Absorption spectra and chirality of single-walled 4 Å carbon nanotubes

WanZhen Liang, GuanHua Chen, Zhaoming Li, and Zi-Kang Tang

Citation: Appl. Phys. Lett. **80**, 3415 (2002);
View online: https://doi.org/10.1063/1.1478155
View Table of Contents: http://aip.scitation.org/toc/apl/80/18
Published by the American Institute of Physics

Absorption spectra and chirality of single-walled 4 Å carbon nanotubes

WanZhen Liang and GuanHua Chen[a)]
Department of Chemistry, The University of Hong Kong, Pokfulam Road, Hong Kong

Zhaoming Li and Zi-Kang Tang
Department of Physics, The Hong Kong University of Science and Technology

(Received 31 January 2002; accepted for publication 13 March 2002)

Absorption spectrum of recently discovered single-walled 4 Å carbon nanotubes is measured. The semiempirical PM3 localized-density-matrix method is employed to evaluate the absorption spectra of three possible 4 Å single-walled carbon nanotubes, (3,3), (4,2), and (5,0). Both experimental and calculated results reveal that these nanotubes have finite optical gaps and strong anisotropic optical responses. When the electric field is perpendicular to the nanotubes, they are transparent to visible lights; and this is confirmed and explained by the calculations. Compared to the measured absorption spectrum, calculated absorption spectra are used to determine the chirality of the nanotubes synthesized in the channels of porous zeolites. © *2002 American Institute of Physics.*
[DOI: 10.1063/1.1478155]

Since the initial finding by Iijima in 1991,[1] and the subsequent report of the synthesis of large quantities of carbon nanoubes (CNTs) by Ebbesen and Ajayan in 1992,[2] CNTs have become the major subject of numerous experimental[3,4] and theoretical investigation.[5] Single-walled carbon nanotubes (SWNTs), in particular, have been studied extensively.[4,6] Electronic and optical properties of the SWNTs have been measured.[3,6] For instance, absorption peaks have been observed between 0.5 and 1.2 eV for SWNTs with diameters ranging from 8 to 15 Å.[6–8] There are quite a few theoretical calculations on the band structures of the SWNTs.[5,9–11] We have reported the calculated absorption spectra of a series of SWNTs.[12] The semiempirical PM3 localized-density-matrix method (LDM-PM3) method[13] was used in the calculations. As early as in 1992, Sawada and Hamada[14] predicted that the existence of extremely thin CNTs. Recently, both multi-walled and single-walled CNTs with 4 Å diameter have been synthesized by the cathodic deposition of arc-discharged graphite rods in a hydrogen atmosphere[15] and by pyrolysis of tripropylamine molecules in channels of porous zeolite $AlPO_4-5$ (AFI) single crystals,[16] respectively. The 4 Å CNTs are the smallest CNTs so far. Unlike other SWNTs that have a distribution of sizes,[4,6–8] single-walled 4 Å CNTs synthesized in channels of porous AFI crystal have a unique diameter.[16] This provides a rare opportunity for us to examine the physical properties of SWNTs of the same size. Single-walled 4 Å CNTs have three possible structures: chiral (4,2), zigzag (5,0), and armchair (3,3) tubes.[15,16] It has been argued that 4 Å CNTs should be either (3,3) or (5,0) because they can be capped by half C_{20}.[15,16] In this letter, we report our measurement of the absorption spectra of 4 Å SWNTs and present calculated absorption spectra of (4,2), (3,3), and (5,0) SWNTs using the LDM-PM3 method,[13] which has been employed extensively to calculate the optical propeties of conjugated organic systems.[12,13] Comparing measured and calculated absorption spectra, we examine the possible structures or chiralities of 4 Å SWNTs synthesized in the channels of porous AFI single crystal.[16]

In our calculations ideal structures are employed, i.e., the SWNTs are constructed by rolling graphite segments along the tube axis with the C–C bond length set to 1.42 Å.[12] Two ends of each SWNT are terminated with hydrogen atoms. Hartree–Fock self-consistent field (SCF) calculation does not converge for neutral (5,0) SWNTs because its electrons cannot fill closed-shell structures.[17] Four extra electrons are added to ensure converging of the SCF calculation. It is found that the extra electrons have little effect on the optical absorption spectra of (5,0) SWNTs, or in other words, that their absorption spectra vary little when the number of carbon atoms reaches 200 or more. The calculated absorption spectra of the three 4 Å SWNTs are shown in Fig. 1. They are (4,2) $C_{332}H_{12}$, (3,3) $C_{420}H_{12}$, and (5,0) $C_{300}H_{10}$, and their tube lengths are 66.0, 84.9, and 68.0 Å, respectively. The cutoff length of 29.0 Å is used in the calculation. All solid lines are the absorption spectra corresponding to electric field **E** aligned along the tube axis while the dashed lines correspond to **E** perpendicular to the tube. For $\omega < 4.0$ eV, three major peaks at 1.16, 1.66, and 2.60 eV are found for (5,0) $C_{300}H_{10}$, two peaks at 1.60 and 2.90 eV for (4,2) $C_{332}H_{12}$, and only one at 1.0 eV for (3,3) $C_{420}H_{12}$. In the case where the external field is polarized along the tube axis, the optical spectra of the three tubes depend very much on the tube lengths, and redshift as the tube lengths increase. The spectral profiles change little after the number of carbon atoms N reaches 200 or more. The optical gaps versus $1/N$ are plotted in the insets for the three SWNTs. The optical gaps redshift as N increases, and depend linearly on $1/N$ for the three types of SWNTs, which were similarly observed for larger diameter SWNTs in Ref. 12. Extrapolating $N \rightarrow \infty$, we find that the optical gaps for (4,2), (3,3), and (5,0) are 1.50, 0.61, and 0.90 eV, respectively. The existence of finite calculated optical gaps has been reported for larger SWNTs such as (5,5), (9,0), and (7,3),[12] and is consistent with the existing experimental results.[6–8] Note that the density func-

[a)]Author to whom correspondence should be addressed; electronic mail: ghc@yangtze.hku.hk

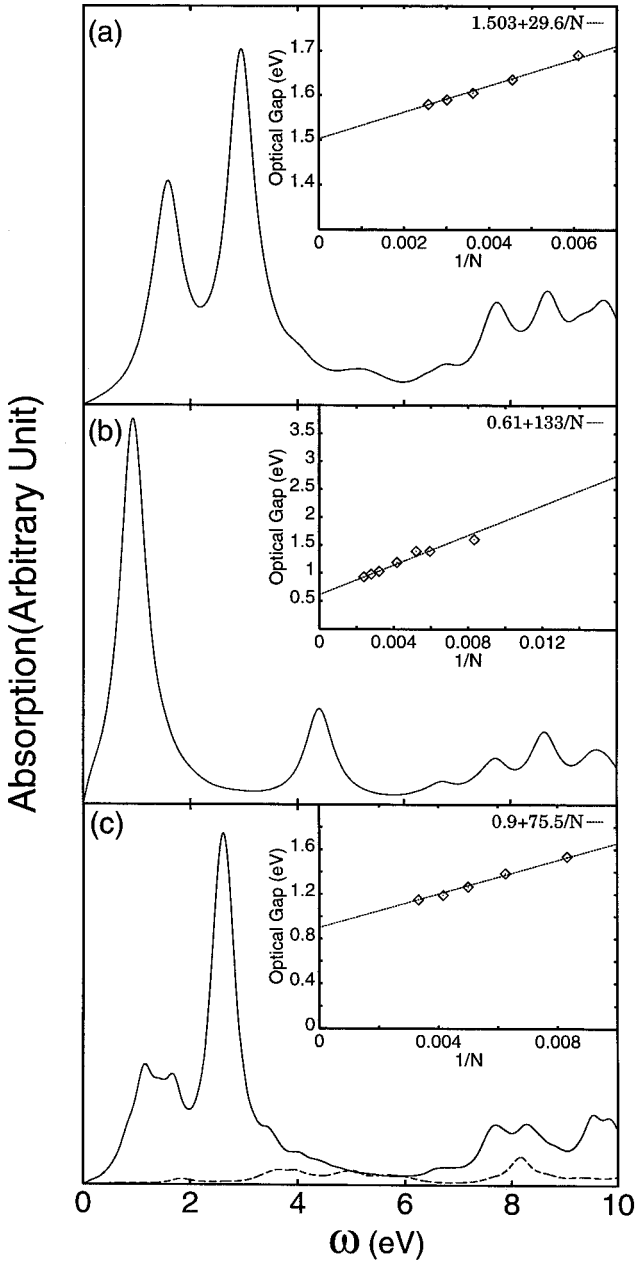

FIG. 1. Calculated absorption spectra of (4,2) $C_{332}H_{12}$, (3,3) $C_{420}H_{12}$, and (5,0) $C_{300}H_{10}$ SWNTs with dephasing parameter $\gamma = 0.2$ eV. External field **E** is polarized along the tube axis except that the dashed line in (c) is the absorption spectrum for **E** $\perp$ Tube. Insets show the optical gaps via $1/N$ for (4,2), (3,3), and (5,0) SWNTs when **E** $\parallel$ Tube.

tional theory (DFT) calculations predict that small diameter SWNTs are metallic due to hybridization of π and σ atomic orbitals.[5] We emphasize that the calculated absorption spectra of (4,2), (3,3), and (5,0) SWNTs are quite different although their diameters are almost identical. The small diameter brings more carbon atoms on the tubes close so that their relative positions and orientations affect very much the electronic structures. This is in contrast to our finding in the Ref. 12 that the absorption spectra of larger SWNTs are determined mainly by their diameters and are insensitive to their chiralities. Since the absorption spectra of the three 4 Å SWNTs are rather different, the measured absorption spectrum of the 4 Å SWNTs in the channels of porous AFI crystals may be used to determine its structure.

We have measured the absorption spectrum of the 4 Å

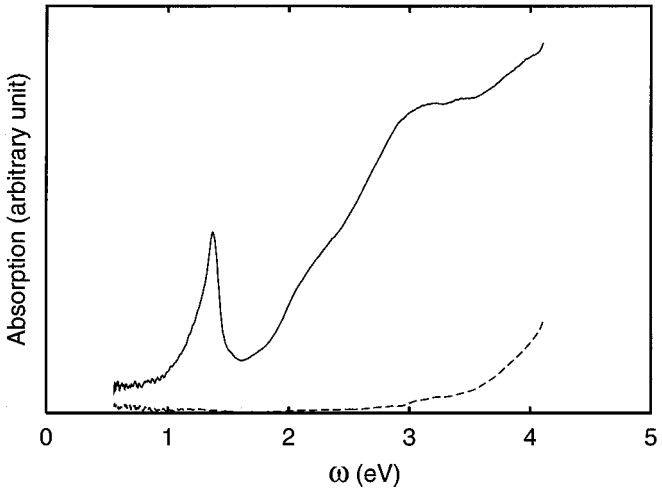

FIG. 2. Measured absorption spectra of the single-walled 4 Å CNT. The solid line is the absorption spectrum for **E** $\parallel$ Tube and the dashed line for **E** $\perp$ Tube.

SWNT. As described in Ref. 16, the 4 Å SWNTs were prepared by pyrolysis of tripropylamine molecules in channels of porous zeolite AFI single crystal. AFI is a transparent microporous crystal. The nanotube containing zeolite single crystal was polished to as thin as 10 μm. Transmission spectra were measured at room temperature. A tungsten–halogen incandescent lamp was used as a light source. The incident polarized light was focused onto the sample by a reflecting microscope objective. The transmission light was collected by another reflecting objective coupled with an optical fiber and dispersed by a 275 mm single-grating monochromator. Figure 2 shows the optical absorption spectra [plotted in optical density, (OD)] of the SWNT-containing AFI crystal for light polarized parallel to the tube axis (**E** $\parallel$Tube, solid curve) and perpendicular to the axis (**E** $\perp$ Tube, dashed curve), respectively. For **E** $\parallel$ Tube, a sharp band at 1.37 eV, a shoulder at 2.1 eV, and a broad band centered at 3.1 eV are observed. The intensities of these absorption bands gradually decrease with increasing polarization angle between **E** and the tube axis. For **E** $\perp$ Tube, these absorption bands vanish eventually and the nanotube is nearly transparent in the whole measured energy region. We could not carry out the measurement in the energy region higher than 4.0 eV, because the epoxy used to hold the sample has strong absorption in the ultraviolet region. The existence of a finite optical gap agrees with the previous[12] and current calculation results. We reported in Ref. 12 that the absorption is much weaker for **E** $\perp$ Tube than for **E** $\parallel$ Tube. Since the absorption spectra of three 4 Å SWNTs are very different, comparing Figs. 1 and 2 may help determine the chirality of the 4 Å SWNT contained in the zeolite AFI crystal.[16]

The absorption spectrum of the (3,3) SWNT has only one major peak below 4.0 eV. When the electric field is parallel to the tube, there are three distinctive absorption peaks below 4 eV for (5,0) SWNTs and two peaks below 4.0 eV for (4,2). Both of them are consistent with the experimental measurement, see Fig. 2. Since the parameters in the PM3 Hamiltonian were not optimized for the time-dependent Hartree-Fock (TDHF) method, which is employed in the LDM method,[13] the calculated absorption spectra are not exactly the same as the experimental spectra. Nevertheless, the

calculated and measured absorption spectra agree qualitatively. We calculate the absorption spectrum of the (5,0) SWNT for electric field $\mathbf{E} \perp$ Tube and compare it to its experimental result. The calculated absorption spectrum for $\mathbf{E} \perp$ Tube is denoted by the dashed line in Fig. 1(c). Clearly, the absorption is very weak in the infrared and visible range, which agrees well with the experimental findings. We observe that the absorption of (4,2) and (3,3) SWNTs is weak as well in the infrared and visible range when $\mathbf{E} \perp$ Tube. It is clear that the (3,3) SWNT alone cannot account for the measured absorption spectrum (see Fig. 2) and it may explain only the first peak at 1.37 eV in the measured spectrum. The calculated absorption spectra of (4,2) and (5,0) are consistent with the measured spectra. Since it is energetically unfavorable to fit half C_{20} caps on (4,2) SWNTs,[16] only H-terminated (4,2) SWNTs may exist. The sharp peak at 1.37 eV in the measured absorption spectrum agrees very well with the first peak in the absorption spectrum of (4,2). This seems to suggest that the (4,2) SWNT is the most likely candidate. However, porous AFI crystals were thermally treated at 500 to 600 °C during synthesis,[16] it is not clear that H atoms inside the pores survive the thermal treatment. This may be resolved by examining the energetics of H-terminated (4,2) or the binding energies of the terminal H atoms, and further calculation is required. If the 4 Å SWNTs synthesized in the porous AFI crystals are of single chirality, they should be either H-terminated (4,2) or (5,0) SWNTs. Of course, a mixture of three SWNTs (4,2), (3,3), and (5,0) cannot be ruled out.

To summarize, we have measured and calculated the absorption spectrum of single-walled 4 Å carbon nanotubes. Unlike those of the larger diameter CNTs whose absorption spectra are determined by their diameters, the absorption spectra of small diameter SWNTs such as (4,2), (3,3), and (5,0) are sensitive to their chiralities as well as their diameters. This sensitivity may be utilized to determine the chiralities of small CNTs. The 4 Å SWNTs are found transparent in the energy range up to 4 eV if the light is polarized perpendicular to the tube axis, which is confirmed and explained by our LDM-PM3 calculation. The strong anisotropy and finite optical gap are observed experimentally for the 4 Å SWNTs, and both observations agree with previous[12] and current calculations. Comparing the measured and calculated absorption spectra, we conclude that 4 Å SWNTs synthesized in porous AFI crystal are either (5,0) CNTs, H-terminated (4,2) CNTs, or a mixture of (5,0), (4,2), and (3,3) CNTs.

Two of the authors (W.Z.L. and G.H.C.) thank ManFai Ng for providing the CNTs structures. The authors thank Dr. Satoshi Yokojima and Professor Ping Shen for stimulating discussions. Support from the Hong Kong Research Grant Council (RGC) and the Committee for Research and Conference Grants (CRCG) of the University of Hong Kong is gratefully acknowledged.

[1] S. Iijima, Nature (London) **354**, 56 (1991).
[2] T. W. Ebbesen and P. M. Ajayan, Nature (London) **358**, 220 (1992).
[3] T. W. Odom, J.-L. Huang, P. Kim, and C. M. Lieber, Nature (London) **391**, 62 (1998).
[4] J. Liu, A. G. Rinzler, H. Dai, J. H. Hafner, R. K. Bradley, P. J. Boul, A. Lu, T. Iverson, K. Shelimov, C. B. Huffman, F. Rodriguez-Macias, Y.-S. Shon, T. R. Lee, D. T. Colbert, and R. E. Smalley, Science **280**, 1253 (1998).
[5] X. Blase, L. X. Benedict, E. Shirley, and S. G. Louie, Phys. Rev. Lett. **72**, 1878 (1994).
[6] J. Chen, M. A. Hamon, H. Hu, Y. Chen, A. M. Rao, P. C. Eklund, and R. C. Haddon, Science **282**, 95 (1998).
[7] M. Ichida, S. Mizuno, Y. Tani, Y. Saito, and A. Nakamura, J. Phys. Soc. Jpn. **68**, 3131 (1999).
[8] H. Kataura, Y. Kumasawa, Y. Maniwa, I. Umeza, S. Suzuki, Y. Ohtsuka, and Y. Achiba, Synth. Met. **103**, 2555 (1999).
[9] N. Hamada, S. Sawada, and A. Oshiyama, Phys. Rev. Lett. **68**, 1579 (1992).
[10] R. Saito, G. Dresselhaus, and M. S. Dresselhaus, *Physical Properties of Carbon Nanotubes* (Imperial College Press, London, 1998).
[11] A. Rubio, D. Sánchez-Portal, E. Artacho, P. Ordejón, and J. M. Soler, Phys. Rev. Lett. **82**, 3520 (1999).
[12] W. Z. Liang, X. J. Wang, S. Yokojima, and G. H. Chen, J. Am. Chem. Soc. **122**, 11129 (2000).
[13] S. Yokojima and G. H. Chen, Phys. Rev. B **59**, 7259 (1999); S. Yokojima and G. H. Chen, Chem. Phys. Lett. **292**, 379 (1998); W. Z. Liang, S. Yokojima, D. H. Zhou, and G. H. Chen, J. Phys. Chem. A **104**, 2445 (2000).
[14] S. Sawada and N. Hamada, Solid State Commun. **83**, 917 (1992).
[15] L. C. Qin, X. Zhao, K. Hirahara, Y. Miyamoto, Y. Ando, and S. Iijima, Nature (London) **408**, 50 (2000).
[16] N. Wang, Z. K Tang, G. D. Li, and J. S. Chen, Nature (London) **408**, 50 (2000).
[17] L. G Bulusheva, A. V. Okotrub, D. A. Romanov, and D. Tomanek, J. Phys. Chem. A **102**, 975 (1998).