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Excitons at the B K edge of boron nitride nanotubes probed by x-ray absorption spectroscopy

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Abstract

We have performed a near-edge x-ray absorption fine-structure (NEXAFS) investigation of multi-walled boron nitride nanotubes (BNNTs). We show that the one-dimensionality of BNNTs is clearly evident in the B K edge spectrum, while the N K edge spectrum is similar to that of layered hexagonal BN (h-BN). We observe a sharp feature at the σ^* onset of the B K edge, which we ascribe to a core exciton state. We also report a comparison with spectra taken after an ammonia plasma treatment, showing that the B K edge becomes indistinguishable from that of h-BN, due to the breaking of the tubular order and the formation of small h-BN clusters.

1. Introduction

X-ray absorption and energy loss spectroscopy are widely used to probe the unoccupied electronic states of materials. In a rough picture, the unoccupied density of states (DOS) of materials can be described through the excitation of one electron from a core level into the conduction band. However, the excited electron deals with a system where one electron has been removed and a core hole has been generated. The relaxation of such a system might be different from that of the ground state, and thus many-body effects, like electron-hole interactions, must be taken into account in explaining excitation spectra [1]. The strength of the interaction of the electron-hole pairs (excitons), coupled by the Coulomb force, is related to the effective screening of valence electrons, namely to the conductivity and the dielectric constant of materials. Insulating and semiconductor materials, for instance, are expected to show strong excitons, especially if charges are confined into low-dimensional systems [2].

In the present work, we have focused our attention on the B K and N K absorption edges of pristine and functionalized

boron nitride nanotubes (BNNTs), by means of a near-edge x-ray absorption fine-structure (NEXAFS) investigation. BNNTs are structurally related to carbon nanotubes (CNTs) [3, 4], pursuing the parallelism between other allotropes (graphite and hexagonal boron nitride (BN); diamond and cubic-BN; amorphous carbon and amorphous BN). The single sheet of h-BN has the same honeycomb lattice as graphene, but with the two atoms of the unit cell chemically inequivalent, leading to a slightly ionic bond character, with the electronic charge mainly centered at the N sites, and opening a gap of about 5.9 eV in the electronic structure [5]. The structure of multi-walled BNNTs (and h-BN), differs from the corresponding one of CNTs (and graphite) for the stacking sequence, where each N atom is on top of a B one and vice versa (AAA... stacking). The structure of BNNTs leads to a defined symmetry of the wavefunctions with respect to the atomic planes, namely σ states arising from s , p_x , and p_y atomic orbitals are oriented along the planes, while π states arising from p_z orbitals are perpendicular to them. In the K edge spectra of boron and nitrogen, transitions are allowed only to the p component of σ and π states. According to the existing literature on BNNTs [6, 7], the p-type

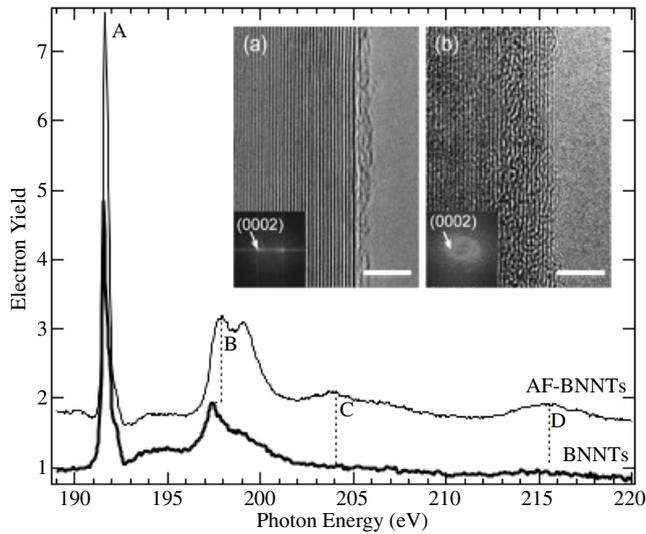


Figure 1. B K edge of pristine (bold line) and amine-functionalized (thin line) BNNTs. In the inset: high-resolution TEM images and Fourier transform images of the wall of (a) pristine BNNTs and (b) AF-BNNTs, from [10]. Scale bar, 4 nm.

partial density of empty states probed by NEXAFS is almost completely insensitive to the orientation of hexagonal layers, namely whether they are flat or rolled up into nanotubes. A slight difference (0.5 eV) was found at the π^* onset of the N K edge [6] and interpreted in terms of curvature/non-planarity effects of the tubes, apparently more pronounced at the N K edge than at the B K one. The similarity between BNNTs and h-BN as probed by both NEXAFS and electron energy loss spectroscopy [8] is somewhat surprising considering the drastic changes of the band structure and dimensionality of the two allotropes [2, 3, 9].

Here, we show that the B K edge does reflect the effect of low-dimensionality in BNNTs, having a strong exciton at the σ^* onset, not observed in layered BN. At the same time though, we demonstrate that N spectra are insensitive to curvature effects, showing a K edge line shape indistinguishable from that of h-BN. We also show that when the tubular order of BNNTs is broken by an ammonia plasma treatment, the B K edge spectrum exhibits the line shape of h-BN. This finding reflects the formation of small two-dimensional clusters and demonstrate that low-dimensionality and local order are a prerequisite to observe exciton states at the σ^* onset of the B K edge spectrum.

2. Experimental details

BNNTs were synthesized on Si substrates by thermal decomposition of B and MgO powders in an ammonia environment at 1200 °C; average diameters and lengths of the tubes were 20 nm and over 10 μm , respectively. Powders are made of bundles of nanotubes randomly oriented in space. Amine-functionalized BNNTs (AF-BNNTs) were obtained via ammonia plasma treatment in a microwave plasma generator. All the details on the preparation and functionalization of our samples are described in [10].

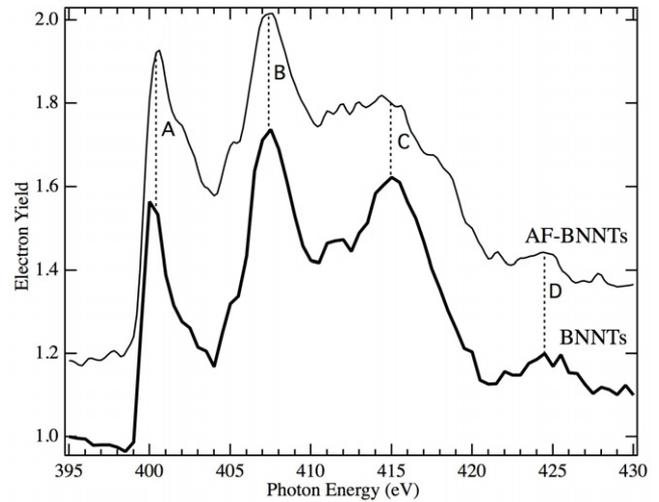


Figure 2. N K edge of pristine (bold line) and amine-functionalized (thin line) BNNTs.

NEXAFS experiments were performed at the Materials Science Beamline (MSB) of Elettra (Italy), using a plane grating monochromator and an ultrahigh vacuum chamber (operating at a base pressure of 2×10^{-10} mbar) equipped with a multichannel 150 mm mean radius electron energy analyzer (Phoibos 150). The electron yield was measured by collecting the secondary electron peak with kinetic energy from 15 to 30 eV vs photon energy, with an overall energy resolution of 150 meV (B K) and 400 meV (N K). Spectra were collected at room temperature with the photon beam incident at the magic angle (54.7° relative to the surface). To eliminate the effect of incident beam intensity fluctuations, the electron yield was normalized using the incident beam intensity obtained from the photoemission yield of a Au grid. The spectra have been processed through pre-edge normalization routines.

3. Results and discussion

Figures 1 and 2 show B K and the N K edge spectra of pristine (bold line) and AF-BNNTs (thin line), respectively. Analogously to the C K edge of graphite and CNTs, B and N K edge spectra of BNNTs were interpreted in terms of transitions from the $1s$ initial state into final states of π (A peak) and σ (B, C and D peaks) symmetry. Specifically, the prominent peak of the B K edge at about 191.6 eV is due to the $B 1s \rightarrow \pi^*(2p_z)$ transition. The sharpness of this peak and its shift of about 1.4 eV towards lower values with respect to the bottom of the conduction band [11] are a clear indication of the excitonic character of this transition. Several theoretical calculations performed on h-BN have confirmed the existence of this core exciton state [12, 13]. Going towards higher energies, the double feature centered at about 198.5 eV is due to the excitation $B 1s \rightarrow \sigma^*(2p_{xy})$, corresponding, in a band theory approach, to the maximum of the DOS at the L and Γ point of the Brillouin zone (BZ), respectively [11]. The peak at about 204 eV (C peak), present in the B K edge spectra of AF-BNNTs and of h-BN [6], and barely visible in that of BNNTs, is due to another transition $B 1s \rightarrow \sigma^*(2p_{xy})$, corresponding

to a maximum of the DOS along the ΓM direction of the BZ. Finally, the peak at about 215 eV (D peak), again barely detectable in the spectrum of BNNTs, is due to a σ^* resonance reminiscent of that observed for c-BN [14].

The N K edge spectrum of BNNTs (figure 2) is composed of four broad peaks. The first, peak A observed at 400 eV, is due to the N $1s \rightarrow \pi^*(2p_z)$ transition; the B, C and D peaks, centered at about 407 eV, 415 eV and 425 eV respectively, are due to σ^* resonances analogous those observed for the B K edge.

Our samples are extremely clean, as judged by the absence of any extra feature due to contaminants, like a sharp peak centered at about 193.8 eV due to boron oxide observed for some other preparation procedures [6, 15].

Figure 1 shows that, while the B K edge spectrum of AF-BNNTs is very similar to that of h-BN [16, 17], the corresponding absorption spectrum of BNNTs exhibits characteristic features. The B peak of the B K edge spectrum shows an intense and sharp onset shifted towards lower values of about 0.5 eV with respect to AF-BNNTs. Due to its sharpness and its shift towards the bottom of the conduction band, we assign this feature to an exciton state of the first σ^* resonance, analogous to the σ^* exciton observed for CNTs and graphite [18]. The reduced intensity of higher energy features (C and D peaks) of the B K edge spectrum (shown in several experiments) is compatible with our interpretation of the excitonic character of the first σ^* transition. A positive core-hole potential, indeed, has the effect of pulling states towards the threshold energy, causing a contraction of the wavefunction and enhancing the spectral weight at the onset of the transition. On the other hand, it is not surprising if bound excitons, like π^* and first σ^* resonances, are seen only at the B K edge and not in the N K spectra. In fact in ionic or polar compounds, due to different screening efficiency, exciton states are more strongly bound at the cation than at the anion site. This finding was recently theoretically predicted and demonstrated on a large variety of materials, like LiF, BeO, c-BN and carbon compounds [1]. We also point out that bound excitons are stronger in the optical response of BNNTs [2] (or CNTs [19]) with respect to the corresponding layered materials, as core-hole effects are markedly enhanced in one-dimensional systems.

We now discuss the effect of the ammonia plasma treatment on the B and N K edges of BNNTs. Our previous investigations showed that the ammonia plasma bombardment generates many defects on the tubular structure (inset figure 1), and radicals of the plasma such as NH_2^* or H^* are expected to terminate the resulting vacancies, as seen by Fourier transform infrared spectroscopy and x-ray photoelectron spectroscopy [10, 20]. The only difference seen here is at the B K edge, while the N K edge retains the same line shape even after the ammonia plasma treatment. Electronic transitions due to $-NH_2$ groups are expected at about 406 eV [21], in coincidence with the onset of the first N σ^* resonance. Considering that atomic hydrogen is not easily detectable, its identification by NEXAFS in our case is even more difficult. Interestingly, after the ammonia plasma treatment, we do not observe any effect of damage due to high

energy ion implantation as reported in the literature for N_2^+ ion implantation of BN thin films [22]. Our B K edge spectrum of AF-BNNTs (figure 1) becomes indistinguishable from that of h-BN, losing the characteristics of pristine BNNTs. We assume that the main effect reflected in the B K edge spectrum of AF-BNNTs is the breaking of the long range tubular order, and the local formation of small h-BN clusters. Moreover, taking into account that the presence of defects, clearly detectable in the π^* resonance of both B and N K edges [7], is not enhanced after the ammonia treatment, we conclude that this finding is an indication that NH_2^* or H^* radicals of the plasma terminate the vacancies. The mean energy of the collected secondary electrons was 22.5 eV, corresponding to an inelastic mean free path of the electrons (and thus depth sensitivity) of about 1 nm. Thus, we believe our approach is sensitive to surface defects.

4. Conclusions

We have reported a NEXAFS investigation of pristine and amine-functionalized BNNTs. Concerning pristine BNNTs, our data show that while the N K edge is similar to that of the layered compound h-BN, the B K edge exhibits some distinctive properties. The double peak centered at about 198.5 eV has a different spectral weight for the two components. Specifically, a sharp peak at the onset of the first σ^* resonance appears, which is due to an exciton state. This electron-hole bound state is enhanced on BNNTs with respect to h-BN due to the one-dimensionality of these compounds.

After the ammonia plasma treatment, we showed that the B K edge exhibits the line shape of h-BN. We explain this effect as due to the local formation of small h-BN clusters, terminated at their edges by the radicals of the ammonia plasma.

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