Growth mechanism of nanocrystals in solution: ZnO, a case study.

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Abstract

We investigate the mechanism of growth of nanocrystals from solution using the case of ZnO. Spanning a wide range of values of the parameters, such as the temperature and the reactant concentration, that control the growth, our results establish a *qualitative* departure from the widely accepted diffusion controlled coarsening (Ostwald ripening) process quantified in terms of the Lifshitz-Slyozov-Wagner theory. Further, we show that these experimental observations can be qualitatively and quantitatively understood within a growth mechanism that is intermediate between the two well-defined limits of diffusion control and kinetic control.

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The kinetics of growth and coarsening of clusters of a minority phase in the background of a majority phase has been studied extensively [1] for many years using analytic [2], computational [3] and experimental [4, 5] methods. In recent times, there has been renewed interest in understanding the growth mechanisms in the nanometric regime [6, 7, 8, 9] to control and manipulate various electronic properties of nano-scale systems. However these studies are concerned with the growth of a solid in a solid medium and the growth of a solid in a solution, that constitutes an important class of synthesis methods, is not extensively investigated in the literature. This is probably due to the common, but not fully substantiated, belief that in the synthesis from solutions, the growth of the nanocrystals occurs via a diffusion limited 'Ostwald ripening' mechanism [10, 11]. Though there exist some reports on non-Ostwald-ripening growth of metal nanocrystals [12], it is almost universally accepted that the growth of semiconducting nanocrystals in the nanometric regime proceeds via a diffusion controlled Ostwald ripening process, as reported so far for TiO_2 [13], InAs and CdSe [14] and ZnO [11] nanocrystal growths. However, there exists a theoretical understanding of the growth kinetics in both the well-defined limits of diffusion controlled growth [15] and growth controlled by reaction kinetics [16]. In this letter, we show that an analysis of our experimental results for the growth of ZnO nanocrystals from solution indicates that the growth process in this case is qualitatively different from the expected Ostwald ripening behavior and belongs to an intermediate regime between the two limiting growth models, namely diffusion limited (Ostwald ripening) and reaction limited growth. We have extended the well-known Lifshitz-Slyozov-Wagner (LSW) theory [17, 18] to include the contribution from kinetically controlled growth. We find that a treatment including the influences of both these processes on the growth kinetics provides a consistent and quantitatively accurate description of all experimental observations.

ZnO is a useful material for a wide range of applications, such as solar cells, luminescent devices and chemical sensors [19, 20]. An intriguing aspect in the preparation of ZnO nanocrystals has been the observation that the presence of a small amount of water in the synthesis influences strongly the size of the nanocrystals [21, 22]. In earlier work [11] on the growth kinetics of ZnO formation in water, it was concluded, on the basis of the time dependence of the average diameter, d, of ZnO nanocrystals, that the growth follows the expected Ostwald ripening process. Besides the well known $d \propto t^{1/3}$ law, Ostwald ripening, characterized by a diffusion limited growth process, also requires specific dependencies of

the growth kinetics on the temperature and the concentrations of the chemical reactants, as predicted by the LSW theory [17, 18]. Therefore, we have investigated in detail the growth kinetics of ZnO nanocrystals in water to establish the dependence of the average size on time, temperature and reactant concentration. Our results show that though the average diameter may be fitted to a cube-root of time dependence at long time scales, the observed dependence on temperature and reactant concentration is *qualitatively* different from what would be expected from an Ostwald ripening process.

A typical growth process involves adding 0.1 mmol of zinc acetate to 100 mL of 100-250 mM solution of double distilled water in iso-propanol (i-PrOH) maintained in a water bath at the required temperature (301-338K). In order to monitor the growth of ZnO nanocrystals in real time during the growth process, we make use of the *in-situ* time-resolved optical absorption spectra recorded from the reaction mixtures. The well-known shifts of the bandgaps, and consequently of the absorption edges with size, [22, 23, 24, 25] provide a reliable way to extract the average size and size distribution of the growing nanocrystal assembly. [26] In order to confirm the results obtained from the absorption technique, we have also carried out transmission electron microscopy (TEM) at a few selected points during the growth. A typical set of optical-absorption spectra for a given concentration of reactants and at a fixed temperature (308 K) is shown in Fig. 1. From the figure it is evident that the bandgap shifts towards lower energy with increasing time, indicating a systematic growth of nanocrystals. Additionally, one can also observe an increase in the absorption intensity with increasing time, suggesting an increase in ZnO concentration with time.
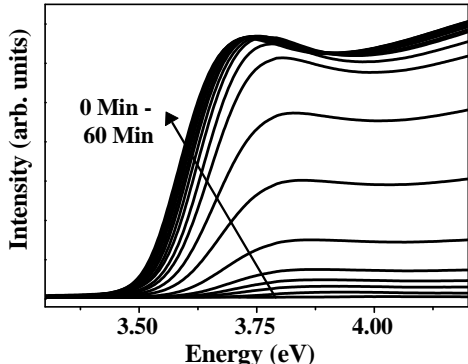

FIG. 1: (a) UV-absorption curves obtained at equal intervals of time for a typical reaction carried out at 308 K with 100 mM of water.

The rate law for diffusion limited growth or coarsening, often termed [27] as Ostwald

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ripening, was derived by Lifshitz and Slyozov [17] and by Wagner. [18] According to this theory the average diameter of the particles has a cube-root dependence on time, following the relation $d^3 - d_0^3 = Kt$, where d is the average diameter at time t and d_0 is the average initial diameter of the nanocrystals. The rate constant K is given by $K = 8\gamma D V_m^2 C_\infty / 9RT$, where D is the diffusion constant at temperature T, given by $D_0 \exp(-E_a/k_B T)$ (E_a is the activation energy for diffusion), V_m is the molar volume, γ is the surface energy and C_∞ is the equilibrium concentration at a flat surface. We show some typical variations of d^3 vs. t for several temperatures in Fig. 2, the points obtained from TEM being shown as open symbols. Though the time-dependence of d^3 deviates from linearity at earlier times, it indeed follows a linear relation at higher time-scales reasonably well (as shown by the thick solid lines), suggesting a dominantly diffusion limited growth in the long time limit. However, it should be noted that an apparently linear dependence of d^3 on t, especially only in the asymptotic limit, does not rigorously establish the validity of the LSW theory, although this criterion has been used [11, 13] extensively in earlier studies of growth of such particles, including the case of ZnO. In general, d^x as a function of t may appear linear within the experimental error limit for a wide range of x-values. We have verified that the present results show acceptable linear behavior for x-values ranging from 2.3 to 4. Therefore, it becomes necessary to explicitly verify the expected dependencies of the rate constant K on the temperature and the concentrations of the reactants, which provide more sensitive and critical testing grounds for the growth mechanism. We have, therefore, analyzed these dependencies in detail.

The dependence of the rate constant K on the temperature, T, arising primarily from the temperature-dependence of the diffusion constant, D, should follow the activated form $K \propto \exp(-E_a/k_B T)/T$. We find that though the observed dependence of K on T is reasonably well-described by this functional form at higher concentrations of water, the fit is far from satisfactory for lower water concentrations. Even more significantly, the activation energy, E_a, obtained from the best-fit curves and plotted (open circles) in the inset of Fig. 2 clearly shows a pronounced dependence on the concentration of water. While a concentration-dependence of the activation energy may arise from chemical diffusion at high water concentrations, the smallness of the highest water concentration (0.46%) employed here and the difficulty in fitting the temperature-dependence of K even for a fixed water concentration to the expected activated form suggest that a purely diffusion-limited growth
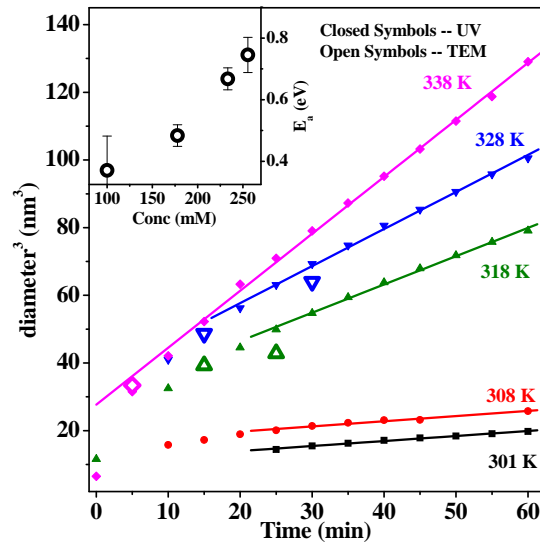
FIG. 2: (color online) The cube of the average diameter of ZnO nanocrystals shown as a function of time for different temperatures at a fixed water concentration (100 mM). The inset shows the variation of the activation energy with the concentration of water.

mechanism with a constant activation energy assumed in the LSW theory cannot describe the growth process of ZnO nanocrystals.

Growth of any nanocrystal via a solution route must be controlled essentially by two processes. One is the diffusion process of the reactants to the surface of the growing crystallite, while the second one is the reaction at the surface of the crystallite to incorporate the reactant as a part of the growth process. The prevalent belief of the diffusion process being rate limiting leads to the standard form of Ostwald ripening with a $d^3 \propto t$ dependence via the LSW theory. The results presented here clearly establish that the details of the growth kinetics, in particular its dependence on temperature and the reactant concentration, invalidate the applicability of this simplified approach, prompting us to probe the possible influence of the surface reaction rate. The reaction involves the dissociation of zinc acetate, providing Zn^{2+} ions. Hydroxyl ions are produced in the solution from the dissociation of water. The nanocrystals of ZnO comprise of tetrahedrally coordinated Zn and O atoms and only the surface Zn atoms are terminated with a hydroxyl ion instead of the oxygen ion. The growth of a nanocrystal occurs by the dehydration of terminating OH^- ions using the freely available OH^- ions in the solution. This is followed by the capturing of Zn^{2+} ions brought near the surface of the nanocrystal by diffusion. The growth of the nanocrystal is further continued by the Zn^{2+} ion capturing an OH^- ion and so on. Thus the reaction,

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namely, $H_2O \rightleftharpoons H^+ + OH^-$, $Zn^{2+} + 2OH^- \rightleftharpoons Zn(OH)_2 \rightleftharpoons ZnO + H_2O$, is controlled both by the diffusion of Zn^{2+} ions and the rate at which the reactions take place at the surface. Hence both these processes have to be taken into consideration in the modeling of the growth process. This interpretation is qualitatively supported by the experimental observations when we take into account the increase of the dissociation constant of water by about two orders of magnitude with increase in temperature, providing a large number of OH^- ions at higher temperatures. This increases the rate of the reaction drastically at higher temperatures. Therefore, it is expected that the growth process would shift towards a diffusion controlled mechanism at higher temperatures. This is entirely consistent with the results shown in Fig. 2, showing that an improved conformity with $d^3 \propto t$ behavior occurs systematically at earlier times at higher temperatures; a similar trend is also seen at higher water concentrations for a given temperature for the same reason.

In order to achieve a *quantitative* description, we note that the rate of change of the radius r of a growing cluster, characterized by the diffusion constant D and the reaction rate constant k_d, is given by [28]

$$\frac{dr}{dt} = \frac{\kappa}{Tr^2} \left(\frac{r/r_b - 1}{1/D + 1/k_d r} \right), \tag{1}$$

where, the constant κ is given by $\kappa = 2\gamma V_m^2 c_\infty / R$ and r_b is the particle radius in equilibrium with the solution. This equation implies that the reaction term is more important for small r, which is consistent with our observation (Fig. 2) of more marked deviations from a purely diffusion controlled growth at early times. Replacing r by the average size d, and assuming, [29] that the ratio of the average radius and the equilibrium radius r_b remains constant in time, Eq.(1) can be integrated to obtain the relation $t = Bd^3 + Cd^2 + const$, with $B = KT \exp(E_a/k_B T)$ and $K \propto 1/(D_0 \gamma V_m^2 c_\infty)$. The coefficient C is of the form $C \propto T/(k_d \gamma V_m^2 c_\infty)$. Thus, this equation not only defines the dependence of the average diameter d on time t, but also separates out the diffusion and reaction terms. This equation also yields the correct dependence of d on t in the two limiting cases: $d^3 \propto t$ in diffusion limited growth ($D/k_d r \ll 1$), and $d^2 \propto t$ in reaction limited growth ($D/k_d r \gg 1$).

We have used this expression to fit the experimentally observed variation of the average diameter d with time t, illustrated for a given water concentration (100 mM) by thick solid lines through experimental data obtained at different temperatures in Fig. 3. The remarkable goodness of fits over the entire range of the data points, in contrast to fits obtained from
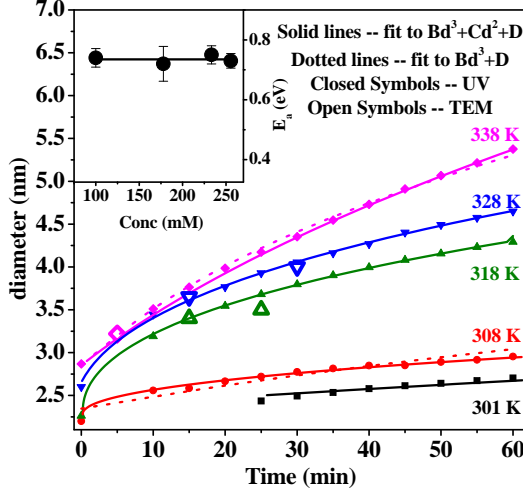
FIG. 3: (color online) The average diameter of ZnO nanocrystals shown as a function of time for different temperatures at a fixed water concentration (100 mM). The solid (dashed) lines show the best fits obtained over the entire data range using the form $Bd^3 + Cd^2 + D$ ($Bd^3 + D$). The inset shows the dependence of the activation energy on water concentration.

the LSW expression $t = Bd^3 + const$, illustrated with dotted lines in Fig. 3 for $T = 308$ and 338 K only, provides a conclusive validation of this description (Eq. 1). Further, we have obtained the values of B for different temperatures and different concentrations of water from the fits. The expected temperature dependence of the coefficient B is given by $B \propto T \ \exp(E_a/kT)$. The activation energy, E_a, obtained from the least square fits to $B(T)$ is plotted as a function of water concentration in the inset to Fig. 3. In sharp contrast to the results for the activation energy obtained earlier assuming only a diffusion controlled growth (shown in the inset of Fig. 2), the new results show a concentration-independent activation energy of 0.735 ± 0.007 eV, as expected. This provides a further validation of the proposed growth mechanism.

We find that the values of B obtained at a fixed temperature for various water concentrations are proportional to the square root of the water concentration, evidenced by the collapse of $B/(water\ concentration)^{1/2}$ vs T plots into a universal curve in Fig. 4. While we still do not have a rigorous explanation for this interesting behavior, such a collapse of the B values may be understood qualitatively in the following way. It is known that the diffusion constant D_0, molar volume V_m, surface energy γ and the equilibrium concentration c_∞ at a flat interface cannot depend on the concentration of water, at least for the small changes in

water concentration used here. However, the growth flux depends on the rate and the extent of reactions occurring near the surface which, in turn, depend on the concentration of the OH^- ions; assuming the concentration of H^+ and OH^- ions to be the same, the concentration of the OH^- should be proportional to the square root of the water concentration. Thus, the observed dependence of B on water concentration is consistent with the local chemistry occurring at the surface.
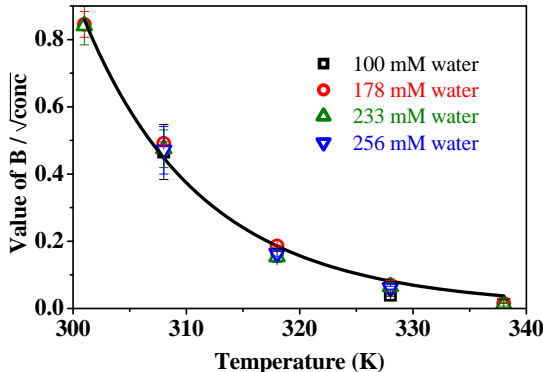

FIG. 4: (color online) The constant B scaled by the square root of water concentration, as a function of temperature for different water concentrations.

In conclusion, we show that a linear dependence of the cube of the average diameter on time is not a critical test to determine the growth mechanism. If the present data set is analyzed in terms of the $d^3 \propto t$ relationship predicted by the LSW theory in the diffusion controlled regime, the estimated activation energy for diffusion shows an unphysical dependence on the concentration of water. This implies a clear departure from the diffusion-limited Ostwald ripening process. However the expression obtained for the time dependence of the average diameter for growth controlled by both the rate of diffusion and the rate of reaction at the surface provides good agreement with experimental results over the entire range of time, temperature and concentration. In addition, this approach provides an estimate for the activation energy for the diffusion process that is independent of water concentration. These observations firmly establish that the mechanism of growth lies in the intermediate regime of diffusion and kinetically controlled growth processes.

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