Biomaterial Surfaces & Interfaces
Room Milo - Session BI-MoE

Soft Surface & Biofunctional Coatings

Moderator: Duncan McGillivray, University of Auckland, New Zealand

6:00pm **BI-MoE2 Functionalisation of Polymeric Biomaterials by Graft Copolymerisation**, ***Lisbeth Grondahl,*** The University of Queensland, Australia **INVITED**

The surface of a material is the first contact with the cellular environment upon inoculation (in vitro) or implantation (in vivo) and as such these surfaces must, at minimum, possess properties amenable to cell adhesion. However, many polymers used as biomaterials lack functional moieties and the overall hydrophobic nature of the polymers encourage non-specific protein adsorption and make them less than ideal for controlled protein attachment and hence directed cell attachment and expansion.

One method of changing the surface properties of polymeric biomaterials is graft copolymerisation of functional polymers thereby providing functional groups and/or reduced hydrophobicity to the material. Work will be presented on graft copolymerisation of both the biodegradable polymer polycaprolactone (PCL), an FDA approved aliphatic semicrystalline polyester studied extensively for tissue engineering, and the biostable polymer expanded polytetrafluoroethylene (ePTFE), used for example in facial reconstruction. The ability to modify the interior of scaffolds and membranes as well as introducing various functional groups (eg. phosphate, carboxylate and amine) will be illustrated. Recent studies on creation of dual functional materials will show how the approach taken (one-pot or consecutive grafting) affects the material properties.

Protein adsorption studies using albumin, lactoferrin and lysozyme illustrate that the surface density of carboxylate groups does not correlate to the amount of adsorbed protein rather a correlation to the degree of grafting was observed indicating penetration of the proteins into the grafted layers. Furthermore, the topology of the graft copolymer is shown to be more important than the functional group in regards to the outcome of in vitro mineralisation when comparing a series of phosphate and carboxylate functionalised surfaces.

6:40pm **BI-MoE4 Blood Compatibility Evaluation of Fluorinated Bioresorbable Polylactic Acid For Coronary Artery Stents**, ***Razieh Khalifehzadeh,*** *B.D. Ratner,* University of Washington, USA

Bioresorbable stents are an emerging, novel treatment for improving long-term stent outcomes. Rigid metallic stents are associated with failure over time partly due to their permanent presence in vessel walls inhibiting physiologic vasomotion and stimulating neointimal hyperplasia. Among various polymers, poly(lactic acid) (PLA) has been extensively used for making bioresorbable stents. PLA undergoes degradation through hydrolysis of ester bonds. The degradation products are lactic acid and oligomers that later metabolize into CO_2 and water.

Despite the various long-term advantages of bioresorbable stents, their reported thrombosis is higher than metallic stents. In an attempt to improve blood compatibility of PLA, we used radio frequency glow discharge (RFGD) to modify the surface of this polymer with perfluoro compound. Fluoropolymers have been shown to lower thrombogenicity and platelet reactivity, and are extensively used in blood contacting materials.

Here, we have developed a process to coat the surface of PLA with perfluoro compound. Electron spectroscopy for chemical analysis (ESCA) was used to analyze the surface composition of these polymers. In addition, contact angle measurements, cell cytotoxicity, and degradation profile were evaluated.

Finally, we will assess the blood compatibility of these modified surfaces by using radiolabeled blood plasma proteins (albumin and fibrinogen) adsorbed onto their surface. The adsorption of plasma proteins is the central event in the biofouling of blood-contacting surfaces, which occurs immediately upon exposure of blood to biomaterial. We hypothesiz that tight binding of adsorbed albumin on fluoropolymers accounts for its success in blood-contacting applications.

7:00pm **BI-MoE5 Multifunctional Bionanotubular Implant Surfaces**, ***Tolou Shokuhfar,*** University of Illinois at Chicago, USA

Bionanotubular surfaces offer exciting progress toward the design of multifunctional medical implants. To bring this to reality, we have synthesized and optimized the mechanical, physical, biocompatibility, and interfacial properties of titania nanotube surfaces using in-situ TEM, SEM, FIB, FTIR, and WCA measurements. We have observed that the fabrication of bionanotubular titania surfaces with elastic modulus close to actual bone promotes osteoblast growth and prevents stress shielding. In addition, bionanotubular titania surfaces could be considered a suitable alternative route for the development of drug-eluting and antimicrobial implants due to the fact that these nanostructures are not an added coating but rather are rooted in the implants and will not delaminate from the surface. Such drug-eluting implants can prevent unnecessary side effects caused by oral administration of drugs, increase drug efficiency, and prevent infection related implant complications and failures.

7:40pm **BI-MoE7 NAP-XPS and EnviroESCA – Surface Analysis Entering New Fields of Applications: XPS from Liquids and Solid-Liquid Interfaces**, ***Thomas Schulmeyer,*** SPECS Surface Nano Analysis, Inc.

For decades XPS has been the well-accepted standard method for non-destructive chemical analysis of solid surfaces. To fulfill this task, existing XPS tools combine reliable quantitative chemical analysis with comfortable sample handling concepts integrated into fully automated compact designs.

Recently however, it has been possible to develop XPS systems that can work far beyond the standard of high or ultrahigh vacuum conditions. Near Ambient Pressure (NAP) XPS has become a rapidly growing field in research, inspiring many scientist to transfer the method to completely new fields of application. By crossing the pressure gap, new insights in complicated materials systems have become possible using either synchrotron radiation or laboratory X-ray monochromators as excitation sources under NAP conditions.

Based on this experience, SPECS Surface Nano Analysis GmbH has developed two lines of products: a portfolio of research instruments with various setups optimized for different applications of NAP-XPS, and EnviroESCA. Both of these revolutionary tools realize the long existing dream in many analytical laboratories: reproducible chemical surface analysis under any environmental condition. EnviroESCA™ allows for different applications, such as extremely fast solid surface analysis of degassing (but also non-degassing) samples, XPS analysis of liquids or liquid-solid interfaces, chemical analysis of biological samples, materials and device analysis under working conditions (in situ/in operando studies of catalysts, electrochemical devices etc.).

In this presentation, the various basic designs showcasing their different applications are introduced. The results primarily show how measurements can be taken from liquids or solid/liquid interfaces, and the essential bits of information that can be derived from these measurements. The applications range from measurements on static and dynamic liquids, biological samples and fuel cells to in-operando measurements on electrodes under potential in static and dynamic electrochemical cells. For the first time, systematic XPS analysis from liquids is possible and evidenced. Thus, realistic opportunities as well as experimental challenges in liquid-XPS analysis will be discussed and summarized.

8:00pm **BI-MoE8 Wearable Microprojection Array Skin Patches for Sampling Biomarkers from the Skin**, ***Jacob Coffey,*** University of Queensland, Australia*; S. Corrie,* Monash University, Australia*; M. Kendall,* University of Queensland, Australia

Microprojection array (MPA) skin patches capture circulating blood biomarkers from the skin as a needle-free alternative to traditional blood sampling. The skin, due to its abundance of superficial capillary vessels offers an alternative route to access circulating biomarkers with minimal invasiveness for more frequent monitoring. This diagnostic potential has been largely unrealised due to the lack of convenient methods to sample biomarkers from the skin. To address this challenge we surface modified MPAs with an anti-fouling polymer (poly(ethylene glycol)) and capture probes that selectively bind circulating disease markers. These MPAs are engineered to penetrate only the upper layers of the skin and selectively bind circulating disease markers, thus avoiding bulk fluid sampling. Accessing the biomarker of interest, however, from the complex milieu of the tissue environment remains a key challenge critical to enable high MPA detection sensitivity.

We report MPAs rapidly sample dengue, malaria, and IgG (antigen-specific) disease markers in animal models. We then characterise the effect of MPA design (length, density, array size) on biomarker capture, which increases with the penetrated surface/tissue contact area of MPAs. Investigating the effect of MPA application and projection design on blood protein extravasation from skin vasculature showed MPA insertion induces blood protein extravasation, which may play a key role in accessing circulating biomarkers *in vivo*. MPAs with improved design rapidly, reliably and

reproducibly sample antigen-specific IgG for immunoassays in 30 sec – currently the best reported sampling time and diagnostic sensitivity using microprojections, making them highly suitable for rapid diagnostic tests.

We also developed 'wearable' MPAs for longer implantation times (24 h) which improves the sampling of low concentration biomarkers up to 6-fold. However, a significant decrease in the functionality of the capture surface was observed during implantation,with an approx 60% decrease in biomarker capture and corresponding increase in non-specific background signal. This suggests significant degradation or fouling of the capture surface *in vivo*. A key remaining challenge is to identify the causes of this functionality loss and to develop stable surfaces for long term *in vivo* sampling. An inflammatory response was also observed in the tisue surrounding the MPA, which may contribute to this surface degredation. Preliminary studies with zwitterionic antifouling polymer coatings (polysulfobetainemethacrylate) show improvemed biomarker capture over shorter sampling times (<10 min), which may offer promise to improve long term sampling.

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