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Advances in Electron Energy-Loss Spectroscopy with High Spatial and Energy Resolution

G. A. Botton[1], E. P. Bellido[1], M. Bugnet[1], N. Gauquelin[1,2], S. Prabhudev[1], D. Rossouw[1,3], S. Stambula[1], S.Y. Woo[1], G.-Z. Zhu[1], H. Zhang[4], J.Y.T. Wei[4]

[1]. Department of Materials Science and Engineering, McMaster University, Hamilton, ON, Canada.
[2]. Now at EMAT, University of Antwerp, Antwerp, Belgium.
[3]. Now with Department of Materials Science and Metallurgy, University of Cambridge, UK.
[4]. CIfAR Quantum Materials Program and Dept of Physics, Univ. of Toronto, Toronto, ON, Canada.

Electron energy loss spectroscopy (EELS) has dramatically evolved since the development of electron monochromators, faster detectors within improved spectrometers, all this within more stable aberration-corrected transmission electron microscopes. These developments allow the acquisition of spectra with atomic resolution and spectroscopic quality that is sufficient to probe the changes in chemical bonding at near-atomic level so that "real materials" questions can be studied. Through energy loss near-edge structure analysis, EELS provide useful chemical state information so that changes in materials, for examples at interface, under extreme high-temperature conditions, or at defects can be probed. This contribution aims to review some of the applications of this technique by demonstrating examples of this work related to the study of interfaces in complex oxides, the quantification of spectra obtained at high-spatial resolution, the detection of spectroscopic changes in nanomaterials subjected to intense light irradiation and the plasmonic response of nanostructures.

Experiments were carried out on two aberration-corrected FEI Titan microscopes (a double-corrected Titan 80-300 Cubed, and an “image-corrected” Titan 80-300), both equipped with monochromators and EELS spectrometers (Quantum 966 and Tridiem 865 respectively), achieving down to 70 meV energy resolution. The capability of mapping at the atomic scale is not simply revealing local changes in composition but it allows us to identify the termination of the surface of substrates, and the chemical species that are in direct contact with the substrate (Figure 1). For the particular case of $La_{2/3}Ca_{1/3}MnO_3$ (LCMO) grown on $YBa_2Cu_3O_{7-d}$ (YBCO) [1], our work has shown that the last atomic plane in YBCO is Ba, while the first atomic plane in LCMO is Mn (Figure 1). Similarly, it is also possible to use EELS mapping to provide unambiguous information on the site preference of transition metals in oxides whereby, in a Ca_2FeMnO_5, Mn is found on octahedral sites and Fe on tetrahedral sides (Figure 2). In disordered systems, this approach has allowed us to directly map the distribution of implanted Pr atoms in $SrTiO_3$ and has demonstrated the expected statistical distribution (Figure 3) of atoms that cannot be resolved based on purely high-angle annular dark-field (HAADF)-contrast imaging [2]. For surfaces, we have been able to determine the valence state of surface atoms in reconstructed $SrTiO_3$ [3]

A good demonstration of the very high energy resolution application in energy loss near-edge structures is shown in our studies of the C K edge in single-wall and multiwall carbon nanotubes[4]. With the improved energy resolution, we have demonstrated that, simultaneous intense light irradiation *(in-situ)* and acquisition of energy-loss spectra, there is a significant change in the excitonic peak portion of the σ* fine structure [4]. This high-sensitivity demonstrates that the local heating and the charge carriers generated by infra-red photons significantly modify the electronic structure of the nanotubes. At very low energy losses, we have also shown the detection of energy loss features down to 0.17eV[5], the lowest feature ever reported. In addition, using numerical deconvolution, we have been able to show improvements in the effective energy resolution of spectra down to a FWHM of 0.01eV[6, 7].

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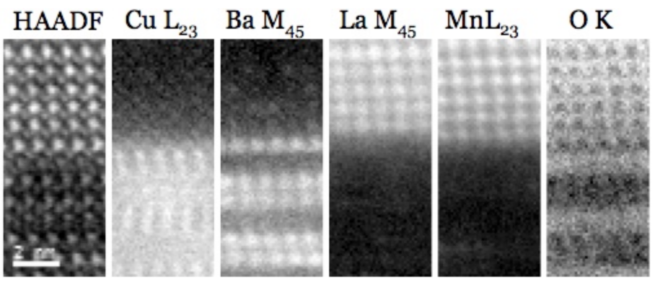

Figure 1, HAADF STEM image and elemental maps of the interface between YBCO (bottom, and LCMO (top) for Cu, Ba, La, Mn and O.

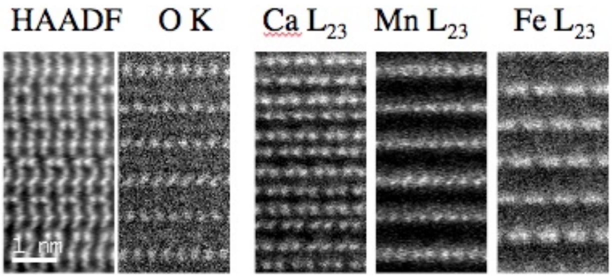

Figure 2, HAADF STEM image and elemental maps showing ordering of Mn and Fe in alternating octahedral and tetrahedral sites respectively with Ca and O separating the layers.

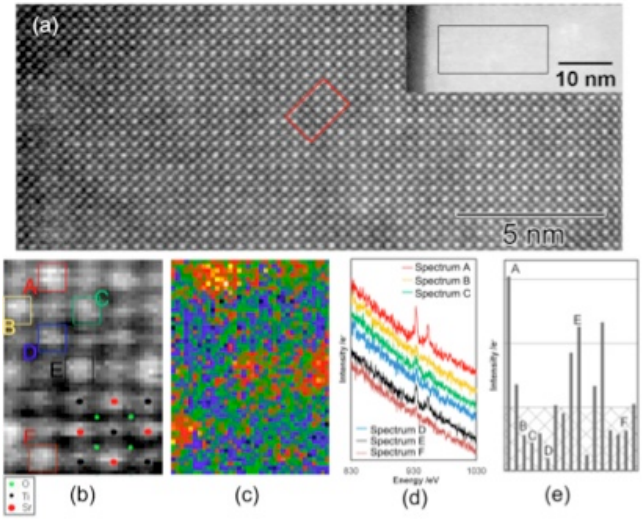

Figure 3, HAADF image of Pr-implanted $SrTiO_3$ (a), and detailed region for EELS analysis (b), elemental map of the implanted Pr (c), energy loss spectra from the selected atomic columns identified in (b) and statistical intensity plot of the edge intensity (e).

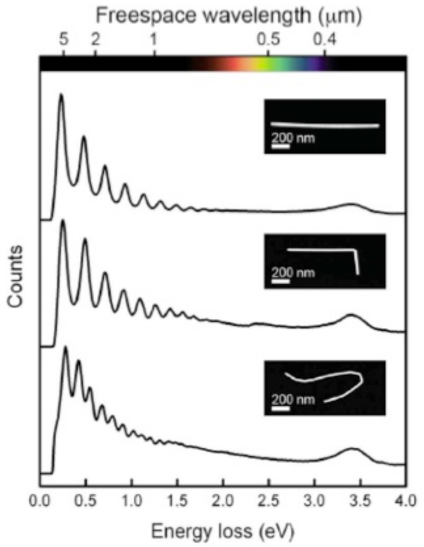

Figure 4, Very low energy loss spectra of Ag nanowires (shown in the inserts) collected with a monochromated microscope with better than 70meV energy resolution.