

Monday Morning, October 15, 2007

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-Blodgett 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 nanostructural 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 seeding⁵ 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}

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

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

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

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

⁵Murphy C. J.; Jana N. R. Adv. Mater. 2002, 14, 80.

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

⁷This 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 metalodielectric 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", "nanoeeggs", "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.

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

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

³F. Hao et Al., Nano Lett. 7(2007)729

⁴D.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 ($\sim 9 \text{ mm}^2$) 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 an enhanced emission with properties similar to a laser. 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 nanodomains.

Finally the residual colloidal mask is removed by ultrasonic bath. The resulting surface is a 2-D crystal constituted by PAA nanodomains surrounded by Gold matrix (2-D Plasmonic Crystal - 2D-PIC). The 2D-PIC 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-PIC 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.

Authors Index

Bold page numbers indicate the presenter

— A —

Agostiano, A.: PL-MoM2, 1
Atwater, H.: PL-MoM3, **1**

— B —

Bao, J.: PL-MoM10, 1
Battula, A.: PL-MoM11, **2**

— C —

Capasso, F.: PL-MoM10, 1
Capitani, G.: PL-MoM2, 1
Ceccone, G.: PL-MoM12, 2
Chen, S.: PL-MoM11, 2
Colpo, P.: PL-MoM12, 2
Comparelli, R.: PL-MoM2, 1
Cozzoli, D.: PL-MoM2, 1
Curri, M.L.: PL-MoM2, **1**

— G —

Giannici, F.: PL-MoM2, 1

— H —

Hara, M.: PL-MoM1, 1
Hohenau, A.: PL-MoM5, **1**

— I —

Ikezoe, Y.: PL-MoM1, 1

— L —

Li, X.: PL-MoM1, 1

— M —

Marabelli, F.: PL-MoM12, 2
Michioka, K.: PL-MoM1, 1

— N —

Nordlander, P.: PL-MoM8, **1**

— P —

Perez-Castillejos, R.: PL-MoM10, 1
Placido, T.: PL-MoM2, 1

— R —

Rioux, R.M.: PL-MoM10, 1
Rossi, F.: PL-MoM12, 2

— S —

Striccoli, M.: PL-MoM2, 1

— T —

Tamada, K.: PL-MoM1, **1**

— V —

Valsesia, A.: PL-MoM12, 2

— W —

Whitesides, G.M.: PL-MoM10, 1

— X —

Xu, Q.: PL-MoM10, **1**