

Investigations of Silver Deposition Dynamics onto Plasmonic Gold Nanorods with Liquid Phase Transmission Electron Microscopy (LP-TEM)

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Summary: Direct visualization of silver deposition onto plasmonic gold nanorods (AuNRs) during LP-TEM is dominated by water radiolysis-induced chemical reduction, indicating observation of plasmonic hot electron-induced photoreduction will necessitate suppression of radiolysis.

Plasmonic photoreduction of secondary metal shells onto plasmonic nanoparticles (NPs) with solution-phase synthesis is a promising method for synthesizing bimetallic plasmonic nanoreactors with tailored morphologies. 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 gold nanorods (AuNRs)—to the morphology of shells formed on AuNR cores. In addition to the ligand environment, the plasmonic properties of AuNRs can affect shell growth in the presence of light. Monochromatic light was previously used to deposit platinum (Pt) and palladium (Pd) onto AuNRs by activating the AuNRs' longitudinal surface plasmon resonance, generating hot electrons capable of reducing the Pt/Pd precursors at the nanorod tips [1,2]. In this study, liquid phase transmission electron microscopy (LP-TEM) is utilized to systematically investigate the relative impact of ligand environment, chemical reduction, and plasmonic excitation on the shell growth mechanism. The electron beam enables visualization of single particle-level processes in solution in real time and interacts with solvent to produce reactive radicals and aqueous electrons capable of reducing and oxidizing metallic precursors *in situ* [3,4]. Furthermore, the electron beam is posited to act as a white light source capable of exciting localized surface plasmons on the AuNRs [3]. These experimental parameters may be leveraged—whether independently or together—to obtain desired shell morphologies of bimetallic plasmonic nanoreactors. Therefore, we have constructed *in situ* LP-TEM experiments to study the reduction of a secondary metal onto AuNRs under the conditions of plasmonic excitation and varying ligand coverage.

As our model system, we investigated deposition of silver 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. Silver shells were observed with LP-TEM to grow into two characteristic morphologies—{111}-faceted bipyramidal shells at higher surfactant coverage and tip-preferential lobes at lower surfactant coverage. *Ex situ* synthesis experiments elucidated the relative impacts of chemical reduction and plasmonic excitation on silver shell morphologies during LP-TEM. Photodeposition formed nanometer-thick silver shells with preferential deposition in inter-rod gaps, while chemical reduction deposited silver at AuNR tips at low surfactant coverage and formed faceted pyramidal silver shells at higher surfactant coverage, consistent with LP-TEM. Deposition locations of silver during LP-TEM were inconsistent with simulations of plasmonic near field and hot electron generation hot spots on single and aggregated AuNRs. Collectively, the results indicate the chemical reduction pathway dominated and obscured plasmon induced metal deposition during LP-TEM, suggesting observation of the latter pathway *via* LP-TEM will necessitate considerable measures to suppress chemical reduction. Ongoing work in our lab is exploring the use of non-aqueous solvents that minimize radiolysis and enable visualizing metal photodeposition independent from chemical reduction.

References

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