A Generalized Three-Stage Mechanism of ZnO Nanoparticle Formation in Homogeneous Liquid Medium

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Abstract: Understanding the influence of relevant parameters on the kinetics of nanocrystal formation, from reaction and nucleation to the final stages of growth in a homogeneous medium, is crucial in the design and synthesis of nanoparticles of desired dimension. ZnO is chosen as a model system to study spherical nanoparticle formation in solution, using a combination of experiments and mathematical modeling. Stable dispersions of ZnO nanocrystals were synthesized in alcoholic solvents at various temperatures, while size-selection between ~1.5 and ~5 nm diameters were achieved by a rapid-quenching to 253 K, with simultaneous use of a capping agent. A priori time-scale calculation of the rate processes involving different elementary events, in conjunction with nanoparticle microscopy and spectroscopic data on particle diameter, has led to an underlying three-stage mechanism for nanoparticle formation. These sequential stages consist of: (I) nucleation of ZnO nanocrystal and growth by molecular diffusion, (II) interparticle coagulative-growth via oriented attachment (OA), and, finally, (III) interparticle growth by Ostwald ripening (OR). Predictions of our mathematical model based on the above mechanism compare favorably with experimental trends on temporal evolution of mean particle diameter, for different alcoholic solvents at various temperatures in the range of 273–353 K. Solvents of lower carbon chain-length and lower temperature independently reduce the rates of both OA and OR facilitating particles of smaller diameter, thereby justifying methanol as the optimum solvent of choice to size-select ZnO nanoparticles in the strong-confinement regime.

1. INTRODUCTION

Development of reliable methods for generating inorganic semiconductor nanocrystal (NC) particles having uniform morphologies (size and shape), crystal structure, and surface properties is important in order to have desirable physicochemical behavior. When the dimensions of the NCs are comparable to the excitonic Bohr radius of the material (i.e., in the quantum-confinement regime), the band-structure is known to change significantly, resulting in dramatic changes in their optoelectronic properties.1–7 The ultrasmall NCs in the strong quantum-confinement regime are also highly reactive due to the presence of unsaturated atoms at the interface, which augments their propensity to grow in size or attach themselves to one another. Given the role of these small NCs in determining specific chemical, catalytic, and optoelectronic properties of the larger nanostructures, it is important to be able to synthesize stable, yet small NC particles with a narrow size distribution and quantify the effect of various physical parameters that control their nucleation and growth.4,8–11 Solution phase colloidal synthesis provides simple and economic routes to generate such small NCs and offers flexibility in the choice of solvents, temperature, and surface passivation agents in order to reduce surface defects, strain, and tendencies of further growth.12–15 ZnO is one of the most versatile and therefore extensively studied metal oxide semiconductors having several applications as UV-blockers, green-phosphors, varistors, sensors, and photocatalysts.6,16,17 Further interest in ZnO arises due to its multifunctional properties like large exciton binding energy (60 meV) coupled with a direct wide band gap ($E_g \sim 3.37$ eV), making it suitable for UV lasers and light emitting diodes.18–20 Due to the obvious importance of ZnO NCs, their size-selected synthesis using solution routes have been studied both experimentally and theoretically.21–26 However, the complete nucleation and growth kinetics have not been explored, even though it has been shown that ZnO NCs as small as ~1.3 nm diameter can be generated by colloidal synthesis routes.27 Such an understanding of the mechanism and kinetics of NC particle formation, starting from an initially homogeneous aqueous solution, would provide directions on how to tune synthesis parameters, so as to achieve a desirable mean particle size and...
size distribution at the end of the synthesis procedure. However, we find that there is no comprehensive model, which could predict the temporal evolution of ZnO NC dimensions, from the very early stages until the end of the process. Therefore, the objective of the present work is to propose a comprehensive nanoparticle formation mechanism in solution using a combination of experiments and mathematical modeling.

2. MECHANISTIC BACKGROUND OF NANOPARTICLE FORMATION

We show that the whole synthesis process of NC particle formation can be schematically represented as in Figure 1, depicting the time history of the evolution of a single particle. However, since different particles in the solution nucleate and subsequently collide or grow at different points in time, from the perspective of the mechanistic evolution of the overall system of a particle-ensemble, nucleation, collision, and growth events occur simultaneously for the particle population under consideration. Final particle size distribution (PSD) obtained therefore is a result of these various events occurring simultaneously. These are as follows: E1, nucleation of a solid ZnO crystal from a required critical number of ZnO molecules in the solvent, the latter formed via a rapid precipitation reaction of a zinc salt by the precipitant; E2, growth of this nucleus by diffusion of ZnO molecules from solution onto the surface of the nucleated particle; E3, interparticle growth by collision and fusion of two particles via the oriented attachment (OA) route; and E4, interparticle growth via exchange (dissolution and diffusion) of molecules between various particles, commonly referred to as Ostwald ripening (OR). In essence, subsequent to the nucleation event E1, a particle can grow by one or all of the growth events, E2, E3, and E4. These individual events are well established in the literature and are also evident from our experimental data (vide infra). For instance, coagulative growth by OA (event E3) is captured by high-resolution transmission electron microscopy (HR-TEM) images at early times (3 min) of growth (Figure 1b and Figure S1, SI). This shows two or three particles fused with each other in the transition stage of their coagulation. In contrast, after 1 h of growth, all HR-TEM images show isolated, nearly spherical, and considerably larger particles, indicating that coagulation is complete by then. From this point onward, OR (event E4) becomes the dominant growth mechanism.

Interestingly, almost all earlier reports involving ZnO have dealt with either initial stages involving only events E1 and E2 or the final stages of growth where only event E4 dominates the growth process. In this context, we summarize the literature findings here. In situ nucleation and diffusion-growth kinetics of ZnO in organic solvents has been studied by Lizandara-Pueyo et al., who revealed that the solvent plays a crucial role in nucleation kinetics.23 The kinetics of OR in alcoholic solvents too have been found to depend on the solvent polarity and reaction temperature. This has been explained in the light of Lifshitz–Slyozov–Wagner (LSW) theory, attributing it to diffusion limited OR.15 Surprisingly, studies on the effect of reactant concentration, counterions, pH, and temperature on ZnO growth kinetics have claimed that the slower diffusion-controlled ripening processes in ZnO qualitatively deviate from the widely accepted LSW model.25,26 In contrast, intermediate stages of ZnO NC growth (event E3) have been rarely addressed by a mathematical model. For instance, for ZnS and SnO2 NCs, attempts have been made to understand the growth kinetics in event E3.28–30 The approach by Hu et al.15 has been extended further by fitting the growth of ZnS NCs via coagulation as well as slower processes like OR, occurring in two consecutive stages.28,31 A special case of coagulation, applicable for II–VI semiconductors like ZnO, is OA, wherein the larger particle is formed by attachment of primary particles along a specific orientation of the crystal.31–34

Therefore, in this work, we aim to develop a complete mechanism and model based on all of the events, from E1 to
E4. The most comprehensive methodology to achieve this is the framework of the population balance equation (PBE), which combines kinetics of nucleation of an individual particle and its collision and growth dynamics into an evolution equation of a population of particles, furnishing characteristics such as mean particle size, standard deviation, etc. Thus, ideally the PBE should include terms corresponding to all events shown in Figure 1. However, considering the complex interplay and simultaneity of dealing with four events mathematically in a single PBE, which in itself has not been attempted before and would be computationally very difficult, it is desirable to break up the process and the equations into different stages. To identify the different stages, we first need to perform a time scale analysis as described below.

2.1. Time Scale Analysis. Time scales of each of the four events are calculated to determine which one of them becomes dominant (i.e., rate determining) during a given time-zone/stage (e.g., beginning, intermediate or end) of the process. These dominant events can be the rate determining steps at each stage of the process. This can potentially lead to the current multistage nanoparticle formation mechanism proposed in this work. Previously, we have modeled nanoparticle size evolution in water-in-oil microemulsions,\(^3\)\(^5\)-\(^3\)\(^7\) a characteristic microheterogeneous system, wherein reaction, nucleation, and growth occur within the physical confinement of nanometer-sized water drops of the microemulsion. However, in the present work, synthesis occurs in the bulk phase of a homogeneous alcoholic solvent. As a result, growth by molecular diffusion and OR, events E2 and E4, respectively, are new events that come in vogue in our present model, making the overall formulation of equations and solution techniques not dealt with previously.

Each time scale is now discussed below:

Reaction Time Scale (\(\tau_r\)). Addition of KOH to Zn-(OAc)\(_2\)·2H\(_2\)O in an alcoholic solvent forms ZnO molecules by precipitation reaction, which is normally considered an instantaneous reaction, compared to all other elementary events.\(^3\)\(^5\)-\(^3\)\(^8\)

Nucleation Time Scale (\(\tau_n\)). Due to precipitation, ZnO concentration in the solvent easily exceeds the very low solubility of ZnO, rendering the solution supersaturated, resulting in nucleation of solid ZnO. Since there are no seed or foreign particles in the solvent, we can assume classical theory of homogeneous nucleation giving the nucleation rate expression as\(^3\)\(^5\)-\(^3\)\(^8\)

\[
{k_n} = \begin{cases} 
0 & l < l_c \\
A \exp \left( -\frac{16\pi \sigma^3 V_m^2}{3(k_B T)^3 (\ln \lambda)^2} \right) & l \geq l_c 
\end{cases}
\]

where \(A\) is the pre-exponential factor, \(\sigma\) is the solid-liquid interfacial energy of nucleus with solvent, \(V_m\) is the volume of a ZnO molecule, \(k_B\) is the Boltzmann constant, \(T\) is reaction temperature, and \(\lambda = C/C_s\) is the degree of supersaturation in liquid phase, with \(C_s\) being the solubility of ZnO and \(C\) being the concentration of ZnO molecules in the solvent at any instant of time (i.e., \(\lambda\) is a function of time). The actual number of molecules in a nucleus is \(l\), whereas \(l_c\) is the critical number of molecules required to form the nucleus. This critical value typically ranges from 2 to 6 molecules,\(^3\)\(^6\)-\(^3\)\(^8\) depending on the type of solute and solvent; for instance, a critical number of 2 is widely used in case of CdS nucleation. \(l_c\) is calculated from \(l_c\) assuming a spherical particle.

Diffusion Controlled Growth Time Scale (\(\tau_g\)). Growth of an individual particle may be limited either by diffusion of molecules from the continuous solvent medium onto the particle surface or by surface reaction step on the growing particle surface itself. NCs have high surface energy, so that surface reaction can be reasonably assumed to be fast relative to the liquid phase diffusion. The growth can then be represented by a simple ZnO transport equation, following the schematic in Figure 1a (stage S-1). The total flux of ZnO molecules to the surface is equated to the rate of growth of a ZnO particle, given by

\[
\frac{4\pi r^2}{r} D_2 (C - C_s) = \frac{d}{dt} \left( \frac{v}{V_m N_A} \right)
\]

where \(r, D, C, C_s, t, v, V_m\) and \(N_A\) are ZnO particle radius, diffusivity of ZnO molecule in solvent, ZnO concentration in the solvent, ZnO concentration at the solid–liquid interface, time, volume of the growing particle, volume of one ZnO molecule, and Avogadro’s number, respectively. Diffusion layer thickness has been assumed to be equal to \(r\). For an instantaneous surface reaction, concentration of ZnO at the interface is equal to its solubility, i.e., \(C_s \approx C\). Typical value of \(C\) used for synthesis ranges from 0.1 to 0.16 M, whereas \(C_s\) for ZnO is of the order of \(10^{-10}\) mol/L (Table S1, SI). Therefore, \(C_s = C \approx C_s \approx C\). The diffusion controlled growth rate of the \(n\)th particle is thus written as

\[
\frac{dL_n}{dt} = 4\pi v V_m N_A D_2 \left( \frac{3v}{4\pi} \right)^{1/3}
\]

Coagulative Growth Time Scale (\(\tau_{coag}\)). Coagulation in the case of ZnO takes place by OA of particles having the same crystallographic orientation. This comprises two steps: attachment of two particles by Brownian collision and subsequent fusion into a single larger particle by solid state diffusion. NCs that are characterized by crystallographic planes with different surface energies fuse by elimination of planes with the highest surface energy, so as to reduce the overall energy of the system. ZnO has a wurtzite crystal structure, and Zn and O are arranged alternately along the \(c\) axis. The top and bottom faces of the crystal terminating with Zn and O ions are polar, whereas the side six planes are nonpolar. The polar plane having positive charge has the highest surface energy, and is the most reactive. Due to charge separation along the \(c\) axis, there is a permanent dipole in the ZnO NC.\(^3\)\(^9\) These NCs therefore align in the direction of the dipole moment, which is the \(c\)-axis of ZnO crystal, and oppositely charged planes (001 and 001) attach with each other. Therefore, we consider coagulation in ZnO only through the OA mechanism.

The frequency of Brownian collision has been modified to incorporate the effect of dipole–dipole and van der Waals’ interactions and probability of OA as follows:\(^3\)\(^9\)

\[
q_p = \frac{1}{32} \left( \frac{1}{W} \right) \left( \frac{2k_B T}{3\mu} \right)^{1/3} \left[ 2 + \left( \frac{v_1}{v_2} \right)^{1/3} + \left( \frac{v_2}{v_1} \right)^{1/3} \right]
\]

where 1/32 is the attachment probability, since only 2 out of 64 relative positions of the NCs (each NC having one polar plane out of a total of 8 crystal planes) can result in a favorable orientation for fusion. \(W\) is the correction factor for dipole–
dipole and van der Waal's interactions.\textsuperscript{39–41} $v_1$ and $v_2$ are volumes of the two colliding NCS, and $\mu$ is viscosity of the solvent.

For particles of the same volume, the collision frequency\textsuperscript{39,40} is thus

$$q_p = \frac{8k_BT}{3\mu} \frac{1}{W}$$

(5)

and the rate of formation of the coalesced particle by coagulation\textsuperscript{39,40} is therefore

$$k_{\text{OA}} = \beta q T N_0$$

(6)

where $\beta$ is the coagulation efficiency, defined as the fraction of collisions that lead to successful coagulation, and $N_0$ is the total number of ZnO particles per unit volume of solution after nucleation and diffusion growth is over. $N_0$ is calculated as

$$N_0 = \frac{6C_vV_mN_A}{\pi d^3}$$

(7)

where $d$ is the mean particle diameter and $C_v$ is molar concentration of dissolved ZnO molecules in the solution, at time, $t = 0$. This is obtained by equating the total moles of reactant present in the liquid phase at time $t = 0$ with the final total moles of ZnO molecules present in the solid phase as ZnO nanoparticles.

Ostwald Ripening Time Scale ($\tau_{\text{OA}}$). Smaller ZnO NCS, due to their higher chemical potential, have higher solubility than the larger particles. Thus molecules from the smaller particles dissolve preferentially in the solution and diffuse through the solvent to grow onto the existing larger ZnO particles. Larger particles thereby grow bigger at the expense of smaller ones. Rate of this diffusion controlled OR is expressed as\textsuperscript{15}

$$d^3 - d_0^3 = k_{\text{OR}}t$$

(8)

where $d$ is the cube of average particle diameter at time $t$, $d_0^3$ is the cube of initial particle diameter, and $k_{\text{OR}}$ is the rate constant for OR given by\textsuperscript{42}

$$k_{\text{OR}} = \frac{8\sigma D(V_mN_A)^2C_v}{9RT}$$

(9)

### 2.2. Conclusions from Time Scales

Table 1 shows time scale values (based on equations in section 2.1) of all elementary events for both solvents at all temperatures, and Table 2 shows the conclusions thereof. All relevant parameter values are listed in Tables 3 and S1. First, it is clear from Table 2 that the nucleation rate is much greater compared to both diffusion and coagulation growth rates. This implies that a large number of nuclei are formed initially in the reactor in a very small time span. These nuclei undergo diffusion-growth to form bigger particles, as long as the solution is supersaturated with respect to ZnO. As explained earlier, nucleation and diffusion growth are considered to occur simultaneously for this

<table>
<thead>
<tr>
<th>solvent</th>
<th>temperature (K)</th>
<th>$\tau_n = 1/(V_k)$ (s)</th>
<th>$\tau_g = 1/(2\pi d_0^2 D C)$ (s)$^a$</th>
<th>$\tau_{\text{OA}} = 1/k_{\text{OA}}$ (s)$^b$</th>
<th>$\tau_{\text{OR}} = (d^3 - d_0^3)/k_{\text{OR}}$ (s)$^{a,cd}$</th>
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<tr>
<td>methanol</td>
<td>298</td>
<td>$4.57 \times 10^{-8}$</td>
<td>$5.85 \times 10^{-10}$</td>
<td>9.05</td>
<td>$1.23 \times 10^3$</td>
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<td></td>
<td>313</td>
<td>$4.61 \times 10^{-8}$</td>
<td>$4.64 \times 10^{-10}$</td>
<td>4.00</td>
<td>$5.41 \times 10^2$</td>
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<td></td>
<td>333</td>
<td>$4.67 \times 10^{-8}$</td>
<td>$3.33 \times 10^{-10}$</td>
<td>1.98</td>
<td>$3.20 \times 10^2$</td>
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<td></td>
<td>353</td>
<td>$4.70 \times 10^{-8}$</td>
<td>$2.47 \times 10^{-10}$</td>
<td>0.78</td>
<td>$1.27 \times 10^2$</td>
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<tr>
<td>ethanol</td>
<td>273</td>
<td>$4.50 \times 10^{-8}$</td>
<td>$3.10 \times 10^{-8}$</td>
<td>4.31</td>
<td>$2.44 \times 10^4$</td>
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<td></td>
<td>283</td>
<td>$4.52 \times 10^{-8}$</td>
<td>$2.94 \times 10^{-8}$</td>
<td>2.57</td>
<td>$8.43 \times 10^3$</td>
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<td>298</td>
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<td>0.72</td>
<td>$3.28 \times 10^3$</td>
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<td>3.77</td>
<td>$1.55 \times 10^3$</td>
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<tr>
<td></td>
<td>333</td>
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<td>$9.47 \times 10^{-7}$</td>
<td>0.07</td>
<td>$9.18 \times 10^2$</td>
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\textsuperscript{a}All growth timescales ($\tau_n$, $\tau_g$, $\tau_{\text{OA}}$) are the required estimated time for different events (E2–E4), calculated based on the growth of a single nucleus ($l = 2$) by diffusion-addition of one ZnO molecule (E2), collision-induced addition of another ZnO nucleus (E3), or ripening-growth by one ZnO molecule (E4), respectively. \textsuperscript{b}$k_{\text{OA}}$ is calculated by using equations\textsuperscript{5, 6, 7} and the value of $\beta$ is taken from SI Table S1. \textsuperscript{cd}$k_{\text{OR}}$ required in $\tau_{\text{OR}}$ is calculated from eq 9. \textsuperscript{e}Use of fitted values of $k_{\text{OR}}$ (from SI Table S1) also gives $\tau_{\text{OA}}$ within 1-2 orders of magnitude of $\tau_{\text{OA}}$ values listed here. This implies that, independent of the estimation method of $k_{\text{OR}}, \tau_{\text{OA}} < \tau_{\text{OA}}$ as concluded later in Table 2.

### Table 2. Conclusions from Time Scale Analysis

<table>
<thead>
<tr>
<th>time scales</th>
<th>conclusions</th>
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<tbody>
<tr>
<td>$\tau_n \ll \tau_g$</td>
<td>nucleation instantaneous compared to diffusion growth</td>
</tr>
<tr>
<td>$\tau_g \ll \tau_{\text{OA}}$</td>
<td>large number of nuclei and monodispersed particles formed</td>
</tr>
<tr>
<td>$\tau_{\text{OA}} &lt; \tau_{\text{OR}}$</td>
<td>diffusion growth much faster than coagulation growth</td>
</tr>
<tr>
<td>$\tau_{\text{OA}} &lt; \tau_{\text{OR}}$</td>
<td>coagulation takes over as concentration of monomers deplete</td>
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<table>
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<tr>
<th>parameter</th>
<th>value</th>
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<td>$C_v$</td>
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<td>our experiment</td>
</tr>
<tr>
<td>$V$</td>
<td>$2 \times 10^{-4}$ m$^3$</td>
<td>our experiment</td>
</tr>
<tr>
<td>$T$</td>
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<td>our experiment</td>
</tr>
<tr>
<td>$C_i$</td>
<td>see SI Table S1</td>
<td>ref 43$^c$</td>
</tr>
<tr>
<td>$\mu$</td>
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<td>ref 43$^d$</td>
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<tr>
<td>$D$</td>
<td>see SI Table S1</td>
<td>ref 43$^e$</td>
</tr>
<tr>
<td>$l_0$</td>
<td>2</td>
<td>ref 38</td>
</tr>
<tr>
<td>$A$</td>
<td>$10^{34}$ m$^{-3}$ s$^{-1}$</td>
<td>fitted parameter</td>
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<tr>
<td>$\sigma$</td>
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<td>refs 15,38</td>
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<tr>
<td>$V_m$</td>
<td>$2.41 \times 10^{-20}$ m$^3$ per molecule</td>
<td>calculated using molar mass, density, and Avogadro Number</td>
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<td>$1/W$</td>
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<td>ref 41</td>
</tr>
<tr>
<td>$\beta$</td>
<td>see SI Table S1</td>
<td>fitted</td>
</tr>
<tr>
<td>$k_{\text{OR}}$</td>
<td>see SI Table S1</td>
<td>fitted</td>
</tr>
</tbody>
</table>

\textsuperscript{c}Methanol. \textsuperscript{d}Ethanol. \textsuperscript{e}Calculated from solubility product. \textsuperscript{f}Calculated using $\mu = A + BT + CT^2 + DT^3$, for ethanol, propanol, butanol, and $\mu = A + (B/T)$ for pentanol and hexanol. \textsuperscript{g}Calculated using the Wilke–Chang equation.

Table 1 that the nucleation rate is much greater compared to both diffusion and coagulation growth rates. This implies that a large number of nuclei are formed initially in the reactor in a very small time span. These nuclei undergo diffusion-growth to form bigger particles, as long as the solution is supersaturated with respect to ZnO. As explained earlier, nucleation and diffusion growth are considered to occur simultaneously for this
Figure 2. Progression of the UV-absorption spectra of ZnO colloids as a function of reaction time in (a) methanol at 333 K and in (b) ethanol at 298 K. Numbers in legends are in min. The y axes do not refer to actual absorbance values; the absorption curves are plotted such that the excitonic peak positions can be identified clearly.

3. RESULTS AND DISCUSSIONS

3.1. Spectrophotometric Monitoring of Nanocrystal Growth. The growth of ZnO NCs after stage S-I is slow enough to be followed using spectrophotometric assay. Figure 2a,b shows the successive UV-visible (UV-vis) absorption spectra at various time-points during the course of stages S-II and S-III. The clear maxima in the absorption spectra between 270 and 345 nm is due to the excitonic transition, which was found to shift to lower energies with increasing time, indicating particle growth. Figure 2a shows that in methanol the smallest NCs could be detected within 30 s into the process (at 333 K), with characteristic excitonic absorption peak (\(\lambda_{\text{max}}\)) at 270 nm (4.59 eV). Based on literature reports, the diameter of these NCs correspond is less than 1.5 nm. The spectral shift associated with NC growth in ethanol at 298 K is shown in Figure 2b. In this situation, at the earliest time point (1 min), the \(\lambda_{\text{max}}\) position was found to be at higher values (~306 nm), indicating formation of larger NCs (~2 nm) at similar growth times. However, even after 5 h of growth in either of the solvents, \(\lambda_{\text{max}}\) Positions for the NCs were found to be ~337 ± 3 nm, suggesting a saturation behavior in the particle-growth kinetics. It is noted that the prominence of peak positions and sharp absorption onset in the red-edge of the excitonic feature reflects narrow size-distributions for ZnO NCs in both these solvents.

Even after long time of growth (>12 h) at various temperatures, the \(\lambda_{\text{max}}\) is found to saturate at ~350 nm, which suggests that in presence of the capping group, tertiary butyl phosphonic acid (TBPA), sustained growth and formation of significantly larger NCs (more than ~10 nm) does not occur under our experimental conditions (see the Experimental Section). The effect of TBPA on the stability of size-selected NCs is evident from Figure 3, which shows the absorption spectra for NCs of three different sizes (with \(\lambda_{\text{max}}\) positions at 275, 303, and 313 nm) collected on the day of preparation, and after 40 and 80 days. The negligible shift in \(\lambda_{\text{max}}\) positions as well as in the overall absorption profiles over extended time-periods demonstrates that TBPA can act as highly effective capping agent to arrest further growth and interparticle association after size-selection by fast thermal quenching (see the Experimental Section). In this context, it is worth mentioning that we have also tried other capping groups (such as polyvinylpyrrolidone), but we find that for our experimental conditions, TBPA is the most effective one in
terms of formation of small particles with narrow size-distributions (see section 3.2).

3.2. Validation of Nanocrystalline ZnO Dimensions. The $\lambda_{1/2}$ value obtained from the excitonic absorption feature (Figure 2a) for the smallest size-selected NCs grown for 30 s in methanol yields a $\Delta E_g$ of 0.91 eV, which, according to the simplified TBM expression, corresponds to $d \approx 1.58$ nm. This value of $\Delta E_g$ is in reasonably good agreement with a previous experimental report ($\Delta E_g \approx 0.95$ eV) where $\sim 1.4$ nm diameter ZnO NC was synthesized. We also performed independent size measurements (TEM and AFM) on NCs formed during the first two hours of growth. Figure 4a–c displays representative TEM images of ZnO samples for 3 min, 1 and 2 h of growth in methanol, for which the $\lambda_{max}$ were found to be 286, 312, and 320 nm, respectively. The PSDs (Figure 4d–f) obtained from the analyses of hundreds of NCs are found to be quite narrow (typically with a standard deviation of $\sim 0.3$ nm), in tune with the sharp excitonic absorption onset. Similarly, AFM height distribution measurements were also performed on capped ZnO NCs spin-cast on a mica surface, which yielded $d$ of $2.8 \pm 0.7$, $3.8 \pm 0.8$, and $6.6 \pm 1.2$ nm for samples prepared for 20 min and 1 and 5 h, respectively (Figure S2, SI). The increasing $d$ obtained from both TEM and AFM measurements were found to be consistent with TBM estimates at respective growth times (Figure S3, SI).

The HR-TEM images (and their Fourier-transforms) of NCs in methanol, grown at 333 K for up to $\sim 3$ min and 1 and 2 h are shown as insets of Figure 4a–c. ZnO NCs grown for 3 min were typically found to have diameters between 1.8 and 2.2 nm, whereas those grown for 1 and 2 h were between 3.2 and 3.6 nm and $\sim 3.8$–4.3 nm, respectively. More importantly, Fourier-transformed HR-TEM images show hexagonal symmetry characteristic of a wurtzite lattice, even for the smallest NCs (Figure 4a inset). The interplanar distance ($\sim 2.6$ Å) obtained from HR-TEM measurements were consistent with the X-ray diffraction for ZnO NCs (Figure S4, SI), corroborating the hexagonal lattice of individual NCs. Interestingly, though the HR-TEM images of bigger NCs show almost spherical shapes with aspect ratios no more than 1.2:1, smaller particles obtained at early growth times routinely show irregular shapes indicating coagulation (Figures 1a, 4a, and S1, SI) to form nanosized clusters. However, no boundary in the form of lattice disorientation between the constituent NCs could be seen in any of these clusters, suggesting that they are attached in such a way that the atomic orientations remain to be continuous across the boundaries.

Figure 3. Long-term stability of capped NCs grown for (i) 1, (ii) 30, and (iii) 60 min and stored in methanol at 277 K. The $y$ axes do not refer to actual absorbance values; the absorption curves are plotted in tune with the sharp excitonic absorption onset. Similarly, the $\lambda_{1/2}$ value obtained from the excitonic absorption feature (Figure 2a) for the smallest size-selected NCs grown for 30 s in methanol yields a $\Delta E_g$ of 0.91 eV, which, according to the simplified TBM expression, corresponds to $d \approx 1.58$ nm. This value of $\Delta E_g$ is in reasonably good agreement with a previous experimental report ($\Delta E_g \approx 0.95$ eV) where $\sim 1.4$ nm diameter ZnO NC was synthesized.

Figure 4. TEM images of ZnO NCs grown for (a) 3, (b) 60, and (c) 120 min in methanol at 333 K. The scale bar is 20 nm. HR-TEM images for the respective samples and their Fourier transforms are shown as insets. The scale bar in the inset is 4 nm. The particle size distributions corresponding to same are shown in panels d–f.

Figure 5 shows the increase in mean particle diameter $d$ of ZnO NCs in both methanol and ethanol at various temperatures ranging from 273 to 353 K, for up to 5 h of nanoparticle growth. The initial time-period (10 min) of growth for the smallest NCs in both the solvents is shown as insets of Figure 5a,b. It is evident that both the solvent medium and the growth temperature play an important role in controlling the initial phases of NC growth. However, at later times, the temperature rather than the solvent has a more profound effect on growth processes and in controlling the eventual size of NCs. The following sections describe how the experimental data for ZnO NC growth over the entire time-span of nanoparticle formation has been successfully predicted using our model.

3.3. Comparison between Model Predictions and Experimental Data. This comparison is obtained by solving the relevant model equation in each stage, starting with eqs A1 and A5 (see the Appendix), to predict $d$ in stage S-I. Depending on the solvent and growth temperature, we obtain $d \approx 1.32$–1.66 nm from our model at the end of stage S-I. These values are then used to solve eqs A6 and A7 (see the Appendix) to calculate increase in $d$ by OA in stage S-II. Similarly, the value of $d$ at the end of stage S-II is used in eq 8 for particle growth by OR in stage S-III. Since a definite criterion for commencement of OR (in time) does not exist, we fitted $d^3$ versus time for both solvents at all temperatures. The time from which the plot showed linearity was taken as the transition time (Figure 6a–d), below which $d^3$ vs $t$ is shown to be nonlinear. These characteristic transition times are listed in Table 4 for methanol...
and ethanol, respectively. It is also clear from Figure 7a,b (discussed later) that the time for the onset of linearity (i.e., onset of stage S-III) does not coincide with the time when nucleation and diffusion growth (i.e., stage S-I) ends, implying that OA indeed occurs in the intermediate period, i.e., it follows diffusion growth and precedes OR. It has been shown that the condition \( \frac{4\sigma V_m}{RT} \ll d \) must be valid for diffusion limited OR to dominate the growth kinetics, giving an alternate estimate of the time of onset of stage S-III.\(^{41}\) In Table 4, we have compared the transition time to stage S-III by both these methods. It is observed that the values from our experimental data (on the onset of stage S-III) is larger than the time required for the above inequality to be valid, suggesting that the inequality condition is already satisfied by the time-instant from which we model growth by the OR route.

Figures 7a and 7b show that both experimental data (symbols) and model predictions (solid lines) display similar trends with respect to time, temperature and solvent. Both show that (i) initially \( d \) grows faster and later slows down with time, (ii) growth rate increases monotonically with temperature, (iii) at a given temperature, nucleation and growth is faster in ethanol, compared to methanol, (iv) formation of smallest NCs are favored in methanol within first few minutes, with growth temperatures playing a minor role, and, finally, (v) at later stages of growth, temperature becomes a dominant parameter and determines final NC size. It is noted that the predictions from the model at initial times (insets of Figure 7) are not very good at low temperature in ethanol. Even though the reasons are not apparent at this time, the model is still able to predict the trends at all temperatures and time in methanol reasonably well. The fitting parameters of the model, namely coagulation efficiency (\( \beta \)) and OR rate constant (\( k_{OR} \)), along with other physical properties of the solvent are listed in Table

![Figure 5](image_url)

**Figure 5.** Temporal evolution of the mean diameter (\( d \)) of ZnO NCs at different growth temperatures between 273 and 353 K in (a) methanol and (b) ethanol. The evolution of \( d \) at initial period of growth (first 10 min) is shown in the insets. The errors-bars in \( d \) were estimated using error in measurements of \( A_{1/2} \) for five independent data sets.

![Figure 6](image_url)

**Figure 6.** Cube of mean diameter (\( d^3 \)) of ZnO NCs plotted against growth times at different temperatures in (a and b) methanol and (c and d) ethanol. Symbols denote experimental data and lines denote the corresponding linear fits. Note that at initial times, it does not follow a linear trend.
S1, SI. The fitted values are well within the range reported in literature.\textsuperscript{15} Since the nanoparticle–solvent system of the present work is same as in ref 15, the fitted constants are expected to be within the same range.

3.4. Transition from Coagulation to OR. We have shown from our time scale analysis that the overall NC growth is a three stage process. For a given solvent and temperature, the rate of coagulation depends upon the total number of particles in the system at the end of stage S-I, frequency of Brownian collision, and the coagulation efficiency in OA, given by eq 6. The OR rate depends upon the difference in number of smaller particles (having higher solubility) versus the number of larger particles (having lower solubility). The effect of these parameters on OA and OR are described below.

Effect of Particle Number and Size. Coagulation causes a decrease in total number of particles in the system, which in turn decreases the rate of coagulation (eq 6). On the contrary, the rate of OR does not depend upon the total number of particles but rather on their size distribution.

Particle size affects the rate of coagulation in two ways, namely (i) the frequency of collision \( q_p \) (ii) the efficiency of coagulation, \( \beta \). The only size dependent term in the collision frequency (eq 5) is the correction factor \( W \). As \( d \) increases with time, for instance, by 50\%, there is a \( \approx 3\% \) reduction in collision frequency (\( q_p \)).

If \( \beta \) is the fraction of collisions that lead to the formation of a larger spherical particle by fusion, the fusion rate is given by\textsuperscript{39,40}

\[
\frac{da}{dt} = -\frac{1}{\tau_f}(a - a_{m})
\]

(10)

where \( a \) is the actual surface area of the aggregate containing two particles at any point during fusion, \( a_{m} \) is the minimum surface area corresponding to a spherical particle formed after complete fusion, and \( \tau_f \) is the characteristic time for fusion, given by\textsuperscript{39,40}

\[
\tau_f = \frac{3k_BT_v}{64\pi\sigma D_{s} V_{m}}
\]

(11)

where \( D_s \) is the solid state diffusivity of atoms or ions. These expressions suggest that the rate of fusion decreases with increase in particle size. This leads to a decrease in rate of coagulation due to decrease in \( \beta \). However, there is no effect of increasing particle size on the rate of OR.

It is worth mentioning that the driving force for sintering and grain growth for granular materials is inversely proportional to the grain (crystal) size.\textsuperscript{47} The driving force for solid state diffusion that leads to fusion is the capillary pressure given by \( 2\sigma/G_t \), where \( G_t \) is the grain or the particle size and \( \sigma \) is the interfacial energy. This inverse relationship is in agreement with our model that the fusion rate decreases with increasing particle size, and also with the observation that the rate of coagulation decreases with time (Figure 7a,b).

It should be noted that the process of coagulation leads to an increase in the width of particle-size distribution.\textsuperscript{48} This enhances the probability of OR at later times. Therefore, one can infer that at a given temperature, the rate of coagulation decreases with time due to decrease in total number of particles and increase in mean particle size. However, rate of OR increases with time due to broadening of particle size distribution.

Variation of Transition Time with Temperature. It can be observed from Figure 6 and Table 4 that the time at which transition from coagulation to OR in either solvent occurs shifts to smaller times at higher temperatures. Similar transition has been reported,\textsuperscript{15,26} wherein the authors have arbitrarily used the

| Table 4. Transition Times in Methanol and Ethanol |
|---------------------------------|-----------------|-------------------|
| temperature (K) | time from \( d^0 \) vs \( t \) (min) | time when \((4\sigma V_m)/(RT) \ll d \) (min) |
| methanol | ethanol | methanol | ethanol |
| 273 | 90 | 273 | 90 |
| 283 | 60 | 283 | 30 |
| 298 | 45 | 298 | 20 |
| 313 | 45 | 313 | 10 |
| 333 | 10 | 333 | 5 |
| 353 | 3 | 353 | - |

Figure 7. Model prediction (solid line) of the evolution of the mean diameter (\( d \)) of ZnO NCs with growth time at various temperatures in methanol (a) and ethanol (b) fitted to the experimental data (symbols). The insets show the experimental data at initial time (up to 60 min) and the model prediction for stages S-I and S-II.
rate law of OR to fit data from 15 min onward, without explaining the mechanism of particle growth before that period.

As the growth temperature is increased, it was observed (Figure 7) that larger \( d \) was obtained at earlier times, which is very likely due to increased rate of coagulation. This increase in \( d \) in turn causes the coagulation rate to be reduced and the particle size distribution to widen even earlier than that at lower temperatures. Moreover, the rate of OR being a strong function of temperature, is also enhanced with increasing temperature. These factors contribute in the reduction of the driving force for coagulation while simultaneously augmenting the driving force for OR with increasing temperature, thus shifting the transition-times to smaller values. This observation is further substantiated from the condition, \((4\pi\rho d^6)/(RT) \ll d\), i.e., at higher reaction temperatures this inequality is valid at even smaller \( d \), which is obtained at smaller growth times (Table 4).

3.5. Rate Controlling Step in OR. It is important to mention that coarsening in this case is limited by the diffusion of molecules through liquid phase, whereas reaction on the surface of ZnO particle is relatively fast, indicating that the former is the rate limiting process. In the formation of ZnO NCs in propanol with water as the base, OR has been proposed to be simultaneously controlled by surface reaction as well as molecular diffusion through liquid medium. The argument of the authors is based on two observations: first, the \( k_{OR} \) does not follow the Arrhenius form at a fixed water concentration, and, second, the activation energy \( (E_a) \) depends upon the concentration of water present in the solution. However, the basic premises of LSW theory are not consistent with these observations which imply that the rate of diffusion alone does not control the coarsening processes. On the contrary, for our experimental data (Figure 8), \( k_{OR} \) follows the expected temperature dependence (i.e., Arrhenius law) in both the solvents. This suggests that \( E_a \) is constant and independent of the base concentration, implying diffusion limited OR.

3.6. Dependence of Overall Growth Rate on Temperature. It is clear from the model as well as the experimental data that all stages of particle growth depend strongly on temperature. We have calculated the rate of coagulation (Figure S5a, SI) using eq 6, which was found to follow the expected enhancement with increasing temperature. The collision frequency \( q_0 \) increases with temperature due to its inverse relationship with viscosity, while the collision efficiency \( \beta \) (related to solid state diffusivity \( \sim kT \)) increases exponentially with temperature following Arrhenius law. Therefore, with increase in temperature, number of collisions between particles leading to fusion is augmented, resulting in an overall increase in the rate of coagulative growth. It was noted that the coagulation rates obtained from our experiments are also consistent to those reported in literature (Figure S5a, SI), especially at lower growth temperatures.\(^\text{15}\)

The rate of OR was also found to increase with temperature (Figure S5b, SI). This is due to several factors such as temperature dependence of ZnO solubility, specific surface energy of the ZnO–solvent interface and the diffusivity of molecular ZnO. Both solubility of ZnO and its diffusivity in the solvent are known to increase with temperature.\(^\text{43}\) However, temperature dependence of specific surface energy of solids is not known in any solvent. We observe that the \( k_{OR} \) in ethanol increases 9 fold when temperature is increased from 273 to 298 K. Over the same temperature range however, solubility of ZnO in ethanol increases by a factor of 4.34 (Table S1, SI) while the diffusivity (inversely related to viscosity) increases by 1.8 times (Table S1, SI). Therefore, solubility and viscosity changes with temperature can account for ~7.8 fold enhancement of OR rates, which is in reasonably good agreement with the observed factor of 9. This suggests that surface energy of ZnO does not vary appreciably over this temperature range and therefore it is likely that surface energy does not contribute significantly to the overall growth rate differentials.

3.7. Dependence of Overall Growth Rate on Solvent. Analyses of both our experimental data and those reported by Hu et al.\(^\text{15}\) in various alcoholic media having higher carbon chain lengths (Figure S5a, SI) show that, both OA and OR rates depend strongly on the choice of solvent. Rate of coagulation by OA was found to increase from methanol to ethanol in the entire temperature range of our experiment. Similar trends are observed from ethanol to hexanol (with the exception of isopropanol), when experimental data from Hu et al. is analyzed using our model. Variation of the coagulation rate constant \( (k_{OA}) \) is due to the interplay of dielectric constant \( \varepsilon \) and viscosity of the medium, both of which can affect the collision frequency \( (q_0) \) between two particles. Due to the existence of repulsive force between two charged particles,\(^\text{49}\) \( q_0 \) and therefore \( k_{OA} \) is reduced significantly (compared to uncharged particles), specially in a medium having higher \( \varepsilon \). In our synthesis, KOH added for precipitation contributes positively charged counterions on ZnO particle surface, which leads to electrical double layer formation around the charged particles. Since the thickness of the double layer is proportional to square root of \( \varepsilon_0 \varepsilon \) (methanol \( \varepsilon = 36 \)) creates thicker double layer and hence, higher repulsive force, compared to that by ethanol \( (\varepsilon = 20) \), thereby reducing \( k_{OA} \) much more in the former solvent. In contrast, with increase in carbon chain-length, solvent viscosity increases mildly, resulting in only a slight lowering of \( q_0 \) between particles, thereby lowering \( k_{OA} \). So, overall, from methanol to hexanol, \( k_{OA} \) is expected to increase, as seen in Figure S5a, SI. The effect of solvent on coagulation efficiency alone is not known.

The rate of diffusion-controlled OR obtained from eq 9 using our experimental data and those reported by Hu et al.\(^\text{15}\) shows similar trends, both with temperature and solvents of increasing carbon chain length (Figure S5b, SI), so that comparison at a particular temperature shows a continuous increase in the rate from methanol to hexanol. The factors that govern rate of OR are molecular volume and diffusivity, solubility, temperature and interfacial energy of ZnO. Molecular volume of ZnO is independent of the solvent. However, at a given temperature, both diffusivity and solubility decreases with increasing carbon.

Figure 8. Temperature dependence of Ostwald ripening rate, i.e., \( k_{OR} \) determined from the slopes of \( d^3 \) vs time curves for methanol (circles) and ethanol (squares). The solid lines show the best linear regressions to the data from 15 min onward, without explaining the mechanism of particle growth before that period.
chain length. Therefore the observed increase in rate at a particular temperature is due to higher interfacial energy in solvents of higher carbon chain length.

3.8. Control of Particle Size Distribution. From the absorption spectra in Figure 2a, we have estimated the percentage coefficient of variation (COV) for our experimental data, up to 120 min of growth (Figure S6, SI). The upper time limit of 120 min is imposed based on the fact that beyond this period, the methodology does not give a reliable estimate of COV. Ideally, one would like to synthesize nanoparticles with COV within 15%, so as to have a reasonably monodisperse PSD. To that end, we notice that for synthesis in ethanol (Figure S6b, SI), the COV is about 15% or less, only when the temperature is below 283 K and growth is not allowed beyond ~30 min. For temperatures 298 K and higher, COV becomes nearly 15% or more within 10 min. This implies a very small operating temperature range for synthesizing particles with less than 15% COV, corresponding to which one cannot have d less than 2.5 nm (Figure 5b). On the contrary, for synthesis in methanol (Figure S6a, SI), COV is less than ~15% at temperatures 333 K or below, if growth is not carried beyond 1 h. Similar to ethanol, here too, COV increases much faster at 353 K, to become ~20% or more within 10 min. However, the larger possible window of growth-time as well as temperature-range (between 313 and 333 K) in methanol allows one to generate ZnO with well-controlled mean particle diameters in the range 1.5 to 3.5 nm (Figure 5a).

4. CONCLUSIONS

ZnO NCs have been synthesized by precipitation in either methanol or ethanol as a solvent at various temperatures ranging from 273 to 353 K. Growth of NCs was arrested by rapid lowering of the reaction temperature (to 253 K) with simultaneous TBPA capping, which results in a stable dispersion of NCs with diameters of ~1.5 to ~5 nm. A mechanism has been proposed and mathematically modeled to predict the above formation pathway. To begin, we consider extremely fast precipitation reaction to be instantaneous. Based on further a priori time scale analysis of the individual events, we propose a three-stage, time-sequenced description: (i) stage S-I, nucleation of ZnO particles and its growth by molecular diffusion; (ii) stage S-II, an intermediate, interparticle coagulative-growth via oriented-attachment; and (iii) stage S-III, final interparticle growth by Ostwald ripening. Accordingly, simultaneous nucleation and diffusion growth in stage S-I is tracked by solving coupled PBE and mass balance equations. These time-scale conclusions are further substantiated by high resolution TEM images for stage S-II, showing transition from a cluster of few NCs to a completely coagulated bigger NC. The effect of ZnO interparticle interactions have also been accounted in the coagulation frequency in this stage. This is followed by the well-known OR route in stage S-III; a very slow growth-mode until the end of the process. Here too, in addition to time scale conclusions, our experimental data clearly show that cube of particle diameter varies linearly with time, from about tens or several tens of minutes until the end of the process-time of five hours. Such cubic law is the signature of diffusion controlled OR growth-mode. Existence of stage S-II is not recognized in most reports on ZnO growth, but is crucial in connecting the rapid nucleation and diffusion growth of stage S-I to the very slow OR growth in stage S-III. This three stage process, proposed on the basis of both estimated time scales and direct experimental proof, constitute the complete particle formation mechanism. Current literature has considered only one or two of these stages and fails to correctly capture the complete evolution of nanoparticle formation in time. Our work therefore addresses this void in the existing literature. Predictions of the model compare favorably with experimental trends on temporal evolution of ZnO NC diameter. The validated mechanism is quite general, and can be applied to study the effect of various parameters (e.g., reactant and capping agent concentrations, reaction time, temperature etc.) for optimizing experimental conditions. All of the fitting parameters used in the model are well within the range of values reported in literature, making our experimental data and model predictions consistent with data published by other research groups.

Finally, explanation of the experimental trend of increasing particle diameter with temperature is ascribed to the increase in all the growth processes with temperature. Similarly, formation of larger particles with increasing carbon chain length of solvents arises because, rates of both OA and OR increase from methanol to ethanol (as in the present work), and from ethanol to hexanol (for data of Hu et al.15). This we justify on the basis of higher interfacial tension, higher viscosity and lower dielectric constant of solvents having increasing carbon chain length. The proposed mechanistic framework, identifying multiple stages based on time-scale calculations, in principle can be used for tracking any other nanostructure evolution. These results therefore open up avenues for further investigation in combining experiments, mechanisms and model calculations of other nanoparticle systems as well.
distributions as indicated by the red-edge of the absorption spectra. Therefore, we have taken precaution to ensure that minimum amount of water is present in the solvents during ZnO synthesis.

5.3. Characterization of ZnO Nanocrystals. Steady-state optical absorption spectra of diluted samples were collected using a UV–visible spectrophotometer (JASCO V570). To determine the morphology and size of the NCs, transmission electron microscopy (TEM) images were recorded in Philips CM200, whereas HR-TEM investigations were performed using a Tecnai F20 TEM/STEM/GIF Supertwin microscope (operating voltage of 200 kV) with field emission gun and a point resolution of 0.24 nm. The TEM samples were prepared by drop casting diluted colloidal ZnO in methanol onto a carbon-coated copper grid, followed by drying at room temperature. Samples for atomic force microscopy (AFM) were prepared by drop casting on a cleaned mica surface, with images taken at ambient condition in tapping mode using Digital Instrument Nanoscope—IV. Main diameter and PSD was calculated by measuring the diameter or height of several (>100) NCs obtained from the TEM and AFM images, respectively. Powder X-ray diffraction of precipitated ZnO NCs was done in a PANalytical X-ray diffractometer, with a step size of 0.02°, using Cu Kα radiation as X-ray source of wavelength 1.5418 Å. All the above measurements were performed at room temperature, unless mentioned otherwise.

5.4. Determination of Nanocrystal Diameter from Absorption Spectra. Tight binding model (TBM) calculations have been shown to predict d for ZnO consistently over the entire size regime of quantum-confined, in contrast to the effective mass approximation (EMA) model,27,46 and therefore, we have used TBM to estimate d. The change in the band-gap (∆Eg) upon quantum-confined was directly obtained from √λ1/2 positions of the excitonic absorption feature,21,51–53 considering the bulk band gap (Eg) of ZnO to be 3.37 eV.18 We have used the simplified TBM expression: ∆Eg = 1.67/d1.4, which has been shown to reliably predict d for ZnO NCs between 2 and 5 nm.46 Error in the estimation of ∆Eg is obtained from the error in measurement of λ1/2 positions at various time-points during growth, which did not exceed ±1 nm. With time, as d increases, the error in ∆Eg translates to an increasing error bar in the estimation of d (see Figures 5 and 7). Estimates of the spread of the size distributions were obtained by calculating the coefficient of variation (COV) following the method prescribed by Viswanatha et al.50 It was however found that estimates of COV was not reliable for long growth-times when larger particles formed, and therefore, COV was estimated only for data up to 2 h.

■ APPENDIX

Model Equations for Evolution of Particle Diameter

Nucleation and diffusion growth (stage S–I): Population Balance Equation (PBE). The PBE used in the form of a number balance of particles in the system, with particle volume, v as the state variable

\[
\frac{dn(v,t)}{dt} + \frac{∂}{∂v} \left[ G(v,t) n(v,t) \right] = k_n δ(v - v_c)
\]  (A1)

where n is the number density of particles per unit dispersion volume, G is the growth rate of a single particle (given as dv/dt), k_n is the nucleation rate of particles, and δ is the Dirac delta function, indicating that nucleation occurs only at the critical volume of a nucleus, v_c. Equation A1 is a balance of rate of change of number of particles in a particular volume range, influenced by nucleation of new particles (term on right-hand side of eq A1) and by diffusion-growth of existing nuclei (second term on left-hand side of eq A1). It is a hyperbolic partial differential equation, solved numerically by the method of characteristics, along with the following known conditions.54

- boundary condition: \( n(v_c, t) = \frac{k_n}{G} \)

- initial condition: \( n(v, 0) = 0 \)

In this technique, eq A1 is converted to a set of ordinary differential equations to track the change in number of particles for each volume range (due to nucleation and growth). The rate of nuclei formation is

\[
\frac{dN_i}{dt} = k_n
\]  (A2)

Total number of particles per unit volume of the system, in a given volume range from \( v_i \) to \( v_{i+1} \) is

\[
N_i = \int_{v_i}^{v_{i+1}} n(v, t) \, dv
\]  (A3)

The rate of change of the number of particles larger than the nuclei is

\[
\frac{dN_f}{dv} = 0
\]  (A4)

where \( i \) stands for particles of volume \( v_i > v_c \).

- The diffusion limited growth rate of particles \( G \) is given by \( dv/dt \) from eq 3.

- The PBE (eq A1) is numerically solved by coupling with the mass balance equation in liquid phase

\[
- \frac{1}{V} \frac{dC}{dt} = \frac{k_n l_i}{N_α} + \frac{d}{dt} \left[ \int_0^{∞} \left( \frac{1}{v_n N_α} \right) n(v, t) V \, dv \right]
\]  (A5)

where \( l_i \) is the critical number of molecules required to form a nucleus, as given by the classical theory of nucleation. The left hand side of eq A5 gives the rate of decrease of moles of Zn species in the solvent-phase, which is equated in the right-hand side to the rate of increase of \( v_n \) species in the solid ZnO phase, by virtue of both nucleation and diffusion-growth. In that, the first term is due to nucleation of ZnO while the second term is due to ZnO molecules added by diffusion growth. Thus, solution of eqs A5 and A6 gives the volume of nanoparticles in stage S-I.

Growth by Coagulation via Oriented Attachment (Stage S-II). End of stage S-I occurs when the solution is no more supersaturated. This signals beginning of stage S-II, wherein particles undergo Brownian collision and only effective collisions lead to their growth by fusion. The variation of mean particle volume \( \langle v \rangle \) and total number of particles per unit volume \( (N) \) can be written from total number density equations as

\[
\frac{dv}{dt} = \frac{q_f β}{2} N(t) v(t)
\]  (A6)

\[
\frac{dN}{dt} = -\frac{q_f β}{2} N^2(t)
\]  (A7)
The factor 1/2 appears in these equations since each effective coagulation of two particles reduces total particle number by one. The initial conditions to be used in eqs A6 and A7 are taken from results obtained at the end of the nucleation and diffusion growth period in stage S-I. The fitted values of coagulation efficiency, β, are reported in Table S1, SI.

**Growth by Ostwald Ripening (Stage S-III).** Finally in stage S-III, the rate law governing the increase in particle diameter due to diffusion limited OR is given by eq 8, from which the ripening rate is calculated as \( k_{OR}/V_m \). The fitted rate constants are given in Table S1, SI.

**ASSOCIATED CONTENT**

Supporting Information

Nomenclature, parameters, two supplementary tables, and six supplementary figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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