

Supporting Information

A Generalized Model for Nano- and Submicron Particle Formation in Liquid Phase, incorporating Reaction Kinetics and Hydrodynamic Interaction: Experiment, Modeling and Simulation

Vivekananda Bal, Rajdip Bandyopadhyaya *

Department of Chemical Engineering, Indian Institute of Technology Bombay,
Powai, Mumbai 400076, India.

* Corresponding author (rajdip@che.iitb.ac.in)

S1. Reaction kinetics

Reaction kinetics plays an important role by directly controlling formation of growth units. For very fast reaction kinetics, reaction is not rate limiting and therefore, successive events responsible for the particle formation are comparatively less affected. When the rate of formation of SiO₂ growth units is slow, then successive events like nucleation and diffusion growth, are affected forthright, whereas events like coagulation and OR are indirectly affected. This necessitates the importance of modeling reaction kinetics in the particle formation model. Reaction kinetics for SiO₂ nanoparticle synthesis from tetraethyl orthosilicate has been derived from our own experiments. We find that overall reaction rate is third order: first order with respect to TEOS, while approximately first order with respect to water and ammonia each. This is in good agreement with the expression obtained by Giesche¹ and the corresponding rate expression (Giesche¹) is given as

$$\frac{dc_{SiO_2}}{dt} = kc_{H_2O}^{1.18}c_{NH_3}^{0.97}c_{TEOS} \quad (1)$$

where, c_{SiO_2} , c_{H_2O} , c_{NH_3} and c_{TEOS} are bulk concentrations of SiO₂, water, ammonia and tetraethyl ortho-silicate, respectively. k is the reaction rate constant. The values of rate constant obtained from our experiment at higher temperature are comparable to that obtained by Giesche,¹ whereas, at low temperature, rate constant values are found to follow the experimental findings of van Blaaderen,² which show comparatively lower values of rate constant.

To briefly describe our procedure of estimating reaction kinetics, it consists of two steps: estimation of concentration of each reactant at certain time intervals and then multivariate regression analysis to develop rate kinetic expression.

- i) In order to calculate the concentration of reactants at different time intervals, sample was collected from reaction mixture and then total mass of silica formed was obtained by following the procedure mentioned in the section S10.

- ii) Once total mass of silica formed was obtained at different time intervals, the corresponding mass of reactants consumed is back calculated from stoichiometry of the reaction.
- iii) This enables us to calculate the concentration of reactants and silica formed at different time, as the initial concentration of reactants are known.
- iv) Thereafter, we calculated the rate of formation of silica at different time intervals by simply dividing change in silica concentration by corresponding time interval.
- v) This gives a subset of data for dc/dt as a function of concentration of reactants.
- vi) This procedure of calculation of concentration of reactants and products at different reaction times was repeated by varying initial concentration of each reactant, while keeping initial concentration of other reactants constant.
- vii) This way, we obtain a large set of dc/dt vs. concentrations at different reaction conditions, at a constant temperature. Next, we performed multivariate regression analysis with this data set in Matlab, to obtain expression of reaction kinetics. Here, rate of formation of silica, dc/dt forms a response variable (Y) and reactants form predictor variables (X_i).

$$Y = \alpha c_{NH_3}^{\beta_1} c_{TEOS}^{\beta_2} c_{H_2O}^{\beta_3} \quad (2)$$

α and β values obtained for different experimental conditions has been given in table S1 below

Table S1: α and β values obtained for different experimental conditions

Experiment	α (mole dm ⁻³) ^{-2.15}	α form literature (mole dm ⁻³) ^{-2.15}	β_1	β_2	β_3
Set 1a (T=293 K)	9.46×10^{-7}	1.09×10^{-6} (Blaaderen et al. ²)	0.956	0.99	1.2
Set 2b (T=305 K)	8.318×10^{-5}	8.18×10^{-5} (Giesche ¹)	0.983	1.01	1.19

The adjusted R_{adj}^2 (coefficient of determination) value for the regression analysis is 0.98. The 95% confidence interval for the regression coefficients are as follows S2

Table S2: Confidence interval (CI) for regression coefficients

Parameter	Confidence interval (CI)
$A (T=293\text{ K})$	$9.46 \times 10^{-7} \pm 0.5$
β_1	0.956 ± 0.023
β_2	0.99 ± 0.03
β_3	1.2 ± 0.031

S2. Nucleation

Nucleation takes place when concentration of growth unit exceeds the saturation solubility. Since there are no seed particles or foreign particles present in the medium, classical theory of homogeneous nucleation³⁻⁴ can be used to model the nucleation rate as

$$n_0 = A \exp \left[- \frac{16\pi\sigma^3 v_m^2}{3(k_B T)^3 (\ln S)^2} \right] \quad (3)$$

where, A is the pre exponential factor, whose value is taken to be 10^{32} , consistent with that for a sparingly soluble material, reported in literature.⁵ σ is the interfacial tension of silica-alcohol system, which is taken as 0.1 J/m^2 , v_m is the molecular volume of SiO_2 . $S = c_{\text{SiO}_2} / c_{\text{SiO}_2,s}$ is the supersaturation of SiO_2 in the liquid phase, where, $c_{\text{SiO}_2,s}$ is the solubility of SiO_2 . Number of molecules in the nuclei may vary from 2-6.⁶ In the present simulation, nuclei (r_{cn}) are assumed to be formed by a cluster of two molecules.

S2.1 Reason of taking stable critical nucleus of 2 molecules

Now, according to the classical nucleation theory, for nucleation of a transient cluster of molecules to take place, the cluster must overcome the activation energy barrier given by the maximum in the total Gibbs free energy change with respect to cluster radius (i. e. $dG/dr = 0$, at free energy maximum). The corresponding critical nucleus radius (r_{cn}) is given as:

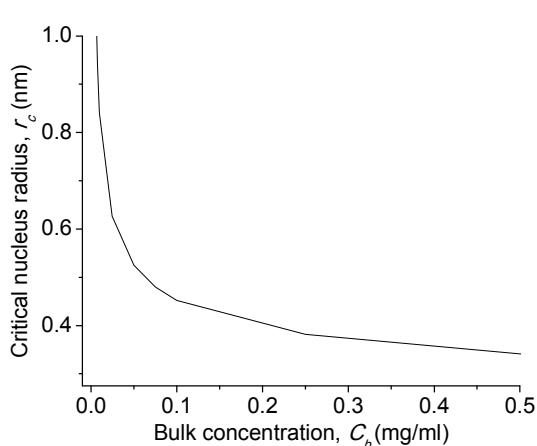
$$r_{cn} = \frac{2\sigma v_m}{kT \ln S} \quad (4)$$

where, σ is the interfacial tension, v_m is the molecular volume, S is the supersaturation level ($c_b/c_{SiO_2,s}$) and A is the pre-exponential factor. Therefore, critical nucleus radius (from eq. 4) will be inversely proportional to logarithm of silica concentration. When concentration reaches close to bulk solubility, critical nucleus radius reaches its largest value.

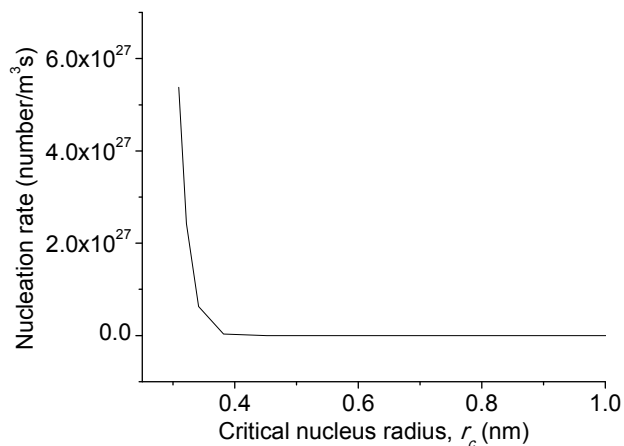
Typically, for the experimental bulk concentration values of silica product-molecules in this case, use of eq. 4 gives a critical nucleus radius corresponding to a fractional number of silica molecules. Since, a fractional number of molecules in a cluster is unrealistic, so we have used the minimum integral number of molecules required to form a stable cluster (i. e. a nucleus) to be consisting of two molecules. Therefore, in our simulation, we have used the silica nucleus to be of two molecules, which corresponds to a critical nucleus radius of 0.29 nm. In section S2 of supplementary material and section 2.3.1 (nucleation) of the main manuscript, we have mentioned that, in the present calculation, we have considered a stable nucleus to be consisting of two molecules, throughout the whole computation.

Now, one can argue that, number of molecules could be any integer number more than two. This has been explained next.

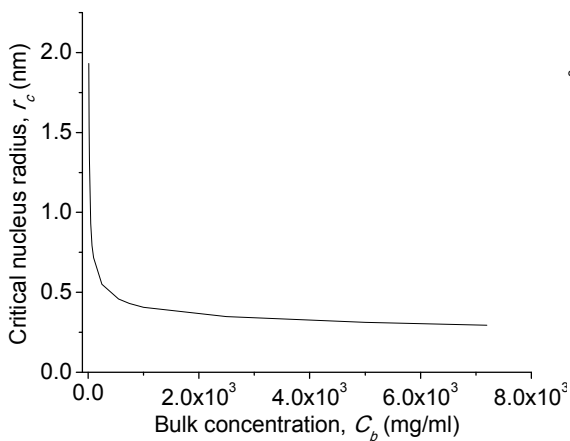
To make it more explicit, let us consider two experimental conditions, set 1a and set 2b, as mentioned in section 5 (experimental section) of the main manuscript and section S6 of supporting information. The values of critical nucleus radius calculated from eq. 4 as a function of bulk concentration (fig. 1a and fig. 1c for set 1a and set 2b, respectively) and corresponding values of nucleation rate calculated from eq. 3 as a function of critical nucleus radius (fig. 1b and fig. 1d for set 1a and set 2b, respectively) are shown in figure 1.



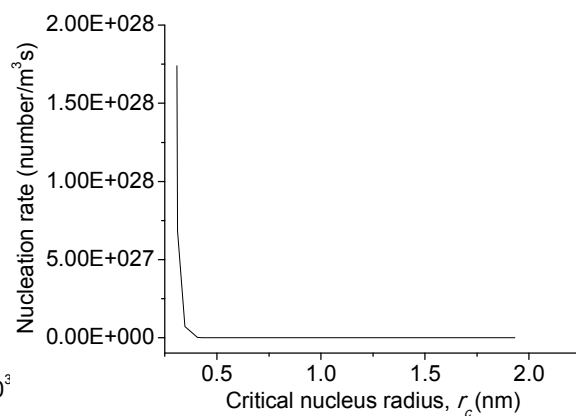
(a)



(b)



(c)



(d)

Fig. S1: (a) Variation of critical radius as a function of bulk concentration (set 1a; saturation solubility, $C_s = 0.00069$ mg/ml) and (b) corresponding nucleation rate as a function of critical radius (set 1a). (c) Variation of critical radius as a function of bulk concentration (set 2b, saturation solubility, $C_s = 4.9$ mg/ml) and (d) corresponding nucleation rate as a function of critical radius (set 2b).

It is observed that, as supersaturation decreases, critical nucleus radius increases, so the nucleation rate decreases. In this particular case, figure 1 shows that, critical nucleus radius can increase from 0.29 nm (2 molecules) to a maximum of up to ~ 0.57 nm (13 molecules), since the

corresponding nucleation rate falls from about $10^{27} \text{ m}^{-3} \text{ s}^{-1}$ down to almost zero, implying critical nucleus can vary from 2-13 molecules. However, whether the critical nucleus is 2 or 13 molecules or some other number in between them (with corresponding radius of 0.29 nm or 0.57 nm or in-between), does not matter, since the final particle diameter of 45 nm or 340 nm is far bigger, consisting of millions or more molecules. It implies that the initial critical nucleus radius has hardly any implication on the final particle diameter, the latter being dominated by the various particle growth mechanisms. This justifies our simplifying assumption of critical nuclei of constant radius of 0.29 nm (with two molecules) throughout the synthesis-time.

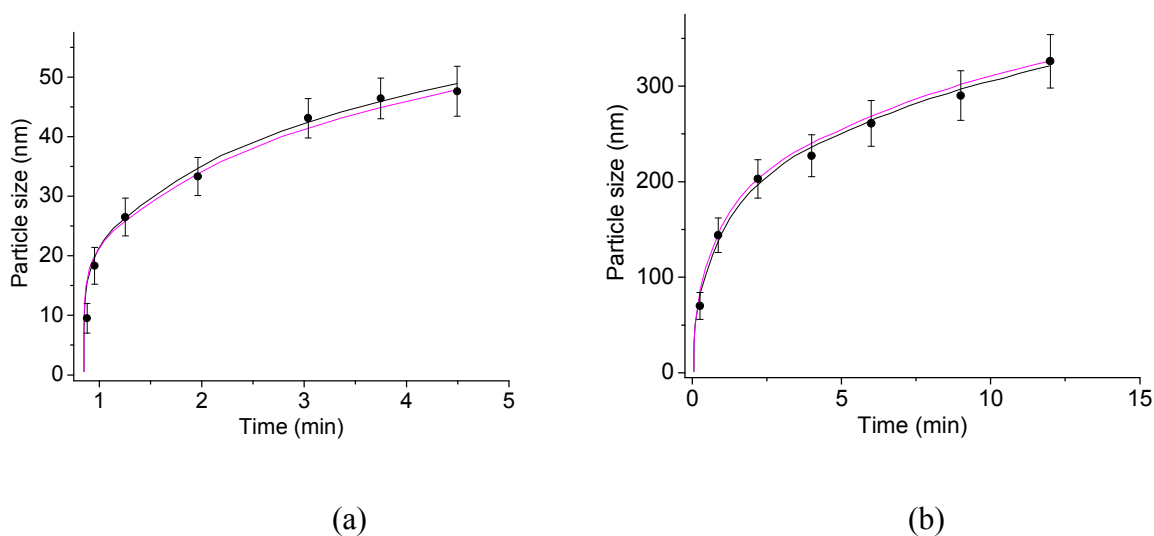


Fig. S2: (a) set 1a and (b) set 2b. Experimental data: symbol (•). Simulation curves: With constant stable critical nucleus radius of 0.29 nm (—) and with variable critical nucleus size (—).

Finally, to ensure the validity of our assumption of constant, critical nucleus of radius 0.29 nm, full scale simulations have been performed in the above mentioned two experimental conditions (exp set 1a and set 2b), by including an additional case of variable critical nucleus radius (eq. 1). This was compared with our base-case simulation results with a critical nucleus of radius 0.29 nm (i. e. nucleus with 2 molecules). The corresponding simulation results have been shown in figure 2a for set 1a and figure 2b for set 2b. In both these cases, simulation results with variable critical nucleus radius or our base-case (with critical nucleus of 2 molecules) do not show any statistically significant variation from one another, in comparison to the larger

experimental error bars. This proves that, initial choice of critical nucleus size does not affect the temporal evolution of the particle size, as also the final particle size; precisely because the overall particle formation phenomena is dependent on many other events too. Hence, this completely justifies our assumption of a constant critical nucleus of two molecules.

S2.2 Reason of selecting pre-exponential factor (A) of value $10^{32} \text{ m}^{-3}\text{s}^{-1}$

In the present calculation, value of pre-exponential factor (A) has been taken as $1 \times 10^{32} \text{ m}^{-3}\text{s}^{-1}$. Literature^{5, 7-12} suggests that, value of pre-exponential factor for insoluble material generally varies in the range of 10^{30} to $10^{36} \text{ m}^{-3}\text{s}^{-1}$. For a highly insoluble material¹³ like BaSO_4 (solubility $\sim 10^{-5} \text{ M}$), A is generally taken as $10^{33-36} \text{ m}^{-3}\text{s}^{-1}$, in which case nucleation rate is very fast, due to the extremely high supersaturation level because of quasi-instantaneous nature of the reaction^{11,14}. Similarly, in case of Fe_3O_4 and ZnO (practically insoluble in water, solubility $\sim 10^{-5} \text{ M}$) in many of the previous studies^{6, 15}, value of A has been taken as 10^{34} , which successfully predicted nanoparticle size and distribution with complete experimental validation. Since amorphous silica is having relatively higher solubility¹⁶⁻¹⁷ (solubility $\sim 10^{-4} \text{ M}$), we have taken the value of A to be $10^{32} \text{ m}^{-3}\text{s}^{-1}$. This is found to predict all our experimental data very nicely.

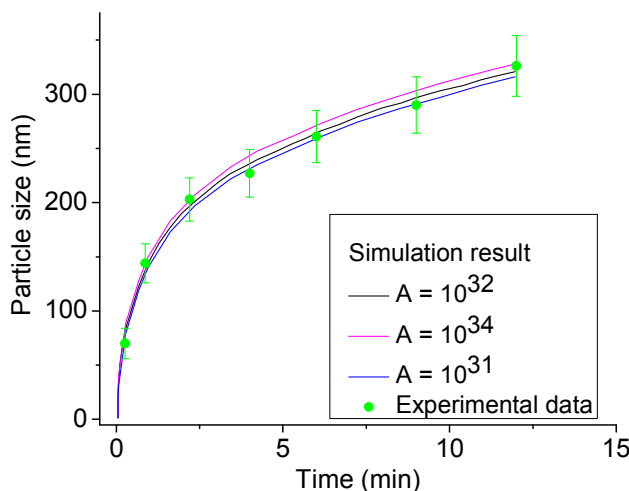


Fig. S3: Effect of pre-exponential factor on mean particle size

In order to further test the sensitivity of pre-exponential factor and thereby to ensure the validity of our assumption, simulation has been carried out for two different values of pre-exponential factor, $10^{31} \text{ m}^{-3}\text{s}^{-1}$ and $10^{34} \text{ m}^{-3}\text{s}^{-1}$. The corresponding simulation results have been shown in figure S3.

It shows that, simulation results show little variation ($\sim 7 \text{ nm}$) from that obtained with assumed value of $A=10^{32} \text{ m}^{-3}\text{s}^{-1}$. At least all the simulation results remain within the error bar.

In the end, in literature, there is no experimentally validated model for calculating the pre-exponential factor for nucleation rate in liquid phase precipitation. There exists some models for gas phase nucleation, but most of these are only a little modification of the classical expression proposed by Volmer and Weber³, based on gas kinetic theory. The corresponding expression is give below:

$$J = A \exp\left[-\frac{16\pi\sigma_{SL}^3 v_m}{3(kT)^3 (\ln S)^2}\right] \quad (5)$$

where, A is the prefactor, S is the supersaturation level, v_m is the molecular volume, and σ_{SL} is the interfacial tension. Expression of the prefactor, in the classical homogeneous nucleation rate, was first introduced by Farkas⁴, based on kinetic theory of gases. The corresponding expression is given below

$$A = Z\phi a^* \quad (6)$$

$$Z = \left(\frac{\Delta G^*}{kT} \cdot \frac{1}{3\pi(n^*)^2}\right)^{1/2}, \Delta G^* = \frac{16\pi\sigma^3 v_m^2}{3(kT \ln S)^2}$$

$$\Phi = \frac{kT}{v_m} \cdot \frac{1}{(2\mu kT)^{1/2}}$$

$$a^* = (36\pi v^2)^{1/3} \cdot n^{*2/3}$$

where, n^* is the number of molecules in critical nucleus, μ is the mass of molecule.

In this regard, most significant contribution to the modification of kinetic pre-factor have been given by Zeldovich¹⁸ to include the effect of Brownian motion in the gas phase nucleation. There is no similar explicit expression of A , available for nucleation in liquid phase (condensed phase). The value of the pre-factor calculated from the above expression is found to be of the order of 10^{13} . This is completely erroneous, if compared with literature^{5,7-9} values for nucleation in condensed phase. Therefore, calculation of pre-exponential factor for nucleation in liquid phase based on classical gas phase nucleation pre-factor gives erroneous values. Therefore, almost all theoretical works for the formation of the crystals or nanoparticles^{6,19-20}, considers the experimentally fitted values of pre-exponential factor (in the range of 10^{30} to $10^{36} \text{ m}^{-3}\text{s}^{-1}$), in their nucleation model.

S2.3 Reason of choosing a surface tension value of 0.1 J/m^2

Value of interfacial tension for amorphous silica-combined water-ethanol system is not reported in literature. It is found from literature that, for almost all of the oxides²¹⁻²², value of interfacial tension lies close to 0.1 J/m^2 . Therefore, in the present calculation, value of interfacial tension has been considered as 0.1 J/m^2 . There are some reports²²⁻²⁵ for interfacial energy of silica-water and silicate-water systems, which suggests that, for silica systems interfacial tension lies close to $0.1\text{-}0.107 \text{ J/m}^2$. Their work further suggests that, energy of silica surface²⁴ ($\sigma_s = 0.455 \text{ J/m}^2$ in air) is reduced by a factor of 4 in presence of absorption of water molecules from vapor and this is further reduced in presence of liquid water²⁶ (Parks, 1984). In case of amorphous silica, though surface enthalpy for hydroxylated surface²⁷ has been shown to be 0.118 J/m^2 , value of surface tension has not been reported so far.

Although many correlations are available for calculation of interfacial energy in liquid-liquid systems,²⁸⁻³¹ there is hardly any kind of model for calculation of interfacial tension at the liquid-amorphous solid interface. We made an attempt to calculate the value of interfacial tension for liquid-solid interface from a theoretical equation (obtained from thermodynamics of surfaces,³²⁻³⁵ by validation with experimental data for nucleation from supersaturated solution. The equation is given as below:

$$\sigma_{SL} = 0.414kT \left(\rho_i^S \frac{N_A}{\tilde{M}_i} \right)^{2/3} \ln \left(\frac{c_i^S}{c_i^L} \right) \quad (7)$$

where, σ_{SL} is the surface tension of solid-liquid interface, $\tilde{M}_i$ molar mass of the component i , ρ_i^S is the solid phase density of component i , c_i^S and c_i^L are the molar concentrations of component i in solid and liquid phase, respectively. This gives a value of 0.1002 J/m², which further supports our assumption of surface tension of 0.1 J/m². There are some experimentally validated correlations available for calculation of interfacial tensions,³⁶⁻³⁷ but these are applicable for ionic crystals only.

In order to check the sensitivity of the final results on the variation of interfacial tension and thereby to further ensure the validity of considering a surface tension value of 0.1 J/m², simulation have been carried out with interfacial tension of 0.107 and compared with the results obtained with 0.1 J/m². The corresponding simulation results are shown in figure S4.

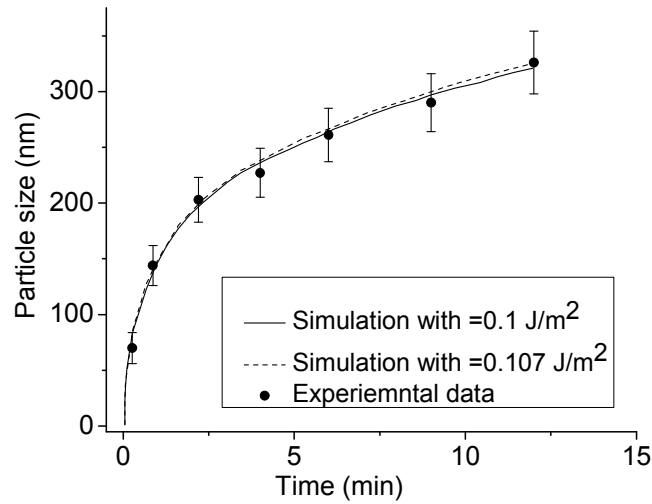


Fig. S4: Effect of surface tension on mean particle size

This shows that, using a surface tension value of 0.1 J/m² does not give any statistically significant difference in prediction of mean particle size. Therefore, we have considered an interfacial tension value of 0.1 J/m².

S3. Diffusion growth

Once nuclei are formed, they start growing by addition of monomeric growth units from bulk of the medium. There are two steps involved in the growth of a single particle: liquid phase transport of growth units to the surface of particle by diffusion and subsequent reaction at the particle surface. Since, the particle surface is highly reactive, surface reaction can be assumed to be very fast compared to the liquid phase transport process. Hence, the rate of diffusion growth is determined by the rate of liquid phase transport of growth units. With this, the rate of diffusion controlled growth can be obtained from solid phase mass balance given below.

$$\frac{d}{dt} \left(\frac{4}{3} \frac{\pi r^3}{v_m N_A} \right) = 4\pi r^2 k_c (c_{SiO_2} - c_{SiO_2,i}) \quad (8)$$

where, N_A is the Avogadro's number, k_c is the mass transfer coefficient and $c_{SiO_2,i}$ is the silica concentration at the surface of particles. k_c is given by D_m/l , in the film theory³⁸ for mass transfer, where, D_m , the molecular diffusion coefficient of SiO_2 in liquid medium, is calculated from Wilke-Chang³⁹ correlation for molecular diffusion in liquid phase. l , the thickness of the fictitious resistance-film of liquid, around the concerned particle, is taken as the radius of the concerned particle as obtained from solving the PBE at any given time. Since the surface reaction is very fast, concentration at the surface of a particle can be approximated as solubility of SiO_2 . Hence, on simplification of the above equation and substitution of $c_{SiO_2,i} \approx c_s$, the rate of diffusion controlled growth becomes

$$\frac{dr}{dt} = \frac{D_m v_m N_A (c_{SiO_2} - c_s)}{r} \quad (9)$$

Since $c_{SiO_2} \gg c_s$, the above equation can be written as

$$\frac{dr}{dt} = \frac{D_m v_m N_A c_{SiO_2}}{r} \quad (10)$$

S4. Brownian coagulation and hydrodynamic correction

In a quiescent medium, nanoparticles move randomly due to thermal fluctuation of solvent molecules and collide with each other. Successful collisions lead to complete fusion of particles, resulting in the formation of a new bigger particle. As in diffusion growth, coagulation can follow two regimes: diffusion limited coagulation and surface reaction limited coagulation. Following the same argument as in the previous molecular diffusion growth process, it can be concluded that, coagulation is a diffusion limited process. Hence, the expression of coagulation kernel proposed by von Smoluchowski,⁴⁰ by solving diffusion equation, can be used to model the coagulation event. The expression for coagulation frequency (q) is given as

$$q(v_i, v_j) = \frac{2k_B T}{3\mu} \left(\frac{1}{v_i^{\frac{1}{3}}} + \frac{1}{v_j^{\frac{1}{3}}} \right) \left(v_i^{\frac{1}{3}} + v_j^{\frac{1}{3}} \right) \quad (11)$$

where, μ is the viscosity of the medium, and v_i and v_j are volumes of colliding particles. In the presence of interparticle forces, coagulation frequency is modified by the form given by Fuchs as

$$q(v_i, v_j) = \frac{2k_B T}{W 3\mu} \left(\frac{1}{v_i^{\frac{1}{3}}} + \frac{1}{v_j^{\frac{1}{3}}} \right) \left(v_i^{\frac{1}{3}} + v_j^{\frac{1}{3}} \right) \quad (12a)$$

where, W is the Fuchs's stability ratio and is given as

$$W = (r_1 + r_2) \int_{r_1 + r_2}^{\infty} \frac{\exp(U / k_B T)}{r^2} dr \quad (12b)$$

where, U is the sum of all interparticle potentials. In the present work, effect of interparticle forces like van der Waal's,⁴¹⁻⁴³ electrical double layer⁴⁴⁻⁴⁵ and solvation force⁴⁶ have been considered into the calculation.

S4.1 Interparticle interaction potentials

S4.1.1 van der Waals potential energy:

The attractive interaction potential energy for two spherical particles is given by⁴¹⁻⁴³

$$V_{vdw} = -\frac{Ha}{6} \left[\frac{2r_1r_2}{r^2 - (r_1 + r_2)^2} + \frac{2r_1r_2}{r^2 - (r_1 - r_2)^2} + \ln \left(\frac{r^2 - (r_1 + r_2)^2}{r^2 - (r_1 - r_2)^2} \right) \right] \quad (13)$$

where, Ha is the Hamaker constant of the corresponding system including the effect of dispersing medium.

S4.1.2 Double layer potential energy

Gouy-Chapman was the first to propose the description of electrical double layer. In the present work, expression for double layer repulsion proposed for both thick and thin double layer⁴⁴⁻⁴⁵ has been considered.

$$V_{edl} = 4\pi r_1 r_2 \bar{Y}_1 \bar{Y}_2 \varepsilon \varepsilon_0 \left(\frac{k_B T}{e} \right)^2 \frac{\exp(-\kappa(r - r_1 - r_2))}{r} \text{ for } 0.5(r_1 + r_2)\kappa \leq 5 \quad (14a)$$

$$V_{edl} = 4\pi \left(\frac{r_1 r_2}{r_1 + r_2} \right) \varepsilon \varepsilon_0 \psi_0^2 \ln \{1 + \exp(-\kappa(r - r_1 - r_2))\} \text{ for } 0.5(r_1 + r_2)\kappa \geq 5 \quad (14b)$$

$$\text{where, } \bar{Y}_i = \frac{8 \tanh\left(\frac{e\psi_0}{4k_B T}\right)}{1 + \left[1 - \frac{2\kappa r_i + 1}{(\kappa r_i + 1)^2} \tanh^2\left(\frac{e\psi_0}{4k_B T}\right) \right]^{\frac{1}{2}}}$$

ψ_0 , ε , ε_0 , e , κ^{-1} are the surface potential, dielectric constant of medium, permittivity of free space, electrical charge and Debye screening length, respectively.

S4.1.3 Solvation potential

The solvation potential can be expressed as⁴⁶

$$V_{sol} = \pi A_s l_d \frac{2(r_1 r_2)}{(r_1 + r_2)} \exp\left(-\frac{r - r_1 - r_2}{l_d}\right) \quad (15)$$

Where, A_s is solvation potential pre-exponential factor, l_d is solvation potential decay length.

S4.2 hydrodynamic correction and mobility functions

Scalar relative-diffusion functions G and H for the diffusion along the centerline and along tangential directions are defined as⁴⁷

$$G(r, r_1, r_2) = \frac{\lambda A_{11} + A_{22}}{1 + \lambda} - \frac{4\lambda A_{12}}{(1 + \lambda)^2} \quad (16a)$$

and

$$H(r, r_1, r_2) = \frac{\lambda B_{11} + B_{22}}{1 + \lambda} - \frac{4\lambda B_{12}}{(1 + \lambda)^2} \quad (16b)$$

where, r , r_1 , r_2 are particle center to center separation distance variable and radiuses of colliding particles, respectively. λ is the colliding particles size ratio. A_{11} , A_{22} , A_{12} , A_{21} , B_{11} , B_{22} , B_{12} and B_{21} are the scalar mobility functions, which are obtained from Batchelor⁴⁷ as follows

$$A_{11} = 1 - \frac{60\lambda^3}{(1 + \lambda)^4 ss^4} + \frac{32\lambda^3(15 - 4\lambda^2)}{(1 + \lambda)^6 ss^6} - \frac{192\lambda^3(5 - 22\lambda^2 + 3\lambda^4)}{(1 + \lambda)^8 ss^8} + O(ss^{-10}) \quad (17a)$$

$$B_{11} = 1 - \frac{68\lambda^5}{(1 + \lambda)^6 ss^6} - \frac{32\lambda^3(10 - 9\lambda^2 + 9\lambda^4)}{(1 + \lambda)^8 ss^8} + O(ss^{-10}) \quad (17b)$$

$$A_{12} = \frac{3}{2ss} - \frac{2(1 + \lambda^2)}{(1 + \lambda)^2 ss^3} + \frac{1200\lambda^3}{(1 + \lambda)^6 ss^7} + O(ss^{-9}) \quad (17c)$$

$$B_{12} = \frac{3}{4ss} + \frac{1 + \lambda^2}{(1 + \lambda)^2 ss^3} + O(ss^{-9}) \quad (17d)$$

$$\begin{aligned}
A_{11}(ss, \lambda) &= A_{22}(ss, \lambda^{-1}) \\
A_{12}(ss, \lambda) &= A_{21}(ss, \lambda) = A_{12}(ss, \lambda^{-1}) = A_{21}(ss, \lambda^{-1}) \\
B_{11}(ss, \lambda) &= B_{22}(ss, \lambda^{-1}) \\
B_{12}(ss, \lambda) &= B_{21}(ss, \lambda) = B_{12}(ss, \lambda^{-1}) = B_{21}(ss, \lambda^{-1})
\end{aligned} \tag{17e -17h}$$

where, ss is the center to center dimensionless separation distance.

S4.3 Hydrodynamic correction function of Honig and co-workers

The expression proposed by Honig and co-workers⁴⁸ for hydrodynamic correction (F) for the motion of two equal spheres is given as

$$F(ss, \lambda = 1) = \frac{6(ss - 2)^2 + 4(ss - 2)}{6(ss - 2)^2 + 13(ss - 2) + 2} \tag{18}$$

S5. Ostwald ripening

Ostwald ripening also known as coarsening occurs because of size dependent solubility of nanoparticles as stated by Gibbs-Thomson equation,

$$c_r = c_{SiO_2, s} \exp\left(\frac{2\sigma V_{mol}}{RT} \frac{1}{r}\right) \tag{19}$$

Where, c_r is the equilibrium surface concentration of spherical particle of radius r . In a system of polydisperse particles, there exists a critical particle size below which particles dissolve because of higher surface energy (high curvature) and above which particles (low curvature) grow with the expense of smaller particles.⁴⁹⁻⁵¹ This process continues till the equilibrium is reached, where particle size in the system becomes equal to the critical size.⁵² Rate of Ostwald ripening is obtained by putting linearized form of Kelvin equation⁵³⁻⁵⁴ to the diffusion flux equation as

$$\bar{r}^3 - \bar{r}_0^3 = k_{OR} t, \quad k_{OR} = \frac{8\sigma D_m V_{mol}^2 c_{SiO_2,s}}{9RT} \quad (20a-20b)$$

Where, $\bar{r}$ is the average particle radius at any time t , $\bar{r}_0$ is the average initial particle radius, k_{OR} is the rate constant for Ostwald ripening, V_{mol} is the molar volume of species, and σ is the interfacial tension. Experimental data shows that for SiO₂ system, a linear relationship between $\bar{r}^3$ vs. t is observed.⁵⁵ This proves that Ostwald ripening takes place in the SiO₂ system. Literature⁵⁶ also tells that amorphous silica shows the Ostwald ripening phenomena and because of higher solubility of amorphous silica compared to other oxides⁵⁷ in water and alcoholic solvent, amorphous silica system shows higher Ostwald ripening rate. Hence, Ostwald ripening is included in this mechanistic model. Time scale analysis shows that sooner after the onset of monomer addition growth, coagulation and Ostwald ripening growth starts.

There has been couple of approaches adopted to incorporate the effect of Ostwald ripening growth in population balance model. Method followed by Layek and Wang group⁵⁸ includes the ripening growth by considering average particle radius as critical radius and then allowing all the particles below the average particle size to dissolve and those above to grow according to the rate obtained by considering critical concentration as bulk concentration (see supplementary material). This works well when the ripening rate is very low and suffers from huge mass balance error whenever there is a fast ripening rate. It is assumed that amount of materials getting dissolved by dissolution of particles, exactly same amount of material is being deposited on the particles. In the present method, PBE and species balance equations are solved simultaneously to capture the dissolution growth process. Since, Ostwald ripening driven dissolution or growth process is essentially a diffusion limited process, therefore the dissolution or growth rate of particles (secondary phase) can be derived by secondary phase mass balance as in the diffusion growth process, resulting in following equation⁵⁹⁻⁶⁰

$$\frac{dr}{dt} = \frac{D_m \nu_m N_A (c_{SiO_2} - c_r)}{r} \quad (21)$$

Mass loss or gain of species in the primary phase due to growth or dissolution process in secondary phase is captured by primary phase species balance equation. This way of incorporating the Ostwald ripening phenomena, obviates the possible sources of mass balance error one encounters in the previous method.

S6. Time scale analysis

Time scale analysis was performed to understand which of the above mentioned five events are the slowest and hence rate limiting, during different stages (time periods) of the particle formation process. In some time periods, rates of multiple events occurring simultaneously may become comparable to each other, while in some time period, a single event may be driving the growth process. This establishes the significance of the multistage mechanism in the nanoparticle size evolution process. Since, rate of all the events mentioned above changes with the process time, time scales in two different stages, namely initial and final period of synthesis has been discussed.

Reaction kinetics affect the whole particle formation process by directly controlling the nucleation, diffusion and curvature dependent growth rate. Reaction time scale is calculated

from the reaction rate kinetics with the expression, $\tau_r = \frac{c_{SiO_2}}{kc_{H_2O}^{1.18}c_{NH_3}^{0.97}c_{TEOS}}$, representing a characteristic time. Larger the time scale, smaller is the amount of material available for growth.

Time scale for nucleation is calculated as $\tau_n = \frac{1}{n_0V}$,⁶¹ where τ_n represents the time required for a single nucleus to form in the system and V is the system volume. Time scale for diffusion growth is calculated from the diffusion limited growth rate using the following expression,

$\tau_{dg} = \frac{v_m}{4\pi V_{mol} D_m (c_{SiO_2} - c_{SiO_2,s})r}$, where, τ_{dg} represents the time required for the particle to grow

by a unit molecular volume. Time scale for coagulation growth is the time required for a single successful collision leading to the complete fusion of colliding particles. Time scale for coagulation can be calculated from the number of Brownian collisions occurring between

particle pairs (per unit time in the system) as, $\frac{qn^2}{2}$, where n is the number density of the

particles. Here, a factor of 2 occurs because each collision is counted twice. Time scale for whole reactor is calculated as, $\tau_{cog,wr} = \frac{2W}{qVn^2}$. Here, W has been calculated from eq. 9b in section S4.

Time scale for coagulation of a single particle is given as $\tau_{cog,sp} = \frac{W}{qn}$ Time scale for Ostwald ripening can be defined as the time required for the particles to grow by unit molecular volume and is calculated as $\tau_{OR} = \frac{v_m}{k_{OR}}$. Results of time scale analysis has been presented in table 3.

In this case initial time scales have been calculated after ~ 5 sec from the start of nucleation,

Two sets of experiments were performed to study the effect of hydrodynamic interaction, reaction kinetics and OR. In each set, two experiments were performed.

Set 1 (low pH and low water content): (a) TEOS= 0.080 (M); NH_4OH = 0.0273 (M); H_2O = 1.622 (M) and (b) TEOS=0.0834; NH_4OH =0.102; H_2O = 3.14 (M). Here, rate of reaction and OR are slow and coagulation drives the growth mechanism.

Set 2 (high pH and high water content): (a) TEOS= 0.192 (M); NH_4OH = 0.857 (M); H_2O = 15.4 (M) and (b) TEOS= 0.158 (M); NH_4OH = 3.8 (M); H_2O = 22.55 (M). Here, both reaction and OR rate are fast and coupled effect drives the growth mechanism.

Table S3: Estimate of time scales

Serial no	Event (time scale)	Expression	Time scale (all time scales are having same unit of sec)
i.	Time scale for reaction to form growth units for whole reactor (τ_r)	$\frac{c_{\text{SiO}_2}}{kc_{\text{H}_2\text{O}}^{1.18}c_{\text{NH}_3}^{0.97}c_{\text{TEOS}}}$	20 (set1 a), 9.80 (set 1b) 11.7 (set2 a), 5.2 (set 2b)
ii.	Nucleation time scale for whole reactor (τ_n)	$\frac{1}{n_0V}$	1.73×10^{-11} (set 1a), 3.7×10^{-11} (set 1b) 1.09×10^{-12} (set 2a), 3.1×10^{-12} (set 2b)

iii.	Diffusion time scale for growth of a single particle (τ_{dg})	$\frac{v_m}{4\pi V_{mol} D_m (c - c_{SiO_2,s}) r}$	2.85×10^{-5} (set 1a), 1×10^{-5} (set 1b) 8×10^{-9} (set 2a), 6.5×10^{-9} (set 2b)
iv.	a) Coagulation time scale for whole reactor ($\tau_{cog,wr}$)	$\frac{2W}{q V n^2}$	3.24×10^{-13} - 2.24×10^{-4} - 1×10^{-2} (set 1a) 2.54×10^{-13} - 1.44×10^{-4} - 1×10^{-1} (set 1b) 8.91×10^{-16} - 6.14×10^{-7} - 3 (set 2a) 6.9×10^{-16} - 1.4×10^{-7} - 7.1×10^{-1} (set 2b)
	b) Coagulation time scale for single particle ($\tau_{cog,sp}$)	$\frac{W}{qn}$	1.24×10^{-3} - 4.3×10^{-2} - 1.9×10^6 (set 1a) 1.72×10^{-3} - 2.44×10^{-2} - 8×10^6 (set 1b) 3.4×10^{-4} - $3.43 \times 10^{-10^3}$ (set 2a) 1.4×10^{-4} - 2.1×10^{-1} - 1.7×10^3 (set 2b)
v.	Ostwald ripening time scale for single particle (τ_{OR})	$\frac{v_m}{k_{OR}}$	2.7×10^{-2} (set 1a), 1.87×10^{-2} (set 1b) 7.29×10^{-6} (set 2a), 5.32×10^{-6} (set 2b)

S7. Input parameters in the simulation

Values of parameters used in simulations are given in the table S4 below

Table S4: List of input parameters

Parameters	Value		Source
A	10^{32}	$m^{-3}s^{-1}$	Randolph ⁵
σ	0.1	J/m ²	Zangwill, ⁶² Oskam and co-workers ⁵¹
ε	80		Ghosh ⁴³
ε_0	8.85×10^{-12}	C ² J ⁻¹ m ⁻¹	Ghosh ⁴³
e	1.6×10^{-19}	C	Ghosh ⁴³

v_m	$4.74 \times 10^{-29} \text{ m}^3$	Calculated from density and molecular weight
V	$30 \times 10^{-6} \text{ m}^3$	Our experiment
$c_{\text{SiO}_2, s}$	$1.15 \times 10^{-8} \text{ mole/dm}^3$ (set 1a, T= 293 K)	Iler; ⁶³ Fournier and Rowe; ⁶⁴
	$2.6 \times 10^{-8} \text{ mole/dm}^3$ (set 1b, T= 293 K)	Chen and Marshall; ⁶⁵ Brinker and Scherer ¹⁷
	$5.1 \times 10^{-5} \text{ mole/dm}^3$ (set 2a, T= 305 K)	
	$8.1 \times 10^{-5} \text{ mole/dm}^3$ (set 2b, T= 305 K)	
V_{mol}	$2.7 \times 10^{-5} \text{ m}^3/\text{mole}$	calculated
Ψ_0	- 8.52 mV (set 1a)	Own experiment (obtained from Malvern Zeta potential measurement)
	- 9.63 mV (set 1b)	
	- 10.3 mV (set 2a)	
	- 11.2 mV (set 2b)	
κ^{-1}	13.3 nm (set 1a)	Our data (calculated from ionic strength)
	10 nm (set 1b)	
	5.1 nm (set 2a)	
	3.3 nm (set 2b)	
l_d	$1 \times 10^{-9} \text{ m}$	Bogush and Zukoski ⁴⁶
A_s	$1.5 \times 10^{-3} \text{ J/m}^2$	Bogush and Zukoski ⁴⁶
r_{cn}	0.29 nm	Calculated from volume of nucleus
D_m	$1.1 \times 10^{-9} \text{ m}^2/\text{s}$ (T= 313 K)	Wilke-chang equation,
	$9.83 \times 10^{-10} \text{ m}^2/\text{s}$ (T= 305 K)	Treybal ³⁹
	$9.8 \times 10^{-10} \text{ m}^2/\text{s}$ (T= 303 K)	
	$9.63 \times 10^{-10} \text{ m}^2/\text{s}$ (T= 293 K)	
μ	0.00192 kgm ⁻¹ s (T= 313 K)	Khattab ⁶⁶
	0.00245 kgm ⁻¹ s (T= 305 K)	
	0.00255 kgm ⁻¹ s (T= 303 K)	
	0.0027 kgm ⁻¹ s (T= 293 K)	
Ha	$6.5 \times 10^{-21} \text{ J}$	Ghosh, ⁴³ Hamaker ⁴¹
k	$1.36 \times 10^{-4} (\text{mole dm}^{-3})^{-2.15}$ (T=313 K)	Giesche, ¹ and van Blaaderen and co-workers ² , in good
	$8.318 \times 10^{-5} (\text{mole dm}^{-3})^{-2.15}$ (T=305 K)	

6.89×10^{-5} (mole dm ⁻³) ^{-2.15} (T=303 K)	agreement with our
9.46×10^{-7} (mole dm ⁻³) ^{-2.15} (T=293 K)	preliminary experimental data

Ψ_0 (Surface potential of the particle): This has been taken as the zeta potential,⁴²⁻⁴³ which is the potential difference between bulk solution and sliding plane (as in Huckel-Onsager equation, since sliding/shear plane is very close to surface, as small as few ionic radius (Ghosh⁴³). Since zeta potential depends on the charge density (number of charged ligands per unit surface area), it does not vary with particle size as long as experimental conditions remain same. Zeta potential of the each of the experimental conditions was measured in Malvern ZetaSizer Nano instrument. Sample from each experiment was collected at three different times and immediately taken for zeta potential measurement. Sample was poured in a cubette. It was found that particles surface is negatively charged. The values of zeta potential have been given in the table S5 for some experimental conditions for representative purpose as follows.

Table S5: Sample zeta potential values for different experimental conditions

Experiment	ξ (mV) at the beginning of synthesis	ξ (mV) at the middle of synthesis	ξ (mV) at the end of synthesis
Set 1a	- 8.52	-8.50	-8.47
Set 1b	- 9.63	-9.62	-9.60
Set 2a	- 10.3	-10.3	-10.2
Set 2b	- 11.2	-11	-11.3

This shows that, zeta potential does not change significantly with time as the synthesis proceeds. Hence, zeta potential value measured at the beginning of the experiment has been used in our simulation.

κ^{-1} (**Debye screening length**): This has been calculated from ionic strength and charge number of ions in the medium as follows

$$\begin{aligned}\kappa^{-1} &= \left[\frac{N_A e^2}{\epsilon \epsilon_0 kT} \sum z_i^2 c_i^\infty \right]^{-1/2} \\ &= \left[\frac{2N_A e^2 I}{\epsilon \epsilon_0 kT} \right]^{-1/2}, \quad I = \frac{1}{2} \sum z_i^2 c_i^\infty\end{aligned}\quad (22)$$

where, N_A is the Avogadro number, e is the elementary charge, ϵ_0 is the permittivity of free space, ϵ is the dielectric constant, z_i is the charge number of ions of type i and c_i^∞ is the concentration of ions of type i . I is the ionic strength of the medium. Ionic strength in the reaction mixture has been calculated from concentration of NH_4OH , as it is the only source of ions in the medium. Dissociation of water and ethanol is negligible as dissociation constants for water and ethanol are 1×10^{-14} and 1×10^{-15} respectively. Since NH_4OH is a weak electrolyte (weak base), it is partially ionized and concentration of dissociated ions has been calculated from equilibrium dissociation constant (K_e) as follows

$$\begin{aligned}\text{NH}_4\text{OH} &= \text{NH}_4^+ + \text{OH}^- \\ K_e &= \frac{c_{\text{NH}_4^+} c_{\text{OH}^-}}{c_{\text{NH}_4\text{OH}}}\end{aligned}\quad (23)$$

where, $c_{\text{NH}_4^+}$, c_{OH^-} and $c_{\text{NH}_4\text{OH}}$ are the concentration of NH_4^+ , OH^- and NH_4OH . K_e is the equilibrium dissociation constant, which is having a value⁶⁷⁻⁶⁸ of 1.8×10^{-5} at 298 K. Temperature dependent form of it has been given by Bates et al.⁶⁹ and Harned et al.⁷⁰ as, $-\ln K_e = \frac{A}{T} + B + CT$, where, $A = 1743.57$, $B = -6.1843$ and $C = 0.017060$. The values of Debye screening length for some of the experimental conditions has been listed in table S6.

Table S6: Calculation of Debye screening length for different experimental conditions

Experiment	c_{NH_4OH} (M)	$c_{NH_4^+}$ (M)	c_{OH^-} (M)	κ^{-1} (nm)
Set 1a	0.0273	0.00066	0.00066	13.3
Set 1b	0.102	0.00123	0.00123	10
Set 2a	0.857	0.0040	0.0040	5.1
Set 2b	3.8	8.49	8.49	3.3

S8. Method of computation

Simulation was carried out numerically using the conventional finite volume technique. The whole computation domain was discretized into finite volumes, using tetrahedral elements. Integration of linear, unsteady state, governing partial differential equations for species balance in the control volumes results in a set of linear ordinary differential equations (ODEs) with time as independent variable. For the PBE, integration over control volume produces a set of linear PDEs with time and particle volume as the independent variables. These spatially discretized equations are discretized in particle volume domain according to the discretization technique proposed by Hounslow and co-workers.⁷¹ with grid spacing following the formulae, $\mathbf{v}_{i+1} = 2^g \mathbf{v}_i$, where, $\mathbf{v}_i$ and $\mathbf{v}_{i+1}$ are positions of i^{th} and $i+1^{\text{th}}$ grids in particle volume domain, and g is a positive integer number. This results in a set of linear ODEs for PBE. Temporal discretization of all these discretized PDEs (PDEs discretized in space and particle volume domain) and particle volume fraction equation (ODE) has been done by integrating them in time domain, using a second order implicit temporal discretization scheme.⁷² A set of linear algebraic equations is thus obtained.

A point implicit linear system solver (Gauss-Seidel iterative method) in conjunction with algebraic multigrid (AMG) solver for coarse grid solution is used for the solution of scalar algebraic equations in each cell node. Least squares cell based spatial discretization scheme was

used for the gradient of scalar variables at the cell center. Codes for nucleation, diffusion growth, coagulation and Ostwald ripening have been written in C++ and used as user defined functions (UDFs) in Fluent.

Physical consistency analysis of the solution from the solver has been performed. It was found that the solution is independent of control volumes with further reduction in grid size. Time step size was varied between 0.1- 0.000001 sec, which on further reduction did not bring any further improvement in solutions, ensuring step-size independence of final results. The solution converged when scaled absolute residuals were less than 0.00001 for all variables. Mass balance check in the system confirmed that the system's total mass remains conserved with a < 3% error in mass balance.

Scaled absolute residuals are defined exactly in the same manner as the relative residuals. In the solver Fluent, it is defined as the ratio of residual in a certain iteration at a particular time step to that of largest absolute value of residual in first five iterations at that time step. After discretization in the finite volume method, the conservation equation for a general variable, suppose ϕ , at a cell p can be written as

$$a_p \phi_p = \sum_{nb} a_{nb} \phi_{nb} + b \quad (24)$$

where, a_p , a_{nb} are coefficients of variable p in the p^{th} cell and in the neighboring cells (nb). b is the contribution of constant part of source term.

The residual of the variable at N^{th} iteration, calculated in the Fluent is the imbalance in the equation (21) summed over all the computational cells i.e.

$$R^\phi = \sum_{cells\ p} \left| \sum_{nb} a_{nb} \phi_{nb} + b - a_p \phi_p \right| \quad (25)$$

Judging the convergence of a variable by the absolute residual values as in the equation above (22) can be erroneous in some cases. Therefore, the above absolute residual is scaled by the largest absolute residual value in the first five iterations in that particular time step as follows

$$\frac{R_{iteration\ N}^{\phi}}{R_{iteration\ 5}^{\phi}} \quad (26)$$

Therefore, for a certain variable to reach the convergence, scaled absolute residual in equation 8 must go below 10^{-5} , as per our imposed convergence criterion i.e.

$$\frac{R_{iteration\ N}^{\phi}}{R_{iteration\ 5}^{\phi}} < 10^{-5} \quad (27)$$

This is to clarify that, in all of the cases in the present work, *except simulation with experimental data set 2b* in section 6.1.1 in figure 3b and in section 6.1.2 in figure 4a in main manuscript, mass balance error was maintained well below 1.12% with the specified convergence criterion of 10^{-5} . In order to decrease the computation time, time step size has been increased at the cost of relatively large mass balance error of 2.7% in case of simulation with experimental data set 2b. In this case, concentration of ammonia as well as water is very high, as mentioned in experimental section 5 in main manuscript. This causes the solubility of silica and hence the Ostwald ripening rate (OR; dissolution-growth rate) to be very high (Iler, Brinker and Scherrer). This, in turn, increases the rate of interphase mass transfer many times. Hence, this needs relatively smaller time step size to capture the change accurately and thereby to avoid the large mass balance error with this specified convergence criterion of 10^{-5} . Using smaller time step size leads to increase in computation time many folds. So, we have used large time step size in case of set 2b.

Simulation has been performed in case of experimental data set 2b with smaller time step size and scaled absolute residual 10^{-6} as convergence criterion instead of 10^{-5} . Mass balance check in this case shows an error of 1.04% at the end of simulation. The corresponding simulation results have been shown in figure S5 below for two different cases. This shows that, with tight convergence criterion and small time step size, though mass balance error decreases to a great extent in both cases (including and excluding hydrodynamic interaction) (to 1.01% from 2.7 %), mean size of particles shows a little increase in value of about 7 nm. Moreover, this modified prediction remains completely within the error bar. Considering all these, it can be said

that, our calculation with 10^{-5} as a scaled absolute residual and 2.7% mass balance error is not too worse.

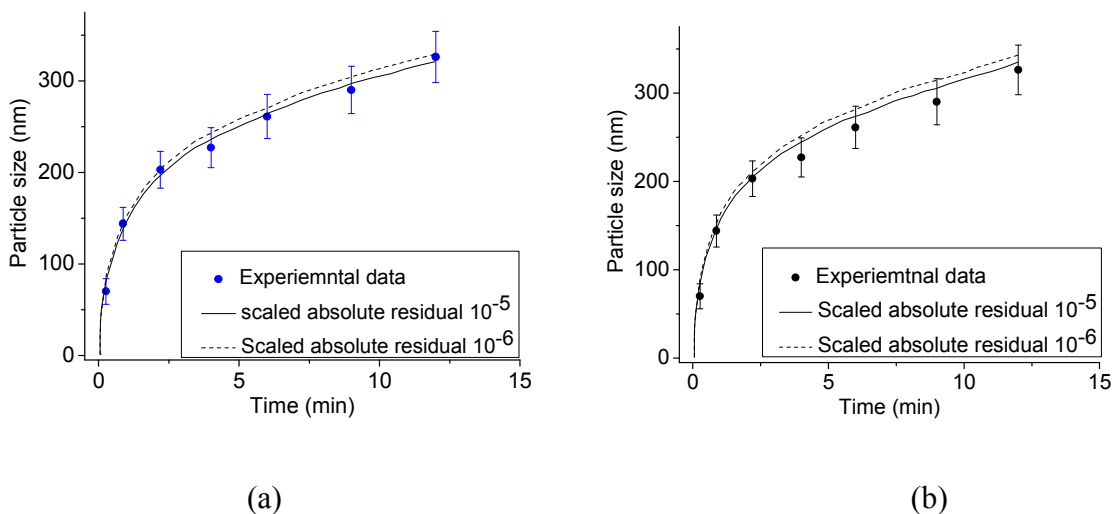


Fig. S5: (a) With hydrodynamic interaction and (b) without hydrodynamic interaction

S9. Experimental method

Material

Tetraethyl orthosilicate ($\text{SiC}_8\text{H}_{20}\text{O}_4$; Sigma Aldrich), ethanol (EtOH ; Gogia & Company, 99% pure) and ammonium hydroxide (NH_4OH ; Merck) were used in our experiment without any further purification. De-ionized Millipore-Milli-Q water was used in all experiments.

Method

Silica nanoparticles were synthesized following Stober's sol-gel method.⁷³⁻⁷⁴ Tetraethyl orthosilicate (TEOS) was used as a precursor. To accelerate the rate of hydrolysis, liquor ammonia was used as a catalyst. Ethanol (Merck) was used as the solvent medium. Experiment was performed at different temperatures in an oil bath, which maintained a constant temperature throughout the experiment. Precipitation was carried out by mixing two previously prepared

mixtures: mixture A- Ethanol, water and ammonia; and mixture B- Ethanol and TEOS. Both the mixtures were mixed together in presence of vigorous stirring in a beaker placed in the oil bath at a certain temperature throughout the experiment. After some time, the reaction mixture became milky white, indicating the formation of nanoparticles. Samples were collected from the reaction mixture through a micropipette at different time intervals and dried immediately. SEM study was then carried out to obtain particle size distribution and thereby understand the particle growth process.

S10. Variation of critical particle radius for OR with solubility and bulk concentration

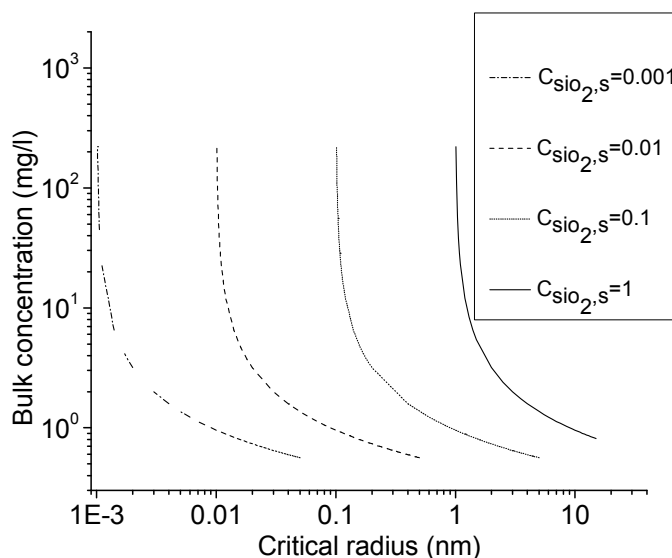


Fig. S6: Variation of critical particle radius for OR with bulk concentration (equation 19 section S5)

Above figure S6 shows that, critical particle radius decreases with increase in bulk concentration, whereas it increases with increase in bulk solubility ($C_{SiO_2,s}$) of material.

S11. Conversion of DLS data to the number density distribution

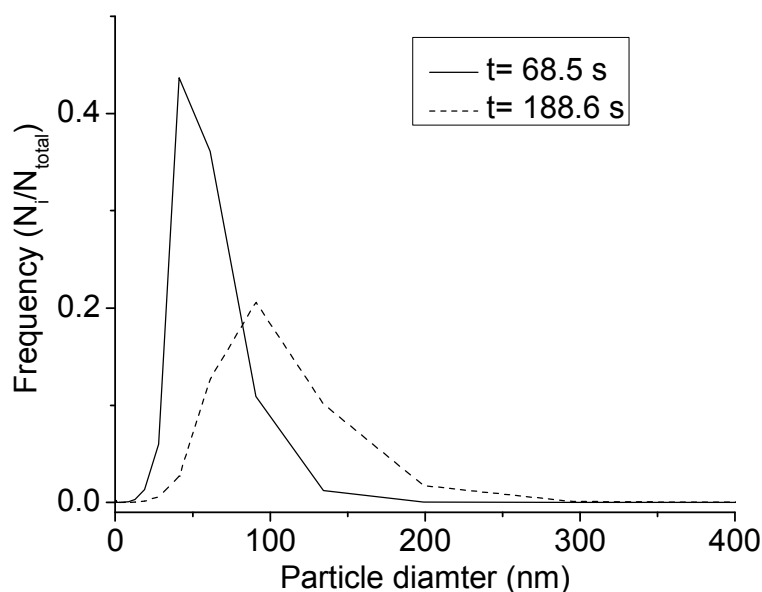


Fig. S7: frequency distribution of particles obtained from DLS

In order to convert the DLS data to the number density distribution, we need to have total mass of silica formed in unit volume of reaction mixture. The detailed experimental procedure has been given below,

- i) Sample was collected from main reaction volume at different times, 68.5 sec and 188.6 sec as mentioned in the figure S7 in the main manuscript and immediately poured into ethanol of volume 15 times higher than the sample collected. This will reduce the reaction rate drastically.
- ii) From this diluted sample, a small volume of 1 ml was immediately poured into a cubette and diluted further to reduce the chance of multiple scattering in DLS. Then DLS measurement was performed and this gives a distribution of particle size in terms of frequency.

- iii) Rest of the sample was centrifuged immediately to collect total mass. Centrifugation was carried out at 19000 rpm in Remi C-24 plus centrifuge for half an hour. Then the mass was washed with ethanol and centrifuged again. This cycle was continued 2-3 times to remove unreacted components and silica molecules.
- iv) To remove ethanol, the collected mass was then dried in an oven and finally, weight was measured.
- v) Once total mass is obtained, we calculate the mass of silica nanoparticles produced in a unit volume of initial mixture.
- vi) From the size distribution (obtained from DLS measurement) and the total mass of sample per unit volume, total numbers of particles are calculated.
- vii) From total number of particles, we calculate the size distribution in terms of number density as shown in figure 7 in main manuscript.

Notation

A	pre-exponential coefficient
A_s	solvation potential pre-exponential factor
A_{11}, A_{22}, A_{12}	mobility functions
B_{11}, B_{22}, B_{12}	mobility functions
c_{H_2O}	concentration of water in primary phase
c_{NH_3}	concentration of ammonia in primary phase
c_r	equilibrium surface concentration of spherical particle of radius r
c_{SiO_2}	bulk concentration of silica in primary phase
$c_{SiO_2,i}$	silica concentration at the surface of particles
$c_{SiO_2,s}$	solubility of SiO_2
c_{TEOS}	concentration of tetraethyl orthosilicate in primary phase
D_m	molecular diffusion co-efficient
D_{12}^0	relative diffusivity of particles in the absence of hydrodynamic interactions
$\overline{\overline{D}}_{12}(r)$	relative translational diffusion tensor
e	electrical charge
e_r	radial unit vector
F	Hydrodynamic correction function provided by Honig ¹⁷
$\hat{F}$	interparticle interaction force
$G(r)$	scalar diffusion functions for the diffusion along the centerline
G_v	volumetric growth rate of particle
$H(r)$	scalar diffusion functions for the diffusion along the tangential direction
Ha	Hamaker constant of the corresponding system
$\hat{j}_i^p$	diffusion flux of species i in the primary phase
J	normal flux for a particle of radius r_2 diffusing to a particle of radius r_1
k	reaction rate constant
k_B	Boltzmann constant
k_c	mass transfer coefficient

k_{OR}	rate constant for Ostwald ripening
l	thickness of fictitious resistance film of liquid around the concerned particle
l_d	solvation potential decay length
m^{ps}	mass transfer from primary to secondary phase
n	number density function of particles
$n(v, 0)$	particle number density in the system initially
$n(0, t)$	particle number density in zeroth bin at time t
n_0	nucleation rate
$\hat{n}$	unit normal vector
N	number of particles crossing each spherical surface concentric with central sphere
N_A	Avogadro's number
$\bar{N}$	total flux of secondary phase species
$\bar{N}_i$	total flux of primary phase species i
p	primary phase
q	coagulation frequency function
r	particle radius variable
$\bar{r}$	average radius of particles at time t
r_{cn}	size of nucleus
$\bar{r}_0$	average initial radius of particle
r_2, r_1	radius of particles colliding
R_i^p	loss or gain of species i due to reaction in the primary phase
s	secondary phase
ss	dimensionless interparticle separation distance
S	super saturation of the SiO_2 in the liquid phase
S_q	source term in the secondary phase
T	temperature
U	sum of interparticle potentials
v	volume of particles
v_i, v_j	volumes of colliding particles
v_m	molecular volume of SiO_2

V	system volume
V_{edl}	electrical double layer potential
V_{mol}	molar volume of species
V_{sol}	Solvation potential
V_{vdw}	van der Waals potential energy
W	stability co-efficient
x	external co-ordinate of the system
$Y_{i,0}$	initial mass fraction of i^{th} species
Y_i^p	mass fraction of species i in the primary phase

Greek letters

α^p	primary phase volume fraction
α^s	secondary phase volume fraction
ε	dielectric constant of medium
ε_0	permittivity of free space
λ	particle size ratio
κ^{-1}	Debye screening length
μ	viscosity of medium
ρ^p	primary phase density
ρ^s	secondary phase density
σ	interfacial tension of silica-alcohol system
τ_{cog}	coagulation time scale
τ_{dg}	diffusion growth time scale
τ_n	nucleation time scale
τ_r	reaction time scale
τ_{OR}	Ostwald ripening growth time scale
ψ_0	surface potential
∇_v	operator in particle volume co-ordinate (internal co-ordinate)

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