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Analysis of Single Nanoparticle Growth Environments to Explain Abnormal Ostwald Ripening of Nanoparticle Ensembles

Taylor J. Woehl[1], Chiwoo Park[2], James E. Evans[3], Ilke Arslan[4], William D. Ristenpart[1,5], and Nigel D. Browning[1,4,6]

[1] Department of Chemical Engineering and Materials Science, University of California, Davis, Davis, CA 95616, USA
[2] Department of Industrial and Manufacturing Engineering, Florida State University, Tallahassee, FL 32306, USA
[3] Pacific Northwest National Laboratory, Environmental and Molecular Sciences, Richland, WA 99352, USA
[4] Pacific Northwest National Laboratory, Fundamental and Computational Sciences, Richland, WA 99352, USA
[5] Department of Food Science and Technology, University of California, Davis, Davis, CA 95616, USA
[6] Department of Molecular and Cellular Biology, University of California, Davis, Davis CA 95616, USA

Nanocrystal growth by *in situ* electron irradiation of aqueous precursors has mainly focused on single particle observations [1, 2] of nanoparticle growth dynamics, paying little attention to ensemble scale growth dynamics. Analysis of nanoparticle growth on the mesoscale by direct observations, using *in situ* liquid electron microscopy, will provide direct comparison of classical ensemble properties to the local nanoscale environments of single nanoparticles.

Silver nanoparticles were grown from dilute solutions of silver nitrate (0.1 mM) by STEM irradiation, which stimulated the crystal growth and provided the imaging signal [3]. Conversion of the precursor into nanocrystals proceeds primarily by a reduction reaction between silver ions and aqueous electrons. The experiments were performed in a continuous flow *in situ* fluid stage (Hummingbird, USA, WA) and imaged continuously with a JEOL 2100F/Cs (S)TEM to produce movies of the nanocrystal growth. Bayesian multivariate statistical methods were applied to analyze 300-400 nanoparticles simultaneously, and extract the particle size distribution for each time frame of the movies [4, 5].

We show that the experimentally measured particle size distribution (PSD) is broader and more symmetric compared to the classical Lifshitz-Sylozov-Wagner (LSW) Ostwald ripening model [6, 7]. The deviation of the PSD from the LSW model has been observed by multiple researchers, however, none have been able to identify the exact mechanism due to purely ensemble scale experimental methods [8]. Through direct *in situ* observations, we demonstrate that the local nanoscale environment of the nanoparticles that do not fit the LSW model varies significantly from the mean field environment. Using this method, we measure parameters of individual non-LSW nanoparticles, such as the coordination number, average nearest neighbor distance, and average nearest neighbor radius [9].

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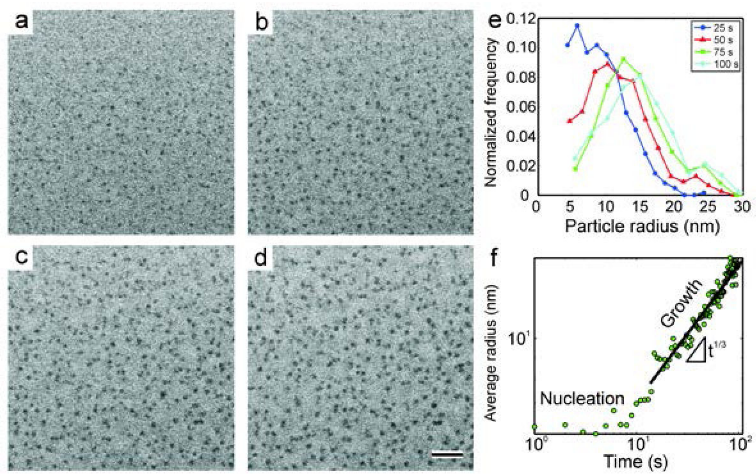

Figure 1. (a)-(d) Time lapsed series of BF-STEM images showing growth of an ensemble of silver nanoparticles starting at 25 seconds from the initial irradiation (20 pA beam current), with 25 second intervals in between panels. The scale bar in (d) is 200 nm. (e) Particle size distribution (PSD) of the ensemble for various times corresponding to each image. (f) Log-plot of the mean nanoparticle radius of the ensemble as a function of time. The black line is a least squares fit to the growth regime only (t > 15 s).

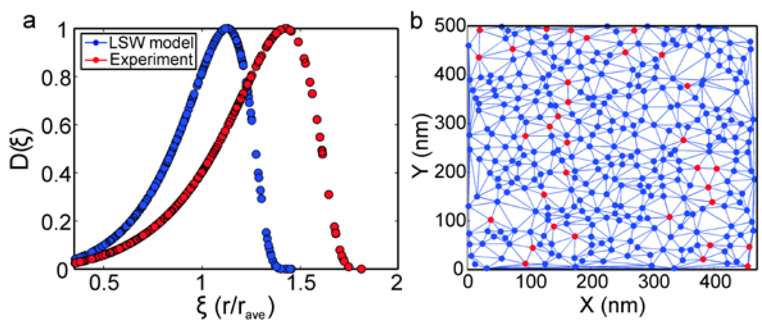

Figure 2. (a) PSD distribution at t = 100 s evaluated using the LSW model. D(ζ) is the LSW distribution function and ζ is the radius of each particle scaled to the average radius. The blue data are experimental data excluding nanoparticles that don't fit the LSW model (r > 1.5*average radius), while the red data include all experimental data. (b) Particle positions at t = 100s. The blue points represent nanoparticles that fit the LSW model, while the red points represent nanoparticles that don't fit the LSW model. The blue grid is a Delaunay triangulation used to calculate the local nanoscale environments surrounding the non-LSW particles.