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In-Situ Nucleation, Growth and Evolution of Au Nanoparticles during Metallization of DNA Origami Visualized with HAADF-STEM

Alejandra Londono-Calderon[1], Lee Bendickson[1,2], Pierre E. Palo[1,2], Marit Nilsen-Hamilton[1,2], Surya Mallapragada[1,3] and Tanya Prozorov[1]

[1.] US DOE Ames Laboratory, Division of Materials Science and Engineering, Ames, IA.
[2.] Iowa State University, Department of Biochemistry, Biophysics and Molecular Biology, Ames, IA.
[3.] Iowa State University, Department of Chemical and Biological Engineering, Ames, IA.

Bio-inspired synthetic methods offer room-temperature pathways to a variety of functional nanostructures with shapes and sizes not realizable via conventional inorganic chemical techniques. For example, DNA origami has been used as a scaffold to create nanoelectronic devices. Among the advantage of DNA-based technologies are low-cost, unprecedented highly-controlled assembly and site-specific binding ability. The majority of published work on recent advances in DNA metallization focuses on either site-specific attachment of discrete metallic nanostructures to the biotemplate [1], electroless plating [2], or by seeding the DNA strands prior to folding to create a starting point for metallic growing [3]. Single-step *in situ* metallization to form continuous nanometer-size metallic surfaces is an alternative pathway. While significant effort has focused on constructing and applying robust templates suitable for metallization, the mechanism of DNA-templated nanoparticle nucleation remains elusive. Fundamental understanding is lacking on how the DNA template dictates nanoparticle formation, attachment, growth, and ultimately, functional properties.

In this work, we used HAADF-STEM imaging to identify specific site interaction between metal precursor complexes and DNA nanostructures during the metallization process. Nucleation events and evolution of metallic particle growth at the surface of DNA triangles were visualized *in situ* by observing direct reduction of $HAuCl_4$ by the electron beam taking place at the surface of the triangles. Initial experiments were carried out on DNA triangles incubated with $HAuCl_4$ and deposited onto Ultrathin C supported film on holey carbon grids (Cu 400 mesh Ted Pella, Inc.) followed by experiments to observe metallization in liquid phase by using a continuous flow fluid cell holder (Hummingbird Scientific). In these experiments, the DNA nanostructures were sealed between the two functionalized SiN windows. $HAuCl_4$ was delivered into the cell, and the DNA incubation with the precursor followed by the removal of excess of $HAuCl_4$ with a buffer solution delivered through the fluid cell. The dynamic metallization of DNA triangles was imaged in liquid phase. HAADF STEM images were acquired with an FEI Tecnai G^2 F20 operating at 200 kV.

Figure 1 shows HAADF STEM images of DNA triangles incubated with $HAuCl_4$ on a Cu grid. E-beam effects on the reduction of Au^{3+} to Au^0 are visible on the progressive increase in size of the initial clusters which act as nucleation points. The initial frame decoration and superficial layer indicate competition between lateral and superficial sites on the DNA template as starting points in the metallization process. Growing events followed an Ostwald ripening mechanism in which smaller clusters are consumed to produce larger Au crystals. DNA metallization can be controlled by tuning the ratio between $HAuCl_4$ and DNA precursors at the time of mixing within the liquid cell. Ongoing experiments involve imaging in a liquid phase and assessment of the electron dose on the metallization

process [4].

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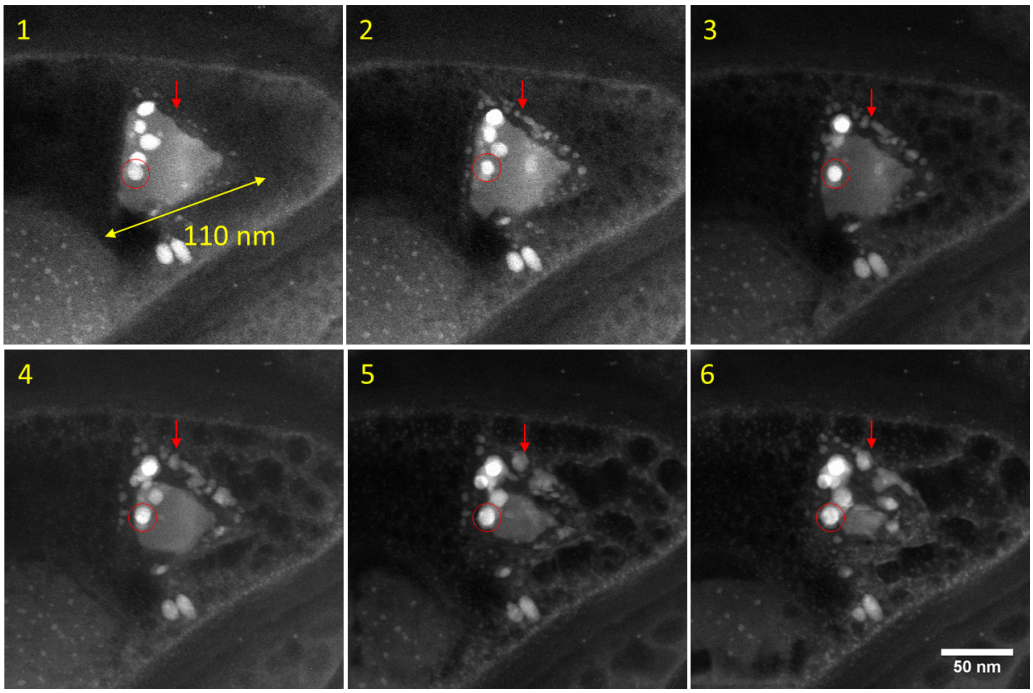

Figure 1. Under the electron beam, Au nanoparticles form on a surface of a ~110 nm DNA triangle incubated with $HAuCl_4$. Precursor is depleted to yield nanoparticles that nucleate and grow, and exhibit hexagonal morphology. The size of a nanoparticle marked with a red circle increases from ~9 nm to ~13 nm; the size of the nanoparticle marked with a red arrow increases from ~4 nm to ~ 12 nm. Nanoparticle growth progression appears to follow the early stages of Ostwald ripening process.

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