



Novel Optical Properties Of Carbon Nano Tube

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Abstract:

Within materials science, the optical properties of carbon nanotubes refer specifically to photoluminescence, and Raman spectroscopy of carbon nanotubes. Spectroscopic methods offer the possibility of quick and non-destructive characterization of relatively large amounts of carbon nanotubes. There is a strong demand for such characterization from the industrial point of view: numerous parameters of the nanotube synthesis can be changed, intentionally or unintentionally, to alter the nanotube quality. As shown below, optical absorption, photoluminescence and Raman spectroscopies allow quick and reliable characterization of this "nanotube quality" in terms of non-tubular carbon content, structure (chirality) of the produced nanotubes, and structural defects. Those features determine nearly any other properties such as optical, mechanical, and electrical properties.

Key words: Carbon nanotube (CNT), Single wall carbon nanotube (SWCNT), Multiwall carbon nanotube (MWCNT)

I.Introduction

Carbon nanotubes are unique "one dimensional systems" which can be envisioned as rolled single sheets of graphite (or more precisely graphene). This rolling can be done at different angles and curvatures resulting in different nanotube properties. The diameter typically varies in the range 0.4–40 nm (i.e. "only" ~100 times), but the length can vary ~10,000 times reaching 18.5 cm. Thus the nanotube aspect ratio, or the length-to-diameter ratio, can be as high as 132,000,000:1,^[1] which is unequalled by any other material. Consequently, all the properties of the carbon nanotubes relative to those of typical semiconductors are extremely anisotropic (directionally dependent) and tunable. Whereas mechanical, electrical and electrochemical (supercapacitor) properties of the carbon nanotubes are well established and have immediate applications, the practical use of optical properties is yet unclear. The aforementioned tunability of properties is potentially useful in optics and photonics. In particular, light-emitting diodes (LEDs)^{[2][3]} and photo-detectors^[4] based on a single nanotube have been produced in the lab. Their unique feature is not the efficiency, which is yet relatively low, but the narrow selectivity in the wavelength of emission and detection of light and the possibility of its fine tuning through the nanotube structure. In addition, bolometer^[5] and optoelectronic memory^[6] devices have been realised on ensembles of single-walled carbon nanotubes. Carbon Nanotubes are expected to play a significant role in the design and manufacture of many nano-material devices in the future. Carbon Nanotubes exhibit many unique properties which generate strong interests in studying their applications. Some of these properties cannot be found in ordinary engineering materials used in our daily lives. Carbon Nanotubes are extremely strong materials and have good thermal conductivity and remarkable electrical properties. Therefore, it is very important to study the characteristic properties of both single and multiwall Carbon Nanotubes. In this paper we are going to study how the topological structures, grain boundaries, electric effect, and quantum size effect dominate mechanical properties of both single and multiwall Carbon Nanotubes.

2.Topological Structure

The single wall Carbon Nanotubes can be imagined as a rolled up sheet of graphite, and is been characterized by its chiral vector (C_h), also called wrapping vector. The chiral vector is given by the two chiral indices, n and m ($n > m$), which are the two integers to

express the chiral vector and describe the primitive vectors of the hexagonal lattice.

$$\bar{C}_h = n * \bar{a}_1 + m * \bar{a}_2 \quad (1)$$

If the directions of the chiral vectors fall within a 30° region, the Carbon Nanotube is called zigzag. For zigzag structure the chiral vector is $(n, m) = (p, 0)$. The armchair structure has $(n, m) = (2p, -p)$ or (p, p) in chiral vector. The remaining cases are the chiral tubes. The relationships between m and n integers are list below.

$$d = \frac{a * \sqrt{(m^2 + mn + n^2)}}{\pi} \quad (2)$$

$$\theta = \sin^{-1} \frac{\sqrt{3m}}{2\sqrt{m^2 + mn + n^2}} \quad (3)$$

$$a = 1.42 \sqrt{3} \quad 0 \leq |\theta| \leq 30^\circ$$

d = diameter of Carbon Nanotubes

Θ = the directions of the inequivalent wrapping vectors

The chiral vectors of Carbon Nanotubes dominate their material properties, especially in electronic properties. Carbon Nanotubes can be either metallic or semi-conducting depend on their chiral vector (n, m) .

Metallic properties dominate when $n-m=0$ or $(n-m)/3 = \text{integer}$

Semi conducting properties dominate when $(n-m)/3 \neq \text{Integer}$.

Theoretically, we will be able to fabricate metallic or semi conducting carbon nanotubes by careful control of d and Θ in the growth of carbon nanotubes.

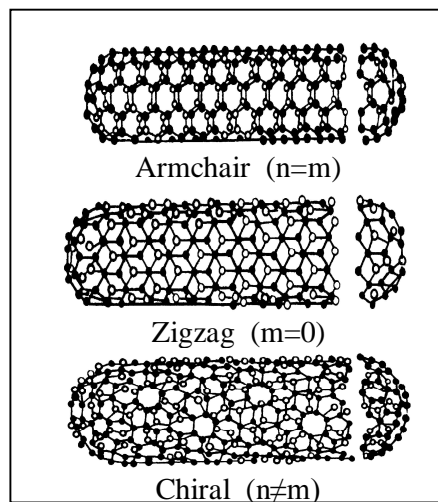


Figure 1: Different structures in Carbon Nanotubes [1]

3. Grain Size And Grain Boundary Effect

The most important deformation mechanism properties in Carbon Nanotubes are defects and dislocations. The point defects and line defects in Carbon Nanotubes have significantly raised the Young's Modulus to value that are higher than conventional materials. Carbon Nanotubes have Young's Modulus in the order of 1 TPa, where most polymer with Young's modulus ranging from 20 to 60 GPa.[2] When applying a stress, Carbon Nanotubes will bend over to surprisingly large angles before they start to ripple off. Carbon Nanotubes usually develop kinks in their structures at failure. The amazing thing about Carbon Nanotubes is that these deformations are elastic - they all completely bounce back to their original shape when the load is removed. Carbon Nanotubes contain a large volume fraction of grain boundaries which provides many significant phenomena in their mechanism properties. As grain size decreases, dislocation activity apparently decreases. For ductile Carbon Nanotubes the empirical Hall-Petch equation has been developed to express the grain-size dependence. In terms of yield stress, this expression is

$$\sigma_o = \sigma_i + kd^{\frac{1}{2}} \quad (4)$$

Where σ_o = yield stress, σ_i = friction stress opposing dislocation motion, k = constant, and d = grain diameter. Similar results can be expressed for hardness as well.

$$H_o = H_i + kd^{-1/2} \quad (5)$$

We can easily observe that as grain size is reduced through the nanoscale region (< 100 nm), the hardness typically increases with decreasing grain size.

4. Electronic Effect

Metallic Carbon Nanotubes are great conductors where electrons can propagate freely. The reason a metallic Carbon Nanotube can conduct electrons is because one of the four valence electrons associated with each carbon atom is delocalized and can be shared by all the carbon atoms. Generally, we classify Metallic Carbon Nanotubes as ballistic conductors: that is, every electron injected into the nanotube at one end should come out the other end. Even though a metallic Carbon Nanotube does have some resistance, this resistance actually is independent of its length and is negligible, which means that Ohm's law does not apply.[13]

Normally, semiconductors don't have many free electrons. The electric current depends on those free electrons; therefore the amount of current that can travel through an

isolated semiconductor is negligible. For example, put a slab of semi-conducting Carbon Nanotubes in the middle of a circuit and it will stop the current. But things change if you put an electric field near that semi-conducting Carbon Nanotube slab. The positive charged metal plate will attract the negatively-charged electrons from inside the body of the semiconductor. (Fig 2) These electrons collect at the surface—suddenly there are free electrons creating a pathway for the current. By controlling the voltage on the metal plate, we can easily flip the current through the semiconductor on and off.

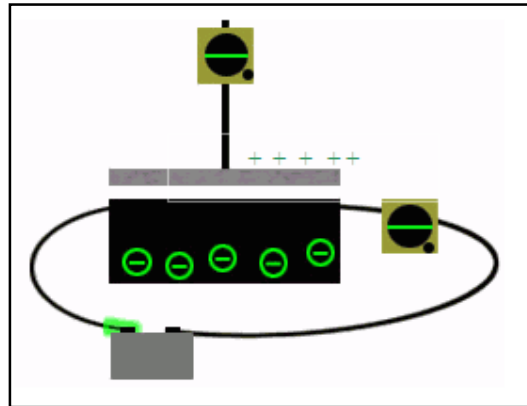


Figure 2: Sketch of field-effect transistors [3]

Semi conducting single wall Carbon Nanotube behaves much like conventional semiconductor transistor and has a very unique electronic property in field-effect transistors (FETs). These important differences are 1. The Carbon Nanotube is one-dimensional, which greatly reduces the scattering probability. As a result, the devices may operate in the ballistic regime. 2. The nanotube conducts essentially on its surface where all the chemical bonds are saturated and stable. Therefore, there is no need for careful passivity of the interface between the nanotube channel and the gate dielectric, i.e. there is no equivalent of the silicon/silicon dioxide interface. 3. The Schottky barrier at the metal-nanotube contact is the active switching element in an intrinsic nanotube device.[4] These properties make the one-dimensional transistor action in nanotubes unique and interesting.

5. Quantum Size Effect

The other important phenomenon of Carbon Nanotubes is the quantum size effect. When the material size has decreased to the nano scale range, material will generate many significant mechanical properties such as dependence of Absorption and Luminescent

Spectra. The absorption and luminescence phenomenon of Carbon Nanotubes can be explained by Quantum Mechanic. One of the manifestations of the size effect in the optical characteristics of nanoparticle is the blue shift (shift to shorter wavelength) of their optical spectrum, which occurs when an excess electron is injected into the nanoparticle. Three different reasons may account for the shift: first, the increase in the excitant energy due to the influence of the electric field of the excess electron; second, the effect of filling the lowest vacant state with the excess electron whose excitation to a higher vacant state requires higher energy; and third, a decrease in the oscillator strength of the excitant transition due to the effect of trapped electrons and holes.[6]

The luminescence spectra are the recombination light generated charges, and have following quantum expression:

$$h\nu = \frac{hc}{\lambda} = E - (D_+ - D_-) + \frac{e^2}{8R} \quad (6)$$

where E is the minimum excitation energy of Carbon Nanotubes, D+ and D- are the depths of the electron and holes trapped. From equation 6, it is obviously that blue shift (shift to shorter wavelength) will be observed as the nanoparticle size decreases.

The quantitative dependence of the minimum electronic excitation energy of a nanoparticle can be approximately by the Heisenberg Uncertainty Principle with respect to the uncertainty in the position (Δx) and the uncertainty in the momentum (Δp).

$$\Delta p \Delta x \geq \frac{\hbar}{2} \quad (7)$$

The particle has no fixed position, but its energy (E) and momentum ($p = \hbar k$) are strictly fixed. For a nanoparticle, the uncertainty in the position depends on the characteristic size of the nanoparticle $\Delta x = d$. The excitation energy of a nanoparticle can be expressed as:

$$E = \frac{\hbar^2 k^2}{2\mu} \quad (8)$$

Where μ is the effective mass.

Before further discussion, we have to assume that the relations between the energy and momentum is independent of the particle size, and that excited energy will change in inverse proportion to the square of the characteristic size of the nanoparticle. A more rigorous analysis of the size effect on the nanoparticle excitation energy (E_n) gives the following relationship:

$$E_n = E_b + E_q \quad (9)$$

Where E_b is the energy of the interband transition in a macroscopic (bulk) semiconductor, E_q is the energy of excitant localization in the nanoparticle:[5] Where the E_q can be found as

$$E_q = \frac{h^2 n^2}{8R^2 \mu} - \frac{1.78e^2}{\epsilon R} - 0.24E_R^* \quad (10)$$

Where n is an integer, R is the radius of the nanoparticle, $\mu = (m_e^{-1} + m_h^{-1})^{-1}$ where (m_e and m_h are the effective mass for electron and hole, respectively), ϵ is the dielectric constant of the semiconductor, and E_R^* is the effective Rydberg Energy. From the experiment we found out that the first term on the right hand side of the equation is predominant, the second term takes into account the Coulomb interaction between the electron and hole inside the nanoparticle, and the third term is responsible for the spatial correlation.[5] It can be seen that the excitant energy of nanoparticle is well described by the $1/R^2$ dependence. Equation 10 is often used to estimate the size of nanoparticle.

6. Optical Absorption

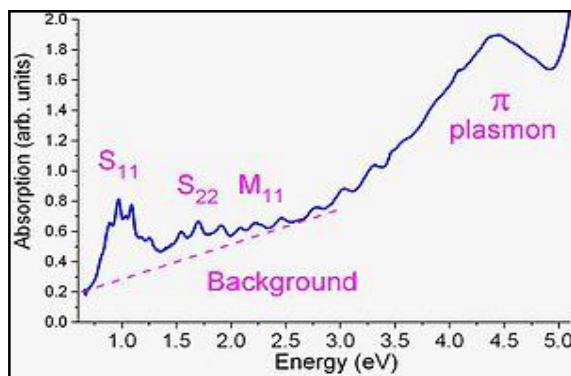


Figure 3: Optical absorption spectrum from dispersed single-wall carbon nanotubes

Optical absorption in carbon nanotubes differs from absorption in conventional 3D materials by presence of sharp peaks (1D nanotubes) instead of an absorption threshold followed by an absorption increase (most 3D solids). Absorption in nanotubes originates from electronic transitions from the v_2 to c_2 (energy E_{22}) or v_1 to c_1 (E_{11}) levels, etc. The transitions are relatively sharp and can be used to identify nanotube types. Note that the sharpness deteriorates with increasing energy, and that many nanotubes have very similar E_{22} or E_{11} energies, and thus significant overlap occurs in absorption spectra. This

overlap is avoided in photoluminescence mapping measurements (see below), which instead of a combination of overlapped transitions identifies individual (E_{22} , E_{11}) pairs. Interactions between nanotubes, such as bundling, broaden optical lines. While bundling strongly affects photoluminescence, it has much weaker effect on optical absorption and Raman scattering. Consequently, sample preparation for the latter two techniques is relatively simple. Optical absorption is routinely used to quantify quality of the carbon nanotube powders. The spectrum is analyzed in terms of intensities of nanotube-related peaks, background and pi-carbon peak; the latter two mostly originate from non-nanotube carbon in contaminated samples. However, it has been recently shown that by aggregating nearly single chirality semiconducting nanotubes into closely packed Van der Waals bundles the absorption background can be attributed to free carrier transition originating from inter tube charge transfer.

7. Carbon Nanotubes As A Black Body

An ideal black body should have emissivity or absorbance of 1.0, which is difficult to attain in practice, especially in a wide spectral range. Vertically aligned "forests" of single-wall carbon nanotubes can have absorbances of 0.98–0.99 from the far-ultraviolet (200 nm) to far-infrared (200 μm) wavelengths. Super black, a coating based on chemically etched nickel-phosphorus alloy, is another material approaching the absorption of 1.0.

These SWNT forests (buckypaper) were grown by the super-growth CVD method to about 10 μm height. Two factors could contribute to strong light absorption by these structures: (i) a distribution of CNT chiralities resulted in various bandgaps for individual CNTs. Thus a compound material was formed with broadband absorption. (ii) Light might be trapped in those forests due to multiple reflections.

7.1. Reflectance Measurements

	UV-to-near IR	Near-to-mid IR	Mid-to-far IR
Wavelength, μm	0.2-2	2–20	25–200
Incident angle, $^{\circ}$	8	5	10
Reflection	Hemispherical-directional	Hemispherical-directional	Specular
Reference	White reflectance standard	Gold mirror	Aluminum mirror
Average reflectance	0.0160	0.0097	0.0017
Standard deviation	0.0048	0.0041	0.0027

Table 1

8. Luminescence

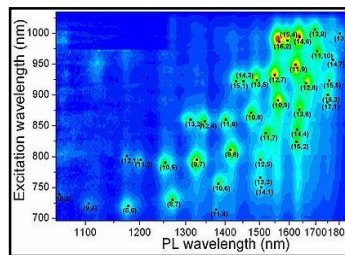


Figure 4: Photoluminescence map from single-wall carbon nanotubes. (n, m) indexes identify certain semiconducting nanotubes

9. Excitation Mechanism

Photoluminescence (PL) is one of the important tools for nanotube characterization. The excitation of PL usually occurs as follows: an electron in a nanotube absorbs excitation light via S_{22} transition, creating an electron-hole pair (exciton). Both electron and hole rapidly relax (via phonon-assisted processes) from c_2 to c_1 and from v_2 to v_1 states, respectively. Then they recombine through a $c_1 - v_1$ transition resulting in light emission. No excitonic luminescence can be produced in metallic tubes — electron can be excited, thus resulting in optical absorption, but the hole is immediately filled by another electron out of many available in metal. Therefore no exciton is produced.

10. Carbon Nanotubes Properties

Photoluminescence from SWCNT, as well as optical absorption and Raman scattering, is linearly polarized along the tube axis. This allows monitoring of the SWCNTs orientation without direct microscopic observation.

PL is quick: relaxation typically occurs within 100 picoseconds.

PL efficiency is usually low (~0.01%), however, there is room for enhancement, e.g., through improving the structural quality of the nanotubes and clever nanotube isolation strategies. For example, the efficiency of 1% has been reported in nanotubes sorted by diameter and length through gradient centrifugation, and it has been further increased to 20% by optimizing the procedure of isolating individual nanotubes in solution.

The spectral range of PL is rather wide. Emission wavelength can vary between 0.8 and 2.1 micrometers depending on the nanotube structure.

Excitons are apparently delocalized over several nanotubes in single chirality bundles as the photoluminescence spectrum displays a splitting consistent with intertube exciton tunneling.

Interaction between nanotubes or between nanotube and another material (e.g., substrate) quenches PL. For this reason, no PL is observed in multi-wall carbon nanotubes. PL from double-wall carbon nanotubes strongly depends on how they were prepared: CVD grown DWCNTs show emission both from inner and outer shells. However, DWCNTs produced by encapsulating fullerenes into SWCNTs and annealing show PL only from the outer shells. Isolated SWCNTs lying on the substrate show extremely weak PL which has been detected in few studies only. Detachment of the tubes from the substrate drastically increases PL.

Position of the (S_{22} , S_{11}) PL peaks depends slightly (within 2%) on the nanotube environment (air, dispersant, etc.). However, the shift depends on the (n , m) index, and thus the whole PL map not only shifts, but also warps upon changing the CNT medium.

11. Application Of Carbon Nanotubes

11.1. Carbon Nanotubes In Batteries And Capacitors

Carbon Nanotubes have the unique electronic characteristics that can be applied as electrodes in batteries and capacitors. Some of these unique properties are high surface area (~1000 m²/g), and good electrical conductivity. But the most importance is their linear geometry which makes their surface highly accessible to the electrolyte.[7]

Research has shown that Carbon Nanotubes have the highest reversible capacity of any carbon material for use in lithium-ion batteries. The other applications of Carbon Nanotubes in batteries and capacitors are Ultra Batteries from MIT [8], and Nanotubes Juice Super Batteries from UC Davis.[9]

12. Conclusion

Carbon Nanotubes exhibit wealth unique properties and incredible phenomena that make them potentially useful in a wide variety of applications in nanotechnology. Until today, many are remain controversial and make Carbon Nanotubes remain an exciting area of research topics. Discovering Carbon Nanotubes properties pushes current technology progress and gain a foothold in science. All these challenges will keep nanotube researchers busy for a long time to come. Carbon Nanotubes are promised to play a significant role in the design and manufacture of many nano-material devices in the future.

13.Reference

1. <http://science.nas.nasa.gov/~deepak/home.html>, Title of Article: Nanomechanics/Materials, By: Deepak Srivastava at OCT, 2004.
2. "Exceptionally high Young's modulus observed for individual carbon nanotubes", M M J Treacy, T W Ebbesen and J M Gibson Nature, vol.381, p678 (1996).
3. <http://www.pbs.org/transistor/science/info/transmodern.html>, Title of Article: Field Effect Transistor, By: The American Institute of Physics, at May 3, 1999.
4. "Electrical-conductivity of individual carbon nanotubes", T W Ebbesen, H J Lezec, H Hiura, J W Bennett, H F Ghaemi and T Thio Nature, vol.382, p54 (1996)
5. www.uaf.edu/chem/467Sp05/lecture19.pdf, Title of Article: Quantum Size Effect and Bulk behavior of Nanostructured Material.
6. <http://www.uaf.edu/chem/467Sp05/lecture19.pdf>. Title of Article: Atomic Scale Friction and Its connection to Fracture Material. By: RW Carpick, EE Flater at Oct 2004.
7. http://www.aist.go.jp/aist_e/aist_today/2003_10/2003_10_p08_09.pdf, Title of Article: Carbon Nanotubes Industrial Application, By Motoo Yumura at Oct 2003.
8. http://www.technologyreview.com/NanThe_applications_of_Carbon_Nanotubes_in_FueoTech/wtr_16326,303,p1.html, Title of Article: The Ultra Battery, By Kevin Bullis at Feb 13 2006
9. http://www.trnmag.com/Stories/2005/032305/Nanotubes_juice_super_batteries_Brief_032305.html, Title of Article: Nanotubes juice super battery at March 20 , 2005
10. <http://www.frost.com/prod/servlet/report-extended-toc>.
11. <http://www.benwiens.com/energy4.html#energy1.5>, Title of Article: The future of Fuel Cell, By Ben Wein at Jan 31 2006.
12. <http://www.ipc.itri.org>, Title of Article: Direct Alcohol Fuel Cell, By: BANNOCKBURN , at Feb 12 2006.
13. <http://physicsweb.org/article/world/13/6/8>, Title of Article: Glass breakthrough, By: Belle Dum at 11 August 2004.
14. http://www.ee.duke.edu/~sorin/papers/ieeenano04_spice.pdf, Title of Article: Semi- empirical SPICE models for Carbon Nanotubes FET Logic. By: Chris Dwyer, Mokey Cheung, and Daniel J Sorin at August 19, 2004.

15. "Nanomechanics of Carbon Nanotubes and Composite". Page215–230, Deepak Srivastava and Chenyu Wei (2003).
16. http://www.cat-science.com/admin/articles/index_050301.html#3
Institut d'Estudis Catalans, By: Alegret, S., Merkoçi, A., Sep 14 2005
17. K. Iakoubovskii et al. (2006). "IR-Extended Photoluminescence Mapping of Single-Wall and Double-Wall Carbon Nanotubes". *Journal of Physical Chemistry B* 110 (35): 17420–17424.doi:10.1021/jp062653t. PMID 16942079.
18. K. Iakoubovskii et al. (2008). "Optical Characterization of Double-wall Carbon Nanotubes: Evidence for Inner Tube Shielding". *Journal of Physical Chemistry C* 112 (30): 11194–11198.doi:10.1021/jp8018414.
19. M. E. Itkis et al. (2005). "Comparison of Analytical Techniques for Purity Evaluation of Single-Walled Carbon Nanotubes". *Journal of the American Chemical Society* 127 (10):3439–8.doi:10.1021/ja043061w. PMID 15755163.
20. Jared J. Crochet et al. (2011). "Electrodynamic and Excitonic Intertube Interactions in Semiconducting Carbon Nanotube Aggregates". *ACS Nano* 5 (4): 2611–2618.doi:10.1021/nn200427r.
21. Zu-Po Yang et al. (2008). "Experimental Observation of an Extremely Dark Material Made By a Low-Density Nanotube Array". *Nano letters* 8 (2): 446–451. Bibcode:2008NanoL...8.446Y.doi:10.1021/nl072369t. PMID 18181658.
22. L. Mizuno et al. (2009). "Supporting Information". *Proceedings of the National Academy of Sciences* 106 (15): 6044–7. Bibcode:2009PNAS..106.6044M. doi:10.1073/pnas.0900155106.PMC 2669394. PMID 19339498.
23. F. Wang et al. (2004). "Time-Resolved Fluorescence of Carbon Nanotubes and Its Implication for Radiative Lifetimes". *Physical Review Letters* 92 (17): 177401. Bibcode:2004PhRvL..92q7401W.doi:10.1103/PhysRevLett.92.177401. PMID 15169189.
24. Jared Crochet et al. (2007). "Quantum Yield Heterogeneities of Aqueous Single-Wall Carbon Nanotube Suspensions". *Journal of the American Chemical Society* 129 (26): 8058–805.doi:10.1021/ja071553d. PMID 17552526.
25. S-Y Ju et al. (2009). "Brightly Fluorescent Single-Walled Carbon Nanotubes via an Oxygen-Excluding Surfactant Organization". *Science* 323 (5919): 1319–1323. Bibcode:2009Sci...323.1319J.doi:10.1126/science.1166265. PMID 19265015.

26. T. Okazaki et al. (2006). "Photoluminescence Quenching in Peapod-Derived Double-Walled Carbon Nanotubes". *Physical Review B* 74 (15): 153404. Bibcode:2006PhRvB..74o3404O.doi:10.1103/PhysRevB.74.153404.