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Using Sub-Sampling/Inpainting to Control the Kinetics and Observation Efficiency of Dynamic Processes in Liquids

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The nucleation and growth of nanostructures from solution has important consequences for materials synthesis, mineralization, atmospheric conditions and climate change, interactions with biological interfaces and energy storage, to name but a few applications. The recent development of in-situ liquid stages for high-resolution (scanning) transmission electron microscopes (S/TEM) has provided a direct means to observe nucleation and growth phenomena in materials under various driving forces, see for example the observation of Li-dendrite formation under electrochemical charge/discharge conditions [1,2]. In all observations using in-situ liquid cells generated by the TEM community so far, the resolution of the images that have been obtained has been limited by the effect of the electron beam changing the local chemistry of the solution. In extreme cases this leads to the formation of bubbles, but more subtle effects can also change the observations if care is not taken – such as depletion and/or charging effects and a change in the local pH that modifies the kinetics of the interactions. To relate these TEM observations to real world examples of nucleation and growth, controlling the dose and extracting the most information for each electron put into the sample is therefore of critical importance.

The recent application of sub-sampling and inpainting in the STEM offers one potential way of extracting more quantitative information from images at lower dose and with more speed [3,4]. In this approach, the image is formed by only acquiring a small random fraction of the pixels in the image and then using inpainting (related to compressive sensing methods [5,6]) to fill in the missing information. While there are limitations in how quickly the scan can currently be performed, the practical application of sub-sampled acquisitions can clearly lead to improved dose/resolution relationships for STEM images. Here, we use these sub-sampling methods to demonstrate that the electron beam control provided by this Bayesian microscopy approach can lead to high quality imaging during an *in-situ* liquid experiment. In addition, the use of sub-sampling to form the image can controllably change the kinetics of the nucleation and growth experiment, leading to morphologies of nanoparticles that are dependent on the overall level of sampling and electron dose.

Figure 1 shows a representative image reconstructed [7] from a sub-sampled movie acquired during the in-situ nucleation and growth of silver nanoparticles. In these experiments, it is the electron beam itself that causes the reduction process to proceed and the particles to precipitate. For each of the sampling experiments that were performed, the images (that form the acquired movies) can be segmented and 3 distinct types of particles can be observed – uniform nanoparticles indicative of a homogeneous mechanism, large flat particles indicative of a heterogeneous mechanism and sharp dendritic structures indicative of high concentration and/or charge mechanisms. The three different types of particles are not

generated in the same numbers for each type of sub-sampling experiment. Noticeably the incubation time between the homogeneous and heterogeneous particles in minimized at the lower sampling rates. Additionally, the dendrite structures are only observed to form when the sampling rate is above 25%. Such differences in the kinetics of the particles types can be attributed directly to the charge deposited in the in-situ liquid cell during the experiment and demonstrates that the sub-sampling of images for in-situ measurements can improve the ability to make observations under low-dose conditions and modify the kinetics of the process. In this presentation, the details of the sub-sampling process and how it can used to control in-situ liquid experiments will be described and the potential for future dynamic experiments will be discussed [8].

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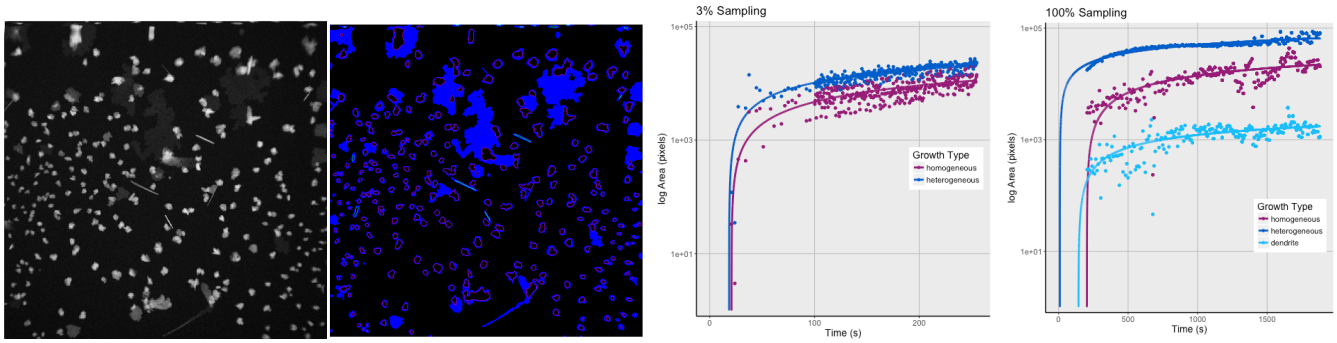

Figure 1. (a) the image reconstructed from the sub-sampled scan can be segmented (b) to track the development of the 3 types of nanoparticles - homogeneous, heterogeneous and dendrite. Analysis of the incubation time and growth rate for the 3 nanoparticle types with (c) 3% and (d) 100% sampling shows a distinctly different phenomena for the two sampling rates.

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