Nanometer-scale Science and Technology Division
Room: 203 - Session NS-MoA

Frontiers in Nanophotonics and Plasmonics
Moderator: N. Camillone III, Brookhaven National Laboratory

2:00pm **NS-MoA1 Probing the Metal-Insulator Transition of Vanadium Dioxide using Gold Nanoantennas**, ***D.W. Ferrara***, *J. Nag, E.R. MacQuarrie, R.F. Haglund*, Vanderbilt University

Vanadium dioxide (VO_2) films and nanostructures in contact with gold (Au) or silver nanostructures can form the building blocks of active metamaterials that can be modulated in response to various stimuli such as the presence of chemical agents, changes in temperature, or irradiation. The semiconducting-to-metal phase transition (SMT) of VO_2, — which can be induced thermally ($T_c = 68^oC$), optically, or electrically — leads to a change in the dielectric function of the film. Since the localized surface plasmon resonance (LSPR) of the metal nanoantenna is sensitive to the local dielectric environment, the SMT allows the optical response of the metal::VO_2 nanocomposite to be tuned. Thus these Au::VO_2 nanocomposites are unique probes of strong-correlation physics because, during the phase transition, the electron-electron interactions in VO_2 that drive the SMT are coupled with the plasmonic excitation of the Au nanostructure.

We fabricated arrays of Au nanoparticles (NPs), 180 nm in diameter and 20 nm high on indium-tin-oxide coated glass by electron-beam lithography. Subsequently, the nanoparticle arrays were coated with a 60 nm VO_2 film by pulsed laser ablation of vanadium metal targets in 10 mTorr oxygen (O_2) background gas, then annealed for 45 minutes at 450°C in 250 mTorr of O_2. Using a Peltier heater and thermocouple mounted on a copper sample holder, temperature-dependent extinction of the array was measured using plain VO_2 film as a reference to determine the LSPR wavelength and linewidth during the SMT.

The LSPR wavelength of the NPs was 1000 nm in the semiconducting state and approximately 840 nm in the metallic state, thus overlapping the VO_2 electronic transitions from the occupied vanadium $3d_{||}$ band to the empty $3d_{\pi}$ band centered at approximately 885 nm. As the film undergoes the SMT, the split $3d_{||}$ bands merge and, with the $3d_{\pi}$ band, form the metallic VO_2 conduction band. Since the Au NPs are sensitive to changes in both the real and imaginary parts of the VO_2 local dielectric function, they serve as a direct probe of the SMT. The results show a 30% decrease in plasmon dephasing time during the transition due to an increase in carrier-carrier scattering in the VO_2. Both Maxwell-Garnett and Bruggeman effective-medium theories predict the decrease in dephasing time during the SMT; however, a linear theory is a more accurate model for the hysteresis in the LSPR wavelength.

2:20pm **NS-MoA2 Metamaterial Nanosensors based on the Metal-Insulator transition in VO_2**, ***K. Appavoo***, *R.F. Haglund Jr.*, Vanderbilt University

The use of solid-solid phase transitions to modulate the plasmonic response of metal nanostructures is a promising approach to nanophotonic technologies, including sensors based on signal modulation in confined nanoscale volumes [1]. Consideration of phase-transforming materials has typically focused on composition, whereas relatively little attention has been paid to the question of size dependence in determining stable phases. However, size effects play a crucial role in determining the coupling with mechanical, optical, chemical or thermal input required to effect the phase transformation [2]. With rapid progress in nanofabrication techniques, size-dependent properties become relevant and systematic studies to assess both the role of nucleation in forming a new state and of the nanoscale dynamical effects are needed.

Here, we describe an example that shows how, by systematically varying the gap between the arms of split-ring plasmonic resonators, the in-arm coupling resonance in a split-ring metamaterial can be used to monitor the metal-insulator transition in discrete volumes of the strongly correlated VO2. Moreover, this "plasmonic hysteresis" technique also provides a means to correlate the electronic phase-transition with its structural counterpart which was previously measured using SERS technique [3]. If the number of intrinsic nucleation sites is directly proportional to the interrogated volume (a reasonable assumption) [4], we have effectively shown that well-crafted plasmonic structures with well-understood modes can be a helpful tool to probe size-dependent effect [5]. Full field 3D finite-difference time-domain simulations show that the physical origins of these non-isotropic electron oscillations leads to concentration of the electromagnetic energy for focused interrogation and high sensitivity.

As an additional example, we briefly describe an investigation into the use of similar nanostructures as chemical sensors based on coupling of autocatalytic reactions at the gold-VO2 interface and molecular recognition moieties. In this case, the detection method involves the change in optical transition of a metamaterial array incorporating VO2 when the heat of decomposition is sufficient to initiate the metal insulator transition.

2:40pm **NS-MoA3 Enhanced Photoluminescence from $Gd_2O_3:Eu^{3+}$ Based Core/Multi-shell Nanoparticles**, ***J. Choi***, *M.R. Davidson, P.H. Holloway*, University of Florida

Core/shell and core/multi-shell nanoparticles with luminescent $Gd_2O_3:Eu^{3+}$ were successfully synthesized by a high boiling-point alcohol (polyol) and solution precipitation methods, respectively. The hetero-structured nanoparticles with Eu doped Gd_2O_3 exhibited intense $^5D_0$-$^7F_2$ photoluminescence (PL) from Eu^{3+} after calcination at 600 ˚C for 2h in air. Photoluminescence excitation (PLE) data showed that while a small fraction of the emission resulted from direct excitation of Eu^{3+}, most of the excitation resulted from adsorption in the Oxygen to Europium charge-transfer band (CTB) between 225 and 275 nm. $Gd_2O_3:Eu^{3+}/Y_2O_3$ core/shell nanoparticles exhibited PL intensities up to 40% larger than from bare $Gd_2O_3:Eu^{3+}$ nanoparticles and $SiO_2/Gd_2O_3:Eu^{3+}/Y_2O_3$ core/multi-shell samples showed quantum yield (QY) up to 72% larger than that of $SiO_2/Gd_2O_3:Eu^{3+}$ core/single-shell nanoparticles. The increased PL and QY were attributed to reduced non-radiative recombination based on longer luminescence decay time. Potential applications of the nanoparticles as scintillation radiation detectors will be discussed.

3:00pm **NS-MoA4 $Au|SiO_2|Yb:Er:Y_2O_3$ Core|Shell Optical Nanoantenna: Experiment & Simulation**, ***V. Jankovic***, *J.P. Chang*, University of California Los Angeles

The conversion of electromagnetic (EM) energy from free propagating radiation to localized energy and vice versa in the radio frequency (RF) and microwave domains is accomplished with the use of antennas. Optical antennas are analogous to their RF and microwave counterparts, but there are crucial differences in their physical properties and scaling behavior because metal is a highly dispersive material with finite conductivity at optical frequencies. Optical antennas are not driven by galvanic transmission lines like RF antennas, instead, localized oscillators such as atomic emitters are brought close to the feed point of the antennas, and electronic oscillations are driven capacitatively.

In this work, Au nanoparticles of different shapes (spheres, rods and stars) were used as antenna elements, Er^{3+} ions in an Y_2O_3 host matrix were used as atomic emitter antenna driving elements while the capacitative gap between the antenna element and the atomic emitter was controlled by deposition of an ultra-thin SiO_2 inner shell between the Au nanoparticle and the $Yb:Er:Y_2O_3$ outer shell. A 4-5nm silica spacer layer was deposited through a controlled TEOS hydrolyzation reaction and was shown to be effective in preventing quenching yet enabling energy coupling between the Au nanorod and the RE-ion doped oxides. Spatially and compositionally controlled $Yb:Er:Y_2O_3$ outer shells were deposited using both wet chemistry methods and radical enhanced atomic layer deposition (RE-ALD).

Upconversion (UC) spectral, power dependence and radiative lifetime measurements with 532nm, 750nm 980 nm and 1064nm laser excitation were used to assess the coupling of the Au optical antenna to the emitter ions as a function of antenna shape, spacer layer thickness and spectral and spatial mode overlap efficiency. Preliminary optical characterization showed a 2X earlier onset of upconversion with 980nm excitation for $Yb:Er:Y_2O_3$ coupled to an Au nanorod antenna compared to pure (uncoupled) $Yb:Er:Y_2O_3$ nanoparticles. Power dependence measurements with 980nm excitation showed a >5 slope indicating a multi-photon absorption induced luminescence process for the Au-coupled erbium and a <2 slope for the uncoupled erbium, indicating a two photon absorption (expected for erbium with 980nm excitation). These optical antenna core|shell particles have potential application in bio-imaging and light trapping for solar and sensor applications.

3:40pm **NS-MoA6 Gap-Mode Plasmonic Cavities: Engineering Light-Matter Interactions in Metallic Structures**, *E.L. Hu,* ***K.J. Russell***, *T.-L. Liu, S. Cui, K. Yeung*, Harvard University **INVITED**

Optical cavities can tightly confine light in the vicinity of optical emitters, enhancing the interaction of light and matter. The modes or optical states of the cavity can be precisely designed and engineered, and in recent years there has been remarkable progress in demonstrations of 'cavity quantum electrodynamics (cQED)' in solid state platforms. Such progress has been

primarily for cavities fabricated in dielectric materials, with a steady improvement in cavity quality, with quality factors, Q, in excess of 10^4 – 10^6 realized for cavities with coupled emitters [1],[2]. These high Q-coupled emitter systems have demonstrated heralded single photon emission [3], ultra-low threshold lasing [4] and strong light-matter coupling [5],[6].

Metal-based optical cavities would have inherently lower Q's (and greater loss) than dielectrics; however, metal cavities utilizing surface plasmon polaritons (SPPs) can have sufficiently small mode volume to produce a substantial Q/V, the quantity relevant for high Purcell factors, a measure of the light-matter interaction. This talk will focus on such *plasmonic cavities*, with optical modes formed within the gap of the two metal layers which defined the cavity [7]. Initial structures comprised silver (Ag) nanowires (NW), 70 nm in diameter and 1 - 3 μm in length, placed into close proximity to a Ag thin film substrate, with the NW axis parallel to the substrate surface. Optically active material was interposed between the nanowire and the Ag substrate: this comprised one to two monolayers of PbS colloidal quantum dots, clad on top and bottom by thin dielectric layers of varying composition and thickness. The fluorescence spectrum of PbS quantum dots within the gap was strongly modified by the cavity mode, with peak position in quantitative agreement with numerical calculations, and demonstrating Q values of ~ 60.

Such plasmonic cavities allow the easy incorporation of a variety of light-emitting active areas, and we have also explored the incorporation of various organic, dye-containing layers within the gap-mode plasmonic cavities. In addition these structures lend themselves to relatively simple modifications of geometry, allowing effective *tuning* of cavity modes, and also control of modes through the use of photonic crystal geometries, fabricated into metal.

The high Q/V possible for these cavities, and the range of organic and nanocrystalline emitters they can accommodate make these important building blocks for the exploration of light-matter interaction in the solid state.

References

[1] S. Noda, M. Fujita, and T. Asano, *Nature Photonics* 1 (2007) 449.

[2] B.-S. Song, S.-W. Jeon, and S. Noda, *Optics Letter* 36 (2011) 91.

[3] P. Michler., et al. *Science* 290 (2000) 2282.

[4] S. Strauf et al., *Phys. Rev. Lett.* 96 (2006) 127404.

[5] J. Reithmaier et al.. *Nature* 432(2004) 197.

[6] K. Hennessy, A. Badolato, et al. *Nature* 445 (2007) 896.

[7] K. Russell and E. Hu, *Appl. Phys. Lett.*97 (2010) 163115.

4:20pm **NS-MoA8 Direct Characterization of Surface Plasmon Enhanced Electromagnetic Fields on Single Ag Nanostructure**, ***W.D. Wei***, *J. Wang, Y. Wang,* University of Florida, *G. Xiong, S. Peppernick, A. Joly, K. Beck, W.P. Hess*, Pacific Northwest National Laboratory

Using two-photon photoemission electron microscopy (2P-PEEM) we have directly explored the optical fields on a single Ag nanostructure and quantitatively measured the field enhancement factor (FEF). The 2PPE intensity from the Ag nanostructure is enhanced by 2 orders of magnitude with respect to the 2PPE intensity from a smooth and homogeneous Ag thin film. This enhancement is attributed to a localized surface plasmon excitation and resonance of the local field, and the FEF is determined to be around 4. The capability of directly correlating the field enhancement with nanostructures makes 2P-PEEM a promising tool to investigate the fundamental optical properties of nanomaterials.

4:40pm **NS-MoA9 Comparisons of Optical and Magneto-Optical Properties between Core-Shell Fe-Ag and Co-Ag Nanoparticles based on Localized Surface Plasmon Resonance**, *L. Wang, C. Clavero, K. Yang, A. Nelson,* College of William and Mary, *K. Carroll, Z. Huba, E. Carpenter,* Virginia Commonwealth University, *D. Gu,* Applied Research Center, ***R.A. Lukaszew***, College of William and Mary

Magnetic transition nanoparticles (NPs) have been developed and studied by many researchers for bio-imaging and bio-sensing applications [1,2] due to their special optical and magneto-optical (MO) properties. Nevertheless, it is possible to enhance the MO effects of the magnetic NPs by combining them with other materials such as noble metals which exhibit intense localized surface plasmon resonance (LSPR) under certain conditions[3,4]. Here, we present our investigations on LSPR enhanced MO effect in magnetic metal core-noble metal shell NPs, such as core-shell Fe-Ag and Co-Ag NPs. These systems present strong Faraday rotation due to LSPR, nevertheless differences are found among them due to their different optical properties. A blue-shift is experimentally observed in the optical and MO spectra peaks from Fe-Ag to Co-Ag NPs with similar Ag shell concentrations and constant NPs sizes. Also, the absorption and Faraday rotation spectra of Fe-Ag NPs are broader than those of Co-Ag NPs. We explain such differences by means of theoretical studies based on an adaptation of the Maxwell-Garnet model to core shell nanoparticles yielding an excellent agreement with the experimental results. The possibility to understand and tune the properties of core-shell nanoparticles reported here will have significant impact in photonic and plasmonic applications.

This work was financed by DARPA under a grant for the development of novel sensors for bio-defense.

---

[1] Gilles K. Kouassi and Joseph Irudayaraj, *Anal. Chem.*, 2006, **78** (10), pp 3234–3241.

[2] Jae-Hyun Lee, Yong-Min Huh, Young-wook Jun, Jung-wook Seo, Jung-tak Jang, Ho-Taek Song, Sungjun Kim, Eun-Jin Cho, Ho-Geun Yoon, Jin-Suck Suh and Jinwoo Cheon, *Nature Medicine* , 2006, **13**, pp 95–99.

[3] Lei Wang, Kaida Yang, Cesar Clavero, Andrew. J. Nelson, Kyler J. Carroll, Everett E. Carpenter, and Rosa. A. Lukaszew, *J. Appl. Phys.*, 2010, **107**, 09B303.

[4] Lei Wang, Cesar Clavero, Zachary Huba, Kyler J. Carroll, Everett E. Carpenter, Diefeng Gu and Rosa A. Lukaszew, *Nano Lett.*,2011, **11**(3), pp1237–1240.

5:00pm **NS-MoA10 Plasmon Induced Current in Metal/Organic Hybrid Nanostructures**, ***D. Conklin***, *S. Nanayakkara, T. Park,* University of Pennsylvania, *J. Stetcher, M. Therien,* Duke University, *D.A. Bonnell*, University of Pennsylvania

Recently we demonstrated a new mechanism of plasmon-induced electronic transport in hybrid metal nanoparticle-molecular devices. The mecahnism realizes enhancements of up to a factor of 200. The hybrid structures consist of arrays of gold nanoparticles linked by (porphinato)zinc(II) oligomers. Here we examine the role of metal particle size, spacing, and molecular length on the transport mechanisms. Understanding the charge transport through the structures allows the relative roles of nano antennae field focusing and hot electron distribution to the current enhancement to be compared. This phenomenon offers a pathway to wide ranging control of the opto electriconic transport properties which enables concepts of energy harvesting, energy transduction and optoelectronic circuits.

5:20pm **NS-MoA11 Direct-bandgap Infrared Light Emission from Tensilely Strained Germanium Nanomembranes**, ***J.R. Sanchez-Perez***, University of Wisconsin Madison, *C. Boztug,* Boston University, *F. Chen,* University of Wisconsin Madison, *F. Sudradjat,* Boston University, *D.M. Paskiewicz, R.B. Jacobson,* University of Wisconsin Madison, *R. Paiella,* Boston University, *M.G. Lagally*, University of Wisconsin Madison

Silicon, germanium, and related alloys, which provide the leading materials platform of electronics, are extremely inefficient light emitters because of their indirect fundamental energy bandgap. This basic materials property has so far hindered the development of group-IV photonic active devices, including diode lasers, thereby significantly limiting our ability to integrate electronic and photonic functionalities at the chip level. Here we show that Ge nanomembranes can be used to overcome this materials limitation. Theoretical studies have predicted that tensile strain in Ge lowers the direct energy bandgap relative to the indirect one. We demonstrate [1] that mechanically stressed nanomembranes allow for the introduction of sufficient biaxial tensile strain to transform Ge into a direct-bandgap, efficient light-emitting material that can support population inversion and therefore provide optical gain. [1] F. Chen, C. Boztug, J. R. Sanchez-Perez, F. Sudradjat, D. M. Paskiewicz, R. B. Jacobson, M. G. Lagally, and R. Paiella, *Direct-bandgap germanium pumped above optical transparency in tensilely strained nanomembranes*, submitted. Research supported in part by NSF and DOE

Authors Index

Bold page numbers indicate the presenter