DOI
30. Wu, J.; Zhu, X.; Li, Q.; et al. Enhancing radiation-resistance and peroxidase-like activity of single-atom copper nanozyme via local coordination manipulation. *Nat. Commun.* **2024**, *15*, 6174. DOI PubMed PMC
31. Yang, B.; Li, B.; Xiang, Z. Advanced MOF-based electrode materials for supercapacitors and electrocatalytic oxygen reduction. *Nano. Res.* **2023**, *16*, 1338-61. DOI
32. Liang, C.; Zhang, T.; Sun, S.; et al. Yolk-shell FeCu/NC electrocatalyst boosting high-performance zinc-air battery. *Nano. Res.* **2024**, *17*, 7918-25. DOI
33. Cheng, K.; Liu, Z.; Jiang, D.; Song, M.; Wang, Y. Jellyfish bio-inspired Fe@CNT@CuNC derived from ZIF-8 for cathodic oxygen reduction. *Nano. Res.* **2024**, *17*, 2352-9. DOI

-
34. Li, Q.; Li, Q.; Wang, Z.; Zheng, X.; Cai, S.; Wu, J. Recent advances in hierarchical porous engineering of MOFs and their derived materials for catalytic and battery: methods and application. *Small* **2024**, *20*, 2303473. DOI
 35. Wen, S.; Yan, L.; Zhao, X. Synergistic effect of structural and interfacial engineering of metal-organic framework-derived superstructures for energy and environmental applications. *Adv. Energy. Mater.*, 2025, 2502432. DOI
 36. Xu, H.; Geng, P.; Feng, W.; Du, M.; Kang, D. J.; Pang, H. Recent advances in metal-organic frameworks for electrochemical performance of batteries. *Nano. Res.* **2024**, *17*, 3472-92. DOI
 37. Wang, X.; Zhang, G.; Yin, W.; et al. Metal-organic framework-derived phosphide nanomaterials for electrochemical applications. *Carbon. Energy.* **2022**, *4*, 246-81. DOI
 38. Liu, J.; Chen, L.; Cui, H.; Zhang, J.; Zhang, L.; Su, C. Y. Applications of metal-organic frameworks in heterogeneous supramolecular catalysis. *Chem. Soc. Rev.* **2014**, *43*, 6011-61. DOI
 39. Bai, J.; Lian, Y.; Deng, Y.; et al. Simultaneous integration of Fe clusters and NiFe dual single atoms in nitrogen-doped carbon for oxygen reduction reaction. *Nano. Res.* **2024**, *17*, 2291-7. DOI
 40. Liu, Y.; Li, Z.; Zeng, Y.; et al. Host-guest engineering of dual-metal nitrogen carbides as bifunctional oxygen electrocatalysts for long-cycle rechargeable Zn-air battery. *Carbon. Energy.* **2025**, *7*, e682. DOI
 41. Xia, B. Y.; Yan, Y.; Li, N.; Wu, H. B.; Lou, X. W.; Wang, X. A metal-organic framework-derived bifunctional oxygen electrocatalyst. *Nat. Energy.* **2016**, *1*, 15006. DOI
 42. Yin, P.; Yao, T.; Wu, Y.; et al. Single cobalt atoms with precise N-coordination as superior oxygen reduction reaction catalysts. *Angew. Chem. Int. Ed.* **2016**, *55*, 10800-5. DOI
 43. Zhang, L.; Meng, Q.; Zheng, R.; et al. Microenvironment regulation of M-N-C single-atom catalysts towards oxygen reduction reaction. *Nano. Res.* **2023**, *16*, 4468-87. DOI
 44. Zhou, T.; Guan, Y.; He, C.; et al. Building Fe atom-cluster composite sites using a site occupation strategy to boost electrochemical oxygen reduction. *Carbon. Energy.* **2024**, *6*, e477. DOI
 45. Guo, W.; Liu, Y.; Zhou, H.; Wu, Y. Multiscale designing principle of M-N-C towards high performance PEMFC. *Microstructures* **2025**, *5*, 2025031. DOI
 46. Cheng, W.; Zhao, X.; Su, H.; et al. Lattice-strained metal-organic-framework arrays for bifunctional oxygen electrocatalysis. *Nat. Energy.* **2019**, *4*, 115-22. DOI
 47. Xiong, Y.; Yang, Y.; DiSalvo, F. J.; Abruña, H. D. Metal-organic-framework-derived Co-Fe bimetallic oxygen reduction electrocatalysts for alkaline fuel cells. *J. Am. Chem. Soc.* **2019**, *141*, 10744-50. DOI
 48. Ma, R.; Li, Q.; Yan, J.; et al. Thermodynamically controllable synthesis of ZIF-8 exposing different facets and their applications in single atom catalytic oxygen reduction reactions. *Nano. Res.* **2023**, *16*, 9618-24. DOI
 49. Yuan, Y.; Zhang, Q.; Li, Y.; et al. Beads-on-string hierarchical structured electrocatalysts for efficient oxygen reduction reaction. *Carbon. Energy.* **2023**, *5*, e253. DOI
 50. Jiao, L.; Wan, G.; Zhang, R.; Zhou, H.; Yu, S. H.; Jiang, H. L. From metal-organic frameworks to single-atom Fe implanted N-doped porous carbons: efficient oxygen reduction in both alkaline and acidic media. *Angew. Chem. Int. Ed.* **2018**, *57*, 8525-9. DOI
 51. Zhuang, Z.; Huang, A.; Tan, X.; et al. p-Block-metal bismuth-based electrocatalysts featuring tunable selectivity for high-performance oxygen reduction reaction. *Joule* **2023**, *7*, 1003-15. DOI
 52. Chen, H.; Zhang, H.; Chi, K.; Zhao, Y. Pyrimidine-containing covalent organic frameworks for efficient photosynthesis of hydrogen peroxide via one-step two electron oxygen reduction process. *Nano. Res.* **2024**, *17*, 9498-506. DOI
 53. Luo, E.; Chu, Y.; Liu, J.; et al. Pyrolyzed M-N_x catalysts for oxygen reduction reaction: progress and prospects. *Energy. Environ. Sci.* **2021**, *14*, 2158-85. DOI
 54. Zhu, X.; Shao, Y.; Xia, D.; et al. When graphitic nitrogen meets pentagons: selective construction and spectroscopic evidence for improved four-electron oxygen reduction electrocatalysis. *Adv. Mater.* **2025**, *37*, 2414976. DOI
 55. Yeager, E. Electrocatalysts for O₂ reduction. *Electrochim. Acta.* **1984**, *29*, 1527-37. DOI
 56. Nørskov, J. K.; Rossmeisl, J.; Logadottir, A.; et al. Origin of the overpotential for oxygen reduction at a fuel-cell cathode. *J. Phys. Chem. B.* **2004**, *108*, 17886-92. DOI
 57. Huang, X.; Zhao, Z.; Cao, L.; et al. High-performance transition metal-doped Pt₃Ni octahedra for oxygen reduction reaction. *Science* **2015**, *348*, 1230-4. DOI
 58. Islam, M. N.; Mansoor Basha, A. B.; Kollath, V. O.; Soleymani, A. P.; Jankovic, J.; Karan, K. Designing fuel cell catalyst support for superior catalytic activity and low mass-transport resistance. *Nat. Commun.* **2022**, *13*, 6157. DOI PubMed PMC
 59. Hu, Y.; Han, X.; Hu, S.; et al. Surface-diffusion-induced amorphization of Pt nanoparticles over Ru oxide boost acidic oxygen evolution. *Nano. Lett.* **2024**, *24*, 5324-31. DOI

-
60. Adabi, H.; Shakouri, A.; Ul Hassan, N.; et al. High-performing commercial Fe-N-C cathode electrocatalyst for anion-exchange membrane fuel cells. *Nat. Energy*. **2021**, *6*, 834–43. [DOI](#)
61. Mu, X. Q.; Liu, S. L.; Zhang, M. Y.; et al. Symmetry-broken ru nanoparticles with parasitic Ru-Co dual-single atoms overcome the volmer step of alkaline hydrogen oxidation. *Angew. Chem. Int. Ed.* **2024**, *63*, e202319618. [DOI](#)
62. Guan, S.; Yuan, Z.; Zhao, S.; et al. Efficient hydrogen generation from ammonia borane hydrolysis on a tandem ruthenium-platinum-titanium catalyst. *Angew. Chem. Int. Ed.* **2024**, *63*, e202408193. [DOI](#)
63. Li, Y.; Niu, S.; Liu, P.; et al. Ruthenium nanoclusters and single atoms on α -MoC/N-doped carbon achieves low-input/input-free hydrogen evolution via decoupled/coupled hydrazine oxidation. *Angew. Chem. Int. Ed.* **2024**, *63*, e202316755. [DOI](#)
64. Hu, Y.; Chao, T.; Li, Y.; et al. Cooperative Ni(Co)-Ru-P sites activate dehydrogenation for hydrazine oxidation assisting self-powered H₂ production. *Angew. Chem. Int. Ed.* **2023**, *62*, e202308800. [DOI](#)
65. Chao, T.; Xie, W.; Hu, Y.; et al. Reversible hydrogen spillover at the atomic interface for efficient alkaline hydrogen evolution. *Energy. Environ. Sci.* **2024**, *17*, 1397–406. [DOI](#)
66. Lien, H. T.; Chang, S. T.; Chen, P. T.; et al. Probing the active site in single-atom oxygen reduction catalysts via operando X-ray and electrochemical spectroscopy. *Nat. Commun.* **2020**, *11*, 4233. [DOI](#) [PubMed](#) [PMC](#)
67. Wang, Q.; Kaushik, S.; Xiao, X.; Xu, Q. Sustainable zinc-air battery chemistry: advances, challenges and prospects. *Chem. Soc. Rev.* **2023**, *52*, 6139–90. [DOI](#)
68. Shao, W.; Yan, R.; Zhou, M.; et al. Carbon-based electrodes for advanced zinc-air batteries: oxygen-catalytic site regulation and nanostructure design. *Electrochem. Energy. Rev.* **2023**, *6*, 11. [DOI](#)
69. Zou, Y.; Su, Y.; Yu, Y.; et al. On the role of Zn and Fe doping in nitrogen-carbon electrocatalysts for oxygen reduction. *Nano. Res.* **2024**, *17*, 9564–72. [DOI](#)
70. Pang, M.; Yang, M.; Zhang, H.; et al. Synthesis techniques, mechanism, and prospects of high-loading single-atom catalysts for oxygen reduction reactions. *Nano. Res.* **2024**, *17*, 9371–96. [DOI](#)
71. Mun, Y.; Lee, S.; Kim, K.; et al. Versatile strategy for tuning ORR activity of a single Fe-N₄ site by controlling electron-withdrawing/donating properties of a carbon plane. *J. Am. Chem. Soc.* **2019**, *141*, 6254–62. [DOI](#)
72. Cao, S.; Sun, T.; Li, J.; Li, Q.; Hou, C.; Sun, Q. The cathode catalysts of hydrogen fuel cell: from laboratory toward practical application. *Nano. Res.* **2023**, *16*, 4365–80. [DOI](#)
73. Jiao, K.; Xuan, J.; Du, Q.; et al. Designing the next generation of proton-exchange membrane fuel cells. *Nature* **2021**, *595*, 361–9. [DOI](#)
74. Bing, Y.; Liu, H.; Zhang, L.; Ghosh, D.; Zhang, J. Nanostructured Pt-alloy electrocatalysts for PEM fuel cell oxygen reduction reaction. *Chem. Soc. Rev.* **2010**, *39*, 2184–202. [DOI](#)
75. Chao, T.; Luo, X.; Zhu, M.; et al. The promoting effect of interstitial hydrogen on the oxygen reduction performance of PtPd alloy nanotubes for fuel cells. *Nano. Res.* **2023**, *16*, 2366–72. [DOI](#)
76. Yu, H.; Li, C.; Lei, Y.; Xiang, Z. Strategic secondary coordination implantation towards efficient and stable Fe-N-C electrocatalysts for the oxygen reduction reaction in PEMFCs. *Angew. Chem. Int. Ed.* **2025**, *64*, e202508141. [DOI](#)
77. Tang, B.; Ji, Q.; Zhang, X.; et al. Symmetry breaking of FeN₄ Moiety via edge defects for acidic oxygen reduction reaction. *Angew. Chem. Int. Ed.* **2025**, *64*, e202424135. [DOI](#)
78. Chen, N.; Lee, Y. M. Anion exchange polyelectrolytes for membranes and ionomers. *Prog. Polym. Sci.* **2021**, *113*, 101345. [DOI](#)
79. Zeng, R.; Li, H.; Shi, Z.; et al. Origins of enhanced oxygen reduction activity of transition metal nitrides. *Nat. Mater.* **2024**, *23*, 1695–703. [DOI](#)
80. Sun, K.; Dong, J.; Sun, H.; et al. Co(CN)₃ catalysts with well-defined coordination structure for the oxygen reduction reaction. *Nat. Catal.* **2023**, *6*, 1164–73. [DOI](#)
81. Li, Z.; Wang, Z.; Zhao, S.; et al. Alkoxy side chain engineering in metal-free covalent organic frameworks for efficient oxygen reduction. *Adv. Mater.* **2025**, 2501603. [DOI](#)
82. Wu, R.; Zuo, J.; Fu, C.; et al. Enhancing rechargeable zinc-air batteries with atomically dispersed zinc iron cobalt planar sites on porous nitrogen-doped carbon. *ACS. Nano.* **2025**, *19*, 20215–24. [DOI](#)
83. Guo, Y.; Zhao, S.; Zhang, N.; et al. Advanced design strategies for Fe-based metal-organic framework-derived electrocatalysts toward high-performance Zn-air batteries. *Energy. Environ. Sci.* **2024**, *17*, 1725–55. [DOI](#)
84. Zhang, H.; Meng, Y.; Zhong, H.; et al. Bulk preparation of free-standing single-iron-atom catalysts directly as the air electrodes for high-performance zinc-air batteries. *Carbon. Energy.* **2023**, *5*, e289. [DOI](#)
85. Sun, C.; Liu, Y.; Lv, Z.; et al. Coordination-environment regulation of atomic Co-Mn dual-sites for efficient oxygen reduction reaction. *Nano. Res.* **2024**, *17*, 6841–8. [DOI](#)
86. Li, J.; Lu, T.; Fang, Y.; et al. The manipulation of rectifying contact of Co and nitrogen-doped carbon hierarchical superstructures toward high-performance oxygen reduction reaction. *Carbon. Energy.* **2024**, *6*, e529. [DOI](#)

-
87. Man, H.; Chen, G.; Wang, F.; et al. Entropy engineering activates Cu-Fe inertia center from prussian blue analogs with micro-strains for oxygen electrocatalysis in Zn-air batteries. *Carbon. Energy*. **2025**, *7*, e693. DOI
 88. Cui, K.; Tang, X.; Xu, X.; Kou, M.; Lyu, P.; Xu, Y. Crystalline dual-porous covalent triazine frameworks as a new platform for efficient electrocatalysis. *Angew. Chem. Int. Ed.* **2024**, *63*, e202317664. DOI PubMed
 89. Zhang, B.; Dang, J.; Li, H.; et al. Orderly stacked “Tile” architecture with single-atom iron boosts oxygen reduction in liquid and solid-state Zn-air batteries. *Adv. Funct. Mater.*, 2025, 2502834. DOI
 90. Wang, Y.; Yang, T.; Fan, X.; et al. Anchoring Fe species on the highly curved surface of S and N Co-doped carbonaceous nanosprings for oxygen electrocatalysis and a flexible zinc-air battery. *Angew. Chem. Int. Ed.* **2024**, *63*, e202313034. DOI
 91. Wang, S.; Zhang, M.; Mu, X.; Liu, S.; Wang, D.; Dai, Z. Atomically dispersed multi-site catalysts: bifunctional oxygen electrocatalysts boost flexible zinc-air battery performance. *Energy. Environ. Sci.* **2024**, *17*, 4847-70. DOI
 92. Khan, I. A.; Qian, Y.; Badshah, A.; Nadeem, M. A.; Zhao, D. Highly porous carbon derived from MOF-5 as a support of ORR electrocatalysts for fuel cells. *ACS. Appl. Mater. Interfaces.* **2016**, *8*, 17268-75. DOI PubMed
 93. Zhao, S.; Yin, H.; Du, L.; et al. Carbonized nanoscale metal-organic frameworks as high performance electrocatalyst for oxygen reduction reaction. *ACS. Nano.* **2014**, *8*, 12660-8. DOI
 94. Chen, Y.; Kang, H.; Cheng, M.; et al. Single-atom catalysts originated from metal-organic frameworks for sulfate radical-based advanced oxidation processes: critical insights into mechanisms. *Adv. Funct. Mater.* **2024**, *34*, 2309223. DOI
 95. Chai, L.; Zhang, L.; Wang, X.; et al. Cube-shaped metal-nitrogen-carbon derived from metal-ammonia complex-impregnated metal-organic framework for highly efficient oxygen reduction reaction. *Carbon* **2020**, *158*, 719-27. DOI
 96. Zhang, S.; Li, S.; Liu, J.; et al. Multiple active cobalt species embedded in microporous nitrogen-doped carbon network for the selective production of hydrogen peroxide. *J. Colloid. Interface. Sci.* **2023**, *631*, 101-13. DOI
 97. Yang, Y.; Sun, Q.; Xue, J.; et al. MOF-derived N-doped carbon nanosticks coupled with Fe phthalocyanines for efficient oxygen reduction. *Chem. Eng. J.* **2023**, *464*, 142668. DOI
 98. Chai, L.; Song, J.; Kumar, A.; et al. Bimetallic-MOF derived carbon with single Pt anchored C4 atomic group constructing super fuel cell with ultrahigh power density and self-change ability. *Adv. Mater.* **2024**, *36*, 2308989. DOI
 99. Du, M.; Chu, B.; Wang, Q.; et al. Dual Fe/I single-atom electrocatalyst for high-performance oxygen reduction and wide-temperature quasi-solid-state Zn-air batteries. *Adv. Mater.* **2024**, *36*, 2412978. DOI
 100. Liu, D.; Srinivas, K.; Ma, F.; et al. Fe species anchored N, S-doped carbon as nonprecious catalyst for boosting oxygen reduction reaction. *J. Alloys. Compd.* **2023**, *937*, 168496. DOI
 101. Zhang, H.; Wang, Y.; Wu, T.; et al. Rational design of porous Fe_xN@MOF as a highly efficient catalyst for oxygen reduction over a wide pH range. *J. Alloys. Compd.* **2023**, *944*, 169039. DOI
 102. Zhang, H.; Li, Z.; Yang, X.; et al. Modulator directed synthesis of size-tunable mesoporous MOFs and their derived nanocarbon-based electrocatalysts for oxygen reduction. *Chem. Eng. J.* **2024**, *486*, 150088. DOI
 103. Liang, Z.; Zhou, G.; Tan, H.; et al. Constructing Co₄(SO₄)₄ clusters within metal-organic frameworks for efficient oxygen electrocatalysis. *Adv. Mater.* **2024**, *36*, 2408094. DOI
 104. Li, H.; Zhang, M.; Zhou, W.; Duan, J.; Jin, W. Ultrathin 2D catalysts with N-coordinated single Co atom outside Co cluster for highly efficient Zn-air battery. *Chem. Eng. J.* **2021**, *421*, 129719. DOI
 105. Rong, J.; Chen, W.; Gao, E.; et al. Design of atomically dispersed CoN₄ sites and Co clusters for synergistically enhanced oxygen reduction electrocatalysis. *Small* **2024**, *20*, 2402323. DOI
 106. Huang, Y.; Chen, Y.; Xu, M.; et al. Catalysts by pyrolysis: Transforming metal-organic frameworks (MOFs) precursors into metal-nitrogen-carbon (M-N-C) materials. *Mater. Today.* **2023**, *69*, 66-78. DOI
 107. Zitolo, A.; Goellner, V.; Armel, V.; et al. Identification of catalytic sites for oxygen reduction in iron-and nitrogen-doped graphene materials. *Nature. Mater.* **2015**, *14*, 937-42. DOI
 108. Arafat, Y.; Azhar, M. R.; Zhong, Y.; Abid, H. R.; Tadé, M. O.; Shao, Z. Advances in zeolite imidazolate frameworks (ZIFs) derived bifunctional oxygen electrocatalysts and their application in zinc-air batteries. *Adv. Energy. Mater.* **2021**, *11*, 2100514. DOI
 109. Nguyen, Q. H.; Tinh, V. D. C.; Oh, S.; et al. Metal-organic framework-polymer complex-derived single-atomic oxygen reduction catalyst for anion exchange membrane fuel cells. *Chem. Eng. J.* **2024**, *481*, 148508. DOI
 110. Yang, Y.; Lou, J.; Zhao, Y.; et al. Ice-templating co-assembly of dual-MOF superstructures derived 2D carbon nanobelts as efficient electrocatalysts. *Chem. Eng. J.* **2023**, *477*, 146900. DOI
 111. Li, X.; Ye, G.; Zhu, W.; et al. Directional construction of low-coordination Fe-N₃ coupled with intrinsic carbon defects for high-efficiency oxygen reduction. *ACS. Nano.* **2024**, *18*, 24505-14. DOI
 112. Bao, G.; Jin, Y.; Fan, Q.; et al. A ZIF-derived hollow carbon nanoframework loaded with FeCu alloy nanoparticles for efficient oxygen reduction reaction and zinc-air batteries. *J. Mater. Chem. A.* **2024**, *12*, 6623-33. DOI

-
113. Xie, M.; Xiao, X.; Wu, D.; et al. MOF-mediated synthesis of novel PtFeCoNiMn high-entropy nano-alloy as bifunctional oxygen electrocatalysts for zinc-air battery. *Nano. Res.* **2024**, *17*, 5288-97. DOI
114. Liao, P. Q.; Shen, J. Q.; Zhang, J. P.; et al. Metal-organic frameworks for electrocatalysis. *Coord. Chem. Rev.* **2018**, *373*, 22-48. DOI
115. Pan, Y.; Gao, J.; Li, Y.; et al. Constructing nitrogen-doped carbon hierarchy structure derived from metal-organic framework as high-performance ORR cathode material for Zn-air battery. *Small* **2024**, *20*, 2304594. DOI
116. Liu, M.; Zhao, J.; Dong, H.; et al. Electrodeposition of Ni/Cu bimetallic conductive metal-organic frameworks electrocatalysts with boosted oxygen reduction activity for zinc-air batteries. *Small* **2024**, *20*, 2405309. DOI
117. Jena, R.; Bhattacharyya, S.; Bothra, N.; Kashyap, V.; Pati, S. K.; Maji, T. K. $\text{Ni}_x\text{Co}_{1-x}\text{O}/\text{NCNT}$ as trifunctional ORR, OER, and HER electrocatalysts and its application in a Zn-Air Battery. *ACS. Appl. Mater. Interfaces.* **2023**, *15*, 27893-904. DOI
118. Lv, C.; Ren, Y.; Li, B.; et al. 1,2,4-triazole-assisted metal-organic framework-derived nitrogen-doped carbon nanotubes with encapsulated Co_4N particles as bifunctional oxygen electrocatalysts for rechargeable zinc-air batteries. *J. Colloid. Interface. Sci.* **2023**, *645*, 618-26. DOI
119. Dong, A.; Lin, Y.; Guo, Y.; et al. Immobilization of iron phthalocyanine on MOF-derived N-doped carbon for promoting oxygen reduction in zinc-air battery. *J. Colloid. Interface. Sci.* **2023**, *650*, 2056-64. DOI
120. Li, J.; Xia, W.; Guo, Y.; et al. Surface curvature effect on single-atom sites for the oxygen reduction reaction: a model of mesoporous MOF-derived carbon. *Chem. Eng. J.* **2023**, *477*, 146841. DOI
121. Li, H.; Zheng, J.; Yang, M.; Duan, J. Electron and configuration engineering of atomic Cu and multi-oxidated Cu_{2+1}O centers via gasifiable reductant strategy for efficient oxygen reduction toward Zn-air battery. *Nano. Res.* **2023**, *16*, 2383-91. DOI
122. Zhao, L.; Zhang, J.; Jin, G.; Jiang, Z. J.; Jiang, Z. Metal-organic framework-derived trimetallic particles encapsulated by ultrathin nitrogen-doped carbon nanosheets on a network of nitrogen-doped carbon nanotubes as bifunctional catalysts for rechargeable zinc-air batteries. *J. Colloid. Interface. Sci.* **2024**, *668*, 525-39. DOI
123. Peng, Y.; Li, S.; Wang, M.; et al. Facet engineering of a two-dimensional metal-organic framework with uniquely oriented layered-structure for electrocatalytic oxygen reduction reaction. *J. Colloid. Interface. Sci.* **2024**, *658*, 518-27. DOI
124. Wang, Q.; Wang, L.; Zhang, S.; et al. MOF-on-MOF-derived $\text{FeCo}@/\text{NC}$ OER&ORR bifunctional electrocatalysts for zinc-air batteries. *J. Colloid. Interface. Sci.* **2025**, *677*, 800-11. DOI
125. Rosyara, Y. R.; Muthurasu, A.; Chhetri, K.; et al. Highly porous metal-organic framework entrapped by cobalt telluride-manganese telluride as an efficient bifunctional electrocatalyst. *ACS. Appl. Mater. Interfaces.* **2024**, *16*, 10238-50. DOI
126. Xue, Y.; Guo, Y.; Zhang, Q.; Xie, Z.; Wei, J.; Zhou, Z. MOF-derived co and fe species loaded on N-doped carbon networks as efficient oxygen electrocatalysts for Zn-Air batteries. *Nano. Micro. Lett.* **2022**, *14*, 162. DOI PubMed PMC
127. Sekar, P.; Vasanthakumar, P.; Shanmugam, R.; et al. Green synthesis of a redox-active riboflavin-integrated Ni-MOF and its versatile electrocatalytic applications towards oxygen evolution and reduction, and HMF oxidation reactions. *Green. Chem.* **2022**, *24*, 9233-44. DOI
128. Yan, Q.; Duan, X.; Liu, Y.; Ge, F.; Zheng, H. A hybridization cage-confinement pyrolysis strategy for ultrasmall Ni_3Fe alloy coated with N-doped carbon nanotubes as bifunctional oxygen electrocatalysts for Zn-air batteries. *J. Mater. Chem. A.* **2023**, *11*, 1430-8. DOI
129. Li, J.; Xia, W.; Xu, X.; et al. Selective etching of metal-organic frameworks for open porous structures: mass-efficient catalysts with enhanced oxygen reduction reaction for fuel cells. *J. Am. Chem. Soc.* **2023**, *145*, 27262-72. DOI
130. Chen, M.; Li, X.; Yang, F.; et al. Atomically dispersed MnN_4 catalysts via environmentally benign aqueous synthesis for oxygen reduction: mechanistic understanding of activity and stability improvements. *ACS. Catal.* **2020**, *10*, 10523-34. DOI
131. Liu, Y.; Li, J.; Lv, Z.; et al. Efficient Proton-exchange membrane fuel cell performance of atomic Fe sites via p-d hybridization with Al dopants. *J. Am. Chem. Soc.* **2024**, *146*, 12636-44. DOI
132. Yi, S. Y.; Choi, E.; Jang, H. Y.; et al. Insight into defect engineering of atomically dispersed iron electrocatalysts for high-performance proton exchange membrane fuel cell. *Adv. Mater.* **2023**, *35*, 2302666. DOI
133. da Silva Freitas, W.; D'Epifanio, A.; Vecchio, C. L.; et al. Tailoring MOF structure via iron decoration to enhance ORR in alkaline polymer electrolyte membrane fuel cells. *Chem. Eng. J.* **2023**, *465*, 142987. DOI
134. Yang, X.; Zhu, B.; Gao, Z.; et al. A vacuum vapor deposition strategy to Fe single-atom catalysts with densely active sites for high-performance Zn-air battery. *Adv. Sci.* **2024**, *11*, 2306594. DOI
135. Tian, H.; Song, A.; Zhang, P.; et al. High durability of Fe-N-C single-atom catalysts with carbon vacancies toward the oxygen reduction reaction in alkaline media. *Adv. Mater.* **2023**, *35*, 2210714. DOI
136. Qu, Q.; Mao, Y.; Ji, S.; et al. Engineering the lewis acidity of fe single-atom sites via atomic-level tuning of spatial coordination configuration for enhanced oxygen reduction. *J. Am. Chem. Soc.* **2025**, *147*, 6914-24. DOI
137. Han, Y.; Wang, Y. G.; Chen, W.; et al. Hollow N-doped carbon spheres with isolated cobalt single atomic sites: superior electrocatalysts for oxygen reduction. *J. Am. Chem. Soc.* **2017**, *139*, 17269-72. DOI

-
138. Guo, Y.; Zhang, Z.; Chen, D.; et al. Precise construction of asymmetrically coordinated PtCuZn trimetallic atom catalysts for efficient oxygen reduction. *Angew. Chem. Int. Ed.* **2025**, *64*, e202507395. DOI
139. Li, Z.; Ji, S.; Liu, Y.; et al. Well-defined materials for heterogeneous catalysis: from nanoparticles to isolated single-atom sites. *Chem. Rev.* **2020**, *120*, 623–82. DOI
140. Liu, L.; Corma, A. Metal catalysts for heterogeneous catalysis: from single atoms to nanoclusters and nanoparticles. *Chem. Rev.* **2018**, *118*, 4981–5079. DOI PubMed PMC
141. Yang, H.; Duan, P.; Zhuang, Z.; et al. Understanding the dynamic evolution of active sites among single atoms, clusters, and nanoparticles. *Adv. Mater.* **2025**, *37*, 2415265. DOI
142. Shen, J.; Chen, J.; Qian, Y.; et al. Atomic engineering of single-atom nanozymes for biomedical applications. *Adv. Mater.* **2024**, *36*, 2313406. DOI
143. Qiu, Y.; Sun, M.; Wu, J.; et al. Boosting oxygen reduction performances in Pd-based metallenes by co-confining interstitial H and p-block single atoms. *Nat. Commun.* **2025**, *16*, 5262. DOI PubMed PMC
144. Yang, X. F.; Wang, A.; Qiao, B.; Li, J.; Liu, J.; Zhang, T. Single-atom catalysts: a new frontier in heterogeneous catalysis. *Acc. Chem. Res.* **2013**, *46*, 1740–8. DOI
145. Chen, Y.; Ji, S.; Chen, C.; Peng, Q.; Wang, D.; Li, Y. Single-atom catalysts: synthetic strategies and electrochemical applications. *Joule* **2018**, *2*, 1242–64. DOI
146. Wang, A.; Li, J.; Zhang, T. Heterogeneous single-atom catalysis. *Nat. Rev. Chem.* **2018**, *2*, 65–81. DOI
147. Zhang, J.; Zhao, Y.; Chen, C.; et al. Tuning the coordination environment in single-atom catalysts to achieve highly efficient oxygen reduction reactions. *J. Am. Chem. Soc.* **2019**, *141*, 20118–26. DOI
148. Yang, J.; Liu, W.; Xu, M.; et al. Dynamic behavior of single-atom catalysts in electrocatalysis: identification of Cu-N₃ as an active site for the oxygen reduction reaction. *J. Am. Chem. Soc.* **2021**, *143*, 14530–9. DOI
149. Li, P.; Guo, Q.; Zhang, J.; Chen, R.; Ding, S.; Su, Y. How the microenvironment dominated by the distance effect to regulate the FeN₄ site ORR activity and selectivity? *Nano. Res.* **2024**, *17*, 5735–41. DOI
150. Ishiki, N. A.; Teixeira Santos, K.; Bibent, N.; et al. Evidence for the stabilization of FeN₄ sites by Pt particles during acidic oxygen reduction. *Nat. Commun.* **2025**, *16*, 6404. DOI PubMed PMC
151. Xie, X.; Peng, L.; Yang, H.; Waterhouse, G. I. N.; Shang, L.; Zhang, T. MIL-101-derived mesoporous carbon supporting highly exposed Fe single-atom sites as efficient oxygen reduction reaction catalysts. *Adv. Mater.* **2021**, *33*, 2101038. DOI
152. Xie, X.; Shang, L.; Xiong, X.; Shi, R.; Zhang, T. Fe single-atom catalysts on MOF-5 derived carbon for efficient oxygen reduction reaction in proton exchange membrane fuel cells. *Adv. Energy. Mater.* **2022**, *12*, 2102688. DOI
153. Yuan, S.; Zhang, J.; Hu, L.; et al. Decarboxylation-induced defects in MOF-derived single cobalt atom@carbon electrocatalysts for efficient oxygen reduction. *Angew. Chem. Int. Ed.* **2021**, *60*, 21685–90. DOI
154. Rong, J.; Gao, E.; Liu, N.; et al. Porphyrinic MOF-derived rich N-doped porous carbon with highly active CoN₄C single-atom sites for enhanced oxygen reduction reaction and Zn-air batteries performance. *Energy. Storage. Mater.* **2023**, *56*, 165–73. DOI
155. Qu, Y.; Li, Z.; Chen, W.; et al. Direct transformation of bulk copper into copper single sites via emitting and trapping of atoms. *Nat. Catal.* **2018**, *1*, 781–6. DOI
156. Jia, Y.; Xue, Z.; Yang, J.; et al. Tailoring the electronic structure of an atomically dispersed zinc electrocatalyst: coordination environment regulation for high selectivity oxygen reduction. *Angew. Chem. Int. Ed.* **2022**, *61*, e202110838. DOI
157. Ma, F. X.; Liang, X.; Liu, Z. H.; et al. Impeding thermal atomization enables synthesizing Fe₂N cluster liganded single Fe-Atom catalyst for highly efficient oxygen reduction reaction. *Angew. Chem. Int. Ed.* **2025**, *64*, e202504935. DOI
158. Ye, W.; Chen, S.; Lin, Y.; et al. Precisely tuning the number of Fe atoms in clusters on N-doped carbon toward acidic oxygen reduction reaction. *Chem* **2019**, *5*, 2865–78. DOI
159. Yan, L.; Mao, Y.; Li, Y.; et al. Sublimation transformation synthesis of dual-atom Fe catalysts for efficient oxygen reduction reaction. *Angew. Chem. Int. Ed.* **2025**, *64*, e202413179. DOI
160. Dey, G.; Jana, R.; Saifi, S.; et al. Dual single-atomic Co-Mn sites in metal-organic-framework-derived N-doped nanoporous carbon for electrochemical oxygen reduction. *ACS. Nano.* **2023**, *17*, 19155–67. DOI
161. Wang, M.; Zhang, Z.; Zhang, S.; et al. Non-planar nest-like [Fe₂S₂] cluster sites for efficient oxygen reduction catalysis. *Angew. Chem. Int. Ed.* **2023**, *62*, e202300826. DOI
162. Liu, M.; Wang, X.; Cao, S.; et al. Ferredoxin-inspired design of S-synergized Fe-Fe dual-metal center catalysts for enhanced electrocatalytic oxygen reduction reaction. *Adv. Mater.* **2024**, *36*, 2309231. DOI
163. Wang, Z.; Ren, J.; Ling, G.; Guo, J.; Lv, Y.; Ren, R. P. Prussian blue-derived atomic Fe/Fe₃C@N-doped C catalysts supported by carbon cloth as integrated air cathode for flexible Zn-air batteries. *Adv. Sci.* **2025**, *12*, 2407631. DOI

-
164. Wang, J.; Lang, S. Y.; Shen, Z. Z.; et al. In situ visualization of interfacial processes at nanoscale in non-alkaline Zn-air batteries. *Nat. Commun.* **2024**, *15*, 10882. DOI PubMed PMC
165. Yao, Y.; Qu, H.; Sun, Z.; Chen, Y.; Yang, S.; Ma, W. Identifying in situ activity and selectivity of oxygen reduction catalysts at the subparticle level. *ACS. Nano.* **2025**, *19*, 18502-12. DOI
166. Liu, M.; Zhang, J.; Su, H.; et al. In situ modulating coordination fields of single-atom cobalt catalyst for enhanced oxygen reduction reaction. *Nat. Commun.* **2024**, *15*, 1675. DOI PubMed PMC
167. Hu, H.; Wang, J.; Liao, K.; et al. Clarifying the active structure and reaction mechanism of atomically dispersed metal and nonmetal sites with enhanced activity for oxygen reduction reaction. *Adv. Mater.* **2025**, *37*, 2416126. DOI

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