

THE IMPACT OF PLASMONICALLY GENERATED HOT-CARRIERS ON SERS ANALYSIS

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Plasmonic nanostructures have paved the way for the development of surface enhanced Raman spectroscopy (SERS); a technique that takes advantage of the Raman signal specific to the molecular vibrational modes. SERS enhances the Raman signal up to 10⁹-fold allowing for lower limits of detection. Through the illumination of the nanostructure with a laser, a localized surface plasmon resonance (LSPR) is excited and further enhances the electric field at the surface of the nanostructure. While the excitation of the LSPR enhances the Raman signal, it can also generate hot carriers that cause the formation of photoproducts that can change the Raman signal. Photoproducts have been reported for various nanostructures in different SERS experiments and can include cross-linking/dimerization, fragmentation, and radical formation. Understanding the parameters and occurrences of these photoproducts will allow for the ability to prevent them when not desired and generate them for further applications. Previously, our group has reported on radical formation with the amino acid tryptophan as well as 4-mercaptobenzoic acid, a common Raman reporter molecule. This work will use changes in the SERS signal to elaborate on the conditions and dynamics of these radical formation reactions associated with the plasmonic activity of nanostructures.