doi:10.1017/S1431927615005656 Paper No. 0486
Microsc. Microanal. 21 (Suppl 3), 2015

Quantitative Analysis of Nucleation and Growth Behavior from *in situ* Liquid Cell Studies

Anton V. Ievlev[1,2], Stephen Jesse[1,2] , Sergei V. Kalinin[1,2], Thomas J. Cochell[3], and Raymond R. Unocic[1,2]

[1] Institute for Functional Imaging of Materials, Oak Ridge National Laboratory, Oak Ridge, TN 37831
[2] Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN 37831
[3] Chemical and Materials Engineering, University of Kentucky, Lexington, KY 40506

Developing a fundamental understanding of nanocrystal nucleation and growth have important implications for a wide range of materials used in catalysis, energy storage, photonic, and electronic applications where the ability to tune crystal size, morphology, and surface chemistry will dictate nanoscale properties and functionality. Here we develop a universal approach for directly probing the kinetic laws, anisotropy, and particle-particle interactions from *operando* experiments of crystal growth and advanced data analytics.

Direct observations of nanocrystal growth from liquid phase precursors can be visualized at high spatial resolution using *in situ* liquid cell scanning transmission electron microscopy (S/TEM) [1]. In this approach, a solution is encapsulated between electron transparent silicon nitride membranes then irradiated with an electron beam to induce a chemical reduction reaction by radiolytically generated aqueous electrons (e_{aq}^-). It has been shown that the electron dose can directly influence the growth behavior from reaction-controlled growth to diffusion-limited growth as interpreted by growth kinetic measurements [2-3]. In the present study a 1 mM K_2PtCl_6 + 0.5 M H_2SO_4 solution was used to study the nucleation and growth mechanisms of Pt nanostructures by performing controlled irradiation studies with an aberration corrected FEI Titan S/TEM operating at 300kV. The focused STEM probe, generally used for imaging, is used here to both stimulate and directly image the chemical reduction processes.

Figure 1 shows a sequence of annular dark field (ADF) STEM images acquired during electron beam irradiation. There are multiple nucleation sites that appear at different time-intervals, which are located either on the top membrane (in focus) or bottom membrane (out-of-focus) within the liquid cell. From the *in situ* dataset, we utilized quantitative image analysis methods to analyze the nucleation and growth behavior of the Pt nanostructures by first performing a binary threshold to each frame followed by automated edge detection, center of mass, and particle tracking algorithms. This approach was used to track two particles indicated in Figure 1c and Figure 2 shows the image analysis results for both particles. The time-resolved edge outlines reveal how the shapes of the particles evolve as a function of time (and cumulative electron dose). The time and angular dependence (in polar coordinates) are shown for the growing particles in terms of absolute and normalized radii. The color scale in Figure 2 correlates to the value of the particle radius for each angle and at each time step. Maps of the absolute radius show a monotonic increase, which suppresses data analysis. Normalization over certain time steps allow for characteristic features of the growth caused by the interaction between particles to be revealed. Cooperative dynamics of particle growth can be presented as a 3D graph (Figure 3). The particles exhibit a diffusion-limited growth behavior. There is a decrease in the growth velocity up to the point of nanoparticle contact, which is suggestive of an influence of overlap of the diffusion fields. The interface of the particles

away from the point of contact and not impeded by an overlap in diffusion fields and continues to grow at a constant velocity. The combination of *in situ* liquid cell microscopy and quantitative image analysis provides new insight into the basics mechanisms that control the nanocrystal growth behavior and reaction kinetics from liquid phase precursor solutions [4].

References:

[1] HG Liao, K Niu, and H Zheng. Chemical Communications 49 (2013) p. 11720-11727.
[2] TJ Woehl *et al*. ACS Nano 6 (2012) p. 8599-8610.
[3] TJ Woehl *et al*. Nano Letters 14 (2014) p. 373-378.
[4] Research supported by Oak Ridge National Laboratory's Center for Nanophase Materials Sciences (CNMS), which is a U.S. Department of Energy, Office of Science User Facility. Quantitative image analysis software available at CNMS.

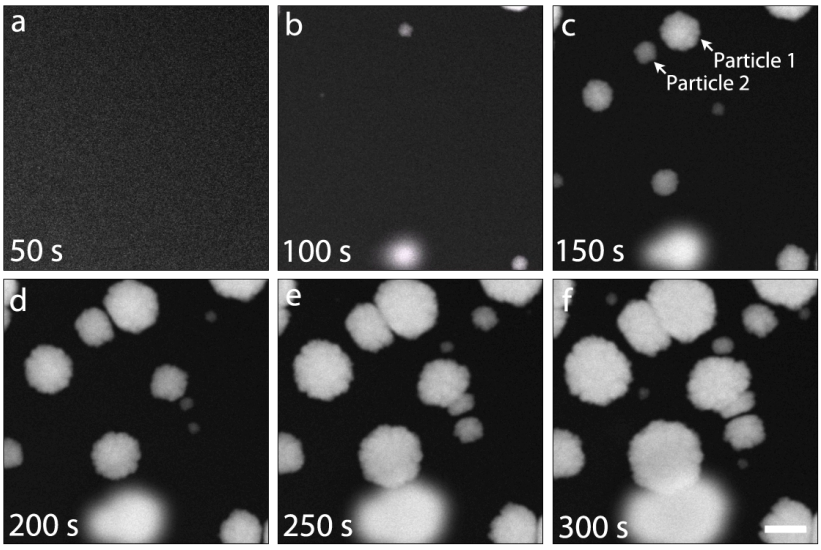

Figure 1. a-f) Time-lapsed ADF STEM images showing the electron beam induced nucleation and growth of Pt from a 1 mM K_2PtCl_6 + 0.5 M H_2SO_4 solution. The electron dose rate is 196 e^-/nm^2s and the scale bar is 200 nm.

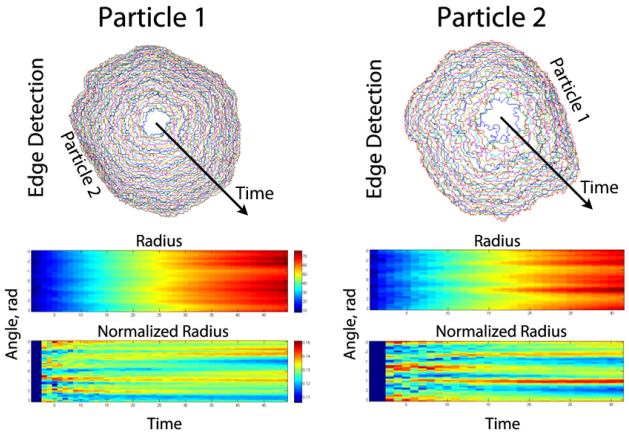

Figure 2. Quantitative image analysis showing the growth evolution of Particle 1 and Particle 2 (Figure 1c) as a function of time. Edge detection used to illustrate shape-evolution during particle growth and extract absolute and normalized values of particle radius as a function of time (shown in polar coordinates)

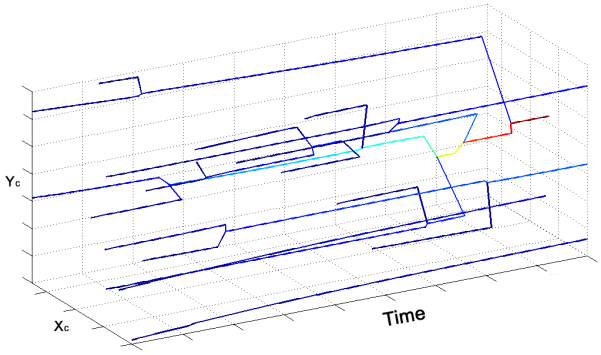

Figure 3. Particles nucleation and growth graph. Each point on the graph corresponds to the particle at the certain time step. Color correlates with particle area.