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Visualization of Gold Nanoparticle Self-assembly Kinetics

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Various types of colloidal nanoparticles are known to self-assemble into hierarchical mesostructures *via* anisotropic interparticle interactions, such as dipolar [1] and electrostatic interactions [2]. Self-assembly strategies are typically designed in an empirical manner or based on equilibrium models of these interparticle interactions, and kinetic considerations are often overlooked. Due to a lack of high spatial and temporal resolution *in situ* observations, little is known about the kinetics of nanoparticle self-assembly. Previous work has suggested that the kinetics of nanoparticle self-assembly process can be likened to multistep chemical [3] and polymerization [4] reactions, where interparticle interactions determine the rate constants for assembly of differently sized and shaped mesostructures [5, 6]. However, it is not clear how the interplay of interparticle interactions and assembly kinetics affect the hierarchical self-assembly process and resulting mesostructure morphology.

Here we use real-time nanoscale observations to measure the self-assembly kinetics of colloidal gold nanoparticles into one dimensional chains. Gold nanoparticles suspended in acetate buffer were observed with *in situ* liquid cell scanning transmission electron microscopy (STEM) to self-assemble into chains of up to 20 nanoparticles over times of several minutes. Real-time kinetic data and *in situ* nanometer resolution images revealed the formation pathway and rate of gold nanoparticle self-assembly to be dependent on the imaging electron beam current (Figure 1). The rate of self-assembly increased proportionally with the beam current, and the self-assembly pathway changed from sequential attachment of nanoparticles to formed chains at low beam currents, to chain-chain attachments at high beam currents. Experimental measurements of the nanoparticle diffusion coefficient revealed that the self-assembly process was diffusion driven, where the nanoparticle mobility dictated the self-assembly rate and pathway. Importantly, through these systematic beam current experiments we revealed that the nanoparticle mobility was the underlying control factor for the self-assembly kinetics. We expect these conclusions will shed light on the role of other mobility-controlling factors on nanoparticle self-assembly, such as nanoparticle size, shape, and suspending solvent [7].

References:

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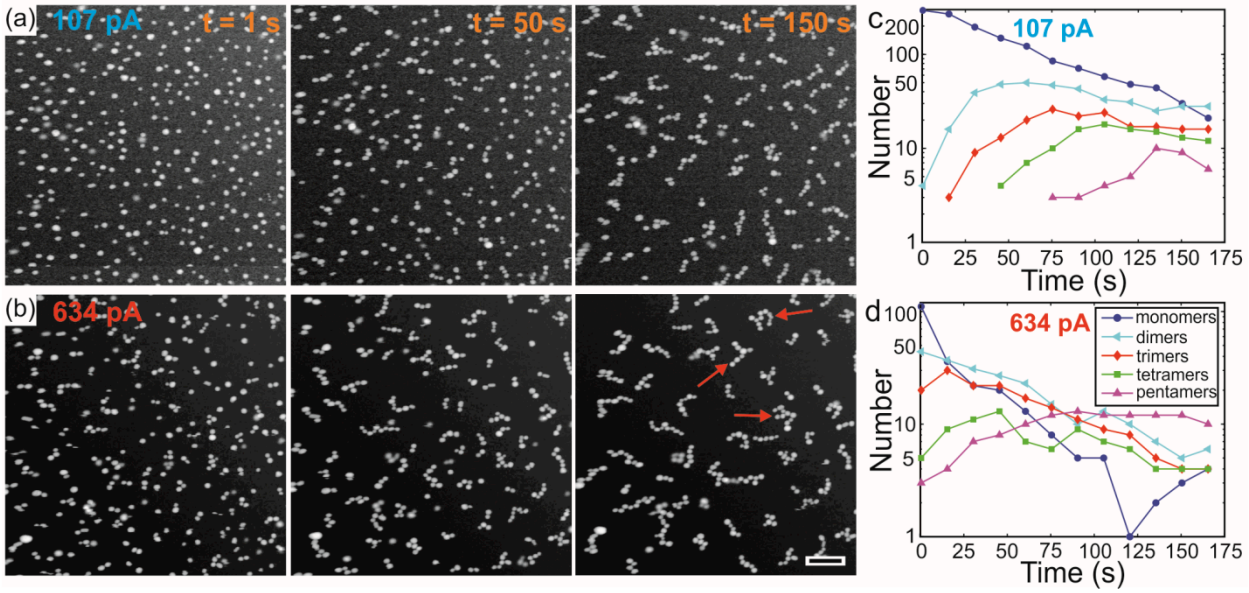

Figure 1. Electron beam dependent gold nanoparticle self-assembly kinetics. Time lapsed annular dark field (ADF) STEM images showing self-assembly of gold nanoparticle chains over 150 s at beam currents of (a) 107 pA and (b) 634 pA. The scale bar in the final panel of (b) is 200 nm. (c)-(d) The number of nanoparticle chains with sizes ranging from 1 – 5 nanoparticles, as a function of time for beam currents of (c) 107 pA and (d) 634 pA.