

REVIEW OPEN ACCESS

Ultrasmall High-Entropy Materials: Nanoscale Effects, Synthesis, and Mechanistic Insights

Yueyue He¹  | Wenbo Wang² | Simon Schweidler¹ | Yanjiao Ma³  | Ben Breitung¹ | Torsten Brezesinski¹ 
¹Institute of Nanotechnology (INT), Karlsruhe Institute of Technology (KIT), Karlsruhe, Germany | ²Helmholtz Institute Ulm (HIU), Ulm, Germany | ³School of Energy and Mechanical Engineering, Nanjing Normal University, Nanjing, China

Correspondence: Yueyue He (yueyue.he@kit.edu)

Received: 5 March 2026 | **Revised:** 9 May 2026 | **Accepted:** 25 May 2026

Keywords: compositionally complex materials | enthalpy | entropy | kinetics | nanoscale effects

ABSTRACT

Ultrasmall high-entropy nanomaterials (USHENMs, <10 nm) merge multicomponent chemistry with size-dependent effects, forming a distinct class of materials with unprecedented properties. This review presents a focused overview of USHENMs and their key advantages, including high defect densities, strong atomic interactions, abundant active sites, fast reaction kinetics, and unique binding energetics. To rationalize their formation, we classify recent synthesis strategies according to the dominant driving force, namely entropy, kinetics, or enthalpy. Entropy-driven routes, commonly involving high-temperature melting-fusion-solidification processes, exploit configurational entropy and enable single-phase USHENMs through various established approaches. Kinetically controlled methods, guided by the LaMer nucleation-growth model, offer effective ways to controlling size and provide the most accessible means of reliably achieving sub-10 nm particles under low-temperature conditions. In contrast, enthalpy-driven routes are rarely reported, and producing USHENMs is particularly challenging because growth is dominated by sluggish, diffusion-controlled processes. At such extreme dimensions, surface and interface enthalpies determine phase stability, even when (bulk) thermodynamics predicts segregation. Finally, the review concludes by emphasizing future needs in long-term stabilization, in situ characterization, and machine-learning-assisted discovery to accelerate progress in materials design and expand application possibilities.

1 | Introduction

Ultrasmall nanomaterials are generally defined as particles with dimensions below 10 nm, often in the range of 1–5 nm. At this scale, the majority of atoms are located on or near the surface, giving rise to properties different from larger nanoparticles or bulk materials [1–7]. These ultrasmall systems have become increasingly important across diverse fields, including electronics [3, 8, 9], energy storage and conversion [10–16], and environmental technologies, where precise control over particle size is critical for achieving desired performance [17–20]. In this context, the concept of ultrasmall high-entropy nanomaterials (USHENMs) has recently gained attention, combining the intrinsic advantages

of nanoscale materials with the compositional diversity of high-entropy systems [21, 22].

The term “high entropy” has been increasingly explored in materials science, particularly for the design and synthesis of nanomaterials with potentially enhanced structural and functional properties [23–27]. Originally proposed in 2004 for metallic alloys [28], the high-entropy concept describes materials composed of five or more principal elements (each typically contributing 5–35 at.%), where the resulting high configurational entropy can promote the formation of single-phase solid solutions, even among elements that are otherwise immiscible, particularly at elevated temperatures. This endows high-entropy materials (HEMs) with

This is an open access article under the terms of the [Creative Commons Attribution](https://creativecommons.org/licenses/by/4.0/) License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited.

© 2026 The Author(s). *Advanced Functional Materials* published by Wiley-VCH GmbH

exceptional tunability and functional diversity, allowing their compositions to be tailored to meet the requirements of targeted applications [23, 29–32]. Consequently, high-entropy systems, characterized by random atomic distributions and vast compositional space, generate strong synergistic effects that surpass the performance of conventional single- or two-component materials [23, 33–36].

In recent years, the development of HEMs has expanded far beyond their metallic roots. While high-entropy oxides (HEOs) demonstrated the potential of entropy stabilization in 2015 [37], subsequent breakthroughs have extended the concept to ceramics [37–41], chalcogenides [42, 43], MXenes [44–46], metal-organic frameworks (MOFs) [47, 48], polyanionic compounds [49–51], and other material classes [52–62]. Most reviews to date have examined HEMs from a general perspective, covering compositions, synthesis methods, and applications, but have placed relatively little emphasis on the ultrasmall size range [63–65]. Inspired by the work of Wang et al. [66], who were among the first to describe HEMs from the macroscopic to the sub-nanometer scale and highlighted the significance of nanoscale effects, the role of particle size has become increasingly important [21, 67]. However, the majority of reviews published over the years have advanced the field in complementary directions without explicitly focusing on size effects, although numerous studies report on ultrasmall systems [68–70]. For example, Yang et al. recently provided a comprehensive overview of major synthesis strategies for high-entropy nanoparticles, but their analysis spans sizes from the nanometer to the micrometer level and does not emphasize the unique potential associated with USHENMs [23]. Likewise, Yao et al. presented a multidisciplinary perspective covering synthesis, characterization, catalysis, high-throughput screening, and data-driven discovery, yet without dedicated discussion of size-dependent behavior below 10 nm [26]. Zhou et al. examined the influence of the high-entropy concept on electrochemical performance, but their analysis does not address how reducing HEMs to the ultrasmall size range alters structural stability or functionality [71]. Collectively, these studies underscore the need for a focused review dedicated to sub-10 nm HENMs, where size plays a central and transformative role in determining structure, stability, and functionality, and new phenomena emerge.

So far, numerous studies across diverse fields have demonstrated that reducing size of HEMs unlocks markedly different and often superior properties compared to their bulk counterparts [66, 71–79]. For example, in biomedicine [22, 80], Ai et al. reported on single-atom PtPdRuRhIr (~1.5 nm) exhibiting peroxidase-like activity that catalyzes endogenous hydrogen peroxide into toxic hydroxyl radicals, enabling effective cancer cell ablation through the synergistic action of enzymatic and photothermal effects. In catalysis [21, 64, 81], Chen et al. demonstrated that ~2 nm PtFeCoNiCuZn intermetallics achieve an ultrahigh mass activity of 2.403 A mg_{Pt}⁻¹ at 0.90 V vs. reversible hydrogen electrode (RHE) for the oxygen reduction reaction, that is, up to 19 times higher than that of commercial Pt/C [82]. Similarly, in electrochemical energy storage [36, 83], Ren et al. showed that USHENMs with abundant active sites are capable of accelerating the oxygen reduction and evolution reactions, enabling quasi-solid-state zinc-air batteries with a power density of 545 mW cm⁻² and stable operation over 165 h at 50 mA cm⁻². In the field of electronics, Yoo et al. developed single-crystalline (MgCoNiCuZn)O

films on epitaxial electrodes for memristor applications [84]. Local structural disordering within the ultrathin films provides customized electronic properties, rendering these devices highly promising for advanced spatiotemporal data-processing systems. Furthermore, recent developments include systems with 10 or more principal elements, in extreme cases even up to 25 [11, 24, 26, 40, 85–88]. Nevertheless, comprehensive summaries of the advantages, synthesis strategies, and formation mechanisms of USHENMs remain scarce.

In this review, we focus on sub-10 nm HENMs, referred to as USHENMs, and highlight the unique advantages that emerge as particle size decreases (Figure 1). We define 1–5 nm as the ultrasmall range and classify 5–10 nm as the transition range. We systematically summarize accessible synthesis strategies, categorized into entropy-, kinetics-, and enthalpy-driven routes, and discuss how each determines particle size. Entropy-driven approaches, typically based on high-temperature melting-fusion-solidification, can yield ultrasmall particles through five main strategies: (i) ultrafast heating and cooling; (ii) localized energy input; (iii) spatial confinement; (iv) matching of precursor properties; and (v) using low-diffusivity supports. Kinetics-driven approaches, guided by the LaMer nucleation-growth model, enable synthesis at low or ambient temperatures. Representative strategies include: (i) using strong reducing agents or highly reactive precursors for burst nucleation; (ii) inducing nucleation through rapid thermal fluctuations; (iii) using high energy input to trigger ultrafast reactions; and (iv) promoting rapid nucleation at moderate temperatures within short reaction windows. In contrast, enthalpy-driven reaction pathways are rarely described, and their mechanisms for size control remain poorly understood, underscoring the need for additional investigations.

Overall, this review establishes a roadmap outlining the unique advantages, synthesis strategies, and formation mechanisms of USHENMs. By bridging nanoscale design principles with compositional complexity, it paves the way for the rational development of next-generation materials, opening new frontiers in catalysis, energy storage, and beyond.

2 | High-Entropy Nanomaterials

2.1 | Size Effects

As shown in Figure 2a, four fundamental effects—high entropy of mixing, sluggish diffusion, lattice distortions, and cocktail effects—are universally observed in HEMs [34, 95]. Instead of a periodic arrangement of one or two types of atoms, they exhibit a random distribution of various types on the same sublattice. This suppresses long-range order and rather results in the formation of disordered solid solutions. Each site experiences a distinct chemical environment, altering local bonding, charge distribution, and electronic structure. Moreover, atomic size mismatches induce compressive and tensile stresses, giving rise to lattice distortions [96]. These distortions diminish the periodicity of the lattice, thereby broadening diffraction peaks and reducing crystal symmetry. Cocktail effects arise from synergistic interactions between the species, while sluggish diffusion reduces ion mobility due to different potential energies of the constituent elements, effectively inhibiting particle agglomeration and

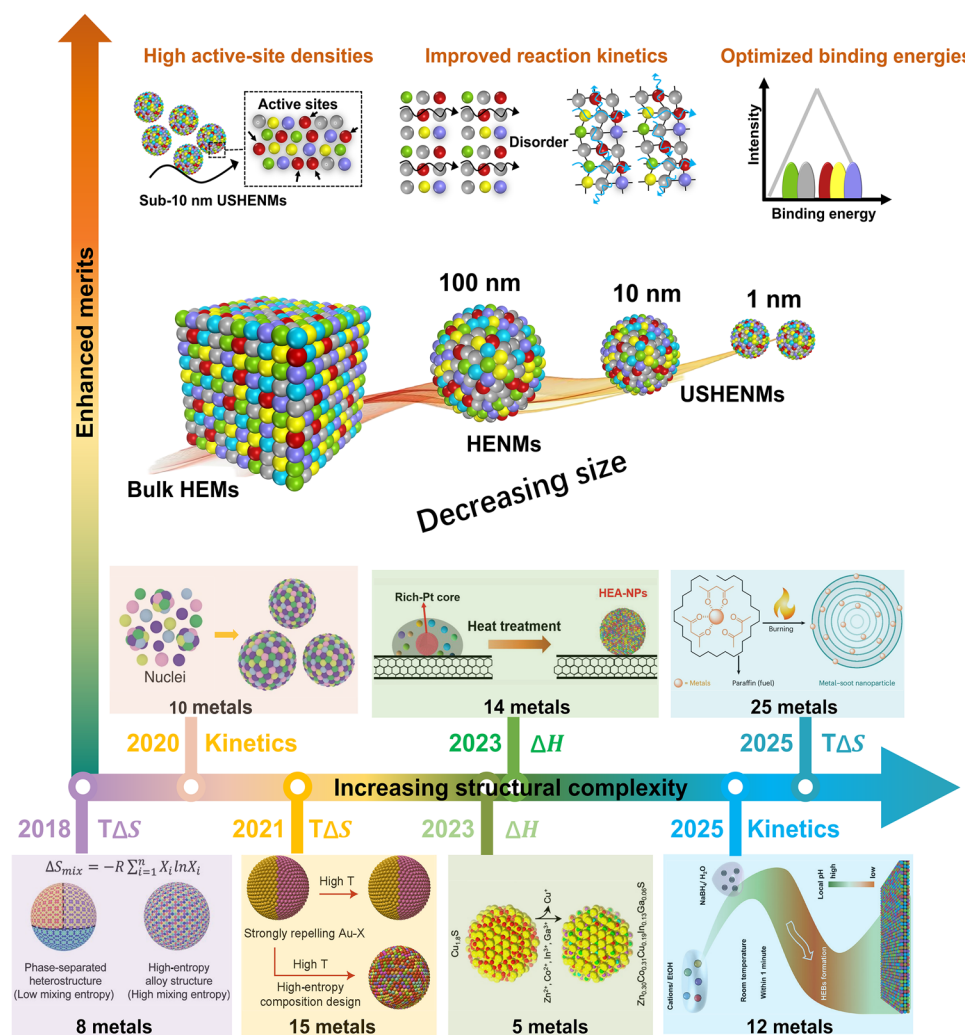


FIGURE 1 | Schematic illustration of the downsizing process, from bulk HEMs to USHENMs, highlighting their key attributes and application potential resulting from increasing structural and compositional complexity. Reproduced with permission [89]. Copyright 2018, American Association for the Advancement of Science. Reproduced from [90]. CC BY 4.0. Reproduced with permission [91]. Copyright 2021, Elsevier. Reproduced with permission [92]. Copyright 2023, American Chemical Society. Reproduced with permission [93]. Copyright 2023, Wiley-VCH GmbH. Reproduced with permission [40]. Copyright 2025, Springer Nature. Reproduced with permission [94]. Copyright 2025, Wiley-VCH GmbH.

preserving nanocrystal integrity during synthesis. Although these effects have been extensively studied in HEMs, their severity in the size range below 10 nm is largely unexplored and is likely to be underestimated [97, 98].

Defects: Classical effects may change in the sub-10 nm size range, as defects in ultrasmall particles often shift from bulk-type (vacancies, dislocations, etc.) to surface-dominated structural ones (disorder). Continuous dislocations in crystals smaller than 5 nm in diameter are rare, leading to increasing non-stoichiometry, bond distortions, and amorphization (rather than well-defined line dislocations). More specifically, when a USHENM is formed, more than half of its atoms reside at or near the surface. At this scale, the material's behavior is determined not only by compositional disorder, but also by pronounced surface and finite-size effects, as well as by curvature-induced strain. Each nanoparticle or nanograin has limited space for strain relaxation, eventually causing local stresses to accumulate. The curved surface and confined volume force atoms into non-ideal lattice positions, further increasing internal

stress/strain. Under these conditions, defect formation becomes energetically favorable, as they can reduce local stresses and lower the total free energy of the system. Consequently, in USHENMs, defects are not merely structural anomalies, but key contributors to their properties. It should also be noted that lattice diffusion in USHENMs is faster than the sluggish diffusion observed in bulk HEMs due to their dimensions. For example, a library of USHENMs, including oxides, nitrides, and borides, has been developed as electrocatalysts for water splitting [25]. They were found to exhibit superior performance owing to the presence of distinct lattice distortions and unsaturated coordination sites, which enhance catalytic activity. Similarly, Sun et al. reported that the resulting USHENMs (nanowires) exhibit pronounced lattice distortions [99], thus modulating the electronic structure [68]. As a representative example of increased structural defects, Niu et al. synthesized nanoscale (MoWVNbTa)C through wire-cut electrical discharge machining of bulk material (Figure 2b) [75]. The sub-10 nm particles, enriched with vacancies, stacking faults, and pronounced lattice distortions (Figure 2c), showed promising catalytic activity

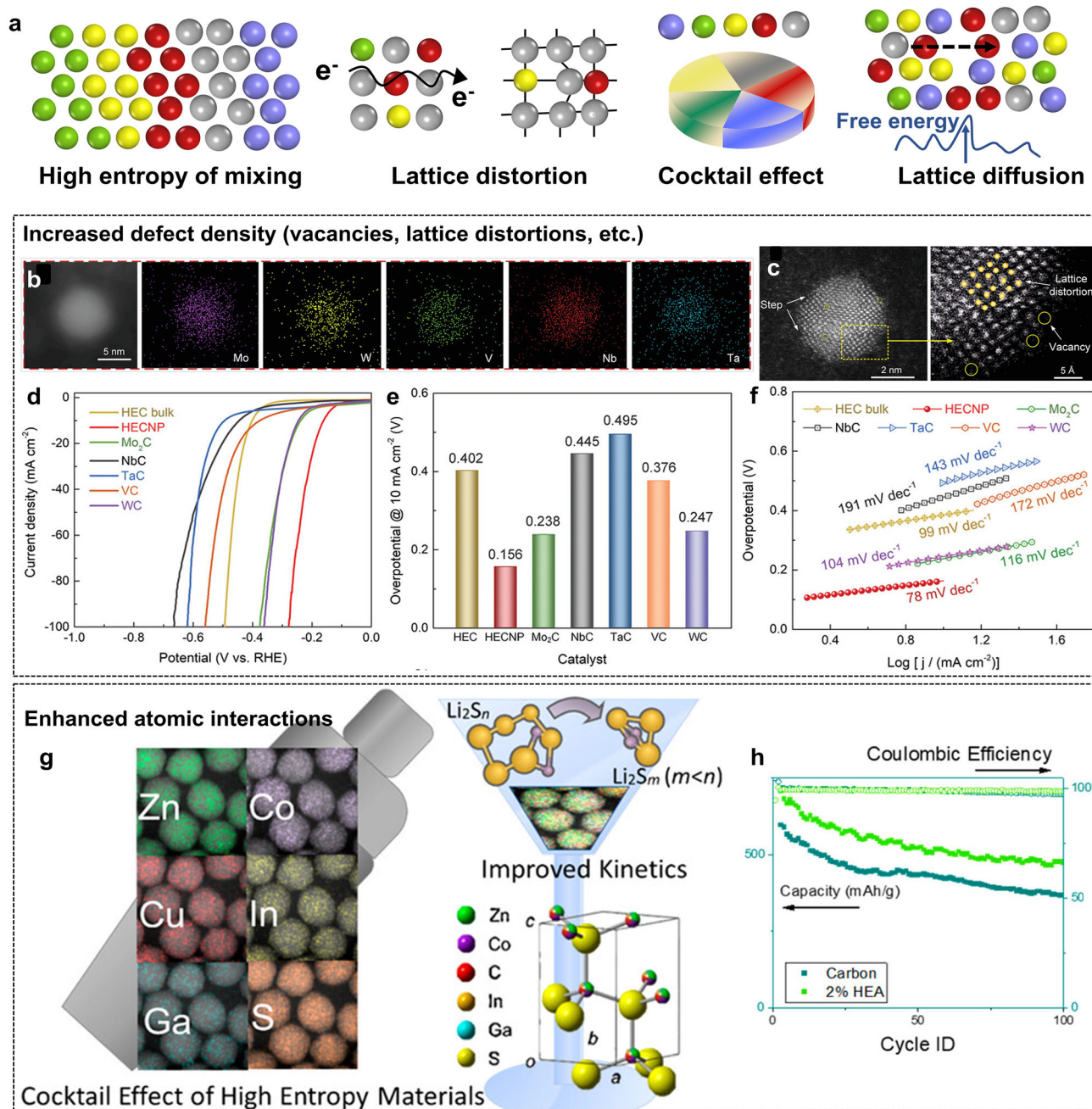


FIGURE 2 | (a) Schematic illustration summarizing four key attributes of HENMs, namely high entropy of mixing, lattice distortions, cocktail effects, and sluggish diffusion. Structural defects in carbide USHENMs and their electrocatalytic performance for the HER in 0.5 M H₂SO₄: (b,c) HAADF-STEM images with corresponding elemental maps and enlarged local views, (d) linear sweep voltammetry curves, (e) overpotentials at a current density of 10 mA cm⁻² (η^{10}), and (f) Tafel slopes. Reproduced with permission [75]. Copyright 2022, Wiley-VCH GmbH. (g,h) Enhanced atomic interactions in USHENMs lead to improved performance of the sulfur cathode in lithium-sulfur batteries. Reproduced with permission [92]. Copyright 2023, American Chemical Society.

(Figure 2d–f) and durability for the hydrogen evolution reaction (HER).

Atomic interactions: While HEMs are often idealized as having fully random atomic distributions, in practice, they exhibit short-range order. In USHENMs, short-range ordering can be more pronounced due to strong surface effects and distinct local interactions. At ultrasmall dimensions, atoms are closely confined, with many occupying low-coordination surface or

interfacial sites. This confinement enhances orbital overlap and charge transfer between dissimilar atoms, increasing the coupling among different elements. The resulting hybridized electronic states can optimize bonding and catalytic activity, thereby enhancing synergistic effects. For example, Theibault et al. reported on (Zn_{0.30}Co_{0.31}Cu_{0.19}In_{0.13}Ga_{0.06})S, where uniformly distributed, nanosized sulfide nanoparticles exhibit a pronounced “cocktail effect” (Figure 2g) [92]. The synergistic interactions between the different atoms effectively mitigate the polysulfide

shuttle phenomenon, resulting in long-term cycling stability in lithium-sulfur batteries (Figure 2h). As another example, very recently, Zhang et al. reported on sub-3 nm PtRuFeCoNiCu particles, densely anchored on carbon fiber paper, exhibiting unique surface functionalities [67]. Specifically, Ru-rich regions facilitate H₂O dissociation, FeCoNiCu sites positively affect hydrogen diffusion kinetics, and Pt-rich regions promote efficient hydrogen recombination. This synergy of dissociation, diffusion, and recombination on the surface of USHENMs enables a record-level HER performance among known catalysts.

In addition to the advantages mentioned above, the benefits of USHENMs can be broadly divided into three main aspects: (i) high active-site density, (ii) accelerated reaction kinetics, and (iii) optimized binding energies.

Active-site density: In bulk materials, most atoms are located deep within the crystal lattice and do not directly interact with the environment, so only a small fraction, those at the surface/interface, is functionally active. USHENMs overcome this limitation because the entire nanoparticle can behave like an “all-surface structure,” in which nearly every atom has catalytic or reactive potential. Their exceptionally high surface-to-volume ratio greatly increases the number of accessible surface atoms per unit mass, thereby maximizing utilization and allowing a much larger fraction of atoms to serve directly as active sites. As an example, Cai et al. recently demonstrated a clear correlation between size and catalytic performance in a series of PtRuPdCoNi particles with precisely controlled sizes of 1.7, 2.3, 3.0, and 3.9 nm (Figure 3a,b) [72]. The smaller ones exhibited increased activity for both the HER and oxygen reduction reaction (ORR), clearly outperforming commercial Pt/C catalysts. Specifically, a reduction in HENM size leads to enhanced HER, due to increased surface atom exposure (density of active sites) [21]. This has been further evidenced by Feng et al. [100], who recently reported that 1.48 nm NiCoMoPtRu nanoclusters exhibit a high mass activity of 12.85 A mg⁻¹ (normalized to the noble metals) for the HER at -0.07 V vs. RHE, nearly twice that of their 6 nm counterparts (6.51 A mg⁻¹) under identical conditions. Feng et al. also reported on ordered 6 nm PtIrFeCoCu particles supported on carbon, featuring a high density of active facets [101]. Theoretical calculations combined with experimental results revealed that the superior ORR performance of HENMs primarily originates from the formation of highly active facets, particularly the (100) facet. Last but not least, Jo et al. compared CoFeNiMoWTe nanosheet arrays (~10 nm) with a spherical CoFeNiMoW counterpart (~100 nm) [102]. The porous nanosheet architecture provides numerous active sites and demonstrated high performance in the (acidic) oxygen evolution reaction (OER) with low overpotential and stable operation for more than 100 h, outperforming the larger particles. When applied in proton exchange membrane water electrolysis, the catalyst achieves 1 A cm⁻² at only 1.81 V and maintained long-term stability with minimal degradation.

Overall, it is evident that USHENMs maximize the utilization of surface atoms, with the exposed ones serving as genuine active sites, thus delivering competitive performance compared to their bulk counterparts [103, 104].

Reaction kinetics: USHENMs exhibit an exceptionally high surface-to-volume ratio, exposing a large fraction of atoms for

catalytic or reactive processes. Their multielement composition produces a chemically diverse surface with numerous active sites, each offering distinct adsorption energies and reaction pathways. This heterogeneity enables reactants (molecules) to find favorable binding configurations, thereby lowering activation barriers and accelerating surface reactions. Moreover, the reduced particle size shortens the average path lengths for charge transport, minimizing resistance and enabling rapid exchange between active material and reactant(s) (Figure 3c). For example, Zheng et al. demonstrated a 5 nm (NiFeCoCuSnMo)O system (Figure 3d), where the dense active sites significantly accelerate redox kinetics in all-solid-state lithium-sulfur batteries by lowering the free energy barrier across the entire sulfur conversion reaction [105, 106]. Similarly, Yang et al. reported a USHENM cathode (Mn_{0.25}Co_{0.25}Ni_{0.25}Cu_{0.25}Fe₂)C for organosulfur batteries, in which the embedded HENMs not only accelerate the reaction kinetics, but also effectively anchor soluble sulfur species, thus suppressing the shuttle effect while reducing the activation energy of redox processes [107]. As a result, the cathode delivers a high initial specific capacity of 527 mAh g⁻¹ at 0.5C and demonstrated good cyclability over 500 cycles, with minimal capacity decay of only 0.078% per cycle. Last but not least, Liao et al. reported that K(Mg_{0.2}Mn_{0.2}Fe_{0.2}Co_{0.2}Ni_{0.2})F₃ (HE-KMF₃) embedded in carbon nanofibers (CNFs) exhibits a higher surface energy and reactivity than single-component KMF₃, enabling strong binding to the CNFs and limiting fluoride nanoparticle growth (~10 nm) [36]. Aside from high-entropy effects, the reduction in particle size shortens the path lengths for ion and electron transport, while the nanoparticle-embedded CNFs promote the formation of a robust mixed-conducting network. As a cathode in potassium-ion batteries, HE-KMF₃@CNFs delivers a reversible specific capacity of 122 mAh g⁻¹ at 20 mA g⁻¹ and shows high stability over 5000 cycles at 500 mA g⁻¹. These studies collectively highlight that downsizing HENMs is a highly effective strategy to accelerate reaction kinetics, overcome energy barriers, and stabilize long-term electrochemical performance.

Binding energy: In USHENMs, the close proximity of dissimilar elements promotes strong electronic hybridization and charge redistribution across the lattice. This interaction modifies the local density of electronic states near the Fermi level, thereby optimizing adsorption energies for intermediates and facilitating electron transfer during redox processes. Maximizing the activity of nanoparticle catalysts requires active sites that bind reactants, intermediates, and products with optimal strength. As described by the Sabatier principle, nanoparticle catalytic performance follows a “volcano” trend, with peak activity achieved when binding is neither too weak nor too strong [63, 108]. In USHENMs, compositional tuning adjusts the *d*-band energy, while short- and long-range interactions between the binding atom(s) and their neighbors modulate the surface electronic structure. Careful selection of elements and stoichiometry in USHENMs enables a near-continuous distribution of binding energies (Figure 3e). Importantly, reducing particle size further shifts binding toward the Sabatier optimum, as the high fraction of low-coordination surface atoms and altered local electronic environments favor intermediate-strength adsorption. This synergy of size and composition allows USHENMs to achieve near-ideal binding energies and thereby maximizes catalytic activity. As an example, density functional theory (DFT) calculations by Cai et al. showed that orbital hybridization engineering combined with nanoscale

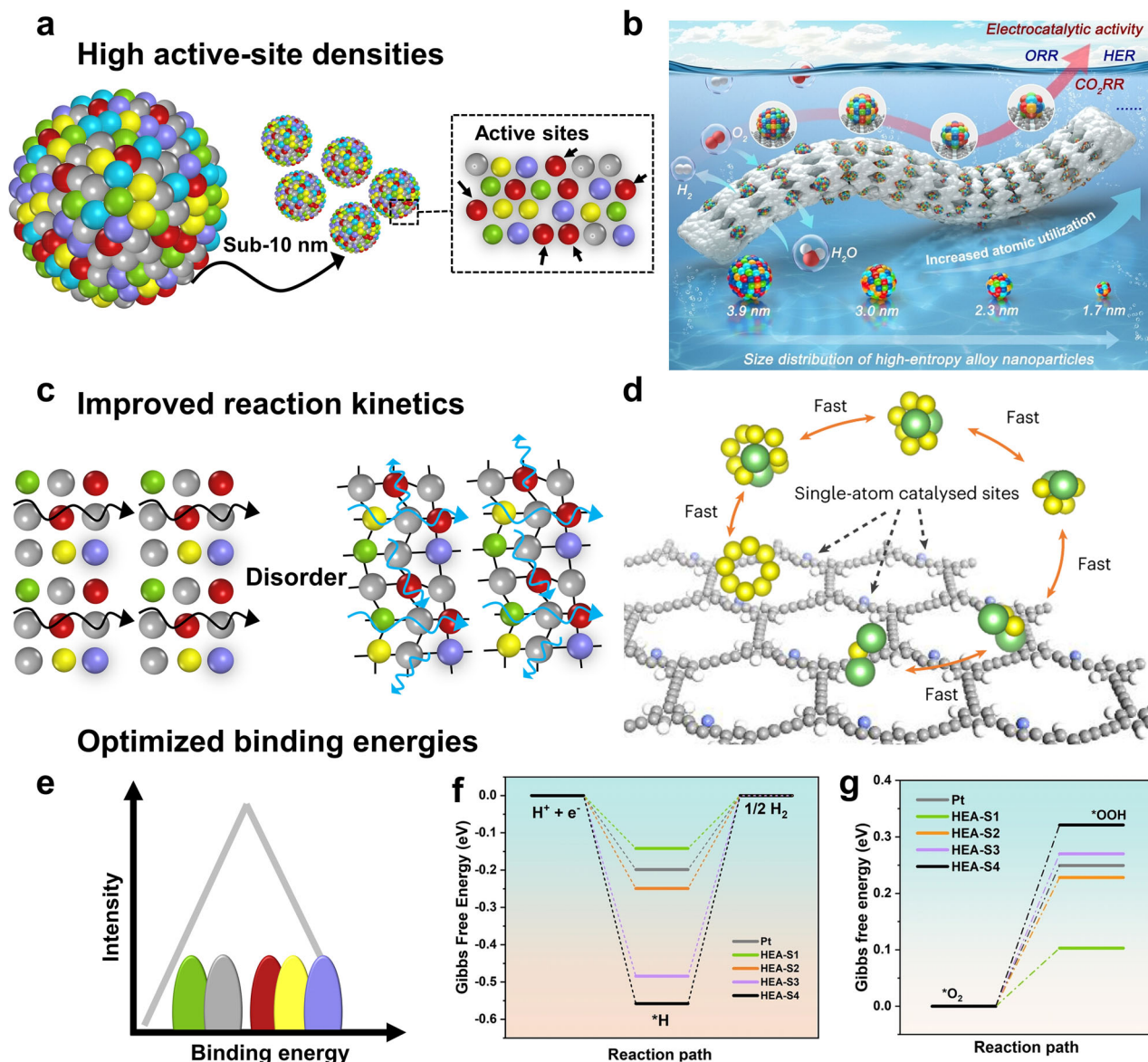


FIGURE 3 | Size effects in USHENMs. (a) Schematic illustration of high active-site densities and (b) corresponding improved catalytic activity toward HER and ORR. Reproduced with permission [72]. Copyright 2025, Wiley-VCH GmbH. (c) Schematic illustration of accelerated reaction kinetics and (d) corresponding improvement in lithium-sulfur solid-state batteries. Reproduced with permission [105]. Copyright 2023, Springer Nature. (e) Schematic of USHENM surfaces with representative binding energy patterns for on-top adsorption of reactants on an idealized infinite single-crystal lattice (excluding step, edge, and defect sites). (f) Calculated hydrogen-adsorption free energy on Pt and HENMs (alloys) with four different sizes, showing reduced energy barriers, and (g) free-energy diagrams of the ORR pathway ($\text{O}_2 \rightarrow \text{OOH}$). Reproduced with permission [72]. Copyright 2025, Wiley-VCH GmbH.

confinement can effectively lower reaction barriers and accelerate reaction kinetics [109]. In particular, smaller particles reduce the hydrogenation barriers of key intermediates, including $\text{O}_2 \rightarrow \text{OOH}$, $\text{CO}_2 \rightarrow \text{COOH}$, and $\text{NO} \rightarrow \text{NHO}$, while optimizing the hydrogen binding energy [72]. Remarkably, the Gibbs free energy for OOH formation on the smallest particles (HEA-S1) is only 0.177 eV, significantly lower than that of larger ones, indicating that size reduction positively affects the electronic structure and enhances electrocatalytic performance (Figure 3f,g).

Finally, the reduced size of HENMs greatly increases the likelihood of defect formation, enhanced atomic interactions, high active-site densities, accelerated reaction kinetics, and optimized

binding energies [69]. Despite these advantages, a comprehensive understanding of nanoscale effects in USHENMs remains limited. In particular, the complex interplay between defect formation and multielement electronic interactions is not yet fully understood and further theoretical and experimental studies are required to unravel how they affect activity and stability.

2.2 | Synthesis

Despite their advantages, USHENMs present substantial challenges in synthesis. Their preparation generally relies on two strategies: (i) top-down methods, which break down bulk HEMs

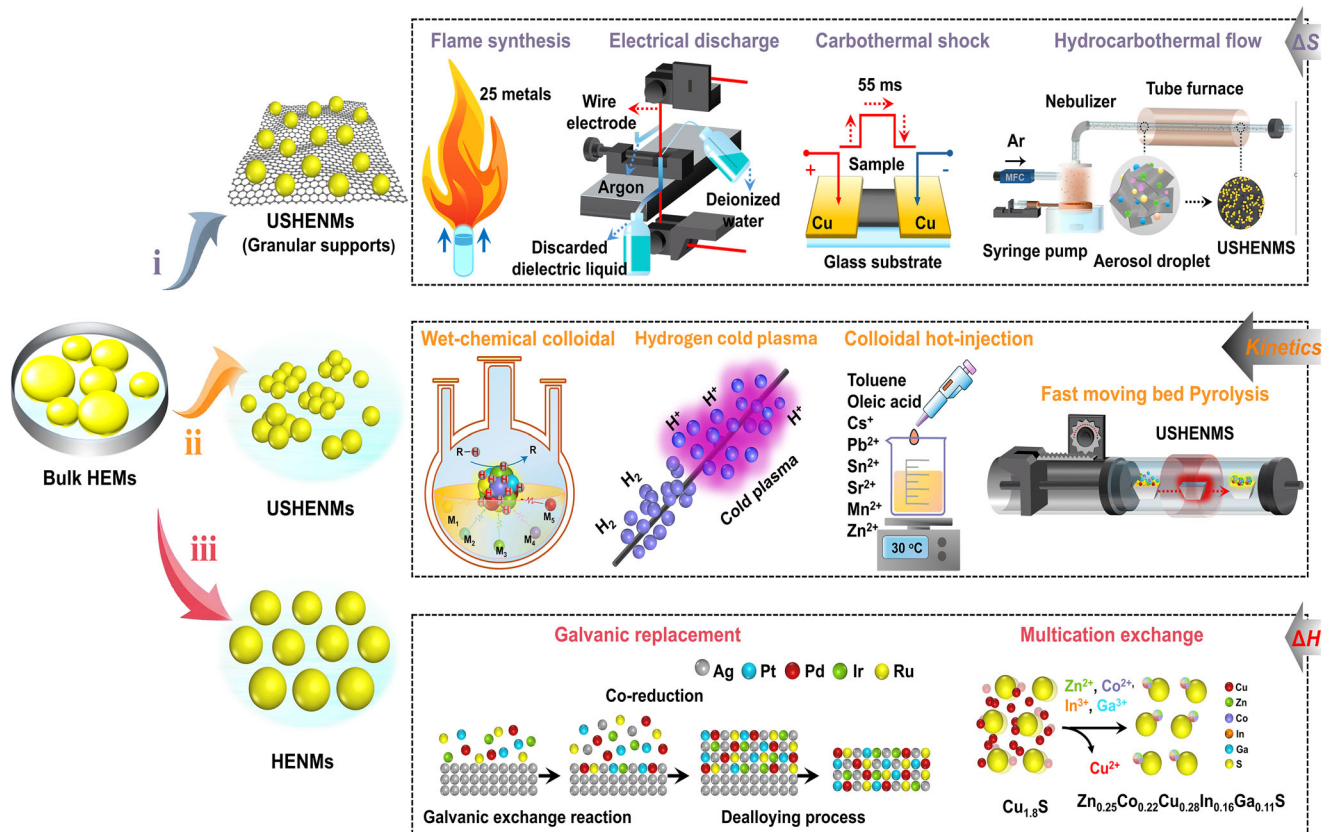


FIGURE 4 | Schematic summary of the existing synthesis methods for USHENMs and their corresponding formation mechanisms. Adapted with permission [40]. Copyright 2025, Springer Nature. Adapted with permission [75]. Copyright 2022, Wiley-VCH GmbH. Adapted with permission [89]. Copyright 2018, American Association for the Advancement of Science. Adapted from [103]. CC BY 4.0. Adapted with permission [110]. Copyright 2025, American Chemical Society. Adapted with permission [76]. Copyright 2022, American Chemical Society. Adapted with permission [30]. Copyright 2025, Wiley-VCH GmbH. Adapted from [90]. CC BY 4.0. Adapted with permission [111]. Copyright 2022, American Chemical Society. Adapted with permission [112]. Copyright 2021, American Chemical Society.

into smaller particles through disassembly or recrystallization, and (ii) bottom-up methods, which directly construct USHENMs from atomic, ionic, or molecular precursors [21, 23]. While the top-down approach is conceptually straightforward, it depends on bulk materials that must first be produced via high-temperature processes, making the overall route energy-intensive and costly due to the additional fragmentation steps. By contrast, bottom-up methods bypass the bulk precursor stage, involve fewer synthesis steps, and are therefore more versatile and energy-efficient, offering greater potential for scalable production of USHENMs. However, achieving uniform atomic-level mixing (compositional homogeneity) remains inherently challenging at the nanoscale. The high surface energy of sub-10 nm particles often induces element segregation, structural instability, and agglomeration during storage and/or electrochemical operation, thus necessitating more stringent synthesis conditions (Figure 4). To address these challenges, the following section discusses recent strategies for realizing high-quality USHENMs.

The formation of USHENMs can be governed by three distinct driving forces: entropy, kinetics, or enthalpy. Since the dominant factor varies among these pathways, we summarize the key aspects underlying USHENM formation and elaborate on the corresponding mechanisms for each route. Although this review clearly distinguishes the contributions of entropy-, enthalpy-,

and kinetics-driven routes, synthesis is typically determined by a complex interplay among these factors. In practice, one can usually identify only the major contribution for a specific method. Therefore, this paper emphasizes the primary driving forces for USHENM formation while recognizing that even when entropy plays a major role at high temperatures, kinetic effects can still exert local effects.

2.2.1 | Entropy-Driven Routes

Entropy-driven formation of USHENMs typically occurs at high temperatures, where configurational entropy becomes the dominant thermodynamic driving force stabilizing multielement solid solutions [Figure 4(i)]. Note that high configurational entropy arises from the random distribution of different elements across equivalent lattice sites. The associated $T\Delta S$ term can compensate for positive mixing enthalpies ($\Delta G = \Delta H - T\Delta S$), enabling a metastable or thermodynamically favored mixed phase. Although high temperatures are often required for the formation of USHENMs in entropy-driven approaches, such conditions can also accelerate atomic diffusion, grain growth, and particle agglomeration, thereby compromising compositional uniformity and performance. To address these challenges, it is important to overcome diffusion barriers among immiscible metals, suppress

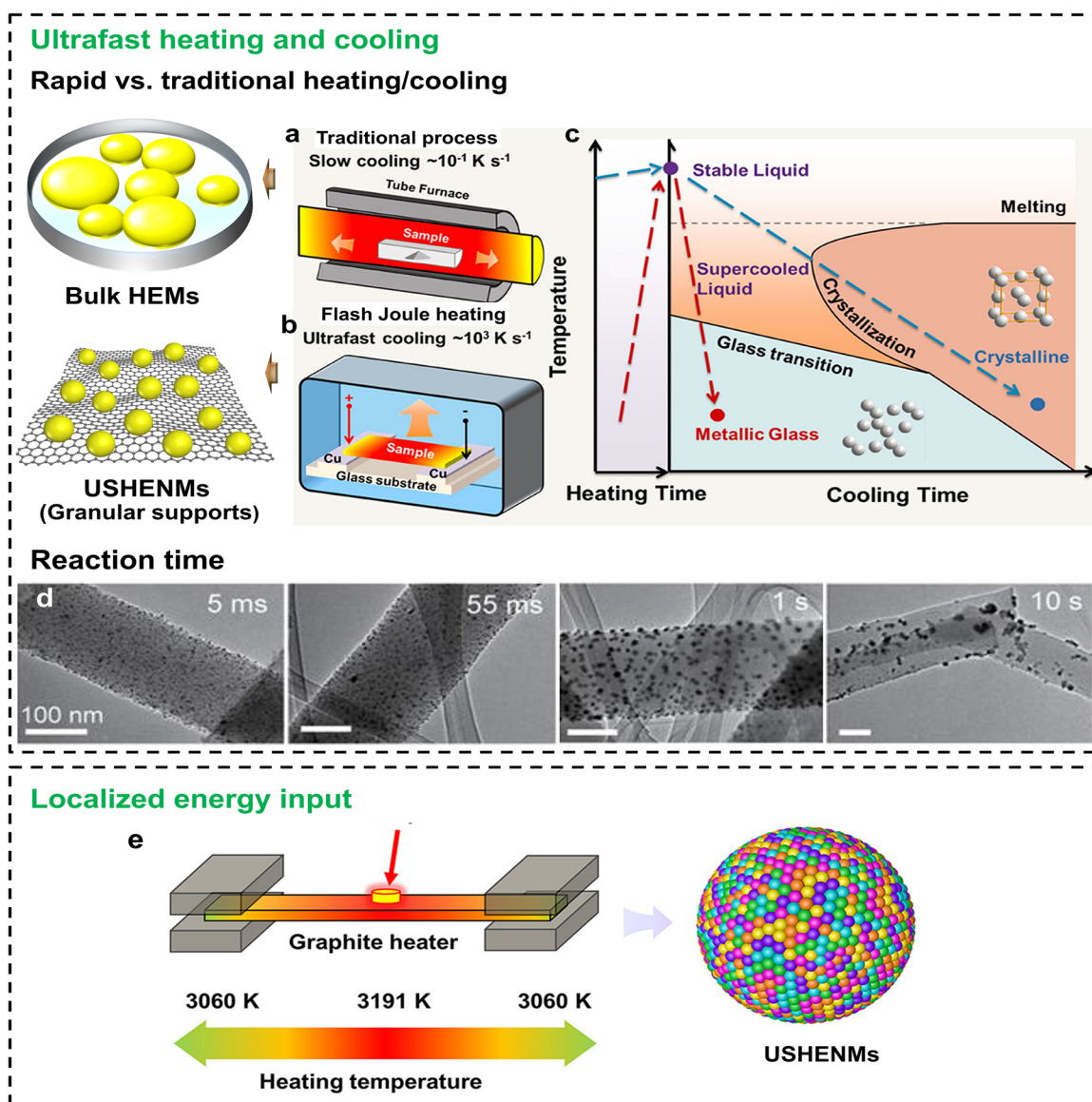


FIGURE 5 | Key factors for synthesizing USHENMs at high temperatures. (a) Traditional heating/cooling process. (b) FJH process with a cooling rate of $\sim 1000 \text{ K s}^{-1}$. (c) Temperature versus time diagram of supercooled liquid alloys and metallic glasses. The blue and red dashed arrows correspond to the thermal profiles of (a) and (b), respectively. Reproduced from [113]. CC BY 4.0. (d) TEM images showing the effect of thermal shock duration on particle size and dispersity. Scale bars: 100 nm. Reproduced with permission [89]. Copyright 2018, American Association for the Advancement of Science. (e) High-temperature platform designed to localize and control energy input. Reproduced from [114]. CC BY-NC-ND.

particle growth and phase segregation during synthesis, and to form solid solutions within extremely short periods of time. Accordingly, this review summarizes five critical factors that enable the realization of ultrasmall particle sizes, namely (i) ultrafast heating and cooling; (ii) localized energy input; (iii) spatial confinement; (iv) compatibility of precursor properties; and (v) low-diffusivity supports.

Ultrafast heating and cooling: The formation of USHENMs requires stringent synthesis conditions, often involving high temperatures and short reaction times, followed by rapid cooling at rates exceeding 10^3 K s^{-1} to “freeze” the system in a non-equilibrium state (Figure 5a–d) [26, 115]. However, ultrafast heating methods are effective only if they are capable of creating a state of high atomic mobility (e.g., local melting). Typically,

they induce localized molten or gas/plasma-like states that ensure the necessary diffusion. Consequently, such synthesis methods enable effective incorporation of otherwise immiscible elements into a metastable (single) phase, while the extremely short reaction time (milliseconds) prevents particle growth [40, 91]. Traditional furnace heating, which is often limited to around 1300 K , has slow heating and cooling rates of only a few tens to a few hundred K min^{-1} , which can lead to element segregation or excessive crystal growth [37]. At present, a variety of rapid heating approaches, including ultrafast sparking synthesis, hydrocarbothermal flow synthesis, flash Joule heating (FJH), or electrical discharge, have enabled the preparation of sub-10 nm HENMs by leveraging fast heating and quenching (for suppressing atomic diffusion) [67, 90, 115–117]. For example, Zheng et al. recently reported on hydrogen-substituted

graphdiyne-assisted ultrafast sparking synthesis (GAUSS) for the formation of 5 nm NiFeCoCuSnMo particles [105]. The GAUSS platform is capable of reaching temperatures of 3286 K within 8 ms, corresponding to a heating rate exceeding 10^5 K s^{-1} . Similarly, FJH is used in the synthesis of USHENMs via carbothermic reactions in graphite heating devices, where temperatures of $\sim 3000 \text{ K}$ are reached within milliseconds [114]. Furthermore, Yao et al. demonstrated that even strongly immiscible metals, such as Au/Ir or Au/Ru, can be successfully integrated into single-phase nanostructures through FJH (1800 K, 50 ms) [91]. Using this strategy, they synthesized highly complex USHENMs (PtPdRhRuIrAuCuFeCoNiCrMnWMoSn) with particle sizes below 10 nm. Benefiting from ultrafast heating, Niu et al. proposed a novel electrical discharge method to transform bulk HEMs into sub-10 nm (MoWVNbTa)C particles [75]. The USHENMs are obtained from the waste liquids produced during wire-cut electrical discharge machining. In this process, a pulsed voltage ionizes the dielectric liquid and forms a plasma channel between the electrodes. Temperatures above 10 000 K lead to rapid surface vaporization and ultrafast quenching of the USHENMs—up to 500 000 times per second—resulting in numerous defects, such as vacancies, stacking faults, and/or severe lattice distortions.

Localized energy input: In methods such as flame synthesis, FJH, laser ablation, or plasma discharge, the energy input is spatially confined to a small region (Figure 5e), typically micrometers to millimeters in size, where temperatures can reach 1500–3000 K in milliseconds [40, 118]. Because only the localized zone attains these extreme conditions, atomic diffusion and coalescence remain restricted to that region. Meanwhile, the adjacent cooling matrix acts as a heat sink, facilitating rapid quenching of the reaction zone and effectively “freezing” the nanoparticles before significant growth or agglomeration can occur. For example, a versatile flame-synthesis process has been shown to produce high-entropy single atoms and nanoparticles on soot-like carbon by blending organometallic precursors into a fuel (paraffin wax), followed by combustion. The localized energy input from the outer flame ($\sim 1800 \text{ K}$) enables strong metal–carbon interactions and bonding among dissimilar species (up to 25 metals) regardless of their thermodynamic compatibility, as recently demonstrated by Liu et al. [40]. For FJH, electrical pulses provide sufficient thermal energy to simultaneously melt and homogenize multiple metal precursors, while the highly localized energy input effectively suppresses bulk growth [119]. By limiting the reaction volume and using ultrashort heating times, FJH enables the synthesis of metastable USHENMs [$2.37 \pm 0.78 \text{ nm}$] of uniform composition [120], which are otherwise not accessible under conventional treatment conditions [83]. Approaches such as GAUSS and carbothermic reduction also use high-temperature synthesis platforms that limit the energy supply to specific areas of the reaction zone. Aside from that, ball milling offers another form of localized energy input on the micrometer scale, where repeated high energy collisions induce continuous fracturing and cold-welding of particles. The high mechanical energy can potentially increase the local temperature to over 1000 K, promoting diffusion in the solid state and triggering chemical reactions between precursor materials [121, 122]. However, the occurrence of such high temperatures remains controversial, as their distribution and duration are uncertain. As an illustrative example, Ni, Cr, Co, Cu, and Fe metal powders with a diameter of $(8 \pm 2) \text{ nm}$ were incorporated into

high-purity graphite powder through mechanical milling and subsequent sonication-assisted dispersion [123]. Although this approach allows for the incorporation of multiple elements with reasonably uniform distribution, it requires prolonged milling times (up to 80 h reported in this work) and can result in severe particle agglomeration, limiting the dispersion quality.

Compatibility of precursor properties: In ultrafast entropy-driven synthesis, the precursors must react synchronously under the same energy input, otherwise uneven nucleation (broad particle size distribution) or even phase segregation may occur due to different reaction kinetics. For example, a facile carbothermal shock (CTS) process proposed by Yao et al. uses rapid heating and cooling ($\sim 2000 \text{ K}$, $\sim 10^5 \text{ K s}^{-1}$, 55 ms) to process metal precursors on an oxygenated carbon support [89]. In their study, particle size was affected by composition, with Pt and Cu identified as being the most and least active, respectively. Notably, the Pt particles had a size of $(6.3 \pm 1.6) \text{ nm}$ (Figure 6a), while the Cu-based ones were significantly larger ($\sim 56.8 \text{ nm}$). This difference arises in part because the chemical composition and solubility of the precursors influence both nucleation rate and growth dynamics, with more reactive precursors forming numerous small nuclei, while less reactive ones lead to fewer but larger particles. Therefore, the use of precursor compositions of similar chemical nature and solubility promotes synchronous melting, nucleation, and co-growth, thereby minimizing element segregation and preventing excessive crystal growth.

Spatial confinement: Structural scaffolds, such as carbon nanotubes (CNTs), mesoporous (carbonaceous) materials, zeolites, or MOFs, can be used to support nanoparticles during high-temperature treatment by providing nucleation sites and preventing aggregation through confinement (Figure 6b,c). In particular, sacrificial templates, such as MOFs, offer an effective way to generate USHENMs embedded in porous carbon, with the scaffold serving to control particle growth [125]. For example, Wang et al. used a zeolitic imidazolate framework (ZIF)-based adsorption-nitridation strategy to incorporate $\sim 5 \text{ nm}$ HENMs into nitrogen-doped carbon dodecahedra, achieving abundant active sites and efficient mass transport [126]. Du et al. recently developed a co-melting-filling-freezing method to produce high-quality 1D HENMs (metal phosphide nanowires), realizing an average diameter of only 1.3 nm [127]. This method involves encapsulating multiple metal cations in single-walled CNTs, followed by post-synthetic modifications, such as phosphorization, sulfurization, or selenization. The CNTs play a versatile role in this process. Specifically, they act both as a porous template (i.e., as nanoreactors for controlled conversion reactions) and as an atomically thin protective shell that stabilizes the resulting nanowires. Very recently, Chen et al. provided an in-depth analysis of how structural scaffolds determine particle size in HENMs [124]. By using quenching-induced confinement of liquid metal droplets in various meso- and microporous molecular sieves (MSs), they achieved precise control over particle size in the range of 1–5 nm. The MSs not only act as spatially confined hosts that anchor the metal species and prevent aggregation, but also as shape-selective templates that enable uniform nanoparticle formation. Under confined, non-wetting conditions, droplets smaller than the pore size exhibit growth behavior similar to that on free surfaces and expand until they match the pore dimensions. If, on the other hand, the droplet size exceeds the

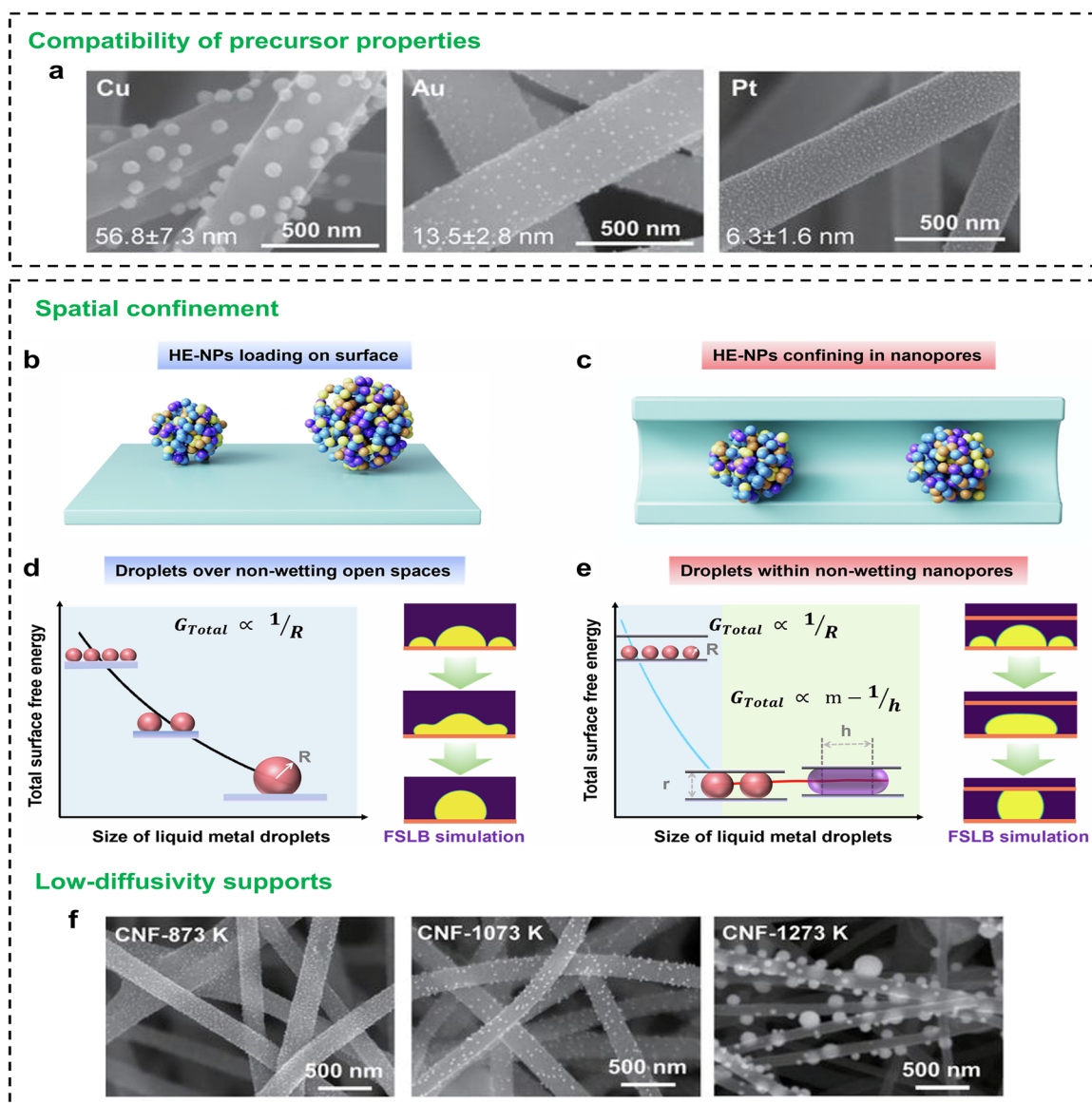


FIGURE 6 | Key factors determining the synthesis of USHENMs at high temperatures. (a) SEM images showing the influence of different precursors in the CTS process on particle size using identical CNF supports. Reproduced with permission [89]. Copyright 2018, American Association for the Advancement of Science. Schematics of HENMs (b) loaded onto surfaces and (c) confined within nanopores. (d, e) The relationship between liquid metal droplet size and total surface Gibbs free energy and corresponding fractional step lattice Boltzmann (FSLB) simulations. Reproduced from [124]. CC BY 4.0. (f) SEM images of AuNi nanoparticles on CNFs carbonized at different temperatures, illustrating the influence of surface defect concentration on particle size and dispersion. Reproduced with permission [89]. Copyright 2018, American Association for the Advancement of Science.

pore diameter, the geometric constraints lead to the formation of a hybrid structure consisting of two hemispherical ends connected by a cylindrical segment, accompanied by a slight increase in total surface energy, as illustrated in Figure 6d,e.

Low-diffusivity supports: Low-diffusivity supports play a critical role in stabilizing USHENMs by limiting atomic diffusion and coalescence during ultrafast (high-temperature) synthesis. From a mechanistic point of view, these supports provide strong interfacial interactions (e.g., metal–nitrogen or metal–carbon bonding) and are capable of anchoring individual atoms or small clusters, while the spatial confinement imposed by porous or defective structures restricts the lateral migration of nuclei.

Representative examples include the CTS and FJH methods, in which precursors are deposited onto carbon supports prior to ultrafast synthesis, as mentioned above [91]. Wang et al. demonstrated that the choice of granular support has a strong influence on particle size by creating a library of HENMs using a pulsed nanosecond laser scanning ablation technique [25]. Under identical laser pulse power densities, the average size of HENMs was markedly different when deposited onto different substrates (~ 10 nm on CNFs, compared to ~ 700 nm on copper foam). The variation in particle size is primarily determined by the substrate-dependent thermal diffusion length [128, 129], expressed as $L_T = \sqrt{D\tau}$, where D denotes the thermal diffusivity and τ the laser pulse width. Copper with a high thermal diffusivity

($\sim 10^{-4} \text{ m}^2 \text{ s}^{-1}$) yields a diffusion length of about 710 nm [25, 130], whereas carbonaceous supports (graphene, CNTs, CNFs) exhibit much lower diffusivities [$(0.1\text{--}7.6) \times 10^{-6} \text{ m}^2 \text{ s}^{-1}$] [25, 131], corresponding to significantly shorter diffusion lengths of 22–195 nm. The greater thermal diffusion length in the case of copper facilitates the formation of larger HENMs with more pronounced melting signatures compared to carbon substrates. In addition, the surface defect concentration of the support has also been found to directly affect the particle size of HENMs. This was demonstrated by carbonizing electrospun polyacrylonitrile (PAN) fibers at different temperatures, thereby generating CNFs with varying defect densities [89]. Lower carbonization temperatures result in smaller particles and more uniform dispersions (Figure 6f), since high-temperature treatment leads to a depletion of O* species on the surface of the CNFs. Building on this understanding, they were able to synthesize PtPdIrRhRu with an average particle size of (3.3 ± 0.8) nm using the CTS method, indicating that USHENMs can be successfully produced by carefully controlling the defect concentration (carbon carrier).

Other related methods reported to date, such as microwave heating [132], aerosol droplet-mediated synthesis [133], laser scanning ablation [134], or arc-discharge plasma approaches [24], have generally resulted in larger HENMs [135]. However, as discussed previously, considering the five critical factors enables the synthesis of sub-10 nm HENMs. For example, for aerosol droplet-mediated synthesis, an aqueous solution of metal salts is nebulized into submicron droplets, with each acting as an independent nanoreactor. This strategy eliminates the need for precursor deposition onto granular supports. Upon rapid on-the-fly heating and quenching, the dissolved salts are directly converted into single-phase HENMs, as demonstrated by Yang et al. [133]. However, He et al. revealed important limitations of this approach [103]. In the absence of a carbon substrate and at high pyrolysis temperatures (1373 K), significant sintering occurs, resulting in large HENMs (~ 60 nm) with a broad particle size distribution. To overcome this, they developed a modified single-step synthesis, in which aerosol droplets containing metal salts, carbon, and water are pyrolyzed at a significantly lower temperature (1123 K) under Ar flow. The addition of carbon provides structural confinement to suppress sintering, while in situ generated H_2 from hydrocarbothermal reactions enables the complete reduction of the metal salts, ultimately resulting in uniform (sub-2 nm) USHENMs.

In summary, although high temperatures often increase the risk of grain growth and coarsening, sub-10 nm particle sizes can nevertheless be achieved through various targeted strategies: (i) minimizing reaction times through high heating/cooling rates to limit atomic diffusion; (ii) localizing energy input to confine the reaction volume and prevent bulk growth; (iii) producing hosts by dispersing atomic or ionic species on high-surface-area supports (having open pores or cavities), such as carbonaceous materials, MOFs, or polymers, or by encapsulating them (solvent droplets) in nanoreactors prior to crystallization; (iv) using precursors with similar reduction properties, decomposition temperatures, and solubilities to promote synchronous melting, nucleation, and growth, thereby minimizing element segregation and improving compositional homogeneity; and (v) carefully selecting support/substrate materials with inherently

low atomic diffusivity to reduce atomic migration and particle coarsening.

2.2.2 | Kinetics-Driven Routes

As discussed above, the entropy-driven synthesis of USHENMs typically relies on rapid thermal processes that demand specialized equipment and additional components, such as conductive substrates, thereby increasing both cost and complexity. However, various milder and more accessible kinetics-driven strategies (requiring lower temperatures or even room temperature) have since emerged, expanding the feasibility of USHENM production [Figure 4(ii)]. Therein, both particle size and compositional uniformity are determined more by the reaction rate than by the thermodynamic equilibrium. It should be noted that, in the context of solution-phase synthesis, the term “high entropy” (used in many articles) often refers primarily to compositional complexity, meaning the introduction of multiple elements rather than to a true entropy effect.

At low temperatures, the contribution of configurational entropy to the mixing free energy (change in Gibbs free energy) is significantly reduced (Figure 7a,b). This often results in a positive ΔG , which thermodynamically favors phase segregation over the formation of homogeneous nanomaterials. From a kinetics perspective, the differing standard reduction potentials (E^0) of metal precursors lead to asynchronous reduction processes. This mismatch causes uneven nucleation and growth, resulting in materials with nonuniform element distribution and relatively narrow compositional ranges, challenges that become more pronounced with the synthesis of sub-10 nm HENMs. Therefore, successful kinetically controlled approaches are based on initiating reactions so quickly that atoms are forced to combine/bond before they can rearrange themselves into thermodynamically stable (in-equilibrium) phases. By promoting rapid nucleation and limiting diffusion, kinetics-driven routes trap the system in a metastable state, thereby enabling the formation of compositionally uniform USHENMs, which, under conditions that are more strongly controlled by equilibrium, would otherwise undergo phase segregation or coarsen. In general, favorable conditions for the kinetics-driven synthesis can be realized across various media, in which the reactants are evenly dispersed.

In the following, we show that kinetic control can be achieved through four main strategies: (i) using strong reducing agents or highly reactive precursors to realize instantaneous nucleation; (ii) triggering reactions through high energy input; (iii) inducing nucleation through sudden changes in temperature; and (iv) promoting rapid nucleation at moderate temperatures within a short period of time.

Using strong reducing agents/reactive precursors: Common wet-chemistry methods, such as sol-gel [136], solvothermal method [137], co-precipitation [47, 96, 138], or colloidal synthesis [139], can produce HENMs, but must be modified to facilitate the formation of USHENMs. Wet-chemistry methods are solution-based synthesis routes, in which metal precursors react under mild conditions, often with strong reducing agents, to prepare nanoparticles [140, 141]. In these approaches, differing redox potentials of the precursors pose major challenges, and the

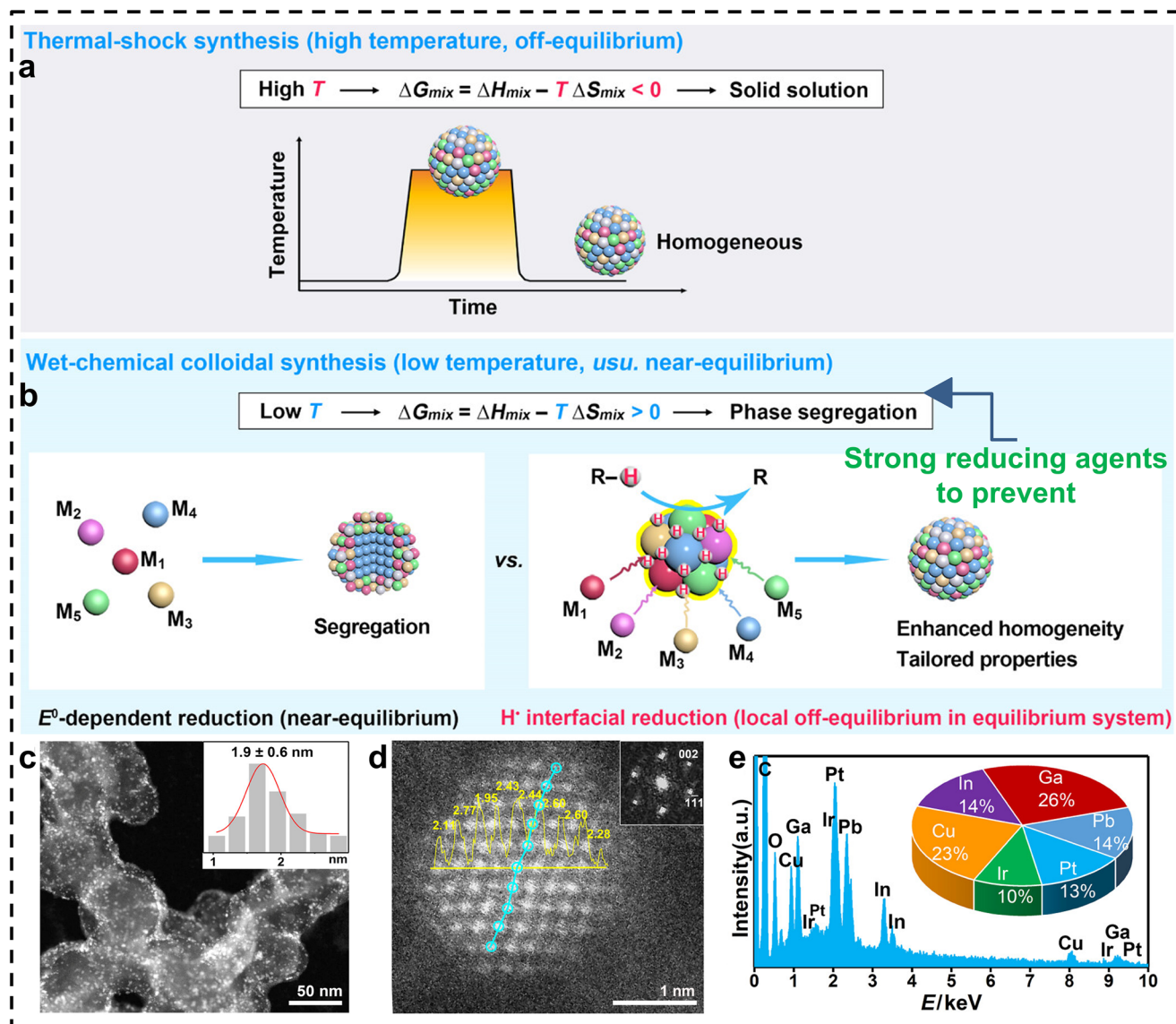


FIGURE 7 | Comparison of synthesis routes for sub-10 nm HENMs. (a) Entropy-driven thermal shock synthesis under off-equilibrium conditions and (b) kinetics-driven wet-chemical, colloidal synthesis. (c) Low- and (d) high-magnification HAADF-STEM images (oriented along the [110] zone axis in panel (d), with cyan circles indicating atomic positions in a distorted lattice and the yellow line representing the intensity profile). Insets: corresponding particle size distribution and Fourier diffractogram. (e) Quantitative EDS analysis. Reproduced with permission [110]. Copyright 2025, American Chemical Society.

methods strongly rely on chemical driving forces rather than high energy input to achieve an even distribution of elements [142, 143]. As an example, Zhang et al. recently developed an innovative colloidal strategy that enables the synthesis of USHENMs (~ 1.9 nm) at a low temperature of ~ 443 K [110]. This approach utilizes the in situ generation of active hydrogen, which acts as a strong reducing agent. The hydrogen is produced through organic dehydrogenation reactions occurring at the free surface of nuclei or seed particles. Because hydrogen has a significantly lower standard reduction potential ($E^0 = -2.3$ V) than most noble and non-noble metals ($E^0 > -1$ V), the authors suggest that this approach creates a near-equilibrium environment (Figure 7b), leading to simultaneous reduction of multiple metal precursors (Figure 7c–e). The claim that in situ hydrogen generation can promote quasi-simultaneous reduction is plausible, but should be treated with caution. Hydrogen diffusion and local concen-

tration are critical, and in some cases, it may not form quickly enough to be effective. As another illustrative example, Sun et al. developed a reduction-diffusion method for synthesizing a library of 17 distinct, Pt-based USHENMs in the form of nanowires, incorporating three to 10 elements (Pt, Rh, Mo, Ir, Co, Ru, Fe, Ni, Mn, and Cr) [99]. This wet-chemistry approach ensures uniform multielement integration and precise control over nanowire morphology and composition at relatively low temperatures (453–493 K, 60–90 min). In this system, CO generated in situ, primarily from the decomposition of $Mo(CO)_6$, which apparently serves a dual role. Specifically, it acts as a strong reductant, promoting the nucleation of metal atoms, and as a structure-directing agent, guiding the formation of 1D nanostructures. Additionally, it suppresses uncontrolled lateral growth and self-seeding of other metal atoms, thereby facilitating the formation of compositionally complex nanowires. Furthermore, the latest work

by Liu et al. reports on a scalable, wet-chemical reduction for the rapid synthesis of libraries of nanosheets, featuring arbitrary combinations of five to 12 metal species and resulting in up to 3302 compositions [94]. This approach makes use of designed reactions between metal cations dissolved in ethanol and NaBH_4 , representing a kinetics-driven, solution-phase reduction method. It also enables the production of over 100 g per batch in less than a minute. Last but not least, Liu et al. developed a low-temperature, polyoxometalate (POM)-assisted solvothermal synthesis strategy that enables precise control over size and shape of particles at the sub-1 nm scale [10]. By employing POM clusters as structure-directing agents, they successfully incorporated multiple immiscible metals (oxides) into well-defined nanowires at only 413 K, creating a tunable library of highly ordered composite materials of flexible composition. When tested as anodes in sodium-ion batteries, the nanowires showed improved cycling performance with increasing compositional complexity. Notably, $(\text{CoZnCuNiFeZrCe})\text{O}_x$ -POM nanowires retained around 92% of their capacity after 5000 cycles at a rate of 10C, underscoring their high stability and promise for long-term electrochemical energy-storage applications.

In conclusion, the use of strong reducing agents/reactive precursors to trigger solution-phase reactions is an excellent strategy for producing sub-10 nm HENMs, offering high efficiency, high yield, low cost, and great versatility in terms of composition.

High energy input: Through the use of specific techniques that directly utilize high energy inputs to trigger simultaneous reactions, such as plasma treatment [76] or ultrasound-assisted synthesis [145, 146], it is also possible to produce sub-10 nm HENMs, as summarized in Table 2. Plasma processes provide a high energy density and generate reactive species that promote the cleavage of chemical bonds in the reactants, thereby enabling efficient reduction. For example, hydrogen cold plasma reduction under ambient conditions was used by Wu et al. to prepare a series of Pt-USHENMs (PtCrTaVFeAl) [76]. This process utilizes $\text{H}^\bullet$ species generated from plasma (Figure 8a) that have a favorable standard reduction potential, enabling the simultaneous reduction of both noble and reactive metal precursors. From a kinetics perspective, the hydrogen plasma provides an extremely strong and instant reducing environment, characterized by nearly zero activation time. This facilitates the co-reduction of multiple metal cations into zero-valent species. As a result, the rapid reduction and nucleation result in uniform (~ 10 nm) particles of spherical shape. Okejiri et al. reported an ultrasound-assisted strategy that exploits acoustic cavitation to directly produce single-phase perovskite $\text{Ru}/(\text{BaSrBi})(\text{ZrHfTiFe})\text{O}_3$ USHENMs (~ 5.9 nm) without the need for calcination [145]. During ultrasonication, cavitation-induced localized high-temperature and high-pressure microenvironments promote rapid nucleation while simultaneously suppressing particle growth, thereby enabling the formation of sub-10 nm HENMs. USHENMs can also be synthesized using flow-reactor systems, where rapid and uniform mixing of precursors and reductants under controlled conditions ensures uniform nucleation and growth. This approach enables the dissolution of multiple cations into separate solutions that are then combined through engineered flow pathways to maintain compositional uniformity during particle formation. As an example, Minami-hara et al. prepared (1.3 ± 0.4) nm IrPdPtRhRu particles using a continuous-flow reactor with liquid-phase reduction at room

temperature (Figure 8b) [144]. The flow design enables rapid mixing of precursors and reductants while controlling nucleation and growth, ultimately resulting in uniform USHENMs.

Sudden change in temperature: USHENMs are often produced by initiating solution-phase reactions through sudden temperature changes, as in the colloidal hot-injection method [80, 147]. In this approach, typically performed at relatively low temperatures, a precursor solution containing metal ions or organometallic compounds is rapidly injected into a preheated solvent containing surfactants or other stabilizing agents. The abrupt change in temperature triggers a burst of nucleation (driven by thermal energy), followed by controlled growth, enabling precise control of particle size, composition, and morphology [148]. For example, Zhang et al. recently synthesized sub-10 nm $\text{Cs}(\text{PbSnSrMnZn})\text{Br}_3$ HENMs using this method (Figure 9a) [30]. In that case, metal acetates were first dissolved in coordinating solvents (oleic acid and toluene), then cesium and tin precursors were added. Nucleation is triggered by the rapid injection of a halide source, completing the reaction within ~ 3 min. Specifically, the strong exothermic interactions between metal cations and halide anions induce nucleation, while ligand coordination stabilizes the surface, ultimately facilitating the formation of structurally stable USHENMs (Figure 9b–e). Notably, even after 8 months of air exposure, the nanomaterials retained both monodispersity and structural integrity. Furthermore, Wood et al. synthesized $(\text{LaCePrNdSmEuGdDyHoErYbScY})\text{OCl}$ nanomaterials by incorporating 13 rare-earth elements into a single phase using a similar method and proposed a library with up to 7099 compositions derived from all possible combinations of five to 13 elements [85].

Overall, the hot-injection method has been shown to enable the synthesis of multicomponent particles across various classes of HEMs, including oxides [35], alloys [29], intermetallics [149], and chalcogenides [31]. In addition, electrospinning in combination with pyrolysis also uses thermal energy to drive rapid (solution-phase) reactions. For example, Yang et al. electrospun a solution of PAN containing metal precursors and multi-walled CNTs into nanofibers, which were subsequently thermally stabilized and carbonized, resulting in uniformly embedded sub-10 nm HENMs in CNFs [107]. Similar results were reported by Liao et al. [36].

A new strategy has recently been reported that differs from conventional thermal methods. It is based on a bilayer ice recrystallization process at sub-freezing temperatures; this enables the synthesis of USHENM particles or aerogels containing up to 11 metal species [78]. In this system, pre-melted ice channels are designed to regulate the controlled release of precursors and reducing agents, facilitating seed formation. It is also believed that these seeds act similarly to de-icing agents and promote the uniform mixing and assembly of elements along the ice grain boundaries.

Rapid nucleation at moderate temperatures: Some thermal-shock methods, while unable to fully melt all species involved, can facilitate rapid nucleation through kinetic control. For example, Zhang et al. reported on a precursor that was heated to 1023 K at a high rate of 2333 K s^{-1} , followed by cooling at 302 K s^{-1} [67]. This extremely fast heating and the short duration of the thermal

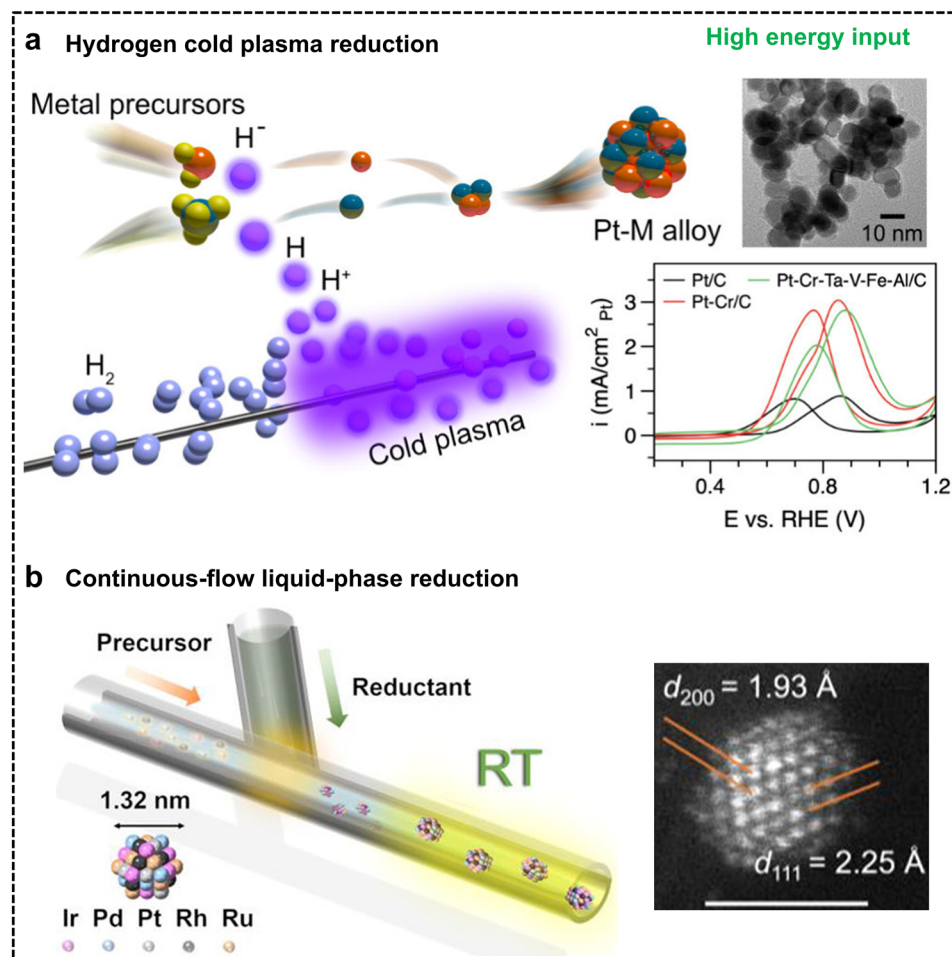


FIGURE 8 | (a) Kinetics-driven hydrogen cold plasma reduction. Reproduced with permission [76]. Copyright 2022, American Chemical Society. (b) Continuous-flow liquid-phase reduction. Reproduced with permission [144]. Copyright 2022, American Chemical Society.

shock not only promote rapid nucleation, but also suppress further particle growth, resulting in HENMs with an average particle size of only 2.3 nm. Furthermore, Gao et al. proposed a fast-moving bed pyrolysis (FMBP) strategy to immobilize USHENMs on a carbon support, achieving a uniform particle size distribution of 2 nm for MnCoNiCuRhPdSnIrPtAu at 923 K in 5 s (Figure 9f) [90]. The extremely small size is due to the rapid pyrolysis process, which induces a high nucleation rate and limits subsequent particle growth. In contrast, the fixed bed pyrolysis (FBP) strategy usually results in phase-separated and larger HENMs (Figure 9g), as the metal precursors are reduced sequentially during the comparatively slow increase in temperature (~ 20 K min⁻¹) according to their different reduction potentials. In short, inducing rapid nucleation through kinetic control via ultrafast temperature ramping proves to be an effective strategy.

Taken together, kinetics-driven strategies for synthesizing USHENMs focus on precise control of nucleation and particle growth. They involve (i) the use of strong reducing agents or reactive precursors, with chemical reductants triggering the simultaneous reaction of multiple metal species; (ii) sudden changes in temperature (hot-injection method), resulting in immediate nucleation at relatively low temperatures; (iii) high energy input-driven nucleation, with techniques such as

plasma treatment, continuous-flow reactors, or ultrasound-assisted precipitation delivering sudden energy to induce ultrafast nucleation and controlled particle growth, typically at low or ambient temperatures; and (iv) rapid nucleation at moderate temperatures (FMBP strategy), with ultrafast ramping generating a high nucleation rate in a short period of time and resulting in USHENMs with minimal phase segregation.

2.2.3 | Enthalpy-Driven Routes

Under low-temperature conditions, where the enthalpies of mixing between elements are moderately negative or similar, the reduction in interfacial energy can cause multiple phases to combine into a single-phase material. At the nanometer scale, surface and interfacial energies strongly affect phase stability and can act as a dominant thermodynamic influencing factor. However, "enthalpy-driven" does not imply that both entropy and kinetics are completely negligible in the formation of USHENMs. Enthalpy-controlled reaction pathways become particularly effective when the particle size falls below a critical threshold, where surface effects outweigh bulk thermodynamics [23]. They require atoms to relocate into lower energy positions, meaning that enthalpy reduction is only possible through atomic

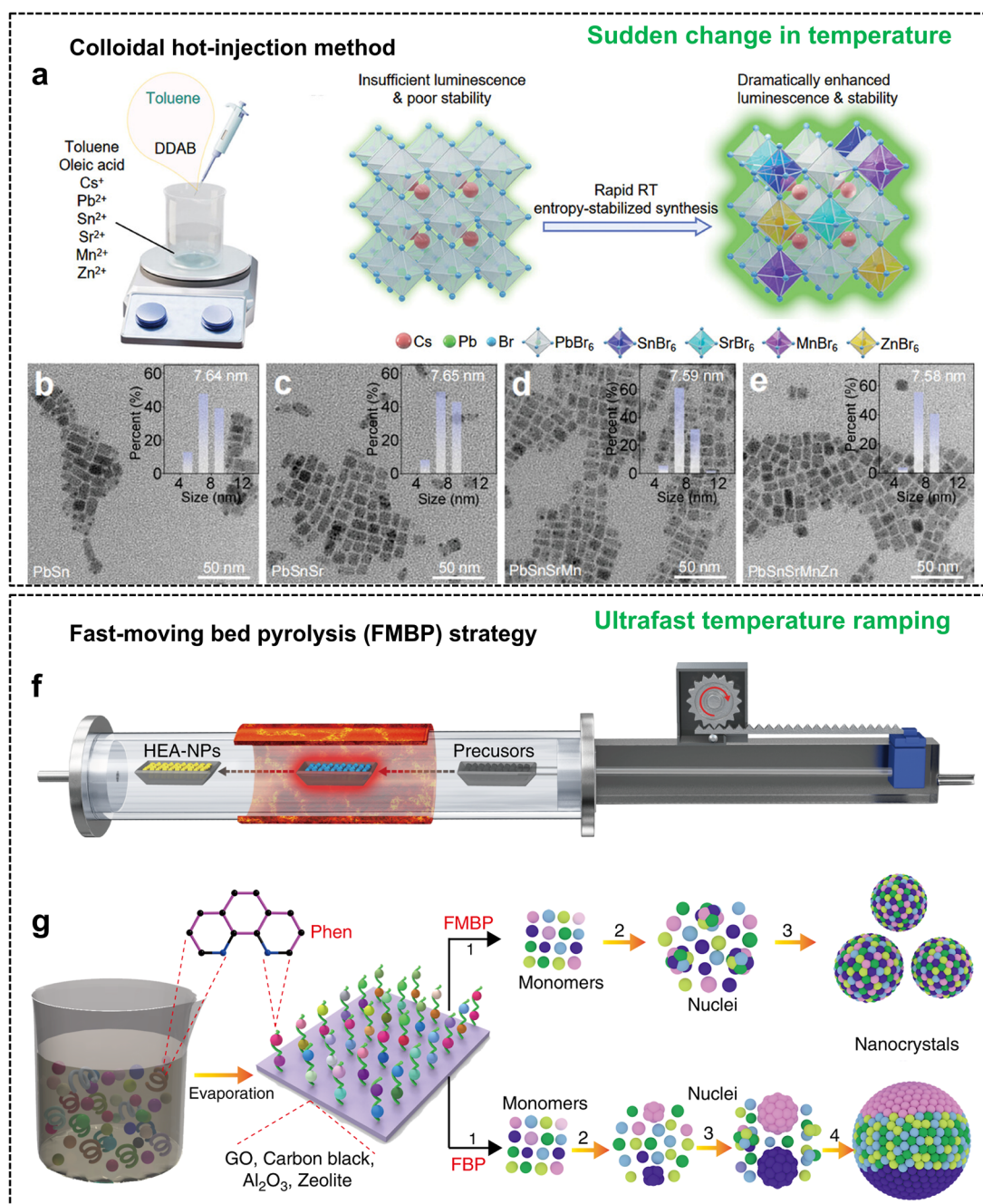


FIGURE 9 | (a) Schematic representation of a colloidal hot-injection process for USHENMs. (b–e) TEM images of particles with increasing compositional complexity: (b) Cs(PbSn)Br₃, (c) Cs(PbSnSr)Br₃, (d) Cs(PbSnSrMn)Br₃, and (e) Cs(PbSnSrMnZn)Br₃. Reproduced with permission [30]. Copyright 2025, Wiley-VCH GmbH. (f) Schematic representation of an FMBP-based experimental setup for the synthesis of HENMs. (g) Schematic representation of the synthesis of uniform and phase-separated HENMs by FMBP and FBP strategies, respectively. Reproduced from [90]. CC BY 4.0.

diffusion. Typically, nanoparticles are used as seeds or templates, and diffusion drives the incorporation of additional elements to produce HENMs. Unlike kinetics- or entropy-driven routes, this approach does not require instantaneous nucleation, rapid reduction, or high temperatures. Rather, the respective HENMs often form through the sequential incorporation of elements via ion diffusion [93], such as through galvanic replacement or ion-exchange reactions [Figure 4(iii)] [111, 112]. However, there are only a few reports on enthalpy-derived HENMs, most of which involve relatively large particles [150–153]. Because the number of studies is limited, the factors that govern the formation of

USHENMs remain poorly understood. Current findings indicate that seed size and reaction conditions, such as temperature and time, play an important role.

As an example, Dey et al. demonstrated the compositional evolution of NiPdPtRhIr nanoparticles, as shown in Figure 10a [31]. In that case, the reaction begins with the rapid formation of Pd-rich seeds at 548 K, after which Ni is incorporated primarily through deposition, followed by significant atomic diffusion, thereby gradually reshaping the early particle structure. Once PdNi domains have formed, Pt begins to incorporate. It is

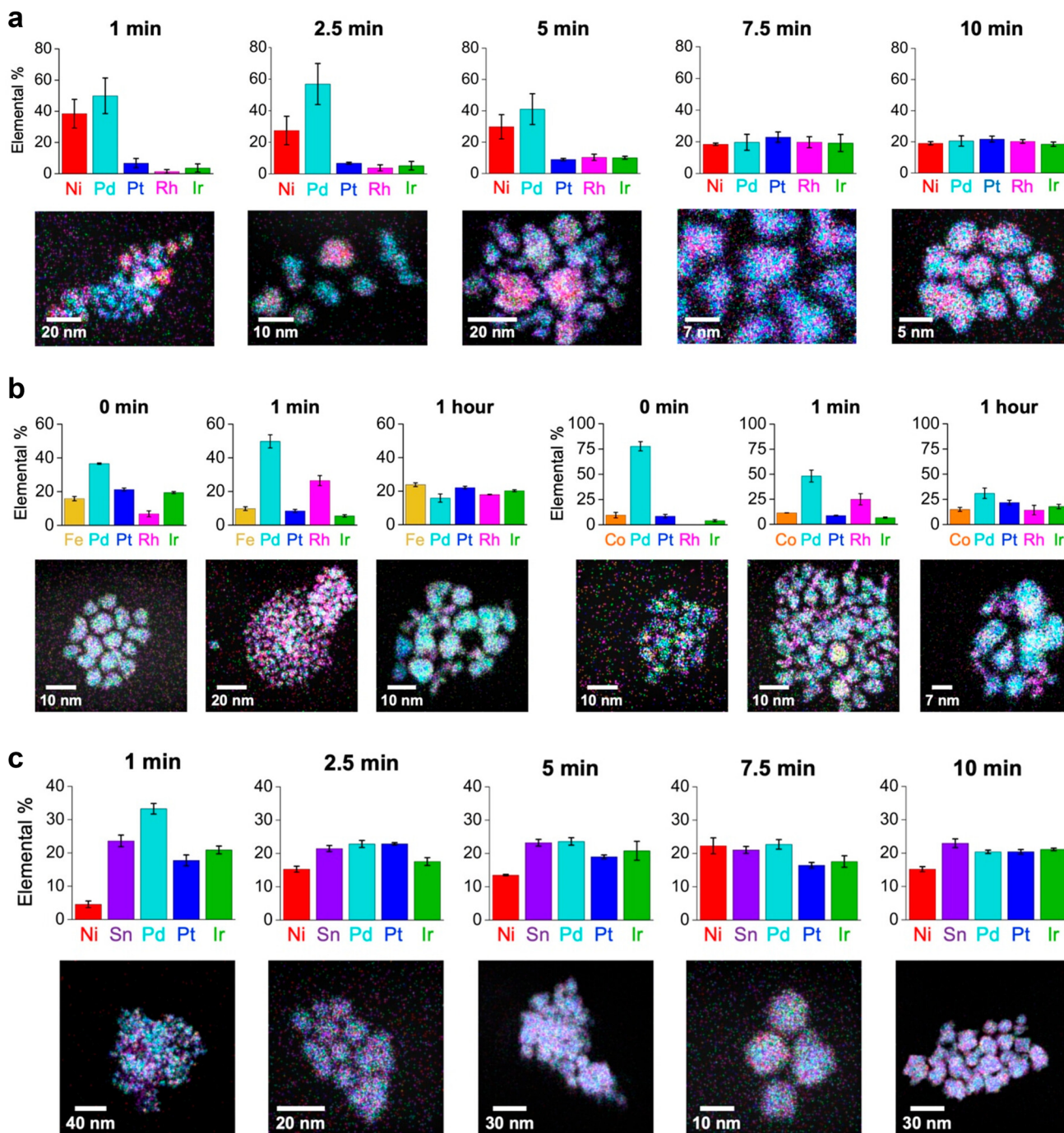


FIGURE 10 | (a–c) Time-dependent formation of NiPdPtRhIr, FePdPtRhIr, CoPdPtRhIr, and NiSnPdPtIr nanoparticles showing their compositional evolution. Reproduced with permission [31]. Copyright 2023, American Chemical Society.

important to note that the introduction of Pt requires the prior presence of Ni and/or Pd and occurs through the slow diffusion of atoms into the growing nanoparticles. Subsequently, a similar diffusion-driven and autocatalytic sequence enables the reduction and incorporation of Rh and Ir. Overall, atomic diffusion plays a central role in this multistage process, as it determines both the sequence and depth of integration of various metals into the final structure. Aside from that, to introduce significant fractions of Fe and Co, the reaction conditions must be adjusted, for example, by increasing the temperature (to 588 K) and extending the dwell time (to 1 h) to promote complete decomposition of

the respective precursors (Figure 10b). In the NiSnPdPtIr system (Figure 10c), Sn likely induces the immediate and rapid reduction of all noble metal species while simultaneously suppressing the formation of PdNi domains (nuclei), a behavior that differs from that observed for the Sn-free counterpart. However, it should be noted that this type of “template modification” is highly system-dependent and cannot be readily generalized. These findings demonstrate that the reaction pathways can vary significantly depending on composition and synthesis conditions, with both factors being important for achieving precise size control.

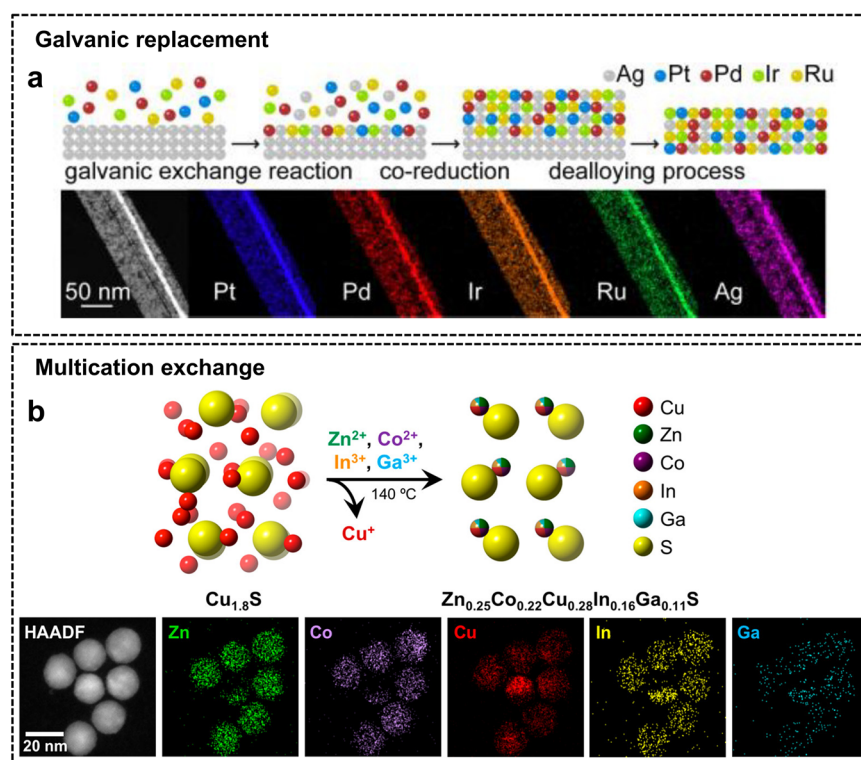


FIGURE 11 | (a) Schematic representation of the galvanic replacement synthesis of HENMs, along with an HAADF-STEM image and corresponding EDS maps. Reproduced with permission [111]. Copyright 2022, American Chemical Society. (b) Schematic representation of multication exchange showing the formation of $\text{Zn}_{0.25}\text{Co}_{0.22}\text{Cu}_{0.28}\text{In}_{0.16}\text{Ga}_{0.11}\text{S}$ from roxbyite $\text{Cu}_{1.8}\text{S}$, along with an HAADF-STEM image and corresponding EDS maps. Reproduced with permission [112]. Copyright 2021, American Chemical Society.

Similarly, Wang et al. prepared 5 nm HENMs comprising up to 14 principal elements, including combinations of strongly immiscible pairs, such as Bi and W [93]. Their method utilizes Pt-rich cores as seeds, followed by an ion diffusion process to introduce additional metals that are otherwise difficult to reduce. The resulting HENMs were further annealed at 973 K, which promotes homogenization, but may also lead to particle growth. This work represents the smallest particle size reported to date for HENMs produced via an enthalpy-controlled reaction pathway. In short, the quality of the template and the initial particle size set the lower limit for enthalpy-driven routes.

In the case of galvanic replacement synthesis, atoms in a preformed nanomaterial (serving as template) are substituted by atoms from solution. The process occurs through oxidation of the sacrificial metal species by ions with higher reduction potentials and is primarily driven by enthalpy, with entropy playing a relatively minor role. For example, Tao et al. prepared 2D HENMs as ribbons with a record thickness of only 0.8 nm and lengths in the micrometer range using Ag nanowires as a template (Figure 11a) [111]. During synthesis, atoms on the nanowire surface are replaced by metal species, such as Pt^{2+} and Pd^{2+} , through galvanic exchange, due to differences in reduction potential. The core was then removed using dilute nitric acid, resulting in freestanding nanoribbons with up to 8 principal elements. Xia et al. further demonstrated that combining the galvanic replacement between Pd nanocubes and K_2PtCl_4 with a co-reduction process using citric acid effectively reduces particle size [154].

In ion exchange, ions within a template material are partially or completely replaced by two or more distinct ions from solution without redox processes taking place. Importantly, the lattice structure remains intact. Due to the large number of available species, cation exchange reactions are generally preferred for HENM formation. For example, McCormick et al. developed a low-temperature, multication exchange strategy to synthesize HENMs with discrete morphologies (~13 nm) [112]. In this post-synthetic approach, preformed binary nanomaterials, such as $\text{Cu}_{1.8}\text{S}$, which serve as sacrificial templates, undergo controlled cation exchange with various ions (e.g., Zn^{2+} , Co^{2+} , In^{3+} , Ga^{3+}) in solution (Figure 11b). An important enthalpic driving force in this process is the strong solvation of the displaced copper by coordinating ligands, such as TOP, OLAM, or benzyl ether, which stabilize Cu^{+} in solution and prevent its reprecipitation. This enables efficient exchange while maintaining the original nanoscale morphology and anionic framework. As the authors emphasized, both enthalpic and entropic factors contribute to the stabilization of the multi-component phase. In particular, enthalpy affects the overall structure by determining if the materials form a single or mixed phase (heterostructure). Leveraging this strategy, Theibault et al. synthesized $(\text{Zn}_{0.30}\text{Co}_{0.31}\text{Cu}_{0.19}\text{In}_{0.13}\text{Ga}_{0.06})\text{S}$ HENMs [(18 ± 2) nm], which exhibit strong catalytic activity toward lithium polysulfide adsorption and conversion [92]. Their nanoscale size and high surface reactivity help mitigate polysulfide shuttling, which is a major limitation in lithium-sulfur batteries, significantly improving both capacity and long-term cycling stability.

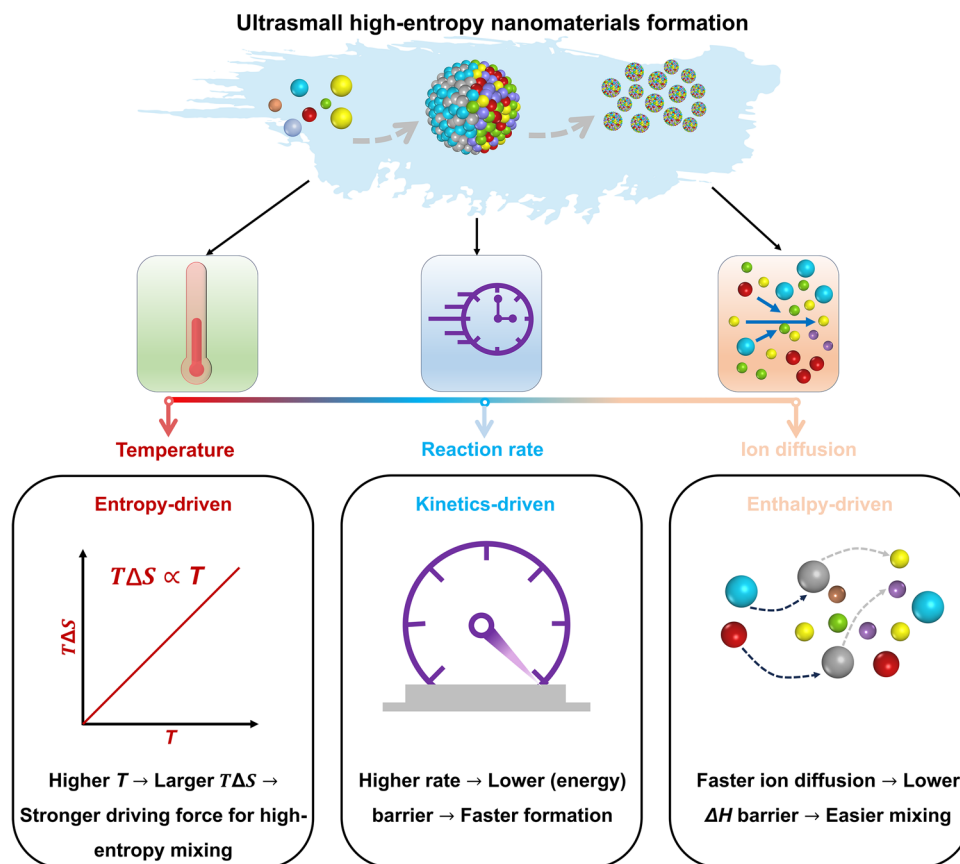


FIGURE 12 | Schematic illustrations highlighting the key factors driving the entropy-, enthalpy-, and kinetics-controlled synthesis of USHENMs.

In general, particle formation is limited by ion diffusion. The incorporation of multiple species requires diffusion to achieve thermodynamic equilibrium, which becomes increasingly inefficient with smaller particles and usually requires elevated temperatures. The latter favors particle growth, thus setting a lower size limit and making it difficult to achieve particles smaller than 5 nm in diameter. This in turn suggests that enthalpy alone is not sufficient to induce the formation of sub-5 nm HENMs. In some cases, local kinetic control or carefully designed growth strategies, such as layer-by-layer growth or ligand stabilization, may enable the formation of ultrasmall particles. Consequently, enthalpy-driven routes are suitable for fine compositional control and the formation of complex structures, but less so for the scalable production of USHENMs. Their applicability is clearly system-dependent, and they are naturally subject to size limitations.

In summary, the formation of USHENMs discussed herein can be broadly classified according to the dominant driving force, meaning entropy, enthalpy, or kinetics (Figure 12). Entropy-driven approaches rely on high configurational entropy to realize compositionally complex mixing, but this typically requires extreme thermal conditions and specialized equipment, with both reproducibility and scalability remaining major challenges. Because of this and the high sensitivity to minor variations in precursor placement, energy input, and/or reaction environment, it is difficult to achieve consistent particle size, composition, and homogeneity across batches. Furthermore, most ultrafast

syntheses are currently limited to small batch sizes, and upscaling to gram or kilogram levels while maintaining favorable particle properties is not trivial. However, they benefit from processing at very high temperatures, which provide sufficient energy to overcome the positive enthalpies of mixing between otherwise immiscible species. Under these conditions, even highly immiscible element pairs can be forced into a single-phase (solid solution) structure [91]. Ultimately, this enables the integration of a wide variety of elements, even those with very different reduction potentials, atomic sizes, and/or bonding preferences.

Kinetics-driven routes offer significant advantages (Figure 13a), as they do not necessarily require high reaction temperatures (entropy contribution), but instead rely on rapid nucleation and growth control under moderate conditions. As a result, such syntheses are more cost-effective, experimentally better accessible, and capable of producing USHENMs with uniform composition and higher yields compared to other approaches. Although the compositional space is more limited than in entropy-driven (high-temperature) routes, they are very attractive for the production of USHENMs due to their practicality and good size control. Enthalpy-driven processes are determined by the intrinsic mixing energetics of the constituent elements, which strongly depends on ion diffusion. Due to these limitations, it is hardly possible to achieve particle sizes below 5 nm with this approach (Figure 13b). Therefore, further development of enthalpy-controlled reaction pathways is necessary.

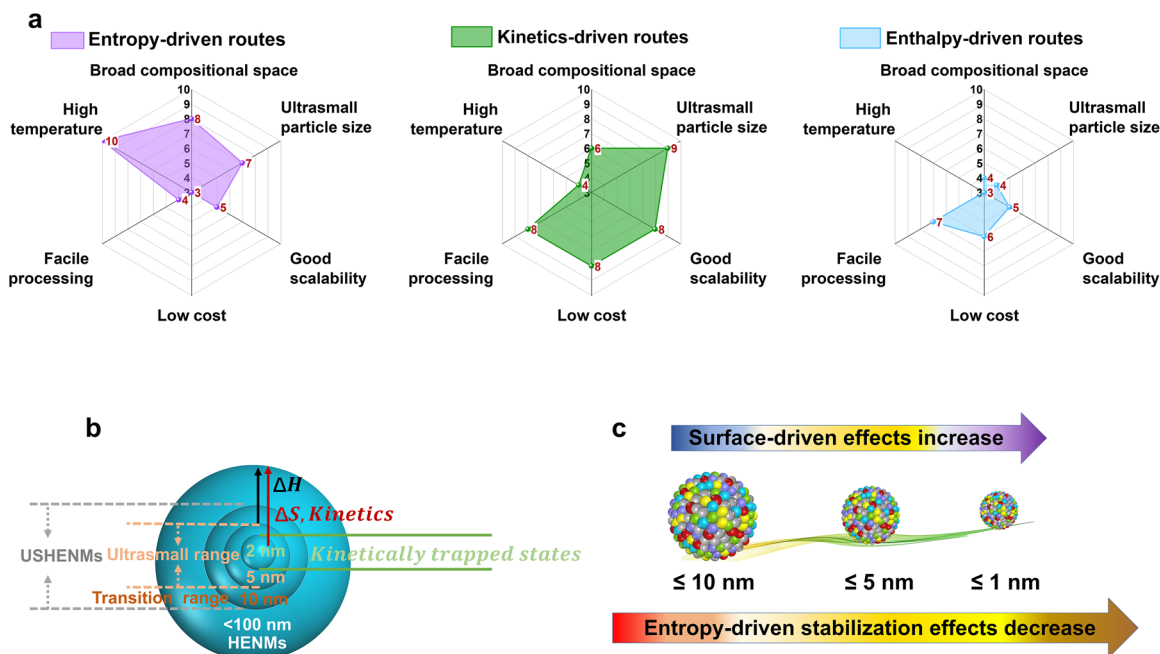


FIGURE 13 | (a) Schematic illustrations highlighting the advantages and limitations of entropy-, enthalpy-, and kinetics-driven synthesis routes. (b) Specific particle size ranges and (c) nanoscale effects.

TABLE 1 | Entropy-driven synthesis strategies for USHENMs.

Method	Temp./K	Particle size/nm	Composition	Formation mechanism	Refs.
Ultrafast sparking synthesis	~3286	~5	NiFeCoCuSnMo	Melting-fusion-quenching (metallic glass)	[105]
Flame synthesis	~1800	<10	FeCoNiCuRuRh PdIrPt	Melting-quenching in flame	[40]
Laser fragmentation in liquids	>2000	<2	AuPtRuRhIr	Melting-fusion-quenching	[118]
Carbothermal shock	~2000	~3	PtPdIrRhRu	Melting-fusion-quenching (metallic glass)	[89]
Mechanical ball-milling and sonication-assisted exfoliation	Not reported	~8	NiCrCoCuFe	Solid-state diffusion and high energy impact	[123]
Electrical discharge	>10 000	<10	(MoWVNbTa)C	Melting-quenching in dielectric medium	[75]
Co-melting-filling-freezing-modification	1023	<2	(MnFeCoCuZn)P	Co-melting-filling-freezing	[127]
Space-confined liquid metal droplet method	1173	1–5	PtMnFeCoCuZn In	Co-melting-filling-freezing	[124]
Hydrocarbothermal flow synthesis	1123	<2	FeCoNiCuPt	Melting-fusion-solidification	[103]
ZIF-derived adsorption-nitridation strategy	1273	~5	(TaMnVCr)NC	Melting-fusion-solidification	[126]

2.3 | Size Evolution (from Sub-10 nm to Sub-1 nm Particles)

As evident from Tables 1 and 2, nanoparticle formation can be achieved via both entropy- and kinetics-driven synthesis

strategies. Entropy-driven approaches include laser fragmentation in liquids, co-melting-filling-freezing methods, space-confined liquid metal droplet methods, and hydro-/carbothermal flow syntheses. In parallel, kinetically controlled routes, such as continuous-flow liquid-phase reduction, fast-moving bed

TABLE 2 | Kinetics- and enthalpy-driven synthesis strategies for USHENMs.

Method	Temp./K	Particle size/nm	Composition	Driving force	Formation mechanism	Refs.
Wet-chemical (colloidal) synthesis	~443	~1.9	PtIrCuInGaPb	Kinetics	Reduction-nucleation-growth	[110]
Continuous-flow liquid-phase reduction	RT	~1.3	IrPdPtRhRu	Kinetics	Reduction-nucleation-growth	[144]
Wet-chemical reduction	<493	<2	PtRhMoIrCoRuFeNiMnCr	Kinetics	Reduction-nucleation-growth	[99]
Fast moving bed pyrolysis	~923	~2	MnCoNiCuRhPdSnIrPtAu	Kinetics	Reduction-nucleation-growth	[90]
Hydrogen cold plasma reduction	RT	~10	PtCrTaVFeAl	Kinetics	Reduction-nucleation-growth	[76]
Electrospinning and pyrolysis	973	<10	(Mn _{0.25} Co _{0.25} Ni _{0.25} Cu _{0.25})C	Kinetics	Solid-state diffusion and carbothermal reaction	[107]
Bilayer ice recrystallization	243	<5	PtAuAgCuInPdRhRuCoBiNi	Kinetics	Rapid nucleation	[78]
Ultrasound-assisted precipitation	RT	~6	Ru/(BaSrBi)(ZrHfTiFe)O ₃	Kinetics	Acoustic cavitation-induced rapid nucleation and precipitation	[145]
POM-assisted solvothermal (colloidal) method	~413	<1	(CoZnCuNiFeZrCe)O _x	Kinetics	Colloidal self-assembly and nucleation under solvothermal conditions	[10]
Colloidal hot-injection method	RT	~8	Cs(PbSnSrMnZn)Br ₃	Kinetics	Rapid nucleation and crystal growth	[30]
Ion-diffusion-mediated (colloidal) synthesis	~600	<10	NiPdPtRhIr, FePdPtRhIr, CoPdPtRhIr	Enthalpy	Ion-diffusion-driven multimetal incorporation into seed cores	[31]
Ion-diffusion-assisted salt reduction synthesis	973	~5	PtZrNbFeCuTaMoHfBiWZn SnPdNi	Enthalpy	Ion-diffusion-driven multimetal incorporation into seed cores	[93]

pyrolysis, and POM-assisted solvothermal methods, can also cover the ultrasmall size range under appropriate conditions. The synthesis of sub-nanometer HEMs (<1 nm) poses a particular challenge, as conventional entropy stabilization fails at this scale. Here, finite-size effects, surface energy, and discrete atomic interactions favor segregation over the stable mixing of multiple elements, necessitating strict kinetic control or spatial confinement [155]. In particular, ligand-mediated wet-chemical synthesis represents a typical kinetically controlled pathway [140], in which the rapid reduction of metal precursors (e.g., acetylacetonates or chlorides) in the presence of strong ligands, such as thiols, oleylamine, or phosphines, leads to burst nucleation and immediate surface passivation, thereby halting growth at the cluster stage. Representative systems include thiol-protected multimetallic clusters and oleylamine-mediated co-reduction systems.

Gas-phase cluster processes (e.g., magnetron sputtering or laser ablation combined with inert gas condensation and mass selection) provide alternative approaches. They create structures from just a few atoms, sorted by size, in the gas phase, which are then deposited onto a substrate (support), resulting in well-defined (high-entropy) atomic clusters. Depending on the system, confinement-assisted synthesis can be associated with both entropy-driven and kinetic strategies. For example, liquid metal droplet methods and hydro-/carbothermal processes can be used to generate ultrasmall clusters in confined environments. More commonly, sub-1 nm particles are stabilized in zeolite cages, MOFs, or defect-rich carbon matrices through solution-based infiltration, followed by reduction or thermal treatment, thereby physically limiting atomic diffusion and aggregation. Overall, while many of the methods mentioned above can produce ultrasmall nanoparticles (1–2 nm in diameter), access to the sub-1 nm range relies primarily on strong ligand stabilization, size selection in the gas phase, or spatial confinement, which effectively suppresses growth.

In ultrasmall systems, the role of entropy stabilization may be less decisive than previously thought (Figure 13c). In contrast, kinetic trapping and surface effects can dominate the energetics and potentially overshadow genuine entropy-driven stabilization. In particular, the balance between thermodynamic stability and kinetic trapping differs fundamentally from that observed in larger particles. This interplay therefore deserves a more critical and nuanced discussion. At this scale, the total free energy is determined primarily by surface energy, lattice strain, and non-equilibrium bonding, while the contribution of configurational entropy is comparatively small. Although high configurational entropy can, in principle, promote mixing, its stabilizing effect decreases strongly as particle size decreases, since the number of atoms involved in bulk disorder becomes limited and surface atoms increasingly determine the overall energetics. As a result, many USHENMs are not thermodynamically stable solid solutions. Instead, they often correspond to kinetically trapped states that arise under conditions of rapid synthesis (e.g., ultrafast heating, burst nucleation, transient melting, etc.). These conditions cause the atoms to be frozen in metastable, mixed configurations before phase separation or ordering occurs. Experimentally verifying true entropy stabilization at this scale is extremely difficult. Regardless, the minimization of surface

energy and kinetic trapping likely play a greater role than entropy-driven stabilization.

Due to their high surface-to-volume ratio, sub-nanometer HEMs exhibit increased surface entropy, due to vibrational, translational, and rotational contributions from undercoordinated atoms [155]. The relative balance of these entropy terms, together with the surface energy, can influence anisotropic cluster formation/assembly. In particular, increased translational entropy favors elongated or belt-like structures, whereas dominant vibrational entropy under strong confinement tends to stabilize more compact, quasi-one-dimensional arrangements (e.g., nanowire-like structures). Overall, morphological evolution is the result of the interplay between surface entropy and surface energy and is not determined by a single factor.

2.4 | Formation Mechanisms

High- and low-temperature (or ambient-condition) syntheses generally activate fundamentally different formation mechanisms for USHENMs. High-temperature routes typically proceed through a melting-fusion-solidification process (Table 1), reflecting their strong dependence on entropy-driven mixing at elevated temperatures. In contrast, low-temperature routes predominantly generate USHENMs through a LaMer-type burst nucleation mechanism (Table 2). However, it should be noted that even under high-temperature conditions, local kinetic effects, such as rapid cooling or quenching, can significantly influence the final particle size.

As illustrated in the respective temperature-time diagram in Figure 5c, this mechanism requires that the maximum temperature ($T_{\max}$) surpasses the melting point of all constituent metals, ensuring complete decomposition of precursors and uniform mixing in the molten state. Upon reaching $T_{\max}$ (Figure 14a,b), the metal precursors melt and fuse into alloy nanodroplets. Rapid cooling, often induced by thermal shock or localized quenching, leads to solidification into either nanocrystalline or amorphous phases. If the cooling rate exceeds the critical value for crystallization ($\sim 1 \text{ K s}^{-1}$), phase segregation is suppressed, stabilizing the high-entropy phase and resulting in compositionally uniform USHENMs [156]. This mechanism is typical of synthesis methods that rely on direct, high-intensity energy input. In ultrahigh-temperature approaches, such as FJH, CTS, or electrical discharge, where temperatures exceed 2000 K, USHENMs usually form via a transient melting pathway. These methods provide a liquid-like environment with extremely high atomic mobility, enabling quasi-simultaneous incorporation of multiple elements into the lattice. This is typically the primary mechanism for achieving homogeneous multielement distributions at the sub-10 nm length scale. Solid-state diffusion contributes to atomic mixing, but is generally slower than the timescale of ultrafast synthesis. Its effectiveness is limited to sub-2 nm particles, unless surface effects accelerate diffusion.

Moderate-temperature methods, such as FMBP, operate below the melting point of most metals, yet provide enough thermal energy to decompose precursors and induce the nucleation-growth processes that characterize the kinetically controlled

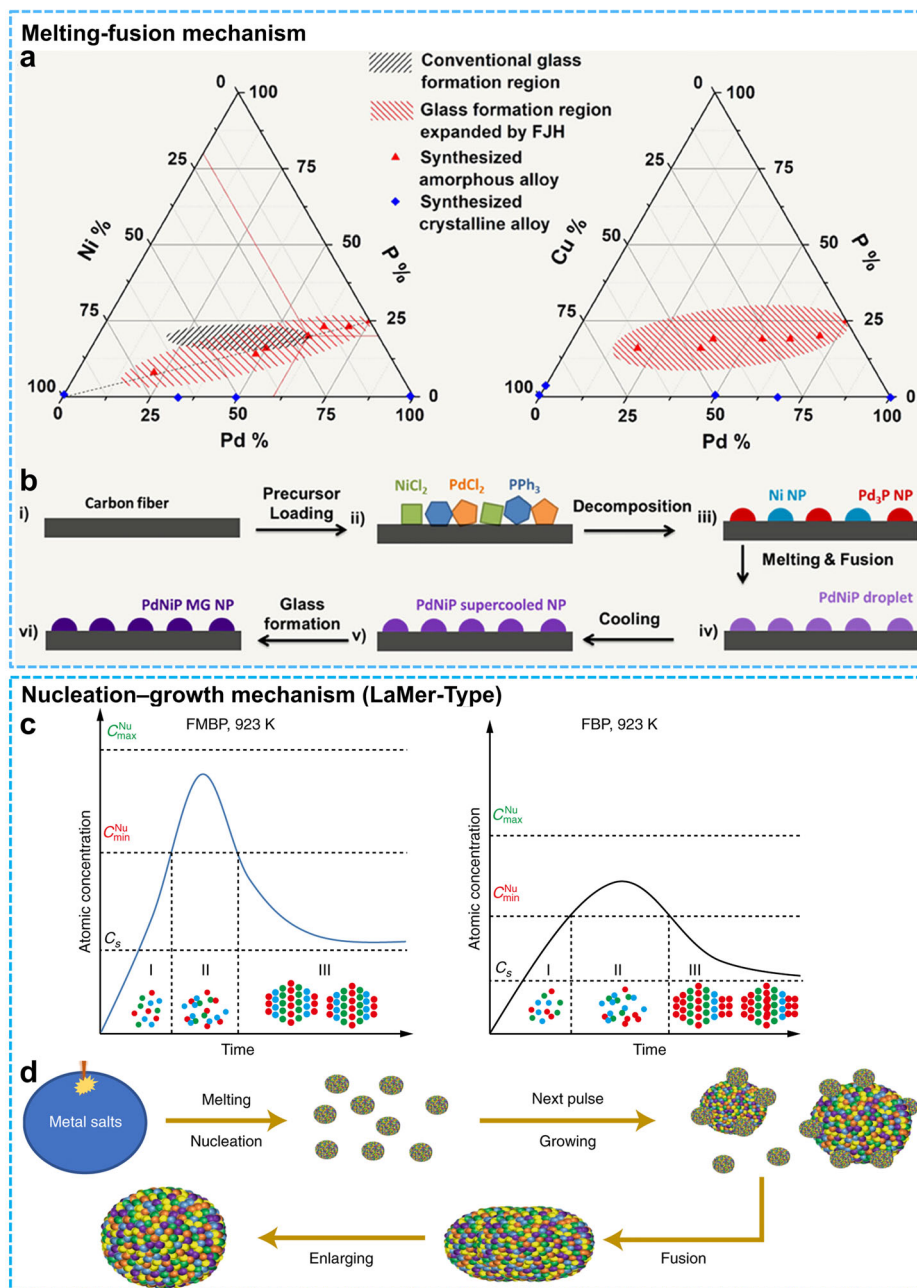


FIGURE 14 | Formation mechanisms of USHENMs. (a) Ternary phase diagrams showing the distribution of crystalline (blue diamonds) and amorphous (red triangles) phases for high-entropy alloys. The black region indicates the conventional glass formation range, while the red region highlights the expanded glass formation region enabled by FJH. (b) Melting-fusion-solidification mechanism illustrating alloy formation during high-temperature synthesis. Reproduced from [113]. CC BY 4.0. (c) Nucleation-growth mechanism of HENM formation via FMBP and FBP. The diagrams illustrate the sequential processes of monomer formation (I), nucleation (II), and nanocrystal growth (III) against the reaction time for each method. Reproduced from [90]. CC BY 4.0. (d) Schematic of nucleation and growth under repeated laser pulse irradiation, depicting enlargement through monomer accumulation and particle fusion. Reproduced with permission [25]. Copyright 2022, Springer Nature.

formation of USHENMs. In such cases, the LaMer nucleation-growth model provides a suitable conceptual framework for nanomaterial formation (Figure 14c,d). This mechanism proceeds via three key stages: [157, 158] (i) monomer generation: thermal decomposition of metal precursors produces reactive atomic species (monomers); (ii) burst nucleation: once the monomer concentration exceeds a critical supersaturation threshold, rapid nucleation events occur; and (iii) particle growth: as the monomer concentration declines, further monomers

deposit on existing nuclei, resulting in controlled particle growth. Also, LaMer conditions are strongly influenced by the reaction medium, ligands, pressure, and gas flow. In the context of FMBP, the decomposition of precursors generates a high concentration of reactive monomers. These monomers have low activation energy barriers for nucleation, enabling the formation of small alloy nuclei. Because of their small critical radius and fast nucleation rate, HENMs with ultrasmall dimensions are readily formed. Moreover, the rate of pyrolysis plays a pivotal role, with

faster pyrolysis leading to a higher degree of monomer supersaturation, which in turn increases the nucleation rate. A higher nucleation rate results in a larger number of nuclei, ultimately producing smaller nanomaterials due to limited monomer supply for growth. Hence, while the LaMer model is traditionally applied to solution-phase syntheses (especially at room temperature), its principles can be adapted to describe the formation of USHENMs in moderate high-temperature gas- or solid-phase environments. However, multielement systems often experience sequential incorporation rather than a single synchronized burst. Below 3 nm, even slight variations in nucleation or growth rate lead to large relative differences in particle composition and size. Ligands or surfactants can preferentially bind to certain metal ions, further disrupting simultaneous nucleation. Therefore, LaMer-type nucleation bursts are barely reproducible for USHENMs. Most successful syntheses rely on non-equilibrium methods, transient molten states, or kinetically trapped growth rather than idealized LaMer behavior. In short, melting-fusion-solidification mechanisms are typically observed under high-temperature conditions, while LaMer-type nucleation-growth processes characterize the moderate temperature (or room temperature)-driven formation of USHENMs.

Entropy-driven formation of USHENMs is strongly temperature-dependent, while kinetic pathways are controlled by reaction rates. The third mechanism, enthalpy-driven formation, primarily involves ion diffusion and is relatively rare; however, it has been described in detail in recent studies [23, 159, 160].

2.5 | Stability and Identification of Homogeneous USHENMs

USHENMs offer exciting scientific and technological opportunities, yet their extremely small dimensions also introduce serious practical challenges. One of the most critical drawbacks is their instability during storage. Due to the high surface energy, the nanoparticles readily agglomerate, oxidize, or undergo structural changes even under mild conditions. As a result, preserving the original size, composition, and surface chemistry over time becomes difficult, which can ultimately compromise their functional performance. Very recently, Krouna et al. [161] investigated the thermal stability of $\text{Au}_{20}\text{Co}_{28}\text{Cu}_{11}\text{Ni}_{20}\text{Pt}_{21}$ nanoparticles (3.0–6.5 nm) from 298 to 973 K using aberration-corrected STEM. Their results showed that atomic diffusion in the temperature range from 773 to 873 K leads to surface segregation of Au and Cu, with a Janus-like configuration becoming evident mainly in coalesced particles, where atomic mobility is higher. At 973 K, diffusion is sufficiently activated to induce clear phase separation in all particles. Interestingly, although higher temperatures would conventionally be expected to increase solid-solution stability, in situ TEM observations revealed a progressive surface segregation of Au and Cu as the temperature increases. At the same time, changes in particle morphology and a reduction in average size were observed, indicating complex thermally-induced reconstruction processes rather than simple stabilization. Overall, this study highlights the limited thermal stability of multi-metallic solid solutions at the sub-10 nm scale, where surface-driven segregation becomes increasingly dominant at elevated temperatures.

To effectively overcome these challenges, it is essential to stabilize the nanoparticle surface and control the storage environment. Surface-engineering strategies, such as ligand capping, polymer encapsulation, or embedding the nanoparticles within protective inorganic or carbon-based matrices, provide a robust barrier against aggregation, oxidation, and undesired structural evolution. Equally important is maintaining a controlled storage environment. Low temperatures, inert atmospheres, and vacuum conditions have all been shown to strongly improve long-term stability. Overall, these approaches form a practical and powerful toolkit for preserving the structural integrity and functional properties of USHENMs.

Characterization presents another major obstacle. The smaller the particles become, the more challenging it is to characterize HENMs. Conventional analytical tools often lack the resolution or sensitivity required to accurately probe such multicomponent materials. To determine whether USHENMs are truly homogeneous single-phase systems or exhibit compositional segregation, it is generally necessary to employ advanced (high-resolution) characterization techniques, such as synchrotron XRD, STEM-EELS [162, 163], 4D-STEM [91], APT [164, 165], and/or XAS [48, 166]. Although limited by particle size broadening, synchrotron-based diffraction can still provide valuable insights into phase composition, lattice strain, and crystallinity, as shown in Figure 15a. Synchrotron XAS, including EXAFS and XANES, is particularly valuable for investigating chemical states and short-range ordering (Figure 15b). APT, a cutting-edge technique, can provide (atomic-scale) 3D compositional maps with extremely high sensitivity. It is particularly powerful for confirming whether the elements are uniformly mixed or show signs of nanoscale segregation, critical questions for USHENMs. STEM-EELS offers higher spatial and chemical sensitivity than EDS, allowing determination of oxidation states, bonding environments, and fine elemental variations within individual nanoparticles. Last but not least, 4D-STEM acquires a complete diffraction pattern at every probe position during a scanning experiment, producing a true 4D dataset (two spatial dimensions + two diffraction dimensions). This capability enables quantitative mapping of strain, local crystallinity, lattice orientation, and phase distribution with high spatial resolution, information that is crucial for understanding the structural disorder and heterogeneity present in USHENMs. As illustrated in Figure 15c–f, localized strain fields can be extracted from a 4D-TEM dataset to visualize lattice distortions. The strain maps are generated by analyzing variations within the individual diffraction patterns at each probe position and comparing them to the average Bragg vector map, thereby revealing subtle structural deviations across the nanoparticles [91].

However, characterizing USHENMs remains extremely challenging because most advanced techniques face fundamental resolution, sensitivity, or damage-related limitations at this size scale. For example, STEM-EELS can, in principle, resolve single atoms, but sub-2 nm systems often suffer from severe beam damage, atomic mobility under the beam, and overlap of EELS edges from multiple elements, which complicates quantitative mapping. 4D-STEM offers strain and lattice-dynamics analysis, yet for clusters containing only a few hundred atoms,

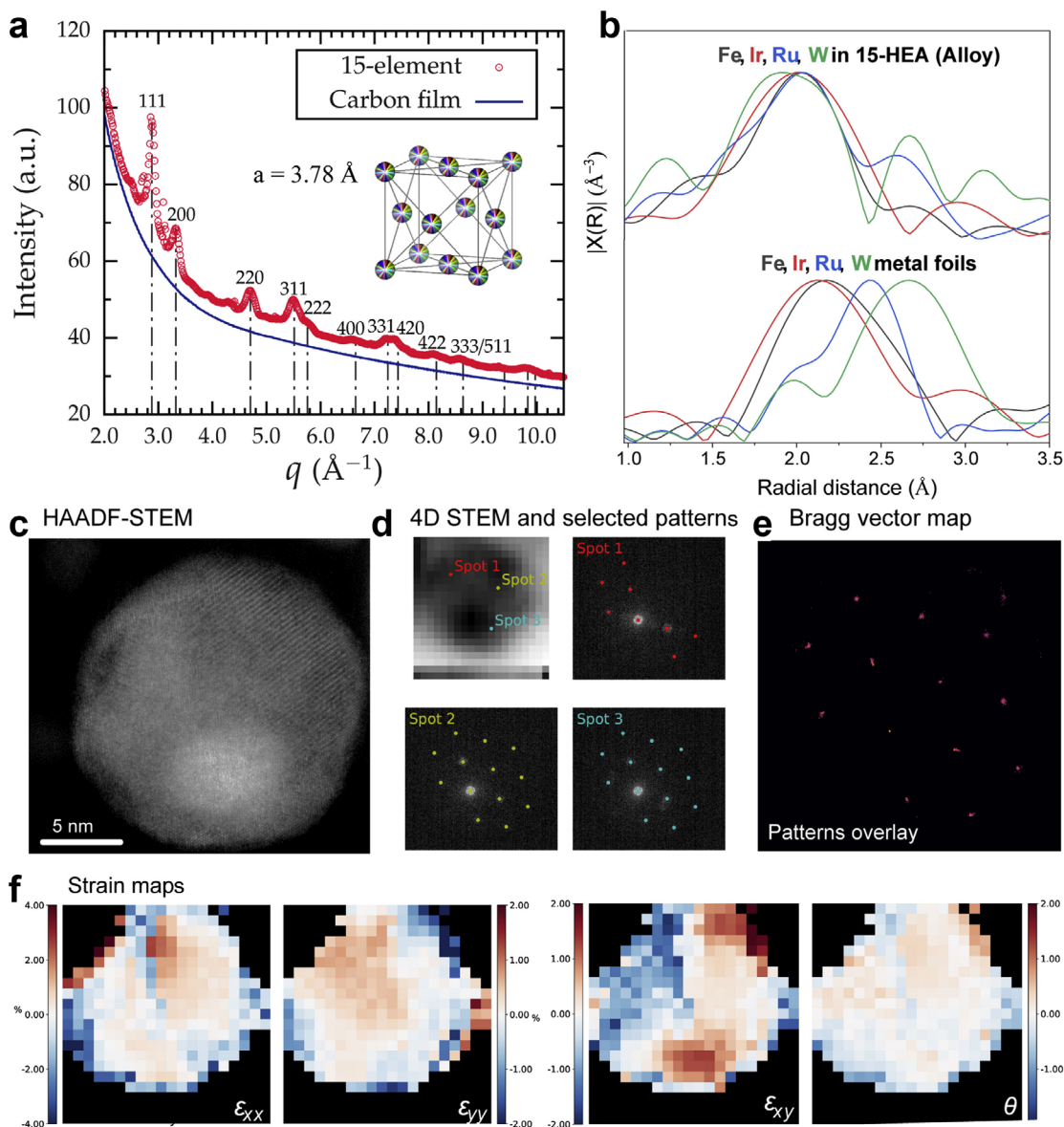


FIGURE 15 | (a) Synchrotron XRD showing an overall single-phase FCC structure. (b) FT-EXAFS analysis of Fe, Ir, Ru, and W compared with their metal foil counterparts, indicating alloy formation through peak shifts. (c) High-magnification HAADF-STEM image of a single nanoparticle used for 4D-STEM analysis. (d) Corresponding virtual ADF image, where each pixel represents a diffraction pattern, with three representative patterns shown. (e) Bragg vector map generated from all diffraction patterns. (f) Resulting strain map, revealing localized lattice strain and structural inhomogeneity arising from the complex elemental mixing. Reproduced with permission [91]. Copyright 2021, Elsevier.

the coherence and diffraction signals are extremely weak, making strain fields and local ordering difficult to interpret. APT provides 3D compositional mapping with near-atomic resolution, but USHENMs tend to field-evaporate inconsistently, leading to preferential loss of certain elements, trajectory aberrations, and unreliable quantification, especially when the particle size is close to the evaporation radius. XAS is powerful for probing local bonding environments, but it yields ensemble-averaged information, meaning subtle heterogeneities, such as local segregation or short-range order, may be masked by averaging across thousands or millions of particles. With continued progress in stabilization strategies and high-resolution characterization tools, the full potential of these remarkable materials can be realized in practical applications.

In general, well-founded claims of homogeneous single-phase USHENMs should be supported by the characterization methods mentioned above. Conventional EDS mapping alone is not sufficient to confirm true homogeneity at the atomic level in ultrasmall systems, as it may overlook phenomena, such as segregation or short-range ordering. In fact, several reports that mention uniform phases show an obvious uneven distribution of elements, suggesting a possible phase separation/segregation. Accordingly, true USHENMs should be confirmed by consistent results from structural, chemical, and electronic characterizations that demonstrate the following: (i) a random, multicomponent atomic distribution at the nanoscale, (ii) the absence of detectable phase separation, cluster formation, or compositional segregation, (iii) uniform local chemical environments across particles, and (iv) spectroscopic signatures

that indicate statistical mixing rather than ordered or segregated domains. Regardless, we emphasize the importance of distinguishing equilibrium-like solid solutions from kinetically stabilized or partially ordered states, particularly in the realm of extremely small dimensions, where surface and kinetic effects dominate.

2.6 | Machine Learning-Based Materials Design and Discovery

HEMs are highly complex systems and downsizing them to the nanoscale often results in unexpected, and in some cases, still poorly understood properties. At the same time, their reaction pathways and characterization methodologies require further refinement. The vast compositional space, coupled with severe lattice distortions and atomic-level heterogeneity, makes it difficult to establish clear composition-structure-property relationships. As discussed above, advanced characterization techniques are essential, yet they remain time-consuming, data-intensive, and experimentally demanding. These challenges limit the pace at which new USHENMs can be explored.

In this context, machine learning (ML) has emerged as a powerful and timely solution. With rapid advancements in data-driven materials science, ML enables efficient prediction of promising element combinations, discovery of mechanistic trends hidden within high-dimensional datasets, and accelerated optimization of multicomponent nanosystems [26, 167, 168]. This paradigm is particularly valuable for HEMs, where the enormous configurational space and associated effects render conventional trial-and-error approaches slow and often ineffective. By integrating ML with high-throughput synthesis and characterization workflows, researchers can more rapidly map the complex landscape of structures and properties, ultimately guiding the rational design of next-generation USHENMs.

Very recently, Perumal et al. demonstrated the potential of this strategy by developing sub-2 nm catalysts composed of 8 transition metals using an active-learning framework (Figure 16a–e) [142]. By integrating Bayesian optimization (BO) with an iterative active-learning model, they efficiently navigated the compositional landscape of octonary USHENMs for both the HER and OER. This closed-loop workflow enabled real-time, user-guided refinement of the model, ensuring rapid convergence toward high-performance compositions while substantially reducing experimental effort. Gaussian process regression was used for property prediction, while SHapley Additive exPlanations analysis and *t*-distributed stochastic neighbor embedding provided interpretable insights into composition-activity trends. Ultimately, this approach identified 10 highly promising compositions that were experimentally validated, highlighting the transformative potential of ML-guided discovery for complex nanoscale systems. Furthermore, Pan et al. utilized a large language model to identify 70 quinary combinations of HENMs, markedly accelerating the discovery of efficient electrocatalysts [169]. Likewise, Shan et al. integrated artificial intelligence (AI) with machine vision automation to screen 56 HENM systems, establishing a comprehensive dataset of 238 precursor composition-activity pairs, a foundation for predictive modeling

of multicomponent materials [170]. Collectively, these advances highlight how ML-driven discovery is revolutionizing the prediction and design of USHENMs, enabling precise control over atomic configuration and property optimization within previously inaccessible compositional regimes.

Although ML, in general, holds great potential, its application to USHENMs also comes with important limitations. High-quality and reliable datasets are essential for building accurate predictive models, yet experimental data are often scarce, inconsistent, or incomplete because of the inherent challenges in synthesizing and characterizing materials at this scale. Such data limitations can reduce model accuracy, introduce bias, and restrict the generalizability of ML predictions. In addition, interpretability remains a significant challenge. Many ML models, particularly deep-learning approaches, function as “black boxes,” making it difficult to understand or validate the physical mechanisms behind their predictions. For complex systems like USHENMs, where mechanistic insights are as critical as performance metrics, these issues can constrain the usefulness and scientific trustworthiness of ML-guided design. Looking forward, the integration of ML with autonomous synthesis, in situ characterization, and quantum-level simulations is expected to establish a smart closed-loop platform for the accelerated discovery of next-generation USHENMs.

3 | Outlook and Conclusions

USHENMs combine compositional disorder with nanoscale effects, giving rise to properties not accessible in the bulk. This review has summarized recent progress in understanding the merits of such materials, including controlling their synthesis, improving their stability, advancing their characterization, and accelerating their discovery through ML approaches. Building on these developments, future advances will depend on addressing several key challenges and opportunities that will determine the next phase of research.

Advancing enthalpy-driven synthesis: Reports on enthalpy-driven routes for USHENMs remain scarce and their underlying control mechanisms are not well understood yet. Unlike entropy- or kinetics-dominated approaches, enthalpy-driven reaction pathways often struggle to achieve ultrasmall particle sizes. Producing sub-5 nm particles is particularly challenging due to limited control over nucleation and sluggish diffusion. Future efforts should focus on elucidating the fundamental thermodynamic processes involved, improving precursor design, and integrating external stimuli (e.g., pressure, reactive atmospheres, or chemical templating) to overcome current limitations and unlock the full potential of enthalpy-driven synthesis of sub-10 nm HENMs.

Toward Homogeneous USHENMs: A key and as yet unresolved challenge in the development of USHENMs is achieving structural and chemical (compositional) homogeneity as particle size decreases from the sub-10 nm range to the sub-5 nm range and ultimately to the sub-nanometer scale. While some single-phase structures can be produced relatively reliably at ~10 nm, further size reduction significantly increases the likelihood of compositional fluctuations, surface segregation, and cluster formation, phenomena that are often unavoidable due to thermodynamic

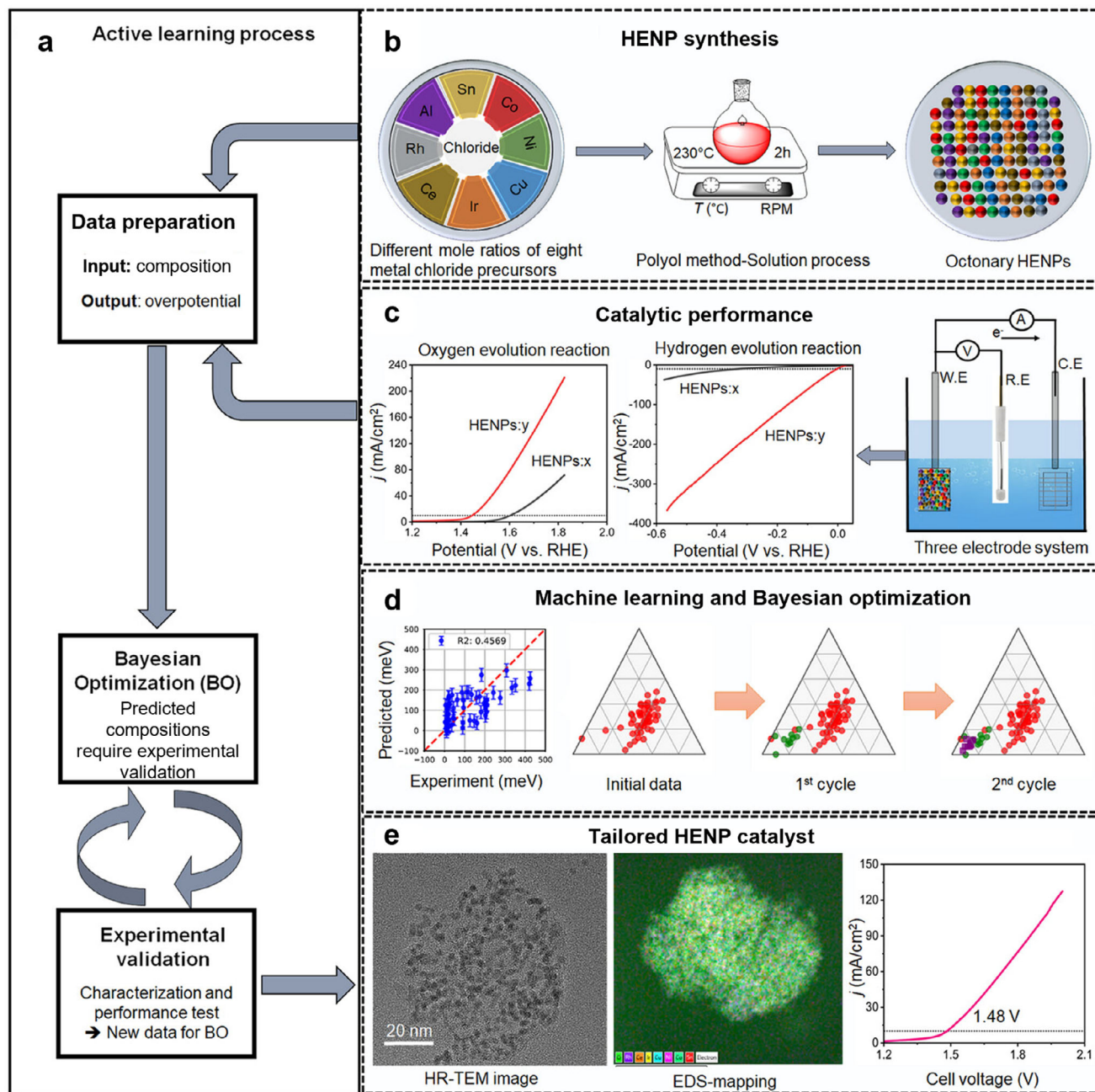


FIGURE 16 | Active learning framework for the discovery of high-entropy nanoparticle (HENP) catalysts for alkaline water splitting. (a) Schematic workflow for identifying low-overpotential materials. (b) Illustration of the synthesis process. (c) Evaluation of HER and OER performance, including linear sweep voltammetry curves for HENPs with the lowest (HENPs-y) and highest (HENPs-x) overpotentials. (d) Visualization of the active learning process using BO. (e) HRTEM image of tailored HENPs, corresponding EDS elemental mapping, and linear sweep voltammetry curve for the overall alkaline water splitting. Reproduced from [142]. CC BY-NC-ND 4.0.

and kinetic constraints. Consequently, although many studies describe USHENMs as single-phase systems, it remains very difficult to demonstrate true homogeneity at the atomic level. These limitations are raising concerns that some of the reported systems may not be solid solutions, but rather metastable or partially segregated structures that lie beyond the resolution limit of conventional characterization techniques.

Addressing this problem requires not only improved characterization, but also the development of synthetic strategies specifically designed to ensure mixing at the atomic scale under

extreme size constraints. Several promising approaches have been identified. First, kinetically controlled synthesis methods, such as rapid quenching, ultrafast reduction, or non-equilibrium deposition, can help “freeze” a uniform distribution of elements before phase separation occurs. Second, strategies for strong coordination or confinement—for example, using ligands, supports, or spatially confined templates (e.g., porous matrices or carbon scaffolds)—can suppress atomic diffusion and prevent segregation during nucleation and growth. Third, the design of precursors at the molecular level, such as single-source or premixed heterometallic complexes, offers a way to ensure uniform element

distribution even before particle formation. Fourth, thermodynamic stabilization through surface and interface engineering becomes increasingly important for dimensions below 5 nm, since surface energy dominates at these scales and can be tailored to favor mixed configurations over segregated ones. In parallel, advanced characterization techniques with atomic resolution, combined with statistical analyses of large particle populations, are essential for rigorously verifying homogeneity and distinguishing single-phase systems from locally segregated structures. Integrating such experimental approaches with theoretical modeling will further clarify the limits of entropy stabilization at ultrasmall scales.

In conclusion, sub-10 nm HENMs embody a unique convergence of compositional complexity (occupational disorder) and nanoscale effects. Future progress will depend on the continued development of reliable frameworks for synthesis-structure verification that are capable of both producing and unambiguously verifying homogeneous USHENMs. Ultimately, they represent an exciting new frontier in materials science and offer opportunities for breakthroughs that cannot be achieved with either bulk HEMs or conventional nanomaterials.

Author Contributions

Y. H. conceived the review topic and drafted the manuscript. W. W. designed the figures. S. S. provided comments on the manuscript. B. B., Y. M., and T. B. contributed to discussions and proofreading.

Acknowledgements

This work is supported by a research start-up fund of Nanjing Normal University (184080H201B41) and Jiangsu Distinguished Young Scholars Fund (BK20250036). S. S. acknowledges funding from the German Federal Ministry of Research, Technology and Space (BMFTR) in the NanoMatFutur program within the project MAP-KAT (03XPM025). The authors acknowledge the use of large language models to improve readability and language.

Conflicts of Interest

The authors declare no conflict of interest.

Data Availability Statement

Data sharing is not applicable to this article as no new data were generated or analyzed.

References

1. S. Chagri, D. Y. W. Ng, and T. Weil, "Designing Bioresponsive Nanomaterials for Intracellular Self-assembly," *Nature Reviews Chemistry* 6 (2022): 320–338.
2. D. Zhang, Y. Chen, M. Hao, and Y. Xia, "Putting Hybrid Nanomaterials to Work for Biomedical Applications," *Angewandte Chemie International Edition* 136 (2024): 202319567.
3. Y. Wang, R. Garg, D. Cohen-Karni, and T. Cohen-Karni, "Neural Modulation With Photothermally Active Nanomaterials," *Nature Reviews Bioengineering* 1 (2023): 193–207.
4. J. Tsai, J. Chen, C. Huang, et al., "A High-Entropy-Oxides-Based Memristor: Outstanding Resistive Switching Performance and Mechanisms in Atomic Structural Evolution," *Advanced Materials* 35 (2023): 2302979.

5. J. Liu, X. Xiong, H. Li, et al., "Application of Solution-Processed High-Entropy Metal Oxide Dielectric Layers with High Dielectric Constant and Wide Bandgap in Thin-Film Transistors," *Micromachines* 15 (2024): 1465.
6. S. Kumar and M. Kumar, "Utilizations of High Entropy Alloy Nanoparticles for Gas Sensors," *Transactions of the Indian National Academy of Engineering* 9 (2024): 679–687.
7. S. Das, S. Chowdhury, and C. S. Tiwary, "High-Entropy-Based Nanomaterials for Sustainable Environmental Applications," *Nanoscale* 16 (2024): 8256–8272.
8. J. Yi and Y. Xianyu, "Gold Nanomaterials-Implemented Wearable Sensors for Healthcare Applications," *Advanced Functional Materials* 32 (2022): 2113012.
9. H. Hu, A. Scholz, C. Dolle, et al., "Inkjet-Printed Tungsten Oxide Memristor Displaying Non-Volatile Memory and Neuromorphic Properties," *Advanced Functional Materials* 34 (2024): 2302290.
10. J. Liu, Y. Li, Z. Chen, et al., "Polyoxometalate Cluster-Incorporated High Entropy Oxide Sub-1 Nm Nanowires," *Journal of the American Chemical Society* 144 (2022): 23191–23197.
11. F. Zhang, T. Gao, Y. Zhang, et al., "High-Entropy Metal Sulfide Nanocrystal Libraries for Highly Reversible Sodium Storage," *Advanced Materials* 37 (2025): 2418890.
12. D. Li, D. Yu, G. Zhang, et al., "High Configuration Entropy Promises Electrochemical Stability of Chloride Electrolytes for High-Energy, Long-Life All-Solid-state Batteries," *Angewandte Chemie International Edition* 64 (2025): 202419735.
13. R. Ge, J. Huo, M. Sun, et al., "Surface and Interface Engineering: Molybdenum Carbide-Based Nanomaterials for Electrochemical Energy Conversion," *Small* 17 (2021): 1903380.
14. Y. Yu, T. Ma, and H. Huang, "Semiconducting Quantum Dots for Energy Conversion and Storage," *Advanced Functional Materials* 33 (2023): 2213770.
15. C. Xia, Y. Zhou, C. He, et al., "Recent Advances on Electrospun Nanomaterials for Zinc–Air Batteries," *Small Science* 1 (2021): 2100010.
16. S. Zhang, B. Ji, K. Ding, Y. Yang, Y. Zheng, and Y. Tang, "Confined Atom Escape and Nucleation Delivering Iridium-Based Nanoparticles with Ultrahigh Mass Activity for Acidic Water Oxidation," *Advanced Energy Materials* 15 (2025): 03229.
17. X. Chen, C. Ke, B. Sun, et al., "Organic Nanomaterials in Memristor-Based Devices for Information Processing and Artificial Intelligence Applications: A Review," *ACS Applied Nano Materials* 8 (2025): 12459.
18. P. Liu, F. Hui, F. Aguirre, et al., "Nano-Memristors With 4 mV Switching Voltage Based on Surface-Modified Copper Nanoparticles," *Advanced Materials* 34 (2022): 2201197.
19. J. Pan, J. Hu, X. Dong, et al., "Enhancement of Stability and Durability in Nanocrystal Memristors With Surface Defect Control for Image Encryption and Storage," *Advanced Functional Materials* 35 (2025): 2500765.
20. K. Chen, N. Li, Y. Luo, and Y. Yao, "High-Performance Hardware Primitives Based on Sub-10 Nm Nanodiodes for Cryptography Applications," *Journal of Materials Chemistry C* 12 (2024): 17878–17889.
21. H. Qi, F. Lu, Q. Li, et al., "Sub-5 Nm Ultrasmall High-Entropy Alloy Nanomaterials for Electrocatalysis," *Advanced Functional Materials* 36 (2026): 19434.
22. Y. Ai, M. He, H. Sun, et al., "Ultra-Small High-Entropy Alloy Nanoparticles: Efficient Nanozyme for Enhancing Tumor Photothermal Therapy," *Advanced Materials* 35 (2023): 2302335.
23. L. Yang, R. He, J. Chai, et al., "Synthesis Strategies for High Entropy Nanoparticles," *Advanced Materials* 37 (2025): 2412337.
24. Y. Liao, Y. Li, R. Zhao, et al., "High-Entropy-Alloy Nanoparticles With 21 Ultra-Mixed Elements for Efficient Photothermal Conversion," *National Science Review* 9 (2022): nwac041.

25. B. Wang, C. Wang, X. Yu, et al., "General Synthesis of High-entropy Alloy and Ceramic Nanoparticles in Nanoseconds," *Nature Synthesis* 1 (2022): 138–146.
26. Y. Yao, Q. Dong, A. Brozena, et al., "High-Entropy Nanoparticles: Synthesis-Structure-Property Relationships and Data-Driven Discovery," *Science* 376 (2022): abn3103.
27. J. W. Yeh, "Recent Progress in High-Entropy Alloys," *Annales de Chimie Science des Matériaux* 31 (2006): 633–648.
28. J.-W. Yeh, S.-K. Chen, S.-J. Lin, et al., "Nanostructured High-Entropy Alloys with Multiple Principal Elements: Novel Alloy Design Concepts and Outcomes," *Advanced Engineering Materials* 6 (2004): 299–303.
29. D. Wu, K. Kusada, Y. Nanba, et al., "Noble-Metal High-Entropy-Alloy Nanoparticles: Atomic-Level Insight Into the Electronic Structure," *Journal of the American Chemical Society* 144 (2022): 3365–3369.
30. L. Zhang, Y. Chen, Z. Zheng, et al., "Rapid Room Temperature Entropy-Stabilized Synthesis Enabling Super-Stable Metal Halide Perovskite Semiconductor Colloidal Nanocrystals," *Advanced Functional Materials* 35 (2025): 2423450.
31. G. R. Dey, C. R. McCormick, S. S. Soliman, A. J. Darling, and R. E. Schaak, "Chemical Insights Into the Formation of Colloidal High Entropy Alloy Nanoparticles," *ACS Nano* 17 (2023): 5943–5955.
32. H. Zhuo, Q. Song, C. Wang, and H. Zhu, "Carbon Dot-Mediated Sub-2 Nm High-Entropy Alloys for Enhancing Hydrogen Evolution Reaction Performance," *Chemical Communications* 61 (2025): 11227–11230.
33. S. Schweidler, M. Botros, F. Strauss, et al., "High-Entropy Materials for Energy and Electronic Applications," *Nature Reviews Materials* 9 (2024): 266–281.
34. W.-L. Hsu, C.-W. Tsai, A.-C. Yeh, and J.-W. Yeh, "Clarifying the Four Core Effects of High-entropy Materials," *Nature Reviews Chemistry* 8 (2024): 471–485.
35. G. R. Dey, S. S. Soliman, C. R. McCormick, C. H. Wood, R. R. Katzbaer, and R. E. Schaak, "Colloidal Nanoparticles of High Entropy Materials: Capabilities, Challenges, and Opportunities in Synthesis and Characterization," *ACS Nanoscience Au* 4 (2024): 3.
36. J. Liao, C. Shao, J. Han, et al., "High-entropy Perovskite Fluoride Ultra-small Nanoparticles Embedded in Carbon Nanofibers Enable Accelerated Redox Kinetic for K Storage," *Energy & Environmental Science* 17 (2024): 7362–7371.
37. C. M. Rost, E. Sachet, T. Borman, et al., "Entropy-Stabilized Oxides," *Nature Communications* 6 (2015): 8485.
38. C. Zhao, F. Ding, Y. Lu, L. Chen, and Y. S. Hu, "High-Entropy Layered Oxide Cathodes for Sodium-Ion Batteries," *Angewandte Chemie International Edition* 59 (2020): 264–269.
39. A. Sarkar, Q. Wang, A. Schiele, et al., "High-Entropy Oxides: Fundamental Aspects and Electrochemical Properties," *Advanced Materials* 31 (2019): 1806236.
40. Z. Liu, E. Goudeli, R. Guo, et al., "Flame Synthesis Achieves Compositionally Tailorable High-Entropy Metal-Containing Nanomaterials," *Nature Chemistry* 17 (2025): 1497–1504.
41. T. Phan-Xuan, S. Schweidler, S. Hirte, et al., "Using the High-Entropy Approach to Obtain Multimetal Oxide Nanozymes: Library Synthesis, in Silico Structure–Activity, and Immunoassay Performance," *ACS Nano* 18 (2024): 19024–19037.
42. L. Lin, K. Wang, A. Sarkar, et al., "High-Entropy Sulfides as Electrode Materials for Li-Ion Batteries," *Advanced Energy Materials* 12 (2022): 2103090.
43. M. A. Buckingham, B. Ward-O'Brien, W. Xiao, Y. Li, J. Qu, and D. J. Lewis, "High Entropy Metal Chalcogenides: Synthesis, Properties, Applications and Future Directions," *Chemical Communications* 58 (2022): 8025–8037.
44. M. Xu, Q. Zhu, Y. Li, Y. Gao, N. Sun, and B. Xu, "Atom-Dominated Relay Catalysis of High-Entropy MXene Promotes Cascade Polysulfide Conversion for Lithium–sulfur Batteries," *Energy & Environmental Science* 17 (2024): 7735–7748.
45. L. Zhang, H. Li, X. Zhang, et al., "Ultra-Rapid Synthesis of High-Entropy MAX Phases and Their Derivative MXenes for Battery Electrodes," *Angewandte Chemie* 137 (2025): 202418538.
46. X. He, Y. Qian, C. Wu, et al., "Entropy-Mediated High-Entropy MXenes Nanotherapeutics: NIR-II-Enhanced Intrinsic Oxidase Mimic Activity to Combat Methicillin-Resistant Staphylococcus Aureus Infection," *Advanced Materials* 35 (2023): 2211432.
47. Y. He, Y. Ting, H. Hu, et al., "Printed High-Entropy Prussian Blue Analogs for Advanced Non-Volatile Memristive Devices," *Advanced Materials* 37 (2025): 2410060.
48. Y. He, S. L. Dreyer, Y. Ting, et al., "Entropy-Mediated Stable Structural Evolution of Prussian White Cathodes for Long-Life Na-Ion Batteries," *Angewandte Chemie International Edition* 63 (2024): 202315371.
49. X. Zhao, Z. Xue, W. Chen, Y. Wang, and T. Mu, "Eutectic Synthesis of High-Entropy Metal Phosphides for Electrocatalytic Water Splitting," *ChemSuschem* 13 (2020): 2038–2042.
50. Q. Wang, A. Sarkar, D. Wang, et al., "Multi-Anionic and -Cationic Compounds: New High Entropy Materials for Advanced Li-Ion Batteries," *Energy & Environmental Science* 12 (2019): 2433–2442.
51. Z. Lun, B. Ouyang, D.-H. Kwon, et al., "Cation-Disordered Rocksalt-Type High-Entropy Cathodes for Li-Ion Batteries," *Nature Materials* 20 (2021): 214–221.
52. J. Gild, Y. Zhang, T. Harrington, et al., "High-Entropy Metal Diborides: a New Class of High-Entropy Materials and a New Type of Ultrahigh Temperature Ceramics," *Scientific Reports* 6 (2016): 37946.
53. P. Sarker, T. Harrington, C. Toher, et al., "High-Entropy High-Hardness Metal Carbides Discovered by Entropy Descriptors," *Nature Communications* 9 (2018): 4980.
54. F. Strauss, J. Lin, M. Duffiet, et al., "High-Entropy Polyanionic Lithium Superionic Conductors," *ACS Materials Letters* 4 (2022): 418–423.
55. E. Castle, T. Csanádi, S. Grasso, J. Dusza, and M. Reece, "Processing and Properties of High-Entropy Ultra-High Temperature Carbides," *Scientific Reports* 8 (2018): 8609.
56. T. Jin, X. Sang, R. R. Unocic, et al., "Mechanochemical-Assisted Synthesis of High-Entropy Metal Nitride via a Soft Urea Strategy," *Advanced Materials* 30 (2018): 1707512.
57. Y. Qin, J.-X. Liu, F. Li, X. Wei, H. Wu, and G.-J. Zhang, "A High Entropy Silicide by Reactive Spark Plasma Sintering," *Journal of Advanced Ceramics* 8 (2019): 148–152.
58. H. Mei, Y. Zhang, P. Zhang, A. G. Ricciardulli, P. Samorì, and S. Yang, "Entropy Engineering of 2D Materials," *Advanced Science* 11 (2024): 2409404.
59. J. Lin, M. Schaller, R. Zhang, et al., "High-Entropy Argyrodite Glass–Ceramic Electrolytes for All-Solid-State Batteries," *Materials Futures* 4 (2025): 025105.
60. J. Lin, M. Schaller, S. Indris, et al., "Tuning Ion Mobility in Lithium Argyrodite Solid Electrolytes via Entropy Engineering," *Angewandte Chemie International Edition* 63 (2024): 202404874.
61. J. Lin, M. Schaller, G. Cherkashinin, et al., "Synthetic Tailoring of Ionic Conductivity in Multicationic Substituted, High-Entropy Lithium Argyrodite Solid Electrolytes," *Small* 20 (2024): 2306832.
62. J. Lin, G. Cherkashinin, M. Schäfer, et al., "A High-Entropy Multicationic Substituted Lithium Argyrodite Superionic Solid Electrolyte," *ACS Materials Letters* 4 (2022): 2187–2194.
63. N. Kar and S. E. Skrabalak, "Synthetic Methods for High-Entropy Nanomaterials," *Nature Reviews Materials* 10 (2025): 638–653.
64. X. Yan, Y. Zhou, and S. Wang, "Nano-High Entropy Materials in Electrocatalysis," *Advanced Functional Materials* 35 (2025): 2413115.

65. A. Khandelwal, G. Mathew, S. Bhattacharya, et al., "Synthesis-Driven Functionality in High-Entropy Materials," *Small* 21 (2025): 01703.
66. X. Wang, Q. Liu, and X. Wang, "High-Entropy Materials: From Bulk to Sub-Nano," *Advanced Functional Materials* 35 (2025): 2504275.
67. Y. Zhang, H. Li, X. Liu, et al., "Sub-3 Nm High-Entropy Alloy Nanoparticles With Triple Functionalities for Efficient Electrolytic Hydrogen Production," *Advanced Materials* 37 (2025): 08975.
68. H. Luo, L. Li, F. Lin, et al., "Sub-2 Nm Microstrained High-Entropy-Alloy Nanoparticles Boost Hydrogen Electrocatalysis," *Advanced Materials* 36 (2024): 2403674.
69. G. Feng, F. Ning, J. Song, et al., "Sub-2 Nm Ultrasmall High-Entropy Alloy Nanoparticles for Extremely Superior Electrocatalytic Hydrogen Evolution," *Journal of the American Chemical Society* 143 (2021): 17117–17127.
70. C. Zhan, L. Bu, H. Sun, et al., "Medium/High-Entropy Amalgamated Core/Shell Nanoplate Achieves Efficient Formic Acid Catalysis for Direct Formic Acid Fuel Cell," *Angewandte Chemie* 135 (2023): 202213783.
71. Z. Zhou, Y. Ma, T. Brezesinski, B. Breitung, Y. Wu, and Y. Ma, "Improving Upon Rechargeable Battery Technologies: On the Role of High-Entropy Effects," *Energy & Environmental Science* 18 (2025): 19–52.
72. H. Cai, H. Yang, S. He, et al., "Size-Adjustable High-Entropy Alloy Nanoparticles as an Efficient Platform for Electrocatalysis," *Angewandte Chemie International Edition* 64 (2025): 202423765.
73. W. Al Zoubi, R. A. K. Putri, M. R. Abukhadra, and Y. G. Ko, "Recent Experimental and Theoretical Advances in the Design and Science of High-entropy Alloy Nanoparticles," *Nano Energy* 110 (2023): 108362.
74. J. Su, Y. Wan, L. Feng, et al., "One-Stone, Two-Birds": Zinc-Rich Metal–Organic Frameworks as Precursors for High-Entropy Zn-Air Battery Electrocatalysts with Hierarchical Pore Structures," *Angewandte Chemie* 137 (2025): 202413826.
75. S. Niu, Z. Yang, F. Qi, et al., "Electrical Discharge Induced Bulk-to-Nanoparticle Transformation: Nano High-Entropy Carbide as Catalysts for Hydrogen Evolution Reaction," *Advanced Functional Materials* 32 (2022): 2203787.
76. D. Wu, L. Yao, M. Ricci, J. Li, R. Xie, and Z. Peng, "Ambient Synthesis of Pt-Reactive Metal Alloy and High-Entropy Alloy Nanocatalysts Utilizing Hydrogen Cold Plasma," *Chemistry of Materials* 34 (2022): 266–272.
77. A. Roy, S. Kumar, A. Guilherme Buzanich, et al., "Synergistic Catalytic Sites in High-Entropy Metal Hydroxide Organic Framework for Oxygen Evolution Reaction," *Advanced Materials* 36 (2024): 2408114.
78. K. Li, X. Sun, Q. Wu, et al., "Synthesizing High-Entropy Alloy Materials and Coatings Using a Bilayer Ice Recrystallization Method," *Nature Synthesis* 5 (2025): 302.
79. L. He, M. Li, L. Qiu, et al., "Single-Atom Mo-Tailored High-Entropy-Alloy Ultrathin Nanosheets With Intrinsic Tensile Strain Enhance Electrocatalysis," *Nature Communications* 15 (2024): 2290.
80. D. Choi, Y. Boo, S. Park, et al., "Ultrasmall High-Entropy-Alloy Nanozyme Catalyzed In Vivo ROS and NO Scavenging for Anti-Inflammatory Therapy," *Advanced Healthcare Materials* 14 (2025): 2402005.
81. P. Wang, S. Guo, Y. Xu, et al., "Upcycling Spent Cathodes from Li-Ion Batteries into a High-Entropy Alloy Catalyst with Reverse Electron Transfer for Li–O₂ Batteries," *ACS Nano* 19 (2025): 17589–17605.
82. T. Chen, C. Qiu, X. Zhang, et al., "An Ultrasmall Ordered High-Entropy Intermetallic with Multiple Active Sites for the Oxygen Reduction Reaction," *Journal of the American Chemical Society* 146 (2024): 1174–1184.
83. R. Ren, T. Liang, Z. Gong, et al., "Integrating High-Entropy Alloy Nanocatalysts With Aligned Porous Air Electrode for High-Power Zinc–Air Battery," *Advanced Materials* 38 (2026): 13348.
84. S. Yoo, S. Chae, T. Chiang, et al., "Efficient Data Processing Using Tunable Entropy-Stabilized Oxide Memristors," *Nature Electronics* 7 (2024): 466–474.
85. C. H. Wood and R. E. Schaak, "Synthetic Roadmap to a Large Library of Colloidal High-Entropy Rare Earth Oxyhalide Nanoparticles Containing up to Thirteen Metals," *Journal of the American Chemical Society* 146 (2024): 18730–18742.
86. R. E. Sikma, D. J. Vogel, R. A. Reyes, M. L. Meyerson, P. G. Kotula, and D. F. S. Gallis, "High-Entropy Metal–Organic Frameworks (HEMOFs): A New Frontier in Materials Design for CO₂ Utilization," *Advanced Materials* 36 (2024): 2407435.
87. W. Xu, H. Chen, K. Jie, Z. Yang, T. Li, and S. Dai, "Entropy-Driven Mechanochemical Synthesis of Polymetallic Zeolitic Imidazolate Frameworks for CO₂ Fixation," *Angewandte Chemie International Edition* 58 (2019): 5018–5022.
88. T. A. A. Batchelor, J. K. Pedersen, S. H. Winther, I. E. Castelli, K. W. Jacobsen, and J. Rossmeisl, "High-Entropy Alloys as a Discovery Platform for Electrocatalysis," *Joule* 3 (2019): 834–845.
89. Y. Yao, Z. Huang, P. Xie, et al., "Carbothermal Shock Synthesis of High-Entropy-Alloy Nanoparticles," *Science* 359 (2018): 1489–1494.
90. S. Gao, S. Hao, Z. Huang, et al., "Synthesis of High-entropy Alloy Nanoparticles on Supports by the Fast Moving Bed Pyrolysis," *Nature Communications* 11 (2020): 2016.
91. Y. Yao, Z. Huang, L. A. Hughes, et al., "Extreme Mixing in Nanoscale Transition Metal Alloys," *Matter* 4 (2021): 2340.
92. M. J. Theibault, C. R. McCormick, S. Lang, R. E. Schaak, and H. D. Abruña, "High Entropy Sulfide Nanoparticles as Lithium Polysulfide Redox Catalysts," *ACS Nano* 17 (2023): 18402–18410.
93. Y. Wang, W. Luo, S. Gong, et al., "Synthesis of High-Entropy-Alloy Nanoparticles by a Step-Alloying Strategy as a Superior Multifunctional Electrocatalyst," *Advanced Materials* 35 (2023): 2302499.
94. D. Liu, P. Guo, Q. Wang, et al., "Local Proton-Mediated Synthesis of a High-Entropy Borate Library," *Advanced Materials* 37 (2025): 2414067.
95. M. W. Glasscott, A. D. Pendergast, S. Goines, et al., "Electrosynthesis of High-Entropy Metallic Glass Nanoparticles for Designer, Multi-Functional Electrocatalysis," *Nature Communications* 10 (2019): 2650.
96. Y. He, S. L. Dreyer, T. Akçay, et al., "Leveraging Entropy and Crystal Structure Engineering in Prussian Blue Analogue Cathodes for Advancing Sodium-Ion Batteries," *ACS Nano* 18 (2024): 24441–24457.
97. H. Shi, T. Dai, X. Sun, et al., "High-Entropy Alloy/Intermetallic Compound Heterostructures for Efficient Hydrazine Oxidation-Assisted Hydrogen Production," *Advanced Materials* 37 (2025): 12081.
98. T. Gu, C. Zhang, L. Xi, L. Ouyang, M. Zhu, and J. Liu, "High-Entropy Electrocatalytic Materials in Zn-Air Batteries: From Fundamentals to Applications," *Advanced Materials* 38 (2026): 12274.
99. Y. Sun, W. Zhang, Q. Zhang, Y. Li, L. Gu, and S. Guo, "A General Approach to High-entropy Metallic Nanowire Electrocatalysts," *Matter* 6 (2023): 193.
100. G. Feng, Y. Pan, D. Su, and D. Xia, "Constructing Fully-Active and Ultra-Active Sites in High-Entropy Alloy Nanoclusters for Hydrazine Oxidation-Assisted Electrolytic Hydrogen Production," *Advanced Materials* 36 (2024): 2309715.
101. G. Feng, F. Ning, Y. Pan, et al., "Engineering Structurally Ordered High-Entropy Intermetallic Nanoparticles With High-Activity Facets for Oxygen Reduction in Practical Fuel Cells," *Journal of the American Chemical Society* 145 (2023): 11140–11150.
102. S. Jo, M. Kim, K. B. Lee, H. Choi, L. Zhang, and J. I. Sohn, "Nonprecious High-Entropy Chalcogenide Glasses-Based Electrocatalysts for Efficient and Stable Acidic Oxygen Evolution Reaction in Proton Exchange Membrane Water Electrolysis," *Advanced Energy Materials* 13 (2023): 2301420.

103. G. He, X. Zhang, J. Liu, J. Chong, G. Ye, and H. Fei, "Hydrocarbothermally Flow Synthesis of Carbon-Supported Small and Dense High-Entropy Alloy Nanoparticles as Electrocatalysts," *Nature Communications* 16 (2025): 8172.
104. X. Li, J. Cao, G. Chen, et al., "A Radical-Assisted Approach to High-Entropy Alloy Nanoparticle Electrocatalysts under Ambient Conditions," *ACS Nano* 19 (2025): 7851–7863.
105. X. Zheng, X. Gao, R. A. Vilá, et al., "Hydrogen-Substituted Graphdiyne-Assisted Ultrafast Sparking Synthesis of Metastable Nanomaterials," *Nature Nanotechnology* 18 (2023): 153–159.
106. J. Hao, Z. Zhuang, K. Cao, et al., "Unraveling the Electronegativity-Dominated Intermediate Adsorption on High-Entropy Alloy Electrocatalysts," *Nature Communications* 13 (2022): 2662.
107. W. Yang, T. Xu, C. Yang, et al., "Selective and Bifunctional Catalytic Electrochemical Conversion of Organosulfide Molecule by High-Entropy Carbides," *Advanced Functional Materials* 34 (2024): 2409450.
108. T. Löffler, A. Ludwig, J. Rossmeisl, and W. Schuhmann, "What Makes High-Entropy Alloys Exceptional Electrocatalysts?," *Angewandte Chemie International Edition* 60 (2021): 26894–26903.
109. H. Cai, S. He, H. Yang, et al., "Highly Exposed Ultra-Small High-Entropy Sulfides with D-p Orbital Hybridization for Efficient Oxygen Evolution," *Advanced Materials* 37 (2025): 2508610.
110. Z. Zhang, P. Yu, Z. Liu, et al., "Off-Equilibrium Hydrothermal Synthesis of High-Entropy Alloy Nanoparticles," *Journal of the American Chemical Society* 147 (2025): 9640–9652.
111. L. Tao, M. Sun, Y. Zhou, et al., "A General Synthetic Method for High-Entropy Alloy Subnanometer Ribbons," *Journal of the American Chemical Society* 144 (2022): 10582–10590.
112. C. R. McCormick and R. E. Schaak, "Simultaneous Multication Exchange Pathway to High-Entropy Metal Sulfide Nanoparticles," *Journal of the American Chemical Society* 143 (2021): 1017–1023.
113. H. Wang, N. Makowski, Y. Ma, et al., "Metallic Glass Nanoparticles Synthesized via Flash Joule Heating," *ACS Nano* 19 (2025): 19806–19817.
114. Z. Wen, Z. Tang, H. Meng, L. Zhuang, H. Yu, and Y. Chu, "Ultrafast Synthesis of High-Entropy Carbides up to 3,273 K for Superior Oxidation Resistance," *Cell Reports Physical Science* 5 (2024): 101821.
115. Y. Yao, Z. Liu, P. Xie, et al., "Computationally Aided, Entropy-Driven Synthesis of Highly Efficient and Durable Multi-elemental Alloy Catalysts," *Science Advances* 6 (2020): aaz0510.
116. G. Zhong, S. Xu, C. Chen, et al., "Synthesis of Metal Oxide Nanoparticles by Rapid, High-Temperature 3D Microwave Heating," *Advanced Functional Materials* 29 (2019): 1904282.
117. R. Chang, H. Li, X. Tian, et al., "In Situ, Rapid Synthesis of Carbon-Loaded High Density and Ultrasmall High Entropy Oxide Nanoparticles as Efficient Electrocatalysts," *Small* 20 (2024): 2309937.
118. C. Zhang, Z. Wang, C. Liu, et al., "Rapid Synthesis of Subnanoscale High-Entropy Alloys With Ultrahigh Durability," *Nature Materials* 25 (2026): 26–34.
119. X. Wang, Y. Zhao, G. Chen, et al., "Ultrahigh-Temperature Melt Printing of Multi-Principal Element Alloys," *Nature Communications* 13 (2022): 6724.
120. J. Ahn, S. Park, D. Oh, et al., "Rapid Joule Heating Synthesis of Oxide-Socketed High-Entropy Alloy Nanoparticles as CO₂ Conversion Catalysts," *ACS Nano* 17 (2023): 12188–12199.
121. Y.-S. Kwon, K. B. Gerasimov, and S.-K. Yoon, "Ball Temperatures During Mechanical Alloying in Planetary Mills," *Journal of Alloys and Compounds* 346 (2002): 276–281.
122. C. Suryanarayana, "Mechanical Alloying and Milling," *Progress in Materials Science* 46 (2001): 1–184.
123. M. Y. Rekha, N. Mallik, and C. Srivastava, "First Report on High Entropy Alloy Nanoparticle Decorated Graphene," *Scientific Reports* 8 (2018): 8737.
124. S. Chen, X. Li, Z. Qu, et al., "Space-Confined Synthesis of Sinter-Resistant High-Entropy Nanoparticle Library," *Nature Communications* 16 (2025): 7383.
125. F. Li, Y. Ma, H. Wu, et al., "Sub-3-nm High-Entropy Metal Sulfide Nanoparticles With Synergistic Effects as Promising Electrocatalysts for Enhanced Oxygen Evolution Reaction," *The Journal of Physical Chemistry C* 126 (2022): 18323–18332.
126. R. Wang, J. Jiao, D. Liu, et al., "High-Entropy Metal Nitride Embedded in Concave Porous Carbon Enabling Polysulfide Conversion in Lithium–Sulfur Batteries," *Small* 20 (2024): 2405148.
127. J. Du, S. Liu, Y. Liu, et al., "One-Dimensional High-Entropy Compounds," *Journal of the American Chemical Society* 146 (2024): 8464–8471.
128. J. E. Miller, A. H. McDaniel, and M. D. Allendorf, "Considerations in the Design of Materials for Solar-Driven Fuel Production Using Metal-Oxide Thermochemical Cycles," *Advanced Energy Materials* 4 (2014): 1300469.
129. W. W. Bewley, C. S. Kim, M. Kim, et al., "Broad-Stripe Midinfrared Photonic-Crystal Distributed-Feedback Lasers With Laser-Ablation Confinement," *Applied Physics Letters* 83 (2003): 5383–5385.
130. H. Meng, X. Yangsu, L. Jing, Z. Jingchao, and W. Xinwei, "Significantly Reduced c-axis Thermal Diffusivity of Graphene-Based Papers," *Nanotechnology* 29 (2018): 265702.
131. Y. Yue, X. Huang, and X. Wang, "Thermal Transport in Multiwall Carbon Nanotube Buckypapers," *Physics Letters A* 374 (2010): 4144–4151.
132. H. Qiao, M. T. Saray, X. Wang, et al., "Scalable Synthesis of High Entropy Alloy Nanoparticles by Microwave Heating," *ACS Nano* 15 (2021): 14928–14937.
133. Y. Yang, B. Song, X. Ke, et al., "Aerosol Synthesis of High Entropy Alloy Nanoparticles," *Langmuir* 36 (2020): 1985–1992.
134. F. Waag, Y. Li, A. R. Zieffuß, et al., "Kinetically-Controlled Laser-Synthesis of Colloidal High-Entropy Alloy Nanoparticles," *RSC Advances* 9 (2019): 18547.
135. M. Cui, C. Yang, B. Li, et al., "High-Entropy Metal Sulfide Nanoparticles Promise High-Performance Oxygen Evolution Reaction," *Advanced Energy Materials* 11 (2021): 2002887.
136. D. Lai, Q. Kang, F. Gao, and Q. Lu, "High-Entropy Effect of a Metal Phosphide on Enhanced Overall Water Splitting Performance," *Journal of Materials Chemistry A* 9 (2021): 17913–17922.
137. M. Ma, E. Chen, H. Yue, G. Tian, and S. Feng, "Entropy Engineering Activation of UiO-66 for Boosting Catalytic Transfer Hydrogenation," *Nature Communications* 16 (2025): 367.
138. Y. Jiang, H. Fu, Z. Zhong, et al., "Atomically Dispersed Rare Earth-Confined High-Entropy Alloy Nanocrystals for Efficient Ammonia Electrosynthesis," *Angewandte Chemie International Edition* 64 (2025): 202515842.
139. R. He, S. Wang, L. Yang, et al., "Active Site Switching on High Entropy Phosphides as Bifunctional Oxygen Electrocatalysts for Rechargeable/Robust Zn–air Battery," *Energy & Environmental Science* 17 (2024): 7193–7208.
140. C. Zhan, Y. Xu, L. Bu, et al., "Subnanometer High-Entropy Alloy Nanowires Enable Remarkable Hydrogen Oxidation Catalysis," *Nature Communications* 12 (2021): 6261.
141. S. Nie, L. Wu, Q. Zhang, Y. Huang, Q. Liu, and X. Wang, "High-Entropy-Perovskite Subnanowires for Photoelectrocatalytic Coupling of Methane to Acetic Acid," *Nature Communications* 15 (2024): 6669.
142. S. Perumal, D. B. Han, T. Marimuthu, T. Lim, H. W. Kim, and J. Seo, "Active Learning-Driven Discovery of Sub-2 Nm High-Entropy Nanocat-

- alysts for Alkaline Water Splitting,” *Advanced Functional Materials* 35 (2025): 2424887.
143. D. Wu, K. Kusada, T. Yamamoto, et al., “Platinum-Group-Metal High-Entropy-Alloy Nanoparticles,” *Journal of the American Chemical Society* 142 (2020): 13833–13838.
144. H. Minamihara, K. Kusada, D. Wu, et al., “Continuous-Flow Reactor Synthesis for Homogeneous 1 Nm-Sized Extremely Small High-Entropy Alloy Nanoparticles,” *Journal of the American Chemical Society* 144 (2022): 11525–11529.
145. F. Okejiri, Z. Zhang, J. Liu, M. Liu, S. Yang, and S. Dai, “Room-Temperature Synthesis of High-Entropy Perovskite Oxide Nanoparticle Catalysts Through Ultrasonication-Based Method,” *ChemSuschem* 13 (2020): 111–115.
146. J. Wang, J. Zhang, Y. Hu, H. Jiang, and C. Li, “Activating Multisite High-entropy Alloy Nanocrystals via Enriching M–pyridinic N–C Bonds for Superior Electrocatalytic Hydrogen Evolution,” *Science Bulletin* 67 (2022): 1890–1897.
147. C.-Y. Wu, Y.-C. Hsiao, Y. Chen, et al., “A Catalyst Family of High-Entropy Alloy Atomic Layers With Square Atomic Arrangements Comprising Iron- and Platinum-Group Metals,” *Science Advances* 10 (2024): adl3693.
148. S. F. Solari, L.-N. Poon, M. Wörle, et al., “Stabilization of Lead-Reduced Metal Halide Perovskite Nanocrystals by High-Entropy Alloying,” *Journal of the American Chemical Society* 144 (2022): 5864–5870.
149. S. S. Soliman, G. R. Dey, C. R. McCormick, and R. E. Schaak, “Temporal Evolution of Morphology, Composition, and Structure in the Formation of Colloidal High-Entropy Intermetallic Nanoparticles,” *ACS Nano* 17 (2023): 16147–16159.
150. X. Wan, R. Zeng, X. Wang, H. Wang, Q. Wei, and D. Tang, “High-entropy Effect with Hollow (ZnCdFeMnCu)_xS Nanocubes for Photoelectrochemical Immunoassay,” *Biosensors and Bioelectronics* 237 (2023): 115535.
151. L. De Trizio and L. Manna, “Forging Colloidal Nanostructures via Cation Exchange Reactions,” *Chemical Reviews* 116 (2016): 10852.
152. H. Cheng, C. Wang, D. Qin, and Y. Xia, “Galvanic Replacement Synthesis of Metal Nanostructures: Bridging the Gap between Chemical and Electrochemical Approaches,” *Accounts of Chemical Research* 56 (2023): 900–909.
153. Y. Hong, S. Venkateshalu, S. Jeong, et al., “Galvanic Replacement Reaction to Prepare Catalytic Materials,” *Bulletin of the Korean Chemical Society* 44 (2023): 4–22.
154. X. Xia, Y. Wang, A. Ruditskiy, and Y. Xia, “25th Anniversary Article: Galvanic Replacement: a Simple and Versatile Route to Hollow Nanostructures with Tunable and Well-Controlled Properties,” *Advanced Materials* 25 (2013): 6313–6333.
155. S. Nie, Q. Liu, L. Wu, and X. Wang, “Surface Entropy-Engineering: Towards General Synthesis of High Entropy Subnano-Oxides,” *Nano Research* 19 (2026): 94908030.
156. J. F. Löffler, J. Schroers, and W. L. Johnson, “Time–Temperature–Transformation Diagram and Microstructures of Bulk Glass Forming Pd₄₀Cu₃₀Ni₁₀P₂₀,” *Applied Physics Letters* 77 (2000): 681–683.
157. V. K. LaMer and R. H. Dinegar, “Theory, Production and Mechanism of Formation of Monodispersed Hydrosols,” *Journal of the American Chemical Society* 72 (1950): 4847–4854.
158. G. M. Pound and V. K. La Mer, “Kinetics of Crystalline Nucleus Formation in Supercooled Liquid Tin 1,2,” *Journal of the American Chemical Society* 74 (1952): 2323–2332.
159. Y. Zhang, Y. J. Zhou, J. P. Lin, G. L. Chen, and P. K. Liaw, “Solid-Solution Phase Formation Rules for Multi-Component Alloys,” *Advanced Engineering Materials* 10 (2008): 534–538.
160. J. Yu, R. He, N. G. Bastús, J. Arbiol, and A. Cabot, “Bringing Order to Chaos in High-Entropy Electrocatalysts,” *ACS Energy Letters* 11 (2026): 2542–2552.
161. S. Krouna, A. Acheche, G. Wang, et al., “Atomic-Scale Insights into the Thermal Stability of High-Entropy Nanoalloys,” *Advanced Materials* 37 (2025): 2414510.
162. K. Wang, W. Hua, X. Huang, et al., “Synergy of Cations in High Entropy Oxide Lithium Ion Battery Anode,” *Nature Communications* 14 (2023): 1487.
163. Z. Ding, Y. Tang, T. Ortmann, et al., “The Impact of Microstructure on Filament Growth at the Sodium Metal Anode in all-Solid-State Sodium Batteries,” *Advanced Energy Materials* 13 (2023): 2302322.
164. B. Gault, A. Chiaramonti, O. Cojocaru-Mirédin, et al., “Atom Probe Tomography,” *Nature Reviews Methods Primers* 1 (2021): 51.
165. G. D. Costa, C. Castro, A. Normand, et al., “Bringing Atom Probe Tomography to Transmission Electron Microscopes,” *Nature Communications* 15 (2024): 9870.
166. Y. Ma, Y. Hu, Y. Pramudya, et al., “Resolving the Role of Configurational Entropy in Improving Cycling Performance of Multicomponent Hexacyanoferrate Cathodes for Sodium-Ion Batteries,” *Advanced Functional Materials* 32 (2022): 2202372.
167. M. Alnaasan, W. Al Zoubi, S. Alhammadi, J.-H. Kang, S. Kim, and Y. G. Ko, “Well-Defined High Entropy-Metal Nanoparticles: Detection of the Multi-Element Particles by Deep Learning,” *Journal of Energy Chemistry* 98 (2024): 262–273.
168. S. Nie, Y. Xiang, L. Wu, et al., “Active Learning Guided Discovery of High Entropy Oxides Featuring High H₂ -Production,” *Journal of the American Chemical Society* 146 (2024): 29325–29334.
169. Y. Pan, X. Shan, F. Cai, H. Gao, J. Xu, and M. Zhou, “Accelerating the Discovery of Oxygen Reduction Electrocatalysts: High-Throughput Screening of Element Combinations in Pt-Based High-Entropy Alloys,” *Angewandte Chemie International Edition* 63 (2024): 202407116.
170. X. Shan, Y. Pan, F. Cai, et al., “Accelerating the Discovery of Efficient High-Entropy Alloy Electrocatalysts: High-Throughput Experimentation and Data-Driven Strategies,” *Nano Letters* 24 (2024): 11632–11640.