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Pacificchem 2010



***Program and Abstracts
of
“Analytical Applications and New
Technical Developments of Soft X-Ray
Spectroscopy” Symposium (#145)***

Dec 18 (Sat) 2010, 7:30 AM- 8:50 PM
Oral session @301A (Hawaii Convention Center)

Dec 19 (Sun) 2010, 10:00 AM-12:00 PM
Poster session @Kamehameha Halls II & III (Hawaii Convention Center)

*Promoting scientific exchange in the Pacific
basin for a healthy and sustainable future.*



Topical Area of *Analytical*

“Analytical Applications and New Technical Developments of Soft X-Ray Spectroscopy” (#145)

Oral session; December 18 (Sat) 2010, 7:30 AM- 8:50 PM
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This symposium focuses on analytical applications and the new technical developments in soft X-ray spectroscopy such as X-ray absorption (XAS), X-ray emission (XES), photoemission (PES), and photon-in photon-out scattering techniques (RIXS). The number of analytical applications that use soft X-ray spectroscopy has been exploding in the last years. Analytical applications range from physical/chemical materials such as metals, semiconductors, superconducting materials, ceramics, to energy-related materials, to nano-structured materials to biological materials such as DNA, soft matter, liquids, and include even food and environmentally important materials. On the instrumental side the field of soft X-ray spectroscopy has flourished as well. New developments include liquid cells that allow better understanding liquid systems and a push for either high resolution or ultra-fast measurements. New X-ray sources, optics, and detector systems complement the new technology in soft X-ray spectroscopy and allow rather new analytical approaches such as microspectroscopy, 3D-imaging and time-resolved measurements for dynamical diagnostics. This symposium will bring together analytical and physical chemists, X-ray physicists, and material scientists and showcase the hot topics in soft X-ray spectroscopy.

Organizer

Yasuji MURAMATSU (University of Hyogo, Japan)

Co-organizers

Hisanobu WAKITA (Fukuoka University, Japan)

Jun KAWAI (Kyoto University, Japan)

Dennis W. LINDLE (University of Nevada, Las Vegas, U. S. A.)

Clemens HESKE (University of Nevada, Las Vegas, U. S. A.)

Louis J. TERMINELLO (Pacific Northwest National Laboratory, U. S. A.)

Anthony W. Van BUUREN (Lawrence Livermore National Laboratory, U. S. A.)

Rupert C. C. PERERA (EUV Technology, U. S. A.)

Alexander MOEWES (University of Saskatchewan, Canada)

Frank LARKINS (University Melbourne, Australia)

Chris GLOVER (Australian Synchrotron, Australia)

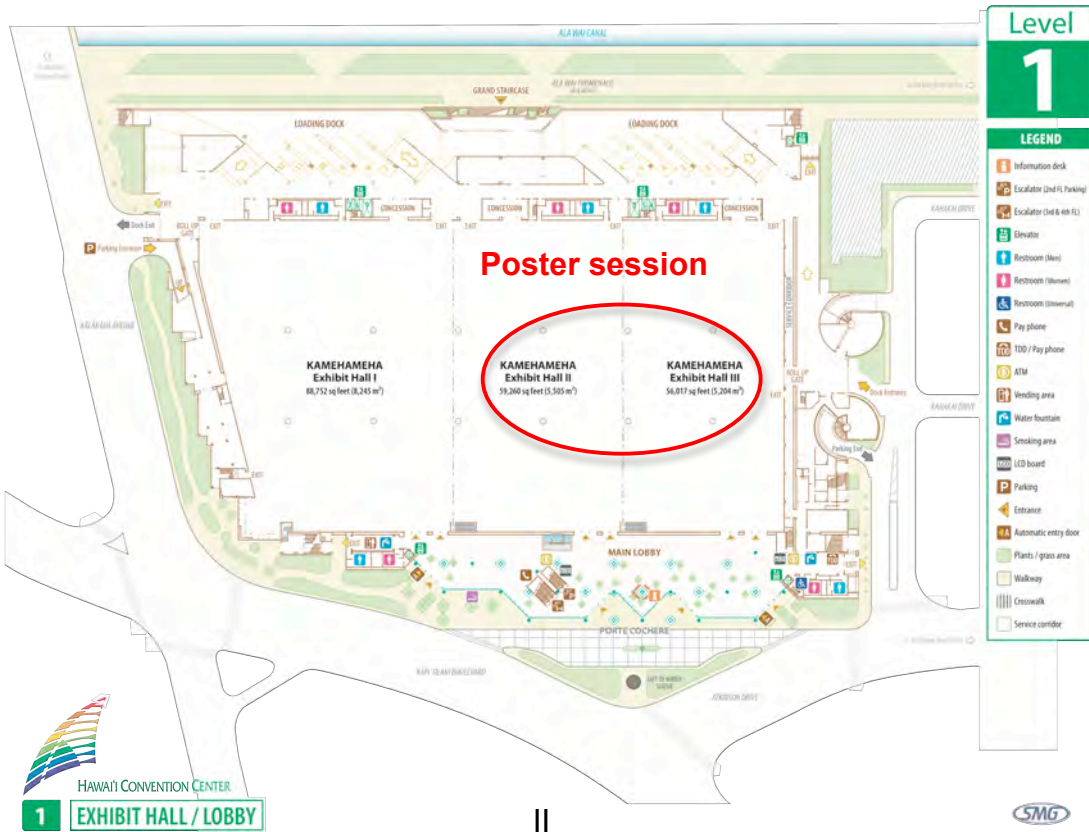
Jinho AHN (Hanyang University, Korea)

Bong Soo KIM (Pohang Light Source, PLS, Korea)

Conference Venue

Hawaii Convention Center

1801 Kalākaua Avenue Honolulu, HI 96815 Phone: (808) 943-3500 Fax: (808) 943-3559



Program

Dec 18 (Sat) 2010 Oral session @ 301A (Convention Center) Presiding Officers: Yasuji Muramatsu, Jun Kawai, Anthony W Van Buuren	
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7:35 AM-7:50 AM	653. Application of soft X-ray PEEM to the observations of electronic structure, valence state and molecular orientation at nanoscale <u>Y. Baba</u> ; T. Sekiguchi; I. Shimoyama; N. Hirao; A. Narita
7:50 AM-8:05 AM	654. Velocity map imaging for the characterization and diagnostics of molecular beams H. Katayanagi; <u>K. Mitsuke</u>
8:05 AM-8:25 AM	655. Ultimate-resolution soft X-ray microspectroscopy <u>R. H. Fink</u> ; J. Raabe; C. Hub; I. Schmid
8:25 AM-8:45 AM	656. Automated assay of internally mixed individual particles using X-ray spectromicroscopy maps <u>R. Moffet</u> ; T. Henn; A. Laskin; M. Gilles
8:45 AM-9:25 AM	657. Recent soft X-ray developments at the Australian Synchrotron <u>R. Lamb</u> ; B. Cowie; A. Buckley; W. Skinner; F. Larkins
9:25 AM-10:05 AM	658. 3-D photoelectron microscopy and soft X-ray emission spectroscopy for nanodevices at spring-8 University of Tokyo beamline <u>M. Oshima</u>
10:05 AM-10:20 AM	659. Ultrahigh resolution soft X-ray emission spectrometer at BL07LSU of SPring-8 <u>Y. Harada</u> ; M. Kobayashi; M. Oshima; Y. Senba; H. Ohashi; T. Tokushima; Y. Horikawa; S. Shin
10:20 AM-10:35 AM	660. Highly efficient soft X-ray emission spectrometer using a transmission grating H. Yamane; T. Hatsui; N. Kosugi
10:35 AM-10:50 AM	661. Angular anisotropy of X-ray emission from acetic acid molecules in solution <u>Y. Horikawa</u> ; H. Arai; T. Tokushima; A. Hiraya; S. Shin
10:50 AM-11:10 AM	662. Silicon drift detector applications in soft X-ray absorption spectroscopy T. Regier; R. Blyth; D. Chevrier; D. Beauregard; A. Achkar; H. Wadati; D. Hawthorn
11:10 AM-11:25 AM	663. Palmtop EPMA <u>J. Kawai</u> ; E. Hiro

Dec 18 (Sat) 2010 Oral session @ 301A (Convention Center) Presiding Officers: Louis J Terminello, Clemens Heske, Alexander Moewes	
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12:50 PM-1:05 PM	699. Electronic states of carbon in iron phthalocyanine-based oxygen reduction catalysts by soft X-ray absorption spectroscopy H. Niwa; M. Saito; M. Kobayashi; Y. Harada; M. Oshima; S. Moriya; K. Matsubayashi; Y. Nabae; S. Kuroki; T. Ikeda; K. Terakura; J. Ozaki; S. Miyata
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	S. G. Minasian; E. R. Batista; K. S. Boland; J. A. Bradley; D. L. Clark; S. D. Conradson; S. A. Kozimor; W. W. Lukens; R. L. Martin; G. T. Seidler; D. K. Shuh; T. Tyliczszak; P. Yang
1:25 PM-1:45 PM	701. Soft X-ray absorption spectroscopy and theory to elucidate the role of 5f electrons in actinide materials R. Copping; B. Jeon; S. Teat; T. Tyliczszak; N. Gronbech-Jensen; A. Canning; G. Szigethy; K. N. Raymond; <u>D. Shuh</u>
1:45 PM-2:25 PM	702. Soft X-ray resonant inelastic scattering: A selective probe in materials science M. Agaker; J. Nordgren
2:25 PM-3:05 PM	703. Application of resonant inelastic X-ray scattering to molecules and solids <u>D. Lindle</u>
3:05 PM-3:20 PM	704. Surface and size manipulation of the magnetic properties of CdSe quantum dots R. Meulenber; J. Lee; S. McCall; K. Hanif; D. Haskel; J. Lang; L. Terminello; <u>T. van Buuren</u>
3:20 PM-3:35 PM	705. In situ X-ray spectroscopy for investigation of advanced materials for electrical energy storage <u>J. R. Lee</u> ; T. M. Willey; M. H. Nielsen; J. Guo; J. Dahn; T. van Buuren
3:35 PM-3:55 PM	706. Understanding bandgap and electronic structure of crystalline materials <u>A. Moewes</u> ; T. Boyko
3:55 PM-4:10 PM	707. Bandgap profile across a silicon oxynitride ultrathin film epitaxially grown on 6H-SiC(0001), studied by XES and XAS <u>H. Tochiyara</u> ; S. Mizuno; T. Shirasawa
4:10 PM-4:25 PM	708. Characterization of graphite-like layered material BC₂N by X-ray absorption and emission spectroscopy <u>M. Kawaguchi</u> ; H. Yamamoto; Y. Muramatsu

(Group Photo)

Dec 18 (Sat) 2010	
Oral session @ 301A (Convention Center)	
Presiding Officers: Rupert C. C. Perera, Tsutomu Kurisaki	
7:00 PM-7:40 PM	811. Recent new soft X-ray spectrometers developed for the analysis of biochemical samples <u>H. Wakita</u> ; T. Kurisaki; S. Matsuo; R. C. Perera; J. H. Underwood
7:40 PM-7:55 PM	812. Characterization of minerals and archeological samples by soft X-ray spectroscopy <u>T. Kurisaki</u> ; D. Tanaka; S. Kokubu; H. Wakita
7:55 PM-8:15 PM	813. Complementary spectro-microscopic techniques: Chemical composition and properties of atmospheric aerosols <u>M. Gilles</u> ; R. Moffet; A. Laskin
8:15 PM-8:35 PM	814. Metals in the environment: Understanding environmental issues through quantitative analysis of X-ray absorption spectroscopy <u>J. Cutler</u> ; J. Warner; L. Van Loon
8:35 PM-8:50 PM	815. Behavior of chlorine in fly ash during dioxin formation <u>M. Takaoka</u> ; T. Fujimori; K. Oshita

Dec 19 (Sun) 2010

Poster session @ Kamehameha Halls II & III (Convention Center)

Presiding Officers: Yasuji Muramatsu

10:00 AM-12:00 PM	893. X-ray absorption spectroscopic characterization of phosphorus-doped TiO₂ with visible-light photocatalytic activity M. Iwase; K. Yamada; T. Kurisaki; H. Wakita
10:00 AM-12:00 PM	894. Adsorption behavior of tellurium oxoanion on d-MnO₂ Y. Katsuyama; C. Numako; Y. Okaue; T. Yokoyama
10:00 AM-12:00 PM	895. Quantitative analysis method of nitrogen in graphitic carbon materials using total-electron-yield soft X-ray absorption spectroscopy T. Amano; Y. Muramatsu; E. M. Gullikson
10:00 AM-12:00 PM	896. Local-structure analysis of the oxidized graphitic carbon dispersoids using soft X-ray absorption spectroscopy N. Inoue; Y. Muramatsu; Y. Aoyama; M. Kawaraya; H. Hisashi; E. M. Gullikson
10:00 AM-12:00 PM	897. Total-electron-yield soft X-ray absorption spectroscopy for the quantitative analysis of carbon materials Y. Muramatsu; E. M. Gullikson
10:00 AM-12:00 PM	898. X-ray fluorescence imaging of growing chemical patterns K. Sakurai; M. Mizusawa
10:00 AM-12:00 PM	899. Measurement of unpaired electron species in dry DNA thin films irradiated with synchrotron soft X-rays around oxygen and nitrogen K-edge studied by EPR T. Oka; A. Yokoya; K. Fujii; Y. Fukuda; M. Ukai

Abstract

653, Oral

Application of soft X-ray PEEM to the observations of electronic structure, valence state and molecular orientation at nanoscale

*Y. Baba*¹; *T. Sekiguchi*¹; *I. Shimoyama*¹; *N. Hirao*¹; *A. Narita*¹

1. Japan Atomic Energy Agency, Ibaraki, Japan.

Up to now, various types of microscopies using micro-focused beams have been developed for the observation of materials. However, for the observation of organic and biological materials, irradiation of micro-focused electron and ion beams causes serious damages on the molecular structures. Also most of the microscopies provide only the information about the surface morphology, elemental composition and crystal structure. It should be noted that the electric and optical properties of a material also depend on the surface electronic structures and valence states at nanometer domains. For thin films of organic molecules, the molecular orientation at nanometer scale also influences the electric and optical properties. In order to observe microscopic images including the above information, we have developed a photoelectron emission microscopy (PEEM) system combined with linearly polarized soft X-rays from synchrotron light source. The PEEM used was an imaging-type, where the total photoelectrons emitted from the surface were expanded using electrostatic lenses, and focused on a screen. By tuning the X-ray energy around the ionization thresholds of the elements, we can observe near-edge X-ray absorption fine structure (NEXAFS) at each microscopic domain in the PEEM images, which gives information about the electronic structures and valence states. For thin films of organic molecules, linearly polarized feature of X-rays also give information about the molecular orientations at nanometer scale. As applications of the present system, we will present the following topics.

- 1) Quick observation (~10ms) of PEEM images by focused soft X-rays using polycapillary lens.
- 2) Chemical-state-selective mapping of silicon compounds at nanometer scale.
- 3) Real-time observation of growth and diffusion of organic silicon thin films.
- 4) Microscopic observation of molecular orientations of organic silicon thin films.

654, Oral**Velocity map imaging for the characterization and diagnostics of molecular beams**

K. Mitsuke^{1, 2}; *H. Katayanagi*^{1, 2}

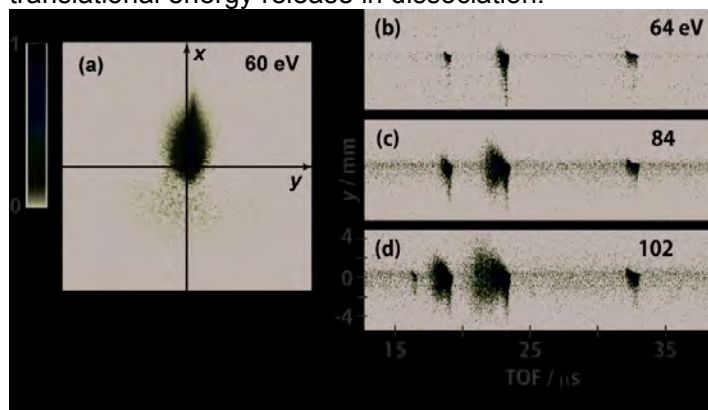
1. Institute for Molecular Science, Okazaki, Japan.

2. Graduate University for Advanced Studies, Okazaki, Japan.

We have developed a velocity map imaging (**VMI**) method to determine the three-dimensional velocity distributions (**3DVD**) of molecular beams used for in-vacuo thin-film deposition techniques, such as molecular beam epitaxy. Our apparatus is based on a photoionization mass spectrometer into which a **VMI** focusing lens system was incorporated to project the **3DVD** of a molecular beam onto a position sensitive detector (PSD) as a two-dimensional (2D) map. Our device is applicable to heterogeneous beams containing multiple chemical species, because their **3DVD** can be reconstructed individually from the 2D map.

We have demonstrated how our **VMI** machine works using a C_{60} beam. C_{60} powder was heated and a beam was generated along the x -axis of the PSD. The beam intersected with synchrotron radiation which propagated along the y -axis. The produced ions were extracted along the z -axis by the lenses, and projected onto the PSD. Photoelectrons were used as the start trigger of TOF measurements. Arrival times t and positions (x, y) of the ions on the PSD were recorded.

Fig. 1a shows the x - y map of the C_{60} beam. An intense stripe in the x -direction is mainly due to C_{60}^{2+} . The x - and y -distributions (**y-Dis**) are found to be governed by the temperature and geometry, respectively, of the C_{60} oven source. The mass-to-charge ratios m/z of the photoions can be obtained from t using the y - t maps of Figs. 1b-1d. The width in the y -direction of each spot is equal to the 1D projection of the **3DVD** of the ions having the same m/z . The marked three spots in Fig. 1b were ascribable to C_{60}^{z+} ($z=1-3$). These spots have narrow **y-Dis**, reflecting the beam sufficiently collimated. Subtle stripes in Figs. 1c and 1d with broader **y-Dis** are seen on the left of the parent ions' spots; the stripes are assigned to the fragments, e.g. C_{58}^{z+} and C_{56}^{z+} , produced by successive ejection of C_2 units from C_{60}^{z+} . The broader **y-Dis** of the stripes are direct evidence for translational energy release in dissociation.



2D maps of the photoions from a C_{60} beam at different photon energies. (a) map of the x - and y -positions. (b)-(d) Maps of the arrival time and y -position.

655, Oral Ultimate-resolution soft X-ray microspectroscopy

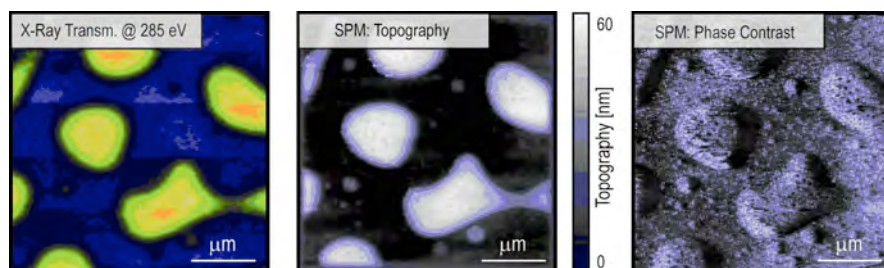
*R. H. Fink*¹; *J. Raabe*²; *C. Hub*¹; *I. Schmid*²

1. Physical Chemistry 2, University of Erlangen, Erlangen, Germany.

2. Paul Scherrer Institute, Erlangen, Germany.

Zone-plate based microspectroscopes are currently installed at all major synchrotron facilities. Based on recent improvements in the fabrication of nanoscaled zone-plates with high aspect ratios lateral resolutions on the order of about 10 nm were achieved. We have set up two spectromicroscopes at bending magnet beamlines of the Swiss Light Source (SLS), which offer versatile experimental opportunities for thin film analysis at ultimate resolution. The PolLux-STXM is a state-of-the-art scanning transmission x-ray microspectroscope. It includes different contrast modes like phase contrast or surface-sensitive detection modes using the parallel detection of secondary electrons emitted from the irradiated spot. NanoXAS is a combined STXM and AFM, thus offering direct correlation of chemical and morphological properties. A modified conductive AFM-tip even allows spatial resolutions below the diffraction limit of the STXM zone plate (goal: 6 nm).

We report on recent applications of these instruments with particular emphasis on in-situ variations, e.g., operation of organic field-effect transistors or solar cells or thermo-responsive microgels. Chemical or electronic modifications are monitored by the spectral changes in the NEXAFS fine structures. Some other prototype experiments include proton-irradiated graphene-layers, polymer blends and block copolymer films, environmentally relevant materials, nanoparticles, or magnetic nanostructures. In the latter case, time-resolved studies with picosecond resolutions are combined with highest spatial resolution to study magnetization dynamics in confined magnetic structures. The project is funded by the BMBF (project 05 KS7WE1).



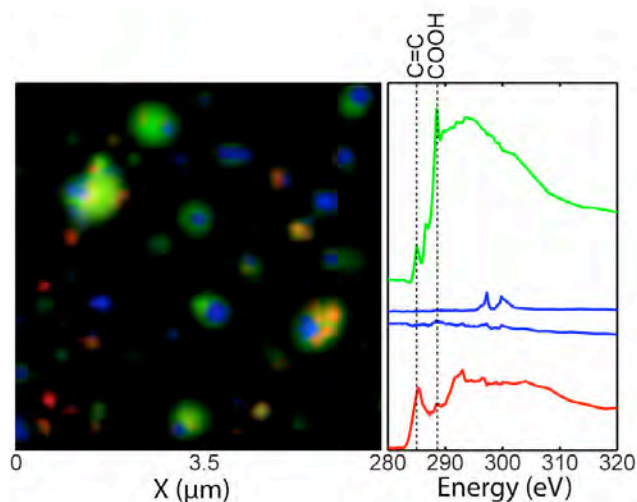
Polymer blend film imaged in the NanoXAS instrument showing x-ray transmission (left), SPM topography (center) and SPM-phase shift (right). All images were recorded in-situ.

656, Oral**Automated assay of internally mixed individual particles using X-ray spectromicroscopy maps***R. Moffet¹; T. Henn¹; A. Laskin²; M. Gilles¹*

1. Lawrence Berkeley National Laboratory, Berkeley, CA, United States.

2. Environmental and Molecular Sciences Laboratory (EMSL), Pacific Northwest National Laboratory, Richland, WA, United States.

We have developed an automated data analysis method for atmospheric aerosols using scanning transmission X-ray microscopy coupled with near edge X-ray fine structure spectroscopy (STXM/NEXAFS). This method is applied to complex internally mixed nanometer-sized aerosol particles containing organic and inorganic material. Several algorithms were developed to exploit spectral features in the energy range from 278-320 eV for quantitative mapping of the spatial distribution of elemental carbon, organic carbon, potassium, and non-carbonaceous elements in mixed particles. Features in this spectral range encompass the carbon K-edge and potassium L2 and L3 edges. Maps of the different chemical components were confirmed with a subsequent analysis using scanning electron microscopy coupled with energy dispersive X-ray analysis. This automated mapping allows for the statistical classification of an arbitrarily large number of particles. Such statistical results are crucial in the field of particle analysis.



Composition map of atmospheric aerosol particles (left) and representative spectra/factors (right) at the carbon K-edge derived by positive matrix factorization (PMF). Organic components are depicted as green, soot as red and inorganics as blue.

657, Invited

Recent soft X-ray developments at the Australian Synchrotron

*R. Lamb*¹; *B. Cowie*²; *A. Buckley*³; *W. Skinner*⁴; *F. Larkins*⁵

1. School of Chemistry, University of Melbourne, Melbourne, VIC, Australia.
2. Australian Synchrotron, Melbourne, VIC, Australia.
3. School of Chemistry, University of New South Wales, Sydney, NSW, Australia.
4. Ian Wark Research Institute, University of South Australia, Adelaide, SA, Australia.
5. University of Melbourne, Melbourne, VIC, Australia.

The state of the art soft X-ray beam-line at the Australian Synchrotron (AS) consists of an elliptically polarising undulator and a plane grating monochromator operating over a wide energy range (90 – 2500 eV). Time consuming sample loading, preparation and experimental incompatibilities significantly reduce the efficiency of the single beamline – particularly for the massive range of sample types/ vacuum spectroscopic analyses.

The primary end-station at the AS, designed specifically for soft X-ray spectroscopy, consists of separate introduction, preparation and analysis chambers deployed around a rotary distribution chamber. Its design was a collaborative effort of the Australian user community together with commercial innovations from both OmniVac (specimen transfer system) and PreVac (two-blade fracture stage). The entire system was commissioned in Taiwan with support from the staff at the NSRRC. A similar instrument design has now been commissioned for a laboratory-based XPS.

The end-station incorporates a number of features including clean UHV, a high resolution electron energy analyser for XPS, a partial yield detector for PEY and TFY NEXAFS spectroscopy, a removable glove box that can be mounted around the sample introduction chamber, a robust specimen transfer system that allows fracture under UHV of materials such as minerals in a two-blade fracture stage, and the ability to cool a specimen before subjecting it to UHV to retain any surface species that might otherwise sublime, and to minimize beam damage of X-ray-sensitive samples.

It is capable of dealing with samples ranging from minerals to single crystal semiconductors without the usual cross-contamination issues.

Some research examples illustrating the end-station performance will be presented. A branch line, currently being developed for imaging applications, will also be discussed.

658, Invited

3-D photoelectron microscopy and soft X-ray emission spectroscopy for nanodevices at spring-8 University of Tokyo beamline

M. Oshima¹

1. Department of Applied Chemistry, The University of Tokyo, Tokyo, Japan.

The University of Tokyo has constructed a new soft X-ray undulator beamline for materials science, that is "University-of-Tokyo Synchrotron Radiation (SR) Outstation" at SPring-8 BL07LSU, in collaboration with RIKEN and JASRI. Eight figure-8-type undulators consisting of four horizontally-polarized undulators and four vertically-polarized ones are installed in a 30 m-long straight section of SPring-8. The undulators can provide us with polarization-controlled soft X-rays (SX) in the photon energy range from 250 eV to 2 keV. Various kinds of experiments including time-resolved photoemission have started to be performed for nano-devices last autumn. The first project is three dimensional photoelectron microscopy, named 3DnanoESCA, where electronic structures of the sample irradiated by several-tens-nm size SX beam can be investigated by angle-resolved photoelectron spectroscopy. The pin-point in-depth profiles of the electronic structures can be obtained by maximum entropy method (MEM) analysis for CMOS gate stacks (TiN/LaO/HfSiON/SiON/Si substrates and so on), quantum dots, environmental catalysts and other nano-fabricated materials. Line profiling of wedge-shape polished surfaces of GaN/ZnO samples can provide us with in-depth chemical profiles and interfacial band bending profiles. The second project is soft X-ray emission spectroscopy with higher energy resolution than 10,000 for biomaterials and polymer electrolyte fuel cells under operation, where sub-micron SX beam is incident on liquid/solid interfaces.

659, Oral

Ultrahigh resolution soft X-ray emission spectrometer at BL07LSU of SPring-8

Y. Harada^{1, 2}; M. Kobayashi^{1, 2}; M. Oshima^{1, 2}; Y. Senba⁴; H. Ohashi⁴; T. Tokushima³; Y. Horikawa³; S. Shin^{3, 5}

1. Applied Chemistry, The University of Tokyo, Tokyo, Japan.
2. Synchrotron Radiation Research Organization, University of Tokyo, Hyogo, Japan.
3. RIKEN/SPring-8, Hyogo, Japan.
4. JASRI/SPring-8, Hyogo, Japan.
5. Institute for Solid State Physics, The University of Tokyo, Chiba, Japan.

An extremely high-resolution flat-field-type slit-less soft X-ray emission spectrometer has been designed and constructed for a long undulator beamline BL07LSU of SPring-8. The spectrometer is optimized for the energy range 300-800 eV by using two cylindrical valid line spacing gratings [1]. The spot size of the illuminated area on a sample is less than 1 μ m which is small enough to achieve $E/\Delta E > 10\,000$. Back-illuminated type CCD detector is used for its high spatial resolution (effectively $\sim 25\mu$ m). Parameters of the gratings are optimized under the following conditions;

1. Keep length from the grating to the detector $L > 1500$ mm and the focal plane at small (~ 20 deg) angle with the incoming beam in order to loosen the restriction by the spatial resolution of the detector.
2. Keep length from the sample to the grating $l < 800$ mm in order to increase the acceptance angle.
3. Overlap the focal plane for the two gratings by sharing all aberration correction parameters of the VLS grating except for b3.

By using optimized ruling parameters and $L = 1961$ mm and $l \sim 600$ mm, high energy resolution $E/\Delta E \sim 10\,000$ is obtained for the optimized energy 500 eV (around O 1s edge). This value includes the restriction by the spatial resolution of the CCD detector. A coma-free operation proposed by V. Stokov et al. [2] is also applied, where l and the incident angle of the grating α are adjusted for any incident energy in order to eliminate defocus and coma aberration. In order to gain high detection efficiency of this photon-hungry experiment, we have added two pre-focusing cylindrical mirrors in non-dispersive direction that has been already installed at BL17SU of SPring-8. In this presentation, details of the optical design and some of the experimental results will be shown.

[1] T. Tokushima et al., Rev. Sci. Instrum. 77, 063107 (2006).

[2] V. N. Stokov et al., PSI Technical Report SLS-SPC-TA-2008-309. PSI, Villigen, Switzerland (2008).

660, Oral**Highly efficient soft X-ray emission spectrometer using a transmission grating**

*H. Yamane*¹; *T. Hatsui*²; *N. Kosugi*¹

1. Department of Photo-Molecular Science, Institute for Molecular Science, Okazaki, Aichi, Japan.
2. XFEL Project Head Office, RIKEN, Sayo, Hyogo, Japan.

The X-ray emission spectroscopy (XES) is a powerful method to study element-specific excitations and occupied partial density of states of gases, liquids, and solids. However, there is a serious problem in the conventional XES using a grazing-incidence spectrometer; that is, a rather low efficiency arising from various factors, e.g., the number of focusing elements for emitted X-rays (horizontal direction only), and the low acceptance angle and quantum efficiency at charge-coupling devices (CCD). Moreover, these factors sacrifice the energy resolution. Such problems are in general solved by the use of high brilliant X-rays of 10^{12} - 10^{13} photons/s. In this case, however, one has to take care of radiation damage, in particular for soft materials such as organic and biomolecular systems.

In order to overcome these problems, we have developed a highly efficient X-ray emission spectrometer using a transmission grating (TG) at UVSOR BL3U [1]. The spectrometer adopts a novel optical design with a Wolter type I mirror, a free-standing TG, and a back-illuminated CCD, which realizes the normal-incidence geometry for the CCD detector. A TG made of SiC with the groove density $D_g = 6250$ lines/mm (160 nm period) was evaluated as a prototype TG. However, the 160 nm period was found to contain serious distortions in the groove structure due to technical difficulties in the e^- -beam lithography. To get a high precision TG, a new TG has been fabricated with $D_g = 5555$ lines/mm (180 nm period). Now we have preliminary obtained the energy resolution of 35 meV for Si 2p region, $E/\Delta E > 3500$, with the high efficiency of 1 spectrum/h for 10^{11} photons/s.

We will discuss 1) the recent progress in our TG spectrometer and 2) site-specific intermolecular interactions of functional organic solids probed by XES.

[1] T. Hatsui *et al.*, *J. Electron Spectrosc. Relat. Phenom.* **144-147**, 1059 (2005).

661, Oral**Angular anisotropy of X-ray emission from acetic acid molecules in solution**

Y. Horikawa^{1, 2}; *H. Arai*¹; *T. Tokushima*¹; *A. Hiraya*²; *S. Shin*^{1, 3}

1. Excitation Order Research Team, RIKEN Harima Institute, Sayo-gun, Japan.

2. Hiroshima University, Higashi-Hiroshima, Japan.

3. Institute for Solid State Physics, The University of Tokyo, Kashiwa, Japan.

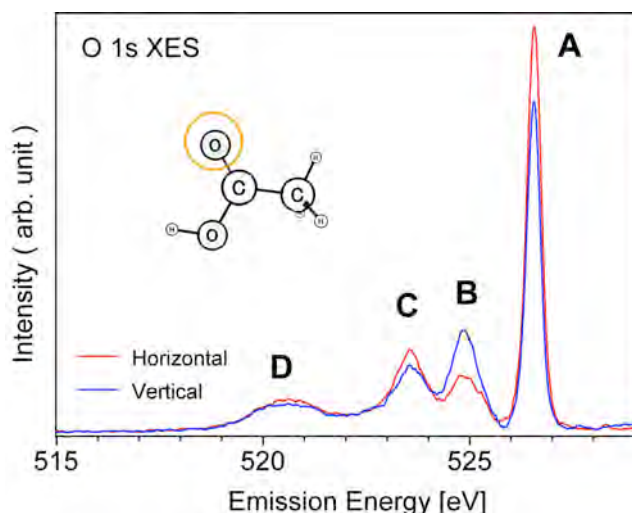
The electronic structure of a material is important for many fields of science, because valence electrons play important roles in properties. Due to its importance in chemistry and chemical physics, some studies have been reported observing electronic structure of liquid using X-ray absorption and emission spectroscopy (XAS and XES). Recently, we have demonstrated site-specific observations of O(C=O) and O(O-H) oxygen for liquid acetic acid under ambient conditions using XES through site-selective excitations [1]. This method was applied to the selective observation of acetic acid in aqueous solution. Occupied valence electronic structures in the neutral and the anionic forms of aqueous acetic acid and their pH dependence have been identified for the first time [2]. These two results suggest that electronic states of acetic acid molecule in solutions are not disturbed so much as expected. In order to investigate the effect of solvation on electronic states in detail, we observe the angular anisotropy of XES from acetic acid in solution.

XES spectra were recorded at synchrotron radiation facility at the beamline BL17SU in SPring-8. The acetic acid solutions were prepared by mixing acetic acid and acetonitrile.

Figure is the O 1s XES spectra for acetic acid in acetonitrile solution. Clear dependence on polarization of excitation light is observed in measured resonant XES spectra, and is simply explained by considering that the molecular orientation is selected by excitation process. Symmetries of each peaks obtained from measured spectra are consistent with the assignment of our previous report [1]. The anisotropy ratios have been evaluated from XES peak intensities. Peak A shows a good fit with the theoretical values, and the trends of peak B expected for free molecules are qualitatively retained.

[1] T. Tokushima and Y. Horikawa et al., Phys. Chem. Chem. Phys. 2009, 11, 1679.

[2] Y. Horikawa and T. Tokushima et al., Phys. Chem. Chem. Phys. 2009, 11, 8676.



XES spectra of acetic acid in acetonitrile obtained for the O(C=O) 1s \rightarrow π^* excitation with horizontal polarization (red line) and vertical polarization (blue line).

662, Oral

Silicon drift detector applications in soft X-ray absorption spectroscopy

T. Regier¹; R. Blyth¹; D. Chevrier¹; D. Beaugard¹; A. Achkar²; H. Wadati³; D. Hawthorn²

1. Canadian Light Source, University of Saskatchewan, Saskatoon, SK, Canada.

2. Department of Physics, University of Waterloo, Waterloo, ON, Canada.

3. Department of Physics and Astronomy, University of British Columbia, Vancouver, BC, Canada.

We report on the integration and operation of a 30 mm² Silicon Drift Detector (SDD) installed on the endstation of the SGM (11ID-1) beamline at the Canadian Light Source (CLS). Development of an EPICS interface layer was completed to allow full control and readout capabilities of the detector within the current beamline control architecture. This facilitates the collection of a complete X-Ray Fluorescence (XRF) spectrum for each excitation energy in a Near Edge X-ray Absorption Fine Structure (NEXAFS) measurement. The new capability allows for the easy identification of 2nd order and scattering contributions to the total fluorescence yield. It also allows for the acquisition of the Partial Fluorescence Yield (PFY) from the on and off resonance elements in the sample. We demonstrate exciting results that show that the Inverse PFY (IPFY) from an off resonant element can, under certain conditions, be used as a self absorption free probe of the bulk X-ray absorption cross section. Examples of these new applications will be presented and discussed for several different sample systems.

663, Oral Palmtop EPMA

*J. Kawai*¹; *E. Hiro*¹

1. Department of Materials Science and Engineering, Kyoto University, Kyoto, Japan

Two pyroelectric single crystals (LiTaO₃), the size of which were 3 x 3 x 10 mm³, were used as a series circuit [1] to electrify a target sample material (one crystal was to electrify the target, and another was to electrify the electron emitter). The crystals were heated or cooled by Peltier devices. The target was bombarded by an electron beam of energy 80 keV [2], to produce characteristic X-ray emission from the sample. The vacuum was 0.01 Torr, and the X-rays continued emitting for 5 minutes. The beam size is now a few mm size, thus EPMA is an abbreviation of Electron Probe Milli Analyzer, but with the use of focusing lens and STM needle as an electron emitter, this will become an Electron Probe Micro Analyzer in the near future. We have checked in fact that the STM needle is a good electron emitter when attached to one end of the pyroelectric single crystal. Cu-Zn alloy (brass) was put on one end of the single crystal and Cu and Zn Ka peaks were detected up to thousands of counts for one thermal cycle of the pyroelectric crystal. The size of the cylindrical glass vacuum vessel was 5 cm length and 4 cm diameter (Fig.1). The X-ray window was Kapton film. X-ray spectra were measured by Amptek Si-PIN or CdTe detector.

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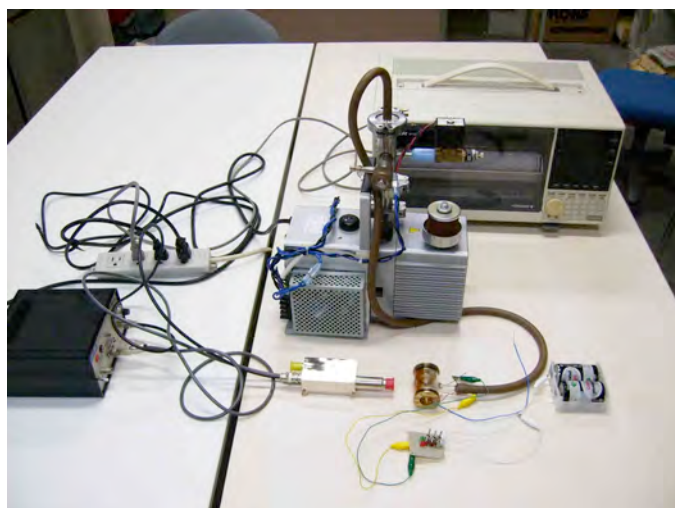


Fig.1 Photo of palmtop EPMA. Electric batteries with polarity changer, rotary pump, Amptek detector & controller, thermocouple recorder, and glass vacuum vessel are shown.

698, Oral

Soft X-ray spectroscopy of materials for photoelectrochemical devices

*C. Heske*¹; *M. Bär*²; *L. Weinhardt*³

1. Chemistry, University of Nevada, Las Vegas, Las Vegas, NV, United States.

2. Solar Energy Research, Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Berlin, Germany.

3. Experimentelle Physik VII, Universität Würzburg, Würzburg, Germany.

The purpose of this talk is to demonstrate how a tool chest of soft x-ray spectroscopies (in particular using high-brilliance synchrotron radiation) is uniquely suited to unravel the electronic and chemical properties of candidate materials for photoelectrochemical (PEC) water splitting. We will show how photoelectron spectroscopy (PES), inverse photoemission (IPES), x-ray emission spectroscopy (XES), and x-ray absorption spectroscopy (XAS) can be suitably combined to derive band gaps as a function of depth, energy level alignments at surfaces and interfaces, local chemical bonding, and insights into chemical stability in ambient environments. As example materials, WO₃ and N-doped ZnO thin films will be discussed.

699, Oral**Electronic states of carbon in iron phthalocyanine-based oxygen reduction catalysts by soft X-ray absorption spectroscopy**

*H. Niwa*¹; *M. Saito*¹; *M. Kobayashi*^{1, 2}; *Y. Harada*^{1, 2}; *M. Oshima*^{1, 2}; *S. Moriya*⁷; *K. Matsubayashi*⁷; *Y. Nabae*⁷; *S. Kuroki*⁷; *T. Ikeda*⁴; *K. Terakura*³; *J. Ozaki*^{5, 7}; *S. Miyata*^{6, 7}

1. Applied Chemistry, School of Engineering, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo, Japan.

2. Synchrotron Radiation Research Organization, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo, Japan.

3. Research Center for Integrated Science, Japan Advanced Institute of Science Technology, Asahidai, Nomi, Ishikawa, Japan.

4. Quantum Beam Science Directorate, Japan Atomic Energy Agency, Kouto, Sayo-cho, Sayo-gun, Hyogo, Japan.

5. Department of Chemical & Environmental Engineering, Graduate School of Engineering, Gunma University, Tenjin-cho, Kiryu, Gunma, Japan.

6. New Energy and Industrial Technology Development Organization, Omiya-cho, Saiwai-ku, Kawasaki, Kanagawa, Japan.

7. Department of Organic and Polymeric Materials, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo, Japan.

The carbon-based materials such as carbon alloy catalysts (CACs) show high oxygen reduction reaction (ORR) activities [1,2] and are expected to be cathode catalyst alternative to Pt for Polymer Electrolyte Fuel Cells. The origin of their ORR activities should be elucidated to further enhance the activities. So far, we have studied the metal phthalocyanine-based CACs and have reported the importance of graphite-like nitrogen and the neighboring carbon at the zigzag edge of graphite [3,4]. Recently, it has been revealed that the catalysts synthesized from iron phthalocyanine/phenolic resin (FePc/PhRs) heat treated at 600 °C show the maximum ORR activity [5]. In order to investigate the relationship between the carbon structure in FePc/PhRs catalysts and the electronic states of carbon in the catalysts have been analyzed by carbon 1s soft X-ray absorption spectroscopy (XAS).

The samples were derived from pyrolyzed FePc and PhRs. The temperature range for the pyrolysis was from 200 °C to 800 °C (Fe200 – Fe800).

C 1s XAS measurements were performed at BL-7A of the Photon Factory, KEK (Japan).

Figure 1 shows C 1s XAS spectra of the FePc/PhRs catalysts. In each samples, π^* resonance peak is observed around ~285 eV. Besides, a shoulder component around ~284 eV (E^*) is observed in the highest ORR active catalysts such as Fe600. This component reflects the unique electronic states called edge states, which is characteristic of the zigzag edge of graphite [6]. This result is well consistent with our previous study that graphite-like nitrogen and the neighboring carbon at the zigzag edge should be ORR active site [3,4].

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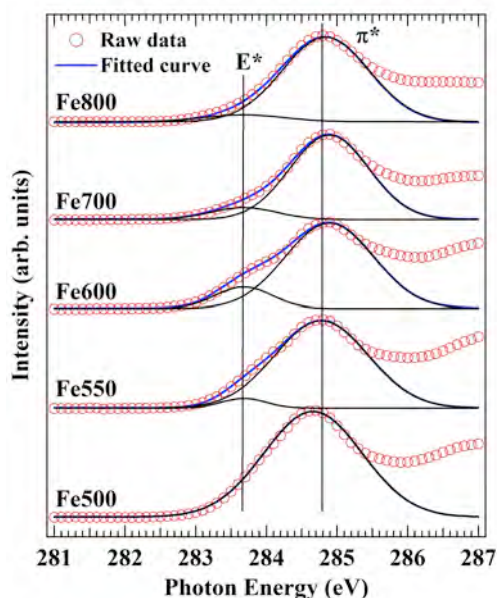
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700, Oral**Quantitative covalency measurements in tetrahedral MO_4^- anions (M = Mn, Tc, Re) using oxygen K-edge XAS and NRIXS spectroscopy**

S. G. Minasian^{1, 2}; *E. R. Batista*¹; *K. S. Boland*¹; *J. A. Bradley*⁴; *D. L. Clark*¹; *S. D. Conradson*¹; *S. A. Kozimor*¹; *W. W. Lukens*²; *R. L. Martin*¹; *G. T. Seidler*⁴; *D. K. Shuh*²; *T. Tyliczszak*²; *P. Yang*³

1. Inorganic, Isotope and Actinide Chemistry, Los Alamos National Laboratory, Los Alamos, NM, United States.

2. Chemical Sciences, Lawrence Berkeley National Laboratory, Berkeley, CA, United States.

3. W.R. Wiley Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, Richland, WA, United States.

4. Physics, University of Washington, Seattle, WA, United States.

The group VII MO_4^- anions provide a foundational model of bonding and electronic structure in a large family of highly reactive compounds that contain metal-oxygen multiple bonds. In this study, the extent of transition metal-oxygen orbital mixing in $\text{K}[\text{MnO}_4]$, $[\text{Ph}_4\text{P}][\text{TcO}_4]$, and $\text{Na}[\text{ReO}_4]$ is quantified using O K-edge X-ray absorption spectroscopy (XAS) and non-resonant inelastic X-ray scattering (NRIXS) measurements. Ground state hybrid DFT calculations with relativistic effective core potentials (RECPs) were used to evaluate the electronic structure in each system, while time dependent-density functional theory (TD-DFT) was used to calculate the energies and intensities of O 1s transitions into empty metal-based orbitals containing O 2p character. Using $\text{Na}[\text{ReO}_4]$ as a well-defined energy and intensity standard, the amount of orbital mixing was quantified in $\text{K}[\text{MnO}_4]$ and $[\text{Ph}_4\text{P}][\text{TcO}_4]$ and verified by TD-DFT. Future efforts will leverage these results to evaluate covalency in actinide-oxygen bonds, where the near degeneracy of O 2p and actinide 5f- and 6d-orbitals are anticipated to provide significant orbital mixing.

701, Oral

Soft X-ray absorption spectroscopy and theory to elucidate the role of 5f electrons in actinide materials

*D. Shuh*¹; *R. Copping*¹; *B. Jeon*^{2, 3}; *S. Teat*⁴; *T. Tyliczszak*⁴; *N. Gronbech-Jensen*²; *A. Canning*^{2, 3}; *G. Szigethy*^{1, 5}; *K. N. Raymond*^{1, 5}

1. Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA, United States.

2. Dept. of Applied Science, Univ. of California, Davis, Davis, CA, United States.

3. Computational Research Division, Lawrence Berkeley National Laboratory, Berkeley, CA, United States.

4. Advanced Light Source Division, Lawrence Berkeley National Laboratory, Berkeley, CA, United States.

5. Dept. of Chemistry, Univ. of California, Berkeley, Berkeley, CA, United States.

The degree of participation of 5f-electrons in bonding is a fundamental issue and probing actinide complexes and materials with soft x-rays is a useful approach to elucidate 5f-electron behavior. Uranyl complexes with the 2,6-Bis(2-benzimidazolyl)pyridine (BBP) ligand have been examined by scanning transmission x-ray microscopy (STXM) at the light element K-edges and f-element N-edges in the soft x-ray region of synchrotron radiation by near-edge x-ray absorption fine structure (NEXAFS) spectroscopy. First-principles electronic structure calculations of the f-electron bonding reveals hybridization of U atom f-like states with oxygen and nitrogen states. Full relaxation of the resultant structure and calculated model structures with different halogen substitutions shows that the angle of the BBP ligand with respect to the uranyl is determined by steric considerations. Plutonium(IV) complexes formed with maltol and bromomaltol ligands have been investigated with the density functional theory formalism within the local density approximation. The ground state of each conformation was evaluated and the LSDA+U approach was employed to more accurately model the strong on-site Coulomb repulsion of Pu 5f-electrons. Full atomic relaxation was carried out for the different complexes and their total energies compared. The results indicate that several conformations can yield similar energy states, corresponding to the mixture of observed conformations found in the crystalline forms of the bromomaltol complexes. Soft x-ray NEXAFS combined with theory can impact the understanding of 5f-bonding in a range of materials and has the potential to aid in the design of special-purpose actinide materials and ligands.

702, Invited

Soft X-ray resonant inelastic scattering: A selective probe in materials science

*M. Agaker*¹; *J. Nordgren*¹

1. Dept of Physics and Astronomy, Uppsala University, Uppsala, Sweden.

Resonant soft X-ray inelastic scattering spectroscopy (RIXS) has evolved into quite a wide-spread technique for the study of the electronic structure of materials in various phases and forms. The demanding quality of X-ray sources associated with this spectroscopy, which used to be an obstacle, is often met at most modern synchrotron radiation facilities today. Also, new developments in instrumentation are continuously adding new capabilities to the method. The chemical selectivity offered by resonant inelastic soft X-ray scattering makes this a suitable technique for the study of complex systems. Additionally, the depth probing capability of soft x-ray spectroscopy allows samples to be studied at ambient conditions, such as e.g. at high pressures, in liquid phase or at buried depths. The talk will address studies of problems in atmospheric corrosion, Li-ion battery materials, and heterogeneous catalysis, aiming at learning about the underlying chemical processes by acquiring detailed information about the electronic structure of these systems in their natural environment. Furthermore, recent design considerations for novel instruments for soft X-ray inelastic scattering spectroscopy will be discussed.

703, *Invited*

Application of resonant inelastic X-ray scattering to molecules and solids

*D. Lindle*¹

1. Chemistry, U. Nevada, Las Vegas, Las Vegas, NV, United States.

Resonant Inelastic X-ray Scattering (RIXS) is a photon-in—photon-out method to probe electronic structure in the valence and core shells of molecules and other forms of matter. While the basic technique has existed since shortly after Roentgen's discovery of x-rays more than a century ago, it has experienced a renaissance the past few decades with the advent of intense, monochromatic, and highly polarized beams of x-rays available from modern synchrotron-radiation facilities. Hand-in-hand with improvements in the x-ray sources have been advances in instrumentation for secondary x-ray-emission spectroscopy. This presentation will emphasize recent results for molecules in both the gas and solid phases, focusing on RIXS near the K edges of chlorine- and sulfur-containing species. Examples will demonstrate the ability to monitor indirectly femtosecond-scale molecular dynamics, as well as the usefulness of measuring polarization of the scattered x-rays as a means to decipher electronic structure and dynamics.

This work is supported by NSF Award No. PHY-0555699. Work at the Advanced Light Source is supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Science Division, of the U.S. Department of Energy under contract No. DE-AC03-76SF00098.

704, Oral

Surface and size manipulation of the magnetic properties of CdSe quantum dots

*T. van Buuren*¹; *R. Meulenberg*^{1, 2}; *J. Lee*¹; *S. McCall*¹; *K. Hanif*³; *D. Haske*⁴; *J. Lang*⁴; *L. Terminello*⁵

1. LLNL, Livermore, CA, United States.

2. Dept Phys & Astron, Surface Sci & Technol Lab, Univ Maine,, Orono, ME, United States.

3. USN, Res Lab,, Washington, DC, United States.

4. Advanced Photon Source, Argonne National Lab, Argonne, IL, United States.

5. PNNL, Richland, WA, United States.

The appearance of magnetism in otherwise nonmagnetic materials had previously been reported for a number of nanoscale systems and is the subject of substantial and ongoing research efforts. This is because coupling the size-dependent optical and electronic properties of the nanocrystalline materials with magnetic behavior opens the possibility for an extended range of technological applications. Significantly, conflicting origins are proposed in the literature for the magnetic behavior exhibited by a range of nanocrystals, which include the presence of dangling bonds on their surfaces, an intrinsic property only present at the nanoscale and an effect of ligands used to passivate the nanostructured material.

We provide conclusive evidence that organic ligands used to coat CdSe nanocrystals have a fundamentally important effect upon their magnetic properties. Using x-ray absorption spectroscopy, magnetometry and x-ray magnetic circular dichroism, the research team demonstrate that the choice of organic ligand can be used to tune the magnetic properties. Moreover, their research indicates that a π -backbonding mechanism between the surface Cd atoms and the organic surfactants is responsible for some of the magnetic behavior of the nanocrystals and that, contrary to previous reports, they are paramagnetic and not ferromagnetic. The potential impact of this research in the field is considerable with the possibility of magneto-optic luminescent nanostructures a point that is emphasized by recognition of the work as a 'Research Highlight' in Nature 2009, 459, 302-303

705, Oral

In situ X-ray spectroscopy for investigation of advanced materials for electrical energy storage

J. R. Lee¹; T. M. Willey¹; M. H. Nielsen²; J. Guo²; J. Dahn³; T. van Buuren¹

1. Lawrence Livermore National Laboratory, Livermore, CA, United States.

2. Lawrence Berkeley National Laboratory, Berkeley, CA, United States.

3. Dalhousie University, Halifax, NS, Canada.

With a projected two-fold increase in worldwide energy consumption during the next 50 years, there is an urgent need for new energy sources to meet the growing demand. A particular emphasis on low- or zero-emission sources (e.g. wind, solar) necessitates the development of more efficient materials for EES with improved capacity and charge/discharge stability. Although numerous materials exhibit great promise for incorporation into next generation devices, their properties are often not well understood and many offer high initial specific capacities only to suffer rapid and unacceptable losses with repeated charge-discharge cycling. In situ characterization of the evolution in electronic structure of these electrode materials during repeated charge-discharge cycling is fundamentally important for more fully understanding the processes of charge storage and degradation, which, in turn, is essential for the development of new EES materials with tailored properties and improved performance. X-ray spectroscopies provide ideal tools with which to obtain enhanced insight into the origins of electrode behavior in EES systems due to their capabilities for direct, element specific, characterization of the electronic densities of states. To date, in situ studies of EES materials have primarily focused on hard x-ray experiments due to the challenges associated with UHV compatibility and high photon attenuation of cells for soft x-ray measurements. Nonetheless, the use of soft x-ray spectroscopies to EES systems is vital since they provide complementary information that cannot be obtained via hard x-ray studies. We report the development of a cell for in situ soft x-ray emission spectroscopy and x-ray absorption spectroscopy studies of EES materials and will discuss experiments focused upon the x-ray spectroscopy characterization of a series of novel electrode materials for application in rechargeable Li-ion batteries. Prepared by LLNL under Contract DE-AC52-07NA27344.

706, Oral

Understanding bandgap and electronic structure of crystalline materials

A. Moewes¹; T. Boyko¹

1. Department of Physics and Engineering Physics, University of Saskatchewan, Saskatoon, SK, Canada.

The bandgap or energy gap in a solid is the energy difference between the top of the valence band and the bottom of the conduction band. The bandgap and the promotion of electrons across it, is exploited in the design of most modern electronic devices such as transistors, laser and photo diodes and solar cells.

Key electronic parameters like conductivity and key mechanical parameters like hardness strongly depend on the bandgap, which is one of the reasons why tailoring the bandgap of materials is an important field in materials science.

We will discuss various methods to determine the bandgap. We use synchrotron-based soft X-ray spectroscopy to measure the bandgap. In the excitation process a photon is absorbed leaving the atom in an excited state with a core hole. The presence of the core hole alters the occupancy of the bands and therefore needs to be accounted for. It will be discussed how to account for the core and we present a study of Solid solutions of silicon nitride (γ -Si₃N₄) and germanium nitride (γ -Ge₃N₄): γ -[Si_{1-x}, Ge_x]₃N₄, (for $0 \leq x \leq 1$). The bandgap of these materials changes non-linearly with concentration x . The experimentally determined bandgaps agree quite well with the trends of our calculations.

We conclude that soft X-ray spectroscopy with synchrotron radiation and Density functional theory calculations provide a reliable way to determine the bandgap of solid-state materials.

707, Oral**Bandgap profile across a silicon oxynitride ultrathin film epitaxially grown on 6H-SiC(0001), studied by XES and XAS**

*H. Tochihara*¹; *S. Mizuno*¹; *T. Shirasawa*²

1. Department of Molecular and Material Sciences, Kyushu University, Kasuga, Fukuoka, Japan.

2. Institute for Solid State Physics, University of Tokyo, Kashiwa, Chiba, Japan.

We found that hydrogen-gas etching of a 6H-SiC(0001) surface and subsequent annealing in nitrogen atmosphere lead to the formation of a silicon oxynitride (SiON) epitaxial layer. A quantitative low-energy electron diffraction (LEED) analysis revealed that it has a hetero double-layer structure: a silicate monolayer on a silicon nitride monolayer via Si-O-Si bridge bonds. Empty- and filled state images of scanning tunneling microscopy confirm the optimized structure model [1]. There is no dangling bond in the determined structure, which explains a fact that the structure is robust against air exposure. Scanning tunneling spectroscopy measured on the SiON layer shows a bulk SiO₂ like bandgap of ~9 eV.

Electronic structures of the SiON layer (~0.6 nm in thickness) were investigated on atomic-layer scale using soft x-ray absorption and emission spectroscopy (XAS and XES) with synchrotron radiation at BL-27SU/SPring-8 and BL-12/SAGA-LS [2]. The element-specific XAS and XES measurements revealed layer-resolved energy-band profiles. Measured gap sizes are 6.3 ± 0.6 eV at the nitride monolayer and 8.3 ± 0.8 eV at the oxide monolayer. The nitride and oxide layers have almost the same energy of conduction-band-minimum (CBM), being ~3 eV higher than CBM of the SiC substrate. The energy-band profiles of the SiON layer are qualitatively reproduced by first-principles calculations.

tochihar@mm.kyushu-u.ac.jp

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708, Oral**Characterization of graphite-like layered material BC₂N by X-ray absorption and emission spectroscopy**

*M. Kawaguchi*¹; *H. Yamamoto*¹; *Y. Muramatsu*²

1. Osaka Electro-Communication University, Neyagawa, Osaka, Japan.

2. University of Hyogo, Himeji, Hyogo, Japan.

Graphite-like layered materials of compositions BC_xN_y ($x = 2.0\sim 2.4$, $y = 0.8\sim 0.9$), are called BC₂N in this paper, were prepared at 1470~2070K by chemical vapor deposition (CVD) method. The electronic structures of BC₂N films were investigated by X-ray emission (XES) and total electron yield X-ray absorption spectroscopy (TEY-XAS) using synchrotron radiation at the Advanced Light Source, Lawrence Berkeley National Laboratory in California. The X-ray emission and absorption spectra in the BK, CK and NK regions of BC₂N were considerably different from those of h-BN and graphite, probably because of hybridization for orbitals of boron, carbon and nitrogen existing in the same layer of BC₂N. TEY-XAS and XES results suggested a band overlap between a conduction band and a valence band for BC₂N. The band overlap for BC₂N is larger than that for graphite and is not like to that for h-BN which has a wide band gap. Angle-resolved XAS indicated the structural orientation of the BC₂N film, which was also observed by X-ray diffraction analysis. Density of states in the occupied 2p orbitals calculated by the discrete variational (DV)-X α method for three types of structural models which were considered on the basis of the CVD reaction, fitted with the measured X-ray emission spectra of BC₂N. The intercalation phenomena of alkali metals into BC₂N are similar to those of graphite, which is probably due to the band overlap and the relatively large intensity of the unoccupied π^* orbital of the material.

811, *Invited*

Recent new soft X-ray spectrometers developed for the analysis of biochemical samples

*H. Wakita*¹; *T. Kurisaki*¹; *S. Matsuo*¹; *R. C. Perera*²; *J. H. Underwood*²

1. Fukuoka University, Fukuoka, Japan.

2. EUV Technology, Martinez, CA, United States.

We recently prepared two new soft X-ray absorption spectrometers: one is a laboratory scale ultra soft X-ray absorption spectrometer for measuring ultra soft X-ray absorption spectra(50-150 eV) of solid samples such as battery materials, soil and rocks, and bone or fossil remains using an ionized plasma X-ray source[1], and the other is a spectrometer for measuring soft X-ray absorption spectra(50-1500 eV) of solution samples such as clean or discharged waters, wet soils, and live specimen of animals and plants at the BL12 of Kyushu Synchrotron Light Research Center, Japan[2]. The former spectrometer consists of four sub-systems:(1) the laser and focusing optics, (2) the target and target chamber, (3) the monochromator, (4) the detector system and sample chamber. Using this spectrometer, we could get sharp spectra of not only several different lithium compounds but alkali and alkaline-earth compounds, and analyzed the spectra by a DV- $X\alpha$ molecular orbital calculation. The latter spectrometric system consists of four sub-systems:(1) the beam-line for incident synchrotron light, (2) a reduction bulb system for vacuum level, (3) a collimator system built-in an X-ray polycapillary, (4) a detector and sample holder system. Using this system, we analyzed the concentration dependency of sodium, magnesium, and calcium cations in aqueous solutions for the biological and environmental purposes by comparing the obtained spectra with theoretical results by the DV- $X\alpha$ calculation. In case of sodium cation in aqueous solution, there exists clear concentration dependency on the spectra and the calculation results give the hydration difference between higher concentrated solution(5-3 molar solutions) and lower solution (1-0.5 molar solutions).We will show the detail of our spectrometers and obtained results.

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812, Oral**Characterization of minerals and archeological samples by soft X-ray spectroscopy**

T. Kurisaki¹; D. Tanaka¹; S. Kokubu¹; H. Wakita¹

1. Chemistry, Fukuoka University, Fukuoka, Japan.

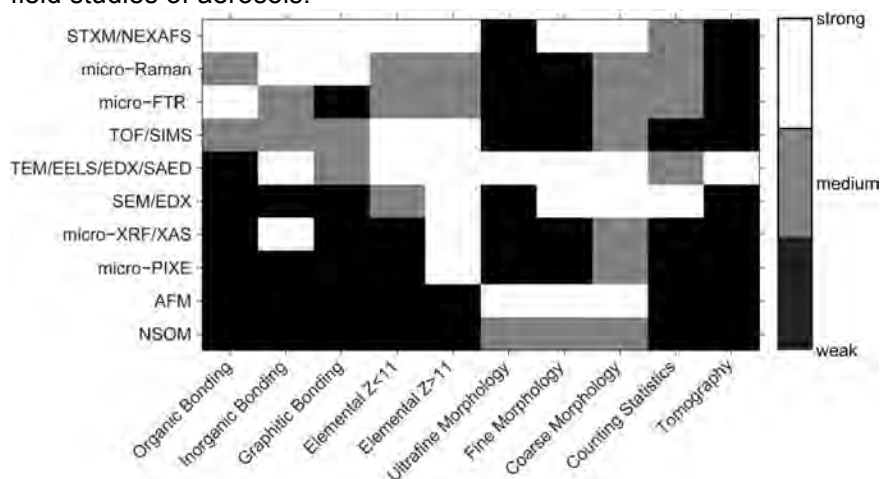
The X-ray absorption spectroscopic method is frequently used for steric and electronic structure analyses because it gives information on the local structure and oxidation state of the absorbing atom. Further, Soft X-Ray Absorption (SXA) method is categorically interested in chemical analysis of various materials in the archeology, environmental science and semiconductor industry. A huntite is called 'a hanto-ishi' and was used as a pigment of the white in ancient Egypt. Chemical formula of this mineral is expressed as $\text{CaMg}_3(\text{CO}_3)_4$. Even if the huntite is a rare mineral and has only a few reports about occurrence, this mineral was used abundantly in ancient Egypt. It is not clear why this rare mineral was used as a pigment of the white in ancient Egypt. Moreover, the first reverberatory furnace in Japan was constructed at Tsukiji, Saga Han(domain) in 1850 because at this time of year non-Asian ships had occasionally arrived to Japan even though Japan had been closed from the outside world by Shogun-policy (Edo Period). To keep the closed-door policy, Japan, even if small area, Han, had to start to construct steal cannon. One of western Han in Japan, Saga Han, also constructed the cannon at several places by using home made reverberatory furnaces. However, these cannons and air-furnaces do not exist now. Therefore the details of the iron manufacture technology are not clear. In this work, we performed the XANES spectra measurement about various minerals such as huntite and dolomite and rusty fragments of iron materials obtained from reverberatory furnace sites. The obtained experimental XANES spectra are analyzed using the calculated theoretical spectra from DV-X α calculations.

813, Oral**Complementary spectro-microscopic techniques: Chemical composition and properties of atmospheric aerosols***M. Gilles¹; R. Moffet¹; A. Laskin²*

1. Chemical Sciences Division, LBNL, Berkeley, CA, United States.

2. W. R. Wiley Environmental Molecular Sciences Laboratory, PNNL, Richland, WA, United States.

Aerosols are widely recognized as key elements in the atmospheric environment. Chemical and morphological data of individual particles are of crucial importance for understanding their formation, reactions, atmospheric history and aging. Microprobe analytical techniques have been extensively used in the past to characterize the size, morphology, phase and composition of particles collected in field and laboratory studies. These techniques coupled with appropriate time-resolved aerosol sampling are capable of generating time-resolved single-particle data, which then can be used to follow in detail the time evolution of specific types of aerosols. In this presentation we give a summary of recent research projects carried out in our laboratory that demonstrates how the use of complementary microprobe methods and other analytical techniques provides new insights into the atmospheric reactions of aerosols, their physical and chemical transformations, and how the obtained data is utilized to define future directions in laboratory and field studies of aerosols.



Comparison of different microscopic and spectroscopic techniques with regards to elemental, chemical, and morphological information. By combining several techniques to probe atmospheric aerosols we obtain insight into their chemical transformation.

814, Oral

Metals in the environment: Understanding environmental issues through quantitative analysis of X-ray absorption spectroscopy

J. Cutler¹; J. Warner¹; L. Van Loon¹

1. Canadian Light Source Inc., Saskatoon, SK, Canada.

Synchrotron-based X-ray Absorption Spectroscopy (XAS) is increasingly being used to analyze and quantify chemical species and elemental oxidation state in natural environments and complex industrial process streams. The characteristics of XAS that make it a popular method of quantitative analysis are the minimal sample preparation required and its element selectivity and sensitivity to changes in oxidation states but many aspects of its quantification capabilities and limitations have not been fully explored.

Although the term "fingerprint" is often used when discussing XAS spectra, the accurate fitting of XAS data requires unique spectral features in both the unknown spectrum being fit and the reference spectra used as fitting standards. We examine a series of mixtures of elements to determine the effect of (i) the number of components, (ii) the matrix (iii) the edge energy, and other aspects of the sample data processing on the fitting quality. We further explore standard fitting techniques to determine their reliability and potential for errors. Overall, the Canadian Light Source is developing an expertise in applying multiple spectroscopic techniques to improve our understanding of complex environmental systems and this presentation will apply these methodologies to a specific case study.

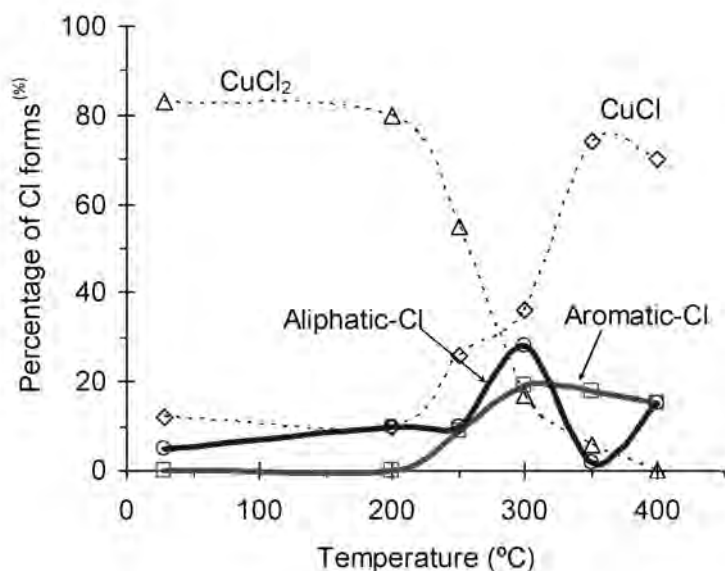
815, Oral**Behavior of chlorine in fly ash during dioxin formation**

*M. Takaoka*¹; *T. Fujimori*²; *K. Oshita*¹

1. Environmental Engineering, Kyoto University, Kyoto, Japan.

2. Research Center for Material Cycles and Waste Management, National Institute for Environmental Studies, Tsukuba, Japan.

In order to control emission of chlorinated dioxins from municipal solid waste incineration, it is important to understand the formation mechanism. A heterogeneous reaction on the surface of fly ash is thought to be most critical reaction and is described as the breakdown reaction of a carbon matrix in fly ash. In this reaction, many researchers regard copper(II) chloride as an influential catalyst and the behavior of copper in fly ash has been examined using various methods. Although chlorine in fly ash is known to be essential factor for the formation, the behavior of chlorine has not yet been clarified. In this study we tried to reveal the behavior of chlorine by the Cl K-edge X-ray absorption near edge structure (XANES). To determine the behavior of Cl, we prepared a model fly ash (MFA), which was a mixture of copper(II) chloride dehydrate (5 wt%), activated carbon (5 wt%), and boron nitride (remainder). The Cl forms present after MFA was heated for 30 min under a 10% O₂ (90% N₂) atmosphere were determined by measuring the Cl K-edge XANES at the Photon Factory (BL-9A and BL-11B) located in Japan. Cl bound to inorganic, aromatic, or aliphatic carbon can be distinguished by the features of a Cl XANES spectrum. When the dechlorination reaction of copper(II) chloride occurred, we found strong evidence of the C-Cl bond. The ratio of Cl connected to aromatic and aliphatic carbons was the maximum at 300 degree based on analyses of Cl K-edge XANES spectra (Fig.1). The C-Cl bond was derived from the dechlorination of copper chloride because the only chlorination source in MFA was copper (II) chloride. Dioxins are known to be generated at the maximum rate in/on fly ash around 300 degree. The results of the temperature profile of aromatic and aliphatic-Cl coincided well with that of dioxins. As a result, it was confirmed that direct chlorination by copper chloride formed dioxins in fly ash.



The percentage of Cl-species as a function of temperature

893, Poster**X-ray absorption spectroscopic characterization of phosphorus-doped TiO₂ with visible-light photocatalytic activity**

*M. Iwase*¹; *K. Yamada*²; *T. Kurisaki*¹; *H. Wakita*^{1, 2}

1. Chemistry, Fukuoka University, Fukuoka, Japan.

2. Advanced Materials Institute., Fukuoka University, Fukuoka, Japan.

Doping TiO₂ with nonmetal such as nitrogen, carbon and sulfur has received a lot of attentions in recent years since it can extend the photoresponse of TiO₂ from ultraviolet to the visible region, which is propitious for using the sunlight as the energy source. As for Phosphorus-doped TiO₂ (P-TiO₂) with visible-light photocatalytic activity, two kinds of P-TiO₂ prepared using phosphate as a precursor of P have been reported. However, some reports showed that P-TiO₂ prepared using phosphate cannot absorb visible light. Thus, we attempted to prepare P-TiO₂ using phosphide as a new method.

P-TiO₂ was synthesized through the hydrolysis of titanium tetraisopropoxide in suspension containing TiP compound, which was prepared by the treatment of titanium tetrachloride with cyclohexylphosphine.

The synthesized P-TiO₂ nanoparticles exhibited a yellow color. The UV-vis diffuse reflection spectra of P-TiO₂ showed a continuous and tailing absorption that extended out to approximately 600 nm. XRD patterns of P-TiO₂ showed the sole presence of anatase phase up to temperatures of 500 °C. Rutile growth began to appear at 550 °C. The phase transformation of pure TiO₂ occurred at a lower temperature. No peak corresponding to hydrocarbon was detected in the IR spectrum of P-TiO₂. XPS spectra of P-TiO₂ showed a P2p binding energy around 134 eV, which indicated that P was incorporated into the titanium oxides. The P2p peak around 134 eV was assigned to P⁵⁺. This showed that the surface of P-TiO₂ was oxidized in synthetic process. The photodegradation of phenol and the appearance of 1,4-benzoquinone were observed in the presence of P-TiO₂ under visible light irradiation while no degradation of phenol and no appearance of 1,4-benzoquinone was observed under the same irradiation condition in the case of ST01, well-known as UV-photocatalyst. We discuss a correlation between the features found by X-ray spectroscopic characterization and the visible light photocatalytic activity.

894, *Poster*

Adsorption behavior of tellurium oxoanion on d-MnO₂

*Y. Katsuyama*¹; *C. Numako*²; *Y. Okaue*¹; *T. Yokoyama*¹

1. Kyushu university, Fukuoka, Japan.

2. Tokushima university, Tokushima, Japan.

Marine ferromanganese crusts (FMMC), which are composed of manganese dioxide and hydrous ferric oxide, form on seamount and rare metals are concentrated into FMMC compared with the amount in the Earth crust. According to Hein's idea about the concentration mechanism of rare metals into FMMC from seawater, cations are sorbed preferentially on the negatively charged surface of hydrous manganese oxide such as MnO₂ in FMMC, while anions including oxoanions are combined to the positively charged surface of the hydrous ferric oxide such as FeOOH. However, molybdenum (Mo), which is present as MoO₄²⁻, has been reported to be concentrated in manganese oxide phase in FMMC. Tellurium (Te) is the highest concentrated element into FMMC compared with the amount in the Earth crust. As Te is present as oxoanion (Te(IV)) in deep seawater like Mo, Te is deduced to be concentrated into manganese oxide phase. In this study, to clarify the sorption mechanism of Te by FMMC, the adsorption behavior of Te on d-MnO₂ having negative surface charge around pH 8 was investigated. It was found that Te(IV) is effectively adsorbed on d-MnO₂ and oxidized at the same time to Te(VI), that is, the sorption of Te into FMMC is controlled by the oxidative-adsorption by overcoming electrostatic repulsion between negative charges of the surface of d-MnO₂ and negative charge of oxoanion of Te.

895, Poster**Quantitative analysis method of nitrogen in graphitic carbon materials using total-electron-yield soft X-ray absorption spectroscopy**

*T. Amano*¹; *Y. Muramatsu*¹; *E. M. Gullikson*²

1. Graduate School of Engineering, University of HYOGO, Himeji, Japan.

2. Center for X-Ray Optics, Lawrence Berkeley National Laboratory, Berkeley, CA, United States.

X-ray absorption spectroscopy (XAS) using a total-electron-yield (TEY) method has been a powerful tool for chemical-state analysis of nitrogen (N) in N-doped graphitic carbon materials and/or C/N alloys. However, some difficulties often arise in TEY-XAS for quantitative analysis, because the TEY signal depends on the electrical property of samples. To achieve the quantitative analysis of nitrogen, we have proposed a new quantitative analysis method of nitrogen in graphitic carbon materials using TEY-XAS. In this method, working curves for quantitative analysis can be obtained from the relative absorption-peak-intensity ratio of NK/CK as functions of the N/C atomic ratio in standard aromatic compounds which have various nitrogenated functional groups.

Twenty-three aromatic compounds having the amine and imine groups were chosen as the standard samples. Soft X-ray absorption spectra in the CK - NK region were measured in BL-6.3.2 at the Advanced Light Source (ALS). Nitrogen in Japanese coals which were mined in Yubari, Hokutan, Mitsui, and Amakusa was analyzed by the working curve obtained from the standard samples.

Fig.1 shows the atomic ratio (N/C) dependencies of the absorption peak intensity ratio ($N\sigma^*/C\sigma^*$) in the standard aromatic samples. The regression line of the relationship with a high correlation factor ($R^2 = 0.97$) and a low standard deviation (0.046) can be regarded as a working curve for quantitative analysis of nitrogen in graphitic carbons. By using this working curve, concentration of nitrogen in the Japanese coals can be estimated as 7%. Additionally, it can be elucidated from the X-ray-absorption near-edge structure (XANES) in the NK region that chemical states of nitrogen in the coals are mainly $-NH_2$ and $-N=$. It is therefore concluded that the proposed TEY-XAS method using the standard aromatic compounds will be useful for not only the chemical-state analysis but also the quantitative analysis of nitrogen in graphitic carbon materials.

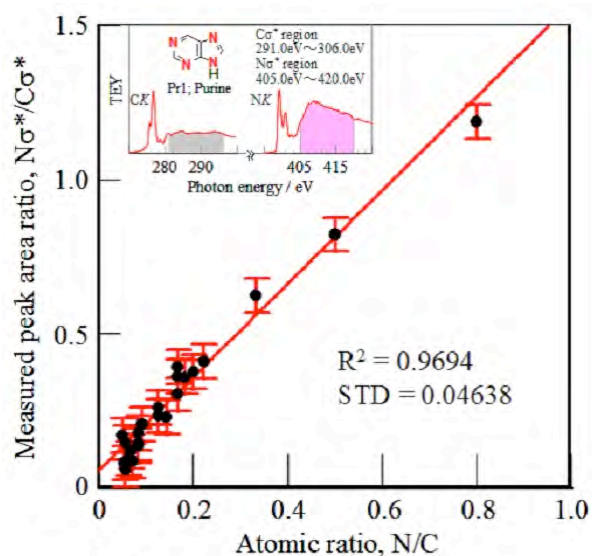


Fig.1 Atomic ratio (N/C) dependencies of the $N\sigma^*/C\sigma^*$ peak area ratio in the TEY-XAS of the selected ten standard aromatic samples. The insert shows TEY-XAS in the CK and NK region of Purine (Pr1). Colored area in the 291.0 - 306 eV and 405.0 - 420.0 eV region can be considered as $C\sigma^*$ and $N\sigma^*$.

896, Poster**Local-structure analysis of the oxidized graphitic carbon dispersoids using soft X-ray absorption spectroscopy**

*N. Inoue*¹; *Y. Muramatsu*¹; *Y. Aoyama*²; *M. Kawaraya*²; *H. Hisashi*²; *E. M. Gullikson*³

1. University of Hyogo, Himeji, Japan.

2. Mikuni color LTD, Himeji, Japan.

3. Center for X-Ray Optics, Lawrence Berkeley National Laboratory, Berkeley, CA, United States.

Graphitic carbons such as carbon black (CB) or carbon nanotube (CNT) have been utilized as dispersoids in various electric device materials. To develop the high-performance carbon dispersoids, local-structure analysis of the oxidized carbon surface is important, because their dispersion characteristics strongly depend on the oxidized surface states. On the other hand, soft X-ray absorption spectroscopy using synchrotron radiation has been a powerful tool for the chemical/electronic-structure analysis of low-Z materials. We have therefore analyzed the local structure of the oxidized graphitic carbon dispersoids using soft X-ray absorption spectroscopy.

Oxidized CB samples were prepared by the conventional ozone (O₃) method. Soft X-ray absorption spectra in the CK - OK region of the oxidized CB were measured in BL-6.3.2 at the Advanced Light Source (ALS) using a total-electron-yield method.

From the absorption peak intensity ratio of OK/CK, it is confirmed that the carbon surface can be surely oxidized by the O₃ method. Additionally, it is elucidated from the OK absorption spectra that the surface can be mainly oxidized with the functional groups of -COOH and/or -C=O. In the CK spectra, the π^* -peak broadening and additional fine structures between the π^* and σ^* peaks were observed in the oxidized CB. However, the peak intensity ratio of π^*/σ^* seemed to be independent of the oxidation. This suggests that the oxygenated functional groups bond to the edge carbon atoms of the hexagonal carbon layers. Theoretical analysis of the estimated local structures using the discrete variational (DV) -X α molecular orbital method agreed with the X-ray absorption spectral profiles. It is therefore elucidated that the oxygenated functional groups bond to the edge carbon atoms in the graphitic carbon clusters of the oxidized CB.

897, Poster

Total-electron-yield soft X-ray absorption spectroscopy for the quantitative analysis of carbon materials

*Y. Muramatsu*¹; *E. M. Gullikson*²

1. Graduate School of Engineering, University of Hyogo, Himeji, Hyogo, Japan.

2. Center for X-Ray Optics, Lawrence Berkeley National Laboratory, Berkeley, CA, United States.

Soft X-ray absorption spectroscopy (XAS) using a total-electron-yield (TEY) method has been a powerful tool for chemical/electronic-state analysis of functional materials. However, some difficulties often arise in TEY-XAS for quantitative analysis, because the TEY signal intensity depends on the electrical property of the samples and the TEY ratios between sample compositions have not been clearly elucidated. To apply the TEY-XAS for the quantitative analysis, we have therefore investigated (1) the TEY ratios between sample compositions [1], and proposed (2) a new quantitative analysis method of oxygen in carbon materials using standard compounds [2].

(1) TEY ratios between sample compositions; From the TEY-XAS measurements of the sp²/sp³-carbon mixtures (carbon black/diamond) and the boron/carbon mixtures (amorphous boron/carbon black), TEY ratios between the compositions can be obtained as 0.12 for diamond to carbon black and as 0.32 for carbon black to boron. By using the measured TEY ratios, TEY-XAS profiles of the mixture samples can be well reproduced by the synthesized spectra. It is therefore confirmed that TEY clearly depends on samples and composition ratio will be quantitatively analyzed from the TEY-XAS measurements considering the TEY ratios among the compositions.

(2) New quantitative analysis method using standard compounds; We have proposed a new quantitative analysis method to measure oxygen in carbon materials by TEY-XAS. In this method, working curves for quantitative analysis can be obtained from the relative absorption-peak-intensity ratio of OK/CK as functions of the O/C atomic ratio in standard organic compounds which have various oxygenated functional groups. This method will be utilized for the characterization of oxygenated carbon materials.

[1] Y. Muramatsu et al., Jpn. J. Appl. Phys., 48, 066514 (2009).

[2] Y. Muramatsu et al., Tanso, 236, 9-14 (2009).

898, Poster

X-ray fluorescence imaging of growing chemical patterns

K. Sakurai¹; M. Mizusawa¹

1. National Institute for Materials Science, Tsukuba, Ibaraki, Japan.

Chemical pattern formation has been extensively studied because of interesting similarity to patterns on biological systems. Chemical reaction-diffusion systems generates spatial variations in the concentration fields of the reacting chemicals. In the present research, time-spatial distribution of elements have been studied by X-ray fluorescence (XRF) imaging using high-flux synchrotron radiation. Though conventional scanning-type XRF imaging has been widely used, the technique requires a long measuring time. To see elements in growing chemical patterns, we have employed novel XRF projection imaging without performing any scans. Some XRF movies of Tarube's artificial cell and oscillating reactions will be presented.

Ref. [1] M. Traube, Arch. Anat. Physiol. u. wiss. Med. 87-129 (1867). [2] K. Sakurai and H. Eba, Anal. Chem. 75, 355-359 (2003).

899, *Poster*

Measurement of unpaired electron species in dry DNA thin films irradiated with synchrotron soft X-rays around oxygen and nitrogen K-edge studied by EPR

*T. Oka*¹; *A. Yokoya*¹; *K. Fujii*¹; *Y. Fukuda*²; *M. Ukai*³

1. Advanced Science Research Center (ASRC), Japan Atomic Energy Agency (JAEA), Ibaraki, Japan.

2. Quantum Beam Science Directorate (QBSD), Japan Atomic Energy Agency (JAEA), Hyogo, Japan.

3. Department of Applied Physics, Tokyo University of Agriculture and Technology, Tokyo, Japan.

In order to clarify the physicochemical mechanism of DNA damage induction by the photoelectric effect due to the excitation/ionization of inner-shell electron in DNA constituent atoms, we have developed an X-band EPR spectrometer system at a synchrotron soft X-ray beamline (BL23SU) in SPring-8, Japan, and measured the short-lived unpaired electron species arising only during irradiation. In the present work, we obtained the 'in situ' EPR spectra of DNA and its related molecules in XANES (X-ray absorption near edge structure) regions around K-edge of oxygen and nitrogen during the monochromatic soft X-ray irradiation.

A calf thymus DNA film and evaporated pyrimidine nucleobase (thymine and cytosine) films were prepared as samples. They were placed in an EPR cavity in a vacuum chamber for the irradiation and the EPR measurement. Monochromatic soft X-ray photons were provided using a grazing-incidence monochromator equipped with variable-line-spacing-plane-gratings (VLSPGM), and the spectra were numerically double integrated to obtain the relative spin concentrations.

The soft X-ray energy dependences of the spin concentration of nucleobase films show similar fine structures to the XANES spectra. The adenine and guanine films also show similar tendencies [1]. However, for the DNA film, the short-lived EPR signal intensity significantly increases above the oxygen K-shell ionizing threshold energy. These results suggest that the induction processes of the unpaired electron due to the inner-shell photoionization are different for a DNA molecule and particular nucleobases. Especially, it is well known that the hydrated water which strongly bonds to the DNA exists even in vacuum. Such hydrated water may play an important role in the induction of unpaired electron. The relationship between the hydrated water and finally arising nucleobase lesions will be discussed.

[1] Yokoya, A.; Fujii, K.; Fukuda, Y.; Ukai, M. *Radiat. Phys. Chem.*, 2009, 78, 1211-1215.

List of Participants

Name	Affiliation	E-mail address*
Amano, Taiji	University of Hyogo, Himeji, Hyogo, Japan.	ew10e001 [at] steng.u-hyogo.ac.jp
Baba, Yuji	Japan Atomic Energy Agency, Ibaraki, Japan	baba.yuji [at] jaea.go.jp
Cutler, Jeffrey	Canadian Light Source Inc., Saskatoon, SK, Canada	jeffrey.cutler [at] lightsource.ca
Fink, Rainer H.	University of Erlangen, Erlangen, Germany	rainer.fink [at] chemie.uni-erlangen.de
Gilles, Mary	Lawrence Berkeley National Laboratory, Berkeley , CA, United States	mkgilles [at] lbl.gov
Harada, Yoshihisa	The University of Tokyo, Tokyo, Japan	harada [at] spring8.or.jp
Heske, Clemens	University of Nevada, Las Vegas, Las Vegas, NV, United States	heske [at] unlv.nevada.edu
Horikawa, Yuka	RIKEN Harima Institute, Sayo-gun, Hyogo, Japan	horikawa [at] spring8.or.jp
Inoue, Natsuki	University of Hyogo, Himeji, Hyogo, Japan	et09o008 [at] steng.u-hyogo.ac.jp
Iwase, Motoki	Fukuoka University , Fukuoka, Japan	mukaisekuto [at] yahoo.co.jp
Katsuyama, Yuka	Kyushu University, Fukuoka, Japan	y_katsuyama [at] mole.rc.kyushu-u.ac.jp
Kawaguchi, Masayuki	Osaka Electro-Communication University, Neyagawa, Osaka, Japan	kawaguti [at] isc.osakac.ac.jp
Kawai, Jun	Kyoto University, Kyoto, Japan	jun.kawai [at] materials.mbox.media.kyoto-u.ac.jp
Kurisasi, Tsutomu	Fukuoka University, Fukuoka, Japan	kurisasi [at] fukuoka-u.ac.jp
Lamb, Robert	University of Melbourne, Melbourne, VIC, Australia	rnlamb [at] unimelb.edu.au
Lee, Jonathan R.I.	Lawrence Livermore National Laboratory, Livermore, CA, United States	lee204 [at] llnl.gov
Lindle, Dennis	U. Nevada, Las Vegas, Las Vegas, NV, United States	lindle [at] unlv.nevada.edu
Minasian, Stefan George	Los Alamos National Laboratory, Los Alamos, NM, United States	minasian [at] lanl.gov
Mitsuke, Koichiro	Institute for Molecular Science, Okazaki, Aichi, Japan	mitsuke [at] ims.ac.jp
Moewes, Alexander	University of Saskatchewan, Saskatoon, SK, Canada	alex.moewes [at] usask.ca
Moffet, Ryan	Lawrence Berkeley National Laboratory, Berkeley , CA, United States	rcmoffet [at] lbl.gov
Muramatsu, Yasuji	University of Hyogo, Himeji, Hyogo, Japan	murama [at] eng.u-hyogo.ac.jp
Niwa, Hideharu	The University of Tokyo, Tokyo, Japan	niwa [at] sr.t.u-tokyo.ac.jp
Nordgren, Joseph	Uppsala University, Uppsala, Sweden	joseph.nordgren [at] fysik.uu.se
Oka, Toshitaka	Japan Atomic Energy Agency, Ibaraki, Japan	oka.toshitaka [at] jaea.go.jp
Oshima, Masaharu	The University of Tokyo, Tokyo, Japan	oshima [at] sr.t.u-tokyo.ac.jp

Perera, Perera	EUV Technology	rupert.perera [at] euvl.com
Regier, Thomas	University of Saskatchewan, Saskatoon, SK, Canada	tom.regier [at] lightsource.ca
Sakurai, Kenji	National Institute for Materials Science, Tsukuba, Ibaraki, Japan	Sakurai.Kenji [at] nims.go.jp
Shuh, David	Lawrence Berkeley National Laboratory, Berkeley , CA, United States	DKShuh [at] lbl.gov
Takaoka, Masaki	Kyoto University, Kyoto, Japan	takaoka [at] environ.mbox.media.kyoto-u.ac.jp
Tochihara, Hiroshi	Kyushu University, Kasuga, Fukuoka, Japan	tochihar [at] mm.kyushu-u.ac.jp
van Buuren, Tony	Lawrence Livermore National Laboratory, Livermore, CA, United States	vanbuuren1 [at] llnl.gov
Wakita, Hisanobu	Fukuoka University , Fukuoka, Japan	wakita [at] fukuoka-u.ac.jp
Yamane, Hiroyuki	Institute for Molecular Science, Okazaki, Aichi, Japan	yamane [at] ims.ac.jp

*[at] should be @