Friday Morning, November 13, 2009

Biomaterial Interfaces
Room: K - Session BI+AS+NS-FrM

Micro and Nanoengineering of Biointerfaces II
Moderator: E.O. Reimhult, ETH Zurich, Switzerland

8:20am **BI+AS+NS-FrM1 Colloid Crystal Surface Patterning for Studying Biointerface Phenomena**, ***P. Kingshott***, Aarhus University, Denmark **INVITED**

Patterning of many types of biomolecules over length scales ranging from micrometers to nanometers is of great interest for biosensors, cell culture dishes, medical implants and tissue engineering. Ideally these devices require attachment of biomolecules at specific locations on solid substrates with precisely controlled chemistry, but to function fully the non-specific adsorption in surrounding regions must be prevented. Currently, the most widely used techniques for patterning are photolithography, soft lithography and electron beam lithography, all of which involve multi-step surface modification directly onto substrates, and are time consuming and expensive. We have shown recently that highly ordered binary colloid patterns, with controllable dimensions, can be generated from simple self-assembly of large and small particles onto surfaces, where single layers of large particles are surrounded by crystals of smaller particles. In addition, when the particles are pre-coated with proteins (e.g. albumin, lysozyme and antibodies) the assembly process also takes place. This opens up the possibility of patterning many proteins on one substrate with controllable dimensions and high order. The crystals are also used to generate chemical patterns since the large particles act as a mask during, for example sputtering of Au, since the region in contact with the substrate remains uncoated. The thickness of gold features can be controlled by the sputtering time. We demonstrate that the resultant Au layer can be coated with a protein resistant mercapto-oligo(ethylene glycol) layer ((1-mercapto-11-undecyl)-tri(ethylene glycol)) that allows selective adsorption of fluorescently labelled proteins, such as FITC-labelled antibodies or rhodamine-labelled albumin, only onto the Si regions of the pattern. In another approach, binary patterns made from silica and amine polystyrene particles are heated at 100 ºC (above glass transition temperature of polystyrene) followed by etching with HF to remove the silica particles creating highly ordered 2- and 3D porous substrates. In summary, we introduce a novel method for generating highly-ordered patterns from colloid crystals that is very fast, inexpensive, and allows patterns of multiple biomolecules over large areas in 2- and 3D.

9:00am **BI+AS+NS-FrM3 Biological Nanoarrays: from Protein-DNA Interaction Studies to Cell Adhesion Investigations**, ***M. Palma***, *J. Abramson, M. Schvartzmann, A. Gorodetsky, C. Nuckolls, M.P. Sheetz, J. Hone, S.J. Wind*, Columbia University

Nanopatterned arrays of biomolecules are a powerful tool to address fundamental issues in many areas of biology.

Combining nanolithography and biomolecular self-assembly strategies, we report on the fabrication of nanopatterned biomimetic surfaces and their use in a variety of biological studies.

We have fabricated arrays of Au/Pd nano-dots of dimensions down to the sub-10nm regime using electron-beam and nanoimprint lithography. Different chemical strategies at surfaces have been pursued to organize biological relevant nanoarchitectures into hierarchical arrays in which structural parameters, such as the spacing and nature of specific functional groups, could be systematically varied and controlled.

The generation of DNA nano-dot arrays allowed us to follow the activity (at surfaces) of a restriction enzyme in real time and at the nanoscale: fluorescence microscopy enabled the monitoring of the kinetics of such protein-DNA interaction.

Furthermore we will show how our nanopatterned biomimetic surfaces can be used to probe the importance of both the geometric arrangement (i.e. spatial ordering of transmembrane proteins, integrins) as well as the role played by peptide sequences as cell binding domains in the formation of cell focal adhesions.

Finally, we will highlight the broader utility and application of such functional nanopatterned surfaces for nanoscopic control and studies: biochemical specificity can be used to selectively place individual nanocomponents with a high degree of control over both position and orientation, as well as to organize functional nanostructures into dense arrays with very fine pitch.

9:20am **BI+AS+NS-FrM4 Arbitrary Topographical Patterns Fabrication by using Two-Photon Photopolymerization**, ***H.J. Jeon***, University of California, Berkeley, *H. Hidai*, Tokyo Institute of Technology, Japan, *D.J. Hwang, K.E. Healy, C.P. Grigoropoulos*, University of California, Berkeley

Two photon photopolymerization (TPP) is a direct laser writing technique, which is known as a powerful tool to make arbitrary 3D structures. Here we demonstrate a method for fabricating high aspect ratio (~10) patterns of varying height by using TPP process in order to study contact guidance of cells. Ridge patterns of various heights and widths were fabricated through single laser scanning steps by low numerical aperture optics, hence at much higher processing throughput. Fibroblast cells were seeded on parallel line patterns of different height (~1.5-μm, ~0.8-μm, and ~0.5-μm) and orthogonal mesh patterns (~8-μm and ~4-μm height, ~5-μm and ~5.5-μm height, and ~5-μm and ~6-μm height). Cells experienced different strength of contact guidance depending on the ridge height. Furthermore, cell morphology and motility on microscale anisotropic cross patterns and parallel line patterns in different aspect ratio (1:2, 1:4, and 1:∞), size of grid (12-, 16-, and 24-μm distance neighboring longer side ridges) was also studied quantitatively. The significant effect of the cross patterns on cell alignment and directionality of migration, and motility was observed on 1:4 cross patterns and parallel line patterns, even though all cross patterns could have an effect on cell attachment and morphology. Overall, it is noted that cell morphology and motility can be influenced by the height of ridges, the aspect ratio of cross pattern and the size of grid.

9:40am **BI+AS+NS-FrM5 2D & 3D Nanoarrayed Chemical Contrasts for Better Biorecognition Kinetics**, ***G.R. Marchesini***, *P. Lisboa, A. Valsesia, C. Pascual, P. Colpo, F. Rossi*, Joint Research Centre, European Commission, Italy

Monitoring biomolecular recognition events with Surface Plasmon Resonance (SPR) heavily relies on the right surface chemistry. Uniform self assembled monolayers with carboxylic functional groups are widely used but might show steric hindrance, thus limiting the interpretation of the biorecognition kinetics. Furthermore, such negatively charged surface needs to be passivated upon immobilization of the ligand to prevent nonspecific electrostatic-driven binding of components from the analyte matrix.

In the present study we evaluate alternatives based on a 2D and 3D array of carboxylic nanodomains on a chemically contrasting matrix. By means of plasma-based colloidal lithography and e-beam lithography we were able to array ≈ 200 nm wide carboxylic motifs having a hexagonal 2-D crystalline structure on a gold surface. The interstitial gold was further modified with contrasting thiol chemistries or vapour enhanced deposition of nonadhesive material like poly ethylene oxide (PEO). The two 2D nanoarrayed chemical contrasts evaluated were carboxylic nanodomains on either a methyl-based or PEO-based matrix.

In addition, the 3D nanoarray based on a carboxylated dextran hydrogel matrix was evaluated for effects on the mass transport. In these cases, mass transport is one of the major challenges when measuring binding kinetics of biointeractants on a surface using a surface plasmon resonance (SPR) biosensor. The presence of a hydrogel on the surface increases the interactant density improving the sensitivity. Nevertheless, this is done at the expense of aggravating the mass transport phenomena.

The influence of the nanoarrayed chemical contrasts combined with the sensitivity improvement due to the band-gap effect on the kinetics of model biomolecular interactants was evaluated using an imaging SPR system and correlated with surface characterization techniques as atomic force microscopy, ellipsometry, and contact angle measurements.

10:00am **BI+AS+NS-FrM6 Spatially Selective Deposition of a Zwitterion with Alkyl Pendant Groups on Periodically Poled Lithium Niobate**, ***Z.Z. Zhang***, *J. Xiao*, University of Nebraska-Lincoln, *D. Wu*, North Carolina State University, *A. Gruverman*, University of Nebraska-Lincoln, *L. Routaboul, P. Braunstein, B. Doudin*, Université Louis Pasteur Strasbourg, France, *O. Kizilkaya*, Louisiana State University, *C. Borca*, Paul Scherrer Institute, Switzerland, *P.A. Dowben*, University of Nebraska-Lincoln

We have spatially selectively deposited a zwitterion compound from the class of N-alkyldiaminoresorcinones (or 4,6-bis-dialkylaminobenzene-1,3-diones, $C_6H_2(NHR)_2(O)_2$), compounds, where R =C_5H_{11}. These molecules have very strong local dipoles as the delocalized benzene π molecule of the zwitterion "core" loses aromatic character due to the large charge separation. This charge separation provides this type of zwitterion molecule with a large electric dipole moment across the "benzene" like plane. Unlike the ferroelectric materials, the electric dipole of this class of zwitterions

when adsorbed on metal surface (and most substrates) is not switchable, which makes these zwitterion compounds more like an electret. We have been able to demonstrate that at least one of this class of zwitterion compound will selective adsorb from solution on periodically poled lithium niobate substrates using infra-red spectra-microscopy. The spatial localization zwitterion on lithium niobate suggests that the ferroelectric poling of lithium niobate either alters the surface chemistry of lithium niobate or that there is some dipole-dipole interaction between the substrate and the zwitterion. We believe the interaction is an interface effect as no alteration in the bulk properties has been observed from spatially resolved near edge X-ray adsorption fine structure (NEXAFS) of the bulk properties. The spatial zwitterion structure is consistent with the periodically poled lithium niobate structure. Crystals of periodically poled lithium niobate (PPLN) with congruent composition (Crystal Technologies) were used as deposition templates. A periodic domain structure (period of ~28 μm) was fabricated by depositing a photoresist mask on the +c sample face and by applying a voltage of 10 kV through a fixture with an electrolyte solution. The mask was removed after poling by means of chemical-mechanical polishing leaving behind a bare ferroelectric surface, prior to the exposure to the zwitterion molecular solution.

Authors Index

Bold page numbers indicate the presenter