Electronic structure of the carbon nanotube tips studied by x-ray-absorption spectroscopy and scanning photoelectron microscopy

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Angle-dependent x-ray absorption near edge structure (XANES) and scanning photoelectron microscopy (SPEM) measurements have been performed to differentiate local electronic structures of the tips and sidewalls of highly aligned carbon nanotubes. The intensities of both π^*- and σ^*-band C K-edge XANES features are found to be significantly enhanced at the tip. SPEM results also show that the tips have a larger density of states and a higher C $1s$ binding energy than those of sidewalls. The increase of the tip XANES and SPEM intensities are quite uniform over an energy range wider than 10 eV in contrast to earlier finding that the enhancement is only near the Fermi level. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1523152]

Carbon nanotubes (CNTs)[1] have attracted enormous attention over the last decade because of both fundamental scientific interests and their potential applications,[2] including the use as electron field emitters.[3,4] For emitters such as CNTs, most electrons are emitted from the tips. Spatially resolved electron energy loss spectroscopy showed that the local electronic structure at the tip could dominantly determine electron emission from a CNT.[5] Since tips have a smaller radius of curvature, the local electronic structures at tips were proposed to be different from those of sidewalls.[6,7] Theoretical investigations showed that the ends of the tube should have different electronic structures due to the presence of topological defects or localized states.[8,9] Carbon K-edge electron energy-loss spectroscopy[10] and x-ray absorption near-edge structure (XANES)[11] measurements for CNTs suggested that the overall features of the electronic states of carbon atoms in the nanotubes are very similar to those of graphite. On the other hand, photoemission measurements found that at the tip, the C $1s$ core level could shift to a higher binding energy and the density of states (DOS) at the Fermi level, E_f, was enhanced.[12] More recently, scanning photoelectron microscopy (SPEM) measurements for the aligned CNTs also revealed that the tip has a larger DOS near E_f than the sidewall.[13] Despite these investigations, the physical origin that causes the increase of DOS at the tips is still under debate. Here, we combine angle-dependent C K-edge XANES and SPEM measurements for

highly aligned CNTs to better understand the enhancement of DOS and the mechanism of electron field emission at the tips.

Angle-dependent C K-edge XANES measurements were performed using a high-energy spherical grating monochromator (HSGM) beamline at the Synchrotron Radiation Research Center (SRRC) in Hsinchu, Taiwan. The C K-edge spectra were obtained using the sample drain current mode at room temperature. SPEM measurements were performed at the U5-SGM undulator beamline of SRRC. The SPEM-end station of the SRRC has been described in detail elsewhere.[14] The vertically aligned CNTs were prepared on the p-type Si(100) substrates by microwave plasma enhanced chemical vapor deposition (MPE-CVD). Before the MPE-CVD process, thin 7 nm thick Fe layers were coated onto the Si substrates by e-beam evaporation. CNTs were subsequently grown using a microwave at a power of 1.5 kW and a chamber pressure of 50 Torr. Using the scanning electron microscope and transmission electron microscopy (TEM), the well-aligned multiwalled CNTs were observed to be $\sim$7 μm long and 10–20 nm in diameter as presented in Figs. 1(a) and 1(b). Details of the preparation of these CNTs can be found elsewhere.[15]

Figure 2 shows the angle-dependent C K-edge XANES spectra of the aligned CNTs. The spectra were normalized using the incident beam intensity, I_0, and keeping the area under the spectra in the energy range between 345 and 360 eV (not fully shown in the figure) fixed. According to the dipole-transition selection rule, the spectra in Fig. 2 are due to transitions from the carbon $1s$ core level to p-like final unoccupied states. The general line shapes of the C K-edge
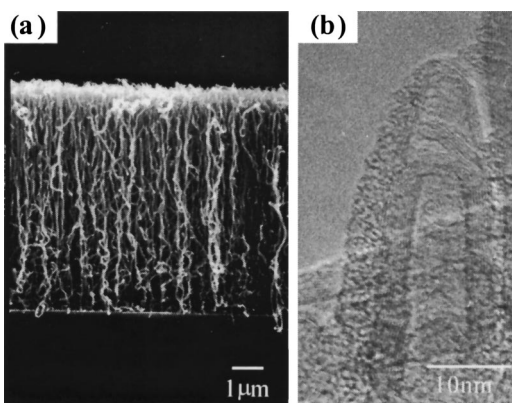
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FIG. 1. (a) Scanning electron microscope image and (b) transmission electron microscope image of the well-aligned multiwalled carbon nanotubes with diameters of 10–20 nm.

FIG. 3. Cross-sectional SPEM C 1*s* image of aligned CNTs.

XANES spectra obtained with different angles of incidence, θ, between the surface normal and the incident synchrotron radiation appear to be similar, though their intensities are different. The two prominent peaks near 286 and 293 eV are known to be associated with the unoccupied π^* and σ^* bands, respectively. Between π^* and σ^* peaks a very weak feature near 288 eV is also observed. This feature can be attributed to the free-electron-like interlayer states in the graphite.[16] The inset in the lower part of Fig. 2 shows that the intensities of the π^*- and σ^*-band features of the aligned CNTs increases when θ decreases from 72° to 0°. Since the intensity is approximately proportional to the density of the unoccupied C $2p$-derived states, the result indicates an increase of the absorption intensity with the decrease of θ not only for the unoccupied π^* states but also for the σ^* state.
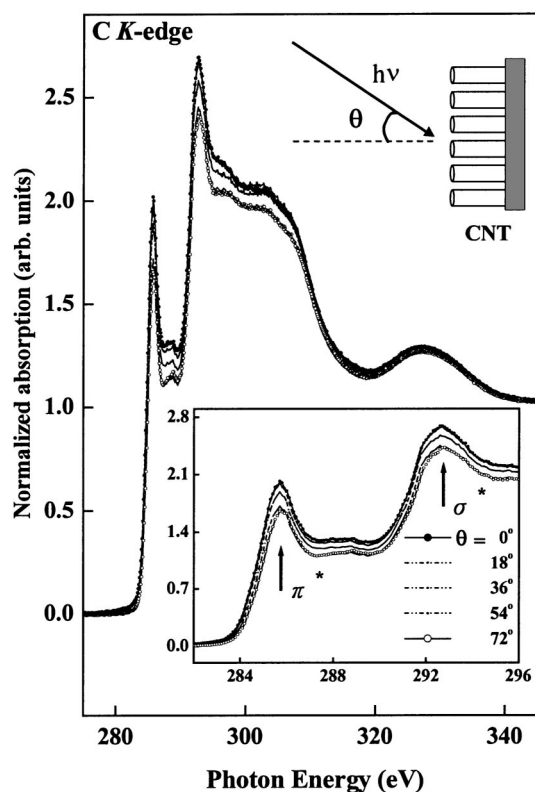

FIG. 2. Normalized C *K*-edge absorption spectra of the aligned carbon nanotubes as a function of θ. The inset shows an enlarged part of the near-edge spectra.
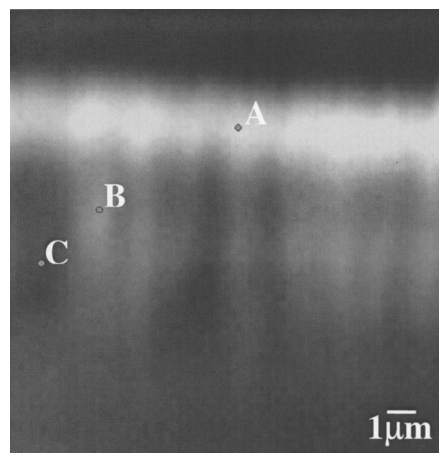
The π^* states are composed of C $2p_x$ and $2p_y$ orbitals, whereas the σ^* state contains the C $2p_z$ orbital. The CNTs are highly aligned, therefore the spectra obtained at normal incidence ($\theta=0°$) and at large incident angle ($\theta=72°$) can be expected to be dominated by contributions from tips and sidewalls, respectively. Thus, our C *K*-edge XANES result shows that the DOSs of both unoccupied π^* and σ^* bands are enhanced at the tip.

Figure 3 shows the C 1*s* SPEM cross-section image of aligned CNTs. The C 1*s* photoelectrons have maximum intensity in the tip region marked by A. In the sidewall region below the tip, there are some less bright areas marked by B, which may contain bent or shorter CNTs. The dark sidewall region marked by C exhibits a shadowing effect.[13,17] The image of tips is clearly much brighter than that of the rest of the parts of the CNTs. We have plotted valence-band and C 1*s* photoemission spectra originated from A, B, and C regions in Figs. 4(a) and 4(b), respectively. Figure 4(a) shows that the tips have a larger valence-band DOS over the whole energy range plotted. Our result is in contrast to previous SPEM measurements by Suzuki *et al.*,[13] which showed the enhancement of tip DOS only near E_f. Figure 4(b) shows that the intensity of region B is not larger than that of region C, though Fig. 3 shows that it is brighter. This may be due to the kinetic energies of the photoelectrons emitted from region B spread due to scattering by surrounding sidewalls and less ordered tip surfaces. Figure 4(b) also shows that the tips have a higher C 1*s* core-level intensity. The C 1*s* spectrum of the tip apparently shifts toward a higher binding energy by ~0.2 eV relative to those of the sidewall spectra. The C 1*s* spectra tail off slowly toward higher binding energies due to core-hole screening by conduction electrons.[18]

Sharp resonance or dangling-bond states due to topological defects near the ends of the capped CNTs were proposed previously for the cause of the increase of DOS at the tips.[8,9,19,20] It was suggested that unpaired π bonds could occur in bent vertical graphite sheets, which could yield localized states in the gap orientated in the direction of the field and might have the optimal stable electronic configuration for field emission.[7] However, Figs. 2 and 4(a) of the unoccupied- and occupied-state spectra show that the difference intensities between the tip and sidewalls are slowly and smoothly varying over an energy range larger than 10 eV. These difference intensities do not show prominent features

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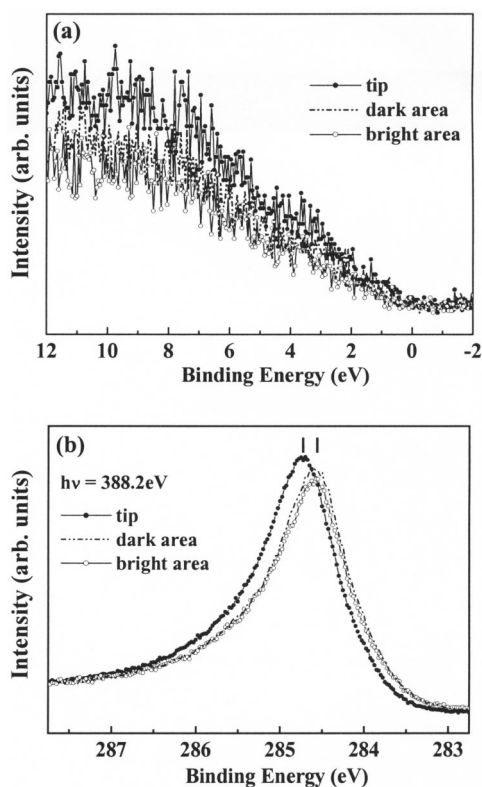
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FIG. 4. (a) Valence-band spectra and (b) C 1s photoemission spectra from the three selected regions marked by A, B, and C shown in Fig. 3, which correspond to tip, bright area and dark area, respectively.

near E_f. They are smoothly varying from -10 eV below E_f (or the valence band maximum) to $+10$ eV above E_f (or conduction band minimum). This suggests that defect and dangling-bond states are not the only origins of the enhancement of DOS at the tip. Because defect and dangling-bond states should be near E_f and not spread over such a large energy range. The differences between previous measurements and ours may be due to that defect and dangling-bond derived features yielded by all nanotubes in our sample overlap to become featureless.

Graphite has degenerate bonding and antibonding π bands at the K point of the hexagonal Brillouin zone, so that it is metallic. When the graphite sheet is rolled into a tube, the circumference boundary condition allows only the nanotubes whose wrapping vector (n_1, n_2) satisfying $n_1 - n_2 = 3m$ ($m = 0,1,2,...$) to remain metallic.[21] The other 2/3 nanotubes are semiconducting. The TEM image in Fig. 1(b) shows that near the tip the radius decreases gradually. Thus, both n_1 and n_2 decrease gradually, so that the metallic condition cannot be maintained approaching the tip cap except $m = 0$. The cap of the nanotube was proposed to be fullerene like with carbon hexagons and pentagons.[22] Due to the lack of planar order the local electronic structure is expected to be nonmetallic as concluded by field emission studies.[21] Thus, overall the semiconducting character is enhanced in the tip region. The corresponding reduction of the valence-band width will give rise to more or less uniformly enhanced DOS because the total number of valence-band states remains the same. Our argument is compatible with previous theoretical investigations. Tight binding calculation suggested that the

increased curvature might alter the local electronic structure at the tips of CNTs.[19,23] The DOS near E_f was also found to increase with the curvature of the CNT graphite sheet.[8,9,19,20] The C 1s binding energy shift and the higher peak in the spectrum of the tip shown in Fig. 4(b) reflect as well the narrowing of the valence bands and the reduction of the screening effect of the C 1s core hole. Goldoni *et al.*[24] also showed that the metallic single-wall carbon nanotubes had a smaller core-hole binding energy than that of semiconducting tubes because the core hole was better screened.

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