

# High-Entropy Alloys in Catalysis: Progress, Challenges, and Prospects

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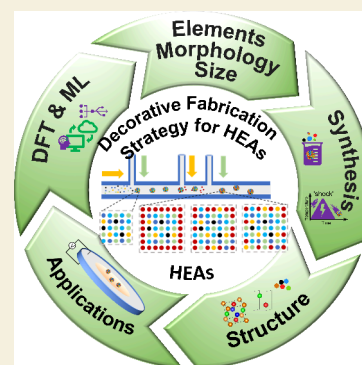
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**ABSTRACT:** High-entropy alloys (HEAs) have become pivotal materials in the field of catalysis, offering unique advantages due to their diverse elemental compositions and complex atomic structures. Recent advances in computational techniques, particularly density functional theory (DFT) and machine learning (ML), have significantly enhanced our understanding and design of HEAs for use in catalysis. These innovative atomistic simulations shed light on the properties of HEAs, enabling the discovery and optimization of catalysis materials for solid-solution structures. This Perspective discusses recent studies that illustrate the progress of HEAs in catalysis. It offers an overview of the properties, constraints, and prospects of HEAs, emphasizing their roles in catalysis to enhance catalytic activity and selectivity. The discussion underscores the capabilities of HEAs as multifunctional catalysts with stable structures. The presented insights aim to inspire future computational and experimental efforts to address the challenges in fine-tuning HEAs properties for improved catalytic performance.

**KEYWORDS:** *high-entropy alloys, catalysis, strategy, synthesis, application*



## 1. INTRODUCTION

High-entropy alloys (HEAs) are a unique class of materials composed of multiple principal elements, typically five or more, that are mixed in approximately equimolar proportions to form a solid-solution structure. While the concentration of each of the principal elements generally ranges from 5 to 35 at. %, achieving near-equimolarity means the elements are present in similar, though not necessarily identical, molar ratios.<sup>1,2</sup> HEAs represent a new paradigm across diverse applications, offering significant opportunities for materials discovery, property optimization, and advanced applications across diverse fields. The exceptional performance of HEAs as functional materials stems from their unique chemical structures, which confer remarkable mechanical properties under harsh conditions. This has led to significant advancements in applications such as catalysis, radiation-resistant materials, soft-magnetic materials, and superconducting materials.<sup>3–5</sup> Additionally, HEAs exhibit the potential to enhance key mechanical properties such as toughness and strength in metallic structural materials, making them particularly suitable for nuclear applications.<sup>6,7</sup> Current research is advancing electrochemical energy conversion by focusing on noble-metal-free alloys and noble/transition metal composites, which demonstrate enhanced catalytic performance.<sup>8–10</sup> Despite challenges such as phase separation due to elemental immiscibility, recent advancements, such as thermal

shock methods, have successfully produced HEAs with homogeneous structures, even when incorporating typically immiscible elements.<sup>11,12</sup>

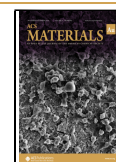
The inherent compositional flexibility of HEAs allows for precise modulation of catalytic activity and selectivity, while their high-entropy mixing confers structural stability, even under extreme conditions.<sup>13</sup> HEAs provide a variety of ideal adsorption sites for multistep reactions. Their multielemental synergy allows active sites to combine various constituent elements, enabling flexible tuning of binding energies for diverse optimization pathways. The entropic stabilization resulting from alloying multiple elements counteracts phenomena such as segregation, phase change, and dealloying, thereby providing structural stability in harsh environments. Moreover, the properties of HEAs provide the potential to replace noble metals with more abundant elements without sacrificing performance.<sup>14</sup> The unique properties of HEAs offer substantial opportunities across various fields, including

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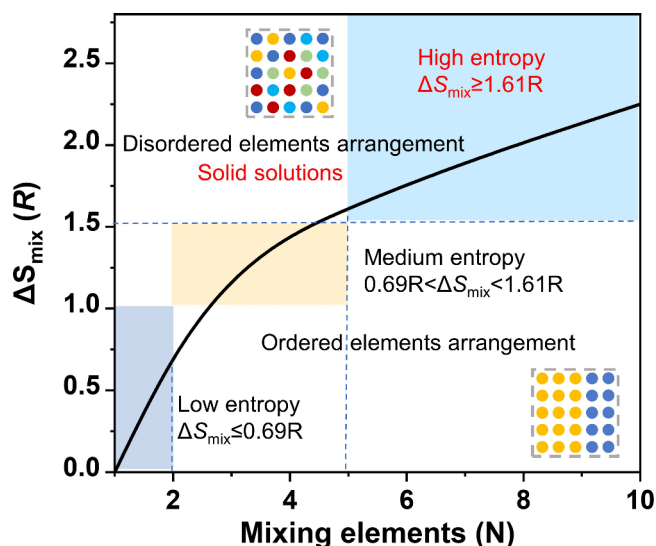
thermoelectricity, water splitting, and energy storage, with promising potential for driving technological advancements, particularly in catalysis.<sup>15–18</sup> Despite these advantages, HEAs present significant challenges in synthesis, characterization, application, and understanding due to their extensive compositional variability and complex atomic arrangements.<sup>13</sup> The relative scarcity of significant active sites on the HEA surface, which must be offset by their increased activity, compounds these challenges.

Accordingly, this Perspective aims to offer a comprehensive overview of recent advancements in HEA materials, highlighting their synthesis, characterization, and applications across various fields. It discusses the components and synthesis methods of HEAs used in electrocatalytic energy conversion reactions as well as their roles in enhancing catalytic activity and selectivity. The focus is on the properties, constraints, and prospects of HEAs within various catalytic applications. The Perspective is organized into the following sections: (i) design method of HEA materials in catalysts, (ii) synthesis and characterization techniques, (iii) applications of HEAs in catalysis, and (iv) challenges and future perspectives on the development.

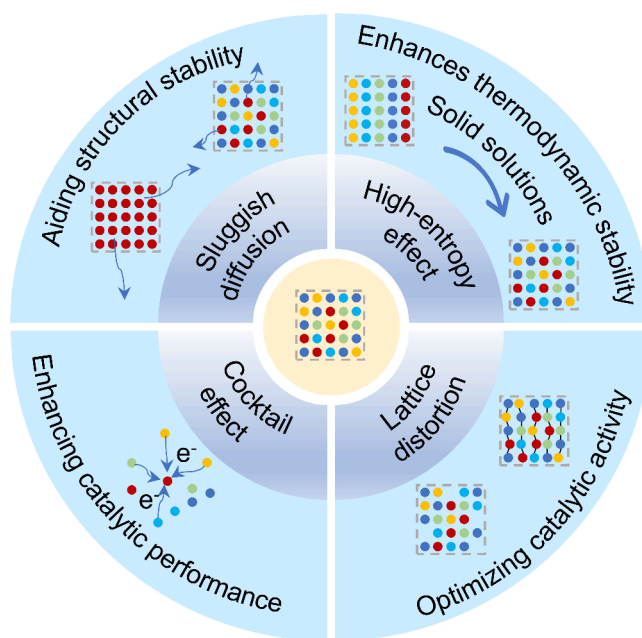
## 2. DEFINITION AND PROPERTIES OF HEAS

Initially, most multielement materials reported in the literature were multiphase rather than single-phase solid solutions.<sup>19,20</sup> Yeh and colleagues hypothesized that adding more elements to an alloy boosts the configurational entropy of mixing sufficiently to overcome the enthalpic contributions, thereby stabilizing solid solutions and preventing the production of potentially harmful intermetallics.<sup>2</sup> By combining numerous elements in nearly equimolar proportions, HEAs offer a revolutionary approach to alloy creation, surpassing the constraints of conventional alloys in binary and ternary forms. The formation of high-entropy nanoparticles (NPs) is driven by a balance between enthalpy and entropy, described by  $\Delta G = \Delta H - T\Delta S$ .<sup>17</sup> The optimal configurational entropy of an ideal solid solution is generally described by  $\Delta S_{\text{mix}} = -R \sum_{i=1}^n c_i \ln c_i$  (where  $R$  is the gas constant,  $n$  is the total number of elements in the HEAs, and  $c_i$  is the molar percentage of each component). As depicted in Figure 1, achieving a high entropy requires incorporating at least five elements in equimolar ratios, where  $\Delta S_{\text{mix}} = R \ln 5 = 1.61R$ .<sup>2,21,22</sup> During solidification, the elevated entropy increases the likelihood of forming a random solid-solution structure over intermetallic complexes. Consequently, HEAs more readily form random solid solutions instead of intermetallic compounds. This innovative understanding of alloy formation lays the groundwork for developing advanced materials with unique properties and applications.

HEAs possess unique microstructures and properties that distinguish them from traditional alloys, characterized by several distinctive features such as sluggish diffusion, the high-entropy effect, the cocktail effect, and lattice distortion, which collectively influence their behavior and performance and offer unique properties for electrocatalysis (Figure 2).<sup>23,24</sup> Sluggish diffusion in HEAs, caused by varying diffusion rates among the different elemental atoms and variations in their potential energies, reduces atomic diffusion rates, thereby enhancing structural stability under harsh conditions.<sup>25,26</sup> The high-entropy effect, arising from the uniform mixing of five or more elements, generates significant mixing entropy that counter-

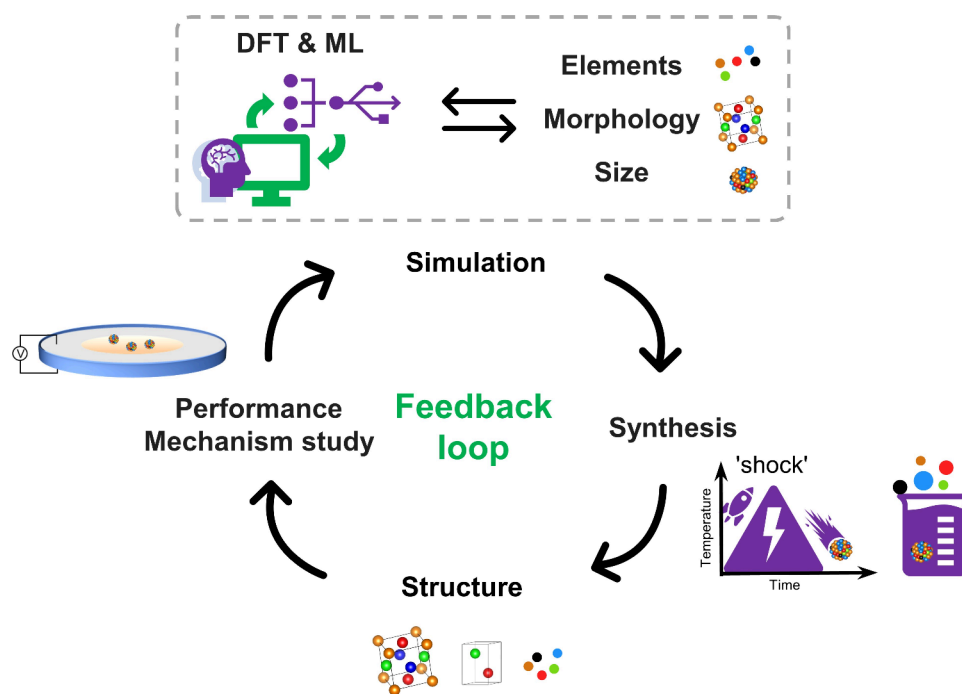


**Figure 1.** Effect of an equimolar number of mixing elements on the mixing entropy.



**Figure 2.** Schematic overview of the properties of HEAs.

balances mixing enthalpy, thereby stabilizing solid solutions and leading to significant catalytic durability in electrocatalysis.<sup>27,28</sup> The cocktail effect arises from the synergistic interactions of diverse elements, enhancing catalytic performance by tuning electronic and geometric structures of HEAs.<sup>29,30</sup> The lattice distortion induced by atomic size mismatches in HEAs enhances catalytic activity through local strain fields and defect formation.<sup>31,32</sup> Together, these effects make HEAs promising candidates for advanced and stable electrocatalytic applications. However, the specific physical mechanisms underlying these effects are not fully understood and require further experimental and theoretical investigation.



**Figure 3.** A strategy for the design of HEAs in catalysis.

### 3. THE DESIGN AND CHARACTERIZATION OF HEAS IN CATALYSIS

Element selection for HEAs is crucial because different reactants require consideration of various intermediate binding energies and compositions, and high immiscibility with dissimilar elements may generate phase-segregated structures. Achieving suitable compositions with optimal element concentrations and structural stability is crucial for improving the catalytic performance of HEAs. A key advancement in catalyst design is the understanding that optimizing activity can be achieved by tailoring the binding energies of reactants or intermediates through alloying, which allows for optimization due to induced electronic interactions. The combination of density functional theory (DFT) and machine learning (ML) in theoretical calculations offers significant opportunities to predict the catalytic properties of HEAs and identify suitable catalysts (Figure 3).<sup>8,32</sup> DFT calculations can elucidate the correlation between chemical compositions in HEAs and specific catalytic reactions.<sup>33</sup> However, modeling a single element combination requires substantial computational power and time. ML has proven to be effective in assisting the prediction of suitable composition. For example, ML enables identification of large amounts of active centers in FeCoNiCuMo HEAs catalysts on 1280 sites for the adsorption energies of reactants and intermediates in CO<sub>2</sub> reduction reaction (CRR) due to their complex atomic structures and broad compositional range.<sup>34</sup>

When selecting compositions for HEAs, it is essential to consider factors beyond theoretical predictions, including oxidation potential, element immiscibility, diverse physicochemical properties, and suitable synthesis methods. Elements like noble metals, along with Fe, Co, and Cu, which have lower oxidation potentials and are positioned in the upper region of the Ellingham diagram, are particularly beneficial for forming HEAs.<sup>35</sup> Due to significant physicochemical differences among elements, achieving natural single-phase mixing is rare. Phase-

segregated structures are more common when using near-equilibrium methods, such as wet chemistry, to synthesize multielemental NPs.<sup>36,37</sup> The surface and microstructure characteristics of HEAs, influenced by various synthetic methodologies, are directly correlated to their suitability for catalytic processes. Therefore, choosing suitable synthetic approaches is crucial for achieving precise control over the composition distribution, atom arrangement, morphology, and phase of HEAs.

#### 3.1. HEA Synthesis

Synthesis approaches for HEAs involve various innovative methods that enhance the efficiency and versatility of HEA production on the selection of component elements. The Gibbs free energy ( $\Delta G = \Delta H - T\Delta S$ ) establishes the thermodynamic limit, highlighting that entropic stabilization increases with elevated temperature. This necessitates a synthesis method where all elements are decoupled from precursors at high temperatures or energies, ensuring that  $\Delta G$  is negative for the element combination. Carbothermal shock (CTS) synthesis provides a rapid, controlled approach to creating multimetallic (up to eight elements) NPs with a wide range of compositions through high-temperature ( $\sim 2000$  K) shocks.<sup>11</sup> The rapid cooling rate ( $105 \text{ K s}^{-1}$ ) in the CTS method significantly influences the extent of nonequilibrium and structural ordering attainable, resulting in homogeneous components. This approach concurrently opens up an innovative way to reduce HEAs from bulk to nanoscale structures.<sup>38</sup> Based on the “shock” concept, various methods such as plasma, microwave-assisted heating, sputtering, combustion-assisted synthesis, and laser irradiation have been utilized to synthesize HEAs, each driven by a strong kinetics-driven mechanism.<sup>39–43</sup> These advancements in synthesis techniques not only broaden the scope of HEAs applications but also enhance their functionality and scalability, making them more viable for practical uses. However, these synthesis methods often require high processing temperatures to

leverage the large configurational entropy in  $\Delta G$ , yield dendritic microstructures, or require complex equipment. While they facilitate the mixing of diverse chemical elements in NPs, elevated temperatures also accelerate atomic diffusion and particle growth, often resulting in particle sizes exceeding 10 nm, for which the unique structural properties of NPs become less dominant.<sup>44</sup>

Electrochemical synthesis offers a notable alternative by allowing controlled nucleation and growth of HEAs via electrodeposition and electro-deoxidation, which can produce HEAs from oxide precursors in organic or molten salt electrolytes, and NPs have been reported to decrease in size down to 10 nm in recent studies.<sup>45</sup> The electrochemical deposition method offers several advantages, including being low cost and requiring minimal equipment, and the tunable properties and composition of NPs can be readily adjusted by varying the electrolyte composition, current density, and applied voltage during the deposition process. However, it also presents challenges such as instability in voltage and current, which can lead to inconsistent nanomaterial synthesis and adversely affect their functional properties.<sup>12,29,45</sup>

The synthesis of HEAs using wet synthesis techniques is also a promising strategy.<sup>14,46</sup> This method offers an alternative to high-temperature synthesis methods by allowing the introduction of a variety of metal precursors to produce the desired HEAs. However, common wet synthesis methods encounter challenges due to variations in the decomposition rates of metal precursors. Through the wet coreduction of metal precursors by using sodium borohydride as the reducing agent, followed by annealing under  $H_2/Ar$  at 350 °C, single-phase HEAs were successfully obtained.<sup>14,46</sup> Kitagawa et al. introduced a novel fabrication approach using a continuous-flow reactor with microfluidic technology and a vortex effect. This approach provides high reproducibility and selectivity of the HEA products. Specifically, a liquid-phase reduction method enabled the synthesis of ultrasmall IrPdPtRhRu HEA NPs with a diameter of 1.32 nm, which exhibit significant activity in the hydrogen evolution reaction (HER).<sup>47</sup>

### 3.2. HEA Characterization

Since HEAs exhibit a single-phase structure with uniformly and randomly mixed constituent elements, characterizing them presents significant challenges due to their complex multi-elemental composition and structural properties (Figure 4). Traditional techniques, such as powder X-ray diffraction (XRD) and selected area electron diffraction (SAED), offer fundamental insights into phase structures, while scanning electron microscopy (SEM) and transmission electron microscopy (TEM) reveal the morphology. Data from energy dispersive spectrometry (EDS) mapping and line scanning of a single alloy can demonstrate that all elements are homogeneously dispersed, with no evidence of elemental segregation, thereby ensuring that HEAs remain free from phase separation. X-ray photoelectron spectroscopy (XPS) gives details about the electronic states and properties. Synchrotron-based X-ray absorption spectroscopy (XAS) offers enhanced resolution for analyzing detailed atomic arrangement, bonding, and electronic properties in HEAs, which is crucial for understanding the electronic and catalytic properties. Advanced methods, such as atomic electron tomography (AET) and four-dimensional scanning transmission electron microscopy (4D-STEM), provide unprecedented 3D structural insights,

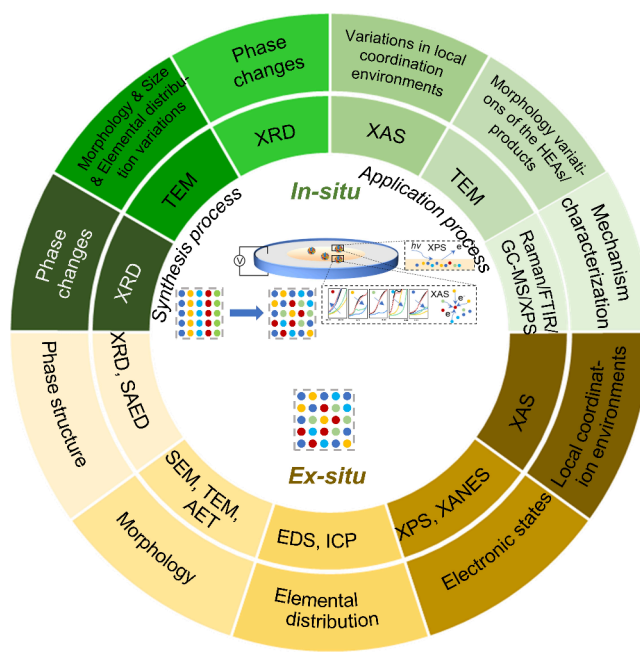


Figure 4. Characterization of HEAs.

revealing local lattice distortions and ordering at the single-atom level.<sup>35,48</sup>

*In situ* characterization techniques can elucidate phase transitions during catalyst synthesis and uncover the mechanisms behind the enhanced catalytic performance. For instance, *in situ* XRD was used to reveal a thermodynamically induced phase evolution during the synthesis of FeCoNiIrRu HEAs. In addition, *in situ* Raman spectra demonstrated the formation of superoxo and OH intermediates on the surfaces of FeCoNiIrRu HEAs, thereby enhancing reaction kinetics for the oxygen evolution reaction (OER) in acidic electrolytes.<sup>49</sup> *In situ* and *operando* XAS was employed to reveal the variations in electronic states, identify active sites, and parse the synergistic effects of HEAs during HER.<sup>46</sup> *In situ* TEM was used to investigate the thermal stability of FeCoNiCuPd HEA NPs on reduced graphene oxide at high temperatures, revealing that the NPs retained their composition, size, and structure at 700 °C, despite a gradual decrease in size due to the preferential sublimation of Cu.<sup>50</sup>

## 4. HEAS FOR CATALYSIS

Given the urgency of addressing climate change coupled with depleting petroleum supplies, developing clean energy technologies, such as water electrolysis,  $CO_2$  conversion, and metal–air batteries, is critical.<sup>51,52</sup> These technologies often require noble metals like Pt, Ru, and Ir for optimal kinetics, while these noble metals are naturally constrained due to limited availability and high costs and rely on catalytic reactions including the following:

- HER
- hydrogen oxidation reaction (HOR)
- oxygen reduction reaction (ORR)
- OER
- nitrogen reduction reaction (NRR)
- CRR

Consequently, developing novel catalysts with superior activity, durability, and affordability is essential for advancing

Catalytic reaction	HER	HOR	OER	ORR	NRR	CRR	Zn-Air battery	Li-S battery	Li-CO <sub>2</sub> battery
<b>Catalyst</b>	IrPdPtRhRu <sup>47</sup> PtPdRhRuCu <sup>54</sup> FeCoNiCuMn <sup>55</sup>		FeCoNiIrRu <sup>49</sup>	CoCuFeNiMnMo <sub>1.5</sub> <sup>9</sup>	FeCoNiCuPd <sup>65</sup>	FeCoNiMnV <sup>70</sup>	FeCoNiZnCu <sup>10</sup>	NiFeCoCuRu <sup>14</sup>	
<b>Synthetic method</b>	Continuous-flow reactor		Facile wet-chemistry	Electrospinning furnace	Mechanical alloying method	Electrospun carbon nanofibers	Pyrolysis method	High-temperature calcination	Chemical reduction
<b>Structure</b>	NPs 1.32 nm fcc		NPs 4.8 nm fcc	NPs 6 nm fcc	Flakes fcc/bcc	NPs 20-30 nm fcc	NPs 16 nm fcc	NPs 10 nm fcc	NPs 2.17 nm hcp
<b>Year</b>	2022		2023	2022	2024	2023	2024	2024	2024

Catalytic reaction	HER	HOR	OER	ORR	NRR	CRR	Zn-Air battery	Li-S battery	Li-CO <sub>2</sub> battery
<b>Catalyst</b>	IrPdPtRhRu <sup>47</sup> PtPdRhRuCu <sup>54</sup> FeCoNiCuMn <sup>55</sup>		FeCoNiIrRu <sup>49</sup>	CoCuFeNiMnMo <sub>1.5</sub> <sup>9</sup>	PtPdFeCoNi <sup>59</sup> CrMnFeCoNi <sup>60</sup>	AuAgPtPdCu <sup>66</sup>	FeCoNiCuMo <sup>34</sup>	FeCoNiCuMn <sup>67</sup>	
<b>Synthetic method</b>	Continuous-flow reactor		Facile wet-chemistry	Electrospinning furnace	Mechanical alloying method	Wet-chemistry reduction	Solution-based approach	Melting and cryogrinding	Cast cum cryo-milling
<b>Structure</b>	NPs 1.32 nm fcc		NPs 4.8 nm fcc	NPs 6 nm fcc	Flakes fcc/bcc	NPs 12 nm fcc	NPs 170 nm fcc	NPs 16 ± 10 nm fcc	NPs 16 nm fcc
<b>Year</b>	2022		2023	2022	2024	2022	2023	2020	2022

Figure 5. State-of-the-art HEAs as catalysts in various applications.

practical clean energy applications. Due to the unique microstructures and superior physicochemical properties of HEAs, HEAs have emerged as promising catalysts to be applied in various energy conversion processes, including the HER, HOR, ORR, OER, NRR, CRR, and metal–air batteries, as depicted in Figure 5. The following section highlights recent research progress.

#### 4.1. HER

The HER can be optimized by creating suitable active sites to selectively promote OH<sup>−</sup> or H<sup>+</sup> intermediates, thereby reducing the hydrolysis energy barrier, enhancing H interaction, and balancing the adsorption of intermediates. HEAs with tunable compositions can regulate intermediate adsorption, improve catalytic activity, and reduce costs. The literature consistently indicates that Pt-based catalysts significantly enhance the kinetics of the HER, thereby making Pt-based HEAs a focus of research in this area.<sup>53</sup> Pt-based HEAs with low contents of expensive noble metals like IrPdPtRhRu and PtPdRhRuCu exhibit impressive catalytic activity, surpassing traditional Pt/C in terms of overpotential and stability and are less costly.<sup>47,54</sup> The study found that the  $\Delta G_{H^*}$  and binding energy of hydrogen on the HEAs surface could be regulated to facilitate hydrogen desorption and release, with specific elements adjusting the electronic structures of active sites, thereby enhancing system entropy. HEA strategy can maintain or even improve the outstanding catalytic activity and stability of Pt while increasing utilization efficiency and lowering expenses.

Moreover, a novel HEA structure incorporating transition metals demonstrated excellent electrocatalytic performance for both the HER and the OER without requiring noble metals.<sup>55</sup> This finding was attributed to differences in electronegativity that drive local electron redistribution and may improve utilization of Cu active sites, affecting the adsorption energies of all adsorbates.

#### 4.2. HOR

In the HOR process, adsorbed H<sup>\*</sup> from H<sub>2</sub> dissociation is formed, and subsequent H<sup>\*</sup> combines with OH<sup>−</sup> to form H<sub>2</sub>O, with the hydroxyl binding energy and hydrogen binding energy (HBE) established as crucial descriptors.<sup>56</sup> Pt group metals are predominantly used for HOR catalysts, primarily due to their relatively strong HBE.<sup>57</sup> For example, PdNiRuIrRh HEA NPs, synthesized via a straightforward wet chemical method, achieved an ultrahigh mass activity (3.25 mA μg<sup>−1</sup>) for the HOR and exhibited performance superior to that of commercial Pt/C, Ir, Rh, Ru, and Pd by 8, 7, 12, 26, and 52

times, respectively. ML-based Monte Carlo simulation revealed that Pd–Pd–Ni/Pd–Pd–Pd and Ni/Ru active sites optimize H<sup>\*</sup> adsorption/desorption and improve HO<sup>\*</sup> adsorption, driving the exceptional HOR performance.<sup>33</sup>

#### 4.3. ORR

Pt-based catalysts have been shown to have better electrocatalytic activity in the ORR process, which involves the reduction and break down of intermediates such as O<sub>2</sub><sup>\*</sup> and the removal of HO<sup>\*</sup>, O<sup>\*</sup>, and H<sub>2</sub>O<sup>\*</sup>. Nanoporous HEAs such as AlCuNiPtMn demonstrate enhanced performance with high specific current densities and stability, outperforming commercial Pt/C materials.<sup>58</sup> PtPdFeCoNi HEA NPs exhibit significantly enhanced catalytic activity, surpassing that of Pt/C by 4.9 times, and demonstrate exceptional stability in the ORR, with durability extending 50 000 cycles.<sup>59</sup> These qualities are attributed to the synergistic effects of lattice distortion, sluggish diffusion, and the high-entropy effect of HEAs. Similarly, noble-metal-free CrMnFeCoNi electrocatalysts exhibit a remarkably high intrinsic activity, comparable to that of Pt under identical conditions, contrary to the expected behavior based on the properties of the constituent elements.<sup>60</sup>

#### 4.4. OER

The OER is characterized by its slow kinetics, involving a four-electron transfer process that necessitates two-step reactions that break and form O–H and O–O bonds.<sup>61,62</sup> One of the primary challenges in the OER is the substantial overpotential required, which greatly limits the rate of water decomposition. Alkaline OER catalysts frequently utilize transition metal-based oxides and hydroxides, while acidic OER catalysts often rely on binary or ternary alloys of noble-metal-free combined with Pt group metals such as Ru and Ir, which provide adsorption sites for HO<sup>\*</sup> and HOO<sup>\*</sup>.<sup>63</sup> The electron transfer from Fe, Co, and Ni (less electronegative elements) to Ir and Ru (more electronegative elements) enhances the activity of Ir in FeCoNiIrRu HEAs, thereby facilitating both the conversion of HOO<sup>\*</sup> intermediates and the production of O<sub>2</sub>.<sup>49</sup>

Meanwhile, inexpensive CoCuFeNiMnMo<sub>x</sub> HEAs demonstrate superior OER performance at slightly elevated Mo content.<sup>9</sup> Phase analysis reveals that mechanically alloyed powders without Mo exhibit a single fcc phase, whereas the addition of Mo introduces a combination of fcc and bcc phases. Electrochemical impedance spectroscopy (EIS) of electrodes shows that CoCuFeNiMnMo<sub>1.5</sub> has a reduced high-frequency resistance and charge transfer resistance, suggesting enhanced charge transfer efficiency and intermediate conversion capabilities at this Mo concentration.

#### 4.5. NRR

To enhance catalytic performance, the focus must be on improving the catalytic capability to adsorb and decompose  $N_2$  in NRR. Theoretical calculations highlight Fe, Mo, Ru, and Rh as promising catalysts for NRR, but their strong H adsorption causes HER side reactions, which can be mitigated by using transition metals like Zr, Ti, Y, and Sc.<sup>64</sup> RuFeCoNiCu HEA NPs achieve high  $NH_3$  yields at low overpotential at 0.05 V versus the reversible hydrogen electrode (RHE). DFT calculation identify Fe surrounded by other elements as the optimal site for  $N_2$  activation and adsorption, while Ni–Ru and Co–Cu pairs have outstanding surface hydrogenation capability at low overpotential.<sup>64</sup> The improved NRR activity and selectivity are attributed to the optimized electronic structures of the FeCoNiCuPd HEA NPs due to B doping. This optimization led to dual-phase B-doped HEAs exhibiting outstanding electrochemical NRR performance with a faradaic efficiency (FE) of 39.2% and a production of  $24.8 \mu\text{mol h}^{-1} \text{cm}^{-2}$  for  $NH_3$ .<sup>65</sup>

#### 4.6. CRR

The electrocatalytic CRR is a multistep process involving various products such as CO, HCOOH,  $CH_4$ ,  $CH_3OH$ , and  $C_2H_4$ .<sup>34</sup> The nature and quantity of products formed, as well as the necessity for extensive proton and electron transfer through multiple intermediates in multielectron reduction reactions, can be profoundly influenced by alloys featuring diverse compositions of metal elements. The multimetallic AuAgPtPd-Cu HEA catalyst demonstrates nearly 100% FE for converting  $CO_2$  into gaseous hydrocarbons at a low potential of  $-0.3$  V versus RHE, attributed to reversed adsorption trends of  $*OCH_3$  and  $*O$  intermediates on Cu (111) and HEA surfaces.<sup>66</sup> Noble-metal-free FeCoNiCuMn HEA NPs/ $TiO_2$  exhibit remarkable stability over 36 h, with significant photocatalytic CRR capabilities, producing  $CH_4$  and CO at rates of 19.9 and  $235.2 \mu\text{mol g}^{-1} \text{h}^{-1}$ , respectively, attaining a 23-fold increase over pristine  $TiO_2$ . The  $*COOH$  and  $*CH_3O$  species have been confirmed as significant intermediates for the synthesis of CO and  $CH_4$  using DFT and *in situ* Fourier transform infrared spectroscopy.<sup>67</sup>

#### 4.7. Batteries

HEAs have been shown to be promising cathode catalysts in battery systems, including Li–S, Zn–air, and Li– $CO_2$  batteries, demonstrating exceptional electrical performance due to their entropy-driven tunable geometric and electronic structures.<sup>10,68–74</sup> NiFeCoCuRu HEAs exhibit excellent stability in Li– $CO_2$  batteries by forming highly active clusters of Ru, Co, and Ni that enhance the adsorption of Li-based compounds, thereby improving the efficiency of both  $CO_2$  reduction and  $Li_2CO_3$  decomposition over extended periods.<sup>14</sup>

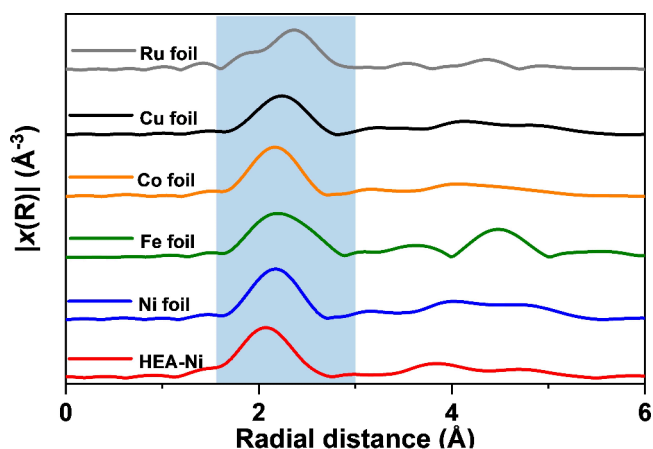
These studies underscore the versatility and promise of HEA NPs as catalysts for advancing clean energy technologies. In most cases, reactions still rely on precious metal-based HEAs; even with low contents of precious metals, they demonstrate impressive catalytic activity, surpassing pure noble metal catalysts in both performance and stability while offering a cost-effective alternative. Due to the irreplaceable nature of noble metals, approaches like core–shell NPs and surface decoration with single-atom HEAs have been reported.<sup>75,76</sup> A reduction in noble metal usage is achieved through surface decoration of noble-metal-free HEA NPs with Pd, which significantly enhances the ethanol oxidation reaction. Two-step high-temperature shock methods were employed, with Pd

atom diffusion controlled by a shorter duration and lower temperature during the second step. This resulted in a high activity and superior stability, surpassing those of commercial Pd/C, binary M@M-Pd (M = Sn, Co, Fe, and Ni), and conventional HEAs.<sup>75</sup> This approach combines increased exposure of active sites with high-entropy coordination to enhance activity and durability and decrease the cost.

### 5. CHALLENGES, OUTLOOK, AND CONCLUSIONS

Considerable advancements have been made in the field of HEAs, demonstrating excellent performance across various catalytic applications. However, to further their development, several challenges remain, particularly in the synthesis methodologies and characterization of HEAs with diverse elements and structures. A deep fundamental understanding of complex electronic interactions and phase and defect effects is essential. Currently, there is a lack of tunable synthesis methods for precise active site generation, which, if developed, would significantly impact the catalytic properties of HEAs and provide valuable feedback to computational models like DFT and ML (Figure 3). Experimental characterization techniques alone, such as XAS, are insufficient to fully characterize HEAs.

For example, Figure 6 illustrates XAS patterns for a multielemental HEA compared to the metallic forms of its



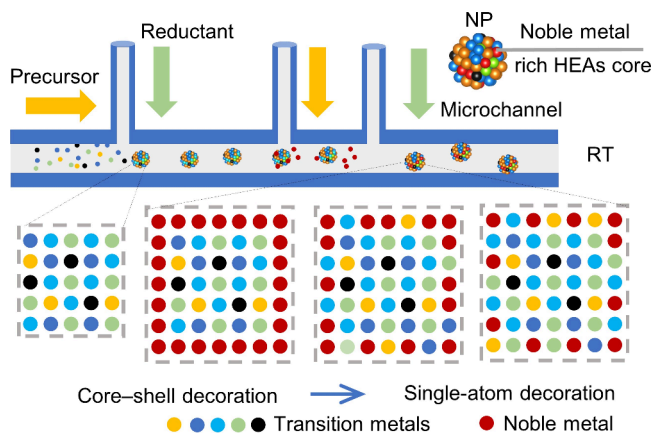
**Figure 6.** XAS comparison of Ni-HEAs to Ni, Fe, Cu, Co, and Ru shells in pure metals.

constituents (Fe, Co, Ni, Cu, and Ru). Single-phase HEAs were obtained via wet coreduction using sodium borohydride, followed by annealing at  $350$  °C under  $H_2/Ar$ .<sup>14,46</sup> The similarity in bond lengths among these materials makes it challenging to discern their individual contributions by using XAS alone. This underscores the necessity of integrating complementary techniques. Computational approaches, such as DFT and ML, can provide insights and understanding of high-performance HEAs that are not easily accessible through experiments alone.<sup>13</sup> The feedback loop between calculation and experiment has the potential to unlock the full potential of HEAs (Figure 3). These complexities, influenced by component composition, crystal structure, and specific applications, present a considerable multivariate challenge.

To facilitate the real-world use of synthesis and application technologies of HEAs, scalability, cost-effectiveness, and stability should be considered during the material design process and when considering their real-world application. Materials with abundant precursors are advantageous, as they

can be used on a large scale and significantly reduce costs. Current productivity levels of HEA materials in research, such as the CTS and wet chemical methods, are typically at the milligram level. Laser scanning ablation technology can reach gram-level production.<sup>11,12,77,78</sup> However, scaling these synthesis methods to industrial levels while maintaining a consistent structure remains a challenge that requires dedicated effort. Additionally, sustainable material production relies on energy-efficient synthesis techniques that minimize waste and have a low environmental impact. Incorporating these factors into the design and synthesis of HEAs materials will enhance the viability and widespread adoption of these synthesis technologies. Although the stability of HEAs is reported to be superior to that of pure noble metals, few studies have achieved stability over thousands of cycles, with most demonstrating only tens or hundreds of hours of stability.<sup>12,59,79</sup> Developing new HEA systems that can operate over extended periods remains a significant challenge.

Leveraging the advantages of wet chemistry methods, which offer low energy consumption and the synthesis of small NPs, it is imperative to further explore and optimize these methods to precisely control the morphology and crystal structure in terms of size, shape, phase, and surface defects. Given that precious metals are optimal for kinetics in most applications, we envision employing noble metal decoration strategies for the design of non-noble HEAs in catalysis by using wet chemistry approaches such as a continuous-flow reactor with microfluidic technology (Figure 7). The concurrent reduction



**Figure 7.** Decoration strategies to the design of HEAs in catalysis by microfluidic technology.

enables the creation of a homogeneous single-phase mixture and maximizes the utilization of precious metal active sites by ensuring their exposure on the surface. This strategy provides a cost-effective and straightforward method for scaling up the synthesis of HEA NPs.

In summary, this Perspective provides a brief overview of the current advancements in HEAs, highlighting their promising potential for effective catalysis. As research progresses, HEA catalysts are expected to play a crucial role in addressing challenges across various applications in energy conversion and storage fields.

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### Notes

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#### ■ NOTE ADDED AFTER ASAP PUBLICATION

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