1475
doi:10.1017/S1431927615008156 Paper No. 0736
Microsc. Microanal. 21 (Suppl 3), 2015

Study Using Low-loss EELS to Compare Properties of TMDs Produced by Mechanical and Liquid Phase Exfoliation

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In recent years, methods for the dispersion and exfoliation of 2D nanostructures of a range of nanomaterials have been successfully developed [1-8], opening up numerous possibilities for a range of innovative technologies [4, 6-10]. As opposed to mechanically cleaving, liquid phase exfoliation can produce large quantities of the material, but to make real applications of liquid phase exfoliated materials feasible there is a need to fully characterize and understand the impact the production route has on the properties of the nanostructures. In addition, very little is known about the effect of flake edges or the presence of surface contaminants on the properties of the materials.
Due to the recent improvements in energy resolution of scanning transmission electron microscopy electron energy-loss spectroscopy (STEM EELS) [11,12] it is now possible to access new information such as the near-infrared/visible/ultraviolet spectral range using this technique. When compared with conventional techniques for measuring optical properties, STEM EELS offers the unique combination of high spatial as well as energy resolution opening up new possibilities for studying properties in a localized manner at an unprecedented energy resolution. For this study we used low-loss STEM EELS using the Nion UltraSTEM100 (SuperSTEM, UK) and the FEI PICO (Jülich, Germany) to compare the optical properties of MoS_2 and other 2D materials produced by mechanical exfoliation and liquid phase exfoliation. Particular attention was being paid to changes in the very low loss EELS (energy losses <10eV) and to relate these to changes in the optical properties when going from multi- to single layered material as well as effects of flake edges [13]. In addition, we studied the effect of surface contamination and orientation dependence of the low loss EELS.

To compare mechanical and liquid exfoliation routes we first analysed MoS_2 produced via both production routes by STEM imaging and STEM EELS analysis of the low-loss region. Overall, we found no difference between the peak positions and their spatial variations between the two materials. The high angle annular dark field dark (HAADF) STEM image of the edge region of a MoS_2 nanosheet produced by mechanical exfoliation is shown in figure **1, A**. A STEM EELS map was acquired over the boxed region shown in figure **1, B** and the corresponding spectra are shown in figure **1, C**. The excitonic lines at 1.9 and 2.1eV [14] are visible in region I in figure **1, C**. These peaks have not previously been unambiguously identified using EELS. The peak in region II in figure **1, C** was the only peak visible in the spectra acquired over or close to the nanosheet edge and it was found to be just below 3eV. In addition, it appeared to slightly shift towards higher energy-losses in spectra acquired over regions further inwards, away from the nanosheet edge. The peak in region III in figure **1, C** was found to increase with increasing layers of material and has previously been associated with interlayer bonding and structure variations [14].

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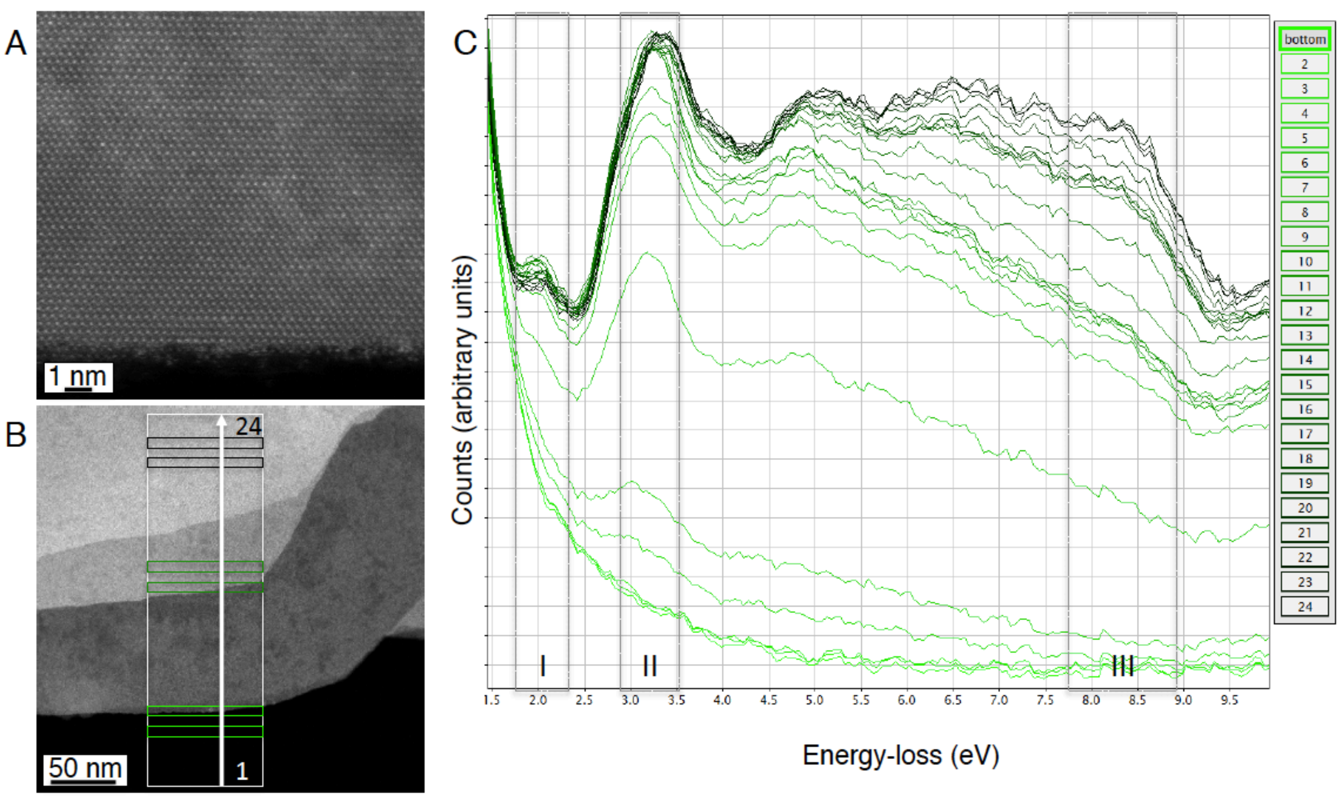

Figure 1. A) HAADF STEM image (Nion, SuperSTEM, Daresbury, UK) of the edge region of a MoS_2 nanosheet produced by mechanical exfoliation. **B**) HAADF STEM Survey image **C**) Summed EEL spectra, normalized to the zero-loss peak and de-noised with mild Principal Component Analysis using 80 components. The spectra were acquired over the regions marked in **B** going from vacuum (spectra 1-3), over the nanosheet edge region (spectra 4-5), over nanosheet steps (spectra 9-12 and spectra 16-19) into the nanosheet with increased thickness (spectra 22-24). The EEL spectra exhibited several changes when moving from the edge to the center, most prominently in energy-loss regions marked I-III.

https://doi.org/10.1017/S1431927615008156