Electronic structure of the Fe-layer-catalyzed carbon nanotubes studied by x-ray-absorption spectroscopy

C. L. Yueh, J. C. Jan, J. W. Chiou, W. F. Pong, M.-H. Tsai, Y. K. Chang, Y. Y. Chen, Y. F. Lee, P. K. Tseng, S. L. Wei, C. Y. Wen, L. C. Chen, and K. H. Chen

Electronic structure of the Fe-layer-catalyzed carbon nanotubes studied by x-ray-absorption spectroscopy

C. L. Yueh, J. C. Jan, J. W. Chiou, and W. F. Pong,[a]
Department of Physics, Tamkang University, Tamsui 251, Taiwan 251, Republic of China

M.-H. Tsai
Department of Physics, National Sun Yat-Sen University, Kaohsiung, Taiwan 804, Republic of China

Y. K. Chang and Y. Y. Chen
Institute of Physics, Academia Sinica, Taipei, Taiwan 107, Republic of China

Y. F. Lee
Synchrotron Radiation Research Center, Hsinchu, Taiwan 300, Republic of China

P. K. Tseng
Department of Physics, Tamkang University, Tamsui 251, Taiwan 251, Republic of China

S. L. Wei, C. Y. Wen, and L. C. Chen
Center for Condensed Matter Science, National Taiwan University, Taipei, Taiwan 106, Republic of China

K. H. Chen
Institute of Atomic and Molecular Science, Academic Sinica, Taipei, Taiwan 106, Republic of China

X-ray-absorption near edge structure (XANES) measurements have been performed to investigate the local electronic structures of the Fe-catalyzed and stabilized carbon nanotubes (CNT) with various diameters. The intensities of the π^*- and σ^*-band and the interlayer-state features in the C K-edge XANES spectra of these CNTs vary with the diameter of the CNT. The white-line features at the C K- and Fe L_3-edges suggest a strong hybridization between the C $2p$ and Fe $3d$ orbitals, which lead to an enhancement of the C K- and reduction of the Fe L_3-edge features, respectively, indicative of a charge transfer from C $2p$ to Fe $3d$ orbitals. The Fe K-edge spectra reveal a $p-d$ rehybridization effect that reduces p-orbital occupation at the Fe site. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1416165]

The discovery of the tubule form of the graphite sheets[1] has attracted enormous attention over the last decade because of its fundamental and technological interests.[2] The formation of the carbon nanotube (CNT) by chemical vapor deposition using transition metal (TM) catalysts has been investigated extensively.[3] The formation of the CNT was found to depend on the initial chemical states of carbon atoms and the specific type of TMs. The use of metallic catalysts gave an improved nanotube yield.[4] TM catalysts were reported to come into close contact with the tube walls and significantly influence the transport properties of those nanotubes.[5] Theoretical investigations revealed that the carbon atoms in the graphite sheet interact strongly with the TM atoms and there is strong hybridization between C p and TM d orbitals.[6,7] The charge transfer effect and the magnetic moment of the TM atoms were found to depend strongly on the metal–graphite interlayer distance and the adsorption site.[7] The curvature of the graphite sheet is also among one of the factors, which was considered to explain the change of the electronic states in CNTs.[8,9] The C K-edge x-ray-absorption near edge structure (XANES),[10] electron energy-loss spectroscopy (EELS), and transmission electron microscopy (TEM)[11,12] measurements were performed for a CNT and revealed that the features of the electronic states of the carbon atoms in the nanotubes are very similar to those of graphite. Up until now, the influence of the TM atoms on the bonding configuration of the carbon atoms in CNT, especially the charge transfer between carbon and TM atoms and the influence of the curvature of the graphite sheet, remains unclear. In this study, we try to improve the understanding of CNTs by performing C K-edge, Fe $L_{3,2}$-edge, and K-edge x-ray absorption measurements for CNTs catalyzed by Fe layers with various thicknesses.

The C K-edge and the Fe $L_{3,2}$-edges XANES measurements were performed using the high-energy spherical grating monochromator (HSGM) beamline with an electron-beam (e-beam) energy of 1.5 GeV and a maximum stored current of 200 mA at the Synchrotron Radiation Research Center (SRRC), Hsinchu, Taiwan. The spectra of the C K and the Fe $L_{3,2}$ edges were measured using the sample drain current mode at room temperature. The Fe K-edge x-ray absorption measurement was also performed in a fluorescence mode at the 15 B and wiggler beamlines of SRRC. The CNTs were prepared on the p-type Si(100) substrates by microwave plasma enhanced chemical vapor deposition (MPE-CVD). Prior to the MPE-CVD process, thin layers of Fe with various thicknesses were coated on the Si substrate by e-beam evaporation. Using the scanning electron microscope, the randomly oriented multiwall CNTs prepared with the 30, 150, and 300 Å Fe layers were observed to be around 10 μm in length and 10 ± 5 nm, 30 ± 15 nm, and 220 ± 100 nm in diameter, respectively. The average diameter of

[a]Author to whom correspondence should be addressed; electronic mail: wfpong@mail.tku.edu.tw
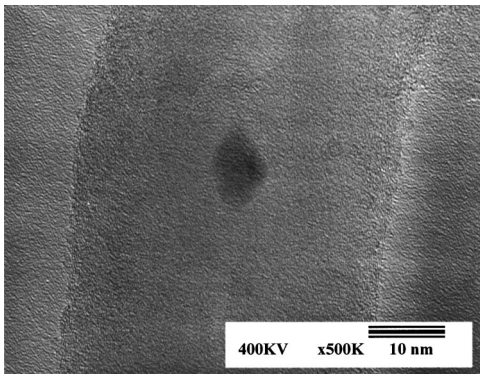
FIG. 1. TEM image shows a metallic Fe cluster inside the nanotube.

the CNT appears to increase with the thickness of the Fe-layer coating. The TEM image in Fig. 1 shows the presence of a Fe cluster, which may be a protrusion from the surface of the Fe layer or a Fe cluster adhered to the CNT wall. The Fe cluster may act as a catalytic growth center of the nanotube. Details of the preparation procedure for these CNTs can be found elsewhere.[13]

Figure 2 displays the C K-edge XANES spectra of the graphite and the three CNTs prepared with 30 Å, 150 Å, and 300 Å Fe layers, respectively. The spectra were normalized using incident beam intensity I_0 and keeping the area under the spectra in the energy range between 314 and 335 eV fixed. The two prominent peaks near 285.7 and 292.7 eV are known to be associated with the unoccupied π^*- and σ^*-bands, respectively.[14,15] The planar graphite sheet in the nanotube is bent into a cylinder. Besides, our CNT samples contain numerous randomly oriented nanotubes. Thus, the π^*- and σ^*-features in our C K-edge XANES spectra are averaged or integrated results over all orientations of the honeycomb planes. Between the π^*- and σ^*-peaks, a weak feature (labeled by a vertical solid line) near 287.5 eV is also presented in Fig. 2. This weak feature was generally not observed in EELS measurements, but was frequently seen in the x-ray absorption spectra of graphite.[15,16] This feature was
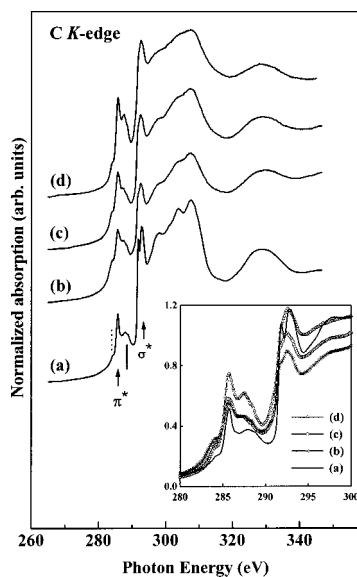
attributed to the free-electron-like interlayer states in the graphite.[14,16] The weak peak around 283.5 eV (labeled by a vertical dashed line) was previously attributed to a defect state of the disordered carbon in diamond films.[17] The inset of Fig. 2 illustrates the relative intensities of the π^*-, σ^*-band, and the interlayer-state features for the three CNTs. The intensities of the π^*- band and interlayer-state features are enhanced relative to those of the graphite. Since the intensities of these features are approximately proportional to the density of the unoccupied C $2p$-derived states, the increased intensities of these features can be correlated with the increased numbers of unoccupied C $2p$ orbitals or a charge transfer from the C $2p$ to Fe $3d$ orbitals to be discussed later. The intensities of the near-edge features increase with the decrease of the CNT diameter, which suggests that the C $2p$ orbitals lose more charge to the $3d$ orbitals of the catalyzing Fe atoms for smaller-diameter CNTs. The observed broadening of the π^*-band was attributed to the curvature of the graphite sheet and the bundle formation of CNTs.[12,18]

Figure 3 displays the normalized Fe $L_{3,2}$-edge XANES spectra of the Fe metal and the three CNT samples. We match the absorption coefficients from the pre-edge region at the L_3 edge to several eV's above the L_2 edge and keep the same area in the energy range between 732 and 749 eV. In Fig. 3, the shapes of the Fe $L_{3,2}$-edge XANES spectra of the CNT samples differ significantly from that of pure Fe. The intensities of the CNT white-line features are also significantly smaller than that of pure Fe. (The intensity of the Fe spectrum has been scaled by a factor of 1/2). The intensities of the white-line features $I(L_3)$ at the Fe L_3 edge are illustrated in the inset of Fig. 3. $I(L_3)$ is determined by subtracting the background intensity described by an arctangent function, as indicated by the dashed line in Fig. 3. Figure 3 shows that $I(L_3)$ for CNTs are significantly lower than that for pure Fe. The lower $I(L_3)$ for CNTs suggests that the local
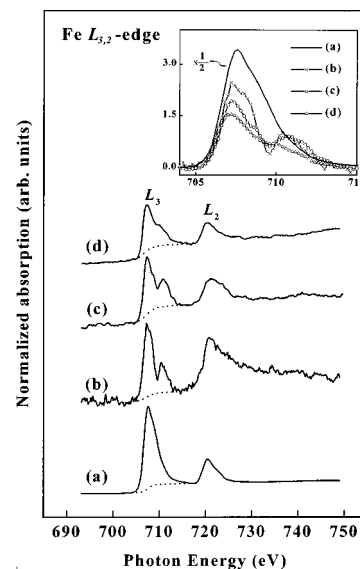

FIG. 2. Normalized C K-edge absorption spectra of (a) the graphite and the CNT with diameters of (b) 220 ± 100 nm, (c) 30 ± 15 nm, and (d) 10 ± 5 nm. The inset displays the enlarged part of the near-edge in a magnified scale.

FIG. 3. Normalized Fe $L_{3,2}$ near-edge absorption spectra of (a) the Fe metal and the CNTs with diameters of (b) 220 ± 100 nm, (c) 30 ± 15 nm, and (d) 10 ± 5 nm. The dashed line represents the extrapolated background at the Fe L_3-edge. The center of the continuum step of the arctangent function was selected at the maximum height of the white-line features. The white-line region of the Fe L_3-edge is shown in the inset in a magnified scale.
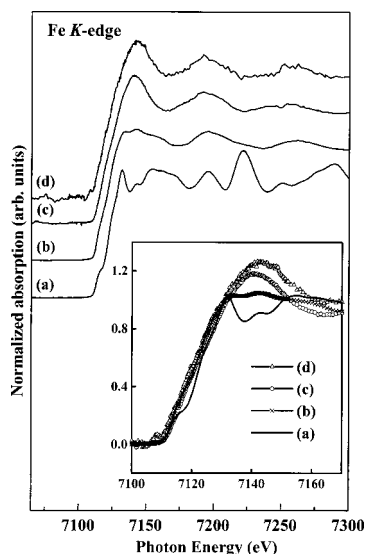
FIG. 4. Normalized Fe K near-edge absorption spectra of the (a) Fe metal and the CNTs with diameters of (b) 220 ± 100 nm, (c) 30 ± 15 nm, and (d) $10 - 5$ nm. The region of threshold edge in the inset is on a magnified scale. (The data for the Fe metal was measured using the total electron yield mode).

atomic structure of the x-ray absorbing Fe atoms in the CNT samples differ from those of pure Fe. Therefore, the Fe cluster should interact strongly with the carbon tube and causes significant changes in the C K-edge spectra stated previously. Figure 3 also shows that $I(L_3)$ gradually increases with the diameter of the carbon tube, suggesting that the number of unoccupied Fe $3d$-derived states increase with the increase of the nanotube diameter. Thus, the $3d$ orbitals of the Fe atoms gain more charge from the carbon $2p$ orbitals for smaller-diameter CNTs consistent with the C K-edge results. Since in our CNT samples Fe exits in the forms of clusters and a thin layer, there are two kinds of Fe–C bonding. The bonding between the Fe cluster and the C atoms on the tube wall will be more like that of iron carbide with strong chemical bonds. While the bonding between the Fe thin layer and the graphite sheet is more like a bonding between two metallic layers. We would like to caution the readers that the transition matrix elements might change noticeably between these two types of Fe–C bonding with different symmetry. The presence of a splitting of the Fe $L_{3,2}$-edge feature may indicate the presence of the crystal field effect.

The direction of the overall charge transfer between the CNT and the Fe cluster can be inferred from their work function differences and the electronegativity of C and Fe atoms. The CNT and Fe metal have work functions of 5.3–5.6 eV[19,20] and 4.5–4.8 eV,[21] respectively, and the electronegativity of C and Fe atoms are 2.55 and 1.83, respectively.[22] Both work function and electronegativity indicate that the overall charge transfer should be from the Fe catalyst to the CNT in opposition to the C $2p$ to Fe $3d$ transfer. Thus, there should be other channels of charge transfer that compensate the C $2p$ to Fe $3d$ transfer. One such channel may be via rehybridization of the $p-d$ orbitals at the Fe site. To see if this is the case, we have also carried out Fe K-edge XANES measurements. Figure 4 shows the normalized fluorescence yield of the Fe K-edge XANES spectra of the three Fe-catalyzed CNTs and Fe metal. The absorption intensity for a CNT just above the edge increases with the decrease of the

CNT diameter and it is larger than that of pure Fe. This result shows that Fe atoms in the CNT samples have more unoccupied p states, which is an indication of the loss of p-orbital charge and this loss of p-orbital charge is larger for smaller-diameter CNTs. Thus, the gain of $3d$-orbital charge may be compensated by the loss of p-orbital charge at the Fe site.

The density of states (DOS) of a CNT in the vicinity of the Fermi level (E_F) was found to increase with the curvature of the graphite sheet for small-diameter CNTs.[8,9,23,24] The degree of delocalization of Fe $3d$ orbitals increases with the thickness of the Fe layer or the size of the Fe cluster. Since delocalization of $3d$ orbitals broadens the $3d$ band and reduces the DOS in the vicinity of E_F, a thinner catalyzing Fe layer or a smaller Fe cluster has a larger DOS near E_F. The enhancement of both DOS's of a CNT and the thin Fe layer or the small Fe cluster near E_F optimizes their hybridization and attractive coupling. Thus, the repulsive strain energy in the nanotube can be compensated and the nanotube can be stabilized. To fully understand the dependence of the diameter of the nanotube on the thickness of the Fe layer requires a growth dynamics study.

[1] S. Iijima, Nature (London) **56**, 354 (1991).
[2] R. Saito, G. Dresselhaus, and M. S. Dresselhaus, *Physical Properties of Carbon Nanotubes* (Imperical College Press, London, 1998).
[3] M. Yudasaka, R. Kikuchi, Y. Ohki, E. Ota, and S. Yoshimura, Appl. Phys. Lett. **70**, 1817 (1997).
[4] T. W. Ebbesen, P. M. Ajayan, H. Hiuram, and K. Tanigaki, Nature (London) **367**, 519 (1994).
[5] L. Grigorian, G. U. Sumanasekera, A. L. Loper, S. L. Fang, J. L. Allen, and P. C. Eklund, Phys. Rev. B **60**, R11309 (1999).
[6] D. M. Duffy and J. A. Blackman, Phys. Rev. B **58**, 7443 (1998).
[7] M. Menon, A. N. Andriotis, and G. E. Froudakis, Chem. Phys. Lett. **320**, 425 (2000).
[8] J. W. Mintmire, B. I. Dunlap, and C. T. White, Phys. Rev. Lett. **68**, 631 (1992).
[9] X. Blase, L. X. Benedict, E. L. Shirley, and S. G. Louie, Phys. Rev. Lett. **72**, 1878 (1994).
[10] M. Imamura, H. Shimada, N. Matsubayashi, M. Yumura, K. Uchida, S. Oshima, Y. Kuriki, Y. Yoshimura, T. Sato, and A. Nishijima, Jpn. J. Appl. Phys., Part 2 **33**, L1017 (1994).
[11] V. P. Dravvid, X. Lin, Y. Wang, X. K. Wang, A. Yee, J. B. Ketterson, and R. P. H. Chang, Science **259**, 1601 (1993).
[12] R. Kuzuo, M. Terauchi, M. Tanaka, and Y. Saito, Jpn. J. Appl. Phys., Part 2 **33**, L1316 (1994).
[13] F. G. Tarntair, L. C. Chen, S. L. Wei, W. K. Hong, K. H. Chen, and H. C. Cheng, J. Vac. Sci. Technol. B **18**, 1207 (2000).
[14] D. A. Fischer, R. M. Wentzcovitch, R. G. Carr, A. Continenza, and A. J. Freeman, Phys. Rev. B **44**, 1427 (1991).
[15] P. E. Batson, Phys. Rev. B **48**, 2608 (1993).
[16] C. J. Pickard, Ph.D. thesis, Christ's College, 1997.
[17] A. Laikhtman, I. Gouzmna, A. Hoffman, G. Comtet, L. Hellner, and G. Dujardin, J. Appl. Phys. **86**, 4192 (1999).
[18] T. Hanada, Y. Okada, and K. Yase, in *The Science and Technology of Carbon Nanotubes*, edited by K. Tanaka, T. Yamabe, and K. Fukui (Elsevier, Oxford, 1999).
[19] E. Hernández, C. Goze, P. Bernier, and A. Rubio, Phys. Rev. Lett. **80**, 4502 (1998).
[20] R. Gao, Z. Pan, and Z. Wang, Appl. Phys. Lett. **78**, 1757 (2001).
[21] *CRC Handbook of Chemistry and Physics*, edited by D. R. Lide, 79th ed. (CRC Press New York, 1998).
[22] *Table of Periodic Properties of the Elements* (Sargent–Welch Scientific Company, Skokie, 1980).
[23] H. Terrones, M. Terrones, E. Hernández, N. Grobert, J.-C. Charlier, and P. M. Ajayan, Phys. Rev. Lett. **84**, 1716 (2000).
[24] H. J. Choi, J. Ihm, Y. G. Yoon, and S. G. Louie, Phys. Rev. B **60**, R14009 (1999).