

Shaping Metallic Nanoparticles toward Integrated Plasmonics and Catalysis

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Noble metal nanoparticles have been of tremendous interest because of their intriguing size- and shape-dependent plasmonic and catalytic properties. The combination of tunable plasmon resonances with superior catalytic activities on the same nanoparticle, however, has long been challenging because plasmonics and catalysis require nanoparticles in two drastically different size regimes. Tunable plasmon resonances is a unique feature of sub-wavelength metallic nanoparticles, whereas heterogeneous catalysis requires the use of sub-5 nm nanoparticles as the catalysts. In the first part of my PhD dissertation, I found a unique way to bridge this size gap between nanoplasmonics and nanocatalysis. I demonstrated that desired plasmonic and catalytic properties can be integrated on the same particle by controllably creating high-index facets on individual sub-wavelength metallic nanoparticles, such as, porous Au nanoparticles, Au nanocrystals enclosed by well-defined high-index facets, multi-faceted Au and bimetallic nanorods. The capabilities to both nanoengineer high-index facets and fine-tune the plasmon resonances through deliberate particle geometry control allow us to use these nanoparticles for a dual purpose: as substrates for plasmon-enhanced spectroscopies and efficient surface catalysts. Such dual functionality enables us to gain quantitative insights into the facet-dependent molecular transformations on Au nanocatalysts using surface-enhanced Raman spectroscopy (SERS) as an ultrasensitive spectroscopic tool with unique time-resolving and molecular finger-printing capabilities.

More recently, I further expand my research interest into plasmonic hot electron-driven

photocatalytic reactions. It has been recently observed that the localized surface plasmon resonance supported by metallic nanostructures plays a crucial role in either driving or enhancing a series of interesting chemical or photochemical reactions. However, key scientific questions concerning about the detailed mechanisms of plasmon-driven photocatalytic reactions are still poorly understood. Therefore, in the second part of my PhD dissertation, I focused on the quantitative understanding of the kinetics and underlying pathways of plasmon-driven photocatalysis. We used SERS to precisely monitor, in real time, the plasmon-driven photoreaction kinetics at the molecule-nanoparticle interfaces. The reductive dimerization of 4-nitrothiophenol and oxidative coupling of thiophenol-derivates were chosen as model reactions to explore the effects of plasmon excitations, molecular adsorption states, local field enhancements, and photothermal processes, on the plasmon-driven photocatalytic reactions. We further discovered the unique capability of plasmon excitation toward decarboxylation of mercaptobenzoic acid, and also acting as plasmonic scissor for aromatic side-chain cleavage.

In summary, the goal of this dissertation is to gain new insights on interfacial molecular transformation kinetics and underlying mechanism of heterogeneous catalysis and plasmon-driven photocatalysis using in situ plasmon-enhanced spectroscopic tool for guiding rational design of high performance nanocatalysts and photocatalysts toward renewable solar energy application.