Tuesday Afternoon Poster Sessions

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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