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Probing Reaction Intermediates, Kinetics, and Surface Chemistry during Nanoparticle Synthesis and Assembly with Liquid Phase TEM

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Liquid phase transmission electron microscopy (LP-TEM) has enabled unprecedented insights into the crystallization mechanisms of solution phase inorganic nanoparticles. A major goal of LP-TEM experiments is to advance fundamental understanding of the nanochemistry of nanoparticle formation during solution phase synthesis, which is expected to spur development of rational synthesis methods. While the formation mechanism of single component metal nanocrystals is well-understood and corroborated by kinetic measurements, there remains a dearth of information on the nucleation and crystallization mechanisms of multimetallic nanoparticles. Compared to the ability of quantum mechanical simulations (*e.g.*, DFT) to predict multicomponent nanoparticles with excellent functional properties (*e.g.*, catalytic activity), methods for rational synthesis of these nanoparticles with prescribed composition and arrangements of atoms lags significantly. Single particle scale probing of the physicochemical processes underlying the formation of multicomponent nanoparticles is critical to develop a theoretical framework for their formation mechanisms. Beyond synthesis of individual colloidal nanoparticles, the ability to self-assemble them into micro- and macroscopic structure is critical to translate nanoparticles into macroscale materials while retaining their unique properties.

Initial work using LP-TEM to visualize nanocrystal formation in liquid focused on identifying novel 'non-classical' formation mechanisms based primarily on *in situ* movies and image analysis of nanoparticle growth kinetics [1,2]. The electron beam acts as the primary source of reactive species for nanoparticle synthesis, where radiolysis of the solvent by the TEM beam generates reactive radicals, such as solvated electrons [3]. Subsequent work utilized electron beam dose rate control to mediate the growth kinetics and mechanisms of nanoparticles and led to a method for systematically probing nanoparticle growth kinetics as a function of solution chemistry [4,5]. In our lab, systematic dose rate-controlled LP-TEM imaging together with complementary characterization, such as mass spectrometry and atomic resolution STEM and EDS, has enabled probing formation mechanisms of single metal and multimetallic nanoparticles while understanding the deleterious effects of radiation damage by the electron beam (Figure 1). Together these techniques revealed that sub-nanometer cluster intermediates were critical to forming alloyed as opposed to phase separated nanoparticles [6]. Ongoing work is painting a picture of how high entropy alloy (HEA) nanoparticles containing 5 or more metals form during solution phase synthesis. Numerical simulations have enabled predicting the concentration of radicals created by the electron beam and radiation damage products from interaction of organic capping ligands with radicals [6,7]. Likewise, we have employed fluorescence microscopy to probe radiation damage to nanoparticle capping ligands by conjugating fluorophores to the nanoparticle surface

following LP-TEM imaging [8]. Together, these works indicated the electron beam significantly modifies organic molecules and polymers used as capping ligands and can either increase or decrease the coverage of capping ligands on the nanoparticle surface. Finally, recent work has revealed the kinetic processes involved in the self-assembly of supraparticles during solution phase synthesis of ultrasmall platinum nanoparticles [9,10]. LP-TEM continues to be an exciting method for probing formation mechanisms of nanoparticles in the liquid phase, and this work shows that introduction of complementary characterization together with deep understanding of the associated radiation chemistry enables discovering important insights into nanoparticle synthesis.

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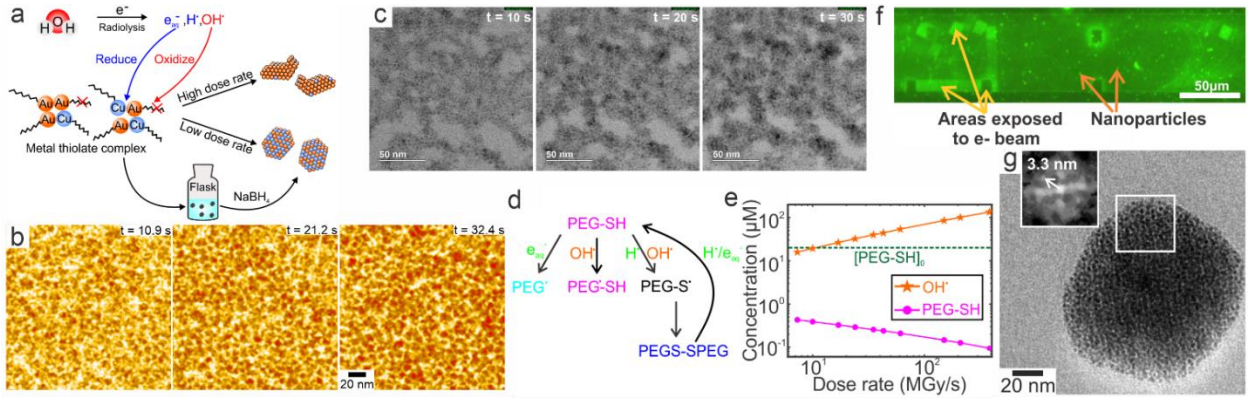

Figure 1. (a) LP-TEM imaging of AuCu alloyed nanoparticle formation probed by electron beam induced reduction. (b) False colored, time lapsed LP-TEM images of AuCu nanocrystal growth. (c) Growth of AgAuPtPdCu HEA nanoparticles observed by LP-TEM. (d) Radical reactions with polyethylene glycol thiol capping ligands and (e) numerical reaction-diffusion simulations of capping ligand concentration (pink) and hydroxyl radical concentration (orange) as a function of electron beam dose rate. (f) Fluorescence microscopy image of aminated polymer capped silver nanoparticles after LP-TEM imaging. (g) Supraparticle consisting of 2 nm platinum nanocrystals formed by electron beam reduction of platinum chloride ions during LP-TEM imaging.

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