

Multiphasic growth dynamics of nanoparticle ensembles

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Abstract

Colloidal nanoparticles are of great interest in modern science and industry, yet the thermodynamic origin of nanoparticle formation remains a mystery and nanoparticle growth frequently exhibits nonclassical dynamics. Here, we tracked hundreds of *in-situ* growth trajectories of a nanoparticle ensemble using an advanced liquid-phase-TEM, and discovered that nanoparticle growth, including coalescence, exhibits monomer supply rate dependent multiphasic dynamics, unexplainable by current theories. Motivated by this finding, we developed a realistic model and statistical theories of growing nanoparticles, providing a unified, quantitative understanding of the mean and fluctuation of nanoparticle size and size-dependent growth rate across various nanoparticle systems and experimental conditions. Our work reveals that the chemical potential in a nanoparticle has a finite maximum at a critical size and exhibits a nonclassical dependence on nanoparticle size. This clear discrepancy from the classical nucleation theory (CNT) results from the strongly non-extensive free energy originating from nanoparticle motion, configurational degeneracy, and edge interaction, which were neglected in the CNT. We also uncover how this chemical potential in a nanoparticle governs formation and growth dynamics of an ensemble of nanoparticles, together with the time-dependent monomer concentration in solution.

The properties of nanoparticles can be tuned by their size and shape, which makes them highly attractive materials in both science and industry¹⁻³. For the last three decades, tremendous effort has been devoted to synthesizing monodisperse nanoparticles of controlled sizes, shapes, and compositions⁴⁻⁶, not only for investigating their unique physicochemical properties but also for various applications such as quantum-dot-enhanced display⁷ and nanocatalysis⁸. Despite extensive research, the thermodynamic origin of nanoparticle formation has not been fundamentally understood and quantitative understanding of nanoparticle growth dynamics has not been achieved⁹⁻¹¹.

Classical nucleation theory (CNT) based on the Gibbs-Thomson model cannot provide a quantitative explanation of monodisperse nanoparticle formation^{12,13}. Early works by Frenkel¹⁴, and Dillmann and Meier¹⁵ showed that the monodispersity of colloidal particles at a stationary state under supersaturation cannot be accounted for by the usual equilibrium statistical thermodynamics. Recently, a nonequilibrium nanoparticle growth process was recorded in real time by liquid-phase transmission electron microscopy (TEM)¹⁶⁻¹⁸. Liquid-phase TEM of individual nanoparticles revealed that the nanoparticle growth pathway is far more complex than assumed in the classical crystallization model¹⁹⁻²². For example, TEM studies presented direct evidence of nanoparticle coalescence and its contribution to the nanoparticle size distribution²³. They also revealed that a specific surface selectively develops, while growth of other surfaces is suppressed, to form faceted nanoparticles, in metal nanoparticles^{24,25}. Various kinetic models have been proposed to explain the growth dynamics of nanoparticles^{9,12,13,26-28}, but none offer a quantitative or fundamental understanding. This is primarily due to the lack of a realistic model of a nanoparticle and an accurate theory describing nanoparticle formation and growth processes, in addition to the lack of large sets of experimental data showing the detailed features of individual growth trajectories of nanoparticle ensembles¹⁶⁻¹⁸.

Here, we develop an advanced *in-situ* liquid-phase TEM and monitor an ensemble of platinum nanoparticle growth trajectories. This direct observation reveals that nanoparticle growth dynamics exhibits multiple kinetic phases. In each of the phases, the mean and variance of nanoparticle size, the growth rate, and its size dependence exhibit their own distinct dynamics, and all these features are sensitive to monomer supply rate. In addition, nanoparticles undergo coalescence with a strongly time-dependent rate that transiently surges and then vanishes. We find these experimental results unexplainable by current theories. Motivated by these findings, we developed a realistic model of a nanoparticle and a statistical mechanical theory. Our model and theory provide not only new physical understanding of nanoparticle nucleation and growth dynamics but also a unified, quantitative explanation of the time-dependent mean and fluctuation of nanoparticle size, and dynamics of the size-dependent growth rate at all stages of nanoparticle growth for various nanoparticle systems under different experimental conditions.

Our work reveals the chemical potential of a monomer in a nanoparticle has a finite maximum value at a critical nanoparticle size and rapidly increases with the size for nanoparticles with smaller than this critical size, in direct contradiction with the CNT. This discrepancy from the CNT is caused by the strongly non-extensive free energy originating from nanoparticle motion, configurational degeneracy, and edge interaction with the surrounding environment, neglected in the CNT. This nonclassical size dependency of the chemical potential plays an essential role in nanoparticle nucleation and multiphasic growth dynamics, including transitions between slow and fast growth and between focusing and defocusing of nanoparticle size.

***In-situ* nanoparticle growth and classification of growth trajectories**

We observed an ensemble of growing metal nanoparticles in real-time using liquid-phase TEM (Fig. 1a, Supplementary Videos 1-4). Multiple *in-situ* liquid-phase TEM movies were recorded, which show growth processes of individual Pt and Au nanoparticles, under different reaction conditions (Methods, Supplementary Video 1 for precursor Pt(acac)₂, Supplementary Video 3 for precursor Pt(COD)Cl₂, where Pt(acac)₂ has a platinum supplying rate higher than Pt(COD)Cl₂ (Supplementary Fig. 1), and Supplementary Video 4 for precursor HAuCl₄). From these movies, we tracked several hundred individual nanoparticle growth trajectories. To accurately track size changes of hundreds of individual nanoparticles in the field of view of the *in-situ* TEM movies, we developed an integrated image processing method, which includes noise removal, edge-contrast optimization, and inconspicuous pixel removal to enhance edge contrast while efficiently reducing noise from instruments and solvent background (Methods). The processed TEM images were then converted via an adaptive binarization method where the threshold for pixel assignment was determined by the locally averaged intensity of neighboring pixels (Fig. 1b and Supplementary Fig. 2)²⁹. The resulting binarized image series conserved the sizes and positions in the original liquid-phase TEM images and enabled unbiased high-throughput measurement of the size and shape of all tracked nanoparticles (Supplementary Videos 1-4, Supplementary Figs. 3-9). All growth trajectories that remained in our field of view for 180 seconds in Supplementary Video 1, for 84 seconds in Supplementary Video 3, and for 193.5 seconds in Supplementary Video 4 are collectively presented in Fig. 1c.

We classified the growth trajectories of nanoparticles into two groups: one showing only monomeric growth (Group-A) and the other exhibiting both monomeric growth and

coalescence growth (Group-B) (Fig. 1a). As these two groups exhibit qualitatively different growth dynamics, we analyzed them separately²⁸. Group-A undergoing monomeric growth makes the dominant contribution to the average size and the size distribution, and the size distribution of Group-A is similar to the distribution of all nanoparticles including Group-A and Group-B (Supplementary Fig. 10); for gold nanoparticles in Supplementary Video 4, there is only Group-A in our experiment. To explain the growth dynamics of Group-A, we developed a realistic model of a colloidal nanoparticle undergoing translation, rotation, and vibration, and electronic interactions with the surrounding environment through its faces and edges. The nanoparticle size-dependency of the Gibbs free energy of this nanoparticle model is qualitatively different from the well-known Gibbs free energy profile assumed in the classical nucleation theory and most current theories and its qualitative shape changes over time with the monomer concentration or the chemical potential of monomers in solution (Fig. 1d).

Monomeric growth dynamics

Monomeric growth dynamics of nanoparticles is decomposable into multiple kinetic phases, which are distinct for each monomer-precursor condition as shown in Fig. 1e (Phase-I-V for platinum nanoparticles generated from precursor $\text{Pt}(\text{acac})_2$, Phase-A-C for platinum nanoparticles from $\text{Pt}(\text{COD})\text{Cl}_2$, with a slower monomer supply rate than $\text{Pt}(\text{acac})_2$, and Phase-1-2 for gold nanoparticles generated from HAuCl_4). For platinum nanoparticle systems, the mean and variance of the nanoparticle size exhibit rapid growth at the initial phase but slower growth in the next phase and then the rapid growth again in the following phases. In comparison, gold nanoparticles exhibit different growth dynamics (Supplementary Note 1 for the details of the phase-dependent mean and variance in each nanoparticle system). We also measured the size-dependent growth rate of nanoparticles at all times investigated, which is enabled by

tracking an ensemble of growth trajectories, and found that the size-dependency of the growth rate also shows strongly dynamic phase-dependent behavior (Fig. 2).

To explain these experimental results, we developed a statistical mechanical theory for a system of nanoparticles growing through reversible association with monomers in solution (Methods). This theory provides a unified, quantitative explanation of various experimental results including the time-profiles of the mean and variance of nanoparticle size, the size distributions, and the size-dependent profiles of the growth rate at all times investigated (Figs. 1e and 2). We emphasize that our theory is based on a realistic nanoparticle model characterized by six parameters that account for essential characteristics of a nanoparticle. Four of these parameters characterize physical properties such as nanoparticle geometry, configurational degeneracy, monomer energy in the face and on the edge of the nanoparticle, relative to the monomer energy in the core. The remaining two parameters characterize the chemical properties of the system, which are related to monomer solubility, the monomer diffusion constant, and the bimolecular rate coefficient of monomer association. In Supplementary Table 1, we present the values of these parameters extracted from our analysis.

We considered a canonical ensemble of our model nanoparticle (Methods) and obtained the monomer chemical potential in a single nanoparticle. As shown in Fig. 1d, the obtained monomer chemical potential, μ_n^s , in an n -mer, a nanoparticle containing n monomers, has a finite maximum at a critical size, in contrast with the Gibbs-Thomson equation underlying the CNT, according to which the chemical potential diverges in the small size limit.

The analytic expression of μ_n^s is given by (Methods)

$$\beta\mu_n^s - \beta\mu_\infty^s = \frac{c_1}{r/\sigma_s} + \frac{c_2}{(r/\sigma_s)^2} - \frac{4 + \alpha}{(r/\sigma_s)^3}. \quad (1)$$

Here, β and r denote, respectively, inverse thermal energy $(k_B T)^{-1}$, with k_B and T being the Boltzmann constant and absolute temperature, and the effective radius of a nanoparticle. r is related to the monomer number, n , in a nanoparticle by $n = (r/\sigma_s)^3 [\equiv 4\pi r^3 \rho_s / 3]$ with ρ_s being the monomer number density in the nanoparticle. c_1 and c_2 in the first two terms on the right-hand-side (r.h.s.) of equation (1) are given by $\frac{2}{3}c_f \Delta \varepsilon_f$ and $\frac{1}{3}c_e \Delta \varepsilon_e$, respectively, where c_f and c_e are nanoparticle-shape dependent parameters, and $\Delta \varepsilon_f$ ($\Delta \varepsilon_e$) denotes the free energy of a monomer at a facial (edge) site with respect to the free energy of a monomer at a bulk site in unit of thermal energy (Supplementary Note 2 for their precise definitions). $\Delta \varepsilon_f$ and $\Delta \varepsilon_e$ are dependent not only on microscopic properties of a nanoparticle but also on the environment surrounding the nanoparticle, including solvent and ligand molecules. $\Delta \varepsilon_f$ or $\Delta \varepsilon_e$ is positive in general; however, $\Delta \varepsilon_e$ or c_2 can be negative because an atom or molecule can bind to a site with a lower coordination number stronger³⁰. 4 and α in the third term originate from the translational and rotational motion and the configurational degeneracy of a nanoparticle, respectively. The free energy associated with translational and rotational motion of a nanoparticle is proportional to $-4 \ln n$, which yields the chemical potential, $-4/n$, or $-4/(r/\sigma_s)^3$ in the third term (equation (10) in Methods). On the other hand, α is a constant that characterizes the n -dependence of the configurational degeneracy, Ω_n , of an n -mer, i.e., $\Omega_n \propto n^\alpha$. For an n -mer with a small number, h , of vacant sites or defects, α is approximately the same as h , because the number of different defect configurations of the n -mer is given by $\Omega_n = n!/(n-h)!h! = n(n-1)\cdots(n-h+1)/h! \sim n^h$, when $h \ll n$. In units of thermal energy, the free energy associated with the configurational degeneracy is given by $-\ln \Omega_n = -\alpha \ln n$,

which yields the chemical potential, $-\alpha/n$, or $-\alpha/(r/\sigma_s)^3$ in the last term of equation (1).

The second and third terms on the r.h.s. of equation (1) give the chemical potential, μ_n^s , its non-classical size dependency as demonstrated in Fig. 1d. For a large particle, the last two terms become negligible, and equation (1) reduces to the Gibbs-Thomson equation, where $\mu_n^s(r)$ monotonically decreases with size.

The non-classical size dependence of $\mu_n^s(r)$ plays a crucial role in the nucleation and growth dynamics. To explain, let us first consider a nanoparticle in a solution of monomers with a constant number density or chemical potential. If the chemical potential, μ_1 , of monomers in solution is higher than $\mu_n^s(r)$, the monomers in solution deposit onto the nanoparticle to increase the particle size. In the opposite case where $\mu_1 < \mu_n^s(r)$, the monomer in the nanoparticle dissolves into the solution to decrease the nanoparticle size. For this reason, the size approaches a particular size, r^* , at which $\mu_n^s(r^*) = \mu_1$ and $\partial\mu_n^s(r)/\partial r|_{r=r^*} > 0$ (Fig. 1d). r^* is a stable fixed point because a nanoparticle with radius r smaller than r^* grows and a particle with r greater than r^* shrinks (Fig. 1d). This type of absolute size focusing is different from the size focusing observed for growing nanoparticles in Phase III, which is discussed below. Absolute size focusing occurs only when the largest nanoparticle in our system is smaller than the critical size, r^{**} , where $\mu_n^s(r^{**}) = \mu_1$ with $\partial\mu_n^s(r)/\partial r|_{r=r^{**}} < 0$. Note that r^{**} is an unstable fixed point around which a nanoparticle with $r < r^{**}$ shrinks and a nanoparticle with $r > r^{**}$ keeps growing, which is the classical Ostwald ripening. If $\mu_n^s(r)$ were a monotonically decreasing function of r , as described by the Gibbs-Thomson equation, absolute size focusing around the stable fixed point r^* would not have occurred; instead, only Ostwald ripening would have occurred.

206 The chemical dynamics of an ensemble of nanoparticles can be quantitatively understood
 207 by equation (1) and the well-known hierarchical kinetic equations for the concentration, ρ_n ,
 208 of n -mers, i.e., $\partial_t \rho_n(t) = J_{n-1}(t) - J_n(t)$, where the net growth rate J_n is given by
 209 $J_n = k_n^a \rho_1(t) \rho_n(t) - k_{n+1}^d \rho_{n+1}(t)$ ($n \geq 1$) and $J_0 = R_M - \sum_{m=1}^{\infty} J_m$ (Methods). Here, k_n^a and
 210 k_{n+1}^d denote the diffusion-influenced rate coefficients of monomer association with n -mers and
 211 dissociation from $(n+1)$ -mers, respectively. R_M denotes the rate of monomer supply defined
 212 by $R_M = \partial_t \rho_{1,T}$ with $\rho_{1,T}$ being the total monomer density, i.e., $\rho_{1,T}(t) = \sum_{n=1}^{\infty} n \rho_n(t)$. In our
 213 liquid TEM experiment, R_M is dependent on the intensity of electron irradiation and the
 214 reactivity of a precursor. It is difficult to measure R_M or $\rho_{1,T}(t)$ directly in our experiment;
 215 however, we circumvent this problem using the general relationship of $\rho_{1,T}(t)$ to the time-
 216 dependent mean nanoparticle size and the mean growth rate coefficient,
 217 $\langle j_n(t) \rangle [\equiv \langle J_n(t) / \rho_n(t) \rangle]$ (Supplementary Notes 3 and 4 for the details).

218 In our model, k_n^a is not simply proportional to the surface area of the nanoparticle
 219 (Methods). Instead, the monomer association rate coefficient per nanoparticle area decreases
 220 with nanoparticle size. This is because the monomer association consists of two steps: the
 221 diffusion-limited encounter of monomers to an n -mer, whose rate coefficient, $k_D(n)$, is
 222 approximately given by $4\pi r D_1$ with r and D_1 being the nanoparticle radius and the diffusion
 223 coefficient of a monomer, and the ensuing association of monomers at the n -mer's surface,
 224 whose rate coefficient, $k_S(n)$, is proportional to the surface area, $4\pi r^2$, of nanoparticle, or
 225 $n^{2/3}$, i.e., $k_S(n) = 4\pi r^2 \kappa_a$ with κ_a being the proportionality constant. According to Collins-
 226 Kimball's theory³¹, k_n^a is given by $k_n^a \cong k_S(n) / [1 + k_S(n) / k_D(n)] = k_S(n) / [1 + (\kappa_a / D_1) r]$, so

227 that the association rate coefficient per nanoparticle surface area,
 228 $k_n^a / 4\pi r^2 (= \kappa_a / [1 + (\kappa_a / D_1)r])$, decreases with the nanoparticle size (Supplementary Fig. 11).
 229 This form of k_n^a serves as a good approximation for a spherical nanoparticle when the
 230 reversibility of monomer association with a nanoparticle is not too large^{31,32}. In our analysis,
 231 we use a more elaborate form of k_n^a to account for a non-spherical geometry of nanoparticles,
 232 which may change over time during nanoparticle growth. The rate of monomer dissociation
 233 from a nanoparticle is not simply proportional to the surface area either, because it is connected
 234 to the monomer association rate by the detailed balance condition^{31,32} (Methods).

235 From the definition of growth rate J_n and the detailed balance condition, we derive the
 236 relationship between growth rate J_n and chemical potential μ_n^s given in equation (1) by

$$237 \quad J_n(t) = k_{n+1}^d \rho_{n+1} \left(e^{-\beta[\mu_n^s - \mu_1(t)]} \rho_n / \rho_{n+1} - 1 \right), \quad (n \geq 1) \quad (2)$$

238 where $\mu_1(t)$ denotes the chemical potential of monomers in solution, which logarithmically
 239 increases with monomer concentration, i.e., $\mu_1(t) = \mu_1^\circ + k_B T \ln \rho_1(t) / \rho^\circ$ with μ_1° and ρ°
 240 being the chemical potential and density of monomer in the standard-state solution,
 241 respectively [Methods for the derivation of equation (2)]. In equation (2) ρ_{n+1} / ρ_n can be
 242 replaced by unity whenever the nanoparticles have a continuous size distribution
 243 (Supplementary Fig. 12). Using our theory based on equations (1) and (2), we provide a unified,
 244 quantitative explanation of the time-dependent mean and fluctuation of the nanoparticle size
 245 and the size-dependent growth rate at all times for various nanoparticle systems under different
 246 experimental conditions (Methods and Figs. 1e and 2). From the quantitative analysis, we
 247 extracted the values of the five parameters characterizing the time-independent

physicochemical properties of nanoparticles for all experimental systems investigated (Supplementary Table 1). In addition, the time-dependent monomer concentration, or the monomer chemical potential in solution, and the shape index were extracted from the experimental data at each time frame (Fig. 4b,c).

In accordance with equation (2), the size-dependence of $J_n(t)$ always exhibits a far more dynamic phase-to-phase variation than the size distribution, $p_n(t) \left(\equiv \rho_n(t) / \sum_j \rho_j(t) \right)$, as shown in Fig. 2. This results from the time-dependent variation of monomer density or the chemical potential difference, $\mu_n^s - \mu_l(t)$, between a nanoparticle and solution in equation (2) (Fig. 3a,b). Since the first term in the parenthesis of equation (2) is the same as $k_n^a \rho_1 \rho_n / k_{n+1}^d \rho_{n+1}$ from the definition of J_n , $\mu_n^s - \mu_l(t)$ is practically the same as the free energy change per association of a monomer with an n -mer, $\exp[-\beta \Delta G_r(n \rightarrow n+1)] \left(= k_n^a \rho_1 \rho_n / k_{n+1}^d \rho_{n+1} \right)$ (Methods), whenever the nanoparticle size distribution is continuous, or whenever $\rho_n \cong \rho_{n+1}$. Therefore, if $\mu_n^s - \mu_l(t) [\cong \Delta G_r(n \rightarrow n+1)] < 0$, the association of monomers and n -mer occurs faster than the reverse dissociation reaction and the nanoparticle grow spontaneously; otherwise, the reverse dissociation reaction occurs faster than the association reaction and the nanoparticle shrink spontaneously.

Under the hyper-saturation condition, in which $\mu_n^s < \mu_l(t)$ for all n , nanoparticle growth occurs spontaneously for all sizes of nanoparticle and the growth rate coefficient $\mu_\infty^s < \mu_l(t) < \mu_n^s$, is positive for all n , which is the case in Phase-I, -III-V of platinum nanoparticles generated from precursor $\text{Pt}(\text{acac})_2$, in Phase-A and-C of platinum nanoparticles from precursor $\text{Pt}(\text{COD})\text{Cl}_2$, and in Phase-1 and-2 for gold nanoparticles from

precursor HAuCl_4 in our experiment (Fig. 3). The growth rate of nanoparticles increases with μ_n^s . On the other hand, if μ_1 for some values of n , those n -mers with μ_n^s higher than μ_1 shrink and their growth rate coefficients j_n are negative, as shown in Phase II of platinum nanoparticles generated from precursor $\text{Pt}(\text{acac})_2$. This transient decrease of nanoparticle size can occur even under supersaturation condition, as shown in Phase B in Fig. 3.

By analyzing the “time-dependent” experimental data for the size-dependent growth rate and size distribution for *in-situ* growth of metal nanoparticles under different precursor conditions using equation (2), we can reconstruct the “time-independent” size dependence of $\mu_n^s - \mu_\infty^s$ using the time-profiles of the solution-phase chemical potential $\mu_1(t)$ extracted from our analysis (Fig. 4a,b). These reconstructed chemical potential differences are found to be in good agreement with equation (1), which are independent of the monomer supply rate either. Note that this chemical potential difference is exactly the same as $\ln(k_{n+1}^d/k_n^a \rho_{1,\infty})$ with $\rho_{1,\infty}$ being the equilibrium solubility of monomers, because of the detailed balance condition (Methods).

In order to demonstrate the general applicability of our model and theory, we also analyzed experimental data for *ex-situ* growth of iron oxide and CdSe nanoparticles synthesized using conventional heat-up⁵ and hot-injection methods³³, respectively (Methods). We confirmed that our model and theory, without any modification, provide a quantitative explanation of these *ex-situ* nanoparticle growth data (Supplementary Fig. 13).

According to our analysis, $\Delta\epsilon_f (\propto c_1)$, or the free energy of a monomer at a facial site, in equation (1) has positive values ; however, $\Delta\epsilon_e (\propto c_2)$, or the free energy of a monomer at an edge site, has negative values for all nanoparticle systems investigated. $\Delta\epsilon_e (\propto c_2)$

exhibits greater system-to-system variation than $\Delta\varepsilon_f (\propto c_1)$ (Supplementary Table 1). Both $\Delta\varepsilon_f$ and $\Delta\varepsilon_e$ increase the maximum value μ_n^{s*} of μ_n^s (Supplementary Fig. 14a,b). However, compared with $\Delta\varepsilon_e$, $\Delta\varepsilon_f$ has a dominant effect on the μ_n^{s*} value. For example, the value of n^* is found to be 1.06, 0.91, 0.79, and 0.74 in descending order for Iron oxide, gold, CdSe, and platinum nanoparticles, respectively, for which μ_n^s values are also in a descending order, given by 4.89, 4.33, 3.41, and 2.87 but μ_n^{s*} values are in an ascending order, given by -5.06, -4.93, -2.82 and, -1.71, in unit of thermal energy. The critical nanoparticle size $\Delta\varepsilon_f$ at which n^* assumes its maximum value decreases with $\Delta\varepsilon_f$ and $\Delta\varepsilon_e$. The value of μ_n^{s*} depends on n^* more sensitively than $\Delta\varepsilon_f$ does (Supplementary Fig. 14b and the caption of Fig. 4).

We note that the time profile of the supersaturation ratio, $\tilde{\rho}_1$, defined by the ratio of the monomer concentration ρ_1 to monomer solubility $\rho_{1,\infty}$, extracted for iron oxide nanoparticle system, is similar to the results reported in ref.³⁴. Our quantitative analysis also reveals that all nanoparticles in the systems we investigated have a geometry similar to a truncated octahedron for all growth phases without showing a systematic time-dependence (Fig. 4c and Supplementary Fig. 15). All tracked nanoparticles in the observation time windows of our *in-situ* and *ex-situ* experiments consistently show quasi-spherical morphology (Supplementary Videos 1-4).

There exists a general relationship between the mean and variance of nanoparticle size, which holds for any growing particle system. This relationship quantitatively explains the time dependence of the relative variance of particle size for various nanoparticle systems (Fig. 4d). The chemical dynamics of any growing particle system can be described by a hierarchical

313 kinetic equation with a suitable choice of growth rate J_n . For an arbitrary J_n , we find that
 314 the variance, $\sigma_n^2(t)$, and mean, $\langle n(t) \rangle$, of nanoparticle size satisfy $\partial_t \sigma_n^2(t) = \partial_t \langle n(t) \rangle$
 315 $+2\langle \delta n(t) \delta j_n(t) \rangle$ with $\langle \delta n(t) \delta j_n(t) \rangle [\equiv \langle n(t) j_n(t) \rangle - \langle n(t) \rangle \langle j_n(t) \rangle]$ denoting the cross
 316 correlation between n and j_n . We note that this equation can also be derived from the
 317 Chemical Fluctuation Theorem in ref ³⁵ (Methods). This relationship between the mean and
 318 variance shows that the mean growth rate, $\partial_t \langle n(t) \rangle$, and the cross correlation, $\langle \delta n(t) \delta j_n(t) \rangle$,
 319 play an essential role in determining the time dependence of the variance. From this equation,
 320 we obtained a simple, approximate expression of the relative variance as a second-order
 321 polynomial in $\langle n(t) \rangle^{-1}$ [equation (13) in Methods], which provides a quantitative explanation
 322 of the monomer supply rate-dependent relative variance under certain conditions
 323 (Supplementary Fig. 16).

324 Our experimental results for platinum nanoparticle systems generated from the two
 325 precursors with different monomer supply rates clearly show that the nanoparticle growth
 326 dynamics is dependent on the monomer supply rate as well as on intrinsic properties of the
 327 nanoparticle system. For example, the relative variance of platinum nanoparticle size tends to
 328 decrease with time for the fast monomer supply condition while it shows the opposite trend for
 329 the slow supply condition (Fig. 4d).

330 It is noteworthy that our theory consistently explains platinum nanoparticles synthesized
 331 under different monomer supply conditions without changing the time-independent
 332 microscopic parameters characterizing our nanoparticle model (Supplementary Table 1 for the
 333 optimized parameter values). This consistency and applicability to three other nanoparticle
 334 systems, gold, iron oxide, and CdSe, demonstrate the robustness of our nanoparticle model and

theory, which confirms the importance of time-dependent monomer concentration and the nonclassical chemical potential in nanoparticle originating from nanoparticle motion, edge interaction, and configurational degeneracy for a quantitative understanding of growth dynamics of a nanoparticle system.

Coalescence growth dynamics

Nanoparticles also grow via mutual coalescence (Fig. 5a)^{18,23,24,36}. The size of the coalescing nanoparticle group, Group-B, abruptly increases over a short period of time (Fig. 5b) in contrast with Group-A that grows continuously. Our experimental data show that platinum nanoparticle coalescence transiently occurs only near the end of Phase-III in our experiment with precursor Pt(acac)₂ (Fig. 5c), where monomeric growth is slow and the nanoparticles manifest a small size fluctuation around the mean, i.e., 1.5 nm ± 0.2 nm, because of size focusing throughout Phase-III. Thus, coalescing nanoparticles have similar radii (Fig. 5a,d). Both the coalescence rate coefficient and the coalescence time distribution are unimodal functions of time (Fig. 5c,e). Individual trajectories of coalescing nanoparticles clearly show that the nanoparticles, which undergo random thermal motion, coalesce when their separation becomes approximately 5.87 nm, close to twice the sum of the nanoparticle radius and the ligand length (Fig. 5f and Supplementary Table 2). The transient coalescence dynamics between growing nanoparticles cannot be explained by the classical chemical kinetics or previously reported theories of diffusion-influenced reaction kinetics for particles with constant size and diffusion coefficient³⁷. The classical Smoluchowski coagulation kinetics³⁸ can explain size distributions of silver nanoparticles growing mainly by aggregation³⁹. However, this theory is inapplicable to Group-B in which nanoparticles grow by both monomeric addition and coalescence (Supplementary Fig. 17), for which the nanoparticle size and hence diffusion coefficient depend on time.

We found it essential to account for two facts in understanding the transient coalescence dynamics. First, nanoparticles are initially separated by a distance far greater than their encounter distance, and second, growing nanoparticles undergo anomalous thermal motion because their diffusion coefficient, inversely proportional to the nanoparticle size, decreases with time (Fig. 5g). In addition, to achieve a quantitative explanation of our experimental data, we assume that the coalescence propensity of nanoparticles greater than a particular size rapidly decreases with size (Fig. 5h). To obtain a mathematical description of this coalescence model, we extended the reduced distribution function formalism, developed for the molecular diffusion-influenced reactions^{32,40}, to encompass growing nanoparticle systems (Methods). The resulting kinetic equation successfully explains the time-profiles of the coalescence rate coefficient and the distribution of coalescence time. According to our analysis, the onset of coalescence is delayed because it takes time for initially separated nanoparticle pairs to form reactive encounter pairs via thermal motion and the encounter pair formation is a rare event. The coalescence time distribution is dependent on the system properties including initial nanoparticle density, reactivity, and monomeric growth dynamics of nanoparticles (Supplementary Fig. 18). The coalescence rate vanishes at times longer than 126 seconds not only because the larger nanoparticles have a smaller diffusion-influenced rate but also because they have a vanishingly small coalescence propensity.

Discussion

The chemical potential in a nanoparticle has a finite maximum value at a critical nanoparticle size, according to equation (1). This is in direct contradiction with Gibbs-Thomson equation, according to which the chemical potential in a nanoparticle diverges in the small size limit. The stark difference of equation (1) from the Gibbs-Thomson equation arises because of strongly

non-extensive free energy originating from nanoparticle motion, configurational degeneracy, and edge interaction with the surrounding environment, overlooked in the CNT. The CNT based on the Gibbs-Thomson equation does provide a useful, approximate result for the crystallization rate⁴¹; however by considering the strongly non-extensive free energy terms, one can explain the nucleation-rate data more accurately than the CNT^{15,42}. Equation (1) reduces to the Gibbs-Thomson equation for an immobile and spherical nanoparticle free of any defect. However, even for a spherical nanoparticle, as long as it moves or has defects, the monomer chemical potential has a finite maximum, satisfying equation (1).

The nonclassical size dependence of the chemical potential, μ_n^s , of a monomer in nanoparticle, given in equation (1), influences the nucleation and growth dynamics of nanoparticles. Since the chemical potential of monomer in a nanoparticle has a finite maximum value, μ_n^{s*} , it is possible to introduce a new concept: the hyper-saturation condition, in which the monomer chemical potential, μ_1 , in solution is higher than μ_n^{s*} . Under the hyper-saturation condition, nanoparticle growth is a spontaneous process for all sizes of nanoparticles, which is the case in Phase-I, III-V on the left panel and Phase-A and -C on the right panel of Fig. 3. On the other hand, under the supersaturation condition in which $\mu_\infty^s < \mu_1 < \mu_n^{s*}$, those nanoparticles with monomer chemical potential μ_n^s higher than μ_1 in solution shrink. This causes the mean nanoparticle size to grow slowly or even shrinks transiently, as shown in Phase-II in the left panel and Phase-B in the right panel of Fig. 1e.

As demonstrated in this work, the present theory based on equation (1) enables a unified, quantitative explanation of growth dynamics of a nanoparticle ensemble for various systems under different experimental conditions, only when it is combined with equation (2), the new

relationship of the net growth rate of a nanoparticle to the difference between the monomer chemical potentials in a nanoparticle and in solution. Our quantitative analysis makes it possible to extract size- and shape-dependent physicochemical properties of a nanoparticle system from the nanoparticle growth dynamics data obtained under a given experimental condition (see, for example, Supplementary Table 1). By repeating this theoretical analysis of nanoparticle growth dynamics for various *in-situ* or *ex-situ* experiments, we can achieve quantitative understanding of how various microscopic properties of nanoparticle depend on experimental conditions. This information is useful for optimizing the experimental condition for the synthesis of nanoparticles with desired properties.

Our *in-situ* liquid TEM experiment, combined with unbiased tracking of nanoparticle ensembles, provides important insights for designing controlled nanoparticle synthesis. For example, the size distribution of Group-A undergoing monomeric growth is narrower than that of Group-B accompanying coalescence (Supplementary Fig. 19). This finding suggests that a synthetic approach that drives more particles to follow the monomeric growth pathway will enhance the monodispersity of the synthesized nanoparticles.

Nanoparticle nucleation and growth dynamics require further research. Liao *et al.* showed that, at short times, all low index facets of platinum nanoparticles exhibit similar growth rates, but at long times beyond our current experimental observation time window, the {100} facets stop growing while the other facets keep growing, resulting in the formation of cube-shaped nanoparticles at long times²⁵. To explain these phenomena, it is necessary to consider the facet dependence of the monomer association rate and the monomer chemical potential in a nanoparticle. Recent studies showed that crystallization in calcium carbonate solutions occurs through multistage pathways involving an intermediate condensed phase^{43,44},

426 and that the size of perovskite nanocrystals formed in cesium lead halide solution is controlled
427 by the halide ion concentration in the solution⁴⁵. We plan to extend the present model and
428 theory to encompass these systems, which we leave for future investigation.

429

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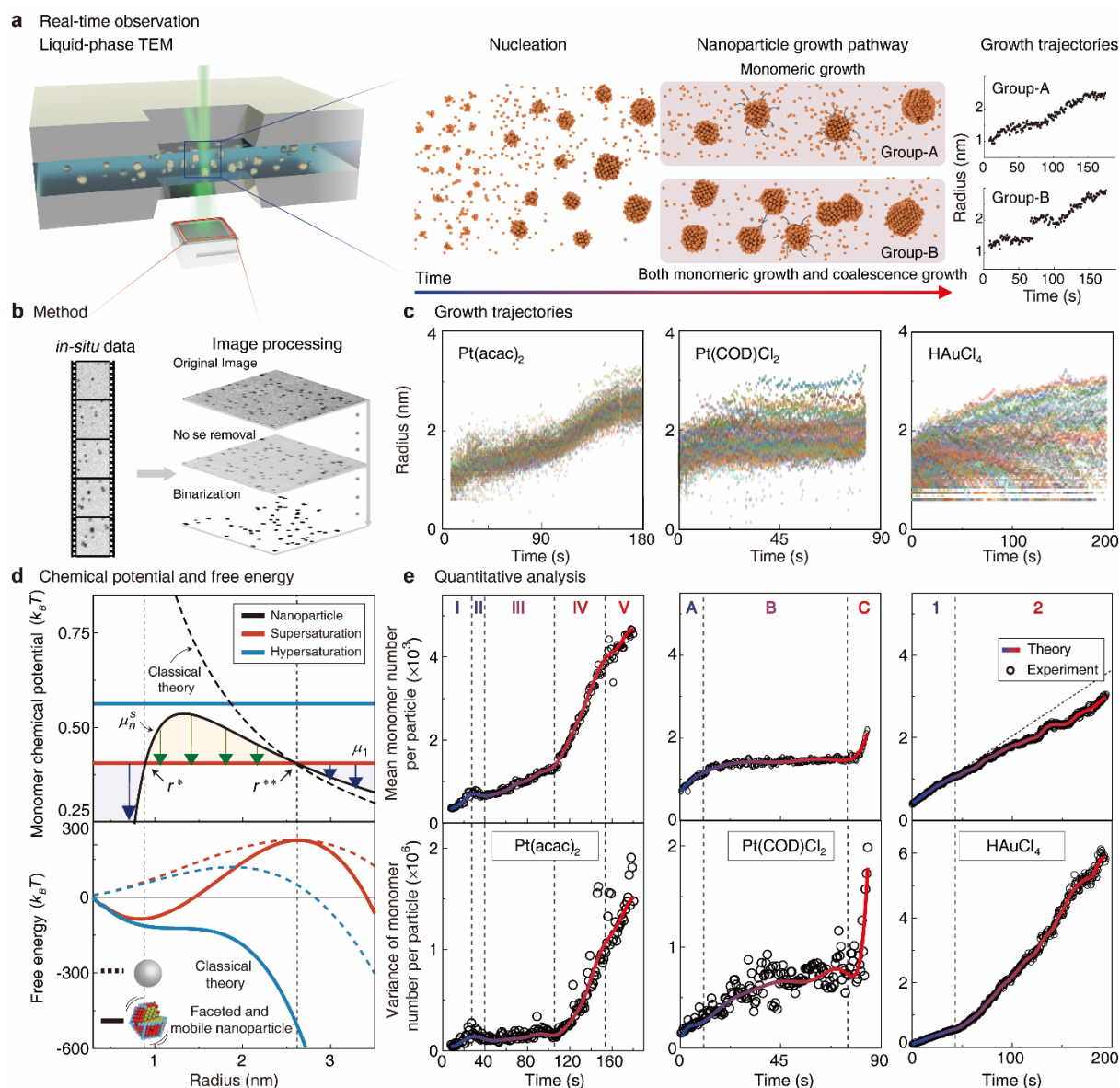


Fig. 1. Thermodynamic origin of nanoparticle formation and multiphasic growth dynamics of nanoparticle ensembles. **a**, Schematic of our experimental measurement of individual growth trajectories of metal nanoparticle ensemble. Left: real time *in-situ* observation of nanoparticle growth using a liquid-phase TEM. Center: Group-A showing only monomeric growth and Group-B exhibiting both monomeric growth and coalescence growth. Right: the pathway-dependent growth trajectories for platinum nanoparticles. **b**, Schematic of TEM image processing including noise removal, edge-contrast optimization, adaptive binarization, and inconspicuous pixel removal to convert *in-situ* TEM images into binarized images. **c**, Individual growth trajectories of hundreds of metal nanoparticles obtained using different precursors. Left: Pt(acac)₂. Center: Pt(COD)Cl₂. Right: HAuCl₄. **d**, Top: Chemical potential, μ_n^s , of monomers in a nanoparticle for our faceted and mobile nanoparticle model (black solid line) and for the classical immobile sphere model (black dashed line), and chemical potential, μ_1 , of monomers in supersaturated solution (red line) and in hypersaturated solution (blue line). For the hypersaturated solution, μ_1 is larger than the maximum of μ_n^s . Absolute

564 size-focusing occurs for nanoparticles with sizes close to r^* until reaching this value, while
565 nanoparticles with size close to r^{**} undergo Ostwald ripening (main text). Bottom: the
566 corresponding Gibbs free energy change associated with the formation of a nanoparticle from
567 monomers for our faceted and mobile nanoparticle model (solid line) and for the classical
568 immobile sphere model (dashed line): supersaturated solution (red) and hypersaturated solution
569 (blue). **e**, Comparison between theory and experiment for the mean and variance of the
570 monomer number per particle: experimental results (circles) and the theoretical results (lines).
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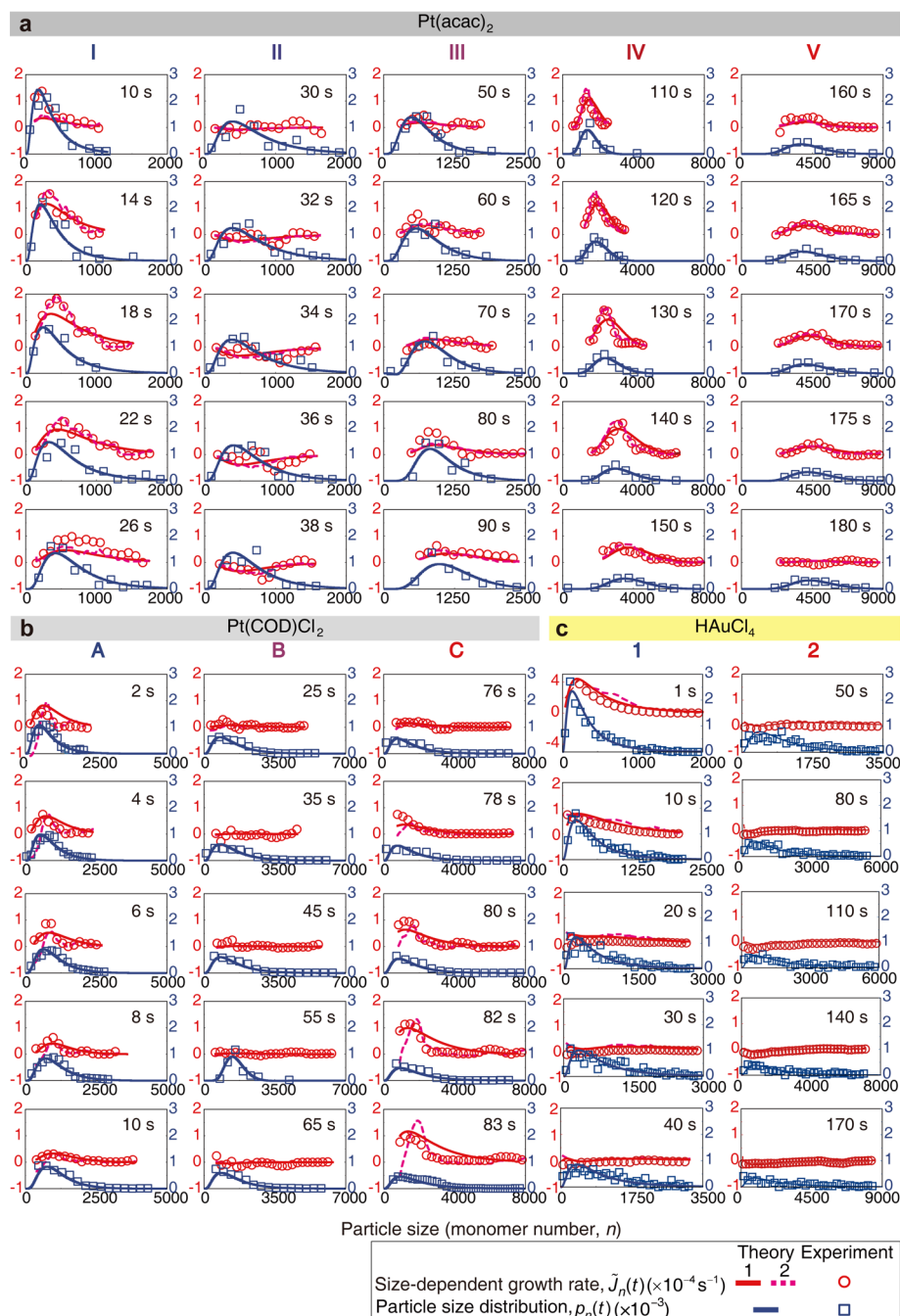


Fig. 2. Size-dependent growth rate and size distribution of nanoparticles at various times. Experimental data (symbols) and theoretical results (lines) (Methods) for scaled size-dependent growth rate $\tilde{J}_n(t) [\equiv J_n(t)/\rho_{1,T}(t_0)]$ in unit of s^{-1} (red) and nanoparticle size distribution $p_n(t)$ (blue): $\tilde{J}_n(t)$ calculated from equation (2) or (S4-9) obtained using the theoretical size distributions (solid line) or experimental size distributions (dashed line). Here, $\rho_{1,T}(t_0)$ denotes the value of the total monomer density, $\rho_{1,T}(t)$, at the beginning of our measurement (see Supplementary Note 4 for the calculation method of $\tilde{J}_n(t)$). **a**, Results for Pt nanoparticles generated from precursor $\text{Pt}(\text{acac})_2$. In Phase-I, the growth rate is positive and a unimodal function of size. However, in Phase-II, the growth rate can be a convex or concave function,

taking on small positive or even negative values. In Phase-III, the growth rate becomes positive again but with far smaller magnitudes than Phase-I or -IV. In Phase-IV, the growth rate resumes a unimodal size dependence but assumes its maximum at sizes far greater than in Phase-I. In Phase-V, the growth rate decreases. **b**, Results for Pt nanoparticles from precursor Pt(COD)Cl₂, which has a slower platinum supplying rate than Pt(acac)₂. In Phase-A, the growth rate is a unimodal function of size, whose peak height decreases with time. In Phase-B, the growth rate plateaus with little fluctuation around zero. In Phase-C, the growth rate resumes a unimodal dependence on size, but the peak height tends to increase with time unlike Phase-A. **c**, Results for Au nanoparticles generated from precursor HAuCl₄. In Phase-1, the growth rate exhibits a similar trend as that for Phase-A in **b**. In Phase-2, the growth rate is slightly negative at small sizes but has small positive values over a wide range of sizes, causing a positive slope of the mean size for gold nanoparticles in Fig. 1e. Our theoretical results for $p_n(t)$ are in quantitative agreement with experimental results at all times and under different monomer supply conditions (Methods).

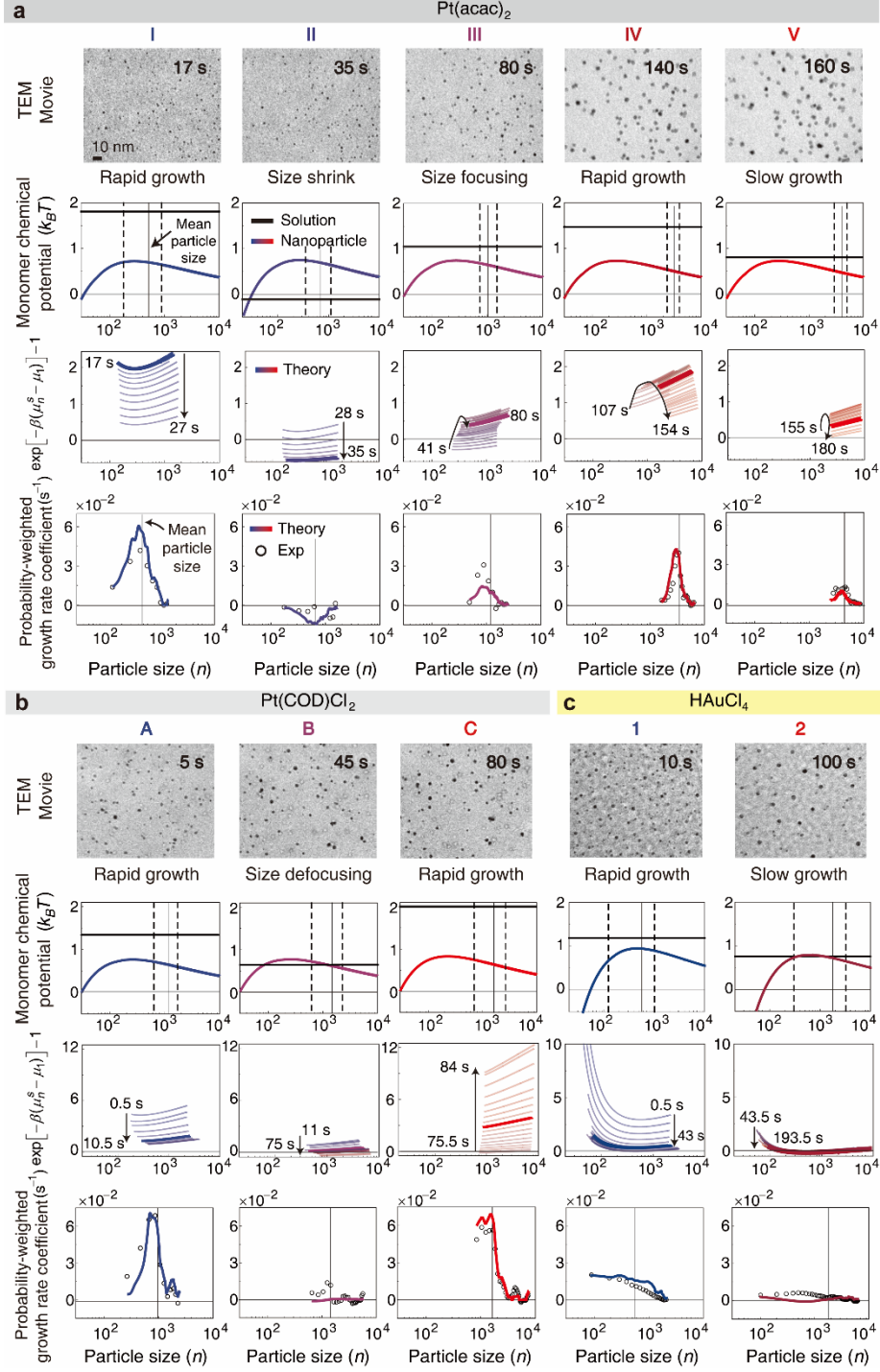


Fig. 3. Phase-dependent dynamics of nanoparticle growth. 1st row: TEM image. 2nd row: Monomer chemical potential, μ_n^s , in nanoparticle phase (colored solid line) and monomer chemical potential, μ_1 , in solution phase (black solid line): the mean particle size (vertical solid line) and error bar (vertical dashed lines). 3rd row: $\exp[-\beta(\mu_n^s - \mu_1(t))]$ with $\beta = 1/k_B T$. $\mu_n^s - \mu_1(t)$ is essentially the same as $\Delta G_r(n \rightarrow n+1) [= -k_B T \times \ln(k_n^a \rho_1 \rho_n / k_{n+1}^d \rho_{n+1})]$ (main text) and is exactly the same as $\Delta G_{n+1} - \Delta G_n (\cong \partial \Delta G_n / \partial n)$,

where ΔG_n denotes the free energy change associated with the formation of an n -mer from n monomers, which has been frequently used in the CNT (see equation (10) in Methods for the precise definition of ΔG_n and Supplementary Fig. 20 for the time-dependent change of ΔG_n for various n). 4th row: Probability-weighted growth rate coefficient, $p_n j_n$: experimental data (circles) and theoretical results (colored lines). p_n and j_n respectively denote the nanoparticle size distribution and growth rate coefficient defined by $j_n \equiv J_n / \rho_n$ [see equation (2) for J_n and ρ_n]. **a,b**, Results for Pt nanoparticles generated from precursor Pt(acac)₂ and from precursor Pt(COD)Cl₂ with a slower monomer supplying rate than Pt(acac)₂. **c**, Results for Au nanoparticles generated from precursor HAuCl₄.

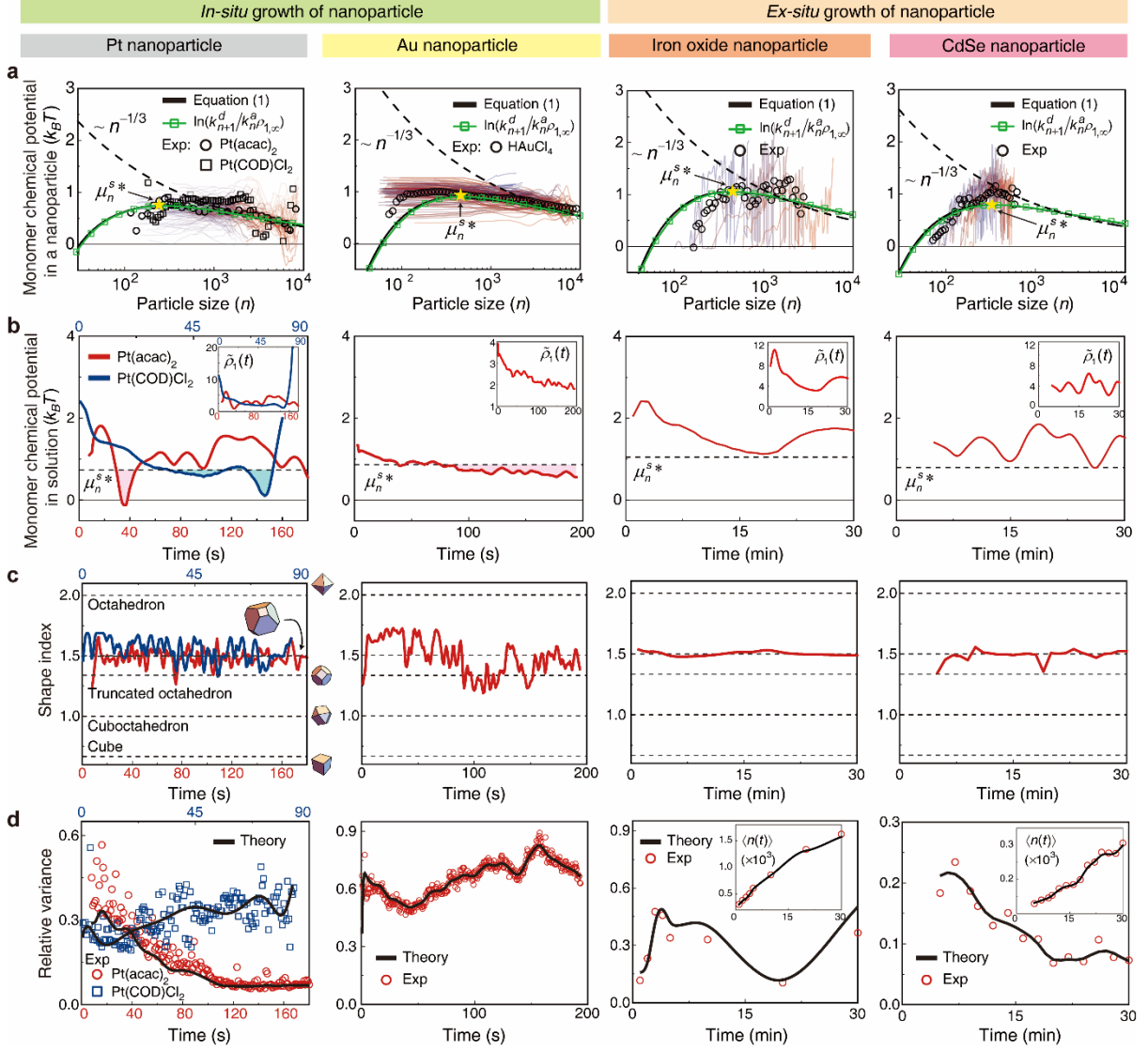


Fig. 4. Physicochemical properties of our colloidal nanoparticle system. Left: Results for *in-situ* growth of platinum nanoparticles (1st column) and gold nanoparticles (2nd column). Right: Results for *ex-situ* growth of iron oxide nanoparticles (3rd column) and CdSe nanoparticles (4th column). **a**, Chemical potential, μ_n^s , in a nanoparticle. The results extracted from the size-dependent growth rate data using equation (2): 1st column: Pt(acac)₂ (circles) and Pt(COD)Cl₂ (squares), and other nanoparticles (circles). The results for individual trajectories at short times (blue thin line) and at long times (red thin line). The result of equation (1) with the optimized parameter values in Supplementary Table 1 (black solid line), which is exactly the same as the logarithm of the ratio between k_{n+1}^d and $k_n^a \rho_{1,\infty}$ (green line with squares). The maximum value, μ_n^{s*} , of the chemical potential at $n = n^*$ is marked by the yellow star: $(n^*, \mu_n^{s*}/k_B T) = (272, 0.74), (481, 0.91), (446, 1.06),$ and $(359, 0.79)$ for platinum, gold, iron oxide, and CdSe nanoparticle systems. The result of the Gibbs-Thomson equation (dashed line). k_n^a , k_{n+1}^d , and $\rho_{1,\infty}$ denote the rate coefficients of monomer association with n -mers and dissociation from $(n+1)$ -mers, and the equilibrium solubility of monomers, respectively. **b**,

Time profile of the chemical potential, μ_1 , in solution extracted from our analysis of the experimental data: 1st column: Pt(acac)₂ (red line) and Pt(COD)Cl₂ (blue line), and the other results (red line). Inset: corresponding supersaturation ratio, $\tilde{\rho}_1(t)$, related to μ_1 by $\mu_1(t) = \mu_\infty^s + k_B T \ln \tilde{\rho}_1(t)$ with μ_∞^s denoting the chemical potential in a macroscopic crystal (Methods). The time profiles of $\tilde{\rho}_1(t)$ for platinum and CdSe nanoparticles show a far more complicated time dependence than those for gold and iron oxide nanoparticles that resembles the LaMer diagram. In **b**, the time region where $\mu_1 \leq \mu_n^{s*}$ (dashed line) is filled with a color: 1st column: platinum from Pt(acac)₂ (pink) and Pt(COD)Cl₂ (cyan), 2nd column: gold (pink). Our *ex-situ* synthesis of iron oxide and CdSe occurs under hypersaturation conditions with $\mu_1 > \mu_n^{s*}$. **c**, Time profile of the nanoparticle shape index extracted from our analysis of the experimental data: 1st column: platinum from Pt(acac)₂ (red line), platinum from Pt(COD)Cl₂ (blue line), and other nanoparticles (red line). Our result indicates that nanoparticles assume a truncated octahedron with shape index about 1.5 throughout our experiment. **d**, Relative variance of nanoparticle size: experimental data: 1st column: platinum from Pt(acac)₂ (red circle), platinum from Pt(COD)Cl₂ (blue square), and other nanoparticles (red circle), and theoretical results (solid line). Inset: Mean sizes for iron oxide and CdSe nanoparticles: theoretical results (lines) and experimental data (circles).

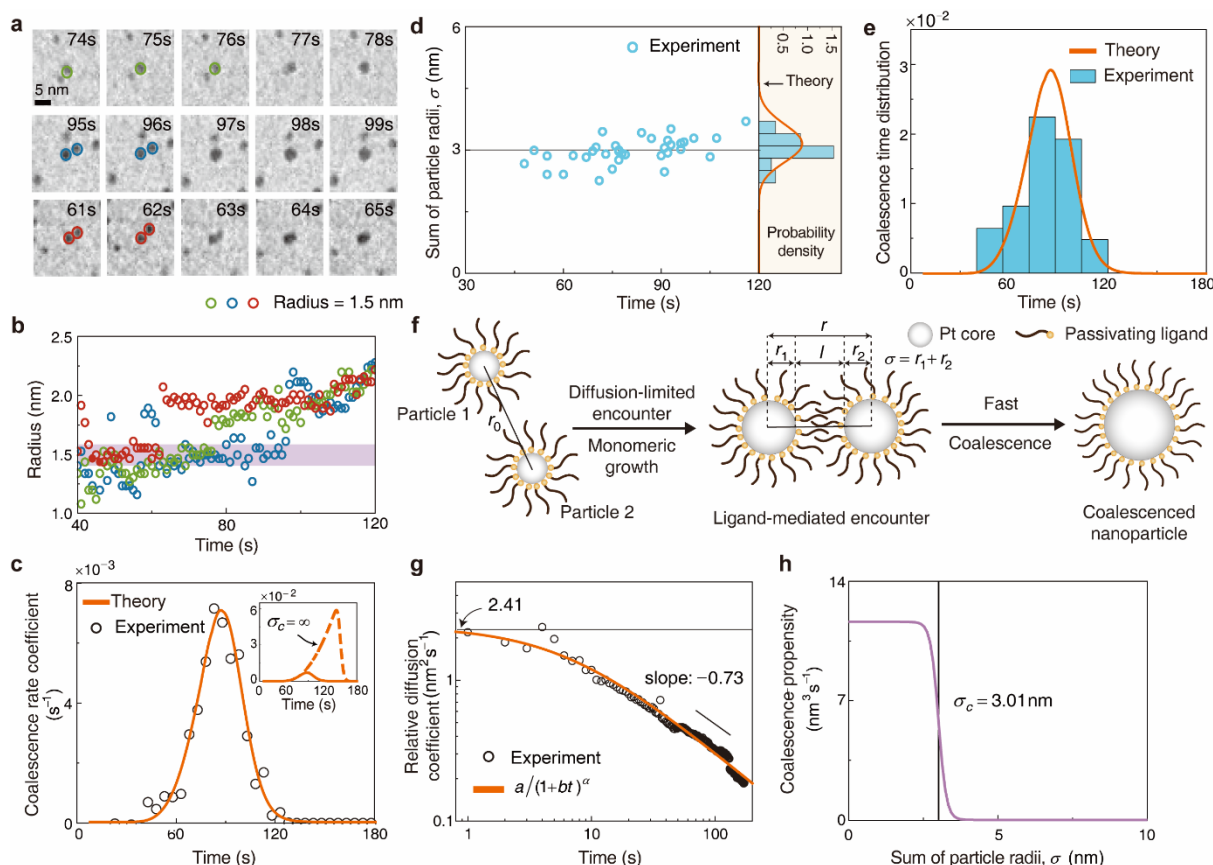


Fig. 5. Frequent coalescence events at a specific nanoparticle size. **a**, TEM images showing three representative coalescence events. Circle: 1.5 nm. Scale bar: 5 nm. **b**, Time-dependent radii of the three nanoparticles shown in a. Coalescence occurs when the nanoparticle radius is about 1.5 nm regardless of coalescing times. **c**, Time-dependent coalescence rate coefficient: theoretical results (solid line) and experimental data (circles). Inset: Coalescence rate coefficient calculated for hypothetical nanoparticle model with a size-independent coalescence propensity (dashed line). **d**, Coalescence times and sum of nanoparticle radii, σ , at each coalescence event (Methods). Right: Probability density of σ : experimental data (bars) and theoretical prediction (solid line). **e**, Coalescence time distribution: theoretical results (solid line) and experimental data (bar). **f**, Schematic of the nanoparticle coalescence process. **g**, Relative diffusion coefficient between a pair of growing nanoparticles. **h**, Size-dependent coalescence propensity extracted from our analysis. The coalescence propensity becomes vanishingly small for nanoparticles with values of σ far greater than 3.0 nm.

Methods

Liquid cell TEM measurement.

For the *in-situ* TEM experiment, we prepared a liquid cell compatible with normal TEM holders. The liquid cell consists of two 100- μm -thick cell bodies, two 25-nm-thick Si_3N_4 windows, and a 100-nm-thick spacer. A precursor solution was prepared by mixing 10 mg of $\text{Pt}(\text{acac})_2$ and 0.1 mL of oleylamine into 0.9 mL of dichlorobenzene, and 0.4 μL of the solution was loaded into the reservoir of the cell. After absorbing the excess solution with filter paper, the liquid cell was sealed with a 600 μm aperture grid using vacuum grease. The growth of the nanoparticles was monitored using JEOL 2010 at an acceleration voltage of 200 kV. The *in-situ* TEM images were obtained at a frame rate of 1 frame per second (fps) with a dose rate of $\sim 1,500\text{ e/s}\cdot\text{\AA}^2$. In Supplementary Video 3 where $\text{Pt}(\text{COD})\text{Cl}_2$ was used as a precursor instead of $\text{Pt}(\text{acac})_2$, the TEM images were recorded at a frame rate of 2 fps to capture initially rapid increases in the nanoparticle. In Supplementary Video 4, a precursor solution was prepared using 0.5 mM of HAuCl_4 and 25 mM of cetyltrimethylammonium bromide (CTAB) ligand with water solvent. The TEM images were recorded at a frame rate of 2 fps.

Image processing.

Image processing was executed using MATLAB code developed by our group to reduce any noise in the TEM images and to generate binarized images for exact assignment of particle size. Gaussian noise in raw TEM images can lead to arbitrary pixels with high contrast, which hampers the generation of binarized images. Therefore, the first step involved applying Gaussian and Wiener filters to remove Gaussian noise. Subsequently, the edge contrast of the particles was enhanced using local Laplacian filtering. Laplacian filtering helps remove insignificant contrast changes and highlight higher contrast changes to improve the accuracy

of particle identification. Finally, the images were binarized with adaptive binarization using the Bradley method²⁹ to correct the background noise in the liquid-phase TEM images. After the binarization procedure, insignificant objects with a size lower than 4 pixels were removed.

Ensemble analysis.

Tracking nanoparticles was performed by comparing correlation factors, F , calculated with the position and size of nanoparticles in a series of TEM images. The correlation factor, F , is defined as $F = (x_{n+1} - x_n)^2 + (y_{n+1} - y_n)^2 + (S_{n+1}^{1/2} - S_n^{1/2})^2$, where x_n , y_n , and S_n respectively denote the x , y coordinates, and area of a nanoparticle at the n th frame. Nanoparticles with the minimum correlation factors in consecutive frames were grouped in the same trajectory. Image drift was corrected using mean displacement of all the tracked particles. The particles moving in and out of the fixed field of view in the *in-situ* TEM movie due to the drift were excluded for further analysis. A watershed algorithm was used to isolate adjacently located particles. The area where the electron beam was strongly irradiated for alignment was excluded from the ensemble analysis, because the area may have different chemical conditions including an unusually high monomer concentration.

Chemicals.

90% oleic acid, 98% $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, 99.8% anhydrous methanol, 99.9% selenium dioxide, and 1-octadecene were purchased from Aldrich. 99.999% cadmium nitrate tetrahydrate, and 99% myristic acid were purchased from Alfa Aesar. Tetrabutylammonium hydroxide (1M solution in methanol) was purchased from Acros. 95% sodium oleate were purchased from TCI. 98% sodium hydroxide was purchased from Samchun. All chemicals were used without further purifications.

Ex situ growth study of iron oxide nanoparticles.

Iron-oleate complexes were synthesized by the two-phase reaction of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and sodium oleate as previously reported⁵. A reaction solution was prepared by dissolving 3.6 g (4 mmol) of the iron-oleate complexes and 1.13 g (4 mmol) of oleic acid in 20 g of 1-octadecene. The solution was degassed at 110 °C, heated to 320 °C at a heating rate of 3.3 °C/min, and aged at 320 °C under an inert atmosphere. Sample aliquots were collected at 1, 2, 3, 4, 5, 10, 20, and 30 min during aging at 320 °C. For purification, 0.1 mL aliquot samples were mixed with 1 mL acetone and 0.1 mL hexane followed and then centrifuged at 13,000 rpm for 5 min. The purification was conducted two times for each sample. We dispersed the aliquot samples in 0.4 mL of hexane and took their TEM image using JEM-2100F (JEOL Inst.) with the magnification of $\times 100,000$ (Supplementary Fig. 21).

Ex situ growth study of cadmium selenide nanoparticles.

Cadmium myristate precursors were synthesized using cadmium nitrate solution and sodium-myristate solution according to the previous literature with some modifications³³. The reaction solution was prepared by dissolving 0.2268 g (0.4 mmol) of cadmium myristate and 0.0444 g (0.4 mmol) of selenium dioxide in 25.2 mL of 1-octadecene. The solution was heated to 220 °C at a heating rate of 10 °C/min and aged at 220 °C in air. Sample aliquots were collected at 5, 7, 9, 10, 12, 14, 16, 18, 20, 22, 24, 26, 28, and 30 min during aging at 220 °C. For purification, 0.2 mL aliquot samples were mixed with 0.6 mL acetone and then centrifuged at 4,000 rpm for 5 min. The purification was conducted one time for each sample. We dispersed the aliquot samples in 1 mL of toluene, measured their absorption using Optizen POP Bio, and took their TEM image using JEM-2010 (JEOL Inst.) with the magnification of $\times 100,000$ (Supplementary Fig. 22).

Estimation of the number of monomers in a nanoparticle.

Quantitative analysis of the sizes of individual nanoparticles was performed by applying our computational algorithm to the binarized images. The size information of the individual particles was obtained by counting the number of pixels in the area that represents the individual particles in the binarized images. The effective radius, r , of a nanoparticle at a given time is calculated from the area of the pixels using the relationship, $r = (S/\pi)^{1/2}$, where S denotes the two-dimensional area of the pixels occupied by the nanoparticle. The number, n , of monomers in the nanoparticle was then estimated as $n \cong (r/\sigma_s)^3 = 4\pi r^3 \rho_s / 3$, exact for a spherical nanoparticle. The discrepancy between the approximate atom number estimated by this formula and the true atom number is small (Supplementary Note 5). Here, the value of the monomer number density, ρ_s , of a platinum nanoparticle is given by $\rho_s = 6.33 \times 10^{21} \text{ nm}^{-3}$ calculated using the mean lattice constant, 3.983 Å, of Pt measured for a few-nanometer-sized Pt particles⁴⁶, which is a little larger than the lattice constant, 3.924 Å, of Pt in the bulk solid phase by ca. 1.5%. The value of the radius, σ_s , corresponding to the effective volume, $\rho_s^{-1} (= 4\pi\sigma_s^3/3)$, per monomer inside a nanoparticle is given by $\sigma_s = 0.156 \text{ nm}$. With the empirical atomic radius, 0.139 nm of Pt, the packing fraction amounts to 0.71, close to the packing fraction, 0.74, of a face-centered cubic lattice, which is the crystal structure of the bulk Pt. For gold nanoparticles, we adopted the σ_s value, 0.159 nm, corresponding to the density of a macroscopic Au crystal. For iron oxide and CdSe nanoparticles, where it is hard to identify a definite chemical composition of a single monomer, the values of σ_s were determined by repeating the optimization procedure of our model to the experimental data for *ex-situ* growth of the two nanoparticles with various values of σ_s , and choosing the best-fitted result: $\sigma_s = 0.350 \text{ nm}$ for iron oxide nanoparticles and $\sigma_s = 0.251 \text{ nm}$ for CdSe nanoparticles.

Derivation of equation (1): the chemical potential of a monomer in a nanoparticle composed of n monomers.

The chemical potential, μ_n^s , of a monomer in a nanoparticle containing n monomers, or an n -mer is related to the Helmholtz free energy, $F_n^s (= -k_B T \ln q_n)$, of a single n -mer as $\mu_n^s = F_{n+1}^s - F_n^s = -k_B T \ln(q_{n+1}/q_n)$. Here, q_n denotes the canonical partition function of a single n -mer in solution. q_n differs from the partition function of a single n -mer in gas phase due to interactions of the nanoparticle with the surrounding environment (Supplementary Note 6); however, q_n can still be decomposed into the translational (q_{trans}), rotational (q_{rot}), vibrational (q_{vib}), electronic (q_{elec}) partition functions, i.e., $q_n = \Omega_n q_{trans}(n) q_{rot}(n) q_{vib}(n) \times q_{elec}(n)$ with Ω_n denoting the configurational degeneracy of an n -mer^{47,48}. Each partition function can be written as a function of n : $q_{trans} \propto n^{3/2}$, $q_{rot} \propto n^{5/2}$, $q_{vib} \propto e^{-\lambda n}$, $q_{elec} \propto q_b^{n_b} q_f^{n_f} q_e^{n_e}$, and $\Omega_n \propto n^\alpha$, leading to

$$q_n = C e^{-\lambda n} n^{4+\alpha} q_b^{n_b} q_f^{n_f} q_e^{n_e} \quad (n \gg 1) \quad (3)$$

with C being the n -independent constant. In equation (3), λ is related to the normalized density, $\tilde{g}(\omega)$, of vibrational states by $\lambda = 3 \int_0^\infty d\omega \tilde{g}(\omega) [\beta \hbar \omega / 2 + \ln(1 - e^{-\beta \hbar \omega})]$ with \hbar being the Planck constant, h , divided by 2π . $\tilde{g}(\omega)$ is normalized such that the whole integration of $\tilde{g}(\omega)$ over vibrational frequency, ω , is equal to unity. We note that an anharmonic contribution to the vibrational partition function can also be accounted for using a suitable density of vibrational states⁴⁹. In equation (3), q_b and $q_f(q_e)$ stand for the electronic partition function of a monomer at a bulk site and a facial (edge) site of an n -mer, respectively.

773 $q_{f(e)}$ is dependent on the microscopic interaction of the nanoparticle face (edge) and the
 774 surrounding environment including ligand and solvent molecules. $n_{b(f \text{ or } e)}$ is the number of
 775 monomers located at bulk (facial or edge) sites, which depends on the size, $n(=n_b+n_f+n_e)$,
 776 and the geometry of a given nanoparticle.

777 We assume that the geometric shape of a nanoparticle is a non-regular truncated
 778 octahedron⁵⁰, whose geometric shape is completely determined by shape index δ . A truncated
 779 octahedron reduces to a regular cuboctahedron when $\delta=1$, a regular truncated octahedron
 780 when $\delta=4/3$, and a regular octahedron in the when $\delta=2$ (Supplementary Fig. 23). We
 781 derive the exact relationship of n_f and n_e to nanoparticle size n and shape index δ
 782 (Supplementary Note 7):

$$783 \quad n_f = \left[8 - 6\delta m - (3\delta^2 - 12\delta + 8)m^2 + \frac{3}{2}(2 - 2/m - \delta)^2 m^2 \Theta(2 - 2/m - \delta) \right] \Theta(m - 2), \quad (4a)$$

$$784 \quad n_e = 12(m - 1)\Theta(m - 1), \quad (1 \leq \delta < 2) \quad (4b)$$

785 where $\Theta(x)$ denotes Heaviside step function defined by $\Theta(x \geq 0) = 1$ and $\Theta(x < 0) = 0$.
 786 See equation (S7-6) for the expression of n_e when $\delta = 2$. From now on, we assume the value
 787 of δ is between 1 and 2. In equation (4), m is the real root of the following cubic equation:

$$788 \quad n = 1 + a_1 m + a_2 m^2 + a_3 m^3, \quad (5)$$

789 where $a_{i \in \{1,2,3\}}$ is a positive-valued function only of δ ($1 \leq \delta \leq 2$), explicitly, $a_1 = \frac{1}{2}\delta + \frac{4}{3}$,
 790 $a_2 = 2 - \frac{3}{4}(2 - \delta)^2$, and $a_3 = \frac{1}{4}(3 + (3 - \delta)^2)\delta - \frac{4}{3}$.

791 When the value of n is large, a simple approximate expression of m can be obtained from
 792 equation (5), which is given by $m \cong (n/a_3)^{1/3} - a_2/3a_3$. When n is greater than 170, the relative

error of this approximate expression for m is less than 1% regardless of the value of δ . Substituting this expression of m into equations (4a) and (4b) and taking the leading terms, we obtain the following analytic expressions of n_f and n_e : $n_f \cong [4 - 3(2 - \delta)^2](n/a_3)^{2/3}$ and $n_e \cong 12(n/a_3)^{1/3}$.

Using equation (3), we obtain the expression of the chemical potential, $\mu_n^s [-k_B T \ln(q_{n+1}/q_n)]$, of a monomer in an n -mer as

$$\beta\mu_n^s = -\ln(e^{-\lambda} q_b) - \Delta n_f \ln \frac{q_f}{q_b} - \Delta n_e \ln \frac{q_e}{q_b} - (4 + \alpha) \ln(1 + \frac{1}{n}), \quad (6)$$

where $\Delta n_{f,e}$ denotes the difference between $n_{f,e}$ of an $(n+1)$ -mer and $n_{f,e}$ of an n -mer, i.e., $\Delta n_{f,e} = n_{f,e}(n+1) - n_{f,e}(n)$. Δn_f and Δn_e decreases with n and vanish in the large n limit. On the r.h.s. of equation (6), the first term is the chemical potential, $\beta\mu_\infty^s$, of monomers in a macroscopic crystal. Equation (6) is essentially the same as equation (1) with $n = (r/\sigma_s)^3$, $\Delta\epsilon_f = -\ln \frac{q_f}{q_b}$ and $\Delta\epsilon_e = -\ln \frac{q_e}{q_b}$ (Supplementary Note 2 for more details). For immobile, perfect spheres free of configurational degeneracy, $\beta\mu_n^s - \beta\mu_\infty^s$ reduces to the Gibbs-Thomson equation, given by $\beta\mu_n^s - \beta\mu_\infty^s = c_1 \sigma_s / r$, shown as the dashed line in the upper panel of Fig. 1d (Supplementary Note 2). However, as long as it moves or has defects, the chemical potential of a monomer deviates from the Gibbs-Thomson equation and has a finite maximum, μ_n^{s*} , at a critical size due to the contribution from the last term on the r.h.s. of equation (1) or (6); for the spherical nanoparticle as well, the absolute size focusing is possible under supersaturation when the monomer chemical potential, μ_l , in solution is lower than μ_n^{s*} .

Free energy change

813 The free energy change, $\Delta G_r(n \rightarrow n+1)$, per association of a monomer with an n -mers
 814 is given by⁵¹

$$815 \quad \Delta G_r(n \rightarrow n+1) = \Delta G_r^\circ(n \rightarrow n+1) + k_B T \ln \frac{\rho_{n+1}/\rho^\circ}{(\rho_n/\rho^\circ)(\rho_1/\rho^\circ)} \quad (7)$$

816 with ρ° denote the density unit. At chemical equilibrium, we have $\Delta G_r(n \rightarrow n+1) = 0$ and

$$817 \quad \Delta G_r^\circ(n \rightarrow n+1) = -k_B T \ln K_{eq}(n \rightarrow n+1) \quad (8)$$

818 with $K_{eq}(n \rightarrow n+1)$ being the equilibrium constant, given by

$$819 \quad K_{eq}(n \rightarrow n+1) = (\rho_{n+1}^{eq}/\rho^\circ)/(\rho_n^{eq}/\rho^\circ)(\rho_1^{eq}/\rho^\circ) = \rho^\circ q_{n+1}^*/q_n^*q_1^* \quad \text{where } q_j^* \text{ denotes } q_j$$

820 divided by system volume⁵². Because of the detailed balance condition, i.e.,

$$821 \quad k_n^a \rho_1^{eq} \rho_n^{eq} = k_{n+1}^d \rho_{n+1}^{eq}, \quad K_{eq}(n \rightarrow n+1) \text{ is the same as } k_n^a \rho^\circ / k_{n+1}^d. \text{ Using this result, equations (7)}$$

822 and (8), we obtain

$$823 \quad \exp[-\beta \Delta G_r(n \rightarrow n+1)] = k_n^a \rho_1 \rho_n / k_{n+1}^d \rho_{n+1} \quad (9)$$

824 in the main text. Whenever the nanoparticle size distribution is continuous, $\Delta G_r(n \rightarrow n+1)$ is

825 essentially the same as $\mu_n^s - \mu_1$ as discussed in the main text. μ_1 denotes the chemical

826 potential of monomers in solution, given by $\mu_1 = -k_B T \ln(q_1^*/\rho_1)$ with ρ_1 and q_1^* being the

827 number density and the volume-scaled partition function of a monomer in the solution phase,

828 respectively.

829 $\Delta G_r(n \rightarrow n+1)$ or $\mu_n^s - \mu_1$ is the same as $\Delta G_{n+1} - \Delta G_n$ where ΔG_n denote the free

830 energy change, associated with the formation of an n -mer from n monomers in solution phase,

831 often discussed in the CNT. ΔG_n is given by $\Delta G_n = F_n^s - n\mu_1$ ¹⁵, where μ_1 . Substituting

equation (3) into this definition, we obtain

$$\beta\Delta G_n = -\ln C - n_f \ln \frac{q_f}{q_b} - n_e \ln \frac{q_e}{q_b} - (4 + \alpha) \ln n - n \ln \frac{\rho_1}{\rho_{1,\infty}}, \quad (10)$$

where $\rho_{1,\infty}$ denotes the monomer solubility, or the concentration of monomers in the solution phase that are in equilibrium with the macroscopic crystal. On the r.h.s. of equation (10), $-4 \ln n$ and $-\alpha \ln n$ in the fourth term respectively originate from $-\ln[q_{trans}(n)q_{rot}(n)]$ and $-\ln \Omega_n$, noting that $q_{trans} \propto n^{3/2}$, $q_{rot} \propto n^{5/2}$, and $\Omega_n \propto n^\alpha$; the differentiation of the free energy term, $-(4 + \alpha) \ln n$, with respect to n yields $-(4 + \alpha)/n$, which is equivalent to the last term on the r.h.s. of equation (1) when n is large enough such that $\ln(1 + n^{-1}) \cong n^{-1}$. $\rho_{1,\infty}$ is determined by equating the monomer chemical potentials, $\beta\mu_1[-\ln(q_1^*/\rho_1)]$ and $\beta\mu_{n \rightarrow \infty}^s[-\ln(e^{-\lambda} q_b)]$, yielding $\rho_{1,\infty} = e^\lambda q_1^*/q_b$. The monomer concentration, ρ_1 , scaled by $\rho_{1,\infty}$ corresponds to the degree of supersaturation, $\tilde{\rho}_1$, i.e., $\tilde{\rho}_1 = \rho_1/\rho_{1,\infty}$. Equation (10) reduces to the corresponding equations in refs ^{15,42} when the numbers, n_f and n_e , of facial and edge monomers are directly proportional to $n^{2/3}$ and $n^{1/3}$, respectively. In Fig. 1d, we show the dependence of $\beta\mu_n^s - \beta\mu_\infty^s$ and $\beta\Delta G_n + \ln C$ on the nanoparticle radius, r , using equations (6) and (10) with $n = (r/\sigma_s)^3$. For immobile, perfect spheres free of configurational degeneracy, $\beta\Delta G_n + \ln C$ is given by $\beta\mu_n^s - \beta\mu_\infty^s = c_1 \sigma_s / r \beta\Delta G_n + \ln C$, shown in Fig. 1d (see Supplementary Note 2 for the details).

Derivation of equations (2): nanoparticle ensemble growth dynamics through monomer association.

The nonequilibrium chemical dynamics of an ensemble of growing particles can be explained

852 by the well-known hierarchical kinetic equations:

$$853 \quad \partial_t \rho_n(t) = J_{n-1}(t) - J_n(t) \quad (n \geq 1) \quad (11)$$

854 with J_n being the growth rate of n -mers. $J_0(t)$ is related to all of the other $J_{n(\geq 1)}$'s by

$$855 \quad J_0 = \partial_t \rho_{1,T}(t) - \sum_{n=1}^{\infty} J_n, \text{ where } \rho_{1,T} \text{ denotes the total monomer density defined by}$$

$$856 \quad \rho_{1,T}(t) = \sum_{n=1}^{\infty} n \rho_n(t) \text{ with } \rho_n(t) \text{ denoting the number density of } n\text{-mers. Note that}$$

$$857 \quad J_n(t) = \partial_t \psi_{n+1}^d(t) \text{ is directly related to the time derivative of the cumulative density, } \psi_n^d(t)$$

$$858 \quad \left[\equiv \sum_{k=n}^{\infty} \rho_k(t) \right] \text{ by } J_n(t) = \partial_t \psi_{n+1}^d(t). \text{ When the total density of the nanoparticles,}$$

$$859 \quad \rho_c \left[\equiv \sum_{i=1}^{\infty} \rho_i \right] \text{ slowly varies over time, the following equations can be obtained from equation}$$

860 (11) (Supplementary Note 3):

$$861 \quad \partial_t \langle n(t) \rangle = \langle j_n(t) \rangle, \quad (12a)$$

$$862 \quad \partial_t \sigma_n^2(t) = \partial_t \langle n(t) \rangle + 2 \langle \delta n(t) \delta j_n(t) \rangle, \quad (12b)$$

863 where $\langle x_n \rangle$ and j_n denote $\langle x_n \rangle = \sum_{n=1}^{\infty} x_n \rho_n / \rho_c$ and $j_n = J_n / \rho_n$, respectively. In

864 equation (12b), the cross correlation, $\langle \delta n(t) \delta j_n(t) \rangle$, between n and j_n is defined by

$$865 \quad \langle \delta n(t) \delta j_n(t) \rangle = \langle n(t) j_n(t) \rangle - \langle n(t) \rangle \langle j_n(t) \rangle. \text{ Integrating equation (12b) with respect to time from}$$

866 t_0 to t and rearranging the resulting equation, we can obtain the following equation for the

$$867 \quad \text{relative variance, } \eta_n^2(t) \left(= \sigma_n^2(t) / \langle n(t) \rangle^2 \right), \text{ when the mean-scaled correlation, } \langle \delta \tilde{n}(t) \delta \tilde{j}_n(t) \rangle$$

$$868 \quad \left[= \langle \delta n(t) \delta j_n(t) \rangle / \langle n(t) \rangle \langle j_n(t) \rangle \right] \text{ assumes its steady-state value:}$$

$$869 \quad \eta_n^2(t) \cong \langle n(t) \rangle^{-1} + f(t_0) \left(\langle n(t_0) \rangle / \langle n(t) \rangle \right)^2 + \eta_n^2(\infty) \left[1 - \left(\langle n(t_0) \rangle / \langle n(t) \rangle \right)^2 \right], \quad (t > t_0) \quad (13)$$

870 where $f(t_0)$ denotes non-Poisson noise defined by $f(t_0) = \eta_n^2(t_0) - \langle n(t_0) \rangle^{-1}$. $\eta_n^2(\infty)$
871 denotes the steady-state value of $\eta_n^2(t)$, which is the same as the steady-state value of
872 $\langle \delta \tilde{n}(t) \delta \tilde{j}_n(t) \rangle$ (Supplementary Note 3 and Supplementary Fig. 24). In Supplementary Note 3,
873 we present the generalization of equations (12) and (13) for the case where $\rho_c(t)$ quickly
874 varies over time.

875 The accurate expression of J_n is complex when monomer association with
876 nanoparticles is a reversible diffusion-influenced reaction³², which is a non-Markov process
877 whose rate at a given time depends on the history of nanoparticle densities. However, when the
878 reversibility of monomer association with nanoparticles is small, J_n can be approximated by
879 the following simple formula:

$$880 \quad J_n(t) \cong k_n^a \rho_1(t) \rho_n(t) - k_{n+1}^d \rho_{n+1}(t) \quad (n \geq 1), \quad (14)$$

881 where k_n^a and k_{n+1}^d are the steady-state rate coefficients of the association reaction between
882 a monomer and an n -mer to form an $(n+1)$ -mer and the dissociation reaction of an $(n+1)$ -mer
883 into a monomer and an n -mer, respectively. Assuming that the reversibility of monomer
884 association with the nanoparticle is small, we use a generalization of the Collins-Kimball
885 formula³¹ to obtain k_n^a for monomer association with non-spherical nanoparticles, which is
886 given by

$$887 \quad k_n^a \cong \frac{A_n \kappa_a \cdot A_n D_1 / r}{A_n \kappa_a + A_n D_1 / r} = 4\pi \sigma_s^2 \kappa_a \frac{c_\delta n^{2/3}}{1 + \frac{\kappa_a \sigma_s}{D_1} n^{1/3}}, \quad (15)$$

888 where κ_a and D_1 respectively denote the bimolecular association rate parameter and the
889 monomer diffusion coefficient. In equation (15), A_n denotes the surface area of the n -mer,

which is related to the effective nanoparticle radius, $r = \sigma_s n^{1/3}$, by $A_n = 4\pi r^2 c_\delta$, where the shape factor, c_δ , is related to the shape index, δ , by (Supplementary Note 8)

$$c_\delta = \frac{3(3^{1/2} - 1)(4 - \delta)\delta + 12 - 8 \cdot 3^{1/2}}{\pi^{1/3}(3\delta^3 - 18\delta^2 + 36\delta - 16)^{2/3}}. \quad (16)$$

k_n^a and k_{n+1}^d satisfy the detailed balance condition, $J_n = 0$ at equilibrium, or $k_n^a/k_{n+1}^d = q_{n+1}^*/q_n^* q_1^*$. Substituting the following expressions for the chemical potentials: $\exp(-\beta\mu_n^s) = q_{n+1}/q_n$ and $\exp[\beta\mu_1(t)] = \rho_1(t)/q_1^*$ into this detailed balance condition, we obtain $k_n^a = k_{n+1}^d \exp[-\beta(\mu_n^s - \mu_1(t))]/\rho_1(t)$. Using this equation, we can rewrite equation (14) as equation (2).

Quantitative analysis of nanoparticle growth data.

It is not easy to measure the absolute number densities, $\{\rho_n(t)\}$, of nanoparticles from our experimental data. However, we can measure the probability distributions, $\{p_n(t) \equiv \rho_n(t)/\rho_c(t)\}$, of nanoparticle size and the associated cumulative probability $\psi_n^p(t) \equiv \sum_{k=n}^{\infty} p_k(t)$, or the probability that a nanoparticle contains n or more monomers at time t . We can derive the hierarchical kinetic equations, (S4-1) for $\psi_n^p(t)$ from equations (11) (14) (Supplementary Note 4). In addition, we also derive a general relationship, equation (S3-14), between the mean and variance of the nanoparticle size (Supplementary Note 3). By comparing equations (S4-1) and (S3-14) with our experimental data for $\partial_t \psi_n^p(t)$ and $\sigma_n^2(t)$, we extracted the values of the adjustable parameters (Supplementary Note 4). The optimized values of the five time-independent adjustable parameters are presented in Supplementary Table 1 for each of the nanoparticle systems we investigated. The time profiles of the remaining

two time-dependent parameters, the degree, $\tilde{\rho}_1(t)$, of supersaturation and the shape index, $\delta(t)$, are presented in Fig. 4b,c, respectively, for each system.

Approximate analytic expression of nanoparticle size distribution.

We found that, at all times, the experimental results for the nanoparticle size distribution, $p_n(t)$, can be represented by the following formula:

$$p_n(t) \cong \frac{1}{(2\pi a_2^2)^{1/2}} e^{-(\ln n - a_1)^2 / 2a_2^2} \sum_{k=0}^{k_{\max}=6} b_k n^k, \quad (17)$$

which is a corrected version of a log-normal distribution⁵³. The values of parameters, a_1 , a_2 , and $\{b_0, b_1, \dots, b_6\}$, were calculated from our theory, i.e., by requiring the first six moments of the nanoparticle size, calculated for our optimized model, to be the same as those of equation (17). With the optimized values of the adjustable parameters at hand, we can easily calculate the higher-order moments, $\langle n^q(t) \rangle$ ($q \geq 3$), using equation (S3-12), the analytical expression of $\langle n^q(t) \rangle$ (Supplementary Note 3). This theoretical prediction is in good agreement with the experimental results for these higher moments $\langle n^q(t) \rangle$ ($3 \leq q \leq 6$) at all times (Supplementary Fig. 25). In addition, the results of equation (17) are in excellent agreement with the experimentally measured size distributions, as shown in Fig. 2. The agreement between theoretical prediction and experimental results for the higher order moments of nanoparticle size and the nanoparticle size distribution demonstrates that our optimized model is robust and can be used to predict various experimental results that are not used for model optimization (see also Supplementary Fig. 26 for how sensitive the resulting model is to variations in adjustable parameter values).

Dynamics of coalescence between nanoparticles undergoing monomeric growth.

To obtain the mathematical description of our coalescence model, we extended Lee and Karplus's reduced distribution function formalism for diffusion-influenced reactions between molecules to describe diffusion-influenced reactions between growing nanoparticles^{32,40}. According to this generalization, the nonequilibrium pair correlation between growing nanoparticles undergoing coalescence satisfies the following reaction-diffusion equation:

$$\partial_t \rho(r, t) = D_r(t) \frac{1}{r} \partial_r^2 (r \rho(r, t)) - \kappa_{\bar{\sigma}(t)} S_{\bar{\sigma}(t)}(r) \rho(r, t), \quad (18)$$

where $\rho(r, t)$ denotes the nonequilibrium pair correlation function for a pair of nanoparticles separated by distance r at time t . In equation (18), the relative diffusion coefficient, $D_r(t)$, depends on time t because the mean nanoparticle size, inversely proportional to the diffusion coefficient, increases with time in our experiment. Here, the time profile of $D_r(t)$ was obtained from the experimental data by dividing the ensemble-averaged variance of the relative displacement, $\Delta \mathbf{r}_{ij}(t) \left[= \mathbf{r}_{ij}(t + t_0) - \mathbf{r}_{ij}(t_0) \right]$, in the two-dimensional TEM image by $4t$, where \mathbf{r}_{ij} is the relative position vector, $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$, with \mathbf{r}_i and \mathbf{r}_j indicating the positions of the i th and j th nanoparticles (Fig. 5g).

Ligand-passivated nanoparticles form an encounter pair, with a ligand-mediated nanoparticle contact, and then undergo fast coalescence. Here, the nanoparticle contact distance is given by the sum of the thickness, l , of the double ligand layer and the two metal core radii of the nanoparticles in the encounter pair. We denote the sum of the two metal core radii as σ . In equation (18), κ_σ and $S_\sigma(r)$ respectively denote the σ -dependent coalescence propensity and the reaction sink function accounting for the coalescence rate depending on the nanoparticle separation; they are explicitly given by

$$\kappa_{\sigma} = \frac{\kappa}{e^{\gamma(\sigma-\sigma_c)} + 1}, \quad (19a)$$

$$S_{\sigma}(r) = e^{-(r-\sigma-l)^2/2v}, \quad (19b)$$

with κ , γ , and v being constants. κ_{σ} , given in equation (19a), becomes vanishingly small when σ is much larger than the most probable core-core contact distance, σ_c , right before coalescence (Fig. 5d,h). In equation (19b), $S_{\sigma}(r)$ is the bell-shaped function centered on the contact separation, $\sigma + l$, between nanoparticles in the encounter pair. In equation (18), we have used the mean time-profile, $\bar{\sigma}(t)$, of the nanoparticle core-core contact distance, effectively accounting for the monomeric growth of the nanoparticle size (Supplementary Fig. 27).

For a given set of the adjustable parameters, equation (18) can be numerically solved with the reflecting boundary condition, $\partial_r \rho(r, t) = 0$, at the moving boundary, $r = \bar{\sigma}(t)$, and the initial condition, $\rho(r, t = 0) = \Theta(r - r_c)$ with $\Theta(x)$ denoting the unit step function defined by $\Theta(x \geq 0) = 1$ and $\Theta(x < 0) = 0$, which assumes that the initial distance between nanoparticles is larger than the cutoff distance, r_c (Supplementary Note 9 and Supplementary Fig. 28). With $\rho(r, t)$ at hand, we can obtain the coalescence rate coefficient,

$$k_f(t) = \int_{\sigma(t)}^{\infty} dr 4\pi r^2 \kappa_{\bar{\sigma}(t)} S_{\bar{\sigma}(t)}(r) \rho(r, t). \quad (20)$$

and the time dependent density of nanoparticles (Supplementary Note 10). By comparing the theoretical results with the experimental data for the time dependent density of nanoparticles, we determined the optimized values of the adjustable parameters (Supplementary Fig. 29 and Supplementary Table 2). The resulting profiles of the scaled coalescence propensity,

$\kappa_{\sigma}\rho_{c,T}(t_0)$, and the scaled coalescence rate coefficient, $k_f(t)\rho_{c,T}(t_0)$, with $\rho_{c,T}(t_0)$ denoting the total nanoparticle density at initial time t_0 , are presented in Fig. 5h, c, respectively.

Finally, the distribution, $\psi(t)$, of the coalescence time presented in Fig. 5e can be calculated from the time profile of $k_f(t)\rho_{c,T}(t_0)$ given in Fig. 5c (Supplementary Note 11). In addition, from the time profile of $\psi(t)$, the distribution of the core-core contact distance right before coalescence can be estimated. Our theoretical result for the distribution of the core-core contact distance right before coalescence, presented in Fig. 5d, was calculated with the time profile of $\psi(t)$ in Fig. 5e (Supplementary Note 11 for more details).

Data availability

All data used in the current research are available upon request to the corresponding authors.

Code availability

The MATLAB code and the Mathematica code used for our data analysis can be found at <https://>

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Author contributions

J.-H.K., J.K., B.H.K., and S.S contributed equally to this work. B.H.K., J.K., S.J., W.C.L., T.H., and J.P. planned the experimental portion of the research. J.-H.K., S.S., and J.S. planned the theoretical portion of the research. B.H.K., Y.S., and J.P. captured the TEM movies. J.K. conducted the image binarization. J.K., J.J., and K.P. conducted the particle tracking. B.H.K., J.K., H.C., and J.W.J. conducted *ex-situ* experiments. B.H.K., J.K., S.J., H.C., B.H., W.C.L., and J.P. conducted the analysis of experimental data. J.S., J.-H.K., and S.S. developed the model of a nanoparticle. J.S. developed the theory explaining nucleation, size-focusing, and defocusing of an ensemble of nanoparticles. J.S., J.-H.K., and S.S developed the theory explaining growth dynamics of an ensemble of nanoparticles. J.S. and J.-H.K. developed the analysis methods of the experimental data. S.S., Jingyu K., M.L. and J.-H.K. performed the quantitative analysis of the experimental data. J.S., J.-H. K., J.K., B.H.K., S.S., T.H.H, and J.P. wrote the manuscript. T.H.H. and J.P. supervised the experimental research. J.S. supervised the theoretical research. All authors contributed to the discussion of results.

1017 **Competing financial interests**

1018 The authors declare no competing financial interests.

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1020 **Additional information**

1021 Supplementary information is available in the online version of this paper. Correspondence

1022 regarding the experiment should be addressed to T.H. and J.P. and correspondence regarding

1023 the theory and analysis to J.S.

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