Supplementary Information

Modelling the Growth and Aggregation of Gold Nanoparticles Using Liquid-Phase Transmission Electron Microscopy

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Derivation of the Lifshitz-Slyozov-Wagner Theory

The derivation of the Lifshitz-Slyozov-Wagner (LSW) theory can be found elsewhere [1,2]. Here, the derivation is shown in detail so that readers can follow through. The LSW equation describing the growth rate of nanoparticles is based on Fick's first law and by considering the following two steps in nanoparticle growth: the first is the diffusion of the monomers from the bulk solution onto the surface of a pre-formed seed, and the second is the reaction of the monomers on the surface. The flux of monomers, *J*, passing through the particle surface could be described by Fick's first law:

$$J = 4\pi x^2 D \frac{dC}{dx} \qquad \textbf{Eq. S1}$$

where *D* is the diffusion coefficient, *C* is the monomer concentration, and *x* is the distance from the center of the particle. At steady state, when *J* is constant over the diffusion layer *x*, **Eq. S1** can be integrated from the surface of a particle with radius *r* to a distance $r + \delta$, where δ is the thickness of the diffusion layer to yield:

$$J = \frac{4\pi D r(r + \delta)}{\delta}(C_b - C_s) \qquad \textbf{Eq. S2}$$

where C_b and C_s are the monomer concentration in the bulk and at the solid/liquid interface, respectively. Under real conditions, the size of the particle is negligible compared to the thickness of the diffusion layer, i.e. $r \ll \delta$, and **Eq. S2** can be simplified to

$$J = 4\pi D r(C_b - C_s) \qquad \textbf{Eq. S3}$$

Similarly, an expression can be written for the rate of surface reaction:

$$J = 4\pi r^2 k_d (C_s - C_r) \qquad \textbf{Eq. S4}$$

where C_r is the solubility of the particle, and k_d is the rate constant of a simple first order deposition reaction. The variable of C_s in **Eq. S3** and **Eq. S4** needs to be eliminated because it is not easily measured in solution. To do so, an expression relating the monomer consumption rate and the rate of change of the particle volume is used:

$$J = \frac{4\pi r^2}{V_m}\frac{dr}{dt} \qquad \textbf{Eq. S5}$$

where V_m is the molar volume. By equating **Eq. S3** and **Eq. S4**, an expression for C_s is obtained:

$$C_s = \frac{D C_b + k_d r C_r}{D + k_d r} \qquad \textbf{Eq. S6}$$

Inserting **Eq. S6** into **Eq. S3** and using **Eq. S5** yields an expression for growth rate of a single nanoparticle as

$$\frac{dr}{dt} = \frac{D V_m}{r + D/k_d}(C_b - C_r) \qquad \textbf{Eq. S7}$$

At the nanometer scale, solubility of a particle is extremely sensitive to its radius and can be described using the Gibbs-Thomson equation, which expresses extra chemical potential that a particle with radius *r* possesses:

$$\Delta\mu = \frac{2\gamma V_m}{r} \qquad \textbf{Eq. S8}$$

The solubility of a nanoparticle C_r can then be expressed as a function of *r*:

$$C_r = C_\infty \exp\left(\frac{2\gamma V_m}{rRT}\right) \approx C_\infty \left(1 + \frac{2\gamma V_m}{rRT}\right) \qquad \textbf{Eq. S9}$$

Similarly, the monomer concentration in the bulk C_b can be written as

$$C_b = C_\infty \exp\left(\frac{2\gamma V_m}{r_b RT}\right) \approx C_\infty \left(1 + \frac{2\gamma V_m}{r_b RT}\right) \qquad \textbf{Eq. S10}$$

where C_∞ is the concentration of a flat particle, and γ is the interfacial energy. Substituting **Eq. S9** and **Eq. S10** into **Eq. S7** gives the general expression describing the size evolution of a single nanoparticle:

$$\frac{dr}{dt} = \frac{2\gamma V_m^2 C_\infty}{RT(1/D + 1/k_d r)} \frac{1/r_b - 1/r}{r} \qquad \textbf{Eq. S11}$$

Next, it is useful to consider the different behaviors of growth and develop **Eq. S11** further to predict the relationship between particle size and time. In the case of a diffusion limited growth, the growth of the particle is controlled by the diffusion of the monomers to the surface. **Eq. S11** is reduced to the form

$$\frac{dr}{dt} = \frac{2\gamma D V_m^2 C_\infty}{RT} \frac{(r/r_b - 1)}{r^2} \qquad \textbf{Eq. S12}$$

Given that the total mass of the system is conserved, the LSW theory shows that the ratio r/r_b is a constant. **Eq. S12** is reduced to

$$\frac{dr}{dt} = K_D \frac{1}{r^2} \qquad \textbf{Eq. S13}$$

Eq. S13 can be easily solved to obtain the time-dependent expression for particle size:

$$r^3 - r_0^3 = K_D t \qquad \textbf{Eq. S14}$$

where r_0 is the average radius of the particle at time $t = 0$, and K is given by the following expression,

$$K_D = \frac{8\gamma D V_m^2 C_\infty}{9RT} \qquad \textbf{Eq. S15}$$

For the growth of particle controlled by the reaction of the monomers at the surface of the particle, then **Eq. S11** is reduced to the form:

$$\frac{dr}{dt} = \frac{2\gamma k_d V_m^2 C_\infty}{RT} \frac{(r/r_b - 1)}{r} \qquad \textbf{Eq. S16}$$

Similar to the case of a diffusion-controlled growth, the ratio r/r_b remains constant if the total mass of the system is conserved. Integrating **Eq. S16** yields the relationship between particle size and time for the case of a reaction-controlled growth:

$$r^2 \approx K_R t \qquad \textbf{Eq. S17}$$

Derivation of Theoretical Particle Size Distribution (PSD)

Based on the LSW theory, the PSD for diffusion-limited growth was described by the following equation:

$$D(\phi) = \kappa_D \phi^2 \left(\frac{3}{3+\phi}\right)^{\frac{7}{3}} \left(\frac{1.5}{1.5-\phi}\right)^{\frac{11}{3}} e^{-\frac{\phi}{1.5-\phi}} \qquad \textbf{Eq. S18}$$

where $D(\phi)$ is the LSW PSD, $\phi = r/< r >$, r the is individual particle radius, and κ_D depends only on time by the relation

$$\kappa_D = \frac{k'}{\left(1 + \frac{t}{\tau_D}\right)^{4/3}} \qquad \textbf{Eq. S19}$$

and τ_D is a time constant given by

$$\tau_D = \frac{9 r_0^3 RT}{64 \gamma D C_\infty V_m^2} \qquad \textbf{Eq. S20}$$

By normalizing $D(\phi)$ using the integral of the distribution, we obtained the LSW probability distribution function for the diffusion-limited case.

The probability distribution function for the reaction-limited case as described by the LSW theory is expressed by the following equation:

$$D(\phi) = \kappa_R \phi \left(\frac{2}{2-\phi}\right)^5 \exp\left(-\frac{3\phi}{2-\phi}\right) \qquad \textbf{Eq. S21}$$

where κ_R depends on time by the relation

$$\kappa_R = \frac{k''}{\left(1 + \frac{t}{\tau_R}\right)^2} \qquad \textbf{Eq. S22}$$

and τ_R is a time constant given by

$$\tau_R = \frac{r_0^2 RT}{\gamma k_d C_\infty V_m^2} \qquad \textbf{Eq. S23}$$

The Smoluchowski equation is often used to analyze the kinetics of particle coalescence [3]. This kinetic model was developed based on the assumption that coalescence occurs only through collisions between pairs of particles, and the change in the number of the particles, n_s, over time is determined by the following equation:

$$\frac{d}{dt}n_s(t) = \frac{1}{2}\sum_{s'} K(s', s - s')n_{s'}(t)n_{s-s'}(t) - n_s(t)\sum_{s'} K(s, s')n_{s'}(t) \qquad \textbf{Eq. S24}$$

In **Eq. S24**, the terms on the right-hand side represent the formation and reduction of clusters of mass, s. The first summation term describes the increase in the number of particles, n_s, due to the aggregation of clusters of mass s' and $s - s'$. The second summary term refers to the decrease in the number of particles, n_s, due to the aggregation of clusters of mass s and s'. The Smoluchowski kernel, $K(s, s')$, defines the rate at which clusters of mass s and s' collide. The Smoluchowski kernel contains the details of the coalescence process; its exact form depends on the spatial correlation between clusters. **Eq. S24** can be used to derive an analytical solution for the PSD and mean particle size over time:

$$F(\phi) = \frac{2W}{\Gamma(\alpha + 1)}(W\phi)^{2\alpha+1}e^{[-(W\phi)^2]} \qquad \textbf{Eq. S24}$$

where $F(\phi)$ is the Smoluchowski PSD, scaled to the average radius, α is the scaling exponent for cluster diffusion, Γ is the standard gamma function, and $W = (\alpha + 1)\Gamma(\alpha + 3/2)/\Gamma(\alpha + 2)$.

References

[1] Lifshitz, I. M.; Slyozov, V. V. The Kinetics of Precipitation from Supersaturated Solid Solutions. *J. Phys. Chem. Solids* **1961**, *19*, 35-50.

[2] Viswanatha, R.; Sarma, D. D. Growth of Nanocrystals in Solution. In *Nanomaterials Chemistry: Recent Developments and New Directions*; Rao, C. N. R.;Müller, A.;Cheetham, A. K., Eds.; Verlag GmbH & Co. KGaA: Weinheim, 2007, pp. 139-170.

[3] Sholl, D. S.; Skodje, R. T. Late-Stage Coarsening of Adlayers by Dynamic Cluster Coalescence. *Phys. A* **1996**, *231*, 631-647.

Figures

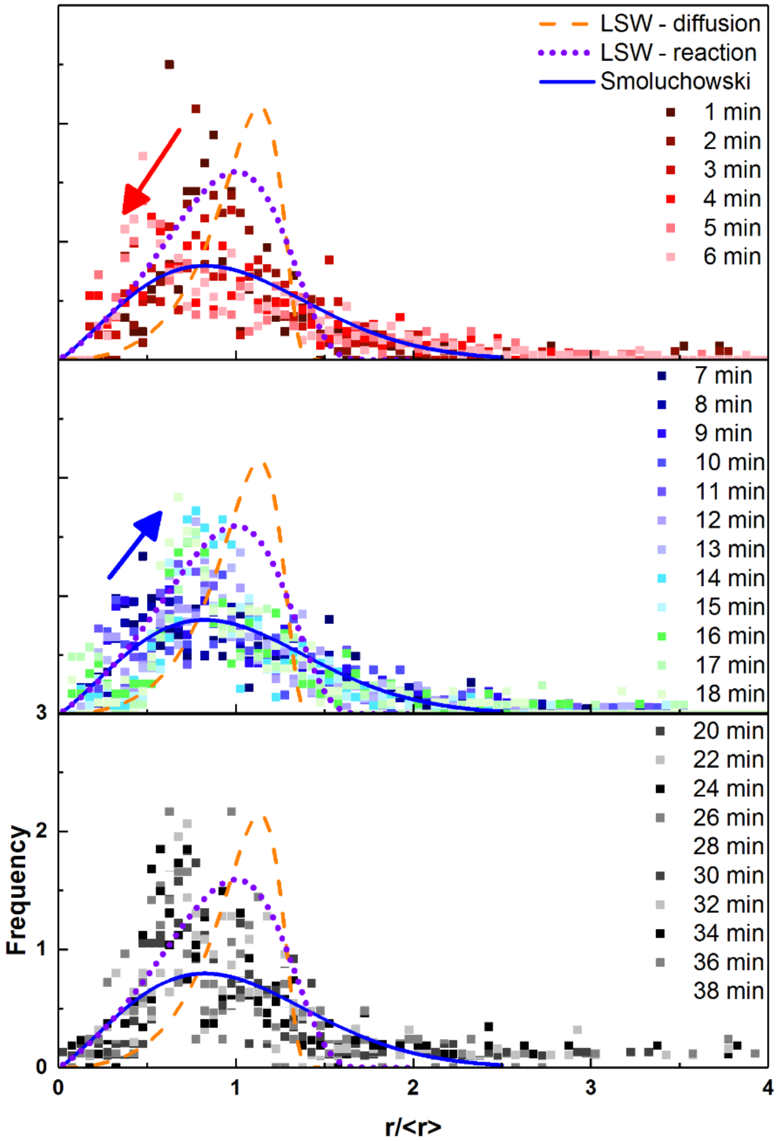

Figure S1. Particle size distribution (PSD) of the experimental radii (colored squares) compared to those predicted from the LSW theory (dashed orange curve for growth by a diffusion-limited process and dotted purple curve for growth by a reaction-limited process) and the Smoluchowski coalescence kinetics (solid blue curve).

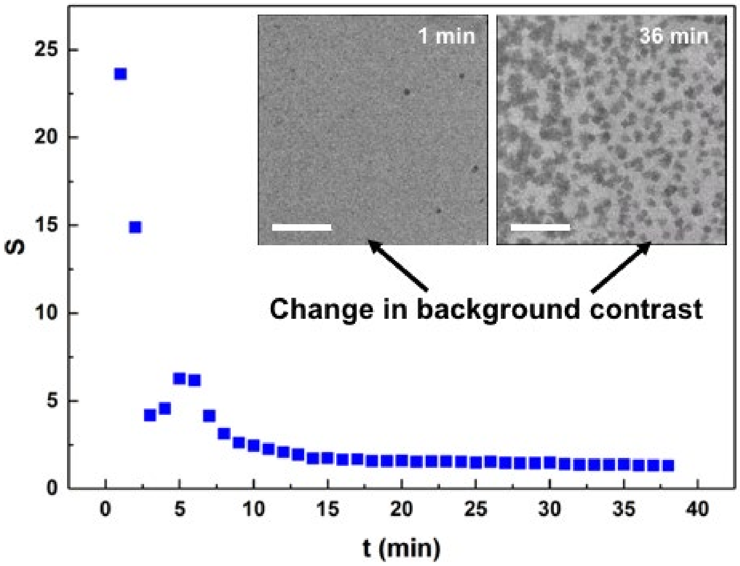

Figure S2. Oversaturation (*S*) as a function of time (*t*). Inset shows the change in contrast of the background at the beginning and at the end of the in situ growth. Scale bars are 200 nm. Considering the possible evaporation of liquid, we may regard the values were obtained under theoretical conditions.

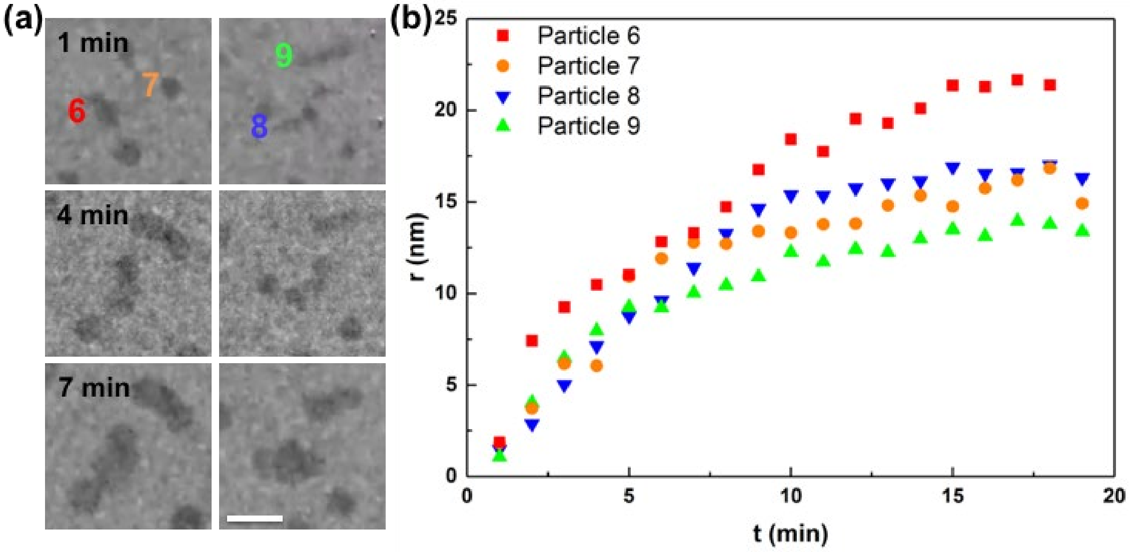

Figure S3. (a) Nanoparticles grown via coalescence, and (b) the radius of the four nanoparticles in (a) over time.