Wednesday Afternoon, October 31, 2012

Nanometer-scale Science and Technology
Room: 12 - Session NS-WeA

Nanophotonics and Plasmonics
Moderator: D. Wei, University of Florida

2:00pm **NS-WeA1 Plasmon Induced Current In Hybrid Nanostructures**, *D.A. Bonnell*, ***D. Conklin***, *S. Nanayakkara*, *X. Chen*, The University of Pennsylvania, *T.H. Park*, University of Michigan, *M. Therien*, Duke University

Interest in plasmon-exciton interactions is increasing owing to potential impact in light harvesting and optical signal manipulation. Recently a new mechanism of plasmon induced current generation was observed in porphyrin-Au nanoparticle hybrid nanostructures.[1] The plasmons associated with the gold nanoparticles enhanced photo conduction by many factors... even an order of magnitude. To understand this phenomena we have first developed an approach to the analysis of temperature dependent transport measurements that can lead to an unambiguous determination of mechanism in complex systems. [2] Then the temperature and wavelength dependent transport is examined as a function of nanoparticle size and distribution and molecule optical properties. [3] A Au-porphyrin combination is designed to distinguish the various potential mechanisms for plasmon induced current. We will show new evidence for a mechanism involving 'hot electron' generation. This has the potential to vastly increase efficiency of energy harvesting devices.

[1] Banerjee et al ACS Nano **4** (2010) 1019-1025

[2] Conklin et al NanoLetters **12** (2012) doi 10.1021/nl300400a

[3] Conklin et al Advanced Materials **21** (2011) 4712–4718.

2:20pm **NS-WeA2 Absorption from Plasmonic Antenna Arrays**, ***K.E. O'Brien***, *P. Wang*, *P.H. Holloway*, *M.R. Davidson*, University of Florida

Photomixing over nano/micro scale plasmonic structures is a novel concept for generating narrow band radiation, specifically in the terahertz (THz) range. The plasmonic structures can serve as antennas for absorbing incoming photons and conversely emit radiation of a lower frequency if it is generated from mixing. In this experiment, antenna structures are excited by two tuned laser diodes to output THz radiation. Various designs for these antennas are have been considered, with presented results focusing on 2 dimensional arrays of elliptical antennas fabricated from Ag using electron-beam lithography and lift-off. The plasmonic antenna arrays exhibit polarization-dependent absorption when excited by visible light in agreement with results from simulations. The effect of varying antenna size on absorption will be discussed, as well as results from photomixing experiments.

2:40pm **NS-WeA3 New Directions in Plasmonics: Pushing the Sensitivity, Space, and Time Limits**, ***R.P. Van Duyne***, Northwestern University **INVITED**

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), localized surface plasmon resonance (LSPR) spectroscopy, sub-wavelength optical microscopy, and nanolithography.

This talk will begin with some background material on the basic physical concepts underlying plasmonics with an emphasis on SERS and LSPR spectroscopy. Next, I will turn to two very recent developments. For the first time, the revolutionary techniques of surface enhanced Raman spectroscopy and femtosecond stimulated Raman spectroscopy (FSRS) have been combined. Thus, plasmonically enhanced broadband Raman spectra using an ultrafast four wave mixing process, which can simultaneously achieve spectral and temporal resolution below the time-energy uncertainty limit, has been achieved! Further we report substantial progress in tip-enhanced Raman spectroscopy (TERS). The isotopologue proof of single molecule specificity in ambient TERS has been demonstrated. We calculated the total TERS enhancement factor to be 1013, which includes a molecular resonance Raman contribution of 107. Further, an ultrahigh vacuum (UHV) TERS instrument has been constructed with atomic resolution of the surface and sub-molecular resolution of the adsorbate. For the first time, multiple vibrational modes for copper phthalocyanine (CuPc) adlayers on Ag (111) have been resolved in TER spectra obtained concurrently with molecular resolution UHV Scanning tunneling Microscopy (STM). All sample preparation and tip degassing are performed in-situ, maintaining atomically clean surfaces, greatly enhancing the stability of the tip-sample junction, and ensuring minimal contamination in the field enhancement region beneath the STM tip. We can now forsee the day when it will be possible to combine UHV-TERS and surface enhanced FSRS to enable single-molecule spectroscopy with simultaneous nanometer spatial resolution and femtosecond time resolution.

4:00pm **NS-WeA7 Near-Field Spatio-Temporal Control of Optical Fields for Spectroscopic Nano-imaging: Ultrafast Spectroscopy Reaching the Single Molecule Limit**, ***M.B. Raschke***, University of Colorado **INVITED**

Combining plasmonic and optical antenna concepts with ultrafast and shaped laser pulses allows for the precise control of an optical excitation on femtosecond time and nanometer length scales. I will present several new concepts extending tip-enhanced spectroscopy into the nonlinear and ultrafast regime for nano-scale imaging and spectroscopy of surface molecules and nano-solids. Examples include the adiabatic nano-focusing on a tip for background free tip-enhanced Raman nano-spectroscopy, and spatio-temporal superfocusing with optical control at the 10 nm-10 fs level. Furthermore, the combination of ultrafast mid-IR femtosecond pulses with scattering-scanning near-field optical microscopy (s-SNOM) allows for the control of the ultrafast free-induction decay of infrared molecular vibrations with an increase in sensitivity of IR surface spectroscopy by 10^9 compared to conventional IR micro-spectroscopy, reaching the single molecule limit.

4:40pm **NS-WeA9 Tuning the Optical Properties of Arrays of Pure and Doped Au Nano Chains**, ***N. Nayyar***, *V. Turkowski*, *T.S. Rahman*, University of Central Florida

We apply time dependent density functional theory to study the absorption spectrum of arrays of nano-scale pure Au chains and those doped with transition metal (TM) atoms. We find that as the number of chains in the array increases the plasmon peak shifts to higher energies and appears in the visible range for an array of three gold chains, each consisting of 10 atoms. Doping with TM atoms also leads to the formation of additional plasmon peaks close in energy to the main one for the undoped case and is especially pronounced for Ni-doped chains. However, the response is very different when we have two chains in the array each doped with one TM atom in the middle. We trace the origin of the additional modes to the interplay between the collective and local plasmon oscillations of the chains. We compare the calculated optical absorption spectrum of the doped chains for several different types of TM atoms at different positions in the chains, and provide rationale for the trends. We also analyze the case of arrays consisting of chains of two different noble metal atoms (Au-Ag) and of arrays in which one chain is of noble metal atoms and the other of TM atoms. We find that the plasmon mode is suppressed when the second chain is composed of TM atoms. In addition we study the effect of plasmon –exciton interaction in arrays of infinite Au chains.

Work supported in part by DOE Grant DE-FG02-07ER46354

5:00pm **NS-WeA10 Synthesis, Characterization and Plasmonic Properties of Horizontally and Vertically Aligned Ag Nanorods and Nanowires**, ***S. Vilayurganapathy***, *A. Pandey*, *A. Devaraj*, *D.E. Perea*, *S. Thevuthasan*, EMSL, Pacific Northwest National Laboratory, *A. Kayani*, Western Michigan University

One dimensional metal nanostructures such as nanorods and nanowires exhibit interesting linear and non-linear optical properties and find various applications as electronic, photonic and sensing devices. The optical properties of these composites are dominated by localized surface Plasmon resonance (LSPR) which results from the oscillations of conduction electrons in response to an external field. The resonant frequency of the electrons depends strongly on size, shape, distribution and the surrounding dielectric medium . By controlling the physical and chemical properties of the nanorods and nanowires the electronic and optical properties of the material can be tuned for appropriate applications. Nanorods and wires with well controlled aspect ratios can be grown by Electrodeposition and Polyol synthesis methods.

We have successfully employed the above two methods to grow both vertically and horizontally aligned Ag nanorods and wires. Vertically aligned and free standing Ag nanorods were grown by electrodepositing Ag onto an Anodized Aluminum oxide (AAO) template containing a sputtered layer of Ag on one side. The length of the nanorods varies linearly as a function of deposition time allowing us to obtain excellent control over the aspect ratio. The template was subsequently etched away using 6 wt. %

Phosphoric acid/1.8 wt. % chromic acid solution leaving behind free standing vertically aligned nanorods. A Polyol process in which we reduce silver nitrate with ethylene glycol in the presence of a capping agent (PVP) was employed to grow nanorods in solution. A high yield of nanorods was obtained after centrifuging. The above grown nanorods were horizontally aligned onto a substrate by the Langmuir-Blodgett method. Scanning electron Microscope (SEM) was used to image the nanorods. The change in plasmonic response of both vertically and horizontally aligned nanorods as a function of aspect ratio as well as the influence of the surrounding dielectric medium on the plasmonic resonance of the nanorods embedded in a dielectric matrix will be discussed.

5:20pm **NS-WeA11 Localized Surface Plasmon Resonances in Silicon**, ***L.-W. Chou***, *N. Shin, S. Sivaram, M. Filler*, Georgia Institute of Technology

Localized surface plasmon resonances (LSPRs) in semiconductors offer new opportunities to engineer the interaction of electromagnetic radiation with solid-state materials. Importantly, the carrier density of semiconductors, and thus LSPR frequency, can be modulated via doping and/or electric field. In addition to realizing novel plasmonic devices, the direct integration of plasmonic and excitonic behavior also promises fundamentally distinct functionality. Here, we demonstrate and systematically control LSPRs in nanoscale Si for the first time. More specifically, Si nanowires are synthesized via the vapor-liquid-solid (VLS) technique with a combination of Si_2H_6 and PCl_3 precursors. PCl_3 simultaneously introduces P atoms to the nanowire core and delivers Cl atoms to the sidewall so as to minimize radial dopant incorporation. This chemistry enables growth sufficiently far from equilibrium such that dopant concentrations can exceed thermodynamic limits. Electron microscopy reveals that these nanowires are single crystalline and <111> oriented with very few lattice defects. Polarization dependent *in-situ* infrared spectroscopy measurements show intense mid-IR absorption bands only for the P-doped nanowires, which we assign to longitudinal LSPRs. A significantly weaker transverse mode is occasionally observed as well. The LSPR frequency can be readily adjusted by varying nanowire length. Mie-Gans theory supports our experimental results and indicates that electrically active dopant concentrations exceed 10^{20} cm^{-3}.

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