Liquid Cell TEM Study of Nanoparticle Diffusion and Interaction in Liquids

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Liquid cell transmission electron microscopy (TEM) has been used to study nanoparticle diffusion [1-3]. However, electron beam interaction with nanoparticles has also been a concern. In general, electron microscope effects can be limited by reducing the electron beam dosage. In this work, we use liquid cell electron microscopy to study nanoparticle diffusion and interaction during nanoparticle self-assembly into a packed two-dimensional lattice. Because the controlled self-assembly of functional nanoparticles into patterns holds promise as a scalable fabrication strategy to systematically produce nanoscale devices, the self-assembly of nanoparticles has a topic of intense interest. However, fluid deposition of nanoparticles is poorly understood and generally not predictable at the present time. Some fundamental questions underlying particle assembly include (1) what are the characteristics of the particle diffusion? and (2) what are the interaction forces between nanoparticles?

We prepare the precursor solution by dissolving $Pt(acac)_2$ and $Fe(acac)_3$ into pentadecane with oleylamine. Pt-Fe nanoparticles are formed in the liquid cell from a precursor solution under electron beam. When nanoparticles are grown into ~5nm, they stop growth and form a two-dimensional film. We track the nanoparticle movement and quantify the interaction between nanoparticles during self-assembly. A custom image analysis algorithm in Matlab enabled quantitative study of assembly and allows for new types of analysis to be applied. A particle detection and tracking algorithm has been developed specifically for noisy and low contrast TEM images containing nanoparticles with a large distribution of sizes and imperfect shapes. The detection step isolates objects at different length scales enabling a threshold function that depends on size and can be adapted to the scale of high and low frequency noise in the image. The advantages of this approach are to capture particles at multiple size scales, avoid any preprocessing of background intensity fluctuations (which occur often over the hundreds of frames in a movie), and distinguish overlapping particles.

By tracking the nanoparticle movement, we found that the chains grow longer by attachment of nanoparticle subunits to the chain ends. As shown in Figure 1, particles largely stay associated with their neighbors from the original chain moving as a group into their final positions in the loosely packed configuration. A few chains split apart into subgroups. Either the chains themselves fold to form locally packed clumps or the chains associate side by side. The statistics show chains are initially similar in length but the distribution broadens significantly at a later stage leading to an increase in length standard deviation. To calculate the interaction forces between nanoparticles, we track the motion of pairs of nanoparticles and their velocity upon being brought into close range. Because the particles are subject to diffusive and drift motion, the metal surface-to-surface distance between particles can be used to obtain a relative individual velocity. The potential combines both a dipole interaction term with a close range isotropic interaction modeled as a Lennard-Jones potential. We have calculated a magnetic moment of

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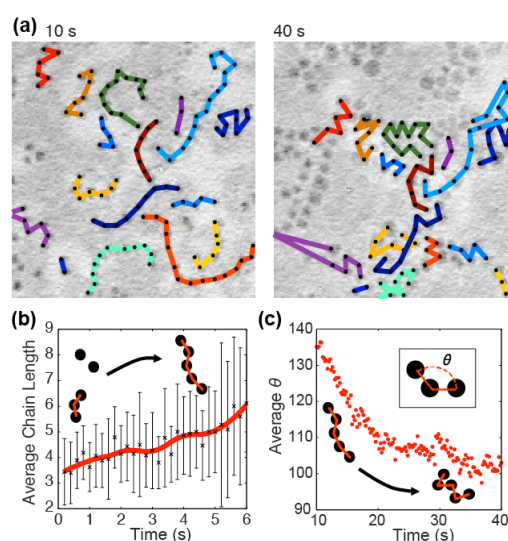

Figure 1. Tracking of dynamic nanoparticle movement in formation of one-dimensional chains. (a) Chains formed at the beginning of self-assembly (10s) and at a later stage (40s) illustrate folding and clumping behavior. (b) Chain growth leads to an increase in average chain length and broadening of length distribution. (c) The average angle change with time. The angle theta is defined by three adjacent particle centerpoints in a chain.
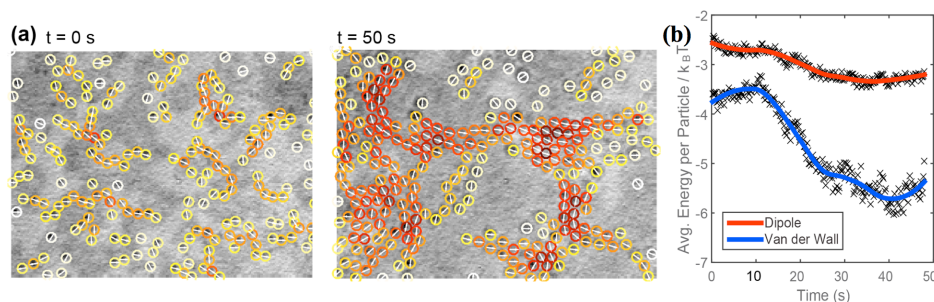

Figure 2. Energy and stability of nanoparticles during self-assembly. (a) Colored circles indicate location of nanoparticles overlaid on the original image. White arrows indicate dipole orientations. The color corresponds to the total energy of an individual nanoparticle computed from the dipole and Van der Waal interaction with nearby particles. (b) The calculated average particle energy evolution over time.