

Nanometer-Scale Science and Technology Room 210 - Session NS+BI-TuA

Molecular and Biological Applications of Nanostructures

Moderator: M.C. Hersam, Northwestern University

2:00pm **NS+BI-TuA1 Nano-Patterned Surfaces Induce Bio-Molecules Oriented Immobilization**, *A. Valsesia, P. Colpo, T. Mezzani, P. Lisboa*, EC-JRC-IHCP Italy; *M. Lejeune, F. Rossi*, EC-JRC-IHCP Italy, Italy

The immobilization of biomolecules in domains with the typical size of the nano-meter or few tenth of nano-meters is one of the most challenging issues of the actual research in the field of biosensors and biochips. In particular the ability to create nanopatterned bio-active surfaces should be addressed to improve the performances of biosensing devices and to study new fundamental problems. From the technological point of view the nano-patterned surfaces can improve or modulate the absorption of proteins, minimize their non-specific absorption, increase the active surface density. In the last few years nano-soft lithography, dip-pen lithography, nano-fountain pen lithography and colloidal lithography were able to produce nano-patterned surfaces with fouling-antifouling contrast. The selective immobilization of the biomolecules on the fouling regions was demonstrated as well as the reduction of the nonspecific absorption in the antifouling matrix. In this work we developed a nano-patterning method which combines the spontaneous formation of molecular monolayers (SAM) and plasma based colloidal lithography. By this approach we have shown that the nano-patterning resolution is not limited in principle and can be accurately controlled by the plasma processing parameters. The techniques was employed for the creation of chemical nano-patterned surfaces with 100 nm motives with a hexagonal 2-D crystalline structure, characterized by COOH terminated SAM nano-spots in a CH₃ terminated thiols matrix. By combining the information arising from the different characterization techniques, it was possible to demonstrate the creation of a chemical contrast with a resolution of 100 nm, without a meaningful change in the morphological properties of the surface. An effective orientation of the biomolecules immobilized on these nano-patterned surfaces was demonstrated by AFM measurements and confirmed using an ELISA antibody immobilization protocol.

2:20pm **NS+BI-TuA2 Surface Nanopatterning for the Control of Cell Behavior**, *C.M. Dekeyser, J. Marchand-Brynaert, A.M. Jonas, Ch.C. Dupont-Gillain, P.G. Rouxhet*, Université Catholique de Louvain, Belgium

Cell adhesion is mediated by proteins of the extracellular matrix, called adhesion proteins. RGD (arginine-glycine-aspartic acid) is the most widely spread peptide sequence responsible for these recognition events. It has been shown that a surface covered by adhesion proteins or grafted with the RGD sequence can induce different cell behaviors, depending on the distribution of the ligands. The aim of the work is to get a better insight into the influence on cell behavior of the distribution of ligands at the nanometer scale. This involves four aspects: creating a nanostructured surface, grafting a RGD ligand or adsorbing an adhesion protein according to defined motifs, passivating the rest of the surface with respect to protein adsorption and evaluating the cell behavior. The nanopatterns are created by means of electron-beam lithography. The challenge here is to draw small motifs (100 nm) on an area (500*500 μm@super 2@), large enough to allow cell adhesion to be studied. This was realized by juxtaposition of patterns (143*143 μm@super 2@) on which electron-beam lithography allowed continuous and regular lines to be drawn. In order to minimize non specific protein adsorption, the passivation of the surface is realized by self-assembly of oligo(ethylene glycol)-terminated silanes on silicon. The influence of various parameters has been examined in order to optimize the treatment in terms of cleanliness, thickness and density (AFM, X-ray reflectometry, XPS) of the obtained layer. Adsorption of different proteins is used to evaluate the inertness of the background and the selective adsorption on the patterns. RGD immobilization is realized by photografting an azide which bears an active ester able to react with the NH@sub 2@ groups of the ligand. The influence of the nanopatterned surfaces on the adhesion and spreading of neural cells will be examined.

2:40pm **NS+BI-TuA3 Enzymatic Nanofabrication: Step-wise Synthesis of DNA Scaffolds on Nanopatterned Oligonucleotide Templates**, *D. Chow, W.-K. Lee, S. Zauscher, A. Chilkoti*, Duke University

Nucleic acid nanopatterns can serve as a template for step-wise synthesis for a variety of complex molecular nanostructures and have significant

potential in materials science, molecular electronics, and biosensing. However, most nanofabrication techniques of nucleic acid scaffolds require DNA to be synthesized separately prior to self-assembly or manipulation at the nanoscale. Enzymes that can polymerize DNA are potentially useful molecular tools for the in situ synthesis of DNA scaffolds. Although these proteins are well studied and commercially available, they have not been previously exploited for enzymatic nanofabrication. This study demonstrates that terminal deoxynucleotidyl transferase repetitively adds mononucleotides to the 3' end of oligonucleotides on gold substrate nanopatterned by e-beam lithography. Without complex multi-step chemistry or biochemistry, the step-wise synthesis of DNA scaffolds leads to significant extension of DNA. This strategy can be modified to create more complex DNA nanostructures by simply replacing natural mononucleotides with unnatural ones, which serve as specific recognition sites along the single-stranded DNA. This enzyme-mediated nanofabrication methodology offers a new route to selectively dock nanoscale components of interest along the vertical direction with nanometer-level precision, and also provides a foundation for fabrication of hybrid molecular ensembles of biotic and abiotic components.

3:00pm **NS+BI-TuA4 Surface Modification and Morphological Stabilization of Silver Nanoparticles**, *V.H. Perez-Luna, A. Dalwadi, S. Lee*, Illinois Institute of Technology

Metallic nanoparticles exhibit unique optical properties due to the oscillation of surface plasmons when excited by visible light. These optical properties are shape dependent and different modes of excitation can occur for anisomeric nanoparticles (e.g. due to transversal and longitudinal oscillation of surface plasmons). Thus, the optical properties of these systems can be changed without modifying their chemical composition. A wide variety of methods for the synthesis of anisomeric metallic nanoparticles (e.g.; triangular slabs, multipods, nanorods) have been developed over the last couple of decades. However, technological applications of these systems have not been extensively implemented in spite of their great potential for surface enhanced emission of fluorescence and Raman scattering. One of the biggest obstacles is the inherent morphological instability of these systems and processing difficulties that may lead to irreversible aggregation. Surface modification of gold and silver nanoparticles with alkane thiol based self-assembled monolayers could help circumvent these problems and allow for technological applications with great potential in biodetection assays. Experimental studies will be presented illustrating the improved morphological stability and tailored properties of surface modified nanoparticles. Experimental evidence of the strong influence exerted by metallic surfaces on emission of fluorescence will be presented. The potential of surface modified Ag and Au nanorods will be discussed with particular emphasis on biological detection assays.

3:20pm **NS+BI-TuA5 Functionalization and Electrical Characterization of Vertically Aligned Carbon Nanofibers**, *K.-Y. Tse, S.E. Baker, E.A. Hindin, T.L. Clare, R.J. Hamers*, University of Wisconsin-Madison

Vertically Aligned Carbon Nanofibers (VACNFs) represent a new form of carbon with potential applications ranging from biosensing to energy storage. We have explored the electrical properties of bare and chemically-functionalized VACNFs in electrolyte solutions using electrical impedance spectroscopy and cyclic voltammetry. Electrical measurements show that the capacitance of the nanofiber forests is directly proportional to the average nanofiber length, demonstrating that the entire fiber surface is electrically active. A comparison of nanofiber forests with planar electrodes shows that the forests have approximately 7 times higher effective surface area. Measurements of DNA hybridization with DNA-modified VACNFs show a similar ratio, showing that the nanofibers have good biological accessibility. We will discuss the factors that control the electrical properties of nanofibers in electrolyte solutions, the effects of nanofiber aggregation, and prospects for the application of nanofibers for biosensing.

3:40pm **NS+BI-TuA6 Single Porphyrin Molecules as Information Storage Elements**, *H. Kim, Y. Kuk*, Center for Science in Nanometer Scale (CSNS), Korea

Redox behaviors of porphyrin molecules have been widely studied for the possible application to molecular-based information storage for two main reasons; i) they form stable radicals whose redox potentials can be tuned by the synthetic design and chelating metal ions. ii) Assembled on the substrate adequately, they exhibit considerably long charge retention times. Recently, it was shown that they can survive silicon device processing,@footnote 1@ which provides a new possibility to molecular electronics. It was, however, confirmed only for a close-packed monolayer of porphyrins to act as information storage. We separated porphyrin

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molecules both from each other and from the substrate by making a mixed self-assembled monolayer of alkanethiol-derivatized porphyrins and alkanethiols on a Au(111) surface. Alkanethiol monolayers can act as an organic insulating layer whose resistance shows approximately exponential dependence on the chain length and the HOMO-LUMO gap is about 9eV. These properties allow us to investigate more intrinsic behaviors of organic molecules attached to alkanethiol monolayers on surface. By means of scanning tunneling microscopy and spectroscopy, we identified the porphyrin groups on the insulating alkanethiol monolayer and resolved the redox states and the charge retention time of a single porphyrin molecule. @FootnoteText@ @footnote 1@ Molecular memories that survive silicon device processing and real-world operation, Z. Liu et al., Science 302, 1543 (2003).

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