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To cite this article: A Seepujak et al 2006 J. Phys.: Conf. Ser. 26 161

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A. Seepujak\textsuperscript{1}, U. Bangert\textsuperscript{1}, A. J. Harvey\textsuperscript{1}, V. D. Blank\textsuperscript{2}, B. A. Kulnitskiy\textsuperscript{2} and D. V. Batov\textsuperscript{2}

\textsuperscript{1} Department of Material Science, University of Manchester, Oxford Road, Manchester M13 9PL, UK

\textsuperscript{2} Technological Institute for Superhard and Novel Carbon Materials, 7a Centralnaya Street, 142092 Troitsk, Moscow, Russia

E-mail: as887@hotmail.com

Abstract. Core EEL spectra of MWCNTs (multi-wall carbon nanotubes) grown in a nitrogen atmosphere were acquired utilising a dedicated STEM equipped with a Gatan Enfina system. Splitting of the carbon K-edge $\pi^*$ resonance into two peaks provided evidence of two non-degenerate carbon bonding states. In order to confirm the presence of a CN$\textsubscript{x}$ bonding state, a full-potential linearised augmented plane-wave method was utilised to simulate core EEL spectra of graphite and graphitic-CN$\textsubscript{x}$ compounds. The simulations confirmed splitting of the carbon K-edge $\pi^*$ resonance in graphitic-CN$\textsubscript{x}$ materials, with the pristine graphite $\pi^*$ resonance remaining unsplit. The simulations also confirmed the increasing degree of amorphicity with higher concentrations (25\%) of substitutional nitrogen in graphite.

1. Introduction

CN$\textsubscript{x}$ materials continue to be a hot topic for study, owing to their predicted exceptional properties e.g. superhardness and elasticity [1-5]. Furthermore, the presence of substitutional nitrogen within a MWCNT has been seen to modify the electronic properties, with all CN$\textsubscript{x}$ nanotubes having been found to possess strong donor states near the Fermi level [1-5, and refs. therein]. Nevertheless, nitrogen incorporation into fullerenes cannot be precisely engineered. High-spatially resolved EEL spectroscopy performed within a STEM (scanning transmission electron microscope), represents an ideal method for investigating modified electronic properties, arising from heterogeneous distributions of nitrogen phases incorporated within MWCNTs.

2. Experimental

The MWCNTs were formed within a water-cooled high isostatic pressure apparatus, with a carrier gas containing pure nitrogen at a pressure of 70 MPa. Details of the MWCNT production are presented elsewhere [6].

EEL spectra were acquired utilising a dedicated VG HB-601 STEM equipped with a CCD-detector based Gatan UHV Enfina system. The STEM possessed a 100 keV cold field emission source, providing a spatial resolution of down to 1 nm, and energy resolution of 0.34 eV, given by the FWHM of the ZLP. Objective / collector aperture semi-angles of 21.3 / 3.14 mrad were used.
The Enfina system allowed utilisation of ‘spectrum imaging mode’ [7], allowing one to map the concentration of a given element. The most important advantage imparted by spectrum imaging e.g. over energy-filtered imaging (GIF), is the provision of an entire EEL spectrum at each pixel of a user-defined 2D acquisition raster. The resultant array of EEL spectra is termed a spectrum image (SI). Post-measurement processing and analysis of the entire SI can be performed e.g. mapping of the relative concentration of constituent elements in a sample. In order to evaluate the experimental core EEL spectra, DFT (density functional theory) calculations were performed utilising the full potential linearised augmented plane-wave (FLAP-W) computer program Wien2K [8].

3. Results and discussion

Experimental core EEL spectra acquired from a segmented MWCNT are detailed in figure 1.

Figure 1. (a) Schematic and STEM BF-image of a MWCNT exhibiting a bamboo-like morphology. Indicated in the BF-image is the acquisition area of the spectrum image, along with the location of several spectra selected for scrutiny. (b) Spectrum images detailing the relative concentration of carbon and nitrogen, within the acquisition area. Black (white) pixels correspond to the least (greatest) relative concentration. (c) Core EEL spectra of the carbon K-edge, corresponding to positions identified in figure 1(a). G represents the core EEL spectrum of a pristine graphite sample.

Quantitative analysis (figure 1(b)) detailed the MWCNT contained a significant amount of nitrogen. The shape of the nitrogen K-edge confirmed the nitrogen was not molecular (i.e. gaseous), but rather a CN_x species. The spectrum images presented in figure 1(b), demonstrate the heterogeneous distribution of nitrogen. At position 2, the composition was carbon 91.9 ± 12.5% and nitrogen 8.2 ± 1.1%; at position 4, the composition was carbon 95.8 ± 13.3% and nitrogen 4.2 ± 0.6%.

The relative concentrations of carbon and nitrogen in figure 1(b) were calculated, by utilising counts over an energy window of 25 eV, from the onset of the core-loss edge. This reduced the effect of the increasing $\pi^*$ peak intensity, in spectra acquired at a large impact parameter with respect to the nanotube axis, from artificially providing a larger elemental concentration. Bond configuration information was deduced by scrutinising core EEL structure; the carbon K-edge at positions 1 to 6, are detailed in figure 1(c). The graphite spectrum (G) exhibits a very intense and narrow $\pi^*$ peak at 286 eV, characteristic of sp^2 hybridisation. The marginally sharper $\pi^*$ peak at the edge (positions 1 and 6),
in comparison to more central locations (positions 2 to 5) can be ascribed to an orientation effect [9], with \( \pi \) states being probed when the polarisation vector of the momentum transfer \( \mathbf{q} \) is parallel to the graphitic basal planes. Notable in spectra acquired at positions 1 to 6, in comparison to that acquired at G, is the absence of a well defined \( \pi^* \) peak. This absence is characteristic of amorphous carbon, and can be ascribed to an increase in sp\(^1\) and sp\(^3\) hybridisation, with a consequent reduction in sp\(^2\) hybridisation. Concomitant with the sp\(^3\) bonding state is the presence of bucking and interlinking of the graphene basal planes [10], resulting in suppression of the 1s\( \rightarrow \pi^* \) electronic transition.

Further notable in spectra 1-6 of figure 1(c), is the splitting of the suppressed \( \pi^* \) peak into peaks at 285.4 eV and 287.5 eV, which is most pronounced at position 2. Splitting of both the carbon and nitrogen K-edge \( \pi^* \) peak has previously been observed in EEL spectra acquired from CN\(_x\) materials e.g. see [2]. Splitting of the nitrogen K-edge is ascribed to the presence of sp\(^2\) and sp\(^3\) hybridised forms of nitrogen, i.e. the presence of pyridinic and bridge-head nitrogen, incorporated within the hexagonal graphite network. Literature [ref. 3 and refs. therein] detail experimentally measured XPS (x-ray photoelectron spectroscopy) carbon 1s spectra, acquired from a CN\(_x\) material, being decomposed into peaks which were assigned as follows. A peak at 284.7 eV was assigned as either sp\(^3\) hybridised carbon in a carbon environment with a low nitrogen concentration, or as sp\(^2\) hybridised carbon with a greater nitrogen concentration. A peak at 285.6 eV was assigned as sp\(^3\) hybridised carbon with one nitrogen neighbour, and a peak at 286.8 eV was assigned as sp\(^3\) hybridised carbon with two nitrogen neighbours.

In order to test whether splitting of the carbon K-edge \( \pi^* \) resonance arises from the presence of both C-C and C-N bonding states, DFT calculations were performed utilising the Wien2K computer program [8]. The muffin-tin radii were set at 1.34 atomic units for both carbon and nitrogen. Core hole effects were neglected. 1000 k-points were utilised to sample the full Brillouin zone of graphite. Owing to the very large diameter of the MWCNT detailed in figure 1, it was assumed that curvature effects would be negligible, hence the nanotube was modelled as a planar medium. Both unit cell and supercell calculations were performed to calculate core EEL spectra of pristine planar graphite and planar graphitic-CN\(_x\) phases, for both a lattice type P was used. Whilst the unit cell calculations only allowed very large concentrations of substitutional nitrogen, the supercell calculations allowed the substitutional nitrogen concentration to be reduced down to as low as one atom per supercell. The energy of the primary electrons was set at 100 keV, with the onset of the core-loss ionisation edge set at 285 eV. Simulated core EEL spectra are illustrated in figure 2, which were not obtained by calculating a spectrum for each inequivalent carbon atom and averaging. Note that the nitrogen concentration of the CN\(_x\) material used for simulation in figure 2(c), is very close to that measured experimentally near position 2, identified in figure 1.

The fine structure of each core EEL spectrum identifies the characteristic bonding phases of the carbon atoms. This may be utilised to deduce the co-ordination fingerprint of a given phase. Fine structure peaks between \( \sim285 \) eV and \( \sim288 \) eV arise from the 1s\( \rightarrow \pi^* \) transition, with fine structure peaks between \( \sim290 \) eV and \( \sim315 \) eV arising from the 1s\( \rightarrow \sigma^* \) transition. A good agreement exists between the pristine graphite spectrum in figure 2(a), and other published core EEL simulations [3,4] of the same material. In figure 2(b), the suppression of the \( \pi^* \) fine structure (in comparison to that of the simulated spectrum of pristine graphite) is consistent with previous observations [2] of a CN\(_x\) material with 22 ± 3 % nitrogen content, and can be ascribed to the decrease (increase) in (sp\(^2\)) sp\(^3\) bonding. The fine structure spectrum of figure 2(c) exhibits largely graphitic characteristics, i.e. prominent features ascribed to the 1s\( \rightarrow \pi^* \) transition.

In both figure 2(b) and 2(c), two fine structure \( \pi^* \) peaks are observed. This gives witness of the presence of two non-degenerate bonding states of carbon, which are consistent with the XPS measurements detailed above i.e. carbon in a carbon environment, and carbon in a nitrogen environment. These two fine structure peaks thus suggest there may be an sp\(^3\) bonding environment. Furthermore, the suppression of the \( \pi^* \) fine structure in figure 2(b) is consistent with the buckling of graphene planes (i.e. an increase in amorphicity). Since this buckling is predicted to occur only when
the nitrogen content exceeds 20% [11], this would conceivably explain the reason for the lack of suppression of the $\pi^*$ fine structure in the spectrum of figure 2(c).

Figure 2. Wien2K simulated core EEL spectra. The narrow line represents the theoretical carbon K-edge ELNES (energy-loss near-edge fine structure), with the bold line representing the broadened spectrum. (a) Planar pristine graphite, (b) planar graphite with 25% substitutional nitrogen, and no vacancies. (c) Planar graphite with 12.5% substitutional nitrogen, and 12.5% vacancies.

The structure of figure 2(c) is very dissimilar to those of figure 2(a) and 2(b). This may be attributed to the presence of the vacancy in the structure model of figure 2(c), resulting in a different characteristic co-ordination fingerprint. It is hoped further experimental measurements will provide a greater understanding of the origin of these differences.

Summary

Experimental core EEL spectra acquired from a CN$_x$ nanotube detailed splitting of the C K-edge $\pi^*$ resonance into peaks at 285.4 eV and 287.5 eV, in the vicinity of a localised high nitrogen concentration. The 285.4 eV peak was assigned as a combination of sp$^2$ or sp$^3$ hybridised carbon in a carbon environment and sp$^3$ hybridised carbon with one or two nitrogen neighbours. DFT calculations suggest the peak at 287.5 eV is attributed to carbon in the presence of a vacancy. The calculations further demonstrate that only in CN$_x$ nanotubes possessing a low substitutional nitrogen concentration (12.5%) is splitting of the C K-edge $\pi^*$ resonance observable, owing to suppressed $\pi^*$ features for higher (25%) nitrogen concentrations. The presence of an experimentally measured unsplit $\pi^*$ peak, cannot therefore be utilised to conclusively determine the absence of degenerate C-C and C-N bonding states.

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