STEM- EELS low loss mapping of carbon nanocones

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Carbon nanocones distinguish themselves from the myriad of known carbon nanostructures by exhibiting discrete apex angles (112.9˚, 84.6˚, 60˚, 38.9˚ and 19.2˚) corresponding to the incorporation of 1 to 5 60˚ disclinations in a hexagonal graphitic sheet [1]. This topography makes the hollow, multiwalled cones very promising for applications in hydrogen storage, sensors and electrodes [2]. The cone samples investigated in this study were produced from crude oil with a plasma arc, and contain a large number of flat discs, which themselves can be considered cones with an apex angle of 180°.

It is of great interest to determine the electronic structure of individual cones for potential future applications. For example; any variation of the electronic structure as function of cone geometry (i.e. apex angle) would have to be taken into careful consideration before any practical application in sensor technology. Electron energy loss spectroscopy (EELS) in the scanning transmission electron microscope (STEM- EELS) provides the perfect tool for these investigations due to its high combined spatial and energy resolution. All data shown here were acquired with a Nion UltraSTEM operated at 60kV to minimize irradiation damage to the carbon cones, with a measured energy spread of 0.30eV. EEL spectra were deconvoluted for thickness and then de-noised using multivariate statistical analysis as implemented in the HREM Research MSA plug-in for Digital Micrograph [3].

The spatial distribution of the dielectric response of carbon nanotubes and carbon onions has previously been investigated by M. Kociak et al. [4]. This was done by comparing results of low loss EELS line scans to the corresponding High Angle Annular Dark Field (HAADF) image intensity profiles. They identified the observed plasmon modes by comparing the acquired EEL spectra to semi-classical simulations of surface plasmon excitations in EEL spectra of carbon onions, relating specific modes to either the in-plane or out-of-plane component of the dielectric tensor [4].

In the present study we have extended the approach of M. Kociak et al. [4] to mapping of the relative contribution and spatial distribution of plasmon modes. This was done by acquiring 2-D EELS low loss spectrum images of suspended carbon nanocones, for all five discrete cone geometries. *Ab initio* simulations using density functional theory are currently being carried out to model the valence structure of the cones and to explain the observed plasmonic distributions. In this study, the tip area of cones was investigated with particular scrutiny. An example of this is shown in Figure 1 for a cone with 4 pentagons at the tip (i.e. corresponding to an apex angle of ~38.9°: Figure 1a). The EELS low loss map in Figure 1b shows an intriguing spatial distribution of the excitation of a surface plasmon mode attributed to both $\pi \rightarrow \sigma^*$ and $\sigma \rightarrow \pi^*$ transitions [4]. The map was integrated over a 4eV window as indicated for the spectrum in Figure 1c. By comparing the EELS map (Figure 1b) to the HAADF micrograph in (Figure 1a), it is clear that the relative intensity of the '$\pi \rightarrow \sigma^*$/ $\sigma \rightarrow \pi^*$' mode peaks at the edge (i.e. the surface) of the cone.

References

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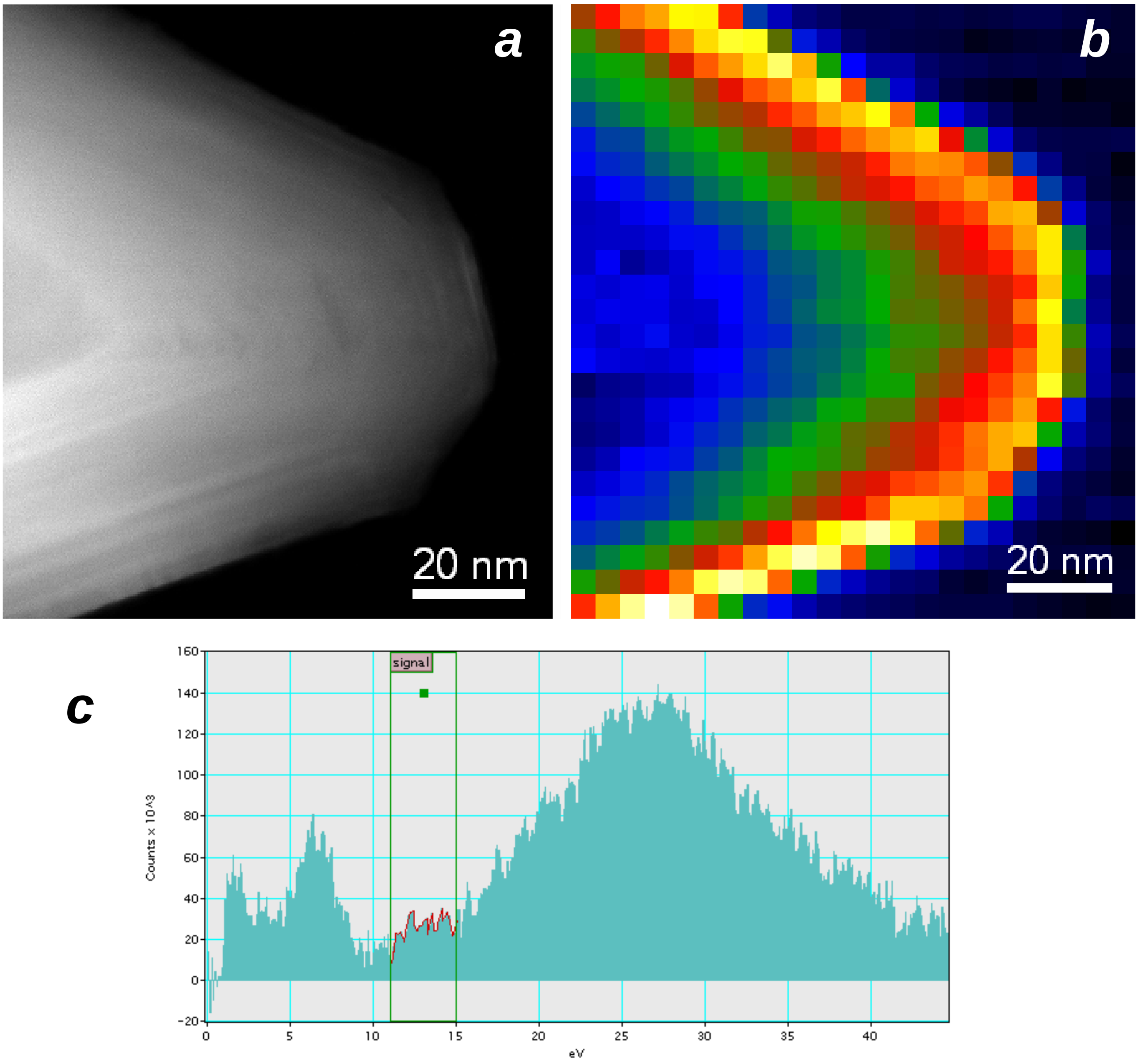

Figure 1a. *HAADF micrograph of the tip of a carbon nanocone (4 pentagons at the tip)* ***b.*** *EELS low loss map showing the spatial distribution of the excitation of the '$\pi \rightarrow \sigma^*$/ $\sigma \rightarrow \pi^*$' surface plasmon mode. This map was integrated over a 4eV window as indicated in the low loss spectrum* ***c*** *(zero loss peak stripped)**.***