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 precursor-scarce 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 sheds 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

Ostwald 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. Coarsening of crystals with directed mass flow from one particle to another and the oscillatory growth have been observed in those studies. In colloidal nanocrystal synthesis, rejoining of precursors into the growth solution can refocus the ensemble of nanoparticles toward a narrower size distribution. 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. Nonetheless, to date this possible dynamics of growth-dissolution at the critical point in liquid-phase 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. Especially, the development of ultrathin liquid cells has significantly advanced our capability to track the growth trajectories of nanocrystals in liquids with nanometer resolution. 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. 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 in-house fabricated liquid cell (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.

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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 °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...
Some particles oscillate total volume of the nanoparticles and from one to another. The oscillation frequency can be dramatically different from the solution) reached a pseudoequilibrium state. The individual detaching to the nanoparticles (growth or dissolution), we consider the two competing processes of precursor attaching or detaching to the nanoparticles. 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 pseudo-equilibrium 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 particle size. Figure 3b shows that the oscillation frequency decreases as the particle size becomes bigger. In Figure 3b, we measured the growth rate \( \frac{dr}{dt} \) 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 \( \frac{dr}{dt} \) 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. As shown by Gass et al. in situ electrochemical plating, a diffusion layer becomes a depletion zone where small clusters within the diffusion layer are

![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.](image-url)
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 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
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
2 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.

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