Plasmonics Topical Conference

Room: 619 - Session PL-MoM

Plasmonic Nanostructures and Plasmon Manipulation

Moderator: J.V. Coe, The Ohio State University

8:00am **PL-MoM1 Local and Surface Plasmon Couplings on Ag Nano-Sheet Composed of 2D Crystallized Ag Nanoparticles**, ***K. Tamada***, *K. Michioka, X. Li, Y. Ikezoe, M. Hara*, Tokyo Institute of Technology, Japan

In this paper, we present our latest result concerning the coupling between propagating surface plasmon on flat gold surface and local plasmon on silver nanoparticles. The silver nanoparticles are deposited on the substrate as 'nano-sheet' composed of two dimensional crystalline layer fabricated at air-water interface, in which the distance between the particle cores is controlled accurately by the thickness of the shell layer and the compressions (e.g., core diameter: 3.7nm, core distance between neighboring particles : 6.6nm). We found the silver nano-sheet deposited on glass to exhibit a significant shift of plasmon absorption band in UV-vis-Near-IR spectra to the longer wavelength (c.a. 50nm), while the peak width was rather reduced (sharpened) in the sheet formation. We determined the dielectric constant of the silver nano-sheet by Kramers-Kronig analyses of the UV-vis-Near-IR spectra, and compared with the value obtained from the SPR angle shift on gold substrate. The SPR curves are broadened distinctively depending on the thickness of sandwiched dielectric layer (in our study, alkanethiol self-assembled monolayers or Langmuir-Blodget films are utilized to control the distance between the nano-sheet and the gold substrate), which evidences the dipole coupling between the gold substrate and the silver nano-sheet. By use of this ideal nanostructual material, we examined several fundamental issues concerning the propagating and the local surface plasmons and their coupling effect on the optical responses.

8:20am **PL-MoM2 Photochemical Synthesis of Shape Controlled Gold Nanoparticles: A Deeper Insight on the Growth Mechanism**, ***M.L. Curri***, *T. Placido, R. Comparelli, M. Striccoli,* National Research Council CNR IPCF Italy*, D. Cozzoli,* National Nanotechnology Laboratory Lecce Italy*, A. Agostiano,* National Research Council CNR IPCF Italy*, G. Capitani,* Università di Bari, Italy*, F. Giannici*, Università di Palermo, Italy

Au nanoparticles are of great interest due to their unusual physical and chemical properties with respect to their bulk equivalent. The field has recently experienced significant growth because of advances in the reproducible synthesis of Au nonspherical nanoparticles with tunable plasmon resonances, and applications of plasmon-resonant nanoparticles in nanophotonics, chemical sensing, and biomedical engineering.[1] Current research has been focused on one-dimensional nanoparticles such as nanorods (NRs) since the morphological anisotropy results in very complex physical properties.[2] Water soluble Au nanospheres and nanorods have been synthesized by using various methods such as templating,[3] photochemistry,[4] seeding[5] and electrochemistry.[6] In this work, we propose a Ag ion mediated photochemical synthesis of gold nanoparticles (NPs) in micellar template under UV irradiation. We performed a systematic study on the role of Ag+ ions in directing the growth of Au NRs, in order to elucidate the mechanism that produces anisotropic particles rather than spheres. The samples have been characterized by UV-Vis-NIR absorption spectroscopy, High Resolution Transmission Electron Microscopy (HR-TEM), Energy Dispersive Spectrometry (EDS), Inductively Coupled Plasma (ICP), and Extended X-ray Absorption Fine Structure Spectroscopy (EXAFS) measurements. Moreover the size and shape distribution has also been investigated by statistical analysis of the experimental data. The overall obtained results allowed us to finely tune the size and the shape distribution of gold NPs and to propose a reasonable mechanism describing the role played by silver ions in directing the growth of gold NRs.[7,8]

[1] Daniel, M.C.; Astruc, D.; Chem. Rev. 2004,104, 293.

[2] Kim, F.; Kwan, S.; Akana, J.; Yang, P. J. Am. Soc. 2001, 123, 4360.

[3] Bohmer, M. R.; Fokkink, L. G. J.; Schonenberger, C.; van der Zande, B. M. I. J. Phys. Chem. B 1997, 101, 852.

[4] Esumi, K.; Matsuhisa, K.; Torigoe, K. Langmuir 1995, 11, 3285.

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[6] Yu, Y. Y.; Chang, S. S.; Lee, C. L.; Wang, C. R. C. J. Phys. Chem. B 1997, 101, 6661-6664. Acknowledgment.

[7] This work was financially supported by the EC-funded project NaPa (Contract no. NMP4-CT-2003-500120)) and by MIUR SINERGY programme (FIRB RBNE03S7XZ).

8:40am **PL-MoM3 Plasmonics: A Route to Optical Metamaterials and Nanoscale Optical Devices**, ***H. Atwater***, California Institute of Technology **INVITED**

The rapidly developing field of plasmonics has captured the imagination of physicists, chemists and engineers because of the unique ability to control optical dispersion and localize light in metallodielectric materials at nanoscale dimensions. Many ideas are currently being generated by researchers, which may ultimately enable plasmonic components to form new metamaterials designs and also building blocks of a chip-based optical device technology with potential imaging, spectroscopy and interconnection applications in ultramicroscopy, computing, communication and chemical/biological detection. In this talk I will describe recent opportunities presented by new plasmonic components including i)design of metal-insulator-metal metamaterials that facilitate dispersion control to enable very high positive as well as negative effective refractive index in the visible and near infrared ii) Si CMOS compatible light near-infrared light sources for coupling into plasmonic networks iii) plasmon-enhanced emission from quantum dots, and iv) active plasmonic devices based on electro-optic and all-optical modulation of plasmon propagation. Finally, amid the exuberance currently felt by plasmonics researchers, it is worthwhile to ponder the potential technological and scientific limitations that we currently face, and how we might take the next steps toward integrated plasmonic circuit and system technologies with compelling applications.

9:20am **PL-MoM5 Surface Plasmon Propagation and Detection**, ***A. Hohenau***, Karl-Franzens University, Graz, Austria **INVITED**

Surface plasmons are hybrid modes of electrons and photons at the interface of a metal and a dielectric. Confinement to two dimensions, resonant field enhancement and femtosecond lifetimes are properties that boost the interest in surface plasmons in a variety of fields as meta-materials, near field optics or molecular spectroscopy. In this talk I will focus on the concepts for the realization of two-dimensional optics with surface plasmons. Basic elements for surface plasmon optics can be realized by nano-fabrication of metal surfaces or local variations of dielectric host media. I will present and discuss the peculiarities of the different approaches to achieve reflection, refraction, wave-guiding of surface plasmons as well as schemes for their integrated detection.

10:20am **PL-MoM8 Plasmon Hybridization: Understanding the Nature of Plasmons in Complex Nanostructures**, ***P. Nordlander***, Rice University **INVITED**

The recent observation that certain metallic nanoparticles possess plasmon resonances that depend very sensitively on the shape of the nanostructure has led us to a fundamentally new understanding of the plasmon resonances supported by metals of various geometries. This picture- "plasmon hybridization",[1] reveals that the collective electronic resonances in metallic nanostructures are mesoscopic analogs of the wave functions of simple atoms and molecules, interacting in a manner that is analogous to hybridization in molecular orbital theory. The plasmon hybridization picture can be applied to an entire family of plasmonic nanostructures of various geometries, such as "nanoshells", "nanoeggs", "nanorice", nanoparticle aggregates, and finite nanoparticles interacting with extended substrates such as metallic films and wires.[2] The approach can also be used to provide a microscopic understanding of the plasmon in highly irregular nanostructures such as "nanostars",[3] electromigrated gaps in bowtie junctions,[4] and individual and concentric nanorings. The new theoretical insight gained through this approach provides an important conceptual foundation for the development of new plasmonic structures that can serve as surface plasmon resonance (SPR) sensors and as substrates for surface enhanced spectroscopies such as surface enhanced Raman scattering (SERS) or surface enhanced infrared absorption spectroscopy (SEIRA), subwavelength plasmonic waveguides, and nanoantennas for on-chip communication.

[1] E. Prodan et Al., Science 302(2003)419

[2] H. Wang et Al., Accounts of Chemical Research 40(2007)53

[3] F. Hao et Al., Nano Lett. 7(2007)729

[4] D.R. Ward et Al., Nano Lett. 7(2007)1396

11:00am **PL-MoM10 Fabrication of Large-Area Patterned Nanostructures for Optical Applications by Nanoskiving**, ***Q. Xu***, *J. Bao, R.M. Rioux, R. Perez-Castillejos, F. Capasso, G.M. Whitesides*, Harvard University

Patterned arrays of metallic nanostructures have many applications in photonics. E-beam lithography or more complicate photolithography such as extreme ultraviolet or x-ray lithography has been applied for the generation of test nanostructures, but they are complex, expensive, not applicable to non-planar surfaces, and incompatible with many materials. Cost-effective and convenient methods for fabrication of patterned metallic nanostructures over the large (mm^2) areas required for applications in nanophotonics are much needed. In this work, we demonstrate the fabrication of arrays of closed and open, loop-shaped nanostructures over a large area (~9 mm^2) by a simple technique (nanoskiving) that combines thin-film deposition by metal evaporation with thin-film sectioning. This method combines deposition of thin metallic films by e-beam evaporation, with nanometer-thick sectioning by ultramicrotome. These arrays of metallic structures fabricated by nanoskiving serve as frequency-selective surfaces at mid-infrared wavelengths. Experiments with structures prepared using this technique demonstrate that a closed-looped structure has a single dominant resonance regardless of the polarization of the incident light, while open structures have resonances that are anisotropic with respect to the polarization of the electric field. Finite-Difference Time-Domain (FDTD) simulations reproduce the scattering spectra of these FSS, provide an explanation of the wavelength of the experimentally observed resonances, and rationalize their polarization dependence based on the patterns of current induced in the nanostructures. Because the thin, polymer slabs containing the nanostructures have some mechanical strength; their manipulation allows the fabrication of certain types of arrays of nanostructures, including those in layers or stacks, which is difficult to fabricate by other conventional methods. We demonstrated the fabrication of multilayered nanostructures containing arrays of U-shaped metallic nanostructure with a layer of parallel nanowires on top, in which nanowire acted as a mid-IR wire grid polarizer to filter the two resonant peaks excited by incident p-polarized light. The ability to fabricate and manipulate free-standing metallic nanostructures will find applications in the fabrication of materials with negative index of refraction, and of three-dimensional metamaterials.

11:20am **PL-MoM11 Extraordinary Transmission and Enhanced Emission with Metallic Gratings having Converging-Diverging Channels**, *S. Chen, **A. Battula***, University of Texas at Austin

Transmission metallic gratings having the shape of converging-diverging channel (CDC) gives an extra degree of freedom to exhibit enhanced transmission resonances. By varying the gap size at the throat of CDC, the spectral locations of the transmission resonance bands can be shifted close to each other and have high transmittance in a very narrow energy band. Hence, the CDC shape metallic gratings can lead to almost perfect transmittance for any desired wavelength by carefully optimizing the metallic material, gap at the throat of CDC, and grating parameters. In addition, a cavity surrounded by the CDC shaped metallic grating and a one-dimensional (1D) photonic crystal (PhC) can lead to a enhanced emission with properties similar to like a â?~laserâ?T. The large coherence length of the emission is achieved by exploiting the coherence properties of the surface waves on the gratings and PhC. The new multilayer structure can attain the spectral and directional control of emission with only p-polarization. The resonance condition inside the cavity is extremely sensitive to the wavelength, which would then lead to high emission in a very narrow wavelength band. Such simple 1D multilayer structure should be easy to fabricate and have applications in photonic circuits, thermophotovoltaics and potentially in energy efficient incandescent sources.

11:40am **PL-MoM12 Biodetection by Nanoscale 2-D Plasmonic Crystal**, ***A. Valsesia,*** European Commission - Joint Research Centre, Italy, *F. Marabelli,* University of Pavia, Italy, *P. Colpo, G. Ceccone, F. Rossi*, European Commission - Joint Research Centre, Italy

Optical detection is a technique of choice for the development of label-free biosensor to detect molecular interactions. In particular methods exploiting the Surface Plasmon Resonances (SPR) of uniform metal films such as gold or silver have become more and more important from the scientific and the commercial point of view. Moreover, the development of advanced surface nanostructuring techniques has allowed the fabrication of biosensing surfaces based on the Localized-SPR (L-SPR) effect. On the other hand the ability to create controlled chemical nanopatterns on the sensor surfaces and to create functional nanostructures is a crucial step for the controlled immobilization of the biomolecular probes in order to optimize their surface bioactivity as well as for the coherence effects on the optical response. In this work we propose a novel optical based biosensing platform combining the sensitivity characteristic of both localized SPR and physico-chemical nanopatterned surfaces. The fabrication method is based on the combination of cold-plasma processes and colloidal lithography techniques. The fabrication process is briefly the following: a layer of Poly Acrylic Acid (PAA) is plasma deposited on a transparent glass slide and nano-structured through a Polystyrene colloidal mask. As the second step, a Gold film is deposited through the residual colloidal mask by Physical Vapor Deposition in order to create a gold matrix surrounding the polymeric nanodomes. Finally the residual colloidal mask is removed by ultrasonic bath. The resulting surface is a 2-D crystal constituted by PAA nanodomes surrounded by Gold matrix (2-D Plasmonic Crystal - 2D-PlC). The 2D-PlC was optically characterized by Angle Resolved - Micro Reflectometry in the spectral range between 400 nm and 1200 nm, inside a continuous flow liquid cell. The micro-reflectance spectra showed different angle dependent absorption resonances attributed to the Surface Plasmon Polaritons - Bloch Waves (SPP-BW) generated at the gold-polymer and gold-ambient (air or liquid) discontinuities and replicated in the Brillouin Zone by the presence of the 2-D crystal. We demonstrated that the SPP-BW resonances are sensitive to the absorption of proteins on the 2D-PlC and the results were confirmed by X-ray Photoelectron Spectroscopy analysis of the surface. The fabricated nanostructured surfaces promise to be an ideal platform for ultra-sensitive label-free biodetectors.

Plasmonics Topical Conference

Room: 619 - Session PL-MoA

Plasmon Dynamics and Magnetoplasmonics

Moderator: J.P. Long, Naval Research Laboratory

2:00pm **PL-MoA1 Nanoplasmonics under Coherent Control**, ***M.I. Stockman***, Georgia State University **INVITED**

Surface plasmon (SP) modes of metal nanostructures can and do localize at the nanoscale in the regions much smaller than the excitation radiation wavelength. Their minimum localization size is limited by the smallest features of the nanostructures and limits of the macroscopic electrodynamics. In practical terms, SPs can localize within just a few nanometers. Local optical fields in a plasmonic nanostructure form nano-sized hot spots where the SPs are localized. In many cases, such a hot spot is a superposition of several or many SP modes. Exciting such a nanoplasmonic system with an optical field that is a coherent superposition of different frequencies, one can impart different phases on the excited SP modes. Due to the interference of these SPs, the intensity of the corresponding hot spot can be changed: the constructive interference leads to the enhanced local fields, and the destructive one to their suppression at any given hot spot. This is a principle of the coherent control of nanoplasmonic energy concentration at the nanoscale proposed theoretically in our paper.[1] The coherent control can be implemented by both continuous-wave excitation and ultrashort pulses that can be considered as a coherent superposition of wide band of harmonics. Since this publication, this coherent control at the nanoscale has been both significantly developed theoretically.[2] and observed experimentally.[3] In this talk, we review the existing knowledge on the ultrafast coherent control of nanoscale optical energy localization in surface plasmonics. We also discuss the latest theoretical ideas including the time-reversal coherent control,[4] carrier-envelope phase effect,[5] and the spatio-temporal coherent control.[6]

[1] M. I. Stockman, S. V. Faleev, and D. J. Bergman, Coherent Control of Femtosecond Energy Localization in Nanosystems, Phys. Rev. Lett. 88, 67402 (2002)

[2] See, e.g., M. I. Stockman, D. J. Bergman, and T. Kobayashi, Coherent Control of Nanoscale Localization of Ultrafast Optical Excitation in Nanosystems, Phys. Rev. B 69, 054202-10 (2004); T. Brixner, F. J. G. d. Abajo, J. Schneider, and W. Pfeiffer, Nanoscopic Ultrafast Space-Time-Resolved Spectroscopy, Phys. Rev. Lett. 95, 093901-1-4 (2005); M. Sukharev and T. Seideman, Phase and Polarization Control as a Route to Plasmonic Nanodevices, Nano Lett. 6, 715-719 (2006)

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[4] X. Li and M. I. Stockman, Time-Reversal Coherent Control in Nanoplasmonics, arXiv:0705.0553 (2007); Phys. Rev. Lett. (Submitted)

[5] M. I. Stockman and P. Hewageegana, Absolute Phase Effect in Ultrafast Optical Responses of Metal Nanostructures, Appl. Phys. A (2007) (In Print)

[6] M. Durach, A. Rusina, K. Nelson, and M. I. Stockman, Toward Full Spatio-Temporal Control on the Nanoscale, arXiv:0705.0725 (2007)

2:40pm **PL-MoA3 Metal Colloids Nano-Antenna for Local Linear and Nonlinear Optical Response**, ***P. Guyot-Sionnest***, *M. Liu*, University of Chicago **INVITED**

The optical absorption and scattering of metal colloids is strongly shape dependent due to collective Plasmon resonances. Such particles are attractive for future optical integration. In particular, very large local electric field can also be achieved, both inside and outside the metal particles, providing means to locally enhance the linear and nonlinear optical response of the colloids and their environment. Of primary interest are structures in which one plasmon mode dominates the spectral response. These are typically elongated structures which exhibit the narrowest spectral response and large field enhancements. An example of such structure is an elongated bipyramid shape recently synthesized for Au colloids. For small particles in the dipole limit, the limiting linewidth of a Plasmon is due to dissipation inherent to the metal and to additional effects of the surface. In this context I will describe Au/Ag core/shell systems. Finally, achieving large nonlinear optical response, so that fast optical switching can be made at the single particle level is an ongoing challenge and initial results on Au nanorods will be presented.

3:40pm **PL-MoA6 Ultrafast Microscopy of Surface Plasmon Dynamics in Silver Films**, ***H. Petek***, University of Pittsburgh **INVITED**

We study the dynamics of localized surface plasmons and propagating surface plasmon polaritons in nanostructured Ag films on femtosecond temporal and nanometer spatial scale by means of interferometric time-resolved two-photon photoelectron emission microscopy (ITR-PEEM). Identical, phase correlated pump-probe pulses excite two-photon photoemission mediated by surface plasmon excitation in silver films; the resulting electron emission is imaged with electron optics. The combination of laser excitation an electron imaging provides <10 fs temporal and 50 nm spatial resolution. We record movies of surface plasmon propagation, dispersion, dephasing, interference and focusing in nanolithographically patterned metal films. The ITR-PEEM method provides a revolutionary advance in ultrafast electron microscopy for visualizing and controlling electromagnetic fields and ultrafast processes on the nano-femto scale.[1,2].

[1] A. Kubo, K. Onda, H. Petek, Z. Sun, Y.-S. Jung, and H.-K. Kim, Nano Letters 5, 1123 (2005).

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4:20pm **PL-MoA8 Ultrafast Studies of Gold, Nickel, and Palladium Nanorods**, ***J.C. Owrutsky***, *A.D. Berry,* Naval Research Laboratory, *G.M. Sando*, Malvern Instruments

Steady state and ultrafast transient absorption studies have been carried out for gold, nickel, and palladium high-aspect ratio nanorods. For each metal, nanorods were fabricated by electrochemical deposition into ~6 µm thick polycarbonate templates using two nominal pore diameters (10 nm and 30 nm, resulting in nanorod diameters of about 40 and 60 nm, respectively). Static spectra of the nanorods for each metal reveal a mid infrared longitudinal surface plasmon resonance (SPR) band as well as a transverse SPR band in the visible for the gold and larger diameter nickel and palladium nanorods. This demonstrates that high aspect ratio nanorods of transition metals have mid infrared SPR bands. Time resolved studies were performed on the gold and nickel nanorods with subpicosecond resolution, 400 nm excitation, and a wide range of probe wavelengths from the visible to the mid-IR as well as using infrared excitation (near 2000 cm^{-1}) and probing at 800 nm. The dynamics observed for both diameters of gold and nickel nanorods include transients due to electron - phonon coupling and impulsively excited coherent acoustic breathing mode oscillations, which are similar to those previously reported for spherical and smaller rod-shaped gold nanoparticles. The results demonstrate that the dynamics of high aspect ratio metal nanorods resemble those for smaller nanoparticles.

4:40pm **PL-MoA9 Magnetoplasmonic Effects in Au/Co/Au Nanodisks**, ***G. Armelles,*** Instituto de Microelectrónica de Madrid (IMM-CNM-CSIC), Spain, *J.B. González-Diaz, A. Garcia-Martin, R. Asenjo, J.M. Garcia-Martin, A. Cebollada,* IMM-CNM-CSIC, Spain, *B. Sepulveda, Y. Alaverdyan, M. Käll,* Chalmers University of Technology, Sweden, *L.l. Balcells*, ICMAB-CSIC, Spain

Noble metal-Ferromagnetic metal nanodisks exhibiting simultaneously localized surface plasmon resonances and magneto-optical (MO) activity were prepared from continuous Au/Co/Au films by colloidal lithography. Up to now, such phenomena have been only observed in continuous films made of Au/Co/Au trilayers. This system exhibits simultaneously well defined propagating surface plasmon resonaces and MO activity,[1] and have been the basis to develop new high sensitive biosensors.[2] However, a nanostructured system exhibiting localized surface plasmon resonances (LSPR) has two main advantages: i) the strong localization of the electromagnetic field around the nanostructures suggests a noticeable enhancement in the MO properties; ii) the spatial localization of electromagnetic fields associated with these resonances would make such a system a promising candidate for the development of high spatial specificity magneto-plasmonic sensing devices. Even though complex onion-like nanoparticles made of noble metals and ferromagnets that exhibit LSPR have been obtained using different chemical methods,[3] no MO activity has been reported in any of them. In this work we show for the first time that such active nanostructures exhibiting optical and MO properties can actually be obtained. The nanodisks (60-110nm diameter) were prepared by colloidal lithography from Au/Co/Au films grown onto glass by sputtering. The absorption spectra of the samples exhibit a peak around 2 eV that can be associated to the LSPR of the nanodisks. As we increase the disk diameter the energy position of the peak shifts towards lower energies. The MO activity was determined measuring the Polar Kerr rotation and ellipticity spectra. These spectra present a well defined structure in the same energy region than that of the absorption peak. Moreover, an enhancement of the MO activity is also observed. The results will be explained with the help of theoretical simulations made with a scattering matrix formalism that takes into account the MO activity.

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[2] B. Sepúlveda et al. Oppt Lett.31,1085 (2006)

[3] Z.Ban et al J. Mater. Chem 15, 4660 (2005); J. Zhang et al. J. Phys. Chem B 110, 7122 (2006); S. Mandal et al J. Mater. Chem 17 , 372 (2007); N. S. Sobal et al. Nano Letters 2, 621 (2002).

5:00pm **PL-MoA10 Magnetoplasmonic Activity in Systems with Interacting Localized and Extended Surface Plasmon Modes**, *A. Garcia-Martin, J.B. Gonzalez-Diaz,* ***A. Cebollada****, J.M. García-Martin, G. Armelles,* IMM-CNM-CSIC, Spain, *M.U. González, G. Badenes, R. Quidant*, ICFO, Spain

In the last years, plasmonics has consolidated as a powerful approach to obtain photonic devices with novel capabilities. To get this progress forward, important efforts are dedicated to developing active and/or externally controlled systems. Magnetic fields can influence the propagation of surface plasmon polaritons (SPP),[1] so the mixing of magnetic and plasmonic materials seems a promising approach for obtaining these externally controlled systems. Up to now, multilayers of noble and magnetic metals have been analyzed and they have shown to present both plasmonic and magneto-optic (MO) effects. Moreover, the MO effect is enhanced in the presence of an excited plasmon in the system.[2] In this work, we present the study of the MO and plasmonic activity in structures exhibiting both SPP and localized surface plasmons (LSP). The samples consist on a continuous Au/Co/Au trilayer deposited on glass by sputtering, covered with a dielectric spacer of SiO2 on top of which an array of Au nanodiscs (100 nm in diameter) have been fabricated by electron beam lithography. This system presents two kinds of surface plasmon resonances: The Au nanoparticles sustain LSP, and the trilayer/silica interface SPP, which can be excited by means of the Au nanoparticles grating. By controlling the parameters of the nanoparticles array, the relative positions of the two plasmon resonances of the system can be engineered.[3] The trilayer also presents MO properties due to the presence of the Co layer. The MO properties of the system have been analyzed measuring the polar Kerr rotation and ellipticity spectra. The trilayer/nanoparticles system shows a different spectrum from that of the trilayer alone. In particular, an increase of the MO signal in the trilayer/nanoparticle spectra appears at the spectral position of the LSP. This increase depends on the coupling strength between the LSP and the SPP, which can be controlled by the periodicity of the array and the thickness of the dielectric spacer. These results open the door to the design of active magnetoplasmonic devices based on interacting localized and propagative surface plasmon modes.

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[2] C. Hermann et al., Phys. Rev. B 64, 235422 (2001).

[3] J. Cesario, R. Quidant, G. Badenes and S. Enoch, Opt. Lett. 30, 3404 (2005).

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-dimentional 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 form 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 repsonse 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. Te 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 ofsurface modification in overcoming morphological instability; and potential applications in biosensing. Specific applications presented involve the combination 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 Moleclues 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 filed will be discussed based on the characteristic behavior of SERS signals observed under relatively strong photo-irradiation.

Plasmonics Topical Conference

Room: 4C - Session PL-TuP

Plasmonics Poster Session

PL-TuP1 A Hydrogel Chip for Biosensing Studied by Imaging Surface Plasmon Resonance, ***O. Andersson***, *A. Larsson, B. Liedberg*, Linköping University, Sweden

In protein microarray biosensors the use of surface enhancing matrices, or hydrogels, is of great interest. Properly constructed biosensor hydrogels exhibit low non-specific binding while allowing for covalent immobilization of ligands with maintained bio-functionality. In earlier work we have developed such a matrix, based on graft copolymerization of poly(ethylene glycol) and 2-hydroxyethyl methacrylate monomers.[1] The matrix was graft polymerized using UV light and was subsequently modified by chemical introduction of carboxyl groups. In this contribution, we demonstrate the construction of a microarray consisting of proteins covalently immobilized to well defined spots of different thicknesses of our PEG-matrix. By using a photo mask and a movable shutter we are able to vary the UV light exposure time of different spots on our surface. This enables construction of surfaces consisting of arrays of spots with physical thicknesses ranging from a few to tens of nanometers. These surfaces were pre-activated with EDC/NHS and proteins were delivered through piezo-dispensation. Biomolecular interactions involving the immobilized proteins were monitored using imaging surface plasmon resonance (iSPR). More specifically, the proteins Human Serum Albumin and Fibrinogen were piezo-dispensed and the response upon flow delivery of their respective antibodies was monitored with iSPR. The dynamic range of iSPR in the Kretschmann configuration is typically limited by the width of the resonance dip. In this work, however, we have employed iSPR at multiple wavelengths to extend the dynamic range and enable measurements in surface spots of different thicknesses.[2] Our results indicate that our sensor surfaces exhibit excellent properties for use as a template in protein micro-array fabrication. This type of thickness gradient surfaces are also useful when optimizing the properties of the hydrogel, for instance with respect to ligand binding, activity and non-specific binding.[3] In addition, the hydrogel thickness gradient array is interesting as a scaffold in the immobilization of nano-particles and as a platform for the construction of more complex heterogeneously composed biosensor matrices.

[1] Larsson A, Ekblad T, Andersson O, Liedberg B. Biomacromolecules 2007, 8, 287-295.

[2] Johansen K, Arwin H, Lundstrom I, Liedberg B. Rev. Sci. Inst. 2000, 71, 3530-3538.

[3] Larsson A, Liedberg B. To appear in Langmuir.

PL-TuP2 Enhanced Optical Response in CdSe Semiconductor via Surface Plasmon Excitation in Gold Nanoparticles, ***R.B. Konda***, *A.K. Pradhan*, Norfolk State University

Recently, surface plasmon resonance in metallic nanoparticles are being explored for a variety of applications including powerful and evolving toolkit for biological detection and molecular sensing, focusing of light, subwavelength photonics, and near-field optical microscopy. Here we show the enhancement of Raman intensity, photoluminescence and absorption in CdSe semiconductor via excitation of surface plasmon resonances in Au nanoparticles insitu pulsed-laser deposited on CdSe semiconductor film surface. CdSe was selected as a model material to illustrate our fabrication method and to demonstrate the physical concept of the enhanced optical properties, such as improving the functionality or performance of photodetectors and related optoelectronic devices, due to plasmon resonance in proximate noble metal nanoparticles. We have also demonstrated enhancement of photocurrent response in p-Si/n-CdSe junction diodes that correspond closely to the nanoparticle plasmon resonance wavelengths via the excitation of surface plasmon resonances in spherical Au nanoparticles deposited on the semiconductor surface. Our results suggest a variety of approaches for improving the performance of devices such as related to enhanced photodetection.

PL-TuP3 Thermoplasmonic Processes in Continuous and Nanostructured Metallic Thin Films, ***A. Passian***, Oak Ridge National Laboratory, *A. Lereu*, ICFO-The Institute of Photonic Sciences, Spain, *R..H. Farahi*, Oak Ridge National Laboratory, *N.F. van Hulst*, ICFO-The Institute of Photonic Sciences, Spain, *T.G. Thundat*, Oak Ridge National Laboratory

Thermoplasmonic processes in continuous and nanostructured metallic thin films The development of optical integrated components such as modulators, filters or switches, has been of continuing interest during recent decades, also in conjunction with developing a new generation of opto-electronic components. In this context, the capability of modulation of light by light naturally appears as a basic goal to achieve toward the emergence of such components. In parallel tremendous progresses have been made in nanofabrication such that nanostructured thin films and surface features may be accomplished with nanometric control. We introduce the concept of surface plasmon (SP) mediated thermo-optical processes to achieve optical modulation. In the first part, SP excitation, supported in thin gold films in the Kretschmann configuration, is demonstrated to lead to a new form of low-frequency modulation of light by light. Thermo-optical processes are shown to be the origin of such a modulation. We report experimental results of the surface response regarding a coupling between several spectrally different Gaussian beams, where a modulated infrared beam is taken as the pump beam and multiple visible continuous beams represent the probes. In the second part, to achieve higher modulation frequency rate, we study nanostructured thin films and nanoparticles where it is expected to see higher dissipation of thermal effects and bring the optical aspect to light. In order to get first some insights, we investigate using spectroscopy and near field scanning optical microscopy (NSOM) the optical response of gold nanostructures placed on a transparent substrate by electron beam lithography. In a second step, a modulated pump beam will be applied to the nanostructured film/nanoparticles and the local illumination from the NSOM tip will be used as a probe signal. We are aiming to achieve higher modulation frequency as well as to utilize lower excitation power. Moreover, the limitation of the excitation power corresponds well with the damage threshold of the nanostructures, a parameter to be taken into account.

PL-TuP4 Gold Nanocrescents with Highly Tunable Infrared Plasmonic Properties for Surface-Enhanced Infrared Absorption Spectroscopy, ***R. Bukasov***, *J.S. Shumaker-Parry*, University of Utah

Gold crescent-shaped nanostructures with uniform size and orientation were fabricated using nanosphere template lithography. The nanocrescents have broadly tunable (900-3600 nm) and strong plasmon resonances (effective cross sections up to 30). The plasmons resonances in the crescents have been shown to be sensitive to the dielectric environment with shifts of the plasmon resonance peak position of up to 880nm/RIU. We will present a new approach to investigate the tunability of nanocrescent plasmons in the infrared (IR) spectral region based on controlling the distance between the tips of the open crescent structures. The tip-to-tip distances in the nanocrescents were varied until a continous ring formed. The crescents were fabricated by controlling the angle of deposition and the angle of rotation between subsequent metal depositions. The number of plasmon resonance peaks in the IR increases from two for completely open crescents to four peaks for closed, continuous crescents. The magnitude of those resonances is dependent upon the orientation of the nanocrescents with respect to the polarization of the incident light. The application of the crescents as a tunable substrates for surface-enhanced infrared absorption (SEIRA) spectroscopy is being investigated. The ability to tune the crescent plasmon resonances farther into the IR by using substrates with higher refractive indices (e.g., from a refractive index of ~ 1.5 for glass to ~3.4 for silicon) is being explored.

PL-TuP5 Single-Nanoparticle Light-Scattering Spectra of Flat Gold Nanoparticles (FGNPs): A Study of the Effect of Nanoparticle Treatment, ***W.D. Tennyson***, *C.E. Allen, D.S. Hartnett, M.D. McCutchen, D.H. Dahanayaka, L.A. Bumm*, The University of Oklahoma

We have investigated the effects of a range of treatments on the surface plasmon modes of individual FGNPs using single-nanoparticle far-field light-scattering spectroscopy. We have explored thermal annealing, surface cleaning, and nanomechanical manipulation of the FGNPs. We can directly measure the effect of the treatments to an individual nanoparticle by correlating the before-and-after spectra with before-and-after microscopy (AFM and SEM). Finding the same nanoparticle again and again can be a significant barrier in correlation, however we have developed a photolithograpically- prepared addressed-grid system to assist finding the particles in multiple measurement platforms. This method also allows facile correlation of the light-scattering spectra to size, shape, thickness, and local environment.

PL-TuP6 Sol-gel Encapsulated Gold-Silica Nanoshells for SERS Based Sensors, *S. Bishnoi*, ***Y.-J. Lin***, Illinois Institute of Technology

Gold-silica nanoshells are important materials for surface enhanced Raman scattering (SERS) based sensors. The individual particles have been found to have enhancements on the order of 10^{10} over normal Raman,[1] preventing the need for the pre-aggregation of particles. The resulting sensors are significantly more reproducible than SERS sensors based on aggregated gold colloids. One challenge in the use of such particles for the creation of in-line Raman sensors lies in the immobilization of such particles to prevent long-term aggregation and other storage issues. To this end, we have used sol-gel methods to immobilize gold-silica nanoshells to create robust SERS based sensors. Using a protocol commonly used to immobilize proteins,[2] we have created biologically friendly SERS sensors for the study of gold binding peptides and proteins. Specifically, by combining tetraethyl orthosilicate (TEOS), methyltrimethoxysilicate (MTMS), phosphate buffer, and gold nanoparticles we have created sol-gels with reduced fluorescence and Raman backgrounds. Since organic solvents have been eliminated in the synthesis, these porous materials are ideal for studying the attachment of biological molecules to gold nanoparticles.

[1] Jackson, J. B.; Halas, N. J. Proc. Natl. Acad. Sci. U.S.A. 2004, 101, 17930-17935.

[2] Soyoun Kim, Youngdeuk Kim, Philseok Kim, Jeongmin Ha, Kyunyoung Kim, Mijin Sohn, Jin-San Yoo, Jungeun Lee, Jung-ah Kwon, and Kap No Lee. Anal. Chem. 2006, 78(21), 7392 -7396.

PL-TuP7 Plasmonic Detection of a Model Analyte in Serum by a Gold Nanorod Sensor, *S.M. Marinakos, S. Chen, A. Chilkoti*, Duke University

We describe the fabrication of a label-free, chip-based biosensor based on the localized surface plasmon resonance (LSPR) of gold nanorods. Gold nanorods were chemisorbed onto a mercaptosilane-modified glass substrate, followed by conjugation of biotin to the nanorods. Streptavidin-binding to biotin was monitored by the wavelength shift of the LSPR peak in the UV-visible extinction spectrum of the immobilized gold nanorods due to the change in local refractive index at the gold nanorod surface induced by streptavidin binding. The limit of detection of the sensor is 94 pM in PBS and 19 nM in serum, and the dynamic range spans 94 pM to 0.19 µM. The advantages of the nanorod-based sensor over a LSPR sensor that we had previously fabricated from gold nanospheres are the significantly lower detection limit and the internal self-reference that the signal of the nanorod sensor provides based on the measurement of peak wavelength shift.

PL-TuP8 Controlled Assembly of Asymmetrically Functionalized Gold Nanoparticles, ***R. Sardar***, *T.B. Heap, J.S. Shumaker-Parry*, University of Utah

Metal nanoparticles have received great attention due to their unique optical properties and wide range of applicability. In this context, programmable assembly of nanoparticles to control particle-particle interactions is a major challenge for the application of nanoparticles in device fabrication and detection systems. Different methods have been developed to achieve asymmetrically functionalized gold nanoparticles including the use of organic bridged ligands, oligonucleotides, and solid phase approaches to form gold nanoparticle dimer, trimer and tetramer assemblies. Of these architectures, dimers are of special interest because of their application as substrates in surface-enhanced Raman spectroscopy (SERS). In addition, one-dimensional nanoparticle chains show potential usefulness in fabrication of optoelectronic devices. We have developed a versatile solid phase synthesis of gold nanoparticle dimers using commercially available organic reagents through an asymmetric functionalization pathway. The method may be used to synthesize dimers for a wide size range of gold nanoparticles. In addition, we demonstrate the synthesis of dimers consisting of two particles with different sizes. The dimer yield varies from ~30% to ~65% depending on the nanoparticles' size. The dimers demonstrate remarkable stability in ethanol without further processing. We have also developed a simple synthetic route to prepare one-dimensional gold nanoparticle chains using asymmetrically functionalized gold nanoparticles and poly(acrylic acid) via a simple amide couple reaction. The length of the synthesized nanoparticle chains varies from 256-400 nm with regular interparticle spacing (~2.7 nm). The synthesized chains display distinct optical properties compared to individual nanoparticles. This methodology also is applicable for gold nanoparticle with different sizes.

PL-TuP9 Optical, Magnetic and Magneto-Optical Properties of Noble-Metal/Ferromagnet Nano-Composite Materials, ***R.A. Lukaszew***, *J.R. Skuza, M. Sestak,* University of Toledo, *N. Dushkina*, Millersville University

Magnetic nanoparticles embedded in noble metal thin films exhibit interesting properties that are function of the microstructure and can be used in relevant applications. Some of these materials can be processed further to achieve a particular magnetic anisotropy of interest while others may exhibit plasmonic enhancement of their optical properties that can be used in a variety of sensing applications, in particular biosensing. The optical, magnetic and magneto-optical properties of these nano-composite materials depend on the materials used, the nano-particle size and distribution, the inter-particle distance, etc. We will present our studies on such composite materials in thin film form. In particular, we will show that ion-implantation of ferromagnetic metal ions onto noble metal thin films is a powerful tool for nano-fabrication of embedded nano-clusters with controlled geomety, i.e. size and distribution. We will present our studies applied to two such systems: FePt and AuCo. In the former case, we have also used thermal treatments to achieve the L10 phase of interest in new generation perpendicular magneto-recording media. In the latter case, we were particularly interested in the enhancement of the surface plasmon resonance (SPR) of the noble metal when combined with a ferromagnetic one, i.e. a magneto-plasmonic material. We will compare the SPR response of a Au/Co/Au trilayer in which the optical response can be tailored varying the thickness of the Co layers, with a nano-composite material made with Co magnetic nano-clusters embedded on a Au thin film matrix. In this latter case, the Co clusters are ion-implanted onto the Au matrix and their size and penetration depth can be tailored by choosing the ion-implantation conditions. We will show our field dependent SPR data on this nanocomposite material.

PL-TuP10 Nanopatterned Polypyrrole Based Surfaces for Enhanced Surface Plasmon Resonance Detection, ***P. Lisboa,*** European Commission, Italy, *M.B. Villiers, C. Brakha, S. Cortes,* INSERM U823, Institut Albert Bonniot Grenoble, France, *A. Valsesia, P. Colpo,* European Commission, Italy, *P. Marche,* INSERM U823, Institut Albert Bonniot Grenoble, France, *F. Rossi*, European Commission, Italy

The interaction between biomolecules and materials is regulated by the chemical properties of the surfaces and by their micro and nano-morphologies. An accurate control of chemical contrasted motives is highly required for the improvement of the sensitivity and the specificity of biosensing devices.[1,2] Polypyrrole (PPy) is a preferential material for bio-analytical sensors thanks to its good environmental stability and excellent biocompatibility, together with the possibility of being functionalised with biological relevant functional groups.@foontote 3@ In this work the gold surface of Surface Plasmon Resonance (SPR) chip was nanostructured to create gold nano-areas over a SiOx matrix by using colloidal lithography. Then, micro spots of modified PPy with ovalbumin (recognition element) and with casein (control) have been created on the nano-structured surfaces and non nanostructured surfaces by electrochemical copolymerization using a microarrayer in potentiostatic conditions. The growth of the modified PPy in the nanostructures takes place only in the gold nano-areas since the surrounded matrix of SiOx presents electrically insulating properties. The effect of the nano-structured PPy surface on the immunoreaction efficiency was evaluated using SPR imaging device. The SPR signals related to the recognition of ovalbumin by different concentrations of anti-Ovalbumin have been measured. The results were compared with a chip with micro spots of uniformly (non nanostructured) modified PPy. Even if the active area of PPy containing Ovalbumin represents only 3% of the area of non nanostructured PPy, the absolute SPR signals resultant from the ovalbumin/anti-ovalbumin reaction was higher by only a factor of 2 in the case of the uniform PPy than in the case of nanostructured surfaces. Nevertheless at lower concentrations, the SPR signal is similar showing that the nanostructured surface improves the biorecognition efficiency at these concentrations. Furthermore, the SPR signals normalised to the active PPy area were higher by a factor of 14 in the nanostructure surfaces for all the antibody concentrations. These results indicate that the nanostructured surfaces improve the immunoreaction efficiency. This is a very promising result regarding the increase of detection sensitivity in analytical devices.

[1] K. Lee. et al Nano-Letters, 2004 4, 1869.,

[2] A. Valsesia, et al, Langmuir 2006, 22, 1763.,

[3] L. Grosjean et al., Analytical Biochemistry 2005, 347, 193-200.

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