Presentation Title: Dynamic Interfacial Behaviors and Photocatalytic Transformations of Ligands on Engineered Plasmonic Nanoparticle Surfaces

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ABSTRACT

We demonstrate that the optical properties of metallic nanoparticles, dominated by localized surface plasmon resonances, can be fine-tuned by either tailoring the surface textures of individual nanoparticles or assembling the nanoparticles into hierarchical mesoscopic suprastructures. The capability to fine-tune the plasmonic properties of surface-textured nanoparticles enables us to use surface-enhanced Raman scattering (SERS) as a plasmon-enhanced spectroscopic tool with unique time-resolving and molecular fingerprinting capabilities to quantitatively correlate the interfacial ligand dynamics with detailed molecular structures in real time under a diverse set of ligand adsorption, desorption, and exchange conditions at both equilibrium and non-equilibrium states. Our time-resolved SERS results provide insights into the effects of nanoscale surface curvature on the binding affinity, cooperativity, structural ordering, and the adsorption/desorption/exchange kinetics of organothiol ligands on colloidal Au nanoparticles. We also use time-resolved SERS as an *in situ* spectroscopic tool to monitor exciton- and plasmonic hot electron-driven photocatalytic chemical transformations, based on which we have been able to identify the key intermediates and resolve the complex reaction kinetics along the multistep photocatalytic molecule-transforming pathways. The insights gained from this work provide a central knowledge framework that guides us to fully understand the dynamic interactions between ligand molecules and optically excited plasmonic nanoparticles that dictate the intriguing interfacial molecular transformations.