Plasmon-Driven Chemistry on Mono- and Bimetallic Nanostructures

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Hot carriers are highly energetic species that can perform a large spectrum of chemical reactions. They are generated on the surfaces of nanostructures via direct interband, phonon-assisted intraband, and geometry-assisted decay of localized surface plasmon resonances (LSPRs), which are coherent oscillations of conductive electrons. LSPRs can be induced on the surface of noble metal (Ag or Au) nanostructures by illuminating the surfaces with electromagnetic irradiation. These noble metals can be coupled with catalytic metals, such as Pt, Pd, and Ru, to develop bimetallic nanostructures with unique catalytic activities. The plasmon-driven catalysis on bimetallic nanostructures is light-driven, which essentially enables green chemistry in organic synthesis. During the past decade, surfaceenhanced Raman spectroscopy (SERS) has been actively utilized to study the mechanisms of plasmon-driven reactions on mono- and bimetallic nanostructures. SERS has provided a wealth of knowledge about the mechanisms of numerous plasmon-driven redox, coupling, and scissoring reactions. However, the nanoscale catalytic properties of both mono- and bimetallic nanostructures as well as the underlying physical cause of their catalytic reactivity and selectivity remained unclear for decades. In my talk, I will focus on the most recent findings reported by our and other research groups that shed light on the nanoscale properties of mono- and bimetallic nanostructures. This information was revealed by tip-enhanced Raman spectroscopy (TERS), a modern analytical technique that has single-molecule sensitivity and subnanometer spatial resolution. TERS findings have shown that plasmonic reactivity and the selectivity of bimetallic nanostructures are governed by the nature of the catalytic metal and the strength of the rectified electric field on their surfaces. TERS has also revealed that the catalytic properties of bimetallic nanostructures directly depend on the interplay between the catalytic and plasmonic metals. We anticipate that these findings will be used to tailor synthetic approaches that are used to fabricate novel nanostructures with desired catalytic properties. The experimental and theoretical results discussed in my talk will facilitate a better understanding of TERS and explain artifacts that could be encountered upon TERS imaging of a large variety of samples. Consequently, plasmon-driven chemistry should be considered as an essential part of near-field microscopy