Electron spectroscopy and defects of hollow boron nitride frameworks

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Boron nitride frameworks of interconnected hollow tetrapods (Aero-BN) exhibiting a porosity beyond 99.99% have been analyzed by transmission electron microscopy based electron energy-loss spectroscopy (EELS). Log-ratio method and low-loss spectra suggest the tetrapods exhibit a wall thickness of only a few nanometers. Despite the high porosity and small wall thickness - and resulting evanescent occupied volume - the frameworks exhibit outstanding mechanical and thermal stability. Of special interest are the optical properties, as boron nitride is a large band-gap dielectric and accordingly does not absorb light in the visible range, making it a potentially ideal support for photocatalytic applications.
Numerous point and triangle defects were found (Fig. 1 a) which may cause measurable magnetic properties in the otherwise paramagnetic boron nitride, as shown by *ab initio* calculations. [1] Also, it was observed that the tetrapod walls - mostly consisting of a single crystalline domain - exhibit regions of overlapping randomly rotated layered BN with parallel c-axes.
Furthermore, a strong but unintuitive dependence between the core-loss intensities of σ* and π* features of the B and N K-edges and angular orientation with respect to the electron beam was found and could be correlated with previous results on few layer boron nitride. These results especially shed light on the correct choice of convergence and collection angle during EELS analysis of electronically anisotropic compounds, such as BN with specific orientation of σ and π orbitals. Unlike investigations on traditional layered structures such as graphene or MoS_2, this angular dependence could be observed without tilting or rotating the sample, as the hollow, tube-like morphology of Aero-BN allows analysis of all potential angles by choosing the right position.

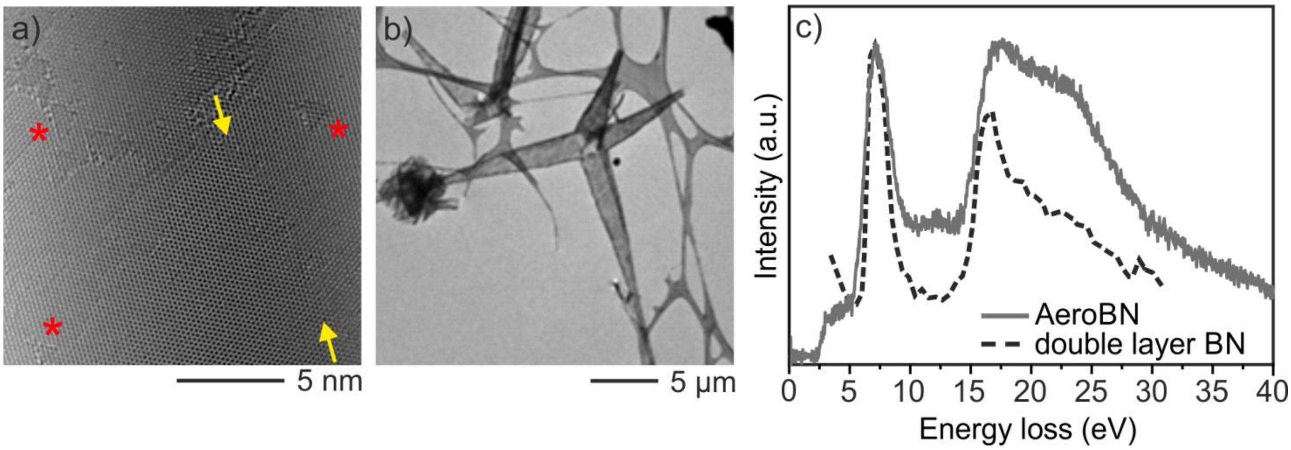

Figure 1: a) High resolution micrograph highlighting point defects (top edge of the image), triangle defects (red asterisks) and a surface step (yellow arrows). b) Morphology of an Aero-BN tetrapod. c) Low-loss EEL spectra of Aero-BN (solid) and double layer h-BN (dashed) as reported by Pan et al. [2] The positions and shapes of the π-plasmon located at around 6 eV match almost perfectly. The positions of the σ-plasmon at 15 eV match while the shape and relative intensity differ slightly. Differences between reference and measured plasmon losses of Aero-BN likely arise due to the curved nature of the latter, defects, and differences in experimental setup. Spectra have been normalized from the onset of the π-plasmon to its apex.

[1] Yang, J., *et al*. Magnetism in boron nitride monolayer: Adatom and vacancy defect. *Surface Science* 604, 1603 - 1607 (2010).

[2] Pan, C. T. *et al.* Nanoscale electron diffraction and plasmon spectroscopy of single- and few-layer boron nitride. *Phys. Rev. B* 85, 045440 (2012).