

Tuesday Afternoon, October 21, 2008

Synchrotron-based Spectroscopy and Spectro-Microscopy Topical Conference

Room: 310 - Session SY+SS+BI-TuA

Synchrotron-based Spectroscopy and Spectro-Microscopy

Moderator: Ch. Wöll, Ruhr-University, Germany

1:40pm SY+SS+BI-TuA1 Ultrafast Surface Dynamics in the Light of Soft X-rays from Free-Electron Lasers: First Results and Perspectives, W. Wurth, University of Hamburg, Germany **INVITED**

To investigate ultrafast electron dynamics and atomic motion in real-time is essential for a fundamental understanding of complex wave packet evolution in materials. As ideal tools for this type of investigation one can envision time-resolved spectroscopic techniques in the XUV or soft x-ray regime using femtosecond pulses. Tools such as angle-resolved photoemission (ARPES), electron spectroscopy for chemical analysis (ESCA), x-ray absorption or emission spectroscopy have proven to be extremely useful to study the electronic structure of complex materials in a static mode. Powerful XUV or soft x-ray sources delivering ultrashort pulses will enable us to obtain element-specific information on dynamic changes in the local electronic structure. With the Free-Electron Laser in Hamburg (FLASH) a unique source for femtosecond XUV-pulses with unprecedented brightness is operational since 2005 and a number of pioneering experiments have been performed with this source during the first user runs. In the talk I will review some of these experiments and present some ideas how femtosecond x-ray pulses from free-electron lasers can be used to study dynamic processes at surfaces and interfaces. I will show first examples for time-resolved experiments performed at FLASH including the investigation of XUV induced changes in optical reflectivity¹ as well as time-resolved photoelectron spectroscopy² and discuss implications for future experiments.

¹C. Gahl et al., Nature Photonics 2, 165 (2008)

²A. Pietzsch et al., New Journal of Physics 10, 033004 (2008).

2:20pm SY+SS+BI-TuA3 Soft X-ray Spectromicroscopy of Protein and Peptide Interactions with Polymer Surfaces, A.P. Hitchcock, B.O. Leung, J.L. Brash, R. Cornelius, McMaster University, Canada, A. Scholl, A. Doran, Lawrence Berkeley National Laboratory **INVITED**

The biocompatibility of a material is dependent on its surface characteristics and how they affect the protein layer which forms upon initial contact with blood or tissue since those proteins mediate subsequent cellular responses. Chemical, mechanical and spatial characteristics are known to play a role in controlling initial protein adsorption. Thus direct measurements of adsorption preferences on structured biomaterials are highly relevant to optimization of biocompatibility. We are using synchrotron based X-ray PhotoEmission Electron Microscopy (X-PEEM) and Scanning Transmission X-ray Microscopy (STXM) to study preferential adsorption of proteins (human serum albumin (HSA), fibrinogen (Fg)) and peptides (sub-6, a cationic antimicrobial) to several phase segregated polymer blend surfaces – PS/PMMA^{1,2} and PS/PLA. The X-ray absorption contrast is sufficient to identify and quantify the polymer and protein/peptide components, and peptides can be differentiated from proteins.³ Single or competitive adsorption is carried out under controlled concentrations, pH, buffer, temperature and exposure times. All of these factors affect adsorption. Image sequences measured in the C 1s, N 1s and O 1s regions are analyzed by pixel-by-pixel spectral fitting to reference spectra. The resulting component maps are placed on quantitative thickness scales, either intrinsically in STXM (when reference spectra are provided on quantitative linear absorbance scales), or by normalizing total signal to a 10 nm measured sampling depth in PEEM. For adsorption on PS/PMMA, under all conditions there is a strong preference to adsorb at the domain interphases, which are thermodynamically favored since both hydrophobic and hydrophilic interactions can be satisfied. Otherwise, HSA and Fg have a preference for PS over PMMA. When sub-6 and HSA are co-adsorbed at neutral pH, there is evidence that the site distribution is controlled by preferential adsorption of a solution complex.⁴ Under basic conditions (pH=11) this complex is unstable and the preferential adsorption becomes similar to that seen when each component is adsorbed independently.

¹ C. Morin et al., J Electron Spec, 137 (2004) 785.

² L. Li et al., J Phys Chem B 110 (2006) 16763, *ibid.*, 112 (2008) 2150

³ J. Stewart-Ornstein et al., J. Phys. Chem. B 111 (2007) 7691

⁴ B.O. Leung et al., Biointerphases 2008, submitted.

3:00pm SY+SS+BI-TuA5 Advances in Scanning Transmission X-Ray Microscopy: Surface Sensitive Electron Spectromicroscopy, B.M. Haines, University of Saskatchewan, Canada, T. Tyliczszak, Lawrence Berkeley National Laboratory, S. Beyhan, S.G. Urquhart, University of Saskatchewan, Canada

Scanning transmission x-ray microscopy (STXM) is a powerful technique that allows for near edge x-ray absorption spectroscopy (NEXAFS) and imaging with chemical speciation at spatial resolutions better than 50 nm. STXM has seen widespread use to study polymers, biological systems, and geochemistry. Many synchrotrons now have at least one beamline dedicated to STXM. It is however a bulk technique with limited surface sensitivity, as such it is not ideal for studying surface phenomenon or monolayers such as Langmuir-Blodgett films where the signal is very weak. Recently we have modified STXM microscopes at the Canadian Light Source and the Advanced Light Source to perform total electron yield (TEY) NEXAFS, which is well suited for studying surface phenomena. We have used TEY-STXM for compositional mapping of phase separated Langmuir-Blodgett films of arachidic acid and perfluorotetradecanoic acid. The films are imaged with the same resolution as STXM with increased contrast and surface sensitivity. TEY-STXM has been used to obtain simultaneous transmission and TEY spectra in addition to compositional maps of Fe₃O₄ carbon supported nanoparticles less than 75 nm in size. The modification of STXM for TEY detection represents a significant new tool for studies conducted with STXM and opens the window for surface sensitive measurements with STXM.

4:00pm SY+SS+BI-TuA8 Recent Advances in Material Research with Synchrotron Infrared Spectromicroscopy at Elettra, A. Perucchi, Sincrotrone Trieste, Italy, S. Lupi, CNR-INFM Coherentia and Universita' di Roma "La Sapienza", Italy, D. Eichert, L. Vaccari, M. Kiskinova, Sincrotrone Trieste, Italy **INVITED**

The infrared beamline SISSI (Source for Imaging and Spectroscopic Studies in the Infrared) at Elettra extracts the infrared and visible components of synchrotron emission for applications of spectroscopy, microspectroscopy and imaging. The applications cover a wide range of research fields, including surface and material science, biochemistry, forensics, geology, biomedicine, microfluidics. We will overview the characteristics of the beamline and discuss recent results. A particular focus will be devoted to the new research opportunities in infrared spectroscopy at high pressures and in the THz range.

4:40pm SY+SS+BI-TuA10 The Brightest Light Downunder, R. Lamb, University of Melbourne and Australian Synchrotron **INVITED**

The Australian Synchrotron, a 3 GeV Instrument located in Melbourne, is the newest facility of its type in the world and is poised to become the single largest scientific and technological user facility in the Southern hemisphere. This talk will outline some of the key aspects of the local Science driving the future developments of the facility. An example of work in the area of nanoscale wetting of surfaces will also be described. Synchrotron small angle x-ray scattering (SAXS) has been used to investigate the in situ immersive wetting of ultrarough surfaces which exhibit superhydrophobicity with extreme water contact angle ($\theta=169$). Reduced scattering contrast observed from rough surfaces when partially or totally wetted reveals significant physical differences between superhydrophobic surfaces not otherwise apparent from conventional contact angle measurements. As a complementary technique to static and dynamic contact angle measurements, transmission SAXS-based immersive wetting measurements promise more predictive models for how complex heterogeneous morphologies affect the phenomenon of wetting.

5:20pm SY+SS+BI-TuA12 Digital In-Line Soft X-ray Holography as Microscopy Technique for Biological Samples, A. Rosenhahn, R. Barth, F. Staier, C. Christoffis, University of Heidelberg, Germany, T. Simpson, S. Mittler, The University of Western Ontario, Canada, S. Eisebitt, BESSY, Berlin, Germany, M. Grunze, University of Heidelberg, Germany

Digital in-line soft X-ray holography (DIXH) is used as lensless microscopy technique to investigate biological samples. The experimental setup follows directly the initial idea of Gabor,¹ a holographic projection microscope based on a diverging photon beam. By creating a large divergence and the use of short wavelength, a lateral resolution better than 400 nm can be achieved without using any optical elements such as zone plates. Objects composed of different materials and thickness are used to determine the imaging properties of holographic microscopy in the VUV and soft X-ray wavelength range.² By tuning the x-ray energy to core resonances, element specific contrast can be obtained.³ These results are promising with respect to the possibility to exploit intrinsic contrast

mechanisms for biological samples. Using fibroblasts and other cells, the sensitivity of the technique to resolve small structures inside these extended objects will be discussed. Although the spatial resolution still needs to be improved, we consider these experiments as starting point for future lensless holospectroscopy and as microscopy approach for highly coherent x-ray sources such as free electron lasers.

¹ D. Gabor, Nature 1948, 161, 777

² A. Rosenhahn, R. Barth, X. Cao, M. Schürmann, M. Grunze, S. Eisebitt, Ultramicroscopy 2007, 107, 1171

³ A. Rosenhahn, R. Barth, F. Staier, T. Simpson, S. Mittler, S. Eisebitt, M. Grunze, Journal of the Optical Society of America A 2008, 25(2), 416.

Authors Index

Bold page numbers indicate the presenter

— B —

Barth, R.: SY+SS+BI-TuA12, 1
Beyhan, S.: SY+SS+BI-TuA5, 1
Brash, J.L.: SY+SS+BI-TuA3, 1

— C —

Christoffis, C.: SY+SS+BI-TuA12, 1
Cornelius, R.: SY+SS+BI-TuA3, 1

— D —

Doran, A.: SY+SS+BI-TuA3, 1

— E —

Eichert, D.: SY+SS+BI-TuA8, 1
Eisebitt, S.: SY+SS+BI-TuA12, 1

— G —

Grunze, M.: SY+SS+BI-TuA12, 1

— H —

Haines, B.M.: SY+SS+BI-TuA5, **1**
Hitchcock, A.P.: SY+SS+BI-TuA3, **1**

— K —

Kiskinova, M.: SY+SS+BI-TuA8, 1

— L —

Lamb, R.: SY+SS+BI-TuA10, **1**
Leung, B.O.: SY+SS+BI-TuA3, 1
Lupi, S.: SY+SS+BI-TuA8, 1

— M —

Mittler, S.: SY+SS+BI-TuA12, 1

— P —

Perucchi, A.: SY+SS+BI-TuA8, **1**

— R —

Rosenhahn, A.: SY+SS+BI-TuA12, **1**

— S —

Scholl, A.: SY+SS+BI-TuA3, 1
Simpson, T.: SY+SS+BI-TuA12, 1
Staier, F.: SY+SS+BI-TuA12, 1

— T —

Tyliszczak, T.: SY+SS+BI-TuA5, 1

— U —

Urquhart, S.G.: SY+SS+BI-TuA5, 1

— V —

Vaccari, L.: SY+SS+BI-TuA8, 1

— W —

Wurth, W.: SY+SS+BI-TuA1, **1**