Wednesday Morning, November 6, 2002

Biomaterials
Room: C-201 - Session BI+AS-WeM

Ambient Surface Science Techniques
Moderator: M. Grunze, Heidelberg Universität, Germany

8:20am **BI+AS-WeM1 A Challenging Problem: Interfaces between Condensed Matter**, ***M. Buck***, StAndrews University, UK **INVITED**

Surface Science has developed a zoo of techniques which allow the characterization of chemistry and structures of surfaces and adsorbates at an impressive level of molecular detail. Unfortunately, the large variety of available techniques dramatically reduces when dealing with systems under non-vacuum environment and, therefore, an understanding on a molecular level is much harder to gain. In addition to problems on the technical side, the situation is further complicated by the fact that "real world" interfaces are, in general, more complex compared to systems studied in surface science, e.g. larger molecular entities with more conformational degrees of freedom, amorphous structures, and additional interactions due to the environment. The talk discusses various routes to unravel the relationship between structures and properties of biomaterials interfaces and highlights problems and possible pitfalls associated with the investigation of such type of interfaces.

9:00am **BI+AS-WeM3 Surface Chemistry of Environmentally Relevant Transition Metal Oxides Studied in Aqueous Solutions using Soft X-ray Spectromicroscopy**, ***B.P. Tonner***, *K. Pecher*, University of Central Florida

The surface chemistry of environmentally relevant inorganic oxides can now be reliably assessed in solution, with high spatial resolution, using a methodology based on x-ray absorption spectroscopy with microfocussing.[1,2] A crucial aspect of this research is that the studies are performed in the presence of a complete water layer, with control of parameters such as buffer concentrations, dissolved oxygen content, and pH. We have concentrated on the fate of Fe and Mn oxides in mineral model compounds, and in addition important nano-scale materials like the 'green rusts.' Spatial chemical inhomogeneities are prevalent in such nano-scale minerals, and are revealed by x-ray spectro-microscopy "chemical state mapping." The state of these studies has matured to the point where chemical intermediates, formed as a result of microbial metabolism, can be reliably detected and identified. This paper will emphasize the quantitative aspects of performing assays of surface transition metal oxide valence distributions using L-edge spectromicroscopy.

[1] Rothe, J., E.M. Kneedler, K.H. Pecher, B.P. Tonner, K.H. Nealson, T. Grundl, W. Meyer-Ilse, and T. Warwick, Journal of Synchrotron Radiation 6, 359-361 (1999).

[2] K. Pecher, E. Kneedler, J. Rothe, G. Meigs, T. Warwick, K. Nealson, and B. P. Tonner, X-ray Microscopy 1999, W. Meyer-Ilse, T. Warwick, and D. Attwood, ed., (American Institute of Physics, NY, 2000) p. 291-300.

9:20am **BI+AS-WeM4 Investigation of Protein Adsorption with Simultaneous Measurements of Atomic Force Microscope (AFM) and Quartz Crystal Microbalance (QCM)**, ***K.-H. Choi***, *J.-M. Friedt, F. Frederix, W. Laureyn, A. Campitelli, G. Borghs*, IMEC, Belgium

We have combined the tapping mode atomic force microscope (AFM) and quartz crystal microbalance (QCM) for the direct investigation and characterization of protein adsorption on various metallic surfaces. The adsorption of proteins, such as human plasma fibrinogen, γ-globulin and collagen, onto the metal/QCM surface were monitored using both methods at the same time when varying the concentration of them. We present the AFM images that shows the surface changes and the adsorption scheme of proteins with molecular resolution according to the shift of resonant vibration frequency of the QCM. The combination of AFM with QCM and the simultaneous measurements of the bio molecule adsorption with two techniques provide us with not only the sensing and detection technique but also the means for understanding the adsorption schemes of bio molecules on the metal surface.

9:40am **BI+AS-WeM5 Real-time AFM Investigations of the Enzymatic Degradation of DNA-polymer Dendrimer Complexes**, ***S.J.B. Tendler***, *H.G. Abdelhady, C.J. Roberts, S. Allen, M.C. Davies, P.M. Williams*, University of Nottingham, UK

Fundamental to surface recognition strategies is the need to develop both interfaces and imaging methods that allow the investigation of biomolecular recognition processes in solution, in-real time. One such set of processes is the enzymatic degradation of DNA, both when naked and when protected by polymeric (bio)materials. This system has clinical relevance in that polyelectrolyte complexes between polyamidoamine (PAMAM) dendrimers and DNA have emerged as potential non-viral vectors for therapeutic DNA delivery. Hence methods for analyzing the ability of PAMAM dendrimers to protect the DNA from degradative enzymes are of clinical significance. Here we have applied atomic force microscopy (AFM) in liquid to visualize at the molecular scale and in real time, the effect of the enzyme DNase I on generation 4 PAMAM dendrimers complexed with DNA (G4-DNA). The formation of G4-DNA is observed to provide a degree of protection to the DNA, the level of which rises with increasing PAMAM dendrimer to DNA ratio and to a certain degree with the time allowed for complexes to form.

10:00am **BI+AS-WeM6 Interaction of Water with Protein Resistant Self-Assembled Monolayers: Neutron Reflectivity Measurements of Water Density in the Interphase Region**, ***D. Schwendel***, *T. Hayashi, A.J. Pertsin, R. Dahint*, University of Heidelberg, Germany, *R. Steitz*, Hahn-Meitner-Institut, Germany, *F. Schreiber*, University of Oxford, UK, *M. Grunze*, University of Heidelberg, Germany

The interfacial behavior of surfaces, colloids, and molecules with water plays a substantial role in surface science and other areas. It is, in particular, responsible for colloid stability, micelle formation, biomembrane fusion, and the resistance of materials against proteins from biological media. These materials are of crucial importance in biotechnology and biomedical applications. One type of such bicompatible surfaces is represented by self-assembled monolayers (SAMs) on Au and Ag composed of undecanethiolates terminated oligo(ethylene glycols), (-O-CH2-CH2-)n (hereafter EGn). Neutron reflectivity measurements on protein resistant methoxy tri(ethylene glycol) (EG3-OMe) and hydroxy terminated hexa(ethylene glycol) (EG6-OH) undecanethiolate self-assembled monolayers (SAMs) in contact with deuterated water reveal the presence of an extended (~5 nm thick) water interphase with a noticeably reduced density (85-90 % of bulk water density). This result is in qualitative agreement with Grand canonical Monte Carlo simulations of water next to the SAM surface. For comparison, neutron reflectivity experiments have also been performed on non-functionalized hydrophobic octadecanethiolate and hydrophilic hydroxy terminated undecylthiolate SAMs. Additionally, neutron reflectivity measurements on protein resistant SAMs formed from hydroxy and methoxy terminated tri(ethylene glycol) (EG3-OH and EG3-OMe) against high concentrated protein solutions of BSA show that the free dissolved protein does not contact the surface but that it is repelled over a distance of few nm. The profiles strongly suggest a BSA depleted water layer at the SAM/bulk interface of 4 to 6 nm while BSA adsorption is observed for non-resistant propoxy terminated tri(ethylene glycol) (EG3-OPr).

10:40am **BI+AS-WeM8 Force Spectroscopy of Self-Assembled Monolayers Containing 'Sandwiched' Oligo(Ethylene Glycol) Interfaces on Gold under Electrolyte Solution**, ***G. Haehner***, *C. Dicke*, University of St Andrews, UK, *S. Herrwerth, W. Eck, M. Grunze*, University of Heidelberg, Germany

Non-specific interactions between biomolecules and (synthetic) organic surfaces, and in particular materials which are resistant to the adsorption of proteins from biological media, are of crucial importance to the fields of biomaterials, biosensors and medical devices. Chemically functionalized (charged and hydrophobic) scanning force microscope probes can mimic local structures of proteins and hence allow it to study the influence of these parameters on the overall observed interaction separately. Oligo(ethylene glycol) (OEG) terminated self-assembled monolayers on gold show high inertness towards the non-specific adsorption of proteins. The underlying mechanism, however, has not yet been resolved completely. It appears that water as well as hydronium and/or hydroxyl ions play a central role. In order to scrutinize the interaction, the accessibility of the OEG interface to molecules/ions from solution was varied. This was accomplished by the molecular structure: the functional (OEG) part was terminated with hydrophobic chains of different length resulting in 'sandwich'-film-structures. Force spectroscopy measurements on these layered structures with hydrophobic probes under electrolyte solution reveal the importance of the different contributing factors to the overall interaction.

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