

Application of MOF Material Modification Strategy in Electrolysis of Water

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Abstract

As a key component of sustainable hydrogen production technology, electrocatalytic water decomposition has promoted the development of various catalysts. Metal organic frameworks (MOFs) have become potential candidate catalysts for oxygen evolution reaction (OER) and hydrogen evolution reaction (HER). However, MOFs materials face challenges related to stability, conductivity and scalability. This review systematically summarizes the basic chemical reactions and reaction mechanisms of electrolytic water reaction, deeply analyzes the application of MOFs materials in electrolytic water, and finally puts forward suggestions for the structural modification strategy of MOFs materials in the future.

Keywords

MOFs Materials; Electrolytic Water; Material Modification.

1. Introduction

The escalating issues of energy poverty and environmental pollution emerged as the primary impetus for the development of green and sustainable energy sources to replace traditional fossil fuels, thereby addressing global warming and climate challenges. Hydrogen energy was regarded as a clean fuel due to its high energy density, ease of storage, transportability, and negligible environmental impact [1]. The existing commercial hydrogen production technology did not align with the principles of environmental friendliness and sustainable development. Nevertheless, the electrolysis of water only generates hydrogen and oxygen, adhering to the ethos of sustainable development, albeit requiring enhanced energy efficiency [2].

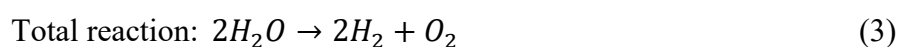
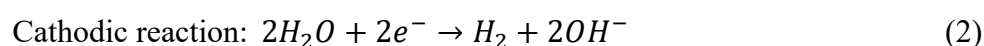
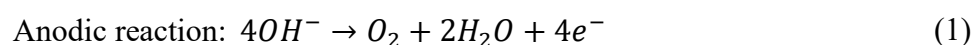
The reaction in electrolytic water is divided into two and a half reactions, hydrogen evolution reaction occurs at the cathode and oxygen evolution reaction occurs at the anode. Under standard conditions, the standard potential relative to the reversible hydrogen electrode (RHE) is about 1.23 V [3]. The OER step involves different adsorption and desorption energies of reactants, products and various reaction intermediates, including O*, OH* and OOH*, leading to complex OER mechanism [4]. To date, the most effective electrocatalysts for oxygen evolution reaction (OER) comprised noble metal-based ruthenium and iridium oxides, while platinum on carbon (Pt/C) served as the benchmark catalyst for hydrogen evolution reaction (HER). However, the limited availability and high cost of these precious metals restricted their applicability on an industrial scale [5]. Due to these limitations, researchers are looking for cheaper alternatives than noble metal catalysts, mainly using more abundant transition metals, such as nickel, cobalt, copper and manganese [6]. The unique 3d orbital configuration of these metals promotes the attachment and separation of intermediates on the catalyst, thus reducing the energy barrier of the complex four electron transfer mechanism. However, transition metals will be affected by pH environment, so the long-term stability and high activity of the catalyst

still need to be studied [7]. Metal organic frameworks are porous coordination compounds formed by self-assembly of metal ions and organic ligands through coordination bonds. Because the inorganic organic combination of MOF can produce unlimited possibilities, it has the characteristics of adjustable pore, ultra-high specific surface area, controllable composition and a variety of coordination modes. Thanks to the high density of metal active sites, the original MOFs with different MO_6 -based inorganic units show great potential in electrocatalysis [8][10]. The tunability and spatial arrangement of MOF structure enable it to introduce various active species to achieve high catalytic activity. However, due to the low conductivity, limited stability, difficulty in adjusting the crystal size of the micro region and the dense structure of MOF materials, the formation of active sites is hindered, resulting in unsatisfactory electrochemical performance [11]. The limited conductivity of most metal-organic framework (MOF) materials stemmed primarily from the non-conjugate nature of organic linkers or coordination bonds. Consequently, considerable efforts were made to enhance the material's conductivity, albeit with restricted success. Designing conductive MOF materials remained a challenging task. Various modification techniques and engineering approaches have since surfaced to address these constraints, all directed towards crafting MOF frameworks with superior stability and reactivity.

Therefore, this paper reports systematically on the modification strategies of MOF in recent years. Firstly, the basic mechanism of electrolyzed water is systematically introduced, including the reaction process of electrolyzed water under alkaline conditions, AEM mechanism and LOM mechanism. Secondly, the challenges faced by MOFs materials are discussed. Finally, the synthesis strategy and structure optimization method of MOF are summarized. It is believed that this paper will provide new ideas for the modification strategy of MOFs, so as to further promote the wide application of MOFs materials.

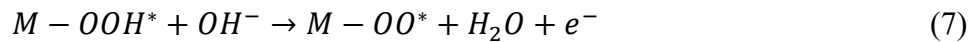
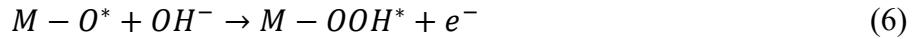
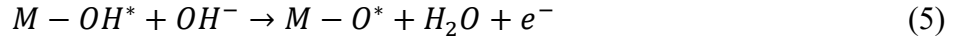
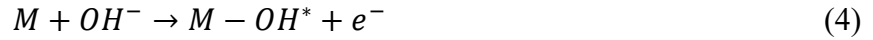
2. Electrolytic Water Mechanism

As a technology for green hydrogen production, electrolyzed water received extensive attention from scientific researchers. It combined with renewable energy, allowing the generated electrical energy to be converted into sustainable and stable chemical energy. The electrolytic water device comprised an electrolyte, a cathode, and an anode. It included two half-reactions: the oxygen evolution reaction at the anode and the hydrogen evolution reaction at the cathode. The application of voltage caused water molecules near the cathode and anode to dissociate, resulting in the formation of H^+ and OH^- , which subsequently generated hydrogen and oxygen, respectively. Based on the type of reactive electrolytes, electrolyzed water technology was categorized into solid electrolyzed water, alkaline electrolyzed water, and proton exchange membrane electrolyzed water [12]. In alkaline electrolytic water, a substantial quantity of hydroxyl ions in the electrolyte amassed on the anode surface, facilitating electron loss and oxygen production via oxidation. The distinct reactions at the anode and cathode were as follows:



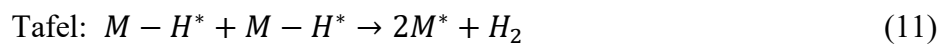
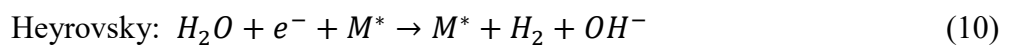
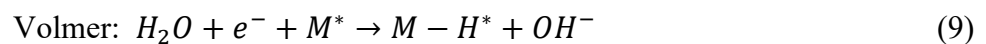
OER as an important semi reaction of electrolytic water, is mainly a process of H_2O or OH^- losing electrons to generate O_2 , which is a four electron transfer reaction. OER had different reaction mechanisms, including the adsorption evolution mechanism (AEM) initiated by metal atoms as active centers and the lattice oxygen oxidation mechanism (LOM) involved in the reaction. In 1986,

Matsumoto and Sato summarized the reaction mechanism for OER reaction under alkaline and acidic conditions. The conventional AEM under alkaline conditions included the following steps [13]:



First, H₂O molecule was adsorbed on the metal active site through electron transfer (* represents the intermediate substance adsorbed on the active site), and the H₂O molecule is deprotonated to generate the hydroxyl intermediate (OH*) in the adsorbed state. In the second step, the hydroxyl intermediate is further deprotonated and converted into the oxygen intermediate (O*) in the adsorbed state, and then the oxygen intermediate further reacts with the proton to form the OOH* in the adsorbed state. The first two steps are affected by the adsorption strength of the intermediate product, and finally release the M site at the metal M active site to generate O₂ molecule and release it. Compared with the AEM mechanism, the difference of LOM mechanism is that lattice oxygen directly participates in the formation of O-O bond, skipping the formation of intermediate OOH*, resulting in lower theoretical overpotential than the AEM mechanism and accelerating the reaction kinetics. However, since the essence of LOM mechanism is that the lattice oxygen of the catalyst participates in the reaction, if the regeneration rate of the catalyst cannot keep up with the consumption rate, it will lead to the accumulation of oxygen vacancies and structural collapse. And with the precipitation of lattice oxygen, some metal ions may be dissolved or segregated, which will lead to activity attenuation [14].

The principle of the main reaction process of hydrogen evolution from HER reaction is the reduction of protons and water molecules, and the process of hydrogen ions obtaining electrons to generate hydrogen. However, due to the different properties of acidic and alkaline conditions, the reaction paths are also different. HER reaction in alkaline electrolyte was mainly introduced. HER was a double electron transfer reaction ($H_2O + 2e^- \rightarrow 4OH^- + H_2$). There were usually two paths: water molecule dissociation adsorption Volmer path, electrochemical desorption Heyrovsky path and chemical desorption Tafel path [14].



The rate of hydrogen evolution reaction in alkaline medium is usually several orders of magnitude slower than that in acidic environment. This occurred because, in an alkaline medium, the cleavage

of the strong covalent H-O-H bond proved to be more significant than that of the weak covalent H_3O^+ . The performance of the alkaline hydrogen evolution reaction (HER) improved effectively through the design of an electrocatalyst that exhibited both good electrolytic water properties and excellent adsorption capacity for hydrogen-producing ions. Based on the reaction path involved in Volmer and Heyrovsky steps, there were four main factors that may affect the performance of alkaline HER, namely, water adsorption at the active site, water decomposition ability, hydrogen binding energy and oxygen ion adsorption strength, which constitute the primary challenge to develop efficient alkaline hydrogen evolution reaction catalysts [15].

3. Defect Engineering

Lattice defect engineering, serving as a precise strategy for material modification, can effectively disrupt the inherent symmetry of the coordination field surrounding the active center, thereby prompting the redistribution and reconfiguration of local electronic states [16]. This perturbation in the electronic structure not only refines the band structure of the active center but also effectively modulates the electronic spin configuration of transition metal ions. Shreyanka et al. [17] utilized a novel method of pulsed laser ablation in liquid (PLAL) technology for etching to synthesize Cu-BTC, Co-BTC, and Ni-BTC with variable sizes. In an alkaline medium, a comprehensive study of the electrochemical reactions of HER and OER was conducted on these MOF materials. Among them, Co-BTC/CC exhibited an overpotential as low as 370 mV for the OER reaction and 437 mV for the HER reaction at a current density of 10 mA cm^{-2} . The bifunctional Co-BTC can also serve as a water electrolyze, achieving excellent stability at a cell voltage of 2.03 V at a current density of 10 mA cm^{-2} , suitable for long-term operation cycles. Chemical characterization results indicate that the highly exposed metal sites at the framework nodes of Co-based MOFs generate oxygen vacancies, which can alter ionic/electronic conductivity and electronic structure, thereby improving catalytic performance. Ji et al. [18] induced lattice strain in NiFe-MOF by using monocarboxylic acid as a linker instead of part of the dicarboxylic acid, leading to changes in the electronic structures of nickel and iron. The original NiFe-MOF was synthesized via solvothermal method using terephthalic acid and Ni/Fe metal sources. When part of the dicarboxylic acid linker was replaced with the monocarboxylic acid benzoic acid linker, the interlayer spacing expanded to 10.6 Å. In terms of catalytic performance, the lattice-strained LS-NiFe-MOF exhibited superior catalytic activity compared to the unstrained NiFe-MOFs. In alkaline electrolyte, LS-6%-NiFe-MOF showed the best electrochemical performance with an overpotential of 230 mV and a Tafel slope of 86.6 mV dec⁻¹ at 10 mA cm^{-2} . After a stability test at a voltage of 1.5 V for 20000 s, the curve of LS-6%-NiFe-MOF showed no significant decay, demonstrating excellent durability and stability. The defect engineering strategy not only enhances the Ni-O-Fe interaction, thereby altering the valence band structure of MOFs, but also changes the coordination environment of metal ions. These reports all involve defect-induced spin state reconstruction, which directly optimizes the adsorption/desorption behavior of key reaction intermediates on active sites, effectively reducing the Gibbs free energy barrier of the rate-determining step of the reaction, and ultimately achieving significant improvement in electrocatalytic reaction kinetics.

4. Doping Engineering

The catalytic activity can be enhanced by incorporating multivalent metal sites or heteroatoms into the crystal lattice of MOFs materials, thereby modifying the electronic structure, chemical composition, and geometric configuration surrounding the active sites of these materials [19]. Cation doping generally entails the incorporation of transition metals, such as Fe, Ni, and Cu, to modulate the d-band electronic configuration of the metal center. Anion doping generally incorporates non-metallic elements, such as N, P, and S, which indirectly regulate the electronic density at the metal center by modifying the charge distribution within the coordination environment and the electron donor/acceptor characteristics of the ligands. Cheng et al. [20] fabricated a nickel-based terephthalic acid (BDC) metal-organic framework, denoted as S-NiBDC, through the incorporation of sulfur (S)

elements into the MOF lattice. The as-synthesized S-NiBDC nanosheet arrays, exhibiting a thickness of approximately 16 nanometers, were grown on nickel foam with a sulfur doping level of 1.67 wt.%. Notably, the S-NiBDC arrays demonstrated exceptional electrochemical performance, featuring a remarkably low overpotential of 310 mV at a current density of 1.0 A cm⁻² and a minimal Tafel slope of 75 mV dec⁻¹. It demonstrates exceptional stability in alkaline hydrogen evolution reactions (HER), outperforming nearly all previously reported MOF-based HER electrocatalysts under high current density conditions, and even surpassing the noble metal Pt/C catalyst (462 mV at 1.0 A cm⁻²). The incorporation of sulfur (S) doping stabilizes the nickel-oxygen bonds, mitigating structural damage to the MOFs and thereby enhancing electrocatalytic stability. The S-modified Ni sites effectively facilitate water activation kinetics, thereby accelerating the alkaline HER process. Guo et al. [21] successfully synthesized a novel flower-like amorphous Co-MI precursor via a straightforward pyrolysis process, wherein MI denotes 2-methylimidazole. Subsequently, the bimetallic CoMo-MI was prepared through a solvothermal reaction followed by crystallization. Further pyrolysis treatment resulted in the formation of CoMo-MI-T (with T representing temperatures of 400, 500, 600, and 700°C). Notably, CoMo-MI-600 exhibited the most outstanding OER performance, attributed to its hierarchical porous nanostructure, optimal N doping, graphitic layers, and well-preserved flower-like morphology. At a current density of 10 mA cm⁻², CoMo-MI-600 demonstrated an overpotential of 316 mV and a Tafel slope of 89.9 mV dec⁻¹. During chronoamperometric measurements, the current density of CoMo-MI-600 remained remarkably stable, maintaining 99.8% at an overpotential of 320 mV for the initial 2 hours. Nevertheless, owing to slight detachment of the sample from the electrode surface over time, the retention rate declined to 87.0% over an extended period of 40000 seconds. Burud et al. [22] employed a straightforward one-step solvothermal approach to synthesize FeBTC, CoBTC, and CoFeBTC, and carried out an in-depth investigation into their OER performance through the incorporation of secondary metal ions. Upon introducing Co ions into FeBTC, CoFeBTC demonstrated a notably low overpotential of merely 310 mV and a Tafel slope of 122 mV dec⁻¹ under alkaline conditions at a current density of 10 mA cm⁻². The stability assessment via i-t curve analysis revealed that CoFeBTC maintained its stability over a 24-hour period, with only a 14% decline in relative current density. A comparative analysis of LSV curves before and after the stability test further corroborated the enhanced durability, as evidenced by a mere 10 mV increase in overpotential. Metal doping augments the synergistic interaction between metals, consequently elevating redox activity, accelerating charge transfer rates, and bolstering structural stability. The incorporation of a secondary metal serves to modulate the intrinsic electronic structure of the framework, thereby generating multiple active sites with distinct oxidation states. This electronic perturbation not only optimizes the adsorption energy of reaction intermediates but also enhances the intrinsic catalytic activity. Furthermore, the inherent porous architecture of bimetallic MOFs provides a high specific surface area and effectively accommodates volumetric expansion during electrochemical cycling, leading to improved structural stability and enhanced energy storage capacity. Collectively, these attributes contribute to superior electrical conductivity, accelerated reaction kinetics, and an overall enhancement in electrocatalytic efficiency.

5. Composite Engineering

After modifying single MOFs materials, their catalytic performance can be significantly enhanced, and the scope of practical applications is also expanded. However, this does not completely solve the inherent challenges of MOFs, as well as the difficulties in improving actual performance due to the limited functionalization of MOFs themselves. Through continuous in-depth research on MOFs, it has been discovered that the organic integration of MOFs with other functional materials (such as conductive substrates, metal nanoparticles, two-dimensional materials, carbon materials, metal oxides, conductive polymers, quantum dots, organic molecules, etc.) not only significantly enhances the electronic transmission ability and structural stability of the materials, but also generates new active sites through interfacial synergistic effects, thereby improving the overall catalytic effect. Bai et al. [23] proposed a novel composite strategy combining MOF with an electrospun carbon nanofiber

(CNF) matrix. Through a controllable MOF-on-MOF approach, they synthesized a CoP/CoFeP heterostructure based on electrospun carbon nanofibers (CoP/CoFeP@CNFs). CoP/CoFeP@CNFs exhibited excellent bifunctional activity and stability in HER and OER. Under alkaline conditions, CoP/CoFeP@CNFs achieved an overpotential of only 113 mV to reach a current density of 10 mA cm⁻² in the HER reaction. Furthermore, the Tafel slope of CoP/CoFeP@CNFs was significantly reduced to 78.2 mV dec⁻¹. Comparative LSV curves after 2000 consecutive CV cycles and a 20-hour i-t curve stability test demonstrated the catalyst's excellent long-term stability. The rich interface structure of CoP/CoFeP@CNFs regulates the geometric configuration of the catalyst, affects the chemisorption process of intermediates, and optimizes the surface reaction sites, thereby enhancing catalytic activity and stability. In the OER reaction, CoP/CoFeP@CNFs exhibited higher catalytic performance, achieving a current density of 10 mA cm⁻² with only 215 mV. Moreover, it had the lowest Tafel slope of 81.01 mV dec⁻¹, indicating faster OER kinetics. Yue et al. [24] developed a novel structure, MOF@POM, by self-assembling a dual-template metal-organic framework (MOF) with a polyoxometalate (POM). MOF@POM exhibits excellent electrocatalytic performance, particularly in oxygen evolution reaction (OER). At a current density of 10 mA cm⁻², MOF@POM demonstrates an extremely low overpotential of 178 mV. Additionally, MOF@POM performs well in alkaline electrolyte membrane water electrolysis (AEMWE). At 25 °C, the cell voltage required for MOF@POM to achieve a current density of 1 A cm⁻² is only 1.83 V, significantly lower than the 1.97 V required for pure MOF. In terms of stability, its current density can be maintained above 2 A cm⁻² for up to 5140 hours, with a decay rate of only 0.02 mV h⁻¹, far superior to traditional metal double hydroxides. By constructing a composite material combining POM and MOF, a robust upper structure is established on the MOF, thereby addressing the dissolution and corrosion issues of active sites in metal (oxy)hydroxides. Current MOF composite engineering has shifted from simple physical composites to deeper structural optimizations such as interface engineering, electronic structure tuning, and construction of atomically dispersed sites.

6. Conclusion

This article systematically reviews the latest advancements in improving metal-organic frameworks (MOFs) to achieve enhanced electrocatalytic water splitting in recent years, with a focus on their applications in hydrogen evolution reaction (HER) and oxygen evolution reaction (OER). Metal-organic framework materials exhibit great potential for applications in constructing coupled hydrogen production systems due to their highly tunable pore structure, abundant active sites, and component diversity. However, MOFs materials face several key challenges. Firstly, the poor intrinsic conductivity of most MOFs limits electron transport. Secondly, their electrochemical stability under acidic and alkaline conditions is insufficient, leading to structural collapse or metal dissociation. Lastly, the synthesis cost of MOFs materials is high, and large-scale preparation is complex. In view of these issues, the following future research directions are proposed: first, defect engineering; second, doping engineering; and third, composite MOFs material engineering. These approaches can effectively adjust the electronic structure of MOFs, expose active sites, and enhance stability, thereby significantly improving catalytic performance.

References

- [1] M.P. Browne, F. Novotny', C.L. Manzanares Palenzuela, J. Šturala, Z. Sofer, M.Pumera. 2H and 2H/1T-Transition Metal Dichalcogenide Films Prepared via Powderless Gas Deposition for the Hydrogen Evolution Reaction[J]. ACS Sustain, Chem. Eng, 2019, 7 (19): 16440-16449.
- [2] L. Ouyang, J. Jiang, K. Chen, M. Zhu, Z. Liu. Hydrogen Production via Hydrolysis and Alcoholysis of Light Metal-Based Materials[J]. A Review, Nanomicro Lett, 2021, 13 (1) :134.
- [3] Hyeonjung Jung, Seokhyun Choung, Jeong Woo Han. Design principles of noble metal-free electrocatalysts for hydrogen production in alkaline media: combining theory and experiment[J]. Nanoscale Advances, 2021, 3(24): 6797-6826.

- [4] James D. Blakemore, Robert H. Crabtree, Gary W. Brudvig. Molecular Catalysts for Water Oxidation[J]. Chem. Rev, 2015, 115:12974–13005.
- [5] Chatenet, M., Pollet, B. G., Dekel, D. R., Dionigi, F., Deseure, J., Millet, P., et al. Water electrolysis: from textbook knowledge to the latest scientific strategies and industrial developments[J]. Chem. Soc. Rev, 2021, 51:4583-4762.
- [6] Lu, X. F., et al. Metal–organic frameworks based electrocatalysts for the oxygen reduction reaction[J]. Angew. Chem. Int. Ed, 2019, 59:4634-4650.
- [7] Zand, Z., Mohammadi, M. R., Sologubenko, A. S., Handschin, S., Bagheri, R., Chernev, P., et al. Oxygen evolution reaction by silicate-stabilized manganese oxide[J]. ACS Applied Energy Materials, 2023, 6(3):1702-1713.
- [8] Camillo Spöri, Pascal Briois, et al. Experimental Activity Descriptors for Iridium-Based Catalysts for the Electrochemical Oxygen Evolution Reaction (OER)[J]. ACS Catal, 2019, 9, 8, 6653-6663.
- [9] Sengeni Anantharaj, et al. “The Fe Effect”: A review unveiling the critical roles of Fe in enhancing OER activity of Ni and Co based catalysts[J]. Nano Energy, 2021, 80, 105514.
- [10] Chunhua Yang, Zhao-Di Yang, et al. Theory-Driven Design and Targeting Synthesis of a Highly-Conjugated Basal-Plane 2D Covalent Organic Framework for Metal-Free Electrocatalytic OER[J]. ACS Energy Lett, 2019, 4, 9, 2251-2258.
- [11] Zhanwu Lei, Tanyuan Wang, et al. Recent Progress in Electrocatalysts for Acidic Water Oxidation[J]. Advanced Energy Materials, 2020, 10(23): 2000478.
- [12] KE EBAŞ A, KAYFECİ M, BAYAT M. Chapter 9-Electrochemical hydrogen generation[M]. Solar Hydrogen Production. Academic Press, 2019: 299-317.
- [13] Y. Matsumoto, E. Sato. Electrocatalytic properties of transition metal oxides for oxygen evolution reaction[J]. Materials Chemistry and Physics, 1986, 14(5): 397-426.
- [14] Congling Hu, et al. Recent progress made in the mechanism comprehension and design of electrocatalysts for alkaline water splitting[J]. Energy Environ Sci, 2019, 12, 2620.
- [15] Zhi Wen Chen, Jian Li, Pengfei Ou, et al. Unusual Sabatier principle on high entropy alloy catalysts for hydrogen evolution reactions[J]. Nature Communications, 2024, 15, 359.
- [16] Yujia He, Wei Liu, Jingquan Liu. MOF-based/derived catalysts for electrochemical overall water splitting[J]. Journal of Colloid And Interface Science, 2024, 661, 409-435.
- [17] Shankar Naik Shreyanka, Jayaraman Theerthagiri, Seung Jun Lee, et al. Multiscale design of 3D metal–organic frameworks (M–BTC, M: Cu, Co, Ni) via PLAL enabling bifunctional electrocatalysts for robust overall water splitting[J]. 2022, 446, 2, 137045.
- [18] Qianqian Ji, Yuan Kong, Chao Wang, et al. Lattice Strain Induced by Linker Scission in Metal-Organic Framework Nanosheets for Oxygen Evolution Reaction[J]. ACS Catalysis, 2020, 10, 10, 5691-5697.
- [19] Jun-Wei Ji, Li-Jing Zhang, et al. Ligand doping engineering induced robust internal electric field in MOFs/BiVO₄ photoanode for water splitting[J]. Chemical Engineering Journal, 2024, 484, 149597.
- [20] Fanpeng Cheng, Xianyun Peng, Lingzi Hu, et al. Accelerated water activation and stabilized metal-organic framework via constructing triangular active-regions for ampere-level current density hydrogen production[J]. Nature Communications, 2022, 13, 6486.
- [21] Yuanyuan Guo, Qi Huang, Junyang Ding, et al. CoMo carbide/nitride from bimetallic MOF precursors for enhanced OER performance[J]. International Journal of Hydrogen Energy, 2021, 46(43): 22268-22276.
- [22] Mahesh Burud, Supriya A. Patil, Vidhya Jadhav, et al. Synergistic Effect of CoFe Bimetallic MOF for Efficient Electrocatalytic OER in Alkaline Media[J]. Energy & Fuels, 2025, 39, 28, 13648-13657.
- [23] Lu Bai, Xin Wang, Minghua Huang, et al. Fabrication of MOF-on-MOF derived heterostructure on carbon nanofibers towards highly efficient electrocatalytic water splitting[J]. Journal of Alloys and Compounds, 2026, 1056, 186621.
- [24] Kaihang Yue, Ruihu Lu, Mingbin Gao, et al. Polyoxometalated metal-organic framework superstructure for stable water oxidation[J]. Science, 2025, 388(6745): 430-436.