NANO LETTERS

In Situ Observation of Oscillatory Growth of Bismuth Nanoparticles

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Supporting Information

ABSTRACT: We study the growth of Bi nanoparticles in an engineered precursorscarce environment in a liquid cell at an elevated temperature (180 °C) using transmission electron microscopy. Observation reveals dynamics of oscillatory growth of individual nanoparticles, pairwise Ostwald ripening and anti-Ostwald ripening and a global collective oscillation. The experimental results suggest a mass-transport zone is present around each particle, which couples to the observed growth kinetics. This study shed light on a new route for system engineering to reverse particle coursing by Ostwald ripening.



KEYWORDS: Liquid cell TEM, in situ TEM, colloidal nanocrystal growth, Ostwald ripening, digestive ripening, depletion zone

stwald ripening, large particles that grow bigger by consuming the smaller species, is a key coarsening mechanism for a variety of physical and chemical processes. It plays an important role in synthesis of monodisperse nanoparticles, geological rock texture formation, and a variety of industrial reactions. In heterogeneous catalytic reactions, Ostwald ripening often leads to undesirable consequences, such as nanoparticle catalysts lost their catalytic activities due to the decreased active surfaces. Since Ostwald ripening is a thermodynamically driven spontaneous process, we believe it is possible to limit this process by controlling the kinetic parameters. The study of anti-Ostwald ripening processes has been of great interest to many researchers. Previous studies have shown that the direction of mass transport can be manipulated by electric biasing.^{1,2} Coarsening of crystals with directed mass flow from one particle to another and the oscillatory growth have been observed in those studies.^{1,2} In colloidal nanocrystal synthesis, reinjection of precursors into the growth solution can refocus the ensemble of nanoparticles toward a narrower size distribution.³⁻⁸ In this case, changes in the precursor concentration modify the chemical potential thus change the particle sizes, which is similar to the effects of an electric biasing. Therefore, one can imagine that the two processes of growth or dissolution of nanoparticles can be reversed if the precursor concentration changes. Similarly, a particle can grow or dissolve if chemical potential fluctuates around the critical point.^{4,9} Nonetheless, to date this possible dynamics of growth-dissolution at the critical point in liquidphase reactions remains undiscovered. It is mainly due to the lack of imaging tools to monitor nanoscale particle growth in liquids. Recently, the development of liquid cells for transmission electron microscopy (TEM) has enabled imaging through liquids with high spatial resolution.¹⁰⁻¹³ Especially, the development of ultrathin liquid cells has significantly advanced

our capability to track the growth trajectories of nanocrystals in liquids with nanometer resolution.¹⁴ Nanoscale reaction processes in liquids can be captured at video rate. The remarkable time and spatial resolution allow us to visualize liquid-phase growth events that would not be observed before.^{13,14} It opens the possibility to design colloidal synthesis with controlled local environment at a length scale that is not accessible in bulk experiments.

In this Letter, we report the first observation of oscillatory growth of Bi nanoparticles in a precursor-scarce colloidal synthesis at an elevated growth temperature (180 °C) in a TEM. The in situ colloidal synthesis was performed in an inhouse fabricated liquid cell¹⁴ (Figure 1a). To produce a precursor-scarce environment, limited numbers of large Bi nanoparticles (with diameters of 80-150 nm) in a solvent mixture of oleylamine (surfactant) and dichlorobenzene (with a volume ratio of 2:8) were loaded into the cell. At an elevated temperature (~180 °C) the free-flowing Bi precursors were provided by dissolution of the preloaded Bi nanoparticles (Supporting Information Figure S1). Heating of the liquid cell was achieved by a furnace-type Gatan heating holder. The in situ observation was performed using a JEOL 3010 TEM operated at 300 kV (thermionic electron gun with a LaB₆ cathode). The TEM-image time series were recorded using a Gatan camera with an acquisition rate of 5 frames/s. The spatial drift of the sample was corrected by the measured drift rate (Supporting Information Figure S2). All images shown in this work have been drift corrected unless otherwise specified.

Received: November 28, 2011 **Revised:** February 1, 2012 Published: February 7, 2012



Figure 1. Overview of the experiment. (a) The construct of a liquid cell that can fit into a commercial TEM heating holder. (I) Three-dimensional view and (II) cross-sectional view of a liquid cell; (III) a TEM heating holder that fits standard 3 mm samples. (b) Number of nanoparticles within the field of view as a function of time. (c) Selected BF-TEM images of the in situ growth of Bi nanoparticles and the corresponding color gradient maps showing oscillatory growth of a pair of nanoparticles. A few nanoparticles with significant changes of volume are marked by arrows in image (III) as a comparison with image (II). The displayed time is in MM:SS format and has been rounded to the nearest integer seconds.



Figure 2. Oscillatory growth of Bi nanoparticles. (a) Trajectories of the total volume of the ensemble and a few selected particles vs time. (b) Trajectories of two particles (P1 and P2) showing pairwise oscillation. (c) The growth correlation plot of the pair of particles shown in (b).

Real time observation of growth trajectories Bi nanoparticles reveals striking dynamics of growth/dissolution oscillations of individual nanoparticles. At room temperature, we did not observe changes of the loaded Bi sources nor did we observe the growth of nanoparticles in any area prior to heating. When the liquid cell was heated to 180 $^{\circ}$ C, dissolution of the loaded Bi sources was initiated. As the Bi precursors diffuse into the surrounding area, Bi nanoparticles started to nucleate and grow on the supporting silicon nitride membrane (Supporting Information Figure S1). Figure 1c shows a few selected sequentially recorded bright-field TEM images in a field of view (see more details of the growth process in Supporting Information Movie S1). Apart from the nanoparticles that had already been present prior to recording, there was an initial outburst of particles (Figure 1b). Following that, rather unexpectedly, nearly all particles started to experience the oscillations of periodic growth/dissolution (see the highlighted nanoparticles in Figure 1c). The total number of nanoparticles within the field of view also fluctuates during the growth. The observed spontaneous dissolution of the particles after it reached certain size indicates the precursor concentration was low and that it varied with time. Nanoparticles are crystalline as



Figure 3. The quantitative growth parameters. (a) The oscillation period as a function of full particle size. (b) The particle size dependent growth rate averaged from all the particles. Dashed line is a linear fit. Inset is growth rate vs particle size of all the particles in the field of view. (c) The particle size dependent dissolution rate averaged from all the particles. Inset is dissolution rate vs particle size of all the particles in the field of view.

demonstrated by the diffraction contrast in imaging (Supporting Information Figure S3).

To explore the growth kinetics in the novel oscillatory growth, we analyzed the volume changes of the nanoparticles along their growth trajectories and further established the correlation between the nanoparticles. To extract the volumes of the nanoparticles, we used a thresholding method to segment the projected area of the particles automatically (see Supporting Information). Because Bi is a heavy element, the obtained bright-field TEM images are dominated by mass contrast of the nanoparticles. Therefore, the projected area of a particle can be segmented by intensities. To avoid systematic errors in measuring particles with different sizes, the threshold is adjusted dynamically for each particle individually. The volume of the particle is calculated from the projected area assuming the particle is spherical. The time-dependent segmentation results of an oscillating particle side-by-side with the original unprocessed data set are shown in Supporting Information Movie S2. It demonstrates the accurate segmentation and the robustness of our method. Using this method, we have tracked the growth trajectories of more than 30 nanoparticles with subsecond time resolution. This allows quantitative study the growth dynamics of individual colloidal nanoparticles at the relevant spatial and temporal resolutions that cannot be obtained by other imaging techniques.

Figure 2a presents the trajectories of a few selected typical particles and the time series of the sum of volumes of all the particles in the field of view. Both individual nanoparticles and the total volume of all the nanoparticles are oscillating around a certain volume. Considering growth of the nanoparticles results from the two competing processes of precursor attaching or detaching to the nanoparticles (growth or dissolution), we believe the system (including all the nanoparticles and solution) reached a pseudoequilibrium state. The individual oscillation frequency can be dramatically different from the total volume of the nanoparticles and from one to another. Some particles oscillate 10× faster than the oscillations of the total volume. This suggests that apart from the large scale collective oscillation there is another degree of freedom at local scales that individual particles are coupled to the neighboring nanoparticles and fluctuate corresponding to their local environment. As a case study, we analyzed the pairwise oscillation of particles P1 and P2 (as denoted in Figure 2b). The anticorrelation between the two particles is evident from the growth trajectories that the growth of one particle is synchronized with the dissolution of the other. There are two

distinct routes for the mass transfer between the two particles. First, one keeps growing while the other keeps shrinking and the process reverses when the shrinking particle completely dissolves. Second, opposite to the slow mass transfer, coalescence between P2 can P1 can occur almost instantaneously. It is noted that although the total volume of these two nanoparticles is not a constant it roughly oscillates around a certain value. The total volume reaches a minimum value when the two particles are almost equal in size. However, the peak volume is achieved when one of the particles is completely consumed. This suggests that these two nanoparticles interact with each other strongly by exchanging precursor through their local environment. Also, the rate of mass transfer from one particle to another (involving diffusion, attachment, and deattachment) fluctuates and is dependent on the particle size. Figure 2c plots the pairwise correlation of the two particles. Each data point is the growth rate of P1 versus the growth rate of P2 in a short time interval. The calculated R value is the Pearson's correlation coefficient between two variables. It is defined as the covariance of the two variables divided by the product of their standard deviations. The absolute magnitude of R is between 0 and 1 with 0 being uncorrelated and with 1 being perfectly correlated. The sign of the coefficient tells whether it is a negative or a positive correlation between the two observables. Using this plot in Figure 2c, we quantified that the correlation coefficient (R)between the pair of particles is -0.78.

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In order to further explore the detailed mechanisms of the oscillatory growth dynamics, we extracted the kinetic parameters of the growth and the dissolution processes. Figure 3a shows that the oscillation frequency decreases as the particles size becomes bigger. In Figure 3b, we measured the growth rate dr/dt as a function of the particle radius for all the nanoparticles growth trajectories. As shown the rate has a 1/r dependency. As for the dissolution process, however, the trend for the dissolution rate dr/dt is not a simple function of particle size. The transition between the growth and dissolution is discontinuous in the first-order derivative. Compared to the growth time scale, the transition time scale is almost negligible (Figure 2a). This phenomenon indicates the complex growth kinetics.

In the classical growth model for colloidal synthesis, there is a widely accepted but not yet experimentally proved diffusion layer around a nanoparticle.⁹ As shown by Gass et al. in in situ electrochemical plating,¹⁵ a diffusion layer becomes a depletion zone where small clusters within the diffusion layer are



Figure 4. The statistics of the correlation between particles. (a) The distance dependent correlation function. Inset is correlation coefficient vs distance of all pairs of nanoparticles within the field of view. The yellow bar plot is the average of all the data points shown in the inset. (b) A schematic of a pair of nanoparticles with the proposed depletion zone. (c) The correlation between the size of each particle and the total volume of the ensemble. The solid horizontal line is the average correlation. The two dashed lines mark the 95.4% confidence interval.

consumed by the bigger/stable clusters. With the similar nature of mass transfer in liquid, we believe the depletion zone concept should be applicable to colloidal synthesis. Especially, when precursor is scarce and nanoparticles are attached to a surface as it is in this case, characteristics of the diffusion layer or depletion zone can have prominent impact on nanoparticle growth trajectories. The analysis of the pair correlation (Figure 2) demonstrates that a depletion zone is likely to be present around particles. To quantitatively test the hypothesis and measure the depletion zone, we measured the correlation coefficient between each pair of particles in the field of view. In the inset of Figure 4a, we show the pairwise correlation coefficients in red crosses with an averaging black line guiding the trend of the data. The yellow bar plot in Figure 4a is a representation of the averaging guide line. The error bar here marks the two standard errors of the mean (95.4% confidence interval). The distance dependent correlation function shows a clear trend. When the distance between particles is larger than 100 nm, the mean value randomly fluctuates showing no significant correlation between particles. When the particles are separated by 50-70 nm, the mean correlation coefficients are positive and the confidence intervals do not cover the line of zero. When particles are further closer (<50 nm), the correlation coefficients become negative. We propose that this trend can be explained using the concept of a depletion zone around each particle (Figure 4b). When the particles are close to each other, their depletion zones are overlapped. It suggests that one growing particle can deplete the mass of the neighbor through the coupled depletion zone. Therefore, their sizes are coupled in an anticorrelated fashion and the correlation coefficients are negative. When the particles are separated slightly further such that their depletion zones are barely touching (Figure 4b), the two particles do not exchange mass with each other directly. Because they share the same local environment, on average they would grow or shrink in synchronous. However, when the particles are further separated, the particles are uncorrelated because they do not share the same local environment. Using this model the thickness of the depletion zone (or diffusion layer) is estimated to be around 20-25 nm.

The presence of a diffusion layer (or depletion zone) around particles can account for mass transport of pairwise oscillations and the growth kinetics. In a precursor scarce environment, the particle grows by consuming the surrounding precursor until it is depleted. Subsequently, the particle has to dissolve since the solubility is much higher than the negligible deposition. Each individual particle could be an oscillator that couples to the local environment as well as the neighbors if their diffusion layers overlap. We believe the size of diffusion layer is highly system specific. Thus, the measured depletion zone in this case, that is, 20-25 nm around a nanoparticle, may not be applied to understanding the growth kinetics in another system. However, this study is the first direct observation on oscillatory growth dynamics in a liquid-phase reaction and it provides direct evidence that a depletion zone surrounding the particle couples with growth trajectories.

In addition to the local environment, we found that on average the particles are positively correlated to the ensemble volume (Figure 4c). This shows a collective oscillation is present at the global scale.

In conclusion, we have created a precursor-scarce environment for colloidal synthesis of Bi nanoparticles in a TEM liquid cell that enables in situ imaging of Bi growth dynamics at nanometer resolution. At 180 °C, we observed in situ oscillatory growth dynamics of Bi nanoparticles on fixed nucleation sites. We have identified both individual and pairwise growth oscillations and collective fluctuations at global length scales. We extracted growth trajectories of more than 30 particles allowing us to analyze quantitative kinetic information of the novel growth phenomenon. We found that different particles can have dramatically different oscillation frequencies, but most particles are positively correlated with the fluctuation in the total volume of the ensemble. We identified that a depletion zone is present around the particles through the calculation of the particle-particle correlation. We also analyzed the size dependent growth and dissolution rate of the particles and found that the growth rate is approximately inversely proportional to the particle radius; however, the dissolution rate is not a simple function of the particle radius. The transition between the growth and dissolution is discontinuous in the first-order derivative. Each individual particle could be an oscillator that couples to the local environment and neighbors. We believe the oscillatory dynamics is associated with the growth/dissolution driven by precursor dependent chemical potential. This study suggests the possibility to counteract the energetically favorable Ostwald ripening process to prevent the coarsening of nanoparticles, which is highly beneficial to many industrial reactions, such as the heterogeneous nanoparticle catalysis. Future studies on the effects of temperature, precursor concentration, surfactants and

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solvent on the oscillatory growth kinetics, and the direct measurement of the local precursor concentration around a nanoparticle will contribute to more depth understanding and controlling of the growth.

ASSOCIATED CONTENT

S Supporting Information

A description of methods, Figures S1–S5, and two supporting movies. 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.

ACKNOWLEDGMENTS

This study was performed using the facility at National Center for Electron Microscopy, Lawrence Berkeley National Laboratory (LBNL), which is supported by the U.S. Department of Energy under Contract No. DE-AC02-05CH11231. We thank the LDRD funding support from LBNL.

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