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Data Analytics Applied to Chemical Transformations in Liquids

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Elucidating the fundamental mechanisms of nanocrystal growth necessitates the utilization of high spatial resolution imaging techniques that are capable of directly imaging individual nucleation and growth events within a liquid phase. By combining time-resolved imaging datasets with quantitative image analysis algorithms, the factors controlling chemical transformations can be determined by analyzing the nanocrystal size and morphological evolution. *In situ* liquid cell microscopy has recently been used to directly image and elucidate mechanisms of nanocrystal nucleation and growth from a precursor solution [1]. In these experiments, the electron beam is used as a source for ionizing radiation to generate radiolytic species, which in turn act as a reducing agent to chemically transform metallic species from their organometallic precursors. The concentration of radiolytic species is influenced by the electron dose, which consequently affects the nanocrystal growth mechanisms and kinetics. For example, Woehl et al. has shown that a change in the electron dose can effectively alter the growth mechanisms from reaction-controlled growth (at low dose) to diffusion-limited growth (at high dose) [2]. The motivation for this work is to develop a robust analytical framework to quantitatively analyze changes in nanocrystal size and morphology using data acquired from electron beam-induced chemical transformations and electrochemical transformation during *in situ* liquid cell experiments [3].

A typical dataset acquired during an *in situ* electrochemical STEM experiment is shown in Figure 1a, where Cu nanocrystals are formed on a glassy carbon working electrode during electrodeposition from a 0.2M $CuSO_4$ solution at a sweep rate of 50 mVs^{-1}. Python codes were developed to extract individual frames from *in situ* videos of the electrodeposition process. Each frame was transformed into a binary threshold image (Figure 1b) then processed further for edge detection (Figure 1c). The resulting data was analyzed to quantify changes in nanocrystal size at the particle and interfacial (fluid-solid interface) level. From these data, growth mechanisms were interpreted by plotting the particle size as a function of time and the morphological evolution of the nanocrystals was tracked.

The Cu nanocrystals were found to originally grow with a spherical morphology from edge detection analysis of several Cu nanocrystals (Figure 2a), and over time become faceted. This is expected since the crystals attempt to minimize the fluid-solid interfacial free energy (γ), and for fcc Cu, the interfacial free energy ranks (lowest to highest) as follows: $\gamma_{\{111\}} < \gamma_{\{100\}} < \gamma_{\{110\}}$ for low index crystallographic facet orientations. From 2D projections (images) of the nanocrystals, the facet orientation can be deduced from the edge detection (Sobel method) processed images. The development of quantitative image analysis codes that capture the dynamics of chemical transformations in liquid cell experiments provides the means to better understand highly localized reaction mechanisms and kinetics occurring at critical fluid-solid interfaces [4].

References:
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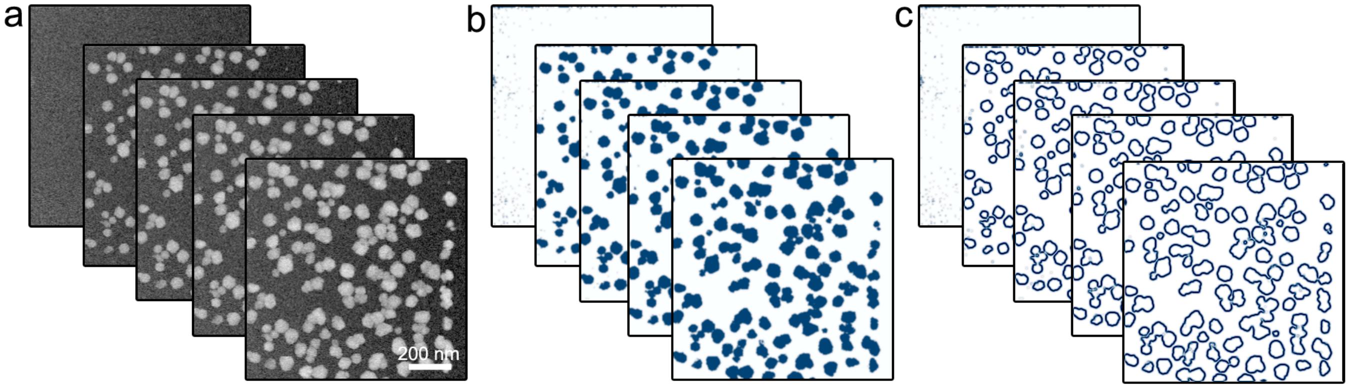

Figure 1. Partial workflow for automated image processing and quantitative image analysis of chemical transformations in liquid cell microscopy experiments. a) Extracted image sequence from *in situ* videos. b) Binary image thresholding. c) Edge detection.

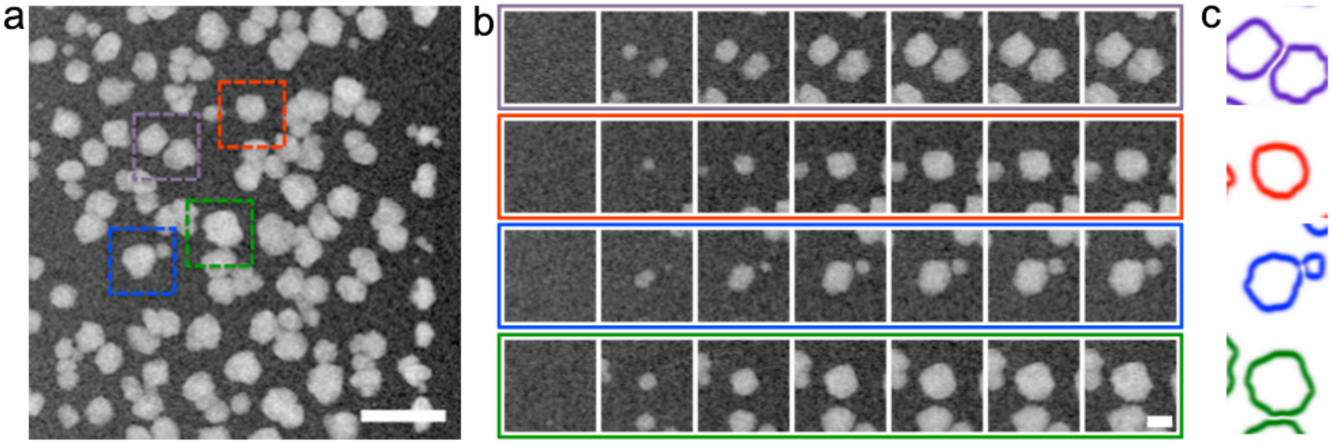

Figure 2. a) Annular dark field (ADF) STEM image of electrodeposited Cu nanocrystals. b) Evolution of several highlighted Cu nanocrystals (colored boxes in 2a). .c) Sobel edge detection processed images highlighting the crystallographic faceting. Scale bar in (a) is 200 nm and 50 nm in (b).