

Unlocking the electrocatalytic potential of porous high-entropy materials: Synthesis, structure, and electrocatalytic performance

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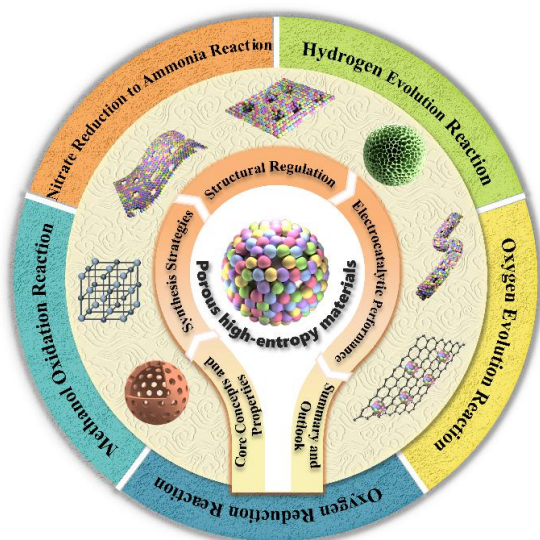
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This review systematically summarizes the synthesis strategies, structural regulation approaches, and electrocatalytic applications of porous high-entropy materials, aiming to provide useful references for research in related fields.

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ABSTRACT: Porous high-entropy materials (PHEMs) integrate the solid-solution characteristics of multiple elements with hierarchical porous structures, combining intrinsic advantages such as high-entropy effects and lattice distortion with structural benefits like high active specific surface area and efficient mass transport channels. They demonstrate remarkable potential in energy conversion reactions including hydrogen evolution, oxygen evolution, and nitrate reduction to ammonia, offering a promising alternative to traditional noble metal catalysts. In recent years, significant progress has been made in the synthesis, structural regulation and electrocatalytic performance research of PHEMs. However, this field is still in the development stage. Currently, there is a lack of comprehensive and systematic understanding of the intrinsic relationship between material composition, microstructure, and macroscopic catalytic performance. **Synthesis methods remain to be systematically summarized**, and the multi-component nature poses challenges in controlling composition and phase structure. Some approaches also suffer from issues such as non-uniform pore size distribution and element segregation, which hinder practical application and commercialization. Therefore, this review systematically outlines the core definition and features of PHEMs, elaborates on the principles and advances of mainstream synthesis strategies, summarizes the governing principles of structural regulation, analyzes their electrocatalytic performance, discusses existing key challenges, and looks forward to future research directions, aiming to provide systematic guidance for related studies.

KEYWORDS: porous high-entropy materials; electrocatalysis; synthesis strategies; structural regulation

1 Introduction

With global carbon emissions and energy consumption on a steady rise, ensuring energy sustainability has emerged as a pressing global challenge[1, 2]. Currently, fossil fuels constitute approximately 95% of the world's energy consumption. It is projected that total energy demand will quadruple by 2050, reaching 28 terawatts (equal to 20 billion tons of oil per year)[3]. To effectively replace fossil fuels and meet future clean energy needs, significant challenges remain in developing large-scale, high-performance energy conversion systems[4-6]. In response, researchers have conducted extensive studies aimed at developing more efficient and cost-effective energy conversion and storage technologies to facilitate the large-scale production and storage of clean energy[7].

As a cornerstone of future energy systems, the development and utilization of renewable energy have drawn global attention. However, constrained by factors such as geographical variability and seasonal fluctuations, its supply remains intermittent and unstable, making it difficult to meet the steadily growing energy demands of modern

society. The key to breaking this bottleneck is to develop efficient energy storage and conversion technologies. Electrocatalysis, which lies at the heart of energy production, storage, and recycling, serves as a crucial bridge between renewable energy sources and end-use applications[8, 9]. Typical electrocatalytic reactions, such as hydrogen evolution reaction (HER), oxygen evolution reaction (OER), oxygen reduction reaction (ORR), methanol oxidation reaction (MOR) and nitrate reduction to ammonia (NO_3RR), are widely regarded as the most promising eco-friendly and sustainable energy conversion strategies[10-18]. However, traditional electrocatalysts currently in widespread use rely heavily on precious metals such as Pt, Ru, Pd and Ir. Their inherent drawbacks, including scarcity, high cost, and limited efficiency under practical conditions, have significantly impeded large-scale industrial application[19, 20]. Although low-loading precious or non-precious metal materials are seen as potential cost-effective alternatives, they often exhibit limitations including suboptimal electronic structure control, sluggish reaction kinetics, and insufficient stability, which prevent them from satisfying practical requirements. Therefore, the development of novel alternative electrocatalysts with high energy conversion

efficiency, low cost and good stability has become a research hotspot and core direction in electrochemistry[21].

In the innovative research of electrocatalytic materials, multi-metal systems demonstrate significantly superior performance compared to single-metal catalysts, owing to their enhanced adaptability in multi-electron transfer processes and reactions with complex active sites[22, 23]. In recent years, the strategic planning for the electrochemical discipline has also explicitly identified multi-component system design and interface regulation as key development directions in the field of electrocatalysis, emphasizing the breakthrough of performance bottlenecks of traditional single-component catalysts through multi-element synergistic effects[24]. In this context, high-entropy materials (HEMs) have attracted wide attention in electrocatalysis for their favorable cost-effectiveness, flexible tunability, excellent catalytic activity and corrosion resistance[3, 25-28]. The high-entropy concept was first introduced into multi-component alloy development back in 2004[29]. Such materials usually contain five or more main elements in near-equimolar ratios (5-35 at.%) and their broad composition and structure space bring unique physicochemical properties such as lattice distortion, slow diffusion and multi-element synergy[30]. These properties can effectively adjust the electronic structure of catalysts and optimize reactant adsorption and product desorption, thereby substantially improving electrocatalytic performance and opening new pathways for material innovation.

Derived from HEMs, porous high-entropy materials (PHEMs) have emerged as a forefront research focus in electrocatalysis in recent years. Their unique structural advantages provide essential support for enhanced electrocatalytic performance, the well-developed pore structure endows the material with a high specific surface area[31], facilitating the exposure of active sites, improving contact between reactant molecules and catalyst, and thereby significantly increasing reaction involvement[32, 33]. Meanwhile, the porous structure effectively enhances mass transport. In typical reactions such as water splitting, connected pores provide efficient channels for fast reactant diffusion and timely product release, which reduces mass transport resistance and improves reaction rate and overall efficiency[34]. In terms of synthesis, preparation methods for PHEMs continue to advance. Template and dealloying methods are two widely used strategies, the template method can precisely control pore size, shape and distribution by employing hard templates such as silica nanospheres or soft templates like surfactant micelles[35, 36]. The dealloying method builds a porous framework by selectively dissolving specific components in the alloy[37]. Different synthesis methods exert a substantial influence on the final structure and performance of porous high-entropy materials. So, selecting and optimizing synthesis methods according to performance needs, enabling the fabrication of PHEMs with optimal structural characteristics and electrocatalytic performance, remains an important and ongoing research direction.

With their obvious structural and performance advantages, porous high-entropy materials show

remarkable potential for electrocatalytic applications. On this basis, a series of HEMs have been widely developed. These include high-entropy alloys (HEAs), high-entropy borides (HEBs), high-entropy oxides (HEOs), high-entropy sulfides (HESs), high-entropy phosphides (HEPs), high-entropy carbides (HECs), high-entropy nitrides (HENs) and high-entropy metal-organic frameworks (HE-MOFs)[38-45]. The structural tunability of these materials gives them unique physicochemical properties, thereby creating broader for various energy-related applications. Among them, the open-pore structure and adjustable porosity of porous HEMs not only facilitate mass and charge transport but can also regulate the diffusion flux of reactants and products within the confined porous space, which contributes to enhanced selectivity toward target products. Coupled with good structural and chemical stability, these materials can maintain excellent electrocatalytic performance during long-term operation, laying a solid foundation for practical industrial applications.

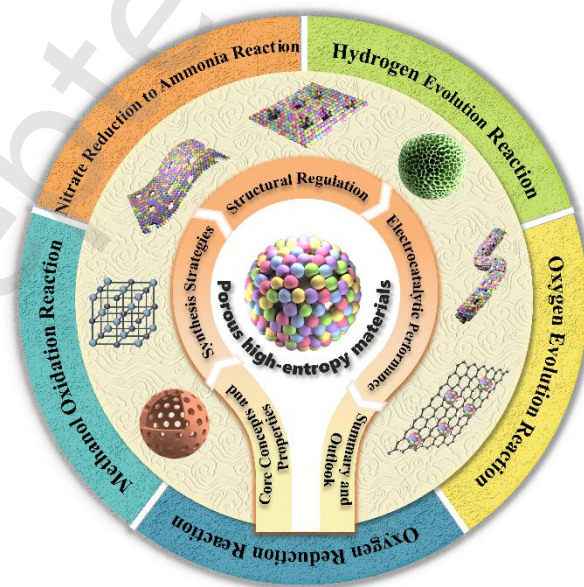


Figure 1. Schematic diagram of the research framework and typical electrocatalytic reaction systems for electrocatalytic porous high-entropy materials.

In summary, as shown in **Fig. 1**, this review systematically explores and summarizes the intrinsic correlation between the synthesis methods, structural characteristics of porous high-entropy materials and their typical electrocatalytic performances such as water splitting, and further investigates their electrocatalytic potential. This study not only deepens the understanding of electrocatalytic reaction mechanisms but also provides new insights and theoretical guidance for designing more efficient electrocatalysts. Furthermore, it contributes to advancing emerging energy sectors, such as hydrogen energy, and accelerates the transition toward a sustainable energy future. Looking ahead, with continuous breakthroughs in synthesis technology and deeper research on structure-performance relationships, porous HEMs are expected to make greater progress in electrocatalysis, offering essential material support for the global energy transition.

2 Definition, core characteristics, and synergistic interplay

2.1 Definition

Porous high-entropy materials represent a novel class of functional materials with synergistic performance via composition design and structure regulation. Their core feature lies in the precise integration of intrinsic properties of high-entropy materials and structural functions of porous materials, forming a unique "composition-structure-performance" trinity system. In terms of composition, high-entropy materials serve as the core performance base. They follow the basic design principles of high-entropy systems, typically prepared by incorporating five or more metallic elements in near-equi-molar ratios, with the atomic concentration of each element maintained within the range of 5-35 at.% [46, 47]. This multi-element equimolar composition creates a vast space of compositions and crystal structures, giving rise to a pronounced high configurational entropy effect. As a thermodynamic driving force, high configurational entropy endows materials with unique physicochemical properties different from traditional single-metal or low-alloy materials[48, 49]. Lattice distortion, slow atomic diffusion and multi-element synergy are the most prominent ones, playing a decisive role in material performance[50, 51]. Among these properties, lattice distortion changes the electronic band structure and surface electron cloud distribution of materials, providing a structural basis for precise regulation of catalytic active sites. Slow atomic diffusion enhances the structural stability of materials during cyclic service, effectively mitigating the loss and agglomeration of active components. Electron transfer and orbital hybridization between multiple elements can precisely optimize the adsorption energy barrier of reaction intermediates on the catalyst surface, thereby accelerating the reaction kinetics process.

2.2 Core characteristics

Structural characteristics. Porous high-entropy materials exhibit excellent structural tunability, which is mainly reflected in three core aspects: pore size control, diverse morphology dimensions, and broad compositional compatibility. In terms of pore size control, precise regulation can be achieved through various preparation strategies. Template methods, including soft- and hard-templating[52, 53], can realize continuous adjustment of mesopore size in the range of 2-50 nm. For macropore structure, pore sizes from 50 nm to the micrometer scale can be controlled by adjusting the diameter of template spheres. Meanwhile, materials can be precisely prepared into diverse morphologies, including 0D, 1D, 2D and 3D complex structures. They are compatible with multiple systems, such as metals, metal oxides, sulfides, carbon materials, and their composites, and these structural characteristics enable them to effectively optimize mass transfer efficiency and active site exposure in energy conversion and storage fields, thereby meeting the requirements of different application scenarios[54].

High specific surface area and efficient mass transfer characteristics. Rich pore structures endow

materials with high specific surface area and efficient mass transfer properties. A large number of pores significantly increase the exposure of active sites. For example, the specific surface area of some macroporous carbon-based high-entropy materials can reach 103-150 m² g⁻¹ [55, 56], while mesoporous metal oxide-based high-entropy materials can also exceed 80 m² g⁻¹ [57, 58]. Interconnected pores (especially mesopore-macropore hierarchical structures) can build efficient mass transfer channels. These structures facilitate electrolyte penetration and ion diffusion, promote the rapid desorption of products such as H₂ and O₂, and inhibit concentration polarization caused by bubble retention. In typical hierarchical structures, the synergy between macropores and mesopores can significantly improve reaction efficiency[55].

Electrocatalytic characteristics. The superior performance of porous high-entropy materials stems from multi-factor synergy. High specific surface area and pore-exposed active sites provide abundant reaction interfaces, thereby enhancing reaction participation. Interconnected pores reduce mass transfer resistance, while the high conductivity of some high-entropy material substrates reduces charge transfer resistance[57, 59]. Together, these features collectively optimize the overall catalytic kinetics. In addition, multi-element doping or composite regulation can precisely adjust the electronic structure of active sites. It optimizes the intermediate adsorption energy barrier and enhances catalytic selectivity and intrinsic activity[56]. At the same time, the porous framework can effectively inhibit the agglomeration and loss of active components, ensuring long-term catalytic stability of materials.

2.3 Synergistic interplay between high-entropy effect and porous structure

The high-entropy effect and the porous structure in porous high-entropy materials do not operate independently; rather, they reinforce each other in ways that collectively enhance electrocatalytic performance. This synergy can be understood from several perspectives.

Active site exposure and electronic modulation. The porous architecture naturally exposes a large number of surface sites, providing abundant reaction interfaces for electrocatalytic processes. Across these exposed surfaces, the high-entropy effect introduces compositional diversity. Lattice distortion arising from atomic size mismatch among different elements can modulate the electronic environment around surface sites, and this effect may be more pronounced at pore edges and curved regions where atomic coordination is already incomplete. For reactions such as HER, OER, or MOR, the density and electronic structure of active sites largely determine catalytic activity. The combination of a porous framework with a high-entropy composition thus offers dual benefits: porosity provides a high density of accessible active sites, while lattice distortion optimizes their electronic structure. Such dual advantages are not easily achieved in single-metal or low-entropy porous materials.

Mass transport and surface reaction kinetics. In electrocatalysis, whether reactants can effectively reach active sites and whether products can detach from the

electrode surface in a timely manner often dictate the overall reaction rate, particularly at high current densities. The open pore network in PHEMs facilitates rapid diffusion of electrolyte ions and efficient release of gas products such as H_2 and O_2 , thereby reducing mass transport overpotentials. Meanwhile, the high-entropy effect can influence surface reaction kinetics through two mechanisms. First, multi-element synergy lowers the energy barriers of key elementary steps, such as water dissociation in HER or O–H bond cleavage in OER. Second, the sluggish atomic diffusion inherent to high-entropy systems helps maintain a stable atomic configuration on pore surfaces during catalysis, preventing undesirable surface reconstruction that could otherwise compromise activity. Together, these features allow PHEMs to sustain high reaction rates at relatively low overpotentials.

Structural and chemical stability under operating conditions. Stability is an essential requirement for practical electrocatalysts. High-entropy alloys and oxides are known for their resistance to phase segregation and elemental leaching, a property attributed to the high configurational entropy that stabilizes the solid solution. In PHEMs, this intrinsic stability is particularly valuable, as porous materials with large specific surface areas tend to undergo accelerated degradation. The high-entropy matrix appears to mitigate this issue by suppressing preferential dissolution of any single element, a common failure mode in multi-metal catalysts. In addition, the porous framework can accommodate lattice strain caused by volume changes during catalytic cycling, thereby inhibiting crack propagation and delaying mechanical failure. This mutual reinforcement between electronic stability (from the high-entropy effect) and mechanical buffering (from porosity) extends the operational lifetime of PHEMs in applications such as water electrolyzers and fuel cells.

Composition-porosity co-optimization for specific reactions. Different electrocatalytic reactions place distinct demands on catalyst composition and pore architecture. For HER, an ideal catalyst requires moderate H^* binding energy along with efficient bubble detachment. High-entropy alloys containing Pt, Ru, or Ni can provide optimized d-band centers, while macropores or mesopores facilitate rapid H_2 release. For OER, transition metal-based high-entropy oxides such as spinel or rock-salt structures benefit from enhanced metal–oxygen covalency driven by lattice distortion, while interconnected mesopores promote OH^- transport and O_2 escape. For MOR, high-entropy alloys with diluted Pt sites help mitigate CO poisoning, and a porous structure accelerates CO_2 release and methanol replenishment. In each case, the synergy between high-entropy composition and porous architecture enables performance optimization that cannot be achieved by tuning either feature alone.

Taken together, the interplay between the high-entropy effect and the porous structure is fundamentally multiplicative rather than additive. The porous framework provides a high density of accessible active sites and efficient mass transport, while the high-entropy composition offers site diversity, tunable electronic properties, and resistance to degradation. Neither feature

alone can deliver all these benefits simultaneously. This synergy distinguishes PHEMs from conventional porous catalysts, which often lack electronic tunability, and from non-porous high-entropy materials, which suffer from limited site accessibility. It is this combination of features that positions PHEMs as a promising class of materials for energy-related electrocatalytic reactions.

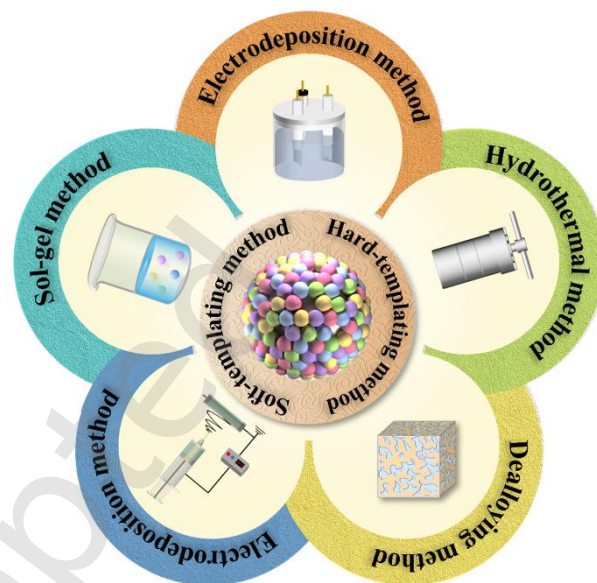


Figure 2. Main synthetic methods of porous high-entropy material.

3 Synthetic strategies for porous high-entropy materials

Fig. 2 systematically summarizes the synthetic strategies for porous high-entropy materials, including template-based methods (hard and soft templates) and template-free methods (dealloying, electrodeposition, electrospinning-calcination, solvothermal /hydrothermal, sol-gel), with each approach possessing distinct mechanisms, advantages and limitations.

3.1 Classification by template method

3.1.1 Hard template method.

The hard template method employs materials with well-defined morphology and rigid structure as core templates, such as polystyrene (PS) colloidal crystals, SiO_2 , metal-organic frameworks (MOFs), Cu nanowires, alumina hollow spheres and mesoporous KIT-6. It relies on the rigid support and clear size characteristics of templates, and combined with processes including impregnation-calcination, solvothermal-pyrolysis, and galvanic replacement-dealloying, this approach enables the construction of mesoporous, macroporous and hierarchical porous structures in high-entropy oxides, alloys, selenides and composite foams. By selecting templates of different sizes and types, the pore structural parameters of the materials can be precisely

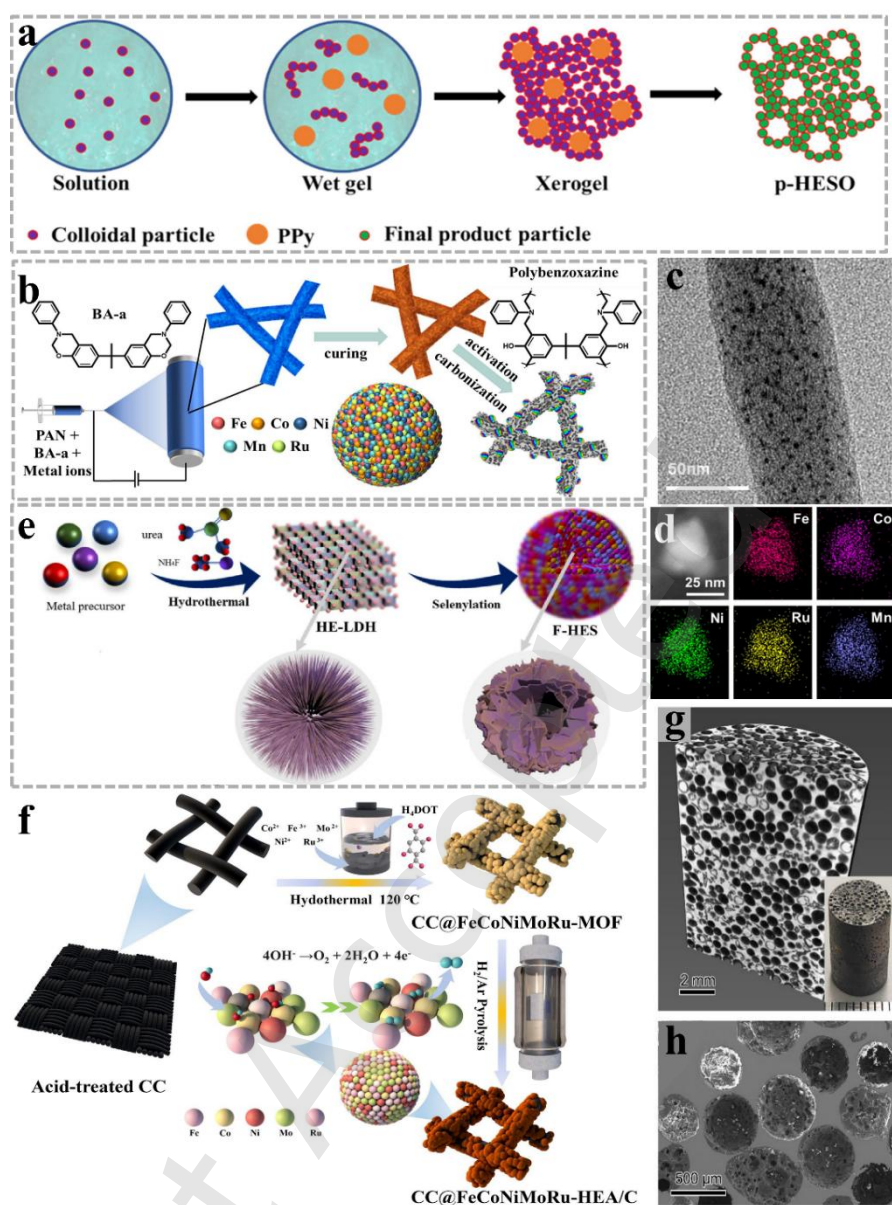


Figure 3. (a) Schematic illustration of the preparation strategy for p-HESO-x. Adapted with permission from ref. [35] copyright 2025, Elsevier. (b) Schematic illustration of the synthesis process for FeCoNiMnRu-HCB_{0.5} catalyst, (c) TEM image and (d) STEM-EDS mapping images of FeCoNiMnRu-HCB_{0.5} catalyst. Adapted with permission from ref. [60] copyright 2025, Elsevier. (e) Schematic illustration of the preparation process for F-HES. Adapted with permission from ref. [61] copyright 2023, Elsevier. (f) Schematic illustration of the synthesis for FeCoNiMoRu-HEA/C on carbon cloth. Adapted with permission from ref. [62] copyright 2024, Elsevier. (g) CT-reconstructed 3D image, (h) SEM secondary electron image of the morphology of a polished section. Adapted with permission from ref. [63] copyright 2023, Elsevier.

regulated, effectively addressing the issues of disordered pores and uncontrollable size in template-free preparation.

Polymer materials are often used as hard templates to construct mesoporous or fibrous porous high-entropy materials due to their excellent processability and highly designable. Typical examples include composite fiber and poly-pyrrole microsphere templates, which are suitable for preparing high-entropy material/carbon composite catalysts and high-entropy spinel oxides, respectively. In the preparation of three-dimensionally ordered macroporous (3DOM) HEOs, Duan et al.[64] used self-assembled polystyrene (PS) microspheres as hard templates.

Multi-metal nitrate precursors were impregnated into the ordered PS array, followed by calcination to obtain the final 3DOM HEOs. The rigid, ordered structure of PS templates ensured the formation of macropores (diameter 254-522 nm) in the HEOs. The high-entropy effect reduces the crystallization temperature, thereby preventing structural collapse after template removal. The obtained 3DOM HEOs have uniform element distribution and high oxygen vacancy concentration. Zhang et al.[35] innovatively used *in-situ* generated poly-pyrrole (PPy) microspheres as hard templates, combined with the sol-gel method, to synthesize porous high-entropy spinel oxides (p-HESO) (Fig. 3a). It

mainly solves the key challenges of particle agglomeration and low specific surface area caused by high temperature in traditional high-entropy oxide synthesis. The synthesis system uses Fe, Co, Ni, Cr and Mn nitrates as metal sources, along with citric acid as the complexing agent. After adding pyrrole monomers into the ethanol-water mixed solution, H_2O_2 is used as the oxidant. *In-situ* polymerization of pyrrole was achieved under water bath conditions at 90 °C. In this process, complexes formed by metal ions and citric acid are uniformly distributed around PPy microspheres, leading to the synchronous formation of a composite wet gel. As rigid hard templates, PPy microspheres initially limit the aggregation range of metal complexes through space occupancy effect. Then it is dried at 110 °C to obtain xerogel, which was subsequently calcined in air at 600 °C for 2 hours. On one hand, PPy microspheres are completely removed by combustion, converting their original spherical spaces into abundant pores. On the other hand, metal complexes decompose at high temperature and transform into single-phase spinel structures. The reductive atmosphere generated during PPy combustion can also induce the formation of oxygen vacancies on the material surface.

In the synthesis of HEM nanofibers, Wang et al.[60] used polyacrylonitrile (PAN)-bisphenol A benzoxazine (BA-a) composite fibers as hard templates to prepared mesoporous HEA/carbon composite catalysts (**Fig. 3b**). The synthesis proceeds as follows: Green nanofibers (NFB_x) loaded with metal salts were prepared by electrospinning, using composite fibers composed of PAN and BA-a as the rigid skeleton templates. Subsequent thermal treatment induced the ring-opening cross-linking of BA-a and the cyclization of PAN, resulting in structurally stabilized polymerized fibers (PNFB_x). This step effectively fixed the distribution of metal salts and enhanced template rigidity. KOH was used as an etchant to modify the pores of the template, converting closed pores inside the fibers into open pores. During pyrolysis, PAN was carbonized to form carbon nanofiber scaffolds, while the metal salts were reduced by carbon to form high-entropy alloy particles, which were uniformly dispersed on the carbon support. Finally, mesoporous materials such as FeCoNiMnRu-HEA/C are obtained (**Fig. 3c and 3d**). The introduction of hard templates effectively inhibits the agglomeration of HEA particles and constructs a porous structure dominated by mesopores (accounting for 94% of total pore volume) with high specific surface area (1014 m² g⁻¹). This structure provides abundant active sites and efficient mass transfer channels for electrocatalytic reactions.

In the synthesis of high-entropy selenides, Jiang et al.[61] used high-entropy layered double hydroxides (HE-LDHs) as hard templates. Through a two-step method of "template preparation-template selenization conversion" (**Fig. 3e**), they successfully synthesized flower-like high-entropy selenides (F-HES, (CoNiFeCuCr)Se). In the approach, sea urchin-like HE-LDH hard templates were first prepared via hydrothermal reaction regulated by urea and NH_4F . NH_4F acts as an etchant to guide the oriented growth of crystals,

ensuring a uniform template morphology with layered porous characteristics. Then, HE-LDH is converted into flower-like high-entropy selenides (F-HES) through ion exchange. Compared with bulk high-entropy selenides (B-HES) prepared by direct selenization without templates, HE-LDH hard templates not only endowed F-HES with flower-like morphology and high specific surface area (172.8 m² g⁻¹) but also ensured uniform distribution of metal elements. As a result, F-HES showed excellent performance in oxygen reduction reaction. It is worth noting that the template-derived porous structure remains stable in the subsequent electrocatalytic process, while also providing a favorable interface for the self-reconstruction of materials, further optimizing the catalytic activity.

The strategy using metal-organic frameworks (MOFs) as templates shows unique advantages. The conversion of FeCoNiCuMnZn-MOF precursors via pyrolysis has been demonstrated as an effective route to prepare porous FeCoNiCuMn high-entropy alloy nanoparticles[65]. In the process, the low boiling point characteristic of Zn element is used, which evaporates and separates during the high-temperature pyrolysis stage, thereby creating internal pore structures of 20-50 nm. By regulating the calcination temperature, the pore size can be further fine-tuned while preserving the high-entropy characteristics and catalytic active sites of the alloy. In addition, Hu et al.[62] used MOFs as core hard templates to construct low-ruthenium (Ru)-loaded FeCoNiMoRu high-entropy alloy self-supported electrodes (**Fig. 3f**). This method uses flexible carbon cloth (CC) as the supporting substrate. First, a five-component FeCoNiMoRu-MOF hard template composite (CC@FeCoNiMoRu-MOF) was formed on the CC surface via a solvothermal reaction. Then it is placed in a H_2/Ar mixed atmosphere for stepwise pyrolysis. The MOF hard template decomposes into a porous carbon skeleton and retains the hierarchical porous structure, while metal precursors were converted into FeCoNiMoRu-HEA nanoparticles with uniform size (10.2±3.0 nm) and uniform dispersion. Finally, CC@FeCoNiMoRu-HEA/C self-supported electrodes are obtained. Relying on porous structure and high specific surface area (product BET specific surface area 96.4 m² g⁻¹), MOF hard templates realize uniform metal dispersion and inhibit particle agglomeration. Wang et al.[38] synthesized porous high-entropy perovskite oxides ($\text{La}(\text{Mn}_{0.2}\text{Fe}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Cu}_{0.2})\text{O}_3$) using MOF gels as hard templates. This method uses multi-metal nitrates as metal sources and 1,3,5-benzenetricarboxylic acid as ligand, forming MOF gel hard templates via a disturbed coordination reaction. After drying and calcination, the MOF template was pyrolyzed to remove the ligand, and the metal components were converted into a single-phase perovskite structure. The MOF gel hard templates played a crucial role in achieving molecular-level uniform dispersion of multi-metal ions, preventing element segregation, and retaining porous structure with high specific surface area and abundant mesopores.

In the preparation of high-entropy alloy-based composite foams, the work by Meng and co-workers[63]

demonstrated a strategy using alumina hollow microspheres as hard templates (**Fig. 3g**). They infiltrated AlCoCrFeNi_{2.1} eutectic high-entropy alloy (EHEA) melt into the template gaps by gas pressure infiltration method, thereby producing EHEA composite foams. The rigid structure of alumina microspheres endows the foam with a uniform porous structure (porosity 28%) (**Fig. 3h**). The FCC/B2 dual-phase structure of the EHEA matrix synergizes with the template, endowing the foam with a quasi-static compressive strength of 309 MPa, an energy absorption efficiency of 0.86-0.91 and a dynamic compressive strength of 455.5 MPa. As a result, the foam has both high strength and excellent energy absorption performance.

The hard template method has prominent advantages. Firstly, the templates have high rigidity and stable size, providing reliable in processes such as high-temperature calcination and solvothermal treatment, they can effectively inhibit material shrinkage and ensure support for the pore structure of high-entropy materials, especially the pore integrity. For instance, PS colloidal crystals and alumina hollow spheres can maintain their structures during calcination or alloy melting. Secondly, the method has high controllability of pore structure. Template size directly determines the pore size of materials. By selecting different templates (such as 530 nm/1.1 μ m PS microspheres and 20-50 nm MOF pores), structures from mesopores to macroscopic macropores can be precisely constructed, featuring excellent pore connectivity and regularity. Thirdly, it is suitable for various types of high-entropy materials. Whether it is dense materials such as high-entropy oxides and alloys, or special-shaped materials such as selenides and composite foams, porous construction can be achieved by the hard template method.

However, the method also has certain limitations. On one hand, template removal is difficult. Some hard templates (such as MOFs and mesoporous KIT-6) need to be removed by strong acid etching or high-temperature calcination, which may corrode or damage the material pore walls and lead to pore structure collapse. On the other hand, the template morphology and size are fixed, making it challenging to flexibly regulate pore diversity. For example, PS microspheres of a single size can only prepare macropores with corresponding pore sizes, and cannot simultaneously construct hierarchical porous structures. In addition, the preparation process of some hard templates is complex and costly. The compatibility between templates and high-entropy material precursors needs to be strictly matched. Otherwise, uneven precursor filling is prone to occur, affecting the uniformity of pore structure.

3.1.2 Soft template method.

The soft template method uses block copolymers (e.g., Pluronic F-127, PS₁₈₀₀₀-b-PEO₇₅₀₀), polymers (e.g., polyacrylonitrile (PAN), bisphenol A benzoxazine (BA-a)) and small-molecule additives (e.g., sodium citrate) as core templates. It relies on the ordered nanostructures formed by template self-assembly. Combined with processes such as

reduction, electrodeposition and electrospinning-carbonization, mesoporous structures can be constructed in various materials, including high-entropy alloys, high-entropy oxides and high-entropy Prussian blue analogs. By regulating template parameters, pore size and pore distribution can be flexibly tailored. This method effectively solves the problems of disordered pores and uneven pore size in template-free preparation.

In terms of mesoporous structure guidance, block copolymers form micelle templates through microphase separation of hydrophobic-hydrophilic segments. These templates directly determine the pore size, distribution and connectivity in the final material. In the element screening of HEA catalysts, Nam et al.[66] first identified four platinum-group metals (PGMs), Pt, Pd, Rh and Ru, as the basic components. Subsequently, by integrating the comprehensive advantages in the screening results (**Fig. 4a**), they selected Mo as the fifth element. Guided by the key requirements of methanol oxidation reaction (MOR) for catalysts, including low resistance, strong adsorption, anti-poisoning and excellent mass transfer, the study adopted the soft template method as the core synthesis strategy. Combined with chemical reduction and electrodeposition processes, it provided key technical support for the construction of efficient MOR catalytic systems. The study selected polystyrene-b-polyethylene oxide (PS₅₀₀₀-b-PEO₂₅₀₀) di-block copolymer as the soft template. The core-shell micelle structure formed by self-assembly in solution to achieve uniform loading and spatial confinement of five metal ions. Through subsequent template removal process, mesoporous structures were constructed, mesoporous PtPdRhRuMo HEA catalysts (**Fig. 4b**) were successfully prepared. The catalysts have two morphologies: nanoparticles (m-HEANP (Mo)) and thin films (m-HEAF (Mo)). Among them, the m-HEANP (Mo) nanoparticles show uniform spherical morphology with a diameter of about 50 nm and obvious mesoporous channels are distributed on their surface. The m-HEAF (Mo) mesoporous films have a continuous two-dimensional thin film structure (**Fig. 4c**). Benefiting from mesoporous characteristics and multi-metal synergistic effect, both products exhibit excellent MOR catalytic performance. Similarly, Zhu et al.[67] used PEO-b-PMMA block copolymer as the soft template to prepare L1₂-phase ordered HEA supported on nitrogen-doped mesoporous carbon nanosheets (OHEA-mNC) (**Fig. 4d**). In the early stage of synthesis, PEO-b-PMMA self-assembles into monodisperse micelles with a size of about 20 nm. Then dopamine (DA) and metal salts are introduced to form metal-catecholamine (MC) complexes, resulting in MC/PEO-b-PMMA composite micelles are formed. These further assembled with graphene oxide (GO) into 2D organic-inorganic superstructures. After annealing in NH₃ atmosphere, nanoparticles with about 10 nm mesopores and uniform element distribution (size 5-10 nm) are obtained. In contrast, annealing in N₂ atmosphere produces FCC disordered-phase HEA (DHEA-mNC). Nandan et al.[68] used PS_{5k}-b-PEO_{2.5k} block copolymer as the soft template to achieve

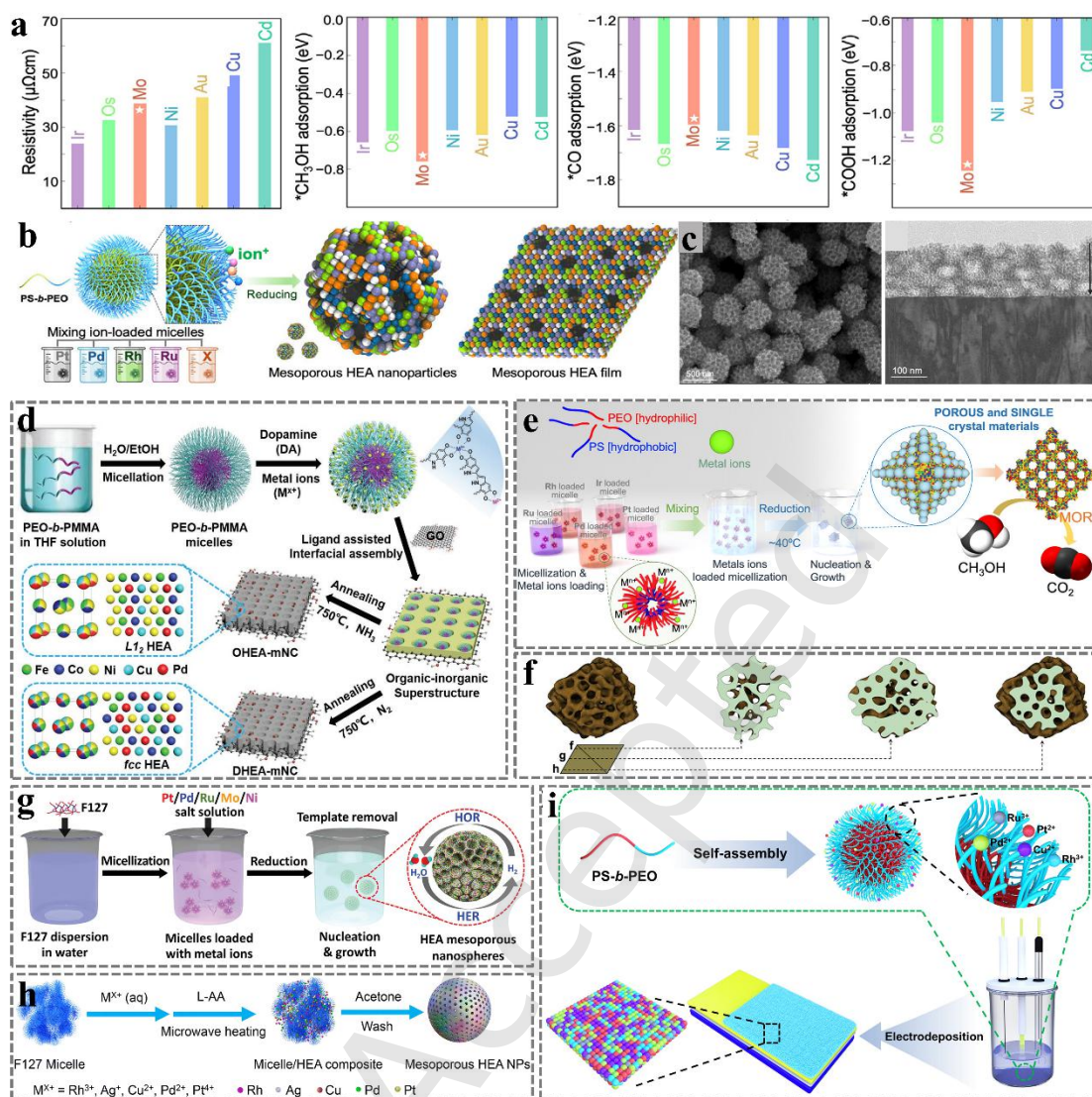


Figure 4. (a) Computational screening of HEA electrocatalysts for MOR on PtPdRhRuX, (b) Schematic illustration of designing quinary HEA-PtPdRhRuX, (c) TEM image of mesoporous HEA-PtPdRhRuMo film. Adapted with permission from ref. [66] copyright 2025, American Chemical Society. (d) Schematic of constructing ordered HEA NPs on 2D nitrogen-rich mesoporous carbon nanosheets. Adapted with permission from ref. [67] copyright 2022, Wiley. (e) Schematic of synthesizing single-crystal porous PtPdRuIrRh high-entropy nanoalloys, (f) Rendering of nanoparticle and its cross-sections. Adapted with permission from ref. [68] copyright 2025, American Chemical Society. (g) Schematic of preparing mesoporous PtPdRuMoNi HEA nanospheres via one-pot wet chemical reduction. Adapted with permission from ref. [69] copyright 2024, Wiley. (h) Microwave-heating fabrication of mesoporous RhAgCuPdPt HEA NPs. Adapted with permission from ref. [70] copyright 2025, The Royal Society of Chemistry. (i) Schematic illustration of the electrodeposition of m-HEA film using block polymers. Adapted with permission from ref. [71] copyright 2024, American Chemical Society.

the controllable preparation of mesoporous single-crystal (SCPHEA) and polycrystalline (PCPHEA) PtPdRuIrRh high-entropy alloys (**Fig. 4e**). During synthesis, PS_{5k}-b-PEO_{2.5k} self-assembles into "PS core-PEO shell" micelles in DMF. The PEO shell enriches Pt, Pd, Ru, Ir and Rh metal ions. Micelle confinement inhibits particle agglomeration and guides mesopore formation, with the target product obtained after washing and removing the template. The crystallization state is controlled by reaction time, single crystals are formed within 1-4 h (e.g., SCPHEA4, size 90 ± 5 nm, FCC structure, mesopores penetrating the particles, **Fig. 4f**), which polycrystals (PCPHEA6) are formed at 6 h.

In addition, Nandan et al.[69] used Pluronic F-127 as the soft template to synthesize mesoporous PtPdRuMoNi

high-entropy alloys (**Fig. 4g**), the hydrophilic segments of micelles formed by F-127 in aqueous solution uniformly wrap different metal ions. This spatial confinement effect restricts ion diffusion and enables the synchronous nucleation and growth of multiple elements during reduction by L-ascorbic acid, ultimately achieving a uniform elemental distribution. The specific surface area of this material reaches $170 \text{ m}^2 \text{ g}^{-1}$, which is nearly 8 times higher than that of the template-free sample. Similarly, Ni et al.[70] employed F127 as the soft template in combination with microwave-assisted heating for efficient synthesis (**Fig. 4h**). F127 self-assembles into micelles in DMF. After mixing with metal salts and L-ascorbic acid, metal reduction and mesopore construction are completed by microwave heating

at 130 °C for 1 min. After template removal with acetone, RhAgCuPdPt mesoporous high-entropy alloy nanoparticles are obtained (size 88 ± 16 nm, pore size 6.8 nm, BET specific surface area $18.97 \text{ m}^2 \text{ g}^{-1}$). The rapidity of microwave heating and the guiding effect of F127 together ensure the single-phase FCC structure and mesopore integrity of the product. In microwave-assisted synthesis, soft templates can combine with the rapid heating characteristics of microwaves to achieve efficient construction of porous structures.

In the electrodeposition process, soft templates guide the directional reduction of metal ions through micelle arrangement in the electrolyte, providing a precise regulation method for the preparation of porous thin film materials. Fu et al.[71] prepared PtPdRhRuCu mesoporous high-entropy alloy films using PS-b-PEO as the soft template (Fig. 4i), micelles were dispersed in the metal salt electrolyte. Under an applied electric field, the micelles directionally adsorbed on the surface of Au-coated Si substrate, forming an orderly arranged "template array". At a potential of -0.2 V (vs. Ag/AgCl), metal ions were reduced and deposited in the inter-micellar regions. The spatial barrier effect of micelles directly forms mesoporous structures. After removing the template by soaking in THF, uniform films with mesopore size of about 25 nm were obtained.

The soft template method has significant advantages. First, soft templates possess a strong self-assembly ability and can form ordered mesoporous structures. By changing the template type, molecular weight or concentration, pore size (20-40 nm, 6.8 nm, etc.) and pore distribution can be flexibly regulated to meet the structural requirements of different high-entropy materials. Second, the template removal process is relatively mild, typically involving washing, calcination and other methods, which will not easily damage the pore integrity of materials. Third, the method exhibits wide applicability. It can be combined with various preparation processes such as reduction, electrodeposition and electrospinning for the porous construction of different types of materials like high-entropy alloys and oxides.

However, this method also presents certain challenges that need to be addressed. On one hand, most soft templates are organic materials with poor high-temperature stability. They are prone to premature decomposition during the calcination process for preparing high-entropy materials, which may lead to pore structure collapse. For instance, some polymer templates cannot maintain their structures above 800 °C. On the other hand, template self-assembly is easily affected by reaction conditions (e.g., temperature, pH, solvent). If parameters are not properly controlled, template agglomeration is prone to occur, resulting in uneven or closed pores of materials and reducing the controllability of pore structures. In addition, some soft templates (e.g., block copolymers) are costly, and trace organic impurities may remain after template removal, which could affect the purity of high-entropy materials.

3.2 Other key synthetic technologies

Template-free methods, benefiting from advantages such as the elimination of additional template removal steps, process simplicity, controllable costs and outstanding scalability potential, play a core role in the preparation of porous high-entropy materials, including HEAs, HEOs, high-entropy intermetallic compounds, etc. Their core principle is to construct porous structures by regulating phase-selective dissolution, reaction kinetics, self-assembly or pyrolysis processes. According to the differences in synthesis mechanisms, technologies such as dealloying, electrodeposition, solvothermal/hydrothermal methods and sol-gel methods achieve differentiated regulation based on distinct process principles, while each has its own advantages and limitations.

3.2.1 Dealloying method.

The dealloying method utilizes the difference in corrosion resistance between different phases (e.g., FCC/BCC, B2 phases) in high-entropy materials. Through chemical or electrochemical etching, it selectively removes active phases (e.g., Al-rich B2 phase, FCC phase) while retaining inert phases as porous skeletons. This approach become a mainstream method for preparing 3D self-supported bulk porous HEMs. It can realize hierarchical structure regulation from nanoscale mesopores to microscale macropores, and is widely applied in electrocatalysis and energy storage fields.

The key advantage of this method lies in the synergistic formation of pores and skeletons, the dissolution of active phases directly generates pores, and inert phases naturally form supporting structures without subsequent pore-forming steps. Wu et al.[72] used $\text{Al}_{16.7}\text{Fe}_{16.7}\text{Co}_{16.7}\text{Ni}_{16.7}\text{Cr}_{16.7}\text{Mn}_{16.7}$ dual-phase HEA as the precursor. After etching with 3 M HNO_3 for 4 h, the Al-Ni-rich B2 phase was selectively dissolved, and retained the Fe-Cr-rich A2 phase to form nanoporous HEA with an average pore size of 84 nm (20-120 nm). After further activation by 500 CV cycles, Cr on the surface dissolved out and an amorphous Mn-Fe-Co-Ni oxide layer was generated in situ. The electrochemically active surface area (ECSA) was 9.6 times that of the un-activated sample. Similarly, a typical selective electrochemical dealloying route has been developed for hierarchically porous high-entropy alloys. Using an arc-melted $(\text{Fe}_{41.08}\text{Co}_{25.31}\text{Ni}_{20.75}\text{Nb}_{12.86})_{97}\text{Pt}_3$ dual-phase alloy as the precursor, the reactive FCC phase is selectively removed in 0.5 M H_2SO_4 , whereas the corrosion-resistant $(\text{FeCoNiPt})_2\text{Nb}$ Laves phase is preserved as the rigid porous ligament. During the dealloying process, uniform $\text{Pt}_3(\text{FeCoNi})$ nanocrystals with a size of ~ 3.5 nm are in-situ formed on the skeleton surface and further stabilized by a thin, protective amorphous NbOx layer[73].

In addition, this method can be combined with secondary modification to optimize structure and performance. For example, Feng et al.[74] adopted a three-step process involving arc melting, dealloying and electrodeposition to prepare NPCCF@Ni composite electrodes (Fig. 5a). First, an equiatomic CoCrFeNiAl high-entropy alloy ingot was obtained by melting Co, Cr, Fe, Ni and Al metals under high-purity argon protected by titanium. Then, the alloy ribbons with a thickness of 30 μm were obtained by melt-spinning. They were soaked in 0.5 M H_2SO_4

solution at 313 K for 12 h to selectively dealloyed the Al-Ni-

rich B2 phase, resulting in maze-like 3D nanoporous CoCrFeNiAl HEA (NPCCF). Finally,

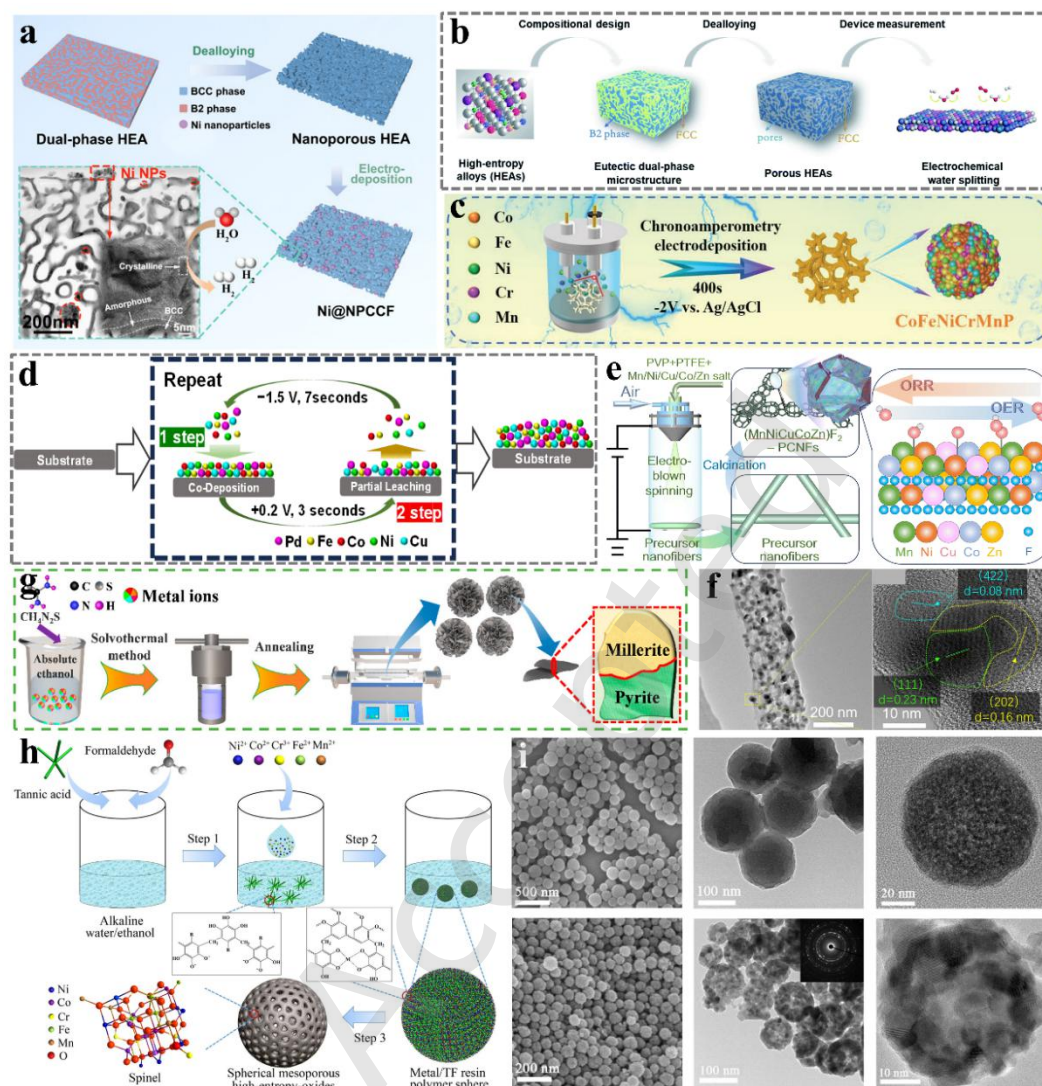


Figure 5. (a) Schematic of preparing self-supporting NPCCF@Ni HER electrodes via electrodepositing Ni NPs. Adapted with permission from ref. [74] copyright 2025, American Chemical Society. (b) Schematic of designing porous high entropy alloys for electrochemical water splitting. Adapted with permission from ref. [75] copyright 2022, Royal Society of Chemistry. (c) Schematic of preparing CoFeNiCrMnP/NF. Adapted with permission from ref. [76] copyright 2023, Wiley. (d) Schematic of preparing polycrystalline Pd-based high-entropy nanostructures (PdFeCoNiCu-PHENs). Adapted with permission from ref. [77] copyright 2024, Royal Society of Chemistry. (e) Schematic of preparing high entropy fluoride modified porous carbon nanofibers, (f) HR-TEM image of (MnNiCuCoZn)F₂-PCNFs. Adapted with permission from ref. [78] copyright 2024, Royal Society of Chemistry. (g) Preparation process and the crystal structure of the high-entropy dual-phase sulfide. Adapted with permission from ref. [79] copyright 2023, American Chemical Society. (h) Schematic of preparing spherical mesoporous HEOs via sol-gel method, (i) SEM and TEM images of Ni-Co-Cr-Fe-Mn-TF polymer spheres. Adapted with permission from ref. [80] copyright 2020, American Chemical Society.

Ni nanoparticles were electrodeposited onto the surface of NPCCF, yielding the NPCCF@Ni composite electrode with uniformly distributed Ni nanoparticles. Similarly, Han et al.[75] took arc melting as the core preparation process and combined it with a selective dealloying strategy to develop a bifunctional porous AlCrFeCoNiW high-entropy alloy electrode (Fig. 5b). First, according to the composition of Ni₃₀Co₃₀Cr₁₀Fe₁₀Al₁₈W₂, metal powders were subjected to arc melting and drop-cast into a copper mold to obtain HEA plates with a thickness of 250 μm. Then it was immersed in 1

M hydrochloric acid solution for selective dealloying. The corrosion-prone BCC phase was removed by regulating the immersion time (12-72 h), while the FCC phase retained to form a 3D porous structure.

3.2.2 Electrodeposition method

The electrodeposition method realizes selective deposition and dissolution of metal ions by regulating electrode potential, current density or electrolyte composition. It can

naturally form porous structures without templates, flexibly prepare HEMs with diverse morphologies, while precisely controlling pore size distribution and active site exposure. This method is widely used in the preparation of HEA-based electrocatalytic materials.

In the constant current/constant potential electrodeposition process, Li et al.[76] used nickel foam (NF) as the substrate, in an electrolyte containing $\text{Co}^{2+}/\text{Fe}^{3+}/\text{Ni}^{2+}/\text{Cr}^{3+}/\text{Mn}^{2+}$ and NaH_2PO_2 (phosphorus source), a three-electrode system was adopted. Continuous deposition at -2 V for 400 s led to the in-situ co-reduction and deposited of metal ions and phosphorus source on the NF surface, generating phosphorus-modified amorphous $\text{CoFeNiCrMnP}/\text{NF}$ composite materials (Fig. 5c). The porous structure was assembled from nanoparticles into a "cauliflower-like" shape with a pore size of 20-50 nm. Similarly, Li et al.[81] adopted direct current electrodeposition, using copper as the substrate and selecting appropriate metal ion sources in an electrolyte adjusted with citric acid, boric acid, and the pH of 2 maintained by 0.025 M H_2SO_4 and 0.075 M HCl. By controlling deposition current and time at room temperature, a porous structure was formed through rapid metal-ion reduction accompanied by vigorous gas evolution. The key parameters were deposition current (0.5 A, 2.5 A, 3 A, 3.5 A) and deposition time (5 min, 6 min, 7 min, 8 min), when the deposition current was 3 A and the deposition time was 7 min, FeCoNiCuMn high-entropy alloy with a 3D porous structure was obtained.

In addition, the two-step potential electrodeposition process can further optimize the porous structure. For example, Liu et al.[77] employed a three-electrode system in an electrolyte containing metal salts such as PdCl_2 and $\text{Fe}_2(\text{SO}_4)_3$. The deposition process periodically alternated two-step potential operations (Fig. 5d), in the first step, a voltage of -1.5 V (vs. $\text{Hg}/\text{Hg}_2\text{SO}_4$) was applied for 7 s to realize co-deposition of all metal atoms. In the second step, the voltage was adjusted to +0.2 V (vs. $\text{Hg}/\text{Hg}_2\text{SO}_4$) for 3 s to induce electro-oxidation leaching of some metal components. This cycle was repeated 15 times to construct a polycrystalline structure rich in grain boundary defects. By adjusting the deposition potential in the second step (e.g., -0.2V or +0.5V), PdFeCoNiCu -pHENSs with different structures (pHENSs-LLP, pHENSs-HLP) can be prepared.

3.2.3 Electrospinning-calcination method.

In the electrospinning-calcination process, Zhang et al.[82] realized the low-temperature preparation of high-entropy oxide nanofibers. Six kinds of acetylacetonates (Ni, Cu, Mn, Co, Zn, Fe) were used as metal sources, and polyvinylpyrrolidone (PVP) was used as the ligand and spinning carrier. After constructing a uniform sol, electrospinning was carried out at a voltage of 25 kV to form a nanofiber membrane, after pretreatment at 200 °C, calcination was performed at 400 °C (adjustable to 1000 °C). The cyclic structure of acetylacetonates ensured uniform metal coordination. During calcination, PVP decomposed to form a hollow porous structure. The final product was spinel-type $(\text{CoNiMnCuZnFe})_3\text{O}_4$ HEO nanofibers with a

mesoporous structure of 6.87 nm pore size. Wang et al.[78] prepared porous carbon nanofibers modified with high-entropy fluorides by combining electrospinning with sol-gel and carbothermal reduction processes (Fig. 5e). Metal salts of Mn, Ni, Cu, Co and Zn were used as raw materials, polyvinylidene fluoride (PTFE) as the fluorine source and pore-forming agent, and PVP as the spinning carrier. The spinning sol was processed by electro-blowing spinning to form precursor fibers, after pretreatment at 250 °C, calcination was carried out at 800 °C in a nitrogen atmosphere. PTFE decomposed to generate fluorine gas, which promoted the conversion of metal salts into $(\text{MnNiCuCoZn})\text{F}_2$ high-entropy fluoride, and a porous carbon fiber carrier was formed at the same time (Fig. 5f). Zinc element induced the fluoride to transform from single crystal to polycrystal. The material exhibited excellent bifunctional catalytic performance in oxygen reduction reaction and oxygen evolution reaction.

3.2.4 Solvothermal/hydrothermal method.

The solvothermal/hydrothermal method uses a high-temperature and high-pressure solvent environment (water or organic solvent) to promote precursor dissolution, reaction and self-assembly. By regulating parameters such as temperature, pH or ligand type, it can induce the formation of porous structures. This template-free approach is capable of synthesizing porous HEMs with low crystallinity and high porosity. It is suitable for regulating complex morphologies such as 2D layered structures and 3D microspheres, and exhibits excellent compatibility with high-temperature-sensitive high-entropy material systems.

In the solvothermal-calcination process, Gonçalves et al. [83] used equimolar acetates of Ni, Co, Mn, Mg and Zn as metal sources, dissolved them in isopropanol with the addition of glycerol. Solvothermal treatment was performed at 180 °C for 10 h to obtain high-entropy glycerate (HE-Gly) microsphere precursors. Subsequent calcination in air at 400 °C/800 °C yielded mesoporous HEO-400 and macropore-mesopore hierarchical HEO-800, respectively. Similarly, Zhao et al.[79] dissolved chlorides of Fe, Co, Ni, Cu, Zn and thiourea in absolute ethanol. Then 0.1 mol L⁻¹ thiourea was added and stirred vigorously to homogenize. the mixture was transferred to a Teflon-lined stainless-steel autoclave and heated at 180 °C for 6 h. Finally, the precursor was annealed at 500 °C for 2 h under argon protection (Fig. 5g), and porous flower-like dual-phase high-entropy sulfide $(\text{FeCoNiCuZn})\text{S}$ was successfully prepared.

The nonequilibrium hydrothermal method can realize the preparation of ultrasmall HEA nanoparticles. For example, Zhang et al.[84] used DMF as the solvent, H_2PtCl_6 , CuCl_2 , etc. as metal sources, and KSCN as the complexing agent. And hydrothermal treatment was performed at 170 °C for 4 h. In this hydrothermal system, DMF underwent catalytic dehydrogenation on the surface of metal cores/seeds to generate active hydrogen ($\text{H}^\cdot$) in situ, constructing a local nonequilibrium environment. It broke through the limitation of differences in metal reduction potentials, realizing synchronous reduction and uniform alloying of multiple metal precursors. A variety of high-

entropy alloy nanoparticles such as $\text{Pt}_{13}\text{Ir}_{10}\text{Cu}_{23}\text{In}_{14}\text{Ga}_{26}\text{Pb}_{14}$ and PtCuNiCoFe were successfully prepared, with sizes adjustable between 1-4 nm and compositions precisely controllable.

3.2.5 Sol-gel method.

The sol-gel method forms a uniform sol through the reaction of multi-metal ions and complexing agents. Combined with subsequent calcination, organic components are pyrolyzed to form mesoporous structures, and metal ions are converted into high-entropy materials at the same time. This approach effectively suppresses element segregation and ensure compositional uniformity. In the sol-gel-calcination process, a method for preparing spherical mesoporous high-entropy oxides was reported by Wang and co-workers[80] (**Fig. 5h**). In this approach, tannic acid (TA) was selected as the polymerization ligand and formaldehyde as the crosslinking agent to construct a sol system with five metal salts of Ni, Co, Cr, Fe and Mn. Metal/tannic acid-formaldehyde resin composite spheres were formed by hydrothermal treatment. Subsequent calcination in air (400-900 °C) decomposed the organic resin, generating mesopores and finally obtaining spherical mesoporous high-entropy oxides with a spinel structure (**Fig. 5i**). The resulting materials exhibited high specific surface area ($42\text{-}143\text{ m}^2\text{ g}^{-1}$) and uniform spherical morphology ($\sim 55\text{ nm}$). Similarly, Balasubramanian et al.[85] employed the sol-gel method combined with hydrothermal treatment and low-temperature calcination to prepare $\text{MnCoNiCuFe}_2\text{O}_4$ high-entropy oxides rich in oxygen vacancies and grain boundaries. Nitrates of Mn, Co, Ni, Cu and Fe were used as

metal sources and ethylene glycol as the solvent to construct the sol. Sodium acetate and polyethylene glycol were added to regulate the reaction environment and mesoporous structure. After hydrothermal and calcination treatment, the product exhibited a mesoporous structure and spinel phase, and showed excellent activity in glucose electrooxidation and glucose oxidation reaction (GOR).

3.3 Comparison of synthesis methods

To provide a clear overview of the various synthetic strategies discussed above, **Table 1** summarizes the relative performance of each method in terms of cost, controllability, scalability, energy consumption, as well as their main advantages and limitations.

Hard and soft templating offer relatively precise control over pore architecture, yet the template removal process is often cumbersome and their thermal stability remains limited. Dealloying and electrodeposition are lower in cost and easier to scale up, making them more attractive for practical applications. Solvothermal and sol-gel methods achieve good compositional uniformity, but their batch yields are limited. Electrospinning-calcination is suitable for continuous production of one-dimensional nanofibers and shows decent scalability, though it requires high-temperature treatment.

The choice of a suitable synthesis method therefore involves trade-offs among cost, controllability, scalability, and energy consumption. Future efforts may combine the advantages of different approaches to strike a balance between precise structural regulation and practical manufacturability.

Table 1. Comparison of synthesis methods for porous high-entropy materials.

Synthetic Method	Cost & Energy	Controllability	Scalability	Energy Consumption	Key Advantages and Limitations
Hard template method	Medium	High	Medium	High	Uniform pore size; difficult template removal
Soft template method	Medium	High	Medium	Medium	Ordered mesopores; poor thermal stability
Dealloying method	Low	Medium	High	Medium	3D self-supporting structure; phase-selective requirement
Electrodeposition method	Low	High	Medium	Low	Diverse morphologies; thickness limited
Electrospinning-calcination	Medium	Medium	High	High	Continuous 1D nanofibers; high-temperature needed
Solvothermal/hydrothermal method	Low	Medium	Low	Medium	Complex morphologies; small batch size
Sol-gel method	Medium	High	Medium	Medium	Molecular-level uniformity; time-consuming

4 Structural regulation of porous high-entropy materials

4.1 Pore size regulation

Pore size regulation of porous high-entropy materials is a critical step for optimizing their structure and performance. Precise control is achieved through two mainstream processes: template method and template-free method.

Different processes rely on specific regulation mechanisms, which in turn exert a crucial impact on the exertion of functions such as electrocatalysis and application effects of the materials.

The template method is an important means for pore size regulation of porous high-entropy alloys, and the synergistic optimization of space holders and sintering processes is highly innovative. Tang et al.[86] first prepared CoCrFeNiMo porous high-entropy alloys using microwave sintering combined with Mg space holders. By varying the Mg content

(0, 10, and 20 wt%), they achieved tailored control over pore

size and specific surface area. As the Mg addition increased,

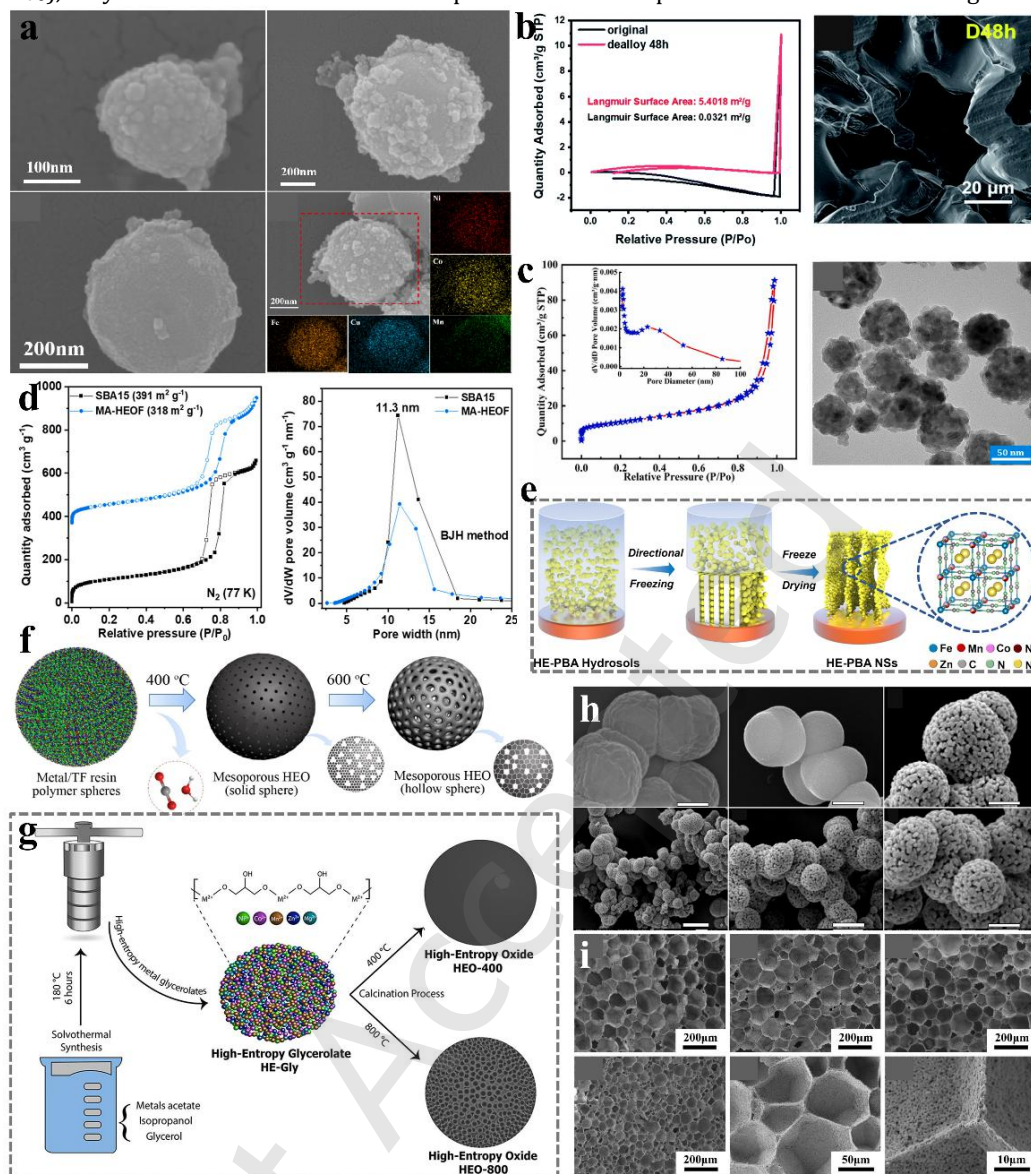


Figure 6. (a) SEM images of HEAs-800, HEAs-950, and HEAs-1000, together with EDS mapping of HEAs-950. Adapted with permission from ref. [65] copyright 2024, Elsevier. (b) N₂ adsorption profiles and SEM image of AlCrFeCoNiW. Adapted with permission from ref. [75] copyright 2022, Royal Society of Chemistry. (c) N₂ adsorption-desorption isotherms and TEM image of OV-GB-MnCoNiCuFe₂O₄. Adapted with permission from ref. [85] copyright 2025, Elsevier. (d) N₂ adsorption isotherms of SBA15 and MA-HEOF at 77 K and BJH-calculated pore size distribution curves. Adapted with permission from ref. [87] copyright 2025, American Chemical Society. (e) Schematic of HE-PBA NSs preparation via hydrosol directional freezing. Adapted with permission from ref. [88] copyright 2025, Elsevier. (f) Schematic illustration of the formation of spherical mesoporous HEOs with solid and hollow structures. Adapted with permission from ref. [80] copyright 2020, American Chemical Society. (g) Schematic of the formation process of HE-Gly and HEO microspheres, (h) SEM images of HE-Gly, HEO-400, and HEO-800. Adapted with permission from ref. [83] copyright 2023, Elsevier. (i) SEM images of (5RE_{0.2})₃NbO₇ ceramic foams with different solid loadings. Adapted with permission from ref. [89] copyright 2022, Elsevier.

the porous structure of the alloy was gradually formed and improved. The CoCrFeNiMo-20Mg sample exhibited a specific surface area of 0.443 m² g⁻¹ and an average pore size of 2.83 μm, markedly superior to the Mg-free sample. The synergistic effect of the microwave sintering process and Mg space holders not only maintained the face-centered cubic single-phase structure of the alloy, but also formed abundant pores through the volatilization of space holders, providing a

new path for precise pore size regulation of porous high-entropy alloys.

Zhao et al.[65] synthesized FeCoNiCuMnZn-MOF precursors via a one-step solvothermal method, and regulated the pore size of the porous FeCoNiCuMn high-entropy alloys by virtue of the low boiling point property of Zn. By regulating the thermal reduction temperature (800, 900, 950, 1000 °C), the sample formed an optimal pore

structure at 950 °C, with an electrochemically active surface area of 3810 cm², uniform pore size distribution and consistent morphology with the MOF precursor. Excessively high temperature (1000 °C) caused particle agglomeration and pore collapse, while excessively low temperature (800 °C) resulted in incomplete Zn evaporation, insufficient pore size and pore volume. By comparing the surface morphologies of HEAs-800, HEAs-950 and HEAs-1000, the abundant porous structure formed after complete Zn evaporation at 950 °C (**Fig. 6a**) and the deterioration of pore structure when the temperature deviated from the optimal value were directly visualized.

The template-free method directly controls pores by optimizing process parameters. In the dealloying method, Han et al.[75] found that the AlCrFeCoNiW eutectic dual-phase HEA formed a pore size of 200-500 nm after selective dissolution of specific phases by etching in 1M HCl for 48 h. After 12 h of etching, the pore size distribution was concentrated without obvious cracks due to phase residue. Insufficient etching (<24 h) led to residual BCC phase and smaller pore size (100-300 nm). After 48 h of etching, the alloy formed a 3D interconnected porous structure, by comparing the adsorption curves and pore size distributions of the original alloy and the sample etched for 48 h (**Fig. 6b**), it can be seen that the Langmuir specific surface area increased from nearly 0 m² g⁻¹ of the original alloy to 5.4 m² g⁻¹. Excessive etching (>72 h) led to pore merging and partial structural collapse, which clearly reflects the significant effect of selective etching on pore formation and pore size optimization.

In the field of porous high-entropy oxides, Balasubramanian et al.[85] prepared mesoporous high-entropy oxide O_v-GB-MnCoNiCuFe₂O₄ via a template-free method combining hydrothermal treatment and low-temperature calcination. Its mesoporous structure was formed by the accumulation of precursor nanoparticles. Through this process regulation, the material obtained mesopore sizes of 2.44 nm and 24 nm (**Fig. 6c**), with a BET specific surface area of 48.5 m² g⁻¹ and a pore volume of 0.241 cm³ g⁻¹. In contrast, the non-high-entropy sample NiFe₂O₄ prepared under the same process only had a BET specific surface area of 29.3 m² g⁻¹ and a pore volume of 0.112 cm³ g⁻¹, which was significantly lower than that of the high-entropy sample. This indicated that the combination of high-entropy effect and hydrothermal-low-temperature calcination process was conducive to forming a better mesoporous structure. Wang et al.[87] used SBA-15 mesoporous silica as the carrier and constructed a NiMgCuZnCoO_x mesoporous amorphous high-entropy oxide film (MA-HEOF) within its mesoporous channels using the solution-phase controlled deposition-precipitation method. By regulating the metal precursor concentration and deposition pH value (slowly decreasing from 12 to 7), precise adjustment of the film thickness and mesoporous structure was achieved. **Fig. 6d** compares the pore structure parameters of the SBA-15 template and MA-HEOF. Utilizing the confinement effect of SBA-15, the material retained the original mesoporous structure of SBA-15 with a size of 11.0-11.5 nm. Although the BET specific surface area decreased from 391 m² g⁻¹ of SBA-15 to 318 m² g⁻¹, the mesoporous

channels were not blocked. This confirms the complete retention of the mesoporous structure and precise regulation of pore size after the deposition of the high-entropy oxide film, providing an effective idea for the pore size control in film-type porous high-entropy oxides.

Relevant pore size regulation studies have also been carried out on high-entropy Prussian blue analogs, high-entropy metal/metal oxide hybrid materials, etc. Gu et al.[88] prepared high-entropy Prussian blue analog (HE-PBA) nanosheets via the self-assembly directional freezing method (**Fig. 6e**). During freezing, the anisotropic growth of ice crystals guided the two-dimensional confined assembly of colloidal nanoparticles. The voids after ice template removal and the gaps between nanoparticles jointly formed a porous structure. The BET surface area of HE-PBA NSs reached 69.2 m²/g with an average pore size of 11.7 nm, providing a new approach for the pore size regulation of two-dimensional porous high-entropy materials. In addition, the work by the research group led by Kim [56] demonstrated the preparation of carbon fiber composites embedded with high-entropy metal/metal oxide hybrid nanostructures (HEMMO/CNF) via electrospinning combined with carbonization. The micropores (0.5-2 nm) of carbon fibers originated from PAN carbonization, while the mesopores (2-50 nm) came from metal particle removal. By adjusting the metal salt concentration (20 wt% was optimal) and stabilization time (2 h), the mesopore volume ratio increased from 28% to 45%. Although the BET specific surface area decreased from 420 m² g⁻¹ to 380 m² g⁻¹, the electrolyte permeability was significantly improved, realizing the synergistic optimization of micropores and mesopores.

Calcination temperature is the core parameter for precise pore size regulation when preparing porous high-entropy oxides via sol-gel, solvothermal and other derivative methods. Meanwhile, the acid etching method can optimize pore size and defect structure simultaneously through structural modification. Wang et al.[80] synthesized spherical mesoporous high-entropy oxides via the sol-gel combined with polyphenol crosslinking method, and clarified that calcination temperature was the key factor for pore size regulation (**Fig. 6f**), the sample calcined at 400 °C had a pore size of 8.3 nm with a BET surface area of 143.4 m² g⁻¹, at 600 °C, the pore size decreased to 7.8 nm and the surface area dropped to 72.2 m² g⁻¹, at 900 °C, the pore size further decreased to 5.5 nm with a surface area of 41.9 m² g⁻¹. Moreover, the pore volume remained at 0.36-0.38 cm³ g⁻¹ throughout the process without obvious collapse, confirming that the gradual adjustment of mesopore size could be achieved by regulating the calcination temperature. In addition, Gonçalves et al.[83] prepared porous high-entropy oxides derived from high-entropy glycerates (NiCoMnZnMg-O) via solvothermal combined with calcination method (**Fig. 6g**). The calcination temperature was the primary factor controlling pore structure, HEO-400 (calcined at 400 °C) had a mesoporous structure with a pore size of 3.5 nm, a BET surface area of 126 m² g⁻¹ and a pore volume of 0.097 cm³ g⁻¹, HEO-800 (calcined at 800 °C) formed a macropore-mesopore hierarchical structure (**Fig. 6h**), with macropores of 50-100 nm and mesopores of 5-8 nm, a BET surface area decreased to 6.7 m² g⁻¹ and a pore volume of 0.038 cm³ g⁻¹. The high-

entropy glycerate precursor had a microporous structure (pore size of 2 nm) with a BET surface area of $342 \text{ m}^2 \text{ g}^{-1}$, showing a controllable pore size evolution from precursor to product. Wang et al.[90] prepared acid-etched high-entropy perovskite oxides ($\text{H}^+\text{-LSE}_x\text{O}$) via the sol-gel combined with acid etching method. The acid etching process effectively introduced nanoscale pores, increasing the BET surface area of $\text{H}^+\text{-LSE}_x\text{O}$ from $10.5 \text{ m}^2 \text{ g}^{-1}$ of LSE_xO to $18.2 \text{ m}^2 \text{ g}^{-1}$, the pore volume from $0.04 \text{ cm}^3 \text{ g}^{-1}$ to $0.08 \text{ cm}^3 \text{ g}^{-1}$, with the pore size concentrated at 5-15 nm. Meanwhile, the oxygen vacancy content increased from 12% to 25%, realizing the synergistic regulation of pore size and defect structure.

For porous high-entropy ceramic materials, the synergistic regulation of slurry solid content and sintering temperature is the key to achieve precise matching of hierarchical pore size and high porosity, which can meet the needs of different functional scenarios. Yang et al.[89] prepared high-entropy niobate ceramic foams via the particle-stabilized foaming method, and achieved pore size regulation by adjusting the solid content of the slurry and sintering temperature. The sample sintered at 1500°C with 20 wt% slurry had the highest porosity (96.12%) with an average pore size of $137 \mu\text{m}$ (Fig. 6i). Increasing the solid content from 20 to 50 wt%, the pore size decreased to $50 \mu\text{m}$, and secondary pores of 1-5 μm were formed at the same time (originating from the gaps between incompletely sintered particles). With the increase of sintering temperature ($1500\text{-}1600^\circ\text{C}$), the pore size decreased slightly ($98\rightarrow 87 \mu\text{m}$). This method realized the synergistic control of high porosity and hierarchical pore size, which was suitable for the demand of thermal insulation performance. Li et al.[91] prepared $(\text{MgCoNiCuZn})\text{O}$ high-entropy ceramic membranes via the diffusion-induced phase inversion combined with high-temperature sintering method. Sintering temperature had a significant effect on pore size, nanopores of 3.433 nm were formed at 850°C with a BET specific surface area of $3.344 \text{ m}^2 \text{ g}^{-1}$, the porosity remained 66-67% at 900°C . At 1000°C , the porosity decreased to 28% due to particle sintering densification. The membrane exhibited an asymmetric structure, with a 2-5 nm spongy microporous surface layer and a 1-5 μm finger-like macroporous sublayer. This hierarchical pore size structure was suitable for the requirements of water permeation and oil interception in the oil-water separation process.

The role and influence of pore size regulation on porous high-entropy materials are mainly reflected in performance optimization and application adaptation. Appropriate pore size can increase the specific surface area and the exposure degree of active sites. For instance, the mesoporous structure (8-12 nm) can significantly increase the specific surface area of the material, providing more active sites for electrocatalytic reactions. Furthermore, the interconnected pore structure accelerates the transport of electrolyte ions and the discharge of reaction gases, reduces mass transfer resistance and optimizes reaction kinetics. For example, Feng et al.[74] found that the mesoporous structure of 20-50 nm could effectively promote mass exchange during the electrocatalytic process. From the perspective of electrocatalytic performance, some materials show excellent performance after pore size regulation. The AlCrFeCoNiW

eutectic dual-phase HEA prepared by Han et al.[75] achieved overall water splitting at 10 mA cm^{-2} with a voltage of 1.55 V in 6 M KOH at 60°C , and retained 103% of its activity after 300 h. At the same time, pore size also affects material stability. A reasonable pore size distribution can alleviate volume expansion during the electrocatalytic process and reduce the risk of structural collapse. For example, Tang et al.[86] found that the porous CoCrFeNiMo high-entropy alloy prepared with the assistance of Mg powder showed no current attenuation in the 24 h constant current test of OER in 1.0 M KOH. In addition, different pore sizes are suitable for different application scenarios. Mesoporous structures are suitable for fields such as electrocatalysis and energy storage, while macroporous structures have more advantages in scenarios such as gas separation and adsorption, realizing the precise matching between material functions and application requirements.

4.2 Dimension and morphology regulation

4.2.1 One-dimensional structures

One-dimensional porous high-entropy materials (1D porous HEMs) are defined by linear or tubular morphologies, generally possess high aspect ratios, and have mesoporous/microporous structures constructed inside or on their surfaces. These structures can be effectively applied to scenarios requiring directional electron transport and mass transfer, serving as crucial structural units in fields like electrocatalysis and energy storage.

Nanowires. Their typical morphology is a confined-grown thin linear structure. For instance, Chen et al.[92] constructed a one-dimensional confined growth environment within the ordered channels of molecular sieves (such as MCM-41, ZSM-5) via the ICQ strategy (incipient wetness impregnation-short-time calcination-rapid quenching). The one-dimensional mesoporous channels of mesoporous MCM-41 (with pore size matching the size of HE-NPs, approximately $3.0\pm 0.5 \text{ nm}$) force HE-NPs to arrange uniformly along the channel direction, forming a continuous linear distribution region. When microporous ZSM-5 is etched by a liquid metal flow, some micropores are interconnected to form "wormhole-like" one-dimensional mesoporous channels, providing additional linear accommodation space for HE-NPs ($4.0\pm 0.8 \text{ nm}$). The channel confinement of both molecular sieves effectively inhibits particle agglomeration, ensures the linear dispersion of HE-NPs along the channel direction, and ultimately endows the material with excellent sintering resistance and catalytic stability.

Nanofibers. 1D porous HEMs often take the form of continuous, slender fibers, which can be prepared through various synthesis routes. The research group led by Zhang[82] successfully constructed typical high-entropy oxide nanofibers (HESO NFs) via sol-gel electrospinning (Fig. 7a). As shown in Fig. 7b, the obtained nanofibers exhibit a continuous linear structure with a diameter of approximately 290 nm, and have hollow channels inside (with an inner diameter of about 20 nm). The outer forms a porous structure (with pore size concentrated at 6.87 nm) due to the decomposition of PVP and acetylacetonate groups.

The fibers extend uniformly along the spinning direction without obvious fractures or branching. The nanocrystals (10-15 nm) inside the fibers stack and grow along the linear

direction, forming continuous one-dimensional crystal connections. In

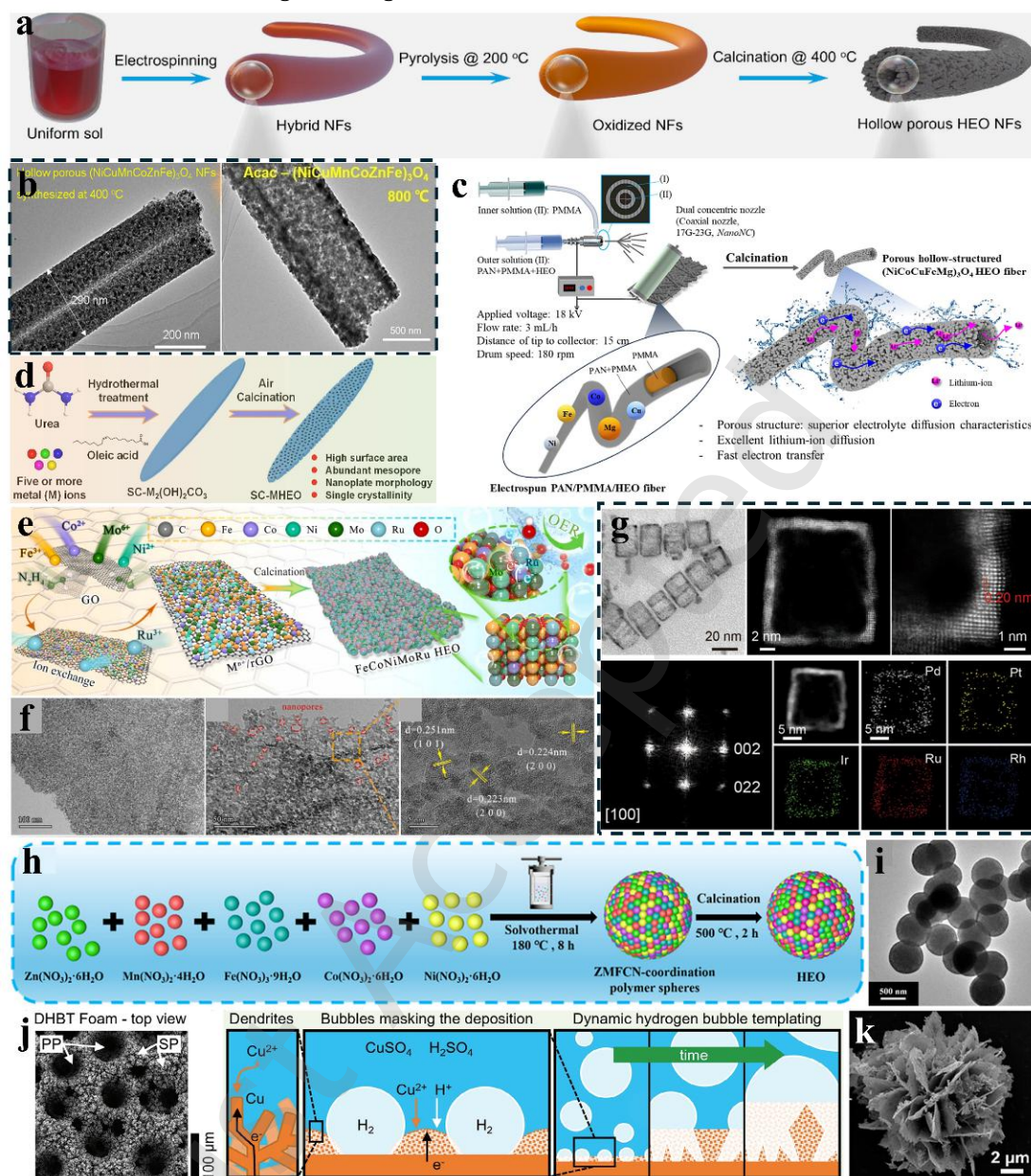


Figure 7. (a) Schematic of preparing hollow porous HESO nanofibers via disjunctive cyclic molecular coordination strategy, (b) EDS mapping of the $\text{Acac}-(\text{NiCuMnCoZnFe}_2)_3\text{O}_4$ NFs. Adapted with permission from ref.[82] copyright 2024, American Chemical Society. (c) Schematic of the synthesis of the porous hollow HEO fibers. Adapted with permission from ref.[93] copyright 2024, Elsevier. (d) BCS-oxide transition strategy for HEOs. Adapted with permission from ref.[58] copyright 2024, Springer Nature. (e) Schematic illustration of the synthesis and (f) TEM images of FeCoNiMoRu HEO. Adapted with permission from ref.[94] copyright 2026, Elsevier. (g) TEM, HAADF-STEM, FFT, and EDS of HEA cubic nanoframes. Adapted with permission from ref. [95]copyright 2025, Wiley. (h) Schematic of preparing M_3O_4 HEO, (i) TEM image of M_3O_4 HEO. Adapted with permission from ref.[96] copyright 2025, the Separation and Purification Technology. (j) SEM image of DHBT foam and time-dependent formation processes. Adapted with permission from ref.[97] copyright 2024, Wiley. (k) TEM image of the hierarchical flower-like quintuple-metal sulfide. Adapted with permission from ref.[79] copyright 2023, American Chemical Society.

addition, Kim et al.[56] constructed a composite system of honeycomb porous carbon nanofibers loaded with FeCoNiCuMn HEA nanoparticles (particle size 45 nm) via electrospinning combined with Joule heating process. This system not only retains the slender morphology and

honeycomb pores of carbon nanofibers, but also achieves functional synergy through the uniform dispersion of HEA nanoparticles.

Hollow nanofibers. As a special subtype of tubular fibers, they can be prepared by coaxial electrospinning

technology. For example, Wang et al.[93] prepared $(\text{NiCoCuFeMg})_3\text{O}_4$ high-entropy oxide porous hollow nanofibers. Their core morphological feature is a one-dimensional hollow tubular structure with a fiber diameter of approximately 500 nm. The tube wall has a uniform thickness and is covered with nanoscale pores, forming a through hollow channel inside. As shown in **Fig. 7c**, during the synthesis process, polyacrylonitrile (PAN) was used as the fiber skeleton matrix and polymethyl methacrylate (PMMA) as the pore-forming agent. The inner and outer layer solutions were delivered separately through a coaxial nozzle. After forming precursor fibers via electrospinning, high-temperature calcination decomposed PMMA to form a porous structure, and at the same time, metal salts were converted into high-entropy oxides while retaining the hollow morphology.

Nanotubes. Nanotubes, characterized by their tubular morphology, can be efficiently prepared by template-assisted methods. Liu et al.[98] successfully prepared PtPdRuIrMCu (M=Mn, Fe, Co, Ni) series high-entropy alloy mesoporous nanotubes via template-induced epitaxial growth method. These nanotubes exhibit a well-defined one-dimensional hollow structure, typically hundreds of nanometers in length, with a diameter of approximately 40 ± 10 nm. The tube wall is remarkably thin, about 1.5 nm (merely several atomic layers thick), and has uniform mesopores (with pore size of 2-100 nm).

4.2.2 Two-dimensional structures

Two-dimensional porous high-entropy materials (2D porous HEMs) are mainly in the form of sheet or film morphologies. Their core advantage lies in atomic-level flat surface characteristics or interlayer pore structures, which can maximize the exposure of surface active and provide an ideal structural platform for surface-dominated reactions (such as electrocatalysis and adsorption).

Nanosheets. Nanosheets typically exhibit a thin-sheet morphology, with their thickness and mesopore distribution tunable via different preparation processes. Wang et al.[58] successfully prepared a series of high-entropy oxide nanosheets (such as $(\text{CoNiMnCuZn})_3\text{O}_4$) via a template-free basic carbonate-oxide conversion strategy. The resulting nanosheets possess a regular 2D sheet structure with a large number of uniform mesopores penetrating inside the sheets (**Fig. 7d**). The pore size ranges from 3 to 10 nm, and the whole structure maintains a single crystal structure without grain boundary defects. The nanosheets have an average length of approximately 2.9 μm , a central width of 460 nm, a thickness of 75 nm, and a specific surface area of $82.2 \text{ m}^2 \text{ g}^{-1}$, which is 6.8 times that of non-porous high-entropy oxides. This two-dimensional single-crystal mesoporous structure not only ensures rapid electron transport, but also exposes sufficient active sites through the mesoporous structure, providing efficient structural support for electrocatalytic reactions. In another approach, Liu et al.[99] prepared 2D porous high-entropy oxide nanosheets via a rapid redox conversion strategy of metal-organic gels. These nanosheets could be thinned down to 3.4-6 nm, and the ultrathin structure further enhances the surface effect.

Ultrathin films. Ultrathin films represent a distinct class of 2D porous HEMs characterized by their thin-layer morphology. Through various synthesis strategies, their mesoporous structure and composition can be precisely tailored. By adopting ligand-assisted interface assembly combined with NH_3 annealing process, Zhu et al.[67] constructed a composite morphology of "two-dimensional mesoporous support-ordered nanoparticles", and prepared structurally ordered high-entropy alloy nanoparticles loaded on two-dimensional nitrogen-doped mesoporous carbon nanosheets (OHEA-mNC). The material features ultrathin carbon nanosheets with uniformly distributed mesopores (~ 10 nm in diameter). The L_{12} -phase ordered high-entropy alloy nanoparticles (with uniform particle size) are tightly and uniformly dispersed on the surface and inside the channels of the mesoporous carbon support without obvious agglomeration. The synergistic effect of the nitrogen-doped carbon substrate and ordered high-entropy alloy nanoparticles optimizes electron conduction and catalytic performance. Feng et al.[40] prepared $\text{Co}_{0.2}\text{Ni}_{0.2}\text{Cu}_{0.2}\text{Mg}_{0.2}\text{Zn}_{0.2}\text{O}$ porous layered high-entropy oxide using GO as the sacrificial template. This material exhibits a typical layered framework structure, where numerous nanoscale pores are distributed between and within the layers. The layered structure is formed by the interconnection of 8-12 nm high-entropy oxide nanoparticles, constructing a continuous porous network. This 2D mesoporous film morphology ensures high specific surface area and low charge transfer resistance of the material. It also achieves tight combination of the catalyst on the substrate, providing favorable conditions for electron transport and mass transfer in the methanol oxidation reaction. Similarly, Wang et al.[94] focused on the preparation of 2D porous nanosheet morphology, and synthesized FeCoNiMoRu series 2D porous high-entropy oxide nanosheets by sacrificial template method (using graphene as the template, **Fig. 7e**). The material exhibits a typical 2D sheet morphology with an ultrathin layer thickness (at the nanoscale). Mesopores of 5-10 nm are uniformly distributed on the surface, and there is no obvious stacking of nanosheets (**Fig. 7f**). The metal elements Fe, Co, Ni, Mo, and Ru are uniformly distributed within the sheets without element segregation or agglomeration. This 2D porous morphology not only maximizes the exposure of active sites, but also shortens the transport distance of ions and electrons during the reaction, providing an efficient structural basis for the oxygen evolution reaction while ensuring the structural stability of the material. In addition, the mesoporous amorphous high-entropy oxide film was prepared by Wang et al.[87] based on solution-phase controlled deposition-precipitation method uses SBA-15 mesoporous silica as the supporting substrate. The film uniformly coats the inner wall of SBA-15 mesopores while completely retaining the mesoporous structure of SBA-15, forming a supported mesoporous film system.

4.2.3 Three-dimensional structures.

Three-dimensional porous high-entropy materials (3D Porous HEMs) feature diverse morphologies, mainly in the form of 3D networks or particles. Their central design

concept is to construct hierarchical pore structures to achieve the synergy between pore distribution and structural support in 3D space, meeting the requirements of complex reaction systems for high specific surface area, efficient mass transfer, and structural stability.

Nanoframes. Nanoframes are defined by their three-dimensional open-frame architecture, which provides exceptionally high specific surface area and structural openness. Lin et al.[95] prepared HEA cubic nanoframes (**Fig. 7g**) using Pd@high-entropy alloy core-shell nanocubes as precursors via a Fe(III)-based wet etching process. The edge thickness of these frames is only 1.2 nm, and the overall structure is hollow without any solid regions. This structural design significantly increases the specific surface area and provides ample space for the contact between reactants and active sites.

Nanospheres. Nanospheres refer to porous high-entropy materials with typical spherical morphology, whose functional properties can be further optimized by constructing mesoporous structures. Nandan et al.[69] synthesized PtPdRuMoNi high-entropy alloy mesoporous nanospheres via a low-temperature wet chemical method assisted by the triblock copolymer (F127). The resulting nanospheres exhibit uniform spherical morphology, with mesopores densely distributed on the surface and inside the spheres. The pore size is concentrated at 10-12 nm, the sphere diameter is approximately 125 ± 10 nm, and the pore spacing is about 16 nm. The synergy between the core-shell element distribution and the mesoporous structure endows the material with a much higher specific surface area than non-mesoporous high-entropy alloys, significantly improving the accessibility of active sites. Wang et al.[96] prepared spinel-type $(\text{Zn}_{0.2}\text{Mn}_{0.2}\text{Fe}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2})_3\text{O}_4$ HEO three-dimensional hierarchical mesoporous microspheres (**Fig. 7h**) via a solvothermal method. These microspheres display a uniform hierarchical mesoporous microsphere structure (**Fig. 7i**), assembled from nanoparticle building blocks that form a continuous internal mesoporous network covering the full mesopore range. The material possesses a specific surface area of $37.295 \text{ m}^2 \text{ g}^{-1}$ and shows excellent structural integrity during electrochemical cycling. Wang et al.[80] synthesized Ni-Co-Cr-Fe-Mn spherical mesoporous high-entropy oxides via a sol-gel method. The material exhibits highly uniform spherical morphology with an average particle size of approximately 55 nm. A continuous mesoporous network is constructed inside the spheres, with the pore size concentrated in the range of 5.5-8.3 nm, and no obvious agglomeration of the spherical particles is observed.

Porous bulk materials. Porous bulk materials primarily exist as three-dimensional monolithic structures with internal porous networks, making them promising candidates for self-supporting electrodes. Li et al.[73] prepared self-supporting porous FeCoNiNbPt high-entropy alloy bulk via a dealloying method. Its core morphological feature is a three-dimensional interconnected porous structure, where ~ 3.5 nm $\text{Pt}_3(\text{FeCoNi})$ nanocrystals are embedded on the surface of the ligaments and wrapped by an amorphous NbO_x protective layer, forming a composite morphology of "nanocrystals-oxide-porous skeleton". Yu et al.[100] adopted a two-step method of "electrochemical

dealloying-anodization" to regulate the surface morphology of microwave-sintered AlCoCrFeNi high-entropy alloy, finally obtaining a porous composite surface. The dealloying process results in the formation of coral-like porous structure on the alloy surface and layered petal-like structure inside. Subsequent anodization further in-situ grows a microstructure with coexisting ice crystal-like and layered structures on the surface. The ice crystal-like structure provides high specific surface area, the layered structure optimizes bubble desorption efficiency, and the overall surface shows hydrophilicity. In another approach, the research group led by Tang[86] prepared porous CoCrFeNiMo high-entropy alloy bulk via microwave sintering technology using Mg powder as the space holder. The Mg powder is removed after sintering, forming pores with an average pore size of $2.83 \mu\text{m}$. The space holder method can effectively regulate the porosity. Han et al.[75] prepared eutectic dual-phase high-entropy alloy (AlCrFeCoNiW) via a selective etching process. The alloy precursor has an FCC/BCC eutectic dual-phase structure. After etching, the BCC phase is removed, forming a porous bulk material with a pore size of 200-500 nm.

Gradient pore structure. Gradient pore structures refer to materials in which the pore size varies progressively within the three-dimensional architecture, which can be achieved through phase composition regulation or template processes. Zhang et al.[101] used FeCoNiCr-Zr eutectic high-entropy alloy with negative mixing enthalpy as the precursor, optimized the multi-length-scale phase composition by adjusting Zr content, and then prepared self-supported bulk high-entropy alloys with tri-scale gradient pores successfully via electrochemical dealloying treatment. Its pore structure includes 2-6 μm micron-scale channels, 80-100 nm nanosheet channels and 3-5 nm mesopores. The nitrogen adsorption-desorption tests confirmed that its specific surface area reached $17.4 \text{ m}^2 \text{ g}^{-1}$. This enables the material to exhibit excellent electrocatalytic performance and stability. Mularzyk et al.[97] prepared a copper-based free-standing metal layer with gradient pores via the dynamic hydrogen bubble template method. Its core morphology is an interconnected vascular-like hierarchical pore structure (**Fig. 7j**). The pore radius shows a gradient distribution, about 5 μm at the bottom and up to 36 μm at the top, with the thickness adjustable between 50-200 μm . During the synthesis process, a zinc interlayer is used to regulate the adhesion between the foam and the substrate to achieve non-destructive peeling. Hydrogen bubbles act as templates to guide the dendritic deposition of copper between the bubbles, forming a "main pore-secondary pore" bimodal pore system. This gradient pore morphology endows the material with diffusion and transport performance significantly superior to that of traditional carbon fiber electrodes, combining the high conductivity of metals and the efficient mass transfer characteristics of porous structures.

Flower-like structures. The characteristic of the flower-like structure is its three-dimensional, flower-like form, which is usually assembled from low-dimensional nano-building blocks. Zhao et al.[79] successfully prepared $(\text{FeCoNiCuZn})\text{S}$ high-entropy sulfide via a two-step

solvothermal-annealing method. The material exhibits a typical hierarchical flower-like morphology (Fig. 7k), appearing as uniformly sized spherical aggregates. These aggregates are self-assembled from numerous ultrathin nanosheets with a thickness of approximately 10 nm. The nanosheets are interwoven and stacked in layers, forming an open and interconnected three-dimensional network with significant internal porosity. The unique flower-like hierarchical morphology and porous assembly characteristics form a synergistic advantage. It improves the interaction efficiency with electromagnetic waves through the high specific surface area of nanosheets, while the three-dimensional interconnected pore structure optimizes impedance matching and scattering effects. In addition, Jiang et al.[61] prepared flower-like high-entropy selenide (F-HES) through a two-step solvothermal method. Initially, a sea urchin-like high-entropy layered double hydroxide (HE-LDH) template was synthesized, followed by a selenization treatment to achieve structural transformation, ultimately resulting in a regularly organized flower-like hierarchical morphology. The material consists of spherical aggregates approximately 200 nm in diameter, which are self-assembled from numerous ultrathin nanosheets merely 5-10 nm thick. These nanosheets exhibit smooth edges and are intricately interwoven and stacked in layers, forming an open and interconnected three-dimensional network structure. Mesopores ranging from 20 to 50 nm are uniformly distributed between the nanosheets. Combined with a high BET specific surface area of $172.8 \text{ m}^2 \text{ g}^{-1}$, it greatly improves the specific surface area and porosity of the material, facilitating full exposure of active sites and improving mass transfer efficiency.

Worm-like structures. Worm-like structures usually refer to aggregated, curved, strip-like forms formed by the aggregation of nanoparticles, which typically contain abundant grain boundary defects. Liu et al.[77] prepared PdFeCoNiCu polycrystalline high-entropy nanomaterials via a two-step potential electrodeposition process. The particles agglomerate to form irregular curved strips, similar to a worm-like morphology. These agglomerates possess a high density of grain-boundary defects, which act as highly active sites for catalytic reactions, making it a promising type of electrocatalytic material.

4.2.4 Interplay between dimensional architectures and porous textures

The dimensionality of porous high-entropy materials not only determines their external morphology but also profoundly influences their internal pore architecture. These characteristics include pore size and distribution, channel connectivity, specific surface area, and tortuosity. Pore structure directly affects the accessibility of active sites and the transport of reactants and products. Understanding how dimensionality shapes pore structure is therefore essential for optimizing electrocatalytic performance.

From a broader catalytic perspective, spatial confinement strategies have been shown to significantly enhance electrocatalytic performance. Zhang and colleagues recently reviewed the application of 1D, 2D, and 3D confined structures in water splitting. They pointed out that confined

spaces can lower reaction barriers by modulating electronic structures and mass transport pathways[102]. This concept has recently been extended to high-entropy material systems. Yang and colleagues published a paper focusing on the dimensionality engineering of high-entropy alloys. It systematically reviews the synthesis strategies and application progress of 1D, 2D, and 3D high-entropy alloys in electrocatalysis[103]. The work indicates that tuning the dimensionality of HEAs can effectively regulate their pore structure, active site exposure, and electron transport properties, thereby improving electrocatalytic performance. These studies provide important background support for understanding the intrinsic relationship between dimensionality and pore structure. Building on this foundation, the present article focuses on porous high-entropy materials. It explores the characteristics of pore structures across different dimensions and their regulatory effects on electrocatalytic performance.

In one-dimensional systems, typical morphologies include nanofibers, nanowires, and nanotubes. Their pore structures often feature mesopores (2–50 nm) distributed along the length or hollow channels running through the interior. This configuration provides low-tortuosity electron transport pathways along the axial direction. Meanwhile, the mesopores or hollow structures create short diffusion distances for electrolytes and reactants. As a result, one-dimensional porous materials exhibit clear advantages in electrocatalytic processes that demand fast reaction rates, such as the HER. However, it should be noted that the pore volume and specific surface area of such materials are often limited by the fiber diameter and the degree of internal pore development.

In contrast, two-dimensional porous high-entropy materials, such as nanosheets or thin films, possess atomic-scale thickness and in-plane mesopores. The ultrathin structure greatly increases the density of active sites per unit volume. The in-plane pores further enlarge the specific surface area and provide additional edge sites. Since the thickness is typically less than 10 nm, most active sites are located at or near the surface, and diffusion limitations are significantly reduced. Such structural features are well suited for surface-sensitive reactions such as the ORR. However, two-dimensional systems lack a three-dimensional pore network. Under high current densities, they may face issues such as insufficient electrolyte wetting and poor gas bubble release.

Three-dimensional porous high-entropy materials, such as nanoporous bulks, foams, aerogels, and nanoframes, exhibit more complex pore structures. Micropores (<2 nm), mesopores (2–50 nm), and macropores (>50 nm) often coexist and interconnect to form hierarchical networks. This multiscale pore system provides an extremely high specific surface area on one hand. On the other hand, it creates continuous channels for electrolyte infiltration and gas product escape. Micropores contribute a high density of active sites. Mesopores facilitate mass diffusion. Macropores benefit convection and bubble release. The synergy among these three pore types enables three-dimensional materials to perform well in high-current-density scenarios such as industrial-scale water electrolysis. Of course, the complexity

of three-dimensional structures also brings challenges. These include maintaining uniform elemental distribution over large scales and preventing pore structure collapse during long-term operation.

The connection from dimensionality to pore structure and then to electrocatalytic performance offers useful

guidance for the further design of porous high-entropy materials. For ease of comparison, **Table 2** summarizes the typical morphologies, structural characteristics, and functional advantages of 1D, 2D, and 3D porous high-entropy materials.

Table 2. Morphology, structural characteristics, and functional advantages of 1D, 2D, and 3D porous high-entropy materials

Dimension	Representative material	Morphology and structural features	Functional advantages	Ref.
1D	FeCoNiMnRu-HCB _{0.5}	Nanofiber with mesopores (94%)	High specific surface area, abundant active sites	[60]
	PtPdRuIrCoCu	Mesoporous nanotube, wall thickness ~1.5 nm	High ECSA, low charge transfer resistance	[98]
	(NiCuMnCoZnFe) ₃ O ₄	Hollow nanofiber with mesoporous outer wall	High specific surface area, favorable electron transport	[82]
2D	(CoNiMnCuZn) ₃ O ₄	Nanosheet with in-plane mesopores, single-crystal	Single-crystal structure enabling fast electron transport	[58]
	OHEA-mNC	Nanosheet supported on mesoporous carbon	Enhanced conductivity from carbon support	[67]
	FeCoNiMoRu	Ultrathin lamellar nanosheet	Maximized exposure of active sites	[94]
3D	Pt ₃ (FeCoNi)@NbO _x	Nanoporous bulk with 3D interconnected pores	Self-supporting, excellent stability	[73]
	FeCoNiCr-Zr	Self-supporting bulk with triple-scale gradient pores (μm to nm)	Gradient pores mitigating bubble impact	[101]
	Pd@HEA	Cubic nanoframe with hollow open framework	Open framework structure, high atom utilization	[95]

4.3 Composition and crystal phase regulation

The regulation of composition and crystal phase in porous high-entropy materials is the core for their adaptation to electrocatalytic applications, which relies on the synergistic effect of element characteristics, process parameters and high-entropy effect. On the one hand, it constructs a stable porous structure, providing sufficient active sites and efficient mass transfer channels for electrocatalytic reactions. On the other hand, it optimizes the crystalline phase to avoid the attenuation of catalytic performance caused by structural collapse or crystal phase distortion, ultimately achieving precise regulation of electrocatalytic performance. Composition regulation serves as the foundation, involving the selection of elements with high intrinsic activity for target reactions, supplemented by additional elements to tailor the electronic structure [104]. Typically, transition metals (Fe, Co, Ni, Cu, Mn) and platinum-group metals (Pt, Pd, Ru) are used as core components, and multi-component strategies are adopted to meet the requirements of electrocatalysis. In terms of ratio and mixing entropy regulation, equimolar or near-equimolar ratios are usually adopted to ensure high mixing entropy ($\Delta S_{\text{mix}} > 1.5R$), which can effectively inhibit element segregation, ensure the uniform distribution of active elements in the porous skeleton, and avoid the imbalance of local catalytic activity. An important direction in compositional design is to exploit differences in the etching activity among elements to regulate the porous structure. For example, the AlCrFeCoNiW high-entropy alloy designed by Han et al.[75] has a composition of Ni₃₀Co₃₀Cr₁₀Fe₁₀Al₈W₂ (atomic percentage). Here, the 3d transition metals (Ni/Co/Fe)

provide high intrinsic electrocatalytic activity, while Cr and W improve mechanical strength and corrosion resistance, and Al plays the key role in forming a dual-phase eutectic system. The initial alloy has a dual-phase eutectic structure of FCC and ordered BCC (B2). By selectively etching the Al-rich B2 phase with 1 M hydrochloric acid, the FCC phase is successfully retained and a three-dimensional porous structure is constructed (**Fig. 8a**). Density functional theory (DFT) calculations reveal that the dealloying process induces changes in charge distribution and atomic orbitals, thereby optimizing the intrinsic electrocatalytic activity, and enabling the electrode exhibit excellent performance in hydrogen evolution reaction and oxygen evolution reaction.

Advanced composition regulation strategies also include the introduction of functional elements, stepwise process regulation and innovation of multi-component preparation methods. Yu et al.[100] prepared AlCoCrFeNi high-entropy alloy by microwave sintering, which mainly contains FCC and BCC phases. This alloy was further modified using a two-step method of electrochemical dealloying and anodization. During dealloying, part of the Cr was selectively removed, and active components such as FeOOH, NiOOH and CoOOH (M-OOH) are generated on the surface after anodization. The electrochemical treatment does not change the main phase structure of the alloy, but only improves the catalytic activity and stability of hydrogen evolution reaction and oxygen evolution reaction through surface composition reconstruction and morphology regulation. Feng et al.[74] established a “selective phase dealloying + electrodeposition modification” route to synergistically regulate composition and crystal phase. Using CoCrFeNiAl quinary equimolar alloy as the precursor, during

dealloying treatment with 0.5 M H_2SO_4 solution, the Al-Ni-rich B2 phase is selectively removed by utilizing the difference in corrosion resistance of each phase, and the Fe-Cr (Co)-rich body-centered cubic (BCC) phase is retained,

forming a labyrinthine nanoporous structure with a ligament size of about 17 nm (**Fig. 8b**). Subsequently, amorphous/crystalline Ni NPs are uniformly loaded on the surface of the porous substrate and internal

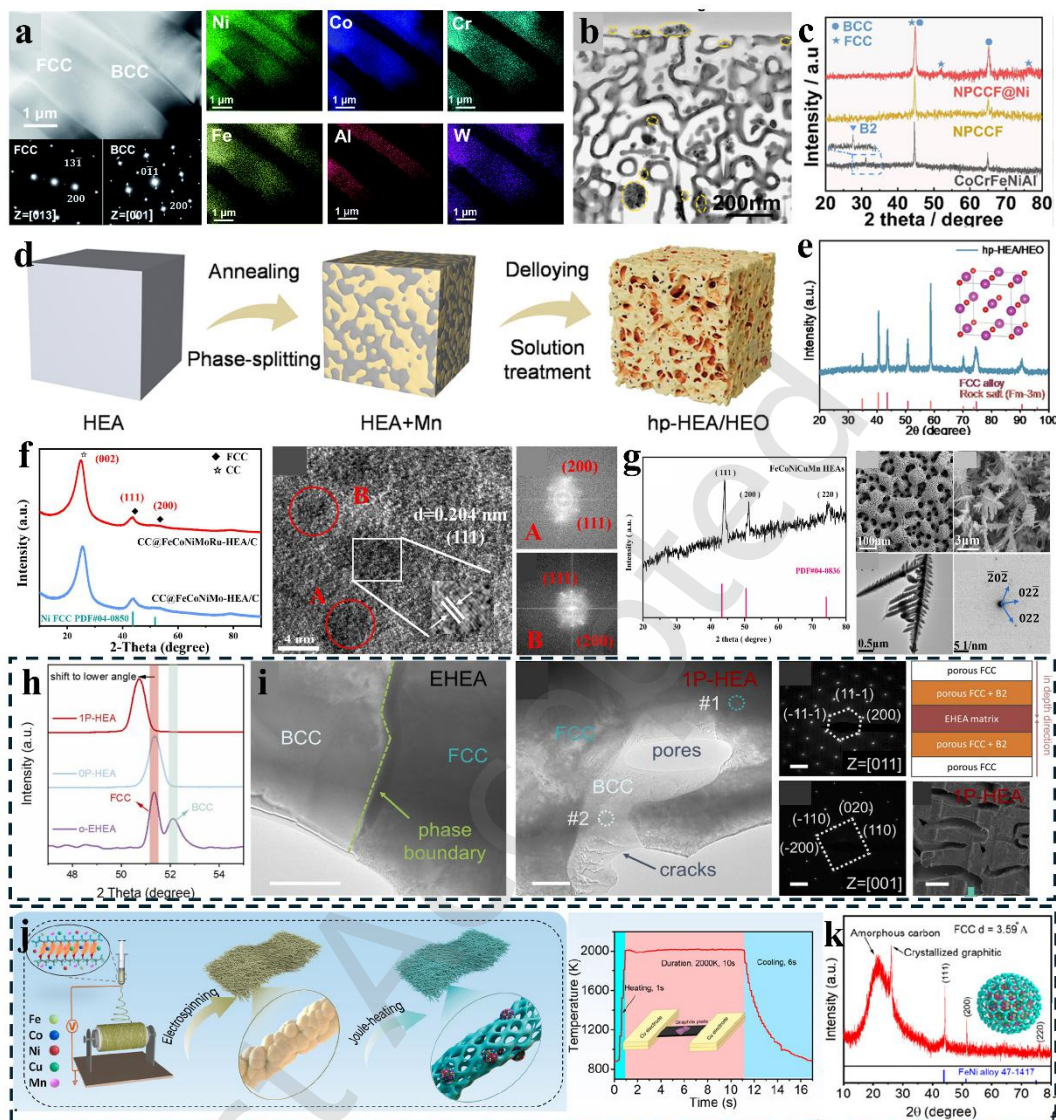


Figure 8. (a) TEM image, HAADF image, SAED pattern and TEM-EDS mapping of the sample. Adapted with permission from ref. [75] copyright 2022, Royal Society of Chemistry. (b) TEM image of NPCCF@Ni, (c) XRD patterns of as-spun CoCrFeNiAl, NPCCF, and NPCCF@Ni. Adapted with permission from ref. [74] copyright 2025, American Chemical Society. (d) Schematic of preparing free-standing hp-HEA/HEO and its structural, morphological characterizations, (e) XRD pattern of hp-HEA/HEO. Adapted with permission from ref. [105] copyright 2024, Wiley. (f) XRD patterns and HRTEM image of CC@FeCoNiMoRu-HEA/C. Adapted with permission from ref. [62] copyright 2024, Elsevier. (g) XRD pattern, SEM image, TEM image and SAED image of the sample. Adapted with permission from ref. [81] copyright 2025, Elsevier. (h) Partial XRD patterns of eutectic high-entropy alloy, (i) HAADF images of EHEA and 1P-HEA (scale bar: 1 μm) and corresponding FCC, BCC phase SAED patterns (scale bar: 5 nm^{-1}). Adapted with permission from ref. [106] copyright 2023, Elsevier. (j) Schematic of preparing HCNF/HEA composite and its digital images before and during Joule-heating synthesis, (k) XRD pattern of the HCNF/HEA composite. Adapted with permission from ref. [107] copyright 2024, American Chemical Society.

ligaments through electrodeposition process, successfully introducing the FCC phase, and finally forming a BCC and FCC composite phase structure (**Fig. 8c**). This strategy realizes the selective retention of core components and crystal phase screening through dealloying, followed by the introduction of functional species and a new crystalline phase via surface modification, increasing the Ni element content by 7 times compared with the original material and

realizing the precise construction of multi-phase structure and gradient optimization of composition.

Cai et al.[57] designed ultra-small high-entropy sulfides (HES , FeCoNiCrMnS_x) with quinary equimolar components of FeCoNiCrMn, and realized structural stability through the dual confinement effect of MOF template and N-doped carbon matrix. In the composition design, S element is introduced to construct a strong hybridization system

between the 3d orbitals of transition metals and the 3p orbitals of sulfur. XAS and DFT calculations confirm that this hybridization effect shifts the d-band center toward the Fermi level, significantly optimizing the crystal electronic. In terms of crystal phase, a single cubic sulfide phase is formed with an interplanar spacing of 2.77 Å for the (200) plane. This synergistic regulation of composition and crystal orientation regulates electron transport characteristics through orbital hybridization and ensures structural stability through crystal phase optimization, providing a new paradigm for the design of high-activity catalysts. The research group led by Pei[105] prepared a self-supporting hierarchical porous high-entropy alloy/oxide composite system with quinary components of NiCoCuFeMn through melting dealloying and high-temperature solution treatment method (**Fig. 8d**), realizing the synergistic regulation of composition and crystal phase. In the composition design, Co, Fe and Mn are electrochemically active elements, Ni and Cu form a high-conductivity network, and the oxygen vacancy content of the oxide phase reaches 37.6% through process regulation. In terms of crystal phase, the HEA matrix is FCC phase, and the oxide phase is rock-salt phase (**Fig. 8e**). The two crystal phases achieve stable coexistence through the coherent interface relationship. This system clarifies the role of each element through the functional division of composition, ensures structural stability through the matching of crystal phases, and provides an important reference for the composition-crystal orientation synergistic design of porous HEAs in the field of energy storage. In addition, Zhang et al.[84] synthesized porous high-entropy alloy nanoparticles by hydrothermal method, with typical compositions such as $\text{Pt}_{13}\text{Ir}_{10}\text{Cu}_{23}\text{In}_{14}\text{Ga}_{26}\text{Pb}_{14}$ and $\text{Pt}_{42}\text{Ni}_{15}\text{Co}_8\text{Cu}_{28}\text{Fe}_7$. The content of noble metals and non-noble metals can be independently and precisely regulated, and the proportion of non-noble metals can exceed 80%. This method uses active hydrogen ($\text{H}\cdot$) generated in situ by DMF dehydrogenation to construct a local non-equilibrium environment, realizing synchronous reduction of multiple metals. The alloy exhibited an FCC crystal structure, with significant lattice distortion (atomic spacing deviation of about $\pm 16\%$) due to the difference in atomic size of multiple elements.

Crystal phase regulation aims to construct stable FCC, BCC or FCC/BCC crystal phases suitable for electrocatalysis, which needs to be carried out by combining multi-component processes and composition design. Annealing temperature is a key parameter affecting the formation and stability of crystal phases. For instance, Hu et al.[62] used multi-component MOF as the precursor to prepare CC@FeCoNiMoRu-HEA/C flexible self-supporting electrode loaded on carbon cloth through pyrolysis. The elements Fe, Co, Ni, Mo, and Ru are uniformly dispersed, with Ru content as low as 5.9 at.%, forming a porous structure with low noble-metal loading. The alloy exhibits a single FCC phase structure (**Fig. 8f**), and lattice defects (stacking faults and dislocations) are generated due to the difference in atomic radius of multiple elements. The three-dimensional open network of carbon cloth further optimizes charge and mass transfer. The crystal phase remains stable during catalysis,

ensuring the high catalytic performance and long-cycle stability of the electrode.

Achieving simultaneous optimization of crystal phase and porous architecture through dynamic processes is another important strategy. For example, Li et al.[81] utilized direct current electrodeposition method, with Fe, Co, Ni, Cu and Mn as the five core components. By precisely regulating the deposition current (3 A) and time (7 min), uniform solid solution of multiple components and directional control of crystal phases were achieved. In this alloy system, the five transition metal elements are uniformly distributed, effectively inhibiting element segregation, and finally forming a single face-centered cubic structure (**Fig. 8g**). The optimization of deposition parameters not only dominates the uniformity of composition, but also indirectly realizes the precise control of crystal phase by regulating the ion reduction rate and bubble template formation process, providing structural guarantee for the subsequent optimization of functional characteristics.

In addition, the catalytic performance of crystal phase can be further optimized by changing the lattice state through doping or high pressure. The $\text{PtBi}_{1.5}\text{Ni}_{0.2}\text{Co}_{0.2}\text{Cu}_{0.2}$ porous aerogel prepared by Ju et al.[11] exhibits a mass activity of 4.19 A mgPt^{-1} for methanol oxidation, which is 12.7 times that of commercial Pt, underscoring the significant impact of crystal phase optimization on specific electrocatalytic reactions. Chen et al.[106] realized the precise regulation of composition and crystal phase of $\text{Ni}_{30}\text{Co}_{30}\text{Fe}_{10}\text{Cr}_{10}\text{Al}_{18}\text{W}_2$ -based porous high-entropy alloy through a two-step process of dealloying-phosphorus doping. For composition control, phosphorus introduced by sealed crucible calcination was uniformly dispersed in the lattice in interstitial/substitutional forms without phosphide formation. The phosphorus doping content of 1P-HEA reached an optimal level of 2.88 at%, and no element segregation occurred in the alloy. For crystal phase control, partial BCC phase was removed from the original FCC/BCC dual-phase eutectic alloy by acid leaching, forming a stable porous FCC+BCC dual-phase structure. After phosphorus doping, the crystal phase characteristics remained unchanged, with no new phase formation or decomposition of the original phase. X-ray diffraction showed that the diffraction peak of the FCC// (111) plane of 1P-HEA shifted to a lower angle, confirming that phosphorus doping induced lattice tensile strain (**Fig. 8h**). High-angle annular dark-field scanning transmission electron microscopy and selected area electron diffraction further verified its layered structure with a single FCC phase on the surface and residual BCC phase inside, showing no obvious phase separation and ordered, complete crystal phases (**Fig. 8i**). In addition, phosphorus doping increased the lattice spacing of the FCC phase from 2.14 Å to 2.22 Å, with a strain value of 1.13% distributed in a gradient along the material depth. Such layered crystal phase characteristics and gradient strain endowed the material with excellent structural stability and electronic structure advantages, thus effectively improving the catalytic performance of hydrogen evolution and oxygen evolution reactions.

The high-entropy effect is the fundamental support for regulating composition and crystal phase, primarily manifested in two aspects: stabilizing the crystal phase and enhancing the catalytic activity. High mixing entropy can inhibit element segregation, ensures the composition uniformity of the porous skeleton, avoids the loss of catalytic sites caused by local corrosion, and stabilizes the metastable crystal phase. For example, Wang et al.[107] realized the precise regulation of composition and crystal phase of FeCoNiCuMn quinary honeycomb porous carbon nanofiber/high-entropy alloy composite material through the synergistic process of electrospinning-Joule heating. This process first prepares a fiber membrane from PVA-PTFE spinning solution containing metal nitrates, and then conducts ultra-fast Joule heating treatment (**Fig. 8j**), which not only ensures composition uniformity, but also realizes stable control of crystal phase. In terms of composition, a multi-component system is constructed where the high-entropy effect promotes uniform elemental dispersion. Each element is present in nearly equiatomic proportion, yielding a mixing entropy of 1.64 R, consistent with the thermodynamic definition of high-entropy alloys. For crystal phase regulation, Joule heating raises the temperature to 2000 K within 1 second, effectively inhibiting phase separation and promoting the formation of a single FCC structure of HEA (**Fig. 8k**). At the same time, regulating the heating time (1-10 seconds) can precisely control the HEA particle size (10-45 nm). In addition, Joule heating promotes the graphitization of HCNF and forms a stable heterojunction interface with HEA, laying a structural foundation for the performance optimization of composite materials.

Through the precise regulation of composition and crystal phase, the electrocatalytic activity, stability and selectivity of porous high-entropy materials can be significantly improved. This is achieved by deliberate control over elemental ratios, etching characteristics, and functional elements in compositional design, combined with optimization of processing parameters and lattice states in crystal-phase engineering. Combined with the supporting role of high-entropy effect, it lays a core foundation for the application of porous high-entropy materials in electrocatalysis, and also provides a clear direction for the subsequent breakthrough of material performance.

5 Electrocatalytic applications of porous high-entropy materials

5.1 Hydrogen evolution reaction (HER)

5.1.1 Introduction and fundamentals for HER

In the process of the global energy structure transitioning toward cleanliness and low-carbonization, hydrogen production via water electrolysis is regarded as one of the crucial approaches to achieve large-scale production of green hydrogen due to its simple process, environmental friendliness, and high purity of produced hydrogen[108]. As a core technology for green hydrogen production, the overall efficiency of electrochemical water splitting is closely related

to the performance of cathode catalysts for the HER[109]. Therefore, the development of highly efficient, stable, and low-cost HER electrocatalysts is of great significance for promoting the practical application of water electrolysis. The HER mechanism mainly follows the Volmer-Heyrovsky or Volmer-Tafel pathway[110], which is essentially a continuous process involving proton adsorption, reduction, and hydrogen molecule desorption on the catalyst surface. The performance of the catalyst mainly depends on three core factors: electronic structure, characteristics of active sites, and mass transfer efficiency. At the electronic structure level, an ideal catalyst should possess a moderate d-band center position to balance the adsorption strength of hydrogen intermediates (H^*). In terms of active sites, high-density and high intrinsic activity sites are conducive to improving reaction kinetics. Regarding mass transfer design, a well-developed pore structure can facilitate electrolyte diffusion and rapid hydrogen release[111].

At present, platinum-based catalysts exhibit excellent HER activity, however, their high cost and scarcity have severely restricted large-scale industrial applications. In recent years, porous high-entropy materials have shown great potential in the field of HER electrocatalysis due to their unique structural tunability and component synergistic effect. Through the synergistic regulation of multiple metal elements, such materials can optimize the electronic structure, expose abundant active sites, and strengthen the mass transfer process by virtue of the porous structure. Thus, they exhibit significant advantages in activity, stability, and adaptability, providing a new material platform and research idea for the development of the next generation of highly efficient and cost-effective HER catalysts.

5.1.2 Precise electronic structure regulation for HER

Precise regulation of the electronic structure is the core logic for porous high-entropy materials to achieve high-efficiency HER catalysis. Through diversified strategies such as multi-element synergy and doping modification, the d-band center of the catalyst can be precisely adjusted to make the hydrogen adsorption free energy approach the ideal value, while significantly improving the intrinsic activity of active sites. The research by Han et al.[75] first verified the effectiveness of multi-element synergistic regulation. After acid leaching of the $Ni_{30}Co_{30}Fe_{10}Cr_{10}Al_{18}W_2$ eutectic dual-phase alloy to remove the B2 phase, Ni/Co/Fe in the FCC phase served as active centers, and Cr/W synergistically regulated the electronic structure, reducing the HER Gibbs free energy change (ΔG_{H^*}) from 0.32 eV to 0.08 eV. In 1.0 M KOH, the overpotential at 10 $mA\ cm^{-2}$ was 101 mV, and the Tafel slope was 112 $mV\ dec^{-1}$, which was far superior to the original HEA. This regulation idea was further expanded in the research of Liu et al.[98] They prepared PtPdRuIrMCu (M=Mn, Fe, Co, Ni) quinary to septenary mesoporous nanotube high-entropy alloys via a template-induced method, with a tube wall thickness of approximately 1.5 nm. In 1 M KOH, PtPdRuIrCoCu mNTs exhibited the optimal HER performance, the overpotential at 10 $mA\ cm^{-2}$ was 35 mV, the Tafel slope was 47.59 $mV\ dec^{-1}$, and the exchange current density was 0.70 $mA\ cm^{-2}$, which was superior to

commercial Pt/C (overpotential 74 mV). The excellent activity originates from the electronic structure optimization induced by 3d transition metals, enhanced mass transport enabled by the mesoporous architecture. Feng et al.[74] obtained labyrinthine nanoporous CoCrFeNiAl by melt spinning and acid etching of arc-melted ingots. After electrodepositing amorphous/crystalline Ni nanoparticles, a

large number of active sites were exposed at the amorphous/crystalline interface, with a double-layer capacitance (C_{dl}) of 131.5 mF cm^{-2} , an overpotential of 50 mV at 10 mA cm^{-2} , and 91% activity retention after 120 h galvanostatic test ($100/500 \text{ mA cm}^{-2}$). Its performance benefits from the high hydrophilicity and large specific surface area of the

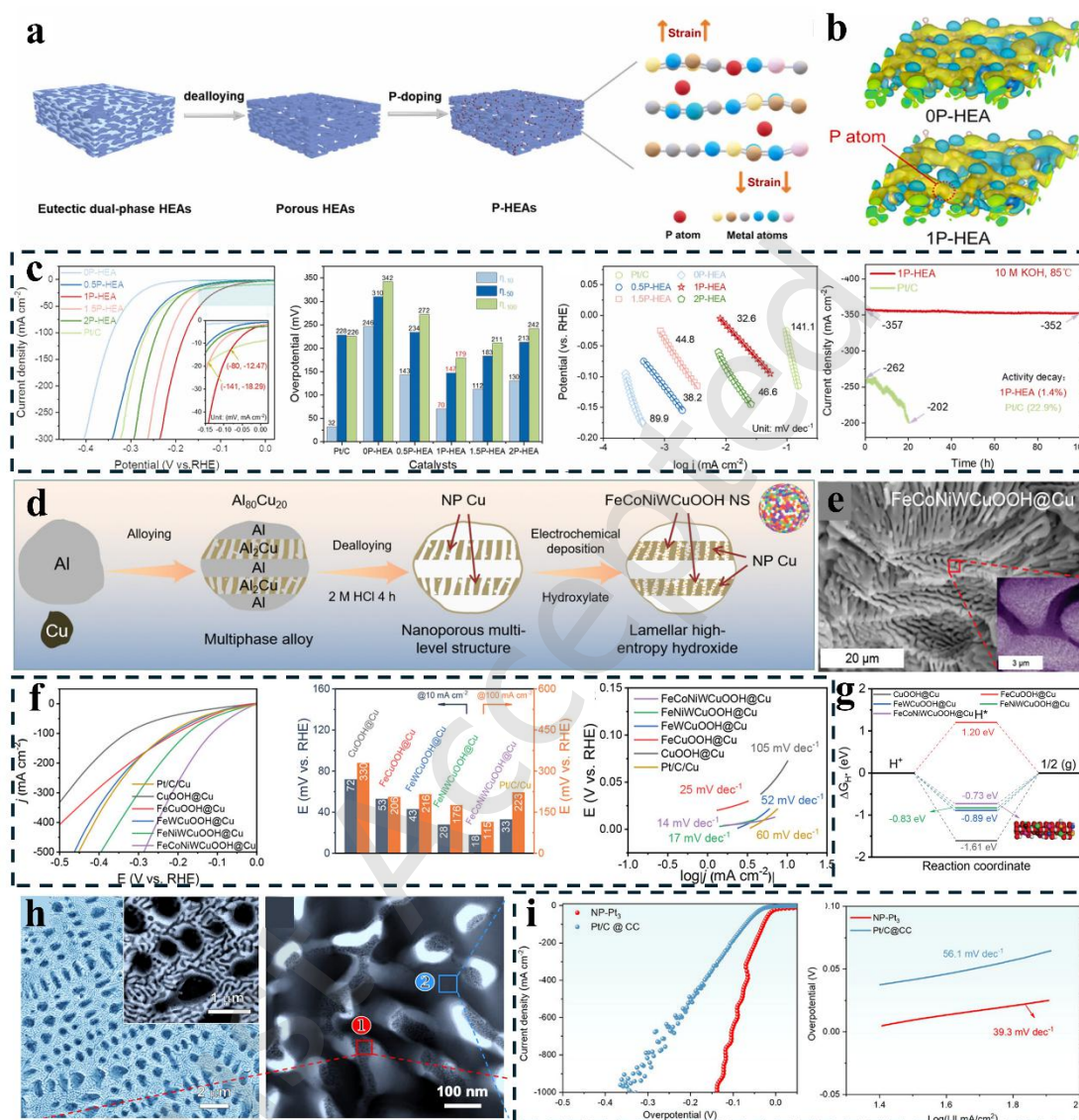


Figure 9. (a) Structural and compositional characterizations of P-doped HEA, (b) Charge density difference of 0P-HEA and 1P-HEA after H adsorption, (c) Electrochemical performance and stability of xP-HEA catalysts: LSV, Tafel curves and stability results. Adapted with permission from ref.[106] copyright 2023, Elsevier. (d) Synthesis diagram of FeCoNiWCuOOH@Cu, (e) SEM images of FeCoNiWCuOOH@Cu, (f) Polarization curves, overpotentials and Tafel slopes of samples in 1 M KOH, (g) HER free energy profiles and structural characterizations of NP-Pt₃ electrode before HER test. Adapted with permission from ref.[112] copyright 2024, Wiley. (h) SEM image of NP-Pt₃, (i) Polarization curves of NP-Pt₃ and Pt/C@CC in 0.5 M H₂SO₄ and their Tafel slopes. Adapted with permission from ref.[73] copyright 2025, Wiley.

nanoporous structure, the optimized hydrogen adsorption free energy (-0.169 eV) after Ni particle modification, and the accelerated charge transfer at the amorphous/crystalline interface.

In addition, Chen et al.[106] innovatively combined doping and strain regulation to prepare P-doped porous high-entropy materials (xP-HEA) via a dealloying-phosphorus doping strategy (Fig. 9a). The underlying mechanism of this process can be elucidated by the charge density difference diagram (Fig. 9b), electronegative P

atoms form lateral electron cloud accumulation with adjacent metal atoms, leading to electron cloud dissipation in the Z direction where H atoms may adsorb (cyan area), which significantly weakens the metal-H bond interaction. Such electronic modulation creates favorable conditions for H^{*} desorption, thereby optimizing the key step in the HER. Benefiting from the structural and electronic regulation, xP-HEA exhibits excellent HER performance under alkaline conditions (**Fig. 9c**), in 1 M KOH, the optimal sample 1P-HEA (P doping amount 2.88 at%) exhibits the most prominent HER activity, surpassing Pt/C at an overpotential of 80 mV, and delivers a Tafel slope as low as 32.6 mV dec⁻¹. The activity decay is only 1.4% after 100 h stability test, confirming the effectiveness of this approach for developing highly efficient and stable HER catalysts.

5.1.3 Design and construction of porous structures for HER

Precise construction of porous structure is another critical factor in enhancing the HER activity of porous high-entropy materials. The hierarchical porous network formed by multiple processes such as dealloying, electrodeposition, and template method can not only increase the specific surface area to expose sufficient active sites, but also accelerate electrolyte penetration and bubble desorption, optimizing reaction kinetics. For example, Li et al.[81] prepared feather-like porous FeCoNiCuMn high-entropy materials via galvanostatic electrodeposition on Cu foil using a two-electrode system. The 30-50 μm porous channels result in a water contact angle close to 0°, and the bubble detachment speed is 3 times faster than that of the Cu substrate, effectively avoiding active site blockage. The HER overpotential at 100 mA cm⁻² is 200 mV, and the charge transfer resistance (R_{ct} =2.3 Ω) is much lower than that of pure Cu. In addition, the self-supporting porous structure can also improve stability. Zhou et al.[10] developed a FeCoNiNbPt porous high-entropy alloy electrode prepared via arc melting, which exhibits a tensile strength of 489.9 MPa, which is 25 times that of nickel foam (NF). There is no activity decay after 100 h galvanostatic test at 1 A cm⁻², and retains 117% of its initial activity after 2000 CV cycles.

Zhang et al.[112] adopted a two-step process of liquid metal dealloying-electrodeposition (**Fig. 9d**), first, the Cu₂₀Al₈₀ alloy was dealloyed in hydrochloric acid to selectively remove Al, preparing a 3D bicontinuous porous Cu skeleton. Then, FeCoNiWCuOOH nanosheets were grown in situ on this skeleton via electrodeposition and electrochemical hydroxylation, constructing a FeCoNiWCuOOH@Cu heterostructured high-entropy oxyhydroxide catalyst (**Fig. 9e**). This catalyst exhibits excellent HER performance under alkaline conditions (**Fig. 9f**), an overpotential of only 18 mV at a current density of 10 mA cm⁻² and as low as 115 mV at 100 mA cm⁻², which is much lower than that of Pt/C/Cu (223 mV). The Tafel slope is also remarkably small, only 14 mV dec⁻¹. In terms of stability, the catalyst maintains 98% of its current after 100 hours of continuous operation at a high current density of 300 mA cm⁻², providing a guarantee for long-term and efficient hydrogen evolution. DFT calculations reveal the

intrinsic origin of its high activity. The hydrogen adsorption free energy diagram (**Fig. 9g**) shows that the ΔG_H of FeCoNiWCuOOH@Cu is -0.73 eV, which is closer to the thermoneutral value, indicating a more favorable balance for hydrogen adsorption and desorption. In a separate study, Nandan et al.[69] prepared mesoporous PtPdRuMoNi high-entropy alloy nanospheres via a wet chemical reduction method using F127 as a soft template, with a pore size of 10-12 nm and a specific surface area of 170 m² g⁻¹. In 0.1 M KOH, the catalyst exhibits a high HER mass activity of 167 A g_{Pt}⁻¹ at an overpotential of 30 mV, significantly exceeding that of commercial Pt/C (34 A g_{Pt}⁻¹). It also achieves a low overpotential of 25 mV at a current density of 10 mA cm⁻² and shows no activity degradation after 10,000 cycles. The superior performance is attributed to the combined effects of lattice distortion, a mesoporous structure, and the Mott-Schottky effect.

5.1.4 Operational versatility and industrial application potential for HER

Through precise regulation of their structure and components, porous high-entropy alloys remarkable operational versatility, which can meet the requirements of different scenarios such as acidic, alkaline, and industrial-grade high-temperature, high-concentration electrolytes, and effectively solve the pain points such as catalyst activity decay and insufficient stability in specific environments. To meet the stringent requirements of acidic proton exchange membrane (PEM) water electrolyzers, Li et al.[73] prepared a self-supporting nanoporous FeCoNiNbPt high-entropy alloy catalyst (NP-Pt₃) via a selective phase dissolution method. Its unique structure consists of Pt₃(FeCoNi) nanocrystals (≈ 3.5 nm) embedded in an amorphous NbO_x protective layer (**Fig. 9h**). In 0.5 M H₂SO₄ electrolyte, this catalyst exhibits excellent HER activity (**Fig. 9i**), the overpotential at a current density of 1 A cm⁻² is only 137 mV, the Tafel slope is 39.3 mV dec⁻¹, and the Faradaic efficiency reaches 95.6%. More notably, it has excellent stability, with minimal activity loss after continuous operation for 2200 h at 1 A cm⁻² and 1 million potential cycles, thereby resolving the trade-off problem between catalyst activity and stability under acidic conditions.

For alkaline electrolysis systems, amorphous/crystalline heterogeneous modification can optimize reaction kinetics. Liu et al.[77] prepared worm-like PdFeCoNiCu polycrystalline high-entropy nanomaterials (PdFeCoNiCu-pHENs) via a two-step potential electrodeposition method. A porous structure rich in grain boundary defects is formed through periodic deposition and partial leaching, with uniform element distribution and coexistence of multiple valence states. In 1 M KOH, the catalyst delivers an overpotential of 38.4 mV at a current density of 10 mA cm⁻² and achieves a current density of 27.9 mA cm⁻² at an overpotential of 50 mV. It also shows a Tafel slope of 29 mV dec⁻¹ and a double-layer capacitance of 11.55 mF cm⁻². Moreover, there is no activity decay after 10,000 LSV cycles, and no significant voltage increase in the 40 h galvanostatic test.

In addition to the fundamental properties of activity and stability, the breakthroughs of porous high-entropy alloys in key practical properties such as CO poisoning resistance and cost reduction have further broadened their industrial application prospects. The research group led by Lin[95] prepared $\text{Pd}_{0.2}\text{Pt}_{0.2}\text{Ir}_{0.2}\text{Ru}_{0.2}\text{Rh}_{0.2}$ cubic nanoframes via Fe(III)-based wet etching using Pd@HEA core-shell nanocubes as precursors. Atomic mixing induces a downshift of the d- band center to -1.35 eV, which weakens CO adsorption. After 15,000 potential cycles, the catalyst retains 97.3% of its initial activity at 0.05 V, and even exhibits a 19.3% activity increase at 0.1 V. When employed as a cathode catalyst in PEM water electrolyzers, it delivers a current density of 473 mA cm⁻² at 1.8 V and 80 °C, and shows a voltage decay of only 2.80 mV h⁻¹ after a 24- hour galvanostatic test at 500 mA cm⁻². In addition, Wang et al.[60] prepared mesoporous carbon-supported FeCoNiMnRu high-entropy alloy catalysts via an electrospinning-activation-carbonization process, with a specific surface area of 1014 m² g⁻¹ and uniformly dispersed HEA particles. In 1 M KOH, the overpotential at 10 mA cm⁻² is 42 mV, which is superior to commercial Pt/C (66 mV). There is no current decay after 20 h constant voltage test at -0.16 V vs. RHE, and the performance is stable after 1000 CV cycles. The mesoporous structure, high- entropy effect, and metal-N bonds that enhance electron transport are identified as the core factors contributing to its superior performance.

5.1.5 Challenges and future perspectives for HER

Although porous high-entropy materials have achieved significant progress in HER, continuous breakthroughs are still needed in three directions. First, deepen the research on multi-metal synergistic mechanisms, combine in-situ characterization and theoretical calculations to reveal the dynamic evolution of active sites during the reaction. Second, scalable and low-cost synthesis processes should be developed, such as Joule heating and microwave sintering technologies, to reduce the energy consumption and cost of high-entropy material preparation. Third, the operational adaptability should be expanded by optimizing porous structures and component design for extreme conditions, such as high temperature and concentrated electrolytes, thereby further enhancing catalyst stability. In the future, with the iteration of material design and preparation technologies, porous high-entropy materials are expected to become core materials to replace traditional noble metal catalysts. This progress will help drive electrochemical hydrogen production toward industrial-scale, cost-effective applications, providing critical support for the global energy transition.

5.2 Oxygen evolution reaction (OER)

5.2.1 Introduction and mechanistic insights for OER

The oxygen evolution reaction (OER) serves as a fundamental half-reaction in various energy conversion technologies, including electrochemical water splitting for hydrogen production, fuel cells, and metal-air batteries. This process involves multi-electron transfer and the

adsorption/desorption of intermediates (e.g., *OH, *O, and *OOH), resulting in slow kinetics and high overpotential[113, 114]. Therefore, the development of efficient and stable OER catalysts is essential to enhance the overall performance of related energy systems. An ideal OER catalyst should possess the combined characteristics of high activity (low overpotential and Tafel slope), high stability (suppression of metal dissolution and structural collapse), and low cost. Although noble metal catalysts (e.g., RuO₂, IrO₂) exhibit high activity, they are limited by high costs and insufficient stability under complex working conditions, making it difficult to meet the demands of large-scale applications.

From the perspective of reaction mechanism, the OER mechanism in alkaline media typically follows the pathway: " $*\text{OH} \rightarrow *O \rightarrow *OOH \rightarrow O_2$ " pathway, with the transformation of *O to *OOH often identified as the rate-determining step[115]. Therefore, precise regulation of the catalyst's adsorption energy for intermediates is the critical for optimizing its performance. Studies have shown that increasing the density of active sites and enhancing electron conductivity are essential for promoting mass transport and charge transfer[116, 117]. In recent years, HEMs have shown significant potential in optimizing electronic structures, increasing active sites, and constructing efficient mass transfer channels through multi-component synergy and structural regulation. In particular, porous high-entropy compounds have emerged as an important direction in OER catalyst design, owing to their tunable physicochemical properties[118].

5.2.2 One and two-dimensional structures for OER

In reported studies, porous high-entropy materials with various structures have exhibited excellent OER performance. For one-dimensional structures, Hang et al.[119] synthesized the high-entropy spinel oxide $(\text{Ni}_{0.2}\text{Co}_{0.2}\text{Zn}_{0.2}\text{Cu}_{0.2}\text{Mg}_{0.2})\text{Fe}_2\text{O}_4$ nanofibers, which leveraged the advantages of 1D structure to deliver an overpotential of 286 mV at 10 mA cm⁻² and a Tafel slope of 136 mV dec⁻¹ in 1 M KOH, outperforming the quaternary $(\text{Ni}_{0.2}\text{Co}_{0.2}\text{Zn}_{0.2}\text{Cu}_{0.2}\text{Mg}_{0.2})\text{Fe}_2\text{O}_4$ (345 mV, 158 mV dec⁻¹) and single-component NiFe_2O_4 (300 mV, 162 mV dec⁻¹). The material exhibited a low charge transfer resistance of 0.34 Ω, indicating high electron transport efficiency. It also showed remarkable stability, with no potential decay observed during a 200 h galvanostatic test, and maintained performance for 300 h under a high current density of 600 mA cm⁻². In-situ characterization confirmed that the oxygen vacancy concentration increased during OER. The active phases FeOOH and CoOOH generated by surface reconstruction synergized with the 1D fiber structure and 8-10 nm mesopores, further improving mass transfer efficiency.

Two-dimensional porous structures also performed remarkably. Wang et al.[94] prepared 2D porous FeCoNiMoRu high-entropy oxide nanosheets using graphene as a sacrificial template through the processes of metal precursor adsorption, reduction, and calcination. This material exhibited excellent OER performance in 1.0 M KOH (Fig. 10a), with an overpotential of only 226 mV at 10 mA

cm^{-2} , far superior to commercial RuO_2 (315 mV). The mass activity reached $1.615 \text{ A mgRu}^{-1}$, which was 18.6 times that of RuO_2 , and the Tafel slope was 46.2 mV dec^{-1} , with no significant performance decay observed during a 40 h stability test. Its high activity and stability are attributed to the high exposure of active sites and fast mass transfer channels provided by the unique 2D porous structure, as well as the electronic synergistic effect among multiple components. Specifically, Fe, Co, and Ni transfer electrons to Ru, while Mo forms charge competition with Ru (Fig. 10b). These interactions collectively regulate the electronic

structure of Ru, stabilize the Ru^{4+} valence state to avoid excessive oxidative dissolution, optimize the adsorption strength of oxygen-containing intermediates, and reduce the energy barrier of the $\text{*O} \rightarrow \text{*OOH}$ step.

5.2.3 High-entropy phosphides and borides for OER

High-entropy phosphides and borides have further optimized catalytic performance through the synergy of non-metal doping and porous structures. The high-entropy phosphide

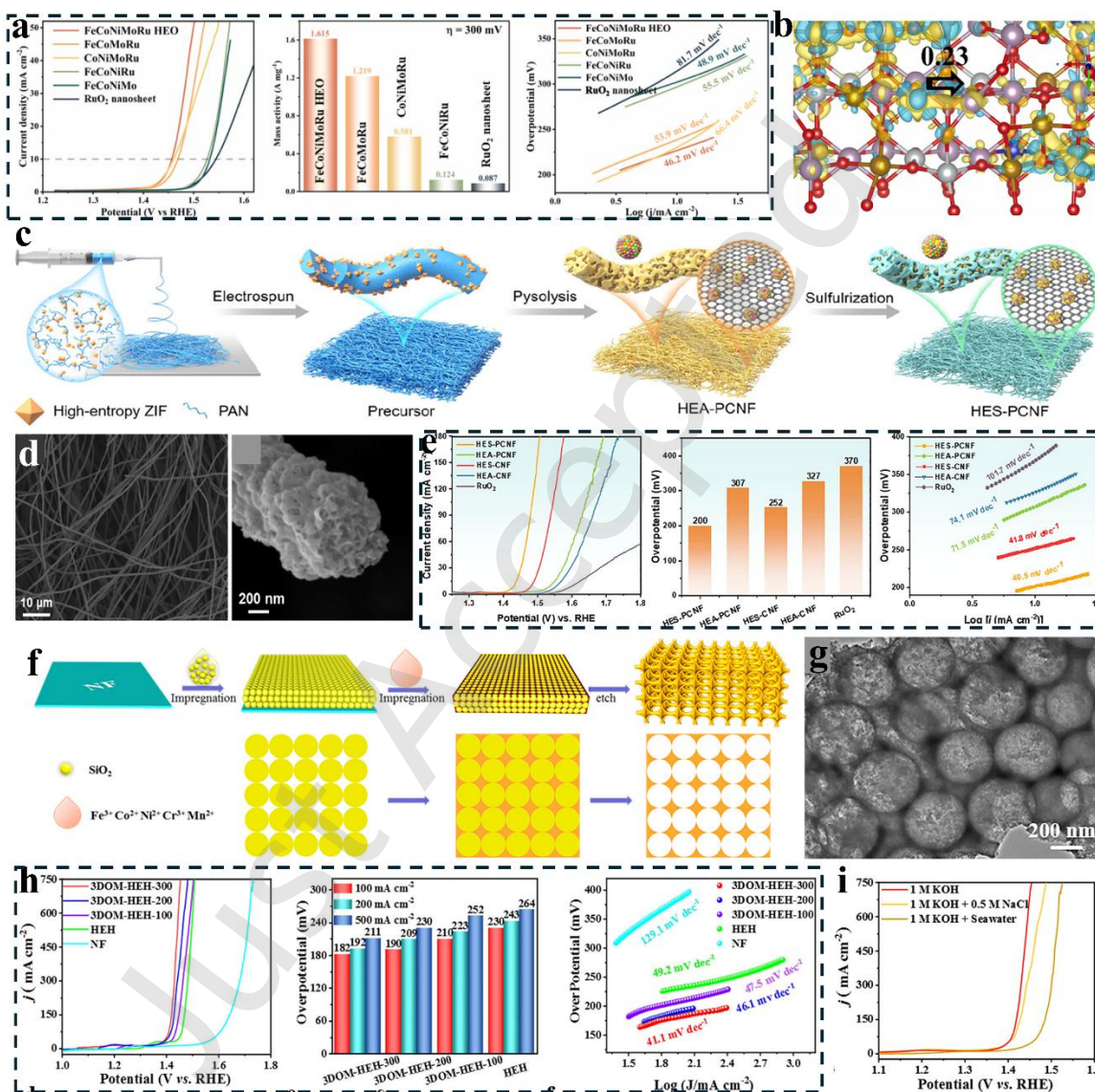


Figure 10. (a) OER polarization curves, mass activities and Tafel slopes of various samples, (b) Charge density difference of FeCoNiMoRu HEO and Mo-Ru charge competition (yellow: charge accumulation; green: charge delocalization). Adapted with permission from ref. [94] copyright 2026, Elsevier. (c) Scheme of the synthesis strategy for HES-PCNF, (d) SEM images of HES-PCNF, (e) LSV curves of various samples, overpotential histogram ($10 \text{ mA}\cdot\text{cm}^{-2}$) and Tafel plots. Adapted with permission from ref. [57] copyright 2025, Wiley. (f) Schematic of 3D ordered macroporous HEH synthesis, (g) SEM images of 3D ordered macroporous HEH, (h) LSV curves, overpotential comparison and Tafel slopes of different catalysts in 1 M KOH, (i) Polarization curves of 3DOM-HEH-300 under different electrolytes. Adapted with permission from ref. [55] copyright 2025, Wiley.

(1P-HEA, P content 2.88 at%) prepared by Chen et al.[106] exhibited an overpotential of 211 mV at 10 mA cm^{-2} , 251 mV

at 50 mA cm^{-2} , with a Tafel slope of 41.3 mV dec^{-1} in 1 M KOH. This performance significantly surpassed that of the non-P-doped sample and commercial RuO_2 . No activity decay was

observed during a 220 h galvanostatic test at 200 mA cm^{-2} , which is attributed to the 1.13% gradient tensile strain introduced by P doping, it can not only adjust the metal d-band center to optimize intermediate adsorption energy, but also accelerate electrolyte penetration and O_2 diffusion through the 3D porous structure. Similarly, the three-dimensional porous FeCoNiMgB high-entropy boride studied by Miao et al.[120] showed prominent kinetic advantages in 1 M KOH, with an overpotential of 234 mV at 10 mA cm^{-2} , a Tafel slope of 36.1 mV dec^{-1} , and a charge transfer resistance of 7.6Ω , outperforming commercial RuO_2 . The amorphous high-entropy metal borate $(\text{CrMnCoNiFe})_{0.2}\text{BO}_x$ prepared by Zhang et al.[121] further highlights the benefits of amorphous structure and mesoporosity. In 1 M KOH, it showed an overpotential of 236 mV at 10 mA cm^{-2} and a Tafel slope of 64 mV dec^{-1} , superior to quaternary metal borates. The high specific surface area ($446 \text{ m}^2 \text{ g}^{-1}$) and mesoporous structure with an average pore size of 9.2 nm provide sufficient active sites and mass transfer channels. The activity slightly increased after 1000 CV cycles, which is attributed to the metal vacancies formed by Cr dissolution and the in-situ generation of active phases such as NiOOH and CoOOH through surface self-reconstruction, further optimizing the catalytic kinetics.

5.2.4 High-entropy chalcogenides and alloys for OER

High-entropy chalcogenides and alloys have also shown excellent catalytic potential for the OER. Cai et al.[57] synthesized ultra-small high-entropy sulfide $(\text{FeCoNiCrMn})\text{S}_x$ supported on porous carbon nanofibers using Zn-based MOF as a sacrificial template (Fig. 10c, d). In 1.0 M KOH, this catalyst exhibited an overpotential of only 200 mV at a current density of 10 mA cm^{-2} and a Tafel slope of 40.5 mV dec^{-1} (Fig. 10e), with activity decay less than 2% after continuous operation for 300 h. The strong hybridization between the 3p orbital of S and the 3d orbital of metals optimizes the adsorption energy of the $^*\text{OOH}$, while the mesoporous structure increases the exposure rate of active sites. Jiang et al.[61] prepared flower-like high-entropy selenide (F-HES) via a two-step solvothermal method. In 1 M KOH, it required an overpotential of 252 mV to achieve 100 mA cm^{-2} , with a Tafel slope of $46.78 \text{ mV dec}^{-1}$. In the overall water splitting test, the cell voltage was 1.73 V at 100 mA cm^{-2} , which is superior to the $\text{RuO}_2//\text{Pt/C}$ system (1.85 V), with no activity decay after 30 h of operation. The flower-like structure and self-reconstruction characteristics make it suitable for bifunctional catalytic applications, while its mesoporosity facilitates rapid gas bubble release and prevents active site blockage. In addition, Huang et al.[122] prepared FeCoNiMnCu high-entropy alloy dendrites via cathode plasma-driven self-assembly process. In 1 M KOH, it exhibited an overpotential of 280 mV at 10 mA cm^{-2} and a Tafel slope of 59 mV dec^{-1} , outperforming commercial RuO_2 and quaternary FeCoNiMn alloy. The dendrite structure and mesopores formed by nanoparticle stacking enhance mass transport. No current decay was observed during a 40 h galvanostatic test at 10 mA cm^{-2} , and the dendrite structure remained intact after 1000 cycles. The oxide/hydroxide double-layer structure formed on the surface avoids component recombination, with the element dissolution

amount $< 0.1 \text{ at.}\%$. The high-entropy effect of the FCC single-phase structure effectively inhibits atomic diffusion and grain coarsening.

5.2.5 Composite catalysts based on high-entropy alloy for OER

Composite catalysts based on high-entropy alloy have also attracted extensive attention. Zhou et al.[10] fabricated a NiAlPt-LDH@PHEA composite by through selective etching the eutectic dual-phase structure combined with surface modification. This catalyst exhibited superior OER performance, achieving an overpotential of 227 mV at 10 mA cm^{-2} , as low as 166 mV at 200 mA cm^{-2} , with a Tafel slope of 25 mV dec^{-1} , consistent with the Volmer-Tafel mechanism. In situ Raman spectroscopy confirmed the reconstruction of the LDH phase into the active Ni-OOH phase during OER. The multi-element synergistic effect of PHEA can promote the formation of high-valence Ni^{3+} , ultimately making its overall water splitting performance superior to the $\text{Pt/C}||\text{RuO}_2$ system and the NiAlPt-LDH@NF system.

Tian et al.[55] successfully prepared a three-dimensionally ordered macroporous FeCoNiCrMn high-entropy hydroxide (3DOM-HEH) catalyst on nickel foam using SiO_2 nanospheres as the template via a simple chemical etching method (Fig. 10f, g). This material exhibits a uniformly interconnected ordered macroporous morphology, possessing both crystalline and amorphous characteristics and a super-hydrophilic surface. In 1 M KOH, with the 3DOM-HEH-300 sample showing low overpotentials of 182 mV and 211 mV at current densities of 100 mA cm^{-2} and 500 mA cm^{-2} , respectively, and a Tafel slope of only 41.1 mV dec^{-1} (Fig. 10h). In addition, the performance decay was only 3.4% after continuous operation for 400 h at 100 mA cm^{-2} . It also exhibited outstanding catalytic activity and stability in alkaline simulated seawater (overpotential 189 mV at 100 mA cm^{-2}) and natural seawater (overpotential 245 mV at 100 mA cm^{-2} , 278 mV at 500 mA cm^{-2} , Fig. 10i). Its excellent performance originates from the high specific surface area and fast mass transfer advantages of the 3DOM structure, the optimized electronic structure due to strong orbital coupling within the high-entropy system, and the synergistic effect of Fe sites selectively adsorbing OH^- and Mn sites inhibiting Cl^- adsorption. In addition, Zhang et al.[101] prepared a self-supporting porous high-entropy alloy catalyst with triple gradient pores (2 nm-6 μm) via electrochemical dealloying of a FeCoNiCr-Zr eutectic high-entropy alloy with negative mixing enthalpy. This catalyst exhibited an overpotential of 215 mV at 10 mA cm^{-2} and 370 mV at 1 A cm^{-2} in 1 M KOH, with a Tafel slope of 44.9 mV dec^{-1} . In particular, it can stably operate for more than 1000 h at a high current density of 2 A cm^{-2} with negligible activity decay. The performance is attributed to the gradient porous structure, which mitigates bubble impact and promotes mass and charge transfer, and the chemical stability of high-entropy intermetallic compounds that inhibits element dissolution. The multi-component oxide/hydroxide active layer generated on the surface during OER further optimizes the catalytic sites, and the multi-element synergistic effect regulates the electronic structure and improves the intrinsic

catalytic activity. Xu et al.[123] reported that a dealloyed dual-phase $\text{Fe}_{20}\text{Co}_{20}\text{Ni}_{20}\text{Cr}_{20}\text{Mo}_{20}$

high-entropy alloy exhibited an overpotential of 370 mV at 40 mA cm^{-2} in 1 M KOH, significantly lower than commercial $\text{IrO}_2\text{-RuO}_2\text{-Ta}_2\text{O}_5/\text{Ti}$ (500 mV) and $\text{IrO}_2\text{-RuO}_2/\text{Ti}$ (542 mV). The nanoporous film formed on the surface (grooves $\approx$ 500 nm, σ phase as the skeleton) increased the active surface area by 30% compared with that before dealloying. During a 60-hour galvanostatic test at 10 mA cm^{-2} , the overpotential change was less than 30 mV. The balance between activity and stability is achieved through the corrosion-resistant σ -phase in the dual-phase structure and the porous network formed by the dissolution of the FCC phase.

5.2.6 Challenges and future perspectives for OER

In summary, porous high-entropy materials have shown significant advantages in OER catalysis through synergistic component and structural design. To advance this promising field, future research could prioritize the following directions: first, further deepen the synergistic regulation of electronic structure and porous morphology, optimize intermediate adsorption and improve mass transfer efficiency through precise doping or multi-scale pore channel design. Second, develop low-cost and scalable synthesis routes, such as microwave method, self-propagating synthesis, etc. These approaches aim to reduce reliance on noble metals and facilitate the practical, large-scale application of these materials. Third, enhance the material adaptability under realistic and complex operating conditions, including high alkalinity, Cl⁻-containing, high temperature, etc. Concurrently, exploring their compatibility with device structures, such as membrane electrodes. These efforts will collectively drive the development of electrochemical water splitting and related technologies toward greater efficiency and broader industrial adoption.

5.3 Oxygen reduction reaction (ORR)

5.3.1 Introduction for ORR

The oxygen reduction reaction (ORR) is a critical process for the efficient operation of fuel cells, which requires high-performance electrocatalysts to reduce the high overpotential of its four-electron and two-electron pathways and accelerate reaction kinetics[124]. However, the large-scale application of proton exchange membrane fuel cells is limited by the high cost and scarcity of Pt-based catalysts. Therefore, developing ORR catalysts with high activity, high stability, and low noble metal content has become an important research goal [125, 126]. Porous high-entropy materials have shown broad application prospects in the ORR field, owing to their tunable components, controllable structures, and flexible catalytic properties enabled by multi-metal synergistic effects[127]. Their performance advantages originate from the synergistic regulation among the high-entropy effect, porous structural, and multi-metal components, the high-entropy effect optimizes the adsorption energy of key intermediates through lattice distortion and electron redistribution caused by the mixing

of multiple metal elements. The porous structure provides efficient mass transfer channels, promotes oxygen diffusion and electrolyte penetration, and increases the accessibility of active sites. Multi-metal components synergistically reduce the reaction energy barrier through electron coupling and functional division of labor, thereby jointly improving ORR activity and stability.

5.3.2 Based on MOF-derived methods for ORR

The metal-organic framework (MOF)-derived strategy offers an effective route for constructing porous high-entropy materials, leveraging the structural controllability of the precursors. For instance, Hu et al. [128] prepared a MOF-derived hollow high-entropy alloy, where the optimized mass transfer was attributed to a "chamber effect". The sample pyrolyzed at 650 °C exhibited an ORR onset potential of 0.97 V vs. RHE, an electron transfer number close to 3.7, and retained 85% of its current density after 1000 cycles, with performance significantly superior to that of the binary CuNi/C catalyst. In a separate approach, Su et al.[129] proposed a "kill two birds with one stone" strategy. Using zinc-rich MOF as the precursor, they took advantage of the low boiling point of Zn to prepare FeCoNiCuMg high-entropy alloy carbon nanocomposites (HEA/NC-5) with a hierarchical pore structure via one-step pyrolysis. The volatilization of Zn not only effectively inhibits metal agglomeration, forming uniformly dispersed single-phase high-entropy alloy nanoparticles (average diameter < 10 nm), but also constructs a three-level porous structure of micropores-mesopores-macropores (specific surface area 291 m² g⁻¹) (**Fig. 11a**). This significantly improved the utilization rate of active sites and mass transfer efficiency. In 0.1 M KOH electrolyte, this material exhibits excellent ORR performance, with an onset potential of 0.94 V vs. RHE, a half-wave potential of 0.84 V, a limiting diffusion current density of 4.94 mA cm^{-2} , and a Tafel slope of 56.8 mV dec⁻¹, outperforming commercial Pt/C (**Fig. 11b**). The electron transfer number is > 3.9 with a low peroxide yield, indicating a dominant 4-electron reaction pathway. The catalyst also showed outstanding long-term stability, retaining 65% of its activity after a 50000 s chronoamperometry test (**Fig. 11c**).

5.3.3 Mesoporous structure design and carrier-composite for ORR

In the design of mesoporous structures and carrier-composite strategies, research focuses on enhancing the utilization and stability of active sites through precise regulation of pore architecture and carrier interactions. Zhang et al. [130] employed an anchoring-carbonization strategy to stably load 2.2 nm PtFeCoNiCuZn high-entropy alloy on ordered mesoporous carbon (**Fig. 11d**). In 0.1 M HClO_4 , the ORR half-wave potential is 0.898 V, the mass activity at 0.9 V is 3.8-6.3 times that of Pt/C, and the ECSA is 102.3 m² g_{Pt}⁻¹ (1.62 times that of Pt/C) (**Fig. 11e**). After 5000 cycles, the activity retention is 98% and the ECSA loss is 3%, far superior to Pt/C. The strong anchoring effect and high-entropy effect ensure stability. In another study, Liu et al.[98] reported PtPdRuIrFeCu mesoporous nanotubes that

delivered a mass activity of $1.94 \text{ A mg}_{\text{Pt}}^{-1}$ at 0.9 V vs. RHE in 0.1 M KOH , which is 7.46 times that of commercial Pt/C. Even after 30000 cycles, the half-wave potential only decays by 7 mV , highlighting the unique advantage of the mesoporous structure in enhancing alkaline ORR stability. Furthermore, Zhu et al.[67] achieved a comprehensive synergistic breakthrough by loading an ordered-phase high-entropy alloy onto nitrogen-doped mesoporous carbon. In 0.1 M KOH , its half-wave potential reaches 0.90 V , 30 mV higher than that of commercial Pt/C. The mass activity at 0.9 V is 10 times that of Pt/C, and the chronoamperometry retention rate after 18 h is 95.37% ,

fully demonstrating the advantages of combining structural ordering with porous carriers.

5.3.4 Novel structural designs and multi-metal synergistic for ORR

Special structural design and multi-metal synergistic strategies further expand the performance limits of porous high-entropy materials. For instance, the high-entropy fluoride $(\text{MnNiCuCoZn})\text{F}_2$ system studied by Wang et al.[78] further embodies the value of multi-metal synergy. In 0.1 M KOH , it achieves a half-wave potential of 0.852 V , close to that of commercial Pt/C, and the electron transfer number is close

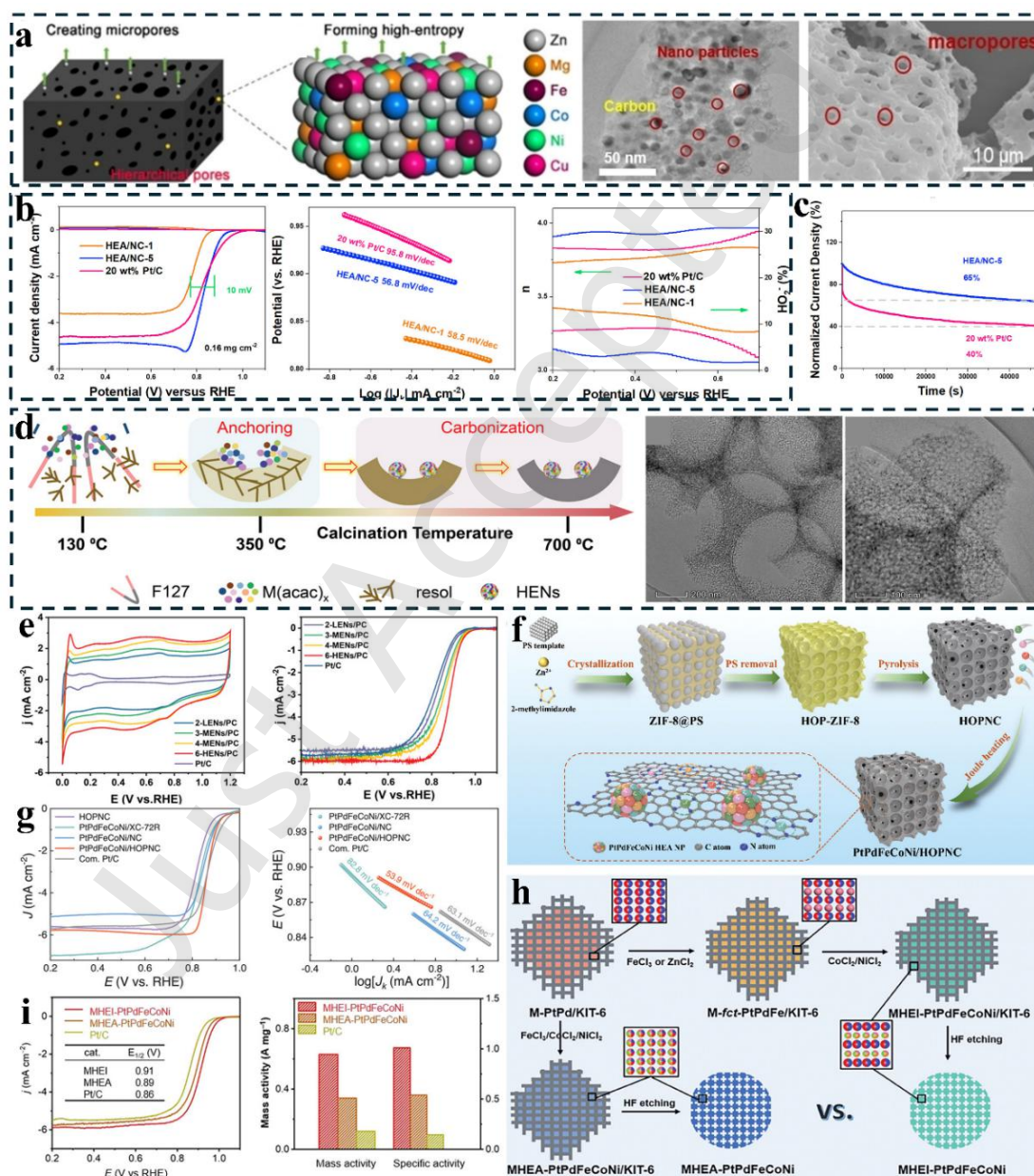


Figure 11. (a) Schematic of preparing hierarchical porous HEA via Zn-assisted method, and TEM, SEM images of HEA/NC-5, (b) Electrochemical and catalytic performance of HEA/NC-5 and 20 wt% Pt/C: LSV curves, Tafel slopes, electron transfer number and HO_2^- yield, (c) Chronoamperometry curves of the HEA/NC-5, 20 wt% Pt/C catalysts. Adapted with permission from ref. [129] copyright 2024, Wiley. (d) Schematic of HENs-carbon interfaces synthesis via anchoring-carbonization, and TEM images of 6-HENs/PC, (e) CV curves and ORR polarization curves. Adapted with permission from ref. [130] copyright 2022, Wiley. (f) Schematic of PtPdFeCoNi/HOPNC synthesis, (g) ORR polarization curves and corresponding Tafel slopes. Adapted with

permission from ref. [131] copyright 2024, Wiley. (h) Schema of concurrent template synthesis of MHEIs and MHEAs, (i) LSV curves of series samples in O₂-saturated 0.10 M KOH and summary of mass/specific activities at 0.90 V. Adapted with permission from ref. [132] copyright 2023, Wiley.

to 4. DFT calculations further reveal that its ORR energy barrier is reduced from 1.80 eV to 1.03 eV, clarifying the optimization effect of multi-metal division of labor and high electronegativity element regulation on reaction kinetics.

Through an ultra-fast Joule heating process, Xie et al.[131] spatially immobilized ≈ 2 nm PtPdFeCoNi high-entropy alloy nanoparticles and multi-metal single atoms on a three-dimensional hierarchically ordered porous nitrogen-doped carbon (HOPNC) framework, preparing a PtPdFeCoNi/HOPNC bifunctional catalyst (**Fig. 11f**). In 0.1 M KOH electrolyte, this material exhibits excellent ORR performance, with a half-wave potential of 0.866 V vs. RHE, a Tafel slope of 53.9 mV dec⁻¹ (**Fig. 11g**). The electron transfer number is close to 4 with low peroxide yield, indicating high reaction selectivity. It also exhibits outstanding long-term stability, showing no obvious shift in half-wave potential after 5000 CV cycles. Furthermore, Wang et al.[132] synthesized mesoporous high-entropy intermetallic compound MHEI-PtPdFeCoNi via a synchronous template strategy (**Fig. 11h**), which has double gyro mesopores (pore size 4.1 nm), L1₀ ordered phase, and fct structure. In 0.1 M KOH, the ORR half-wave potential is 0.91 V (50 mV higher than Pt/C), the mass activity at 0.9 V is 0.63 A mg⁻¹, and the specific activity is 1.01 mA cm⁻², which are 1.85 times that of the disordered alloy and 5.25 times that of Pt/C, respectively (**Fig. 11i**). After 50,000 cycles, it retains 87.3% of its activity, and chronoamperometry shows only a 13% loss after 48 h. DFT calculations confirm that multi-factor synergy effectively lowers the ORR energy barrier.

5.3.5 Challenges and future perspectives for ORR

In the future, the development of porous high-entropy materials in the ORR field can be promoted from the following aspects: in terms of component design, further reduce the noble metal content, explore low-cost and high-activity element combinations, and clarify the multi-element synergistic mechanism through the combination of theoretical calculations and experiments. In terms of structural regulation, it is essential to develop precise synthesis methods to achieve controllable fabrication of complex architectures, such as hierarchical pore channels and core-shell structures. Coupling these with in-situ characterization technology will help to deeply reveal the dynamic correlation between material structure and performance. From the perspective of application integration, catalyst and electrode structures should be optimized according to the practical requirements of different fuel-cell systems, aiming to enhance their durability under complex operating conditions. This will accelerate the transition of these materials from laboratory research to real-world applications, thereby providing key material support for the development of next-generation high-efficiency energy conversion devices.

5.4 Methanol oxidation reaction (MOR)

5.4.1 Introduction for MOR

The accelerating depletion of fossil energy resources has triggered a dual crisis of sustainable energy supply and environmental security. Compared with hydrogen, methanol has the advantages of convenient storage and transportation and compatibility with existing infrastructure, making direct methanol fuel cells (DMFCs) a highly promising electrochemical energy technology. Therefore, the development of high-efficiency and cost-effective catalysts for the MOR is particularly crucial[133]. Porous high-entropy materials exhibit unique advantages in MOR catalysis through the organic combination of high-entropy effect, porous structure, and multi-metal synergistic effect. From the perspective of electronic structure, lattice distortion and electron transfer driven by multi-element mixing entropy can regulate the metal d-band center and optimize the adsorption energy of key intermediates such as *CH₃OH, *CO, and *OH. For example, electron transfer from non-noble metals to Pt can induce lattice compressive strain, which can not only weaken the excessive adsorption of CO to alleviate catalyst poisoning but also promote the generation of OH species [134]. In terms of reaction kinetics, the hierarchical porous structure provides efficient mass transfer channels for reactants and products, while the three-dimensional interconnected network is conducive to reducing charge transfer resistance. Regarding anti-poisoning ability, the functional division of labor of multi-metal components and the "active site redundancy" mechanism can maintain the overall catalytic activity when some sites are poisoned, significantly improving long-term stability. In addition, the multi-metal coupling effect forms diverse active sites, which further optimize the material performance combined with structural regulation.

5.4.2 Aerogels and mesoporous structure for MOR

High-entropy alloy aerogels and mesoporous structural materials are two important systems in current research. Ju et al.[11] constructed anthill-like PtBi_{1.5}Ni_{0.2}Co_{0.2}Cu_{0.2} high-entropy alloy aerogels (HEAAs) via a co-reduction-freeze-drying strategy. The three-dimensional porous network achieves uniform distribution of multiple metals, significantly improving the exposure of active sites and mass transfer efficiency. XPS and DFT confirm that multi-metal synergy shifts the d-band center of Pt and optimizes the electronic structure. In the acidic MOR, the mass activity of this catalyst reaches 4.19 A mg_{Pt}⁻¹, which is 12.7 times that of Pt/C. Its CO adsorption strength is weaker than that of PtBi alloy and Pt/C, showing excellent anti-poisoning ability. A DMFC assembled with this catalyst delivers a peak power density of 115 mW cm⁻² and a current density of 0.49 A cm⁻² (0.2 V), outperforming commercial Pt/C-based batteries.

These results highlight the promising application potential of high-entropy alloy aerogels in fuel cells.

Porous high-entropy alloy materials with mesoporous structures can achieve breakthroughs in MOR performance through precise regulation. For instance, Fu et al.[71] used PS-b-PEO as a soft template to prepare mesoporous PtPdRhRuCu high-entropy alloy films via electrodeposition, with a mesopore size of about 25 nm, and abundant defects (Fig. 12a). In the 1.0 M KOH + 1.0 M CH₃OH, the catalyst exhibits excellent performance in MOR (Fig. 12b), with a mass activity reaches 4.2 A mg_{Pt}⁻¹, which is 7.2 times and 35 times that of mesoporous Pt films and commercial Pt, respectively. Its specific activity is 8.58 mA cm⁻², the

forward/reverse scan peak current ratio is 2.87, showing excellent anti-CO poisoning ability. The performance advantages stem from the ~25 nm mesopores enhance mass transfer and active-site exposure, the low work function (4.80 eV) accelerates electron transfer, and lattice distortion provides abundant active centers. DFT calculations further confirm that multi-metal sites reduce the energy barriers of methanol dehydrogenation and *CO desorption, providing valuable insight for fuel cell anode catalysis. In another study, Nam et al.[66] prepared PtPdRhRuMo high-entropy alloys with Mo activation centers via machine learning-assisted design. From the perspective of the theoretical potential energy surface

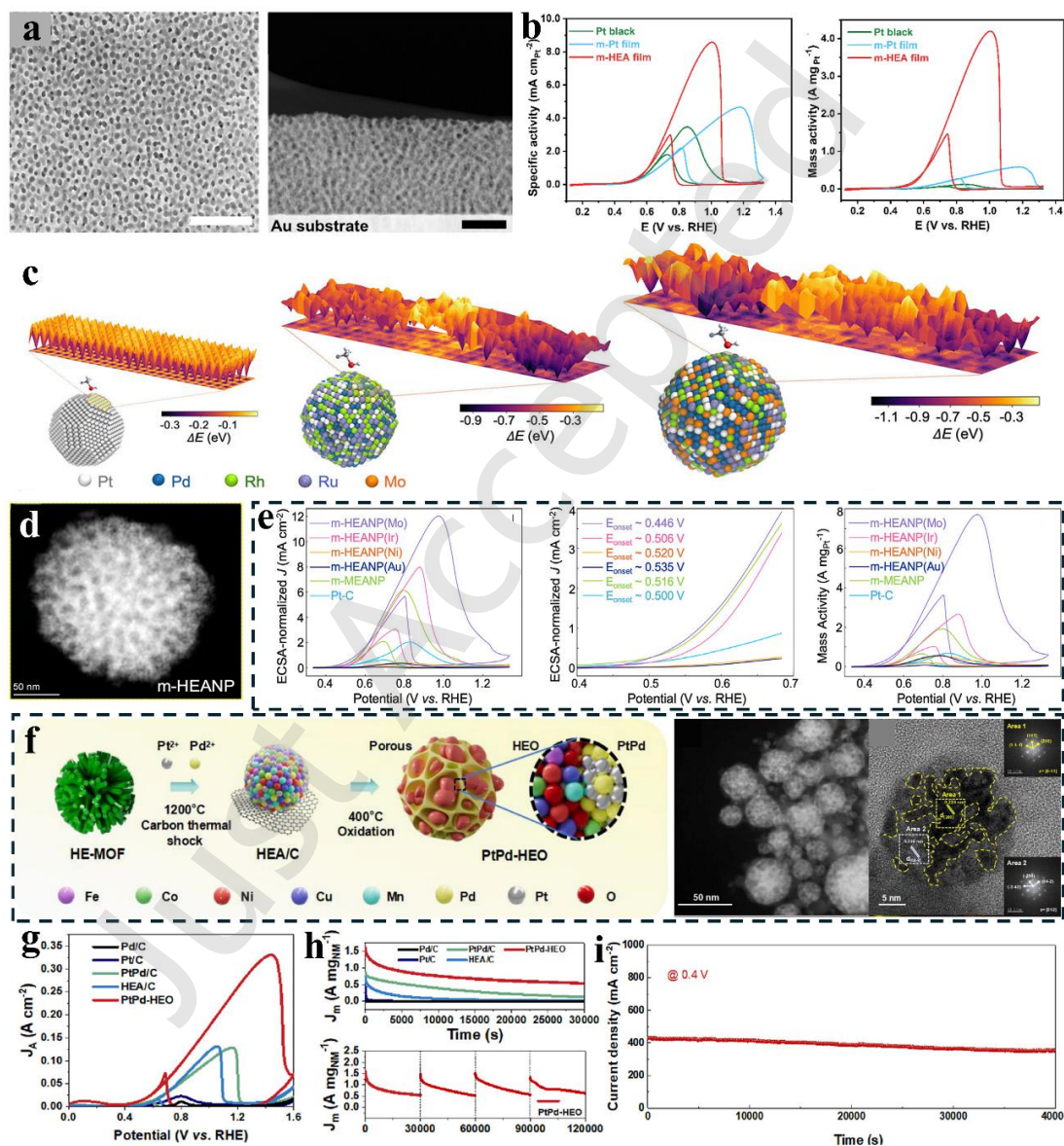


Figure 12. (a) Top-view SEM image and cross-sectional TEM image of the m-HEA film, (b) Specific activity and mass activity of m-HEA film, m-Pt film, and Pt black in N₂-saturated 1.0 M KOH + 1.0 M CH₃OH. Adapted with permission from ref. [71] copyright 2024, American Chemical Society. (c) Methanol adsorption potential energy landscapes on Pt(111), MEA and HEA surfaces, (d) HAADF-STEM image, (e) MOR electrochemical performance of m-HEANP(Mo) and other catalysts: ECSA-normalized CV profiles, onset potentials and Pt-loading based mass activities. Adapted with permission from ref. [66] copyright 2025, American Chemical Society. (f) Schematic of preparing PtPd-HEO and its microstructure characterization: HAADF-STEM, HRTEM images and inverse FFT patterns of PtPd alloy and HEO, (g) Current density of samples in 1.0 M KOH + 1.0 M CH₃OH, (h) I-t curves of samples at 0.70 V vs. RHE and long-term I-t curve of PtPd-HEO, (i) Stability test results of DMFCs assembled with PtPd-HEO. Adapted with permission from ref. [135] copyright 2025, Wiley.

(Fig. 12c), the energy difference of methanol adsorption sites on the single Pt (111) surface is only 0.3 eV, resulting in weak selective capture ability. The PtPdRhRu medium-entropy alloy (MEA) surface has a charge differentiation, which increases the energy difference to 0.9 eV and improves the adsorption capacity. For PtPdRhRuMo HEA surface, under the effect of Mo electron donors, forms a strong adsorption center with an energy difference of 1.1 eV, and the methanol adsorption free energy is as low as -0.76 eV, far superior to that of single Pt (-0.32 eV) and MEA (-0.52 eV), thus providing a favorable foundation for subsequent reactions. In the 1.0 M KOH + 1 M CH₃OH, the mesoporous nanoparticles (Fig. 12d) and films of this HEA have a maximum specific activity of 18.20 mA cm⁻² (8.3 times that of commercial Pt/C) and a mass activity of 9.89 A mg_{Pt}⁻¹ (Fig. 12e). And the CO oxidation onset potential is negatively shifted, showing excellent anti-poisoning ability, achieving a high degree of agreement between theoretical and experimental performance. Similarly, the PtPdRuIrCoCu mesoporous nanotubes prepared by Liu et al.[98] exhibit a MOR mass activity of 1.46 A mg_{Pt}⁻¹ in a 0.1 M KOH + 0.5 M CH₃OH. The high electrochemically active surface area and low charge transfer resistance brought by the mesoporous structure further verify the dual promotion of mesoporous tubular structures on active site exposure and mass transfer.

5.4.3 Heterostructures and polycrystalline nanomaterials for MOR

High-entropy heterostructures and polycrystalline high-entropy nanomaterials provide more diverse options for MOR. Yang et al.[135] used MOF-derived high-entropy alloys as precursors to construct mesoporous PtPd-high-entropy oxide heterostructured catalysts via in-situ oxidation (Fig. 12f). In 1.0 M KOH + 1.0 M CH₃OH, the MOR onset potential of this catalyst is 0.47 V, which is significantly negatively shifted compared with the reference catalyst (Fig. 12g). The area activity is 331 mA cm⁻² and the mass activity is 8.38 A mg⁻¹, far exceeding Pt/C and others. After a 30000 s chronoamperometry test at 0.70 V, the activity retention rate is 34%, and 85% of the activity can be recovered after 4 cycles (Fig. 12h). It can stably operate for 40000 s at a voltage of 0.4 V (Fig. 12i), with overall performance substantially exceeding PtPd/C and Pt/C- based cells, thereby providing a new paradigm for the application of high- entropy heterostructures in fuel- cell anodes.

In addition, the PdFeCoNiCu polycrystalline high-entropy nanomaterials prepared by Liu et al.[77] exhibit excellent MOR performance in alkaline media. The catalyst shows a specific activity of 52.48 mA cm⁻² and a mass activity of 20.98 A mg_{Pd}⁻¹, which are 2.6 times and 9.24 times higher than those pure Pd nanostructures (Pd-Ns), 6.02 and 9.24 times higher than commercial 20 wt% Pd/C, and 4.95 and 6.94 times higher than commercial 20 wt% Pt/C, respectively. At the same time, it also exhibits a more negative MOR onset potential, indicating a lower reaction energy barrier. Furthermore, Wang et al.[136] synthesized ultra- fine porous high- entropy alloys via reduction in

H₂/Ar at 700 °C. By leveraging lattice strain to regulate the electronic structure, they achieved simultaneous enhancement of both MOR activity and stability in acidic solutions, providing an example of improving performance through process optimization.

5.4.4 Challenges and future perspectives for MOR

Looking ahead, the development of porous high-entropy materials in the MOR can be promoted from multiple dimensions: in terms of component design, it is necessary to further reduce the amount of noble metals and screen high-activity and low-cost element combinations combined with theoretical calculations. In terms of structural regulation, hierarchical porous structures can be constructed through template methods, dealloying and other technologies to increase the electrochemically active area. In terms of application, it is necessary to enhance the wide pH adaptability of materials, optimize their compatibility with fuel cell components, and promote the improvement of single-cell performance. At the same time, with the help of in-situ characterization and multi-scale calculations, establish a "composition-structure-performance" structure-activity relationship model to accelerate the transformation of materials from laboratory research to industrial application.

5.5 Nitrate reduction reaction to ammonia (NO₃-RR)

Human activities, including excessive agricultural fertilization and large-scale industrial production, have led to the excessive accumulation of nitrate (NO₃⁻) in water, triggering a series of health, environmental and economic issues. Among various nitrate removal strategies, the electrochemical nitrate reduction reaction (NO₃-RR) for ammonia (NH₃) production is regarded as a promising green conversion route, as it integrates wastewater treatment with the production of a high-value chemical[137-140]. However, the conversion from NO₃⁻ to NH₃ involves multi-step reaction pathways and complex intermediates, and its efficiency and selectivity still need to be improved[141]. Recent studies have identified the regulation of active hydrogen (*H) as a key factor in enhancing NO₃-RR performance[142]. Porous high-entropy materials provide a new idea for breaking through the above bottlenecks through the synergistic effect of high-entropy characteristics and porous structures. At the electronic structure level, the multi-metal mixing entropy can drive lattice distortion and electron transfer, optimize the adsorption energy of key intermediates such as *NO₃, *NO₂ and *NO by regulating the d-band center, and thus balance the reaction energy barriers of each step. In terms of reaction pathways, different metal components can form synergistic sites with clear division of labor, constructing an efficient and complete catalytic cycle. Meanwhile, the porous structure can accelerate the mass transfer process, expand the electrochemically active surface area, which is conducive to improving ammonia yield and reaction kinetics [143].

In recent years, existing literatures have systematically investigated the NO₃-RR performance of porous high-

entropy materials, with numerous results confirming their high efficiency and stability. In the aspect of noble metal-based high-entropy systems, Zhu et al.[144] constructed a library of Pt-based high-entropy intermetallic compound (HEI) catalysts supported on two-dimensional nitrogen-doped mesoporous carbon (N-mC) via ligand-assisted interfacial assembly combined with a two-step carbonization strategy. Among them, $\text{Pt}_{0.8}\text{Fe}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Cu}_{0.2}/\text{N-mC}$ exhibited the best performance. In the 1.0 M KOH + 0.1 M KNO_3 , its NO_3^-/RR onset potential reached 0.20 V vs. RHE, and the current density was the highest (Fig. 13a). At -0.8 V vs. RHE, the ammonia yield reached $25.52 \text{ mg h}^{-1} \text{ cm}^{-2}$, which was 2.78~2.92 times that of the latter two (Fig. 13b). Meanwhile, it was compatible with a wide pH range of 1~14 and nitrate concentration $\geq 0.1 \text{ M}$, and the ammonia Faradaic

efficiency (FE_{NH_3}) still exceeded 97% after 20 cycles (Fig. 13c). Mechanistic studies revealed that the Pt-X bridge sites and Pt sites of HEI synergistically optimized the reaction energy barriers, ensuring high-efficiency catalysis (Fig. 13d).

As another representative of porous high-entropy materials, Li and co-workers[145] synthesized PdCuSnCoNi high-entropy metallene aerogels (HEMAs) via a seed-mediated route, integrating the structural advantages of high-entropy alloys, metallenes, and three-dimensional aerogels. The material features a 3D self-supported porous network assembled from ultrathin metallene subunits with a thickness of approximately 1.38 nm, achieving a BET surface area of up to $269 \text{ m}^2 \text{ g}^{-1}$. In an electrolyte of 0.5 M K_2SO_4 containing 500

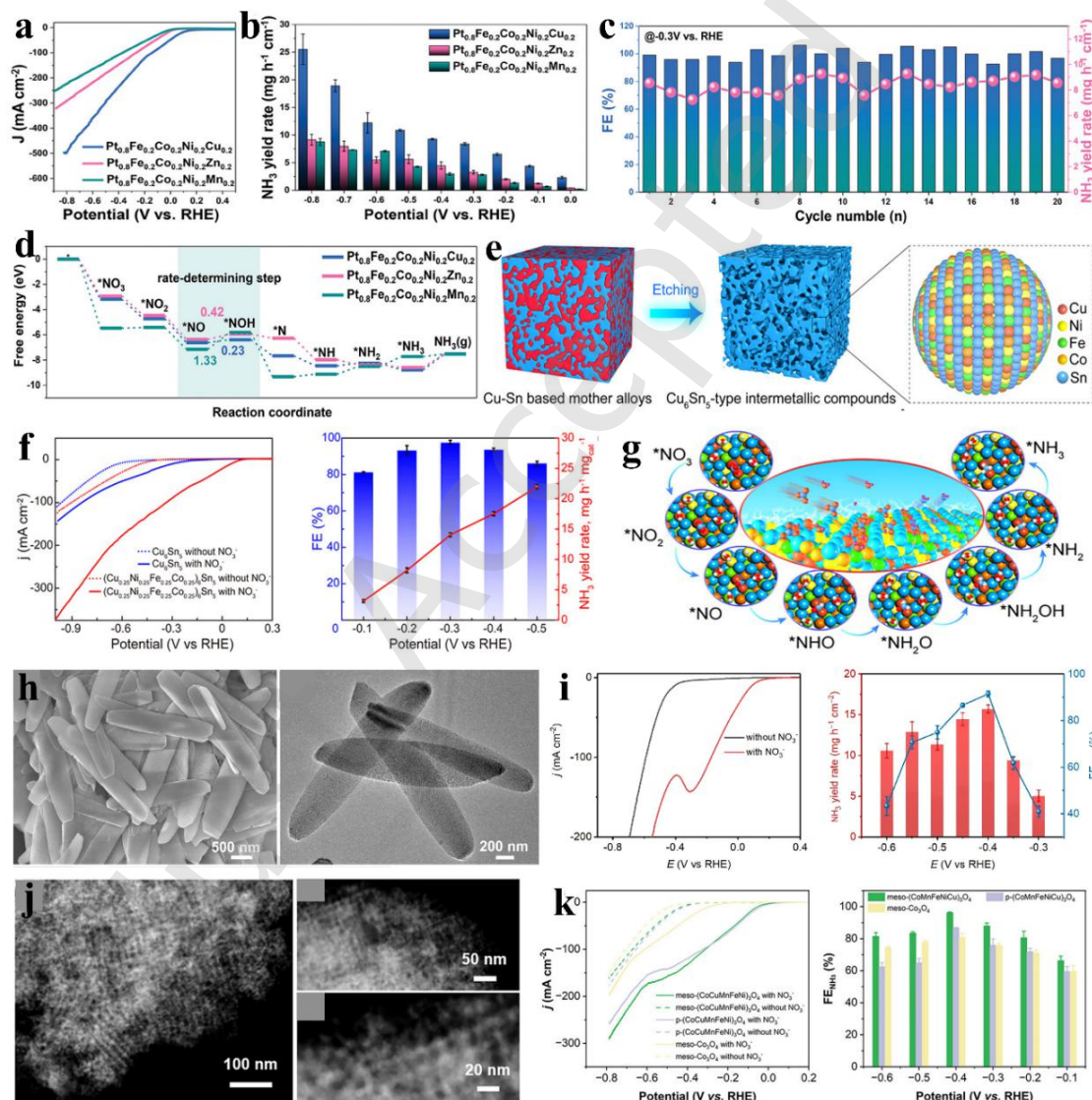


Figure 13. (a) LSV curves of three samples, (b) NH_3 yield rates of various samples, (c) Electrocatalytic NO_3^-/RR cyclic stability test at -0.3 V versus RHE, (d) Free energy diagrams of various samples and their (110) surfaces. Adapted with permission from ref. [144] copyright 2024, Wiley. (e) Schematic illustration for the preparation of nanoporous Cu_6Sn_5 -type intermetallic compounds, (f) LSV curves, NH_3 yield rates and faradaic efficiency of two samples, (g) Schematic of NO_3^-/RR on $(\text{Cu}_{0.25}\text{Ni}_{0.25}\text{Fe}_{0.25}\text{Co}_{0.25})_6\text{Sn}_5$. Adapted with permission from ref. [146] copyright 2025, Wiley. (h) High-resolution TEM image, and corresponding FT pattern, (i) LSV curves, NH_3 yield rates and FE_{NH_3} . Adapted with permission from ref. [58] copyright 2024, Springer Nature. (j) Low- and high-magnification HAADF-STEM images of the sample, (k) LSV curves of meso- $(\text{CoMnFeNiCu})_3\text{O}_4$ and counterparts and FE_{NH_3} . Adapted with permission from ref. [143] copyright 2025, the Separation and Purification Technology.

mg L⁻¹ N-KNO₃, the catalyst delivers an NH₃ Faradaic efficiency of 99.5% at -0.8 V vs. RHE and a yield rate of 4117.8 μg h⁻¹ mg_{cat}⁻¹ at -1.1 V vs. RHE. The multi-metal synergy effectively balances the production and consumption of active hydrogen and lowers the energy barrier of the rate-determining step, thereby suppressing the competing hydrogen evolution reaction.

Beyond noble metal-based systems, non-noble metal porous high-entropy materials also show great promise. Xiang et al.[146] prepared nanoporous Cu₆Sn₅-type high-entropy intermetallic compounds via a selective dealloying strategy (**Fig. 13e**). Among these, (Cu_{0.25}Ni_{0.25}Fe_{0.25}Co_{0.25})₆Sn₅ exhibited industrial-grade NO₃⁻RR performance for ammonia production. After adding 0.1 M KNO₃ to the 1.0 M KOH, the current density of the catalyst increased significantly, and the NO₃⁻RR onset potential was significantly more positive than that of the HER, proving that it could efficiently suppress the HER and preferentially catalyze NO₃⁻ reduction (**Fig. 13f**). And, at -0.3 V vs. RHE, the FE_{NH3} reached 97.09±1.15%, with the ammonia yield of 17.80±1.12 mg h⁻¹ mg_{cat}⁻¹. The presence of Sn contributed to the suppression of the HER, and the overall process followed a reaction pathway involving the gradual hydrogenation of nitrate to ammonia (**Fig. 13g**). This work provides a new direction for the design of non-noble-metal NO₃⁻RR catalysts.

Similarly, Wang et al. [58] prepared two-dimensional single-crystalline mesoporous high-entropy oxides (SC-MHEO) (**Fig. 13h**), among which (CoNiMnCuZn)₃O₄ SC-MHEO exhibited excellent performance. In the 1.0 M KOH + 0.1 M KNO₃, the catalyst exhibited a significantly higher current density compared to the NO₃⁻-free system, and the NO₃⁻RR onset potential was lower than that of the reference samples, indicating its stronger activation ability for NO₃⁻. At -0.4 V vs. RHE, the FE_{NH3} reached 91.5%, and the ammonia yield was 15.73 mg h⁻¹ cm⁻² (**Fig. 13i**). The activity retention rate exceeded 95% after 12 cycles, and it was compatible with a wide nitrate concentration range of 10~1000 mM, showing significant adaptability to nitrate-containing water bodies with different pollution levels. In a separate study, He et al.[143] prepared a series of high-entropy mesoporous metal oxides via nanocasting method using mesoporous KIT-

6 as the hard template (**Fig. 13j**). In the 1.0 M KOH + 0.1 M KNO₃, the (CoMnFeNiCu)₃O₄ attained an FE_{NH3} of 96.3%, and an ammonia yield of 1.83 mmol h mg⁻¹ (**Fig. 13k**). After 20 consecutive cycles, neither FE_{NH3} nor yield decreased significantly, and the stability was far superior to that of single-metal Co₃O₄ and the corresponding alloy. The high-entropy effect significantly reduced the hydrogenation-deoxygenation energy barrier.

Looking forward to the future, the development of porous high-entropy materials in the NO₃⁻RR can be promoted from the following aspects: in terms of material design, it is necessary to further reduce the noble metal content and screen low-cost and high-activity element combinations combined with theoretical calculations. In terms of structural regulation, it is necessary to develop controllable preparation strategies for hierarchical pores and low-dimensional morphologies to improve mass transfer efficiency and active site utilization. In terms of practical application, it is necessary to expand the adaptability of materials under complex water quality conditions such as wide pH range and high salinity, and promote their integration with components such as electrolyzers and separation membranes to achieve the leap from laboratory research to engineering application. At the same time, with the help of in-situ characterization and multi-scale simulation, the structural evolution and catalytic mechanism of materials during the reaction process should be deeply revealed to provide guidance for the rational design of high-performance NO₃⁻RR catalysts.

5.6 Summary of electrocatalytic performance

To provide a concise overview of the electrocatalytic performance of porous high-entropy materials across different reactions, **Table 3** summarizes the representative catalysts and key performance metrics for HER, OER, ORR, MOR, and NO₃⁻RR. The selection prioritizes materials with outstanding performance in each reaction, while also ensuring diversity in dimensional types (1D, 2D, 3D) and material systems, so that the summary is broadly representative.

Table 3. Summary of representative electrocatalytic performance of porous high-entropy materials.

Reaction	Representative material	Dimension	Electrolyte	Key metrics	Performance	Ref.
HER	PtPdRuIrCoCu	1D	1 M KOH	η ₁₀ , Tafel slope	35 mV, 47.59 mV dec ⁻¹	[98]
	NP-Pt ₃	3D	0.5 M H ₂ SO ₄	η ₁₀₀₀ , Tafel slope	137 mV, 39.3 mV dec ⁻¹ , stable 2200 h	[73]
	FeCoNiMnRu-HCB _{0.5}	1D	1 M KOH	η ₁₀ , Tafel slope	42 mV, 148.7 mV dec ⁻¹ , stable 20 h	[60]
	1P-HEA	3D	1 M KOH	η ₁₀ , Tafel slope	80 mV, 32.6 mV dec ⁻¹ , stable 100 h	[106]
	FeCoNiMoRu	2D	1 M KOH	η ₁₀ , Tafel slope	226 mV, 46.2 mV dec ⁻¹ , stable 40 h	[94]
OER	3DOM-HEH-300	3D	1 M KOH	η ₁₀₀ , Tafel slope	182 mV, 41.1 mV dec ⁻¹ , stable 400 h	[55]
	FeCoNiCr-Zr	3D	1 M KOH	η ₁₀ , Tafel slope	215 mV, 44.9 mV dec ⁻¹	[101]

	(FeCoNiCrMn) S_x @PCNF	1D	1 M KOH	η_{10} , Tafel slope	stable >1000h 200 mV, 40.5 mV dec ⁻¹ , stable 300 h	[57]
	PtPdRuIrFeCu	1D	0.1 M KOH	MA, $E_{1/2}$	1.94 A mg _{Pt} ⁻¹ , $E_{1/2}$ =0.94 V, 30000 cycles	[98]
ORR	HEA/NC-5	3D	0.1 M KOH	$E_{1/2}$, Tafel slope	0.84 V, 56.8 mV dec ⁻¹ , stable 50000 s	[129]
	PtPdFeCoNi/HOPNC	3D	0.1 M KOH	$E_{1/2}$, Tafel slope	0.866 V, 53.9 mV dec ⁻¹ , 5000 cycles	[131]
	m-HEANP(Mo)	1D	1 M KOH	MA, SA	9.89 A mg _{Pt} ⁻¹ , 18.20 mA cm ⁻²	[66]
MOR	PtPd-HEO	3D	1 M KOH	MA, stability	8.38 A mg ⁻¹ , stable 40000 s	[135]
	PdFeCoNiCu	1D	1 M KOH	MA, SA	20.98 A mg _{Pd} ⁻¹ , 52.48 mA cm ⁻²	[77]
	(CoNiMnCuZn) ₃ O ₄	2D	1 M KOH + 0.1 M KNO ₃	FE, yield	91.5%, 15.73 mg h cm ⁻² , 12 cycles	[58]
NO ₃ ⁻ RR	(Cu _{0.25} Ni _{0.25} Fe _{0.25} Co _{0.25}) ₆ S n ₅	3D	1 M KOH + 0.1 M KNO ₃	FE, yield	97.09±1.15%, 17.80±1.12 mg h mg _{cat} ⁻¹	[146]
	(CoMnFeNiCu) ₃ O ₄	3D	1 M KOH + 0.1 M KNO ₃	FE, yield	96.3%, 1.83 mmol h mg ⁻¹ , 20 cycles	[143]

Note: η_{10} and η_{1000} denote overpotentials at 10 and 1000 mA cm⁻², respectively; $E_{1/2}$ is the half-wave potential; MA is the mass activity; SA is the specific activity; FE is the Faradaic efficiency; n is the electron transfer number.

As shown in **Table 3**, porous high-entropy materials exhibit excellent performance across all five electrocatalytic reactions, though their advantages vary by reaction type. For HER and OER, where gas evolution is involved, the enhanced mass transport from porous structures and the optimized electronic structures through compositional regulation collectively improve reaction efficiency. For ORR and MOR, dimensional effects and multi-metal synergy play more critical roles in tuning reaction pathways and poisoning resistance. For NO₃⁻RR, the combination of the high-entropy effect and pore confinement helps balance intermediate adsorption and conversion. Overall, the electrocatalytic advantages of porous high-entropy materials arise from the synergy between high-entropy components and porous architectures, which together enable favorable performance across diverse reaction systems.

5.7 Advances in theoretical calculations and In Situ characterization techniques

In recent years, theoretical calculations and in-situ characterization techniques have matured, benefiting the study of electrocatalytic mechanisms in PHEMs. In the past, electrocatalysis research relied mostly on ex-situ characterization and trial-and-error experiments, making it hard to see the real active sites and dynamic changes of catalysts under working conditions. Now, advances in density functional theory (DFT) calculations and in-situ/operando techniques allow researchers to observe, at the atomic scale, how multi-element synergy, lattice distortion, and charge redistribution affect catalytic performance. This means research is moving from "describing phenomena" to "designing materials based on mechanisms."

5.7.1 Density functional theory calculations

DFT calculations help researchers understand the electronic origin of catalytic activity in PHEMs. A key theme in improving these materials is tuning the d-band center through multi-element synergy, lattice distortion, and interfacial interactions, thereby optimizing the adsorption energy of key intermediates and lowering reaction barriers.

For the OER, Liu et al.[147] found that in FeCoNiMnZn high-entropy layered double hydroxide (HELDH-SO₄²⁻), selective leaching of Zn creates cation vacancies, while SO₄²⁻ adsorption further tunes the electronic structure. As shown in the reaction pathway diagram (**Fig. 14a**), the OER on SO₄²⁻-FeCoNiMnZnOOH-Vc involves four proton-coupled electron transfer steps. The charge density difference map (**Fig. 14b**) reveals that adsorbed SO₄²⁻ and defect sites formed after Zn leaching help stabilize *OH. Density of states analysis (**Fig. 14c**) shows a notable increase in DOS near the Fermi level, and the Gibbs free energy diagram (**Fig. 14d**) shows that Zn leaching lowers the *O formation barrier from 2.45 eV to 1.71 eV, shifting the rate-determining step from *O formation to *O desorption. In addition, in the NiCoFeCuMnOOH-SO₄²⁻ catalyst obtained by Lei and colleagues[148] via electrochemical reconstruction, SO₄²⁻ preferentially adsorbs on Co sites, significantly lowering the water dissociation barrier from 1.24 eV to 0.81 eV.

For the NO₃RR, Li and colleagues[145] prepared PdCuSnCoNi high-entropy metallene aerogels. DFT calculations reveal that the multi-metal synergy optimizes the reaction pathway. The d-band center of this material shifts down to -1.91 eV, weakening intermediate adsorption. The energy barrier for the *NO₃ → *NO₂ step is only 0.44 eV, much lower than the 0.86 eV of the reference sample. Moreover, the energy barrier for *H → H₂ (0.86 eV) is higher than the maximum barrier for NO₃RR, indicating that active hydrogen prefers to participate in nitrate hydrogenation rather than the HER.

For the MOR, the mesoporous PtPd-HEO heterostructure constructed by Yang et al.[135] shows that strong interfacial

interaction with the HEO component shifts the PtPd d-band center down from -1.99 eV to -2.26 eV. The CO stripping voltammetry curves (Fig. 14e) confirm that this heterostructure has excellent CO tolerance, showing the absence of the CO_i oxidation peak that is typically observed on conventional Pt/C and PtPd/C catalysts. Reaction pathway analysis (Fig. 14f) reveals that this system bypasses the conventional CO pathway and follows a formate-dominated route. The free energy diagram (Fig. 14g) further shows that the barrier for converting CHO* to HCOOH* is only 0.31 eV, much lower than the 1.24 eV for CO* formation, which is consistent with the enhanced CO tolerance observed in Fig. 14e.

For the HER, Wang et al.[149] coupled Pt-based high-entropy alloy clusters with super-hydrophilic CeO₂, finding that the interfacial Pt-O-Ce bond acts as a charge transfer channel, sharply reducing the water dissociation barrier from 0.50 eV to 0.18 eV, and optimizing the ΔG_{H^*} on surface Pt sites to near-neutral -0.05 eV. In the nanoporous NP-Pt₃ catalyst prepared by Li and colleagues[73] via dealloying, the calculated ΔG_{H^*} at the Pt₃(FeCoNi) hollow site (Fig. 14h) is -0.063 eV, close to the

ideal value. DOS analysis (Fig. 14i) shows that compressive lattice strain from smaller atoms like Fe, Co, and Ni shifts the d-band center downward. Meanwhile, the high-entropy effect raises the Pt vacancy formation energy to 2.58 eV, much higher than the 0.88 eV of pure Pt, significantly enhancing corrosion resistance.

5.7.2 In-situ characterization techniques

The development of in-situ characterization techniques allows researchers to track, in real time, the structural evolution of catalysts, the adsorption behavior of intermediates, and the dynamic changes of active sites during electrochemical reactions, providing key experimental validation for the theoretical predictions above.

In OER studies, Liu et al.[147] used in-situ Raman spectroscopy to track the structural evolution of HELDH-SO₄²⁻. The in-situ Raman spectra (Fig. 14j) and their contour plot (Fig. 14k) show that as the potential increases, the Ni-O peaks at 462 and 525 cm⁻¹ shift from Ni^{II}-O to Ni^{III}-O, confirming the

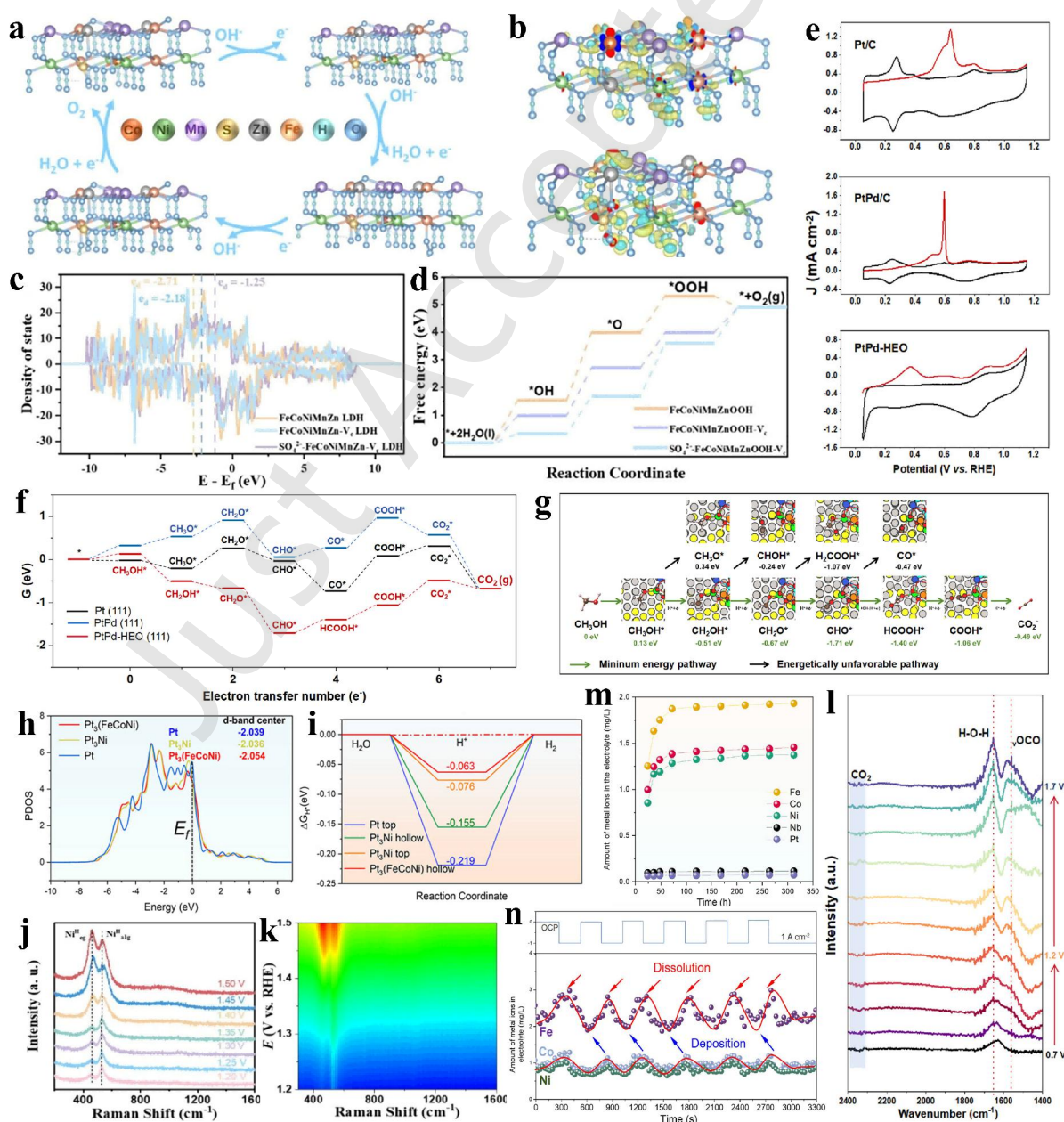


Figure 14. (a) Reaction pathway diagram of OER on SO_4^{2-} -FeCoNiMnZnOOH-Vc, (b) corresponding charge density difference maps, (c) density of states (DOS) of different models, and (d) OER Gibbs free energy profiles of different models. Adapted with permission from ref. [147] copyright 2026, American Chemical Society. (e) CO stripping voltammetry of Pt/C, PtPd/C, and PtPd-HEO catalyst, (f) selective MOR pathway diagram of PtPd-HEO heterostructure, and (g) free energy diagrams of the optimal MOR pathway on Pt, PtPd, and PtPd-HEO catalyst. Adapted with permission from ref. [135] copyright 2025, Wiley. (h) Calculated ΔG_{H^+} of Pt, Pt_3Ni , and $\text{Pt}_3(\text{FeCoNi})$ models in NP- Pt_3 catalyst, (i) corresponding DOS calculations. Adapted with permission from ref. [73] copyright 2025, Wiley. (j) In situ Raman spectra of HELDH- SO_4^{2-} , (k) corresponding contour plot. Adapted with permission from ref. [147] copyright 2026, American Chemical Society. (l) In situ ATR-SEIRAS spectrum of PtPd-HEO catalyst. Adapted with permission from ref. [135] copyright 2025, Wiley. (m) Dissolution concentrations of Fe, Co, Ni, Pt, and Nb elements in NP- Pt_3 electrode during the durability test (error bars represent standard deviation of three independent replicates), and (n) applied potential (start-stop cycles) and the corresponding dissolution profiles of Fe, Co, and Ni elements in NP- Pt_3 electrode. Adapted with permission from ref. [73] copyright 2025, Wiley.

reconstruction of the catalyst into an active oxyhydroxide phase. Zhang et al.[150] detected the *OOH intermediate on the surface of a B2 NiAl-type high-entropy intermetallic catalyst using in-situ ATR-FTIR, and revealed the active phase transition from M-O to M-OOH using in-situ Raman spectroscopy. In addition, in-situ DEMS experiments using ^{18}O -labeled water showed a low $^{34}\text{O}_2/^{32}\text{O}_2$ ratio, indicating effective suppression of the lattice oxygen oxidation mechanism, which explains the excellent long-term stability of this catalyst.

In NO_3^- RR studies, Li et al.[145] used in-situ ATR-IRAS to detect *NO_2 (1108 cm^{-1}) and *NH_2 (1638 cm^{-1}) intermediates on PdCuSnCoNi HEMAs. Online DEMS confirmed the formation of NO_2 , NH_2OH , and NH_3 products. EPR experiments showed that the DMPO-H signal weakened significantly upon NO_3^- addition, directly proving that active hydrogen participates in the nitrate hydrogenation process. In addition, Lei and colleagues[148] observed NH_2OH , NH_4^+ , and a clear H signal around 2140 cm^{-1} on NiCoFeCuMnOOH- SO_4^{2-} , indicating good water dissociation capability of this catalyst.

In MOR studies, Yang and colleagues[135] used in-situ ATR-SEIRAS and found that the spectrum of the PtPd-HEO heterostructure completely lacks the CO_1 band commonly seen on Pt/C, and instead shows a new formate band at 1561 cm^{-1} (Fig. 14l), indicating that the HEO component successfully shifts the reaction pathway from the CO poisoning route to the formate route.

In HER studies, Wang et al.[149] used operando FTIR and observed a clear red shift and increased intensity of the H-O-H bending vibration, and a blue shift of about 40 cm^{-1} for the Pt-H bond, on Pt-HEA-cluster/ CeO_2/C . This indicates that CeO_2 enhances water affinity and also benefits H_2 desorption. Li^+ poisoning experiments further confirmed that Ce sites are the main water dissociation centers. And, Li and colleagues[73] monitored the dynamic dissolution-deposition equilibrium of NP- Pt_3 using in-situ ICP-OES: Fe, Co, and Ni dissolve at open-circuit potential, and their concentrations drop rapidly after switching to working potential (Fig. 14m). The potential cycling curves (Fig. 14n) confirm the establishment of this dynamic equilibrium, and in-situ TEM shows that the catalyst structure remains nearly unchanged after 2200 hours.

Overall, theoretical calculations and in-situ characterization techniques work together, allowing researchers to understand the structure-activity relationship of PHEMs from both electronic

structure and dynamic evolution perspectives. DFT calculations provide atomic-scale predictions of active sites, reaction pathways, and energy barriers, while in-situ characterization validates these predictions under real reaction conditions. This combination not only deepens the understanding of core mechanisms like the high-entropy effect, lattice distortion, and charge redistribution, but also pushes electrocatalyst design from "trial and error" toward "rational design," laying a foundation for developing next-generation efficient and stable electrocatalysts.

6 Conclusions and outlook

6.1 Conclusions

As a breakthrough material in electrocatalysis, porous high-entropy materials' core advantage lies in integrating the multi-element mixing characteristics of high-entropy chemistry with porous structure design. They not only retain the inherent high-entropy effect, lattice distortion effect, slow diffusion effect, and cocktail effect of high-entropy systems, but also gain larger specific surface area, smoother mass transfer channels, and more interface defects through porous structures. This enables the materials to simultaneously have excellent reaction activity, fast reaction kinetics, and stable structural performance, providing a new design concept for the innovative development of energy conversion and storage technologies. This review systematically summarizes the comprehensive research progress of this material: at the basic concept level, its essence is the organic combination of multi-element mixing of high-entropy alloys and hierarchical porous structures. Its core feature is the synergistic regulation of component diversification and structural hierarchy. At the synthesis method level, among existing technical routes, the hard-templating method can prepare materials with uniform pore size. The soft-templating method can construct multi-layer porous structures, and dealloying method, thermal shock method, electrodeposition method, etc., can also realize material preparation. These methods can produce products with different compositions and pore characteristics to meet the differentiated needs of various electrocatalytic reactions; at the structure regulation level, by adjusting pore size (micropores, mesopores, macropores, and

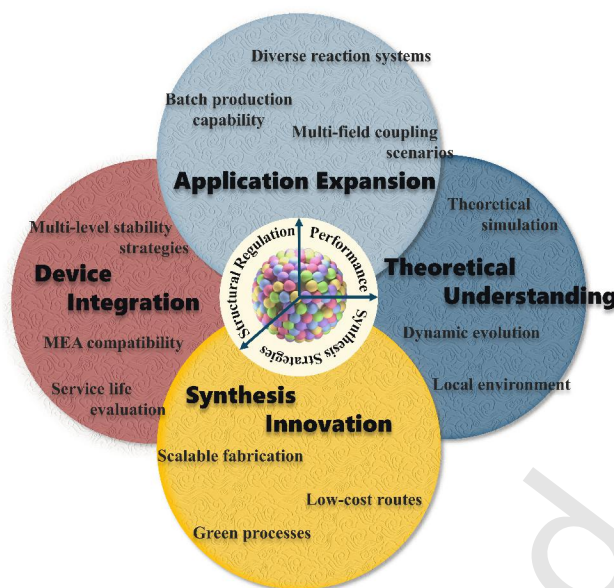


Figure 15. Porous high-entropy materials for electrocatalysis, from structural regulation to performance breakthroughs and future pathways.

mixed pores), material morphology (1D, 2D, 3D), chemical composition, and crystal phase, the reaction active sites, mass transfer efficiency, and electronic structure of the material can be precisely regulated. At the electrocatalytic application level, this material has been successfully applied in various reaction scenarios such as HER, OER, ORR, MOR, and NO_3RR , effectively solving some performance bottlenecks faced by traditional catalytic materials.

In summary, porous high-entropy materials have provided innovative technical solutions for the electrocatalysis field. In the future, it is necessary to continuously deepen the understanding of their structure-performance relationship mechanism, optimize material synthesis and structure regulation technologies, and promote their transformation from basic laboratory research to large-scale industrial applications, thereby providing a new direction for global energy transition and the achievement of carbon neutrality goals.

6.2 Outlook

Porous high-entropy materials have shown considerable promise in electrocatalysis, yet their transition from laboratory-scale samples to industrial-grade devices still faces notable challenges. Theoretical understanding remains to be deepened, the scalability of synthetic methods requires further validation, stability issues under operating conditions are not yet fully resolved, and explorations into device integration have only just begun.

As illustrated in **Fig. 15**, future research might proceed along four directions to gradually move the field toward practical applications.

Regarding theoretical understanding. Most existing studies focus on the correlation between static structures and macroscopic performance, while the dynamic evolution of materials during electrocatalytic processes has received less attention. Future work may combine in-situ characterization with theoretical simulations to examine the evolution of atomic arrangement, element migration, and pore structures during reactions. At the same time, how the

microenvironment inside pores (e.g., pH, ion concentration, electric field distribution) influences reaction pathways remains unclear and deserves further investigation. Clarifying these issues could provide a more reliable theoretical basis for the rational design of catalysts.

Regarding synthetic methods. Current techniques still have room for improvement in terms of batch production, cost control, and batch-to-batch consistency. From the perspective of engineering-scale application, dealloying is relatively amenable to large-scale production, although precise control over pore size distribution remains a limitation. Template methods can achieve relatively regular pore structures, yet the template removal process is cumbersome and yields are generally low, making the economics less than ideal. Electrodeposition is operationally simple and energy-efficient, but in most cases it yields only thin films or coatings. Electrospinning is suitable for continuous fabrication, though it comes with relatively high energy and solvent consumption. Solvothermal and sol-gel methods can achieve molecular-level homogeneous mixing, but they suffer from long production cycles and limited batch yields. Different methods have their own applicable scenarios, and none currently strikes an ideal balance among scalable fabrication, low-cost routes, and green processes. Future efforts might pay more attention to emerging synthetic strategies such as ultra-fast high-temperature techniques (e.g., Joule heating and microwave sintering), which feature short synthesis times and relatively low energy consumption, offering certain advantages for continuous production. Meanwhile, adopting non-noble metal substitution strategies and developing accompanying recycling technologies may represent viable paths to reduce material costs and promote industrialization.

Regarding performance optimization and device integration. Materials may face issues such as oxidative corrosion, element leaching, and pore structure collapse under actual reaction conditions. More importantly, most studies still rely on evaluations at the rotating disk electrode level, which differ from the service conditions in practical electrolyzers and fuel cells. Future work might construct

multi-level stability strategies: at the atomic level by introducing corrosion-resistant elements or leveraging the high-entropy effect to suppress selective leaching; at the mesoscale by designing core-shell or gradient structures with protective layers to isolate corrosive media; and at the macroscale by establishing unified accelerated aging test protocols to simulate typical service conditions.

In terms of device integration, research on porous high-entropy materials in membrane electrode assembly compatibility is still at an early stage. Major bottlenecks include the interfacial adhesion strength between the catalyst layer and the membrane, potential damage to pore structures caused by bubble detachment at high current densities, and the leaching of non-noble metal elements under high-potential oxidizing environments. For fuel cells, corrosion stability in acidic media, detachment of active components due to carbon support corrosion, and effective construction of the three-phase reaction interface remain key unresolved challenges. A few studies have attempted single-cell performance validation, but operating durations are mostly short, still far from the service life requirements for industrial applications. Future efforts could further optimize membrane electrode assembly fabrication processes, conduct longer-term single-cell tests, and gradually establish performance degradation databases under different operating conditions to provide references for catalyst screening and device matching.

Regarding application expansion. Current research is mostly concentrated on several common electrocatalytic reactions. Considering that porous high-entropy materials possess a rich variety of active site types and tunable electronic structures, it may also be worthwhile to expand their applications to diverse reaction systems, such as carbon dioxide reduction, electrooxidation of biomass derivatives, and the coupling of nitrate reduction with organic oxidation. At the same time, advancing batch production capabilities, conducting long-term stability verifications in real devices, and establishing device performance databases encompassing polarization curves, electrochemical impedance spectra, and durability metrics could represent important steps toward practical applications. Furthermore, the performance of these materials under multi-field coupling scenarios (e.g., photoelectric synergy, thermoelectric synergy) also deserves attention. Developing testing standards and evaluation systems tailored to real-world operating conditions may help facilitate the transition of such materials from fundamental research to engineering-scale applications.

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

Jingying Li: writing-original draft, investigation, conceptualization. Xiaolong Wang: writing-review & editing. Han Lv: supervision. Zhihui Huan: supervision. Hongdong Li: writing-review & editing, supervision, project administration. Lei Wang: writing-review & editing, supervision, project administration.

Informed consent

Not applicable.

Ethics statement

Not applicable.

Use of AI statement

None.

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