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Topical Review

High-entropy oxides as energy materials: from complexity to rational design

Zhong Yang, Xianglin Xiang, Jian Yang and Zong-Yan Zhao*

Faculty of Materials Science and Engineering, Kunming University of Science and Technology, Kunming 650093, People's Republic of China

E-mail: zzy@kust.edu.cn

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Abstract

High-entropy oxides (HEOs), with their multi-principal-element compositional diversity, have emerged as promising candidates in the realm of energy materials. This review encapsulates the progress in harnessing HEOs for energy conversion and storage applications, encompassing solar cells, electrocatalysis, photocatalysis, lithium-ion batteries, and solid oxide fuel cells. The critical role of theoretical calculations and simulations is underscored, highlighting their contribution to elucidating material stability, deciphering structure-activity relationships, and enabling performance optimization. These computational tools have been instrumental in multi-scale modeling, high-throughput screening, and integrating artificial intelligence for material design. Despite their promise, challenges such as fabrication complexity, cost, and theoretical computational hurdles impede the broad application of HEOs. To address these, this review delineates future research perspectives. These include the innovation of cost-effective synthesis strategies, employment of *in situ* characterization for micro-chemical insights, exploration of unique physical phenomena to refine performance, and enhancement of computational models for precise structure-performance predictions. This review calls for interdisciplinary synergy, fostering a collaborative approach between materials science, chemistry, physics, and related disciplines. Collectively, these efforts are poised to propel HEOs towards commercial viability in the new energy technologies, heralding innovative solutions to pressing energy and environmental challenges.

Keywords: high entropy oxides, new energy materials, theoretical calculations, material design, electrochemical energy storage, photo(electro)catalysis

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* Author to whom any correspondence should be addressed.

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1. Introduction

The unsustainable exploitation of fossil fuels has precipitated a critical need for sustainable and renewable energy sources, driving the quest for innovative functional materials to propel new energy technologies. Photocatalytic, electrocatalytic, and photoelectrochemical processes, alongside lithium/sodium-ion batteries, have risen as pivotal for energy conversion and storage, with photocatalysis notably advancing hydrogen production and carbon dioxide reduction; electrocatalysis, integral to energy transformation, is extensively applied in reactions such as the oxygen evolution reaction (OER), enhancing energy conversion efficiency and reducing consumption [1, 2]. Disordered alloys and solid-solutions have garnered attention for their intrinsic catalytic activity and activation capabilities, attributed to their disordered structure and surface heterogeneity [3–5]. However, their stability under environmental temperature fluctuations remains a concern. High-entropy alloys (HEAs), inspired by disordered alloys, diverge from traditional alloy design by embracing chemical disorder, utilizing equimolar multi-principal-elements and aperiodic atomic occupation, thereby enhancing configurational entropy and stability [6]. The advent of 'Entropy Engineering' has invigorated the development of high-entropy materials (HEMs), offering new avenues for optimizing material performance across high tech fields such as energy, microelectronics, and information storage.

The development of HEMs, including high-entropy oxides (HEOs), represents a significant advancement in materials science, particularly for applications in energy conversion and storage [7]. The evolution from HEAs to HEOs and beyond has been driven by the desire to create materials with unique properties arising from their multi-component nature [8]. HEAs, which are alloys containing five or more elements in near-equal proportions, were the precursors to HEOs. They were initially developed to achieve superior properties such as enhanced strength and corrosion resistance due to the high configurational entropy that stabilizes the solid solution phase. Over time, the concept was extended to oxides, leading to the development of HEOs. HEOs are characterized by their complex, multi-component structure, which provides a wide range of tunable properties [9]. Compared to HEAs, HEOs offer a rich selection space in terms of composition and crystal structure types, allowing for more flexibility and adjustability in electronic structure, transitioning from single metal conductor materials to compounds, including conductors, semiconductors, and insulators. This makes HEOs particularly attractive for applications in the field of new energy due to their abundant active sites, adjustable specific surface area, stable crystal structure, and unique geometric compatibility. For instance, HEOs have been explored for their potential in OER electrocatalysis, as evidenced by recent studies.

The development of HEOs has been facilitated by advances in synthesis methods, such as sol–gel processes, flame spray synthesis, and other advanced techniques, enabling the production of HEOs with specific properties tailored for their intended applications. As the field progresses, researchers are focusing not only on the synthesis and characterization of HEOs but also on understanding the fundamental principles that govern their properties. Computational modeling and theoretical studies have been instrumental in predicting and explaining the behavior of HEOs, as well as in guiding the design of new materials with improved performance. Looking beyond HEOs, the concept of HEMs continues to evolve, with researchers exploring the potential of other HEMs, such as sulfides and nitrides, for various applications. The future of HEMs is likely to involve the development of new synthesis strategies, a deeper understanding of their properties, and the expansion of their use into a broader range of technologies, particularly in the fields of energy and catalysis. In summary, the transition from HEAs to HEOs and beyond not only reflects the deepening of scientific research and the diversification of materials but also reveals the surpassing and advantages of HEOs in multiple fields. With further understanding of the structure and properties of HEOs, it is expected that they will play a more critical role in future energy conversion and storage technologies. The ongoing research and development in this field promise to further expand the horizons of HEMs.

The complexity of HEOs, while a source of unique effects and performance advantages, presents challenges in composition design, synthesis, and mechanism exploration. Despite outlining the structure, synthesis, properties, and applications of HEOs, existing studies lack a systematic summary of design principles and innovative methods. This review aims to bridge this gap, reviewing the fundamental scientific principles of HEOs and the material design's core role in their advancement. It emphasizes the importance of theoretical calculations and simulations in guiding design and exploring the design space of HEOs, providing a deeper understanding of their structural characteristics and informing synthesis method selection. This review comprehensively overviews the atomic structure and characterization techniques of HEOs, discusses synthesis methods, and analyzes microstructural features, systematically summarizing design strategies and descriptors. It concludes with a perspective on the prospects of HEOs in energy applications, identifying future research directions, offering new insights for rational design, and fostering academic and technological innovation of HEOs.

2. Features and preparation of HEOs

2.1. General features

HEOs, a subclass of oxide materials and HEMs, are characterized by a principal-element that includes five or more equimolar metal cations [10–13]. This concept, which originated from HEAs, is noted for superior mechanical properties and corrosion resistance. Recent research advancements have applied this concept to oxides, leading to the development of innovative materials that exhibit core effects, such as high-entropy effects, lattice distortion, sluggish diffusion, and cocktail effects [14]. These characteristics confer on HEOs a broad potential for applications across various fields. Unlike HEAs, HEOs typically feature uniform anionic and cationic sublattices. Research by Rost *et al* suggests that HEOs may display a higher degree of cationic disorder compared to HEAs [8]. Ideally, the HEOs lattice exhibits long-range periodicity while maintaining compositional disorder and a uniform distribution, with lattice sites randomly occupied by constituent atoms. This configuration results in elevated configurational entropy, which aids in stabilizing a single-phase crystalline structure, thereby uncovering properties not found in conventional materials. This structural feature significantly influences their fundamental physicochemical properties and is closely linked to their performance in applications such as catalysis and electrochemical energy storage.

Configurational entropy is a critical concept in understanding HEOs and plays a pivotal role in their thermodynamic stability. It refers to the entropy contribution arising from the distribution of different species within a crystal lattice. In the context of HEOs, configurational entropy is maximized when the constituent elements are randomly and uniformly distributed across the available lattice sites, leading to a high number of microstates for the system. The configurational entropy S_c of a multi-component system can be calculated using the formula derived from statistical thermodynamics as the following equation (1):

$$S_c = k_{\mathrm{B}} \ln \Omega \tag{1}$$

where k_{B} is Boltzmann's constant, and Ω is the number of distinct configurations the system can have, which is directly related to the thermodynamic probability of the system. For an ideal mixture of N species with equal probabilities of occupying lattice sites, the configurational entropy can be expressed as the following equation (2):

$$S_c = -k_B \left[\left(\sum_{i=1}^{N} x_i \ln\left(x_i\right) \right)_{\text{cation}-\text{site}} + \left(\sum_{j=1}^{N} x_j \ln\left(x_j\right) \right)_{\text{anion}-\text{site}} \right] \tag{2}$$

where x_i and x_j is the mole fraction of the ith cation and jth anion species.

In HEMs, the configurational entropy is particularly significant because it contributes to the material's overall stability. At finite temperatures, the entropic contribution to the free energy can outweigh the enthalpic contributions, leading to the stabilization of phases that would not be stable based on enthalpy considerations alone. This is especially relevant in the case of HEOs, where the configurational entropy can drive the formation of solid solutions with unique properties. It is important to note that the configurational entropy is maximized when all species are present in equal amounts, as any deviation from this equimolar ratio reduces the number of possible configurations and thus the entropy. This principle is utilized in the design of HEOs to achieve high entropy and the associated benefits in terms of material properties. Therefore, configurational entropy is a key factor in the development and understanding of HEOs, providing a thermodynamic basis for the stabilization of complex, multi-component materials with unique and tunable properties.

HEOs have exhibited outstanding performance in various advanced energy technologies, including electrocatalysis, solid-state batteries, and supercapacitors [15, 16]. In electrocatalysis, HEOs function as efficient catalysts for both the oxygen reduction reaction (ORR) and the OER, benefiting from their multiple active sites and adjustable electronic structures. As electrode materials in solid-state batteries, they demonstrate high energy density and cycling stability, while their application in supercapacitors is marked by high power density and extended cycle life. In the realm of lithium-ion batteries (LIBs), HEOs are noted for their high lithium-ion conductivity and structural stability, making them promising candidates for future energy storage solutions [14]. Their role in water-splitting electrocatalysis is critical as well, where their multi-element active sites contribute to reduced overpotentials and enhanced catalytic efficiency [17]. Additionally, in solid oxide fuel cells (SOFCs), HEOs serve as electrode materials characterized by high ionic conductivity and electrochemical stability. The ongoing development of material synthesis and characterization techniques is likely to further highlight the pivotal role of HEOs in energy conversion and storage technologies.

Advanced imaging technologies such as aberration-corrected scanning transmission electron microscopy (STEM) allow researchers to observe and quantify sub-angstrom scale structural changes in HEOs, including local and lattice distortions [18]. These structural details are essential for understanding their physicochemical properties and performance in applications like catalysis and energy storage. The fundamental distinction between HEAs and HEOs lies in the microstructural composition, with HEOs incorporating anionic sublattices while preserving a uniform distribution of metallic cations. Future research may focus on achieving an equimolar high-entropy configuration in anionic sublattices, potentially enhancing the S_c value of HEOs. In figure 1, Rost *et al* demonstrated this fundamental distinction using random binary alloys and random pseudo-binary oxides [8]. The introduction of anionic sublattices in HEOs, in conjunction with the random distribution of metallic cations, can significantly augment the S_c value [14]. This feature permits a more intricate arrangement and a broader region of crystal structures in HEOs compared to HEAs.

HEAs are predominantly defined by metallic bonding, characterized by its non-directional nature, facilitating the random distribution of atoms within the lattice. Conversely, HEOs may display a variety of bonding types, such as ionic, covalent, and metallic, owing to the presence of both metallic cations and non-metallic anions. This multiplicity in bonding can result in a wider array of properties for HEOs, including ionic conductivity, which is not commonly observed in HEAs. The thermodynamic stability of HEAs is typically linked to the equilibrium between enthalpy and entropy, where a high S_c can counteract a positive enthalpy of mixing, thus stabilizing the solid solution phase. HEOs also depend on this equilibrium, but the presence of anionic sublattices introduces more complex interactions between enthalpy and entropy. For example, structural transitions in HEOs can entail substantial

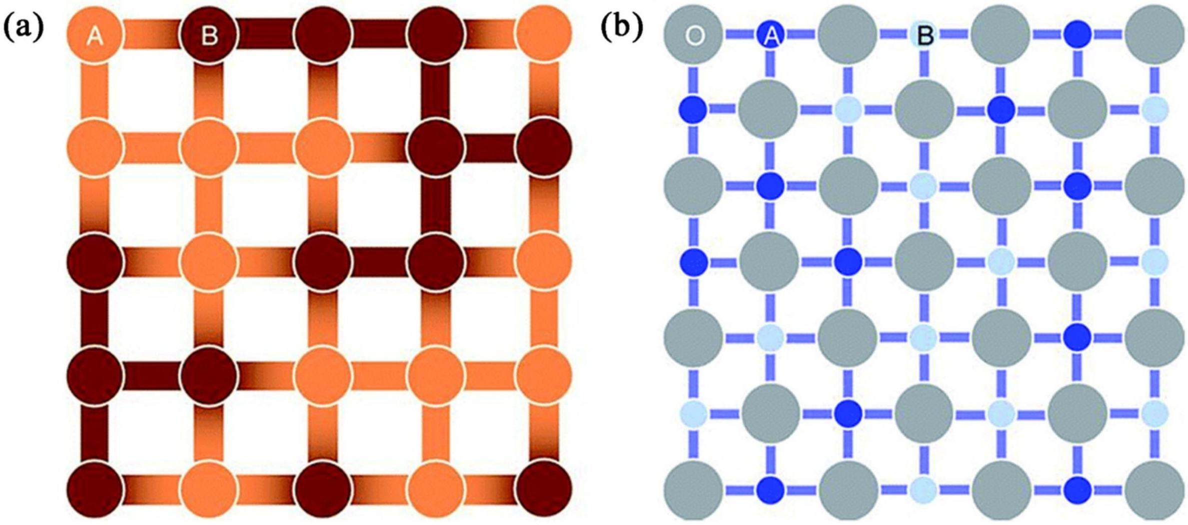

Figure 1. Schematic comparison of structural elements in (a) random binary alloys and (b) random pseudo-binary oxides. The illustration highlights the variance in electronegativity through the shading of atomic representations, with darker shades indicating higher electronegativity. Additionally, the localization of negative charge is emphasized by the darker bonds. In the pseudo-binary oxide scenario, the uniform anion sub-lattice is shown to consistently separate the nearest neighbor cations, providing a clear distinction in their spatial arrangement. Reproduced from [8]. CC BY 4.0.

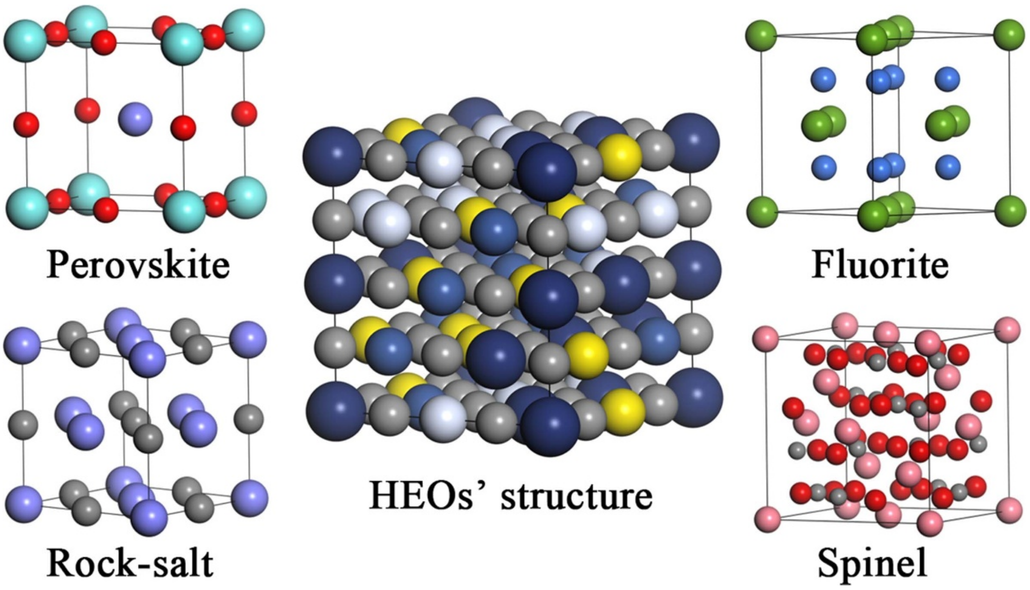

Figure 2. Structural variability in high-entropy oxides (HEOs): the central illustration depicts a supercell of a rock salt structured HEO, with anions represented as dark grey spheres and cations distributed in a stochastic pattern. The unit cells are derived from HEOs that have been successfully synthesized, showcasing the diversity in their structural configurations.

enthalpy changes, which are modulated by the S_c value. Thus, while HEAs and HEOs both capitalize on high S_c for stabilization, the presence of anionic sublattices and diverse bonding types in HEOs introduces additional complexity and variability. This not only promotes thermodynamic stability and the formation of a single-phase structure but also expands the potential properties and applications of HEOs beyond those of HEAs.

Figure 2 categorizes HEOs into various classes based on their crystal structures, including spinel, perovskite, fluorite, and rock-salt types. Each class exhibits distinct characteristics and advantages; for example, spinel and perovskite types have shown exceptional electrochemical performance as electrode materials in LIBs due to their structural flexibility and tenability [19, 20]. Conversely, fluorite and rock-salt types are valued for their potential in high-temperature applications, attributed to their high thermal stability and robust mechanical properties. The compositional and structural versatility of HEOs introduces significant opportunities for material design. By meticulously controlling the elemental composition and microstructure, the properties of HEOs can be finely tuned to fulfill the requirements of specific applications. For instance, a uniform anionic sub-lattice enhances both catalytic activity and stability [17]. Moreover, the principal-elements in HEOs allow for a wide range of crystal phases, exhibiting complex diversity including not only the common types mentioned but also lesser-known forms such as rutile [21], pyrochlore [22], and ferromanganese [23], along with novel structures like dual-phase [24], mixed crystalline-amorphous [25], and two-dimensional variants [26]. The reported diversity and complexity in crystal structures, summarized in table 1, underscore the need for a comprehensive understanding of these features to design high-performance HEOs customized for particular applications. This knowledge is essential for leveraging the full potential of HEOs in advanced technological applications.

HEOs are complex, multi-component systems characterized by intricate interactions among constituent elements during formation, profoundly influencing their properties. These interactions, along with the surrounding chemical environment, crystal structure, and oxidation state variations during transitions, contribute to distinctive physical phenomena and unique effects [61]. The unique effects observed in HEOs include high entropy, severe lattice distortion, slow diffusion, and synergistic cocktail effects. The high-entropy effect is crucial for stabilizing non-periodic structures, enhancing both thermodynamic and kinetic stability. This stability ensures that HEOs maintain structural integrity under extreme conditions, making them ideal for catalytic reactions subjected to high temperatures [8]. Lattice distortions within HEOs are known to influence the electronic structure, optimizing catalytic activity and affecting light absorption characteristics. For instance, these distortions stabilize the active sites in copper ions during CO oxidation, boosting catalytic efficiency [62]. In photocatalytic CO_2 reduction, the adjustable bandgap and enhanced light absorption properties facilitate effective photocatalysis [24]. Furthermore, the slow diffusion rate in HEOs preserves the composition and structure over extended periods, increasing the durability and stability of catalysts. This attribute is particularly valuable in high-temperature catalytic processes, where it prevents sintering and loss of active components [47, 63]. In SOFCs, slow diffusion in electrode materials contributes to prolonged structural integrity and extended battery life [36]. The cocktail effect, arising from the interactions among different metal elements, produces a synergistic impact that enhances overall material performance. This effect is notably beneficial in electrocatalytic reactions such as oxygen reduction and evolution reactions, where multiple elements contribute to a flexible electronic structure and a diverse array of active sites, thus improving the efficiency and stability of these reactions [36, 47]. These findings underline the broad application potential of HEOs in new energy technologies, presenting innovative material solutions for energy conversion and storage challenges. Continued advancements in material synthesis and characterization are expected to further elevate the role of HEOs in future energy applications.

2.2. Distribution and local environments of principal-elements in HEOs

HEOs are characterized by a random distribution of five or more principal-elements in equimolar proportions, forming a disordered solid-solution structure. This disorder enhances the configurational entropy of oxides and significantly improves their phase and thermodynamic stability. The high-entropy effect promotes complex interactions among elements, leading to phenomena such as lattice distortion and retarded atomic diffusion, which are beneficial for the catalytic and energy storage performances of HEOs. Enhanced compatibility among the principal-elements reduces the overall free energy, preventing phase separation and reinforcing phase stability [8, 10].

Advanced characterization techniques, such as energy dispersive x-ray spectroscopy (EDS) and x-ray photoelectron spectroscopy (XPS), are employed to analyze the distribution of principal elements at micro-regional levels or on surfaces [13]. Transmission electron microscopy in conjunction with high-angle annular dark field (HAADF) STEM and EDS mapping, reveals elemental distributions and chemical compositions at the nanoscale. These methods provide a deeper understanding of the microstructure of HEOs and their impact on performance. Research employing these techniques confirms that cations in HEOs are uniformly distributed within the lattice, showing no signs of local aggregation or segregation, thus indicating enhanced phase stability under high-entropy conditions [14, 15]. For example, as shown in figure 3, studies have demonstrated uniform mixing of elements in various HEO compositions, such as (CoFeNiCrMn)O and multi-element nanoparticles like (PtPdCoNiFeCuAuSn), synthesized using novel methods like carbothermal shock synthesis [64, 65]. Additionally, atom probe tomography (APT) studies on various structures of HEOs, such as rock-salt, brownmillerite, and perovskite, have confirmed the atomic-scale uniformity of elemental distribution, which is crucial for their stability and function in high-entropy environments [14].

Raman spectroscopy is an effective tool for analyzing the local microenvironments of metal oxides and can differentiate between intrinsic and extrinsic defects. The observed blue or red shifts in Raman bands correlate with lattice modifications induced by cation presence in the crystal structure, which also reflects the variation in M–O bond distances. As shown in figure 4, research by Sarkar *et al* on rare earth element doping in CeO_2 using Raman spectroscopy revealed that doping caused a redshift and broadening in Raman signals, indicative of lattice expansion and an increase in oxygen vacancies conducive to M–O bond formation [66]. The Raman spectroscopy analysis offers compelling insights into the microstructure of HEOs, with a notable redshift of approximately $15\ \text{cm}^{-1}$ observed in the F_{2g} vibrational mode for ME-REOs, suggesting significant lattice distortion. Moreover, the detection of a broad band at around $570\ \text{cm}^{-1}$ is attributed to oxygen vacancies, a critical factor in the material's properties.

Table 1. A concise overview of recent literature on high-entropy oxides (HEOs): this compilation summarizes the reported crystal structures, compositions, synthesis techniques, and emerging energy applications of HEOs, highlighting the advancements in the field over recent years.

Crystal phase	Composition	Synthesis method	Application	References
Perovskite	$(La_xK_{0.4-x}Ca_{0.2}Sr_{0.2}Ba_{0.2})\text{-}TiO_{3+\delta}$	Solid-state sintering	Optoelectronics	[27]
	$(La_{1/6}Pr_{1/6}Nd_{1/6}Gd_{1/6}Sr_{1/6}Ba_{1/6}Mn)O_3$	Solid-state sintering	Photocatalysis	[28]
	$BaSn_{0.16}Zr_{0.24}Ce_{0.35}Y_{0.1}Yb_{0.1}Dy_{0.05}O_{3-\delta}$	Sol–gel method	Solid oxide fuel cells	[29]
	$(La_{0.2}Nd_{0.2}Sm_{0.2}Ca_{0.2}Sr_{0.2})MnO_3$	Sol–gel method	Solid oxide fuel cells	[30]
	$(Na_{0.2}Bi_{0.2}Ba_{0.2}Sr_{0.2}Ca_{0.2})TiO_3$	Solid-state method	Solid-state refrigeration	[31]
	$(Bi_{0.2}Na_{0.2}K_{0.2}La_{0.2}Sr_{0.2})TiO_3$	Citrate acid method	Electrical energy storage	[32]
	$(Li_7La_3Al_{0.5}T_{i0.5}V_{0.5}Zr_{0.5})O_{12}$	SSR	Li-S battery	[33]
	$La_{0.7}Bi_{0.3}Mn_{0.4}Fe_{0.3}Cu_{0.3}O_3$	Sol–gel auto combustion method	Supercapacitor	[34]
	$La(Cu_{0.2}Cr_{0.2}Ni_{0.2}Fe_{0.2}Co_{0.2})O_3$	Multiple sol–gel annealing method	Solar cells	[35]
	$La(CrMnFeCo_2Ni)O_3$	Facile co-precipitation method	Electrocatalysis	[36]
	$La_{0.8}Sr_{0.2}(Cr_{0.2}Mn_{0.2}Fe_{0.2}Co_{0.2}Ni_{0.2})O_3$	Electrospinning and sintering process	Electrocatalysis	[37]
	$TiZrHfNbTaO_{11}$	High-pressure torsion method	Photocatalysis	[38]
	$(Mg_{0.2}Ti_{0.2}Zn_{0.2}Cu_{0.2}Fe_{0.2})O$	Solvothermal	Lithium-ion batteries	[39]
Spinel	$(FeCoNiCrMn)_3O_4$	Dealloying	Supercapacitors	[40]
	$(CoCrFeMnNi)_3O_4$	Reverse Coprecipitation	Electrocatalysis	[41]
	$(Fe_{0.35}Co_{0.33}Zn_{0.32})(Mn_{0.71}Fe_{0.90}Co_{0.03}Ni_{0.36})O_4$	Supercritical hydro-thermal process	Electrocatalysis	[42]
	$NiFeXO_4$ (X = Mo,Ni,Co,Fe,Al,Cr)	Eutectic dealloying process	Electrocatalysis	[43]
	$(Co_{0.2}Mn_{0.2}Ni_{0.2}Fe_{0.2}Zn_{0.2})Fe_2O_4$	High-energy ball milling	Electrocatalyst	[44]
	$(CoNiCuZnMg)Fe_2O_4$	Soft-templating and dip-coating	Photocatalyst	[45]
	$(Ni_{0.2}Co_{0.2}Mn_{0.2}Fe_{0.2}Ti_{0.2})_3O_4$	Simple solid-state sintering method	Lithium ion batteries	[46]
	$Mg_{0.2}Co_{0.2}Ni_{0.2}Cu_{0.2}Zn_{0.2}$	Sol–gel	CO oxidation	[47]
	$(Co_{0.2}C_{r0.2}Fe_{0.2}Mn_{0.2}Ni_{0.2})_3O_4$	Nebulized spray pyrolysis	/	[48]
	$(Cr_{0.6}Mn_{0.6}Fe_{0.6}Co_{0.6}Ni_{0.6})O_4$, $(Mn_{0.2}Fe_{0.2}Co_{0.2}Ni_{0.2}Cu_{0.2})Cr_2O_4$, $(Mn_{0.2}Fe_{0.2}Co_{0.2}Ni_{0.2}Cu_{0.2})Fe_2O_4$, $(Mn_{0.2}Co_{0.2}Ni_{0.2}Mg_{0.2}Zn_{0.2})Fe_2O_4$	Solid-state sintering	Supercapacitor	[49]
Rock-salt	$(CoNiMnZnFe)_3O_{3.2}$	Mechanical alloying	Electrocatalysis	[50]
	Li-(FeCoNiCuZn)O	Wet-soaking treatment	Electrocatalysis	[51]
	$(Mg_{0.2}Co_{0.2}Ni_{0.2}Cu_{0.2}Zn_{0.2})O$	Joule heating	Anode for Li batteries	[52]
	$Ce_{1-x}(TM)_xO_{2-y}$ (TM = Al, Fe, La, Mn, Nd, Pr, Sm, Y, and Zr)	Sol–gel method	CO oxidation	[53]
Fluorite	$Ce_{0.2}Zr_{0.2}La_{0.2}Pr_{0.2}Y_{0.2}O_2$	Aqueous sol–gel	Photocatalysis	[54]
	$(Eu_{0.2}Bi_{0.2}Y_{0.2}La_{0.2}Cr_{0.2})_2O_3$	Electrospinning	Dielectric materials	[55]
Face-centered -cubic	$(Mg_{0.2}Co_{0.2}Ni_{0.2}Cu_{0.2}Zn_{0.2})O$	Sol–gel combustion method	Photocatalysis	[56]
	$(NiCoMnCuZn)WO_4$	Electrospinning	Lithium–sulfur batteries	[57]
Coexisted crystalline and amorphous	$FeCoNiCrMnO_x$	Sol–gel method	Water splitting	[25]
Layered oxide	$Na_{0.83}Li_{0.1}Ni_{0.25}Co_{0.2}Mn_{0.15}Ti_{0.15}Sn_{0.15}O_{2-\delta}$	Solid-state sintering	Na-ion battery	[58]
	$Na_{0.67}(Mn_{0.45}Ni_{0.18}Co_{0.18}Ti_{0.1}Mg_{0.03}Al_{0.04}Fe_{0.02})O_2$	Solid-state chemistry		[59]
2D structure	$Cu_2Zn_1Al_{0.5}Ce_5Zr_{0.5}O_x$	PVP templated method	Photothermal-catalysis	[60]

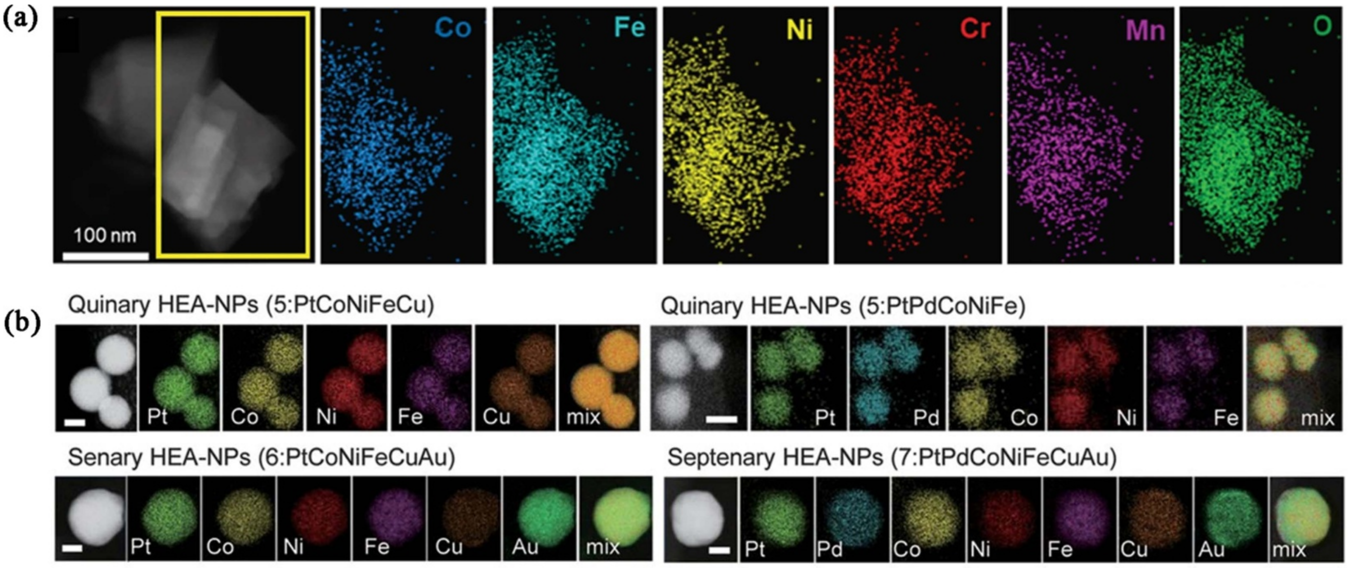

Figure 3. Elemental distribution in high-entropy alloy nanoparticles (HEA-NPs): (a) energy-dispersive x-ray spectroscopy mapping of Co, Fe, Ni, Cr, Mn, and O is depicted. Reproduced from [64]. CC BY 4.0. (b) Scanning transmission electron microscopy maps of high-angle annular dark field (HAADF) images and corresponding elemental maps are presented for quinary (PtFeCoNiCu and PtPdCoNiFe), senary (PtCoNiFeCuAu), and septenary (PtPdCoNiFeCuAu) compositions, with a scale bar of 10 nm. From [65]. Reprinted with permission from AAAS.

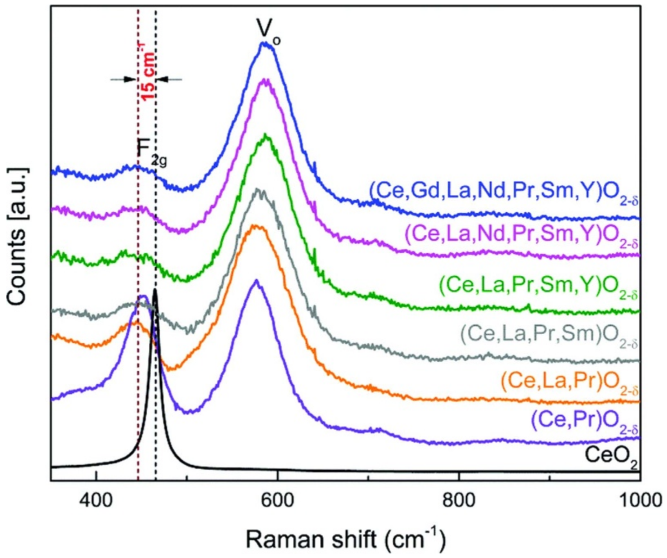

Figure 4. Comparative Raman spectroscopy of pure CeO_2 and mixed-element rare-earth oxides (ME-REOs). Utilizing a He–Ne laser with a wavelength of 633 nm, the Raman spectra are presented. The F_{2g} vibrational mode characteristic of ceria is observed at 465 cm^{-1}. In contrast, ME-REOs exhibit a redshift of approximately 15 cm^{-1}, indicative of structural modifications. Additionally, a broad band at around 570 cm^{-1} is detected in all ME-REOs, which is associated with the presence of oxygen vacancies (V_o) within the material's lattice. Reproduced from [66] with permission from the Royal Society of Chemistry.

These precise spectral observations not only validate the utility of Raman spectroscopy in probing the intricate microstructural details of HEOs but also underscore its indispensability in advancing the understanding of these complex materials. Extended x-ray absorption fine structure (EXAFS) has also been applied to investigate the local structure of high-entropy spinel (MgNiCoZn)O. The EXAFS analysis indicated uniform oscillations of all constituent elements in reciprocal space, suggesting homogeneity in their local structures and chemical environments [8].

HEOs feature a random distribution of metal elements leading to lattice distortion and slowed element diffusion, properties that confer unique physicochemical attributes on the material. In new energy materials, the distribution of principal-elements in HEOs offers a plethora of active sites for catalysis, enhancing the adsorption and activation of reactants via adjustments in lattice distortion and electronic structure. For example, in lithium–sulfur batteries, HEOs act as sulfur hosts, stabilizing sulfur species and promoting sulfur conversion reactions, thus improving the electrochemical performance. In LIBs, the even distribution of metal ions in electrode materials boosts electrical conductivity and structural stability, enhancing cycle stability and energy density. In SOFCs and electrocatalysis, the uniform distribution of elements within HEOs is crucial for maintaining performance and durability at high temperatures, and significantly affects catalytic activity and selectivity, respectively. This distribution is pivotal in diversifying reaction pathways and enhancing selectivity [15, 67].

The definition of high entropy in HEOs necessitates a uniform distribution of principal-elements, which must balance order and disorder within their local environments. This balance underscores the unique properties of HEOs and presents challenges for their characterization in experimental analyses. Advanced atomic-level characterization techniques, such as three-dimensional atom probe tomography (3D-APT) and four-dimensional electron energy loss spectroscopy (4D-EELS), are well-suited to address these requirements. However, these methods are complex and expensive. To overcome these challenges, it is essential to develop more accessible and cost-effective characterization techniques. Simultaneously, integrating electronic and atomic-level theoretical calculations is crucial for achieving ultra-high spatiotemporal resolution in studying the distribution and local environments of principal elements in HEOs. Such integrative approaches will enhance our understanding of the physicochemical behaviors of HEOs in real-world material contexts and elucidate the physical origins of their unique properties.

2.3. Preparation, synthesis, and processing

The preparation of HEOs is crucial for realizing their unique properties and effects, and it requires adherence to several fundamental criteria. First, the fabrication method must ensure the homogeneous integration of five or more cations within a single phase to maintain the material's single-phase structure [14]. Furthermore, it is essential to prevent the aggregation of elements and phase separation to preserve the high-entropy characteristics of HEOs [68]. Additionally, the process should meticulously control the microstructure, including grain size, phase purity, and defect density of products. The technique must also be scalable to meet industrial production demands [69]. Preparation methods for HEOs are generally divided into top-down and bottom-up approaches. Top-down methods, such as mechanical alloying and chemical vapor deposition (CVD), start with bulk materials and reduce them to nanoscale structures through physical or chemical processes [70]. In contrast, bottom-up strategies like sol–gel and co-precipitation begin at the atomic or molecular level, offering enhanced control over microstructure and chemical composition [71]. Recent advancements in HEO fabrication techniques have led to significant improvements. For instance, HEOs with high ionic conductivity have been synthesized at reduced temperatures by optimizing synthesis conditions [72]. Additionally, mechanical alloying followed by heat treatment has been effective in producing HEOs with enhanced electrochemical properties [16]. These techniques are broadly categorized based on the phase state of the reactants into solid-state, liquid-phase, and vapor-phase methods. The advantages and disadvantages of common synthesis methods for HEOs are summarized and compared in table 2.

Solid-state methods, such as mechanical alloying and high-temperature sintering, are traditional fabrication techniques that require high temperatures and extended processing times to achieve elemental mixing and phase stabilization. High-temperature solid-state reaction methods are conventional for synthesizing HEOs. In these methods, equimolar ratios of metal oxides are mechanically milled to ensure uniform mixing, followed by pressing and sintering in air to obtain a stable high-entropy solid solution structure [73]. For instance, Rost *et al* successfully synthesized bulk materials of $(Co_{0.2}Cu_{0.2}Mg_{0.2}Ni_{0.2}Zn_{0.2})O$ with a single rock-salt structure using CoO, CuO, MgO, NiO, and ZnO as raw materials through high-temperature solid-state reactions [8]. Building on this foundation, Rost demonstrated the reversible transition between low-temperature multiphase and high-temperature single-phase by altering the content of the penta-elemental composition, confirming that HEOs are entropy-driven. As depicted in figure 5, Wu *et al* introduced a Joule heating method using nickel foils to overcome the prolonged heating times associated with conventional muffle furnaces [74]. This method enables the rapid synthesis of HEOs, achieving decomposition and formation within tens of seconds. It has been successfully applied to synthesize high-entropy rock-salt oxides (MgFeCoNiZn)O, high-entropy perovskite oxides, and spinel oxides. This approach leverages the rapid increase in temperature and entropy over a brief period to mitigate the effects caused by phase transformations in the spinel phase. For HEOs with special crystal structures, such as pyrochlore-type HEOs, achieving the desired density often requires several hours of high-temperature processing. Therefore, more efficient preparation processes are needed. Mao *et al* reported an ultrafast oxide densification method, known as reactive flash sintering, and successfully prepared pyrochlore-type $(La_{0.2}Nd_{0.2}Sm_{0.2}Eu_{0.2}Gd_{0.2})_2Zr_2O_7$ at 1200 °C in just a few seconds [75]. This method achieved a product density of 99% of the traditional solid-state method, which requires 1600 °C for 6 h. Lin *et al* have successfully synthesized four novel rock-salt structured HEOs at ambient temperature through a simple mechanochemical reaction: $(Zn_{0.2}Ni_{0.2}Co_{0.2}Mn_{0.2}Fe_{0.2})O$, $(Zn_{0.17}Ni_{0.17}Co_{0.17}Mn_{0.17}Fe_{0.17}Cu_{0.17})O$ and $(Zn_{0.14}Ni_{0.14}Co_{0.14}Mn_{0.14}Fe_{0.14}Cu_{0.14}Mg_{0.14})O$ [76]. The high-energy planetary ball-milling process was employed to handle air-sensitive and thermally unstable ions present in the raw

Table 2. A brief table of the advantages and disadvantages of common synthesis methods for HEOs.

Synthesis method	Advantages	Disadvantages
Solid-state reaction method	Low cost High productivity Simple preparation process Widely used for bulk materials	High energy consumption Low efficiency Easy to mix impurities
Flame/nebulized spray pyrolysis	High purity Good uniformity Simple operation	High energy consumption Produce harmful gases
Co-precipitation Hydrothermal synthesis	High purity, Good uniformity Simple operation and No harmful gas	pH value changes frequently Environment of each metal particle Constantly changes
Solution combustion synthesis	Energy saved, Multiple particle sizes Simple operation	Toxic gas remaining
Sol–gel method	Low synthesis temperature Tempered condition Special morphology	Complicated preparation process Highly costed

materials, such as Fe^{2+} and Mn^{2+}, while simultaneously incorporating Li^{+}. This straightforward synthesis method, utilizing readily available binary oxide precursors, opens up possibilities for the creation of a wide array of innovative HEOs and oxyfluoride compounds.

Liquid-phase methods, such as sol–gel, co-precipitation, and hydrothermal/solvothermal processes, facilitate the synthesis of HEOs at lower temperatures and promote the uniform distribution of components. In the sol–gel method, metal alkoxides or metal organic salts are used as precursors to form a homogeneous sol in a solvent, followed by gelation to create a three-dimensional gel network. The final oxide material is obtained after drying and heat treatment, typically producing materials with high specific surface areas and excellent thermal stability [47]. Miao *et al* successfully synthesized hollow-structured HEA oxides with enhanced OER activity and stability by combining metal–organic framework templates with an ion-exchange strategy [77]. Co-precipitation involves the simultaneous precipitation of various metal ions in a solution to form a uniform precursor, followed by heat treatment to produce HEOs. This method is noted for its simplicity, low cost, and ability to achieve uniform component distribution [36]. Hydrothermal/solvothermal methods leverage high temperature and pressure conditions to synthesize high-quality nanomaterials within a relatively short time. Mints *et al* employed a machine learning model, trained on experimental data from 350 different nanoparticles, to simulate the OER performance of an AuIrOsPdPtReRhRu composition [78]. They identified the optimal catalyst as a mixture of AuIrOsPdRu and used microwave-assisted solvothermal synthesis to prepare 350 HEO nanoparticles of varying compositions.

Vapor-phase methods, including spray pyrolysis, CVD, magnetron sputtering, pulsed laser deposition (PLD), and atomic layer deposition, facilitate precise atomic-scale control during the fabrication of HEOs thin films and nanostructures. These techniques are celebrated for their rapid reaction rates and high product purity, enabling exact manipulation of thin films and nanostructures—critical for developing high-performance HEO materials [79]. Brandt *et al* synthesized Co- and Cr-free spinel-type HEOs using spray pyrolysis, positioning these as next-generation anode materials [80]. Salian and Mandal pioneered the use of PLD to create various HEO films, examining the effects of processing parameters on film structure and stability [81]. Similarly, Kotsonis *et al* employed PLD to produce $(MgNiCoCuZnSc)_{0.167}O$ thin films on various substrates, assessing phase stabilization impacts [82]. Kirnbauer *et al* generated single-phase crystalline $(AlCrNbTaTi)O_2$ thin films on silicon and sapphire substrates via reactive pulsed direct current magnetron sputtering [83]. Zhou *et al* developed rare earth zirconate HEOs with double ceramic layer thermal barrier coatings using atmospheric plasma spraying, focusing on their thermal stability [84].

The techniques used in HEOs preparation significantly influence their performance, with uniform principal-element distribution and single-phase structures essential for optimal properties. Fine-tuning synthesis parameters allows for the regulation of grain size and morphology, optimizing electrochemical activity and stability. The heat treatment is vital for stabilizing phases with high-entropy characteristics. For example, while HEOs produced via solid-state methods generally show enhanced mechanical properties and thermal stability, they may suffer from grain coarsening issues. Conversely,

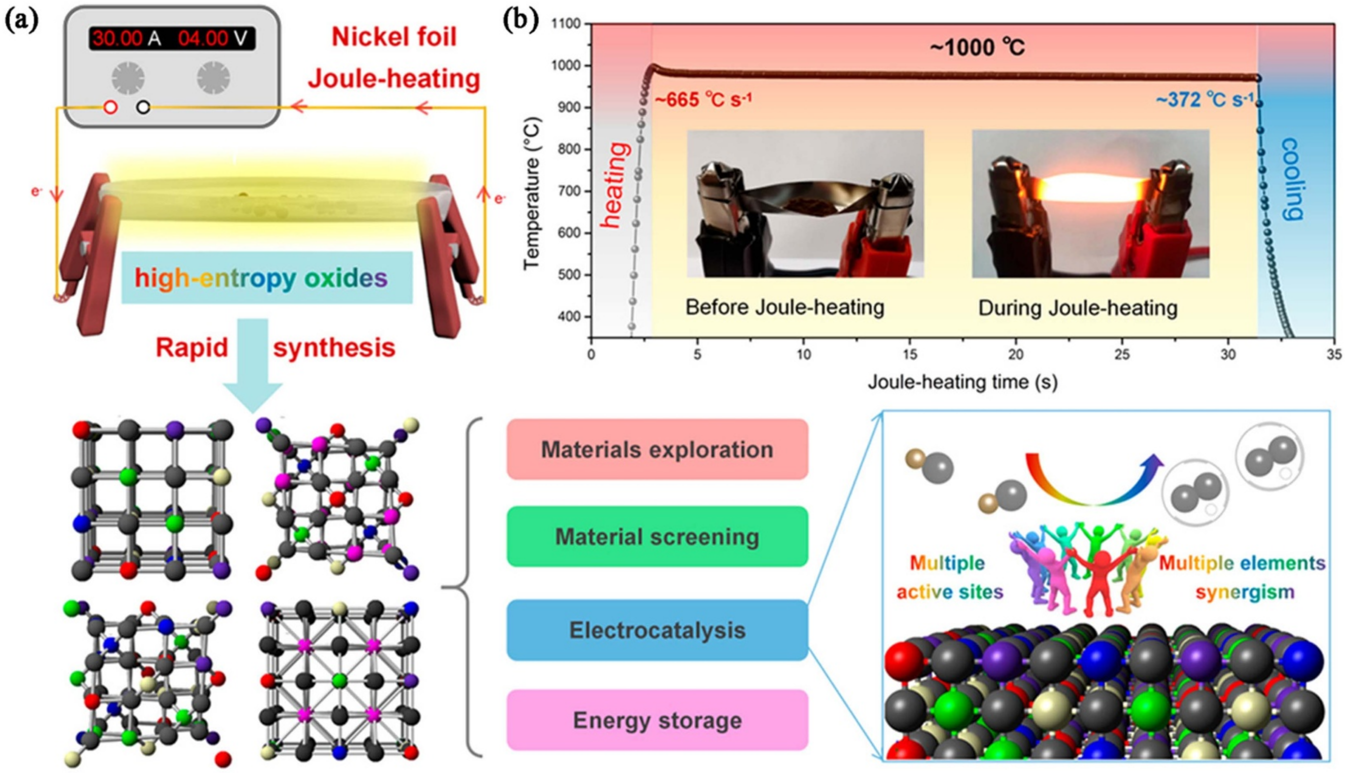

Figure 5. Schematic illustrations for the fabrication and catalytic mechanism of high-entropy oxides (HEOs). (a) The process of synthesizing HEOs with diverse structural systems is depicted through the Joule heating of nickel foil, a technique applicable for various studies and catalytic applications. In this representation, gray spheres symbolize oxygen atoms, while spheres of distinct colors denote different metal elements. (b) The temperature profile of the nickel foil during Joule heating is charted, with an inset image illustrating the Joule-heating process. Additionally, a schematic is provided to elucidate the presence of multiple active sites and the synergistic catalysis effect on HEOs, highlighting the material's potential in catalytic applications. Reprinted with permission from [74]. Copyright (2022) American Chemical Society.

liquid-phase and vapor-phase methods tend to yield HEOs with higher specific surface areas and catalytic activity. Additionally, variables like temperature, pressure, and atmospheric conditions during fabrication can affect the microstructure and performance of these materials [85]. As the field evolves with emerging fabrication techniques, further research is required to understand the mechanisms underlying these processes to precisely control the structure and properties of HEOs.

3. Applications of HEOs as energy materials

HEOs are primarily composed of transition metals arranged in a disordered and uniformly distributed fashion, distinguishing them from conventional transition metal oxides doped with impurities. This unique chemical composition and structure confer various performance advantages, enhancing physical properties and introducing new phenomena, with significant implications for the energy materials sector. The benefits of HEOs primarily arise from their high configurational entropy, which supports the formation of a single-phase solid solution, thereby enhancing the material's stability and thermodynamic characteristics. Due to the expansive scope of the HEOs and the variability in elemental compositions, HEOs with diverse structures exhibit unique performance features. This versatility makes HEOs highly applicable across various new energy technologies, including catalysis, energy conversion, energy storage, and sensing. For instance, in catalysis, the abundance of active sites and the tunable electronic structure of HEOs have shown exceptional activity and stability in reactions such as the ORR and the OER. Furthermore, HEOs have demonstrated considerable potential in energy conversion and storage applications, such as in solar cells, fuel cells, and LIBs. Their high electrical conductivity, chemical stability, and optimized energy conversion efficiency open new avenues for improving the performance of energy devices. To provide a clearer overview of the diverse applications of HEOs in the field of new energy, we have compiled recent literature on the crystal structure, composition, synthesis methods, and applications of HEOs into table 1. This table highlights the complexity of HEOs in these aspects, underscoring the significant challenges they present in experimental research work. This summary aims to facilitate a deeper understanding of multifunctional applications and the ongoing developments of HEOs.

The potential of HEOs as energy materials is not only anchored in their fundamental physicochemical properties but

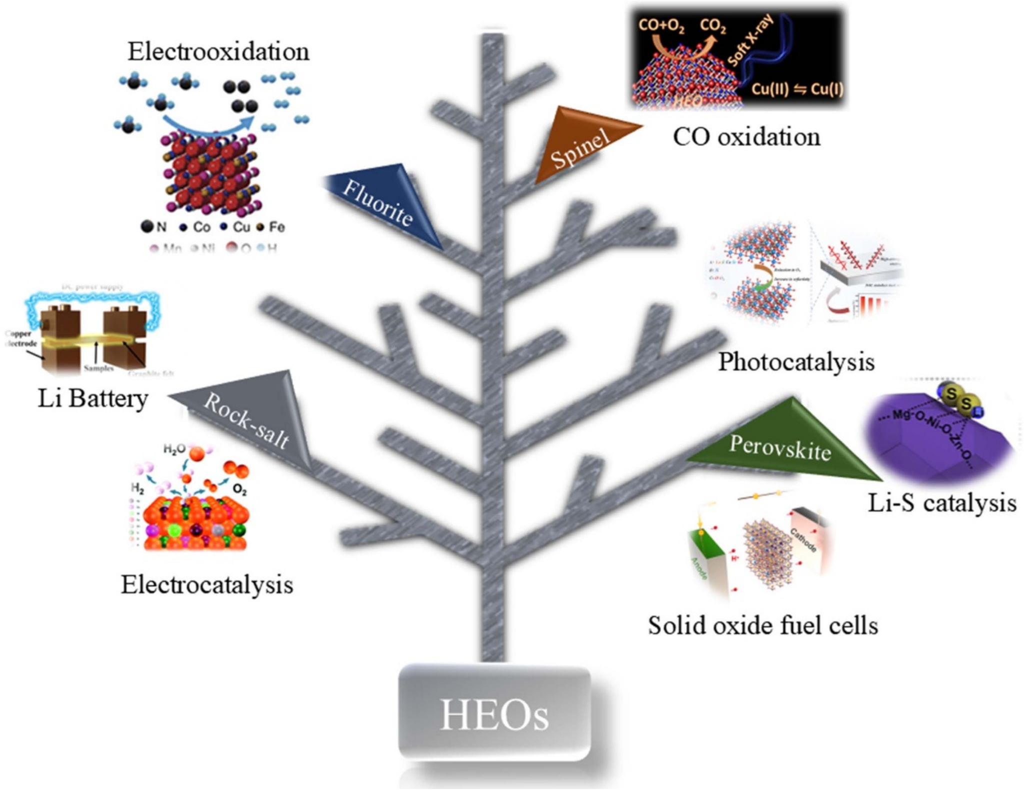

Figure 6. Functional tree of high entropy oxides (HEOs) in the field of new energy technology. Different crystal structures have different primary application performances, but they can still intersect and cross boundaries with each other. This feature is also one of their unique advantages over HEAs.

also in performance enhancements facilitated by advanced material design and engineering. Through precise control of synthesis conditions and post-treatment techniques, the microstructure of HEOs can be finely tailored to optimize their functionality for targeted applications. Modifications such as grain size, morphology, and compositional adjustments are critical for enhancing electrochemical activity and cyclic stability, which are crucial for developing robust energy storage solutions. As research on HEOs advances, their application scope within the energy materials sector is expected to expand significantly. Future studies will likely explore innovative synthesis methods, material designs, and performance optimization strategies, aiming to harness HEOs' full potential in energy conversion and storage. Additionally, a deeper understanding of HEOs will enhance their utility in addressing critical energy and environmental challenges, underscoring their importance in sustainable technology development. This ongoing research promises to further elucidate the versatile applications of HEOs, paving the way for their increased integration into advanced energy systems. To visually elucidate the diverse performances of HEOs across various domains, figure 6 categorizes HEOs into four predominant branches. A diagrammatic representation, analogous to the branching structure of a tree, is employed to outline the distinct applications associated with different crystal structures, which facilitates a clear and logical understanding of the material's multifaceted utility.

3.1. Solar cells

HEOs demonstrate unique advantages in solar cell applications, including tunable electronic structures, superior photoelectric conversion efficiencies, exceptional durability, and stability under extreme conditions. Their robust mechanical properties and high-temperature resistance underscore their potential in advancing photovoltaic technology.

Kumbhakar *et al* utilized high-throughput computation to screen a series of rare earth HEOs and highlighted the significant impact of synthesis atmosphere on the bandgap of these materials. The reversible modulation of the bandgap, ranging from 2.0 to 3.5 eV, can be achieved for multivalent rare earth cations such as Ce, Pr, Tb, when subjected to calcination under oxidizing and reducing atmospheres. This feature provides flexibility for the light absorption and electronic structure regulation of HEOs in solar cells [86]. As shown in figure 7, Zhang *et al* prepared transparent p–n junction $CuAlO_2/WO_3$ solar cells with self-cleaning functions using a multi-step sol–gel annealing process and introduced a high-entropy perovskite oxide $La(Cu_{0.2}Cr_{0.2}Ni_{0.2}Fe_{0.2}Co_{0.2})O_3$ as a buffer layer. This structure not only achieved a high transmittance of 85%–90% but also realized a remarkable enhancement of approximately 6.2×10^3 times in photoelectric conversion efficiency, reaching about 1.19% [35]. The incorporation of HEOs optimized the carrier dynamics balance, adjusted the Fermi level, improved the quantum yield, and facilitated

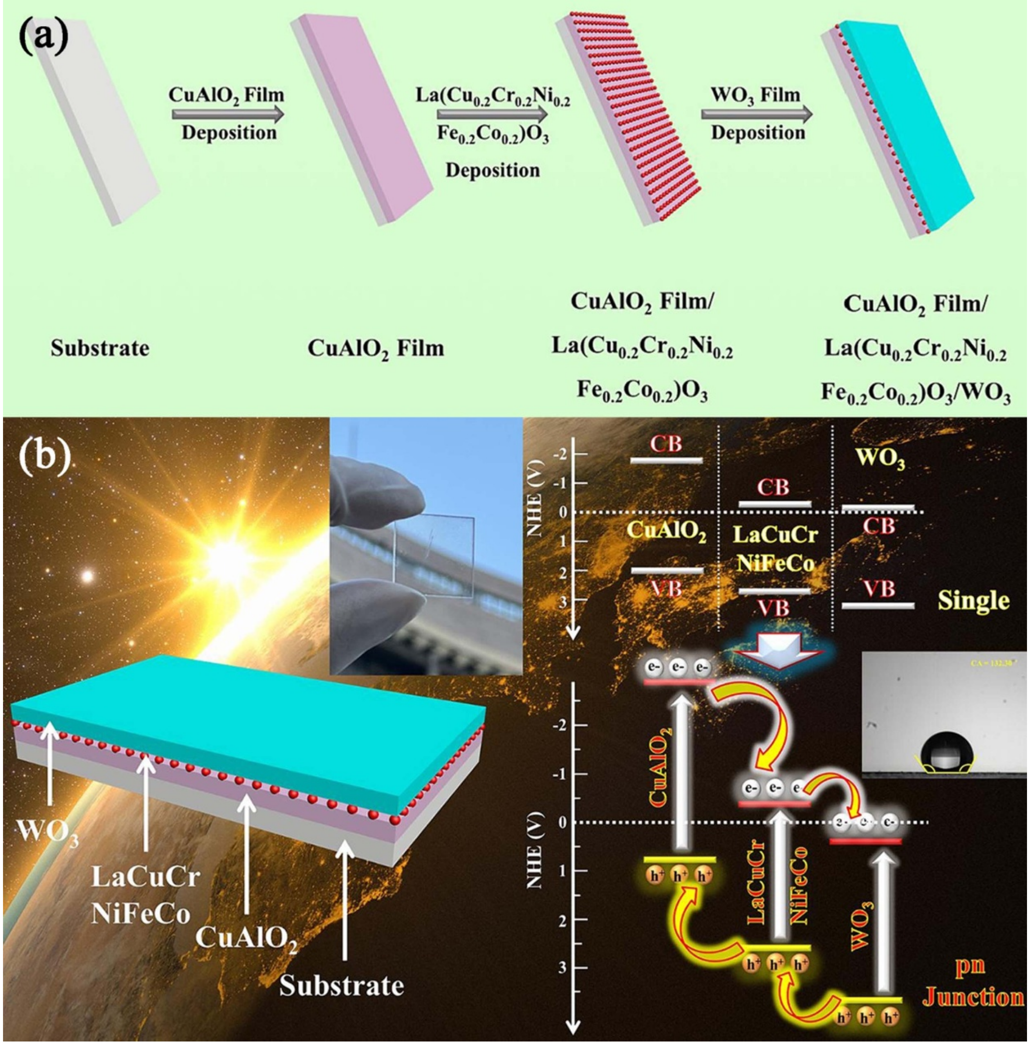

Figure 7. Enhanced transparency in photovoltaic p–n junctions through high-entropy perovskite oxide modification. (a) The process for creating a transparent p–n junction in the $CuAlO_2/WO_3$ system is illustrated, utilizing a high-entropy perovskite oxide transition layer, $La(Cu_{0.2}Cr_{0.2}Ni_{0.2}Fe_{0.2}Co_{0.2})O_3$, to achieve improved optical properties. (b) A demonstration of the prepared mechanism for the transparent photovoltaic p–n junction is presented, showcasing the integration of the high-entropy perovskite oxide layer and its role in enhancing the junction's performance. Reprinted from [35], © 2024 Elsevier B.V. All rights reserved.

the injection and transport of additional charge carriers, achieving dual optimization of transparency and photovoltaic conversion efficiency.

The potential of HEOs extends beyond improving photoelectric conversion efficiency; they also enhance the stability and durability of solar cells. The high-entropy effect leads to lattice distortion and slow atomic diffusion, contributing to improved thermal stability and anti-aging performance, which are vital for long-term operational reliability. Furthermore, the compositional diversity and structural tunability of HEOs provide a wide spectrum for designing novel solar cell materials. By precisely controlling synthesis parameters and post-treatment techniques, the optoelectronic properties of HEOs can be further refined to suit various solar cell technologies. Ongoing research should focus on developing innovative synthesis strategies, exploring the mechanisms behind optoelectronic property regulation, and effectively implementing HEOs in solar cell applications. This approach will help to maximize their utility and contribute to the evolution of photovoltaic technologies.

3.2. *Electrocatalysis*

In recent advancements, the application of HEMs in electrocatalysis has been significantly demonstrated. Yang *et al* present a high-entropy aqueous electrolyte that enables stable zinc–air battery operation from −60 °C to 80 °C, with remarkable retention of room-temperature power density even at extreme lows [87]. Hu *et al* innovate with a selenium-mediated synthesis approach for constructing multilayered multicomponent nanocrystals. These nanocrystals, when employed as catalysts in alkaline polymer electrolyte fuel cells, deliver exceptional power densities and enduring stability [88]. HEOs have also emerged as a prominent class of materials in electrocatalysis, noted for their exceptional catalytic activity, stability, and durability. These attributes stem from the high-entropy nature of these materials and the synergistic effects among their constituent elements. Specifically, in crucial electrochemical processes such as the hydrogen evolution reaction, OER, and ORR, HEOs have shown outstanding catalytic performance.

The OER is known for its slow kinetics, yet the integration of HEOs has been effective in creating multiple active sites, substantially improving OER activity. The synergistic action of primary metal components such as Fe, Co, Ni—along with additional elements like Cu, Mn, Nb, Cr, La—presents new methods for enhancing OER performance. Notably, Co^{3+} sites have been effective in reducing the OER overpotential [89]. The valence state oscillations between $Mn^{3.5+}$ and $Mn^{3.7+}$ are also crucial for achieving minimal OER overpotentials. Furthermore, an increased number of oxygen vacancies enhance adsorbate adsorption capacity, thus reducing the overpotential [90]. Nguyen *et al* developed a perovskite-type HEO, $La(CrMnFeCo_2Ni)O_3$, which, with a high ratio of Co^{3+}/Co^{2+}, achieved an OER overpotential of just 325 mV at a current density of 10 mA cm^{-2}, demonstrating exceptional long-term electrochemical stability [36]. They also discovered that an increased cobalt content significantly enhanced OER activity. The morphological design of HEOs plays a critical role in optimizing electrocatalytic performance. Porous nanostructures, which offer a large specific surface area, are now a research focus, providing more active sites and thereby enhancing OER activity. As illustrated in figure 8, the porous spinel nanowires $NiFeXO_4$ (X = Mo, Ni, Co, Fe, Al, Cr) designed by Zhang *et al* displayed remarkable performance in water splitting technology, achieving a low overpotential of 195 mV at a current density of 10 mA cm^{-2} and maintaining stable catalysis over 115 h [43]. This enhancement is attributed to both the porous structure and increased intrinsic activity, as well as enhanced covalency resulting from multivalent cation substitution and interactions between metal 3d and oxygen 2p orbitals.

Entropy engineering fabrication methods for HEOs, as demonstrated by Zhang *et al*, have produced spinel-type $(Co_{0.2}Mn_{0.2}Ni_{0.2}Fe_{0.2}Zn_{0.2})Fe_2O_4$ with notable OER catalytic performance. This material exhibited an overpotential of 326 mV and a Tafel slope of 53.6 mV Dec^{-1} in 1M KOH solution, along with exceptional stability in long-term OER activity tests [44]. The lattice distortion introduced a significant number of high-density oxygen vacancies, increasing the electrochemically active surface area and substantially enhancing OER catalytic efficiency. Increased structural entropy suppressed the rapid degradation of the catalytic surface structure, reducing the loss of oxygen vacancies and maintaining the catalyst's excellent stability. As illustrated in figure 9, the perovskite-type $La_{0.8}Sr_{0.2}(Cr_{0.2}Mn_{0.2}Fe_{0.2}Co_{0.2}Ni_{0.2})O_3$ (HE-LSMO) nanofibers, prepared by Tian *et al* through an electrospinning calcination method, effectively modulated the binding strength of soluble polysulfides due to their unique porous fiber structure and the introduction of various metal elements [37]. As a bifunctional electrocatalyst, HE-LSMO nanofibers demonstrated a high areal capacity of 6.6 mA·h·cm^{-2} and good cyclic stability in the S/HE-LSMO cathode with a sulfur loading of 8.4 mg cm^{-2}. The chemically disordered multication structure of HEOs endows them with excellent electrochemical performance, with the synergistic action among cations being a key factor for their superior performance [91].

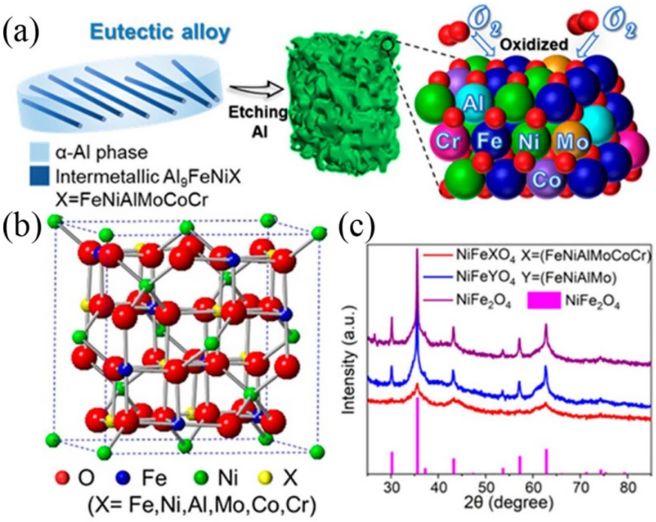

Figure 8. Characterization of porous spinel $NiFeXO_4$ nanowires. (a) The synthesis process of porous spinel $NiFeXO_4$ nanowires is depicted, highlighting the methodological approach for creating these nanostructures. (b) A crystallographic model of the spinel $NiFeXO_4$ structure is presented, illustrating the arrangement of its constituent atoms. (c) XRD patterns of the as-prepared porous nanowires are shown, providing insights into their crystalline nature and phase purity. Reprinted with permission from [43]. Copyright (2023) American Chemical Society.

The application of HEOs in electrocatalysis has demonstrated substantial potential and varied advantages. Owing to the high-entropy effect and synergistic interactions among multiple elements, HEOs not only enhance catalytic activity and stability but also optimize the kinetics of electrocatalytic reactions. This optimization is achieved by modulating electronic structures and increasing the number of active sites. In critical electrochemical processes like the OER and ORR, HEOs significantly reduce the overpotential of these reactions through the formation of abundant oxygen vacancies and regulation of the valence states of metal ions, thus boosting overall catalytic efficiency. Furthermore, the morphological design of HEOs, particularly through the creation of porous nanostructures, has improved their electrocatalytic performance by providing more active contact sites, enhancing the material's intrinsic activity, and increasing the specific surface area. In practical terms, the synthesis strategies, structural regulation, and performance optimization of HEOs are currently prominent areas of research. Researchers have developed various HEOs materials with excellent electrocatalytic properties through entropy engineering and innovative morphological designs. These materials have demonstrated exceptional capabilities in accelerating electrochemical reaction rates, improving energy conversion efficiency, and enhancing

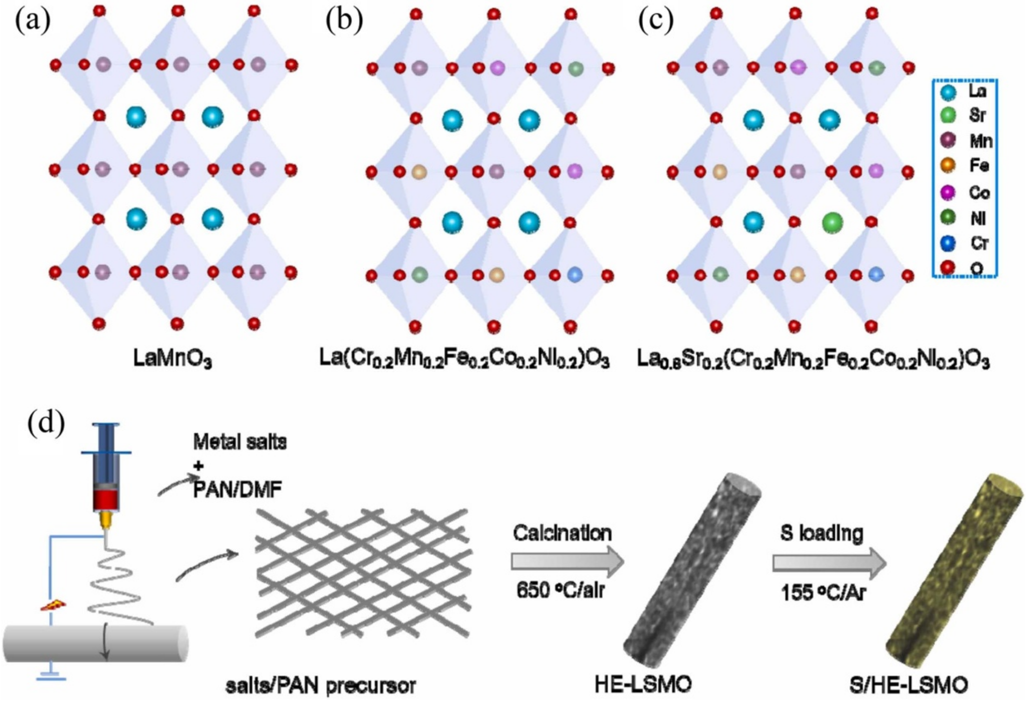

Figure 9. Comprehensive overview of high-entropy perovskite oxides and their nanofiber derivatives. (a)–(c) Schematic representations elucidate the high-entropy design principles and atomic occupancy patterns within perovskite oxide structures, showcasing the complexity and variability inherent in these materials. (d) The preparation process for high-entropy oxide nanofibers and their sulfur-based composites is outlined, detailing the steps involved in fabricating these advanced materials for various applications. Reprinted from [37], © 2022 Elsevier Ltd. All rights reserved.

long-term stability. With ongoing advancements in understanding the structure-performance relationship of HEOs and continual innovations in synthesis technologies, HEOs are expected to assume a more critical role in future electrocatalytic and energy conversion applications.

3.3. Photo(electro)catalysis

HEOs are increasingly recognized as promising candidates in the realm of photo(electro)catalytic materials, attributed to their adjustable composition, bandgap, and exceptional thermal stability. By finely tuning the molar ratios of constituent atoms, researchers can synthesize HEOs with varied crystal structures, defects, and band structures, optimizing their performance in photocatalytic applications.

Edalati *et al* have successfully synthesized HEO photocatalyst, $TiZrHfNbTaO_{11}$, through mechanical alloying and high-temperature oxidation [38]. This HEO demonstrates significant absorption in the visible spectrum, a bandgap of 2.9 eV, and possesses appropriate valence and conduction band structures for water splitting. It effectively facilitates photocatalytic hydrogen production. Similarly, Akrami *et al* reported that dual-phase HEOs comprising $TiZrNbHfTaO_{11}$ exhibit remarkable photocatalytic activity without the need for co-catalysts. Their efficiency in converting CO_2 to CO rivals that of traditional photocatalysts like anatase TiO_2 and $BiVO_4$, and is comparable to P25 TiO_2 [24]. Moreover, as shown in figure 10, rare earth-based HEOs, exemplified by $Ce_{0.2}Zr_{0.2}La_{0.2}Pr_{0.2}Y_{0.2}O_2$, have demonstrated superior photocatalytic activity [54]. This is evidenced by a hydrogen production rate of 9.2 μmol mg^{-1} h^{-1}, significantly surpassing the rate observed with pure CeO_2 at 0.8 μmol mg^{-1} h^{-1}. The effectiveness of these HEOs can be attributed to their tunable bandgaps ranging from 1.91 to 3.0 eV, high specific surface areas, and the abundance of oxygen vacancies. These features collectively enhance the separation and transport of photogenerated carriers, thereby boosting photocatalytic efficiency.

Einert *et al* synthesized ordered mesoporous spinel-type $(CoNiCuZnMg)Fe_2O_4$ thin films using the sol–gel method, which exhibit a high specific surface area, robust visible light absorption, and suitable band positions for water splitting reactions [45]. As a photoanode, the disorder multi-principal element composition enhances electron transport. In electrocatalytic OERs, this thin film required an overpotential of 420 mV to reach a current density of 10 mA cm^{-2} in 1 M KOH solution. Furthermore, as shown in figure 11, two-dimensional sub-nano HEOs nanosheets were prepared via a simple solvothermal method induced by polyoxometalate (POM) clusters [92]. These nanosheets, characterized by abundant active sites and precise elemental regulation, show exceptional bifunctional oxygen catalytic activity under light, significantly enhancing the kinetics of the OER. Notably, $CoFeNiMnCuZnO_x$ sub-nano sheets achieved an overpotential of 165 mV at the same current density, displaying improved performance under light compared to dark conditions. The half-wave potential for the ORR under light was 0.802 V,

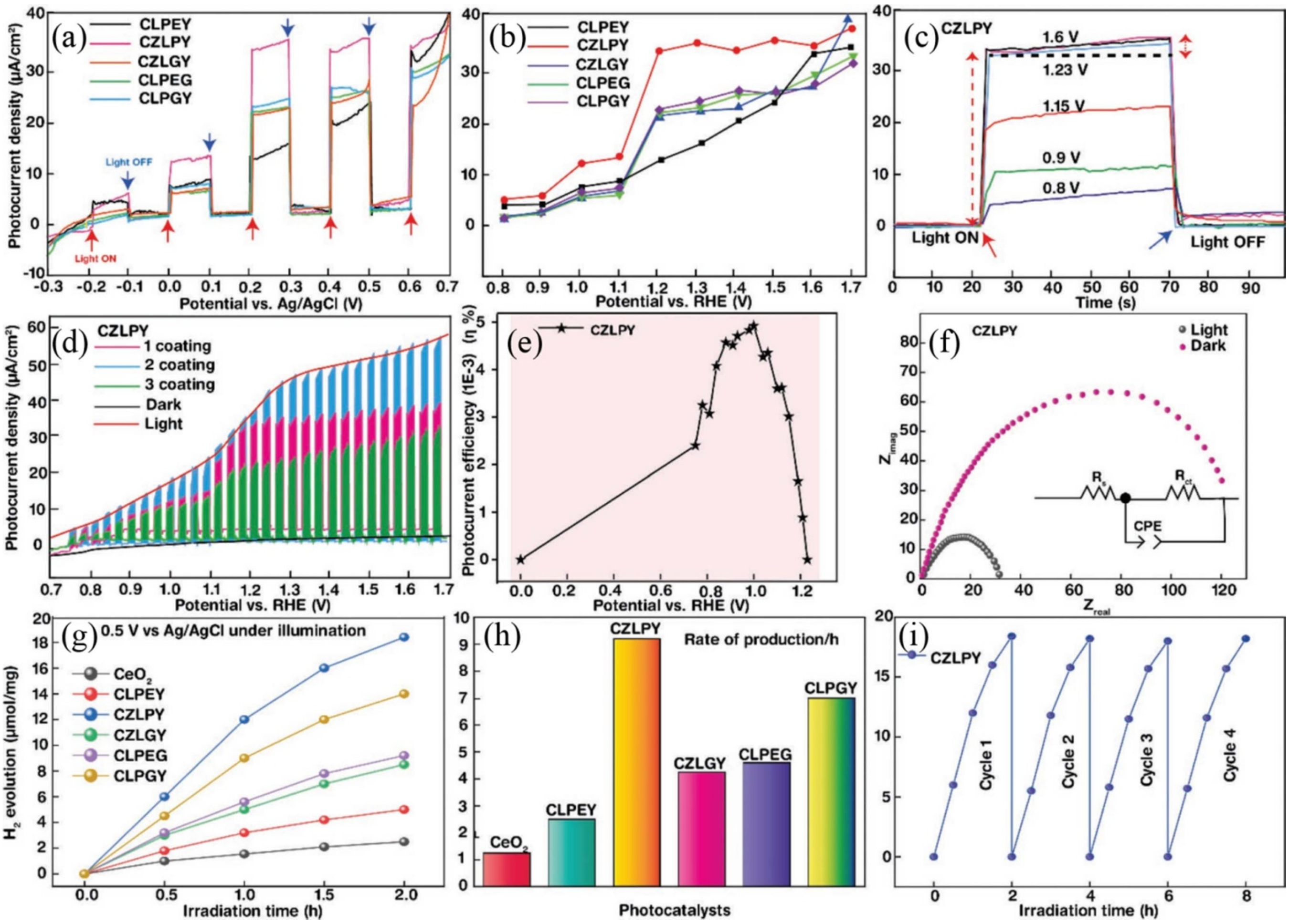

Figure 10. Comparative photoelectrochemical performance of high-entropy catalysts: (a) LSV plots for CLPEY, CZLPY, CZLGY, CLPEG, and CLPGY under chopped light and dark conditions, with potentials measured against Ag/AgCl and RHE. (b) The transient photoswitching response of the CZLPY electrode at different potentials is shown. (c) The effect of coating thickness on the LSV performance of the CZLPY electrode is analyzed. (d) The applied bias photon-to-current efficiency (ABPE) for the CZLPY electrode is plotted against potential. (e) Electrochemical impedance spectroscopy data for the CZLPY electrode under light and dark conditions. (f) Hydrogen evolution rates and (g) production rates for the catalysts under solar irradiation. (h) Stability test results for the CZLPY catalyst over multiple cycles. [54]. John Wiley & Sons. © 2022 Wiley-VCH GmbH.

demonstrating potential for high-performance zinc-air battery catalysts.

HEOs have emerged as novel catalysts in the photo(electro)catalytic domain, offering optimized bandgap and electronic structures that enhance light absorption and charge carrier mobility. HEOs excel in photocatalytic water splitting and CO_2 conversion, attributed to their unique lattice defects, strain, and high-density oxygen vacancies. Researchers have developed HEOs with high specific surface areas and porous structures using techniques like mechanical alloying, sol–gel methods, and POM-induced solvothermal methods. Such structural properties not only increase active sites but also promote efficient charge separation and transport, boosting catalytic efficiency. Specifically, rare earth-based and spinel-type HEOs have demonstrated significant hydrogen production rates and CO_2 conversion efficiencies, highlighting their practical value in energy conversion and environmental protection. As understanding of their structure-performance relationships deepens and synthesis technologies evolve, HEOs are poised to play a pivotal role in future photo(electro)catalytic applications, offering innovative solutions to energy and environmental challenges.

3.4. Lithium ion batteries (LIBs)

LIBs, integral to modern electronics and electric vehicles, are limited by the capacity and durability of current anode materials. HEOs, with their notable entropy stabilization and lithium-ion storage capacities, offer advancements in anode material performance.

The application of HEOs in LIBs is primarily focused on the development of anode materials, especially when used in full-cell configurations in conjunction with $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ cathodes, they can achieve excellent cycling performance [93]. HEOs such as $(FeCoNiCrMn)_3O_4$ are considered promising candidates for long-life anode

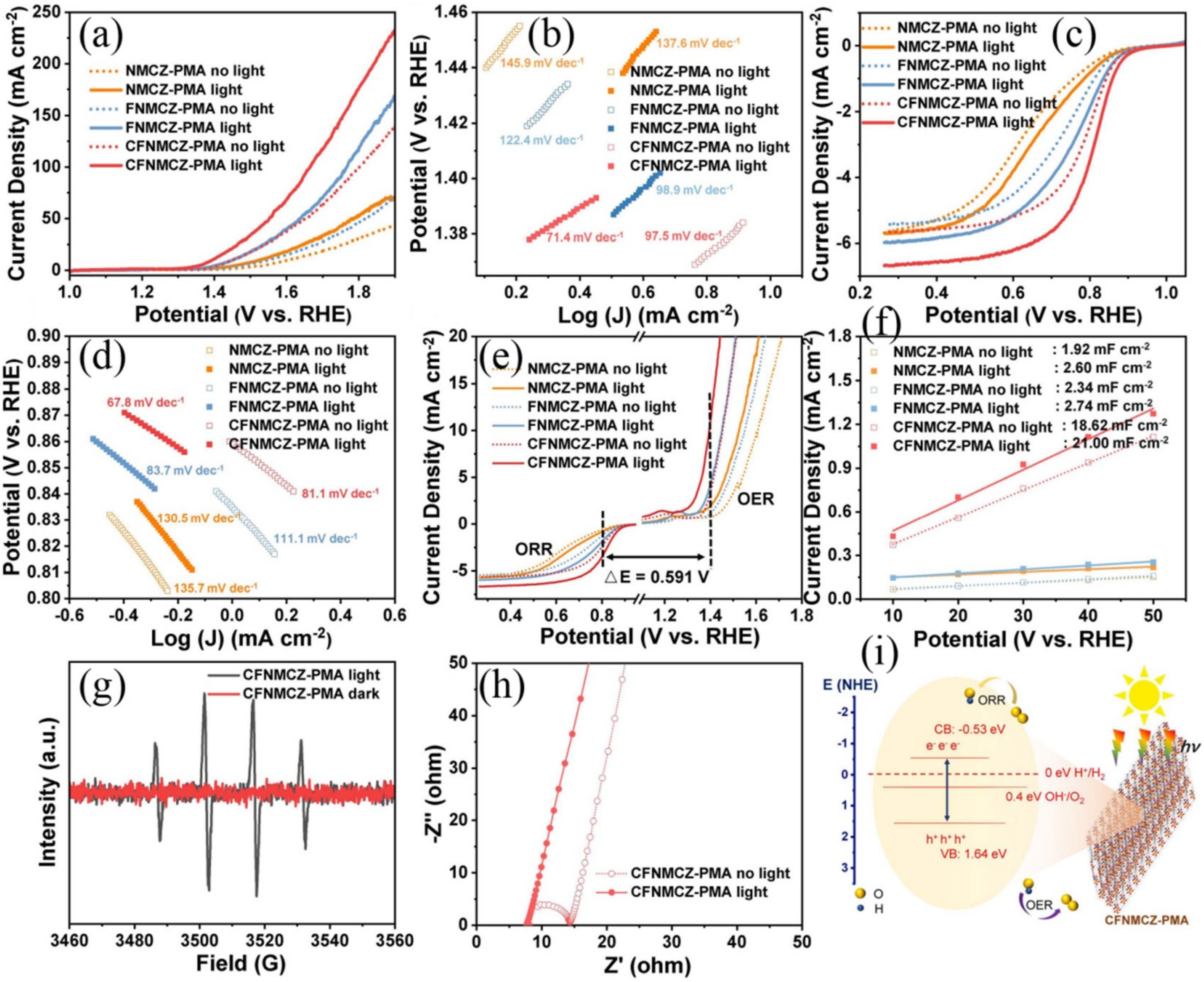

Figure 11. Photoelectrocatalytic behavior of engineered SNSs under illumination: (a) linear sweep voltammetry (LSV) curves for the oxygen evolution reaction (OER) in 1 M KOH at a rotation rate of 1600 rpm. (b) The Tafel slope analysis derived from the OER polarization data. (c) Polarization curves for the oxygen reduction reaction (ORR) in 0.1 M KOH under identical rotation conditions. (d) Tafel slope analysis for the ORR polarization data. (e) Composite polarization curves depicting the overall performance of the ORR and OER. (f) Assessment of the double-layer capacitance of the SNSs. (g) Electron paramagnetic resonance (EPR) spectra of CFNMCZ-PMA SNSs under both dark and light-irradiated conditions. (h) Electrochemical impedance spectroscopy (EIS) profiles of CFNMCZ-PMA SNSs, comparing their behavior with and without light exposure. (i) A schematic representation of the photoenhanced reaction mechanisms for both ORR and OER processes occurring on CFNMCZ-PMA SNSs. Reprinted with permission from [92]. Copyright (2024) American Chemical Society.

materials due to their stable crystal structure and high theoretical capacity. Nevertheless, a deeper understanding of the crystal structure and lithium storage mechanism of these materials is still needed to promote their further application and development in LIBs [94]. The rock-salt type ($Mg_{0.2}Co_{0.2}Ni_{0.2}Cu_{0.2}Zn_{0.2}$)O is one of the more studied HEOs for LIB anodes, exhibiting high Li^+/Na^+ ionic conductivity and, along with other HEOs like $(Co_{0.2}Cr_{0.2}Fe_{0.2}Mn_{0.2}Ni_{0.2})_3O_4$, $(CoNiZnXMnLi)_3O$ (X = Fe, Cr) $(Mg_{0.2}Ti_{0.2}Zn_{0.2}Cu_{0.2}Fe_{0.2})_3O_4$, $(Al_{0.2}CoCrFeMnNi)_{0.58}O_{4-\delta}$, and $(FeNiCrMnMgAl)_3O_4$, they constitute an important direction in the research of LIB anode materials [39, 95].

The microstructure of the electrode, including particle size, porosity, spherical structure, and thickness, also significantly affects the electrochemical performance. The evolution of these factors during the charge and discharge process plays a decisive role in the battery's cycle stability and rate capability. The HEOs of $(FeCoNiCrMn)_3O_4$ successfully prepared from oxidized HEAs of FeCoNiCrMn powder, has shown good cycle stability, attributed to its high-entropy characteristics, special crystal structure, and narrow bandgap [94]. (Mg,Ni,Zn,Cu,Co)O reported by Ghigna *et al* demonstrated a reversible specific capacity of 600 mAh g^{-1} at a current density of 89 mA g^{-1}, and after 10 cycles at a high current density of 1800 mA g^{-1}, the reversible capacity

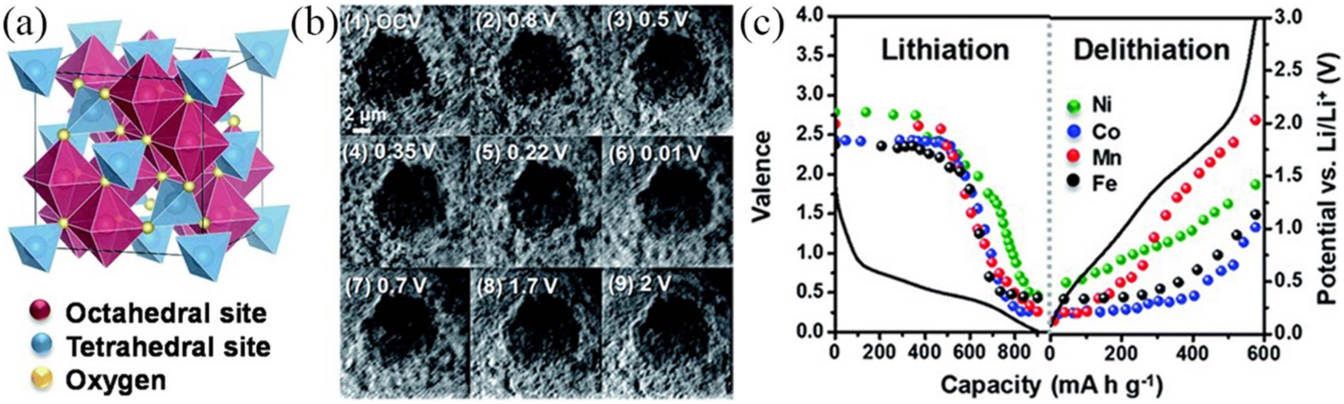

Figure 12. Structural and in operando characterization of spinel NCMFT for lithium-ion batteries: (a) the lattice structure of the spinel NCMFT is presented, illustrating its crystallographic configuration. (b) In operando transmission x-ray microscopy images of NCMFT when utilized as an anode in lithium-ion batteries, capturing the dynamic structural changes during operation. (c) Valence state variations of Fe, Co, Mn, and Ni are analyzed at various voltages, providing insights into the electrochemical behavior of the material. Reproduced from [46] with permission from the Royal Society of Chemistry.

could be fully restored [96]. (Mg,Ni,Zn,Cu,Co)O studied by Kheradmandfard showed a reversible specific capacity of 400 mAh g^{-1} at a current density of 100 mA g^{-1}, and after 1000 cycles at a current density of 1000 mA g^{-1}, the capacity remained at 325 mAh g^{-1} without significant decay [97]. Furthermore, as shown in figure 12, the spinel-type $(Ni_{0.2}Co_{0.2}Mn_{0.2}Fe_{0.2}Ti_{0.2})_3O_4$, as an anode material, exhibited a reversible specific capacity of 560 mAh g^{-1} at a current density of 100 mAh g^{-1}, with no capacity decay after 100 cycles [46]. Breitung *et al* have concentrated their research on utilizing the multi-component nature of HEOs to bolster the electrochemical performance of LIBs [98–100]. A significant outcome observed across these studies is the enhancement of cycling stability and the achievement of specific capacities surpassing 600 mAh g^{-1}, attributed to the stabilization of the rock-salt structure in HEOs. The formation of a robust solid-electrolyte interphase, as demonstrated by differential electrochemical mass spectrometry, effectively reduces the gassing behavior in HEO-based anodes. Additionally, the introduction of lithium into the HEO lattice triggers a phase transition from spinel to rock-salt, coupled with the partial oxidation of specific elements, indicating adjustable redox properties. This research highlights the significance of entropy stabilization in the formation of single-phase structures and emphasizes the necessity to tackle issues such as initial cycle efficiency and voltage hysteresis. Together, these findings lay the groundwork for the development of next-generation LIBs employing HEOs, presenting a promising path for advanced energy storage solutions.

HEOs are increasingly recognized for their potential as anode materials in LIBs. These materials utilize their entropy stabilization effect to enhance lithium-ion storage, potentially overcoming the capacity and durability constraints of existing anodes. HEOs are distinguished by their high theoretical capacities, superior electrochemical performance, and robust cycling stability, particularly in full-cell configurations, positioning them as optimal candidates for durable LIBs. Research indicates that meticulous control over synthesis conditions and microstructural design is critical for optimizing the electrochemical attributes of HEOs. For example, the enduring cycle stability of $(FeCoNiCrMn)_3O_4$ HEO underscores the significance of high-entropy effects in improving battery performance. Furthermore, HEOs with varied crystal structures, such as rock-salt and spinel types, have demonstrated remarkable reversible specific capacities and cycling stability, validating the high-entropy approach in materials engineering. Future investigations should aim to deepen the understanding of lithium storage mechanisms within HEOs, enhance their crystal structure and micromorphology, and develop innovative synthesis techniques to advance anode material performance.

3.5. *Solid oxide fuel cells (SOFCs)*

SOFCs represent a highly efficient energy conversion technology capable of directly transforming chemical energy into electrical energy. They achieve efficiencies up to 85% while maintaining low emissions. The energy conversion in SOFCs is facilitated by the simultaneous occurrence of ORRs and hydrogen oxidation reactions. Despite their efficiency, the operational requirement for high temperatures, typically between 800 °C and 1000 °C, poses challenges. These temperatures can lead to decreased electrochemical stability and reduced mechanical durability of electrode materials. This limitation necessitates further research into material enhancements to sustain performance under such demanding conditions.

To enhance the service life of electrodes and address issues caused by high temperatures, researchers have explored the application of HEOs to strengthen structural stability and improve the electrochemical performance of SOFCs. HEOs, known for their high activity and stability at elevated temperatures, are particularly suitable as cathode materials under high pressure. In Intermediate-temperature SOFCs, rare-earth-site

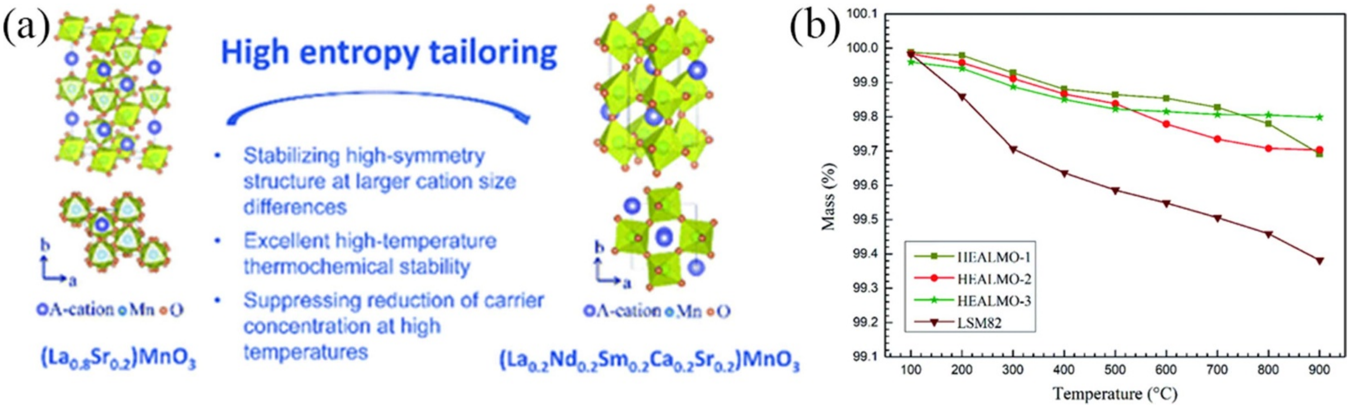

Figure 13. Thermodynamic stability and high-entropy engineering of manganese oxides. (a) The transition from $(La_{0.8}Sr_{0.2})MnO_3$ to the high-entropy analogue $(La_{0.2}Nd_{0.2}Sm_{0.2}Ca_{0.2}Sr_{0.2})MnO_2$ is depicted, showcasing the tailoring of composition for enhanced properties. (b) The weight change profiles of HEALMO-1, HEALMO-2, HEALMO-3, and LSM82 as a function of increasing temperature are presented, reflecting their thermal stability characteristics. Reproduced from [30] with permission from the Royal Society of Chemistry.

high-entropy double perovskite oxides with different molar ratios have been evaluated for use as cathode materials. Studies have indicated that an increase in configurational entropy significantly positively affects the crystal structure, conductivity, electrochemical performance, and material stability, with equimolar HEOs demonstrating excellent electrochemical activity at 700 °C [101]. The application of HEAs and HEOs in SOFC technology emphasizes their advantages in high strength and uniformity of component diffusion. Unlike the spinel-type HEOs used in LIBs, perovskite-type HEOs have a wider range of applications in SOFCs, with more exchangeable positions in their structure and a higher content of metal elements in the electrode to ensure high stability during SOFC operation. As shown in figure 13, in the ABO_3 perovskite structure, the A site typically contains a large number of rare earth elements for constructing the structural framework, while the B site's transition metals provide catalytically active redox pairs [30]. The B-site sublattice, acting as an electron-dominated sublattice, can have its conductivity greatly enhanced in p-type conductors by introducing dopants at the A site or B site, creating electron holes and lattice oxygen vacancies.

SOFCs, as efficient electrochemical devices, are often constrained by the stability and durability of electrode materials at elevated temperatures. HEOs, characterized by their exceptional structural stability and electrochemical activity, provide promising alternatives for advancing SOFC technology. These materials enhance conductivity, improve electrochemical performance, and extend cell longevity. Specifically, rare earth-site high-entropy double perovskite oxides utilized as cathode materials in intermediate-temperature SOFCs have shown superior electrochemical properties. The optimization of configurational entropy is crucial for enhancing material conductivity and stability. Equimolar ratios in HEOs help maintain effective electrochemical activity and lower operational temperatures. Perovskite-type HEOs are particularly advantageous for SOFC electrode applications due to their structural versatility and high elemental diversity. Doping at the A and B sites can fine-tune the electronic structure and oxygen vacancy concentration, thus improving conductivity and catalytic activity. Future research should focus on refining synthesis methods and microstructural control of HEOs to continually advance SOFC performance. Moreover, a deeper understanding of the high-entropy effects on material properties will facilitate the design of more efficient, stable, and cost-effective energy conversion materials, accelerating the commercialization of SOFC technology.

3.6. *Supercapacitor*

Electrochemical supercapacitors, recognized for their novel high-power energy storage capabilities, stand out due to their exceptional energy and power density, rapid charging and discharging abilities, broad operational temperature range, and low decay rates. Unlike traditional carbon materials that utilize electrostatic storage mechanisms, metal oxide-based supercapacitors achieve enhanced energy storage through Faradaic reactions.

In supercapacitors, the redox potential of single metal oxides is typically fixed, while HEOs, containing multiple metal elements, provide a rich array of redox pairs. This not only enhances the energy storage capacity but also improves electronic conductivity. The multi-metallic characteristic confers significant advantages to HEOs in the application of supercapacitors, particularly in terms of cyclic stability. The electrode material is where HEOs play a pivotal role in supercapacitors. Notably, HEOs doped with heterovalent cations exhibit excellent electrochemical performance due to their complex lattice structures and abundant redox active sites. As shown in figure 14, researchers have successfully fabricated a variety of spinel-structured HEOs, such as spinel-type $(Al_{0.2}Co_{0.2}Cr_{0.2}Mn_{0.2}Ni_{0.2})_3O_4$, $(CoCrFeMnNi)_3O_4$, $(FeCoCrMnZn)_3O_4$, perovskite-type $La(CoCrFeMnNiAl_x)_{1/(5+x)}O_3$, $La_{0.7}Bi_{0.3}Mn_{0.4}Fe_{0.3}Cu_{0.3}O_3$, and ilmenite-type $(Zr_{0.5}Ti_{0.5}Ce_{0.5}Hf_{0.5})O_7$, etc [34, 102].

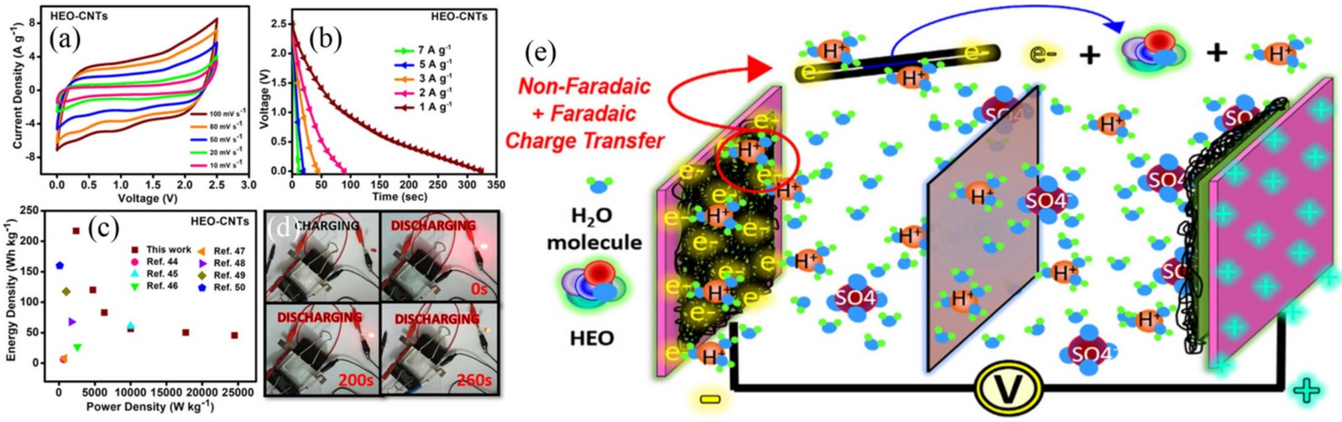

Figure 14. Electrochemical performance of high-entropy oxide–carbon nanotube (HEO–CNT) nanocomposites in flexible energy conversion systems. (a) Cyclic voltammetry (CV) plots of the HEO–CNT nanocomposite-based flexible capacitive energy storage (fc-EC) device using the [BMIM]ee[TFSI] electrolyte, measured at various scan rates. (b) Galvanostatic discharge (GD) plots of the same system at different current densities. (c) A Ragone plot illustrating the energy and power densities of the HEO–CNT-based fc-EC, benchmarked against prior studies. (d) Practical application demonstrations, including the illumination of a red light-emitting diode (LED) and the valuation at various stages of charge and discharge. (e) Charge transfer characteristics of carbon nanotubes (CNTs) decorated with high-entropy oxide catalyst nanoparticles. Reprinted with permission from [102]. Copyright (2019) American Chemical Society.

These materials have not only demonstrated high specific capacity and excellent cyclic stability but also their synthesis strategies and structural optimization have provided new directions for the development of supercapacitors.

The integration of HEOs into supercapacitors represents a significant advancement in energy storage materials. Leveraging their multi-metal redox pairs and high electronic conductivity, these materials surpass traditional carbon-based supercapacitors in energy storage potential under Faradaic mechanisms. The varied lattice structures and abundant active sites of HEOs offer numerous opportunities for enhancing supercapacitor performance. With ongoing improvements in understanding the structure-performance relationships of HEOs and innovations in synthesis techniques, these materials are expected to play a pivotal role in future supercapacitor technologies, addressing the demands for high-power, high-energy-density, and durable energy storage systems.

3.7. Other applications

HEOs, endowed with unique compositional and structural properties, are increasingly employed beyond traditional photoelectrochemical energy storage and conversion applications. Their expansion into diverse technological arenas underscores the broad application potential of these materials.

In the field of photo-thermal catalysis, a two-dimensional Cu-based HEOs $Cu_2Zn_1Al_{0.5}Ce_5Zr_{0.5}O_x$ has been demonstrated as an outstanding CO_2 hydrogenation catalyst. This material not only achieved a photothermal energy conversion efficiency of 36.2% but also reached a CO productivity of 248.5 mmol g^{-1} h^{-1}, with its performance further enhanced to 571 1 under specific conditions [60]. This accomplishment not only reflects the advantage of HEMs in enhancing the stability and activity of catalysts but also paves a new way for the development of photo-thermal catalytic technology. Additionally, the application of HEOs in the field of infrared radiation materials is equally noteworthy. As depicted in figure 15, researchers successfully synthesized a spinel-type HEO $(CuMnFeCr)_3O_4$ using a solid-state synthesis reaction and utilized cold spraying technology to deposit it onto a stainless-steel substrate, creating an infrared radiation coating with high radiative thermal efficiency and significant thermal stability [103]. The infrared emissivity of the coating in the 0.78–2.5 μm and 2.5–16 μm bands has been effectively enhanced, with the high-entropy effect ensuring its long-term chemical and thermal stability.

These examples highlight the significant value of HEOs' multifunctionality in various domains beyond energy and catalysis. As research continues to deepen the understanding of HEOs' properties, it is expected that these materials will increasingly influence numerous scientific and technological fields. The interdisciplinary applications of HEOs underscore their wide relevance in materials science. With advancing insights into their structure-performance relationships, HEOs are poised to impact additional technical disciplines significantly. Future research should focus on uncovering new uses for HEOs while refining their synthesis techniques and performance characteristics to address the specialized demands of diverse industrial applications.

4. Rational design and screening of high-performance HEOs

4.1. Necessity and urgency of computational design for HEOs

HEOs, characterized by their unique multi-principal-element composition and structural diversity, hold significant promise for advancing new energy technologies. Nevertheless, the vast compositional range and complex structures of these

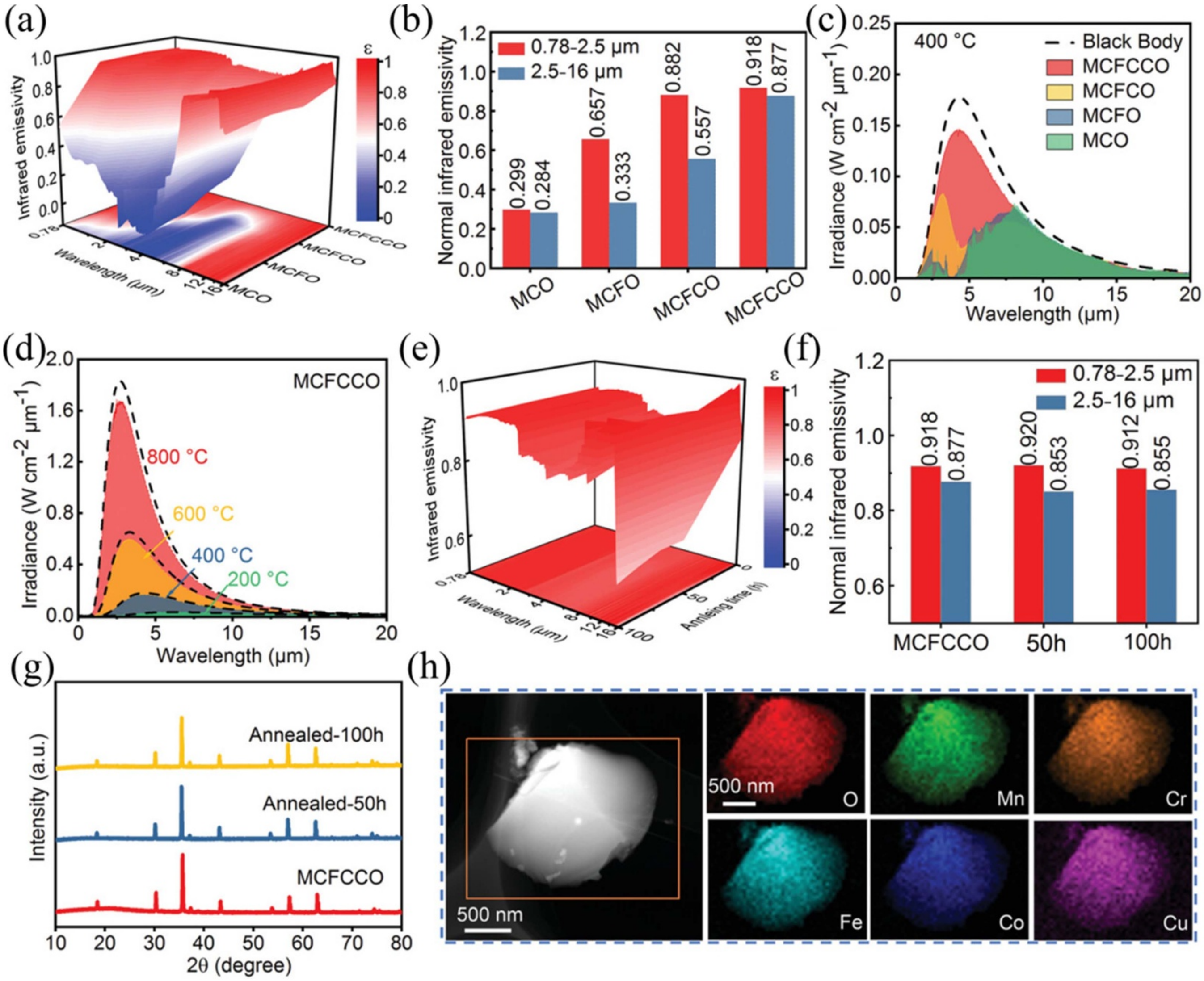

Figure 15. Infrared radiation properties of multi-metal spinel oxides. (a) Three-dimensional (3D) mappings of the infrared spectral emissivity for MCO, MCFO, MCFCO, and MCFCCO ceramic materials at room temperature (RT). (b) The corresponding normal infrared emissivity values for the ceramics shown in (a). (c) Comparison of the irradiance between theoretical blackbody radiation (dotted lines) and the respective spinel oxides (solid lines) at 400 °C. (d) Irradiance profiles of a theoretical blackbody and MCFCCO at temperatures of 200 °C, 400 °C, 600 °C, and 800 °C. (e) 3D emissivity mappings of MCFCCO ceramics annealed at 1300 °C for durations of 50 and 100 h in air. (f) The corresponding normal emissivity values for the annealed MCFCCO ceramics depicted in (e). (g) X-ray diffraction (XRD) patterns of the MCFCCO ceramics subjected to the same annealing conditions. (h) Transmission electron microscopy (TEM) mappings of the MCFCCO ceramics annealed at 1300 °C for 100 h, revealing microstructural details. [103]. John Wiley & Sons. © 2023 Wiley-VCH GmbH.

materials, alongside the multifunctional requirements of new energy applications, pose substantial challenges. These challenges include material synthesis, characterization, performance optimization, and mechanism exploration. As traditional experimental approaches reach their limits, the role of theoretical calculations and simulations becomes increasingly crucial [7, 9, 72, 104, 105].

Theoretical calculations offer profound insights at the electronic- and atomic-levels, predicting material properties, guiding experimental synthesis, enhancing research efficiency, and reducing costs. In the synthesis of HEOs, achieving precise control over the uniform distribution and single-phase nature of multiple principal components is critical, yet this process often faces significant uncertainties. Theoretical calculations can elucidate the distribution of different principal-elements, their thermal stability and phase space, and their impacts on the microstructure and macroscopic properties of the material [106]. First-principles calculations and molecular dynamics simulations are pivotal for understanding the structural characteristics and stability of materials at the atomic-level and for predicting their physical and chemical properties [107, 108]. The integration of density functional theory (DFT) with molecular dynamics simulations facilitates the prediction and optimization of key performance indicators such as electronic properties, ionic conductivity, and thermal stability prior to actual material synthesis. High-throughput computational screening and inverse design strategies are especially crucial in the research and development of HEOs. High-throughput techniques enable the performance prediction of numerous potential materials, swiftly identifying candidates with promising application potential [86]. Conversely, inverse design strategies begin with specific application objectives to determine the suitable material composition and structure [109, 110]. When combined with artificial intelligence (AI), machine learning, and data mining technologies, these strategies significantly enhance the rationality and efficiency of material design [111–113]. The role of theoretical calculations in new energy applications is indispensable. They not only predict the performance of HEOs under specific conditions but also provide crucial guidance for their practical application. First-principles calculations elucidate electron transfer mechanisms in electrochemical reactions, offering a theoretical foundation for designing more efficient energy storage and conversion materials. Additionally, theoretical simulations can expose the reaction mechanisms and degradation processes of materials under various operational conditions, guiding material design and device optimization.

Theoretical calculations and simulations are indispensable in the development of HEOs. They enable researchers to understand the underlying physical mechanisms of HEOs deeply and guide the experimental design, thereby accelerating the discovery and optimization of new HEOs. Future research should advance computational methods to better handle the complexity of HEOs and integrate these methods with experimental efforts, thereby driving forward the science of new energy materials.

4.2. Exploration of stability and structure activity relationship

HEOs are characterized by their complex compositional diversity and multi-principal-element configuration, which significantly influence material properties and stability. Typically composed of five or more principal-elements in near equimolar ratios, minor variations in each constituent can profoundly impact microstructural attributes and overall material behavior [106]. Therefore, employing theoretical calculations and simulations becomes pivotal in predicting the thermodynamic stability and structure-property relationships of HEOs.

These computational techniques facilitate forecasting phase stability under diverse environmental conditions, including variations in temperature and pressure. By doing so, they streamline synthesis optimization, mitigate experimental redundancy, and reduce costs. Studies underscore the critical role of achieving homogeneous atomic-scale distribution and stable single-phase structures in enhancing catalytic efficiency [114]. For example, Jiang *et al* highlighted the pivotal role of the Goldschmidt tolerance factor in the thermal stability of cubic perovskite solid solutions. They established that tolerance factors close to unity ($0.97 \leqslant t \leqslant 1.03$) for all six components are indicative of forming a single-phase high-entropy perovskite [68]. Similarly, Krawczyk *et al* utilized DFT to investigate the electronic structure of $(\mathrm{Gd_{0.2}Nd_{0.2}La_{0.2}Sm_{0.2}Y_{0.2}})\mathrm{CoO_3}$, revealing a bandgap of 1.18 eV, classifying the material as a semiconductor. Their findings underscored the potential for computational methods to enhance the design of efficient photocatalysts by exploring various compositions [115]. Furthermore, DFT calculations by Nguyen *et al* examined different HEO systems, including halite (Mg, Zn, Mn, Co, Ni) and spinel (Cr, Fe, Mn, Co, Ni) structures. Their simulations elucidated that composition variations significantly influence structural preferences, with lower Mn concentrations favoring halite structures and higher Mn concentrations stabilizing spinel formations [116]. These computational insights align with experimental synchrotron x-ray diffraction observations, affirming the utility of theoretical approaches in predicting and understanding the structural characteristics of HEOs. In conclusion, integrating advanced computational methodologies not only enhances our fundamental understanding of HEOs but also holds promise for optimizing their synthesis and functional properties in diverse applications.

The application of machine learning and high-throughput methods has greatly accelerated the discovery of new HEOs. Mints *et al* utilized a machine learning model based on experimental data from 350 different nanoparticles to simulate the OER performance of an AuIrOsPdPtReRhRu composition. They identified AuIrOsPdRu-based HEOs as the optimal catalyst and predicted the phase transition behavior and stability of these materials under varying conditions [78]. Furthermore, AI-aided design and high-throughput computational methods have significantly contributed to the study of HEOs. For example, Monte Carlo simulations estimating phase composition, oxygen vacancy concentration, and local ion segregation as functions of temperature and oxygen partial pressure, coupled with theoretical calculations, have been employed in the synthesis of various multi-component oxides with a pyrochlore composition. This approach has enhanced the purity of pyrochlore-type HEOs and reduced experimental costs [117]. In practical applications, Fu *et al* proposed a controllable synthesis strategy based on the element's self-lattice framework, achieving phase-controlled synthesis of HEOs ultra-thin-film [118]. By precisely controlling the ratio and distribution of elements, this strategy optimizes the phase structures of HEOs, thus improving their performance and application prospects.

The interpretation of structure-property relationships is crucial in HEOs design, where theoretical calculations and simulations serve as powerful tools. First-principles calculations allow researchers to predict the electronic structure, band structure, mechanical properties, and light absorption characteristics of materials, offering guidance for designing materials with specific electrochemical properties. For instance, as depicted in figure 16, first-principles calculations and simulations effectively predict and optimize the light absorption and photothermal conversion performance of HEOs. Spinel-type HEOs exhibit a 95.5% solar light absorption rate across the full spectrum (300–2500 nm) and can raise the material surface temperature from room temperature to 63.2 °C within

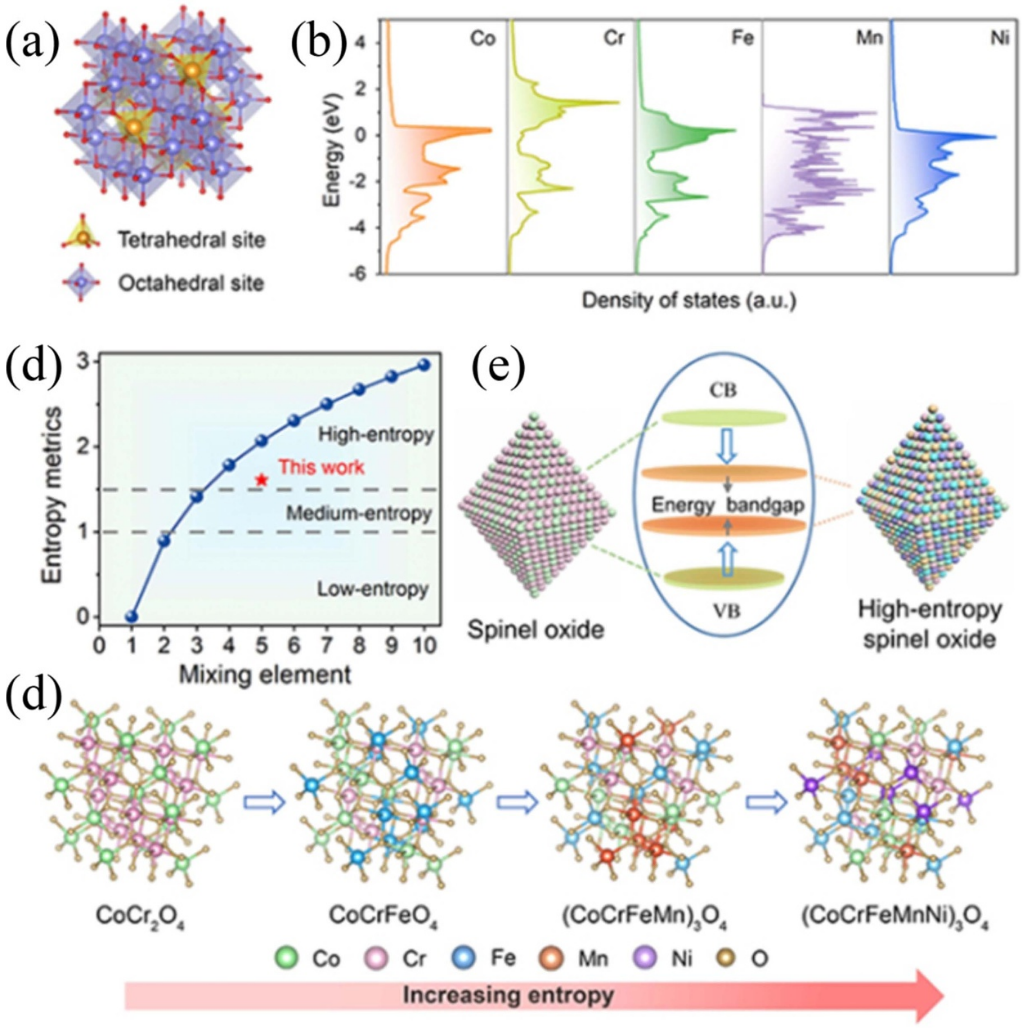

Figure 16. High-entropy spinel oxides: design and electronic structure. (a) The distribution of cations within the spinel oxide lattice is illustrated, highlighting the uniformity of multi-element incorporation. (b) The density of states (DOS) contributions from each cation in $(CoCrFeMnNi)_3O_4$ are delineated, emphasizing the electronic structure's complexity. (c) It is demonstrated that the prepared spinel oxides achieve high-entropy oxide (HEO) status. (d) The configurational entropy of the spinel oxides is shown to increase with the addition of cations, underscoring the impact on material properties. (e) The capacity of high-entropy spinel oxides to modulate the band gap is elucidated, a feature pivotal for their applications. Reprinted from [120], © 2023 Elsevier Inc.

120 s under 1 kW m^{-2} simulated solar irradiation, demonstrating excellent solar absorption and photothermal conversion characteristics [103, 119, 120]. These results highlight perovskite-type HEO nanofibers as catalysts for lithium–sulfur batteries, showcasing exceptional catalytic performance. DFT calculations indicated that the confinement of multiple metal elements within a single perovskite phase leads to high configurational entropy, creating various active sites that regulate polysulfide adsorption properties [37].

Traditional characterization methods, such as XPS, Raman spectroscopy, and XAFS, possess inherent limitations in analyzing catalytic active centers (including defects, stress, and electronic structure) within HEOs. While XRD and SEM provide insights into material crystal structure and morphology, they fall short in capturing the complex interactions and microstructural details of multi-principal-element HEOs [106]. *In-situ* characterization techniques are pivotal for understanding material behavior under operational conditions, yet computational simulations offer deeper atomic-scale insights, complementing experimental data and elucidating micro-mechanisms of material performance. Hu *et al* demonstrated a Cr-induced spontaneous reconstruction strategy for synthesizing FeCoNiMnCr HEA and HEO hetero-structure catalysts, revealing electroactive sites with robust valence states crucial for stable OER activity [121]. Furthermore, Ye *et al* employed first-principles calculations and aberration-corrected microscopy to investigate lattice distortion effects in high-reflectivity HEOs, optimizing perovskite-type materials $(La_xK_{0.4-x}Ca_{0.2}Sr_{0.2}Ba_{0.2})TiO_{3+\delta}$ (x = 0.1, 0.15, 0.2, 0.25, 0.3) with up to 94% reflectivity by suppressing oxygen vacancies [27]. Their work outlines a viable pathway for designing stable, high-reflectivity HEOs through precise control of multi-principal-element compositions.

Determining the crystal structure and local chemical environment of HEOs remains challenging. Moniri *et al* proposed a lattice distortion descriptor and studied chemical short-range order (CSRO) in three-dimensional HEOs, utilizing atomic electron tomography to reveal local lattice distortions associated with CSRO and twinning phenomena [122]. Their findings underscore the complex nature of local structural distortions in HEAs, where twinning occurs in energetically unfavorable regions affecting CSRO. Therefore, by combining atomic electron tomography [123], lattice distortion parameters, twin order parameters [124], and CSRO parameters [125, 126], it was found that local lattice distortion in HEAs is related to CSRO, and twinning occurs in regions where energy is not favorable for CSRO.

The role of theoretical calculations and simulations is crucial in investigating the stability and structure-property relationships of HEOs. These tools not only facilitate a profound comprehension of the fundamental mechanisms underlying materials but also provide invaluable guidance for experimental design. This synergy accelerates the exploration and refinement of novel materials. Future research efforts should focus on advancing computational methodologies to effectively address the intricate nature of HEOs. Integrating these advancements with experimental approaches will foster significant progress in the field of new energy science.

4.3. Performance prediction and optimization

Optimizing the performance of HEOs remains a persistent challenge in materials science research. Experimentally, improving catalytic activity and structural stability through adjustment of synthesis parameters requires a comprehensive understanding of material behavior under diverse operating conditions [127, 128]. Theoretical calculations and simulations are pivotal in this regard, facilitating optimization of HEOs composition and structure to enhance their efficacy in new energy technologies, as well as predicting material behavior in targeted applications [106].

In new energy applications, the surface/interface microstructure and catalytic activity of HEOs serve as crucial performance metrics. Researchers enhance these characteristics by adjusting the ratios of principal-elements and the crystalline structure, thereby improving both catalytic efficiency and stability. Theoretical calculations and simulations play a pivotal role in this optimization process, elucidating the microstructure, electronic structure, and surface reaction kinetics of HEOs across various composition combinations. This systematic approach not only optimizes their performance but also guides the experimental synthesis of advanced catalytic materials [129]. DFT calculations have been instrumental in understanding the nature of catalytic active sites in HEOs. For instance, the catalytic activity of AuIrOsPdRu-HEO derives from active sites primarily composed of Ru and Ir, with Pd further enhancing their performance. Additionally, Os contributes by roughening the surface, thereby improving overall catalyst performance, while Au fulfills a structural support role [78]. For the OER, spinel-type non-noble metal-based HEOs, optimized through DFT calculations and synthesized using a straightforward solvothermal approach to form small $(FeCoNiCrMn)_3O_4$ nanoparticles, have exhibited notable catalytic activity and stability [130]. Furthermore, combined DFT calculations and XPS studies have demonstrated that the multi-cation composition of perovskite-type HEOs enhances catalytic activity in water oxidation reactions [16]. This enhancement arises from the synergistic effects of oxidizing and reducing different transition metal cations during the adsorption of reaction intermediates. Defects and strain structures within HEOs also exert significant influence on their catalytic performance. DFT calculations have revealed that inherent defects and strain structures facilitate the generation of surface hydroxide species on the catalyst, thereby enhancing catalytic activity in photocatalytic CO_2 conversion [24].

Theoretical calculations and simulations serve as crucial tools for elucidating the mechanisms behind distinctive phenomena such as the high-entropy effect, lattice distortion effect, sluggish diffusion effect, and cocktail effect. These effects manifest unique mechanisms within HEOs in comparison to HEAs, yet their precise mechanisms and implications remain incompletely understood. Zhong *et al* highlighted disparities between HEOs and conventional HEAs, suggesting that 'high-entropy blending' could optimize electronic and ionic conductivity, offering a novel approach for designing advanced HEOs [131]. The diverse metallic elements present in HEOs yield varied electronic configurations. These configurations, through mixing and rearrangement, contribute to optimizing the overall electronic structure of the material. Orbital hybridization resulting from high-entropy strategies can effectively heighten the likelihood of electron transitions. This process introduces a multitude of oxygen vacancies via variable-valence metal elements, thereby narrowing the material's bandgap. Concurrently, the lattice distortion effect reduces the symmetry of lattice vibrations, endowing spinel-type $(MnCrFeCoCu)_3O_4$ with outstanding near-blackbody radiation capabilities [103]. In spinel-type HEOs, lattice distortion induces twisting, generating numerous densely-packed oxygen vacancies that increase the electrochemically active surface area. This enhancement significantly bolsters the catalytic efficiency for OER [44]. As depicted in figure 17, the 'cocktail effect' in HEOs widens the d-band and reduces reactivity in comparison to single-metal oxides, thereby facilitating efficient electron transfer and optimizing rate performance [132]. Furthermore, the robust lattice strain field of HEOs exhibits considerable tolerance towards the electrostatic repulsion of highly charged Zn^{2+} ions, thereby endowing aqueous zinc-ion batteries with exceptional cycle stability.

Performance prediction and optimization of HEOs are pivotal for advancing their application in new energy technologies. Theoretical calculations and simulations are now indispensable for comprehending and designing these materials. By precisely predicting microstructure, electronic configuration, and surface reaction dynamics across

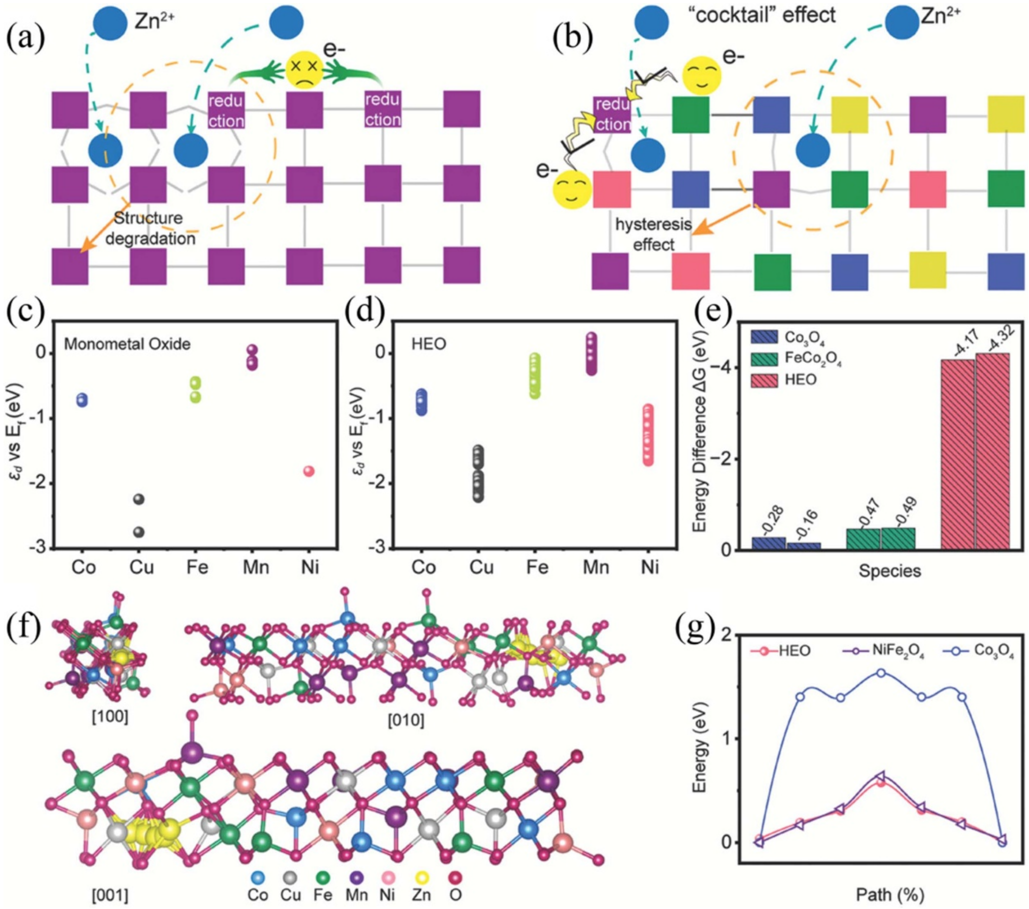

Figure 17. Comparative framework of electrode materials for aqueous zinc-ion batteries (AZIBs). (a) A schematic representation of traditional metal-oxide structured electrode materials is provided, outlining their conventional electron pathways. (b) In contrast, high-entropy electrode materials are depicted with their intricate multiple electron paths, enhancing the electrochemical performance in AZIBs. (c) The ε_d value for monometallic oxides is presented, followed by (d) the corresponding value in Co-HEO, illustrating the difference in electron density upon zinc ion adsorption. (e) The formation energy post Zn^{2+} intercalation is compared between monometallic oxide and Co-HEO, highlighting the energetics of the process. (f) The migration pathways of Zn^{2+} within the Co-HEO structure are delineated, showcasing the material's ability to facilitate ion transport. (g) The migration energy profile across monometallic oxides, bimetallic oxides, and Co-HEO is presented, emphasizing the impact of high-entropy configurations on ion mobility. [132]. John Wiley & Sons. © 2023 Wiley-VCH GmbH.

diverse compositional blends, researchers can systematically enhance HEO performance and direct experimental synthesis. Theoretical techniques like DFT calculations elucidate active site characteristics and elucidate the role of multi-principle-element synergies in catalytic processes. Concurrently, computational simulations are crucial for exploring specialized effects such as the high-entropy phenomenon, lattice distortion, sluggish diffusion, and cocktail effects. A profound grasp of these phenomena provides a foundational framework for mechanistic studies and optimizing HEOs performance. Furthermore, theoretical calculations and simulations illuminate material performance in specific applications, such as photocatalysis, electrocatalysis, and energy storage. Forecasting and optimizing these performances not only expedite new material discovery but also reduce developmental costs and enhance research efficiency. Future investigations should continue harnessing and advancing computational methodologies to navigate the intricacies of HEOs, integrating them with experimental research to propel advancements in new energy materials science. Through interdisciplinary collaboration, significant strides in the rational design and optimization of HEOs are anticipated.

4.4. Multiscale modeling and simulation

Multiscale modeling and simulation play a pivotal role in computational materials science, providing robust algorithmic support for understanding the multiscale properties and structural simulation of HEOs [133]. This approach bridges various levels from microcosmic to macroscopic, facilitating a comprehensive comprehension of the behavior and synthesis processes of HEOs. The synthesis of HEOs demands precise conditions, balancing crystal structure, electronegativity, and coordination numbers. Conventional synthesis methods often introduce microstructural variations and alter electronic properties, thereby influencing material performance.

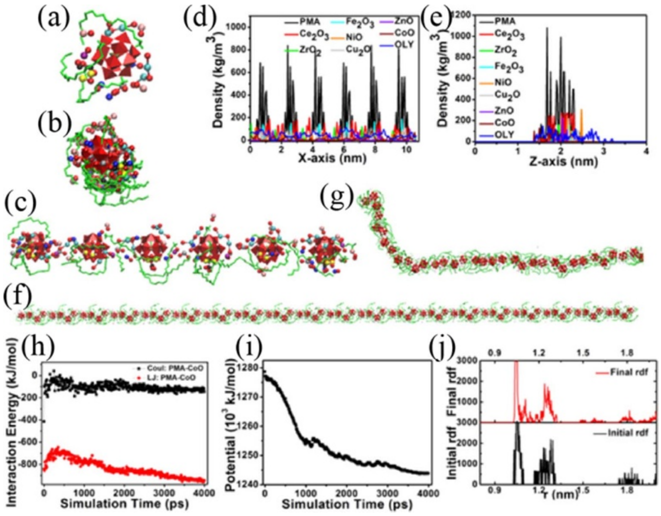

Figure 18. Molecular dynamics of CoZnCuNiFeZrCeO$_x$-PMA spinel nanowires. (a) Structural model of the nanowire building block with color-coded elements. (b) and (c) Views of a six-block nanowire before simulation. (d) and (e) Density distributions of components in the nanowire. (f) Initial 80 nm nanowire. (g) Post-simulation bending of the nanowire. (h) Interaction energy and (i) potential energy changes during bending. (j) Radial distribution function (RDF) for PMA central atoms pre- and post-bending. Reprinted with permission from [139]. Copyright (2022) American Chemical Society.

Furthermore, transitioning these materials from laboratory to industrial scales necessitates addressing critical factors such as consistency, repeatability, and cost-effectiveness [15, 106, 128, 134, 135]. The integration of multiscale modeling and simulation enables a profound exploration of how synthesis processes impact the formation of HEOs and facilitates the development of novel synthesis strategies.

Molecular dynamics simulations have been employed extensively to investigate the local structure of HEOs. Anand *et al* utilized molecular dynamics to construct 23 536 supercells for rock-salt type HEOs within the (Mg,Co,Cu,Ni,Zn)O system. Each supercell contained 1000 cations and 1000 anions, employing the Buckingham interatomic potential to capture detailed local structures [136]. Their findings revealed that supercells with high stable energy exhibited fewer Cu^{2+}–Cu^{2+} pairs and more Cu^{2+}–Zn^{2+} pairs, with no observed special ordering among the other 13 types of pairings. In another study, Ye *et al* constructed 100 supercells of rock-salt type $(Hf_{0.2}Zr_{0.2}Ta_{0.2}Nb_{0.2}Ti_{0.2})C$, each containing 64 atoms with a random distribution of metal atoms and cation stoichiometry close to equimolar [137]. Subsequently, DFT calculations were employed to fully relax these supercells, providing insights into total energy and atomic positions. The analysis of atomic displacements indicated that anions generally displace more than cations, suggesting that lattice distortion in these HEOs primarily occurs within the anionic sublattice.

The inverse structure mapping scaling algorithm utilizes the kinetic Monte Carlo structure evolution algorithm, known for its efficacy in calculating material structures at mesoscale and larger scales. This approach is applied to simulate the atomic and molecular scale structural features of HEAs, HEOs, and multiphase organizations. It further extracts and reduces the symmetry of nanoscale atomic clusters from material samples at mesoscale and above ($>10^3$ atoms and $50 \times 50 \times 50$ nm^3). From simulation results at mesoscale, symmetry irreducible cluster cells and their relative proportions inform an inverse structure mapping algorithm akin to Monte Carlo methods. This algorithm facilitates the mapping of macroscopic disordered material structure features to nanoscale and smaller supercell models [133]. Wan *et al* developed multiscale modeling methods integrating data from various scales to enhance the characterization and understanding of HEOs [138]. Their approach incorporates machine learning techniques to enable seamless information transfer and coupling across different scales, thereby revealing the hierarchical nature and distinctive behaviors of HEOs. In a related study illustrated in figure 18, the formation of sub-nano wires in HEOs, induced by POMs, was investigated via molecular dynamics simulations. The findings highlight the interaction and co-assembly of POMs with multi-metal oxides, driven by Coulombic and van der Waals forces, elucidating the mechanism behind HEOs formation [139].

Multiscale modeling and simulation technology plays a pivotal role in the investigation of HEOs. By integrating simulations across multiple scales, from microcosmic to macroscopic, researchers gain comprehensive insights into the structural and property dynamics of materials. This approach offers new perspectives and methodologies crucial for the rational design and optimization performance of HEOs. Methods such as molecular dynamics simulations and first-principles calculations facilitate precise predictions and control behavior of HEOs, spanning from atomic configurations to larger scales. These techniques elucidate intricate details including cation pairing, lattice distortions, and electronic structures within HEOs, thereby providing foundational insights into their stability and functional properties. Moreover, advancements in inverse structure mapping algorithms and kinetic Monte Carlo simulations significantly

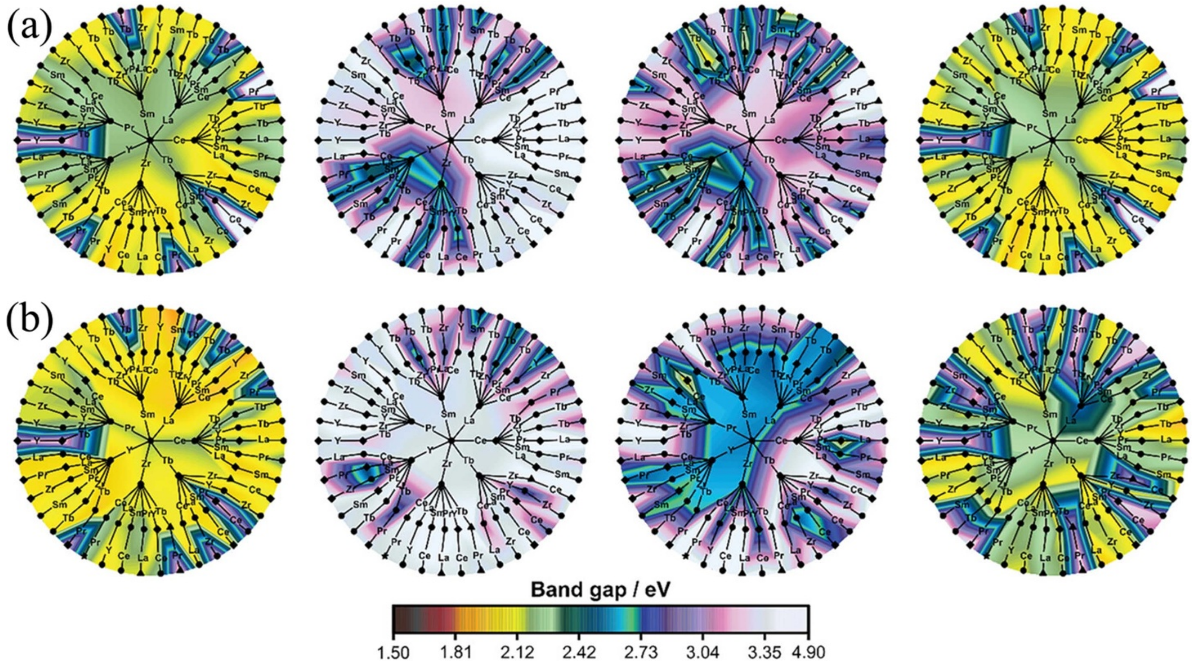

Figure 19. Band gap energies of rare-earth oxides (REOs) at elevated temperatures. Contour plots illustrate the variation in band gap energies of REOs at (a) 700 °C and (b) 900 °C, with the calcination atmosphere sequentially transitioning from air to argon, 10% H_2/argon, and back to air. Reproduced with permission from [86]. CC BY-NC 4.0.

enhance cross-scale simulation capabilities. These tools enable detailed microstructural feature analysis of HEMs, further augmenting our understanding and predictive capabilities. Additionally, the integrated application of multiscale modeling approaches, bolstered by machine learning technologies, facilitates seamless information coupling across different scales. This integration introduces innovative avenues to capture the hierarchical nature of HEOs and uncover their multiscale characteristics. In conclusion, multiscale modeling and simulation not only deepen our comprehension behavior of HEOs but also furnish a theoretical foundation and strategic guidance for the discovery and optimization of novel HEOs. This underscores its critical significance and expansive applicability within the realm of materials science research.

4.5. High-throughput computing and screening

The design of HEOs is inherently intricate, primarily due to the vast array of possible constituent element arrangements. Each element's proportion and distribution play pivotal roles in determining the material's overall performance. Achieving precise control over these factors is crucial for optimizing HEOs, thereby presenting a significant challenge [140, 141]. In specific applications like energy storage and catalysis, HEOs must satisfy rigorous performance criteria. For example, electrode materials used in SOFCs must endure high temperatures and mechanical stresses [127]. Given the extensive compositional space involved, traditional experimental screening methods are inherently inefficient. Alternatively, leveraging high-throughput screening through theoretical calculations and simulations offers a promising avenue. This approach enables rapid evaluation of numerous material combinations, thereby expediting the discovery and optimization of novel materials [106, 142].

In figure 19, Kumbhakar *et al* demonstrated the synergistic potential of theoretical prediction and experimental validation [86]. They conducted a thorough assessment of 5300 two-dimensional octahedral oxohalides, identifying HEOs with significant electron mobility and energy levels compatible with solar cell architectures. Their screening revealed the reversible tuning capability of multivalent rare earth cations (e.g. Ce, Pr, Tb) on the bandgap under varying redox atmospheres, achieving bandgap adjustments from 2.0 to 3.5 eV. Hong *et al* integrated high-throughput synthesis, computational modeling, and machine learning techniques to establish a descriptor combination for predicting the formation of HEMs. This approach not only enhanced the efficiency of HEM discovery and design but also opened new avenues for applying high-throughput predictive methods in materials genomics engineering [143]. These examples underscore the potential of high-throughput computational techniques in advancing HEO research, providing robust tools and platforms from fundamental theoretical investigations to practical applications.

High-throughput computation and screening are increasingly pivotal in HEO research due to the intricate compositional space and rigorous performance demands. Traditional experimental methods struggle to meet these challenges. High-throughput computation rapidly evaluates numerous material combinations, thereby accelerating the discovery and optimization of new materials. Through integrating theoretical predictions with experimental validation, researchers have identified HEOs with tailored properties, making them promising for high-performance optoelectronic and energy storage applications. Machine learning and data-driven approaches further improve the efficiency and accuracy of high-throughput screening, offering fresh perspectives for materials genomics engineering applications. Despite the significant potential of high-throughput computation in HEO research, its application remains developmental compared to simpler oxides. Future efforts should focus on refining these computational methods to address the complexities of HEOs and collaborating closely with experimental research. This synergy will advance the science of HEOs and facilitate their practical application development.

4.6. AI and inverse design

In the review by Wang *et al*, which offers insights into the discovery and refinement of high-entropy energy materials through the age of big data, the authors posit that a foundational comprehension of the interplay between atomic-level processes, structures, properties, and performance is essential for the pre-screening and selection of prospective materials [111]. They contend that emerging computational technologies, such as AI and machine learning, can eclipse the constraints of traditional electronic structure methodologies, thereby enabling the exploration of complex material systems exhibiting novel phenomena. Furthermore, the integration of reverse engineering with high-throughput techniques and AI is anticipated to become a practical reality in laboratory settings, facilitating the autonomous fabrication and characterization of a diverse array of samples. This synergistic approach is projected to accelerate the advancement and utilization of HEMs in the realms of energy conversion and storage, particularly for materials with intricate compositions that are poised to redefine the landscape of new materials research.

The inverse design approach offers an innovative pathway for the systematic design of HEOs, starting from desired properties and deducing potential material compositions and structures. This approach guides researchers in purposefully designing novel HEOs, thereby enhancing the efficiency of material discovery and facilitating breakthroughs in performance [106]. In the prediction and identification of active sites on HEOs catalyst surfaces, establishing and optimizing clear thermodynamic and kinetic models is crucial. Utilizing machine learning tools for statistical analysis on large datasets enables effective screening and identification of new high-activity structural catalysts. The inherent long-range disorder of HEOs presents challenges for direct structural and property studies. However, computational methods such as the inverse structure mapping algorithm can simulate HEOs' microstructure, serving as a valuable complement to experimental investigations [133]. Various machine learning algorithms, including traditional methods and deep neural networks, play crucial roles in HEOs research. To establish robust machine learning models, comprehensive and precise data collection, feature engineering, and rigorous model training and selection through cross-validation are essential steps [138]. These advancements in computational techniques promise to further enhance the understanding and application of HEOs in optoelectronics and beyond, driving the field towards new frontiers of materials science.

Lin *et al* allocated Cr, Co, Fe, Mn, and Ni to lattice sites using crystal constants and formation energies derived from DFT calculations of the spinel structure as training data for machine learning models. Their study revealed that the distribution of different metal cations on the A and B sites of HEOs significantly influences lattice constants and formation energies [144]. Moreover, the formation energy of this lattice exhibits an inverse relationship with Cr content, and machine learning predictions align closely with DFT results, demonstrating deviations in lattice constants and formation energies of only 1%–2%. This approach using machine learning or neural networks marks a novel direction for investigating complex materials such as HEOs [141]. Machine learning methods offer efficient avenues for first-principles-based modeling and prediction in HEO research. Li *et al* employed high-throughput DFT calculations to generate extensive datasets, utilizing machine learning models for material characterization across various chemical structures [145]. Debnath *et al* explored the application of forward and inverse design paradigms in refractory HEAs design, investigating the potential of deep learning in material innovation [146]. Tetsassi Feugmo *et al* introduced a neuroevolutionary method combining artificial neural networks and evolutionary algorithms for structure generation in HEAs, achieving inverse design by analyzing distribution functions and atomic characteristics [147]. Kar *et al* applied reverse synthetic design to develop HEA nanoparticles, establishing design principles for colloidal synthesis of core–shell nanoparticles as precursors for predictable synthesis of dispersed HEA nanoparticles [148].

In figure 20, Li *et al* introduced an algorithm aimed at mapping the mesoscopic (above 50 nm) atomic disorder arrangement characteristics of high-entropy and multiphase materials [133]. They developed a novel reverse structure scaling top-down algorithm to optimize an equivalent supercell atomic model at the nanoscale. This approach provides significant guidance for cross-scale simulations of various material samples, including HEAs, HEOs, and multiphase organizational materials. Figure 21 illustrates the application of generative learning in accelerating the optimized design of dielectric HEOs. This method addresses the challenge of component dimensionality encountered during HEO development and employs reverse screening across five groups of HEOs. Through directed experiments, Li *et al* achieved an eightfold improvement in dielectric energy storage performance [149]. Zhou *et al* devised a generative adversarial neural network method that relies on human input to explore potential glass-forming regions within the alloy composition space. This approach proves particularly effective for navigating the intricate composition landscape of metallic HEOs glasses [150].

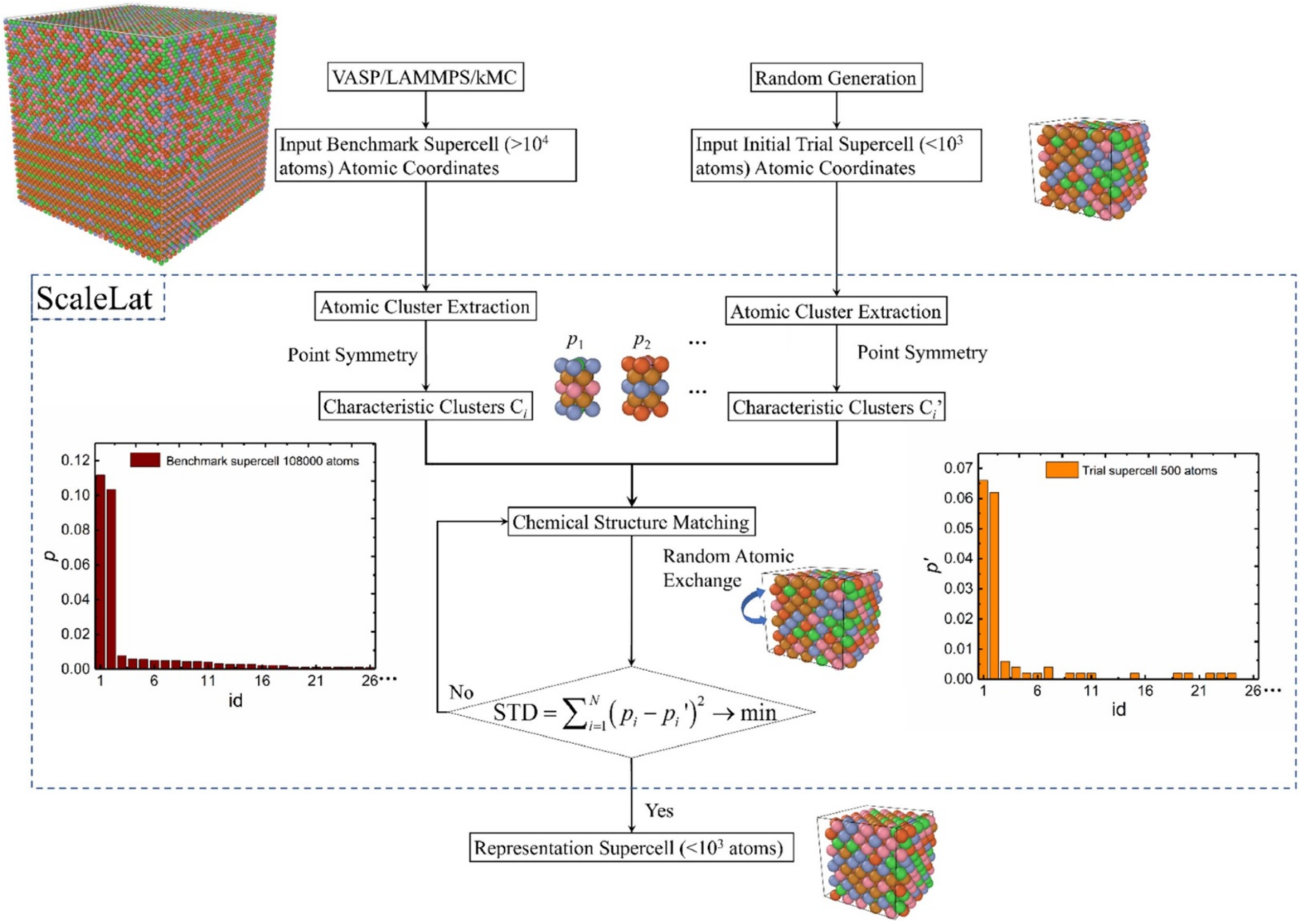

Figure 20. Workflow of the ScaleLat software for structural prediction. The diagram delineates two distinct computational pathways employed by the software, each tailored to leverage the atomic-scale specificity of material structures. Reprinted from [133], © 2024 Published by Elsevier B.V.

These advancements underscore the application of advanced computational techniques in the design and characterization of complex materials, paving the way for enhanced performance in various technological applications.

These research cases illustrate the pivotal role of AI and inverse design in the investigation of HEOs, advancing material design from empirical exploration to systematic rationalization and precision. The inverse design approach significantly enhances the prospect of discovering materials with novel properties by deducing potential compositions and structures that align with desired performance criteria. Coupled with high-throughput computing and machine learning methodologies, researchers can swiftly screen and pinpoint prospective high-performance HEOs, effectively mitigating the dimensional constraints in HEMs research. Machine learning models, particularly deep neural networks, exhibit substantial promise in analyzing the phase structure and stability of HEOs, as well as in constructing simulation models. Through meticulous analysis of training data and adept feature engineering, these models can predict the properties and behaviors of HEOs, providing robust theoretical underpinnings for experimental investigations. Furthermore, the deployment of advanced computational techniques like the inverse structure mapping algorithm offers profound insights into material structural characteristics spanning from macro-scale to nanoscale, thereby enhancing comprehension of the microstructure of HEOs. The development and application of these methodologies not only advance the systematic design of HEOs but also introduce fresh research paradigms to the field of materials science. In essence, AI and inverse design showcase formidable capabilities in HEO studies, unlocking novel pathways for discovering and utilizing future materials, heralding a more efficient and innovative new era in HEMs research and application.

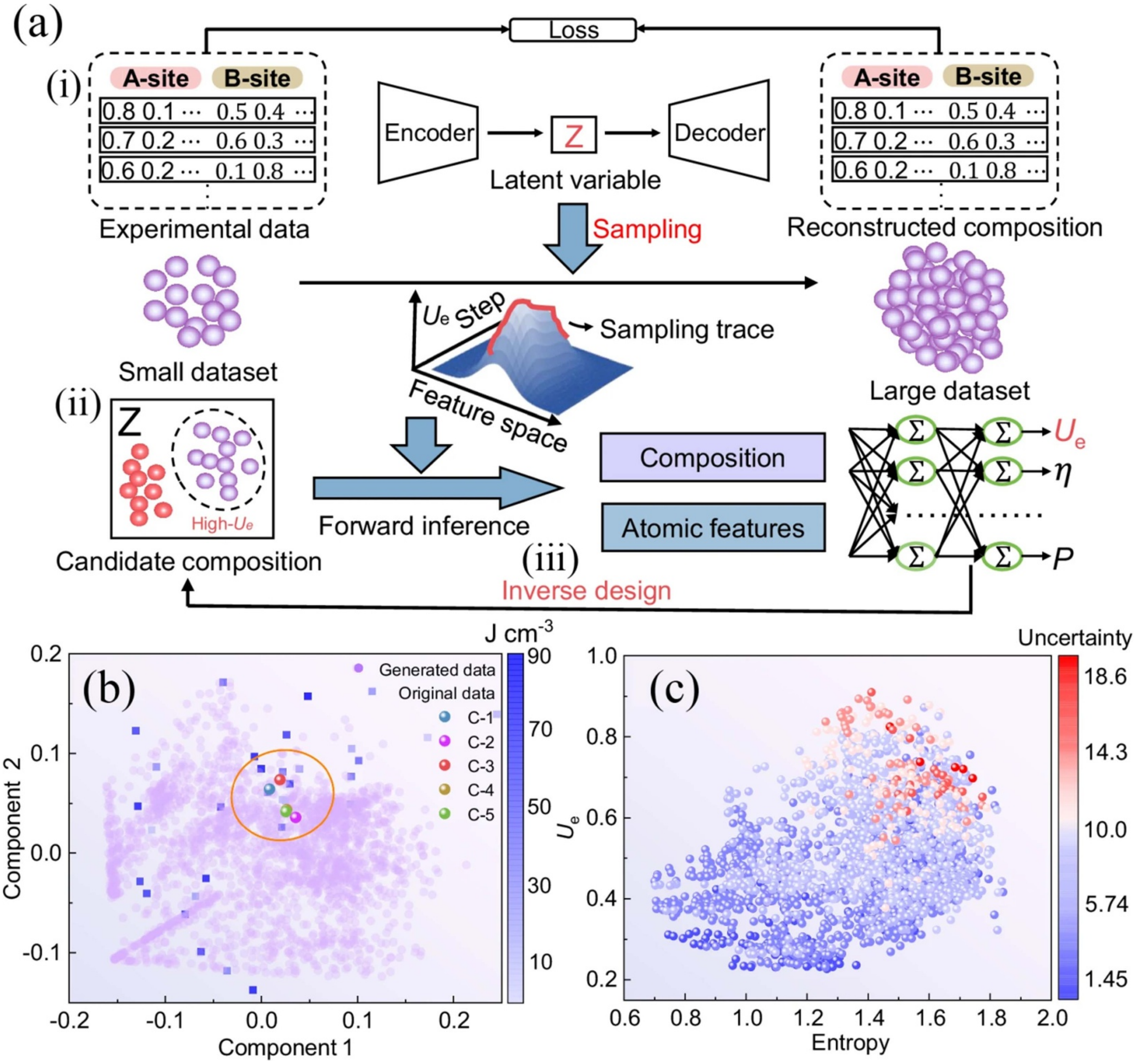

Figure 21. Generative learning approach to high-entropy dielectric material design. (a) The depicted framework outlines a three-step generative learning model for the design and discovery of high-entropy dielectric materials, encompassing: (i) the generation of latent space vectors z, (ii) the classification and sampling of material compositions, and (iii) the processes of forward inference and inverse design. (b) The latent space distribution is illustrated, with purple circles indicating the 2144 sets of high-performance data generated by the model, blue squares representing the original experimental datasets, and solid spheres of various colors corresponding to the five novel sets of components forecasted by the model. (c) A plot of entropy versus normalized internal energy (U_e) for potential materials is presented, with the color-coding of data points indicative of their associated uncertainty levels. Reproduced from [149]. CC BY 4.0.

5. Conclusions

HEOs represent a novel category of multi-principal-element oxides, distinguished by their exceptional physical, chemical, and electrochemical properties. These include the unique high-entropy effect, lattice distortion, sluggish diffusion, cocktail effect, and tunable electronic structure, alongside fundamental physicochemical properties and abundant active sites. In recent years, HEOs have garnered considerable attention for their applications in new energy technologies, particularly in electrochemical energy storage, electrocatalysis, and photo(electro)catalysis. The study of HEOs underscores their pivotal role in advancing energy technologies, heralding new opportunities for innovative applications and paving the way for future advancements in material science and energy research.

The challenges faced by HEOs are primarily twofold. Firstly, their preparation involves complexity and significant costs despite their promising performance, limiting their practical applicability. This complexity often leads to stability issues during synthesis and application, such as phase separation and structural distortion, further hindering their deployment. Secondly, theoretical calculations and design for HEOs present formidable challenges due to their intricate composition and structure. The complexity necessitates the development of robust thermodynamic and kinetic models to predict and identify optimal chemical catalytic reaction sites. Key research focuses include accurately predicting structure-performance relationships and designing new materials with specific functionalities. The development of HEOs as energy materials necessitates a comprehensive understanding of their vast principal component combination space, diverse crystal structures, versatile fundamental physicochemical properties, unique effects, and applications in new energy sectors, all rooted in the complexities of HEOs. To advance HEOs as energy materials, it is crucial to integrate material calculation and simulation closely with rational design.

6. Future perspectives

Despite inherent challenges in synthesis and practical deployment, the revolutionary potential of HEOs in the field of new energy technologies is enormous. The complexity of HEOs stems from the richness of their principal-element combination space, the diversity of their crystal structures, and the flexibility of their physical properties and effects. This requires that every step of the further development and development of HEOs be closely integrated with theoretical calculations and simulations, and that more advanced theoretical models be developed to effectively predict and determine the quantitative structure-activity relationship of HEOs, thereby unleashing their full potential. Recognizing these challenges, the following strategic research directions need to be closely monitored to effectively promote the transformative development of HEOs in the field of new energy technologies.

(1) Synthesis innovations: Paramount among future endeavors is the refinement of synthesis techniques. Emerging methods, such as molten salt processes and flash sintering, promise substantial reductions in production costs while enhancing purity and accessibility for commercial uses. These techniques are poised to yield HEOs with tailored morphologies and significantly elevated specific surface areas—attributes critical for maximizing catalytic site exposure and, consequently, catalytic efficiency.

(2) Advancements in characterization methods: The progression of *in-situ* characterization techniques will be essential for an intimate understanding of the microchemical structures of HEOs. Technologies such as 3D-APT and 4D-EELS offer ultra-high-resolution spatiotemporal analysis, permitting detailed observation of material behaviors under operational conditions, thereby enabling optimization of material properties *in situ*.

(3) Design of functional energy materials: The targeted design of new materials with bespoke functionalities represents a crucial research trajectory. Through strategic post-treatment modifications, it is possible to enhance the physicochemical attributes of HEOs, customizing them for specific applications such as energy storage and catalysis.

(4) Theoretical and computational advances: A profound comprehension of the unique properties of HEOs is indispensable. Advanced characterization tools coupled with theoretical calculations will play a pivotal role in elucidating the relationships between structure and performance, thereby laying a robust theoretical groundwork for material innovation. Moreover, enhancing theoretical calculation methodologies, particularly through the integration of machine learning, will facilitate the statistical analysis of vast datasets, enabling the prediction and identification of novel, highly active catalytic structures.

(5) Interdisciplinary collaborations: Strengthening interdisciplinary partnerships across materials science, chemistry, physics, and beyond is essential for the broad application of HEOs in emerging energy technologies. Such collaborations are likely to spur innovative solutions and breakthroughs in the field.

(6) Exploration of energy applications: The investigation of HEOs across diverse catalytic reactions—including but not restricted to CO oxidation, CO_2 hydrogenation, and electrocatalysis in lithium–sulfur batteries—offers a fertile ground for research. Developing HEOs with distinctive structural features, such as cation defects and activated lattice oxygen, could further augment their catalytic efficacy. Additionally, exploring the potential of HEOs in nascent areas like photocatalysis and thermocatalysis might open new avenues for energy conversion technologies.

The journey ahead for HEOs is complex but filled with promise. An integrated approach that combines computational modeling, material synthesis, and rational design will accelerate the development of HEOs as next-generation energy materials, leading to significant contributions to the field of energy science and technology.

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Author contributions

Yang Z collected and organized literature, and wrote the original paper; Xiang X and Yang J reviewed and revised the paper; Zhao Z -Y proposed ideas, organized literature, reviewed and revised the paper.

Conflict of interest

The authors declare no conflict of interest.

ORCID iD

Zong-Yan Zhao https://orcid.org/0000-0001-8953-3150

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