Quantifying the Nucleation and Growth Kinetics of Electron Beam Nanochemistry with Liquid Cell Scanning Transmission Electron Microscopy

Mei Wang,1 Chiwoo Park,2 Taylor J. Woehl1,*

1Department of Chemical and Biomolecular Engineering, University of Maryland, College Park, MD
2Department of Industrial and Manufacturing Engineering, Florida State University, Tallahassee, FL

*Corresponding author, email: tjwoehl@umd.edu

Abstract

In this article, we report on complex nanochemistry and transport phenomena associated with nanocrystal formation by electron beam induced growth and liquid cell electron microscopy (LCEM). We synthesized silver nanocrystals using scanning transmission electron microscopy (STEM) electron beam induced synthesis and systematically varied the electron dose rate, a parameter solely thought to regulate nanocrystal formation kinetics via the rate of metal precursor reduction. Rationally modifying the solution chemistry with tertiary butanol to scavenge radical oxidizing species established a strongly reducing environment and enabled repeatable LCEM experiments. Interestingly, nanocrystal growth rate decreased with increasing electron dose rate despite the predicted increase in reductant concentration. We present evidence that this counterintuitive trend stems from increased oxidizing radical concentration and radical recombination at high magnifications, which together decrease rate of precursor reduction. Nucleation rate was proportional only to imaging magnification, which we rationalized based on local radical accumulation at high magnification causing increased supersaturation and fast nucleation. Radiation chemistry and reactant diffusion scaling models yielded new scaling laws that quantitatively explained the observed effects of electron dose rate on nucleation and growth kinetics. Finally, we introduce a new reaction kinetic model that enables unraveling nucleation and growth kinetics to probe nucleation kinetics occurring at sub-nanometer length scales, which are typically not accessible with LCEM. Our systematic investigation of nanocrystal formation kinetics with LCEM indicates that the intricacies of radiation chemistry and reactant
transport must be accounted for to effectively harness radical scavengers and electron beam induced growth to systematically probe nanocrystal formation kinetics. We expect the empirical trends, scaling laws, and reaction kinetic model presented here will be indispensable tools for in situ electron microscopists and materials chemists alike when designing, analyzing, and interpreting LCEM nanocrystal formation data.

**Keywords**

Liquid cell TEM, nanocrystal synthesis, kinetic model, in situ electron microscopy, nucleation

**Introduction**

A unique aspect of colloidal nanochemistry compared to conventional molecular and supramolecular chemistry is the influential role of formation kinetics on resulting nanocrystal characteristics, such as size, shape, and surface structure. Because nanocrystal functional properties derive from these characteristics, formation kinetics effectively serve as an additional degree of control over nanocrystal properties in addition to the material composition. Colloidal nanocrystal formation proceeds by a complex combination of chemical and physical kinetic processes; precursor reduction is a chemical reaction, while nucleation is a physical phase transformation. Nanocrystal growth occurs by physical processes, such as aggregation and monomer attachment, chemical processes, such as autocatalytic growth, or a combination of both. In particular, effects of nucleation on colloidal nanocrystal formation remain enigmatic due to difficulty in quantifying nucleation kinetics. Overall, the complex chemical and physical processes involved in nanocrystal formation are intimately interlaced during synthesis. Separating and elucidating fundamental mechanisms for each kinetic process represents a significant current challenge to the nanomaterials research community, which if solved will enable deterministic synthesis of new nanostructures with increased complexity compared to current generation nanocrystals.

Nanocrystal formation kinetics have been experimentally investigated with various approaches, including bulk reaction kinetic measurements, UV spectroscopy, high energy x-ray diffraction...
In situ SAXS in particular is a powerful approach for resolving nanocrystal formation with high spatial resolution, as it allows detection of sub-nanometer sized nuclei and the time dependent particle size distribution (PSD), and can be quantified for interpretation by reaction kinetic models. However, in situ SAXS is limited in that it cannot resolve growth kinetics of individual nanocrystals with diverse shapes.

LCEM is unique among these approaches due to its ability to provide direct microscopic images of nanocrystal formation with high spatial and temporal resolution. Nanocrystal formation with LCEM is most often stimulated with the imaging electron beam, which reduces metal precursors into metal nanocrystals via the creation of radical species by radiolysis. Several fundamental challenges remain to be solved to enable utilizing LCEM to quantify nanocrystal formation kinetics in a manner similar to in situ SAXS. These include elucidating the local electron beam-induced solution chemistry, separating nucleation from growth kinetics, and enabling quantitative analysis of statistically relevant and repeatable data sets. Separating nucleation and growth kinetics is difficult because LCEM imaging in most transmission electron microscopes (TEM) only achieves nanometer scale resolution, while nuclei are sub-nanometer in size. Nucleation kinetics can be inferred by measuring the nucleation induction time, but direct systematic measurements of nucleation kinetics have yet to be realized with LCEM. Repeatability and reproducibility of electron beam induced nanocrystal formation has been a major challenge for LCEM researchers. Due to the small sample size, minute amounts of contaminants can significantly alter solution chemistry. For this reason, nanocrystal formation studies with LCEM are often limited to a few observations from a handful of experiments. Recent work has demonstrated improved repeatability during LCEM experiments through design of new microchips, modeling the effects of the electron beam on solution chemistry, and use of graphene and its derivatives to mitigate electron beam damage.

In this article, we demonstrate design and quantitative analysis of a parametric set of LCEM experiments probing the nanochemistry of electron beam induced nanocrystal formation. This study was enabled by innovations in rational control of solution chemistry, multitarget single nanoparticle tracking, scaling models for complex electron beam interactions, and a new reaction kinetic model for nanocrystal formation.
formation. We utilized a well-known model system of silver nanocrystal formation by electron beam reduction using scanning TEM (STEM) and systematically varied the electron dose rate, an important parameter thought to control the formation kinetics of nanocrystals and their growth mechanisms.\textsuperscript{26, 28-29}

This large data set (10 unique kinetic conditions, 23 total experiments, 3 unique samples) uniquely enabled us to search for and discover counterintuitive correlations among the nanocrystal formation kinetics that reveal new nanochemistry and physics associated with electron beam induced nanocrystal formation. Surprisingly, we found that neither nucleation nor growth kinetics correlated directly with the electron dose rate. We develop two scaling laws based on radiation chemistry and reactant diffusion that provide new scaling expressions that show excellent correlation with nucleation and growth kinetics. We developed a reaction kinetic model that enables uncovering nucleation kinetics at early synthesis times, which are typically invisible to LCEM imaging. Together, these results indicate that electron dose rate is not simply a ‘quantitative knob’ for tuning nanocrystal nucleation and growth kinetics, but that more complex nanochemistry and physical processes must be considered when designing and interpreting quantitative LCEM experiments.

Results

Electron beam induced solution chemistry

The area averaged dose rate of the electron beam during STEM imaging, $\dot{d}$, quantifies the average amount of energy absorbed in the imaging area during LCEM imaging and is defined as $\dot{d} = \frac{i_e S}{A}$, where $i_e$ is the beam current, $S$ is the density normalized stopping power of water (2.798 x 10\textsuperscript{5} eV m\textsuperscript{2} kg\textsuperscript{-1} at 200 kV), and $A$ is the surface area of the STEM image, which is inversely proportional to the square of the image magnification.\textsuperscript{28} Electron dose rate is thought to be a universal parameter for controlling nanocrystal formation rate during electron beam induced nanocrystal formation because it controls radical reducing agent concentration, \textit{infra vide}.\textsuperscript{35} This suggests dose rate can be varied systematically to investigate nanocrystal formation kinetics and mechanisms in the same way that rate of reduction can be varied in wet
chemical synthesis. Coupled with simulations to predict dose rate-dependent reducing agent concentrations, LCEM experiments could enable discovery of quantitative correlations between nanocrystal nucleation and growth kinetics, precursor conversion kinetics, and nanocrystal formation mechanisms. With this premise in mind, we performed a parametric set of silver nanocrystal formation experiments using LCEM and varied electron beam current from 21 – 207 pA and image magnification between 80 – 150 kx to vary the electron dose rate between values of $10^5 – 10^7 Gy/s$. All together, we probed 10 unique dose rates in 23 experiments by parametrically varying beam current and magnification.

The imaging electron beam induces radiolysis of water molecules to form a mixture of both oxidizing and reducing radicals via the fundamental water radiolysis reaction:

$$H_2O \rightarrow e^- H_3O^+, OH^-, e_{aq}^-, H^+, OH^-, H_2O_2, H_2, HO_2$$ (Figure 1). Oxidizing species ($OH^-, O_2$) concentrations exceed those of reducing species ($e_{aq}^-, H^+$) in pure water by more than an order of magnitude (Figure 2a); these significant oxidative back reactions complicate nanocrystal formation kinetics and make it significantly different than common wet chemical syntheses. Nanocrystals still form in pure water due to the larger reducing reaction rate constants compared to oxidizing reactions, but can appear ‘fluffy’ due to simultaneous reduction and oxidation. To eliminate oxidative back reactions and establish purely reducing conditions more representative of wet chemical synthesis, we added 100 mM tertiary-butanol to each precursor solution, a molecule we found to serve as a dual scavenger. Tertiary-butanol directly scavenges $OH^+$ radicals, which in turn creates a radical byproduct that rapidly scavenges oxygen gas created by radiolysis (Figure 1). Numerical kinetic simulations showed that addition of tertiary-butanol decreases oxidizing radical concentration by two orders of magnitude compared to pure water (Figure 2b), leading to strongly reducing conditions for dose rates used in our experiments (Figure 2c). Based on the excellent experimental repeatability we observed, we believe that tertiary butanol also acts to normalize the solution chemistry across each sample by effectively overwhelming minute variable amounts of organic contamination in each sample that could react with oxidizing radicals.
Nanocrystal formation kinetics

Electron beam induced silver nanocrystal formation in the presence of tertiary butanol produced ~500 – 1000 nanocrystals, which were observed to nucleate and grow over several minutes and had final sizes ranging from 5 – 20 nm in diameter (Figure 3a). High resolution TEM (HRTEM) revealed the nanocrystals were crystalline silver and predominantly spherical in shape (Figure 3b,c). Importantly, we found that nucleation and growth overlapped in time, evidenced by the emergence of new nanocrystals simultaneous with their growth in time (Figure 3a). Due to this overlap, the average nanocrystal radius and number of nanocrystals as a function of time were ineffective quantitative measurements of growth and nucleation rate (see supplementary material).

To facilitate progress in quantifying nucleation and growth kinetics, we instead analyzed growth trajectories of single nanocrystals over time using multtarget particle tracking,43-44 which enabled delineating nucleation from growth kinetics. Figure 3d shows an example of single particle tracking for a small subset of nanocrystals from a single LCEM movie. The red stars indicate the time that each nanocrystal was detected, i.e. the nucleation induction time,26 while the black lines are linear fits to the nanocrystals’ growth trajectories. The nucleation induction time is inversely proportional to the nucleation rate and is commonly used to quantify nucleation kinetics because nuclei cannot be detected at the instant they form.12 Figures 3e and 3f show exemplary histograms of the growth rates and nucleation induction times for ~500 nanocrystals in a single LCEM movie. To reduce the substantial number of nucleation times and growth rates to two kinetic measurements for each experiment, we define the median growth rate (\(\bar{R}\)) and nucleation induction time (\(t_{\text{ind}}\)), shown by the dashed vertical lines.

Nanocrystal nucleation and growth kinetics were compared to the electron dose rate used for their synthesis, which is thought to control nanocrystal formation kinetics. Surprisingly, we found no universal correlations between nucleation and growth kinetics and dose rate (see supplemental material). Examining the growth rate data more closely, we found that nanocrystal growth rate decreased with increasing magnification for a constant beam current, while growth rate increased with beam current at constant magnification, albeit with a weak positive correlation (Figure 4a). The latter positive correlation is
expected due to increased concentrations of radicals at high beam currents, but the former indicates growth rate **decreases** with dose rate when increasing magnification. *This result is counter to all prior LCEM observations*, which have exclusively shown growth rate is proportional to dose rate.\textsuperscript{28-29} Indeed, this result indicates that the dependence of growth rate on electron beam parameters is more complex than previously thought and cannot simply be described by a universal parameter like dose rate.

**Nanochemistry of nanocrystal growth kinetics**

Why does nanocrystal growth rate decrease with increasing magnification (and dose rate)? Further interrogation of the data revealed that the growth rate for constant beam current followed a power law dependence on dose rate of $R \sim \dot{d}^{-1/2}$. Interestingly, the ratio of reducing species to oxidizing species concentration decreased with dose rate following the same power law, ostensibly due to depletion of the radical scavenger (Figure 2c). However, plotting growth rate as a function of $\dot{d}^{-1/2}$ yielded a plot where the growth rate data did not collapse onto a single curve (see supplementary material). Clearly the radiolysis kinetics alone do not explain the trend and there remain more complex underpinning chemical/physical phenomena. For further insight, we turn to the initial steps of radiolysis, which occur on time scales of picoseconds inside isolated spherical clusters of radicals called spurs.\textsuperscript{45} While spurs are typically separated in space, spur overlap at high dose rates causes enhanced radical recombination, which decreases concentration of reducing and oxidizing radicals.\textsuperscript{46-47} Grogan et al. developed scaling expressions for average interspur distance ($d_{spur}$) and spur density ($\rho_{spur}$) as a function of electron dose rate (see supplementary material).\textsuperscript{34} Based on typical spur size and the normal distribution of radicals within, two spurs are predicted to overlap and effect increased radical recombination when they are $\leq 6$ nm apart. **Figure 4b** shows that for all experimental conditions here the interspur distance is $\leq 6$ nm and that interspur distance decreases and spur density increases with increasing beam current and magnification. Therefore, we posited that by considering spur overlap as a correction factor for radical concentration, all the growth rate data will collapse onto a single curve. Indeed, when we recast the growth rate in terms of
the dose rate divided by the spur density, raised to the power of $\beta = -1/2$, viz., $(\frac{d}{\rho_{spur}})^{-1/2}$, we find an unambiguous correlation with the growth rate with a Pearson’s correlation coefficient of $R = 0.94$ (Figure 4c). This quantitative correlation, together with the experimental trends we observed, strongly supports the idea that this scaling argument directly correlates with the rate of precursor reduction during nanocrystal formation.

**Nucleation kinetics and reactant transport**

Like growth rate, nucleation induction time did not correlate universally with dose rate but revealed correlations when holding electron beam parameters constant. Median nucleation time decreased approximately linearly with magnification for constant beam current (Figure 5a). Changing magnification during STEM imaging affects several physical parameters during the experiment, namely the interpixel spacing during the image raster and the total volume of liquid being irradiated by the electron beam (*i.e.* the interaction volume$^{26}$). Increasing magnification and decreasing interaction volume could possibly increase the driving force for radical diffusion away from the nanocrystal growth area, but this would yield an opposite trend compared to what we observe. Instead, we focus on radical diffusion in the vicinity of the electron probe during STEM imaging. The STEM electron probe is ~1 nm in diameter and rasters across the sample surface at high velocity, intermittently pausing at each pixel for 5 $\mu$s (the pixel dwell time) to deliver electrons to form an image. At each pixel location, radicals are locally generated in the liquid and diffuse away due to large concentration gradients; the spacing of these local radical sources decreases with increasing magnification. We posit that the decreased pixel spacing at high magnification diminishes local concentration gradients and diffusive driving forces, which effects local accumulation of radicals. Large local radical concentrations rapidly reduce silver precursor, leading to a large supersaturation ratio and rapid nucleation kinetics. To quantitatively test the proposed mechanism, we compare the characteristic time scale for interpixel radical diffusion, $\tau_D$, with the characteristic flight time of the electron beam between two pixels, $\tau_{flight}$ (see supplementary material). As radical diffusion becomes faster than the beam
movement ($\tau_D \ll \tau_{flight}$), we expect there will be a more significant concentration of radicals surrounding an adjacent pixel when it is irradiated, smoothing concentration gradients and diminishing diffusive driving forces. This is expected to lead to shorter nucleation induction times. Indeed, recasting nucleation induction time as a function of the ratio between these time scales, $\tau_D/\tau_{flight}$, reveals an unmistakable positive correlation in line with our proposed physical mechanism ($R = 0.86$). This correlation is interesting because it indicates that at least for these experimental conditions, *beam current and thus the expected concentration of reducing radicals, had negligible effects on nucleation kinetics*. Figure 6 summarizes the proposed mechanisms for the effects of radiation chemistry and reactant transport on the nanocrystal nucleation and growth kinetics.

**Reaction kinetic model for nanocrystal formation**

The limited spatial resolution of LCEM, typically on the order of a couple nanometers, currently limits our ability to directly investigate kinetics of sub-nanometer scale processes like nucleation. The limited spatial resolution also indicates that the results of conventional particle tracking, such as average size and number of particles over time (see supplementary material), are influenced by both nanocrystal nucleation and growth. While single particle tracking can indirectly separate nucleation from growth kinetics, we desire a more general method to directly probe early-time nucleation kinetics occurring below the resolution limit of LCEM.

To this end, we developed a reaction kinetic model to uncover nucleation kinetics. We draw our inspiration from seminal work by Finke et al., who interpreted nanocrystal formation in terms of pseudo-elementary reactions for nucleation and growth. A pseudo-elementary reaction is the sum of many sequential reactions, only one of which is rate-limiting, and enables simplifying the complex kinetics of nanocrystal formation into a few tractable reactions. Our reaction kinetic model is as follows:

\[
Ag^+ + S \xrightarrow{k_N} N \tag{1}
\]

\[
Ag^+ + N_{surface} \xrightarrow{k} 2NP_{surface} \tag{2}
\]
Equation (1) represents nucleation, where $S$ are nucleation sites and $N$ are silver nuclei. Equation (2) represents growth of nuclei into nanocrystals that cannot be observed with LCEM, $NP_1$. Equation (3) represents growth of nanocrystals below LCEM detection into nanocrystals observed in experiments, $NP_2$.

Several aspects of the new kinetic model are worth noting. First, it is based on a two-step nucleation and autocatalytic growth reaction mechanism, which is commonly invoked for slow nanocrystal formation reactions. However, recent experiments have shown the wide-spread applicability of this type of reaction model for both slow and fast nanocrystal growth kinetics. Secondly, our reaction kinetic model includes an intermediate growth reaction (equation 2) that takes into account growth of nanocrystals with sizes below the image spatial resolution. Ex situ HRTEM images confirmed the presence of silver nanocrystals below the resolution limit of LCEM and the particle tracking algorithm ($<2$ nm) (Figure 3b,c). Because nanocrystals form on the silicon nitride membrane surface and only within the electron irradiated area, each reaction above is inherently a surface reaction in terms of surface concentration of each species. Nanocrystals only form on the membrane surface, so there is limited area available for nucleation and growth. To account for this unique aspect of LCEM, we included an additional species in the nucleation reaction that accounts for the limited number of nucleation sites, $S$.

Experimental measurements of nanocrystal PSD as function of time were transformed into total surface molarity of nanocrystals, $[NP_2]$, and assuming mass-action kinetics the rate expressions were numerically integrated and fit to the kinetic data to determine each rate constant (See supplemental material for details). The plots of $[NP_2]$ have a characteristic initial lag time, ostensibly due to finite nucleation rate and growth of nanocrystals below the resolution limit of LCEM (Figure 7a). Examples of the reaction model fits to experimental data for nanocrystal formation at two different magnifications are shown in Figure 7a. We can see that the reaction model fits our experimental data very well compared to kinetic models that don’t include the intermediate growth step or the nucleation site species (see supplementary material). The time course of each species concentration at 100 kx magnification in Figure
7b shows that nucleation sites were depleted over time as nucleation began. The nuclei concentration peaked between 15-20 seconds, characteristic of ‘burst’ nucleation and similar to prior kinetic models for nanocrystal formation.9 Once nuclei formed, Ag⁺ reduced on the nuclei surface to effect growth of small nanocrystals that were not observed by LCEM (NP₁). Shortly after formation of NP₁, larger nanocrystals that were detected in LCEM images, NP₂, emerged. This reaction cascade provides a qualitative explanation for the time lag in appearance of nanocrystals, which is due to a combination of nucleation and growth kinetics. Only by implementing this reaction kinetic model were we able to unravel and quantify the contribution of these two effects to the lag time. The time course of the 150 kx data set is shown in Figure 7c. Each of the time-dependent species concentrations showed qualitatively similar trends compared with the lower magnification. At higher magnification, the peak in nuclei concentration occurred earlier indicating that higher magnification yielded faster nucleation, in agreement with our single particle tracking measurements (Figure 5). It is remarkable that the fitted growth rate (k_G) and nucleation rate (k_N) constants derived from this ensemble kinetic model followed identical trends as the median growth rate and nucleation induction time derived from single particle tracking (Figure 7d,e). This agreement with experimentally measured formation kinetics provides strong evidence that our reaction kinetic model is truly capturing the nanocrystal formation kinetics.22 Most importantly, this reaction kinetic model reveals sub-spatial resolution details about nucleation kinetics. Specifically, it reveals that nucleation occurs in a burst at early times and that the main precursor conversion channel shifts from nucleation to growth as surface sites are depleted. The nucleation site parameter, S, is solely responsible for capturing this kinetic behavior and was therefore critical to enable successful implementation of this model. This reaction kinetic model should be generally applicable to all LCEM nanocrystal formation experiments, as it captures specific aspects of LCEM including the limited number of nucleation sites and limited spatial resolution. Additional reactions could be included to account for nanocrystal growth by aggregation.9,49

Discussion
Considering our results showing nucleation and growth kinetics were not universally correlated with dose rate, we must reassess how to undertake quantitative investigations of nanocrystal formation with LCEM. For instance, testing whether nanocrystal nucleation can be explained by classical nucleation theory (CNT) or more complex 2-step mechanisms, one could vary the supersaturation ratio and measure resulting nucleation rate. If CNT is an accurate model, the natural logarithm of nucleation rate \((J)\) should be directly proportional to the inverse square of the logarithm of supersaturation ratio \((S)\), viz. \(\ln(J) \propto \frac{1}{\ln(S)^2}\). While prior results suggested the supersaturation ratio could be varied systematically by varying the dose rate, our new results establish this is not the case for silver nanocrystal formation using STEM imaging. In fact, the supersaturation ratio during electron beam induced nanocrystal formation is on the order of \(10^4 - 10^5\), suggesting that nucleation rate may be so large that changes in dose rate and rate of precursor reduction are not significant enough to observe changes in nucleation rate. Progress in utilizing LCEM to investigate nanocrystal nucleation mechanisms will be enabled by more detailed modelling of radical diffusion during STEM imaging or through utilizing new liquid heating sample cells that enable varying sample temperature. More detailed modeling should be aimed at deriving quantitative relationships between the nucleation scaling laws developed here and local supersaturation ratio, which is the fundamental parameter underlying nucleation kinetics.

The outlook for varying dose rate during STEM imaging to systematically investigate growth mechanisms is promising due to the observed power law dependence of growth rate on effective rate of precursor conversion with a correction factor for spur separation. However, several fundamental challenges still need to be addressed. Given the correlations we have established between growth rates and spur density, the effects of beam current and magnification on growth rate are more complex than previously thought. In comparison, Alloyeau et al. and Park et al. observed a simple power law dependence of gold nanocrystal growth rate on electron dose rate. Because other groups have not observed this effect, we expect that the nanocrystal composition, reacting radical identity, and the imaging mode (TEM vs STEM) play key roles in whether spur overlap is important. Grogan et al. predicted that spur overlap likely does not occur
for TEM imaging due to the larger size of the parallel TEM beam, which explains why Park et al. did not observe effects of spur overlap. It is possible that the precursor chemistry determines whether spur overlap plays a significant role in the nanochemistry. Large concentrations of hydrogen radicals are formed in the presence of tertiary butanol, which dominate reduction of silver ions (cf. Figure 2c). Electron beam induced growth of gold nanocrystals is typically attributed to reaction with aqueous electrons, which are not affected as significantly by spur overlap. This may explain why Alloyeau et al. did not observe effects of spur overlap on growth rate of gold nanocrystals. While adding tertiary butanol established more reducing conditions in our experiments, it also caused a dose rate-dependent ratio between reducing and oxidizing radical concentration, which was directly reflected in the nanocrystal growth kinetics. Taken together, this suggests that researchers should consider several factors when designing quantitative LCEM nanocrystal growth (or dissolution) experiments, including the identities of the reacting radicals and precursors, imaging mode, radical scavenger reactions, and whether spur overlap will significantly affect radical concentrations.

**Conclusions**

We systematically investigated the nanochemistry of electron beam induced formation of silver nanocrystals using LCEM. Single particle tracking and a nanocrystal formation reaction kinetic model enabled decoupling nucleation and growth kinetics to discover complex and counterintuitive correlations between formation kinetics, the electron beam stimulus, and solution chemistry. While electron dose rate has been thought to universally control nanocrystal formation rate, we found no universal correlations between it and nucleation and growth kinetics. Instead we discovered growth rate correlated with a power law dependence on the dose rate, normalized to the spur density. Nucleation kinetics were independent of beam current and correlated with interpixel radical diffusion times scales. Importantly, these results indicate that nucleation and growth kinetics are controlled by independent electron beam parameters, which suggests each kinetic process could be independently investigated by careful design of experiments. Our results indicate that the details of radiation chemistry and reactant transport must be carefully considered to effectively utilize radical scavengers and the electron beam as a stimulus for nanocrystal formation.
Acknowledgements

T.J.W. acknowledges partial funding from Oak Ridge Associated Universities (ORAU, Award #17061851) and University of Maryland start-up funds. M.W. acknowledges funding from a Harry K. Wells Fellowship from the University of Maryland Energy Research Center. C.P. acknowledges partial funding from Air Force Office of Scientific Research (Grant #FA9550-18-1-0144).

Experimental Methods

A 10 mM silver nitrate (AgNO₃) stock solution was prepared by dissolving salt (Alfa Aesar, ACS, 99.9+%) in DI water (18.2 MΩ) and then diluted to 0.1mM together with tertiary butanol (Sigma-Aldrich ≥99.5%). For the experiments, an aqueous solution of 0.1 mM AgNO₃ and 0.1 M tertiary butanol was used as the precursor solution. The precursor solution was degassed by bubbling with argon gas for one hour before experiments.

All experiments were performed on a Protochips liquid cell sample holder (Poseidon Select). The liquid cell sample was prepared by sandwiching two silicon chips (Protochips) together dry. A free standing 50 nm thick silicon nitride window with a dimension of 550×50 µm on each chip allows the electron beam to pass through. 150 nm gold spacer posts on one of the silicon chips defined the liquid thickness and allowed liquid to flow between them. Prior to experiments, both chips were rinsed by acetone followed by methanol and then plasma cleaned (Harrick Plasma, PDC-32G) for 3 minutes to remove organic contamination and make the surface hydrophilic. Precursor solution was stored in a 5 mL gas-tight glass syringe (Hamilton 700) and was pumped between the two E-chips by syringe pump (Harvard Apparatus) with a flow rate of 300 µL/hr for an hour to remove any air bubbles before liquid cell experiments. The liquid cell electron microscopy experiments were performed on a JEOL JEM-2100F TEM operated in scanning mode (STEM) with an accelerating voltage of 200 kV. STEM was operated with Digital Micrograph using a 1024*1024 pixel image size and 5 µs dwell time to generate movies. Movies were recorded with Camtasia Studios at 10 frames/s. Prior to each particle growth experiment, precursor
solution was flowed for 5 minutes at a flow rate of 300 µL/hr. After liquid cell experiments, silicon E-chips were rinsed by DI water for the ex-situ HRTEM. The ex-situ HRTEM images were acquired on a JEOL JEM-2100 LaB₆ TEM. Images were acquired with Gatan Digital Micrograph and processed by Image J. See supplemental materials for details on LCEM nanocrystal growth movie image analysis.⁴³-⁴⁴

References


7. Watzky, M. A.; Finke, R. G., Nanocluster size-control and "magic number" investigations, experimental tests of the "living-metal polymer" concept and of mechanism-based size-control predictions leading to the syntheses of iridium(0) nanoclusters centering about four sequential magic numbers. *Chemistry of Materials* **1997**, *9* (12), 3083-3095.


**Figures**

*Figure 1.* Electron beam induced silver nanocrystal nucleation and growth process.
Figure 2. Radiolysis simulations of oxidizing and reducing radiolysis species as a function of electron dose rate. Steady state concentrations of species formed in (a) deaerated DI water and (b) deaerated 0.1 M aqueous tertiary-butanol. (c) The ratio of reducing species (aqueous electrons, hydrogen radicals) to oxidizing species (hydroxide radicals, oxygen) as a function of dose rate in deaerated DI water (blue circles) and deaerated 0.1 M tertiary-butanol (red diamonds).
Figure 3. (a) Time lapsed bright field STEM images of silver nanocrystal formation over time. (b)-(c) HRTEM images of silver nanoparticles. (d) Plot of 10 particle trajectories over time showing linear growth rate fits and nucleation induction times. (e) Distribution of growth rates and (f) nucleation induction times for a single LCEM data set. The dashed lines in (e) and (f) denote the median values.
Figure 4. Nanocrystal growth kinetics are explained by oxidizing radicals and spur density. (a) Median growth rate (\(\bar{R}\)) as a function of electron dose rate. The marker size is representative of the magnification used for that experiment. (b) Top: The average spur separation (\(d_{spur}\)) as a function of beam current and magnification. Bottom: the spur density (\(\rho_{spur}\)) as a function of beam current and magnification. (c) Median growth rate follows a power law dependence on the dose rate normalized to the spur density. The power law coefficient, \(\beta = -1/2\), was determined from the power law dependence of the concentration ratio of reducing to oxidizing radiolysis species on dose rate by the radiolysis simulations in Figure 2c.
Figure 5. Nucleation kinetics are explained by interpixel radical diffusion. (a) Median nucleation time as a function of dose rate. (b) The ratio of the interpixel radical diffusion time scale to interpixel electron beam flight time as a function of magnification. (c) Median nucleation induction time as a function of the time scale ratio defined in (b).
**Figure 6.** Schematic showing proposed mechanisms for effects of radiation chemistry and reactant transport on (a) growth and (b) nucleation kinetics.
Figure 7. (a) Exemplary reaction kinetic fits of nanocrystal formation at two different magnifications. (b) Model-derived time course for each species at (b) 100 kx and (c) 150 kx. (d) Fitted growth rate constants as a function of the growth rate scaling law shown in Figure 4c. (e) Fitted nucleation rate constants as a function of the nucleation scaling law shown in Figure 5c. Solid lines are best fits determined by linear least squares fitting.
TOC Graphic