

Thursday Afternoon, October 23, 2008

Biomaterial Interfaces

Room: 202 - Session BI+TF+MI+NS+NC-ThA

Plasmonics and Magneto/Plasmonics Aimed at Biosensing

Moderator: F. Höök, Chalmers University of Technology, Sweden

2:00pm BI+TF+MI+NS+NC-ThA1 Optical Meta Materials and Nano Plasmonics, X. Zhang, University of California, Berkeley INVITED

Recent theory predicted a new class of meta structures made of engineered sub wavelength entities - meta "atoms" and "molecules" which enable the unprecedented electromagnetic properties that do not exist in the nature. For example, artificial plasma and artificial magnetism, and super lens that focuses far below the diffraction limit. The metamaterials may have profound impact in wide range of applications such as nano-scale imaging, nanolithography, and integrated nano photonics. I'll discuss a few experiments that demonstrated these intriguing phenomena. We showed, for the first time, the high frequency magnetic activity at THz generated by artificially structured "meta molecule resonance", as well as the artificial plasma. Our experiment also confirmed the key proposition of super lens theory by using surface plasmon. We indeed observed optical superlensing which breaks down so called diffraction limit. I'll also discuss nano plasmonics for imaging and bio-sensing. The surface plasmon indeed promises an exciting engineering paradigm of "x-ray wavelength at optical frequency".

2:40pm BI+TF+MI+NS+NC-ThA3 Gold and Silver Nanocrescents as Tunable Substrates for Surface Enhanced Infrared Absorption Spectroscopy, R. Bukasov, J.S. Shumaker-Parry, University of Utah

Controlling the size, shape, and orientation of metal nanoparticles in order to tune and optimize the particles' optical properties for specific applications remains a challenge in the field of plasmonics. Tuning the localized surface plasmon resonance (LSPR) wavelength as well as the localized field enhancements is especially important for spectroscopy applications such as surface enhanced Raman spectroscopy (SERS) and surface enhanced infrared absorption spectroscopy (SEIRA). Although SERS has received a lot of attention with the engineering of nanoparticle-based substrates, the activity in SEIRA development has been less, most likely due to the lack of tunable substrates for the IR spectral region. We describe the development of gold and silver nanocrescents as tunable substrates for SEIRA studies. We use nanosphere template lithography to fabricate gold and silver crescent-shaped structures which exhibit multiple, polarization-sensitive plasmon resonances that are tunable from the visible through the infrared. Large electromagnetic field enhancements are expected due to the sharpness of the crescent's tips and the ability to bring these sharp tips into close proximity to each other. Using the crescent-shaped structures as substrates, we demonstrate the importance of spectral tunability for maximizing signal enhancements in SEIRA. The nanocrescent area normalized SEIRA signal enhancement increases from 7,700 to 46,000 with an increase in the extent of overlap of the nanocrescents' LSPR frequency with the frequency of the probed molecular vibration. The broad tunability of the nanocrescents' LSPR properties makes the structures excellent candidates for a range of spectroscopic and sensing applications including SEIRA.

3:00pm BI+TF+MI+NS+NC-ThA4 Use of Angle-Resolved SPRi for the Characterization of Protein Binding and Agglomeration Dynamics, M.S. Golden, J.A. Ruemmele, A. Whitty, R.M. Georgiadis, Boston University

Transient protein-protein interactions are essential on almost every level of cellular function. In addition, protein aggregates play various roles in cell signaling pathways and have been implicated in the onset of many neurodegenerative conditions such as Alzheimer's disease. Although various structures of protein complexes have been widely studied, the mechanisms involved in protein binding events are not clearly understood, and the transient dynamics of this formation have proven difficult to study. Investigation of the mechanisms of protein agglomeration and binding, however, is essential to elucidating the role of these structures in diseases. Here we exploit the multi-array quantitative capabilities of angle-resolved surface plasmon resonance imaging (SPRi) to perform kinetic and thermodynamic measurements of protein-protein interactions. Specifically, the agglomeration and small molecule inhibition of Tumor Necrosis Factor (TNF) family members whose primary role is the regulation of immune cells is under investigation. Surface fabrication techniques coupled with

multi-channel microfluidic delivery will be employed in order to introduce protein binding partners and small molecules to the surface. Effects of density, orientation, and heterogeneity of surface immobilized protein molecules on protein binding efficiency and kinetics will be investigated and optimum surface fabrication conditions will be identified. In addition, a unique multi-wavelength SPRi approach will be implemented to simultaneously determine dielectric constants and thicknesses of protein layers on a surface. These studies will therefore allow aggregate and nonaggregate structures at the surface to be clearly differentiated. The results of these fundamental studies will allow a broader understanding of how proteins act cooperatively.

3:20pm BI+TF+MI+NS+NC-ThA5 Sensitivity Enhancement of Surface Plasmon Resonance Imaging by Nanoarrayed Organothiols, P. Lisboa, A. Valsesia, I. Mannelli, P. Colpo, F. Rossi, JRC-European Commission, IHCP, Italy

The implementation of sensor platforms providing high sensitivity of detection is a crucial step for the design of the new analytical device generation for biosensor developments. Designing platform with active/non-actives region at nanoscale has shown already a drastic increase of detection sensitivity.^{1,2} The use of organothiols to create nanopatterns has been already studied showing that this type of chemistry is indicated to produce chemical contrasts for bio-applications.³ In this work, the effect of organothiols-nanopattern in Surface Plasmon Resonance imaging (SPRi) detection was studied. The gold surface of the SPRi chip was divided in two areas, one modified with a chemical nano-contrast based in two different organothiols (thiolated polyethylene oxide (PEO) and Mercaptohexadecanoic acid (MHD) and the other modified uniformly with MHD. The SPRi study was based on the detection of the immunoreaction between Human IgG and anti-Human IgG (Ab specific) by comparing the results obtained with nanostructured and uniform carboxylic surface. First Human IgG was immobilised on the chip and after the recognition of different concentrations of anti-Human IgG was realised. The achieved SPRi signal was higher in the case of the nanostructured areas for all the tested concentrations. Since the active surface with carboxylic functionalities presented only 3% of the total area, one would expect the detection signal to be 3% of the signal obtained for the uniform MHD surface. The fact that the signal from the nanostructures is higher than in the MHD surfaces in SPRi detection is related to an amplification of signal due to the 2D crystalline character of the structures. This type of arrangement presents the geometry of a photonic crystal leading to the interaction between the Surface plasmon polariton modes and the regular modulation of the dielectric constant of the surface above the gold film modifying the plasmon effect and consequently increasing the measured reflectivity. These results indicate that SPRi detection performance can be improved by the rational functionalisation of the prism surface with 2D crystalline nanopatterns. Moreover adhesive - nonadhesive nanopatterns are recognized to be good platforms for the correct immobilization of the biomolecules on biosensing surfaces.

References

- ¹K. Lee, et al., Nano-Letters, 2004 4, 1869.
- ²A. Valsesia, et al., Langmuir 2006, 22, 1763.
- ³P. Lisboa, et al., Applied Surface Science, 2006, 253, 4796.

4:00pm BI+TF+MI+NS+NC-ThA7 New Developments in Magneto-Plasmonic Devices, C. Clavero, J.R. Skuza, K. Yang, R.A. Lukaszew, College of William and Mary INVITED

In recent years Surface Plasmon Resonance (SPR) sensors have been extensively used in bio-sensing applications. SPR is a charge density oscillation at the boundary between a metal and a dielectric material that gives rise to highly confined fields at the interface. As a consequence the SPR excitation condition is very sensitive to changes in refractive index in the dielectric medium and hence to bio-molecules adsorbed at the metal surface. Nevertheless, the required detection sensitivity for low concentrations of small molecules exceeds current SPR sensors. A new kind of sensors combining plasmonic and magneto-optical (MO) properties, i.e. magneto-plasmonic devices, is being actively investigated. In particular, Au-Co-Au trilayers have been found to increase sensitivity in this type of biosensors.¹ This is due to MO activity enhancement in the Co film caused by the high electro-magnetic field created by SPR.² We will report on Au-Co-Au thin film tri-layers grown on glass using UHV magnetron sputtering. The optimization of growth conditions and accurate control of films thickness is critical to achieve a remarkable increase in MO activity and hence in overall sensitivity. A practical issue in these multilayer systems is the bad adhesion of Au to glass causing degradation of the sensor when exposed to a water flux. We will show how to circumvent this problem by inserting Cr or Ti thin buffer layers. A different approach to magneto-plasmonic materials, namely fabrication of Au-Co nano-composite

materials in thin film form, will also be presented. These materials are expected to exhibit enhanced MO response due to localized surface plasmon resonances (LSP) within the Co nano-particles and also considerable reduction of light absorption associated with ferromagnetic materials thus increasing the overall sensitivity of the bio-sensor. Parameters such as shape, size and inter-particle distance can be tuned to control the optical and magnetic properties of the material. Au-Co nano-composite materials in thin film form were obtained by magnetron sputtering co-deposition of Au and Co where parameters such as Au and Co concentration, deposition temperature and film thickness were accurately controlled. Finally, different optical configurations for the excitation of the surface plasmon resonance will be discussed.

¹ B. Sepulveda et al. *Opt. Lett.* 31, 1085 (2006).

² V. I. Safarov et al. *PRL* 73, 3584 (1994).

4:40pm **BI+TF+MI+NS+NC-ThA9 Grafting Thermoresponsive Polymers on Gold Nanoparticles with Atom Transfer Free Radical Polymerization**, *S. Chakraborty, V.H. Perez-Luna*, Illinois Institute of Technology

Thermoresponsive polymer brushes on colloidal gold were formed through Atom Transfer Free Radical Polymerization (ATRP) of N-isopropylacrylamide (NIPAAm) in aqueous media. In this approach, the “grafting from” technique was used with Atom Transfer Radical Polymerization (ATRP) to grow polymer chains from the surface of gold nanoparticles (~20nm). ‘Grafting from’ using the ATRP technique enables more uniform/homogenous coverage of polymer chains on the surface of gold nanoparticles. Other advantages of ATRP are the growth of polymer chains without chain termination or chain transfer and that the presence of an active initiator site at the end of the growing polymer chain facilitates synthesis of block copolymers. In the present work, PNIPAAm was grown from the surface of nanoparticles with the help of 2-bromopropionyl bromide as the initiator. The reaction was carried out at room temperature under inert atmosphere and aqueous conditions. The system was found to exhibit thermoresponsive behavior with increase in temperature above 32°C. This behavior could be exploited to develop aggregation based assays. The hybrid polymer-gold nanoparticle system was characterized using Optical Absorption Spectroscopy, Fourier Transform Infra-Red Spectroscopy (FTIR) and Dynamic Light Scattering (DLS). These analytical techniques confirmed the growth of polymer chains in the reaction scheme yielding the final product. The ability to make block copolymers with this metal-polymer hybrid system opens up a wide range of applications such as drug delivery systems, detection assays and bioseparations.

5:00pm **BI+TF+MI+NS+NC-ThA10 Reconfigurable Core-satellite Nanoassemblies as Molecularly-Driven Plasmonic Switches**, *D.S. Sebban, J.J. Mock, D.R. Smith, T.H. LaBean, A.A. Lazarides*, Duke University
INVITED

Colloidal metal nanoparticles support localized surface plasmon resonances that are sensitive to the presence of molecules, materials, and other polarizable particles that assemble in their near fields. Biomolecule nanoparticle conjugates have been implemented in various molecular detection applications in formats that allow monitoring of plasmonic response. Each specific format has vulnerabilities as well as advantages. For instance, monolayers of immobilized particles functionalized with receptors respond sensitively to target molecules and can be used to track kinetics, but are equally sensitive to non-specific adsorbates, a disadvantage shared with traditional, thin film surface plasmon resonance (SPR). Other formats, such as target induced particle aggregation offer strong plasmon modulation, but involve a complex bulk phase process that presents a significant barrier to quantitative interpretation of the optical data. 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, and ultimately, to yield a signal that is distinguishable from plasmonic variations associated with non-specific interactions. In the coupled system upon which we report, DNA nanostructures tether satellite particles to a core particle of like or unlike composition. 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 structurally using dynamic light scattering and transmission electron microscopy and optically using elastic scattering spectroscopy. We demonstrate that DNA nanostructures provide molecular control of interparticle separation by correlating measured plasmonic signals with simulated signals derived from models based upon measured structural parameters. In order to study the sensitivity of core-satellite spectral response to colloid material properties, single assembly scattering spectroscopy and multi-color CCD image analysis are used to monitor perturbation of the core plasmon resonance induced by assembly of satellites of various composition.

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