Examining Deposition Dynamics of Silver onto Gold Nanorods with Liquid Phase Transmission Electron Microscopy

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Gold nanorods (AuNRs) exhibit strong and tunable plasmon resonances owing to their anisotropic morphology. Combining the plasmonic properties of AuNRs with other functionalities by synthesizing AuNR-based particles with controlled morphology can therefore benefit numerous areas, such as catalysis, biomedical therapies, and molecular sensing [1,2]. Such particles are generally synthesized by depositing a secondary material onto AuNR seeds to obtain core-shell particles, with solution-phase synthesis being a promising route to efficiently prepare large quantities of particles with controlled morphology [2-4]. However, the ligand environment of colloidal AuNRs is known to influence the shell growth process. Previous studies have related the concentration of hexadecyltrimethylammonium bromide (CTAB)—widely used as a capping ligand to direct anisotropic growth and inhibit aggregation of commercially synthesized AuNRs—to the morphology of shells formed on AuNR cores [1,4,5]. In addition to the ligand environment, the plasmonic properties of AuNRs can also affect shell growth when the process occurs in the presence of light. Monochromatic light was previously used to deposit platinum (Pt) onto AuNRs by activating the AuNRs' longitudinal surface plasmon resonance, generating hot electrons capable of reducing the Pt precursor at the nanorod tips [6]. Systematic efforts to characterize the effects of ligands and plasmonic behavior are needed to understand their respective contributions to the shell growth mechanism and how these factors may be leveraged—whether independently or together—to obtain desired shell morphologies. Liquid phase transmission electron microscopy (LP-TEM) is a promising tool to investigate these questions. Aside from being able to visualize single particle-level processes in solution in real time, the electron beam interacts with solvent to produce reactive radicals and aqueous electrons capable of reducing and oxidizing metallic precursors *in situ* [7]. Furthermore, the electron beam is posited to act as a white light source capable of exciting localized surface plasmons on the AuNRs [8].

In view of the considerations discussed, we have constructed *in situ* LP-TEM experiments to study the reduction of a secondary metal onto AuNRs under conditions of plasmonic excitation and varying ligand coverage. As our model system, we investigated deposition of Ag onto CTAB-covered AuNRs from a dilute aqueous silver nitrate ($AgNO_3$) precursor solution, employing the electron beam to establish a chemically reducing environment within the liquid cell [7]. In an *in situ* experiment using $[AgNO_3] = 0.25$ mM and $[CTAB] \sim 1$ mM, Ag deposited preferentially at the nanorod sides to ultimately form faceted, bipyramidal shells around the AuNRs (**Figure 1a**). However, decreasing CTAB concentration by repeated washing of the nanorods with water promoted tip-selective growth (**Figure 1b**). These results agree with prior work regarding the effect of CTAB concentration on the morphology of AuNR-seeded Au overgrowth, where selective desorption of CTAB from the nanorod tips leads to tip-specific

growth [5]. LP-TEM experiments showed little to no Ag deposition at plasmonic hot spots between closely spaced nanorods, suggesting that the observed growth mechanism was not plasmonically driven [2]. Companion *ex situ* experiments utilizing a broadband visible light source with or without a chemical reductant (ascorbic acid) present supported the *in situ* observations. Namely, high CTAB concentration inhibited deposition of Ag on the AuNRs, whereas conformal, faceted Ag shells grew under reduced CTAB concentrations. Furthermore, when using both light and chemical reductant (most closely resembling LP-TEM conditions), faceted Ag shells formed on CTAB-stripped AuNRs, while when using light only, Ag deposited most abundantly at plasmonic hotspots (**Figure 2**) [2,9]. Overall, this work elucidates the relative contributions of plasmonic and chemical induced metal reduction during LP-TEM imaging of nanorod shell growth and suggests chemical reduction by radicals is the predominant shell growth mechanism, while plasmonic effects did not contribute significantly [10].
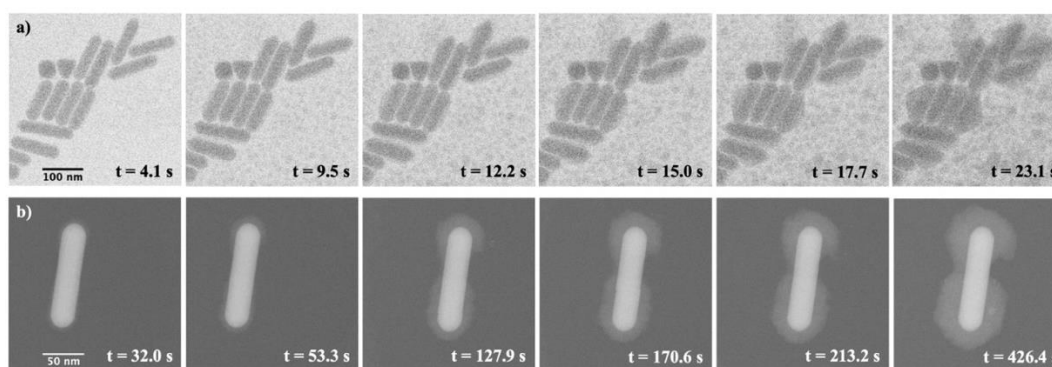

Figure 1. a) Time lapsed images from *in situ* LP-TEM deposition of Ag on AuNRs. b) Time lapsed images (dark field) during *in situ* deposition of Ag on AuNRs. The CTAB concentration was reduced compared to (a) by washing the nanorods 3 times with DI water.
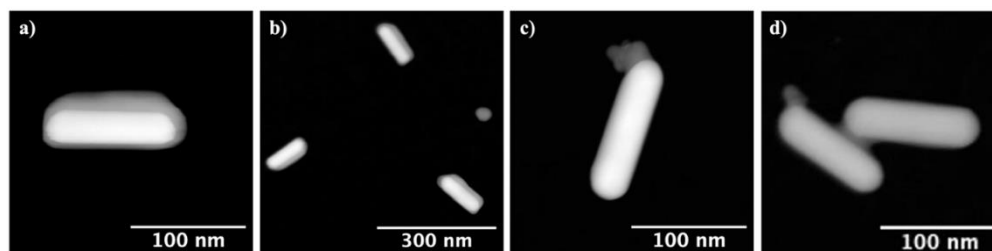

Figure 2. HAADF-STEM images of single and multiple AuNR-Ag core-shell particles. a,b) Ag formed faceted shells when reduced by both chemical (ascorbic acid) and hot electron reduction (white light illumination). c,d) Under plasmonic growth conditions, Ag deposited predominantly in areas between adjacent nanorods or on sites corresponding to plasmonic hotspots.

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