

Probing Defects and Impurity-induced Electronic Structure Changes in Single and Double-layer Hexagonal Boron Nitride Sheets with STEM-EELS

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While graphene is rapidly moving from the laboratory to the factory floor, a sustained research effort has been applied to studying how it interfaces with the other components of emerging graphene-based electronic devices [1]. As a result, other two-dimensional materials with structures analogous to graphene but with complementary properties, have attracted renewed attention [2]. Single-layer hexagonal boron nitride (h-BN) is one such material whose wide band gap of ~ 5.9 eV arguably makes it the thinnest possible insulator [3]. Impurities, defects or structural tailoring have however the potential to dramatically modify the electronic structure and therefore the properties of these two-dimensional crystal membranes. The recent advances in atom-by-atom chemical analysis using annular dark field scanning transmission electron microscopy [4] provide the perfect tool to image directly defects or edge structures in h-BN sheets, or to identify unambiguously impurities within the lattice. We combine here *Z*-contrast STEM imaging at 60kV acceleration voltage on a Nion UltraSTEM100 with electron energy loss spectroscopy (EELS) in both low- and core-loss regimes to probe defect-induced changes in the electronic structure of single and double layer h-BN.

As is the case for graphene, the plasmon structure of single and bi-layer h-BN is quite unique: fig. 1a. While these valence EELS results generally agree with *ab initio* DFT simulations carried out with WIEN2k, the detailed shape of the calculated π -plasmon for pure h-BN shows slight discrepancies with experimental spectra. In particular, a shoulder systematically present at ~ 7.5 eV in the experiments is not reproduced by simulations. Careful image analysis reveals the integration within the h-BN lattice of about 4% of O and C atoms, as single O atoms or C-C/C-O short chains (rather than clusters): fig. 1b. The incorporation in the corresponding amounts of these impurities into large supercells for further WIEN2K simulations leads to a much improved agreement with the experiments (fig. 1c) and confirms the large influence of O impurities on the electronic structure of h-BN [5].

Similarly, lattice relaxations occurring at the edges of a bi-layer h-BN sheet lead to noticeable electronic structure changes. Rather than staying flat, the edges fold and bond together: fig. 2a-b. This reconstruction is obvious through the strain-induced contrast in ADF images, also observed in simulated images of the relaxed structure calculated by DFT. Core-loss *B K* EEL spectra acquired at specific atomic positions along and away from the folded edge show distinct EELS fine features, notably a change of the π^* to σ^* ratio, in extremely good agreement with *ab initio* simulations: fig. 2c. Understanding such atomic scale chemical and physical effects in 2D crystal membranes will no doubt prove essential for nano-engineering attractive properties for these novel materials.

References

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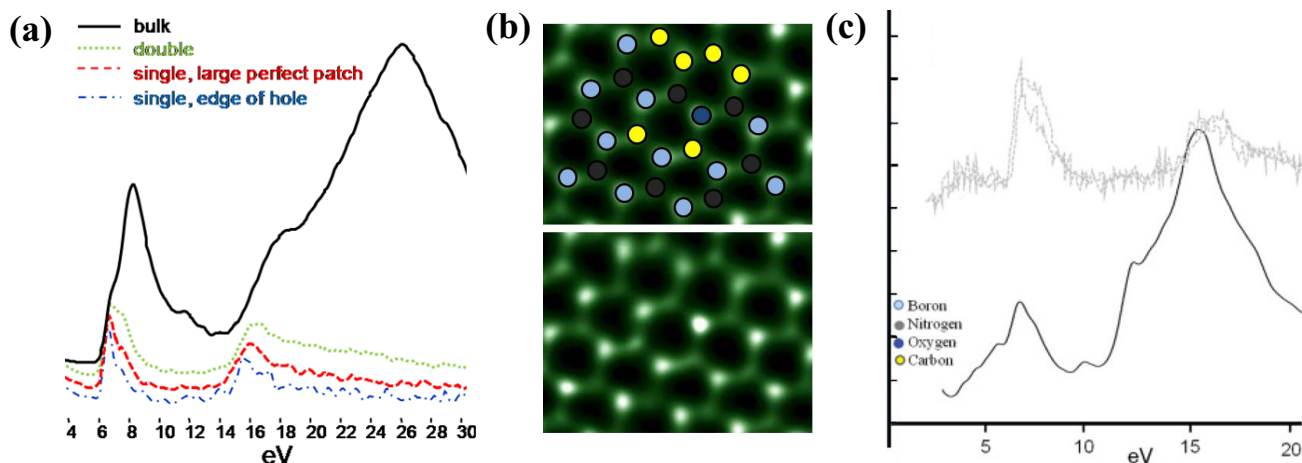


FIG. 1. (a) Experimental spectra from single layer (both from a large layer and in aloof mode at the edge of a hole), double layer and bulk (10+ layers) h-BN. A shoulder at 7.5eV is clearly visible on the π plasmon (arrow) but is not reproduced in simulations of pure h-BN. (b) Histogram intensity analysis [4] of HAADF images reveals the presence of $\sim 4\%$ of C and O impurities. (c) WIEN2k calculation of an EEL spectrum (solid black line) from a structure similar to that of (b), showing that the 7.5eV shoulder from experimental spectra (grey line above) is well reproduced. [5]

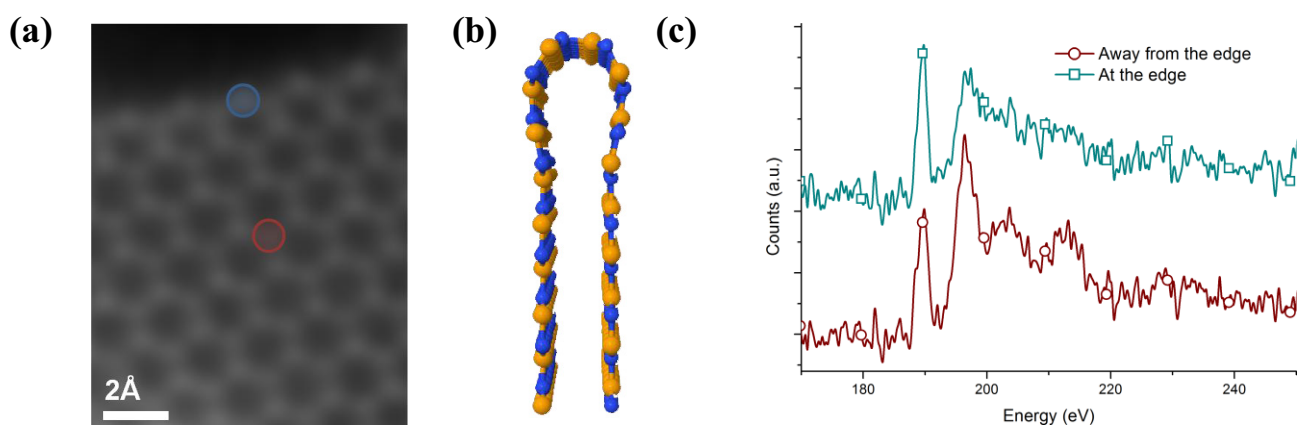


FIG. 2. (a) Low-pass filtered ADF image of the folded edge of a bi-layer h-BN sheet (the number of layers was identified through VEELS and by contrast analysis). The lattice relaxation at the edge results in strain-induced contrast. (b) Edge-on model of the folded sheet: the relaxed atomic positions were calculated by DFT. (c) B K EELS spectra acquired at the positions marked in (a). Clear π^* to σ^* ratio differences can be observed, in agreement with *ab initio* WIEN2k calculations (not shown).