Biomaterial Interfaces
Room 2014 - Session BI-ThM

Plasmonic Methods and Sub-micron Structures for Biology and Medicine

Moderator: S. Zauscher, Duke University

8:00am **BI-ThM1 Light Exposure Affects the Adsorption of Colloidal Gold onto Monolayers of 3-Mercaptopropyltrymethoxysilane**, *K. Pandya, O. Ogunsanwo,* ***V.H. Perez-Luna,*** Illinois Institute of Technology

Light exposure affects the capability of thiol-terminated monolayers to adsorb colloidal gold particles. This effect was determined by forming monolayers of 3-mercaptopropyltrimethoxysilane (MPTMS) on silica surfaces in the presence of white light, red light (635 nm) and under dark conditions. Surface characterization by means of wettability, ellipsometry and FTIR spectroscopy was carried out to determine differences in surface properties for the different preparation methods. Monolayers prepared under different conditions of light exposure (white light, red light and absence of light) were exposed to colloidal gold solutions in order to study the adsorption of gold nanoparticles. The adsorbed colloidal gold monolayers were characterized by optical absorption spectroscopy. In spite of the strong affinity of the thiol group for gold, samples that were exposed to white light did not adsorb gold nanoparticles to a significant extent. In contrast, monolayers prepared using red light or under dark conditions were capable of adsorbing gold nanoparticles at levels comparable to amine-functionalized surfaces. These findings may offer some insights as to differing literature reports on adsorption of colloidal gold to thiol-functionalized surfaces. The thiol groups may undergo oxidation in the presence of oxygen and white light to from sulfonate groups that do not promote adsorption of gold nanoparticles. Hence MPTMS monolayers exposed to light may not present sufficient thiol groups for subsequent attachment of gold. Surface analysis of samples exposed to white and red light and those kept in the dark verify this hypothesis.

8:20am **BI-ThM2 Label Free Nanoscale Optical Biosensors**, ***A. Chilkoti,*** Duke University **INVITED**

I will describe the use of nanoparticles for the fabrication of label-free, surface optical biosensors by exploiting the localized surface plasmon effect exhibited by individual nanoparticles of gold and silver. We have immobilized gold nanoparticles onto glass slides, functionalized the surface of the gold nanoparticles with biological ligands, and shown that these nanoparticle decorated surfaces enable ligand binding to be detected by the shift in the extinction spectrum of individual nanoparticles. This assay is analogous to conventional, planar SPR with the added advantage of being performed in widely available, low-cost UV-visible spectrophotometers and its facile extension to array based sensors. The extension of this detection modality using gold nanorods and the increased sensitivity afforded by these anisotropic particles will also be discussed. Finally, recent results on reducing the size of the optical transducer to the ultimate limit of a single nanoparticle through the use of dark-field microscopy will be discussed, which opens up the intriguing possibility of obtaining single molecule sensitivity.

9:00am **BI-ThM4 Non-Cross-Linking Aggregation of DNA-Fnctionalized Nanoparticles for Single-Base Substitution Assay**, ***M. Maeda,*** RIKEN, Japan **INVITED**

For the detection of DNA single-base substitutions, gold nanoparticles (GNPs) has been attracting considerable interests, because GNP aggregation accompanied by the surface plasmon shift can be clearly recognized with the naked eye. The method is in general a sandwich assay in which a target DNA molecule cross-links two DNA-functionalized GNPs by hybridization. In contrast, we recently discovered that GNPs also aggregate with a non-cross-linking (NCL) manner; formation of fully complementary duplexes on GNP surfaces induces the aggregation at relatively high salt concentration. Interestingly, the NCL aggregation exhibits extraordinary selectivity against terminal mismatches; single-base mismatches at the free ends of the duplexes make very stable dispersions (e.g., no aggregation). Unlike conventional hybridization-based assays, this system can detect the terminal mismatches without precise temperature control. Because of this surprising selectivity for terminal mismatches, rapid and reliable SNPs typing after single-base primer extension is possible without time-consuming analysis such as mass spectrometry. NCL interaction between fully-matched DNA duplex on GNPs (FM-Au) and duplex on a gold substrate was studied using SPR imaging. A significant increase in intensity was observed where the substrate-anchored DNA probe hybridized with its fully-matched target showing a blunt end. In contrast, no change in intensity was observed with the one-base mismatched target. The FM-Au specifically discriminates the terminal base-pairing at the sensor surface.

9:40am **BI-ThM6 Nano-Crescents as Tunable Plasmon-Based Sensing Platforms**, *R. Bukasov, M. Hukill,* ***J.S. Shumaker-Parry,*** University of Utah

Crescent-shaped gold nanostructures exhibit localized plasmon resonances that are tunable from the visible to the infrared. A combination of polymer nanosphere templating, metal film deposition and ion beam etching produces a large number of crescents with defined and uniform size, shape, and orientation on a substrate. Ensemble measurements show the crescents exhibit multipolar plasmon resonances that are tuned from 600 to 2800 nm by controlling the crescents' structural properties. In addition to the template size, the diameter to thickness aspect ratio and the distance between the crescent tips also influence the crescents' optical properties. The crescents' plasmon resonances exhibit a strong dependence on the local dielectric environment, with sensitivity factors of up to 800 nm/refractive index unit, depending on the crescent size and the plasmon resonance wavelength. The high sensitivity, the tunability of the crescents' optical properties over a wide wavelength range, and the bare crescent surface readily available for functionalization with receptor molecules make the crescents strong candidates for development as sensors.

10:00am **BI-ThM7 Plasmonic Coupling in Biomolecule Linked Nanoparticle Assemblies**, ***A.A. Lazarides,*** Duke University, US; *D.S. Sebba, E.R. Irish,* Duke University

Metal nanoparticle assemblies support delocalized plasmon resonances that are highly sensitive to interparticle spacing, when particles are positioned within the near fields of their neighbors. We have observed near field coupling in biomolecule-linked core/satellite structures and have observed, further, controllable plasmon band modulation when the assemblies are linked by reconfigurable tethers. The nature of the modulation depends upon both the strength of the plasmon coupling and the composition of the component particles. Accurate electrodynamic calculations confirm the observed relationships between assembly structure, composition, and optical properties. Approximate, analytic, dipole coupling models provide insight into the material-dependence of the observed band modulation phenomena.

10:20am **BI-ThM8 Semiconductor Quantum Dots for Bioimaging: Bandgap Engineering and Surface Engineering**, ***A.M. Smith,*** *S. Nie,* Georgia Institute of Technology and Emory University **INVITED**

The development of high-sensitivity and high-specificity probes beyond the intrinsic limitations of organic dyes and fluorescent proteins is of considerable interest to many areas of research, ranging from single-molecule biophysics to in-vivo medical imaging. Recent advances have shown that nanometer-sized semiconductor particles can be covalently linked with bioaffinity molecules such as peptides, antibodies, nucleic acids, and small-molecule inhibitors for use as fluorescent probes. In comparison with organic fluorophores, quantum dots (QDs) exhibit unique optical and electronic properties such as size- and composition-tunable fluorescence emission, large absorption coefficients, and significantly improved brightness and photostability. Despite their relatively large sizes (2-8 nm), bioconjugated QD probes behave like fluorescent proteins (4-6 nm), and do not suffer from serious kinetics or steric-hindrance problems. In this mesoscopic size range, QDs also have high surface area-to-volume ratios that can allow multivalent functionalization with many diagnostic (e.g., radioisotopic or magnetic) and therapeutic (e.g., anticancer) agents. We present recent developments in bioconjugated QD probes and their applications in ultrasensitive molecular and cellular imaging. We have generated new classes of QDs with tunable near-infrared emission (700-900 nm) for high-sensitivity imaging deep within living animals and in highly autofluorescent fixed tissue specimens. These QDs are brighter and have narrower emission bandwidths than comparable QDs reported in the literature, approaching the spectral properties of commonly used visible QDs. Using polymeric encapsulation, we have also engineered the surfaces of these and other QDs for ultra-high stability under a variety of harsh conditions, such as high salt buffers, acidic solutions, and oxidizing environments that would normally quench the QD fluorescence and potentially degrade the semiconductor core.

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