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## **3D atomic structure and local chemical order of medium/high-entropy nanoalloys**

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**Medium- and high-entropy alloys (M/HEAs) mix multiple principal elements with near-equiatomic composition and represent a paradigm-shift strategy for designing new materials for metallurgy<sup>1-8</sup>, catalysis<sup>9-14</sup>, and other fields<sup>15-18</sup>. One of the core hypotheses of M/HEAs is lattice distortion<sup>5,19,20</sup>, which has been investigated by different numerical and experimental techniques<sup>21-26</sup>. However, determining the three-dimensional (3D) lattice distortion in M/HEAs remains a challenge. Additionally, the presumed random elemental mixing in M/HEAs has been questioned by x-ray/neutron study<sup>27</sup>, atomistic simulations<sup>28-30</sup>, energy dispersive spectroscopy (EDS)<sup>31,34</sup>, and electron diffraction<sup>32,33</sup>, which suggest the existence of local chemical order in M/HEAs. However, the 3D local chemical order has eluded direct experimental observation since the EDS integrates the composition of atomic columns along the zone axes<sup>7,33,34</sup> and diffuse electron reflections may originate from**

**planar defects instead of local chemical order<sup>35</sup>. Here, we determine the 3D atomic positions of M/HEA nanoparticles using atomic electron tomography<sup>36</sup>, and quantitatively characterize the local lattice distortion, strain tensor, twin boundaries, dislocation cores, and chemical short-range order (CSRO). We find that the HEAs have larger local lattice distortion and more heterogeneous strain than the MEAs and strain is correlated with CSRO. We also observe CSRO-mediated twinning in the MEAs, that is, twinning occurs in energetically unfavoured CSRO regions but not in energetically favoured CSRO ones, which represents the first experimental observation of correlating local chemical order with structural defects in any material. We expect that this work will not only expand our fundamental understanding of this important class of materials, but also could provide the foundation for tailoring M/HEA properties through engineering lattice distortion and local chemical order.**

Strength and ductility are two important material properties, but are mutually exclusive in most materials<sup>37</sup>. Recent experiments have demonstrated that several M/HEAs can overcome this strength-ductility tradeoff<sup>3-8,38-40</sup>. The high strength of M/HEAs stems from the different elemental components acting as solutes<sup>41</sup>, local chemical order<sup>30</sup> and heterogeneous lattice strain<sup>25,26</sup>, which raise the energy barrier of dislocation motion<sup>35</sup>. While dislocation glide in face-centred cubic (fcc) metals leads to high ductility with reduced strength<sup>37</sup>, twinning in M/HEAs provides a distinct plasticity mechanism that obstructs dislocation motion and gains strength while remaining ductile<sup>42</sup>. This twinning-induced, simultaneous increase of strength and ductility in M/HEAs has spurred both mechanistically-driven and property-discovering investigations for structural applications<sup>3,7,38-40,43</sup>. However, the degree and influence of atomic segregation and

CSRO on twin formation remain unclear in both M/HEAs and other alloys. Recent atomistic simulations have indicated a link between CSRO and twinning in MEAs<sup>28,30</sup>, but there is no experimental evidence.

Furthermore, CSRO, lattice distortion, and surface strain strongly affect the catalytic activity of M/HEAs<sup>9-14</sup>. Unlike conventional catalysts, M/HEAs confine different elements into the same lattice, which distorts the lattice structure and induces strain<sup>12,13</sup>. The lattice distortion and surface strain along with the chemical diversity of adsorption sites increase the activity, selectivity and durability of M/HEA catalysts<sup>9,13,44-46</sup>. However, our current understanding of the lattice distortion, strain, and CSRO in M/HEA catalysts remains limited due to the dearth of 3D space and atomic scale information from diffraction, spectroscopy, electron microscopy, and atomistic simulations<sup>9-14</sup>. Here, we employed atomic electron tomography (AET) to determine the 3D atomic coordinates of NiPdPt-based M/HEA nanoparticles. We quantified the 3D lattice distortion, strain tensor, dislocations, twin boundaries and CSRO of the M/HEAs at the atomic scale. We observe a correlation between strain and CSRO in the M/HEAs and a direct link between CSRO and twinning in the MEAs.

### **3D local lattice distortion and strain tensor in M/HEAs**

We chose NiPdPt-based M/HEA nanoparticles as a model in this study as they are not only catalytically active<sup>14,47-49</sup>, but also provide sufficient image contrast for AET to identify their atomic species/types<sup>36</sup>. The M/HEA nanoparticles were synthesized by a carbothermal shock method<sup>50</sup> (Methods, Extended Data Table 1), and the distribution of the eight elements in the HEAs was confirmed by EDS maps (Extended Data Fig. 1). The AET experiments were performed with a scanning transmission electron microscope in the annular dark-field mode (Methods). Tomographic tilt series were acquired from six

MEA and four HEA nanoparticles (Extended Data Table 2). These nanoparticles were stable under the electron beam by examining the consistency of the images taken before, during and after the data acquisition. After image pre-processing, each tilt series was reconstructed by an advanced tomographic algorithm and the 3D atomic coordinates were traced, classified, and refined to produce an experimental atomic model (Methods). The experimental precision of the 3D atomic coordinates was estimated to be 19.5 pm (Extended Data Fig. 2). While we resolved the atomic species in the MEA nanoparticles as Ni, Pd, and Pt, the eight elements in the HEA nanoparticles were classified into three types (Co and Ni as type 1; Ru, Rh, Pd, and Ag as type 2; Ir and Pt as type 3) because the atomic numbers of several elements only differ by 1 and cannot be distinguished by AET<sup>36</sup>. The number of atoms and the atomic species/types of the ten M/HEAs are shown in Extended Data Table 2.

Figure 1a-d and Extended Data Fig. 3 show the experimental 3D atomic models of the ten M/HEA nanoparticles, exhibiting a single-phase fcc structure. To quantify the local lattice distortion of the M/HEAs, we compared each atom and its nearest neighbours with a reference fcc lattice to determine the 3D atomic displacement (Methods). Figure 1e-h shows the 3D atomic displacements for two representative MEAs and two HEAs, termed MEA-1, MEA-2, HEA-1, and HEA-2, respectively. The mean and standard deviation of the atomic displacements of the four nanoparticles are  $0.23 \pm 0.11$  Å,  $0.26 \pm 0.12$  Å,  $0.29 \pm 0.12$  Å, and  $0.37 \pm 0.12$  Å, respectively (Fig. 1i-l). A statistical analysis of these data shows that the HEAs have larger local lattice distortion than the MEAs (Extended Data Table 3). From the experimental 3D atomic coordinates, we also determined the local strain tensor of the M/HEAs using a method described elsewhere<sup>51</sup> (Methods). Figure 2 shows the six components of the local strain tensor for MEA-1,

MEA-2, HEA-1 and HEA-2, where the compressive, tensile, and shear strain range from -8% to +8%. To quantify the local heterogeneity of the strain tensor, we calculated the standard deviation and the smoothness energy (Methods). The standard deviation measures the average amount of deviation from the mean, whereas the smoothness energy quantifies the local fluctuation. The larger the smoothness energy, the larger the local fluctuation. Figure 2e and f show that the HEAs have more heterogeneous strain than the MEAs.

Next, we characterize twins and dislocations in the M/HEAs. Among the ten M/HEAs, three are twin-free, two have a single twin, four have double twins, and one has a grain boundary and double twins (Methods, Fig. 1a-d, Extended Data Fig. 3). The abundant presence of the single and double twins in M/HEAs is different from conventional nanoparticles, which have fewer twins except for decahedral multiply twinned nanoparticles<sup>52,53</sup>. Compared to the MEAs, the HEAs have more diffuse twin boundaries with each boundary spreading to the neighbouring atomic layers (Extended Data Fig. 4a-e). We also observe that the HEAs are more prone to having dislocations than the MEAs. Extended Data Fig. 4f-i shows the cores of several Shockley partial dislocations and screw dislocation in the M/HEAs and the corresponding Burgers vectors.

### **Experimental observation of CSRO-mediated twinning**

To quantify the local chemical order in the M/HEAs, we compute the CSRO parameters ( $\alpha_{ij}$ ) between each atom and its nearest neighbours<sup>55,30</sup> (Methods). For pairs of the same species/types ( $i = j$ ), a positive  $\alpha_{ii}$  means a tendency to segregate, and a negative  $\alpha_{ii}$  does the opposite. For pairs of different species/types ( $i \neq j$ ), a negative  $\alpha_{ij}$  means favourable inter-mixing, and a positive  $\alpha_{ij}$  does the opposite. A quantitative analysis of CSRO and

strain indicates that the HEAs have more heterogeneous CSRO than the MEAs and CSRO is correlated with strain in the M/HEAs (Fig. 2e and f). Figure 3a, b and Extended Data Fig. 5a-d show the 3D distribution of the six CSRO parameters ( $\alpha_{\text{NiNi}}$ ,  $\alpha_{\text{PdPd}}$ ,  $\alpha_{\text{PtPt}}$ ,  $\alpha_{\text{NiPd}}$ ,  $\alpha_{\text{NiPt}}$ , and  $\alpha_{\text{PdPt}}$ ) of twin-free MEA-1. The 3D distribution is heterogeneous with the formation of pockets of local chemical order, indicating that CSRO can propagate from the angstrom- to the nanometer-scale. To quantify the local chemical order, we averaged every CSRO parameter for each atomic layer along the [111] direction (Fig. 3c, d, Extended Data Fig. 5e-h). We observe that all the average  $\alpha_{\text{NiPt}}$  values are negative and the majority of the average  $\alpha_{\text{PdPt}}$  values are positive, indicating the tendency of the inter-mixing between Ni and Pt atoms and the separation between Pd and Pt atoms. To validate our experimental observations, we performed density functional theory (DFT)-based calculations to predict energy-favoured CSRO in a twin-free NiPdPt MEA (Methods). Figure 3i shows the histogram of the six average CSRO parameters of the twin-free MEA between the DFT calculations and experimental observations, confirming a favourable bonding between Ni and Pt atoms and an unfavourable bonding between Pd and Pt atoms in twin-free MEAs.

As a comparison, we calculated the six CSRO parameters for the double-twinned MEA-2. Figure 3e, f and Extended Data Fig. 5i-l show the 3D distribution of the six parameters, in which the yellow planes represent the twin boundaries. The CSRO of the double-twinned MEA are more heterogeneous than that of the twin-free MEA. Some pockets of local chemical order are connected to each other to form elongated structures that extend over a few nanometers. Figure 3g, h and Extended Data Fig. 5m-p show the histograms of the six average CSRO parameters of each atomic layer parallel to the twin boundaries. The majority of the  $\alpha_{\text{NiPt}}$  and  $\alpha_{\text{PdPt}}$  values are positive and negative,

respectively (Fig. 3g, h), which are the opposite of the  $\alpha_{\text{NiPt}}$  and  $\alpha_{\text{PdPt}}$  of the twin-free MEA-1 (Fig. 3c, d). The average  $\alpha_{\text{NiPt}}$  and  $\alpha_{\text{PdPt}}$  values of the double-twinned MEA are the reverse of those of the twin-free MEA as well as the DFT calculations of a twin-free MEA (Fig. 3i). These observations indicate that the separation of the favourable atomic species (Ni and Pt) and the inter-mixing of the unfavorable atomic species (Pd and Pt) facilitate the formation of the twins, which are further corroborated by the analysis of the other double-twinned MEA nanoparticle (Extended Data Figs. 6).

To investigate the impact of CSRO on the twin formation energy ( $E_{\text{TF}}$ ) of the MEAs, we used the experimental 3D atomic coordinates and species as direct input to molecular dynamics (MD) simulations and calculated  $E_{\text{TF}}$  as a function of the twin position (Methods). We first applied this approach to a single-twinned MEA. Figure 4a-e shows the change of  $E_{\text{TF}}$  by moving the twin from the 0<sup>th</sup> to the 10<sup>th</sup> atomic layer along the [111] direction, where the 0<sup>th</sup> layer means twin-free. Four representative atomic configurations are shown in Fig. 4a-d with the twin marked in yellow. We observe that  $E_{\text{TF}}$  changes from negative to positive when the twin is moved from atomic layer 5 to 6 (Fig. 4e). The experimentally determined twin position is in layer 5 (yellow bar), which is next to the minimum  $E_{\text{TF}}$  in layer 4. Next, we used the experimental 3D atomic coordinates of the double-twinned MEA-2 as input to MD simulations to calculate  $E_{\text{TF}}$  as a function of the twin separation. While fixing one twin, we moved the other twin layer-by-layer along the [111] direction and computed the corresponding  $E_{\text{TF}}$  (Fig. 4f-i). We find that  $E_{\text{TF}}$  changes from negative to positive between a twin separation of 5 and 6 atomic layers. The experimentally determined twin separation is 5 layers (yellow bar in Fig. 4i), which is next to the minimum  $E_{\text{TF}}$  with a twin separation of 4 layers. We analyzed the other double-twinned MEA nanoparticle and obtained consistent results (Extended



Data Fig. 7). All these observations show a correlation between the CSRO and twinning in the MEAs, that is, energetically-unfavourable CSRO lowers the  $E_{TF}$ . As the samples were synthesized by heating metal precursors to  $\sim 2,000$  K in  $\sim 50$  ms, followed by rapid cooling at  $\sim 10^5$  K/s (Methods)<sup>50</sup>, this quenching process essentially freezes the CSRO in the molten alloy since there is no sufficient time for atomic diffusion to appreciably change the CSRO. Therefore, we conclude that CSRO mediates the formation of twins in the MEA nanoparticles.

Compared to the MEAs, the HEAs exhibit greater local chemical fluctuation. Extended Data Figs. 8a-f and 9a-f show the 3D distribution of the six CSRO parameters for a twin-free and a double-twinned HEA, which are more heterogeneous than those of the MEAs (Fig. 2e). The increase of the chemical complexity from the three-element MEAs to the eight-element HEAs leads to a larger distortion of the twin geometry as manifested in the formation of atomic steps along the twins of both the MEAs and HEAs (Extended Data Fig. 4b-e), with the latter containing multiple such steps that disrupt stacking of the neighbouring atomic planes. To examine the correlation between CSRO and twinning in the HEAs, we calculated the six average CSRO parameters of the atomic layer along the [111] direction for a twin-free HEA (Extended Data Fig. 8g-l). In comparison, the six average CSRO parameters for a double-twinned HEA are shown in Extended Data Fig. 9g-l. We observe the reverse of  $\alpha_{13}$  between the twin-free and double-twinned HEAs, indicating that the separation of the favourable atomic types 1 and 3 facilitates the formation of the twins in the HEAs (Extended Data Fig. 9m). Because our current AET experiment can only classify the eight elements in the HEAs into three types, we cannot calculate the  $E_{TF}$  from the experimental 3D atomic coordinates and types of the HEAs as in the case of the MEAs.

## Conclusions and outlook

Lattice distortion and CSRO are two fundamental features that strongly affect the unique properties of M/HEAs. Despite significant insights from various experiments<sup>21-33</sup>, direct 3D structure information remains elusive. Here we overcome this major limitation by advancing AET to determine the 3D atomic positions of M/HEAs and quantitatively characterize their local lattice distortion, strain tensor, dislocation cores, and CSRO in three dimensions. We find a correlation between strain and CSRO in the M/HEAs. We also observe CSRO-mediated twinning in the MEAs, which confirms the DFT calculations of the NiPdPt MEA (Fig. 3i) and the atomistic simulations of the CrCoNi MEA<sup>28,30</sup>. Owing to the tunability of CSRO during materials manufacturing, our 3D atomic-scale insights into the correlation between CSRO and twinning could expand the horizon for the design of M/HEAs and other alloys with targeted structure-property relationships. As a general tomography method, AET can also be combined with EDS to quantitatively characterize the CSRO in bulk M/HEAs, where the samples can be fabricated into sharp needles or thin films by focused ion beam.

Furthermore, M/HEA catalysts have shown performance improvements over conventional alloys for various multi-step reactions<sup>12,14</sup>, including ammonia oxidation/decomposition<sup>9,50</sup>, carbon dioxide reduction<sup>44,45</sup>, and methane combustion<sup>56</sup>. M/HEA catalysts also possess near-continuum adsorbate binding energies with greater structural stability<sup>12,14,49</sup>. Thus, determining the 3D atomic structure of M/HEA catalysts and measuring their 3D local lattice distortion and strain could pave the way for their rational design in a largely untapped range of compositions and structures. The present case-study of NiPdPt-based M/HEA nanoparticles provides unprecedented insights into the heterogeneous distribution of strain and CSRO, and represents an important step in

this direction. Recently, we have demonstrated that the experimental 3D atomic coordinates from AET can be used as direct input to DFT and machine learning to identify the active sites of Pt alloy nanocatalysts for the oxygen reduction reaction<sup>57</sup>. Immediate extension of this approach to M/HEA nanoparticles could open the door to uncovering yet-unknown attributes of this emerging class of catalysts. Looking forward, we expect that the ability to determine the 3D atomic structure and local chemical order of M/HEAs will extend to both the metallurgical community's pursuit of superior strength-ductility combinations, and the catalysis community's quest toward optimized surface adsorption energies.

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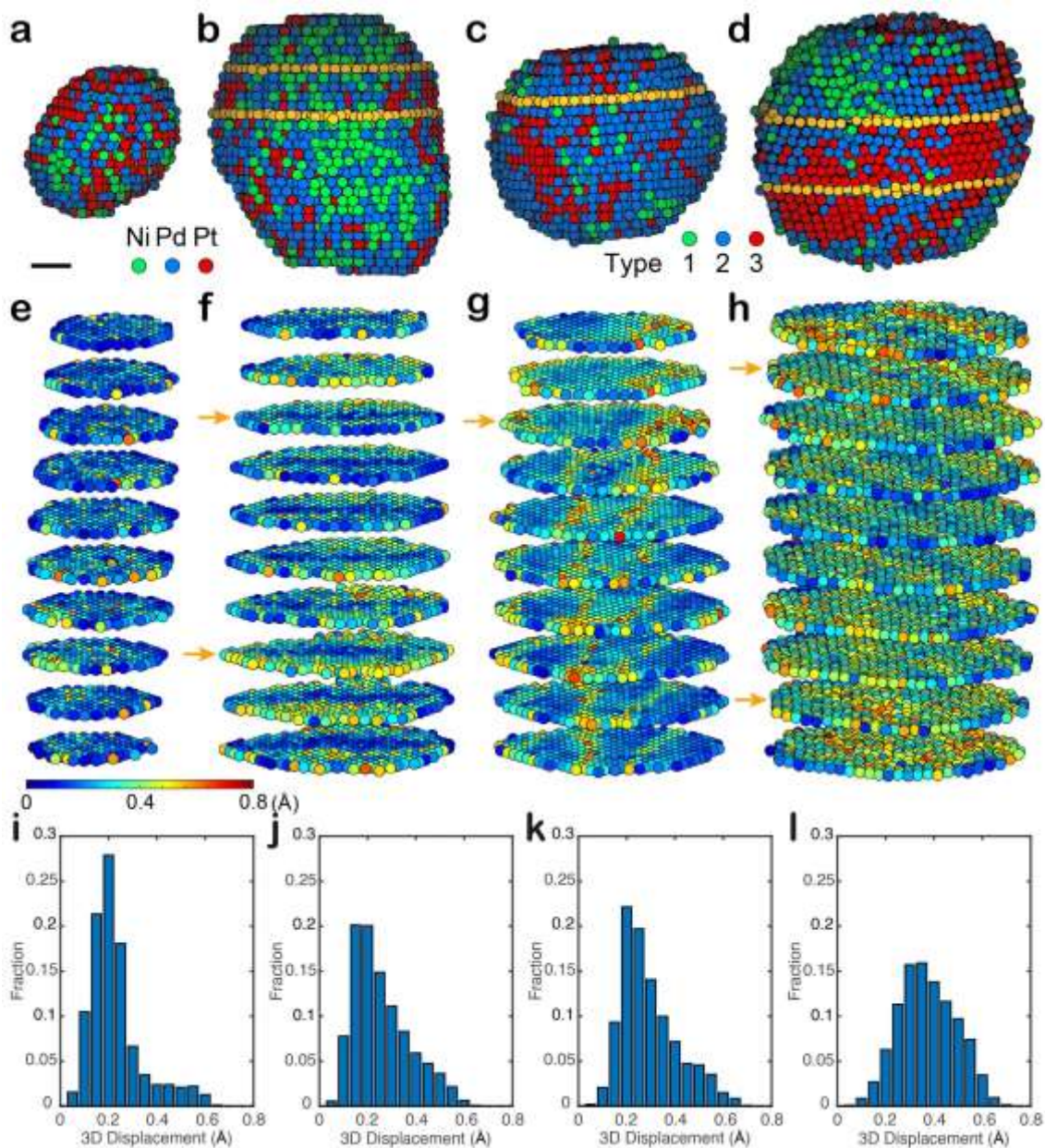
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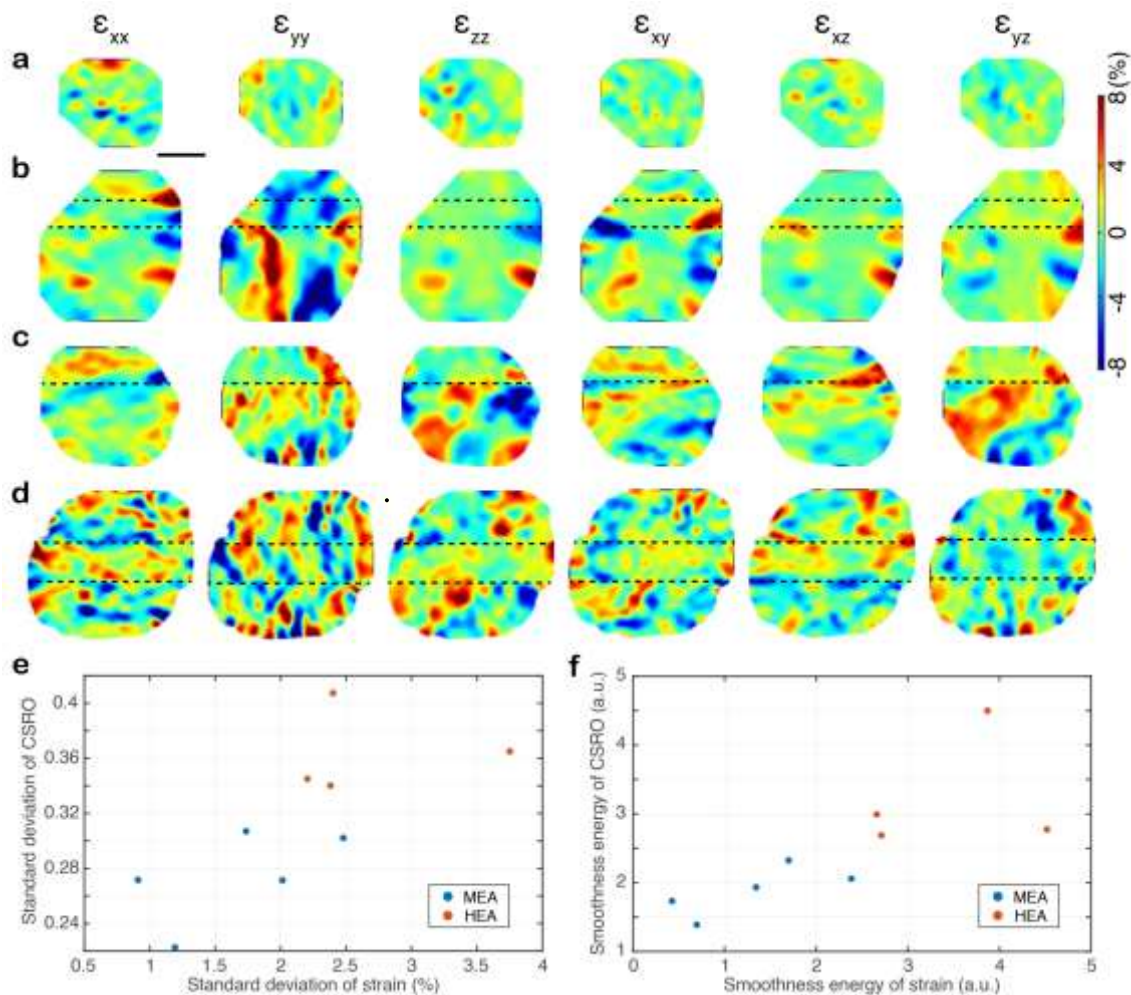
## Figures and Figure legends



**Fig. 1 | The 3D atomic structure and lattice distortion of M/HEA nanoparticles. a-d,** Experimental atomic models of two MEAs and two HEAs, named MEA-1 (a), MEA-2 (b), HEA-1 (c), and HEA-2 (d), respectively, in which the yellow circles represent the atoms along the twin boundaries. Scale bar, 1 nm. **e-h,** Atomic layer-by-layer visualization of the 3D displacements of MEA-1, MEA-2, HEA-1, and HEA-2, respectively, where the yellow arrows point to the twin boundaries. **i-l,** The distributions

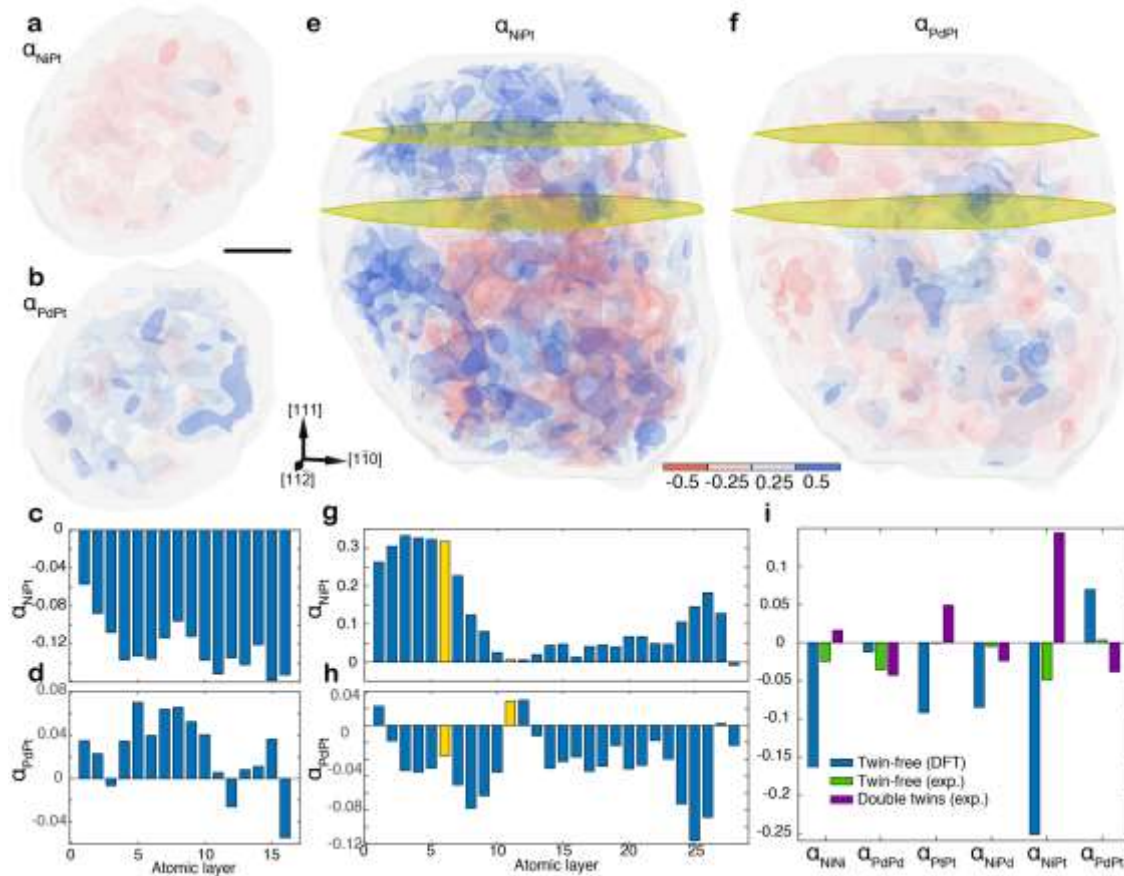


of the 3D atomic displacements of MEA-1, MEA-2, HEA-1, and HEA-2 with the mean and standard deviation as  $0.23\pm 0.11$  Å,  $0.26\pm 0.12$  Å,  $0.29\pm 0.12$  Å, and  $0.37\pm 0.12$  Å, respectively.



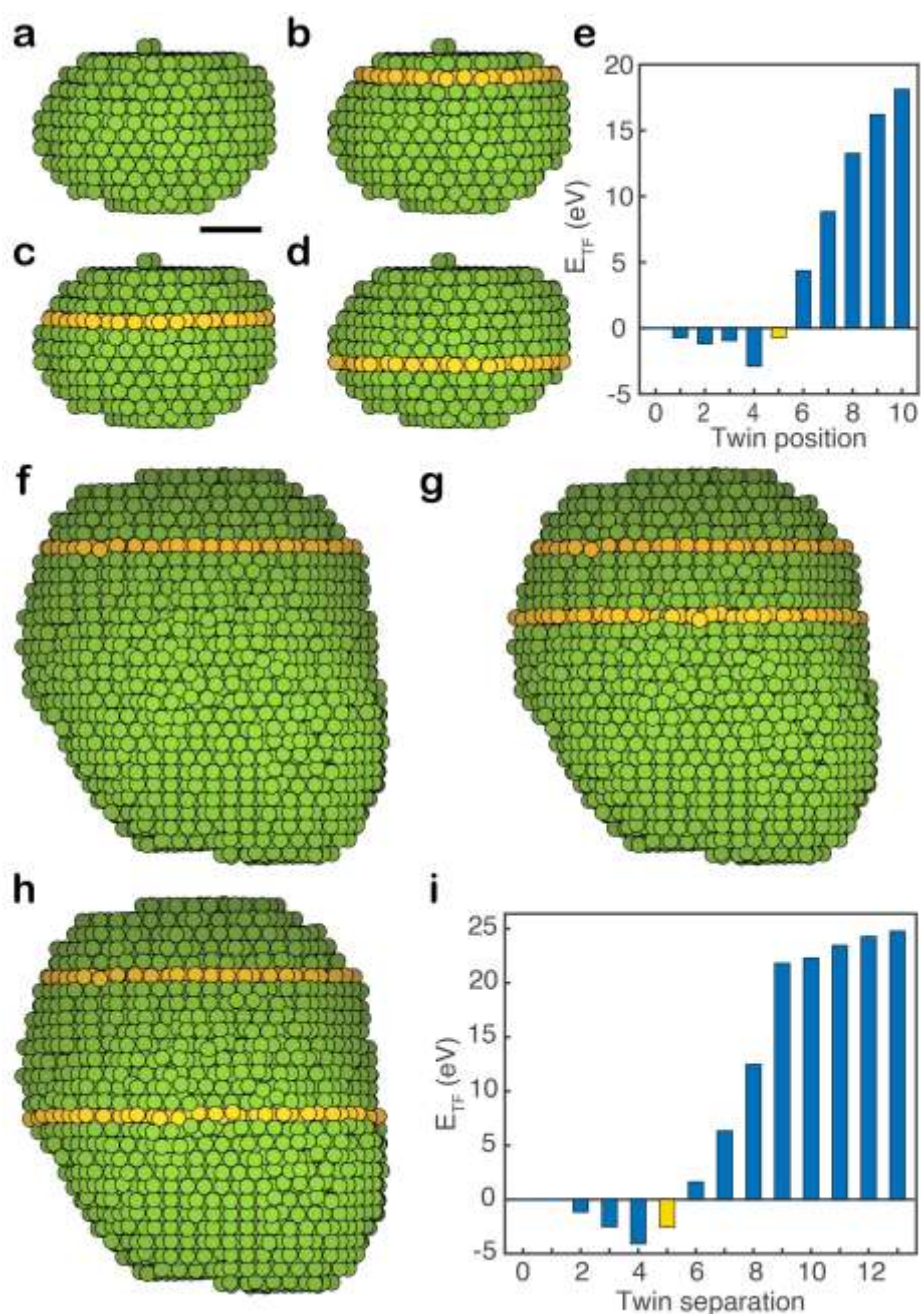
**Fig. 2 | 3D strain tensor measurements of the M/HEA nanoparticles. a-d,** Six components of the local strain tensor of a representative atomic layer in MEA-1 (a), MEA-2 (b), HEA-1 (c), and HEA-2 (d) along the  $[1\bar{1}0]$  direction, in which the dashed lines represent the twin boundaries. Scale bar, 2 nm. **e,** Standard deviation of strain and CSRO for five MEA and four HEA nanoparticles, which quantifies the average amount of deviation from the mean. MEA-5 is excluded in the calculation due to a grain boundary

(Extended Data Fig. 3c). **f**, Smoothness energy (i.e., local fluctuation) of strain and CSRO for the M/HEA nanoparticles, which represents the local fluctuations of strain and CSRO.



**Fig. 3 | Experimental observation of the correlation between CSRO and twinning in MEAs.** **a, b**, 3D distribution of  $\alpha_{NiPt}$  and  $\alpha_{PdPt}$  in the twin-free MEA-1. Scale bar, 1 nm. **c, d**, Histogram of the average  $\alpha_{NiPt}$  and  $\alpha_{PdPt}$  for each atomic layer along the [111] direction, indicating the tendency of the inter-mixing between Ni and Pt atoms and the separation between Pd and Pt atoms. **e, f**, 3D distribution of  $\alpha_{NiPt}$  and  $\alpha_{PdPt}$  in the double-twinned MEA-2 (the twins marked with yellow planes), exhibiting more heterogeneous CSRO than the twin-free MEA-1 (**a** and **b**). **g, h**, Histogram of the average  $\alpha_{NiPt}$  and  $\alpha_{PdPt}$  values for each atomic layer along the [111] direction (the yellow bars indicate the twin positions), which are the opposite of the  $\alpha_{NiPt}$  and  $\alpha_{PdPt}$  for the twin-

free MEA-1 (c, d). i, Histogram of the six average CSRO parameters of a DFT-calculated MEA, the twin-free MEA-1, and the double-twinned MEA-2.



**Fig. 4 | The twin formation energy ( $E_{TF}$ ) calculated from the experimental 3D atomic coordinates and species of the MEAs. a-d, Calculation of  $E_{TF}$  of a single-twinned MEA by moving the twin (yellow circles) from the 0<sup>th</sup> (top) to the 10<sup>th</sup> atomic layer along the [111] direction, with four representative atomic configurations showing the twin in layer**

0 (i.e., twin-free) (**a**), 3 (**b**), 5 (**c**) and 8 (**d**). Scale bar, 1 nm. **e**, Histogram of  $E_{TF}$  as a function of the twin position, in which  $E_{TF}$  changes from negative to positive from atomic layer 5 to 6. The experimentally determined twin is in layer 5 (yellow bar), which is next to the minimum  $E_{TF}$  in layer 4. **f-h**, Calculation of  $E_{TF}$  of the double-twinned MEA by fixing one twin (yellow circles in **f**) and moving the other twin along the [111] direction, where three representative atomic configurations show a twin separation by 0 (i.e., a single twin) (**f**), 5 (**g**), and 10 atomic layers (**h**). **i**, Histogram of  $E_{TF}$  as a function of the twin separation, in which  $E_{TF}$  changes from negative to positive between a twin separation of 5 and 6 layers. The experimentally determined twin separation is 5 atomic layers (yellow bar), which is next to the minimum  $E_{TF}$  with a twin separation of 4 layers.

## METHODS

**Sample synthesis.** The M/HEA samples were prepared by a carbothermal shock method<sup>50</sup>. Metal precursors in ethanol (0.05 M) were mixed into the desired multielement composition (Extended Data Table 1) and dipped onto carbon heater for Joule heating, where reduced graphene oxide was used as the substrate for dispersion and stabilization. After room temperature drying, metal precursors on the reduced graphene oxide were rapidly heated to a high temperature ( $\sim 2,000$  K for  $\sim 50$  ms) by Joule heating followed by rapid cooling ( $\sim 10^5$  K/s). This sample synthesis procedure enabled us to fully mix various elements into M/HEA nanoparticles<sup>14,50</sup>.

### AET data acquisition

The AET experiments of ten M/HEA nanoparticles were performed using the TEAM 0.5 microscope with the TEAM stage at the National Center for Electron Microscopy, operated in ADF-STEM mode at 200 or 300 kV (Extended Data Table 2). At each tilt angle, a nearby nanoparticle or a sample feature was used as a fiducial to align and focus the image, thereby reducing the unnecessary exposure of the region of interest to the electron beam<sup>58</sup>. To minimize the drift distortion and electron dose at each tilt angle, three to four sequential images were taken with a dwell time of 3  $\mu$ s. The total electron dose of each tilt series was optimized to be between  $4.9 \times 10^5$  and  $1.1 \times 10^6$   $e^-/\text{\AA}^2$  to reduce the beam damage (Extended Data Table 2).

For each sample, we confirmed the structural stability upon beam exposure by comparing images before, during, and after the acquisition of the tilt series.

### **Image pre-processing**

A multi-step image pre-processing protocol was performed on each AET dataset as outlined below.

i) Drift correction. To compensate for sample drift during data acquisition, we collected three to four images at each tilt angle, computed the cross-correlation coefficient between the images and identified the relative drift vectors by the maximum cross-correlation. We used a step size of 0.1 pixel as the drift in typical ADF-STEM images is smaller than one pixel. We applied the drift correction to each image along the slow scan direction, and corrected for it by interpolating the raw images with drift-corrected pixel positions. The drift-corrected images were then averaged to form a single image at each tilt angle.

ii) Image denoising. To remove the Poisson and Gaussian noise from the drift-corrected images, we used the block-matching and 3D filtering (BM3D) algorithm<sup>59</sup>, which has been successfully used to denoise experimental AET datasets<sup>60,61</sup>. To optimize the BM3D denoising parameters for each dataset, we first estimated the level of each noise type (Poisson and Gaussian) in the image stack. Then, these noise levels were added to several simulated ADF-STEM images of model nanoparticles with similar size and elemental distribution as the experimental data. The denoising parameters leading to the maximum cross-correlation between the simulated images and the experimental images were applied to the experimental data.

iii) Background subtraction. For each denoised image, we used Otsu thresholding in MATLAB to generate a mask of the nanoparticle, which is slightly larger than its boundary. Using the background outside the masked region, we performed Laplacian interpolation to estimate the background level inside the masked zone and subtracted it from the denoised image<sup>60</sup>.

iv) Image alignment. The background subtracted images were aligned by the common line method along the tilt axis and the centre of mass method perpendicular to the tilt axis, which are capable to align experimental tilt series with a sub-pixel accuracy<sup>58,62</sup>.

### **Tomographic reconstruction**

Each pre-processed dataset was reconstructed by the REal Space Iterative REconstruction (RESIRE) algorithm<sup>63</sup>. RESIRE iteratively minimizes the difference between the experimental and calculated images of a sample using gradient descent. By incorporating angular refinement and spatial alignment, RESIRE is

superior to other tomographic reconstruction algorithms<sup>63</sup>. A typical RESIRE reconstruction converges after about 200 iterations. Following an initial reconstruction and an iterative process of angular refinement and spatial alignment, the background of the new set of images was re-evaluated and re-subtracted. The resulting images, after undergoing further angular refinement and spatial realignment, were used to generate the final 3D reconstruction by RESIRE.

### **Determining the 3D atomic coordinates and species/types**

From the final 3D reconstructions, we determined the 3D atomic coordinates and species/types using the following steps.

- i) Each reconstruction underwent spline interpolation to produce a finer grid using an oversampling ratio of 3, from which all the local maxima were identified. Using a polynomial fitting method<sup>60</sup>, we identified the positions of all the peaks (i.e., potential atoms) from a  $0.8 \text{ \AA} \times 0.8 \text{ \AA} \times 0.8 \text{ \AA}$  volume around each peak. An initial list of the potential atoms was obtained by searching through all the fit peak positions with the constraint that the minimum distance between neighbouring peaks is  $2 \text{ \AA}$ , given that all the interatomic distances in our samples are larger than this value.
- ii) To remove the non-atoms from this list, we performed K-means clustering of the integrated intensity of the local volume around each potential atom position<sup>64,65</sup>.
- iii) By overlaying the 3D atomic positions with the 3D reconstructions, we manually checked the atomic positions and corrected a small fraction ( $< 1\%$ ) of unidentified or misidentified atoms. Such manual correction is routine for atom tracing and refinement in macromolecular crystallography<sup>66</sup>.
- iv) The distribution of the integrated intensity of each atom is affected by several factors, including the atomic number, the electron probe size, the inner and outer angles of the detector, sample drift, angular errors, the missing wedge, and noise. To accurately classify the Ni, Pd and Pt atoms in MEAs and the three types of atoms in HEAs, we used K-means clustering<sup>64,65</sup>, which has been demonstrated as a robust method to obtain consistent results from different independent runs<sup>60,67</sup>.
- v) We performed local reclassification of all the atomic species/types. Each atom was defined to be at the centre of a  $10 \text{ \AA}$ -radius sphere. The average intensity distribution of the three atomic species/types was computed within this sphere. We then computed the  $L_2$  norm of the intensity distribution between the central atom and the average Ni, Pd and Pt or type-1, -2, and -3 atoms. The atom was assigned to the species/type

with the smallest  $L_2$  norm. After repeating this step for all the atoms, an initial experimental 3D atomic model of the sample was obtained.

vi) The 3D atomic coordinates of the initial model were refined by minimizing the error between the experimental and computed images using gradient descent as described elsewhere<sup>65</sup>. Convergence of the iterative process was verified by monitoring the  $L_2$  norm error.

### Local lattice distortion and strain tensor measurements

The local lattice distortion is defined as the deviation of the experimental atomic positions in the M/HEA nanoparticles from those in a perfect fcc lattice. For each atom, its local lattice distortion ( $\Delta d_i$ ) was calculated by,

$$\Delta d_i = \frac{1}{N} \sum_j |\mathbf{r}_{ji} - \mathbf{r}_{ji}^0| \quad (1)$$

where  $N$  is the number of the nearest neighbours of atom  $i$ ,  $\mathbf{r}_{ji}$  is the experimental 3D coordinates of the  $j^{\text{th}}$  nearest-neighbour atom, and  $\mathbf{r}_{ji}^0$  is the perfect fcc lattice structure that is aligned to  $\mathbf{r}_{ji}$  based on the three Euler angles determined by a breadth-first search algorithm<sup>60</sup>. A cut-off of a quarter of the nearest-neighbour bond length was applied to eliminate the contribution from some surface atoms with a large deviation. The strain tensor measurements follow a procedure described elsewhere<sup>51</sup>. Briefly, the atomic displacements were calculated from the measured atomic positions and a perfect fcc lattice structure. The atomic displacements were convolved with a 2-Å-wide 3D Gaussian kernel to increase the signal-to-noise ratio and precision, but reduce the 3D resolution to  $\sim 4$  Å. The strain tensor was obtained by numerical differentiation of the 3D atomic displacements, where a mask was applied to remove the edge effect<sup>51</sup>.

### The CSRO parameters

After identifying the nearest neighbours of each atom, we computed the CSRO parameters ( $\alpha_{ij}$ ) between the central atom ( $i$ ) and its nearest neighbours ( $j$ ) by<sup>55,30</sup>

$$\alpha_{ij} = \frac{p_{ij} - c_j}{\delta_{ij} - c_j} \quad (2)$$

where  $p_{ij}$  denotes the average probability that a  $j$ -type atom is the nearest neighbour to an  $i$ -type atom,  $c_j$  signifies the average concentration of  $j$ -type atoms, and  $\delta_{ij}$  is the Kronecker delta function. To eliminate the boundary effect, we removed the surface atoms of each M/HEA nanoparticle from the calculation of the CSRO parameters. Following this procedure, we computed the six CSRO parameters, which are

bounded between -1 and +1, for every atom in the M/HEA nanoparticles. To obtain a local CSRO distribution such as those in Fig. 3, Extended Data Figs. 5, 6, 8 and 9, we interpolated the CSRO parameters onto 3D grids and convolved them with a Gaussian kernel. The width of the Gaussian kernel was determined by the first valley of the pair distribution function of the nanoparticle, corresponding to the first nearest-neighbour shell distance.

### The twin order parameter

From the experimental 3D atomic coordinates, we fit the nearest neighbour atoms around each atom to a perfect fcc and hexagonal close-packed (hcp) lattice by the breadth-first search algorithm<sup>60</sup>. If a nearest neighbour atom has a deviation larger than a cut-off of 0.75 Å, we set its deviation to be the cut-off value. This step was to eliminate the effect of some surface atoms with a large deviation. The twin order parameter ( $\eta$ ) was calculated by<sup>68</sup>

$$\eta = \frac{d_{\text{fcc}} - d_{\text{hcp}}}{d_{\text{max}}} \quad (3)$$

Where  $\eta = 1$  and  $-1$  represent a hcp and fcc structure, respectively,  $d_{\text{fcc}}$  and  $d_{\text{hcp}}$  are the sum of the deviation of the nearest-neighbour atoms from a perfect fcc and hcp lattice, respectively, and  $d_{\text{max}}$  is the maximum deviation. In this study, we also calculated  $\eta$  using different cut-off values and obtained consistent results. With  $\eta$ , we can identify an intrinsic, extrinsic stacking fault or a twin boundary by calculating the separation between two hcp layers: 0 for an intrinsic stacking fault, 1 for an extrinsic stacking fault, and  $\geq 2$  for a twin boundary. In our experimental data, the separation between two hcp layers is  $\geq 2$ , indicating that these are twin boundaries instead of intrinsic or extrinsic stacking faults.

### Correlation between strain tensor and CSRO

To quantify the local heterogeneity of the strain tensor and CSRO, we calculated the standard deviation and the smoothness energy<sup>69</sup>. The standard deviation ( $\sigma$ ) of strain or CSRO quantifies the average amount of deviation from the mean, defined as

$$\sigma = \sqrt{\frac{1}{6} \sum_{\beta} \sigma_{\beta}^2} \quad (4)$$

where  $\sigma_{\beta}$  is the standard deviation of each component of strain or CSRO. The smoothness energy ( $S_E$ ) is defined as<sup>69</sup>

$$S_E = \frac{1}{6N} \sum_{n,i,\beta} (\Delta_i f_{\beta}^n)^2 \quad (5)$$



where  $f_{\beta}^n$  is component  $\beta$  of the strain tensor or CSRO,  $n$  is the  $n^{\text{th}}$  voxel of a volume containing  $N$  voxels,  $\Delta_i$  is the  $i^{\text{th}}$  component of Laplacian with  $i$  equal to  $x$ ,  $y$  or  $z$ .  $S_E$  averages the square of the second derivative of the local strain tensor or CSRO and quantifies the local fluctuation in each dataset. Larger  $S_E$  means larger local fluctuation (i.e., more heterogeneous). Figure 2e and f show the standard deviation and the smoothness energy of the strain tensor and CSRO for the M/HEA nanoparticles, where a mask was applied to remove the edge effect. This quantitative analysis shows that i) the HEAs have more heterogeneous strain and CSRO than the MEAs and ii) strain is correlated with CSRO in the M/HEAs.

### DFT calculations

DFT-based lattice Monte Carlo (MC) approach<sup>28</sup> was utilized to reveal the characteristic CSRO for the NiPdPt MEA and NiCoRuRhPdAgIrPt HEA. The 256-atom configurations were generated as a special quasi-random structure<sup>70</sup>. The MC simulations were run for 3,000 steps, corresponding to about 12 swap trials per atom, at an MC temperature of 600 K. Energy calculations were performed using the Vienna *ab initio* simulation package<sup>71,72</sup>. A plane wave cut-off energy was chosen at 380 eV, and the Brillouin zone integrations were performed using Monkhorst–Pack meshes<sup>72</sup> with a single k-point ( $\Gamma$ ). It adopted projector augmented wave potentials<sup>73</sup> with the Perdew–Burke–Ernzerhof generalized-gradient approximation<sup>74</sup> for the exchange–correlation functional. From the DFT results, the lattice distortion parameter<sup>23</sup> was calculated as 0.089 Å and 0.11 Å for the NiPtPd MEA and NiCoRuRhPdAgIrPt HEA, respectively, which confirm our experimental observations (Fig. 1i-l).

### The twin formation energy of the MEAs

We calculated the twin-formation energy of the NiPdPt MEAs from the experimentally measured 3D atomic coordinates using the LAMMPS software package<sup>75</sup> with the empirical EAM potential<sup>76</sup>. The experimental 3D atomic coordinates of the MEA nanoparticles were obtained from the AET experiments. To eliminate the boundary effect, the surface atoms of each MEA nanoparticle were not used in the MD calculations. For the supercell, the shrink-wrapped non-periodic boundary conditions were imposed along all three directions. As illustrated in Fig. 4 and Extended Data Fig. 7, the migration of the twin boundary was carried out by gradually shifting the close-packed (111) atomic planes along the  $\langle 112 \rangle$  direction by the Burgers vector of the Shockley partial  $b_s = \frac{a}{6} \langle 11\bar{2} \rangle$ . For the twin boundary at different position, the twin formation energy was calculated by the energy difference between the twinned and twin-free configurations after energy minimization.

### Data availability

All the raw and processed experimental data will be immediately posted on an open-access repository (<https://github.com>) after the paper is published online.

### Code availability

All the MATLAB source codes for the 3D reconstruction, atom tracing, and data analysis of this work will be immediately posted on an open-access repository (<https://github.com>) after the paper is published online.

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**Author contributions** J.M. directed the project; Y. Yao and L.H. synthesized the samples; J.Z., P.E. and J.M. discussed and/or carried out the AET experiments; Y. Yang, Y. Yuan, S. M. and J.M. performed image reconstruction, atom tracing and classification for the AET experiments. S.M., Y. Yang, Y. Yuan, L.Y., F.Z., Y.L., J.D. and J.M. analysed the data and interpreted the results; J.D. performed the DFT calculations and MD simulations with input from S.M., Y. Yang, Y. Yuan and J.M.; J.M., S.M. and Y. Yang wrote the manuscript. All authors commented on the manuscript.

**Competing interests** The authors declare no competing interests.

**Addition information**

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