

Recent Applications of Sub-20meV Monochromated STEM-EELS: from Phonon to Core Losses in Real and Momentum Spaces

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A new generation of electron beam monochromators has recently pushed the energy resolution of (scanning) transmission electron microscopes deep into the sub 20meV range [1]. In addition to the obvious increase in resolution which has made exploring the phonon region of the EELS spectrum possible [1], the increased flexibility of these instruments is proving hugely advantageous for materials science investigations. The energy resolution, beam current and electron optics can be adjusted seamlessly and traded off each other as necessary within a greatly increased range, as will be illustrated on a number of systems studied using a Nion UltraSTEM100MC ‘Hermes’ instrument recently installed at the SuperSTEM Laboratory.

In an early application to the field of two-dimensional materials, the cubic (*c*-BN) and hexagonal (*h*-BN) phases of boron nitride were shown to give rise to markedly different phonon excitations in EELS [2]. A better understanding of this phonon response can be achieved by observing the dependence of the phonon peak under different optical conditions, mapping the energy of the peaks in momentum space and showing a very limited dispersion with momentum, as expected for these optical phonons. Similarly, the low loss spectrum of carbon nanotubes contains a variety of characteristic losses, such as van Hove singularities which are of great importance to understand their electronic behavior and the role of defects in their electronic structure [3]. Observing these directly both in real and momentum space down to sub-20meV energy resolution for nanotubes with increasing number of walls provides insights into the possible structural origins of these excitations.

Moving up in energy loss, the band gap of semi-conductors is known to be strongly affected by structural variations such as composition or crystalline defects. Local compositional changes in Cu(InGa)Se₂ solar cell absorber layers lead to subtle band gap changes [4], and we show how the increased energy resolution achieved through monochromation can provide an increased precision on these nm-scale measurements. We also highlight how peaks associated with excitonic effects in MoS₂ nano-flakes exhibit a clear spatial dependence at step edges and on terraces of varying thicknesses, comparing these results to theoretical calculations explicitly taking into account the electron-hole interactions.

Finally the flexibility afforded by the new generation of monochromators allows us to balance beam intensity and energy width to obtain unprecedented signal-to-noise levels at energy resolution tailored to match the intrinsic width of the observed excitation, as demonstrated in mapping localized plasmon

resonances in Ag plasmonic nanostructures [5] or in linking the crystal field splitting changes in Ti $L_{2,3}$ core loss fine structure across an A-site deficient perovskite to observed structural variations in atomic site occupancies [6].

References

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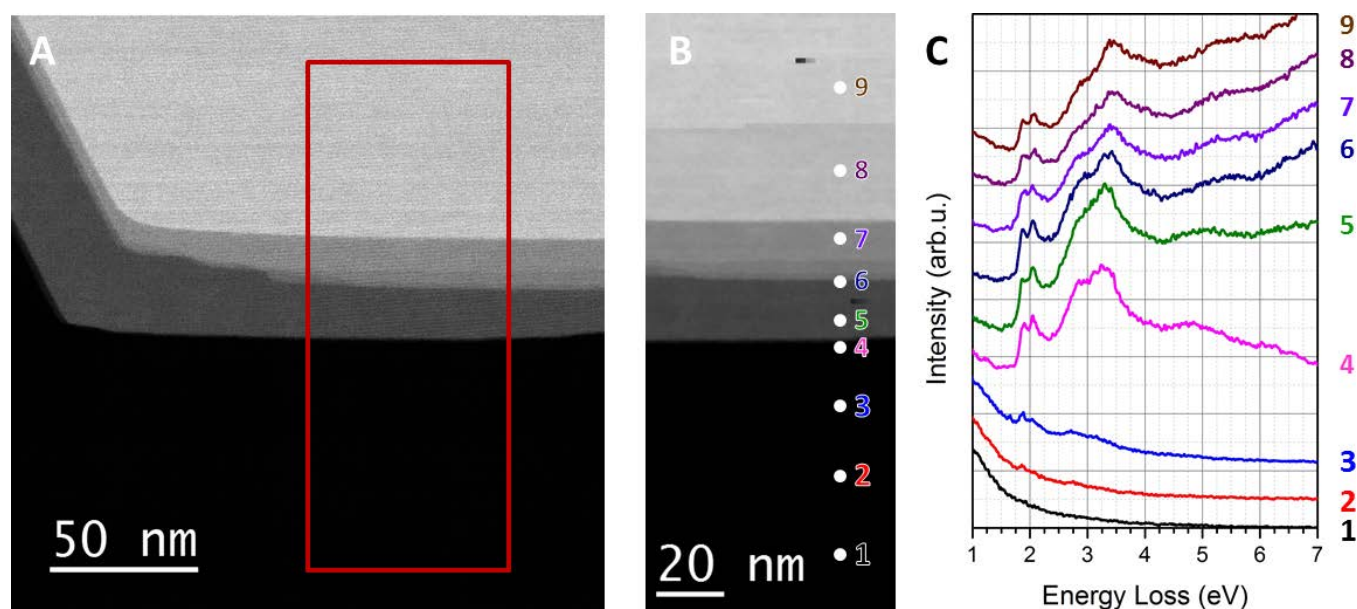


Figure 1. Low loss spectra of a MoS₂ nano-flake. The spectra were acquired at positions across step edges and terraces on a mechanically exfoliated nano-flake, as indicated on the survey image, A. The spectra were averaged horizontally at position marked on the simultaneously acquired HAADF image B to provide a higher signal-to-noise. The peaks at 1.9 eV, C, whose splitting is only resolvable thanks to an energy resolution of ~ 16 meV, are shown to be of an excitonic nature and exhibit a clear variation as a function of probe position. Data acquired at 60kV acceleration voltage on a Nion UltraSTEM100 MC, configured to form a 1.5\AA probe, with ~ 10 pA of beam current once monochromated to 16meV energy resolution.