

**Department of Chemistry
Kolthoff Lectureship in Chemistry
Monday, September 20-Wednesday, September 22**

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**Lecture 1:
Molecular Plasmonics:
Nanoscale Spectroscopy and Sensing
3:45 p.m. Monday, September 20,
230 Science Teaching & Student Services
Reception following in 117/119 Smith Hall**

During the last few years, there has been an explosion of interest and activity in the field of plasmonics. The goal of plasmonics is to control and manipulate light on the nanometer length scale using the properties of the collective electronic excitations in noble metal films or nanoparticles, known as surface plasmons. An improved understanding of the interactions between adsorbed molecules and plasmonic nanostructures (i.e., molecular plasmonics) is having a significant impact in a number of research areas. These include surface-enhanced Raman spectroscopy (SERS), [1] localized surface plasmon resonance (LSPR) spectroscopy for chemical and biological sensing, [2,3] sub-wavelength optical microscopy, [4, 5] and nanolithography [6].

This introductory lecture will begin with some background material on the basic physical concepts of plasmonics. Since plasmonics is a materials driven subject, a unifying theme will be the fabrication of nanoparticles and surfaces with size and shape-tunable nanoscopic features using nanosphere lithography (NSL), electron beam lithography (EBL), and chemical synthesis. Size and shape tunability leads to an exquisite degree of control over the magnitude and spatial extent of the surface electromagnetic fields that surround optically excited nanoparticles. In turn, this has enabled fundamental new insights into the electromagnetic (EM) field enhancement mechanism underlying both LSPR and SER spectroscopy. For example, the EM mechanism makes very specific predictions about the intertwined relationship between SERS and LSPR at the ensemble averaged level that are demonstrated by experiment. [8] I will conclude this lecture with an overview of SERS applications focussing in on recent work to develop an *in vivo* SERS glucose sensor, [9] a SERS sensor for gas phase chemical agents, [10] and the use of SERS to identify colorants in Art Conservation Science.[11]

References

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**Lecture 2:
Single Molecule and Single Nanoparticle Surface Enhanced Raman Spectroscopy
9:45 a.m. Tuesday, September 21, 331 Smith Hall**

In 1997, two groups independently reported the startling observation of single molecule surface enhanced Raman spectroscopy (SMSERS). [1, 2] Over time the, the evidence for the existence of SMSERS as well as the magnitude of the enhancement factor was called into question. This lecture will focus on our efforts to provide a robust existence proof for SMSERS. In addition, we attempt to answer fundamental questions such as (1) what is the largest possible enhancement factor (EF), and (2) what nanostructure produces the largest EF will be given. Our approach to answering these questions involved the development of new tools using SMSERS, single nanoparticle SERS and single nanoparticle LSPR spectroscopy spatially correlated with high resolution transmission electron microscopy (HRTEM). [3]

The existence of SMSERS has been proven employing a frequency-domain approach with two isotopologues of rhodamine 6G (R6G) that provide unique vibrational signatures. [4] When an average of one molecule is adsorbed per Ag nanoparticle, only one isotopologue is typically observed under a dry N₂ environment. The frequency-domain proof was subsequently used to study the structure of SMSERS active nanoparticle assemblies by HRTEM [5] and electrodynamics theory [5] as well as to perform excitation spectroscopy measurements. [6] The isotopologue proof has recently been extended to the crystal violet (CV) system. [7]

Understanding the relationship between single particle structure and SERS activity represents a significant challenge for plasmonics. To this end, the structural and optical properties of SERS nanoantennas comprised of aggregated Au nanoparticles that are coated with organic reporter molecules and encapsulated by a SiO₂ shell have been determined using correlated transmission electron microscopy (TEM), SERS, LSPR, and theory [8] The results show that the distribution of SERS enhancement factors (EFs) for a structurally and optically diverse set of nanoantennas is remarkably narrow. The EFs are uncorrelated to aggregation state and localized surface plasmon resonance (LSPR), but are crucially dependent on the size of the interparticle gap.

References

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Lecture 3: High Resolution and High Throughput Plasmonic Biosensors 3:45 p.m. Wednesday, September 22, 331 Smith Hall

Recent developments have greatly improved the sensitivity of optical sensors based on the localized surface plasmon resonance (LSPR) of noble metal nanoparticle arrays and single nanoparticles. The basic concepts of the LSPR and a description of its exquisite sensitivity to nanoparticle size, shape and local dielectric environment will be briefly reviewed [1]. The development of single nanoparticle LSPR spectroscopy spatially correlated with high resolution transmission electron microscopy (HRTEM) [2] to define the structure-function relationship of plasmonic biosensors will be discussed. Recent examples from our laboratory using LSPR biosensors to detect molecular binding events and conformation changes will be presented [3]. The remainder of the talk will focus on progress in areas that represent significant future challenges: (1) pushing the sensitivity of plasmonic biosensors towards the single-molecule detection limit, (2) combining LSPR with complementary molecular identification techniques such as matrix assisted laser desorption ionization mass spectrometry (MALDI-MS) [4], (3) the development of new instrumentation for high throughput plasmonic biosensing [5], and gas sensing with plasmonic nanosensors [6].

References

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