

Quantification of High Spatial and Temporal Resolution

In-Situ TEM/STEM/DTEM Observations

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Many processes in materials chemistry are dependent on the local environmental conditions (temperature, voltage, stress, gas, liquid etc). Therefore, although recent years have seen a paradigm change in the performance of (scanning) transmission electron microscopes ((S)TEM), with unprecedented improvements in spatial, spectroscopic and temporal resolution being achieved, a full utilization of these new capabilities *to study chemical processes* requires precise control of the environment around the sample. Here, the development and implementation of an in-situ liquid stage (used for experiments often described as being *in-situ* or *operando*) will be discussed that permits the study of samples in solution. With this stage, obtaining reproducible and quantifiable results requires a complete calibration of the effect of the electron beam on the process being studied. After calibration of the beam (and in some cases the use of experimental conditions where its effect is negligible), detailed quantitative measurements of the nucleation and growth of individual nanoparticles or different phases within nanoparticles can be determined and compared directly with ex-situ results. Here it is the ability of the electron microscope to obtain direct images that provides unique insights into the processes taking place).

As an example of the type of experiment that can be performed, if the effect of the electron beam is calibrated and quantified, it can be used to mimic the effect of a reducing agent in solution [1]. In the case of the growth of Ag nanoparticles, a dose of less than $0.5 \text{ e}^-/\text{\AA}^2/\text{s}$ resulted in no observable growth, while a total dose of $12 \text{ e}^-/\text{\AA}^2$ was needed to see any nucleation at all (Figure 1). Controlling the dose in this way allowed the comparison of growth modes with classical models for nucleation and growth, i.e. although the initiation process is different in-situ and ex-situ the growth modes are the same. Furthermore, by employing statistical clustering analysis to track and group all the different growth modes seen in the complete experiment, it was found that while the average nanoparticle radius scaling agrees with the classical Ostwald ripening model, the distribution is artificially broadened by abnormal aggregative growth of nanoparticles [2] (Figure 2). These aggregative growth modes could potentially be the first stage in the creation of new nanomaterial synthesis routes and more complete theoretical models to account for aggregative growth [3].

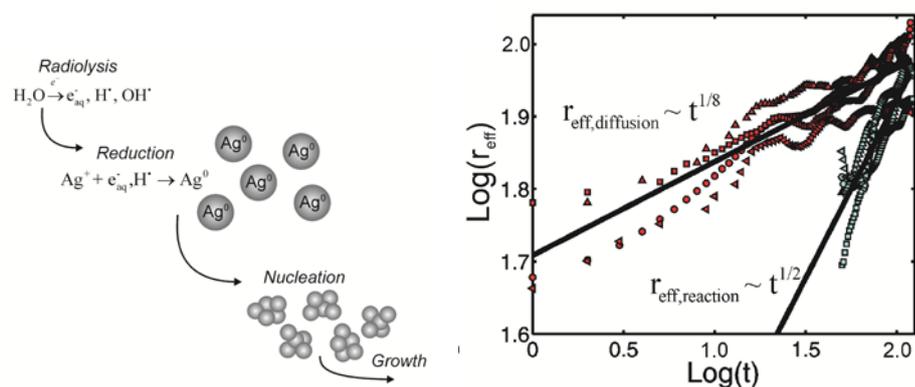


Figure 1: Controlling the dose rate in the microscope leads to control of nucleation and growth phenomena by radiolysis (a). High and low dose regimes result in different growth modes, with reaction limited growth being consistent with ex-situ observations.

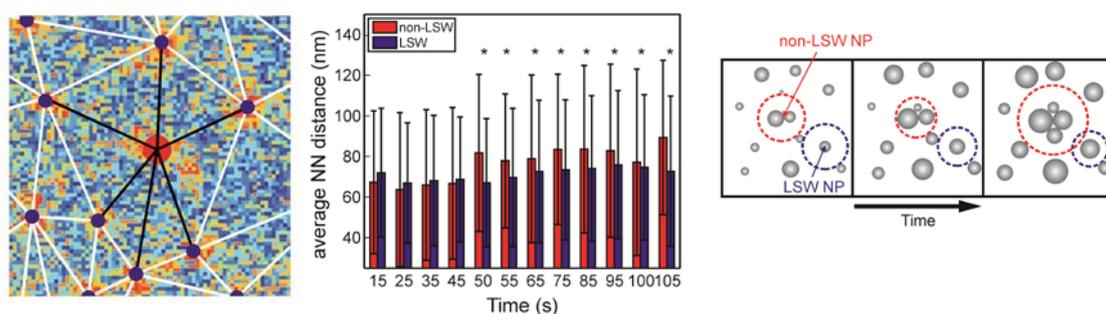


Figure 2: The mean nearest neighbor distance of non-standard (i.e. inconsistent with the Lifshitz-Slyozov-Wagner (LSW) model) nanoparticles is significantly higher than for the LSW model. (a) BF STEM image showing a non-standard nanoparticle (red) and its nearest neighbors (blue). The white lines connecting the centroids are created using a Delaunay triangulation. The black lines are the inter-particle distances. (b) The mean nearest neighbor distances of **all** the particles during growth - asterisks denote a statistically significant difference between the LSW and non-LSW populations (c) Schematic time-series of aggregative growth of non-LSW nanoparticles vs. simple growth of LSW nanoparticles. The dashed circles represent the depleted area surrounding the particle (red for non-LSW, blue for LSW).

References

- [1] T. J. Woehl, J. E. Evans, I. Arslan, W. D. Ristenpart, N. D. Browning, *ACS Nano* **6**,8599-8610 (2012)
- [2] T. J. Woehl, C. Park, J. E. Evans, I. Arslan, W. D. Ristenpart, N. D. Browning, *Nano Letters***14**, 373-378 (2014)
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