Novel Trends in Synchrotron and FEL-Based Analysis Focus Topic

Room 9 - Session SA+2D+AC+MI-WeM

Recent Advances of Diffracting/Scattering and Spectroscopic Methods for Correlated and 2D Materials

Moderators: Hans-Peter Steinrück, University Erlangen-Nuernberg, Germany, Kristina Edström, Uppsala University, Sweden

8:00am **SA+2D+AC+MI-WeM-1 Studies of Surfaces and Catalysis in real time with X-ray Free Electron Laser**, ***Anders Nilsson***, Stockholm University, Sweden **INVITED**

In heterogeneous catalysis, reactants adsorbed on surfaces are converted to products, which eventually desorb via various intermediates. The transition state separates reactants and intermediates from products and the free energy required to reach it determines the kinetics of an elementary chemical reaction. Many surface reaction intermediates are, however, transient species with a short residence time and the population of species in the transition state region is near-zero making their observation a challenge during steady state conditions. Ultrafast pump-probe techniques have, however, opened up opportunities by promoting a sufficient population of molecules in transient states to allow detection on short time scales. Here recent results on probing chemical reactions on surfaces using X-ray free-electron lasers LCLS (Linac Coherent Light Source) at SLAC National Accelerator Laboratory) will be presented. Four examples will be shown CO desorption, Oxygen activation, CO oxidation and CO hydrogenation on Ru(0001). We demonstrate that both transient intermediates and the transition state region can be detected in surface chemical reactions.

8:40am **SA+2D+AC+MI-WeM-3 New Generation RIXS of 3*d*-TM Oxides**, ***Giacomo Ghiringhelli***, Politechnico Milano, Italy **INVITED**

Resonant inelastic soft x-ray scattering huge potential is quickly becoming reality. RIXS is element and site selective, like x-ray absorption spectroscopy. It is momentum resolved, like x-ray diffraction. And it probes several kinds of excitations at a time, from charge transfer and electron-hole pair generation, to orbital (*dd* or *ff*) excitations, to spin waves and lattice modes, unlike any other energy loss spectroscopy. Moreover, the elastic component of the spectra carries information on commensurate and incommensurate orders, such as charge density waves (CDW) and orbital order. The ERIXS endstation at the ID32 beam line of the ESRF is the founder of a new generation of RIXS instruments capable of exploiting all the strongpoints of this technique, thanks to the very high resolving power (30,000 at 1 keV), the diffractometer-like manipulator and the full control of photon polarization provided by the combination of the APPLE II source and the polarimeter on the analyzer.

I will review some of the results obtained in the first year of operations of ID32, with a special focus on cuprate superconductors studied at the Cu L_3 edge. High resolution RIXS has been used to determine the relation between crystal structure and the extent of hopping integrals in parent compounds, revealing why apical oxygens are detrimental to superconductivity [1]. Ultra-high resolution RIXS has provided a direct measurement of the momentum-dependent electron phonon coupling in undoped and superconducting samples, and has revealed new collective modes related to charge density waves (CDW) in underdoped Bi2212. Polarization analysis has definitively demonstrated the spin-flip character of the mid-IR spectral region in superconducting compounds. And the quasi-elastic part of RIXS spectra has brought new evidence of the universality of charge ordering phenomena in cuprates, including striped cuprates [2] and single layer Bi2201. Finally the feasibility of high resolution RIXS in standing wave geometry has been successfully demonstrated, adding depth control on this bulk sensitive technique.

[1] Y. Y. Peng, G. Dellea, M. Minola, M. Conni, A. Amorese, D. Di Castro, G. M. De Luca, K. Kummer, M. Salluzzo, X. Sun, X. J. Zhou, G. Balestrino, M. Le Tacon, B. Keimer, L. Braicovich, N. B. Brookes and G. Ghiringhelli, [https://arxiv.org/abs/1609.05405]

[2] H. Miao, J. Lorenzana, G. Seibold, Y.Y. Peng, A. Amorese, F. Yakhou-Harris, K. Kummer, N. B. Brookes, R. M. Konik, V. Thampy, G. D. Gu, G. Ghiringhelli, L. Braicovich, M. P. M. Dean, [https://arxiv.org/abs/1701.00022]

9:20am **SA+2D+AC+MI-WeM-5 Resonant Inelastic X-ray Scattering on Low-Dimensional Correlated Transition Metal Oxides and Oxide Heterostructures**, ***Thorsten Schmitt***, Paul Scherrer Institut, Switzerland **INVITED**

Resonant inelastic X-ray scattering (RIXS) is a powerful bulk-sensitive photon-in / photon-out spectroscopic probe of the electronic structure of condensed matter with atomic and orbital sensitivity. It is a unique tool for studying excitations from the electronic ground state in correlated transition-metal oxides, being directly sensitive to lattice-, charge-, orbital- and spin-degrees of freedom. In this talk, we report RIXS investigations of the $LaTiO_3$ layers in $(LaTiO_3)_n/(LaAlO_3)_5$ superlattices undergoing a transition from Ti^{3+} to Ti^{4+} oxidation state upon reducing n and thickness as well as temperature-driven metal-insulator transitions in thin films of $CaVO_3$.

$(LaTiO_3)_n/(LaAlO_3)_5$ superlattices (SL) composed of a band-insulator ($LaAlO_3$) and a Mott-insulator ($LaTiO_3$) present an enhanced insulating character when n is reduced. We prepared a set of SLs (n=10, 5 and 2 unit cells) and investigated these with X-ray absorption spectroscopy (XAS) and RIXS. XAS shows a clear change in the Ti valence going progressively from the nominal Ti^{3+} ($3d^1$, n=10 u.c.) for bulk $LaTiO_3$ to an almost pure Ti^{4+} ($3d^0$, n=2 u.c.). RIXS reveals two spectral developments when reducing the $LaTiO_3$ thickness n: 1) reduction of intra-t_{2g} / intra-e_g splitting and increase of t_{2g} to e_g separation and 2) increase of the charge transfer excitation spectral weight. The changes in the energy of the orbital levels observed as a function of n reveal a clear change of the local TiO_6 distortion. We suggest that an inverse Jahn-Teller effect, inducing the octahedra to assume higher symmetry, is responsible for the observed orbital energy shifts. This peculiar effect is partially caused by strain, triggering a $3d^1 \rightarrow 3d^0$ electron transition at the interfacial Ti sites.

Bulk $CaVO_3$ is a correlated paramagnetic metal. Thin films of $CaVO_3$ undergo a metal-insulator transition (MIT) when the thickness is reduced below ca. 20 u.c.. Our XAS and RIXS measurements at the V L-edge across this dimensionality driven MIT in $CaVO_3$ reveal a large transfer of spectral weight from fluorescent to Raman modes upon entering the insulating state. We observe a large reduction in the charge excitation bandwidth and V-O covalence across the thickness and temperature-driven MIT. Further analysis of the charge modes suggests a bandwidth-controlled MIT, assisted by the presence of strong correlations.

11:00am **SA+2D+AC+MI-WeM-10 Doping of Graphene Exploited with Spectromicroscopy**, ***Carla Bittencourt***, University of Mons, Belgium **INVITED**

Limitations in characterisation and theoretical modelling tools have been a major obstacle for the engineering of novel functional materials with properties enhanced by their nanoscale morphology, because detailed understanding of the structure–property–operando relationships are required. In this perspective technology has entered in a period of convergence between theory and characterisation tools, traditional spectroscopic techniques are being combined with microscopy to characterise individual nano-objects. In this context advances in the design and fabrication of x-ray focusing systems allow modifying conventional X-ray spectroscopies using synchrotron light to be used to study individual nanostructures and selected regions of a nanoscale sample. These spectroscopies are amongst the most powerful tools in material science providing elemental, electronic, structural and chemical information. Recent trends include in-operando analysis of individual nanostructures.

In my talk I will report recent results obtained using spectromicroscopy techniques to study the doping of suspended graphene flakes. The nitrogen doping of suspended graphene was performed via ion implantation. We will show that inclusion of up to 20 at.% nitrogen can be reached, while maintaining a sp^2-network. The evolution of nitrogen species: pyridinic, graphitic, and pyrrolic, at different doping stages and annealing temperatures is observed by scanning X-ray photoelectron microscopy (SPEM). Variations in the ratio between sp^2 nitrogen species is observed for increasing treatment time; thermally heating the doped carbon nanostructure results in quenching of the sp^3 component, suggesting the graphitic nitrogen as the most thermal stable species. The effect of the interaction of molecular oxygen with nitrogen doped graphene will be discussed.

11:40am **SA+2D+AC+MI-WeM-12 Multi-modal and Multi-dimensional Synchrotron Investigation of Functional Materials**, ***Karen Chen-Wiegart***, Stony Brook University/Brookhaven National Laboratory **INVITED**

Multi-modal and multi-dimensional characterization at synchrotrons can provide unprecedented information for complex, heterogeneous materials

system. A multi-modal approach combines multiple synchrotron techniques to gain complementary information. Furthermore, with imaging techniques specifically, multi-dimensional imaging includes techniques such as tomography, spectroscopic microscopy, or in *situ/operando* imaging. These capabilities are particularly powerful when used to study complex structures with morphological and chemical heterogeneity. This talk will address the applications in energy storage and conversion materials, including Li-ion batteries, Li-S batteries, and solid-oxide fuel cells. Other examples, including nano-/meso-porous metals, cultural heritage and surface treatment on metals will also be briefly discussed.

Author Index

Bold page numbers indicate presenter