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TOPICAL REVIEW — Artificial intelligence and smart materials innovation: From fundamentals to applications

High-entropy alloys in synergistic electrocatalytic conversion applications

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High-entropy alloys (HEAs), with multi-principal-element composition, are gaining attention for their structural stability and mechanical properties. Extensive research has focused on using HEAs as electrocatalysts in the conversion of single-component reactions, such as hydrogen evolution reaction (HER), oxygen evolution reaction (OER), carbon dioxide reduction reaction (CO_2RR), etc. However, their potential in the application of synergistic conversion of pollutants (e.g., carbon dioxide (CO_2) and nitrogen oxides (NO_x)) has been largely overlooked. This review overviews HEAs' fundamental concepts and characteristics, and delves into their advantages in transition metals and optimization strategies for the synergistic conversion process. It offers a novel approach for sustainable environmental remediation and resource utilization.

Keywords: high-entropy alloys, electrocatalytic materials, optimization strategy

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1. Introduction

Alloys are extensively used in diverse applications due to their favorable properties. For example, magnesium is popular in the automotive and aerospace industries with its high strength-to-weight ratio, and aluminum can be used as a negative electrode material with high energy density and good cycle stability.[1,2] Moreover, nanoscale alloys display remarkable ductility, mechanical strength and thermoelectric properties, as shown by both experimental and theoretical studies.[3–7] Although these factors can effectively enhance the properties of alloys, relying on only a single main element significantly restricts the range of possible alloy combinations and hinders the development of new generations of alloy materials. Consequently, innovative approaches are crucial for broadening the diversity and applications of alloys. The predominant method to enhance the performance of metallic materials has been the introduction of new alloying elements into the primary element, thereby creating a family of alloys based on the main element.[8,9]

Recently, a novel approach has emerged where multiple principal elements are combined in high concentrations to form a stable state, giving rise to high-entropy alloys (HEAs).[10–12] HEAs can transcend the limitations of conventional alloy development while maintaining unique microstructural stability.[13,14] Mechanically, HEAs exhibit a broad range of yield strengths, from 300 MPa ($AlCoCrFeNiTi_x$)[15] to around 10^3 MPa (NbMoTaW),[16] which can be adjusted by altering the concentrations of the constituent elements.[17–19] Remarkably, HEAs retain these distinctive mechanical properties at both elevated (e.g., Al_xCrFeCoNi,[20] CrMnFeCoNi,[21] FeCoNiCrMn[22]) and cryogenic temperatures (e.g., $Al_{0.3}$CoCrFeNi[23]). These examples illustrate the distinctive benefits of HEAs when contrasted with conventional alloys.

In recent decades, the use of fossil fuels has led to critical environmental issues, especially the emissions of carbon dioxide, which can cause the greenhouse effect. To address environmental concerns, the development of a clean energy system and the transformation of carbon dioxide are crucial. Extensive research has focused on using HEAs as electrocatalysts in the conversion of single-component reactions, such as hydrogen evolution reaction (HER), oxygen evolution reaction (OER), carbon dioxide reduction reaction (CO_2RR), etc. However, their potential in the application of synergistic conversion of pollutants (e.g., carbon dioxide (CO_2), nitrogen oxides (NO_x), volatile organic compounds (VOCs), sulfur oxide exhaust gas and organic dyes) has been largely overlooked. The synergistic conversion of pollutants, such as carbon dioxide (CO_2) and nitrogen oxides (NO_x) holds great significance and is highly worthy of in-depth research. The si-

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multaneous conversion of these pollutants can not only effectively reduce greenhouse gas emissions and alleviate air pollution, but also transform pollutants into valuable chemicals or fuels, which can improve resource efficiency and create new economic value. High-entropy alloys have shown promising potential in the synergistic electrocatalytic conversion of multiple pollutants, offering an innovative approach to addressing environmental and energy challenges. In principle, the unique structural complexity of HEAs, arising from their multi-principal-element composition, can significantly enhance electrocatalytic performance. The lattice distortion and electronic structure modulation in HEAs are induced by the atomic size mismatch and electronegativity differences among the constituent elements. For the multiple pollutants NO_x and CO_2, the combination of internal strain energy from atomic-size disparity and fluctuations in the electronic field energy due to electron cloud redistribution creates a rich diversity of active sites, which can effectively stabilize reaction intermediates and lower activation barriers. As a result, HEAs are capable of simultaneously promoting the reduction of CO_2 and the decomposition of NO_x, thereby achieving efficient and selective conversion of these pollutants into valuable chemicals or fuels. This multifunctional capability makes HEAs a compelling candidate for sustainable environmental remediation and resource utilization.

This review presents the latest advancements in the synergistic electrocatalytic conversion of multiple pollutant properties of HEAs, with a focus on the physical insights into the synergistic electrocatalysts' structure, performance and mechanism. This article is structured as follows. Section 2 provides a brief overview of the basic concepts and characteristics of HEAs, including their definition and structural characteristics such as crystalline, quasicrystalline and preparation methods. Section 3 discusses the synergistic electrocatalytic conversion of CO_2 with NO_x, synergistic multi-path electron transfer and lattice oxygen activation in OER, and synergy between incorporation and intrinsic tensile strain in MOR, highlighting the intrinsic advantages of HEAs in transition metals and the optimization strategy of HEAs. Finally, Section 4 offers a brief conclusion and outlook for future experimental and theoretical studies.

2. Basic insights into HEAs

2.1. Definition of HEAs

Initially, HEAs were defined as solid-solution alloys containing more than five elements, each with an equal or near-equal atomic percentage (at.%), and each component having an atomic fraction greater than 5 at.% and lower than 35 at.%.[24] These multicomponent alloys are positioned far from the peripheries and vertices of the phase diagrams, challenging traditional material design paradigms.

The mixing entropy of materials ($\Delta S^0_{\rm mix}$) can be calculated using the following equation:

$$\Delta S^0_{\rm mix} = \Delta S^0_{\rm conf} + \Delta S^0_{\rm vib} + \Delta S^0_{\rm mag} + \Delta S^0_{\rm elec}, \tag{1}$$

where $\Delta S^0_{\rm conf}$, $\Delta S^0_{\rm vib}$, $\Delta S^0_{\rm mag}$ and $\Delta S^0_{\rm elec}$ represent the configurational entropy, vibrational entropy, magnetic dipole entropy and electronic randomness entropy, respectively. Notably, $\Delta S^0_{\rm conf}$ plays a crucial role in the total mixing entropy. For an alloy with equal atomic ratios, it can be calculated using Boltzmann's assumption

$$\begin{aligned}\Delta S_{\rm conf} &= -R\left(\frac{1}{n}\ln\frac{1}{n}+\frac{1}{n}\ln\frac{1}{n}+\cdots\frac{1}{n}\ln\frac{1}{n}\right)\\ &= -R\ln\frac{1}{n} = R\ln n,\end{aligned} \tag{2}$$

where R is the gas constant (approximately 8.3145 J·mol^{-1}·K^{-1}) and n is the number of constituent elements. The formula indicates that integrating various elements into the alloy encourages a random distribution of atoms. This randomness prevents the separation and ordering of seed phases within the alloy. Consequently, this leads to an increase in configurational entropy, which aids in forming a single solid-solution phase and enhances the alloy's properties.

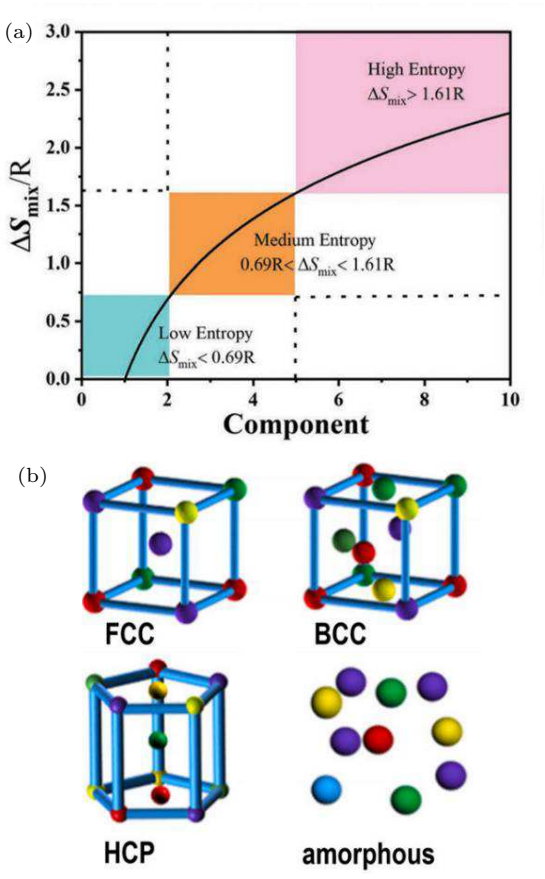


Fig. 1. Characteristics of high-entropy alloys: (a) correlation between ΔS mix changes and components and (b) structures in high-entropy alloys, from Ref. [25] from Wiley, Copyright 2022.

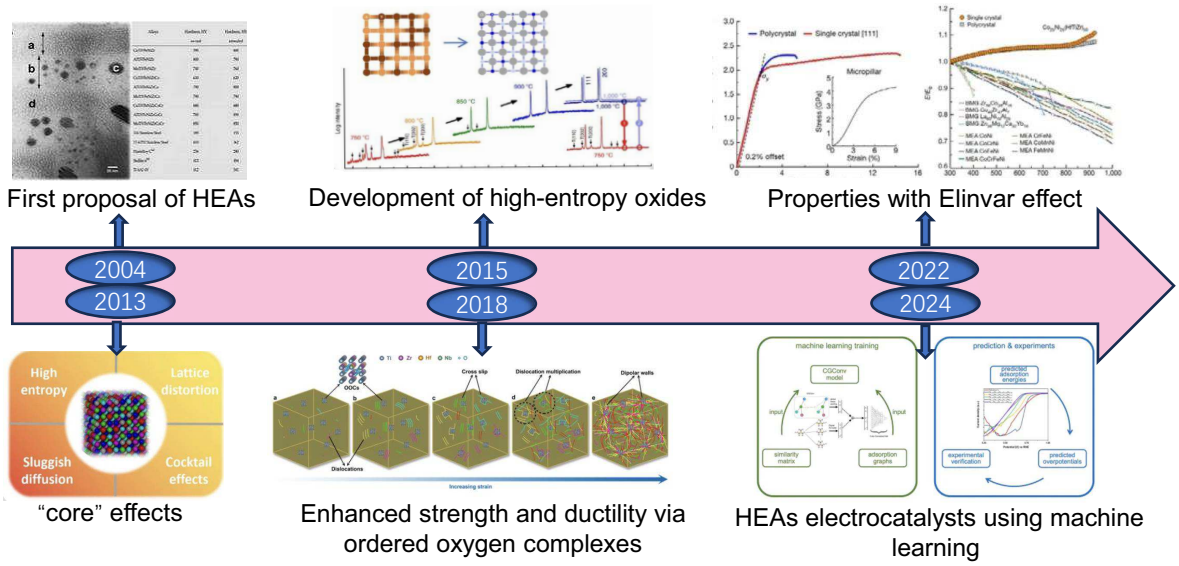


Fig. 2. Development of HEAs from 2004 to 2024, covering many aspects such as experimental preparation, characterization, optical and electronic properties, theoretical simulation in quantum computing and application exploration in spintronics and other fields.[25,36–38]

As an example, in Fig. 1(b), the structure of HEAs includes the face-centered cubic (FCC), body-centered cubic (BCC), amorphous, hexagonal close-packed (HCP) and HEAs.[10] As shown in Fig. 1(a), an alloy is generally considered to be an HEA when composed of five or more elements and meets the criterion $\Delta S_{\text{conf}} \geq 1.5R$. Theoretically, it is believed that high configurational entropy can stabilize random solid solutions, which leads to the formation of HEAs and broadens the HEA concept.[26] Consequently, quaternary alloys that meet the high-entropy criteria are also designated as HEAs.[27–29] Figure 2 illustrates the development of HEAs based on the timeline. High-entropy alloys are characterized by four core effects: the high-entropy effect, sluggish diffusion effect, severe lattice distortion effect and cocktail effect.[24] In 2004, Yeh *et al.*[30] first proposed that the high-entropy effect is a distinctive feature of HEAs since it promotes the formation of single-phase solid solutions, resulting in much simpler microstructures than previously anticipated. Increasing the number of constituent elements allows the enthalpy of mixing in a random state to approach that of a fully ordered state, making the random solid solution more competitive, especially when aided by high mixing entropy. Specifically, the rise in configurational entropy can lower the free energy of the system, facilitating the formation of solid-solution phases, particularly at elevated temperatures. While it is generally believed that high configurational entropy helps stabilize and optimize random solid solutions, it is also observed that most HEAs tend to form simple structures.[31]

The sluggish diffusion effect refers to the notably slow atomic diffusion processes in HEAs, which can be advantageous for developing certain microstructures. Comparisons show that the diffusion coefficients of elements in HEAs are lower than those in pure metals and stainless steels, indicating slower diffusion and phase transformation kinetics.[32] This sluggishness arises because atoms in HEAs occupy random positions, so when an atom attempts to move into a vacancy, the local atomic environment varies. If an atom moves into a low-energy site, it tends to become trapped, making further movement difficult, while in high-energy sites, the opposite occurs. In both scenarios, atomic diffusion is impeded.[33] This phenomenon can help explain why nano-sized precipitates form readily but grow slowly in HEAs since the formation of nuclei is easy, but their growth is hindered.

The severe lattice distortion effect in HEAs is often contrasted with traditional alloys that have a predominant element. In HEAs, however, the lattice sites are randomly occupied by different atoms, leading to variations in atomic sizes, bonding configurations and lattice potential energies among neighboring atoms. This pronounced lattice distortion has a significant impact on the mechanical properties of HEAs, such as increasing their hardness and strength.[34]

The cocktail effect, first introduced by Ranganathan,[35] refers to the synergistic interactions that occur when multiple elements are mixed in HEAs. This effect suggests that the outstanding properties of HEAs arise not only from the inherent characteristics of individual elements or simple mixing but also from the unique interactions between the various elements present.[19]

2.2. Preparation methods of HEAs

The synthesis of nanostructured HEAs presents significant challenges, primarily due to the complexity of precisely controlling the thermodynamic and kinetic mixing processes of various elements. Differences in crystal structure, atomic size and valence electron configuration make homogeneous mixing and structural stability difficult, especially since mi-

gration and aggregation can easily occur at high temperatures. Therefore, a thorough discussion of synthesis methods is needed to precisely control the size, phase structure and compositional distribution of HEAs.

Currently, the synthesis methods for HEAs can be broadly classified into three categories: solid-state, liquid-phase and gas-phase methods. Solid-state methods (such as mechanical alloying and high-energy ball milling) are cost-effective and suitable for large-scale production but offer limited control over particle size and morphology. Liquid-phase methods (including arc melting and laser melting) can produce solid-solution HEAs, but require high temperatures. Gas-phase methods (such as molecular beam epitaxy and atomic layer deposition) are more technically demanding and require sophisticated equipment. In addition, emerging techniques, such as dealloying, solvothermal synthesis and ultrasonication-assisted wet chemistry, have enabled the creation of diverse nanostructured HEAs under various conditions. With the continuous development of both traditional and novel synthesis methods, exploring strategies for producing HEAs with desirable properties remains a critical research focus. The synthesis of nanoscale HEAs relies not only on the selection of constituent elements and their simultaneous reduction but also on understanding their growth mechanisms. Recently, innovative approaches, such as fast-moving bed pyrolysis, wet chemical method, sputtering deposition and electrospinning method, have emerged to tackle the challenges in preparing nanostructured HEAs. This section reviews these advanced synthesis methods and their impact on structural control.

2.2.1. Fast-moving bed pyrolysis

Fast-moving bed pyrolysis (FMBP) has recently gained attention as an effective method for synthesizing ultrasmall, highly dispersed HEAs on various substrates, including carbon materials, zeolites and γ-Al_2O_3 (Fig. 3). By adjusting the temperature and nucleation rate, the size and composition of HEA nanoparticles can be precisely controlled. FMBP enables the formation of homogeneous HEAs with fast nucleation and low free energy, preventing phase separation. For example, Gao *et al.* used FMBP to immobilize 2 nm HEA nanoparticles on a granular matrix at high temperatures. The method can produce HEA NPs with up to ten elements (e.g., MnCoNiCuRhPdSnIrPtAu) by simultaneously pyrolyzing mixed metal precursors at ultra-fast heating rates, resulting in small, uniform particles.[39] These FeCoPdIrPt NPs exhibit superior HER performance and stability compared to commercial Pt/C catalysts.[39] Overall, FMBP shows great potential for producing highly crystalline, multi-component HEAs with uniform distribution, making it promising for electrocatalysis and energy storage applications. However, it requires specialized equipment to achieve the necessary high temperatures and rapid heating conditions.

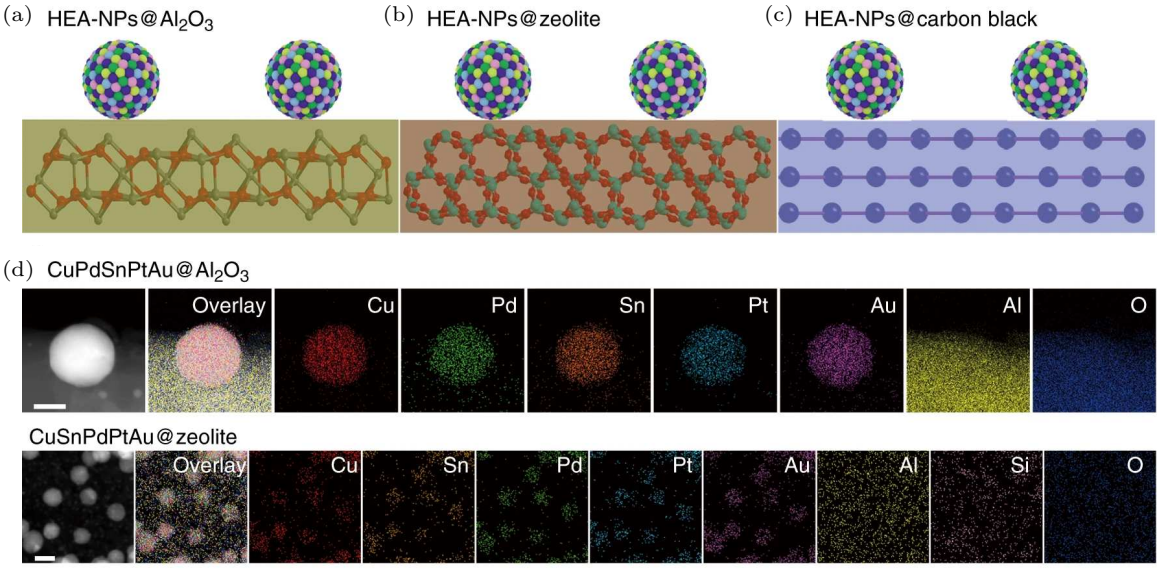


Fig. 3. Schematic diagrams for HEA-NPs dispersed on (a) γ-Al_2O_3, (b) zeolite and (c) carbon black using the FMBP experimental setup. (d) Elemental maps for quinary (CuPdSnPtAu) supported on Al_2O_3 and zeolite, (loading of HEA-NPs on γ-Al_2O_3 and zeolite was 10 wt%). Reproduced with permission from Ref. [39] from Nature Publishing Group, Copyright 2020.

2.2.2. Wet chemical method

Wet chemical synthesis is an increasingly promising route for preparing HEAs in materials science. This method enables the incorporation of various metal precursors to produce HEAs, providing an alternative to traditional high-temperature techniques.[40–42] A key advantage of wet chemical synthesis is the ability to precisely control the growth of HEA nanoparticles by tuning parameters such as reaction temperature, reducing agents, surfactants, ligands and reaction time.[43,44] Typically, as shown in Fig. 4, metal precursor solutions are added to a preheated mixture of reducing (e.g., triethylene glycol,

TEG) and stabilizing agents (e.g., polyvinylpyrrolidone, PVP) under controlled conditions to yield HEA nanoparticles.[45] Recent advances include predictive strategies for engineering HEA nanocrystals with specific spatial compositions by quantitatively controlling reduction kinetics and mixing entropy during the dropwise addition of multi-metal precursors.[46] For example, studies on quinary HEA nanocrystals with platinum-group metals have shown that maintaining steady precursor ion states is essential for producing various structures such as typical PdPtRhIrRu, dendritic PdPtRhIrRu and Pd@PdPtRhIrRu core–shell nanocrystals. The stoichiometry of these nanocrystals can be tuned by adjusting the metal precursor ratios, expanding possibilities for catalyst design. While one-pot synthesis tends to yield phase-separated particles due to sequential reduction, dropwise addition promotes synchronized nucleation and uniform HEA nanocrystals. Further modulation of droplet intervals and precursor redox potentials can generate dendritic or core–shell structures, with dendritic PdPtRhIrRu HEAs displaying enhanced activity and durability for hydrogen evolution reaction (HER) and hydrogen oxidation reaction (HOR). In addition, the use of soft templates, such as diblock copolymers during chemical synthesis, allows for the formation of mesoporous HEA nanostructures. For instance, Yamauchi *et al.* developed a one-pot wet-chemical reduction method using poly(ethylene oxide)-block-poly(methyl methacrylate) (PEO-b-PMMA) micelles as templates to synthesize mesoporous nanospheres (MNs) composed of multiple metals, including Pt, Pd, Rh, Ru and Cu.[47]

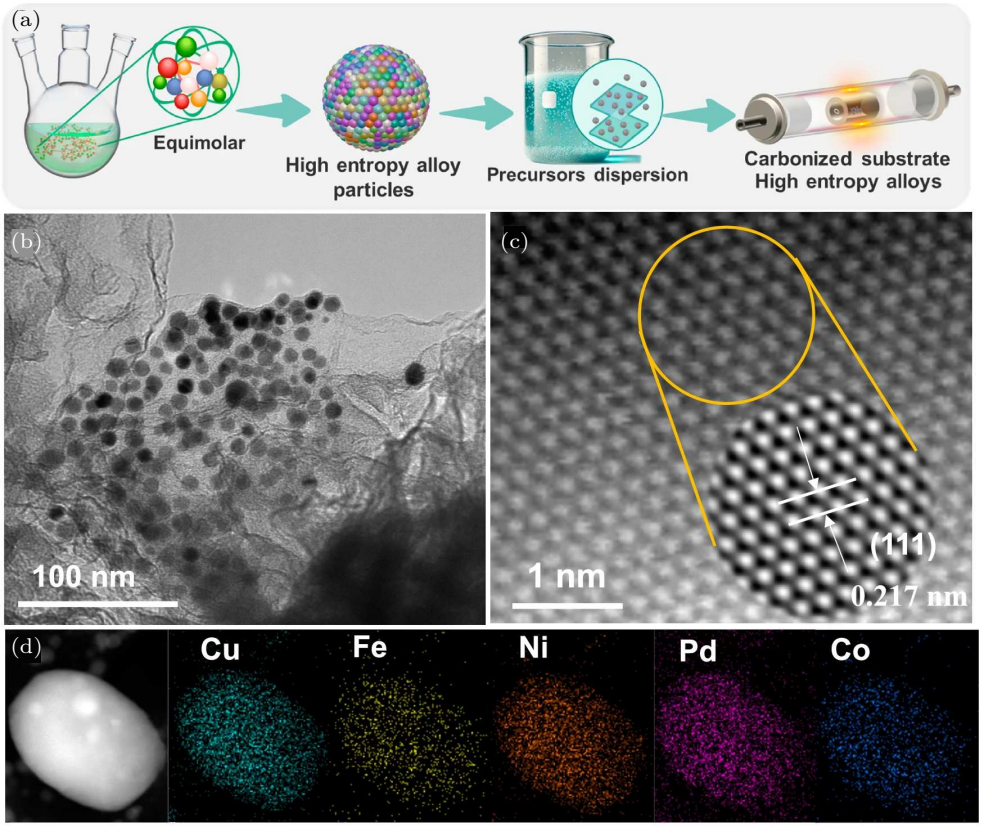


Fig. 4. (a) Schematic diagram for the wet-chemical synthesis process of HEAs. (b) TEM images of HEAs. (c) Aberration-corrected HAADF-STEM image and the corresponding inverse FFT pattern of HEAs (highlighted in the yellow circle). (d) Elemental mapping for HEAs (scale bar, 5 nm). Reproduced with permission from Ref. [48] from Nature Publishing Group, Copyright 2025.

2.2.3. Sputtering deposition and electrospinning method

Sputtering deposition is a widely used method for depositing thin films or nanoparticles onto substrates. Typically, a polymer solution or melt is electrospun in a strong electric field. As the electric field acts on the droplet at the tip of the needle, its shape transforms from a sphere into a cone, and a filament is then drawn out from the cone's tip. For example, FeMnCoCrC HEA coatings have been fabricated on high-speed steel substrates via magnetron sputtering, utilizing a specific range of substrate bias voltages. More recently, Schuhmann and colleagues introduced an enhanced sputtering deposition approach to produce highly dispersed CrMnFeCoNi HEA nanoparticles (NPs).[49] This technique spits metal atoms into an ionic liquid rather than onto a traditional substrate by bombarding the target substance with an argon plasma. Within the ionic liquid, the ejected metal atoms nucleate and subsequently grow into the final HEA NPs. This technique not only works with different substrates but also allows control over the size of the HEAs. However, its reliance on specialized equipment and vacuum conditions may lead to increased costs. Furthermore, HEA thin films with excel-

lent homogeneity and purity can be produced by customizing sputtering deposition. By fine-tuning sputtering parameters — such as power, the distance between the target and substrate, and the type of sputtering gas — the properties of the resulting coatings can be precisely controlled. Overall, sputtering deposition is a versatile technique for fabricating HEA thin films and NPs with exact compositional and dimensional control. Furthermore, sputtering deposition techniques have been successfully integrated with the electrospinning method. In electrospinning, an electric field causes a droplet at the tip of a needle to drastically change from a spherical to a conical shape. This droplet then stretches and solidifies into continuous fiber filaments. The cooperative interaction between metal ions and polymer chains during electrospinning enables the atomic-level uniform dispersion of various metal species on the polymer nanofiber, which lays the groundwork for synthesizing HEA NPs. Subsequent high-temperature annealing — performed in inert, oxidizing or reducing atmospheres — determines the final state of these nanoparticles. For instance, Zhu *et al.* demonstrated the successful fabrication of HEA NPs using electrospinning.[50] To promote the *in situ* formation of HEA NPs on carbon nanofibers, they first electrospun FeCoNiIrRu salts/PVP nanofibrous membranes and subsequently annealed them in an argon environment. The interaction between these HEA NPs and the carbon nanofibers effectively restricted the nanoparticle growth, resulting in an average diameter of approximately 6 nm. Although the use of electrospinning for HEA fabrication is still emerging, its potential for large-scale nanomaterial production makes it a promising avenue for future exploration. Furthermore, edge reconstruction technology also plays an important role in controlling material properties during material preparation. For example, edge electrons and phonon states can be eliminated by unique edge reconstruction in phosphene nanoribbons, thus improving material properties. This provides a new idea for the preparation of high-entropy alloys.[51]

3. Electroreduction properties

3.1. Intrinsic advantages of HEAs in electrocatalytic applications

In recent years, HEAs have demonstrated superior performance in the representative field of electrocatalytic energy conversion, playing a key role as catalysts with significant application prospects in electrochemical applications. However, the search for ideal HEA catalysts to reduce the energy of catalytic reactions remains challenging. Over the past decade, HEAs with various chemical compositions and structures have emerged as prominent competitors in catalytic applications. Notably, significant progress has been made in the development of nanostructured HEAs within the field of electrocatalysis. Furthermore, the special qualities of HEAs present special chances for novel and flexible active sites. These active sites can be tailored for certain uses by carefully choosing the elements' composition and arrangement.[52–54] The arrangement of surface atoms determines the complexity of high-entropy configurations, which also leads to different adsorption modes for reactants and intermediates. Furthermore, functional differences in the various metal components drive the redistribution of charge on the surface of the catalyst. This, in turn, results in uneven electronic distribution across the entire surface, enhancing the potential of HEAs and thereby reducing the energy barriers during the catalytic process. In addition to catalytic activity, the inherent property of slow diffusion in HEAs ensures that catalysts possess strong stability during the reaction process, even in high-temperature, oxidative, acidic or alkaline environments. Therefore, the subtle interactions between geometric and electronic structures in HEAs contribute to improved catalytic activity, selectivity and stability, indicating that HEAs are candidates to play a role in the search for efficient catalysts.[55–58]

Non-precious metal catalysts, especially those composed of 3D transition metals, often have comparable properties. To exceed the catalytic activity of noble metal catalysts, these metals with OER catalytic activity include Fe, Co and Ni. In catalyst applications, compounds and complexes of these elements can provide unique electronic properties and reaction activity.[59,60] The multi-component structure can combine the above elements with catalytic activity advantages. Thus, 3D transition metal-based HEAs catalysts offer the following advantages: (i) cost-effective. Compared to precious metal catalysts (e.g., platinum, iridium), 3D transition metals are generally cheaper and more abundant, and although high-entropy alloys may contain some expensive elements, they can be used more conveniently with proper design. It is advisable to replace or reduce the use of precious metals, thereby reducing costs. (ii) Catalytic activity. Due to the synergistic effect of multiple elements, high-entropy alloys may exhibit higher catalytic activity than single elements or traditional alloys. (iii) Optimized electronic structure. The electronic structure of multiple elements in the alloy interacts with each other, which can lead to a more favorable relationship. The electronic state distribution and band structure, which improve the catalytic efficiency, are comparable to or even higher than those of noble metal catalysts. Catalytic activity, especially under specific reaction conditions. (iv) Flexible adjustability. The electronic structure and coordination environment of 3D transition metals can be achieved by synthesis methods and ligands. The design is adjusted, and high-entropy alloys can achieve rich crystal structures and surface characteristics by adjusting the alloy composition, which offers a wide range of possibilities for optimizing catalytic performance. (v) High stability. High-entropy alloys typically have high thermal stability and cor-

rosion resistance, which is essential for demanding reactions (e.g., high pH or high overpotential) that are significant. Some selected examples in electrocatalysis with HEAs are listed in Table 1.

Table 1. Summary of the synthetic method and electrocatalytic application of high-entropy alloys.

Composition	Structure	Catalytic application	Ref.
RuRhCoNi(Ir)	FCC	NH_3 decomposition	[61]
RuRhCoNiIr	phase separation	NH_3 decomposition	[61]
FeCoNiCuMo	FCC	NH_3 decomposition	[62]
PtPdRhCoCe	FCC	NH_3 oxidation	[63]
PtPdRhNi	FCC	ORR	[64]
PtPdFeCoNi	FCC	ORR	[64]
PtRuCuOsIr	FCC	ORR, MOR	[65]
PdAuAgTi	–	ORR	[66]
CrMnFeCoNi	–	ORR	[49]
AlNiCoIrMo	FCC	ORR	[67]
AlNiCuPt*M* (M = Ir, Pd, V, Co, Mn)	FCC	ORR	[68]
AlNiCuPtPdAu	FCC	HER, OER	[69]
CoCrFeMnNi	FCC	HER	[70]
PtAuPd(RhRu)	FCC	HER	[71]
MnFeCoNiCu	FCC	OER	[72]
CuAgAuPtPd	FCC	MOR	[73]
AgAuCuPdPt	FCC	CO_2RR	[74]

ORR: oxygen reduction reaction; MOR: methanol oxidation reaction; HER: hydrogen evolution reaction; OER: oxygen evolution reaction; CO_2RR: CO_2 reduction reaction.

3.2. Electroreduction of CO_2

The electrochemical reduction of CO_2 (CO_2RR) represents a promising strategy for establishing a closed carbon cycle and offering a sustainable pathway to convert CO_2 into valuable products such as ethanol (CH_2OH). CO_2 diffuses to reach catalytically active sites and undergo reduction under electrochemical conditions. Beyond its potential to meet the growing demand for renewable energy sources, CO_2RR plays a critical role in mitigating environmental challenges linked to anthropogenic CO_2 emissions.[75] Reaction parameters, such as the electrolyte's pH and the catalyst selection, have a significant impact on the effectiveness and result of CO_2RR. These factors collectively govern the reaction mechanisms and product selectivity.[76] The adsorption of CO_2 molecules onto the catalyst surface is the first step in the typical process for electrochemical CO_2RR. Carbonate (CO_3^{2-}) can be created when CO_2 and OH^- ions combine in an alkaline environment. The adsorbed CO_2 or its derivatives (such as CO_3^{2-}) are then reduced by electron transfer, usually involving several electrons. Proton (H_+) participation is essential in subsequent steps to drive the reaction forward.

During the electron and proton transfer processes, various intermediates, such as CO, $HCOO^-$, CHO and CH_2O, are formed. These intermediates further react to produce desired products, including CO, CH_4, and ethanol (CH_3CH_2OH).[77,78] However, the process is challenged by large overpotentials, which often result in low selectivity for target products. In aqueous environments, the competing hydrogen evolution reaction (HER) further complicates CO_2 reduction, leading to the undesired formation of H_2.

To address these challenges, the development of highly effective, selective and stable electrocatalysts that can improve CO_2RR performance and advance its practical application in carbon cycling and renewable energy production is imperative. Among transition metals, Ag, Zn and Au, along with their derivatives, favor the desorption of CO as the primary product due to the weak CO adsorption energies.[79,80] In contrast, In, Sn, Bi and Pb show even weaker CO adsorption, leading to a preference for formate production.[81] Conversely, metals with strong CO affinity, such as Fe, Pt, Co, Ni and Pd, are prone to active site poisoning, shifting the reaction toward the hydrogen evolution reaction (HER) and resulting in excessive H_2 formation. A moderate CO affinity, however, promotes the formation of multi-carbon products. The most efficient catalysts for converting CO_2 to C_{2+} products are copper (Cu) and its compounds because they make it easier for carbon-containing intermediates to couple, which is a necessary step in the production of C_{2+} species.[82]

The diversity of CO_2RR products highlights the importance of intermediate adsorption strengths on electrocatalysts. By optimizing material composition and surface structure, the adsorption energies of intermediates can be tailored to enhance selectivity and efficiency. HEAs, offer unique electronic properties, such as d-band center (the average energy level of a metal's d-orbitals, influencing its catalytic activity by affecting adsorbate bonding), and electron density distribution, which influence CO_2 activation and intermediate stability. Furthermore, HEAs' slow diffusion and strong entropy effect encourage the creation of NPs with large specific surface areas and numerous active sites, which improves CO_2RR performance. Nellaiappan *et al.* synthesized AuAgPtPdCu HEA NPs via melting and cold grinding.[74] These NPs demonstrated high activity in CO_2-saturated electrolytes, achieving nearly 100% Faradaic efficiency (FE) for gaseous products at 0.3 V versus RHE, with minimal liquid byproduct formation. The altered electronic structure of the HEA surface favors hydrocarbon production by lowering energy barriers for CH_4 and C_2H_4 formation while increasing the barrier for CO formation. Theoretical calculations reveal that intermediates such as $^*OCH_3$ and $^*O$ exhibit distinct adsorption energies on AuAgPtPdCu HEA NPs compared to pure Cu(111), reducing energy barriers for critical CO_2RR steps. Cavin *et al.* developed a layered high-entropy transition metal dichalcogenide (TMDC) alloy, (MoWVNbTa)S_2 HEA (Figs. 5(a) and 5(b)).[55] This material exhibited exceptional selectivity and activity for CO production, achieving a 0.51 A·cm^{-2} current density and a

turnover frequency of 58.3 s^{-1} at ~ -0.8 V versus RHE. Vanadium (V) and niobium (Nb)-enriched edge sites are responsible for the improved performance since they lower reaction barriers and CO desorption energies. The 2D stratified structure maximizes active site exposure and modulates conversion efficiency via interlayer interactions, combining compositional diversity with high surface area for improved electrochemical performance. Li *et al.* synthesized PdCuAuAgBiIn high-entropy alloy aerogels (HEAAs) with a 3D self-supported, nano-porous architecture via a freeze–thaw method (Fig. 5(c)).[55] The 3D framework optimized intermediate adsorption/desorption dynamics, reducing H_2 production and enhancing selectivity for formate. The CO_2 adsorption capacity of HEAAs surpassed that of Pd metal aerogels, highlighting the structural advantages of HEAs in promoting CO_2RR efficiency.

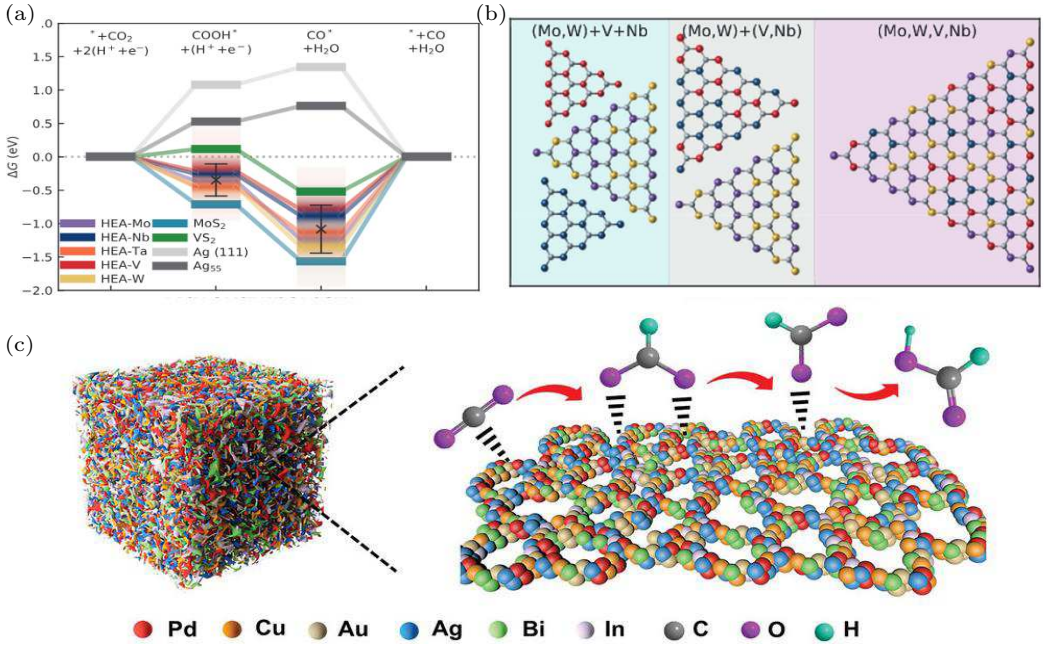


Fig. 5. (a) Free energy for each step of the catalytic reaction with molecules adsorbed to the V site. (b) Schematics for applying the HEA screening technique to (Mo,W,V,Nb). Reproduced with permission from Ref. [55] from Wiley, Copyright 2021. (c) Schematic for boosted HCOOH generation over PdCuAuAgBiIn HEAs. Reproduced with permission from Ref. [83] from Wiley, Copyright 2023.

The catalytic efficacy of HEAs in CO_2RR stems from several key factors. A variety of surface-active sites, electronic structure manipulation to customize intermediate adsorption, geometric morphology control for increased reactivity, intermediate adsorption energy optimization for advantageous pathways, and metal element synergy. These mechanisms collectively enable HEAs to convert CO_2 into valuable chemicals at low potentials, positioning them as promising catalysts for electrochemical energy conversion and carbon capture technologies.

Despite challenges due to varying metal reduction potentials and miscibility, Liu *et al.* successfully fabricated a series of HEAAs via the freeze–thaw method.[83] Notably, the PdCuAuAgBiIn HEAAs demonstrated exceptional performance, achieving nearly 100% Faradaic efficiency (FE) for C1 products between -0.7 V and -1.1 V versus the reversible hydrogen electrode (VRHE), with a maximum FE for formic acid of 98.1% at -1.1 VRHE. This outperformed PdCuAuAgBiIn high-entropy alloy particles (HEAPs) and Pd metallic aerogels (MAs). In a flow cell, the current density reached nearly 200 $mA{\cdot}cm^{-2}$ with an FE for formic acid of 87%. The outstanding CO_2RR performance was attributed to strong metal interactions and surface unsaturated sites in the PdCuAuAgBiIn HEAAs, optimizing the adsorption and desorption of $HCOO^*$ intermediates and enhancing HCOOH production. This study offers a simple synthesis strategy for HEAAs and paves the way for developing efficient catalysts.

3.3. Synergistic conversion of CO_2 and NO_x

Although there are numerous examples in the electrocatalysis of HER, OER, OMR, NRR and CO_2RR with HEA electrocatalysts, there is little investigation on the synergistic conversion of CO_2 and NO_x with HEA electrocatalysts. Ordered intermetallic compounds, as an effective strategy for alloying, can enhance electrocatalytic activity by providing more active sites for intermediate adsorption during single-step catalytic reactions. However, in multi-component catalytic processes, such as the co-catalytic synthesis of urea from CO_2 and NO_3^-, these ordered structures often struggle to facilitate simultaneous adsorption of multiple intermediates. This limitation tends to favor individual reaction pathways and hinders efficient C–N coupling. To address this challenge, Wu and coworkers[84] synthesized a medium-entropy intermetallic (MEI) compound composed of Au, Cu, Ir and Co, and in-

troduced Pd to disrupt its ordered arrangement (Fig. 6). This modification resulted in a HEA counterpart, PdAuCuIrCo, designed for co-catalytic urea synthesis. *In situ* spectroscopic analyses revealed that the MEI predominantly produces NH_3 through the reduction of NO_3^-, whereas the HEA favors the formation of C–N coupling products. Theoretical calculations demonstrated that the HEA exhibits a lower $^*NO_2$ adsorption energy compared to the MEI, reducing the energy barrier for both C–N coupling and hydrogenation steps. This facilitates effective co-adsorption of $^*CO_2$ and $^*NO_2$, promoting simultaneous reactions, while the MEI excessively stabilizes $^*NO_2$, leading primarily to NH_3 formation via a single pathway. The HEA achieved a high urea production rate of 52.43 $mmol{\cdot}h^{-1}g^{-1}$ and a Faradaic efficiency of 22.57% at −0.9 V, significantly outperforming the MEI.

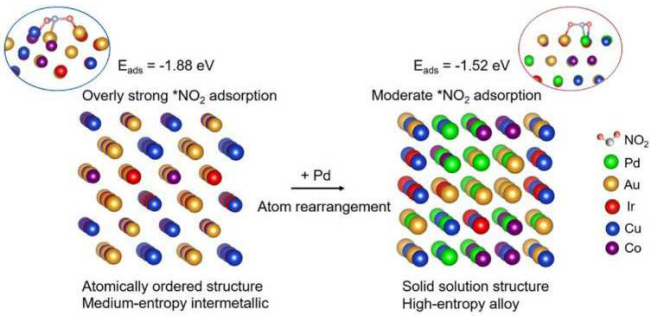


Fig. 6. Structural configurations of MEI and Pd-containing HEA, showing an ordered structure and a disordered solid solution structure, respectively. Circles represent the $^*NO_2$ adsorption models. Reproduced with permission from Ref. [84] from Wiley, Copyright 2025.

3.4. Synergistic multi-path electron transfer and lattice oxygen activation in OER

Synergistic effects of multi-elements in high-entropy alloys can activate the lattice oxygen mechanism effectively and enhance the activity of the oxygen evolution reaction. Yu[85] *et al.* reported a $NiFeCoCrW_{0.2}$ HEA electrocatalyst, which boosts OER. The Ni oxidation process in the alloy is enhanced by multipath electron transfer, and the weaker Co–O bond contributes to the effective lattice oxygen mechanism at the Ni–Co double site (Fig. 7). It is also found that the evolution mechanism of oxygen changes from the adsorbate evolution mechanism to the lattice oxygen oxidation mechanism with the increase in alloy element amount, which is related to the fine regulation of the metal-oxygen band center and the decrease of the metal-oxygen bond strength during oxygen desorption. In addition, the contribution of dynamic surface reconstruction and self-healing ability to the long-term stability of high-entropy alloys, as well as the change in activity under different pH conditions, are also emphasized, which are closely related to the multi-element synergistic effect of alloys. Finally, the $NiFeCoCrW_{0.2}$ high-entropy alloy designed by the research team showed excellent oxygen evolution reaction activity and long-term stability at low overpotential, providing a new idea for developing high-performance oxygen evolution reaction electrocatalysts. Furthermore, high-entropy alloys have significant advantages in the synergistic conversion of CO_2 and SO_2. By adjusting the composition and structure of the alloy, the researchers successfully achieved efficient electrochemical reduction of the two gases. Certain high-entropy alloy catalysts are capable of simultaneously converting CO_2 to carbon-based fuels (such as formic acid or methanol) and SO_2 to sulfides or sulfates in the same reaction system. This synergistic transformation not only improves resource utilization but also reduces the number of cycles.

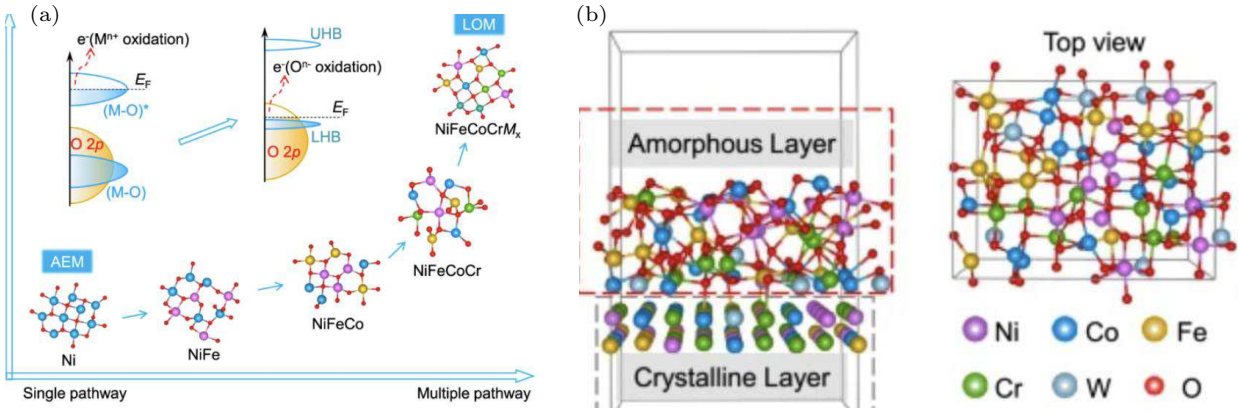


Fig. 7. Schematic of how multi-path electron synergism facilitates lattice oxygen activation in $NiFeCoCrW_{0.2}$. (a) Schematic of lattice oxygen activation and (b) views of the $NiFeCoCrW_{0.2}$ oxide model with top amorphous layers for DFT calculations. Reproduced with permission from Ref. [85] from Nature, Copyright 2025.

3.5. Synergy between incorporation and intrinsic tensile strain in MOR

In the realm of catalysis, the strategic incorporation of HEAs can significantly influence their catalytic performance via synergistic incorporation and intrinsic tensile strain. Furthermore, alcohol fuel cells have attracted much attention due to their high energy efficiency and environmental friendliness. However, their commercial application is limited by the high cost of Pt-based catalysts and CO poisoning issues. The main problem is to improve catalytic activity, durability and CO

tolerance through catalyst design. Guo *et al.*[86] synthesized Mo_1-PdPtNiCuZn ultra-thin nanosheets for HEA electrocatalysts in MOR. The synergy between Mo and tensile strain optimizes the electronic structure and surface energy, enhancing catalytic activity and stability. This makes the catalyst exhibit excellent methanol oxidation performance in alkaline media and provides an effective solution to the CO poisoning problem. During the methanol oxidation reaction (MOR), Ni and Mo act as electron depletion centers, effectively promoting electron transfer on the HEA surfaces. Simultaneously, the efficient d–d orbital coupling between Pt, Pd, Cu and Zn plays a pivotal role (Fig. 8). This interaction reduces the energy barrier associated with electron transfer during the oxidation process and helps stabilize the valence state of Pt sites. This stabilization is crucial for maintaining the intermediates of MOR. This carefully designed combination of elements provides an optimal surface configuration, a favorable electronic microenvironment, and ideal adsorption/desorption sites for the reaction. These features collectively ensure the proper adsorption of key intermediates, thereby enhancing the formate-dominated MOR. The results show that the introduction of Mo and the intrinsic tensile strain cooperate to optimize the electronic structure of Pt sites, inhibit CO adsorption, and reduce the reaction energy barrier, thus significantly improving the catalytic performance.

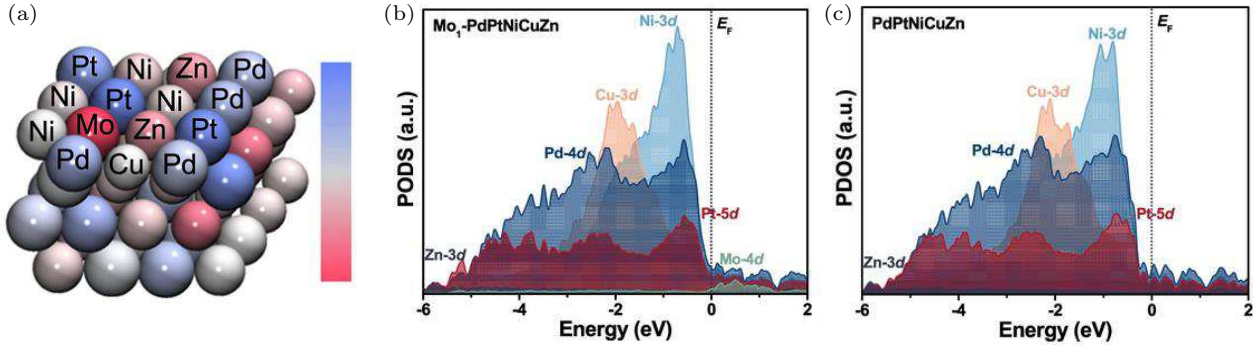


Fig. 8. Schematic of Mo incorporation and intrinsic tensile strain synergy effect in Mo_1-PdPtNiCuZn HEA electrocatalysts. (a) Bader charge simulation for Mo_1-PtPdFeCoNi. PDOSs of (b) Mo_1-PdPtNiCuZn and (c) PdPtNiCu. Reproduced with permission from Ref. [86] from Nature, Copyright 2025.

3.6. Optimization strategy of high-entropy alloy

3.6.1. Constituent regulation

A cornerstone of designing effective HEA catalysts lies in the 'rational selection of constituent metal elements', guided by the specific requirements of the target reaction system. Each metal possesses inherent chemical and physical properties — its electronic structure (particularly the d-band center relative to the Fermi level), its affinity for different reactants and intermediates, its redox potential, and its structural role within the alloy lattice. By carefully combining elements with complementary or synergistic properties, researchers can engineer HEA surfaces with optimized characteristics for enhanced catalytic performance.

In high-entropy alloys, the electronic structure of the alloys can be changed by adjusting the composition, and then the catalytic performance will be affected. Similarly, sumarene monolayer, as a new type of 2D material, exhibits an ideal band gap, ultra-high carrier mobility and strong exciton binding energy through its unique kagome analog lattice. This effective control of the electronic structure provides a new idea for the composition design of high-entropy alloys.[87] Systematic studies and extensive experimental exploration have begun to map the landscape of element utilization in HEA catalysis. As summarized by Miracle *et al.*[88] through an analysis of published research (illustrated conceptually in Fig. 9(a), where usage frequency is represented), a core group of transition metals consistently appears in HEA catalyst formulations. The most frequently employed elements include iron (Fe), cobalt (Co), nickel (Ni), manganese (Mn), chromium (Cr), copper (Cu), aluminum (Al) and titanium (Ti). The prevalence of these specific elements is not arbitrary. Fe, Co and Ni are well-established electrocatalysts, particularly for reactions involving oxygen and hydrogen, due to their favorable d-electron configurations and ability to adopt multiple oxidation states.

Iridium (Ir) and ruthenium (Ru), typically in their oxide forms (IrO_2, RuO_2), are considered the state-of-the-art OER catalysts, particularly in acidic media.[89,90] HEAs provide a promising platform for developing efficient and stable non-precious metal OER catalysts. Combinations involving Co, Ni, Fe and Mn are frequently explored to facilitate proton-coupled electron transfer steps. The high-entropy structure can generate a diverse range of active sites and potentially stabilize high-valence states of these metals under operating conditions, which are often crucial for OER activity. The aim is to create synergistic sites where the binding energies of the different OER intermediates are collectively optimized, breaking the scaling relations that often limit single-metal or binary oxide catalysts.

Platinum (Pt) and palladium (Pd) are the undisputed benchmarks for HER catalysis, exhibiting near-zero overpotential due to their optimal hydrogen binding energy (HBE)

— strong enough to adsorb hydrogen intermediates but weak enough to allow facile H_2 desorption, as predicted by the Sabatier principle and visualized in volcano plots.[91,92] By incorporating small amounts of Pt or Pd into a multi-element HEA matrix (e.g., CoCrFeNiPd), the precious metal atoms can be highly dispersed, maximizing their utilization efficiency.

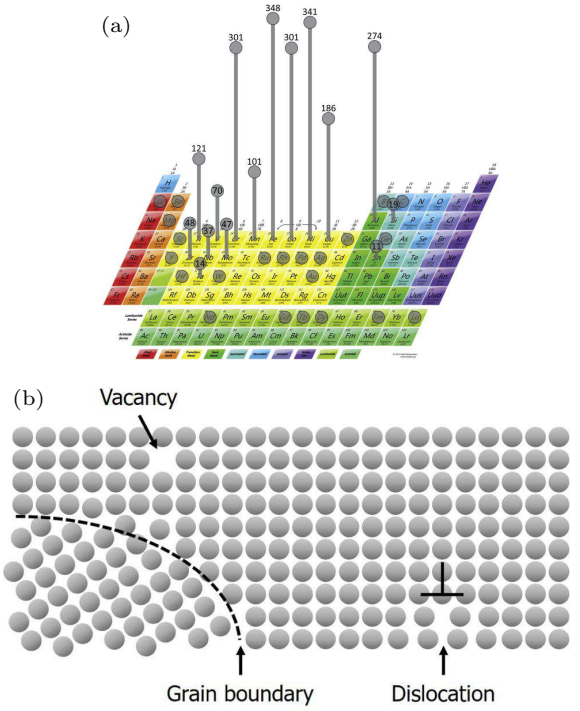


Fig. 9. (a) Utilization frequency of elements in the 408 multi-component alloys (MPEAs) that were assessed. Reproduced with permission.[88] Copyright 2017, Elsevier Ltd. (b) Typical defects present in HEAs. Reproduced with permission.[97] Copyright 2019, Elsevier Ltd.

Cr is typically incorporated to enhance the stability and corrosion resistance of the catalyst, particularly under harsh acidic or alkaline conditions, where it can also participate electronically in the catalytic process.[93,94] Cu, as highlighted later, holds a unique position in CO_2 reduction but is also used more broadly for its conductivity and alloying characteristics. Among elemental metals, copper (Cu) stands out for its unique ability to catalyze the reduction of CO_2 to multi-carbon (C_{2+}) products, such as ethylene (C_2H_4) and ethanol (C_2H_5OH), which are significantly more valuable than single-carbon products such as carbon monoxide (CO) or formic acid (HCOOH).[95,96] However, elemental Cu catalysts often require high overpotentials and suffer from competing HER, limiting efficiency and selectivity. HEAs incorporating Cu offer exciting possibilities. By alloying Cu with other metals (e.g., Fe, Co, Ni, Zn, Au, Ag), researchers aim to precisely tune the electronic structure of the Cu sites and modify the local reaction environment. These modifications can potentially alter the binding strengths of key intermediates (*CO, *CHO, etc), suppress the competing HER and steer the reaction pathway towards desired C_{2+} products at lower overpotentials. The multi-element surface may also offer distinct sites for different elementary steps, promoting C–C coupling.

Al and Ti, while sometimes participating directly in surface reactions (e.g., forming active oxide layers or modifying support interactions), are often included for structural reasons, potentially reducing density, improving mechanical stability, or acting as deoxidizers during synthesis, thereby influencing the final microstructure and surface state.[96] The enhanced performance often observed in HEA catalysts compared to their single-component counterparts stems fundamentally from the coordination and synergistic interactions between the multiple metal elements. These interactions manifest in several ways. The presence of neighboring atoms with different electronegativities and electronic configurations leads to charge redistribution and hybridization of electron orbitals. This can shift the d-band center of active sites, a critical descriptor for adsorption energies. By carefully selecting elements, the d-band center can be tuned to optimize the binding strength of key reaction intermediates, aligning with the Sabatier principle for maximum activity. For geometric effects, the diverse local atomic arrangements on the HEA surface create unique geometric sites (ensembles) that may not exist on single-crystal surfaces or simpler alloys. These specific arrangements can influence how reactants adsorb and interact. Furthermore, surrounding atoms (ligands) electronically influence the central active atom, modifying its catalytic properties (ligand effect). The net result of these electronic and geometric effects is the ability to fine-tune the adsorption energies of reactants, intermediates and products. HEAs can potentially break the linear scaling relationships that often constrain traditional catalysts (where improving the binding of one intermediate detrimentally affects another). By providing a heterogeneous surface with a distribution of binding sites or sites with non-standard binding properties, HEAs can potentially achieve optimal binding for multiple steps in a complex reaction sequence. In addition, the stable solid solution structure, and the presence of elements such as Cr can improve corrosion resistance. Furthermore, the variety of sites might make the catalyst less susceptible to poisoning by strongly adsorbing species that could block active sites on a more uniform surface.

The strategic selection of constituent metals is the linchpin for designing high-performance HEA catalysts. By leveraging the known catalytic strengths of individual elements and combining them with abundant, synergistic transition metals (Fe, Co, Ni, Mn, Cr, etc) within the unique HEA framework, researchers can create materials with tailored electronic structures and optimized surface adsorption properties. The resulting coordination between multiple metals often leads to catalytic activity, selectivity and stability surpassing those of single-component systems, particularly unlocking potential for efficient bifunctional and multifunctional catalysis crucial

for advancing clean energy and sustainable chemical production technologies. The vast compositional space of HEAs, guided by an understanding of element-specific contributions and inter-element synergies, promises a continued wave of innovation in catalyst discovery. In addition, in 2D materials, the zigzag edge reconstruction of the α-phase pleated monolayer can lead to strong space charge separation. This edge reconstruction also provides a new perspective for the composition design of high-entropy alloys, which is helpful to optimize their electronic properties.[98]

3.6.2. Defect project

In any crystalline material, a defect represents a deviation from the perfect, repeating arrangement of structural units (atoms or molecules). When these units are incorrectly positioned or missing, defects such as vacancies (missing atoms), dislocations (misaligned planes of atoms), grain boundaries (interfaces between different crystal orientations), or stacking faults are generated.[99] These imperfections inevitably disrupt the local geometric and electronic environment (as conceptually illustrated in Fig. 6(b)). From a thermodynamic perspective, defects are inherently metastable. Their formation increases the system's internal energy and free energy compared to the perfect crystal lattice.[100] This higher energy state translates directly into higher chemical reactivity. Consequently, atoms located at or near defect sites often exhibit altered coordination numbers, strained bond lengths and modified electronic densities. These perturbations make defect sites prime locations for adsorbing reactant molecules, often binding them more strongly or weakening their internal bonds compared to pristine surface sites.[101] As such, defects frequently act as intrinsic catalytic active centers, playing a crucial role in initiating and facilitating chemical transformations.

High-entropy alloys, by their very nature, provide a particularly fertile ground for defect formation.[102] The inherent chemical complexity, involving multiple elements with varying atomic sizes, electronegativities and preferred crystal structures, naturally leads to significant lattice distortion and internal strain. This complexity makes it challenging for the alloy to achieve a perfectly ordered lattice during synthesis and processing, resulting in a higher baseline concentration and diversity of defects compared to simpler metals or alloys. The types of defects commonly encountered include vacancies, complex dislocation networks, numerous grain boundaries (especially in nanocrystalline HEAs), and localized compositional fluctuations that act as electronic defects.[103] This intrinsic richness in structural imperfections is one of the underlying reasons for the promising catalytic activities observed in many as-synthesized HEAs. Recognizing the potent influence of these imperfections, researchers have elevated their manipulation from a mere consequence of synthesis to a deliberate strategy known as defect engineering. This approach aims to intentionally introduce, control and stabilize specific types of defects within the HEA structure to optimize its catalytic activity, selectivity and stability. Defect engineering has proven to be an important and highly effective pathway to enhance catalyst performance beyond simply tuning the elemental composition. In addition, the surface reconstruction, oxidation mechanism and stability of Cd_3As_2 show that the surface characteristics of Cd_3As_2 have significant influence on its overall properties, which is similar to the challenge faced by defect engineering of high-entropy alloys.[104]

3.6.3. Strain engineering

Strain in materials, particularly in HEAs, significantly impacts the atomic and electronic structure by altering the distances between atoms and the symmetry of the lattice. This change in the original state of atomic bonds can be due to stretching or compressing the chemical bonds, leading to variations in lattice parameters. HEAs, characterized by their multi-component nature, are particularly susceptible to lattice strain because of the differing atomic sizes and lattice parameters of their constituent elements. Wu *et al.* conducted a study using density functional theory (DFT) simulations to explore the strain effects in Fe, Co, Ni, Pd and Pt.[105] Their findings highlighted that under specific conditions, such as low refractive index surfaces like (110) and (100), Ni and Co behaved as predicted by conventional strain theories.[106] However, Fe, Pd and Pt exhibited deviations, suggesting that precise strain modulation could potentially induce phase transitions. This insight is crucial for future research into the electrocatalytic properties of HEAs, where fine-tuning the strain could lead to enhanced catalytic performance.

The influence of strain on the electronic structure is particularly notable in the movement of the d-band center. Tensile strain tends to elevate the d-band center, while compressive strain has the opposite effect, lowering it.[107] This shift in the d-band center directly affects the adsorption energy of intermediates in the catalytic process.[108] An upward shift enhances the adsorption energy, which can be beneficial for certain catalytic reactions. Wang *et al.* demonstrated this concept in their study on PtFeCoNiCu HEAs.[109] By heating these alloys at different temperatures (400 °C and 700 °C), they induced varying degrees of strain. The HEA sample heated at 400 °C exhibited stronger compressive strain, resulting in a downward shift of the d-band center. This manipulation of strain and the consequent electronic structure changes open up new avenues for tailoring the properties of HEAs for specific applications, particularly in catalysis.

Strain plays a pivotal role in modifying the lattice and electronic structures of HEAs, influencing their catalytic properties. The ability to control strain through thermal treatments or other methods provides a powerful tool for optimizing the performance of these alloys in various applications,

especially in the field of electrocatalysis. Future research in this area could lead to the development of HEAs with tailored properties for efficient energy conversion and storage systems. Similarly, study of the surface reconstruction and stability of materials is also helpful to the performance optimization of high-entropy alloys. For example, particle swarm optimization and machine learning are used to study the surface of Fe_3O_4 (001), which can provide a reference for its surface strain regulation.[110]

4. Conclusion and prospect of HEA electrocatalysts

The multi-element alloy nature of HEAs, characterized by site-occupancy disorder and lattice order, allows for the optimization of their surface electronic structures. This optimization results in superior catalytic performance compared to low-element systems. In addition, the strength of adsorption energy can be modulated by adjusting the type and proportion of metal elements. Electrocatalytic reactions such as HER, HOR, OER, ORR and CO_2RR involve multi-step processes. The uniform distribution of several active sites on the catalyst surface can mitigate the limitations of interdependence, thereby enhancing binding energy and improving catalytic activity.

Despite the promising potential of HEAs as electrocatalysts, current studies are primarily focused on exploring the synthetic methods and screening element combinations.

This review delves into the concept of HEAs and outlines the primary synthesis methods. It also discusses the design of HEA catalysts for various electrochemical reactions, including HER, OER, CO_2RR and AOR. Especially in the synergistic conversion of CO_2 and NO_x, which is rarely discussed in previous reviews. The optimization strategy of HEA electrocatalysts is also illustrated, and the challenges and prospects are concluded.

4.1. The current challenges

High-entropy alloy electrocatalysts represent an emerging class of catalytic materials with significant promise, yet they also face several key challenges. To address these challenges and enhance our understanding of HEAs in electrocatalysis, several research directions are proposed. First, integrating theoretical and experimental approaches is crucial for elucidating the catalytic mechanisms of HEAs. Priority should be given to creating novel models, computational tools, and techniques to ascertain the factors affecting performance and the dynamic evolution of active sites in HEAs. Second, electrocatalytic processes can be favored by the abundance of active sites that can be produced by carefully regulating the size and content of HEAs. The microscopic inhomogeneity and surface atomic resolution of HEAs require improved structural characterization, which includes local stress distribution and chemical valence studies. Under various circumstances, phase engineering might enable HEAs with the same composition to display distinct crystal forms. Lastly, the design of composite materials with interface or core–shell structures should be incorporated into the advancement of HEAs. These cutting-edge materials might find use in catalysis and other areas.

The complexity in material design and synthesis consisting of five or more principal elements in near-equimolar ratios lies on vast combinatorial possibilities. The interplay of factors such as atomic size mismatch, electronegativity differences and crystal structure variations complicates the prediction and design of materials with tailored properties, posing challenges for optimizing electrocatalytic performance. While techniques such as arc melting, sputtering and chemical vapor deposition can produce HEAs, each method has drawbacks. Arc melting may introduce impurities and inhomogeneous composition, while sputtering and CVD often require high-vacuum conditions and costly equipment, hindering scalability. Precise control over composition, structure, and morphology during synthesis remains a persistent challenge.

Despite their high-entropy effects, lattice distortion and atomic miscoordination, HEA electrocatalysts do not always exhibit superior activity. Further research is needed to fine-tune their electronic structure and surface properties to boost catalytic efficiency for target reactions. Many HEA catalysts suffer from poor reaction selectivity, generating unwanted byproducts that reduce efficiency and economic viability. Developing strategies to enhance selectivity for desired reaction pathways is critical. Under electrochemical operating conditions, HEAs may degrade due to element leaching, structural collapse or surface passivation. Ensuring durability in harsh environments remains a major hurdle for practical deployment.

The complex, multi-element nature of HEAs makes traditional computational methods (e.g., DFT) inadequate for accurately predicting their electronic structures and catalytic behavior, limiting rational design efforts. Electrocatalytic reactions involve multi-step processes (mass transfer, charge transfer, reaction kinetics), and the interactions between HEAs and reaction intermediates are poorly understood. Advanced *in situ* characterization and multiscale simulations are needed but remain underdeveloped.

Variations in testing conditions and evaluation criteria across studies hinder fair comparisons between HEA catalysts, complicating the identification of optimal materials. Most research is confined to lab-scale experiments, with limited assessment of performance under industrial conditions (e.g., long-term stability, resistance to poisons). Bridging this gap is essential for commercialization. The inclusion of noble or

rare-earth metals in some HEAs raises expenses, restricting large-scale adoption. Cost-effective alternatives without sacrificing performance are needed.

Scaling up HEA synthesis while maintaining uniformity in composition and performance is difficult. Developing low-cost, industrially viable production methods is a key priority. Because of their remarkable combined features, HEAs are showing a growing amount of promise in electrocatalytic research. HEAs might become important materials in the realm of structural and functional materials in the future. Several challenges remain in understanding the catalytic mechanisms and practical applications of HEAs. For instance, precise shape control of HEAs is difficult to achieve, and there is insufficient control over the local atomic occupancy within HEAs. Although the morphology, crystal structure and elemental distribution in HEAs can be well characterized, there is still no definitive evidence linking these structural features to electrocatalytic performance. Furthermore, the complex surface and internal structures of HEAs, coupled with the multistep nature of electrocatalytic reactions, make it challenging to fully understand the catalytic structure-activity relationship.

4.2. Future research direction

4.2.1. In-depth study of the relationship between structure and performance

Employ advanced computational techniques, such as density functional theory (DFT), to examine the electronic structure of HEAs. Focus on key parameters such as electron density distribution, d-band center position and density of states to understand how these influence electrocatalytic behavior. Use these insights to predict optimal compositions and atomic arrangements tailored for specific electrocatalytic reactions. Utilize cutting-edge characterization tools including high-resolution transmission electron microscopy (HRTEM), x-ray diffraction (XRD) and extended x-ray absorption fine structure (EXAFS) spectroscopy to reveal atomic-scale features of HEAs. Investigate crystal structures, lattice constants and atomic coordination environments to clarify their impact on catalytic performance. Perform systematic electrochemical assessments to measure parameters such as electrochemical active surface area, catalytic activity, selectivity and durability. Correlate these performance metrics with structural data to deepen the understanding of how microstructural factors govern electrocatalytic efficiency, thereby guiding the design of superior HEA catalysts.

4.2.2. Exploration of emerging application areas

Extend HEA electrocatalyst research beyond traditional reactions (e.g., oxygen reduction and hydrogen evolution) to emerging energy technologies. For instance, explore their role in water electrolysis to simultaneously enhance the HER and OER, improving electrolyzer efficiency. Investigate their potential as photoelectrocatalysts in solar-driven water splitting and CO_2 reduction to boost renewable energy conversion.

Investigate HEAs for catalyzing environmentally relevant reactions such as nitrate and perchlorate reduction in contaminated water. Leverage their unique electronic structures for efficient and selective pollutant degradation. In addition, explore their application in the electrochemical breakdown of organic contaminants, aiming to broaden the scope and effectiveness of water purification technologies. Explore the utility of HEA electrocatalysts in biomedical fields, including biosensors and bioelectrochemical devices. Their high catalytic activity, combined with biocompatibility, makes them promising candidates for sensitive biomolecule detection and innovative diagnostic or therapeutic platforms. Beyond traditional electrocatalytic reactions, HEA electrocatalysts will be explored for emerging energy conversion and storage applications such as water electrolysis for hydrogen production and solar energy conversion.

4.2.3. Environmental protection and sustainable development

Develop greener synthesis approaches adhering to green chemistry principles to minimize the use of hazardous substances and reduce waste. Focus on environmentally benign techniques, such as hydrothermal synthesis and sol–gel processes, utilizing water or other sustainable solvents to manufacture HEA electrocatalysts. HEA electrocatalysts will be studied for their potential in environmental remediation, including nitrate reduction, perchlorate reduction and electrochemical degradation of organic pollutants.

Prioritize the recycling of precious metals and valuable elements from spent HEA catalysts to conserve resources and reduce environmental impact. Innovate effective recycling protocols and explore regeneration techniques that allow multiple reuse cycles, thereby extending catalyst lifespan and resource efficiency. Conduct thorough evaluations of the environmental footprint of HEA electrocatalysts throughout their entire lifecycle — from raw material extraction and synthesis to application and disposal. Identify potential ecological risks and develop strategies to mitigate adverse effects, ensuring that HEA catalyst development aligns with broader goals of environmental protection and sustainable development.

Acknowledgments

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References

[1] Wang S, Jiao S Q, Song W L, Chen H S, Tu J G, Tian D H, Jiao H H, Fu C P and Fang D N 2018 *Energy Storage Mater.* **12** 119

[2] Zhang J, Miao J, Balasubramani N, Cho D H, Avey T, Chang C and Luo A A 2023 *J. Magnesium Alloys* **11** 3867
[3] Liu X X, Ma S G, Wang J J, Zhao D, Jiao Z M, Zhang T W, Qiao L, Chen X Z and Wang Z H 2024 *J. Mater. Res. Technol.* **29** 5539
[4] Jing K, Liu R, Xie Z M, Ke J G, Wang X P, Fang Q F, Liu C S, Wang H, Li G and Wu X B 2022 *Acta Mater.* **227** 117725
[5] Yang T, Zhao Y L, Li W P, Yu C Y, Luan J H, Lin D Y, Fan L, Jiao Z B, Liu W H, Liu X J, Kai J J, Huang J C and Liu C T 2020 *Science* **369** 427
[6] Ren K, Huo W, Chen S, Cheng Y, Wang B and Zhang G 2024 *Chin. Phys. B* **33** 057202
[7] Xing R and Liu X 2024 *Chin. Phys. B* **33** 16202
[8] Li X, Lu L, Li J, Zhang X and Gao H 2020 *Nat. Rev. Mater.* **5** 706
[9] Xie L, Sun H, Wen Y, Hua L and Zhang L C 2025 *Prog. Mater. Sci.* **153** 101488
[10] V B and M A X 2024 *Heliyon* **10** e26464
[11] Yang Y F, Hu F, Xia T, Li R H, Bai J Y, Zhu J Q, Xu J Y and Zhang G F 2025 *J. Alloys Compd.* **1010** 177691
[12] Wen P, Du C, Tao G and Ding G 2024 *Chin. Phys. B* **33** 116103
[13] Pickering E J and Jones N G 2016 *Int. Mater. Rev.* **61** 183
[14] George E P, Curtin W A and Tasan C C 2020 *Acta Mater.* **188** 435
[15] Jiao Z M, Ma S G, Chu M Y, Yang H J, Wang Z H, Zhang Y and Qiao J W 2016 *J. Mater. Eng. Perform.* **25** 451
[16] Zou Y, Ma H and Spolenak R 2015 *Nat. Commun.* **6** 7748
[17] Niu C, LaRosa C R, Miao J, Mills M J and Ghazisaeidi M 2018 *Nat. Commun.* **9** 1363
[18] Liang Y, Wang L, Wen Y, Cheng B, Wu Q, Cao T, Xiao Q, Xue Y, Sha G, Wang Y, Ren Y, Li X, Wang L, Wang F and Cai H 2018 *Nat. Commun.* **9** 4063
[19] Ding Q, Zhang Y, Chen X, Fu X, Chen D, Chen S, Gu L, Wei F, Bei H, Gao Y, Wen M, Li J, Zhang Z, Zhu T, Ritchie R O and Yu Q 2019 *Nature* **574** 223
[20] Bloomfield M E, Christofidou K A, Mignanelli P M, Reponen A P M, Stone H J and Jones N G 2022 *J. Alloys Compd.* **926** 166734
[21] Zou Y, Wheeler J M, Ma H, Okle P and Spolenak R 2017 *Nano Lett.* **17** 1569
[22] Ren K, Chen J, Wang H and Huang Z 2021 *J. Phys. Conf. Ser.* **2044** 012051
[23] Li D, Li C, Feng T, Zhang Y, Sha G, Lewandowski J J, Liaw P K and Zhang Y 2017 *Acta Mater.* **123** 285
[24] Zhang Y, Zuo T T, Tang Z, Gao M C, Dahmen K A, Liaw P K and Lu Z P 2014 *Prog. Mater. Sci.* **61** 1
[25] Zhai Y, Ren X, Wang B and Liu S 2022 *Adv. Funct. Mater.* **32** 2207536
[26] Li W, Xie D, Li D, Zhang Y, Gao Y and Liaw P K 2021 *Prog. Mater. Sci.* **118** 100777
[27] Huo W, Fang F, Zhou H, Xie Z, Shang J and Jiang J 2017 *Scr. Mater.* **141** 125
[28] Li Z, Pradeep K G, Deng Y, Raabe D and Tasan C C 2016 *Nature* **534** 227
[29] Wang X, Guo W and Fu Y 2021 *J. Mater. Chem. A* **9** 663
[30] Yeh J W C S K, Lin S J, Gan J Y, Chin T S, Shun T T, Tsau C H and Chang S Y 2004 *Adv. Eng. Mater.* **6** 299
[31] Cantor B 2021 *Prog. Mater Sci.* **120** 100754
[32] Tsai K Y, Tsai M H and Yeh J W 2013 *Acta Mater.* **61** 4887
[33] Huo W Y, Wang S Q, Zhu W H, Zhang Z L, Fang F, Xie Z H and Jiang J Q 2021 *Tungsten* **3** 161
[34] Huo W, Liu X, Tan S, Fang F, Xie Z, Shang J and Jiang J 2018 *Appl. Surf. Sci.* **439** 222
[35] Ranganathan S 2003 *Curr. Sci.* **85** 1404
[36] Lei Z, Liu X, Wu Y, Wang H, Jiang S, Wang S, Hui X, Wu Y, Gault B, Kontis P, Raabe D, Gu L, Zhang Q, Chen H, Wang H, Liu J, An K, Zeng Q, Nieh T G and Lu Z 2018 *Nature* **563** 546
[37] Chang Y, Benlolo I, Bai Y, Reimer C, Zhou D, Zhang H, Matsumura H, Choubisa H, Li X Y, Chen W, Ou P, Tamblyn I and Sargent E H 2024 *Matter* **7** 4099
[38] Cantor B, Chang I T H, Knight P and Vincent A J B 2004 *Mater. Sci. Eng. A* **375** 213
[39] Gao S, Hao S, Huang Z, Yuan Y, Han S, Lei L, Zhang X, Shahbazian Yassar R and Lu J 2020 *Nat. Commun.* **11** 2016
[40] Fu S, Zhu C, Du D and Lin Y 2016 *ACS Appl. Mater. Interfaces* **8** 6110
[41] Mori K, Hashimoto N, Kamiuchi N, Yoshida H, Kobayashi H and Yamashita H 2021 *Nat. Commun.* **12** 3884
[42] Xu Z, Zhang X, Wang X, Fang J, Zhang Y, Liu X, Zhu W, Yan Y and Zhuang Z 2021 *ACS Nano* **15** 7131
[43] Li H, Sun M, Pan Y, Xiong J, Du H, Yu Y, Feng S, Li Z, Lai J, Huang B and Wang L 2022 *Appl. Catal. B* **312** 121431
[44] Niu B, Zhang F, Ping H, Li N, Zhou J, Lei L, Xie J, Zhang J, Wang W and Fu Z 2017 *Sci. Rep.* **7** 3421
[45] Kusada K, Mukoyoshi M, Wu D and Kitagawa H 2022 *Angew. Chem. Int. Ed.* **61** e202209616
[46] Chen L, Song Z, Zhang S, Chang C K, Chuang Y C, Peng X, Dun C, Urban J J, Guo J, Chen J L, Prendergast D, Salmeron M, Somorjai G A and Su J 2023 *Science* **381** 857
[47] Kang Y, Cretu O, Kikkawa J, Kimoto K, Nara H, Nugraha A S, Kawamoto H, Eguchi M, Liao T, Sun Z, Asahi T and Yamauchi Y 2023 *Nat. Commun.* **14** 4182
[48] Yao Z, Chen Y, Wang X, Hu K, Ren S, Zhang J, Song Z, Ren N and Duan X 2025 *Nat. Commun.* **16** 148
[49] Löffler T, Meyer H, Savan A, Wilde P, Garzón Manjón A, Chen Y T, Ventosa E, Scheu C, Ludwig A and Schuhmann W 2018 *Adv. Energy Mater.* **8** 1802269
[50] Zhu H, Zhu Z, Hao J, Sun S, Lu S, Wang C, Ma P, Dong W and Du M 2022 *Chem. Eng. J.* **431** 133251
[51] Li S Q, Liu X, Wang X, Liu H, Zhang G, Zhao J and Gao J 2022 *Small* **18** 2270011
[52] Löffler T, Savan A, Garzón Manjón A, Meischein M, Scheu C, Ludwig A and Schuhmann W 2019 *ACS Energy Lett.* **4** 1206
[53] Jin Z, Lyu J, Zhao Y L, Li H, Lin X, Xie G, Liu X, Kai J J and Qiu H J 2020 *ACS Mater. Lett.* **2** 1698
[54] Qiu H J, Fang G, Wen Y, Liu P, Xie G, Liu X and Sun S 2019 *ACS Mater. Lett.* **1** 526
[55] Cavin J, Ahmadiparidari A, Majidi L, Thind A S, Misal S N, Prajapati A, Hemmat Z, Rastegar S, Beukelman A, Singh M R, Unocic K A, Salehi Khojin A and Mishra R 2021 *Adv. Mater.* **33** 2100347
[56] Chen Z J, Zhang T, Gao X Y, Huang Y J, Qin X H, Wang Y F, Zhao K, Peng X, Zhang C, Liu L, Zeng M H and Yu H B 2021 *Adv. Mater.* **33** 2101845
[57] Sarkar A, Wang Q, Schiele A, Chellali M R, Bhattacharya S S, Wang D, Brezesinski T, Hahn H, Velasco L and Breitung B 2019 *Adv. Mater.* **31** 1806236
[58] Zhang L, Cai W and Bao N 2021 *Adv. Mater.* **33** e2100745
[59] Chen W, Luo S, Sun M, Wu X, Zhou Y, Liao Y, Tang M, Fan X, Huang B and Quan Z 2022 *Adv. Mater.* **34** 2206276
[60] Qu J, Elgendy A, Cai R, Buckingham M A, Papaderakis A A, de Latour H, Hazeldine K, Whitehead G F S, Alam F, Smith C T, Binks D J, Walton A, Skelton J M, Dryfe R A W, Haigh S J and Lewis D J 2023 *Adv. Sci.* **10** 2204488
[61] Yao Y, Liu Z, Xie P, Huang Z, Li T, Morris D, Finfrock Z, Zhou J, Jiao M, Gao J, Mao Y, Miao J, Zhang P, Shahbazian Yassar R, Wang C, Wang G and Hu L 2020 *Sci. Adv.* **6** eaaz0510
[62] Xie P, Yao Y, Huang Z, Liu Z, Zhang J, Li T, Wang G, Shahbazian Yassar R, Hu L and Wang C 2019 *Nat. Commun.* **10** 4011
[63] Yao Y, Huang Z, Xie P, Lacey S D, Jacob R J, Xie H, Chen F, Nie A, Pu T, Rehwoldt M, Yu D, Zachariah M R, Wang C, Shahbazian Yassar R, Li J and Hu L 2018 *Science* **359** 1489
[64] Yao Y, Huang Z, Li T, Wang H, Liu Y, Stein H S, Mao Y, Gao J, Jiao M, Dong Q, Dai J, Xie P, Xie H, Lacey S D, Takeuchi I, Gregoire J M, Jiang R, Wang C, Taylor A D, Shahbazian Yassar R and Hu L 2020 *Proc. Natl. Acad. Sci. USA* **117** 6316
[65] Chen X, Si C, Gao Y, Frenzel J, Sun J, Eggeler G and Zhang Z 2015 *J. Power Sources* **273** 324
[66] Mao Y, Chen J, Wang H and Hu P 2015 *Chin. J. Catal.* **36** 1596
[67] Jin Z, Lv J, Jia H, Liu W, Li H, Chen Z, Lin X, Xie G, Liu X, Sun S and Qiu H J 2019 *Small* **15** 1904180
[68] Li S, Tang X, Jia H, Li H, Xie G, Liu X, Lin X and Qiu H J 2020 *J. Catal.* **383** 164
[69] Qiu H J, Fang G, Wen Y, Liu P, Xie G, Liu X and Sun S 2019 *J. Mater. Chem. A* **7** 6499
[70] Waag F, Li Y, Ziefuß A R, Bertin E, Kamp M, Duppel V, Marzun G, Kienle L, Barcikowski S and Gökce B 2019 *RSC Adv.* **9** 18547
[71] Liu M, Zhang Z, Okejiri F, Yang S, Zhou S and Dai S 2019 *Adv. Mater. Interfaces* **6** 1900015
[72] Huang K, Zhang B, Wu J, Zhang T, Peng D, Cao X, Zhang Z, Li Z and Huang Y 2020 *J. Mater. Chem. A* **8** 11938

[73] Katiyar N K, Nellaiappan S, Kumar R, Malviya K D, Pradeep K G, Singh A K, Sharma S, Tiwary C S and Biswas K 2020 *Mater. Today Energy* **16** 100393

[74] Nellaiappan S, Katiyar N K, Kumar R, Parui A, Malviya K D, Pradeep K G, Singh A K, Sharma S, Tiwary C S and Biswas K 2020 *ACS Catal.* **10** 3658

[75] Tan X, Yu C, Ren Y, Cui S, Li W and Qiu J 2021 *Energy Environ. Sci.* **14** 765

[76] Hao Q, Liu D X, Zhong H X, Tang Q and Yan J M 2023 *Chem Catal.* **3** 100542

[77] Birdja Y Y, Pérez Gallent E, Figueiredo M C, Göttle A J, Calle Vallejo F and Koper M T M 2019 *Nat. Energy* **4** 732

[78] Woldu A R, Huang Z, Zhao P, Hu L and Astruc D 2022 *Coord. Chem. Rev.* **454** 214340

[79] Kim C, Jeon H S, Eom T, Jee M S, Kim H, Friend C M, Min B K and Hwang Y J 2015 *J. Am. Chem. Soc.* **137** 13844

[80] Mistry H, Reske R, Zeng Z, Zhao Z J, Greeley J, Strasser P and Cuenya B R 2014 *J. Am. Chem. Soc.* **136** 16473

[81] Kim C, Dionigi F, Beermann V, Wang X, Möller T and Strasser P 2019 *Adv. Mater.* **31** 1805617

[82] Reske R, Mistry H, Behafarid F, Roldan Cuenya B and Strasser P 2014 *J. Am. Chem. Soc.* **136** 6978

[83] Li H, Huang H, Chen Y, Lai F, Fu H, Zhang L, Zhang N, Bai S and Liu T 2023 *Adv. Mater.* **35** 2209242

[84] Chen X, Tan Y, Yuan J, Zhai S, Su L, Mou Y, Deng W Q and Wu H 2025 *Adv. Energy Mater.* **15** 2500872

[85] Zhang T, Zhao H F, Chen Z J, Yang Q, Gao N, Li L, Luo N, Zheng J, Bao S D, Peng J, Peng X, Liu X W and Yu H B 2025 *Nat. Commun.* **16** 3327

[86] He L, Li M, Qiu L, Geng S, Liu Y, Tian F, Luo M, Liu H, Yu Y, Yang W and Guo S 2024 *Nat. Commun.* **15** 2290

[87] Shi X, Gao W, Liu H, Fu Z G, Zhang G, Zhang Y W, Liu T, Zhao J and Gao J 2022 *Small* **18** 2203274

[88] Miracle D B and Senkov O N 2017 *Acta Mater.* **122** 448

[89] Zhang T, Sun J and Guan J 2023 *Nano Res.* **16** 8684

[90] Xiao L, Han J, Wang Z and Guan J 2023 *Int. J. Hydrogen Energy* **48** 23776

[91] Jin D, Qiao F, Chu H and Xie Y 2023 *Nanoscale* **15** 7202

[92] Tang T, Wang Z and Guan J 2023 *Coord. Chem. Rev.* **492** 215288

[93] Wang C L, Guo H D, Fang J, Yu S X, Yue X Q, Hu Q H, Liu C W, Zhang J X, Zhang R, Xu X S, Hua Y and Li Y X 2023 *Pet. Sci.* **20** 1155

[94] Xu D D, Zhou B L, Wang Q Q, Zhou J, Yang W M, Yuan C C, Xue L, Fan X D, Ma L Q and Shen B L 2018 *Corros. Sci.* **138** 20

[95] Zhang H, Liang Q and Xie K 2024 *iScience* **27** 108973

[96] Roy D, Mandal S C and Pathak B 2022 *J. Phys. Chem. Lett.* **13** 5991

[97] Yang G, Zhao Y, Lee D H, Park J M, Seok M Y, Suh J Y, Ramamurty U and Jang J i 2019 *Scr. Mater.* **161** 23

[98] Zhang Y, Zhao Y, Bai Y, Gao J, Zhao J and Zhang Y W 2021 *Nano Lett.* **21** 8095

[99] Li M, Zhang C, Li M, Liu F, Zhou L, Gao Z, Sun J, Han D and Gong J 2022 *Chem. Eng. J.* **429** 132450

[100] Singh M K 2014 *J. Cryst. Growth* **396** 14

[101] Jia Y, Jiang K, Wang H and Yao X 2019 *Chem* **5** 1371

[102] George E P, Raabe D and Ritchie R O 2019 *Nat. Rev. Mater.* **4** 515

[103] Rudolph P 2016 *Prog. Cryst. Growth Charact. Mater.* **62** 89

[104] Gao J, Cupolillo A, Nappini S, Bondino F, Edla R, Fabio V, Sankar R, Zhang Y W, Chiarello G and Politano A 2019 *Adv. Funct. Mater.* **29** 1900965

[105] Wu T, Sun M and Huang B 2020 *Small* **16** 2002434

[106] Wang L, Lai K C, Huang L, Evans J W and Han Y 2020 *Surf. Sci.* **695** 121532

[107] Luo M and Guo S 2017 *Nat. Rev. Mater.* **2** 17059

[108] Zhang Y, Wang D and Wang S 2022 *Small* **18** 2104339

[109] Wang D, Chen Z, Huang Y C, Li W, Wang J, Lu Z, Gu K, Wang T, Wu Y, Chen C, Zhang Y, Huang X, Tao L, Dong C L, Chen J, Singh C V and Wang S 2021 *Sci. China Mater.* **64** 2454

[110] Liu H, Zhao Y, Qiu S, Zhao J and Gao J 2023 *Chin. Phys. B* **32** 056802