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Isothermal solidification for high-entropy alloy synthesis

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Summary

Kinetically trapping the high temperature states through rapid cooling solidification is widely used for synthesis of high-entropy alloys (HEAs), especially those with intrinsic immiscible elemental combinations¹⁻⁴. However, strategies need to be developed to overcome the fundamental limitations of rapid cooling solidification in controlling the crystallinity, structure, and morphology of HEAs. Here, we introduce an isothermal solidification strategy for synthesis of HEAs by rapidly altering the metal alloy composition through liquid-liquid interface reactions at low temperatures, e.g. from 25 °C to 80 °C. We use gallium (Ga)-based metal as the sacrificial reagent and mixing medium. By directing the reactions to the interfaces between the Ga-based liquid metal and an aqueous metal ion solution, the foreign metal ions can be reduced at the interfaces and incorporated into the liquid metal quickly. HEAs with various crystallinity (single crystal, mesocrystal, polycrystal, amorphous), morphology (0-dimension, 2-dimension, 3-dimension), and compositions can be achieved through the isothermal solidification. Ga can be completely consumed resulting in Ga-free HEAs. If desired, Ga can be one of the metal elements in the final products. In-situ liquid phase transmission electron microscopy (TEM) studies and theoretical analysis unveil the isothermal solidification mechanisms. Our direct observation reveals the liquid metal motion enhanced elemental mixing and the solidification process with fluctuating nucleation dynamics. The isothermal solidification marks a powerful strategy for HEA synthesis through an unexplored pathway of kinetically trapping the high-entropy states.

Main Text

High-entropy alloy (HEA) nanomaterials have attracted significant interest due to their prospective applications in catalysis^{1,5-9}, batteries¹⁰ and others¹¹. For the intrinsically immiscible

metal element combinations under thermodynamic equilibrium, employing the method of rapid cooling from the high temperature (e.g., above 2000 K) states is effective for trapping the high entropy states to obtain HEAs^{1-4,12}. Such HEAs synthesis by rapid cooling solidification predominantly yields nanoparticles with little control over their structure and morphology^{2,6,8}. Wet-chemical approaches provide versatility in lower temperature synthesis of HEAs with various particle sizes, morphology, and structure^{2,13-15}, but they are mainly applicable to combinations of miscible elements in equilibrium thermodynamic processes. To date, innovative approaches remain to be explored to overcome the limitations imposed by these techniques.

In this work, we introduce an isothermal solidification strategy for synthesis of HEAs at low temperature. By directing the metal ion reduction reactions to the interfaces between the Ga or Ga-based liquid metal and an aqueous salt solution, the formation of HEAs with control of crystallinity, morphology and structure is realized, including those with intrinsically immiscible metal element combinations. We monitor the dynamic solidification processes at the atomic level using state-of-the-art liquid-cell TEM technology to reveal the underlying mechanisms. The isothermal solidification of HEAs marks a breakthrough in HEA synthesis, providing a viable alternative to rapid cooling for trapping the liquid alloy states.

Principles of isothermal solidification

Figure 1a illustrates the fundamental principle of the isothermal solidification strategy for HEAs synthesis, where the high entropy states are achieved through rapid composition changes under a constant temperature. The formation of HEAs involves two steps: (I) the metal ions from the salt solution are reduced by Ga at the interfaces between the liquid metal and the salt solution (liquid-liquid interface). The reduction reaction is restricted to the liquid-liquid interface due to

68 the nature of the reaction ($\text{Ga} + \frac{3}{x}\text{M}^{x+} \rightarrow \text{Ga}^{3+} + \frac{3}{x}\text{M}$, where Ga is from the liquid metal, M is the
 69 foreign metal from the salt solution, and x represents the valence state). (II) The generated foreign
 70 metal atoms readily dissolve into the liquid metal. Since Ga-based liquid metals (e.g., Ga or Ga-
 71 based alloys, **Extended Data Figs. 1 & 2, Supplementary Fig. 1**) interact strongly with other
 72 metal elements, they are ideal solvents for the dynamic mixing of metal elements^{12,16,17}. The liquid-
 73 liquid interface reaction facilitates the rapid incorporation of newly formed metal atoms into the
 74 liquid metal alloy, thus the reaction is continuously refreshed and an accelerated composition
 75 increase of the liquid metal alloy can be achieved due to the spontaneous rapid incorporation of
 76 foreign metal atoms as well as the consumption of Ga metal in the liquid metal^{18,19}. The abrupt
 77 composition change leads to the liquid metal alloy entering a supercooled state, triggering
 78 isothermal solidification to kinetically trap the high entropy states. For HEAs synthesis using Ga
 79 liquid metal, the reducibility and miscibility of metals are governed by two parameters^{20,21} (**Fig.**
 80 **1b**): the reducibility of metal ions by Ga is estimated by $\frac{3}{x}\Delta G_{\text{M}^{x+}} - \Delta G_{\text{Ga}^{3+}}$, which accounts for the
 81 feasibility of the reduction reaction in Step I. The miscibility of metals with Ga is represented by
 82 the mixing enthalpy (ΔH_{mix}), which describes the readiness of the foreign metal to alloy with Ga
 83 in Step II. The ΔH_{mix} values were calculated based on Miedema's model for equimolar (1:1) solid-
 84 state mixtures of Ga-X pairs at room temperature²². Because the product composition varies during
 85 isothermal solidification and the mixing process occurs in the liquid state, we treat these ΔH_{mix}
 86 values as a qualitative indicator for the tendency to form a solid solution in Step II based on phase
 87 formation rules^{23,24}. According to these criteria, elements positioned in the first and fourth
 88 quadrants of **Fig. 1b** correspond to those that can undergo spontaneous reduction from their
 89 aqueous metal chloride solutions. Moreover, elements positioned near the left of the vertical
 90 boundary (e.g., Cd, V, Co) can also undertake reduction upon thermal heating.

We exemplify this isothermal solidification strategy using the Ga-Cu binary alloy²⁴, which features a low solubility of Cu in liquid Cu-Ga alloy at temperatures below 100 °C (less than 3%). The widely used rapid cooling solidification of the high temperature Ga-Cu liquid alloys leads to kinetically trapping of the alloy mixture, as highlighted by the red arrow (**Fig. 1c**). However, as an alternative route highlighted by the blue arrow, drastically increasing the miscibility of Cu in liquid Ga creates an oversaturated liquid alloy (a supercooled liquid state) and the subsequent isothermal solidification yields a high-Cu-content alloy.

We successfully synthesized binary Cu-Ga alloys using the isothermal solidification method at a constant temperature of 60 °C. Energy-dispersive X-ray spectroscopy (EDS) analysis (**Fig. 1d**) reveals that the Cu content reached up to 95%, with the two elements homogeneously distributed. In addition, the isothermal solidification may also generate Ga-free alloys, e.g., Cu-Pd alloys are achieved (**Fig. 1e**). The isothermal solidification can effectively synthesize HEAs with arbitrary elemental compositions (**Fig. 1f, Supplementary Fig. 2, Supplementary Table 1**).

In-situ TEM dynamics

To uncover the underlying mechanisms of isothermal solidification for HEAs synthesis, we conduct direct observation of the alloying process at the atomic level using advanced liquid cell TEM (**Figs. 2 & 3, Supplementary Videos 1 & 2**). In a simplified model system, we introduce Cu as a single additional element into the host liquid metal of Ga-based alloy (e.g., GISZ, composed of Ga, In, Sn, Zn) to form single-crystal high-entropy alloy nanoparticles (HEA-NPs), specified as GaSnInZnCu.

We track the dynamic evolution of the HEA-NPs formation. At the initial stage (**Fig. 2a**), the liquid metal nanoparticle is encased in a Ga₂O₃ shell (**Extended Data Fig. 1**), which transforms

into GaOOH through hydrolysis reaction in the aqueous solution²⁵. Ga from the liquid metal reacts with cations in the solution (e.g., H^+ and Cu^{2+}), generating H_2 gas and Cu metal atoms. The formation of H_2 is marked by the appearance of nanobubbles at the GaOOH-liquid metal interface (indicated by yellow arrows in **Fig. 2b**). The generated Cu atoms are incorporated into the liquid metal, as evidenced by EDS characterization of the final HEA (**Fig. 2e**). Small gas bubbles coalesce into a larger bubble while the liquid metal circulates along the inner shell (indicated by indigo arrows) (30-58 s). This hydrogen gas-assisted stirring greatly enhances the metal element mixing (**Supplementary Video 3** and **Supplementary Figs. 3 & 4**). As the reaction proceeds, gas bubbles continue to evolve, driving the bubble expansion (**Fig. 2a-c**). Simultaneously, Ga is gradually depleted from the liquid metal while Cu atoms continuously join in (**Fig. 2c**). After 121 seconds, the fluidity of the liquid metal alloy quickly decreases, signaling its transition to a solid state (**Fig. 2d**). The temperature remains at 60 °C throughout the alloying and solidification processes, indicating that the isothermal solidification. During the final crystallization, the gas bubble briefly expands before contracting and the liquid metal undergoes slight reshaping before it is finally stabilized (**Fig. 2c**). High-resolution TEM (HRTEM) imaging (**Fig. 2d**, **Supplementary Fig. 5**) and EDS characterization (**Fig. 2e**, **Supplementary Fig. 6**) of the entire particle confirm the single-crystal structure and homogeneous distribution of metal elements within the resulting HEA-NPs. Therefore, the dynamic evolution of the HEA-NPs formation can be summarized as hydrogen gas bubble assisted mixing followed by isothermal solidification of the liquid alloy and reshaping during final crystallization.

Figure 2c reveals that the isothermal solidification of the liquid alloy takes several seconds, which is contradictory to the common notion that the supercooled liquid alloy would undergo fast solidification²⁶. To explore this further, we conduct atomic-resolution observation of the dynamic isothermal solidification (**Supplementary Video 2**). As shown in **Fig. 3**, we find oscillatory

solidification of the liquid alloy. The H₂-gas driven dynamics result in continuous splitting and reforming of the metal alloy domains. For instance (**Fig. 3a**), Domain 2 with an initial crystalline structure converts to an amorphous liquid-like structure after it rapidly merges with Domain 1. During the progression, crystallization occurs repeatedly, and then it breaks down into an amorphous structure upon interaction with new domains. The oscillatory nucleation and disruption are illustrated (in **Fig. 3b & c**) by tracking the crystal center position and measuring the projected area of the crystalline domains with time. Notably, phase transitions between crystalline and amorphous states may occur within a single observation frame (0.1 s) (**Fig. 3c**). This implies that the solidification is fast, which helps effectively trap the high-entropy state of liquid metal.

Theoretical analysis of nucleation and solidification in this scenario supports our observation. According to classical nucleation theory²⁷, nucleation rate first increases with degree of supercooling, but eventually begins to decrease due to the retarding effect of a low absolute temperature on the rate of appearance of critically sized nuclei. This trend is captured by Eq. 1, in which ΔT is the degree of supercooling, T is the absolute temperature, ΔS_V is the difference in entropy between the solid and liquid phases, γ is the interfacial energy between the solid and liquid phases and K is a geometrical prefactor. Since our experiments take place at low temperatures, we speculate that the isothermal solidification process may occur in this regime with extreme supercooling and a suppressed nucleation rate resulting from a delay in the solidification process.

$$J = K \exp \left[\frac{-16\pi\gamma^3}{3k_B T \Delta S_V^2 (\Delta T)^2} \right] \quad (1)$$

We also hypothesize that when solid nuclei do appear, their growth is inhibited by the mixing motion introduced by hydrogen bubbles produced from the reduction of H⁺, which destroys the nuclei and further delays solidification. This is consistent with our in-situ observation that the hydrogen gas assisted stirring of the liquid repeatedly disrupts the crystallization. Finally, we note

that at the beginning of the synthesis process, no Ga is present in the aqueous phase and as a result, there exists a favorable thermodynamic driving force for the dissolution of Ga. The Ga dissolution, in combination with the metal ion reduction reactions at the interfaces followed by the quick incorporation of foreign metal atoms into the Ga liquid metal alloy, drives the rapid composition changes leading to kinetically trap high-entropy states during the isothermal solidification process.

Crystallinity and morphology control

Utilizing the isothermal solidification strategy, we adjusted the reaction temperature and metal salt concentration to control the solidification rates. This allowed us to precisely regulate the structure and crystallinity of the resulting HEAs (**Fig. 4, Supplementary Figs. 7-8, Supplementary Tables 2-3**). The study specifically targets on a system consisting of thermodynamically immiscible elements^{7,28}: Ga, Pt, Pd, Au, Cu, and Pb (see **Supplementary Table 4**). Due to the differences in atomic size, electronegativity, and lattice parameters among these metals, phase separation often occurs during thermodynamic processing (**Extended Data Fig. 3, Supplementary Table 5**), which makes this alloy an ideal candidate for exploring synthesis under non-equilibrium conditions.

At 40 °C, metal atoms, produced through a gentle reaction, dissolved into the liquid Ga and mixed thoroughly. As the melting point of the liquid alloy (which varies with its elemental composition) rises above 40 °C, the alloy solidified from a supercooled state, forming a uniform solid solution with high crystallinity (**Fig. 4a&b, Supplementary Fig. 9**). For small particles (size below 100 nm), we use HRTEM images of entire particles and FFT analysis to confirm their single-crystal structure (**Supplementary Fig. 10**). For large particles, we use selected area electron diffraction (SAED) patterns to verify their single-crystal nature (**Supplementary Fig. 8**). However, not all particles are perfect single crystals—some exhibit lattice defects. For example, the HRTEM

image (**Supplementary Fig. 11**) shows various defects within a HEA particle, including lattice mismatch, lattice distortion, and local structural disorder. These defects may result from factors such as atomic radius variations and lattice differences among different metal elements²⁹. At higher temperatures (e.g., 60 °C), the solidification rate increased, the time required to achieve perfect crystallization is not sufficient. Consequently, the nanoparticles exhibit a mesocrystalline structure with a distinctive architecture (**Fig. 4c, Extended Data Fig. 4, Supplementary Figs. 12**): large porous spherical particles (100-300 nm) composed of numerous smaller nanoclusters (2-5 nm). In general, the solidification of liquid alloys often results in volume shrinkage, which can contribute to the formation of a porous structure³⁰. Additionally, the higher rate of gas generation can cause gas to become trapped within the alloy, further promoting the porosity²⁹. Notably, within this mesocrystalline matrix, we observe local lattice distortions and bending (**Extended Data Fig. 4**), likely due to the stress induced by gas generation and the high surface tension of the liquid metal prior to solidification. By further increasing the temperature to 80 °C, polycrystalline HEA-NPs with a flower-like morphology are produced (**Fig. 4d, Supplementary Fig. 13**). EDS mapping reveals that nearly all the Ga is consumed, leaving the remaining five elements evenly distributed throughout the particles. The complete consumption of Ga may stem from an accelerated solidification rate³¹. The polycrystalline phase and flower-like morphology may arise from dynamic heterogeneities and the mobility asymmetry of supercooled liquids²⁹. The observed crystallinity variations with temperature are consistent with our theoretical predictions (**Supplementary Fig. 14**).

Interestingly, amorphous HEAs are achieved by doubling the concentration of metal precursor solution at 40 °C while keeping all other parameters constant (**Fig. 4e, Supplementary Figs. 15-16**). This adjustment boosts the influx of foreign metals at the liquid-liquid interface by preserving their diffusion rate. Consequently, foreign atoms enter liquid metal and accumulate

rapidly, thus promoting solidification. In this case, we get spherical HEA-NPs with an amorphous phase. The solid spherical shape indicates that no gas entered the particle during the reaction at 40 °C, akin to the case in **Fig. 4b**. The uniform distribution of metal elements demonstrates that the metal atoms have diffused sufficiently, resulting in thorough mixing. Hence, we deduce that the amorphous structure arises from the swift dissolution of foreign metal atoms, leading to deep undercooling of the liquid alloy, followed by the prompt solidification of the liquid alloy. As foreign atoms enter, the melting point of the liquid alloy quickly surpasses its temperature. Nevertheless, without crystal nucleation, the liquid metal maintains its supercooled state to maintain its liquid form. Once solidification is triggered, it proceeds rapidly leading to an amorphous solid.

The precise control over the crystallinity of these HEAs confirms the presence of distinct supercooled states and the varied solidification rates during isothermal solidification synthesis. In contrast to the rapid cooling solidification synthesis methods¹⁻³, the isothermal solidification provides the opportunity to control the crystallinity and morphology of HEAs (**Supplementary Table 6**). Notably, we have achieved precise control over the crystallinity of HEAs, successfully synthesizing mesocrystalline HEAs for the first time (see **Extended Data Figs. 4-5**).

Diversified synthesis of HEAs

The isothermal solidification strategy demonstrates its robust capabilities for controlled synthesis of a diverse array of HEA nanomaterials, beyond the HEA-NPs. In terms of composition control, a broad range of metallic elements can be incorporated into the liquid Ga metal, successfully forming quinary, senary, septenary, octonary, nonary, decennary, and even undecennary HEAs (**Fig. 4, Supplementary Figs. 17-21, Extended Data Figs. 6-7**). Additionally, Ga can be completely consumed to produce Ga-free HEAs (**Fig. 4d, Extended Data Fig. 6**,

Supplementary Figs. 22-23). As illustrated in **Fig. 5a**, we have synthesized HEAs with more than 20 distinct elements, each possessing unique crystal structures, melting points, and atomic radii. This capability highlights the versatility in generating a broad spectrum of HEA-NPs with diverse elemental combinations (**Fig. 5a, Supplementary Table 7**). HRTEM and EDS confirm the compositional homogeneity of these nanoparticles, showing no phase or elemental segregation (**Extended Data Fig. 8 and Supplementary Figs. 24-25**).

In addition to the mixing of diverse elements, the morphology and crystallinity of these HEAs can also be tuned, similar to the HEA-NPs in **Fig. 4**. By adjusting the reaction kinetics at liquid-liquid interfaces, we can synthesize a spectrum of structures spanning from zero-dimension to three-dimension, including solid, porous, hollow spheres, nanoflowers, nano dendrites, 2-dimension porous nanosheets, as well as three-dimension networks and hierarchical structures (**Fig. 5b, Extended Data Figs. 6, 7, 9, 10, Supplementary Figs. 26-27**).

HEA-NPs with 0-dimension morphology (including solid, porous, flower-like nanoparticles) are typically obtained by utilizing spherical liquid metal precursors (as opposed to flakes of Ga) (**Extended Data Fig. 10, Methods**). At 30 °C (**Extended Data Fig. 10a**), when liquid Ga metal is used as precursor (marked by red outline), the resulting HEA-NPs tend to form phase-separated structures resembling egg-yolk and core-shell configurations. By increasing the temperature to 40 °C, HEA-NPs with solid sphere shapes can be achieved (marked by red outline) in **Extended Data Fig. 10b**. Further increasing the temperature to 60°C and 80°C, HEA-NPs with porous spherical, flower-like, dendritic, and snowflake-like morphologies can be obtained (**Extended Data Fig. 10 d, f, Fig. 4c-d**). This implies that raising the reaction temperature may enhance the uniform distribution of elements, formation of porous structures, and more diversified morphology in HEAs. By controlling the size of the liquid metal precursor, we can tune the sizes of the resulting high-entropy nanomaterials (**Supplementary Fig. 28**). This approach enables the synthesis of

high-entropy nanomaterials with a range of sizes (**Supplementary Fig. 29**). Moreover, further investigations have demonstrated that, under identical reaction conditions, variations in precursor size do not affect elemental distribution or HEA formation (**Supplementary Fig. 30**).

Interestingly, using liquid Ga alloy instead of pure Ga precursor, we can obtain HEA-NPs with porous structure at 40 °C and even room temperature (~25 °C) (highlighted by yellow outline in **Extended Data Fig. 10a & b**). Employing a liquid alloy precursor with a lower melting point yields similar effects as increasing the reaction temperature. This may be attributed to the lower melting point of the liquid Ga alloy further promotes the reduction reaction at the interfaces and the foreign metal atoms mixing. At the elevated temperatures (e.g., 60 °C or above), the impact of the liquid metal precursor is not notably pronounced, and both liquid Ga and liquid Ga-based alloys can yield porous or more diversified structures (**Extended Data Fig. 10d & f, Fig. 4c & d**).

Without the addition of HCl to the metal salt solution, the formation of HEAs at low temperatures (e.g., 30 °C, and 40 °C) is hindered, as the oxide on the surface of the liquid metal acts as a passivation layer blocking the interface reaction. However, increasing the temperature can resolve this issue, allowing for the formation of HEAs with various morphologies (**Extended Data Fig. 10c & e**). We further find that ellipsoidal HEA-NPs are generated when spherical liquid metal precursors are employed (marked by indigo outline in **Extended Data Fig. 10c**), HEAs with irregular shapes are obtained as irregular metal precursors are used (marked by green outline in **Extended Data Fig. 10c**), and 2-dimension film metal precursors are utilized to synthesize 2-dimension nanosheets, 2-dimension networks, 2-dimension hierarchical structures, and some other intricate structures (marked by white outline in **Extended Data Fig. 10c & e**). Accompanying the morphological changes, the crystallinity can also be modified, enabling the synthesis of HEAs with single-crystalline, mesocrystalline, polycrystalline, and amorphous structures depending on the rate of isothermal solidification (**Fig. 4, Fig. 5c, Extended Data Figs. 5-7**).

Conclusion

We demonstrate an isothermal solidification strategy for the synthesis of HEAs with controlled crystallinity, morphology, and composition at low temperatures. By directing the metal ion reduction reactions to the liquid-liquid interfaces, the foreign metal mixing rate is significantly enhanced. The fast metal mixing combined with the rapid Ga consumption effectively induce liquid alloys with high concentration of solute metal above the thermodynamic solubility limitation at low temperatures. The gas bubble-enhanced mixing and fluctuations of crystallization during isothermal solidification highlight an unexplored pathway to kinetically trap the high entropy state. This strategy broadens the scope of HEA synthesis and discovery, allowing the creation of previously unattainable HEAs with diverse structural configurations. The liquid-liquid interface reaction enables unhindered solidification, resulting in intricate solidification patterns at room temperature with promising applications, such as three-dimension printing of metals, catalysis, batteries, etc. Further exploration of the diverse HEAs has the potential to expand their applications across broader fields, spanning material science, chemistry, and biomedicine.

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Methods

Chemicals

All chemicals used in this study were commercially available, and no further purification was required. These include gallium (Ga; 99.99%), indium (In; 99.99%), tin (Sn; 99.999%), zinc (Zn; 99.8%), aluminum (Al; 99%), vanadium(III) chloride (VCl_3 ; 97%), cadmium chloride (CdCl_2 ; 99.99%), iron(III) chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$; 98.0%-102%), cobalt(II) chloride hexahydrate ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$; 98%), nickel(II) chloride hexahydrate ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$; 99.9%), copper(II) chloride dihydrate ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$; 99.0%), zinc chloride (ZnCl_2 ; 98%), lead(II) chloride (PbCl_2 ; 99.999%), palladium(II) chloride (PdCl_2 ; 99%), platinum(II) chloride (PtCl_2 ; 99%), rhodium(II) chloride hydrate ($\text{RhCl}_3 \cdot x\text{H}_2\text{O}$; 38-40%), bismuth(III) chloride (BiCl_3 ; 99.99%), tungsten(VI) chloride (WCl_6 ; 99.9%), gold(III) chloride hydrate ($\text{HAuCl}_4 \cdot x\text{H}_2\text{O}$; ~50% Au basis), silver nitrate (AgNO_3 ; 99.0%), 1-dodecanethiol (98%), 2-propanol (99.5%), acetone (CH_3COCH_3 ; 99.9%), and hydrochloric acid (HCl ; 37%) were purchased from Sigma-Aldrich. Rhenium(III) chloride (ReCl_3 ; 61.4-65.9% Re) was purchased from Thermo Scientific Chemicals. To prepare the solutions, an ultrapure purification system (Milli-Q advantage A10) was used, which produced deionized water with a resistance of 18.2 M Ω cm.

Preparation of Ga and Ga alloy nanoparticle precursors

We used two methods for the synthesis of Ga NPs. The first approach involves the synthesis of Ga NPs using a previously reported sonication technique³². Specifically, a mixture of Ga (100 mg, 1.43 mmol), 1-dodecanethiol (289 mg, 1.43 mmol) and 2-propanol (10 mL) was placed in a vial and sonicated for 2 h. Then, the obtained NPs were separated by centrifugation and washed three times with acetone to remove the remaining 1-dodecanethiol. Finally, the Ga NPs were re-dispersed in acetone for storage.

The second method involves scratching ~0.02 mg liquid Ga metal onto a carbon film substrate to form irregular thin film flakes (**Supplementary Fig. 31a**). These thin film flakes were remarkably stable due to the formation of oxide layers on the Ga surface. Subsequently, by immersing the Ga/Ga-oxide flakes coated substrate in a 0.1M HCl aqueous solution for 3 seconds triggered a reaction with the oxide layer, transforming the irregular Ga/Ga-oxide thin film flakes into Ga metal nanoparticles (**Supplementary Fig. 31b**).

Galinstan was prepared by mixing Ga, In, and Sn metals at 250 °C until complete melting. The weight ratio of Ga:In:Sn was 68.5:21.5:10.0. GISZ alloys were prepared by mixing Ga, In, Sn, and Zn metals with various compositions in quartz tubes under a vacuum of approximately 5×10^{-4} Pa and heated at 250 °C for several hours until complete melting in a thermostatic oil bath³³. After melting, the alloys were cooled to room temperature and transferred into sealed vials using a plastic transfer pipette for further use. We used the same scratching method to prepare Galinstan and GISZ nanoparticles with different film flakes. Furthermore, we immersed the Ga-based alloy-loaded substrate in a 0.1M HCl aqueous solution for 3 seconds to get Galinstan and GISZ nanoparticles. After all nanoparticle formation, we gently placed the sample into deionized water to remove chloride for further use.

The preparation of Ga-Cu and Cu-Pd binary alloys

First, a commercial Au TEM grid coated with a carbon film was used as the substrate. A thin layer of liquid Ga metal (~0.02 mg) was applied to the carbon film side by gentle scratching. Subsequently, we immersed the Ga-loaded TEM grid in a 0.1M HCl aqueous solution for 3 seconds. The HCl removed the native oxide layer on the Ga surface, allowing the liquid Ga to spontaneously break into numerous nanoparticles due to surface tension. The Au grid, now loaded with Ga nanoparticles, was thoroughly rinsed with deionized water to remove residual chloride

ions and then dried. It was then placed on an IKA RCT magnetic hotplate, heated and maintained at a constant temperature of 60 °C. A drop of CuCl₂ aqueous solution was added and allowed to react for two minutes. The resulting sample was washed again with deionized water, yielding Ga–Cu binary alloy particles as shown in **Fig. 1d**. By substituting the copper salt solution with a gold or palladium salt solution, binary Ga–Au and Ga–Pd alloys can also be synthesized (**Supplementary Figs. 32-33**).

For the synthesis of Cu–Pd binary alloy nanoparticles (**Fig. 1e**), Ga particles were heated and maintained at 80 °C. An aqueous solution of PdCl₂ was used in place of CuCl₂. All other experimental conditions and procedures were identical to those used for the synthesis of the Ga–Cu alloy.

The preparation of single crystal GaCuPdPtAuPb HEA-NPs

To synthesize GaCuPdPtAuPb HEA-NPs, a nickel TEM grid coated with a carbon film was used as the substrate to eliminate any potential elemental interference from the grid during alloy formation. Ga nanoparticles were prepared using the second method (scratching method) to load on the substrate. The Ga particles were then heated and maintained at 60 °C on an IKA RCT magnetic hotplate. Subsequently, 0.1 M mixing aqueous solutions (30 µl) of CuCl₂, PbCl₂, PdCl₂, PtCl₂, and HAuCl₄ were dropped onto the carbon film and allowed to react for two minutes. The resulting sample was rinsed thoroughly with deionized water to obtain the single-crystalline HEA-NPs shown in **Fig. 1f**.

The preparation of GaCuPdPtAuPb HEA with tunable morphologies and structures

To prepare GaCuPdPtAuPb HEA with adjustable morphology and structure, we also used the scratching method to form Ga nanoparticle precursor on a nickel TEM grid coated with a carbon

film. The TEM grid loaded with Ga nanoparticles was heated to 40 °C, after which a 0.1 M mixed aqueous solution (30 µl) containing HCl, CuCl₂, PbCl₂, PdCl₂, PtCl₂, and HAuCl₄ was dropped onto the carbon film and allowed to react for two minutes. The resulting sample was thoroughly rinsed with deionized water to yield the single-crystalline HEA-NPs shown in **Fig. 4b**. While keeping the reaction steps and conditions unchanged, we adjusted only the heating temperature of the TEM grid to 60 °C and 80 °C. This led to the formation of GaCuPdPtAuPb HEA-NPs with a mesocrystalline structure at 60 °C (**Fig. 4c**), and CuPdPtAuPb HEA-NPs with a polycrystalline structure at 80 °C (**Fig. 4d**). If the other reaction conditions are kept constant and the salt concentration is doubled relative to the conditions in **Fig. 4b**, an amorphous GaCuPdPtAuPb alloy can be obtained (**Fig. 4e**).

HEA nanomaterials preparation

To prepare the other HEA-NPs, we heated carbon-supported TEM grids containing Ga, Galinstan, and GISZ alloy NPs on an IKA RCT magnetic hotplate stirrer at RT, 40, 60, or 80 °C for 2 minutes. It should be noted that we selected various TEM carbon film grids depending on the synthesis of different HEAs to better assess the influence of the TEM grid on experimental outcomes. Then, we added a drop of a mixture of various metal salt solutions (0.1 M for each salt) to the grid, with or without 0.1 M HCl. After one minute of reaction, we removed the remaining liquid and washed away the residual salt with deionized water. Then, the sample was loaded into a TEM for characterization.

For preparing HEA nanomaterials with different shapes, we used the scratching method to load Ga-based liquid metal onto a carbon substrate, creating various irregular thin films. The oxide layer forms spontaneously on the liquid metal surface, stabilizing the irregular film shape. Next, we applied salt solutions containing various metal cations (0.1 M for each salt) onto the substrate

to react with the Ga-based liquid metal at different temperatures (25-80 °C) for 2 minutes, generating various non-granular HEAs. To prepare HEAs with more elements, Al was introduced to the Galinstan or GISZ alloys before adding salt solutions.

Material characterizations

The TEM characterizations were conducted using an image-corrected FEI ThemIS microscope operating at 60-300 kV. The microscope is equipped for fast EDS mapping and S/TEM imaging. All TEM and HRTEM were captured using an FEI Ceta2 camera. For EDS spectra and mapping, an FEI EDS detector with four windowless SDDs was employed. It provides a solid angle of 0.7 steradians and 140 eV energy resolution, enabling elemental mapping with high signal-to-noise ratio. During the TEM characterization process, we selected different TEM grids, washers, and clips based on the element combinations of the HEA nanomaterials.

In-situ liquid cell experiment for HEA-NPs formation

To study the alloying mechanisms of liquid metal with foreign metal source in the liquid phase environment, carbon film liquid cells were used in this experiment. First, we deposited the liquid GISZ alloy onto a carbon-supported gold grid by the scratching method. Next, the grid was swiftly immersed in a 0.1M HCl solution for 1 second, followed by rinsing with deionized water, effectively forming GISZ nanoparticles onto the carbon-supported grid. After drying, 100 nl of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ aqueous solution (0.1 M) and 10 nl of 0.1M HCl solution were dropped onto the GISZ-loaded carbon film. We covered the wet grid with another grid. After the liquid cell was assembled, it was loaded into the microscope for imaging. An FEI ThemIS 60-300 STEM/TEM with Cs-corrector was used for in situ imaging, and a beam current density of $\sim 100 \text{ e}^- \text{ nm}^{-2} \text{ s}^{-1}$ was used for the study.

Exclude the influence of electron beam effects

To rule out the influence of the electron beam on the conclusions drawn from the in-situ experiments, we conducted three systematic control experiments: ex-situ experiments without electron beam exposure, in-situ experiments without heating, and in-situ experiments with the electron beam blocked.

The ex-situ control experiment without electron beam exposure excluded the influence of the electron beam on the alloying process. For all ex-situ processes of HEA alloying, we can reach the high-entropy state after the reaction with no electron beam involved (**Fig. 1f, Fig. 4**). Therefore, the formation of HEA-NPs observed under controlled electron beam conditions can reflect the actual situation of ex-situ synthesis.

Under the same electron beam conditions, the in-situ control experiment without heating showed no alloying phenomena (**Supplementary Fig. 34**), confirming that alloying does not occur in the absence of heating. Therefore, we know thermal heating triggers the alloying process.

Third, in our in-situ experiment with thermal heating at 60°C, we found particles outside the viewing field that were not exposed to the electron beam during the reaction could still form HEAs (**Supplementary Fig. 35**), which demonstrates that HEA formation is independent of the electron beam.

Therefore, based on these findings, we confirm that the formation of HEA in our in-situ experiment is driven by thermal heating rather than the electron beam.

ICP-OES Characterization

The as-synthesized HEA powders containing Ga, Pb, Pd, Pt, Cu, and Au were dissolved using freshly prepared aqua regia (3:1 v/v HCl:HNO₃). After the acid was added to the powders, the

suspension was sonicated at room temperature for 15 minutes to promote initial dissolution. The mixture was then gently heated to 60 °C on a hotplate until complete visual dissolution of the solids was observed. Additional aqua regia was added dropwise as needed to ensure full digestion. Following digestion, the solution was cooled to room temperature, and a measured aliquot was diluted with 2% HNO₃ (v/v) prior to ICP-OES analysis. All solutions were prepared using ultrapure water. ICP-OES measurements were carried out using an Agilent 5800 Series VDV ICP-OES instrument. Axial viewing mode was selected for the detection of each element. An internal standard (Yttrium) was used to correct for instrumental drift and matrix effects. Calibration accuracy and stability were verified using both an initial calibration verification standard and a continuing calibration verification standard. A reagent blank was also analyzed to correct for background contamination.

XPS characterization

XPS analysis was performed on the 6 elements ((GaCuPdPtAuPb) HEA-NPs (**Supplementary Figs. 36-37**). XPS analysis was conducted using a Thermo Scientific™ K-AlphaPlus™ instrument, equipped with a monochromatic Al K α radiation source emitting at 1486.7 eV. The measurement area was configured to an elliptical shape of 200 × 400 μ m, and a flood gun was employed for charge compensation. For spectral acquisition, the pass energy settings were 200 eV for survey spectra and 50 eV for high-resolution spectra, with an energy resolution maintained at 0.1 eV. The analysis chamber maintained the pressure of approximately 1×10^{-9} mbar during data acquisition. Data processing was executed using the Thermo Scientific Advantage XPS software, with peak fitting performed through a combination of Gaussian/Lorentzian shapes and a Shirley background subtraction. Reference for all peak positions was established using the C 1s peak from adventitious carbon at 284.4 eV. XPS spectra covered

several binding energy regions, including XPS Survey, Ga 3*d*, Cu 2*p*, C 1*s*, O 1*s*, Pt 4*f*, Au 4*f*, Pb 4*f*, and Pd 3*d* orbitals, ensuring comprehensive surface composition analysis.

Data Availability Statement

All data generated or analyzed during this study are available in the paper and its Supplementary Information.

Additional references

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Author contributions Q. Z. and H.Z. conceived this work. Q.Z. designed and performed the in-situ TEM experiments. Q.Z., and Y.C. performed the ex-situ experiment about HEA synthesis, HEA characterization. Y.L. performed electrocatalytic tests under the supervisor of Y.H.. L.C. performed the XPS characterization and analyzed the XPS data. M.C.G. supplied discussion of

547 thermodynamic and kinetic theory for the synthesis method under the supervision of K.A.P..
548 Q.Z., Z.S., Y.C., Qi.Z., K.B., L.H., and H.Z. carried out data analysis. Q.Z. and H.Z. co-wrote
549 the manuscript with input from all authors. This work was done under the supervision of H.Z.

550 **Competing interests** Authors declare that they have no competing interests.

551 **Additional information**

552 **Supplementary information** The online version contains supplementary material available at

553 **Corresponding and requests for materials** should be addressed to Haimei Zheng.

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555 Figure legends

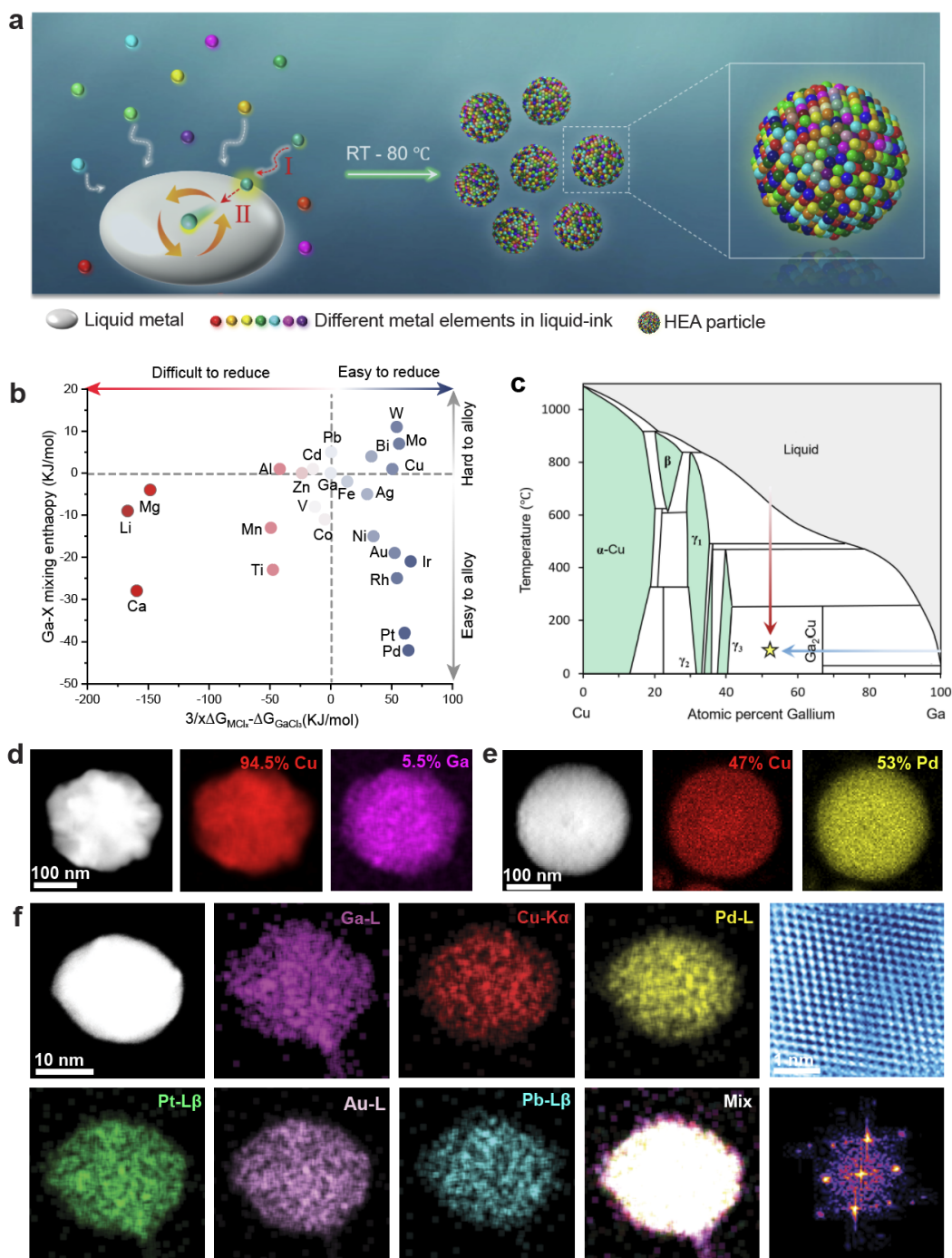


Fig. 1 | Fundamental principles of ISS synthesis of HEA at low temperatures. **a**, Schematic of HEA synthesis via ISS achieved through a liquid-liquid interface reaction. The synthesis process consists of two stages: (I) reduction of foreign metal ions at the interface between the liquid metal and salt solution; (II) solidification of the resulting metal atoms into a HEA within the liquid metal phase. **b**, Thermodynamically informed design map. The reducibility ($\Delta G_{chloride} - \Delta G_{GaCl_3}$) of metals is considered to assess the feasibility of the reduction reaction in Step I. Metals corresponding to ions positioned to the right of the dashed line can be spontaneously reduced by gallium (Ga) at

room temperature. The mixing enthalpy between Ga and other metals serves as an indicator of alloy miscibility in Step II. It is noted that we only list the mixing enthalpy of binary alloys here (The values of binary liquid alloys are calculated using the Miedema model at an equi-atomic composition)²⁹. For multi-element alloys, the miscibility is governed by the mixing entropy of the entire element system. **c**, Phase diagram of a representative Cu-Ga binary alloy, demonstrating two solidification routes. Traditional cooling solidification requires high temperatures to melt the metal, followed by rapid cooling to stabilize the high-entropy state (indicated by the red arrow). For ISS, the high-entropy state of liquid alloy can be trapped by rapid change in the composition through liquid-liquid interface reaction at low temperatures (blue arrow guides). **d**, Scanning TEM (STEM) elemental mapping of a representative Ga-Cu alloy. **e**, STEM elemental mapping of a representative Pd-Cu alloy. **f**, STEM elemental maps, HRTEM image, and fast Fourier transform (FFT) pattern of an individual HEA-NP, showing the formation of a solid-solution structure by ISS synthesis at 60 °C.

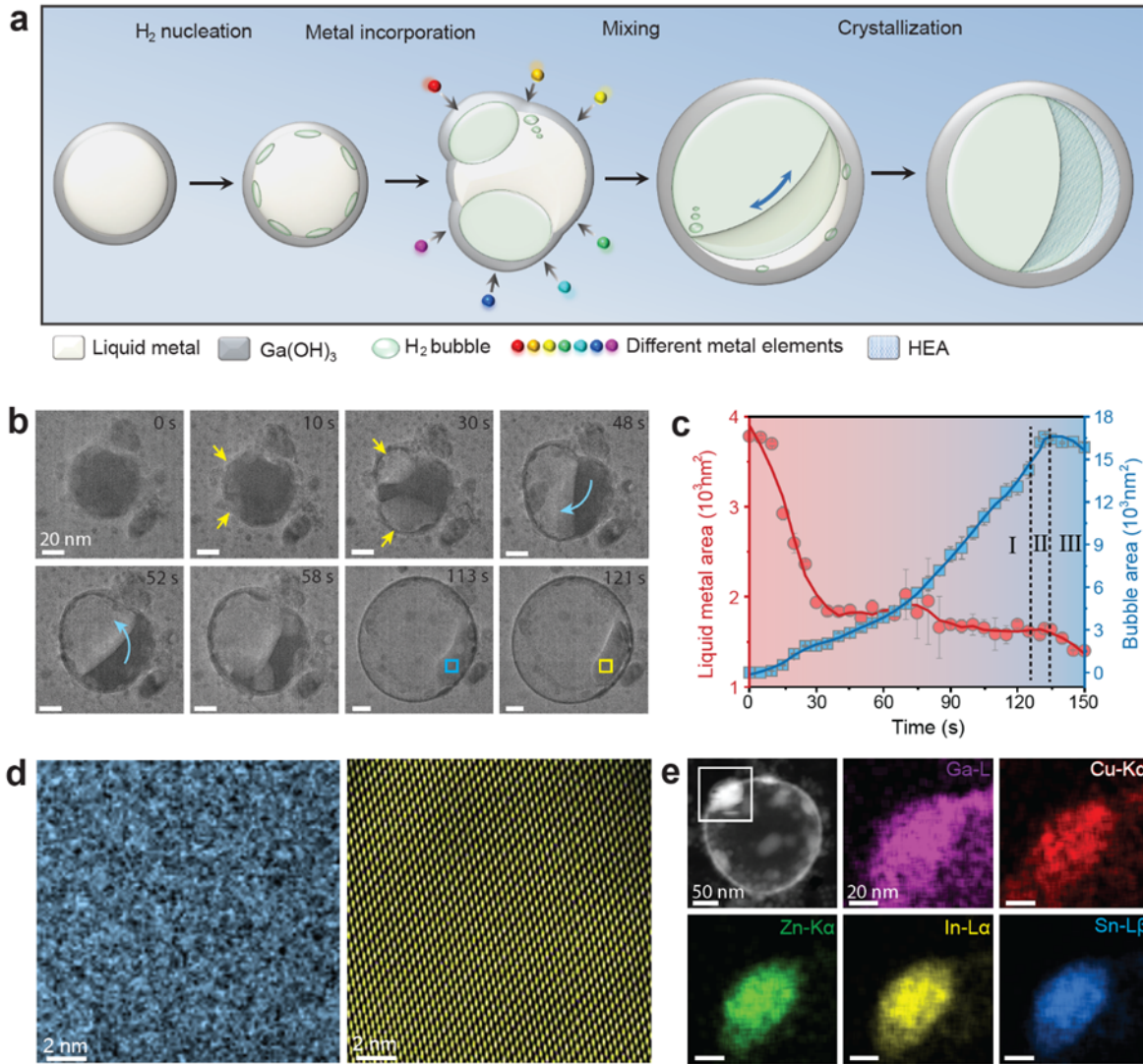


Fig. 2 | Mechanisms of ISS alloying during the formation of HEA nanoparticles (HEA-NPs) revealed through in-situ heated liquid-phase TEM. **a**, Schematic of HEA-NP formation, illustrating the steps of H₂ nucleation, metal incorporation, mixing, and crystallization. **b**, Sequential in-situ TEM images capture the formation of a HEA-NP (GaInSnZnCu) within a liquid environment at 60 °C. Yellow arrows highlight H₂ bubble nucleation and growth, while the indigo arrow indicates the stirring direction of the liquid metal alloy. **c**, Projected areas of the metal alloy and bubbles over time. Intervals I, II, and III represent stages in the dynamic process. Data are presented as mean ± standard deviation (s.d.), based on 3 independent measurements (n = 3), with error bars representing s.d. **d**, High-resolution TEM images show structural features of the same area before and after solidification of the liquid metal alloy, corresponding to the blue and yellow squares in (b). **e**, EDS mapping reveals the elemental distribution within the synthesized HEA-NP.

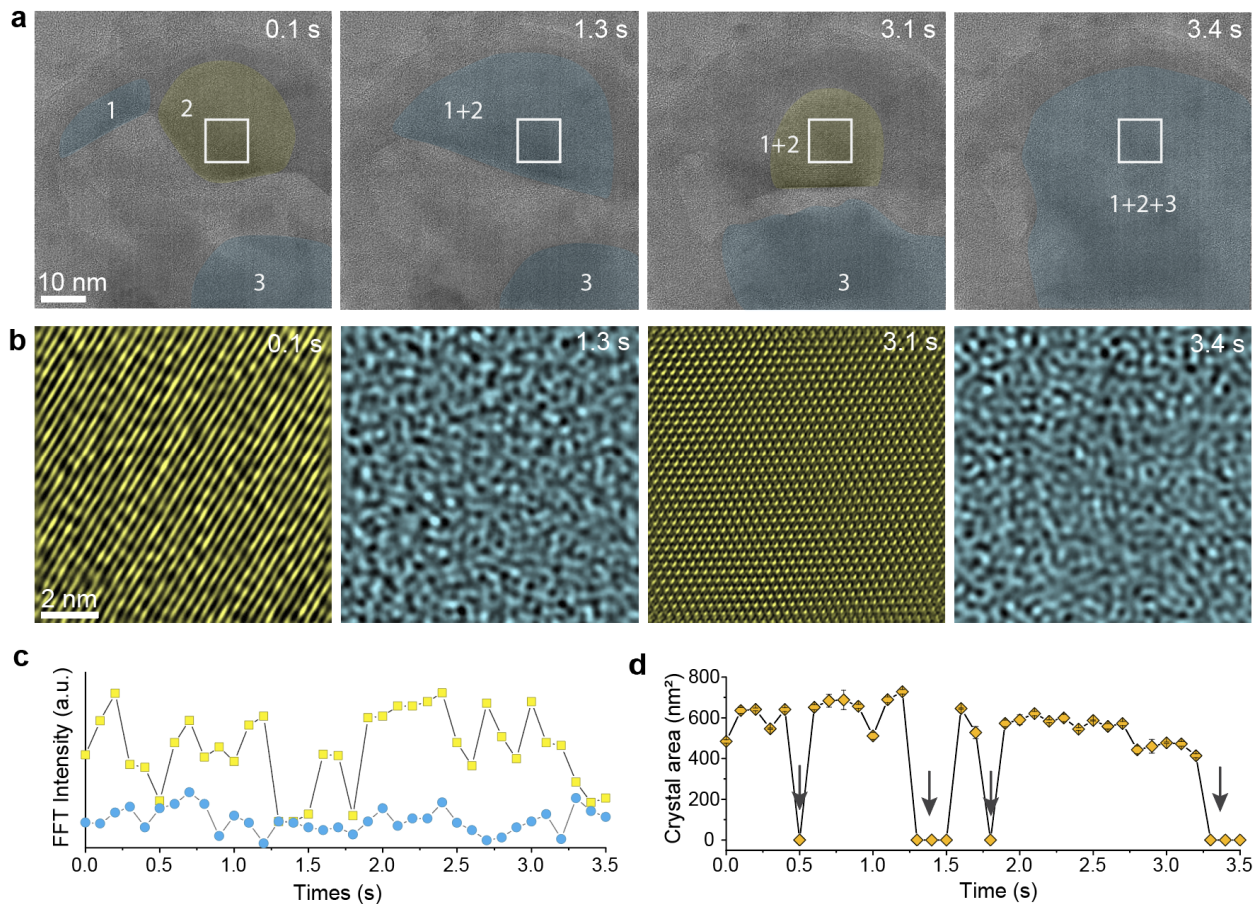


Fig. 3 | Structural fluctuations during the nucleation of liquid alloy crystals. **a**, Sequential images illustrate the fluctuations in alloy nucleation. Blue highlights the amorphous regions, while yellow indicates the crystalline regions. **b**, The HRTEM images of the white square area show the specific structures during the transformation. **c**, Maximum intensity of the FFT image as a function of time, with signals from a carbon film area indicating the background noise levels (negative control) of this analysis, measured in arbitrary units (a.u.). **d**, Nanocrystal area changes over time. The gray arrows point out the moments of amorphization.

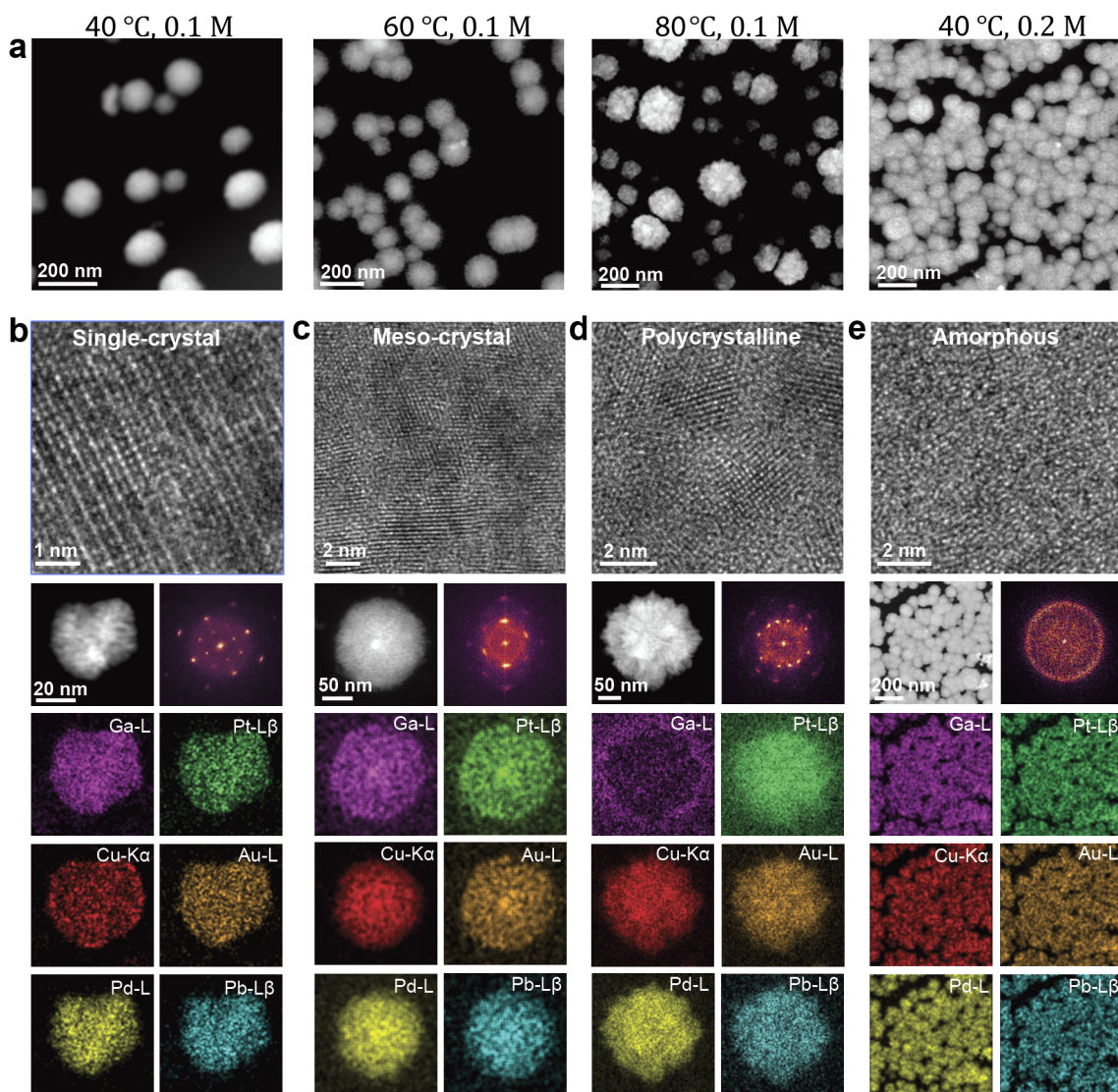


Fig. 4 | The controllable synthesis of HEA-NPs with varying crystallinity and morphology. a, STEM images of synthesized HEA-NPs (GaPtPdPbAuCu) obtained at different temperatures and concentrations of metal ion precursors: 40 °C, 0.1 M; 60 °C, 0.1 M; 80 °C, 0.1 M; and 40 °C, 0.2 M. **b-e,** High-resolution TEM images, along with corresponding FFT patterns and EDS mappings, depict representative HEA-NPs synthesized under the following conditions: **(b)** 40 °C with 0.1 M metal salt concentration, **(c)** 60 °C with 0.1 M metal salt concentration, **(d)** 80 °C with 0.1 M metal salt concentration, and **(e)** 40 °C with 0.2 M metal salt concentration.

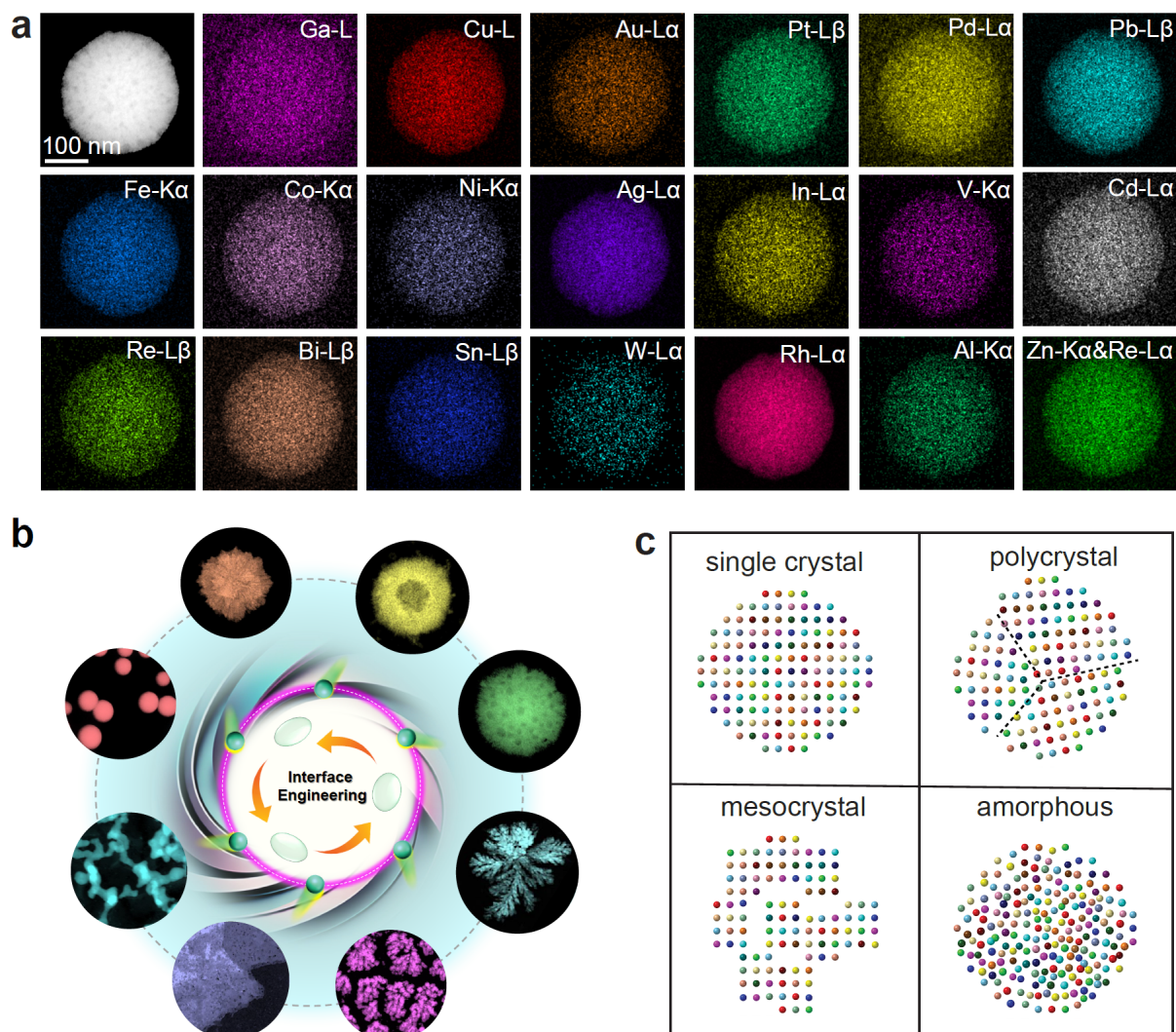
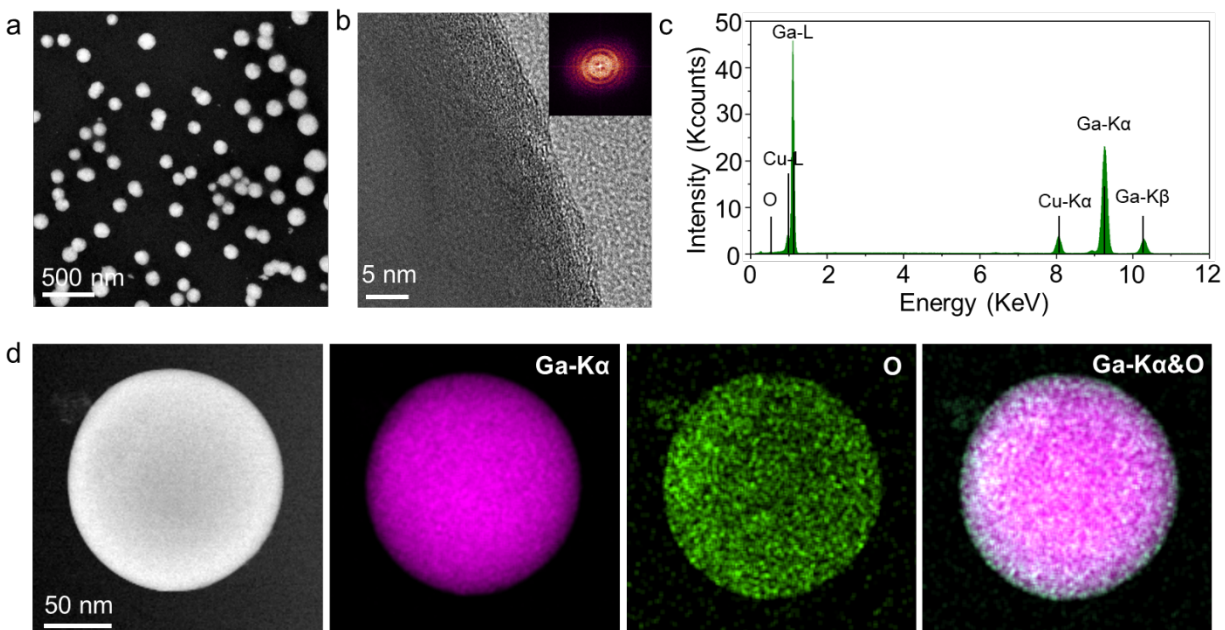
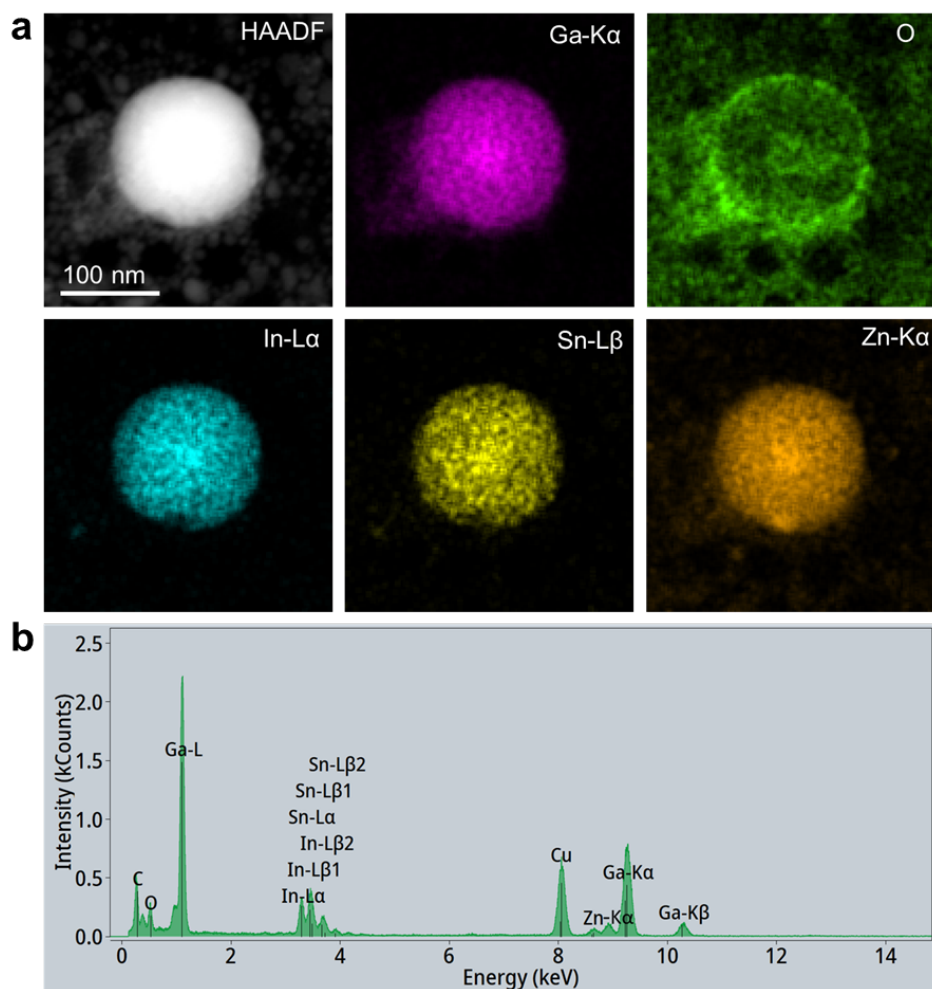


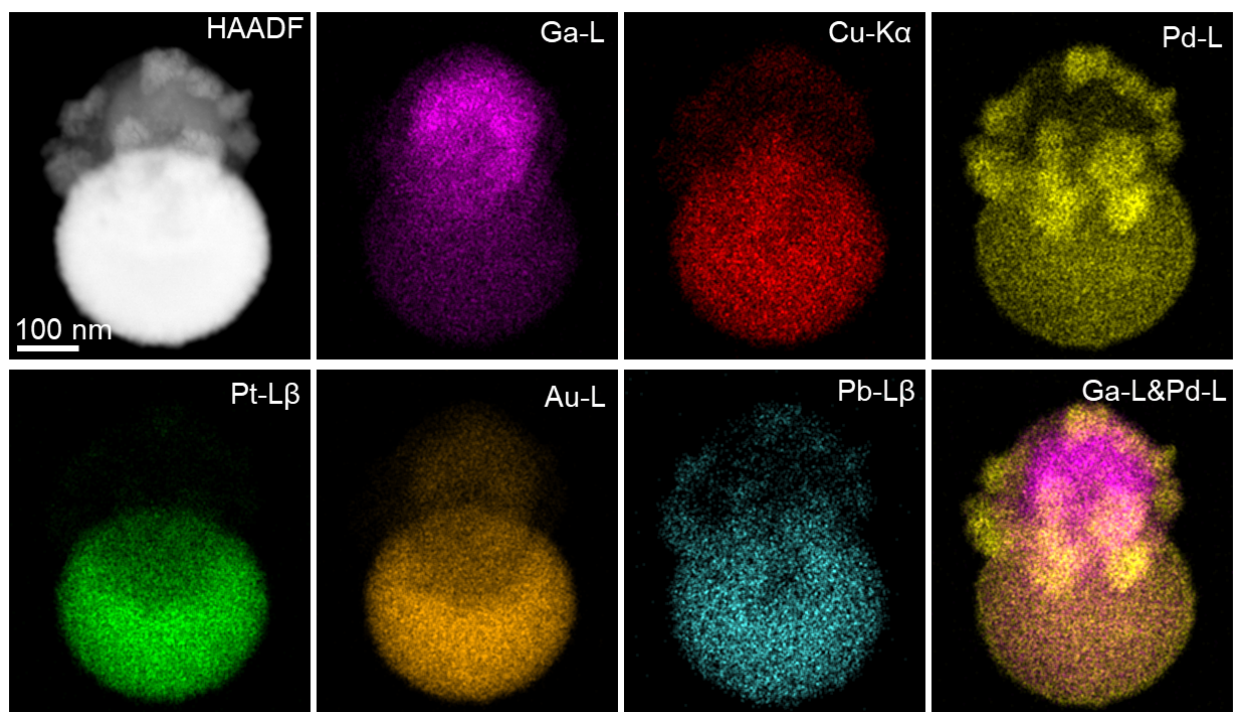
Fig. 5| The ISS method is efficacious for synthesizing HEA nanomaterials (HEA-NMs) with controlled elemental composition, morphology, and crystallinity. a, Elemental maps show HEA-NMs can incorporate as many as 20 metal elements. **b,** HEA-NMs with diverse shapes and morphologies can be attained after modiating the interface reaction. **c,** Schematic shows the controllable crystallinity (single crystal, mesocrystalline, polycrystalline, and amorphous structures) of synthesized HEA-NMs.



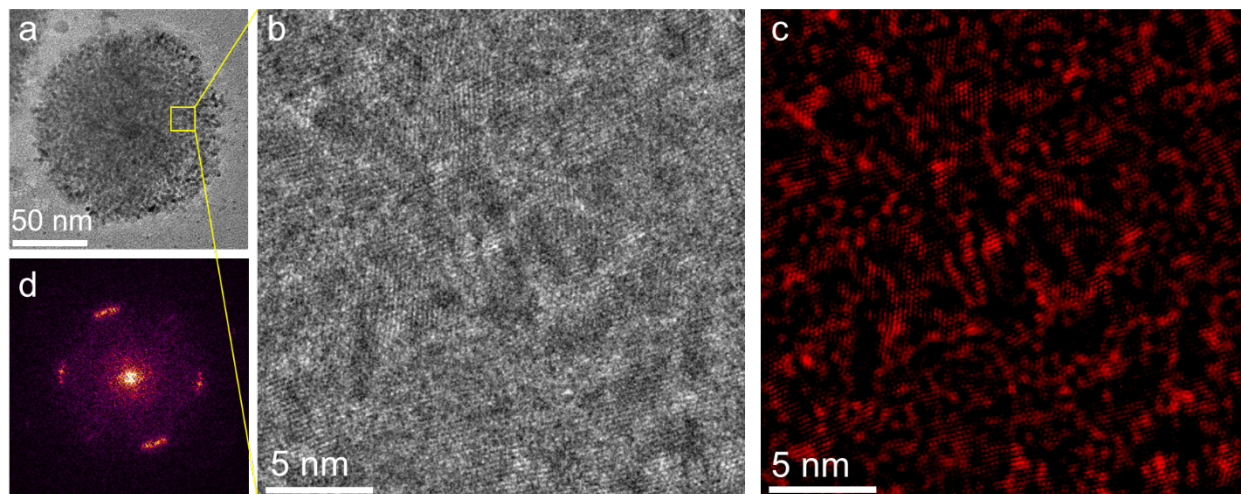
Extended Data Fig. 1 | TEM characterization of Ga nanoparticles. **a**, A low-magnification STEM image reveals the size the size characteristics of Ga nanoparticles. **b**, The HRTEM image, along with the corresponding FFT pattern of the Ga nanoparticle, indicates its amorphous structure. **c**, A STEM-EDS spectrum of a Ga nanoparticle confirms the presence of Ga and O elements, with Cu signals originating from the supporting Cu grid. **d**, STEM-EDS mapping of a Ga nanoparticle: HAADF image, Ga-K α map, O map, and Ga-K α &O map. The presence of O exclusively distributed on the shell part demonstrates the existence of an oxide shell.



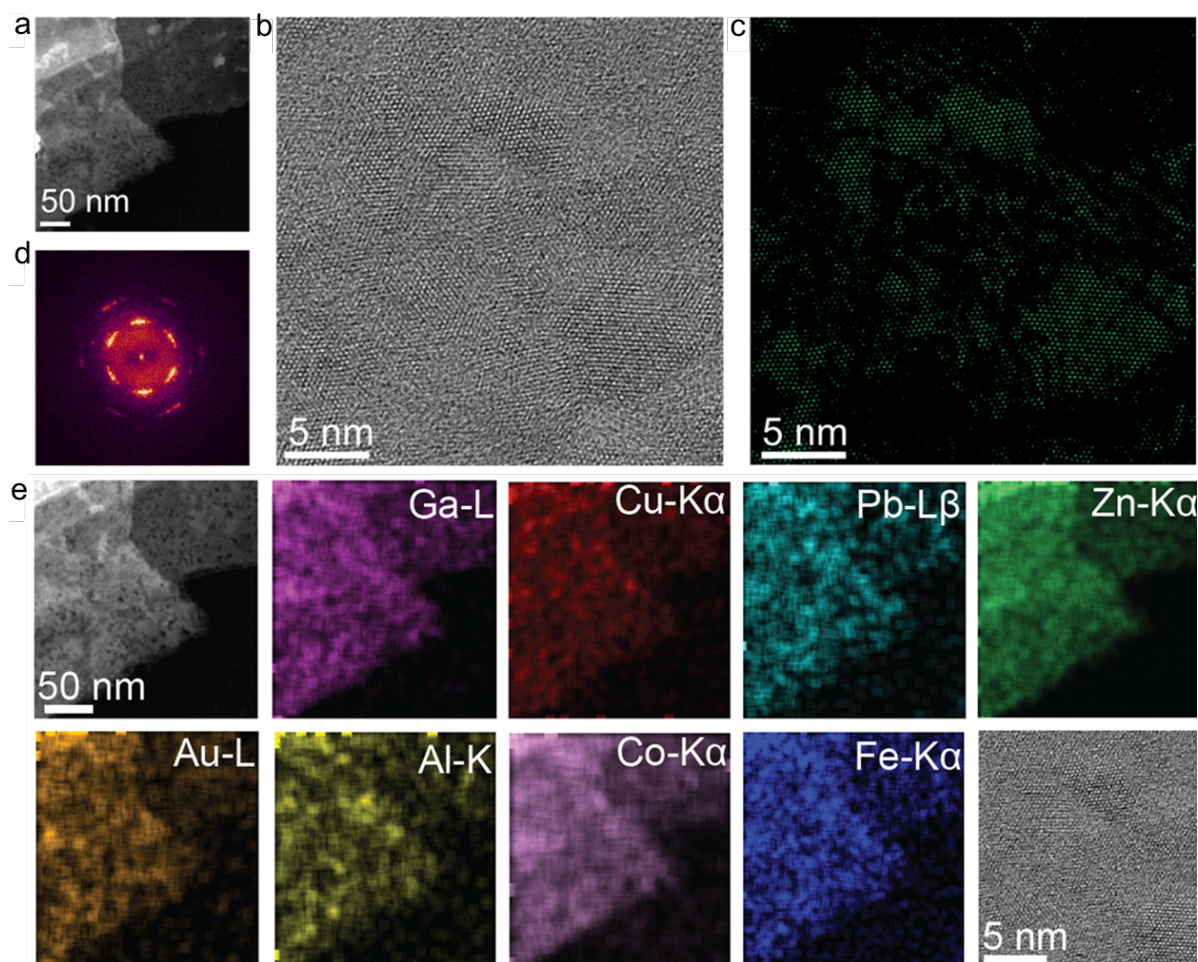
Extended Data Fig. 2 | EDS characterization of a GISZ nanoparticle. **a**, STEM-EDS mapping of a GISZ nanoparticle including HAADF image, Ga-K α map, In-L α map, Sn-L β map, Zn-K α map, O map, and Ga-K α &O map. The presence of O exclusively distributed on the shell part demonstrates the existence of an oxide shell. **b**, The STEM-EDS spectrum of a GISZ nanoparticle confirms the presence of Ga, In, Sn, Zn, and O elements, with Cu signals attributed to the underlying Cu grid.



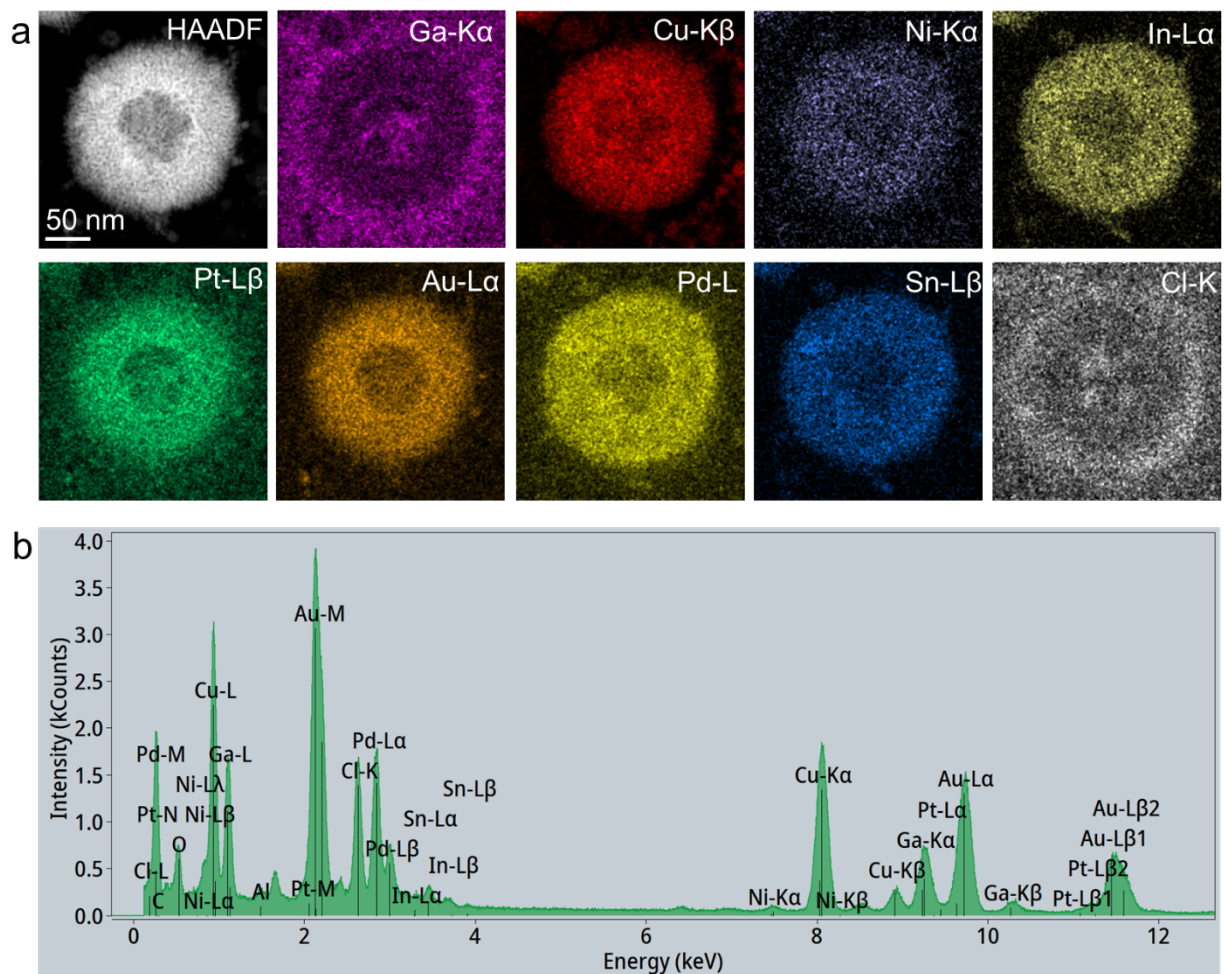
Extended Data Fig. 3 | TEM characterization of HEA with phase separation. STEM-EDS mapping of the heterostructured HEA nanoparticle includes HAADF imaging along with elemental maps: Ga-L, Cu-K α , Pd-L, Pt-L β , Au-L, Pb-L β , and a combined Ga-L & Pd-L map. The EDS mapping reveals a non-uniform elemental distribution within the nanoparticles, with the Ga-L & Pd-L map distinctly highlighting phase segregation.



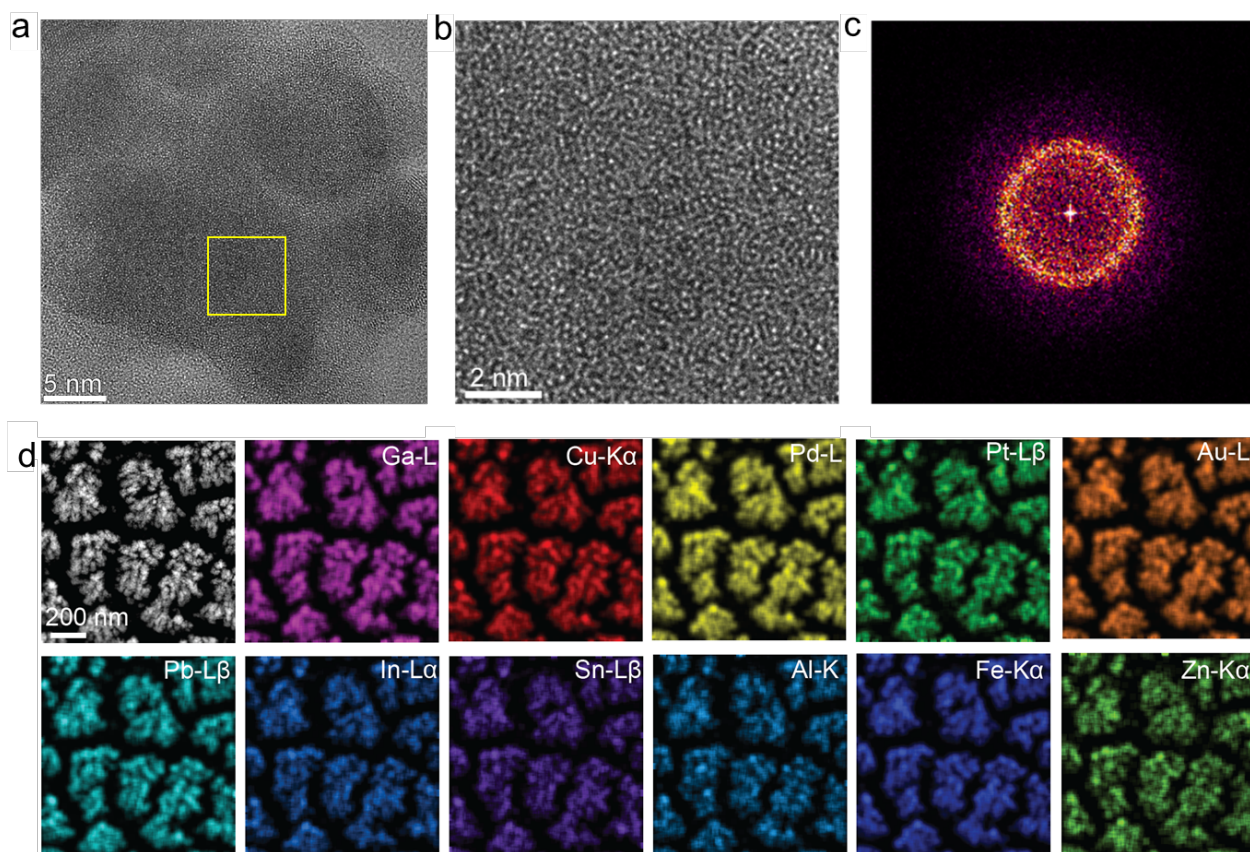
Extended Data Fig. 4 | TEM characterization of a mesocrystal HEA-NP (related to Fig. 4c).
a, A low-magnification TEM image reveals a large, porous spherical particle composed of numerous smaller nanoclusters. **b**, The zoomed-in view and **(c)** pseudo-color images illustrate the mesocrystal structure. **d**, The corresponding FFT pattern indicates that the crystalline domains are not perfectly aligned, showing evidence of rotational misalignment and lattice bending.



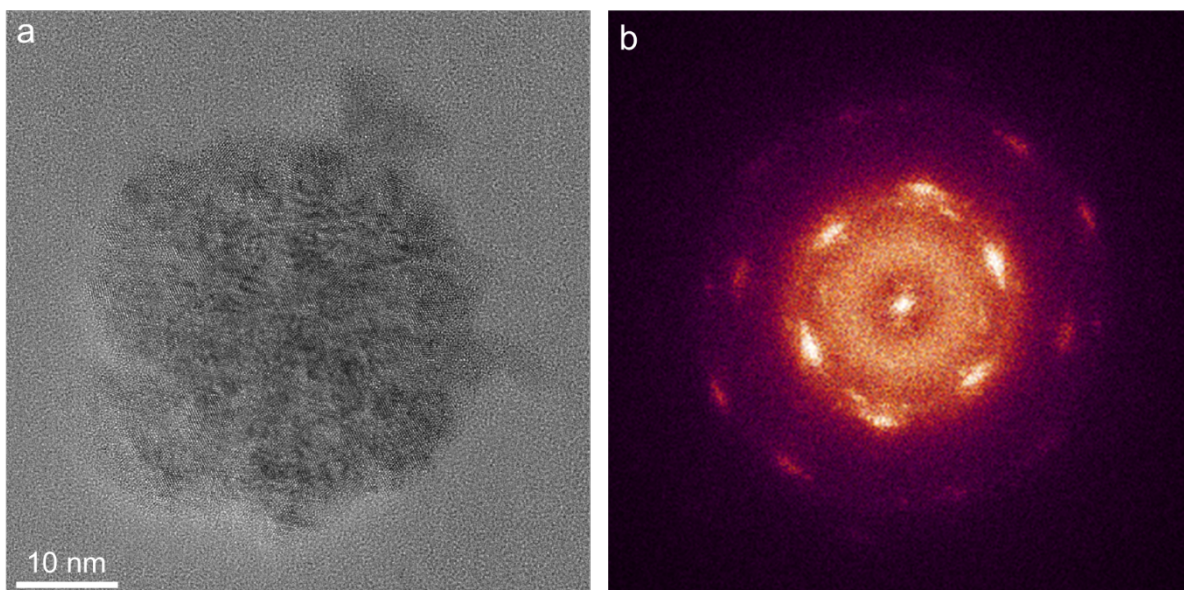
Extended Data Fig. 5 | Characterization of mesocrystal HEA nanosheets. **a**, A low-magnification STEM image highlights the 2D morphology of the HEA nanosheets. **b**, The HRTEM image reveals their mesocrystal structure, with individual single-crystal domains exhibiting parallel crystallographic alignment while remaining spatially separated. **c**, An IFFT image of the HRTEM emphasizes the distinct, separated crystal domains. **d**, The corresponding FFT pattern indicates that the crystalline domains are not perfectly aligned, showing signs of rotational misalignment. **e**, EDS maps demonstrate that the elements are uniformly distributed throughout the nanosheets.



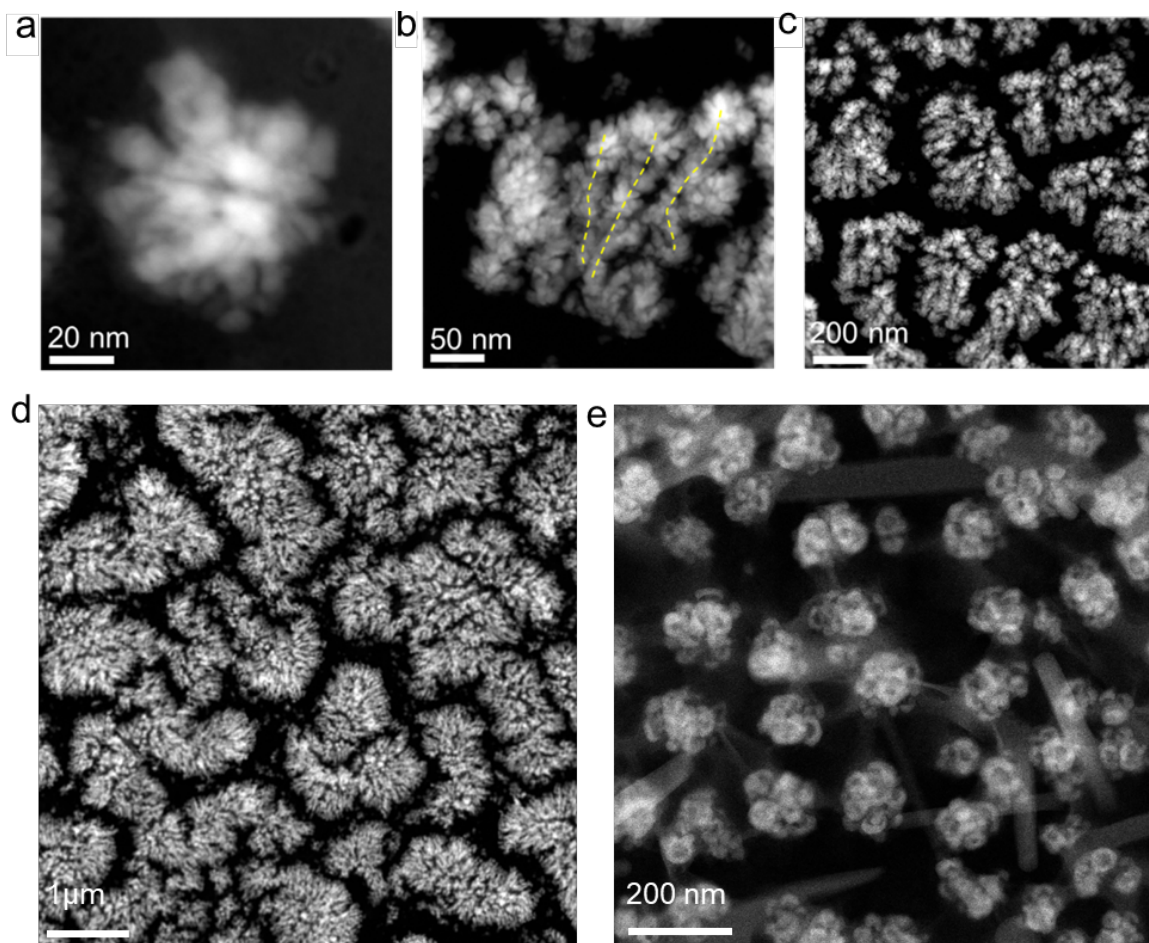
Extended Data Fig. 6 | EDS characterization of the HEA-NP using Galinstan precursor at 40 °C. **a**, STEM-EDS mapping of the HEA-NP: HAADF image, Ga-K α map, Cu-K α map, Ni-K α map, In-L α map, Pt-L β map, Au-L α map, Pd-L map, Sn-L β map, and Cl-K map. The EDS mapping reveals uniform elemental distribution within the nanoparticle. Cl does not belong to the HEA composition. **b**, The EDS spectrum of the HEA nanoparticle reveals the presence of C, O, Ga, Cu, Ni, In, Pt, Au, Pd, and Cl elements. C, O, and Cl originate from the carbon supporting film and residual salts.



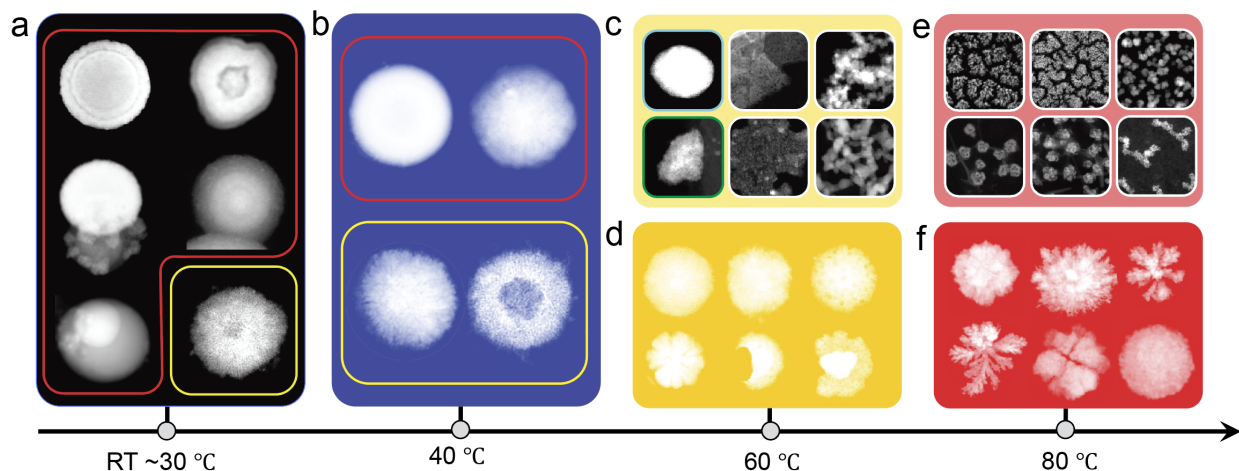
Extended Data Fig. 7 | Structural analysis of hierarchical HEAs. **a**, TEM image of the basic flower structure. **b**, HRTEM and the corresponding FFT (**c**) show the basic blocks have amorphous structure. **d**, EDS maps of the 3D hierarchical nanostructures show its elemental distribution.



Extended Data Fig. 8 | TEM characterization of HEA with 20 elements (correspond to Fig. 5a). **a**, HRTEM image reveals the crystal structure of the HEA-NPs. **b**, The corresponding FFT pattern reveals its mesocrystal structure.



Extended Data Fig. 9 | Configuration analysis of some 3-D hierarchical HEAs. **a-c**, The 3-D HEA structure in the shape of “grape bunches”. **a**, Flower structure of the basic building block. **b**, The flower structures align together to form chain. Yellow dashed lines highlight the chain structure. **c**, Chain-like structures come together to form large “grape bunch” structure. **d**, The 3-D HEA structure in the shape of in the shape of feathers. **e**, The 3-D HEA structure in the shape of in the shape of plum blossoms.



Extended Data Fig. 10 | Morphology diagram of HEA nanomaterials. STEM images show the diverse morphology of HEAs. **a:** To synthesize nanoparticles in panel (a), we utilize sphere-shaped liquid gallium (marked with red outline) or liquid gallium alloy (marked with yellow outline) as precursors. Additionally, we introduce HCl into the metal salt solution to eliminate the surface oxide of the Ga and Ga alloy particles. **b, d, f:** The synthesis conditions for the particles depicted in panel (b), (d), and (f) mirror those in panel (a), but with elevated reaction temperatures of 40 °C, 60 °C, and 80 °C. **c:** we employ spherical shape (marked with indigo outline), irregular shape (marked with green outline), and 2D-film (marked with white outline) liquid Ga/Ga alloy precursors, without the addition of HCl in the metal salt solution, and the reaction temperature is 60 °C. **e:** For HEA synthesis, we use 2D-film liquid Ga/Ga alloy precursors and the reaction temperature is 80 °C.