

Advanced metal–organic frameworks for next-generation energy storage and conversion: From nanoscale design to widespread applications

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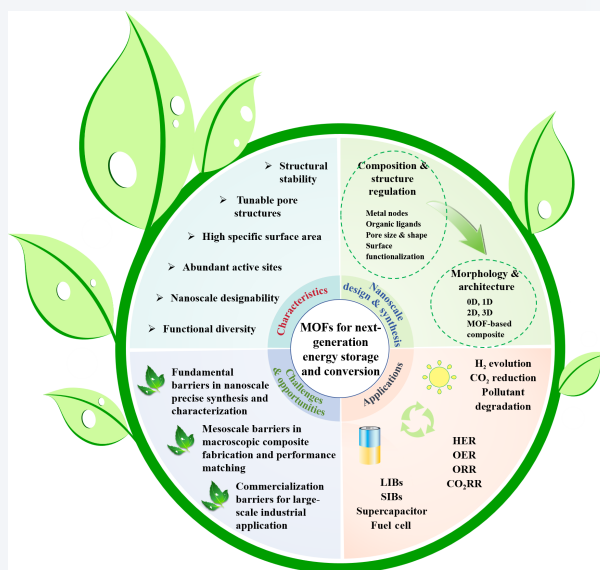
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ABSTRACT: Metal–organic frameworks (MOFs), as an emerging class of porous crystalline materials, exhibit immense potential in the field of energy storage and conversion due to their high specific surface area, tunable pore structures, and abundant active sites. This review summarizes the latest research progress of MOFs in next-generation energy technologies. Spanning from nanoscale design to macroscopic applications, the structure–performance relationships and critical roles of MOFs in electrochemical energy storage, electrocatalysis, and photocatalysis are systematically explored. Initially, nanoscale design principles and controllable synthesis strategies for MOFs are introduced, covering the selection of metal nodes and organic linkers, the modulation of pore size and geometry, and surface functionalization. Subsequently, the applications of MOFs in electrochemical energy storage systems, such as lithium-ion batteries, sodium-ion batteries, supercapacitors, and fuel cells, are discussed. Furthermore, their superior performance in electrocatalytic reactions, including the hydrogen evolution reaction, oxygen evolution reaction, oxygen reduction reaction, and carbon dioxide reduction reaction, is highlighted. In addition, the potential of MOFs in photocatalytic fields, such as photocatalytic water splitting for hydrogen production, carbon dioxide reduction, and pollutant degradation, is examined. Finally, the major challenges hindering the transition of MOFs from laboratory research to scalable applications are summarized, and their significant role in driving the energy revolution and achieving sustainable development goals is envisioned. Through this review, new insights and directions are provided for MOF research in the energy sector, aiming to facilitate their widespread application in future energy technologies.



KEYWORDS: metal–organic frameworks, energy storage, energy conversion, nanoscale design, sustainable development

1 Introduction

With sustained global economic growth and expanding populations, worldwide energy demand is on a significant upward

trajectory. Long-standing reliance on fossil fuels has not only exacerbated the risk of resource depletion but also precipitated severe environmental and socio-economic challenges across energy production, transmission, and consumption [1, 2]. Combustion of fossil fuels, a primary source of greenhouse gas emissions, directly accelerates global warming [3]; concurrently, the resulting air pollutants pose critical threats to public health [4, 5]. Confronted by this escalating urgency, the international community has universally recognized the imperative of transitioning toward clean, renewable, and efficient energy systems, establishing sustainability as the cornerstone of energy policy [6–8]. This profound energy transition

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fundamentally hinges on breakthroughs in novel materials and advanced technologies to achieve efficient energy conversion, storage, and utilization, ultimately paving the way for a low-carbon or zero-carbon future.

The development and deployment of novel functional materials are regarded as pivotal pathways to resolving the energy crisis and achieving carbon neutrality. Metal–organic frameworks (MOFs), as a class of crystalline materials with porous architectures, exhibit more pronounced performance advantages over traditional non-MOF materials in addressing the aforementioned energy challenges. MOFs are constructed from metal ions or metal clusters as nodes, interconnected by organic linkers [9]. The resulting three-dimensional (3D) network structures not only possess specific surface areas and porosities far exceeding those of conventional porous materials, such as activated carbon and zeolites [10], but their pore sizes and shapes can also be regulated with atomic-level precision through the selection of different metal centers and organic linkers. This enables the customization of pore environments and the precise construction of active sites tailored to specific requirements in energy storage and conversion processes [11], a structural characteristic that is difficult to achieve with traditional inorganic porous materials and carbon materials. Meanwhile, the highly diverse compositional constituents of MOFs allow researchers to flexibly modulate the electronic structure, surface hydrophilicity/hydrophobicity, and catalytic activity of materials through strategies, such as ligand modification and multi-metal synergy, enabling precise functional customization for different energy reactions. Compared with currently commercialized non-MOF energy materials, MOFs demonstrate particularly significant advantages in scenarios requiring ion sieving, multi-active-site synergy, and gas adsorption/activation [12]. The core performance of MOF-based materials has already surpassed that of most traditional non-MOF benchmark materials, providing entirely new material options for breaking through existing energy technology bottlenecks. These unique structural and performance characteristics furnish a solid foundation for the application of MOFs in numerous fields, particularly energy-related technologies. Currently, MOFs and their derivatives are extensively investigated for electrochemical energy storage systems, as they offer abundant active sites to facilitate ion transport, while their stable frameworks contribute to enhanced cycling stability and rate capability of electrode materials [13]. Their high conductivity and rapid response characteristics significantly boost the energy and power density of supercapacitors [14]. Moreover, owing to their unique optical absorption properties and electron transfer efficiency, the application of MOFs in photocatalysis is equally noteworthy [15].

Although several review articles have discussed the applications of MOFs in the field of energy storage and conversion, the majority of existing reviews either focus on a single application direction, such as electrocatalysis or energy storage devices, or concentrate on the systematic compilation of materials synthesis methodologies. A systematic integration spanning the full chain from molecular design to device application has yet to be established. Furthermore, the integration of cutting-edge breakthrough research in the MOF field over the past three years remains insufficient, and critical analyses of practical device-level challenges confronting industrial implementation are relatively scarce. Based on these considerations, this review aims to comprehensively revisit and analyze the latest advances in MOF materials from nanoscale design to macroscopic

application, with particular emphasis on their role in next-generation energy storage and conversion. As shown in Fig. 1, we explore the principles of nanoscale design for MOFs, including how ideal morphological control and composite construction are achieved through the modulation of metal nodes, organic ligands, and surface modification. Subsequently, the paper delves into specific application cases of MOFs in electrochemical energy storage, electrocatalysis, and photocatalysis, highlighting their advantages over traditional materials. Finally, we assess the primary obstacles currently hindering the large-scale deployment of MOFs and outline future research directions, such as intelligent design, multifunctional integration, and the establishment of performance evaluation standards. It is hoped that this review will provide valuable insights for professionals in the field and inspire further research endeavors dedicated to MOF materials, collectively advancing the energy revolution and the realization of sustainable development goals.

2 Nanoscale design and controllable synthesis of MOFs

2.1 Composition and structural regulation of MOFs

2.1.1 Selection of metal nodes and organic ligands

The structural design of MOFs represents a systematic engineering endeavor involving the synergistic optimization of metal nodes and organic linkers [16, 17], with typical examples of metal nodes and organic linkers illustrated in Fig. 2. The selection of metal nodes extends beyond single-type metals to encompass mixed-metal systems. Metal centers typically comprise transition metals, rare-earth elements, or other main-group metals, which offer diverse oxidation states and geometric configurations that subsequently govern the stability, electrical conductivity, and other critical properties of MOFs. The diversity and flexibility of metal nodes enable researchers to optimize the physicochemical performance of MOFs through modulation of metal types or adjustment of their ratios. Mixed-metal MOFs, achieved by introducing a secondary metal species with distinct oxidation states or coordination environments, exhibit substantially richer structural characteristics and broader potential applications compared to their single-metal counterparts [18]. The core advantage of this bimetallic or multimetallic strategy lies in the resultant synergistic effects: Electronic interactions between different metal ions can optimize the material's band structure, while multiple metal sites can simultaneously activate reactant molecules, thereby significantly enhancing catalytic activity and selectivity, outcomes that are difficult to achieve with single-metal MOFs. At the synthetic strategy level, researchers have developed several mature routes for the preparation of mixed-metal MOFs, including one-pot co-assembly, postsynthetic ion exchange, and seed-mediated growth. Among these, the postsynthetic ion exchange strategy has garnered considerable attention due to its capacity to introduce novel metal active centers while preserving the topological integrity of the parent framework [19], as illustrated in Fig. 3(a). These multi-metal–organic frameworks (MMOFs), leveraging their tunable active sites and superior synergistic effects, demonstrate exceptional performance surpassing conventional single-metal MOFs in catalysis, electrocatalysis, photocatalysis, and sensing applications.

The selection of organic linkers similarly necessitates

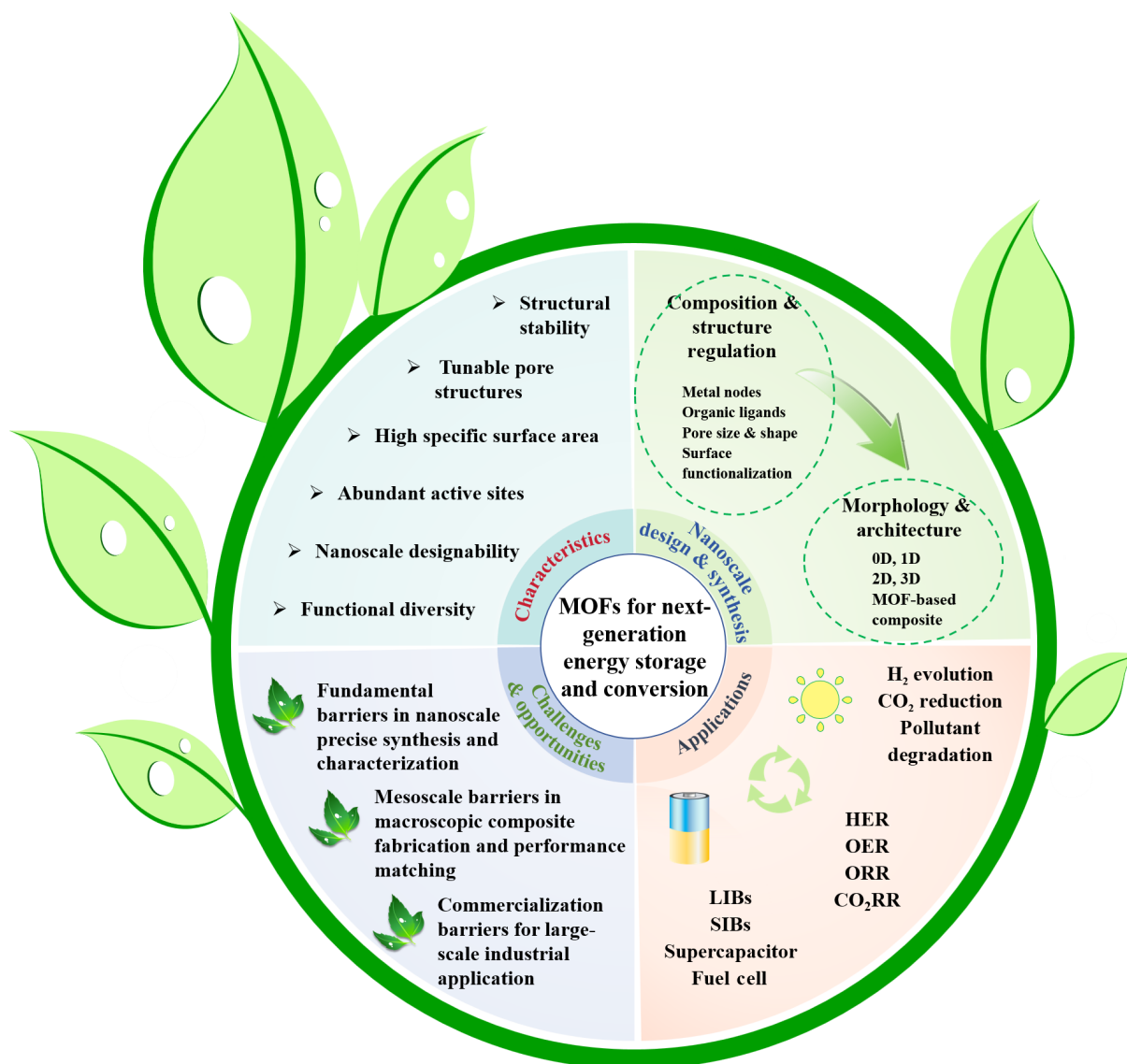


Figure 1 Schematic diagram of the overall framework of MOFs materials from nanoscale design to macroscopic applications.

comprehensive consideration of multiple factors. On one hand, the length, geometric configuration, and connectivity of linkers directly determine the pore dimensions, channel geometries, and topological structures of MOFs; on the other hand, the chemical composition of linkers profoundly influences the surface properties, hydrophilicity/hydrophobicity, and reactivity of MOFs. To accommodate diverse application scenarios, researchers continually explore the design and synthesis of novel linkers. Linkers can be engineered to incorporate specific functional groups, thereby introducing chemical reaction sites or enhancing the material's physical properties. The introduction of nitrogen- or oxygen-containing functional groups can enhance the hydrophilicity of MOFs, facilitating their dispersion in aqueous systems; conversely, hydrophobic functional groups can augment structural stability in humid environments. Prior studies have demonstrated that thiol ($-SH$) functionalized MOFs achieve removal efficiencies exceeding 99.9% for heavy metal Pb^{2+} ions [20]. Furthermore, the construction of MOFs utilizing photoactive or electroactive organic linkers constitutes a core design strategy for achieving efficient light harvesting and charge separation [21]. Such photoactive linkers are

capable of generating long-lived charge-separated states upon photoexcitation, and through the periodic framework structure of MOFs, enable effective spatial separation and directional migration of electrons and holes [22].

The advent of solvent-assisted ligand incorporation (SALI) has provided a strategic avenue for the functionalization of MOFs. The core mechanism of SALI involves the introduction of functional organic ligands into unsaturated secondary building units (SBUs) within the MOF via coordination bonds. Distinct from traditional modification methods that rely on covalent or non-covalent interactions, SALI achieves functionalization through direct coordination between the ligand and the metal nodes [23], as illustrated in Fig. 3(b). The primary advantages of this technique are manifold: First, SALI is typically conducted at room temperature or under mild heating, ensuring compatibility with thermally sensitive functional molecules, such as radical polymerization initiators, photoswitches, and bioactive molecules. Second, it exhibits high universality regarding the types of ligands introduced, encompassing carboxylic acids, phosphonic acids, sulfonic acids, and others. Third, unlike post-synthetic exchange (PSE), SALI

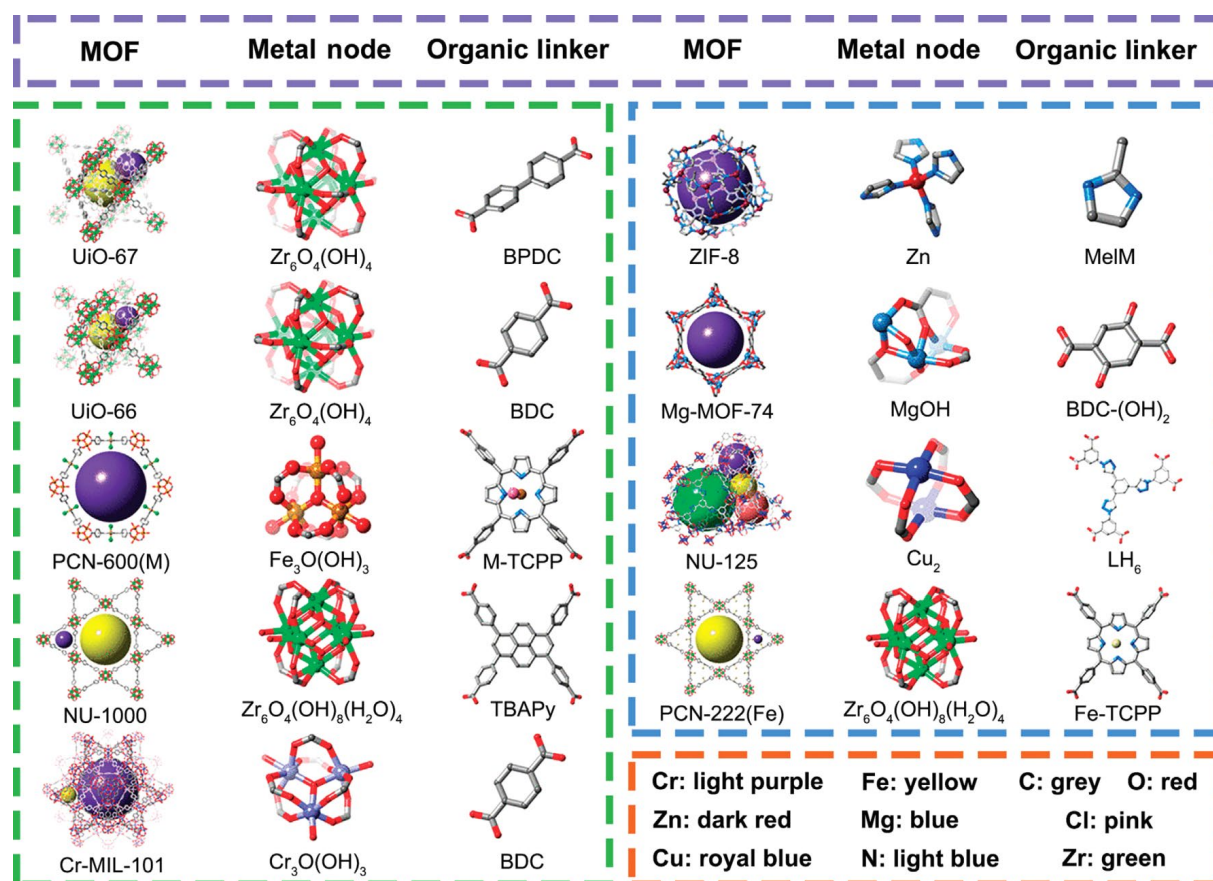


Figure 2 Typical examples of metal nodes and organic ligands. Reproduced with permission from Ref. [17], © Wiley-VCH GmbH 2024.

functionalizes the framework by adding ligands to under-coordinated metal nodes rather than replacing existing structural linkers. This characteristic ensures that the topological structure and porosity of the MOF remain largely unchanged pre- and post-modification. Through SALI, researchers can precisely introduce functional groups into MOF channels to modulate the polarity or acidity/basicity of the pore microenvironment, thereby enhancing recognition capabilities for specific substrates. Furthermore, when combined with metal nanoparticles, the non-structural ligands introduced via SALI can serve as anchoring sites to effectively stabilize the nanoparticles and prevent agglomeration, significantly improving the catalytic activity and selectivity of the composite materials [24].

In recent years, driven by advances in computer-aided design, theory-guided ligand screening has emerged as a pivotal paradigm in MOF research. This approach not only accelerates the discovery of new materials but also predicts their performance, thereby substantially enhancing research efficiency. Traditionally, MOF development relied heavily on trial-and-error methods, where researchers explored potential candidates through iterative experimentation of metal node and organic linker combinations. However, given the vast chemical configuration space of MOFs, comprising theoretically infinite combinations of thousands of topologies, hundreds of metal nodes, and billions of organic linkers, traditional empirical exploration is no longer sufficient to effectively cover this immense design space [25]. To address this challenge, research strategies integrating multi-scale molecular simulation with artificial intelligence have been developed, driving a paradigm shift from empirical exploration to rational design in MOF

materials [26]. On the theoretical front, density functional theory (DFT) elucidates coordination modes between ligands and metal nodes and the stabilization mechanisms of reaction intermediates at the electronic structure level, providing atomic-scale insights into how functional modifications influence catalytic activity [27]. Meanwhile, grand canonical Monte Carlo (GCMC) simulations predict adsorption isotherms and selectivity for specific gas molecules in ligand-modified MOFs, allowing for the assessment of separation performance prior to synthesis [28]. In the realm of data-driven research, machine learning has been extensively applied [29, 30]. By establishing non-linear mapping relationships between MOF structures and properties within databases, machine learning enables the performance evaluation of massive candidate materials within seconds [31, 32]. Currently, several critical MOF structural databases have been constructed, with the computation-ready, experimental MOF (CoRE MOF) database being the most widely utilized. The latest version includes key attributes, such as machine learning-predicted stability metrics and heat capacity, providing a robust data foundation for high-throughput screening [33]. The integrated application of these methods empowers researchers to make rational decisions based on structural design and target application characteristics. Consequently, the selection of metal nodes and organic ligands has evolved into a comprehensive process that leverages computational tools to facilitate the efficient development of novel MOF materials.

2.1.2 Regulation of pore size and shape

The precise regulation of pore size and shape constitutes one of the most critical design elements in MOF engineering [34]. The

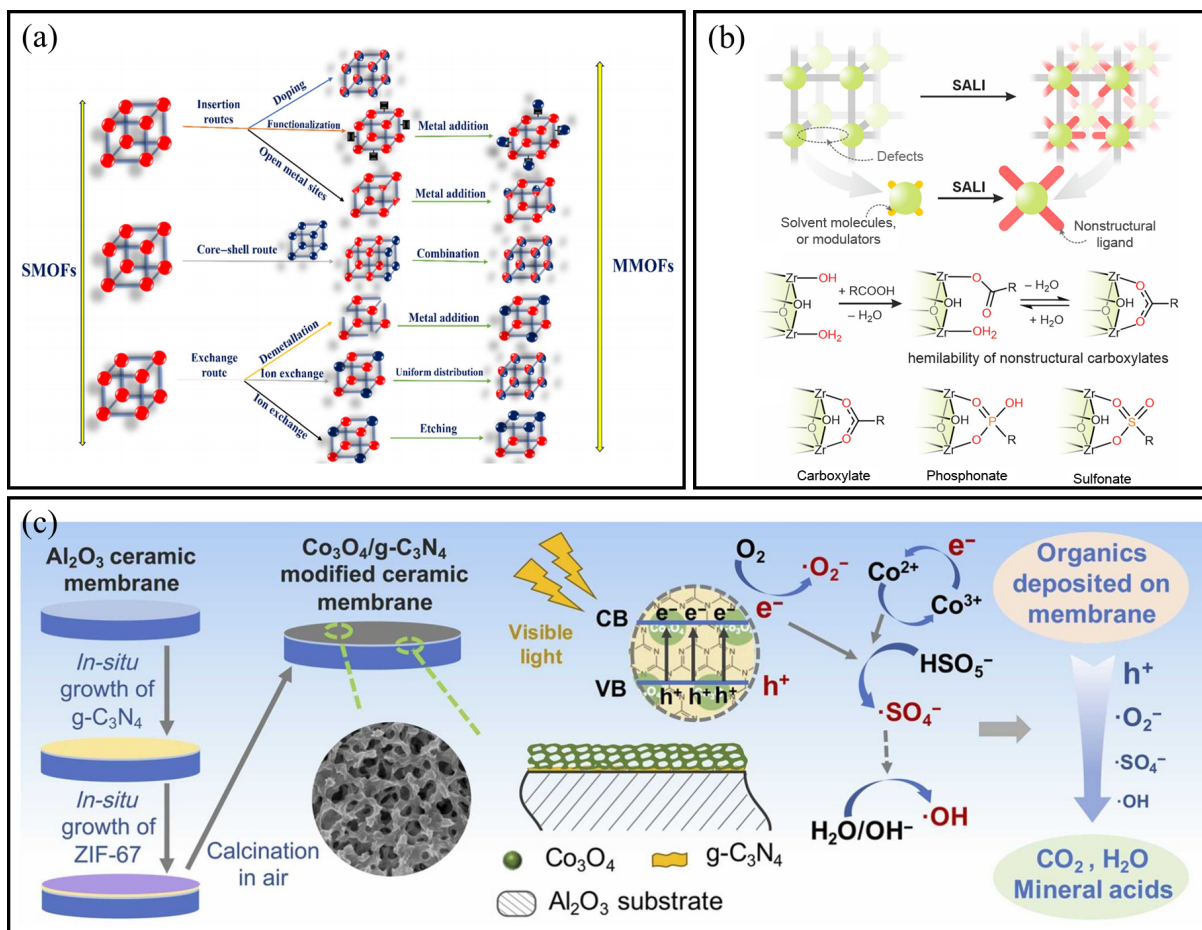


Figure 3 (a) Post-synthesis strategy of MMOF. Reproduced with permission from Ref. [19], © The Royal Society of Chemistry 2026. (b) Mechanism of SALI technology in MOFs. Reproduced with permission from Ref. [23], © The Royal Society of Chemistry 2025. (c) Mechanism by which Co-CN-M materials remove emerging pollutants. Reproduced with permission from Ref. [51], © Elsevier B.V. 2025.

exquisitely tunable porous architecture within MOFs exerts profound influence over their physicochemical properties, particularly in the realms of gas adsorption and separation, catalytic reactions, and energy storage and conversion. Through systematic adjustment of the inter-node distances and angles, or through modification of the linker length, geometric configuration, and connectivity, control over the internal pore geometry of MOFs can be achieved [35]. This reticular chemistry-guided capacity for accurate modulation renders MOFs ideal candidates for gas adsorbents and separation membranes, as they can be tailored according to the dimensions, shape, and even polarity characteristics of target molecules. In carbon dioxide capture, rational design of MOF aperture sizes enables efficient kinetic separation of carbon dioxide (CO₂) from other gaseous species; in the separation of hydrocarbon mixtures within the petrochemical industry, a mixed-linker synthetic strategy combining long and short linkers has been employed to construct customized isosceles triangular pore windows within face-centered cubic (fcc)-topology Zr-MOFs. This distinctive pore geometry facilitates highly efficient sieving of hexane isomers, with selectivity exceeding 200 fold for linear hexane over monobranched hexane [36].

Furthermore, subtle variations in pore geometry significantly influence mass transport efficiency and reaction kinetics within the channels; consequently, for applications requiring efficient mass transfer, structural optimization of the pore architecture represents

an essential approach for enhancing device performance [37]. The regulation of pore dimensions and shapes extends beyond mere geometric modifications, encompassing intricate physicochemical mechanisms, among which the “gate-opening effect” serves as a paradigmatic example of dynamic behavior in MOFs. When the pore apertures of MOFs undergo reversible transformation under external stimuli, such as specific pressure, temperature, or molecular presence, unique gate-opening adsorption behavior emerges: Prior to reaching a critical pressure or threshold condition, the channels remain virtually impermeable to guest molecules, yet upon satisfaction of the triggering conditions, the pores abruptly open and permit rapid molecular ingress. A Zn-MOF material featuring a “rigid-yet-flexible” structural motif has been reported, which possesses a 2 fold interpenetrated framework and exhibits distinctive gate-opening behavior upon acetylene (C₂H₂) adsorption. This dynamic structural transition induces substantial pore modulation; the interlayer spacing of benzene rings expands from 3.09 to 3.34 Å, thereby enabling pore dimensions that selectively accommodate acetylene molecules while effectively excluding carbon dioxide (CO₂), despite the nearly identical kinetic diameters of the two species [38]. Similarly, the ZSTU-6 material, constructed with methyl-decorated two-dimensionally orthogonally arranged channels, has achieved reverse molecular sieving whereby CO₂ is “fully open” while C₂H₂ remains “closed” under ambient temperature and pressure, with a CO₂/C₂H₂ adsorption ratio

reaching 36.2 [39]. This threshold-driven adsorption mechanism holds particular significance in molecular sieving applications, as it permits entry or egress exclusively by specific molecules with matching dimensions and shapes, thereby substantially enhancing separation selectivity.

A series of sophisticated synthetic methodologies have been developed to achieve precise modulation of MOF pore parameters across multiple scales [40]. At the microscopic level, the crystal morphology and defect concentration of MOFs can be precisely controlled by manipulating modulators in solvothermal synthesis. Meanwhile, unconventional heating methods, such as microwave-assisted or ultrasound-assisted synthesis, allow for effective regulation of particle size distribution and pore uniformity by influencing nucleation and crystal growth kinetics. Among these approaches, the utilization of water molecules as green modulators to induce defect formation and hierarchical porosity has garnered significant attention in recent years. Taking the classic Zr-MOF (UiO-66) as an exemplar, the introduction of water molecules acts as a competitive coordinating modulator. Water molecules partially substitute terephthalic acid ligands in coordination with zirconium (Zr_6) clusters, thereby generating “missing-linker” structural defects while maintaining the stability of the original topology, ultimately resulting in a hierarchical pore structure characterized by the coexistence of mesopores and micropores [41]. This controllable defect-construction strategy is, in essence, a precise modulation of the metal-node coordination environment. The loss of linkers exposes coordinatively unsaturated metal sites (CUSs) on the otherwise fully coordinated Zr_6 clusters; these open metal sites (OMSs) can directly serve as Lewis acidic catalytic centers for substrate activation [42]. Defect engineering enables the tuning of the Lewis acid strength of the active centers by altering the coordination geometry and electronic structure of the metal nodes, thereby influencing their adsorption and activation capabilities toward substrates. With respect to catalytic site density, a direct quantitative correlation exists between defect concentration and the number of active sites, with each missing linker corresponding to one or more exposed CUS. The systematic control of defect density through the adjustment of water modulator dosage allows for precise regulation of the number of catalytic sites [43]. Studies have demonstrated that the relationship between defect density and catalytic activity does not follow a simple monotonically increasing trend; instead, the two exhibit a volcano-type curve. Beyond a critical defect density, excessive defect generation compromises framework structural stability and consequently diminishes catalytic performance. This defect-chemistry strategy, which achieves directional performance optimization through precise regulation of defect type and concentration [44], can provide a reference for the rational design of MOF defect engineering. For instance, in the ring-opening reaction of styrene oxide, catalytic activity reaches its maximum when approximately two linkers are missing per Zr_6 cluster, with further increase in defect density leading to performance decline due to framework degradation [45]. Despite the higher density of open Zr catalytic sites in “missing-linker” defects (UiO-66L), its catalytic activity in multiple model reactions is inferior to that of “missing-cluster” defects (UiO-66C), and is even comparable to that of defect-free UiO-66 [46]. This finding reveals a complex trade-off between catalytic site density and intrinsic activity; under certain circumstances, excessively high site densities may induce local diffusion resistance due to self-adsorption effects of reactants, thereby inhibiting rather than

promoting the catalytic reaction. Furthermore, the type of defects can be directionally regulated by the choice of modulator. The use of monocarboxylic acid modulators predominantly introduces “missing-linker” defects, whereas strict control of water content can induce “missing-cluster” defects in the absence of acidic modulators, generating more pronounced coordination distortions while simultaneously forming mesoporous structures [47].

It is worth noting that the heterogeneity of pore structures may induce electromagnetic field enhancement effects or molecular-level confinement effects within specific regions, thereby facilitating distinct chemical reaction pathways or improving energy conversion efficiency. Consequently, gaining an in-depth understanding of the structure–performance relationships between such complex pore architectures and macroscopic material properties, and elucidating the underlying mechanisms through advanced characterization techniques and theoretical simulations, is imperative for the rational design and development of high-performance MOFs tailored for specific applications.

2.1.3 Surface functionalization modification

Surface functionalization represents a pivotal strategy for endowing MOFs with specialized capabilities and expanding their application horizons. By introducing functional moieties or coating additional material layers onto MOF surfaces, the surface properties of the materials can be significantly improved while preserving the integrity of the underlying framework. Approaches to surface modification are primarily categorized into post-synthetic modification (PSM) and *in-situ* modification during synthesis. Within PSM strategies, a distinct “aggressive” ligand exchange method has been proposed, wherein functional ligands in solution selectively replace existing ligands within the MOF framework to achieve precise customization of surface functions. Another strategy involves an “additive” MOF-on-MOF growth approach, where the epitaxial growth of one MOF layer upon another allows for the independent regulation of core and shell (or surface) functionalities. This modular design philosophy has vastly enriched the toolkit for MOF functionalization.

Modulating the hydrophilicity or hydrophobicity of MOFs via surface modification is an effective means of enhancing their performance in specific environments. For instance, post-synthetic modification of MOF-808 using ethylenediaminetetraacetic acid (EDTA) introduces abundant hydrophilic carboxyl functional groups [48]. This modification enables the EDTA-modified MOF-808 (E-MOF-808) to achieve a water uptake capacity of up to 0.39 g/g at 25% relative humidity (RH), more than five times that of pristine MOF-808. Theoretical calculations further elucidate that this performance enhancement stems from the high affinity between surface hydrophilic groups and water molecules. Simultaneously, the optimized pore structure significantly bolsters the material’s cycling stability, exhibiting negligible capacity decay after 50 adsorption–desorption cycles. This case clearly demonstrates how surface group engineering can transform MOFs into efficient atmospheric water harvesters. Furthermore, surface modification can be employed to improve the biocompatibility and cytotoxicity profiles of MOFs, facilitating their utility in biomedical applications, such as drug delivery vehicles. Composites formed by encapsulating magnetic nanoparticles within a MOF matrix not only enable targeted delivery via external magnetic fields but also serve as contrast agents for magnetic resonance imaging (MRI), enhancing imaging contrast by shortening the relaxation times [49].

In solar energy conversion systems, MOFs can function as light absorbers or charge transport media. When their surfaces are modified, they can synergize more effectively with semiconductor nanoparticles to promote the separation and migration of photo-generated carriers, thereby improving photoelectric conversion efficiency. Utilizing liquid-phase epitaxy, MOF-199 nanoisland films with diameters of approximately 20 nm have been constructed on dielectric layers [50]. The d-d transitions of metal ions within the MOF structure, coupled with conjugated structures formed with organic linkers, provide stable multichannel charge trapping sites for the device. This design enables the phototransistor to achieve a high photoresponsivity of 650.1 A/W and excellent long-term plasticity, while simultaneously mimicking the short-term and long-term plasticity functions of biological synapses. This validates that MOF surface layers can participate in charge transport processes by modulating energy level structures, rather than merely serving as insulating dielectrics. In the realm of photocatalytic water treatment, constructing heterojunctions between MOF-derived materials and other semiconductors can effectively suppress electron-hole pair recombination. As illustrated in Fig. 3(c), a membrane (M) material (Co-CN-M) formed by compositing zeolitic imidazolate framework-67 (ZIF-67)-derived Co_3O_4 with graphitic carbon nitride ($\text{g-C}_3\text{N}_4$) enhances charge transfer and promotes the $\text{Co}^{2+}/\text{Co}^{3+}$ cycle via a p-n heterojunction interface. Consequently, it exhibits superior performance in degrading bisphenol A through the synergy of peroxymonosulfate (PMS) activation and photocatalysis, demonstrating the advantages of a synergistic photo-Fenton-like effect [51].

Beyond chemical modification and heterostructure construction, surface engineering at the physical level, such as coating technologies, constitutes a critical step toward the practical deployment of MOFs. Coating MOFs onto electrodes, polymer films, or glass substrates through layer-by-layer self-assembly, *in-situ* growth, and electrochemical deposition effectively enhances their sensitivity and selectivity in electrochemical sensors, or endows the substrates with multifunctional characteristics for optical and environmental applications [52]. In summary, surface functionalization not only augments the functional diversity of MOFs, enabling them to address interdisciplinary challenges spanning energy conversion, environmental remediation, and biomedicine, but also opens avenues for their application across a broader spectrum of fields. With the deepening of interfacial engineering research on MXene-MOF composites (MXOFs) [53], and the utilization of smart-responsive polymers to decorate MOFs for achieving “on-off” switching of catalytic activity [54], more innovative surface modification methodologies are anticipated to emerge in the future, further propelling MOF materials toward intelligent and multifunctional development.

2.2 Morphology control and nanostructure construction of MOFs

2.2.1 zero-dimensional (0D), one-dimensional (1D), two-dimensional (2D), and 3D MOF nanomaterials

The dimensional design of MOF nanomaterials represents one of the core strategies for modulating their physicochemical properties and determining their applicability in energy storage and conversion devices. Based on spatial dimensional differences, MOFs can be classified into 0D, 1D, 2D, and 3D structures, with each morphology exhibiting distinct performance advantages and

application scenarios attributable to its unique geometric characteristics [55]. Variations in particle size and morphology significantly influence the specific surface area, as well as the type and quantity of active sites in MOFs, thereby altering their catalytic activity, adsorption capacity, or electrochemical properties; consequently, precise control over the dimensionality and morphology of MOFs constitutes a critical pathway for optimizing material performance [56].

0D MOFs primarily refer to isotropic materials, such as nanoparticles and nanospheres, whose most salient feature is an exceptionally high specific surface area accompanied by abundant exposed active sites. Upon reduction of MOFs from the microscale to the nanoscale, their surface properties undergo substantial changes, including the exposure of numerous unsaturated coordination sites, elevated surface energy, and increased defect density [57]. The small-size effect of nanoparticles enables the provision of a greater number of contact interfaces, thereby accelerating reaction rates and enhancing detection sensitivity. Furthermore, 0D MOF nanoparticles can be readily dispersed in liquid-phase systems through facile dispersion methods, facilitating operation and recovery. However, due to their small-size effect, high surface energy, and thermodynamic instability, nanoparticles are prone to aggregation during practical application, resulting in diminished effective specific surface area and reduced active site density. To address this issue, the introduction of hydroxyl species onto the surface of MOF-derived materials through alkaline etching treatment has been demonstrated to preserve the dispersed state of nanoparticles. This approach increases surface charge density and utilizes electrostatic repulsion to suppress nanoparticle aggregation, while the crystal reconstruction process simultaneously generates surface defects that further modulate surface properties and enhance the accessibility of active sites [58].

1D MOFs, encompassing structures, such as nanorods (NRs), nanowires, nanofibers, and nanotubes, are characterized by the anisotropic transport advantages conferred by their high aspect ratios. These structures facilitate continuous electron/ion transport pathways, significantly shortening carrier diffusion distances and reducing resistive losses. More importantly, 1D architectures can effectively buffer the mechanical stress induced by volume expansion during charge-discharge cycles, thereby extending the service life of electrode materials. Regarding synthesis strategies, 1D MOFs can be fabricated via template methods, electric field-induced assembly, and temperature-regulated structural evolution. For instance, citric acid was utilized to induce the *in-situ* uniform coating of ZIF-67 on silicon nanoparticle surfaces; subsequent heat treatment successfully yielded silicon-carbon anode materials reinforced with carbon nanotubes (CNTs) and featuring a dual-carbon stress-buffering layer [59]. Studies confirm that this structure exhibits minimal stress gradients in the fully lithiated state, effectively mitigating structural collapse caused by stress concentration. Consequently, the electrode maintains a capacity retention rate of 88% after 500 cycles at a current density of 0.5 A/g.

2D MOF nanosheets (NSs) have garnered significant attention for their ultrathin morphology, large surface area, tunable porosity, and modular chemical properties, serving as efficient support materials for electrocatalysts or components in high-performance supercapacitors [60]. Compared to their 3D bulk counterparts, the atomic-level thinness of 2D nanosheets results in an extremely high proportion of surface atoms, maximizing the exposure of active sites. Simultaneously, their intrinsic anisotropy enables directional

charge transport, which is particularly advantageous in electrochemical systems. In the realm of electrocatalysis, 2D MOF nanosheets demonstrate superior catalytic performance in key processes, such as the oxygen evolution reaction (OER), hydrogen evolution reaction (HER), oxygen reduction reaction (ORR), CO₂ reduction reaction (CO₂RR), and nitrogen reduction reaction (NRR). In energy storage applications, ranging from supercapacitors to lithium-ion and lithium-sulfur batteries, 2D structures enhance redox kinetics, ion transport efficiency, and active site accessibility [61].

3D MOF network structures provide an ideal platform for gas storage and separation owing to their complex and ordered hierarchical pore systems. Such 3D architectures not only accommodate substantial quantities of gas molecules but also enable selective adsorption through the modulation of pore size and geometry, thereby improving separation efficiency. A super-microporous 3D MOF material constructed from Cu(II) nodes and multidentate ligands has been proposed [62]. This material exhibits high selectivity and separation efficiency for N₂/CO₂ and CH₄/CO₂ mixtures, along with excellent cycling stability. Furthermore, it demonstrates favorable catalytic activity in CO₂RR, particularly favoring the production of industrially valuable ethylene. This bifunctional 3D MOF, capable of both gas separation and catalytic conversion, offers new insights into material design for integrated carbon capture and utilization. It is worth noting that 3D MOFs can exist either as micron-scale bulk crystals or as 3D hierarchical structures assembled from low-dimensional nano-building blocks. The latter category constructs macroscopic 3D monoliths with mesoporous-macroporous hierarchical structures by assembling 0D nanoparticles, 1D nanowires, or 2D nanosheets. This approach preserves the high activity of the nanounits while facilitating the diffusion and transport of macromolecules [63].

MOF nanomaterials of varying dimensions possess distinct structural advantages and application niches. With the continuous advancement of synthetic methodologies, precise control over MOF dimensionality has become achievable through strategies, such as modulator regulation, external field intensification, bottom-up interfacial growth, and top-down exfoliation. As illustrated in Fig. 4, three core mechanisms primarily govern MOF morphology control [64]: the coordination modulation mechanism, the protonation/deprotonation mechanism, and the surfactant adsorption mechanism. The coordination modulation mechanism achieves morphology control by introducing monodentate modulators that share chemical functionalities with the organic ligands. These modulators compete with multidentate ligands for metal ion coordination sites, slowing crystal growth rates by regulating the coordination equilibrium. This promotes the formation of additional nuclei while suppressing amorphous precipitation, thereby enhancing crystallinity. The protonation/deprotonation mechanism involves modulators altering the acidity or alkalinity of the reaction system to influence the protonation state of the ligands. Alkaline modulators increase solution pH, promoting ligand deprotonation and increasing the concentration of organic anions available for coordination with metal ions; this accelerates nucleation rates, leading to the generation of smaller nanocrystals. Conversely, acidic modulators inhibit coordination by protonating the ligands. The surfactant adsorption mechanism relies on the selective adsorption of amphiphilic molecules onto specific crystal facets. Surfactants bind to these facets via van der Waals forces, electrostatic interactions, etc., lowering their surface energy. This

inhibits growth in that direction while promoting development on other facets. Collectively, these three mechanisms form the foundation of MOF morphology control, enabling precise regulation from nanoparticles to complex hierarchical structures through the synergistic adjustment of reaction kinetics and thermodynamics.

2.2.2 Construction of MOF-based composites

The construction of MOF-based composites represents a critical strategy for overcoming the inherent limitations of single-component MOFs and expanding their application boundaries. Although pristine MOFs possess high specific surface areas, tunable pore architectures, and abundant metal active sites, their poor electrical conductivity and limited chemical stability severely restrict practical applications in electrochemical energy storage and related fields. Through the integration of MOFs with functional guest materials, including carbon nanotubes, graphene, conductive polymers, and metal oxides, not only can the deficiencies of individual components be compensated, but synergistic effects between constituents can also generate novel material systems with comprehensive performance advantages.

In the field of electrochemical energy storage, the composite strategy combining MOFs with CNTs has been extensively adopted [65]. Carbon nanotubes exhibit high electrical conductivity, excellent mechanical strength, and large specific surface areas; when composited with MOFs, CNTs serve as conductive pathways facilitating rapid electron transport, while the MOF component provides abundant active sites for ion adsorption and storage. Khan et al. [66] synthesized a composite of yttrium-vanadium bimetallic MOF (BMOF) with CNTs (VY-MOF@CNT) via an ultrasound-assisted hydrothermal method, as illustrated in Fig. 5(a). This material formed a distinctive conductive network architecture: CNTs functioned not merely as “highways” for electron transport, but also established hierarchical ion diffusion pathways through uniform dispersion. Electrochemical testing demonstrated that the VY-MOF@CNT electrode achieved a specific capacitance of 1661 F/g at a current density of 2 A/g; the assembled symmetric supercapacitor device delivered an energy density of 60 Wh/kg and retained 92% of its capacitance after 10,000 cycles. This performance enhancement was attributed to a dual charge storage mechanism: the synergistic contribution of electric double-layer capacitance from CNTs and pseudocapacitance from Y/V redox centers.

The shuttle effect constitutes one of the core challenges facing the commercialization of lithium-sulfur batteries, whereby lithium polysulfide intermediates dissolve into the electrolyte and diffuse to the negative electrode, resulting in rapid capacity decay and decreased Coulombic efficiency. To address this issue, a Co(SCN)₂(pyz)₂ (where pyz denotes pyrazine) MOF featuring a two-dimensional channel structure was synthesized through a liquid-phase diffusion method and subsequently composited with a polypropylene separator to form a multifunctional membrane [67]. This MOF exhibited exceptional adsorption capability toward lithium polysulfides, effectively suppressing the shuttle effect. Lithium-sulfur batteries assembled with this composite separator achieved an initial discharge specific capacity of 2060.48 mAh/g at 0.1 C, substantially exceeding the 883.77 mAh/g obtained with unmodified separators; under 1 C rate, the Coulombic efficiency remained stable throughout extended cycling, demonstrating superior cycling stability and prolonged operational lifespan.

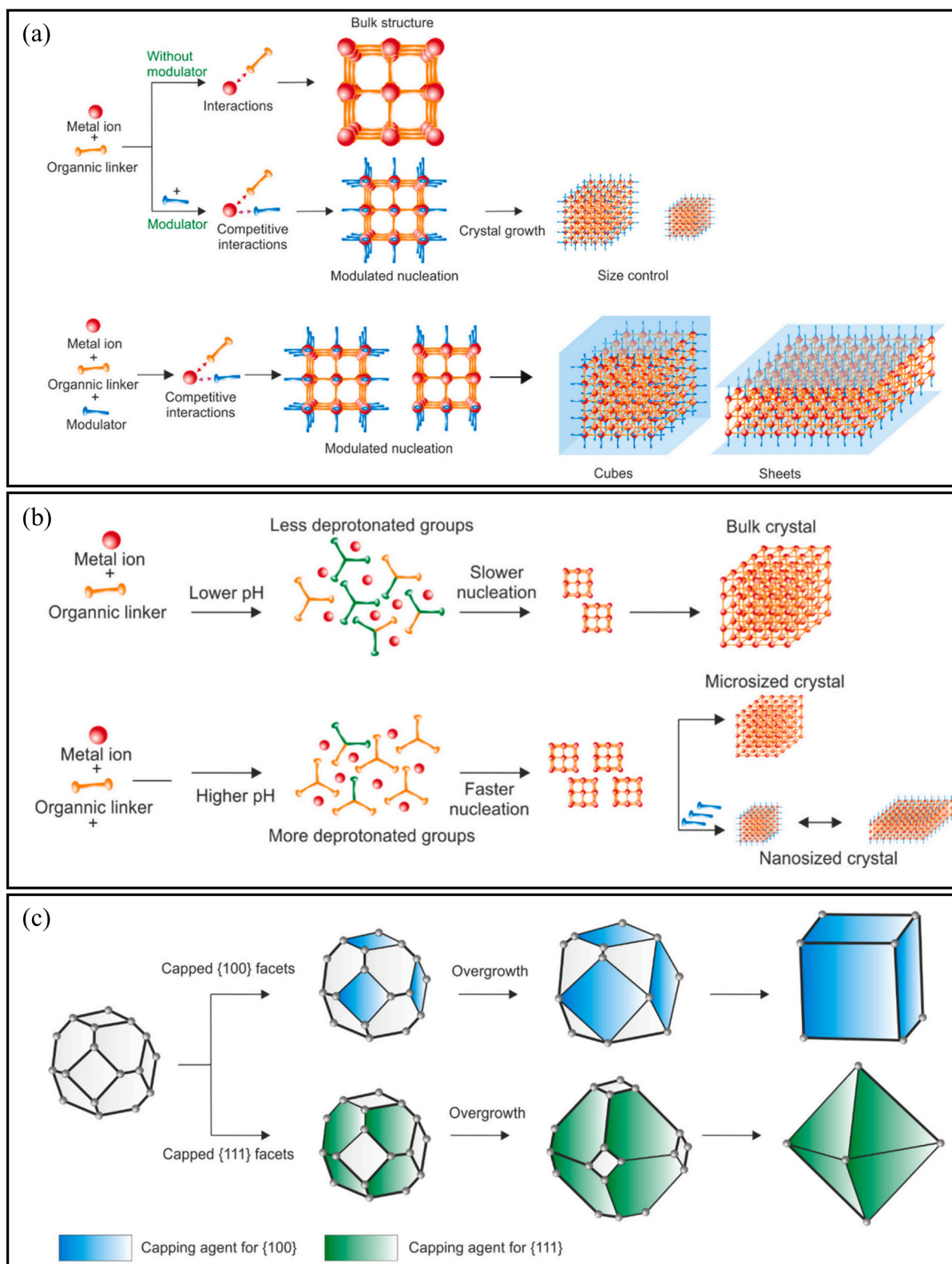


Figure 4 Core mechanisms of MOFs morphology control. (a) Coordination regulation mechanism. (b) Protonation/deprotonation mechanism. (c) Surfactant adsorption mechanism. Reproduced with permission from Ref. [64], © Łuczak, J. et al. 2023.

Furthermore, amino-functionalized titanium-organic framework materials were employed for separator modification [68], with this design ingeniously integrating multiple suppression mechanisms (as depicted in Fig. 5(b)): First, the -NH_2 groups reduced the sub-

nanometer pore apertures of the Ti-MOF from 0.95–1.10 to 0.83–0.86 nm, utilizing size-sieving effects to completely block polysulfide permeation; second, the positively charged -NH_2 groups captured the blocked polysulfides through electrostatic adsorption,

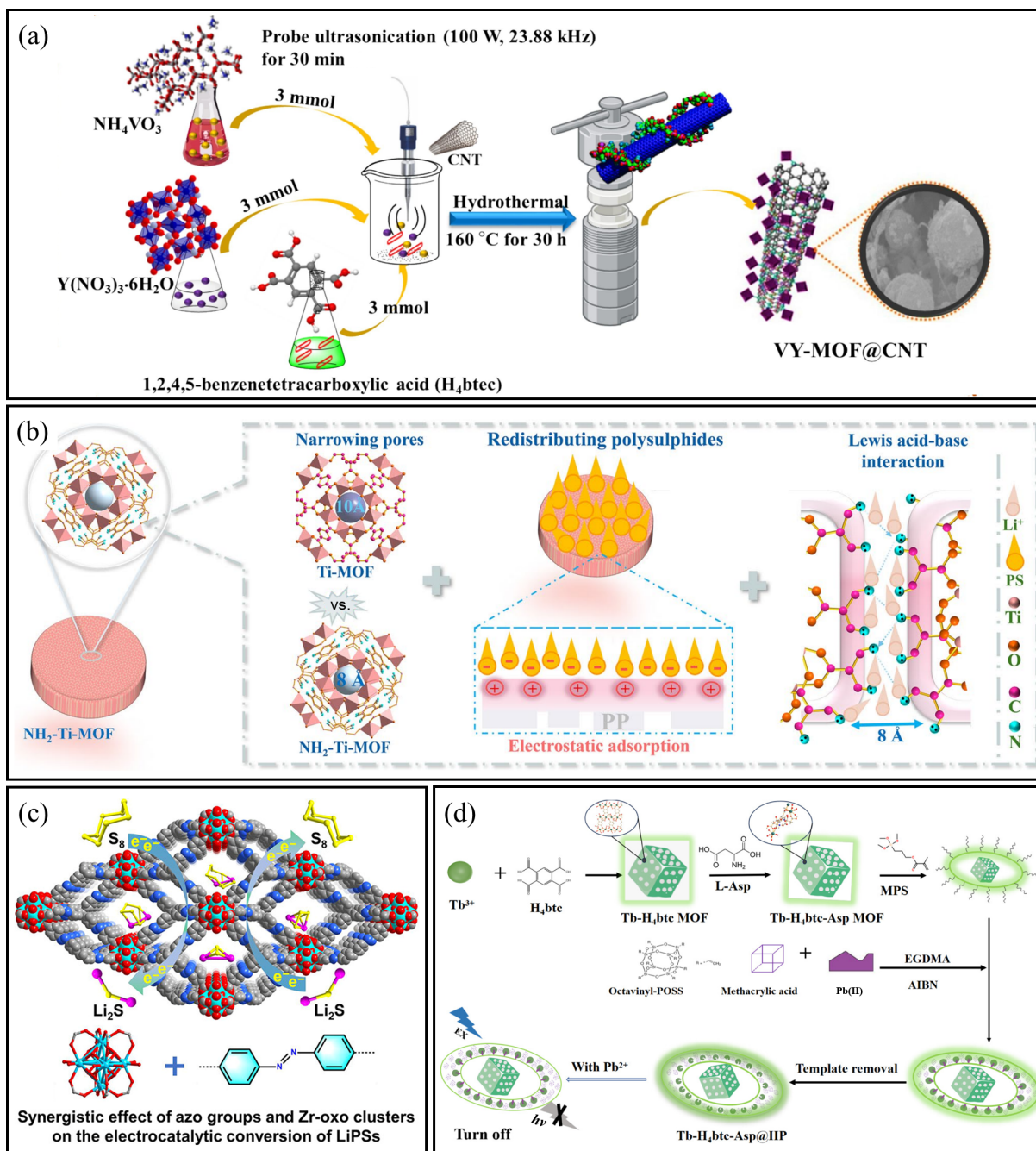


Figure 5 (a) Synthesis of VY-MOF@CNT. Reproduced with permission from Ref. [66], © Elsevier Ltd. 2025. (b) Mechanism of $\text{NH}_2\text{-Ti-MOF}$ modification of lithium-sulfur battery separator, including size sieving effect, electrostatic adsorption, and Lewis acid-base interaction. Reproduced with permission from Ref. [68], © Kang, X. Y. et al. 2025. (c) Influence of synergistic effect on electrocatalytic conversion. Reproduced with permission from Ref. [69], © American Chemical Society 2025. (d) Preparation of $\text{H}_4\text{btc-Asp@IIP}$. Reproduced with permission from Ref. [70], © American Chemical Society 2025.

enabling their return to the positive electrode for re-participation in electrochemical reactions; finally, the Lewis acid-base interactions between $-\text{NH}_2$ and Li^+ facilitated the formation of directed, rapid lithium-ion transport channels. Based on this “sieving-adsorption-reutilization” synergistic mechanism, lithium-sulfur batteries with $\text{NH}_2\text{-Ti-MOF}$ -modified separators exhibited a capacity decay rate of merely 0.045% per cycle after 1000 cycles, demonstrating exceptional long-term cycling stability. Recently, an azo-bridged three-dimensional MOF material (zirconium-based azo-functionalized metal-triazole acrylate carboxylate (Zr-MTAC)) was constructed through the integration of azo-functionalized

linkers with Lewis acidic zirconium-oxo clusters, as shown in Fig. 5(c), and was employed as a cathode host material for lithium-sulfur batteries [69]. The design of this material incorporated dual functionalities: On one hand, Zr-MTAC could effectively capture polysulfides through physical confinement and chemical adsorption; on the other hand, the abundant azo groups served as electron transport channels to facilitate charge transfer during polysulfide conversion.

Biomass-derived multifunctional materials, as a class of environmentally friendly pollution remediation materials, can achieve efficient adsorptive removal of multiple pollutant categories

through structural regulation [71, 72], and their green and sustainable design philosophy can inspire the development of MOF-based composite materials. Luo et al. proposed a design strategy for a solar-assisted bimetallic MOF-derived fibrous composite [73]. The carboxylated multi-walled carbon nanotubes and hygroscopic bimetallic MOFs were loaded onto a multilayer glass fiber carrier via a bottom-up interfacial-induced assembly method. The MIL-100(Fe,Al)-3 skeleton, constructed through bimetallic node defect engineering, possesses a specific surface area of up to 1535.28 m²/g and a pore volume of 0.76 cm³/g, surpassing the hygroscopic capacity of the parent MOF and other reported MOFs. Benefiting from the hierarchical structure of the fibrous rods and the solar-driven self-heating interface of the photothermal layer, the customized BMOF crystals achieved efficient loading and optimized water adsorption-desorption kinetics. Ultimately, under medium-to-high humidity outdoor conditions, the system completed six adsorption-desorption cycles per day, yielding a water harvesting capacity of 1.45 g/(g-day). However, for these composites to transition towards practical utility, challenges, such as high costs and complex synthesis processes must be overcome. An approach combining post-coordination modification with surface ion imprinting technology offers a viable solution, exemplified by the development of a Tb-H₄btc-Asp@IIP (where btc denotes 1,2,4,5-benzenetetracarboxylic acid, Asp denotes aspartic acid, and IIP denotes ion-imprinted polymer) luminescent sensor [70]. As shown in Fig. 5(d), aspartic acid functionalization constructs a protective ion-imprinted polymer layer approximately 90 nm thick on the MOF surface. This allows the composite to retain 90.2% of its original fluorescence intensity after 30 days in an aqueous environment and enhances thermal stability up to 286 °C, while simultaneously achieving highly selective detection of Pb(II) with a limit of detection as low as 3.19 ng/mL. This strategy not only enhances the chemical and thermal stability of MOFs but also endows them with specific recognition capabilities, providing a feasible pathway for the controlled preparation of multifunctional composites. With the continuous development of facile and efficient synthesis methods, such as *in-situ* growth and wet chemistry, along with ongoing in-depth research into MOF modification, MOF-based composites are advancing towards greater robustness and processability, making them increasingly suitable for industrial production and real-world applications.

In summary, the nanoscale design and controllable synthesis of

MOFs constitute a multidisciplinary research domain. This field demands not only a profound understanding of the fundamental building blocks and structural characteristics of MOFs but also mastery of various advanced synthesis and processing techniques. Looking ahead, with the establishment and refinement of theoretical models and continuous innovation in experimental techniques, it is anticipated that MOFs will assume an increasingly critical role in next-generation energy storage and conversion technologies.

3 Applications of MOFs in energy storage and conversion

Building upon the fundamental principles of nanoscale design and controllable synthesis outlined in the preceding section, this section delves into the practical applications of MOFs in energy storage and conversion systems, as shown in Fig. 6. The unique structural attributes of MOFs endow them with unparalleled versatility for addressing critical challenges in electrochemical energy storage, electrocatalysis, and photocatalysis. From advanced battery technologies to sustainable fuel production, MOFs have emerged as transformative materials capable of bridging the gap between molecular-level engineering and macroscopic energy solutions. Herein, we systematically explore the structure-performance relationships that underpin their functionality in these domains, highlighting key breakthroughs, mechanistic insights, and future opportunities for scaling their impact in next-generation energy technologies.

3.1 Electrochemical energy storage

3.1.1 Lithium-ion batteries (LIBs)

The application of MOFs and their derivatives in LIBs has emerged as a cutting-edge research frontier in the energy materials field, offering novel pathways to overcome the limitations of conventional electrode materials. With the ever-increasing demand for high-performance energy storage devices driven by renewable energy systems and electric vehicles, LIBs, as the dominant energy storage technology, face critical challenges encompassing enhanced energy density, extended cycle life, and improved safety. Traditional graphite anodes exhibit relatively low theoretical capacity and suffer from structural degradation induced by solvent molecule

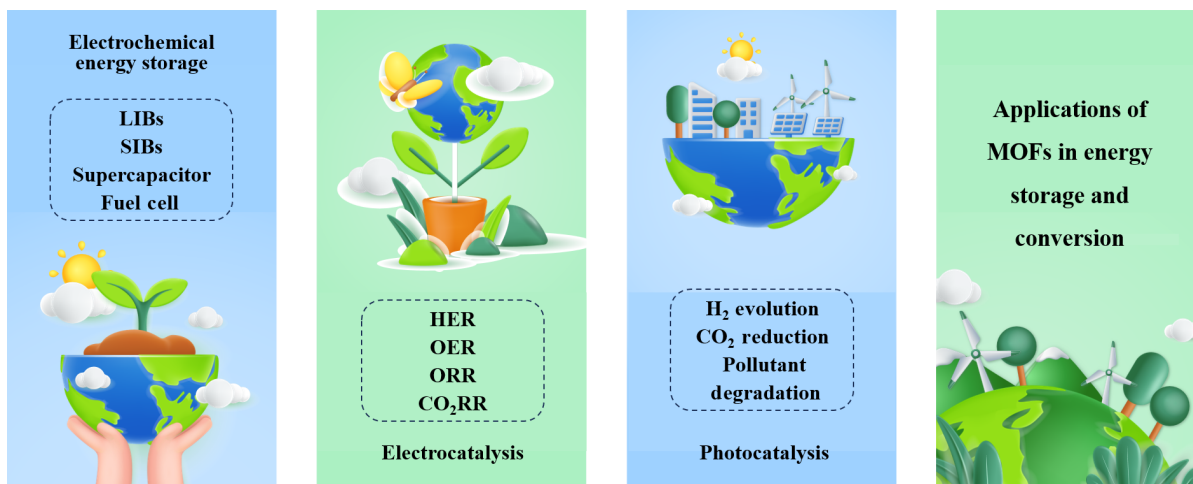


Figure 6 Applications of MOFs in energy storage and conversion.

intercalation; meanwhile, transition metal oxides (TMOs), despite their high theoretical capacities, are constrained by poor electrical conductivity and volumetric expansion effects during cycling. MOF materials, through precise regulation of the coordination modes between metal nodes and organic linkers, enable pore engineering and active site design; their derived materials can further inherit high porosity characteristics while substantially enhancing electrical conductivity, thereby providing multidimensional solutions for performance breakthroughs in LIBs.

In electrode material design, the direct application and derivatization strategies of MOFs demonstrate complementary advantages. Taking the nickel-based MOF-derived microflower-like carbon framework (P/Ni@C) as an exemplar [74], as illustrated in Fig. 7(a), the phosphorus modification-generated P–O–C bonds effectively mitigate the volumetric expansion of red phosphorus, while the high conductivity of the carbon framework enables the composite material to maintain a high reversible capacity of 1184.6 mAh/g after 400 cycles at 200 mA/g. This structural design not only addresses the inherent deficiencies of red phosphorus anode materials but also achieves uniform dispersion of active substances through the morphological hereditary effect of MOF precursors. Regarding conductivity enhancement, the triazacoronene (TAC)-based two-dimensional conductive MOF (Cu-TAC) exhibits a narrow band gap of 0.31 eV attributable to its “superbenzene-type” multi-nitrogen nanographene structure, with high-density lithium storage sites enabling a capacity of 772.4 mAh/g at 300 mA/g [75]. The extended conjugated system formed through π - π stacking in this material significantly improves electron transport efficiency, while its interlayer spacing (3.4 Å) facilitates rapid lithium-ion intercalation/deintercalation. To address the polysulfide shuttle effect, a trimetallic Ni-Co-Mn MOF-pillared multilayer graphene separator was developed, which

constructs ion-sieving channels and delivers a lithium-sulfur battery capacity of 1634 mAh/g at 0.1 C with a capacity decay rate of merely 0.034% over 2000 cycles [76]. This design leverages the strong adsorption of polysulfides by OMSs within the MOF, combined with the highly conductive graphene network, achieving spatial confinement and electrochemical *in-situ* conversion of polysulfides. In the organic anode domain, the polythiol-supported dicarboxylate iron-based MOF (Fe-TTTP) maintains a stable capacity of 310 mAh/g after 5000 cycles at 2000 mA/g through the synergistic mechanism of the $\text{Fe}^{3+}/\text{Fe}^0$ redox couple and the C=O/C–O superlithiation reaction [77]. Its rigid framework structure effectively suppresses the dissolution of organic small molecules into the electrolyte, while the incorporation of iron nodes further enhances the intrinsic electrical conductivity of the material. Additionally, nanofiber composites prepared through the combination of electrospinning technology with MOFs can enhance mechanical strength through porosity regulation, rendering them suitable for lithium-sulfur batteries and sodium/potassium-ion batteries [78]. The design of one-dimensional MOF-derived architectures also provides a regulatory approach for stabilizing lithium metal anodes. A nitrogen-doped amorphous zinc-carbon multichannel fiber developed in existing research [79] leverages the synergistic effect between the volume buffering effect of the multichannel structure and the lithiophilic nature of zinc sites to effectively induce uniform lithium deposition and suppress dendrite growth, offering a reference for the structural design of MOF-derived carbon-based lithium host materials.

Although MOF-derived TMOs possess high theoretical capacities, poor conductivity and volume expansion during cycling remain critical bottlenecks. Studies indicate that performance can be significantly enhanced through strategies, such as compositing with carbon nanotubes/graphene, nitrogen doping, and the use of

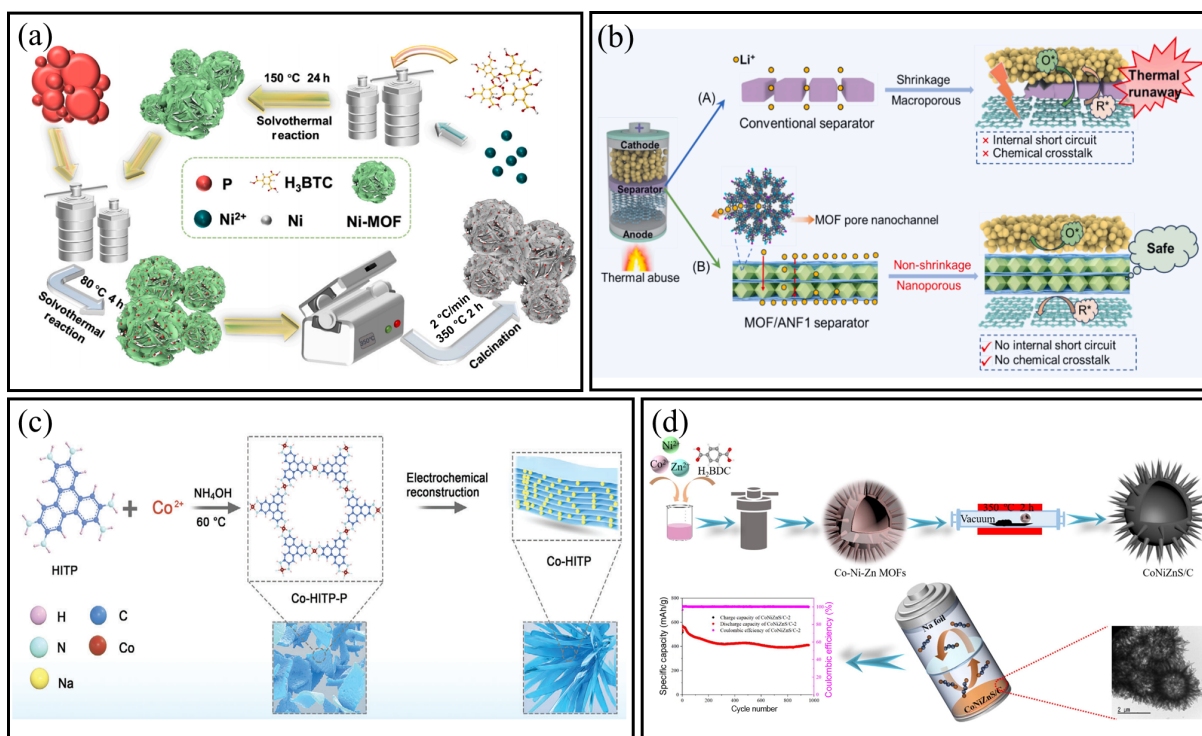


Figure 7 (a) P@Ni-MOF and P/Ni@C composites. Reproduced with permission from Ref. [74], © Elsevier Ltd. 2023. (b) Thermally stable high-performance diaphragm. Reproduced with permission from Ref. [86], © Elsevier B.V. 2024. (c) Synthesis of Co-HITP MOF. Reproduced with permission from Ref. [95], © Wiley-VCH GmbH 2024. (d) CoNiZnS/C composite. Reproduced with permission from Ref. [99], © Elsevier Inc. 2022.

mixed metals [80–82]. Notably, certain MOF-derived TMOs exhibit a “capacity-increasing” phenomenon during cycling; this is potentially attributed to progressive pore formation induced by electrolyte penetration and the catalytic activation effects of metallic nanoparticles [83]. MXene-encapsulated porous Ni-NDC (where NDC denotes naphthalene dicarboxylic acid) nanosheets effectively expand interlayer spacing via interlayer hydrogen bonding interactions. This structure suppresses MXene oxidation while constructing a 3D conductive network, enabling the electrode to deliver a capacity of 579.8 mAh/g after 100 cycles at 100 mA/g, significantly outperforming pure Ni-NDC [84]. This interface engineering strategy offers new insights for the compositing of MOFs with two-dimensional materials.

In the realm of functional modification for separators and electrolytes, the incorporation of MOFs has transcended the limitations of traditional polyolefin separators, such as poor thermal stability and low ionic conductivity. The electrospun separator (ZTP), composed of UiO-66(Zr/Ti) and polyvinyl alcohol (PVA), leverages high-density OMSs to enhance anion complexation capability. This configuration increases the lithium transference number and reduces ion transport activation energy, thereby endowing batteries with favorable low-temperature performance [85]. Such performance enhancement stems from the strong adsorption of PF_6^- by Zr/Ti bimetallic nodes and the selective transport of lithium ions through MOF channels. Regarding thermal safety, MOF/Aramid nanofiber (MOF/ANF1, where 1 is defined as the index corresponding to 10 wt.% of ANF mass fraction in the MOF/ANF composite) composite separators with a 10 wt.% ANF content exhibit a decomposition temperature exceeding 500 °C and possess self-extinguishing properties [86]. As illustrated in Fig. 7(b), their high ionic conductivity of 1.01 mS/cm enables the battery to achieve a capacity of 147.3 mAh/g after 200 cycles at 1 C. This design ingeniously combines the mechanical strength of ANFs with the porosity of MOFs, achieving a balance between safety and electrochemical performance. Furthermore, poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP)-based separators incorporating MOF-808 and UiO-66- NH_2 have been shown to reduce cell resistance [87]. Among these, UiO-66- NH_2 exhibits superior interfacial stability due to hydrogen bonding between amino groups and the electrolyte. Although partial structural collapse of the MOF may occur during cycling, the residual porous framework effectively retards capacity fading.

Regarding the degradation mechanisms of MOF-based electrodes during long-term cycling, systematic studies in recent years have demonstrated that the decay is primarily governed by the synergistic interplay between solid electrolyte interphase (SEI) evolution and structural collapse. The high specific surface area of MOF materials, coupled with abundant unsaturated coordination sites, catalyzes electrolyte decomposition during the initial charge/discharge process, inducing the *in-situ* formation of an SEI layer [88]. When the surface functional groups of MOFs are precisely regulated, they can guide the formation of a thin, dense, and uniform SEI layer enriched with inorganic components, which not only facilitates rapid lithium-ion conduction but also prevents sustained contact between the electrolyte and active sites, thereby suppressing parasitic reactions [89]. However, if excessive surface defects or highly active coordinatively unsaturated sites are present in the MOF, they will catalyze excessive electrolyte decomposition, generating a thick, porous, and unstable SEI layer with a disproportionately high organic content. Such an SEI layer

undergoes repeated rupture and regeneration during cycling in response to volumetric deformation, continuously depleting active lithium while substantially increasing interfacial impedance, leading to irreversible capacity decay. Studies have confirmed that unpassivated unsaturated metal sites tend to catalyze the excessive decomposition of fluorinated carbonate additives, and the resulting unstable SEI layer undergoes repeated rupture and regeneration in subsequent cycles, persistently consuming active lithium and causing a marked increase in interfacial impedance, which is recognized as one of the core contributors to capacity fade [90]. Concurrently, the incorporation of fluorinated ligands into the MOF framework can provide a sustained fluorine source during cycling, thereby inducing the formation of a LiF-rich stable SEI layer and effectively enhancing the long-term cycling stability of the electrode [91]. On another front, MOF structural collapse primarily stems from two mechanisms: First, the repeated redox or alloying/dealloying reactions of metal nodes during charge/discharge induce drastic volume expansion, and when the internal stress exceeds the tolerance threshold of the framework coordination bonds, it leads to the rupture of ligand-metal coordination bonds and pore collapse; second, the dissolution or decomposition of organic linkers under high-voltage or strongly reducing environments causes irreversible damage to framework integrity [92]. Structural collapse not only results in the encapsulation and deactivation of internal active sites but also triggers the pulverization and detachment of electrode materials, disrupting the continuity of the conductive network. Taking cobalt-based MOF anodes as an example, their structural degradation during long-term cycling is predominantly manifested as pore collapse caused by coordination bond rupture and the deactivation of active sites, which in turn induces severe capacity decay [93]. It is noteworthy that the fresh surfaces generated by MOF structural fragmentation will further catalyze abnormal SEI growth, while a thick and high-impedance SEI layer exacerbates the non-uniformity of ion transport, leading to localized stress concentration on MOF particles and further accelerating structural disintegration. This synergistic effect is the key factor underlying the abrupt capacity drop observed in MOF electrodes during extended cycling.

3.1.2 Sodium-ion batteries (SIBs)

In recent years, significant progress has been made in the application of MOFs to SIBs. Their unique structural tunability, high specific surface area, and abundant redox-active sites provide novel pathways for addressing key challenges in SIBs, such as sluggish kinetics, severe volume expansion, and poor conductivity. Compared to traditional LIBs, SIBs have garnered attention due to the abundance and low cost of sodium resources; however, the larger ionic radius and mass of sodium result in more severe structural strain and sluggish ion diffusion kinetics for electrode materials during charge–discharge processes. Through the precise design of the coordination environment between metal nodes and organic linkers, MOF materials can construct electrode materials with expanded pore structures and multiple redox centers, offering an ideal platform for the efficient storage and rapid transport of sodium ions [94].

Regarding anode materials, MOFs and their derivatives exhibit superior sodium storage performance through structural design and composition regulation. The layered single-crystal MOF material Co-HITP (HITP stands for 2,3,6,7,10,11-hexamino-triphenylene; Fig. 7(c)) forms expanded interlayer

spacing and abundant active sites via *in-situ* electrochemical reconstruction [95]. Its stable single-crystal structure benefits from the synergistic effects of d- π hybridization and π - π interactions, allowing the minimal structural unit to store up to 14 Na⁺ ions. It delivers a high reversible capacity of 450.1 mAh/g at 0.2 A/g and achieves ultra-long cycling stability. This material design overcomes the limitations of dissolution in electrolytes and structural instability found in traditional organic anodes, providing a pathway for developing high-stability SIB anodes. For alloy-type anodes, lead nanospheres encapsulated in porous carbon (Pb@C) prepared via MOF derivation effectively mitigate the volume expansion of lead during alloying through the physical confinement of the carbon skeleton [96]. The unique core-shell structure enables the material to maintain a reversible capacity of 379.1 mAh/g at 2 A/g, with a capacity retention of 88.2% after 6000 cycles and a capacity loss of only 0.00748% per cycle. This design not only enhances the cycling stability of the electrode but also offers insights into the resource utilization of lead pollutants. MOF-derived transition metal sulfide/selenide hollow architectures represent another highly promising anode system for sodium-ion batteries. Through sequential ion-exchange strategies, copper-doped CoSe, hierarchical microboxes [97] and copper-substituted CoS₂@Cu₂S double-shelled nanoboxes [98] can be prepared. Such materials leverage the synergistic effect between the volume buffering effect of hollow structures and the electronic structure modulation induced by heteroatom doping to concurrently enhance sodium storage kinetics and cycling stability, providing a pathway for the structural design of MOF-based transition metal chalcogenide anodes. Transition metal sulfides are promising anode candidates due to their high theoretical capacity, yet they face challenges, such as poor conductivity and capacity fading, caused by phase transitions during cycling. As shown in Fig. 7(d), hollow sea urchin-like CoNiZnS/C microspheres prepared using a trimetallic Co-Ni-Zn MOF precursor significantly enhance sodium ion storage kinetics through multi-metal synergistic effects and abundant phase interface defects [99]. The optimized CoNiZnS/C-2 material exhibits a high initial Coulombic efficiency of 96.52%, maintains a capacity of 477.0 mAh/g at a high rate of 5.0 A/g, and retains over 85% of its capacity after 960 cycles. This multi-metal sulfide design strategy effectively balances the trade-off between capacity and stability by regulating phase boundary density and hollow structures.

In the field of cathode materials, the rigid framework structure and tunable redox centers of MOFs offer solutions to issues, such as low capacity and structural instability, in traditional cathodes. The 2D conjugated MOF Cu-TBA (TBA denotes octahydroxytetrabenzoanthracene) features a rhombic topology and narrow band gap characteristics [100]; its metallic band structure facilitates rapid electron transport, delivering a reversible capacity of 153.6 mAh/g at 50 mA/g with negligible capacity decay after 3000 cycles at 1 A/g. By combining experiments with theoretical calculations, a three-step reaction mechanism for sodium storage was revealed, involving the redox activity of unsaturated bonds in the organic ligands and valence changes in Cu²⁺. Compared to the hexagonal structure of Cu-HHTP (HHTP stands for 2,3,6,7,10,11-hexahydroxytriphenylene), the rhombic topology of Cu-TBA significantly enhances electrochemical performance by lowering the lowest unoccupied molecular orbital (LUMO) energy level of the linkers and narrowing the band gap. Prussian blue analogues (PBAs), a special class of MOFs, have become a research hotspot for

SIB cathodes due to their open framework structure and multi-electron transfer characteristics. High-quality sodium-rich monoclinic nickel hexacyanoferrate nanocubes (NiHCF-NCs) synthesized via a disodium diethylenetriaminepentaacetate (Na₂DTPA)-assisted co-precipitation method possess a nanocube morphology and low defect concentration [101]. Their unique low-strain sodium storage mechanism allows the material to maintain a capacity of 64.5 mAh/g at a high rate of 4000 mA/g, with a capacity retention of 97.1% after 2000 cycles. Compared to bulk materials prepared by traditional co-precipitation, NiHCF-NCs exhibit higher sodium content and fewer [Fe(CN)₆]⁴⁻ vacancies, resulting in significantly improved structural stability. The assembled NiHCF-NCs//NaTi₂(PO₄)₃@C full cell maintains excellent performance after 5000 cycles, demonstrating the immense potential of PBAs in practical SIB applications.

3.1.3 Supercapacitors

Supercapacitors represent energy storage devices intermediate between conventional capacitors and batteries, distinguished by their high-power density, rapid charge/discharge capability, and extended cycle life. The application of MOFs and their derivatives in supercapacitors is manifested primarily in two aspects: First, as electrode materials directly participating in charge storage processes; second, as templates or precursors guiding the formation of other functional materials. Regarding the former, MOFs inherently possess large specific surface areas and abundant active sites, enabling their direct utilization as electric double-layer capacitor (EDLC) or pseudocapacitive electrode materials. The latter role of MOFs as templates or precursors is more pronounced, as a series of functional materials with distinctive morphologies and architectures can be derived from MOFs. These materials inherit the high specific surface area and favorable conductivity of the parent MOFs while simultaneously exhibiting enhanced electrochemical activity and superior mechanical strength.

Recently, an ultrathin Ni₁₁(HPO₃)₈(OH)₆ nanosheet array and Ni/Co bimetallic phosphides were prepared via a templating method [102], among which Ni/Co-POH-2 (Ni/Co molar ratio of 2) demonstrated exceptional electrochemical performance, achieving a specific capacitance of 1905.60 F/g at 1 A/g, with the assembled asymmetric supercapacitor delivering an energy density of 36.59 Wh/kg, as illustrated in Fig. 8(a). This achievement highlights the advantages of MOFs as precursors in modulating material morphology and electronic structure. Through *in-situ* phosphorus doping during the hydrothermal conversion process, synergistic optimization of open-framework architecture and high conductivity was realized, while the vertical orientation of the nanosheet array effectively facilitated electrolyte ion diffusion and charge transport. Notably, the introduction of bimetallic Ni/Co further enhanced the redox activity of the material through electronic coupling effects, whereas the crystallographic stability of the MOF-derived products ensured cycling performance, with a capacitance retention of 67.98% after 5000 cycles, thereby providing a new paradigm for the application of transition metal phosphides in supercapacitors.

In terms of material design strategies, multidimensional modification approaches can overcome the intrinsic bottlenecks of poor electrical conductivity and insufficient mechanical stability in MOFs. On one hand, utilizing wood tracheid inner walls as biotemplates for Ni/Co-MOF loading, the Ni/NiO/CoO-CW-4 (CW denotes carbonized wood and 4 denotes after 4 h of acid

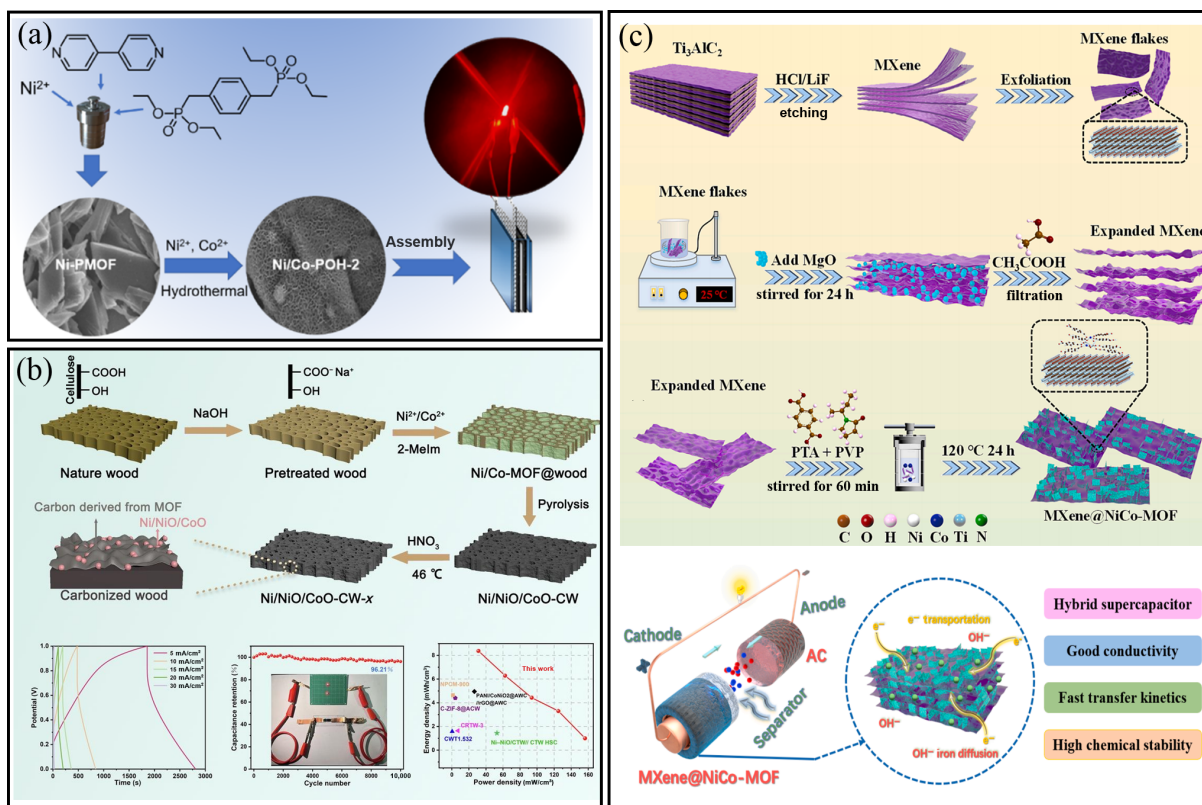


Figure 8 (a) Synthesis and assembly of Ni/Co-POH nanosheet array. Reproduced with permission from Ref. [102], © American Chemical Society 2024. (b) Synthesis and properties of Ni/NiO/CoO-CW. Reproduced with permission from Ref. [103], © Elsevier Inc. 2024. (c) MXene@NiCo-MOF synthesis and its application in hybrid supercapacitor (HSC). Reproduced with permission from Ref. [104], © Elsevier B.V. 2024.

etching) electrode obtained after carbonization–oxidation–acid etching treatment exhibited an areal capacitance of 16.76 F/cm² [103], as shown in Fig. 8(b); the performance enhancement originated from the conductive network provided by the hierarchical porous structure of wood and the pseudocapacitive contribution of MOF-derived metal oxides. On the other hand, as depicted in Fig. 8(c), an MXene@NiCo-MOF composite electrode was constructed through weak coordination of metal ions with surface hydroxyl groups on MXene to form oxygen vacancies, achieving a specific capacitance of 2078.1 F/g [104]. In this architecture, MXene not only resolved the interlayer stacking issue of MOFs, but its high conductivity also significantly reduced charge transfer resistance, while DFT calculations confirmed that the redox-active centers of NiCo-MOF possess excellent electron/ion transport characteristics. More sophisticated structural modulation is exemplified in the design of Dawson-type polyoxometalate-based MOFs (POMOFs), wherein CUST-833 achieved a specific capacitance of 430 F/g through “conjugated acid-base pairs” formed by uncoordinated N atoms on the organic linkers; its proton conduction mechanism provides a theoretical foundation for the development of novel ionic supercapacitors [105]. These cases collectively demonstrate that through strategies encompassing interfacial engineering, heterostructure construction, and proton transport channel design, the charge storage kinetics of MOF-based materials can be systematically optimized.

Theoretical understanding, ranging from material systems to energy storage mechanisms, is continuously deepening. The application of MOFs in supercapacitors primarily involves two mechanisms: electric double-layer capacitance (EDLC) and

pseudocapacitance. Conductive or redox-active MOFs achieve efficient charge transport and redox response through reversible valence changes at metal centers and synergistic interactions with organic ligands [106]. The high crystallinity of MOFs ensures a more uniform distribution of charge storage sites, while their permanent porosity guarantees sufficient electrolyte infiltration, characteristics that are difficult to achieve simultaneously in traditional porous carbon materials. Through precise modulation of the MOF skeleton structure, targeted optimization of specific surface area and pore size distribution can be realized [107]. Notably, MOF derivatives often inherit the porous structure of their precursors while possessing higher conductivity; this “structural inheritance” effect provides a crucial pathway for developing novel composite electrodes. The current consensus suggests that breakthroughs in the performance of MOF-based supercapacitors require a comprehensive consideration of multiple factors, including the electronic configuration of metal nodes, the conjugation degree of organic ligands, and the ion affinity of the pore environment, to achieve synergistic optimization of energy storage performance through cross-scale regulation.

3.1.4 Fuel cells

Fuel cells, which directly convert chemical energy into electrical energy, occupy a pivotal position in the future energy landscape due to their high efficiency and eco-friendly nature. The core roles of MOFs in fuel cells are mainly manifested in three aspects: serving as precursors for single-atom catalysts (SACs), modifying proton-conducting membranes, and acting as supports for cathode ORR catalysts. MOF-derived single-atom catalysts exhibit significant

potential in enhancing fuel cell reaction kinetics due to their maximum atom utilization efficiency and well-defined active center structures. By employing a chelation-assisted selective etching strategy, open-porous Fe-N-C single-atom catalysts (OP-Fe-NC) can be constructed [108], as shown in Fig. 9(a). This material achieves a half-wave potential of 0.89 V in acidic media and an current density of 29 mA/cm² at 0.9 V_{ir-free} in membrane electrode assemblies (MEA). Furthermore, the high metal loading capacity and tunable pore characteristics of MOFs make them ideal templates for preparing M-N-C catalysts. For instance, the CoFe-NC-polypyrrole (PPy) catalyst (Fig. 9(b)) exhibits a half-wave potential of 0.915 V in alkaline media and a peak power density of 352 mW/cm² in anion exchange membrane fuel cells (AEMFC) [109]. These achievements indicate that MOF-based SACs significantly enhance ORR activity and stability by optimizing electronic structures and lowering reaction energy barriers, providing a viable path for replacing noble metal catalysts.

In the field of proton-conducting membranes, MOFs effectively address the issue of declining proton conductivity under low humidity in traditional perfluorosulfonic acid (PFSA) membranes through the synergistic action of their pore structure and functional groups. Composite membranes prepared by incorporating Ni-MOFs into sulfonated polymers (sulfonated poly(ether ether ketone) (sPEEK)) enhance water retention capabilities via the MOF's high specific surface area and hydrophilicity [110]. This results in an approximately 40% increase in proton conductivity at 80 °C

and 100% relative humidity, with a power density reaching 319 mW/cm². Similarly, hybrid membranes of NH-Zr frameworks and PFSA [111], as illustrated in Fig. 9(c), induce the construction of proton hopping channels through the formation of acid-base pairs (N-H and -SO₃H). Consequently, proton conductivity improves by 33% and peak power density by approximately 20% compared to pristine membranes under low humidity (40% RH). More notably, hydrogen-bonded MOF nanosheets exhibit anisotropic proton conduction properties, with conductivity in the thickness direction reaching 4.4×10^{-3} S/cm (90 °C, 100% RH) [112]. Their non-porous structure also significantly suppresses hydrogen permeation, stabilizing the open-circuit voltage of H₂/O₂ fuel cells at 1.0 V. Thus, MOFs can achieve efficient proton conduction via the Grotthuss mechanism and structural design.

MOFs also demonstrate innovation in applications as cathode catalyst supports and in low-platinum (Pt) fuel cells. By regulating the pyrolysis conditions of MOFs, nitrogen-doped carbon materials with controllable mesopore sizes can be prepared; their pore size distribution directly influences the dispersion of Pt nanoparticles and mass transfer efficiency. The E-Pt/NC₅ ("E" is the abbreviation of "etched", indicating that this catalyst has undergone ammonia etching treatment) catalyst (Fig. 9(d)) achieves a mass activity of 1.52 A/mg and a peak power density of 0.8 W/cm² (H₂-air) under ultra-low platinum loading [113]. On another front, the intrinsic conductivity limitations of MOFs can be resolved by compositing with conductive materials. For example, the introduction of single-

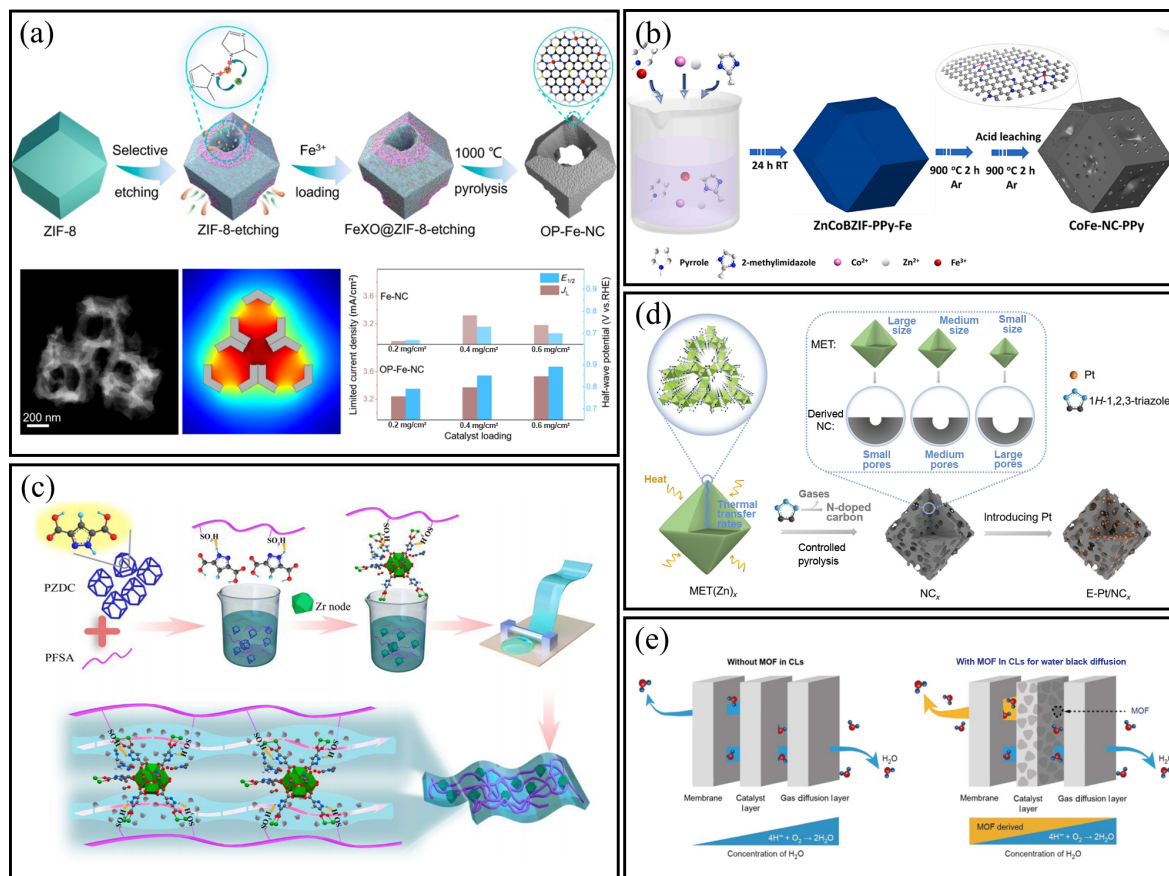


Figure 9 (a) Preparation and characteristics of OP-Fe-NC. Reproduced with permission from Ref. [108], © American Chemical Society 2023. (b) Preparation of CoFe-NC-PPy. Reproduced with permission from Ref. [109], © Elsevier B.V. 2024. (c) Formation of NH-Zr mixed membrane. Reproduced with permission from Ref. [111], © Zhang, W. X. et al. 2023. (d) Synthesis of E-Pt/NC₅. Reproduced with permission from Ref. [113], © Wiley-VCH GmbH 2023. (e) MOF playing a water storage role in the catalyst layer. Reproduced with permission from Ref. [115], © The Royal Society of Chemistry 2023.

atom Cu-N₄ sites in Cu-7,7,8,8-tetracyanoquinodimethane (Cu-TCNQ)/graphene oxide (GO) composites allows them to surpass Pt/C in half-wave potential in alkaline media, boosting alkaline polymer electrolyte fuel cell (APEFC) power density to 320 mW/cm² [114]. Additionally, MOFs used as additives in cathode catalyst layers can promote reverse water diffusion through a water-storage effect. As shown in Fig. 9(e), this maintains a current density of 0.88 A/cm² under low humidity, although excessive MOF content (≥ 7 wt.%) increases interfacial resistance due to particle agglomeration [115]. Collectively, these cases demonstrate that the multifunctional design of MOFs requires balancing porosity, conductivity, and active site density to achieve comprehensive performance enhancement in fuel cells.

3.2 Electrocatalysis

3.2.1 HER

The HER is a critical step in the electrolysis of water for hydrogen

production and holds significant importance for the realization of clean energy production and utilization. Although traditional noble metal catalysts possess outstanding catalytic activity, their high cost and limited reserves restrict widespread application. Consequently, the development of low-cost, high-performance non-noble metal catalysts has become a research hotspot. MOFs can regulate pore size and shape by introducing different metal nodes and organic linkers, thereby optimizing proton transport pathways and improving HER efficiency. Furthermore, MOFs possess large specific surface areas and abundant active sites, which significantly increase contact opportunities with reactants and facilitate catalytic reactions.

In acidic media, the HER activity of MOFs can be significantly enhanced by precisely modulating the electronic structure of metal centers. A hybrid structure constructed from iron-based MIL-100 and Ti₃C₂T_x MXene nanosheets (MIL/Ti₃C₂T_x, Fig. 10(a)) inhibits the interlayer agglomeration of MXenes and forms a porous structure [116]. It exhibits a low overpotential of 107 mV and a

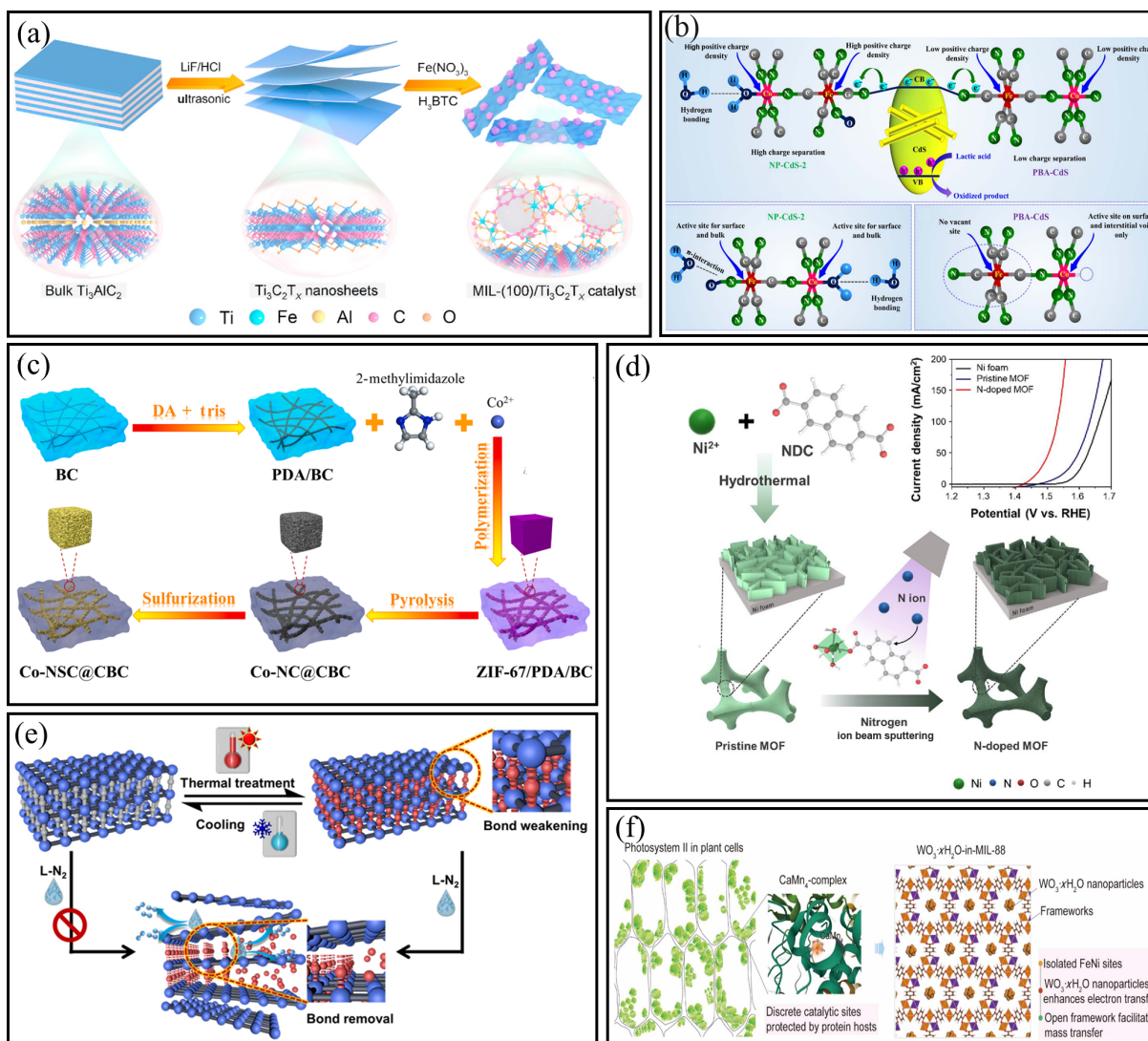


Figure 10 (a) Synthesis of MIL/Ti₃C₂T_x. Reproduced with permission from Ref. [116], © Elsevier Ltd. 2023. (b) Mechanism of MOFs optimizing electron transfer pathways. Reproduced with permission from Ref. [117], © The Royal Society of Chemistry 2023. (c) Preparation of Co-NSC@CBC. Reproduced with permission from Ref. [118], © Elsevier Inc. 2024. (d) Synthesis of NIBS@NiNDC. Reproduced with permission from Ref. [123], © Elsevier B.V. 2024. (e) Preparation of ultrathin 2D MOF nanosheets. Reproduced with permission from Ref. [128], © Wiley-VCH GmbH 2024. (f) Structural design of WO₃·xH₂O-in-MIL-88. Reproduced with permission from Ref. [130], © The Royal Society of Chemistry 2024.

Tafel slope of 61 mV/dec in 0.5 M H_2SO_4 ; this performance enhancement stems from the synergy between the high conductivity of MXene and the active sites of MIL-100. Similarly, when CoFe-based MOFs (CoFe-nitroprusside (CoFe-NP)) serve as cocatalysts for CdS nanorods, ligand regulation (substituting $-\text{NO}$ for $-\text{CN}$) alters the charge density of metal centers and extends the lifetime of charge-separated states, achieving a photocatalytic HER rate of 1735 mmol/(g·h), nearly seven times higher than that of pure CdS [117]. These studies reveal the mechanism by which MOFs optimize electron transfer pathways through ligand engineering and interface design. Figure 10(b) illustrates the mechanism of optimizing electron transfer pathways via ligand engineering and interface design. By replacing the $-\text{CN}$ ligands in PBAs with the strong π -acceptor $-\text{NO}$, CoFe-NP significantly alters the electronic structure of the metal centers, resulting in increased positive charge densities on Fe and Co, which facilitates the acceptance of photo-generated electrons from the CdS conduction band (CB). This ligand regulation enhances metal-to-ligand charge transfer (MLCT) and interfacial electronic coupling, forming an efficient n-n type heterojunction that promotes charge separation. Additionally, the axial distortion induced by $-\text{NO}$ makes Fe sites more accessible to substrates, while the $-\text{CN}$ bridge acts as an electron channel to further accelerate electron transfer from CdS to the MOFs. Long-lived charge-separated states observed in NP-CdS-2 via transient absorption spectroscopy (TAS) confirm the critical role of ligand engineering in extending carrier lifetimes.

In the realm of alkaline HER, MOF-derived transition metal sulfides and carbides exhibit promising performance due to their platinum-like electronic structures. The Co_9S_8 porous carbon-based catalyst (Co-NSC@CBC (NSC denotes N-doped sulfurized carbon and CBC denotes carbonized bacterial cellulose), Fig. 10(c)), prepared via pyrolysis and sulfurization using ZIF-67 as a precursor, exhibits an overpotential of 138 mV and a Tafel slope of 123 mV/dec in 0.5 M H_2SO_4 [118]. Its performance is attributed to the strong electronic coupling between Co-NSC nanoparticles and the bacterial cellulose carbon substrate. Molybdenum-based MOF derivatives have garnered attention for their d-band centers being close to that of platinum; through heteroatom doping and heterostructure construction, the Gibbs free energy of hydrogen adsorption can be regulated, rendering them significantly superior to undoped samples [119]. Furthermore, hollow Ni/NiO/C composites (H-Ni/NiO/C) promote H-OH bond cleavage through metal/metal oxide synergistic effects, achieving a low overpotential of 87 mV in alkaline media [120]. Their hollow structure not only increases the exposure of active sites but also optimizes mass transport processes. MOF-derived non-noble metal catalysts can approach or even surpass the performance of platinum-based catalysts through component and morphology regulation.

The integration of MOFs with carbon materials further addresses their intrinsic deficiency in electrical conductivity. Hybrid systems comprising graphene and MOFs form continuous conductive networks through π - π stacking or chemical bonding; graphene not only enhances charge transport efficiency but also reinforces stability by suppressing framework collapse of the MOFs [121]. Theoretical studies have demonstrated that the sluggish kinetics of alkaline HER are intimately correlated with the adsorption behaviors of multiple reaction intermediates (adsorbed hydrogen (H_{ad}), adsorbed hydroxide (OH_{ad}), and adsorbed water ($\text{H}_2\text{O}_{\text{ad}}$)), and the pore dimensions and functional groups of MOFs can precisely modulate the adsorption energies of these

intermediates [122]. Notably, the crystallographic anisotropy of MOFs also influences HER performance; two-dimensional MOF nanosheets exhibit superior activity relative to bulk materials due to exposure of additional active crystal facets, yet their long-term stability remains to be improved through cross-linking or encapsulation strategies. These findings provide multi-scale design principles for MOF-based HER catalysts, necessitating systematic consideration from atomic-level coordination environments to macroscopic morphology optimization.

3.2.2 OER

The OER constitutes another critical step in water splitting for hydrogen production, typically occurring at the anode. Although OER is a four-electron transfer process, it is confronted with a high activation energy barrier, resulting in a relatively low reaction rate. Currently, the most widely employed OER catalysts remain precious metal oxides, such as RuO_2 and IrO_2 ; however, their high cost and resource scarcity constrain large-scale applications. The exploration of efficient non-precious-metal OER catalysts has therefore become one of the focal points of research.

The unique structural tunability, high specific surface area, and abundant active sites of MOFs provide extensive latitude for the optimization of electrocatalytic performance. Studies on nitrogen doping of two-dimensional MOFs through ion beam sputtering (IBS) technology have revealed that nitrogen IBS (NIBS) can precisely regulate the surface chemistry of Ni-naphthalene-2,6-dicarboxylic acid MOF (NiNDC), as illustrated in Fig. 10(d), forming three functional nitrogen species: pyridinic nitrogen (accelerating reaction kinetics), pyrrolic nitrogen (stabilizing catalyst structure), and graphitic nitrogen (enhancing conductivity) [123]. The ratio among these three species can be controlled by adjusting the acceleration potential (AP); the optimized NIBS@NiNDC requires merely 222 mV overpotential to achieve a current density of 10 mA/cm^2 , with a Tafel slope as low as 88 mV/dec, and demonstrates stable operation for 120 h at a high current density of 100 mA/cm^2 . The coordination environment of nitrogen species profoundly influences OER activity by modulating the electronic structure of metal active centers and the adsorption energies of intermediates. As critical organic connecting units within MOFs, the type, coordination mode, and electron-donating capability of nitrogen ligands determine the valence state of metal nodes, the position of the d-band center, and the local charge distribution [124]. Simultaneously, nitrogen ligands themselves or their derived nitrogen-doped carbon structures can participate in electron conduction, optimizing charge transfer pathways. More importantly, through precise design of nitrogen ligand structures, the linear scaling relationships between the adsorption energies of different OER intermediates can be disrupted, thereby reducing the reaction energy barrier. This mechanism provides a clear rationale for surface engineering of MOFs: the introduction of specific nitrogen species through postsynthetic modification, the construction of nitrogen-containing heterointerfaces, or the induction of nitrogen-containing active reconstruction layers during the OER process can systematically optimize the electronic structure and reaction kinetics of catalysts, achieving synchronous enhancement of activity and stability [125].

A profound correlation exists between the microscopic structure of MOFs and their OER activity, and the introduction of single-particle electrochemical strategies has provided novel perspectives for understanding this relationship. Taking sheet-like nickel-based

MOFs as an exemplar, single-particle-level investigations through scanning electrochemical cell microscopy (SECCM) have revealed a negative correlation between particle thickness and OER activity, while an increased proportion of (001) crystal facets significantly enhances catalytic performance [126]. The elucidation of this structure–activity relationship benefits from the precise tracking of MOF-derived processes by *in-situ* characterization techniques, ensuring the accuracy of structural information. Further studies have demonstrated that the dynamic reconstruction behavior of MOFs during the OER process can be modulated through the introduction of organic carboxylic acid linkers into the electrolyte. The addition of biphenyl dicarboxylic acid (BPDC) to alkaline electrolyte can retard the reconstruction rate of Ni-BPDC-MOF and NiFe-BPDC-MOF, suppressing the formation of ordered β -Ni(OH)₂ and promoting the generation of disordered α -Ni(OH)₂ [127]. This phase transition modulation enables the catalyst to achieve a low overpotential of 355 mV under 0.02 M additional linker conditions, and the mechanisms of aging delay and stability enhancement were confirmed through *in-situ* Raman spectroscopy and X-ray diffraction.

Dimensional engineering and amorphization strategies for MOFs provide crucial pathways for performance breakthroughs. Through a directional chemical bond intervention method combining thermal decomposition with liquid nitrogen exfoliation, ultrathin 2D MOF nanosheets with thicknesses less than 10 nm can be prepared [128], as shown in Fig. 10(e). This technique selectively weakens interlayer bonds while maintaining intralayer stability, utilizing the drastic expansion stress generated by liquid nitrogen quenching to achieve efficient exfoliation, thereby exposing more active sites without capping agents. On another front, converting FeNi-MOF into an amorphous catalyst (A-FeNi) via *in-situ* amorphization allows it to inherit the high specific surface area and porous structure of the MOF. Simultaneously, leveraging high coordination numbers and Fe/Ni site synergies enables the achievement of ultra-low overpotentials of 152 and 232 mV in 1 M KOH, a Tafel slope of merely 17 mV/dec, and stable operation for 400 h at 100 mA/cm² [129]. Furthermore, integrating tungstic acid (WO₃·xH₂O) into the MIL-88 framework (Fig. 10(f)) achieves molecular-level isolation of FeNi sites, preventing intermolecular decomposition [130]. The optimized 15% WO₃·xH₂O-in-MIL-88 exhibits an overpotential of 263 mV at 10 mA/cm², a low Tafel slope of 39 mV/dec, and a mass activity of 190.6 A/g (at 300 mV overpotential). Its hydrophilicity and the *in-situ* formed Fe–O–O–Ni structure significantly enhance water molecule diffusion efficiency, demonstrating excellent performance even in alkaline seawater. Therefore, through precise regulation of the chemical composition, crystal structure, electronic state, and interface environment of MOFs, their OER catalytic activity and durability can be systematically optimized, laying a material foundation for the development of clean energy conversion technologies.

3.2.3 ORR

The ORR is one of the core reactions in energy conversion devices, such as fuel cells and metal–air batteries. Traditionally, Pt and its alloys have been widely used as ORR catalysts; however, due to their high cost and poor durability, the search for alternative non-noble metal catalysts has become an urgent necessity. MOFs and their derivatives have demonstrated broad application prospects in this field. By designing the metal nodes and organic linkers of MOF

precursors, carbon-based materials with atomically dispersed active sites can be derived. In FeCo alloy nanoparticles loaded on 1D carbon nanofibers (FeCo/N-CNFs), the uniform distribution of Fe and Co forms synergistic active centers [131]. Their highly graphitized carbon structure provides directional charge transfer channels, while the electronic coupling between M–N_x sites and pyridinic N/graphitic N significantly reduces the *OOH formation energy barrier, resulting in a half-wave potential of 0.88 V. This performance stems from the modulation of the d-band center via metal–support interactions: Charge redistribution in the FeCo alloy leads to increased 3d electron filling in Co, weakening the excessive adsorption of oxygen intermediates, while unpaired electrons in Fe promote O₂ activation. At the atomic scale, the advantage of MOF-derived catalysts lies in the programmability of the coordination environment; strong interactions between metal nodes and the nitrogen-doped carbon matrix during pyrolysis stabilize single-atom sites, while mesoporous structures accelerate mass transport and gas diffusion. This hierarchical structural synergy provides an ideal electron–proton transport network for ORR.

Regulating the morphology and active site exposure of MOFs through facet engineering is an effective strategy for enhancing ORR performance. As shown in Fig. 11(a), 2D ZIF-L (L denotes leaf-like) grows confined along the *c*-axis under the induction of cetyltrimethylammonium bromide (CTABr), forming 1D ZIF-NR [132]. Its derived material, Co-NCR (NCR stands for N-doped carbon nanorod), retains the rod-like morphology and hierarchical porous structure, with cobalt nanoparticles encapsulated in a nitrogen-doped carbon matrix exhibiting excellent ORR activity. Bromide ions from CTABr preferentially adsorb onto the (002) facet, weakening the bonding between Zn²⁺ and 2-methylimidazole through coordination competition. During pyrolysis, this directional structure promotes the uniform encapsulation of cobalt nanoparticles within the nitrogen-doped carbon matrix, forming abundant Co–N_x active sites. Further research indicates that the performance advantages of MOF-derived materials stem not only from morphological effects but are also closely related to their electronic structure. When ZIF-8 encapsulates triethylenediamine cobalt complexes ([Co(en)₃]³⁺), high-temperature pyrolysis results in Co-SAC/NC where cobalt exists as single atoms anchored on a nitrogen-doped carbon support [133], as illustrated in Fig. 11(b). Cobalt atoms primarily exist in a Co–N₄ coordination configuration with a coordination bond length of 1.38 Å, and no Co–Co scattering paths are detected in the second shell. DFT calculations reveal that the synergy between adjacent Co–N₄ sites significantly lowers the *OOH formation energy barrier, while high-density active sites further optimize electron transfer pathways, achieving a half-wave potential of 0.88 V. Notably, high-density single-atom sites also optimize charge transport pathways, bringing the electron transfer number close to 4.0, indicating that the four-electron pathway dominates.

In the investigation of bimetallic-site MOF systems, two-dimensional phthalocyanine (Pc)-based MOFs exhibit distinctive electronic coupling effects. As illustrated in Fig. 11(c), taking the Ni-Co bimetallic MOF as an exemplar, both experimental and theoretical calculations collectively confirm that Co sites dominate ORR activity, while the introduction of the second metal (Ni) modulates the d-band center position of Co through interlayer interactions, thereby influencing the adsorption strength of oxygen intermediates [134]. The Ni sites exert a significant influence on reaction selectivity, with their two-electron ORR selectivity

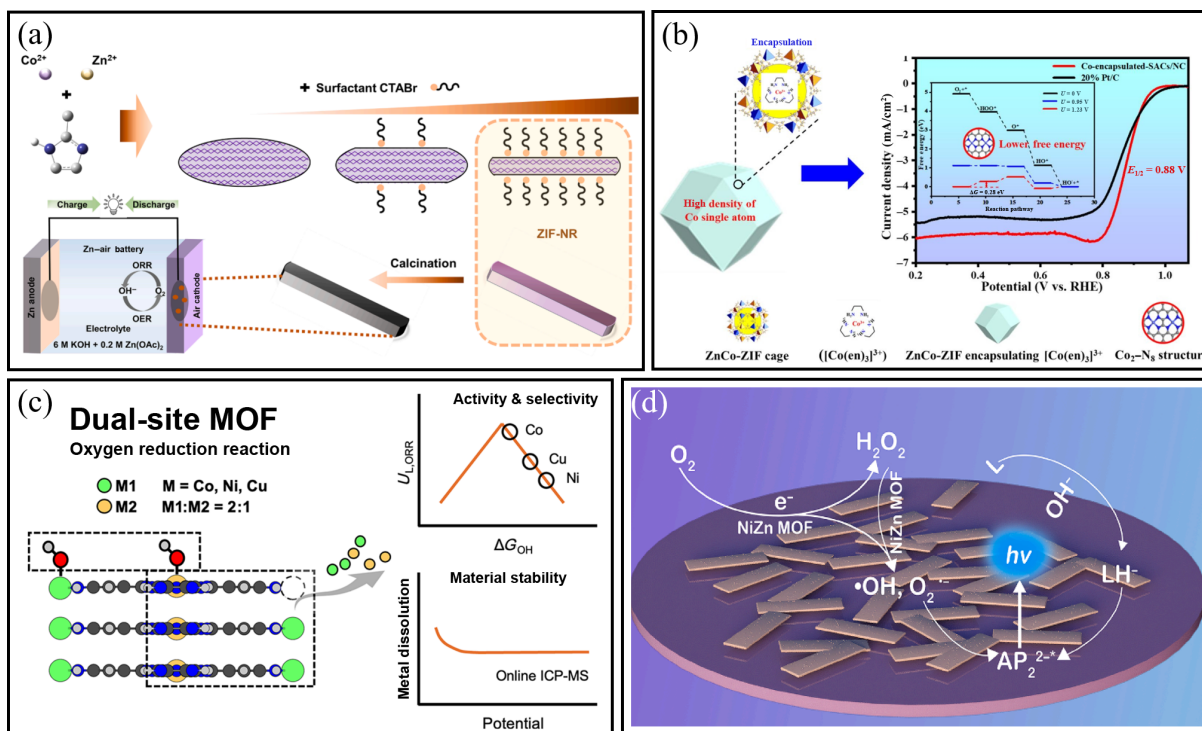


Figure 11 (a) Preparation and application of ZIF-NR. Reproduced with permission from Ref. [132], © Elsevier Inc. 2023. (b) Formation and performance of Co-SAC/NC. Reproduced with permission from Ref. [133], © Elsevier Inc. 2023. (c) Computational model of MOFs ORR selectivity, activity, and stability. Reproduced with permission from Ref. [134], © American Chemical Society 2024. (d) ECL reaction mechanism of NiZn MOF/luminol system. Reproduced with permission from Ref. [136], © Elsevier B.V. 2023.

exceeding 46%, substantially higher than the 4% observed for Co sites. This disparity originates from the differential capacity of distinct metals to regulate the $^*\text{OOH}$ dissociation energy barrier. *In-situ* characterization combined with theoretical calculations further reveals that Co sites exhibit optimal stability under alkaline conditions, whereas Cu sites are prone to structural reconstruction, providing atomic-scale guidance for the stability design of bimetallic MOFs. Similarly, within composite MOF material systems, the interfacial engineering between CoFe-layered double hydroxide (LDH) and Ni-MOF demonstrates synergistic enhancement effects. Upon modification of the Ni-MOF layered structure with CoFe-LDH in a wrinkled ribbon morphology, the formed heterointerface not only expands the specific surface area but also induces electron transfer from Fe to Co, optimizing oxygen adsorption energy [135]. The exchange current density of this composite material is substantially enhanced, enabling the maximum power density of microbial fuel cells (MFCs) to reach 211 mW/m²; the performance enhancement mechanism can be attributed to accelerated charge transport at the interface and exposure of additional edge active sites.

MOF materials also exhibit unique advantages in the selective regulation of ORR pathway. Through precise control of the thermal treatment conditions of NiZn MOF, a 2D nanosheet structure loaded with NiO nanoparticles can be obtained; this material demonstrates 76% H_2O_2 selectivity and 61% Faradaic efficiency in the two-electron ORR [136]. The introduction of Zn modulates the local coordination environment of Ni, elevating the O–O bond cleavage energy barrier and thereby promoting H_2O_2 generation. This selective modulation capability has been applied to enhance luminol electrochemiluminescence (ECL) systems, wherein *in-situ* generated H_2O_2 catalyzed by the MOF serves as the core reaction

intermediate, significantly amplifying ECL signal intensity and ultimately enabling the construction of a highly sensitive biosensor. The reaction mechanism illustrated in Fig. 11(d) demonstrates that in this system, the active intermediates and final products of the 2e[−] ORR can synergistically promote luminol cathodic luminescence. Concurrently, the charge repulsion between luminol and the catalyst surface under alkaline conditions can attenuate its nonspecific adsorption without interfering with the ORR process, thereby achieving efficient coupling of the catalytic and luminescence processes. From the materials design perspective, the modular synthetic characteristics of MOFs permit the precise regulation of metal nodes, organic linkers, and pore environments to achieve directional control over the ORR reaction pathway (four-electron or two-electron), offering possibilities for tailoring electrocatalysts toward specific application scenarios. A comprehensive assessment of existing research indicates that the performance optimization of MOF-based ORR catalysts necessitates systematic consideration of three hierarchical factors: atomic-scale modulation of metal electronic states, nanoscale distribution of active sites and their interaction with supports, and microscale hierarchical pore architecture and morphology design. The synergistic interplay among these three hierarchical levels collectively determines the ultimate catalytic performance of the material.

3.2.4 CO₂RR

The CO₂RR refers to the process of converting CO₂ into value-added chemicals or fuels, holding significant importance for mitigating global climate change and realizing carbon cycling. The application of MOFs in CO₂RR leverages their core advantages of structural tunability and multifunctionality, with electrical

conductivity emerging as a critical factor. The 2D structure of the Pc-based conductive MOF ($\text{NiPc-Ni}(\text{NH})_4$) achieves high conductivity through the extensive overlap of d- π conjugated orbitals between nickel nodes and phthalocyanine units [137]. It exhibits superior CO_2RR performance in an H-type electrolytic cell, reaching a CO Faradaic efficiency of 96.4% at -0.7 V. DFT calculations confirm that the Ni-N_4 units within the phthalocyanine rings serve as catalytic active sites, while the planar $\text{Ni}(\text{NH})_4$ nodes accelerate proton/electron transport. This structure-function relationship provides a pathway for designing efficient electrocatalysts.

From the perspective of reaction mechanisms, the role of MOFs in CO_2RR involves multi-scale regulation. At the molecular level, the electronic structure of metal centers directly influences the activation energy barrier of CO_2 , while organic linkers can stabilize reaction intermediates through hydrogen bonding or electrostatic interactions [138]. In $\text{NH}_2\text{-MIL-68(In)}$, the introduction of amino groups enhances CO_2 chemisorption and efficiently converts CO_2 into formic acid via a proton-coupled electron transfer process, achieving a Faradaic efficiency exceeding 94% [139]. At the mesoscopic level, the pore size and surface chemistry of MOFs determine mass transport efficiency and the local microenvironment, thereby influencing product selectivity. ZIF-series MOFs can suppress the competitive HER and improve CO_2RR selectivity by modulating the hydrophobicity of imidazole linkers. Furthermore, the coordination environment of metal nodes in MOFs is capable of mimicking natural enzyme active centers, optimizing reaction pathways through geometric and electronic effects to lower the formation energy barriers of key intermediates [140]. Notably, the stability of MOFs in electrocatalysis remains a concern; consequently, some studies have focused on constructing MOF/carbon composites or introducing conductive polymer networks to enhance structural stability while maintaining high catalytic activity.

In CO_2RR , the regulation of product selectivity essentially depends on the relative strength of the adsorption free energy between the key reaction intermediate COOH and CO. Ligand engineering enables the modulation of intermediate binding energies by tuning the electronic structure of the MOF framework, thereby directionally optimizing catalytic performance. The electron-donating/withdrawing nature of ligands can directly influence the adsorption strength of the COOH intermediate by altering the charge density at the metal center. Studies have demonstrated that in benzimidazole-based ligands, higher electron density at sp^2 -hybridized carbon atoms can effectively lower the energy barrier for COOH formation [141]. The Hammett equation is commonly employed to describe the remote electronic effects of substituents on the catalytic activity of MOF metal nodes, and researchers have further proposed a predictive model based on ligand orbital energy levels, providing theoretical guidance for designing metal-node catalytic activity through the regulation of ligand and substituent electronic properties [142]. Regarding the secondary coordination sphere, investigations on trinuclear metal-cluster MOFs ($\text{Fe}_2\text{NiTPTB-OH}$, TPTB denotes 4,4',4''-(triphenylene-1,5,9-triyl)tris(2-hydroxybenzoic acid)) have revealed that the introduction of $-\text{OH}$ functional groups in proximity to catalytic sites can form hydrogen-bonding interactions with the COOH intermediate, achieving dual-site synergistic stabilization and bringing the COOH adsorption energy to an optimal value [143]. Furthermore, the highest occupied molecular orbital (HOMO) energy level of the ligand exhibits a positive correlation with the

binding strength of the CO intermediate [144]; the higher the ligand HOMO energy level, the stronger its charge-transfer capability toward the metal site, leading to increased electron density in metal d orbitals and thereby enhancing π -backdonation to CO. These ligand electronic effects on intermediate binding energies can, in essence, all be attributed to the modulation of the d-band center position of the active metal center. Theoretical studies on two-dimensional conjugated MOFs have indicated that the adsorption energies of COOH/HCOO as well as the number of electrons transferred during the CO_2RR process are all determined by the position of the d-band center at the active site [145]. Research on silver-cluster-based MOFs has further confirmed that imidazole ligands, by virtue of their stronger Lewis basicity and σ -donating capability, can induce a significant upward shift of the d-band center of Ag_{12} clusters, thereby optimizing the adsorption of the *COOH intermediate and lowering the reaction energy barrier, achieving a CO Faradaic efficiency of 98.5% in acidic electrolyte [146]. Therefore, systematic modulation of the d-band center through simultaneous tuning of metal species and organic ligands enables the directional design of CO_2RR product selectivity.

3.3 Photocatalysis

3.3.1 Photocatalytic hydrogen evolution

Photocatalytic water splitting for hydrogen production represents one of the pivotal pathways toward realizing clean energy generation and utilization, bearing significant importance for alleviating global energy crises and mitigating greenhouse gas emissions. Conventionally, semiconductor materials, such as TiO_2 , have been extensively employed in photocatalytic water splitting reactions; however, they suffer from low quantum efficiency and insufficient visible-light absorption, which constrain their practical applications.

Research on MOFs in the field of photocatalytic water splitting for hydrogen evolution has evolved from single-material design to complex systems involving multidimensional synergistic optimization. The core mechanisms encompass three critical aspects: metal node synergy, heterojunction interfacial engineering, and molecular-level electronic structure modulation. The introduction of high-entropy MOFs (HE-MOFs) signifies a substantial breakthrough in materials design, wherein synergistic effects among multiple metal nodes significantly enhance charge transfer efficiency. HE-MOF single crystals (HE-MOF-SC) and their NSs (HE-MOF-NS) achieved visible-light-driven hydrogen evolution through p-type semiconductor characteristics [147], as illustrated in Fig. 12(a). The nanosheets, benefiting from reduced thickness and increased specific surface area, attained a hydrogen evolution rate of 13.24 mmol/(h·g); this performance was attributed to band structure optimization and enhanced carrier separation efficiency resulting from the high-entropy effect. Similarly, a trimetallic MOF ($\text{Ho}_6\text{-Cd}_4\text{Ni}_{1-x}\text{-NS}$) achieved a hydrogen evolution rate of 40.06 mmol/(g·h) through precise modulation of the ratio between photosensitive (Cd) and photothermal (Ni) single sites. The underlying mechanism involves the localized high temperatures generated by photothermal sites promoting reaction kinetics, while uniformly dispersed single sites form ultrashort electron transport pathways that effectively suppress charge recombination [148]. As depicted in Fig. 12(b), under illumination, the photosensitive Cd-NS sites are effectively excited and generate abundant photo-generated electrons, which are transferred through the linkers to adjacent Ni-NS sites. The uniformly distributed Cd-

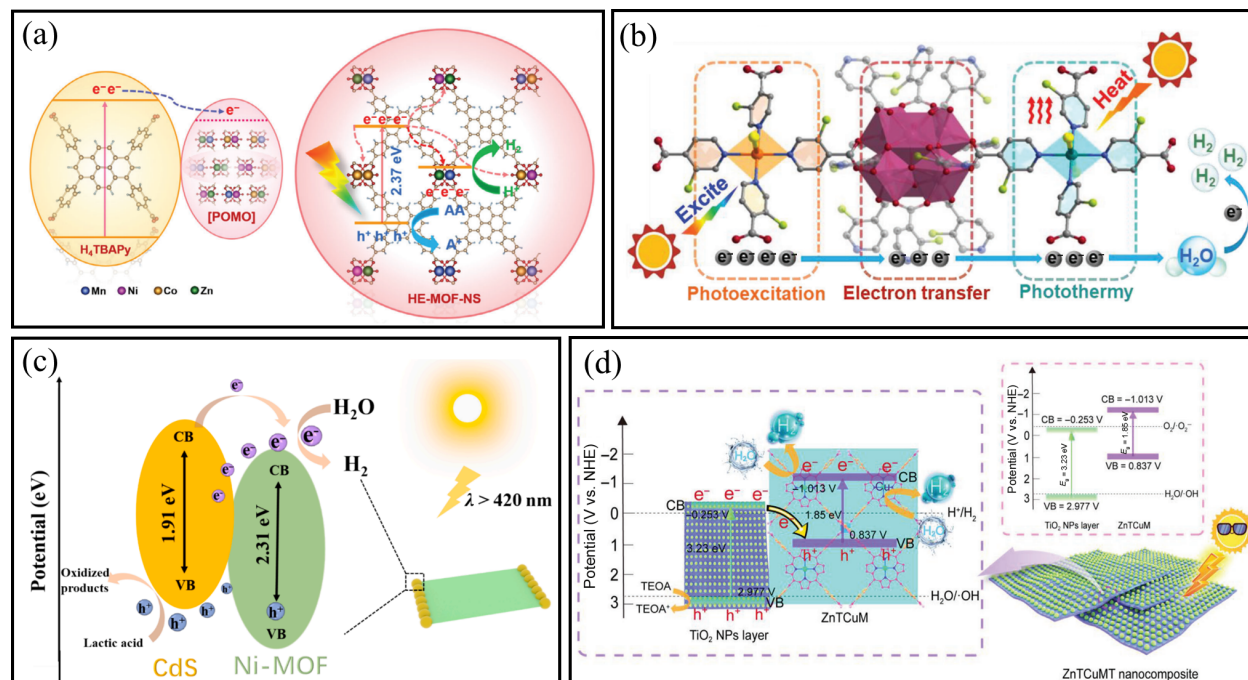


Figure 12 (a) Hydrogen production mechanism of HE-MOF-NS. Reproduced with permission from Ref. [147], © Wiley-VCH GmbH 2024. (b) Mechanism of action and electron transport of $\text{Ho}_6\text{-Cd}_3\text{Ni}_4\text{-NS}$. Reproduced with permission from Ref. [148], © Wiley-VCH GmbH 2024. (c) Hydrogen production mechanism of CdS/Ni-MOF. Reproduced with permission from Ref. [149], © Elsevier Inc. 2024. (d) Photocatalytic hydrogen evolution mechanism of ZnTCuMT. Reproduced with permission from Ref. [152], © Wiley-VCH GmbH 2024.

NS and Ni-NS sites synergize with Ho_6 -clusters to form ultrashort electron transfer pathways, enabling efficient electron transport and suppressing photo-generated carrier recombination effects, while the sustained photothermal effect accelerates the reaction rate, thereby enhancing photocatalytic reaction efficiency.

In heterostructure construction, composite strategies combining MOFs with inorganic semiconductors demonstrate remarkable advantages. A heterojunction system comprising CdS nanoparticles directionally loaded at the edges of Ni-MOF nanosheets achieved a hydrogen evolution rate of 19.6 mmol/(h·g) [149]; the performance enhancement originated from the promotion of charge separation by Ni-MOF as a cocatalyst, coupled with geometric optimization through the edge-loading strategy that reduced carrier transport distances. As shown in Fig. 12(c), under visible-light irradiation, CdS generates photo-generated electrons that are transferred to Ni-MOF through the 0D/2D interfacial heterojunction, while holes are consumed by sacrificial agents [150]. Ni-MOF functions as a cocatalyst to promote H_2 generation, suppress CdS photocorrosion, and enhance stability and activity. Another study achieved a hydrogen evolution rate of 15,584 $\mu\text{mol}/(\text{g}\cdot\text{h})$ through the combination of *in-situ*-derived TiO_2 nanosheets with salicylaldehyde-supported Co(II) sites ($\text{Co-sal-NH}_2\text{-MOF@TiO}_2$) [151]; extended X-ray absorption fine structure (EXAFS) analysis confirmed that the stable coordination environment of Co(II) synergized with the heterojunction units formed with TiO_2 to optimize the band structure, enhancing photo-generated electron-hole pair separation efficiency by 105–354 fold. A more sophisticated Z-scheme mechanism was validated at the interface between porphyrin-based MOFs (ZnTCuMT-200) and TiO_2 [152], wherein surface-engineered heterojunctions enhanced hydrogen evolution activity by 28.2 fold. Direct recombination of TiO_2 conduction band electrons with MOF valence band holes preserved high-reduction-potential electrons, while the broad-spectrum

absorption of porphyrin linkers and Cu^{2+} catalytic sites further enhanced light harvesting and surface reactions. Specifically, upon photoexcitation, TiO_2 conduction band electrons transfer to the ZnTCuM valence band and recombine with holes, while ZnTCuM conduction band electrons reduce water to generate H_2 , and TiO_2 valence band holes oxidize triethanolamine (TEOA), as illustrated in Fig. 12(d). This direct Z-scheme pathway promotes charge separation, preserves strong reduction/oxidation capabilities, and enhances photocatalytic activity and stability.

In MOF-based photocatalytic hydrogen evolution systems, the separation, migration, and recombination dynamics of photo-generated charge carriers are the core determinants of catalytic efficiency, and TAS serves as the key technique for elucidating these ultrafast photophysical processes. TAS enables the capture of transient absorption signals following photoexcitation with femtosecond-to-nanosecond time resolution, thereby directly tracking the formation and decay of charge-separated states and providing direct experimental evidence for verifying charge transfer pathways in heterojunctions. In the study of CdS/Ce-UiO- NH_2 heterojunction photocatalysts, TAS combined with electrochemical spectroscopy confirmed that this heterostructure facilitated charge separation, generating long-lived holes and electrons, and achieved an external quantum efficiency of 2.2% under 420 nm irradiation [153]. Notably, unlike conventional electron-accepting Zr-UiO, this study revealed a reversed charge separation direction in the CdS/UiO heterojunction, wherein Ce-UiO- NH_2 acts as an electron donor rather than an electron acceptor in this system. In the $\text{Pt@NH}_2\text{-UiO-66/CdS}$ ternary composite photocatalyst, TAS directly observed that the carrier dynamics followed an efficient photo-generated hole transfer-band-trap pathway, and it is this unique charge separation mechanism that endows the system with a remarkably high apparent quantum efficiency (AQE) of 40.3% (at

400 nm) and excellent long-term stability [154]. Furthermore, femtosecond TAS (fs-TAS) has also been employed to reveal differences in carrier dynamics in MOF-based Z-scheme heterojunctions. In an MOF-derived $\text{In}_2\text{O}_3/\text{rGO}/\text{C}_3\text{N}_4$ ternary Z-scheme system, fs-TAS confirmed that the introduction of an rGO electron mediator extended the average carrier lifetime from 240.48 ps in the binary system to 448.16 ps, directly demonstrating the critical role of rGO in suppressing charge recombination [155]. Regarding defect engineering modulation, ultrafast transient absorption spectroscopy studies have shown that $\text{UiO}-66\text{-NH}_2$ with an appropriate level of structural defects exhibits the fastest relaxation kinetics and the highest charge separation efficiency, whereas excessive defects retard relaxation and diminish charge separation efficiency [156]. In the ZIF-67 system, optical transient absorption (OTA) and X-ray transient absorption (XTA) spectroscopies confirmed the formation of a long-lived charge-separated state with ligand-to-metal charge transfer (LMCT) characteristics following photoexcitation, providing crucial theoretical underpinning for its photocatalytic applications [157]. The aforementioned cases provide direct experimental validation of charge separation mechanisms in MOF-based photocatalytic hydrogen evolution heterojunctions, demonstrating that rational heterojunction and defect engineering design can not only effectively promote the separation of photo-generated charges but also significantly enhance photocatalytic hydrogen evolution performance by extending carrier lifetimes.

Nanoscale regulation and electronic structure modification provide a deeper optimization path for MOFs' photocatalysis. The Ag_{25} nanoclusters doped with heteroatoms (MAG_{25} , $\text{M} = \text{Pd}/\text{Pt}/\text{Au}$) encapsulated in $\text{UiO}-66\text{-NH}_2$ form a Z-type heterojunction. Among them, $\text{AuAg}_{24}@\text{UiO}-66\text{-NH}_2$ exhibits an activity of 3.6 mmol/(g·h) [158]. The ultrafast transient absorption spectroscopy confirms that MOF encapsulation has changed the electronic state of Ag and promoted the excitation energy dissociation. The post-functionalization of semiconductor MOFs (DPT-MOF, where DPT denotes 3,6-di(4-pyridyl)-1,2,4,5-tetrazine) through click chemistry introduces fluorine atoms, increasing the H_2O_2 yield to 1676 $\mu\text{mol}/(\text{g}\cdot\text{h})$. The strong electron-withdrawing effect of the fluorine atoms prolongs the charge lifetime and optimizes the conduction band position, revealing the potential of ligand modification for precise control of MOF electronic structure [159]. These studies clarify the regulatory mechanism of the interaction between the electronic state of the active sites and the carrier at the atomic scale, providing a theoretical basis for the design of efficient MOF-based photocatalysts. Current research has formed a multi-level optimization strategy from metal node design, heterostructure construction, to molecular-level modification. The core scientific issues focus on how to achieve efficient separation and utilization of photo-generated charges through the regulation of structure-performance relationships.

3.3.2 Photocatalytic CO_2 reduction

In photocatalytic CO_2 reduction, MOFs absorb solar energy via photosensitive ligands or metal clusters to excite electron-hole pairs, thereby driving the CO_2 reduction reaction. The synergistic interaction between metal nodes and organic ligands within MOFs facilitates the chemisorption and activation of CO_2 , while their porous architecture promotes the diffusion of reactants and products, consequently enhancing photocatalytic performance. Although the primary products of photocatalytic CO_2 reduction are

C_1 compounds, such as CO and CH_4 , regulating the pore environment and active site distribution of MOFs holds promise for achieving the selective generation of C_{2+} products [160].

Amino functionalization serves as a core modification strategy, significantly optimizing the optoelectronic properties of MOFs through the strong electron-donating characteristics of amino groups ($-\text{NH}_2$). Specifically, the introduction of amino groups reduces the material's band gap, broadens the visible light absorption range, and enhances catalytic activity by improving the separation efficiency of photo-generated electron-hole pairs [161]. Taking $\text{NH}_2\text{-MIL}-125(\text{Ti})$ as an example, amino modification not only promotes CO_2 adsorption (due to acid-base interactions with CO_2) but also provides active sites for the protonation process, driving the reduction reaction towards multi-electron product pathways [162, 163]. Furthermore, structural crystal engineering further optimizes the light-harvesting capability and carrier transport kinetics of materials by precisely modulating the topology, pore size, and metal node/linker combinations of MOFs. Figure 13(a) illustrates the mechanism of photocatalytic CO_2 reduction over {112} faceted $\text{NH}_2\text{-MIL}-125(\text{Ti})$ (T112). The design of high-index facets exposes more unsaturated metal sites, enhancing CO_2 adsorption and activation capabilities, while promoting the transfer of photo-generated electrons to adsorbates through energy level matching [164]. However, single-component MOFs are often limited by narrow photoresponse ranges and high carrier recombination rates, necessitating composite strategies to overcome these bottlenecks.

Composite structure design compensates for the performance deficiencies of single materials through multi-component synergistic effects. In the $\text{NH}_2\text{-UiO}-66/\text{Au}/\text{In}_2\text{O}_3$ system, Au nanoparticles extend light absorption to the near-infrared region via the surface plasmon resonance (SPR) effect and form Schottky junctions with In_2O_3 to directionally separate electrons; meanwhile, $\text{NH}_2\text{-UiO}-66$ provides high specific surface area and amino active sites to strengthen CO_2 capture and proton-coupling processes [165]. This ternary structure achieves efficient spatial separation of photo-generated carriers: Electrons from the conduction band of In_2O_3 migrate to Au nanoparticles, while holes in the valence band of $\text{NH}_2\text{-UiO}-66$ participate in oxidation reactions, ultimately increasing the CO production rate to 45 times that of pure In_2O_3 . Similarly, heterojunctions formed between MOFs and semiconductors or metal oxides can establish energy band gradients that drive electron transfer from photosensitizers to catalytic sites [166]. It is worth noting that stability remains a critical challenge for the practical application of composites. As some MOFs are prone to structural collapse in aqueous phases or under illumination, their durability must be enhanced by increasing ligand rigidity, modifying with hydrophobic groups, or regulating crystallinity [167].

The regulation of product selectivity relies on the precise control of the active site microenvironment and reaction pathways. While copper-based MOFs typically generate C_1 products, nitrogen doping strategies can reconstruct their electronic structure, steering the reaction towards C_2 product pathways [168]. Figure 13(b) depicts the photocatalytic process of N-doped $\text{NH}_2\text{-CuBDC}$ (BDC denotes 1,4-benzenedicarboxylate) materials. Using 2-methylimidazole as an N-dopant, N-doped MOFs with a sheet-like structure were prepared via room-temperature stirring. Under illumination, N-doping increases the electron density at Cu catalytic sites and accelerates photo-generated charge transfer. Cu-N sites stabilize CO and CHO intermediates, promoting C-C coupling to

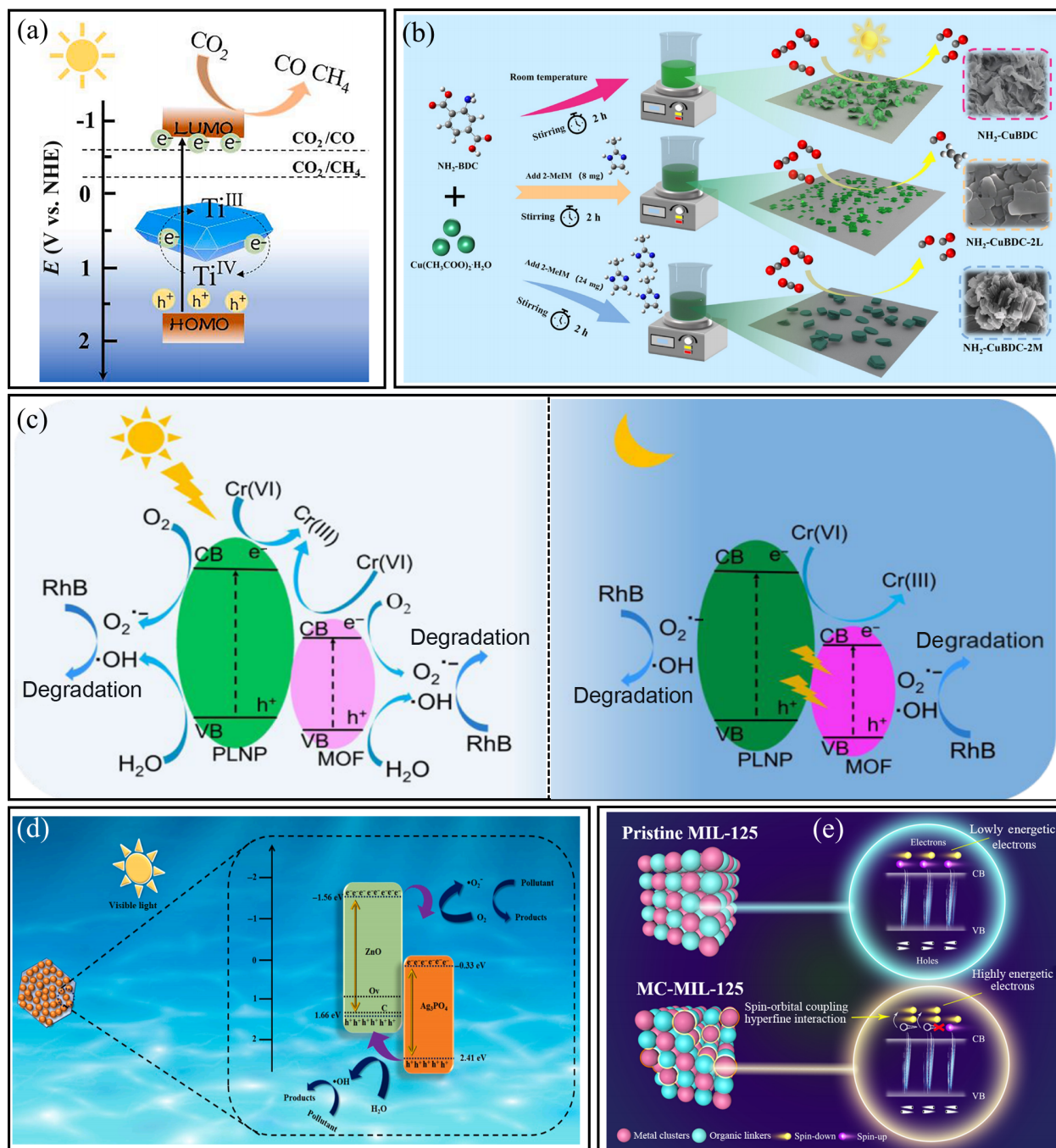


Figure 13 (a) Photocatalytic CO_2 reduction mechanism of Ti_{12} . Reproduced with permission from Ref. [164], © Elsevier B.V. 2021. (b) Synthesis and photocatalysis of N-doped $\text{NH}_2\text{-CuBDC}$. Reproduced with permission from Ref. [168], © Science China Press 2024. (c) Photocatalytic mechanism of PLNPs/MOFs. Reproduced with permission from Ref. [169], © American Chemical Society 2023. (d) Photocatalytic degradation mechanism of SNs in the AZ2 heterostructure. Reproduced with permission from Ref. [170], © Elsevier B.V. 2023. (e) Mechanism of spin polarization-induced CB flexibility to enhance photocatalytic performance. Reproduced with permission from Ref. [171], © Elsevier Inc. 2022.

form CO-CHO , which ultimately realizes the efficient conversion of CO_2 to C_2H_4 , whereas the pristine MOF generates only the C_1 product CO .

3.3.3 Photocatalytic degradation of pollutants

Photocatalytic degradation of pollutants represents a significant direction in environmental remediation, aiming to harness solar energy for the decomposition of organic pollutants into harmless small molecules, such as water and carbon dioxide. Recent studies

have optimized the photocatalytic performance of MOFs through diverse strategies, including the integration with persistent luminescent (PL) materials, heterostructure construction, functional linker incorporation, and defect engineering for electronic structure modulation. He et al. developed a $\text{Zn}_3\text{Ga}_2\text{Ge}_2\text{O}_{10} \cdot 0.5\% \text{Mn}/\text{NH}_2\text{-MIL-101(Fe)}$ composite system that covalently bonds PLNPs with MOFs, achieving round-the-clock photocatalysis [169]. The core mechanism of this system lies in the absorption of solar light by PLNPs to generate ultralong afterglow, which transfers excitation

energy to the active sites of MOFs through persistent luminescence resonance energy transfer (PLRET), enabling sustained and efficient degradation of rhodamine B (RhB) and Cr(VI) for over 12 h even in dark environments, as illustrated in Fig. 13(c). The high specific surface area and porous architecture of MOFs provide abundant sites for pollutant adsorption, while photoexcitation generates electrons and holes [172]; the persistent luminescence characteristic of PLNPs addresses the bottleneck of conventional photocatalysts' dependence on continuous illumination. Notably, the covalent bonding ensures efficient interfacial charge transport and reduces the recombination of photo-generated electron-hole pairs, with this synergistic effect rendering the degradation efficiency of the composite material substantially superior to that of individual components.

In heterostructure design, a ZIF-8-derived C-ZnO/Ag₃PO₄ (AZ2) system significantly enhanced photocatalytic activity through oxygen defect engineering and interfacial engineering [170]. The presence of oxygen defects in AZ2 not only broadens the visible-light absorption range but also serves as electron traps to suppress carrier recombination. The Type-II heterojunction formed between Ag₃PO₄ and ZnO facilitates directional migration of photo-generated electrons, while the ZIF-8-derived carbon matrix enhances electrical conductivity. The photocatalytic degradation mechanism of sulfonamide antibiotics (SNs) by the AZ2 heterostructure is depicted in Fig. 13(d). Solid-solution preparation modulates the photocatalyst band gap to an optimal position, enhancing visible-light absorption; oxygen defects modify the surface structure and function as hole scavengers, effectively reducing photo-generated electron-hole recombination. Upon illumination, electrons undergo valence band transitions and react with O₂ to generate ·O₂⁻, while holes interact with H₂O to produce ·OH; both species cooperatively govern SNs degradation. The heterostructure promotes charge separation, while oxygen defects enhance light absorption and carrier utilization efficiency, synergistically achieving efficient degradation. Furthermore, this study reveals the structural heritability of MOF-derived materials—high-temperature pyrolysis preserves the high specific surface area while newly generated metal oxides form intimate interfaces with semiconductors; this structure–performance relationship provides a paradigm for designing stable and efficient heterojunction photocatalysts.

Linker modification and defect engineering constitute two additional critical strategies for modulating the intrinsic photocatalytic properties of MOFs. The AgTz-4 (Tz denotes the triazole-based ligand) MOF significantly enhanced light absorption and optimized band structure through the introduction of high-content thiophene groups [173]. The electron-rich nature of thiophene induces a negative shift in the conduction band position of the MOF, enhancing its reducing capability, while its π -conjugated system promotes photo-generated charge separation. Compared to the isostructural AgTz-3, AgTz-4 exhibited degradation rate enhancements exceeding 2 fold for both rhodamine B and salazosulfapyridine, confirming the structure–activity relationship between linker electronic properties and photocatalytic activity. On the other hand, defect engineering studies on Ti-based MOFs (MIL-125) have revealed the modulation mechanism of spin polarization on conduction band flexibility [171]. As shown in Fig. 13(e), through controlled defect concentration, the upward shift of the material's d-band center enhances H⁺ adsorption capacity, resulting in a four-order-of-

magnitude improvement in hydrogen evolution rate. The high mobility of conduction band electrons induced by defects effectively suppresses charge recombination, while the broadened valence band enhances oxidation capability, enabling MIL-125-5% to exhibit exceptional performance in both pollutant degradation and hydrogen evolution. Consequently, through atomic-scale precise regulation of the electronic structure of MOFs, directional optimization of photocatalytic performance can be achieved.

To intuitively quantify the latest research progress of MOFs in the field of next-generation energy storage and conversion, Table 1 summarizes and categorizes their principal research achievements. The design and synthesis strategies for MOFs are diverse, encompassing solvothermal synthesis, one-pot synthesis, ion exchange, template transformation, coprecipitation, and *in-situ* electrochemical reconstruction, with each method exerting distinctive influences on the structure and performance of the final products. MOFs and their derivatives prepared through these methods exhibit fundamental characteristics, including high porosity, large specific surface area, favorable stability, abundant active sites, and excellent electrical conductivity. Key parameters, such as specific surface area, reversible capacity, proton conductivity, and overpotential, often demonstrate superior performance, capable of meeting specific application requirements. Research has revealed that the performance of MOFs can be significantly enhanced through the regulation of metal centers and organic ligands, optimization of synthesis conditions, and construction of composite structures, thereby maximizing their performance utilization and providing novel solutions to complex problems in the energy storage and conversion field. Concurrently, their extensive application value in lithium-ion batteries, sodium-ion batteries, supercapacitors, fuel cells, electrocatalysis (HER, OER, ORR, CO₂RR), and photocatalysis has been demonstrated. Specifically, in the battery field, they can effectively enhance capacity and cycling stability; in the supercapacitor field, they exhibit high specific capacitance and excellent energy density; in the fuel cell and electrocatalysis fields, they demonstrate outstanding activity and durability as efficient catalysts or supports; and in the photocatalysis field, they manifest substantial value in photocatalytic water splitting, CO₂ reduction, and pollutant degradation, underscoring the important value of MOF materials in addressing energy and environmental issues. Although MOFs have demonstrated tremendous potential surpassing traditional commercial battery materials in laboratory research, their transition to practical application still faces severe technical bottlenecks. Compared with mature graphite anodes or lithium cobalt oxide cathodes in traditional commercial batteries, most MOF materials suffer from intrinsically low electronic conductivity, insufficient chemical stability in electrolytes, and structural collapse readily induced by volume changes during charge/discharge processes, which directly limit their long-cycle life and rate performance. Furthermore, MOF materials universally encounter engineering challenges, including low tap density, high synthesis costs, and difficulties in scale-up preparation. Across different applications, the emphasis of these bottlenecks varies: In lithium/sodium-ion batteries, conductivity and cycling stability constitute the primary obstacles; in lithium–sulfur batteries, the anchoring and catalytic conversion capability toward polysulfides still requires enhancement; in supercapacitors, how to balance high specific capacitance with high energy density is critical; while in electrocatalysis and photocatalysis, greater attention is paid to the

Table 1 Comparison of representative MOF materials for energy storage and conversion

Materials	Synthesis methods	Structure	Basic characteristics	Key parameters	Major findings	Applications	References
Cu-TAC	Solvothermal synthesis	Rod-like microcrystals	High electrical conductivity, dual redox-active centers	Reversible capacity: 772.4 mAh/g (300 mA/g); capacity retention: 83% (600 cycles); band gap: 0.31 eV	The conductive 2D framework with TAC ligands provides abundant active sites, delivering superior capacity and long-term cyclability	Li-ion battery anode	[75]
NCM-MOF@G	Bottom-up integration	Multilayer pillared structure	Polysulfide sieving, catalytic conversion, flame-retardant	Initial capacity: 1634 mAh/g (0.1 C); decay rate: 0.034% per cycle (2000 cycles)	The pillared interlayer structure effectively blocks polysulfide shuttling and catalyzes conversion, enabling high capacity and long life for Li-S batteries	Li-sulfur battery interlayer	[76]
Fe-TTTP	Solvothermal synthesis	2D layered/3D architecture	High theoretical capacity, insolubility, redox-active centers	Reversible capacity: 950 mAh/g (at 50 mA/g); rate: 95 mAh/g (at 10,000 mA/g); cycling: 310 mAh/g (5000 cycles at 2000 mA/g)	The multi-thiol-supported structure prevents dissolution in electrolyte, enabling superior cycling stability and high rate performance for LIBs	Li-ion battery anode	[77]
Ni-NDC/MXene	Hydrothermal; vacuum filtration	3D porous interpenetrating nanosheets	Enhanced conductivity, buffered volume expansion, high porosity	Reversible capacity: 579.8 mAh/g (100 cycles at 100 mA/g); long-term: 310 mAh/g (500 cycles at 1 A/g)	Encapsulating porous Ni-NDC nanosheets with MXene improves conductivity and structural stability, overcoming volume expansion issues	Li-ion battery anode	[84]
UiO-66(Zr/Ti); UiO-66(Zr/Hf)	Cation exchange	Nanoparticles encapsulated in PVA nanofibers	High porosity, high density of OMSs, strong anion complexation	Li ⁺ transference number: 0.83 (Zr/Ti); ionic conductivity: 7.79 mS/cm; capacity retention: 75% (1000 cycles at 1 C)	Heterometallic MOFs in separators enhance Li ⁺ conductivity and transference number, significantly improving rate capability and cycle life	Li-ion battery separator	[85]
Co-HITP	<i>In-situ</i> electrochemical reconstruction	2D nanoribbon/single-crystal	High conductivity, stable single-crystal structure, expanded layer spacing	Reversible capacity: 450.1 mAh/g (at 0.2 A/g); decay rate: ~0.001% per cycle (15,000 cycles at 8 A/g)	<i>In-situ</i> reconstruction creates a stable, conductive single-crystal structure with abundant sites, enabling ultra-long cycle life and high capacity	Na-ion battery anode	[95]
CoNiZnS/C	Solid sulfidation of MOF precursor	Hollow sea urchin-like microspheres	Abundant phase boundaries, buffers volume expansion, rich voids	Initial Coulombic efficiency: 96.52% (at 0.1 A/g); cycling stability: 410.7 mAh/g (960 cycles at 2.0 A/g); rate performance: 477.0 mAh/g (at 5.0 A/g)	The unique hollow microsphere structure with multiphase boundaries provides abundant active sites and effectively buffers volume changes, leading to high performance and stability	Na-ion battery anode	[99]
Cu-TBA	Solvothermal synthesis	Rhombic 2D layered/rod-like	High surface area, metallic band structure, high conductivity	Reversible capacity: 153.6 mAh/g (at 50 mA/g); cyclability: ~100% retention (3000 cycles at 1 A/g); surface area: 613 m ² /g	The rhombic topology and narrow energy gap enhance charge transfer and active site utilization, leading to superior capacity and stability compared to its hexagonal counterpart	Na-ion battery cathode	[100]
NiHCF-NCs	Na ₂ DTPA-assisted coprecipitation	Nanocubes	High crystallinity, low-strain, few defects, high Na content	Specific capacity: 81.3 mAh/g (at 10 mA/g); rate capability: 64.5 mAh/g (at 4000 mA/g); capacity retention: 97.1% (2000 cycles)	The controlled crystallization process yields high-quality nanocubes with few defects, resulting in a low-strain mechanism that ensures outstanding cycle life and rate capability	Na-ion battery cathode	[101]
Ni/Co-POH-2	Template conversion	Ultrathin nanosheet arrays	Large specific surface area, high structural stability, superior conductivity, synergistic bimetallic effect	Specific capacitance: 1905.60 F/g (at 1 A/g); energy density: 36.59 Wh/kg; retention: 67.98% (after 5000 cycles)	Ni/Co-POH-2 shows optimal electrochemical performance due to uniform porous nanosheet morphology and complete conversion of MOF precursor. Bimetallic synergy enhances charge storage and rate capability compared to monometallic counterparts	Supercapacitors	[102]

(Continued)

Materials	Synthesis methods	Structure	Basic characteristics	Key parameters	Major findings	Applications	References
Ni/NiO/CoO-CW-4	Template/ <i>in-situ</i> growth (carbonization, oxidation, acid-etching)	3D hollow carbon structure on wood tracheids	High graphitization degree, exceptional conductivity, optimized pore size distribution, abundant functional groups	Areal capacitance: 16.76 F/cm ² (at 5 mA/cm ²); energy density: 0.67 mWh/cm ² ; retention: 96.21% (after 10,000 cycles)	Surface modification with Ni/Co-MOF derivatives creates a 3D hollow structure enhancing ion transport. Acid-etching removes unstable metals, optimizing surface chemistry and conductivity, leading to superior areal capacitance and cycling stability in solid-state devices	Symmetric supercapacitors	[103]
MXene@NiCo-MOF	<i>In-situ</i> growth on expanded MXene (hard template assisted)	Hierarchical nanosheets on 2D layers	High electrical conductivity, rich oxygen vacancies, large specific surface area, enhanced OH ⁻ adsorption	Specific capacitance: 2078.1 F/g (at 1 A/g); energy density: 40.23 Wh/kg; retention: 84.4% (after 10,000 cycles)	Expanded MXene prevents restacking and induces oxygen vacancies in NiCo-MOF, enhancing conductivity and active sites. DFT confirms reduced band gap and stronger OH ⁻ adsorption, resulting in high capacitance and excellent rate performance in hybrid supercapacitors	Hybrid supercapacitors	[104]
Dawson-type POM-based MOFs	One-step synthesis	Block crystals	High redox capability, stability, high proton conductivity	Specific capacitance: 225, 305, and 430 F/g (at 1 A/g); proton conductivity up to 2.35×10^{-4} S/cm	CUST-833 exhibits highest capacitance due to conjugated acid-base pairs facilitating rapid proton transport. Theoretical calculations confirm enhanced performance via proton conduction rather than electronic conductivity	Proton supercapacitors	[105]
NH-Zr framework	One-step synthesis	Nanoparticles	Good stability, tunable composition, high water retention	Proton conductivity: 0.292 S/cm (80 °C, 100% RH); 0.031 S/cm (80 °C, 40% RH); max power density: 0.726 W/cm ² (40% RH)	The <i>in-situ</i> constructed NH-Zr framework induces reorganization of proton-conducting groups and forms acid-base pairs, enhancing proton conductivity under low humidity. The hybrid membrane shows superior performance and stability compared to pristine PFSA	Proton exchange membrane fuel cells (PEMFCs)	[111]
E-Pt/NC _x	One-step synthesis	Nanoparticles	High porosity, large specific surface area, many active sites	Mass activity: 1.52 A/mg Pt; peak power density: 0.80 W/cm ² (H ₂ -air); Pt loading: 0.05 mg/cm ²	Controllable mesopores in N-doped carbon derived from MET(Zn) allow for optimal Pt NP dispersion and mass transport. The optimized catalyst achieves high mass activity and power density with ultralow Pt loading, surpassing commercial Pt/C	Low-Pt fuel cells; ORR electrocatalysts	[113]
Cu-TCNQ/GO	One-step synthesis	Nanosheets	Excellent conductivity, many active sites, good stability	Resistivity: 2.7 Ω/cm (decreased by 3 orders of magnitude); half-wave potential: 0.92 V; power density: 320 mW/cm ² ; Brunauer-Emmett-Teller (BET) surface area: 678 m ² /g	The Cu-TCNQ/GO composite significantly improves conductivity and ORR activity compared to pure Cu-TCNQ. It exhibits a high half-wave potential of 0.92 V and excellent durability in alkaline media, outperforming commercial Pt/C in specific metrics	APEFCs; ORR catalyst	[114]
UiO-66(Zr)-(COOH) ₂	One-step synthesis	Nanoparticles	High porosity, good stability, high water content	Water content: ~29.4 wt.% (11.3% physisorbed + 18.1% dehydroxylation); current density improvement: from 0.63 to 0.88 A/cm ² at 0.6 V (30% RH)	UiO-66(Zr)-(COOH) ₂ acts as a water reservoir in the cathode catalyst layer, promoting water back-diffusion to the membrane under low humidity. This significantly improves PEMFC performance at low RH without direct membrane modification	PEMFCs; cathode catalyst layer additive	[115]
MIL-100(Fe) combined with Ti ₃ C ₂ T _x MXene	<i>In-situ</i> solvothermal assembly	2D porous nanoarchitecture	Large surface area, high porosity, excellent conductivity, active sites	Onset potential: 29 mV; overpotential: 107 mV at 10 mA/cm ² ; Tafel slope: 61 mV/dec; charge-transfer resistance: 35.5 Ω; double layer	The MIL(40%)/Ti ₃ C ₂ T _x hybrid prevents MXene restacking and combines high conductivity with abundant active sites, resulting in significantly enhanced electrocatalytic HER performance and long-term stability	Electrocatalytic HER in acidic media	[116]

Materials	Synthesis methods	Structure	Basic characteristics	Key parameters	Major findings	Applications	References
CoFe-NP and CoFe-PBA loaded on CdS	Low-temperature synthetic method; ligand substitution strategy	Nanorods with cocatalyst coating	Tunability, active sites, charge separation efficiency	HER rate: 1735 $\mu\text{mol}/(\text{g}\cdot\text{h})$ (NP-CdS-2); AQE (%): 1.37% (at 400 nm); cocatalyst loading: 0.12 wt.%; band gap: ~ 2.4 eV	Replacing -CN with strong π -acidic -NO in CoFe-NP increases positive charge density on metal centers, enhancing electron transfer from CdS and providing more active sites for superior photocatalytic HER	Photocatalytic HER	[117]
Ni-MOF (derived into H-Ni/NiO/C)	Two-step process; template-assisted	Hollow nanospheres	High porosity, large surface area, active sites, stability	Overpotential: 87 mV at 10 mA/cm ² ; Tafel slope: 91.7 mV/dec; charge transfer resistance: 75 Ω ; double layer capacitance: 4.89 mF/cm ²	The H-Ni/NiO/C hollow composite exhibits superior HER activity due to synergistic effects of metal/metal oxide and hollow architecture, facilitating H-OH bond breaking and charge transport	HER in alkaline media	[120]
MOF 2D-sheets (Ni-bic-4,4'bpy) and derivatives (MOFD-1, MOFD-2)	Hydrothermal synthesis, followed by <i>in-situ</i> electrochemical/chemical derivation	Nanosheet	High surface area, tunable conductivity, active grain boundaries, structure-activity correlation	Thickness: 50–800 nm; turnover frequency (TOF) correlates negatively with thickness; activation energy for OH ⁻ transport: 0.146 eV (MOFD-1); grain boundary Ni sites have lower ΔG (1.80 eV) than bulk (2.95 eV)	A negative correlation exists between sheet thickness and OER activity due to the higher fraction of active (001) facets and grain boundaries in thinner sheets. Thin sheets facilitate electrolyte penetration and charge transfer, revealing that edge activity depends on thickness and crystal plane exposure	OER at single-particle level	[126]
A-FeNi	One-step synthesis	Nanosheet	High porosity, large surface area, good stability, active sites, tunability	Overpotential: 152 mV (at 10 mA/cm ²), 232 mV (at 100 mA/cm ²); Tafel slope: 17 mV/dec; BET surface area: 117 m ² /g; durability: > 400 h (at 100 mA/cm ²)	The amorphous A-FeNi inherits ligands and coordination from FeNi-MOF, providing abundant active sites and fast kinetics. Fe sites modulate electronic structure, while Ni sites aid initial adsorption, resulting in superior OER performance and durability compared to crystalline counterparts	OER in alkaline electrolyte	[129]
15%-WO ₃ -xH ₂ O-in-MIL-88 (FeNi-MIL-88 hybrid)	Solvothermal synthesis (MIL-88) followed by impregnation/gelation of tungstic acid	Nanoparticle	High porosity, good stability, improved conductivity, hydrophilicity, isolated active sites	Overpotential: 263 mV (at 10 mA/cm ²); Tafel slope: 39 mV/dec; TOF: 0.135 s ⁻¹ ; mass activity: 190.6 A/g; stability: >100 h (alkaline), > 70 h (seawater)	Encapsulating tungstic acid in MIL-88 pores isolates FeNi active sites and enhances hydrophilicity, facilitating water diffusion and electron transfer. The 15% loading optimizes conductivity and porosity, yielding superior OER activity and stability in both alkaline and seawater environments compared to pure MIL-88	OER in alkaline and seawater electrolytes	[130]
Pc-based dual-site MOFs	Solvothermal synthesis/one-step synthesis	2D layered AA-eclipsed stacking	Tunable dual metal sites, high porosity, good crystallinity, adjustable OER selectivity	BET surface area: 119–548 m ² /g; crystal domain size: 7.4–12.3 nm; M1 site content: 60%–70%	Dual-site MOFs allow precise tuning of OER activity and selectivity. Co-containing MOFs show higher 4e ⁻ activity. Dissolution studies reveal stoichiometric loss patterns affecting long-term stability	ORR electrocatalyst	[134]
CoFe-LDH@Ni-MOF	Simple hydrothermal method	Lamellar stacked structure	Large BET surface area, high pore volume, enhanced electrochemical activity, good stability	Max power density in MFC: 211 mW/m ² ; pore volume: 0.094218 cm ³ /g; redox peak at -0.80 V	The composite structure promotes OER performance in MFCs, achieving higher power density and better stability compared to individual components	MFC cathode catalyst	[135]
NiPc-Ni(NH) ₄	Solvothermal synthesis	2D nanosheets	High electrical conductivity, high Ni loading, large BET surface area, highly dispersed Ni sites	BET surface area: 172 m ² /g; Ni content: 17.18 wt.%; max CO Faradaic efficiency: 96.4% (at -0.7 V); CO current density: 24.8 mA/cm ² (at -1.1 V)	NiPc-Ni(NH) ₄ exhibits excellent CO ₂ reduction performance with high Faradaic efficiency for CO production over a wide potential range, outperforming most 2D and 3D MOF electrocatalysts due to high conductivity and active site density	CO ₂ RR electrocatalyst	[137]

Materials	Synthesis methods	Structure	Basic characteristics	Key parameters	Major findings	Applications	References
HE-MOF-NS	One-pot solvothermal synthesis followed by ultrasonic exfoliation	2D nanosheets	High entropy effect, large specific surface area, p-type semiconductor, excellent water stability, efficient charge transfer	H ₂ evolution rate: 13.24 mmol/(g·h); band gap: 2.37 eV; charge transfer resistance: 4233 Ω; electron lifetime: 809 ps	High-entropy strategy incorporating Ni, Mn, Co, and Zn enhances charge transfer via the cocktail effect. The 2D nanosheet structure provides abundant active sites and short diffusion paths, resulting in significantly higher photocatalytic hydrogen production activity compared to single-metal MOFs	Photocatalytic hydrogen production	[147]
H ₀ -Cd _{0.76} Ni _{0.24} -NS	One-pot solvothermal synthesis followed by sulfurization treatment	3D framework with uniformly dispersed single-sites	Synergistic photosensitive and photothermal effects, ultrashort electron transfer pathways, high stability, no cocatalyst required	H ₂ evolution rate: 40.06 mmol/(g·h); AQE: 29.37% (at 420 nm); band gap: 2.41 eV; photothermal temperature rise: up to 65.5 °C	Uniform organization of photosensitive Cd-NS and photothermal Ni-NS single-sites creates synergistic effects. This arrangement shortens electron transfer paths and suppresses charge recombination, leading to superior visible-light-driven hydrogen evolution without cocatalysts or photosensitizers	Photocatalytic hydrogen evolution	[148]
DPT-MOF, PA-MOF, EFB-MOF	One-pot hydrothermal synthesis followed by postsynthetic click-type reaction	Rod-like nanocrystals with 3D layered structure	Tunable optical properties, electrical conductivity, high charge separation efficiency, chemical stability	BET surface area: 166–187 m ² /g; band gap: 2.03–2.54 eV; H ₂ O ₂ production rate: up to 1676 μmol/(g·h); electrical conductivity: ~ 10 ⁻⁶ S/cm	Postsynthetic fluorine functionalization via click chemistry tunes band positions and prolongs charge lifetime. EFB-MOF achieves highest non-sacrificial photocatalytic H ₂ O ₂ production due to efficient electron trapping by fluorine groups, demonstrating the potential of conductive MOFs in artificial photosynthesis	Photocatalytic hydrogen peroxide production	[159]
Tl12	Solvothermal synthesis with controlled facet exposure	NH ₂ -MIL-125(Ti) with exposed high-index {112} facets	High specific surface area, narrow HOMO-LUMO gap, efficient charge separation and migration, strong CO ₂ adsorption	Band gap: 2.45 eV; AQY: 0.097%; photoelectron effectiveness: 100.46 μmol/(g·h)	Exposing high-index {112} facets on NH ₂ -MIL-125(Ti) narrows the band gap and accelerates charge separation, resulting in CO and CH ₄ yields 33 and 31 times higher than low-index facet samples	Photocatalytic CO ₂ reduction to CO and CH ₄	[164]
NH ₂ -UiO-66/Au/In ₂ O ₃	Solvothermal synthesis: Au nanoparticles and NH ₂ -UiO-66 decorated on In ₂ O ₃ nanorods	In ₂ O ₃ nanorods decorated with NH ₂ -UiO-66 MOF and Au nanoparticles	High CO ₂ adsorption capacity, enhanced visible light absorption, improved charge separation efficiency, good stability	CO yield: 8.56 μmol/(g·h); band gap: 2.79 eV; charge transfer resistance: 5581 Ω	The co-modification of NH ₂ -UiO-66 and Au on In ₂ O ₃ nanorods significantly enhances CO ₂ adsorption and charge separation. CO yield is 45 times that of pure In ₂ O ₃	Photocatalytic CO ₂ reduction to CO	[165]
C-ZnO/Ag ₃ PO ₄	Solution method	Heterostructure nanoparticles	High surface area, oxygen vacancies, good stability, efficient charge separation	Degradation efficiency: 98.5% in 90 min; rate constant: 0.0361 min ⁻¹ ; band gap: 3.22 eV; conduction band: -1.56 eV	The ZIF-8 derived C-ZnO/Ag ₃ PO ₄ heterostructure (AZ2) exhibits superior photocatalytic activity due to oxygen vacancies and efficient electron-hole separation. It achieves 98.5% degradation of sulfonamides under visible light, outperforming pristine components	Photocatalytic degradation of antibiotic pollutants	[170]
AgTz-3 and AgTz-4	Solvothermal synthesis	2D nanosheets	Good stability, tunable composition, structural diversity	Photodegradation rate constants: 0.055 mg/(L·min ⁻¹), 0.24 min ⁻¹ ; band gap width: 3.55 eV; conduction band: -1.72 V vs. RHE	Incorporating thiophene groups enhances photocatalytic activity. AgTz-4, with higher thiophene content, shows superior degradation efficiency for RHB and SSZ compared to AgTz-3 due to optimized band structure and increased light absorption	Photocatalytic degradation of organic pollutants	[173]
MIL-125-5%	Defect engineering via thermal treatment	Nanoparticles	High surface area, good stability, tunable	H ₂ evolution: 16,507.27 μmol/(g·h); band gap: ~ 3.12 eV; conduction	Moderate defect density optimizes CB position via spin polarization, enhancing electron	Photocatalytic water splitting	[171]

intrinsic activity of active sites, long-term durability, and the separation efficiency of photo-generated charge carriers. Therefore, future research must systematically address these bottlenecks through various potential advanced means to propel MOF materials from the laboratory toward industrial application.

4 Challenges and opportunities of MOFs from nanodesign to macroscopic applications

MOF materials hold substantial value in the field of energy storage and conversion; however, their progression from nanoscale design to macroscopic application remains confronted with numerous challenges. These challenges encompass not only the precise synthesis and characterization of materials but also the preparation and optimization of composites at the macroscopic scale, alongside scientific and technological barriers in scalable deployment. This section delves deeply into these critical issues and analyzes the development opportunities for MOFs in future energy technologies.

4.1 Fundamental barriers in nanoscale precise synthesis and characterization

The precise synthesis and structural elucidation of MOFs at the nanoscale constitute the foundation for achieving high-performance applications. The structural complexity and diversity of MOFs demand a high degree of controllability in the synthetic process to ensure the acquisition of anticipated physicochemical properties. In constructing MOFs with specific functionalities, precise control over metal node selection, organic linker design, and the coordination mode between the two is required. This involves not only molecular-level assembly but also meticulous regulation of parameters, such as reaction temperature, pressure, and solvent environment. The core controversies currently existing in the field are first concentrated on the mechanism of defect engineering. Although researchers generally acknowledge that regulating defect density can optimize the number of active sites, no unified conclusion has been reached regarding whether “missing-linker” or “missing-cluster” defects are more conducive to enhancing energy storage performance. Existing studies even present mutually contradictory results: Some reports indicate that higher defect densities enhance activity, while other works find that excessive defects compromise framework stability and degrade performance. This controversy essentially stems from differences in defect formation energies and charge transport mechanisms across different MOF systems, and universal theoretical models capable of predicting the contributions of different defect types to energy storage remain lacking. Furthermore, significant controversy exists regarding the characterization of dynamic framework structures. MOFs often undergo reversible framework deformation and gate-opening structural changes during energy storage charge/discharge processes; however, existing characterization techniques are predominantly *ex-situ* tests, making it difficult to capture *in-situ* the dynamic evolution of nanoscale structures during charge/discharge. Different research teams frequently arrive at divergent conclusions regarding the phase transition evolution pathways of the same MOF system, and the interpretation results from advanced characterization techniques, such as synchrotron radiation and *in-situ* electron microscopy, also often trigger discussions on result universality due to differences between the characterization environment and actual device operating conditions. At the synthesis methodology level, conventional solvothermal methods,

although capable of generating high-quality MOF crystals, suffer from prolonged reaction times and high energy consumption. In recent years, emerging technologies, such as microwave-assisted synthesis, ultrasonic treatment, and electrochemical deposition, have enhanced synthetic efficiency and enabled precise control over MOF morphology and structure under milder conditions; however, batch-to-batch stability in large-scale synthesis remains difficult to guarantee. Moreover, controversy exists regarding the origins of energy storage performance differences in MOFs of identical composition obtained via different synthetic routes. The debate focuses on whether residual synthetic byproducts affect the intrinsic material performance, or whether subtle structural differences constitute the core cause of performance variations. At the characterization technology level, conventional techniques, including X-ray diffraction, scanning electron microscopy, and transmission electron microscopy, struggle to comprehensively resolve the dynamic evolution processes and local detailed features of MOFs. It is necessary to integrate high-resolution characterization techniques, such as synchrotron radiation spectroscopy, nuclear magnetic resonance, and atomic force microscopy, to capture responsive behaviors under different external stimuli. Meanwhile, although computational methods, such as density functional theory simulations and machine learning screening, can assist in materials design, the predictive accuracy of existing models for the dynamic structural evolution of MOFs still warrants improvement. Significant deviations frequently exist in key parameters, such as adsorption energies and band gaps, obtained from different computational methods, introducing uncertainty into the mechanistic interpretation of experimental results.

4.2 Mesoscale barriers in macroscopic composite fabrication and performance matching

The preparation and optimization of MOF composites constitute a critical step in translating their exceptional properties to the macroscopic scale. Relying solely on MOFs often proves inadequate for meeting the demands of complex operating conditions, necessitating the construction of synergistic performance systems through composite formation with other functional materials. Substrate material selection lies at the core of composite system design. Carbon materials (graphene, carbon nanotubes, etc.) are frequently employed as supporting frameworks owing to their excellent electrical conductivity and chemical stability, which can enhance overall structural mechanical strength and provide efficient electron transport pathways. Metal oxides can augment catalytic capability through abundant active sites; however, insufficient interfacial adhesion between the substrate and MOFs leads to elevated charge transfer impedance and detachment of active materials during cycling. Significant controversy currently exists in the field regarding interfacial interaction mechanisms. On one hand, researchers generally acknowledge that heterojunctions formed between MOFs and substrates can facilitate charge separation and transfer; however, no consensus has been reached on how to quantitatively regulate the relationship between interfacial binding strength and charge transfer efficiency. On the other hand, some studies indicate that excessive interfacial interactions alter the intrinsic electronic structure of MOFs, thereby weakening the intrinsic activity of active sites, and no unified interfacial design criterion has been established. In terms of electrode shaping processes, controversy centers on the relationship

between MOF loading and device performance. Excessively high loading readily induces agglomeration, diminishing the effective specific surface area, whereas insufficient loading fails to exploit the high activity advantages of MOFs. Concurrently, the impact of different shaping processes on the structural integrity of MOFs remains disputed. Advanced shaping technologies, such as 3D printing, enable the fabrication of electrodes with complex architectures, yet whether the high-temperature sintering process will destroy the MOF framework structure remains a subject of inconsistent research conclusions. Moreover, contradictory reports exist regarding the structure–performance relationships between porosity and ion transport efficiency for electrodes obtained through different processes. Although composite methods, such as *in-situ* growth, impregnation coating, and self-assembly, have been developed, each approach harbors distinct limitations: *In-situ* growth yields intimately bonded interfacial structures, yet the uniformity of scale-up preparation remains difficult to control; impregnation coating is amenable to large-scale production, but excessive MOF loading readily induces agglomeration, diminishing the effective specific surface area; self-assembly techniques are suitable for fabricating specialized morphological structures, yet the process complexity is high and cost control remains challenging. Regarding microstructural modulation, heterojunctions formed at the MOF–substrate interface can facilitate electron transfer; however, the quantitative regulation mechanism of interfacial interactions remains unclear, and the structure–performance relationships governing MOF loading, distribution patterns, and overall performance have yet to coalesce into a unified paradigm. At the processing level, bulk materials fabricated via conventional powder metallurgy, tableting, and sintering methods exhibit low densification and abundant internal defects. Emerging shaping technologies, such as 3D printing and freeze casting, enable the customization of components with complex geometries, yet they still suffer from poor compatibility with existing industrial production lines. Furthermore, controversy exists regarding whether emerging processes can genuinely enhance the practical energy storage performance of devices in terms of cost–benefit ratio: Some studies argue that customized architectures can significantly improve mass transfer efficiency, while opposing views contend that the cost increase associated with additional processes far exceeds the performance gains.

4.3 Commercialization barriers for large-scale industrial application

The transition of MOFs from laboratory to industrial-scale application necessitates overcoming multiple commercialization barriers, including cost, stability, batch production, processing, and recycling. The most critical unresolved controversy in this field centers on the trade-off between stability and performance. Researchers generally acknowledge that the stability of MOFs under practical energy storage conditions can be enhanced through post-modification and composite modification; however, such modification processes typically incur additional costs and inevitably block partial pores and reduce active sites. Regarding how to balance stability enhancement with performance loss, no universal optimization standard currently exists, and the vastly differing stability requirements across various application scenarios render the establishment of a unified evaluation system difficult. Regarding cost control, the synthesis of high-performance MOFs currently relies predominantly on expensive metal nodes or complex organic linkers, resulting in persistently high raw material

costs. Developing green and environmentally friendly synthetic routes, substituting precious metals with earth-abundant transition metals, and designing simplified organic linkers represent the core pathways for cost reduction. However, MOFs synthesized via low-cost approaches often fail to meet application requirements in terms of performance, necessitating the establishment of a cost–performance balance evaluation system. Moreover, significant controversy exists within the field concerning which low-cost strategy holds the greatest industrialization prospect: One group of researchers advocates for water-based green synthetic routes, arguing that they can substantially reduce solvent costs and environmental hazards; the opposing view contends that MOFs obtained from aqueous synthesis exhibit poor crystallinity and insufficient batch stability, making it difficult to meet the consistency requirements of energy storage devices. Another group of researchers proposes using industrial-grade raw materials to simplify synthetic steps, while skeptics argue that impurities in industrial raw materials significantly affect the nucleation and growth of MOFs, making performance reproducibility difficult to guarantee. In terms of stability, MOFs are susceptible to structural collapse or deactivation under practical application conditions due to factors, such as humidity, temperature, and pH. Although stability can be enhanced through strategies, including the introduction of cross-linkers, post-synthetic modification, and the construction of composite materials, such modification processes often incur additional costs or compromise partial porosity and active sites. Concerning batch production, conventional solvothermal synthesis suffers from long reaction times and low yields. Emerging technologies, such as continuous flow reactors, spray drying, and freeze casting, can achieve large-scale preparation, yet the batch consistency and structural integrity of the products require further validation. Furthermore, the high investment threshold of emerging large-scale synthesis technologies remains controversial regarding their suitability for promotion among small and medium-sized enterprises. Additionally, three critical issues must be addressed in practical device applications: First, the low packing density of MOFs leads to insufficient active material loading per unit volume, directly diminishing device energy density, and whether densification processes will damage the pore structure and ion transport performance of MOFs remains a subject of divergent experimental conclusions; second, the poor adaptability of electrode fabrication processes, conventional doctor-blade coating exhibits weak interfacial adhesion and facile detachment of active materials, while vacuum filtration and electrodeposition struggle to fabricate high-loading thick electrodes, which process is more suitable for large-scale production of MOF-based electrodes has yet to achieve industry consensus; third, inadequate binder compatibility, traditional PVDF binders block MOF pores, and aqueous binders exhibit weak interfacial adhesion with hydrophobic MOFs, resulting in elevated interfacial impedance and degraded cycling stability, while research on the compatibility of novel binders with MOFs remains in its infancy. Regarding recycling, efficient reversible synthesis and deconstruction technologies for MOFs remain lacking; the resource utilization rate of discarded MOFs is low, and this readily causes environmental pollution and cost wastage. Moreover, whether it is necessary to establish a dedicated MOF recycling system or whether existing electrode material recycling processes can be adapted has yet to achieve a unified industry perspective.

5 Conclusions and perspectives

As an emerging class of porous crystalline materials, MOFs have

garnered widespread attention in the field of energy storage and conversion due to their high specific surface area, tunable pore structures, and abundant active sites. This review has systematically summarized recent advancements in MOFs across electrochemical energy storage, electrocatalysis, and photocatalysis, comprehensively exploring structure–performance relationships from nanoscale design to macroscopic applications. Despite the superior performance demonstrated by MOFs at the laboratory scale, significant challenges remain in bridging the gap between nanoscale design and large-scale practical implementation.

Looking ahead, the evolution of MOFs is poised to advance towards intelligent design, multifunctional integration, and the establishment of standardized performance evaluations. First, with the progress of artificial intelligence and machine learning, intelligent design is set to become a pivotal trend. By constructing extensive databases and integrating deep learning algorithms, potential target materials can be rapidly screened, and smart recommendations for new MOF designs can be generated. This data-driven approach not only accelerates the discovery process but also predicts performance outcomes, thereby substantially enhancing research efficiency. Second, multifunctional integration represents a key strategy for augmenting the comprehensive performance of MOFs. Through compositing MOFs with other functional materials and optimizing their composition and structure, synergistic enhancements can be achieved. This enables the materials to possess diverse properties, such as efficient energy conversion, robust mechanical strength, and superior conductivity, meeting a broader spectrum of application requirements. Furthermore, the establishment of performance evaluation standards is imperative for fostering the healthy development of the MOF industry. Currently, the standardization system for MOF materials remains incomplete, characterized by a lack of unified metrics and testing protocols, which hinders their widespread adoption. Consequently, establishing a robust performance evaluation framework and formulating scientific testing standards will be a priority for future research. Standardization efforts will not only help regulate market order and ensure product quality but also facilitate collaboration among different laboratories, collectively propelling the advancement of MOF technologies. Finally, with the application of more advanced technologies and methodologies, it is anticipated that a greater number of high-performance MOF materials will enter the market, making substantial contributions to resolving energy and environmental challenges.

It has been empirically demonstrated that MOFs play an indispensable role in driving the energy revolution and achieving sustainable development goals. Confronted by the dual pressures of global climate change and resource scarcity, the development of clean, efficient, and renewable energy sources has become an international consensus. By virtue of their unique physicochemical properties, MOFs exhibit broad application prospects in energy storage and conversion. MOFs and their derivatives provide abundant active sites that facilitate ion transport, thereby increasing the energy and power density of batteries. Moreover, they can exhibit high conductivity and rapid response characteristics, significantly boosting device performance. As effective catalysts or catalyst supports, MOFs participate in critical chemical reactions, such as HER, OER, ORR, and CO₂RR, holding significant importance for achieving low-carbon emissions and clean energy utilization. Additionally, MOFs play vital roles in gas adsorption and separation, thermal catalysis, and sensing, further expanding

their scope of application and promoting technological development in related fields.

In conclusion, as an emerging multifunctional material, MOFs hold vast potential in the realm of energy storage and conversion. With deepening research and technological progress, it is believed that innovative MOF materials will continue to emerge, providing robust support for addressing global energy and environmental challenges. Researchers will continue to strive towards overcoming existing technical bottlenecks and exploring greener, more efficient synthesis processes, contributing to the development of the MOF industry. Through continuous effort, MOFs are expected to become one of the key materials for building a low-carbon economy and achieving sustainable social development, aiding humanity in progressing towards a brighter future.

Data availability

Not applicable.

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Declaration of competing interest

All the contributing authors report no conflict of interests in this work.

Author contribution statement

H. W.: Conceptualization, investigation, formal analysis, resources, writing – original draft, writing – review & editing. X. X. G.: Formal analysis, visualization. L. Y.: Methodology, visualization, project administration, writing – original draft, writing – review & editing. S. P. F.: Investigation, formal analysis. All the authors have approved the final manuscript.

Use of AI statement

None.

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