Research Progress and Future Directions of Metal-Organic Framework-Derived Single-Atom Catalysts for Electrolytic Water Splitting

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Abstract. Addressing the high cost and limited efficiency of precious metal catalysts in water electrolysis for hydrogen production, single-atom catalysts (SACs) have emerged as promising alternatives due to their nearly 100% atomic utilization and exceptional catalytic activity. However, their tendency to migrate and agglomerate under operational conditions poses a significant challenge to their practical application. Metal-organic frameworks (MOFs), with their well-defined pore structures and ultra-high specific surface areas, offer an ideal platform to address these issues by precisely anchoring and stabilizing single atoms. Based on this premise, this review focuses on single-atom catalysts derived from metal-organic framework precursors. It systematically summarizes the synthesis strategies, performance tuning mechanisms, and recent advances in their application for water electrolysis. Furthermore, the key challenges currently hindering their large-scale preparation and long-term stability are critically analyzed. This review aims to provide theoretical insights and research directions for the design of highly efficient and cost-effective catalysts for sustainable hydrogen production.

1 Introduction

Amid global efforts to transition energy systems and achieve carbon emission peak targets, hydrogen energy is emerging as a strategic clean energy source. Its electrolytic hydrogen production technology, which delivers higher purity and zero-carbon emissions compared to other energy sources, is recognized as the future of green hydrogen's large-scale application [1]. However, commercialization still faces challenges such as slow kinetics in the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER). Despite the exceptional activity of platinum group and iridium/ruthenium-based catalysts, their scarcity and high costs hinder widespread adoption [2]. Additionally, non-precious metal catalysts struggle with issues like low active site utilization and poor structural stability [3].

Single-atom catalysts (SACs) have garnered widespread attention and research [4, 5] due to their theoretical 100% atomic utilization, well-defined active center structures, and tunable electronic properties, which demonstrate exceptional performance in practical applications.

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However, challenges such as metal atom migration and aggregation during preparation, as well as difficulties in large-scale synthesis, remain unresolved [6]. Metal-organic frameworks (MOFs) offer novel solutions for SACs through their periodically arranged metal nodes, precisely controllable pore structures, and ultra-high specific surface areas [5, 7]. Enhancing SACs via MOFs-based precursor or carrier preparation, thermal treatment, and modification can significantly improve their performance [8]. MOF-derived SACs have become a key research focus for improving water electrolysis catalytic performance and reducing dependence on precious metals. This paper systematically reviews the application of MOF-based SACs in water electrolysis for hydrogen production, highlighting their advantages through synthesis strategies, performance tuning mechanisms, and catalytic performance in hydrogen evolution, oxygen evolution, and water splitting reactions. By comparing them with precious metal and conventional non-precious metal catalysts, the study demonstrates their superiority in atomic utilization, activity, and cost-effectiveness. The paper not only addresses current challenges in large-scale preparation and stability but also provides effective directions for developing efficient and low-cost hydrogen production catalysts in the future.

2 Reaction mechanism and catalysts of electrolysis of water

2.1 Reaction mechanism of electrolysis of water

The essence of electrolysis of water is the decomposition of water molecules into hydrogen (H_2) and oxygen (O_2) through redox reactions driven by an electric field. As shown in Fig. 1, the total reaction equation is:

$$2H_2O \rightarrow 2H_2\uparrow + O_2\uparrow \quad (1)$$

The hydrogen evolution reaction (HER) at the cathode occurs under acidic conditions, where H^+ accepts electrons to form H_2. The equation is as follows:

$$2H^+ + 2e^- \rightarrow H_2\uparrow \quad (2)$$

Under alkaline conditions, the equation for H_2O accepting electrons to form H_2 and OH^- is:

$$2H_2O + 2e^- \rightarrow H_2\uparrow + 2OH^- \quad (3)$$

The core of the reaction is the equilibrium control of hydrogen adsorption and desorption.

The oxygen evolution reaction (OER) at the anode occurs under acidic conditions. The equation for the loss of electrons by H_2O to form O_2 and H^+ is:

$$2H_2O \rightarrow O_2\uparrow + 4H^+ + 4e^- \quad (4)$$

Under alkaline conditions, the equation for the loss of electrons by OH^- to form O_2 and H_2O is:

$$4OH^- \rightarrow O_2\uparrow + 2H_2O + 4e^- \quad (5)$$

OER involves a four-electron transfer process, characterized by complex reaction steps and high energy barriers, which serves as the rate-limiting step in water electrolysis [9].

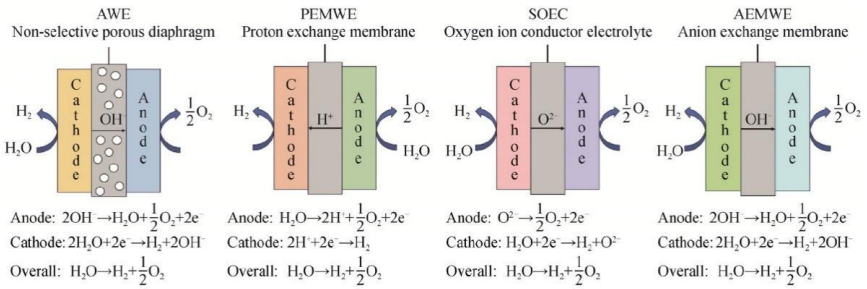

Fig. 1. Schematic diagram of the basic principle of electrolytic hydrogen production technology [10].

2.2 Comparison of electrolysis water catalysts and their performance

Water catalysts in electrolysis are considered the basic materials to achieve the high efficiency of the hydrogen production and minimize expenses. At present, they may be ridiculously classified into three types, all of which have considerable disparities in terms of activity, stability, cost, and application scenarios.

2.2.1 Precious metal catalyst

Platinum (Pt), iridium (Ir), ruthenium (Ru) and their oxides constitute largely the type of catalysts that are used and they have excellent catalytic activity. They have been identified as being the most promising catalysts to the existing hydrogen evolution reactions (HER, Pt-based), and oxygen evolution reactions (OER, Ir/Ru-based). In addition, the catalysts are shown to have very low overpotential in acidic conditions, high-efficiency electron transfer as well as high short-term stability [11]. But yet the big scale use of them is a difficulty due to the absence of resources and their high cost. An example is that ruthenium-based catalysts are likely to get oxidized and dissolved by conditions of high-potential, and they lack long-term stability [12]. They are normally used in precision laboratory research as well as small-scale electrolysis equipment with severe conditions.

2.2.2 Non-noble metal based catalyst

The present research will target MOF-derived single-atom catalysts, such as transition metal alloy/ oxide/hydroxide/sulfide/ nitride/as well as Fe-N-C, Co-N-C, Ni-N-C single-atom catalysts and ruthenium-modified MOF-derived carbon materials. The benefits of these catalysts include low-cost manufacture and plentiful quantity of reserves [13], almost 100% atom utilization, and high quantities of active sites, uniformly distributed. Their performance is further boosted by the fact that the exact energy of adsorption of reaction intermediates using coordination environment modulation is optimized. Like the above-mentioned types, these catalysts have low overpotential properties in hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) and even better performance. Also, owing to the special structure of MOF-derived carbon carriers, they have ultra-high surface area of specific surface area, and three-dimensional porous structures, which develops their mass transfer efficiency greatly. Resilient cooperation between the individual atoms, as well as the carrier, works well to avoid the loss of metal atoms that provides a long-lasting stability [14]. Nevertheless, single-atom catalysts have not reached perfection yet because they still struggle with several problems, including underdeveloped mass production procedures and the tendency of aggregation of single-atom catalysts in batch production. Also, the fact that they partially depend on the precious metal catalysts requires cost optimization. These catalysts

are nowadays used in medium pressure alkaline water electrolysis facilities, high-current-density electrolysis facilities in industry, and in renewable energy coupled hydrogen production facilities.

2.2.3 Metal-free carbon-based catalyst

The main types of the third one include nitrogen-doped graphene, porous carbon nanotubes, heteroatom (nitrogen, sulfur, phosphorus) co-doped carbon materials. These materials are most likely to be made up of carbon; they have a number of important merits which are immense low cost, chemical stability, high electrical conductivity and raw materials are readily available. Nevertheless, these catalysts have the poorest catalytic activity, elevated hydrogen and oxygen potential, unbalanced distribution of active sites, low activity, inadequate catalytic selectivity and contains intrinsic deficiencies in the alkaline systems. Their major disadvantages render their current applicability in small scale electrolysis units with low efficiency and low current density, albeit them being applicable with other catalysts.

Out of the three mentioned types of catalysts, the MOF-derived single-atom catalyst in the second non precious metal system exemplifies such benefits as cost-effectiveness, high stability, high atom utilization efficiency and high activity. This breakthrough has served well to tackle the performance drawbacks that have failed the development of conventional non-precious metal and precious metal catalysts and this could possibly be a key material in breaking the commercialization bottleneck in hydrogen production by the electrolysis of water. The scholarly worth of this study as well as its importance to industry is high.

2.3 The effect of MOF structure on single atom catalyst

MOF precursors are used in high-performance single-atom catalysts (SACs). In the absence of periodic metal nodes and tunable channels that serve as an accurate anchoring point, the migration and aggregation of metal atoms during the pyrolysis process are likely, which causes a low active site density and inadequate stability of single-atom catalysts. The optimum catalytic efficiency requires the MOF structure to comprise of high density and uniform distribution of metal nodes, multi abundant of nitrogen coordination sites as well as multi-layered channels (micro/mesoporous) structures. These properties allow creating highly loaded single atoms and creating active sites of M-Nx that remain stable after the pyrolysis process, thus creating carbon carriers with large specific surface areas and good mass transfer efficiency. It is only in such circumstances that the advantages of atomic utilization efficiency and stability of single-atom catalyst can be fully achieved.

3 The loading mechanism, properties and structure of MOF-derived single-atom catalysts and element control

3.1 Single atom loading mechanism and key technology

The metal-organic frameworks (MOFs) have been an important natural medium of single-atom catalysts. The physical confinement and chemical coordination of the metal atoms onto MOF precursors or its derivatives is done by the exact process of single-atom loading. The main idea of reaching this is the inhibition of metallic atom migration and aggregation to establish high-density, highly-dispersed distribution of single atoms. In this regard, various unique loading processes and technical methods are created.

3.1.1 In-situ conversion of precursor metal nodes loaded

The technique involves the use of metal nodes (e.g., Zn^{2+}, Co^{2+}, Fe^{3+}, Ni^{2+}) of MOFs as a source of single atoms. This is done by high-temperature pyrolysis so as to carbonize the organic ligands in MOFs to produce nitrogen-doped carbon carriers. Instead, the metal nodes are minimized to elemental metals anchored on the carbon carrier surface via coordination of nitrogen, to produce single-atom catalyst M-N-C-type M-N-C-type M-N-C-type catalysts (M atoms). It does not need any other source of metal, has an easy and efficient loading process and the loading capacity of the mono atom depends mostly on the metal quantity of the MOF precursor.

3.1.2 Impregnation adsorption loading of exogenous metal ions

In the case of MOF-derived carriers of carbon (e.g. porous carbon following MOF pyrolysis, nanocage structures), exogenous metal ions (also Ru^{3+}, Pt^{4+}, Ir^{3+}, Cu^{2+}) are impregnated on the carrier surface. Such metal ions are then reduced (chemically or photo reduced or thermally) to be converted to single atoms, which are then attached to defect sites or heteroatom coordination sites on the carrier. The type of single atoms can be easily controlled which is good because the loading level is maximized by controlling the metal ion concentration and the impregnation time.

3.1.3 Space confined auxiliary load

Agglomeration is avoided by building physical barriers and chemical traps into MOF precursors by adding guest molecules, which may be nitrogen-containing polymers (e.g., polyaniline, melamine), carbon quantum dots, or metal-organic complex into the reagent and reducing the migration paths that metal atoms can follow during not only the pyrolysis reaction but also the subsequent finalizations.

3.1.4 Precise atomic layer deposition

The Atomic Layer Deposition (ALD) technique is a method of loading single atoms into the reaction chamber by alternating between introducing metal precursors (e.g., trimethylaluminum, tungsten hexacarbonyl) and reactive gases (e.g. H_2, O_2) into it and performing deposition on the MOF or its derivative substrates at an atomic scale. This system has high loading precision, single atoms are uniformly distributed, and loading quantities can be accurately controlled, but the equipment is expensive and therefore, only used in large scale.

3.2 Regulation mechanism of catalytic performance

Stability, selectivity, and activity of SACs, which are based on MOF, are highly reliant on the atomic level structure. This is an outcome of accurate regulation using composition, synthesis and post-processing strategies of MOF precursors, which attain three significant mechanisms.

3.2.1 Element composition and synergistic effects

Metallic centers (e.g., cobalt, iron, nickel or ruthenium) have inherent electronic structures (d-band centers) giving them specific metal center selectivity. These selectivity tune

adsorption strengths of H star in hydrogen evolution reaction (HER) and adsorption capacity of oxygen containing intermediates in oxygen evolution reaction (OER) to different extents. The atomic control of the heteroatoms is performed through doping the support with atomic species (mainly nitrogen with the addition of sulfur, phosphorus, etc.) to create heteroatomic configurations M-Nx. This coordination changes charge distribution and electronic density, thus maximising adsorption energy. Various forms of nitrogen (e.g., pyridine nitrogen, graphite nitrogen, etc.) are also observed to have different effects on the promotion of particular reactions. The bimetallic/metallic coordination effect is a two-case effect, which means that the addition of the second metal atom (e.g., cobalt/iron, nickel/ruthenium) as an interaction site with other metal atoms is possible, leading to synergistic catalysis. The method alters the reaction pathways, decreases energy stages at the key points and eventually increases activity and stability.

3.2.2 Coordination environment regulation

The unsaturation and electronic state of the metal center (characteristic of 2-6) depend directly on the coordination number of the center. Low numbers of coordination are related to high reactivity whereas, high numbers of coordination stabilize the metal center, therefore, it is important to pick the best amount of coordination. Secondly, the adsorption behavior of reaction intermediates is fine-tuned by the action of electronegativity differences between the type of coordinating atoms (N, O, S). In addition, defect engineering adds carbon defects or metal holes to MOF-transformed carbon carriers to generate more active sites and changing the local electronic state of nearby single-atom sites to control catalytic activity.

3.2.3 Optimization of carrier structure

Skimming morphology and pore structure of carriers to elevate specific surface area and hierarchy of pore structure (micropores, mesopores, macropores) gained upon MOF precursors are key improvement efforts. Two-dimensional nanosheets are given as an example, which helps to move the electrons and open active sites, whereas three-dimensional porous networks or nanocage structures have better ability to transfer the mass between electrons and products, especially when the density of current is high. The other method of enhancing performance through carrier alteration is the stability anchoring. MOFs yield nitrogen-doped carbon matrix on which there are strong M-N-C bonds that offer constant anchoring sites to single atoms. This plays the effective role of inhibiting the atomic migration, aggregation, or leaching during catalysis, which is used as a structural base of long-term stability.

4 Application performance analysis and prospects

The MOF-derived single-atom catalysts (SACs) are superior in supporting the three fundamental reactions of water electrolysis in comparison with the noble metal-based and non-noble metal-based catalysts due to almost-theoretical atomic utilization and highly tunable electronic structure.

4.1 High-performance applications and data comparison

MOF-derived non-precious metal-based SACs show excellent results in the study of hydrogen evolution reaction (HER). As an example, cobalt individual atoms accurately decorated with V 2 CT o MXene supports have much better performance than control

samples without MOF structure or traditional carbon supports. The high extent of hybridization between the cobalt 3d orbital and substrate oxygen 2p orbital is an effective one in maximizing the hydrogen adsorption free energy, which facilitates the catalyst to reach the overpotential that would support 10 mA/cm^2 current density in an alkaline media, equivalent to commercial Pt/C catalysts. By comparison, under such conditions, traditional non-precious metal catalysts or simple carbon-supported catalysts have overpotentials of tens to hundreds of millivolts on average [15].

In the case of the oxygen evolution reaction which is rate-determining (OER), MOF SACs are more effective. By controlling defects and coordinations, the use of the two-dimensional Fe-MOF-derived catalysts has a reduction of close to 100 mV overpotential versus conventional iron-based catalysts (e.g., Fe_2O_3 or supported Fe/C) with no particular modulation of MOF precursor structure. In addition, cobalt / nickel bimetallic catalysts that are fabricated through MOF strategy on MXene surfaces are stable at a current density of 500 mA/cm^2 industrial conditions despite continuous loading in excess of 100 hours, which is much longer than the MOF strategy under identical operating conditions limits many other conventional catalysts under these conditions.

When used in wholly hydrolyzed processes, a high-performance stability of MOF SACs plays a vital role in the overall performance of the electrolyzers. The electrolysis platform that has been prepared using a single-atom ruthenium (Ru)-functionalized Co_3S_4 -bound MOF-derived bifunctional catalyst shows great efficiency in the combination with variable renewable energy patterns, e.g., solar and wind energy. It has many times the hydrogen production and continuous operation stability under intermittent power supply conditions than do systems with conventional cobalt sulfide or ruthenium-based nanoparticle catalysts, enabling important technical assistance to renewable energy-based hydrogen production [1].

4.2 Key challenges and future outlook

Although there has been major advancement in the domain of laboratory-based research, the derivation of SACs through MOF continues to confront daunting issues in switching off the theoretical ideals into laboratory application.

The biggest challenge in present industries use is large-scale production. Synthesis strategies in existent syndromes whether direct pyrolysis or spatial confinement methods can only be used in small scale syntheses at the gram level. As the scale gets up to production of kilo-mole scale, there is a bound to be some problems associated with metallic atoms namely the problem of aggregation, distribution of active sites and moving costs up to the sky. In addition, despite the remarkable long-term stability of single-atom catalysts, there are not enough industry-scale challenges. Even in such harsh environments as high acids/strong bases or high current densities, the works of catalysts are in danger to experience loss of their metal atoms, corrosion of their carbon carriers, and structural losses, not satisfying the industrial standards of stability during thousands of hours of work. The theoretical shortage presenting in the atomic-level design of active sites renders the optimization of performance challenging and optimistic, and use of empirically-adjusted performance is not fully concluded. Lastly, the high-performance SACs rely either on precious metal such as ruthenium and platinum, or highly complex preparation methods, remains a serious issue in terms of cost management.

Innovation of technology and innovation of theory are two dimensions that should be given attention in future research. Cosmogonic emphasis ought to be placed on the investigation of process level scalable green synthesis technologies, including continuous pyrolysis, template-based batch production, and the investigation of low-cost MOF precursors such as biomass to ensure reduced costs. Also interface engineering, such as the creation of protective layers (e.g., carbon layers or oxide layers) and optimization of

coordination environments to increase the strength with which single atoms bind to carriers, can be used to increase the stability of such systems by increasing the pH tolerance regime, and enhancing current fluctuation adaptability. In theory, the design of active sites can be directed by higher-order computational methods, such as density functional theory (DFT), and cutting-edge characterization technologies, such as spherical aberration-corrected electron microscopy and X-ray absorption fine structure (XAFS), can clarify the mechanism of catalysis at the atomic level, which would allow the problem of empirical regulation.

As industry, academia, and research are very strongly integrated and the technology improves, MOF-derived SACs will become a key catalytic technology to catalyze the hydrogen transition in the world towards the goal of the so-called dual carbon by overcoming the existing bottlenecks.

5 Conclusion

The present paper presents a systematic review of the recent development in the research on MOF-derived SACs in the context of water electrolysis, focusing on its synthesis techniques (direct pyrolysis, mixed metal approach, spatial confinement approach), performance optimization methods (defect engineering, coordination environment engineering, support and morphology engineering), and its application in HER, OER, and in general, in the water splitting reaction. Having high atomic utilization, tunable electronic structures, and desirable catalytic properties, MOF-derived SACs provide a viable solution to the issues of expensive and inefficient generation of hydrogen by precious metal catalysts using water electrolysis.

The most critical challenges in the field are also determined with scalability in production, long-term stability, accurate regulation, and cost regulation, and specific directions of research are proposed in the future. As notable improvement in synthesis and gradual apply more control theories and even closer integration of industry-academia-research collaboration MOF-derived SACs will become fundamental catalysts of industrial-level hydrogen generation through water electrolysis, which can offer the key to the transition toward energy and the attainment of carbon peaking and carbon neutrality objectives.

References

1. M. Yue, H. Lambert, E. Pahon, et al. Hydrogen energy systems: A critical review of technologies, applications, trends and challenges. Renewable and Sustainable Energy Reviews **146**, 111180(2021)
2. J. Zhou, S. Qiu, X. Hou, T. Ni, C. Zhang, S. Dai, X. Wang, G. Wang, H. Jiang, M. Huang, Defect‐Driven Stepwise Activation of Metal–Organic Frameworks Toward Industrial‐Level Anion Exchange Membrane Water Electrolysis. Angewandte Chemie **137**, e202503787(2025)
3. D. Li, M. Chen, D. Liu, et al. Engineering ruthenium species on metal–organic frameworks for water electrolysis at industrial current densities. Advanced Energy Materials **15**, 2404714(2025)
4. N. Song, J. Jiang, S. Hong, et al. State-of-the-art advancements in single atom electrocatalysts originating from MOFs for electrochemical energy conversion. Chinese Journal of Catalysis **59**, 38-81(2024)
5. A. Amjad, M. Murtaza, SAA. Shah, et al. Atomically precise MOF-Based electrocatalysts by design: Hydrogen evolution applications. Fuel **385**, 134021(2025)
6. X. Yang, A. Wang, B. Qiao, et al. Single-atom catalysts: a new frontier in heterogeneous catalysis. Accounts of Chemical Research **46**, 1740-1748(2013)

7. H. Furukawa, KE. Cordova, M. O'Keeffe, et al. The chemistry and applications of metal-organic frameworks. Science **341**, 1230444(2013)
8. D. Li, HQ. Xu, L. Jiao, et al. Metal-organic frameworks for catalysis: State of the art, challenges, and opportunities. EnergyChem **1**, 100005(2019)
9. C. McCrory, S. Jung, IM. Ferrer, et al. Benchmarking hydrogen evolving reaction and oxygen evolving reaction electrocatalysts for solar water splitting devices. Journal of the American Chemical Society **137**, 4347-4357(2015)
10. D. Shukai, Z. Xiong, Y. Zhangtao, C. Mingxuan, et al. Research Progress on Key Materials for Alkaline Electrolysis Cells. Journal of Silicate **52**, 06, 1841-1860(2024)
11. T. Reier, M. Oezaslan, P. Strasser. Electrocatalytic oxygen evolution reaction (OER) on Ru, Ir, and Pt catalysts: a comparative study of nanoparticles and bulk materials. Acs Catalysis **8**, 1765-1772(2012)
12. S. Cherevko, S. Geiger, O. Kasian, et al. Oxygen and hydrogen evolution reactions on Ru, RuO2, Ir, and IrO2 thin film electrodes in acidic and alkaline electrolytes: A comparative study on activity and stability. Catalysis Today **262**, 170-180(2016)
13. J. Song, C. Wei, ZF. Huang, et al. A review on fundamentals for designing oxygen evolution electrocatalysts. Chemical Society Reviews **49**, 2196-2214(2020)
14. H. Fei, J. Dong, Y. Feng, et al. General synthesis and definitive structural identification of MN4C4 single-atom catalysts with tunable electrocatalytic activities. Nature Catalysis **1**, 63-72(2018)
15. T. Ni, X. Hou, H. Wang, L. Chu, S. Dai, M. Huang, Controllable defect engineering based on cobalt metal-organic framework for boosting oxygen evolution reaction. Chinese Journal of Structural Chemistry **43**, 100210(2024)