Tuesday Afternoon, November 4, 2003

Applied Surface Science
Room 324/325 - Session AS+BI-TuA

Biomaterials Characterization

Moderator: J.E. Fulghum, University of New Mexico

2:00pm **AS+BI-TuA1 Spatially Defined Immobilization of Biomolecules on Microstructured Polymer Substrate***, **A. Hozumi**, N. Shirahata,* National Institute of Advanced Industrial Science and Technology, Japan*; S. Asakura, A. Fuwa,* Waseda University, Japan*; Y. Yokogawa, T. Kameyama,* National Institute of Advanced Industrial Science and Technology, Japan

ã€€The spatial arrangement of biomolecules on solid surfaces with artificial control in the micro~nanometer scale has attracted attention in biotechnical and biomedical applications. Here we report a simple method by which a number of biomolecules can be immobilized onto positions spatially defined in micrometer-scale. Our approach demonstrated here is based on the photodecomposition and hydrophilization of polymeric material using vacuum ultraviolet (VUV) light of 172 nm radiated from a Xe@sub 2@@super *@ excimer lamp. Each poly (methyl methacrylate) (PMMA) substrate was irradiated for 30 min at 10@super 3@ Pa with VUV light through a photomask contacting the PMMA surface. As confirmed by atomic force microscopy, after VUV-irradiation, microwell arrays composed of about 2 nm in diameter and 350 nm in depth were successfully formed on the PMMA substrates. Next, using such microstructured PMMA substrates, we demonstrated spatial arrangement of biomolecules. The microstructured sample was immersed into a solution containing antibodies labeled with fluorescence for 30 min. The antibodies were selectively adsorbed on the microwells in which the surfaces were photooxidized, while the surrounding regions where they were not unirradiated regions remained free of adsorption, as evidenced by fluorescence microscopy. This specific adsorption was probably due to the differences in chemical properties between the VUV-irradiated and unirradiated regions, as well as due to the geometrically effect. Indeed, according to water-contact angle measurements and X-ray photoelectron spectroscopy analysis, the VUV-irradiated PMMA surface became highly hydrophilic with its water-contact angle changing from 80Ã…Ã£ to 25Ã…Ã£ due to the formation of polar-functional groups, such as C=O and O-C=O, on the surface. Such chemically and geometrically defined microwells are expected to serve as spatially arranged active sites for the immobilization of a wide variety of biomolecules.).

2:40pm **AS+BI-TuA3 Low-Temperature STM Manipulation of Single Bio Molecules***, **J.J. Benson**, V. Iancu, A. Deshpande, S.-W. Hla,* Ohio University, Athens

Single porphyrin molecules adsorbed on Cu(111) surface are investigated by using a variety of manipulation procedures and spectro/microscopy measurements with a low temperature UHV STM at 6 K. The tunneling I/V and dI/dV spectroscopy techniques are used to probe the electronic properties of the single molecules with atomic level precision.@footnote 1@ Mechanical stability of single molecules is also examined using 'lateral manipulation' techniques with the STM-tip.@footnote 2@ In this procedure, the STM-tip is brought very close to the molecule to increase tip-molecule interactions (approximately one angstrom from the molecule). Then the tip is moved across the surface. Due to the tip-molecule interaction, the molecule is pushed across the substrate to relocate it to specific surface sites. Detailed internal conformation changes of the molecule can be directly monitored through the corresponding STM-tip height signals during the lateral manipulation process. These combined STM manipulation/spectroscopy investigations elucidate detailed information about the electronics and mechanical properties of the porphyrin molecules at sub-nanometer level resolutions. @FootnoteText@@footnote 1@F. Moresco et al, Phys. Rev. Lett. 86, 672-675, (2001). @footnote @@S.-W. Hla, K.-H. Rieder, Ann. Rev. Phys. Chem. 54, 307-330, (2003). .

3:00pm **AS+BI-TuA4 Base-dependent Displacement of Thiolated DNA Films by Mercaptohexanol (MCH)***, **H. Kimura-Suda**,* National Institute of Standards and Technology*; D.Y. Petrovykh,* University of Maryland & Naval Research Laboratory*; L.J. Whitman,* Naval Research Laboratory*; M. Tarlov,* National Institute of Standards and Technology

The immobilization of DNA on surfaces is the basis for DNA microarrays and many emerging nanotechnology applications. It has been demonstrated that the attachment of thiolated DNA probes to gold surfaces is an effective approach for construction of DNA-based sensors and diagnostics. One challenge with the use of thiolated DNA is reproducibly controlling the surface coverage and hybridization activity of adsorbed probes. A two-step method, where first the gold substrate is exposed to a solution of thiol-modified single-stranded DNA (HS-DNA), followed by exposure to a solution of mercaptohexanol (MCH), is a common approach for controlling the coverage and orientation of DNA probes. In this protocol, MCH both passivates the surface against nonspecific adsorption of DNA targets and "activates" DNA probes by displacing adsorbed nucleotides from the gold surface. The MCH treatment also displaces DNA probes from the gold surface resulting in less steric hindrance for hybridization. Nonetheless, the displacement of thiolated DNA by MCH remains poorly understood. In this study, we focused on base-dependent displacement of HS-DNA films from gold upon MCH exposure. Self-assembled monolayers of thiolated homo-oligonucleotides [HS-(dA), HS-(dT), HS-(dC), HS-(dG)] on gold surfaces were produced and characterized before and after exposure to MCH with FTIR and XPS. Surprisingly, we find that the displacement of HS-DNA on gold by MCH is strongly base-dependent. For example, most HS-(dT) is removed or displaced, whereas most HS-(dC) remains on the surface. In this talk we will present a selectivity series for the base dependent displacement of homo-oligonucleotides by MCH and discuss the origin of this effect. We will demonstrate that base dependent displacement effects can account for dramatic variations in probe coverage for probes of different base composition.

3:20pm **AS+BI-TuA5 Neuron Pathfinding and Surface Chemistry, Patterning and Reactions***, **T.P. Beebe, Jr.**,* University of Delaware **INVITED**

Biomaterials interfaces are at the heart of new approaches to control cell-surface interactions, and modern surface analytical techniques can now provide molecular-scale information about surface modifications, coverages and patterning or relevant ligands and proteins. These approaches can inform our understanding of the relationship between surface chemistry, surface structure and biological function. Using the biomedical problem of repair to damaged central nervous system tissue as the motivation for biomaterials interface characterization and cell-surface interactions, we will present several approaches to surface modification and surface characterization in conjunction with cell-surface biophysical measurements. The tools for these studies are AFM, XPS, TOF-SIMS and fluorescence microscopy and labeling.

4:00pm **AS+BI-TuA7 In-situ Spectroscopic Study of Thermal Phase Transition of Supported Hybrid Bilayer Membranes***, **C.S.-C. Yang**, K.A. Briggman, J.C. Stephenson, L.J. Richter,* National Institute of Standards and Technology

Hydrated phospholipid structures (Langmuir-Blodget films, supported bilayers, vesicles, etc.) have been widely studied as model systems for biological membranes. We report a study of the thermal phase transitions of fully hydrated hybrid bilayer membranes, i.e. phospholipid monolayers self-assembled onto a Au surface previously modified by a self-assembled monolayer of octadecane thiol (ODT). Using Sum Frequency Generation, a non-destructive interface-sensitive nonlinear optical probe, the structure and conformation of both the ODT and phospholipid alkyl chains have been characterized as a function of temperature from 25 to 60 °C. There is very little change in the ODT alkyl chain order over the temperature range studied. There are significant changes in the lipid chain order that are attributed to the transition from the ordered gel phase to disordered fluid phase, allowing us to determine the phase transition temperatures of the two-dimensional lipid layer. The gel-fluid phase transitions for a series of saturated phospholipids in the hybrid bilayers are observed at ~ 10 °C higher temperatures than those in corresponding multilamellar vesicles.

4:20pm **AS+BI-TuA8 Spectroscopic Quantification of Covalently Immobilized Oligonucleotides***, **A.V. Saprigin**, C.W. Thomas, C.H. Patterson, M.S. Spector,* Naval Research Laboratory

Quantitative determination of surface coverage, film thickness, and molecular orientation of DNA oligomers covalently attached to aminosilane monolayers has been obtained using complementary infrared and photoelectron studies. Spectral variations between the different nucleic acids are observed in surface immobilized oligomers for the first time. Carbodiimide condensation was used to covalently attach phosphorylated oligonucleotides to silanized aluminum substrates. Fourier-transform infrared (FTIR) spectroscopy and X-ray photoelectron spectroscopy (XPS) were used to characterize the surfaces after each modification step. Infrared reflection-absorption spectroscopy of covalently bound DNA provides orientational information. Surface density and layer thickness are extracted from XPS data. The surface density of immobilized DNA, 2-3Ã—10^13 molecules/cm^2, was found to depend on base composition. Comparison of antisymmetric to symmetric phosphate stretching band intensities in reflection-absorption spectra of immobilized DNA and

transmission FTIR spectra of DNA in KBr pellet indicates that the sugar-phosphate backbone is predominantly oriented with the sugar-phosphate backbone lying parallel to the surface, in agreement with the 10-20 Ã… DNA film thickness derived from XPS intensities.

4:40pm **AS+BI-TuA9 Photoionization for Trace Measurement of DNA on Surfaces**, ***J.F. Moore***, *W.F. Calaway,* Argonne National Laboratory*; B.V. King,* University of Newcastle, Australia*; J.W. Lewellen, S.V. Milton, M.J. Pellin,* Argonne National Laboratory*; M. Petravic,* Australian National University*; I.V. Veryovkin,* Argonne National Laboratory*; G.L. Woloschak,* Northwestern University

Recent developments in vacuum ultraviolet (VUV) lasers allow new photoionization techniques to be applied to surface and interface analysis problems. Single photon ionization of laser desorbed nucleosides and DNA was performed using a molecular F@SUB 2@ laser (wavelength 157 nm, pulse energy 8 mJ, pulse length 10 ns) and a tunable free electron laser (wavelength 120 - 265 nm, pulse energy 0.1 mJ, pulse length 300 fs). Results including detection limit and degree of fragmentation are compared for several systems including guanosine and single-stranded DNA of 10-30 base pair lengths. The tunability of the free electron laser to a wavelength just above the ionization potential of the analyte molecule can be used to enhance selectivity and sensitivity of the analysis. There are clear applications of this sensitive, selective, spatially resolving technique that is capable of identifying mutated or adducted DNA with little sample preparation. These uses will be elaborated on in the context of our results and plans for further technique development, and operational experience with the free electron laser. @FootnoteText@ This work is supported by the U. S. Department of Energy, BES-Materials Sciences, under Contract W-31-109-ENG-38.

5:00pm **AS+BI-TuA10 Utilization of Polyatomic Primary Ion Sources for Analysis of Drug Delivery Systems by Secondary Ion Mass Spectrometry (SIMS)**, ***C.M. Mahoney***, *G. Gillen,* National Institute of Standards and Technology

The utilization of cluster primary ion beams in SIMS has become very popular in the last decade due to the increased secondary ion yields as compared to monoatomic sources.@footnote 1-4@ In particular the analysis of organic materials has gained considerable interest as these cluster primary ion beam sources (in particular SF@sub 5@@super +@) have resulted in the enhancement of characteristic molecular secondary ion yields and have decreased the beam induced damage.@footnote 4@ Furthermore, the increased sputter rate with decreased beam damage has allowed for depth profiling in organic films and polymers for the first time with limited success.@footnote 4@ Here we explore the applicability of cluster SIMS in the analysis of various materials utilized in drug delivery. The effects of SF@sub 5@@super +@ bombardment on molecular secondary ion yields will be explored in various biodegradable polymers (polylactic acid, polyglycolic acid and polycaprolactone) as well as several model drugs (theophylline, 4'-hydroxyacetanilide, amyloid probe). The enhancement in the sensitivity will then be applied to imaging applications where it will be shown that imaging with SF@sub 5@@super +@ enhances the signal intensity as compared to Ar or Cs primary ions resulting in more sensative imaging capabilities. This will be useful in many systems where the concentration of drug is very low (e.g. biological samples, ppb-ppm range). Dynamic SIMS analysis (utilizing SF@sub 5@@super +@) of a series of polylactic acid films doped with varying concentrations of 4'-hydroxyacetanilide will also be discussed. @FootnoteText@ @footnote 1@ Kotter, F.; Benninghoven, A. Applied Surface Science 133 (1998) 47.@footnote 2@ Appelhans, A.D.; Delmore, J. Anal. Chem. 61 (1989) 1087.@footnote 3@ Gillen, G.; King, R.L.; Chmara, F. J. Vac. Sci. Technol. A 17(3) (1999) 845.@footnote 4@ Gillen, G.; Roberson, S.; Rapid Commun. Mass Spectrom. 12 (1998) 1303.

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