

Commentary

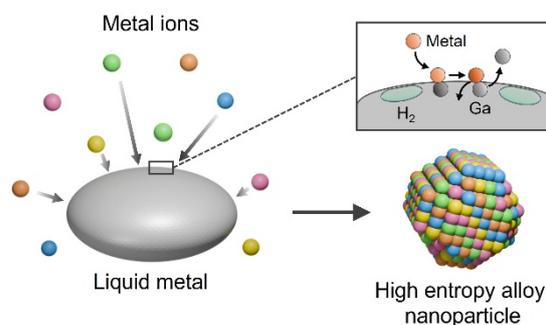
Kinetic Trapping of High-Entropy Alloys via Fast Reduction and Mixing in a Liquid Metal

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Abstract: High-entropy alloy nanoparticles have emerged as a promising material platform for catalysis, sensing, energy storage, and biomedical applications, but their synthesis is often constrained by high temperature or energy inputs, as well as the intrinsic immiscibility of the constituent elements. A recent study in *Nature* introduces an isothermal solidification approach, in which metals are rapidly reduced and mixed in a sacrificial liquid metal, enabling the formation of nanoparticles containing up to 20 elements with controlled structure and morphology.



Keywords: high-entropy alloy; isothermal solidification; liquid metal; nanoparticle synthesis; *in-situ* transmission electron microscopy

Alloying elements has been employed to modify material properties since the Bronze Age, with well-known examples including the addition of tin into copper and chromium into iron to enhance hardness and corrosion resistance [1]. At the nanoscale, tuning the composition of nanoparticles (NPs) can similarly optimize their chemical, physical, and mechanical properties, such as surface reactivity, chemical stability, structural robustness, and stiffness, enabling superior performance in catalysis, sensing, energy storage, and biomedicine. While earlier studies mostly focused on bi- or tri-metallic NPs, since first proposed in 2004 [2], the concept of high-entropy alloys (HEAs) introduced materials composed of five or more elements in near-equiatomic proportions. These multicomponent NPs offer highly tunable chemical compositions and improved structural stability, as the increased entropic contribution with increasing number of elements can overcome the enthalpic contribution and stabilize solid solutions.

The most typical method in synthesizing HEA NPs involves high temperature/energy annealing followed by rapid cooling, which promotes mixing of elements while skipping their structural aggregation, phase segregation, and surface reconstruction. Notable examples include carbothermal shock [3], electroshock [4], and laser scanning ablation [5], techniques that typically require specialized and sometimes complex instrumentation. Alternatively, wet-chemical strategies such as multi-cation exchange [6] or co-reduction [7,8] have emerged as convenient approaches, usually operating at relatively low reaction temperatures by carefully controlling metal insertion or reduction rates. However, these methods are often limited by the miscibility of elements involved, and the products are majorly governed by thermodynamics.

Aside from co-reduction, galvanic replacement provides another strategy for alloying metals driven by differences in reduction potentials, in which a sacrificial metal template reacts with ions of more noble metals. Liquid metal, in particular gallium (Ga), stands out as a unique substrate due to its non-toxicity, low melting point, high metal solubility, and low reduction potential ($E_0[\text{Ga}^{3+}/\text{Ga}] = -0.529 \text{ V}$ vs. standard hydrogen electrode), endowing it with strong reducing capability and an ideal medium for atomic-level metal mixing [9]. Reporting in *Nature*, Zheng and co-workers demonstrated an isothermal solidification approach to synthesize HEA NPs containing up to 20 elements at temperatures below 100 °C by employing Ga as both the reductant and reaction



medium (Figure 1A) [10]. Beyond simple galvanic replacement [11], this approach can produce Ga-free HEA NPs with tunable size, structure, and morphology.

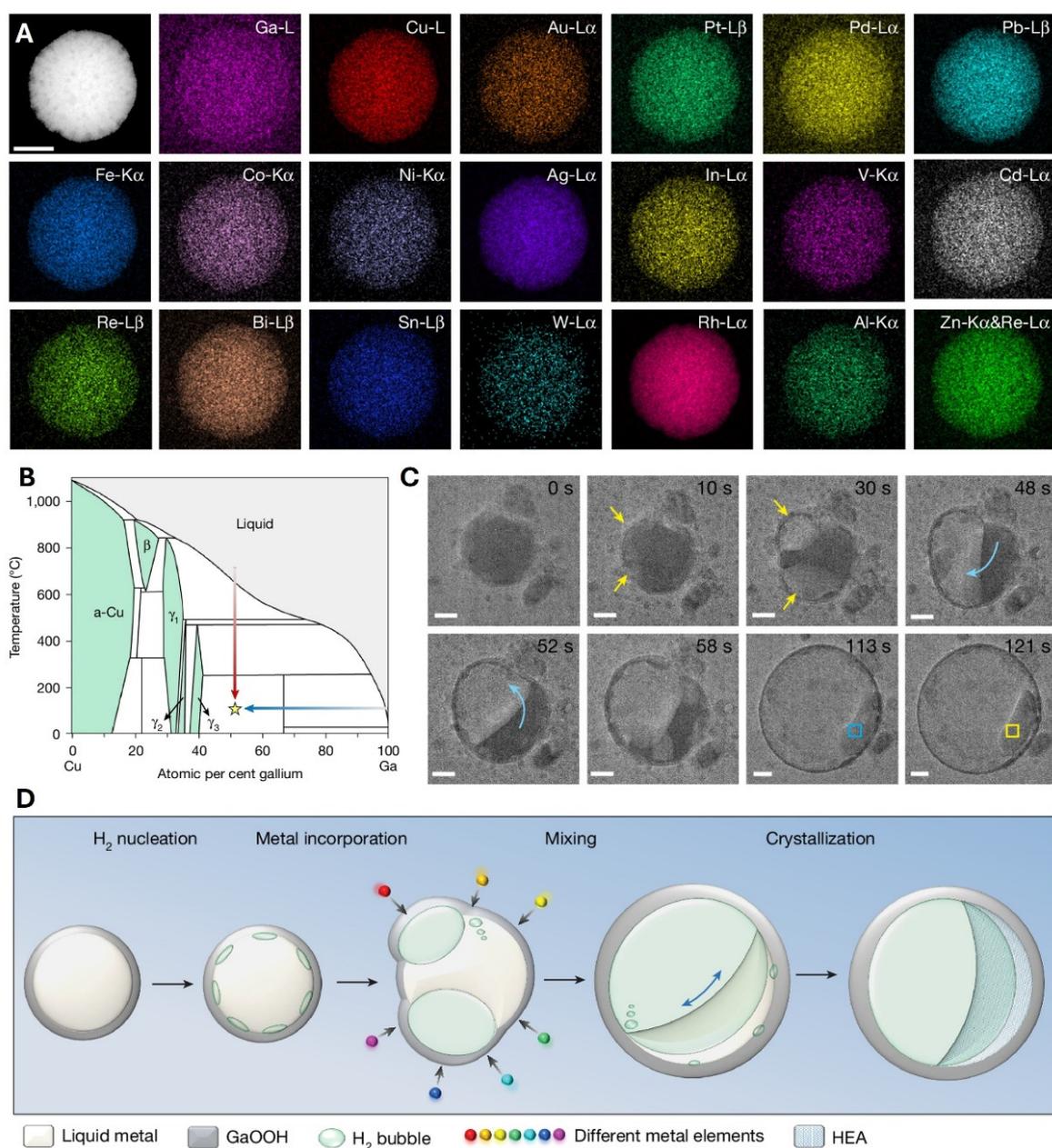


Figure 1. (A) Elemental mapping by energy dispersive X-ray spectroscopy (EDS) showing a HEA NP containing up to 20 metals, which was synthesized using isothermal solidification. (B) Phase diagram of a representative Cu–Ga binary alloy, demonstrating two solidification routes. The rapid cooling solidification traps the high-temperature states to form HEAs, as indicated by the red arrow. The isothermal solidification, in contrast, traps high-entropy state by rapidly changing the composition at low temperatures, as marked by the blue arrow. (C) *In-situ* TEM images capture the formation of a HEA NP (GaInSnZnCu) within a liquid environment at 60 °C. Yellow arrows highlight H₂ bubble nucleation and growth, whereas the blue arrow indicates the stirring direction of the liquid metal alloy. (D) Schematic of the formation of HEA NPs, showing the steps of H₂ nucleation, metal reduction and incorporation, metal mixing and crystallization.

Two steps are involved in isothermal solidification: (i) fast reduction of metal salts at the interfaces between the Ga-based liquid metal and aqueous metal ion solution ($Ga + \frac{3}{n} Me^{n+} \rightleftharpoons Ga^{3+} + \frac{3}{n} Me$), and (ii) dissolution of the reduced metal atoms into Ga, followed by their dynamic mixing. Different from the rapid cooling solidification which kinetically traps the high-temperature states to form HEAs (indicated by the red arrow in Figure 1B), isothermal solidification traps the high-entropy state by rapidly changing the composition at low temperatures (as highlighted by the blue arrow). The abrupt composition change leads to the liquid metal alloy

entering a supercooled state, triggering elemental oversaturation in the liquid metal and their precipitation as HEA NPs. Note that Ga can be largely excluded in the final product by controlling its consumption and metal solidification rates, leaving alloys made of only desired elements. This distinguishes isothermal solidification from previously reported liquid metal-assisted synthesis of HEA NPs at high temperatures [12], where Ga remains incorporated in the final product.

The solidification process was further captured by in-situ transmission electron microscopy (TEM) to unveil the atomistic mechanisms (Figure 1C,D). This state-of-the-art imaging technique allows two interesting observations: (i) hydrogen bubbles were generated during the reduction process, and their stirring effectively enhanced the metal element mixing; (ii) oscillatory nucleation and disruption were observed, which supports the proposed rapid solidification. The disruption to the formation of crystals is likely induced by the stirring of evolving hydrogen bubbles.

Beyond simply producing HEA NPs, isothermal solidification also has capability in controlling crystal structure and morphology by tuning reaction temperature and metal salt concentration. With increasing temperature, mesocrystalline (at 60 °C) and polycrystalline (at 80 °C) NPs were obtained, which can be attributed to rapid solidification, dynamic heterogeneities, and mobility asymmetry of supercooled liquids. Reacting at a lower temperature (40 °C) while doubling the concentrations of metal precursors led to the formation of amorphous spherical NPs, potentially arising from the swift dissolution of metal atoms, deep undercooling of the liquid alloy, and prompt solidification. In terms of morphology, with increasing reaction temperature, HEA NPs tended to exhibit more uniform elemental distribution, more porous structures, and more diversified morphologies. A variety of shapes including solid spheres, porous spheres, flow-like, dendritic, and snowflake-like structures have been observed. The size of HEA NPs could also be tuned from 140–250 nm by controlling the size of the liquid metal droplets.

Despite its advantages, the isothermal solidification method still requires further development. For instance, scalable synthesis is necessary to meet the demand of a large quantity for practical applications. Additionally, since the shape and size of the HEA NPs are also affected by liquid metal droplets, achieving high-purity products remains a challenge. Nevertheless, this approach based on rapid reduction and mixing of metals in liquid metal nanoreactors offers an innovative platform for producing NPs that are otherwise difficult or tedious to synthesize, such as single-atom alloys and multi-layer structures, potentially through careful control of metal salt concentrations and drop-wise precursor addition. Moreover, its coupling with density functional theory (DFT) and machine learning (ML) holds great promise for accelerating the identification of elemental compositions for specific applications [13]. The nanoreactors could also be extended beyond liquid metals to micelles or bioreactors, enabling selective element incorporation or alternative reduction mechanisms (e.g., photocatalysis). In summary, isothermal solidification provides a one-step, low-temperature route to HEA NPs with controllable size, morphology, and crystal structure, offering significant promise for applications in catalysis, batteries, and beyond.

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