

Tuesday Morning, October 16, 2007

Plasmonics Topical Conference

Room: 619 - Session PL+BI-TuM

Plasmon-mediated Sensing and Biosensing

Moderator: J.C. Owrutsky, Naval Research Laboratory

8:00am **PL+BI-TuM1 Combining Surface Plasmons, Enzyme Chemistry and Nanoparticles for Ultrasensitive Biosensing**, *R.M. Corn, H.J. Lee, A.W. Wark*, University of California-Irvine **INVITED**

Surface bioaffinity biosensors have become invaluable biotechnological tools for the rapid, multiplexed detection of biomolecules. In the last decade, a number of surface-sensitive spectroscopic techniques based on changes in the local optical index of refraction near an interface upon adsorption have emerged as attractive alternatives to traditional fluorescence-based detection methods for surface bioaffinity biosensing. For example, we have successfully applied surface plasmon resonance imaging (SPRI) to measure the bioaffinity adsorption of DNA, RNA, antibodies, proteins and biomarkers. In this talk we will describe our recent efforts to create the next generation of ultrasensitive biosensors which use a combination of (i) surface enzyme chemistry and (ii) nanoparticle surface incorporation. For example, SPRI, DNA microarrays, nanoparticles and poly(A) RNA polymerase can be used together for ultrasensitive microRNA profiling measurements at femtomolar concentrations. In addition, we will also describe a new optical technique, nanoparticle-enhanced diffraction gratings (NEDG), that can be used to create novel ultrasensitive biosensors.

8:40am **PL+BI-TuM3 Polarization-Dependent Surface Enhanced Raman Scattering from Silver Nanoparticle Arrays**, *W. Luo, P. Chu, D.L. Mills, R.M. Penner, J.C. Hemminger*, University of California, Irvine

One specially promising method to design Surface Enhanced Raman Scattering (SERS) substrates is to fabricate silver nanoparticle arrays with nanoscale gaps that can carry strong and localized surface plasmon resonances. Studies have revealed that dramatic SERS phenomena require interparticle spacings to be around 10 nm or less which is hard to achieve with current fabrication technologies. We present the straightforward fabrication of ordered spherical silver nanoparticle arrays with gaps less than 10 nm on Highly Oriented Pyrolytic Graphite (HOPG). Physical Vapor Deposition (PVD) of silver on HOPG under controlled experimental conditions results in the self-assembly of rows of silver nanoparticles. Straight rows of particles are obtained that extend over distances as large as 100 microns. Arrays of rows of particles are parallel over similar distances. Since these 2-dimensional particle arrays are organized over 100's of microns they are easily addressed in conventional optical experiments. Using thiophenol adsorbed on the silver particles as probe molecules, highly polarization-dependent enhanced Raman scattering has been observed from these particle arrays. When light is polarized along the axis of the nanoparticle arrays, the enhanced Raman spectra are much stronger than when light is polarized perpendicular to the axis of the nanoparticle arrays. Theoretical calculations of the electromagnetic response of the interacting nanoparticles to a light field will also be presented. Ongoing research with these arrays includes a number of different studies. Among these is the use of the particle arrays as a collection of "nano-electrodes". For example, electrodeposition of semiconductors on the silver nano-arrays has been accomplished with the subsequent observation of enhanced photoluminescence.

9:00am **PL+BI-TuM4 Nanoplasmonic Sensing of Surface and Bulk Modifications of Metallic Nanoparticles using Localized Surface Plasmon Resonances: Studies of Hydrogen Uptake in Supported Pd Nanoparticles and Oxidation of Al Nanoparticles**, *I. Zorić, C. Langhammer, E. Larsson, B. Kasemo*, Chalmers University of Technology, Sweden

We propose a novel nanoplasmonic sensing scheme for optical, real time, monitoring of property changes in metal nanoparticles. The property changes can be both bulk and/or surface changes induced e.g. by interaction with the surrounding medium. To sense these changes we use the localized surface plasmon resonance (LSPR) of the nanoparticle as signal transducer for remote optical readout. The high sensitivity of the LSPR (i.e. plasmon energy and extinction cross-section) to electronic, structural and shape changes, taking place in the nanoparticle, makes the latter an extremely sensitive and non-invasive probe for studies of surface and bulk changes in nanoparticles. Furthermore, since the LSPR seem to be a rather universal feature for nano-confined metallic systems the proposed sensing method is

quite universal. The supported metallic nanodisks were fabricated by the hole-mask colloidal lithography method relying on electrostatically self-assembled polystyrene beads as evaporation masks. The method is suitable for fabrication of large-areas covered by nanostructures allowing for easy spectroscopic studies. The proposed sensing scheme was used to study: a) metal hydride formation in nanometer sized Pd disks exposed to hydrogen atmosphere and b) oxidation of Al nanodisks. In both cases we have quantified the optical response by complementing the optical studies with gravimetric studies (QCM-D). In the latter case the same processes were studied by monitoring the frequency and dissipation shifts when Pd or Al nanoparticles, prepared on the of the quartz crystal microbalance electrode, were exposed to the hydrogen and oxidizing environment respectively. In addition, AFM and SEM studies were used to characterize the morphological changes induced during the process of interest. The most important results include: a) hydrogen pressure-composition isotherms covering the solid solution (α) phase, the coexistence region of the α and hydride (β) phases, and finally the pure hydride phase at large hydrogen pressure. Similarities and differences to the corresponding isotherms for 2D continuous Pt films are also presented. b) Al nanoparticle oxidation kinetics in water shows an initially fast oxide growth followed by a transport limited slower kinetics accompanied by oxide shell cracking. We also show how extension of this sensing approach from nanoparticles to thin films can be made by using LSPR of the 100nm diameter holes made in continuous films.

9:20am **PL+BI-TuM5 Surface Modification of Metallic Nanoparticles for Plasmonics Applications: Potential, Challenges and Advances in the Field**, *V.H. Perez-Luna*, Illinois Institute of Technology **INVITED**

Nanoparticles of noble metals such as gold and silver exhibit size and shape dependent optical properties that are sensitive to changes in the dielectric environment and degree of aggregation. These properties arise from collective oscillations of plasmons excited by incident light. For metals such as gold and silver resonant excitation of particle plasmons can be tuned to occur in a wide region of the visible and near infrared spectrum by proper manipulation of size and morphology. In addition to their interesting optical properties, excitation of particle plasmons by light give rise to enhanced electric fields in the vicinity of nanoparticles. The enhanced electric fields hold enormous potential for biosensing applications using Surface Enhanced Raman Scattering and Surface Enhanced Emission of Fluorescence. Despite this potential, some applications remain largely unexploited due to inherent morphological instability of anisotropic metallic nanoparticles, irreversible aggregation, and difficult surface modification when templating surfactants such as hexadecyltrimethyl ammonium bromide are used to synthesize anisotropic nanoparticles. Surface modification can overcome these obstacles but has not received sufficient attention. This presentation will focus on understanding displacement reactions at the surface of nanorods and model crystalline gold surfaces; the effect of surface modification in overcoming morphological instability; and potential applications in biosensing. Specific applications presented involve the combination of polymers and nanoparticles for detection; creation of environmentally sensitive nanostructured surfaces; and photostability of fluorophores in the vicinity of metallic nanorods. New opportunities and future challenges will be discussed.

10:40am **PL+BI-TuM9 Environmental Sensitivities of Localized Surface Plasmon Resonances of Immobilized Nanoparticles: Substrate Modulation of Generic Bulk Phase Results**, *M.M. Miller, S. Chen, A. Chilkoti, A.A. Lazarides*, Duke University

The plasmon bands of metal nanoparticles are known to be sensitive to the refractive index of the environment. The magnitude of the sensitivities vary widely for resonances supported by particles of various shape, size, and composition. Through spectral simulation, however, it has been shown that the resonant frequency of particles suspended in a medium have sensitivities to refractive index of the medium that are determined with high accuracy by the plasmon frequency and the dielectric properties of the particle and medium, when the particle is composed of a single component and of modest phase volume.^{1,2} Immobilized particles, in contrast, display sensitivities to the exchangeable component of their media that are reduced relative to those of suspended particles and expected to be dependent upon the nature and localization of the mode and its interaction with the substrate. Here, we report measurements and simulations of the refractive index sensitivities of a family of gold nanorods immobilized on glass, and a comparison of the immobilized particle sensitivities with the generic sensitivities of plasmons supported by suspended particles. The refractive index sensitivities of the immobilized rods are found to be well predicted by a band location dependent sensitivity function reduced from the generic solution phase sensitivity function by a constant scale factor derived from

comparison of simulation and theory. The applicability of the result to immobilized particles of other shapes, sizes, and compositions will be discussed within the framework of sensitivity theory.

¹ Miller, M. M.; Lazarides, A. A. "Sensitivity of Metal Nanoparticle Surface Plasmon Resonance to the Dielectric Environment" *J. Phys. Chem. B* 2005, 109, 21556-21565

² Miller, M. M.; Lazarides, A. A. "Sensitivity of Metal Nanoparticle Plasmon Resonance Band Position to the Dielectric Environment as Observed in Scattering" *J. Opt. A: Pure Appl. Opt.* 2006, 8, S239-S249.

11:00am **PL+BI-TuM10 Controlled Plasmonic Coupling in Reconfigurable Nanoparticle Assemblies**, *D.S. Sebba, T.H. LaBean, A.A. Lazarides*, Duke University

Metal nanoparticles (MNPs) support localized surface plasmon resonances that are sensitive to particle shape, size, composition, and the presence of other polarizable particles and materials. Advances in MNP synthesis and surface chemistry have yielded biomolecule nanoparticle conjugates that interact specifically with oligonucleotides, peptides, and proteins. The specific recognition properties of these components have been exploited in responsive plasmonic systems with formats that range from amorphous solution phase particle networks to immobilized colloidal monolayers and individually responsive particles. For molecular detection applications, various formats have various advantages, with single particle sensors generally offering ease of control and multi-particle systems offering strong plasmon modulation. Here, we report plasmon modulation in pre-formed, few particle assemblies linked by reconfigurable DNA nanostructures. The investigation is motivated by the potential of reconfigurable few particle assemblies to provide control of plasmon coupling in a format that displays high responsiveness per molecule. In the coupled system upon which we report, DNA nanostructures tether satellite MNPs to a core MNP. The DNA nanostructures use duplex DNA to control interparticle separation and are responsive to target strands that modulate interparticle helix length. The reconfigurable assemblies are characterized in two states, using dynamic light scattering and transmission electron microscopy to monitor structure and scattering spectroscopy to monitor plasmonic properties. A two state structural model is tested by comparison of spectroscopic data with spectra calculated for structures defined by core/satellite stoichiometry from TEM and interparticle separations from measurements in DNA-linked networks. Thermodynamic properties derived from melting transition data collected from the reconfigurable DNA linker ex-situ are reported and reviewed as a source of insight into DNA nanostructure control of system stability.

11:20am **PL+BI-TuM11 Metal Films with Arrays of Tiny Holes: Infrared Plasmonic Scaffolding for Spectroscopy**, *J.V. Coe, K.R. Rodriguez, S. Teeters-Kennedy, H. Tian, J.M. Heer*, The Ohio State University **INVITED**

The surface plasmon (SP) mediated, extraordinary transmission of metal arrays of subwavelength holes has been moved into the infrared (IR) region in order to overlap with the traditional range of molecular vibrations. SP-enhanced IR absorption spectra are recorded (using standard FTIR instrumentation) of metal-supported self-assembled alkanethiol monolayers, phospholipid bilayers, gramicidin (an antibiotic peptide) and cholesterol in phospholipid bilayers, as well as hexadecane thin films. The interaction of a SP resonance and a vibrational excited state has been examined by tuning a SP resonance (both by film thickness and angle of the mesh) through the primary rocking vibration of the hexadecane molecule producing vibrational band intensity changes, peak shifts, and lineshape changes. The nature of the enhancements will be discussed.

12:00pm **PL+BI-TuM13 Photo-Recognition and Control of a Small Number of Molecules at Metal Nano-Gap Arrayed on Solid Surface**, *K. Murakoshi*, Hokkaido University, Japan

Detection, recognition, and control of single molecules are a common theme in recent advanced technologies. It has been demonstrated that the surface-enhanced Raman scattering (SERS) phenomenon can drastically increase the scattering cross section, which is comparable to that of fluorescence at high quantum yield. Although the importance of single-molecule SERS (SM-SERS) has been well recognized from the early stage of its discovery, there are only a few examples supporting the observation of SM-SERS. In the present study, well-ordered, periodic metal nano-dot dimer arrays were prepared. The gap distance between two metal dots was optimized to show intense SERS in an aqueous solution. The system was also applied to control the adsorption of target molecules. In-situ Raman spectroscopic measurements with 785 nm excitation were carried out in aqueous solution using metal nano-gap array. Intense Raman signals were observed when the metal dimer structure was optimized. The SERS activity was dependent upon on the structure of the metal dimer with a distinct gap distance, suggesting that the intense SERS originates from the gap part of the dimer. Characteristic time-dependent spectral changes were observed both in Stokes and anti-Stokes region. In the system of Au dots array, relatively stable SERS signals was observed even under relatively strong

photo-irradiation. Possibility of the molecular manipulation by electromagnetic field will be discussed based on the characteristic behavior of SERS signals observed under relatively strong photo-irradiation.

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