Tuesday Afternoon, October 21, 2008

Biological, Organic, and Soft Materials Focus Topic
Room: 201 - Session BO+PS+AS+BI+SS-TuA

Plasma-deposited Polymer and Organic Surfaces in Biological Applications

Moderator: E.R. Fisher, Colorado State University

1:40pm **BO+PS+AS+BI+SS-TuA1 High Throughput Surface Chemical Analysis of Polymer Microarrays: Wettability, Protein Adsorption and Cell Response Correlations**, *M. Taylor, A.J. Urquhart,* The University of Nottingham, UK, *Y. Mei, D.G. Anderson, R. Langer,* MIT, *M.C. Davies, **M.R. Alexander***, The University of Nottingham, UK **INVITED**

In the search for new and improved biomaterials, combinatorial material discovery approaches are increasingly being explored. A significant development in the production of polymer libraries by parallel synthesis was the move from preparation of macroscopic samples,[1] to on-slide polymerisation as microarrays in nano-litre volumes.[2] Such microarray material libraries may readily be interrogated by automated surface analysis equipment. Recently, high throughput surface analysis of a library of 576 different acrylate copolymers in triplicate on one slide using water contact angle (WCA), XPS and ToF SIMS highlighted the difference in the bulk and surface composition of the polymer spots, and consequently the need for surface analysis data when determining structure-property relationships.[3] The complexity of SIMS data, multiplied by the number of different samples necessitates the use of multivariate analytical approaches. Using partial least squares (PLS) analysis, relationships between SIMS fragments and WCA have led to identification of moieties controlling wettability across the wide range of copolymers synthesised on one microarray.[4] Comparison of human embryonic stem cell number on the spots with SIMS spectra have identified further SIMS fragments that correlate with high or low cell-polymer affinity. Protein adsorption measurements have been undertaken in an attempt to rationalise the cell adhesion data.[5] The correlations identified, and the information on the relationship between the surface structure and cell response or wettability will be discussed in this exploration of the high throughput approach.

[1] Brocchini S et al. Structure-property correlations in a combinatorial library of degradable biomaterials. Journal of Biomedical Materials Research 1998 42 66.

[2] Anderson DG, et al. Nanoliter-scale synthesis of arrayed biomaterials and application to human embryonic stem cells. Nature Biotechnology 2004 22 863.

[3] Urquhart AJ, et al. High throughput surface characterisation of a combinatorial material library. Adv Mats 2007 19 2486.

[4] Urquhart AJ et al. TOF-SIMS analysis of a 576 micropatterned copolymer array to reveal surface moieties that control wettability. Anal Chem 2008 80 135.

[5] Taylor M et al. A Methodology for Investigating Protein Adhesion and Adsorption to Microarrayed Combinatorial Polymers. Rapid Macromol Comm 2008 (in press).

2:20pm **BO+PS+AS+BI+SS-TuA3 Plasma Medicine**, ***A. Fridman***, Drexel University **INVITED**

Novel engineering and science approaches sustaining human health, such as for example radiation biology and laser medicine, represent a significant segment of technological developments around the world. Recent breakthrough discoveries of the highly energetic but non-damaging direct treatment of living tissues with non-thermal plasma enable to create new branch of the engineering medicine, PLASMA MEDICINE, which creates qualitatively new possibilities of healing, treating of previously untreated diseases, deactivation of dangerous pathogenic organisms, development of new direct methods of medical diagnostics. New types of non-thermal atmospheric plasma discharges are able to operate directly contacting human body and other living tissues, which significantly increase effectiveness of the tissue sterilization, treatment of wounds, skin and other diseases, as well as direct medical diagnostics. Obviously success of the plasma medicine depends on deep fundamental understanding of physics, chemistry and biology of the non-thermal plasma interaction with living tissues, and engineering of the relevant non-thermal plasma discharges, which is to be discussed in the presentation. Recent achievements in plasma biotechnology also address many aspects of the challenging problem of deactivation of viruses and bacteria that cannot be disinfected by traditional methods. Disinfecting large volumes of air in buildings and hospitals economically is now possible with room-temperature atmospheric pressure plasma. Similarly, atmospheric plasma technology can be employed to sterilize medical equipment, clothing, and building walls; to disinfect living tissue without side effects, and to disinfect and preserve food and water without damage. In addition, plasma technology can also be used to create innovative tools for sensing, detection and identification of dangerous pathogenic organisms as well as to characterize success of the cleansing processes. Essential advantage of the plasma biotechnology is its potential for universal availability, due to the technology's exclusive reliance on electrical power. It avoids many logistical difficulties associated with delivery, storage and disposal that typically hinder chemical and pharmaceutical approaches to sustainable health. Plasma technology can also be easily scaled from point-of-use devices to centrally operated plants capable of cleaning massive quantities of material. The key element of recent plasma technology developments is its use as a catalyst of many natural biological processes. As such, plasma can provide highly energy efficient treatment of biological materials, which is also to be discussed in the presentation.

3:00pm **BO+PS+AS+BI+SS-TuA5 Plasma Polymer Patterning of PDMS for Microfluidic Application**, ***S. Forster***, *A.G. Pereira-Medrano, M. Salim, P.C. Wright, S.L. McArthur,* University of Sheffield, UK

Microfluidic systems are becoming increasingly important for a wide range of bioengineering applications including proteomics and protein separations. Polydimethylsiloxane (PDMS) has proved to be the most popular material for microfluidic device production in the laboratory due to its many advantages over traditional materials. However, PDMS has some fundamental problems, namely a lack of functionality present at the surface, high protein fouling and inability to retain stable surface modification due to its motile hydrophobic monomer. These factors can lead to the loss of specificity and sensitivity in many bioassays. Plasma polymerisation is a method of depositing a uniform polymeric coating onto a surface, while retaining the desired functionality of the monomer. Hence, plasma polymerisation presents a versatile approach for surface modification and patterning of device channels. The wide range of monomers available for plasma polymerisation makes this approach even more suitable for use in systems where multiple surface properties within a single device are required. The aim of this work was firstly to investigate methods to produce stable plasma polymer patterns on PDMS. The coatings chosen include acrylic acid and maleic anhydride for their functional groups and tetraglyme to reduce non-specific protein adsorption. Patterning using photolithographic techniques and subsequent specific biomolecule immobilisation was achieved. Surface characterization using XPS and ToF-SIMS was used to ensure the spatial, chemical and biomolecule resolution of the device surfaces produced. This ability to combine microfluidics with spatially defined reactive regions on a 'non-fouling' background was then used in a number of applications to show the diversity and efficiency of the devices. Protein digestion by immobilized trypsin using single flow-through experiments in PDMS devices was improved using plasma polymer functionalized channels. The results achieved using mass spectrometry showed an increase in speed and sensitivity of the digestion as well as superior device reliability. Finally, plasma functionalized channels were used to investigate the effect of ampholyte adsorption onto device walls in isoelectric focusing (IEF). By coating channels with a tetraglyme plasma polymer an increase in sensitivity and reproducibility of IEF measurement was achieved. This technique can also increase the 'lifetime' of the device by ensuring channel properties were unchanged.

4:00pm **BO+PS+AS+BI+SS-TuA8 Plasma Etching for Selective Removal of PMMA from nm-scale PS/PMMA Block Copolymers for Lithographic Applications**, ***A.E. Wendt***, *Y.H. Ting, C.C. Liu, X. Liu, H.Q. Jiang, F.J. Himpsel,* University of Wisconsin-Madison, *P.F. Nealey,* University of Wisconsin, Madison **INVITED**

Diblock copolymers films, in which polymer components segregate into nano-scale domains, have been shown to have tremendous potential in fabrication of nm-scale surface topographies. Applications range from microelectronics fabrication to the study of how topography affects the growth and behavior of living cells or microorganisms. Use of block copolymers as a template for pattern transfer requires selective removal of one polymer component, and has motivated our study of plasma etching of polystyrene (PS) and polymethyl-methacrylate (PMMA), the two components of the PS-PMMA diblock copolymer. To better understand the mechanisms of the etch process for these materials, we have surveyed the effects of etch gas mixture and ion bombardment energy (taking advantage of our capability to produce a narrow ion energy distribution at the substrate), in combination with chemical analysis of the resulting etched surfaces. Of particular interest are the mechanisms of surface roughening, which shows a complex dependence on plasma process conditions that is not easily explained. A review of the literature on factors contributing to surface roughness, such as intrinsic inhomogeneity in the film, local deposition/micro-masking, shadowing effects and redeposition will be presented. We ultimately propose a mechanism for roughening of PS that involves micro-masking by inhomogeneous modification of surface chemical composition (rather than deposition) in oxygen-containing plasmas. Support from the UW NSF MRSEC for Nanostructured Materials is gratefully acknowledged.

4:40pm **BO+PS+AS+BI+SS-TuA10 Correlation of Macroscopic Surface Qualities of Poly-Parylene with Plasma-Specific Parameters**, ***G. Franz***, *F. Rauter, M. Häge*, University of Applied Sciences, Germany

In the course of our research how deposition conditions teleologically influence the morphology and various physical properties of the surface of various derivates of parylene, we followed the Yasuda approach to correlate the deposition rate of polymeric films with external parameters (flow rate and power) to define three different regimes of growth.[1,2] Since external parameters, especially the pressure, influence the polymerization in an opposite manner (rising the pressure causes an increase in the collision rate, but a decrease in electron temperature) we studied the deposition of parylene vapors with and without pulsed microwave plasmas to correlate outcome parameters such as surface energy, roughness, and deposition rate with respect to plasma density and electron temperature (Langmuir and OES) by varying the molar fraction of the monomeric species, diluted by the noble gas argon, the total pressure and the power. For this end, we determined the vapor pressure of the dimer and the chemical equilibrium between the monomer and the dimer by varying the evaporation temperature and the cracking temperature, resp., and cross-checked this equilibrium by mass spectrometry. This method has been extended to explain the onset of volume polymerization which becomes manifest by slight tarnishing of the polymer. Following Yasuda, this happens when a certain ratio of number density of the monomeric species to plasma density is exceeded. After having established stable process windows, two further tracks have been followed, namely copolymerization with CF_4 (volume polymerization) and hydrophilic functionalization. Following Gogolides, the surface roughness has been correlated to contact angle measurements.[3] The super-hydrophobic character is mainly due to surface roughening (nanotexturing) in the case of normal CVD. However, plasma treatment leads to super-hydrophobic character also for smooth surfaces. Subsequent treatment with O_2 generates long-term stable hydrophilic surfaces. To calibrate the effect of momentum transfer and to separate the chemical effect of etching, this has been compared with Ar etching.

[1] H.K. Yasuda, and Q.S. Yu; J. Vac. Sci. Technol. A 19, 773 (2001)
[2] Q. Yu, C.E. Moffitt, D.M. Wieliczka, and H. Yasuda; J. Vac. Sci. Technol. A 19, 2163 (2001)
[3] A.D. Tserepi, M.-E. Vlachopoulou, and E. Gogolides; Nanotechnology 17, 3977 (2006).

5:00pm **BO+PS+AS+BI+SS-TuA11 Plasma Processing of Nanostructured Polymeric Surfaces for the Development of Immunosensors**, *A. Valsesia*, ***P. Colpo***, *I. Mannelli, G. Ceccone, F. Rossi*, European Commission Joint Research Centre, Italy

Immunosensors play a very important role for the development of Point-of-Care analysis thanks to their rapid and sensitive detection capabilities.[1] Among others, the control of the interface between the transducer and the biological probes is a crucial issue since the bio-interface is the essential element that guaranty the bioactivity of the immobilized biological probes.[2] The control of the bio-interface is typically addressed by functionalizing the surface with special chemical groups. Besides, new nanobiotechnology-based tools have led to more sophisticated approaches that use for instance nanostructured surfaces. Benefits have been already shown in terms of the improvement of immunoreaction efficiency.[3] In this work we propose a new method for fabricating nanostrucured surfaces combining the use of colloidal masks with different plasma processes. In this method, Plasma Polymerization Processes are able to produce pinhole-free functional layers with different properties. The choice of the precursor together with the appropriate plasma processing parameter ensures the production of stable functional layers which can be used for the production of the chemically contrasted nanopatterns. Also the deposition of the colloidal mask in a controlled way is essential: for example, mass sensitive detectors (like Quartz Crystal Microbalance, QCM) require the use of very large areas in order to obtain measurable signals. Also plasma etching plays a very important role: it is important to choose the suitable processing parameters enabling the fabrication of nanostructured surface which are not limited in the patterning geometry and resolution. After the optimization of the nanofabrication process, the surfaces of immunosensors have been nanostructured. In particular we transferred the nanostructures on the crystals of QCM for on-line monitoring of the protein adhesion. The nanostructures accelerate the kinetics of absorption and increase the density of absorbed molecules, resulting in higher bioactivity of the immobilized proteins and consequently in an improvement of the immunosensing performances.

[1] K. R. Rogers, Applied Biochemistry and Biotechnology - Part B Molecular Biotechnology 2000, 14, 109-129.
[2] B. Kasemo, Current Opinion in Solid State and Materials Science 1998, 3, 451-459.
[3] A. Valsesia, P. Colpo, T. Meziani, P. Lisboa, M. Lejeune, and F. Rossi, Langmuir 2006, 22, 1763-1767.

5:20pm **BO+PS+AS+BI+SS-TuA12 Use of Multivariate Analysis Techniques to Predict Cellular Response to Plasma Polymerized pNIPAM**, ***J.E. Fulghum***, *K. Artyushkova, A. Lucero, H.E. Canavan*, University of New Mexico

The primary objective of this work is to investigate the correlate structural properties of a thermoresponsive polymer, poly(N-isopropyl acrylamide) (pNIPAM), with its ability to reversibly adhere cells. PNIPAM undergoes a sharp property change in response to a moderate thermal stimulus at physiological temperatures (~32 °C). This behavior has generated great interest in the biomaterials community, and pNIPAM is being investigated as a "smart" release coating to harvest intact cell monolayers. Many techniques are used to deposit pNIPAM, including electron beam irradiation and solution deposition (e.g., silanes and self-assembled monomers). Recently, we constructed a radio frequence (rf) plasma reactor for plasma polymerization of NIPAM (ppNIPAM) from the vapor phase based on a previous design. Plasma polymerization is a sterile, solvent-free, and compatible with surfaces of any geometry or chemistry. These factors make plasma polymerization extremely useful for cell and tissue culture, which often rely on plastic tissue culture plates. Due to the inherently energetic conditions of the plasma, parameters such as maximum rf wattage, location/position of the samples in the chamber, and monomer flow have on the resulting films. In this work, pNIPAM films resulting from those varying conditions are characterized using X-ray photoelectron spectroscopy (XPS) for film composition, interferometry for film thickness, contact angles for thermoresponse, and cell detachment for cell releasing properties. Using multivariate analysis, the structural information of the films obtained at various polymerization conditions will be correlated with their thermoresponsive and cell-releasing behavior. In this way, we will predict the conditions that will optimize film composition for bioengineering applications.

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