

Wednesday Morning, October 17, 2007

Applied Surface Science

Room: 610 - Session AS-WeM

Chemical Imaging at High Spatial Resolution and Nanoscale Materials

Moderator: K.G. Lloyd, DuPont

8:00am **AS-WeM1 Local Chemical Measurements with the Scanning Tunneling Microscope**, *P.S. Weiss*, The Pennsylvania State University
INVITED

Interactions within and between molecules can be designed, directed, measured, understood and exploited at unprecedented scales. We look at how these interactions influence the chemistry, dynamics, structure, electronic function and other properties. Such interactions can be used to advantage to form precise molecular assemblies, nanostructures, and patterns, and to control and to stabilize function. These nanostructures can be taken all the way down to atomic-scale precision or can be used at larger scales. We measure these interactions and the electronic perturbations that underly them using scanning tunneling microscopy. In these and other measurements, we collect substantial data sets in order to generate distributions with the statistics of ensemble-averaging techniques, while still retaining all the single-molecule and environmental information. This requires new automated tools for acquisition and analyses. We use molecular design, tailored syntheses, intermolecular interactions and selective chemistry to direct molecules into desired positions to create nanostructures, to connect functional molecules to the outside world, and to serve as test structures for measurements of single or bundled molecules.

8:40am **AS-WeM3 Chemical Characterisation on the Nanoscale: Imaging XPS and Scanning Auger Microscopy with Ultimate Spatial Resolution**, *M. Maier, T. Berghaus, D. Funneman, K. Winkler*, Omicron NanoTechnology, Germany, *N. Barrett*, CEA-DSM/DRECAM/SPCSI, CEA Saclay, France, *O. Renault*, CEA-Leti, Minatec, France

In this contribution we briefly summarize the current status of Imaging XPS (iXPS) and Scanning Auger Microscopy (SAM). Novel instrument concepts are presented, one in either field achieving ultimate resolution beyond today's limits. In iXPS a great obstacle for higher resolution is the limited X-ray brilliance in the analysis area in combination with the small electron acceptance angle of current spectrometers. Today commercial laboratory instruments are limited to approx. 3 μm resolution at best. Acquisition times as well as time for experiment set up increase unacceptably when the attempt is made to utilise this kind of resolution routinely. In particular with those instruments acquiring each image pixel sequentially by either scanning the X-ray beam or the analysis spot. We present first results of the NanoESCA instrument recently installed at LETI. A new lens concept provides a huge progress for the acceptance angle of photo electrons. This is combined with a patented aberration compensated analyser allowing the acquisition of typically 640x512 image pixels in a single shot. This offers the unique possibility to achieve sub micron image resolution routinely as well as small spot spectra from well defined areas below 1 μm diameter, within reasonable acquisition times. In the field of SAM, the spatial resolution depends mainly on the performance of its electron source. Crucial parameters are the probe diameter, the electron energy, and the beam current density. As state of the art a spatial resolution on the order of 10 nm and slightly below has been demonstrated recently on the most advanced commercial instruments, using beam energies as high as 20 keV. However, the Auger cross section increases for lower beam energies and the scattering volume in the sample decreases. Thus operation at lower beam energies is desirable, but the probe diameter still shall not increase to a counteracting extent. We present SAM measurements acquired with a new electron source employing a patented lens system optimised for low beam energies and high current density. This concept enables the highest so far reported SAM resolution of 5 nm (at 10kV). Even at beam energies as low as 1keV more than 1 nA beam current can be focussed into <10nm spotsizes. Furthermore we describe the combination of SEM/SAM with complementary techniques, such as STM/AFM, 4 Probe STM, SEMP, or EBSD to provide information on topography, electronic structure, magnetic domains, or crystal orientation.

9:00am **AS-WeM4 Application of Chemical Imaging in the Pharmaceutical Industry**, *X. Dong, C.A.J. Kemp*, Eli Lilly and Company
Chemical imaging methods have seen increased utilization within the pharmaceutical industry due to their ability to provide insight into the

composition and product performance of solid oral dosage forms. The primary imaging tools used for this type of characterization include EDS, NIR, Raman, NMR, and TOF-SIMS. This presentation will focus on the use of imaging tools for studying the detailed composition of dosage forms and packaging materials, and the inhomogeneous discoloration of API stored in USP-approved materials. Additionally, data will show that TOF-SIMS can be a pivotal tool for trouble-shooting by combining high mass resolution spectra with high spatial resolution images. The strengths and limitations of various imaging techniques (chemical and physical) will also be discussed.

9:20am **AS-WeM5 In-situ Surface Analysis by Optical Means**, *C.M. Eggleston*, University of Wyoming
INVITED

Understanding natural geochemical systems requires investigating fundamental reactions (adsorption, dissolution/growth, electron transfer, catalysis) at a variety of solid-solution interfaces. The availability of techniques for characterizing solid-liquid interfaces in-situ has made this task simpler. Such techniques include synchrotron-based X-ray absorption spectroscopies (e.g., EXAFS, XANES), scanning probe microscopes (STM, AFM, and their variations), and developments in Raman and IR spectroscopies. Here, we explore some perhaps less well-known techniques: Optical second harmonic generation (SHG), optical waveguide lightmode spectroscopy (OWLS), and photocurrent measurements coupled to impedance spectroscopy. SHG is a nonlinear optical technique. Briefly, the interface represents a noncentrosymmetric setting between two centrosymmetric bulk phases. Intense laser light impinging on an interface can produce a few photons of doubled-frequency (second harmonic) whose intensity and polarization can be related to the concentration - and possibly orientation - of adsorbed species. We have used SHG to observe the adsorption of organic molecules to oxide surfaces and to study the structure of water near charged oxide surfaces. OWLS operates on the basis of small changes in the effective refractive index of a waveguide of sub-wavelength thickness as the result of molecular adsorption to the waveguide surface. We are using OWLS to study the adsorption of proteins, particularly outer membrane cytochromes from iron-reducing bacteria, on oxide surfaces. This technique has proven crucial in studying the adsorption of small amounts of protein. Furthermore, comparison of quartz crystal microbalance (QCM) adsorption results (which includes associated water in the adsorbed mass) to OWLS results (which excludes associated water) shows that of the total adsorbed mass, only 27% is protein in these cytochromes. Our work with semiconducting oxide electrodes necessitates electrode characterization with regard to flatband potential, charge carrier density, and other properties. In addition, these and photocurrent transient techniques allow us to locate electronic states both at the semiconductor surface and within its bulk bandgap. This presentation will briefly show how such states may be located and studied using photocurrent transient spectroscopy and impedance spectroscopy in the case of iron oxide photocatalysts.

10:40am **AS-WeM9 Synchrotron Radiation Induced X-ray Photoelectron Emission Microscopy (SR-XPEEM) with Aberration Corrected Energy Filterin**, *N. Barrett*, CEA-Saclay, FR, *O. Renault*, CEA LETI Minatec, FR, *L.-F. Zagonel*, CEA Saclay, FR, *A. Bailly*, CEA LETI Minatec, FR, *J. Charlier*, *J. Leroy*, CEA Saclay, FR, *J.C. Cezar*, *N. Brookes*, ESRF, FR, *M. Senoner*, Fed. Inst. Mtls Testing, Germany, *J. Maul*, *T. Berg*, *F. Schertz*, *G. Schönhense*, Univ. of Mainz, Germany

The combination of high brightness photon source and aberration corrected energy filtering has allowed new progress in the field of electron emission microscopy for nanoscience and nanotechnology. The first commercially available NanoESCA instrument (OMICRON GmbH) has been recently commissioned and tested at the CEA Nanocharacterization centre (Minatec) in Grenoble and on beamline ID08 at the ESRF. We first present the principles of spectromicroscopy, and in particular the use of an electrostatic PEEM column together with an energy aberration corrected double hemispherical analyzer. The objective immersion lens and the high extraction voltage considerably improve lateral resolutions. The use of a contrast aperture reduces the chromatic aberrations in the PEEM column. The accurate focus tracking of the instrument allows imaging at the secondary electron threshold and across specific core levels at chosen kinetic energies. The resulting lateral resolution better than 150 nm and energy resolution give an imaging capability with full chemical state sensitivity. The principles will be illustrated by several examples. The core level intensity contrast is demonstrated with a multilayer certified standard sample of GaAs/GaxAl1-xAs variable multilayer. The energy resolved chemical mapping will be illustrated via the preferential molecular grafting on a heterogeneous Au-Si substrate. Finally, the depth resolution thanks to the variable photoelectron escape depth is employed to do non-destructive position detection of pre-solar grains coming from a meteorite, prior to

nano-SIMS analysis. The perspectives include reaching the ultimate resolution limits using an optimized synchrotron beamline, the development of valence band imaging and the study of single nanodevices.

11:00am **AS-WeM10 Directed Growth of Ordered Metal Nanostructures on Crystalline Cellulose Templates**, *G.J. Exarhos, Y. Shin*, Pacific Northwest National Laboratory

A form of nano-crystalline cellulose, isolated from carbohydrate-derived materials like paper or cotton, serves as a reducing template that drives formation of ordered regions of metal nanoparticles or nanorods when placed in aqueous metal precursor solutions under hydrothermal conditions. Uniform sized gold, silver, palladium, platinum, copper, nickel, selenium and other metal or metal-oxide nanocrystals were observed to rapidly nucleate and preferentially grow along the ordered hydroxyl-rich regions of the substrate. The ordered metals display catalytic, electrical and optical properties that would not normally be present in larger crystals. For example, a marked enhancement in the rate of degradation of organic dyes in water under uv-irradiation has been measured when selenium-decorated templates were immersed in methylene blue solutions. Materials have been characterized by means of XRD, FESEM, TEM, and optical methods. The mechanistic of the growth process will be discussed based upon these structural measurements and the known reducing properties of carbohydrate materials. Prospective uses of these materials for catalysis and in optical applications also will be described.

11:20am **AS-WeM11 Critical Issues Concerning the Use of Nanomaterials In Aerospace Platforms**, *P.T. Lillehei*, NASA Langley Research Center **INVITED**

Revolutionary aerospace vehicle designs are enabled by the use of lightweight structural composites. These composites must possess structural integrity and multifunctionality features, such as lightning strike protection, for the vehicle to fully realize the weight savings. NASA and the aerospace industry are aggressively pursuing the use of nanomaterials as both structural reinforcements and as an enabler of multifunctionality. Optimal utilization of nanomaterials in multifunctional aerospace platforms will demand an understanding of the fundamental principles that govern their behavior at the nanoscale. For example, NASA has established that a critical factor governing the electrical conductivity characteristics of a nanomaterial or nanocomposite is the degree of dispersion of the nanomodifier in the host matrix. However, before conductive nanomaterials can be considered for use in applications such as lightweight, flexible, surface mountable materials for lightning strike protection, a set of robust, field-ready quality assurance/control (QA/QC) standards must be developed. The research described in this presentation establishes a means of quantifying the dispersion of carbon nanotubes in high-performance, aerospace polymers. Work can now begin on developing the field ready QA/QC implementations of these techniques.

12:00pm **AS-WeM13 Functionalization and Characterization of Gold Nanoparticles**, *S.D. Techane, L.J. Gamble, D.G. Castner*, University of Washington

Gold nanoparticles (AuNPs) are non-toxic and have a high percentage of surface atoms, which gives them special electronic properties and reactivities. Since these properties are dependent on the size, shape and surface chemistries of the AuNPs, one can vary these quantities to achieve desirable applications for AuNPs in biomedicine, microarray and biosensor fields. In this research, AuNPs of different diameters (14nm - 50nm) were synthesized with a citrate reduction method and later functionalized with various chain lengths (3, 6, 8, 11, and 16 carbon chain) of carboxyl terminated alkyl thiol by direct displacement of the citrate ions. To obtain a hydrophobic surface, functionalization with 1-dodecanethiol was tried using a two step functionalization method. The size, shape, and size distribution of the AuNPs were characterized with transmission electron microscopy (TEM) and ImageJ, where the distribution in terms of 3σ ranged from 2.5 to 20nm, depending on the average diameter of the AuNPs. Surface chemistries of the self assembled monolayer (SAMs) of alkyl thiol were analyzed with X-ray photoelectron spectroscopy (XPS) and time-of-flight secondary ion mass spectrometry. Comparison between SAMs of 16-mercaptohexadecanoic acid (C/O = 8 and C/S = 16) on AuNPs and flat Au surface was done to verify the applicability of XPS data analysis method for curved nanoparticle surfaces. Surface atomic composition ratios: C/S (26 for AuNPs and 42 for flat Au), C/O (5 for AuNPs and 8 for flat Au), C/Au (1.7 for AuNPs and 1.2 for flat Au) exhibited some differences between the two surface types. These differences indicate the need to develop specific XPS data analysis methods to accurately represent the surface chemistries of curved nanoparticles surfaces. XPS results for the two-step functionalization method, which uses thioctic acid as an intermediate, showed 11% oxygen surface composition with 6% carboxyl carbon indicating incomplete displacement of the intermediate carboxyl thiol and a need for a better functionalization method to achieve hydrophobic surface.

AuNPs with carboxyl terminated SAMs are being used to investigate adsorption thermodynamics of short chain peptides onto these surfaces. Protein assay, XPS, and NMR are being used to characterize the adsorbed peptides.

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