

Tip-Enhanced Raman Imaging of Plasmon-Driven Chemistry on Mono- and Bimetallic Nanostructures

Dmitry Kurouski¹,

1. Department of Biochemistry and Biophysics, Texas A&M University, College Station, Texas 77843, United States 2. Institution/Organization, address

E-mail: dkurouski@tamu.edu

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 or Ru, to develop bimetallic nanostructures with unique catalytic activities [1]. The plasmon-driven catalysis on bimetallic nanostructures is light-driven, which essentially enables green chemistry in organic synthesis. During the past decade, surface-enhanced 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 mechanisms of numerous plasmon-driven redox, coupling and scissoring reactions. However, 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 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 sub-nanometer spatial resolution, Figure 1 [2]. TERS findings show 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 [3-4]. TERS also revealed that catalytic properties of bimetallic nanostructures directly depend on the interplay between catalytic and plasmonic metals [5]. We anticipate that these findings will be used to tailor synthetic approaches that are used for fabrication of novel nanostructures with desired catalytic properties. Experimental and theoretical results that will be 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 the essential part of near-field microscopy.

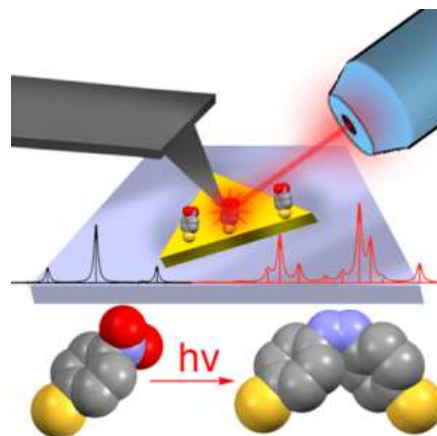


Figure 1. Tip-enhanced Raman imaging of plasmon-driven reactions at the nanoscale.

References

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