Electronic Supplementary Material (ESI) for Nanoscale.

Supplementary Information

Visualizing Formation of High Entropy Alloy Nanoparticles with Liquid Phase Transmission Electron Microscopy

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2. **Supplementary Video 2:** BF-STEM movie of HEA nanoparticle formation with a metal:ligand ratio of 1:2. Magnification = 1,500,000 ×, beam current = 23 pA, and dose rate = 212 MGy/s. Frames from this movie were used to generate Fig. 4b.

3. **Supplementary Video 3:** BF-STEM movie of preformed HEA nanoparticle aggregation with a metal:ligand ratio of 1:1 and no metal ions present. Frames from this movie were used to generate Figs. 6d.
   Magnification = 1,500,000 ×, beam current = 74 pA, and dose rate = 682 MGy/s.

4. **Supplementary Video 4:** False-colored, cropped, contrast-enhanced version of Supplementary Video 3. The movie was processed in ImageJ (FIJI version). The initial movie was first processed by a running average filter (Walking Average in the Multi Kymograph tool) to decrease noise, with the frame average taken over 10 frames. The image contrast was then inverted and a false color map was applied (Fire map in ImageJ) and the contrast was maximized to make small nanoparticles visible. Frames from this movie were used to generate Fig. 6d.

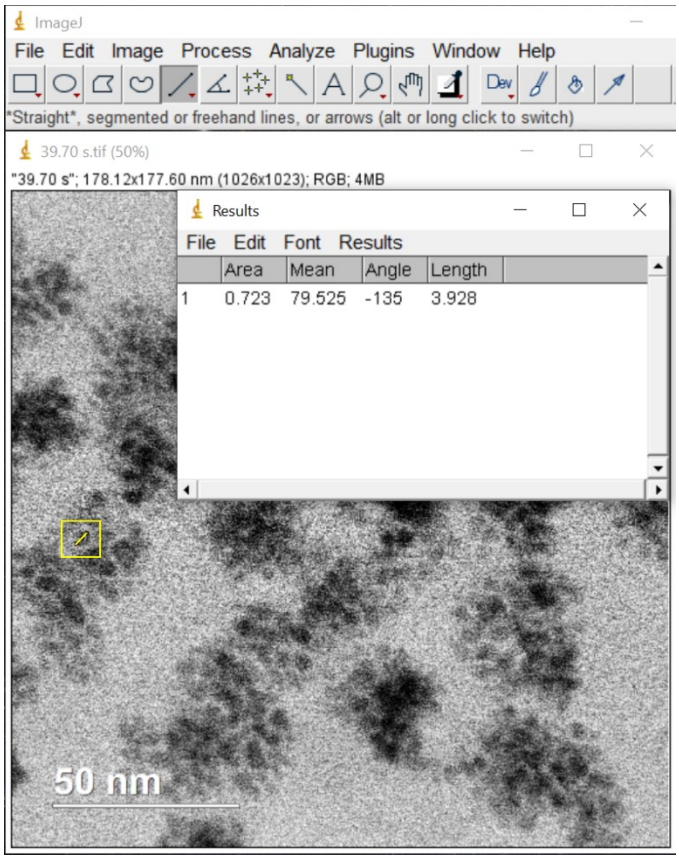

Fig. S1 ImageJ measurement of particle diameter by manually drawing a line on the selected particle (particle shown in the yellow box). This method was used to measure the nanoparticle growth kinetics shown in Fig. 4c and Fig. S7.

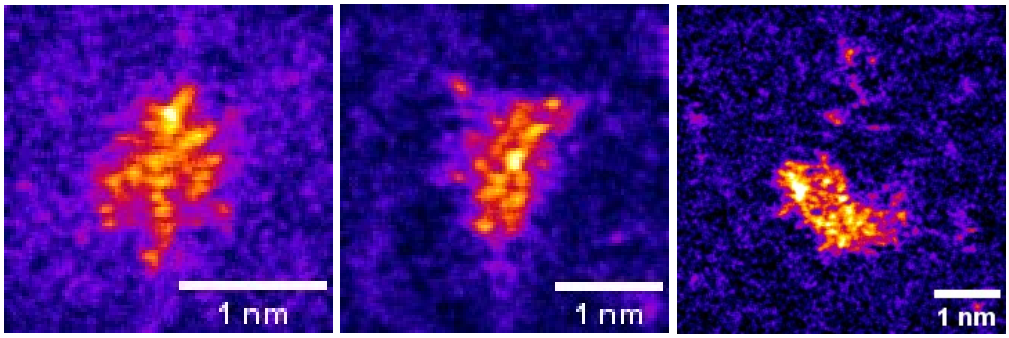

Fig. S2. Dry state HAADF-STEM images showing the atomic structure of sub-nanometer clusters in an HEA nanoparticle reaction solution. The images have been cropped, false colored, and contrast enhanced. Atoms appear as orange or yellow contrast.

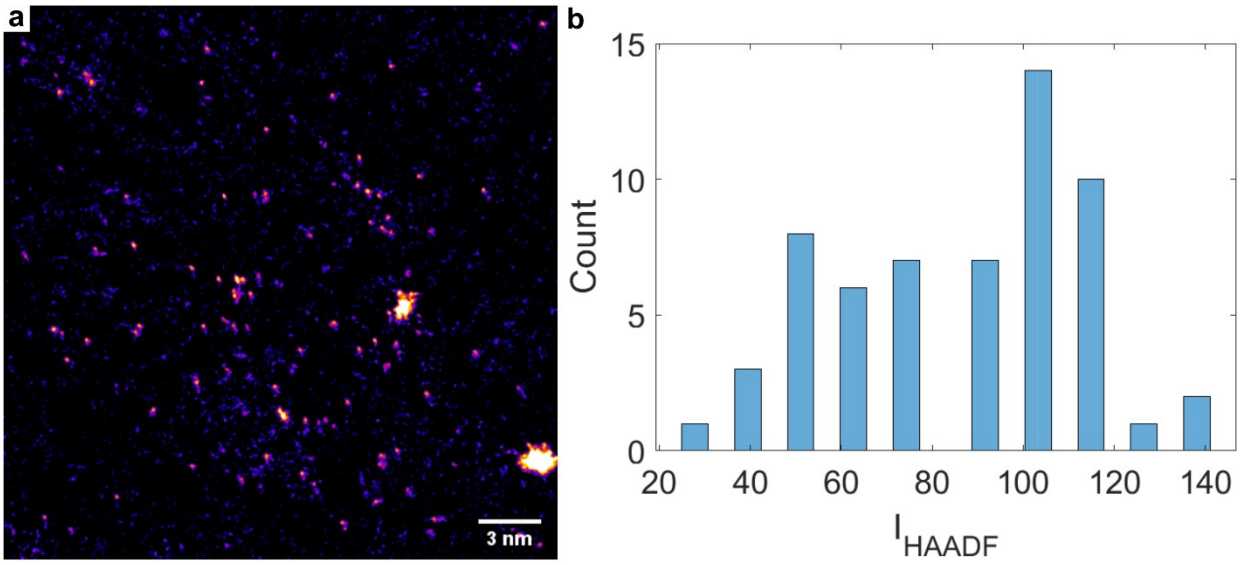

Fig. S3. Single-atom intensity analysis of a HAADF-STEM image. (a) False colored HAADF-STEM image of a 1:1 metal:ligand ratio sample of HEAs showing single atoms and small clusters. Atoms and clusters appear in purple, pink, and orange. (b) Histogram of atom intensities in (a), excluding the two large clusters on the right of the image. The difference in I_{HAADF} between the lowest and highest intensity atoms in the image is about 7 times, which corresponds to the expected image intensity ratio between copper (Z_{Cu} = 29) and platinum (Z_{Pt} = 78) atoms, $\left(\frac{Z_{pt}}{Z_{Cu}}\right)^2 = 7.3$.

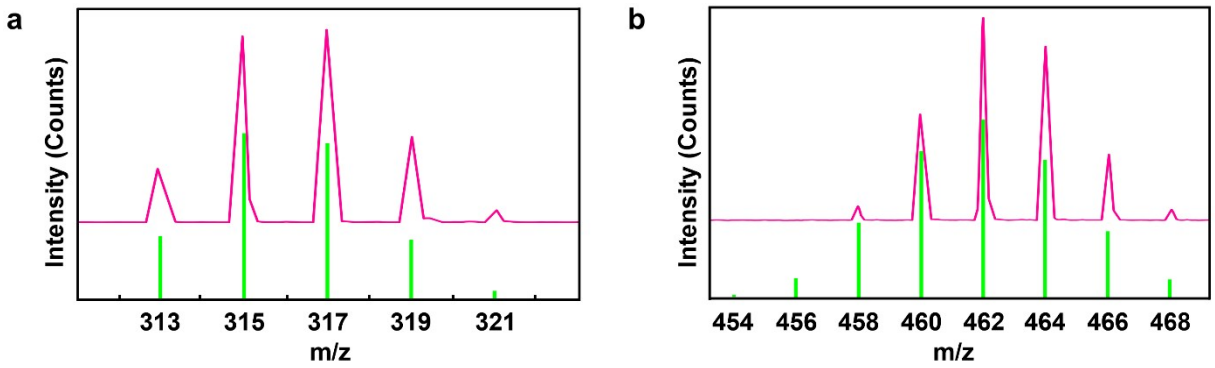

Fig. S4. Experimental MALDI-TOF MS of metal clusters (pink) and simulations (green). (a) $[Ag_2CuClH]^-$ and (b) $[PdAg_2Cu_2BH]^-$. The green simulated spectra are generated using a freely available online tool by Scientific Instrument Services (SIS).

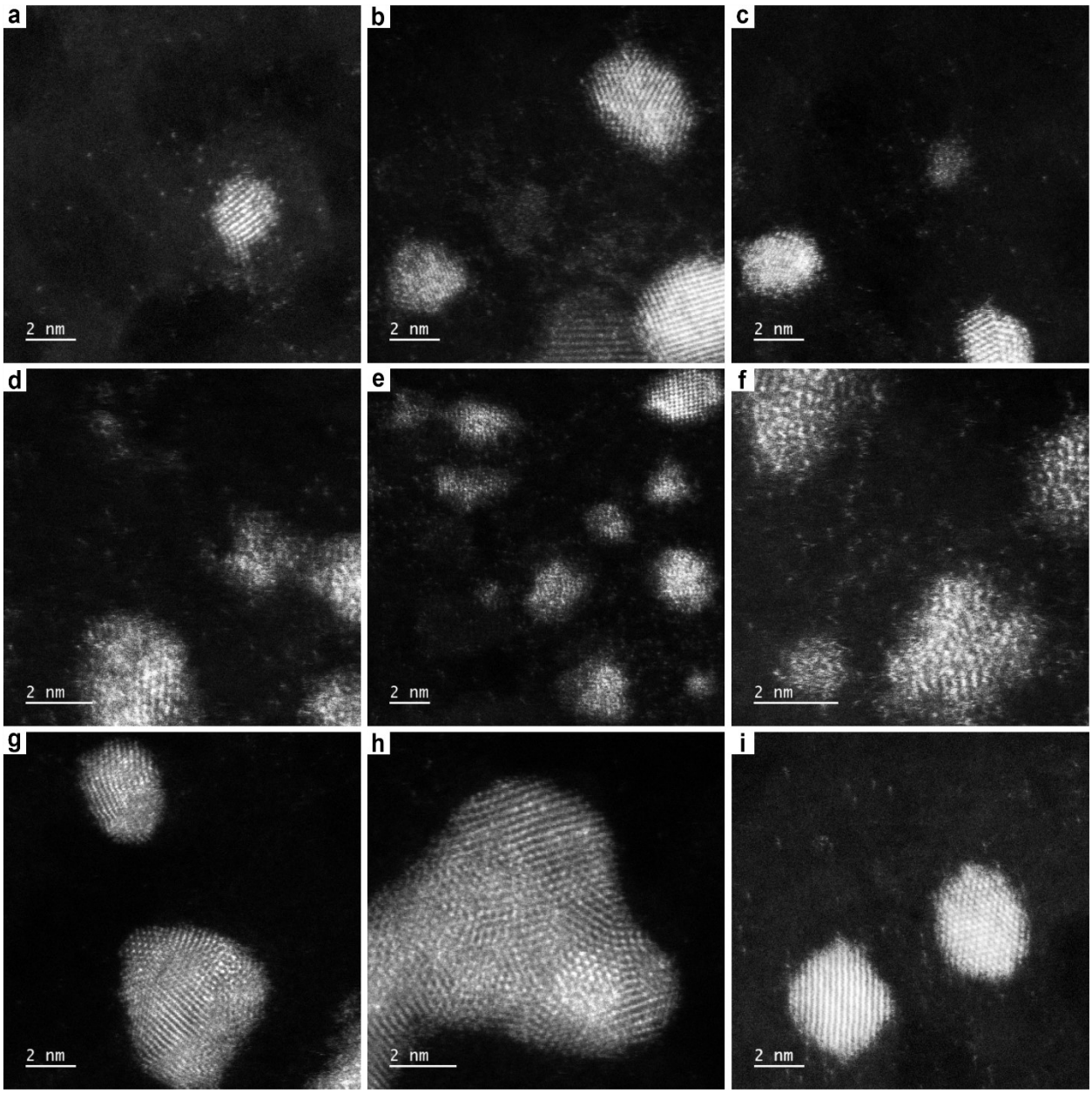

Fig. S5. HAADF-STEM images showing different types of nanoparticles formed at different metal:ligand ratios. HAADF-STEM images of HEA reaction solutions with metal:ligand ratios of (a-c) 1:1, (d-f) 2.5:1, and (g-i) 5:1.

Table S1. EDS quantification of HEA nanoparticle composition.

	Cu Atomic %	Pd Atomic %	Ag Atomic %	Pt Atomic %	Au Atomic %
Spectrum 1	22.45	30.9	12.85	2.2	31.6
Spectrum 2	21.81	28.21	15.9	1.45	32.64
Spectrum 3	18.54	42.69	15.29	2.73	20.75
Spectrum 4	11.57	72.89	11.39	0.64	3.51
Spectrum 5	26.62	23.83	4.85	16.72	27.97

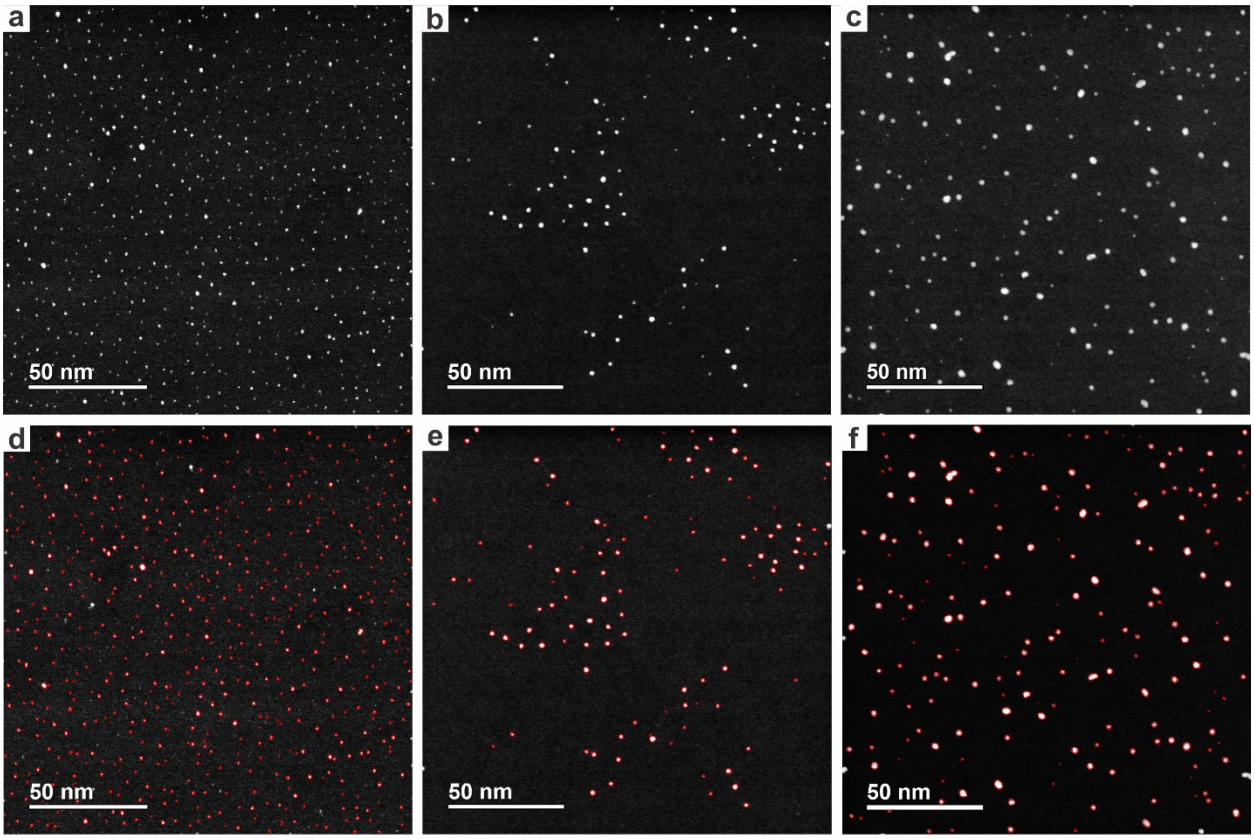

Fig. S6. Exemplary STEM images used to generate PSDs for particles synthesized by different metal:ligand ratios (a-c) and particle outlines drawn by an automated MATLAB script for particle sizing (d-e). The metal:ligand ratios are (a,d) 1:1, (b,e) 2.5:1, and (c,f) 5:1.

Table S2. Aqueous electron concentrations for each LPTEM dose rate used in this work.

	Dose Rate (MGy/s)	**e_{aq}^- concentration (µM)**
Fig. 4a	362	5.77
Fig. 4b	212	4.39
Fig. 5a	212	4.39
Fig. 5b	205	4.32

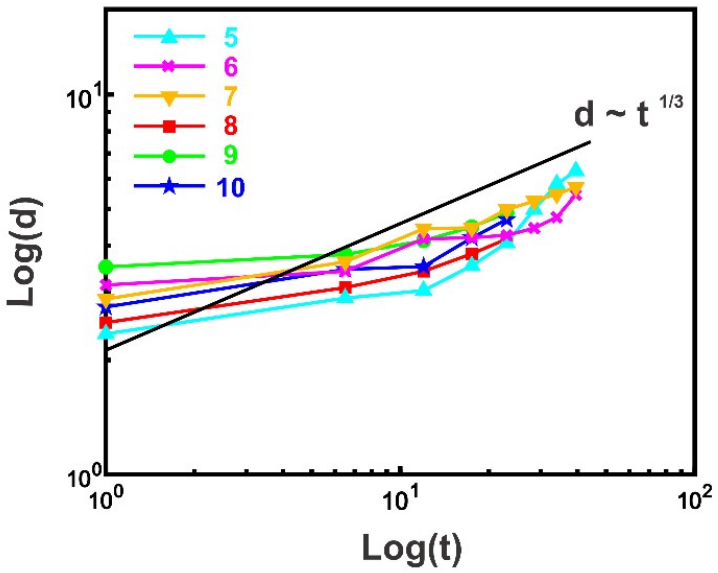

Fig. S7. Nanoparticle diameter (d) as a function of time (t) for 6 particles shown on a double logarithmic plot. The particles are denoted by numbers 5 to 10 in **Fig. 4a** and **Fig. 4b**. The particle diameter shows a $t^{1/3}$ dependence at times > 10 s.

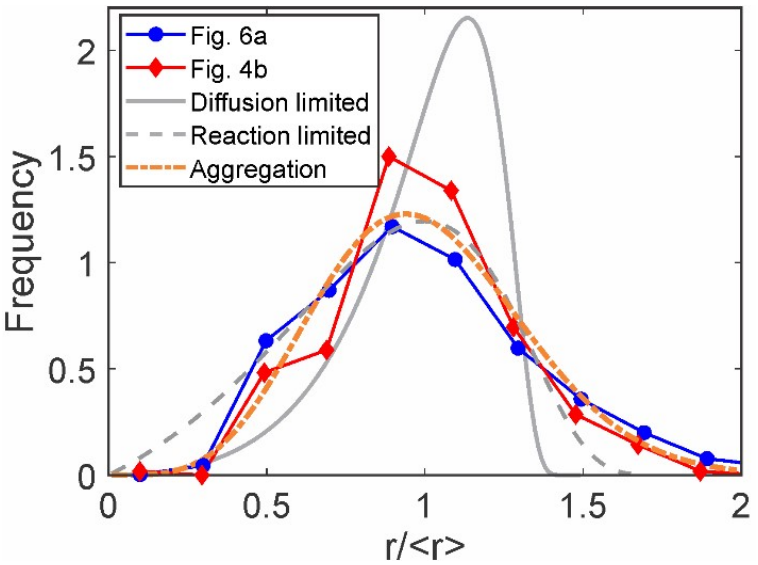

Figure S8. PSDs of HEA nanoparticles generated by LPTEM (blue circles) and $NaBH_4$ reduction (red diamonds) compared to theoretical PSDs calculated by the LSW model (diffusion limited growth (gray solid line) and reaction limited growth (dashed gray line)) and the Smoluchowski model (Aggregation, dashed orange line).[1-3] The x-axis is the reduced nanoparticle radius, which is the particle radius (r) divided by the average particle radius, <r>. The nanoparticles from **Fig. 6a** were synthesized with 6.96 mM $NaBH_4$. The final frame of Supplementary Video 2 was used to generate the PSD from **Fig. 4b**.

Table S3. Sum of squared errors (SSE) between experimental data and theoretical PSDs.

	Diffusion limited	**Reaction limited**	**Aggregation**
Fig. 4b	29.5	31.0	0.256
Fig. 6a	27.2	28.9	0.086

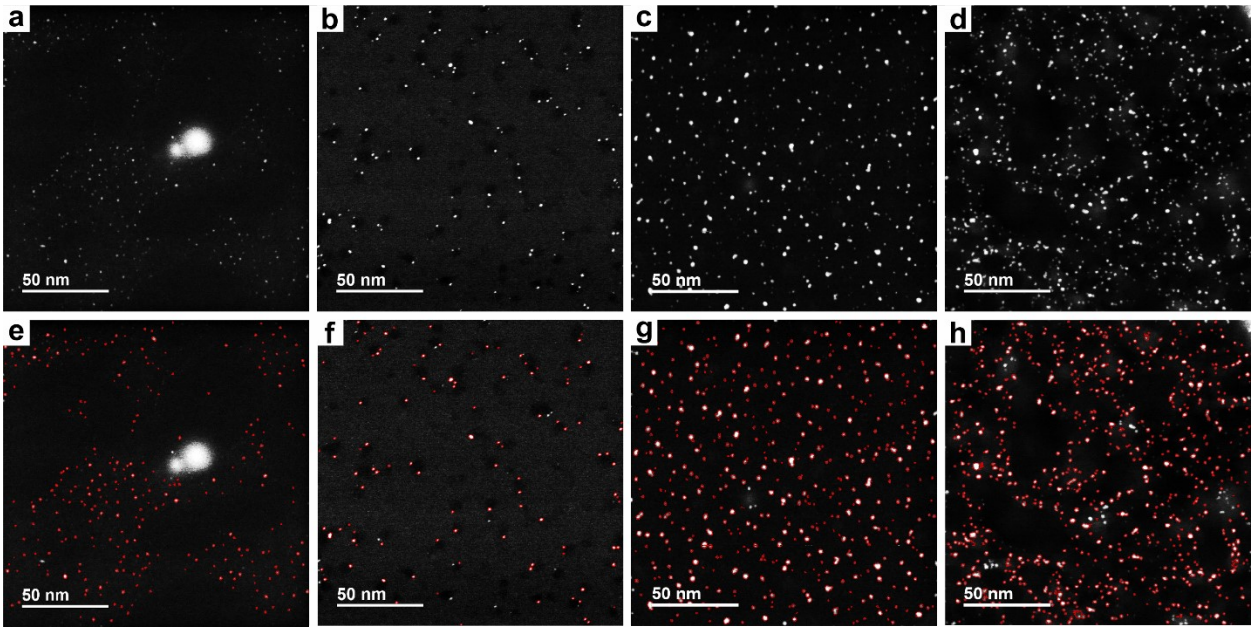

Fig. S9. Exemplary STEM images used to generate PSDs for particles synthesized by different $NaBH_4$ concentrations (a-d) and particle outlines drawn by an automated MATLAB script for particle sizing (e-h). The $NaBH_4$ concentrations were 0.42 mM (a,e), 1.01 mM (b,f), 3.52 mM (c,g), and 6.96 mM (d,h).

References

1. T. J. Woehl, C. Park, J. E. Evans, I. Arslan, W. D. Ristenpart and N. D. Browning, *Nano Letters*, 2014, **14**, 373-378.
2. D. S. Sholl and R. T. Skodje, *Physica A*, 1996, **231**, 631-647.
3. R. Viswanatha and D. D. Sarma, in *Nanomaterials Chemistry: Recent Developments and New Directions*, 2007, ch. 4, pp. 139-170.