

Capturing High-Entropy Alloy Particle Growth by Liquid-Phase Transmission Electron Microscopy

Jiayue Sun¹, Asher Leff^{2,3} and Taylor J. Woehl^{4*}

¹ Department of Chemistry and Biochemistry, University of Maryland, College Park, MD, United States.

² Sensors and Electron Devices Directorate, Combat Capabilities Development Command, United States Army Research Laboratory, Adelphi, MD, United States.

³ General Technical Services, LLC, Wall Township, NJ, United States.

⁴ Department of Chemical and Biomolecular Engineering, University of Maryland, College Park, MD, United States.

* Corresponding author: tjwoehl@umd.edu

The emergence of liquid-phase transmission electron microscopy (LP-TEM) has brought researchers into an era where the chemical reactions can be observed dynamically in the solution phase with nanoscale spatial resolution. The application of the LP-TEM has overcome the limitations of the conventional dry-state TEM and enabled *in-situ* studies of biomolecule assemblies [1], polymer assemblies [2], and formation and growth of nanoparticles in liquid solution [3].

High-entropy alloy (HEA) particles have exciting potential as new functional materials for chemical catalysis and energy storage. Current methods to form HEA nanoparticles utilize the high-temperature carbothermal shock solid-state synthesis method [4] or electrodeposition of precursor droplet synthesis method [5], with relatively few facile solution-phase synthesis reactions demonstrated. One reason for the lack of colloidal synthesis methods for HEA nanoparticles is that the formation mechanisms of HEA nanoparticles remain unclear due to their rapid formation within seconds. Prior work has suggested solution-phase nanoparticles form by classical nucleation and growth mechanisms. Here we utilize LP-TEM and systematic flask synthesis to demonstrate that the formation of HEA nanoparticles occurs by ligand desorption mediated aggregation of metastable intermediate alloy clusters.

Herein, HEA nanoparticles containing Au, Ag, Cu, Pt, and Pd were formed in water by the chemical co-reduction of metal salt precursors with sodium borohydride in the presence of poly (ethylene glycol) methyl ether thiol (PEGSH) ligands at room temperature. PEGSH is the surface protecting ligand and it plays a critical role in the HEA nanoparticle synthesis to stabilize the nanoclusters and aggregation of metal atoms. Sodium borohydride, apart from being the reducing agent, has been found to desorb and replace thiol ligands from the nanoparticle surface [6], which induces nanoparticle or nanocluster aggregation. High resolution TEM imaging showed that intermediate nanoclusters appeared in the reaction solution after synthesis of HEA nanoparticles (Figure 1a). A competition between PEGSH binding, which stabilizes intermediates, and borohydride ions displacing PEGSH, which drives cluster aggregation, mediated the formation of HEA nanoparticles. This competition between PEGSH binding and stabilizing nanoclusters and borohydride ions destabilizing nanoclusters is evidenced by an increase in particle size and aggregation with increasing sodium borohydride concentration relative to ligand concentration (Figure 1b-h).

LP-TEM synthesis of HEA nanoparticles using solvated electrons as the reducing agent manifested similar reaction conditions to sodium borohydride reduction. HEA nanoparticles were observed to grow by self-growth and aggregation in time lapsed movies taken with LP-TEM (Figure 2a-c). High-

resolution scanning TEM (HRSTEM) and energy-dispersive x-ray spectroscopy (EDS) showed the 1-5 nm HEA nanoparticles formed by LP-TEM contained all 5 elements (Figure 2d). Overall, our results are consistent with a growth mechanism involving sodium borohydride-induced ligand desorption and aggregation of intermediate alloy clusters [7].

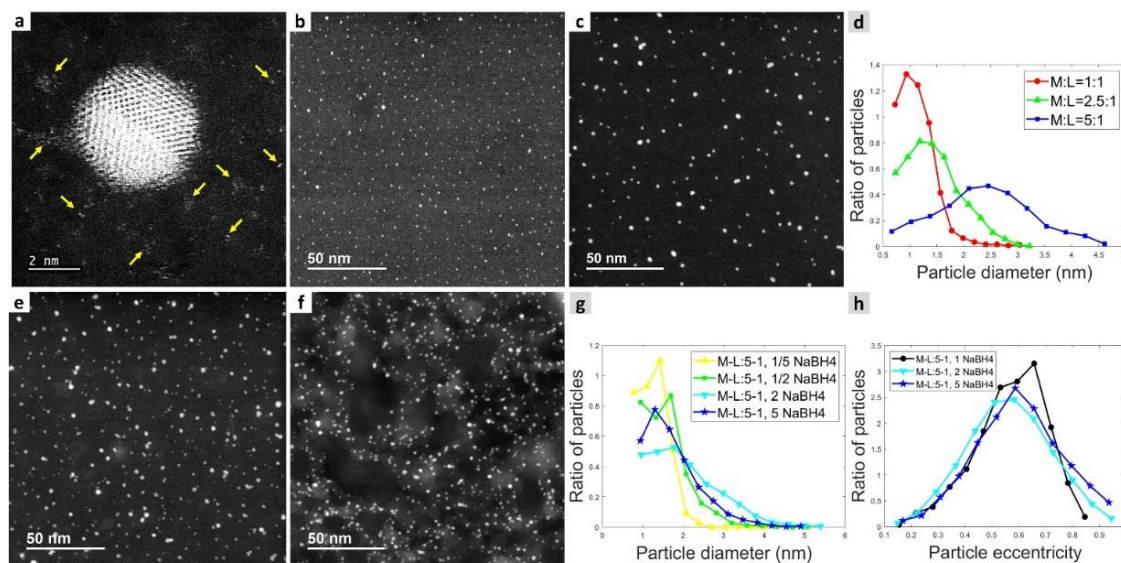


Figure 1. (a) HAADF-STEM image of a HEA particle surrounded by sub-nanometer clusters (yellow arrows). (b, c) HAADF-STEM images of HEA particles with metal:ligand ratio 1:1 and 5:1. (d) Particle size distributions of HEA particles with metal:ligand ratios of 1:1, 2.5:1, and 5:1. (e, f) HAADF-STEM images of HEA particles (metal:ligand ratio 5:1) with NaBH₄ amount of 2 times and 5 times. (g) Particle size distribution of HEA particles with different NaBH₄ amount. (h) Particle eccentricities with NaBH₄ of 1 time, 2 times, and 5 times.

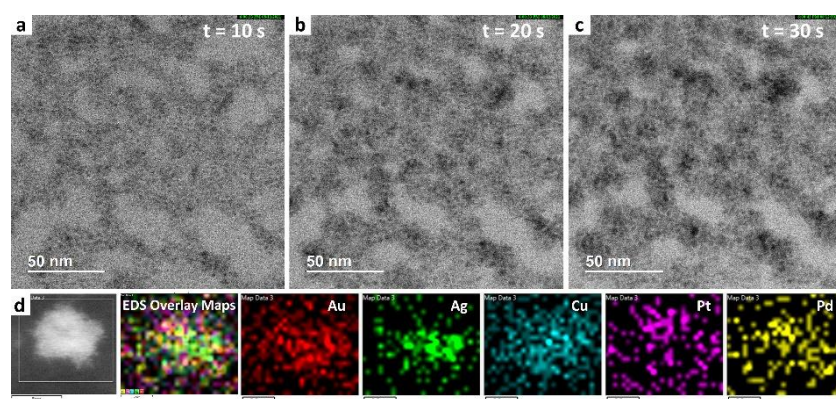


Figure 2. (a-c) Time-lapses images of HEA growth during LP-TEM at the magnification of 1,500,000 and beam current of 23 pA (dose rate = 212 MGy/s). (d) HAADF-STEM image (left) and EDS mapping of a single HEA particle formed during LP-TEM imaging.

References:

- [1] Touve, M. A. et al., *Nat. Commun.* **10** (2019), p. 1-12. doi:10.1038/s41467-019-12660-1
- [2] Korpanty, J. et al., *Nat. Commun.* **12** (2021), p. 1-8. doi:10.1038/s41467-021-26773-z
- [3] Wang, M. et al., *ACS Nano* **15** (2021), p. 2578-2588. doi:10.1021/acsnano.0c07131
- [4] Yao, Y. G. et al., *Science* **359** (2018), p. 1489-1494. doi:10.1126/science.aan5412
- [5] Glasscott, M. W. et al., *Nat. Commun.* **10** (2019), p. 1-8. doi:10.1038/s41467-019-10303-z
- [6] Ansar, S. M. et al., *Nano Lett.* **13** (2013), p. 1226-1229. doi:10.1021/nl304703w
- [7] We acknowledge funding support from the National Science Foundation under grant No. 2045258.