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Concluding remarks: Achievements, challenges, and trajectories for high-entropy alloy nanoparticles

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The field of high-entropy alloy nanoparticles (HEA-NPs) had to move and indeed has moved beyond the early enthusiasm of simply "mixing five or more elements and hoping the configurational entropy will do some magic" in terms of chemical and physical properties. What the 2025 *Faraday Discussion* made clear is that, at the nanoscale, entropy is often a minor player. Phase stability, structure, and functional properties are instead dominated by kinetics, surface reconstruction, defects, segregation, decomposition, and – more often than we like to admit – (unnoticed) interstitial contamination (C, O, N, H, B, S) picked up during synthesis and during particle exposure to "real-world" environments. Bulk HEAs can still "hide" a bit behind their mostly metastable single-phase character and complex diffusion mechanisms, and often even exploit these features to their advantage, but nanoparticles have no such luxury. Their huge surface-to-volume ratio, rapid synthesis pathways, and exposure to harsh operational environments reveal the true thermodynamic and kinetic transient features of most reported compositions. We see decomposition, demixing, surface reconstruction, and dynamic ensemble behaviour that have in part little to do with the ideal solid-solution picture painted a decade ago. These profound differences between bulk HEAs and nanosized ones provide opportunities to be embraced and exploited for well-targeted and theory-guided development steps. The community therefore should feel encouraged to pivot. Instead of chasing ever more complex average compositions, we must focus on what really governs the usually transient features and stability of these particles, particularly at the surface and their dynamical states in real environments, and how we can deliberately exploit kinetic barriers, short-range ordering, defects and their chemical decoration, and surface dynamics to achieve emergent properties unattainable in conventional nanoscale alloys. Theory and simulation must leave the $O(N^3)$ constraints of traditional DFT behind and embrace large-scale, accurate machine-learning potentials and property-driven screening of the astronomical configuration space. Synthesis has to become far more chemically aware and reproducible, with rigorous control (and transparent reporting) of interstitials, decomposition and decay kinetics when the particles are used. And finally, functional

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validation can no longer rely on post-mortem snapshots; we need genuine *operando* insight into displaced reaction features, ordering, dynamical reconstruction, composition, and dynamics of those atomic clusters that actually do the catalytic or magnetic work. If we accept that HEA nanoparticles are inherently kinetically highly variable, defect-rich, surface-dominated objects, then more adequate design metrics need to be found, going beyond the so far primarily used single mean-field metric of configurational (bulk) entropy. This could open a pathway towards a more systematic, realistic and holistic design approach for true nanoparticle multifunctionality and their real-world stability. Papers presented at the 2025 *Faraday Discussion* have shown that opportunities along these lines might be lurking in the fields of magnetically active catalysts, noble-metal-lean electrocatalysts, or materials that combine corrosion resistance, thermal stability, and high activity in one particle. The road ahead is demanding, but the potential payoff for more sustainable catalysis and magnetic applications and beyond is high. This boils down to the statement that it is time to stop treating high-entropy nanoparticles as merely "miniaturized" bulk HEAs and start treating them as the fascinating new materials class they really are.

Introduction

This paper renders some concluding remarks about the 2025 *Faraday Discussion* on High-Entropy Alloy Nanostructures.

High-Entropy Alloys (HEAs) were originally defined as metallic materials consisting of five or more principal elements mixed in near equiatomic proportions.[1-4] The core concept is to exploit the associated high configurational entropy for stabilizing solid solutions residing on simple crystal structures. While the mixing entropy indeed plays an essential role in this, Gibbs thermodynamics states that it is not the mixing entropy of a single compound alone that determines the occurrence of phases in equilibrium.[5] Rather, the stability and occurrence of phases are determined by the total free energy minimum in terms of the common tangent construction considering all possible phases in such composition and structure spaces.[6]

Specifically, intermetallics, stabilized by their strong directional bonds (*i.e.*, by the enthalpy contribution in the Gibbs framework), play an important role in that context. They often form in such materials after prolonged heat treatment, an effect which shows that most HEAs reported to date are in a kinetic transient.[7,8] This is not at all a principal obstacle for using these materials, it is just important to understand what that means for their stability when exposing them to heat or – as in the current case – reducing their dimensions into nano-space.

This means that scale-related kinetic and thermodynamic features of HEAs become particularly apparent when synthesizing them as nanoparticles,[9-12] where substantial kinetic effects (*e.g.*, fast surface diffusion) and thermodynamic effects (*e.g.*, the Gibbs–Thomson relation, decoration according to the isotherm and Wulff surface) can become more essential for phase stability than the mixing entropy. Considering these aspects seems to provide a more solid basis for the rational development of nanosized HEAs. This means that mixing elements is not an aim in itself in this field.[13-16] Instead, a *Quo Vadis* analysis for the field demands to revisit and re-evaluate fundamental phase stability and kinetic assumptions and extracting from this a targeted, theory-based approach to

identify and realize emergent phenomena unattainable by traditional alloys.[17–21] This requires moving past the simplistic initial description of HEAs as "ideal solid solutions" and embracing the reality that HEA nanoparticles are inherently kinetically driven, with stability and performance dictated by local chemical ordering, surface dynamics, surface reconstruction features, contamination from synthesis, decomposition, and the precise control of the interplay of structural defects and their defect-specific chemical decoration.[22,23]

The latter point is important when it comes to the predictive design of composition–structure–property relations, because such complex nanomaterials obtain many of their features less from their average chemical composition but from defects. Bulk HEAs are monolithic, primarily solid–solution phases (mostly metastable) where the multiple principal elements can lead to specific nanostructure features such as nano-twins, nano-precipitates, ordered domains, nano-grains or stacking faults—defect types that can be achieved by tweaking the stacking fault energy or the bulk energy landscape of the materials.[24,25] Their nanostructure features are intentionally created defects within this bulk, to enhance mechanical and functional properties without altering the core alloy's single-phase stability.[25–27]

In contrast, nanoparticles made from HEAs represent a separate material class where the high surface-to-volume ratio dictates behavior.[11,12] During synthesis (e.g., from the gas phase), rapid cooling often prevents true thermodynamic equilibrium, leading to decomposition into multiple phases and surface enrichment of the element with the lowest surface energy. Furthermore, their immense surface area makes them highly susceptible to light-element (particularly carbon and oxygen) contamination from precursor solvents or atmospheric hydrocarbons, which can form a surface carbide layer or adsorbates, drastically altering catalytic or magnetic response and sintering resistance compared to their bulk counterparts.

These thoughts are meant to reflect that a main challenge in HEA nanoparticle research lies in the shift from postulating the validity of bulk-like alloy synthesis approaches that target particle stabilization by mixing entropy alone as a governing material design metric to learning what really determines the (transient) stability of such particles, keeping also the chemical and structural long-term effects of synthesis and use in harsh environments in mind.[28–31] This becomes particularly essential when aiming to link compositional complexity to specific functional features, such as magnetism,[32–37] catalysis,[28,30,38–41] conductivity,[42–46] thermal expansion[47–49] or corrosion[29,50–55] etc.

These critical issues identified at the *Faraday Discussion* meeting converge along several strategic axes: navigating the immense configuration space computationally, understanding kinetic instability and decomposition under operational conditions (including the roles of defect structures), understanding and controlling effects from chemical contamination arising from synthesis transparent, assessing their impact, and developing *operando* and artificial intelligence validation methodologies.

Theory-guided exploration of the configuration space

The vastness of the compositional and structural landscape is today the primary bottleneck preventing the rational design of new HEA systems.[17,56–59] The

theoretical foundation for exploring this space must transcend trial-and-error methodologies. One main suggestion as an outcome of the *Faraday Discussion* meeting thus lies in developing theory- and artificial intelligence-guided material design and search strategies,[60] that also take the thermodynamics, kinetics, and synthesis-related chemical contamination of nanosized HEA particles into account.[28,61,62]

This becomes a particularly challenging task when considering that the states of such multicomponent systems are defined by an $8N$-dimensional configuration space, where N is the number of atoms. This space encompasses not only all the atomic positions and chemical species but also spin and surface states and all relevant electronic excitations. The magnitude of this challenge is quantitatively severe: for a modest system of $N = 100$ atoms, assuming only ten data points on each coordinate, the number of possible configurations approaches 10^{800}. Exhaustive, high-fidelity exploration of this space is impossible.[56]

Traditional Density Functional Theory (DFT), the cornerstone of modern materials simulation, exacerbates this problem due to its intrinsic scaling behavior of $O(N^3)$ with system size. This limitation renders the rigorous calculation of fundamental properties, particularly those requiring large supercells (*e.g.*, simulating nanodefects or finite-temperature thermodynamic ensemble averaging), prohibitively expensive. For example, a direct thermodynamic simulation of even a relatively simple alloy using a 250-atom supercell can demand the computation of approximately 600 000 DFT energy values—a task requiring extensive allocation on high-performance supercomputers. Consequently, reliance on traditional DFT simulations for high-throughput screening (to match corresponding experimental high-throughput screening of multi-element alloys[16,63–66]) of chemically complex materials is fundamentally limited by this computational intractability.[49,67,68]

The rigorous treatment of configurational complexity requires adopting strategies that replace expensive electronic structure calculations with effective atomistic models, thereby reducing the computational scaling behavior. Progress hinges on large-scale simulations, leveraging GPU-accelerated Monte Carlo (MC) and Molecular Dynamics (MD) techniques, which aim to achieve linear or near-linear scaling, allowing for the simulation of systems exceeding one billion atoms. This capability is essential for revealing the complex, multi-scale interplay of order and disorder, including the formation and evolution of short-range ordered clusters and nanophases comprising millions of atoms under finite-temperature conditions.

The necessity for simulating vast configuration spaces at relevant length scales mandates the deployment of advanced machine learning interatomic potentials (MLIPs).[69–73] These potentials are today successfully trained to reproduce the high accuracy of first-principles methods (DFT) while drastically improving computational efficiency.[69,71,73–84] The development of highly accurate AI Cluster Expansion potentials or similar ML-derived models is identified as a critical requirement. A crucial objective for these advanced potentials is the accurate simulation of segregation, decomposition, surface, stability, ordering and phase transformation effects. They also allow bridging time and length scales, a feature which is essential for predicting the dynamics of catalytic processes on nanoparticle surfaces.

Given the unmanageable size of the configurational space, theoretical guidance must also prioritize filtering the space based on desired functionality rather than phase stability alone. The search strategy must shift the focus toward property-driven metrics. Functional descriptors must replace traditional thermodynamic metrics. Examples include magnetic moments, coercivity, thermoelectric figures of merit, and electrochemical parameters, such as the hydrogen binding energy for catalysis. High-throughput calculations of fundamental surface properties, such as surface energies and work functions, coupled with the adsorption energy of specific intermediates, serve as highly effective predictors for catalytic performance.

Nanoparticle decomposition and the interstitial effect

For nanostructured HEAs, stability under functional conditions is predominantly kinetic, often diverging significantly from bulk thermodynamic predictions. The primary concern is not just the initial phase formation, but the resistance to decomposition and demixing when subjected to thermal, mechanical, or electrochemical stresses. The discussion requires a clear distinction between thermodynamic stability (minimal tendency for compound formation) and kinetic stability (resistance to decomposition over time under operational potentials). Experimental observations, particularly in electrocatalytic environments, show that HEA nanoparticles often demonstrate localized decomposition, forming defined clusters or phases (*e.g.*, clear separation into PtPd and FeNiCo patches). These findings confirm that HEA nanoparticles frequently operate in metastable states, where kinetic barriers, rather than thermodynamic minima, dictate performance.

Key factors governing this kinetic stability are ordering, segregation and phase transformation phenomena. For example, the development of HEA nanoparticles with SRO (short-range ordering), driven by local bonding preferences, significantly influences kinetic processes. Specifically, SRO can suppress defect evolution by reducing defect jump frequencies and trapping defect motion, thereby dictating thermal stability and resistance to degradation. Designing alloys with tailored SRO states therefore provides a direct mechanism for enhancing kinetic barriers and long-term stability in HEA nanoparticles.

The discussion also revealed that a critical, yet often unquantified, source of instability and structural variation is the presence of non-measured interstitial contaminants, specifically carbon (C), nitrogen (N), oxygen (O), hydrogen (H), and boron (B). These elements, often overlooked in compositional analysis, exert significant influence on the material's internal degrees of freedom, including quench sensitivity, glass formation tendency, and the stabilization of point defects. The community recognizes the necessity of adopting "defect phase thermodynamics" and generalizing the adsorption isotherm to explicitly account for these interstitials.[85] Point defects and interstitials, stabilized by C, N, O, or H, are not simply impurities but rather inherent components that drastically influence the stability and the configuration space of the surface. For instance, high carbon content can dictate the crystallinity state of laser-ablated HEA nanoparticles, influencing their tendency toward amorphization. The lack of rigorous

control over these contaminants during synthesis, particularly in processes like ball milling or laser ablation, results in low reproducibility and scientific uncertainty.

Under reactive conditions, HEA nanoparticles undergo pronounced dynamic instability. *In situ* Transmission Electron Microscopy (TEM) studies have captured various phenomena in that context including demixing events, decomposition, ordering, Kirkendall effects, and formation of voids.[86–91] These phenomena are relevant to sustained functionality, particularly in catalysis, as they fundamentally alter the surface architecture. Detailed studies of HEA nanoparticle oxidation, for instance, reveal that the oxidation rate of HEA nanoparticles is significantly slower than that of their monometallic counterparts, exhibiting a logarithmic rather than the parabolic rate predicted by Wagner's theory. This kinetic suppression stems from the chemical complexity of the HEA lattice, which effectively disrupts the fast, cooperative diffusion pathways necessary for the formation of thick, continuous oxide layers. The outward diffusion of specific transition metals (Fe, Co, Ni, Cu) is observed, leading to the formation of disordered oxide layers while stabilizing noble elements (Pt) in the core region.

These kinetic mechanisms suggest that the field must broaden its focus from designing solely the bulk alloy composition to managing the nanoscale "defect effects" and associated dynamic processes that the alloy leverages when synthesized and operated as a nanoparticle. By engineering compositional complexity, researchers implicitly design a material that exhibits superior kinetic stability under complex service conditions by impeding large-scale elemental transport and promoting beneficial surface segregation patterns.

The surfaces of functional high entropy nanoparticles are dynamic ensembles: state of *operando* validation

Functional applications of HEA nanoparticles, particularly in electrochemistry and catalysis, rely on the dynamic state of the surface, which is chemically, structurally and dynamically distinct from the bulk interior. This active interface presents the most significant challenge in validation and mechanistic understanding. This requires decoding the bulk–surface relationship: a scientific inquiry for HEA nanoparticle design is therefore better understanding of the relationships between the bulk and the surface: "Does the surface 'know' the bulk and *vice versa*?". While bulk composition is readily measurable, the active surface structure and composition are highly sensitive to the operating environment, temperature, exposure history, and adsorbed species. Computational simulations utilizing techniques like Monte Carlo reveal that HEA surfaces are intrinsically susceptible to segregation, even for noble-metal systems (*e.g.*, Ag enrichment and Pt depletion observed on AuAgCuPdPt nanoalloys). This segregation is not a static property but is dynamically induced by temperature, reaction atmosphere, and surface coverage.

Similar considerations apply to surface segregation and reconstruction dynamics. Catalytic systems operate *via* dynamic cycles, commonly referred to as Ertl-cycling, which involve continuous reconstruction of the reaction zone.[92] The chemical and structural state observed in *post-mortem* analysis (*e.g.*, clusters,

patches, or surface oxides) often bears limited resemblance to the truly active state under *operando* conditions. Capturing this dynamic evolution—where the surface configuration space is constantly changing—is vital for developing accurate predictive models.[93,94] The chemical complexity of HEA surfaces translates into a wide diversity of binding sites.[61,62,95] Consequently, the adsorption energy of reaction intermediates can probably not be characterized by a single value, as is common for conventional catalysts. To address this complexity, the field requires generalized theory of the adsorption isotherm and the prediction of the multiplicity of chemically and/or magnetically active sites in complex alloys that incorporates the complex local interactions, surface entropy terms, segregation, dynamics, and coverage dependencies inherent to multicomponent surfaces. This demands developing a robust "chemical defect theory" that formalizes the role of local chemistry and defects in determining adsorption energetics.

The discussions also showed that a certain gap in current knowledge lies also in the understanding of the physical definition and spatial extension of the active interface, *i.e.*, the question about the true quantification of the active reaction zone. This boils down to the question: "How displaced are the reactions—how thick is the reaction interface?". This quantification of the reaction zone thickness is crucial, as it defines the functional boundary between the stable bulk solid solution and the dynamically reconstructing catalytic layer.

To achieve this spatial and chemical resolution, advanced *operando* analysis is mandatory. This involves coupling high-resolution structural techniques with chemical detection. Specific requirements include utilizing *in situ* STEM/TEM holders to observe demixing, void formation, and structural reorganization, coupled simultaneously with mass spectroscopy (MS) tracking to correlate structural dynamics with gas-phase reactant consumption and product evolution. Furthermore, quantitative metrics for the reaction zone thickness can be derived from techniques such as *operando* X-ray reflectivity or conductivity measurements, which have demonstrated the ability to distinguish and measure the thickness of the formed surface phase *versus* the bulk thickness. This ability to quantitatively measure the structural dynamics of the reaction interface through *operando* methods provides the necessary link to validate theoretical models and definitively ascertain if the observed phase is, in fact, the active phase responsible for performance. Without this quantifiable correlation, the field risks misattributing functional activity based on static, *post-mortem* data.

Challenges associated with nanoparticle synthesis

The theoretical and characterization challenges outlined above place demand on synthesis methodology.[75] To achieve predictable functionality, the field must improve towards better chemically controlled and kinetically informed chemical design. A critical task lies in improving the documentation, reproducibility, and impurity control of these materials. The synthesis of colloidal HEA nanoparticles is a significant challenge due to the complex chemical landscape involved in co-reducing multiple metal precursors. Each constituent metal exhibits unique reactivity profiles, reduction rates, and threshold energies. If the reduction kinetics are not precisely synchronized, the variance in reaction rates inevitably leads to compositional gradients and detrimental phase separation. Studies show

that simpler synthesis methods, such as one-pot approaches, frequently yield multiple phases, whereas highly controlled techniques, such as hot-injection synthesis, are essential for achieving monodisperse, ultra-small (1–3 nm) single-phase HEA nanoparticles, even in highly miscible noble-metal systems (*e.g.*, RhIrPtPdRu).

Furthermore, the issue of interstitial contaminants (C, N, O, H) must be addressed through control of the synthesis environment and precursors. The chemical state of these contaminants, often acting as metallic bond interruptors, can drastically alter the crystalline state, stability, segregation, surface activity, phase separation, phase formation *etc.*, particularly in laser ablation or mechanical alloying methods where contamination is often implicit.

A related objective—once equipped with such understanding and improved chemical control—is the precise control of local atomic structure and morphology. Traditional synthetic routes, such as high-temperature heating followed by rapid cooling, typically stabilize bulk HEA structures but lack the precision required for functional nanostructures. Some of these methods still lack fine control over size, uniformity, and shape—nanoscopic features that are known to dominate catalytic performance and surface chemistry. Solution-based approaches, like continuous-flow reactors or wet chemistry methods, are critical for tuning these parameters while minimizing energy consumption.

A trajectory vision: property-driven multifunctional nanoparticle HEAs

The complexity inherent to HEAs can now be exploited to deliver integrated performance metrics that are hard to attain by conventional alloys. Yet, we must strive beyond aiming to mimic "Monolithic Performance" metrics and rather aim at the multifunctionality of such materials, embracing aspects such as easy synthesis, low-cost elements, defined contamination tolerance, corrosion resistance, catalytic performance, and long-term stability – just to give an example of the facets to be reconciled in a single nanoparticle material.[45] This means that the field must strategically move beyond attempting to outperform existing commercial bulk materials (*e.g.*, steels, Al, Ti alloys) in a single dimension (1D property space). HEAs have shown first results in their capacity for multifunctionality—the symbiotic combination of disparate properties within a single material framework.[45] Examples of this multifunctional synergy are beginning to emerge such as magneto-catalysis and electrochemically-tuned non-noble systems.

Magneto-catalysis is a promising topics: it targets the strategic incorporation of magnetic elements (Fe, Co, Ni) into Pt-group metal catalytic HEA nanoparticles (*e.g.*, PtPdFeCoNi)[96–99] allowing for the development of magnetically separable catalysts. The magnetic core facilitates easy recycling and recovery after reaction completion, while the magnetic field may also influence the electronic structure and spin polarization of the surface, potentially tuning catalytic selectivity. Electrochemically active[40,41,62] non-noble systems are essential to avoid using strategic and scarce elements in catalysis: the HEA strategy allows for the design of non-noble systems (*e.g.*, transition metal HEAs) that demonstrate high-efficiency electrocatalysis (*e.g.*, for the Hydrogen Evolution Reaction (HER) or

Oxygen Evolution Reaction (OER)). This performance is achieved by leveraging differences in electronegativity among constituent elements, which drive localized electron redistribution at active sites (*e.g.*, enhancing Cu utilization), ultimately affecting adsorption energies and minimizing reliance on expensive noble metals.

Accelerating the design of these integrated property profiles requires sophisticated computational support. Artificial Intelligence (AI) and Machine Learning (ML) approaches are indispensable for multi-objective optimization, allowing for the rapid identification of compositions that simultaneously satisfy competing functional requirements, such as high mechanical hardness and magnetic softness.[49,56,100–104]

Among the many possible multifunctionality metrics mentioned above, societal relevance and sustainability must not be underestimated. Future research guidance should align with global societal demands, emphasizing applications such as CO_2 capture and conversion, high-efficiency hydrogen storage, and sustainable energy conversion.[105] The initial reliance on highly expensive, noble-metal-rich HEAs presents a substantial sustainability challenge.[106] A critical visionary path involves prioritizing the design of lean-alloy or non-noble HEA nanoparticles that can reproduce the superior kinetic stability and catalytic diversity typically associated with Pt-group metals.[107] The HEA complexity, when rationally deployed, offers a powerful tool to enhance active site utilization and extend catalyst lifetime, mitigating the need for high-concentration precious metal loading.[28,31]

Conflicts of interest

There are no conflicts to declare.

Data availability

No primary research results, software or code have been included, and no new data were generated or analysed as part of this article.

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