Direct observation of aggregative nanoparticle growth: Kinetic modeling of the size distribution and growth rate

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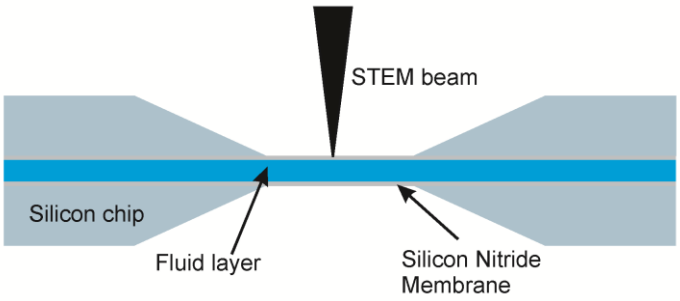

Figure S1. *In situ* liquid STEM experimental apparatus. A thin layer of aqueous silver precursor (~800 nm) is sandwiched between two silicon nitride coated silicon chips.

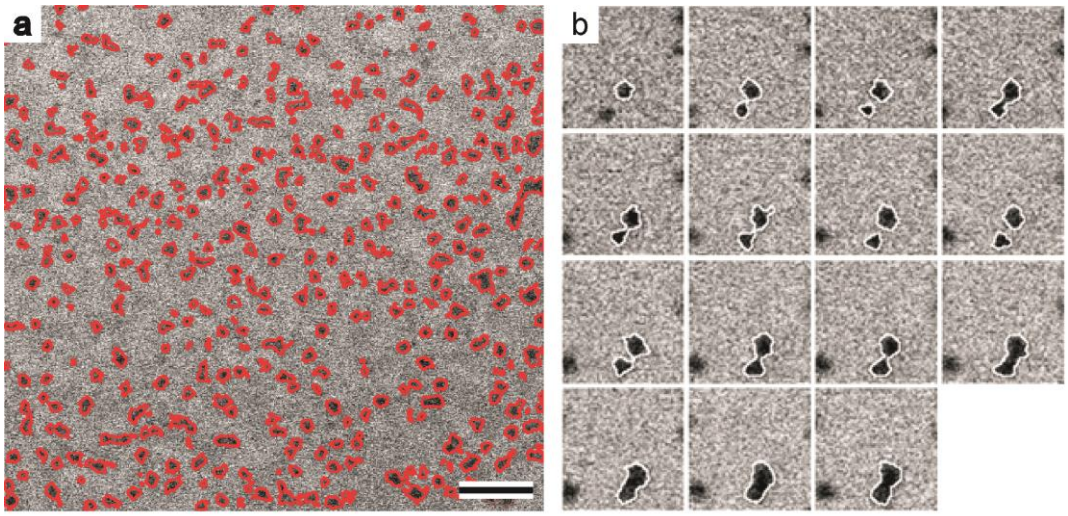

Figure S2. Sample Results of Image Segmentation and Particle Tracking. (a) Nanoparticle outlines at t = 105 s (cf. Figure 2a), extracted by the image segmentation method. The red outlines are the nanoparticle boundaries overlaid on the bright field STEM image. The scale bar is 200 nm. (b) Tracked trajectories of two nanoparticles, the first frame is at t = 40 s, with 2

second intervals in between frames. The nanoparticles experience multiple aggregation/disaggregation events during the series.

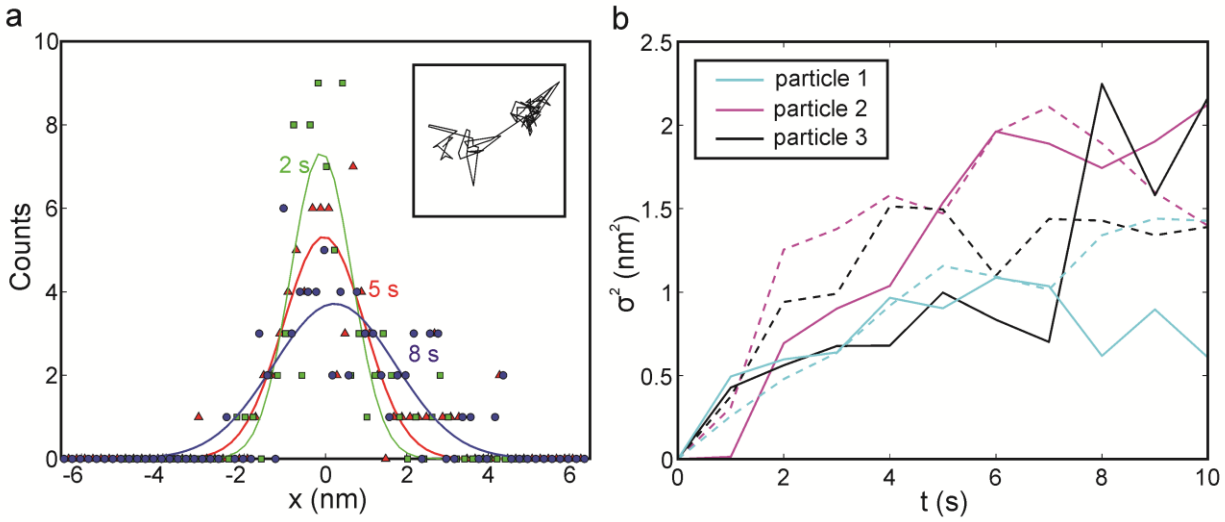

Figure S3. Brownian motion of nanoparticles during growth. (a) Probability distribution of displacements of a nanoparticle in the x-direction for various time steps indicated in the plot. Solid lines are non-linear least-squares Gaussian fits of the displacements. Inset is the trajectory of the nanoparticle over 80 seconds in a 10 by 10 nm area. (b) The mean squared displacement (MSD), σ^2, as a function of time for three representative nanoparticles, indicated by different colors in the plot. The solid lines are for motion in the x-direction, and the dashed lines are in the y-direction. σ^2 is the square of the variance of the Gaussian probability distribution fits. The Gaussians and trajectory in (a) are for particle 1. For Brownian motion in 2-dimensions, $\sigma^2 = 2Dt$, yielding diffusion coefficients of 0.12 nm^2/s, 0.14 nm^2/s, and 0.10 nm^2/s for particle 1, 2, and 3 respectively.[1]

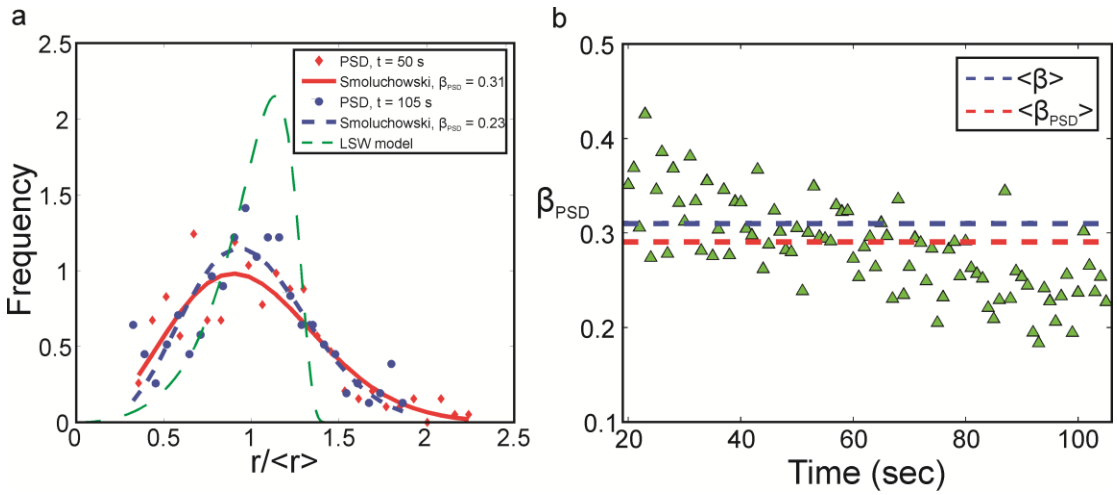

Figure S4. Variation of the Smoluchowski PSD, experimental PSD, and fitting parameter as a function of time. (a) Plot of the predicted LSW PSD for Ostwald ripening and the PSD derived from Smoluchowksi kinetics fit to the experimental PSD's at t = 50 s (red) and 105 s (blue). The Smoluchowski PSD's were obtained using non-linear least squares fitting. The PSD's are normalized to the mean radius and their total integral. The sum of the squared error (SSE) is 6.6 (50 s) and 5.1 (105 s) for the LSW model and 0.68 (50 s) and 0.91 (105 s) for Smoluchowski kinetics, indicating a much better quantitative fit for the Smoluchowski model. (b) The Smoluchowski as a function of time for each Smoluchowski PSD fit. $\langle\beta_{PSD}\rangle = 0.29$ (red dashed line) and $\langle\beta\rangle = 0.31$ (blue dashed line) are plotted for comparison.

Movie S1: Full data set of silver nanoparticle ensemble growth depicted in Figure 1. The magnification is M = 100,000, beam current is 20 pA, and the dwell time is 5 µs. The pixel size is 3.13 nm/pix. The movie was recorded with a frame rate of 1 fps, and is displayed at 5 fps. Only nanoparticles in focus were tracked for their sizes.

Supplemental note: Theoretical framework for LSW model and Smoluchowski aggregation kinetics

Lifshitz-Slyozov-Wagner (LSW) model

The LSW model takes a mean field approach to Ostwald ripening, where all parameters in the model are the averaged across the entire ensemble. The LSW model predicts power law growth of the following form in the diffusion limited regime:[2]

$$\langle r \rangle^3 - \langle r_0 \rangle^3 = \frac{8\sigma D V_m^2 c_\infty}{9RT} t \quad \text{(Supp. Eq. 1)}$$

Here <r> is the average particle radius, $\langle r_0 \rangle$ is the average particle radius at t = 0, σ is the interfacial energy of the particles, D is the diffusion coefficient of the precursor ion, V_m is the molar volume of the particle material, c_∞ is the equilibrium solubility of the particles, R is the universal gas constant, T is the temperature, and t is time. An analytical particle size distribution (PSD) can be obtained in the long-time asymptote:

$$D(\phi) = \phi^2 \left(1 + 8Kt/r_0^2\right)^{-4/3} \left(\frac{3}{3+\phi}\right)^{7/3} \left(\frac{1.5}{1.5-\phi}\right)^{11/3} \exp\left(\frac{-\phi}{1.5-\phi}\right) \quad \text{(Supp. Eq. 2)}$$

Here D(φ) is the LSW PSD, φ = r/<r>, r is the individual particle radius, and K is the term leading t in Supp. Eq. 1. Normalizing D(φ) by the integral of the distribution yields the well-known LSW probability distribution function (cf. dashed blue line Figure 3). To facilitate direct comparison to the LSW model PSD, all experimental radii are normalized to the respective mean nanoparticle radius for that time, and then normalized by their total integral (cf. red dots Figure 3).

Smoluchowski aggregation kinetics

The classical Smoluchowski equation is a result of the solution of the time-dependent diffusion equation for the particle concentration in an ensemble of particles coarsening by aggregation:[3]

$$\frac{d}{dt}n_s(t) = \frac{1}{2}\sum_{s'} K\left(s', s-s'\right) n_{s'}(t) n_{s-s'}(t) - n_s(t)\sum_{s'} K(s,s') n_{s'}(t) \qquad \text{(Supp. Eq. 3)}$$

Here n_s is the time dependent concentration of aggregates with mass s, and K is the collision frequency for the given aggregate sizes. The first summation on the right represents the increase in n_s due to aggregation of clusters of mass s' and s - s', while the second summation represents the decrease in n_s due to aggregation of clusters of mass s and s'. An analytical solution for the PSD and mean particle size time scaling in the long-time asymptote can be derived from Supp. Eq. 3 assuming the collision frequency is time invariant and spatially uncorrelated, i.e. the collisions are due to random Brownian motion.[4]

$$F(\phi) = \frac{2W}{\Gamma(a+1)}\left(W\phi\right)^{2a+1} e^{-(W\phi)^2} . \qquad \text{(Supp. Eq. 4)}$$

Here, F(φ) is the analytical PSD scaled to the average particle radius, a is the scaling exponent for cluster diffusion, i.e. $D \sim N^{-a}$, where N is the number of atoms in the cluster. Similar to the LSW model, the mean particle radius experiences power law growth of the following form:

$$\langle r \rangle - \langle r_0 \rangle = Kt^{\beta_{PSD}} . \qquad \text{(Supp. Eq. 5)}$$

Unlike Ostwald ripening the growth exponent, β_{PSD}, depends on the mechanism for particle diffusion, and is related to the cluster diffusion scaling exponent by $\beta_{PSD} = 1/2(a+1)$. For Brownian motion of a particle, the Stokes-Einstein relation describes the size dependent diffusion coefficient of the particle:

$$D \sim \frac{k_B T}{r}. \qquad \text{(Supp. Eq. 6)}$$

Here k_B is Boltzmann's constant. Assuming that the particles are 2-dimensional clusters, the Stokes Einstein equation in terms of N scales as follows:

$$D \sim \frac{k_B T}{N^{1/2}}. \qquad \text{(Supp. Eq. 7)}$$

This shows that the scaling exponent for cluster diffusion by Brownian motion is a = 1/2 (i.e. $D \sim N^{-1/2}$), yielding a predicted growth exponent of $\beta_{PSD} = 1/3$. Experimentally we obtain time averaged values of $\langle a \rangle = 0.78 \pm 0.33$ and $\langle \beta_{PSD} \rangle = 0.29 \pm 0.05$ (Figure S3b), well within the range of the exponents predicted for diffusion by Brownian motion. The time dependent β_{PSD} in our experiments may be due to the fact that Supp. Eq. 7 is a simple estimate of the diffusion coefficient that doesn't take into account the nanoparticle's proximity to the window.

References

1. Russel, W. B.; Saville, D. A.; Schowalter, W. R., *Colloidal Dispersions*. Cambridge UP: Cambridge, 1989.
2. Lifshitz, I. M.; Slyozov, V. V. *Journal of Physics and Chemistry of Solids* **1961,** 19, (1-2), 35-50.
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