

## The Mechanisms for Preferential Attachment of Nanoparticles in Liquid Determined Using Liquid Cell Electron Microscopy, Machine Learning, and Molecular Dynamics

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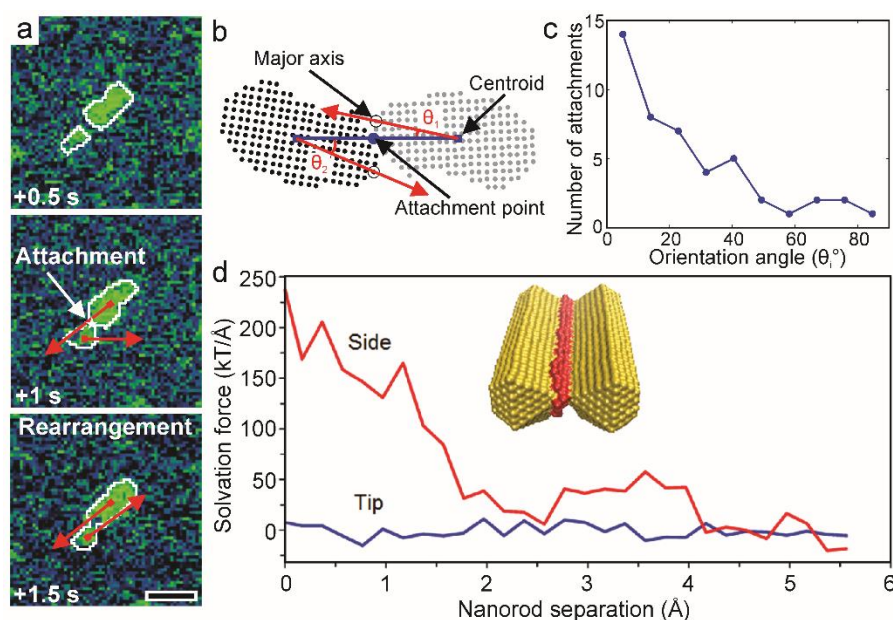
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Optimization of colloidal nanoparticle synthesis techniques requires an understanding of underlying particle growth mechanisms. Non-classical particle-mediated growth mechanisms are particularly important as they affect nanoparticle size and shape distributions and can lead to formation of superstructures [1]. Nanomaterial growth by non-classical particle-mediated growth mechanisms is complex and often proceeds *via* multiple assembly pathways simultaneously [2]. Ensemble techniques for characterizing the dynamics of these growth pathways, such as x-ray or visible light spectroscopy, average the dynamics associated with these multiple pathways, making them impossible to distinguish. Liquid cell electron microscopy has emerged as an *in situ* technique providing an ideal combination of high spatial resolution visualization of nanomaterial structure and *in situ* dynamics. Measurements of growth and assembly dynamics and nanoparticle interactions from *in situ* movies are typically performed manually using simple image analysis algorithms; however, these simple algorithms suffer from human error and bias and lack in statistics [3]. The use of advanced machine learning-based image analysis algorithms [3] to interpret dynamic liquid cell electron microscopy *in situ* movies promises to provide insights into complex nanoparticle growth pathways.

Here we employ liquid cell scanning transmission electron microscopy (STEM), machine learning-based image analysis [4], and steered molecular dynamics (SMD) simulations to demonstrate that the experimentally observed preference for end-to-end attachment of silver nanorods is a result of weaker solvation forces occurring at rod ends [5]. Silver nanoparticle growth and attachment processes were directly observed and initiated *via* liquid cell STEM [6]. Silver nanocrystals grew on the silicon nitride window surface, with their size increasing monotonically with time through monomer addition (of reduced silver ions) as well as aggregation of neighboring nanocrystals [7]. For the experimental parameters used in this study, nanoparticles often grew into asymmetric shapes, such as nanorods (Figure 1a). These mobile particles were observed to eventually attach to neighboring particles, and showed a preference for end-to-end attachment. Machine learning-based image analysis algorithms were used to identify interparticle attachment events and extract the orientation angles of the nanorods at the time of attachment (Figures 1b and 1c) [4]. SMD revealed that when the side of a nanorod approached another rod, perturbation of the surface-bound water at the nanorod surface created significant energy barriers to attachment (Figure 1d). Additionally, rod morphology (i.e., facet shape) effects can explain the majority of the side attachment events that are observed experimentally [8].

## References:

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**Figure 1.** (a) False colored bright field (BF) STEM images of an attachment event. The two nanoparticles (outlined in white) rearranged and attached over a period of about 2 seconds, after which the orientation angles were measured. (b) Representative schematic demonstrating machine learning-based algorithm for orientation measurement of two rod-shaped nanoparticles undergoing attachment. Each orientation angle is measured from the line connecting the nanoparticle's centroid to the attachment point and the line defining the major axis of the nanoparticle. (c) Histogram of attachment count as a function of orientation angle for 23 attachment events. (d) Solvation force-displacement curves for tip and side coalescence. The increase in solvation force for side coalescence is due to water monolayer compression (inset).