Journal of Nanoscience and Nanoengineering
Vol. 2, No. 5, 2016, pp. 34-39
http://www.aiscience.org/journal/jnn
ISSN: 2471-8378 (Print); ISSN: 2471-8394 (Online)

Finding the Chirality of Semiconducting DWCNT Using Empirical Equation of Radial Breathing Mode Frequency of RRS and Optical Transition Energy

Adnan Siraj Rakin*, S. M. Mominuzzaman

Department of Electrical and Electronic Engineering, Bangladesh University of Engineering and Technology, Dhaka, Bangladesh

Abstract

The main objective of this work is to obtain the Chirality of inner and outer tube of double walled carbon nanotube successfully for the first time taking the interaction effect of the walls of Double Walled Carbon Nanotubes (DWNT) into account. Once the diameter is obtained from the Radial Breathing Mode (RBM) Frequency of Resonant Raman Spectroscopy (RRS) then this can be used as a base to form an equation with the chiralities of inner and outer tube which was previously shown for Single walled carbon nanotube. By Taking the interaction effect into account both the RBM frequency and Optical transition energy relation with diameter were modified for DWNT. This improved equation gave accurate diameter of the tubes from Radial Breathing Mode frequency with almost no error. Since from RRS the diameter and Optical transition energy is known and their relation with chirality can be used to solve for the chirality of both inner and outer tube. While solving those two equations the interaction effect between the tubes were also taken into account by building a proper algorithm.

Keywords

Double Walled Carbon Nanotube, Raman Spectroscopy, Optical Transition Energy, Chirality

Received: September 18, 2016 / Accepted: September 26, 2016 / Published online: November 2, 2016

1. Introduction

Over the last few years a significant amount of work have been done on Carbon nanotube. The difficulty in characterizing double wall carbon nanotube due to inter wall interactions is evident. To overcome these challenges there is an urge for developing new improved technique for determining the diameter, optical transition energy and chirality of double wall carbon nanotube.

The most widely used description of the electronic band structure of graphene is an empirical tight-binding model [1, 2]. The electronic band structures of carbon nanotubes were calculated by using zone folding approximation as well as by using 1st-principle calculations [3, 4]. Curvature mixes the in plane σ and out of-plane π states of graphene [5]. It there by shifts the electronic bands towards the Fermi level. TB model with the nearest-neighbour approximation can provide a simple way to calculate band gap of semiconducting SWCNT, despite its failure in the overall quantitative predictions of the electronic energies [7, 8]. The absorption spectrum is often further approximated by considering only the van-Hove-related transition energies E_{ii} [6, 7]. The expression for the band gap of semiconducting SWCNT with chirality (n, m) is: $Eii=\gamma_0/d$ Where, i=1, 2, 3, 4…. denotes First, second, third and fourth and so on transition energy from band to band.

* Corresponding author Adnan Siraj Rakin adnanrakin@gmail.com
E-mail address: adnanrakin@gmail.com (A. S. Rakin), mominuzzaman@yahoo.com (S. M. Mominuzzaman)

This relation is always found true except for SWCNT with very small diameter, where curvature effect dominates its properties [9]. Another important optical property that needs to be taken into account is the excitonic effect. An electron and a hole in a crystal can form a bound state called an exciton [10]. Different Authors Have proposed Modification to the linear relation of Transition Energy with diameter for Single Walled Carbon Nanotube. Later, correction of γ was proposed by many authors to include curvature effect [11]. Jamal, G. R. A. et al Modified the value of γ showing that it has a relation with chirality [12]. In this Work those Equations were modified to form an empirical equation for Double Walled Carbon Nanotube Taking the interaction effect and outer wall screening into account.

Another Important aspect of this work is Resonant Raman Spectroscopy. In double walled carbon nanotubes (DWNTs), the WRBM and diameter relationship is more complex than in SWNTs because additional factors like wall to wall stresses and charge transfer can shift the WRBM [13]. Previous investigation indicated that RBM frequencies have a systematic upward shift for the SWCNTs in the bundles compared with the isolated ones due to the van der Waals interaction [14, 15]. Here it was assumed that the influence of the van der Waals interaction between the outer and the inner tube in a DWCNT is the same as that in SWCNT bundles.

Raman Spectroscopy [20], Rayleigh scattering [21] and Photoluminescence excitation [22] have been previously used for nondestructive chirality characterization. Raman spectroscopy has been used to find the chirality of double walled carbon nanotube by different researcher [23]. DWCNT have been used to excite with different excitation energy to determine the chirality of double walled carbon nanotube [24]. Another new technique that was used in determining the chirality of double walled carbon nanotube is by using the two RBM frequencies of the nanotube [25]. Here an empirical equation based Chirality assignment technique has been presented.

2. Experimental Data

`By combining Tunable Raman spectroscopy with Raman mapping procedures and electron beam lithography it is possible to obtain the Raman spectra of the individual constituents of the same isolated DWNT. In an attempt to build an empirical equation Radial Breathing Mode frequency and optical transition energy data for particular inner and outer tubes were required whose chirality would be known as well.

The values of both the up shift and down shift of DWNTs' RBM frequencies are not constant, but vary with inter layer spacing and their chiralities. In their work M Xia et el and co [16] calculated theoretically by using the modified continuum model which takes the inter wall spacing and chirality effect into account. From their work the approximated radial breathing mode frequency can be written as, $W_{rbm} = A/d+B\times c_o$ $cm^{-1,}$ Where A and B are constants and c_o depends on the inter layer spacing. These data's were Curve fitted using Matlab to get the values of the constants of our Empirical equations. For Optical Transition Energy the data's were collected from the experiments of Shimamoto et el [17] and it was assumed that the optical transition energy for which both the inner and outer wall carbon nanotube would be in resonance with excitation energy would actually be equal to the energy found from PL experiments.

3. Procedure and Results

a. W_{RBM} VS Diameter Relation:

Radial Breathing Mode frequency is inversely proportional to the diameter [26]. Influence of chirality certainly plays a role in W_{RBM} of the tube however due to the interaction effect of double walled carbon nanotube this effect becomes minimum. In this work chirality effect is neglected when compared to curvature and inter tube interaction effect [27]. Different calculations have shown that the upshift of the inner tube RBMs can be as high as 12 cm^{-1}. Such an upshift of the RBM frequency does not only occur for inner tubes in DWCNTs but also for SWCNTs in bundles [18]. In both cases this shift is due to the van der Waals interaction with the surrounding tubes. However, in the case of the concentric tubes the interaction is between a tube outside and a tube inside whereas in the case of the bundles it is between two tube outsides. From those observations we assume that inter wall interaction affects the radial breathing mode frequency exponentially. As the diameter of the tube decreases curvature of these small nanotubes affects the radial breathing mode frequency more. That would give an empirical equation as following

$$w = \frac{a}{d} + c.e^{f.dd} + \frac{g}{d^2} \quad (1)$$

First part is the inverse relation with diameter while the second part is the shifting due to interaction and third part takes the chirality effect into account. Here a, c, f, g are constants, w is RBM frequency dd is diameter difference and d is diameter. By using curve fitting in matlab we get the values of constants.

For inner tube,

a=216.8; c =16.65; f =-.6523; g =6.68.

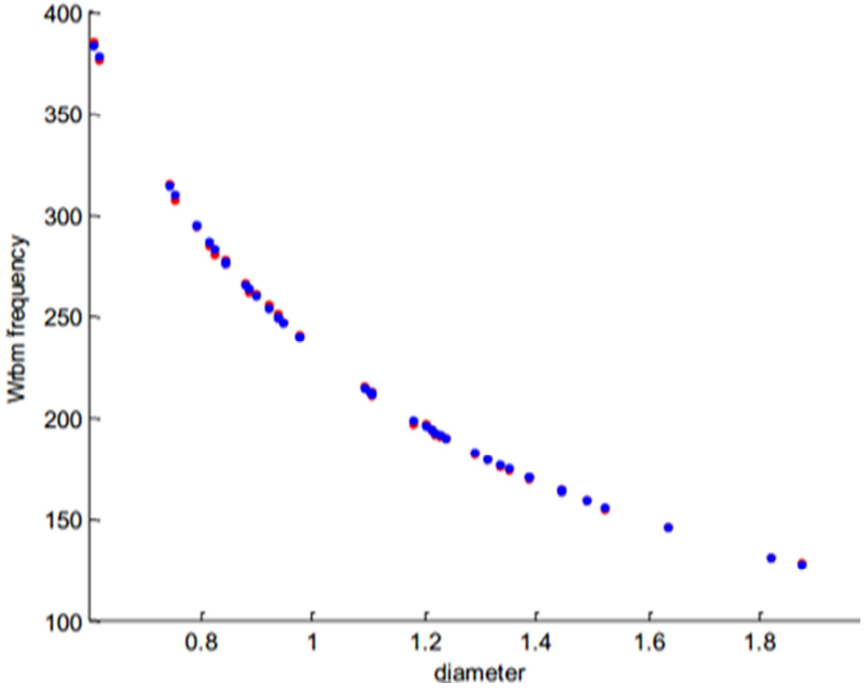

Fig. 1. Inner tube $W_{RBM\ vs}$ Diameter plot. Red dot are experimental value [16] and Blue dot are values found from the developed equation.

For outer tube,

a=218; c=14.13; f=-0.7713; g=7.285.

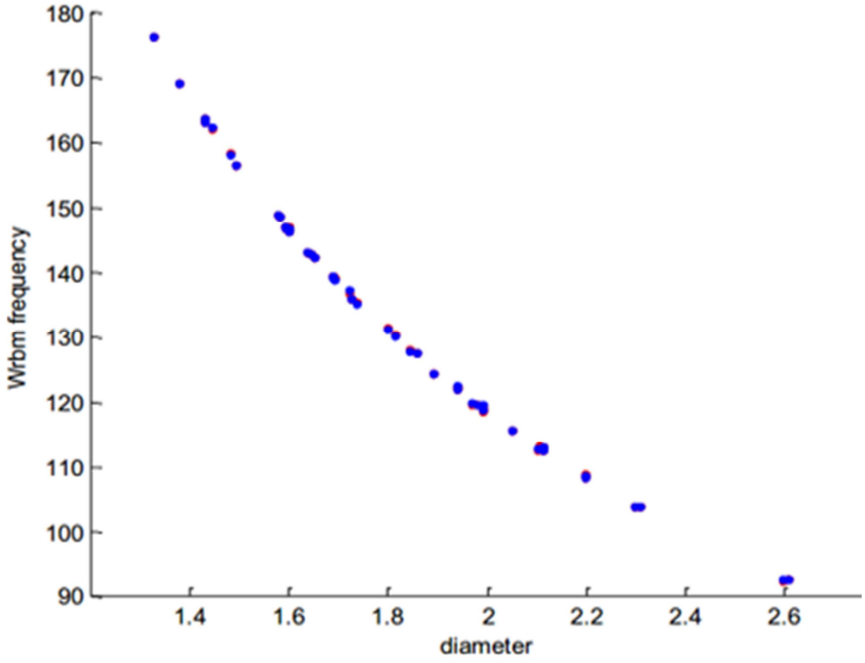

Fig. 2. Outer tube $W_{RBM\ vs}$ Diameter plot. Red dot are experimental value [16] and Blue dot are values found from the developed equation.

So the experimental results of M Xia et el and result obtained from the developed equation is identical.

b. Optical Transition Energy VS Diameter Relation:

For single walled nanotube it was confirmed that band gap of SWCNT has a part which is proportional to $\cos(3\theta)/R^2$ where R and θ is radius and chiral angle of SWCNT respectively [19]. From that it is derived that $\cos(3\theta)/R^2$ is proportional to 1/2n-m [12]. The binding energy or cohesive energy of carbon atom in a CNT decrease with increasing curvature.

The 2D short-range interactions are reduced by dielectric media around CNTs due to dielectric screening of Coulomb interactions, leading to red shift in the exciton energy levels in CNTs. Screening effect would be dominant in the inner tube due to outer wall protection [28]. Since interaction effect shifts the energy of the inner tube we add a constant factor in our equation to take this factor into account. Combining these effect an equation similar to the already existing SWNT equation can be estimated [12]. For double walled tube the equation would look like this:

$$E_{11}(S) = k.\frac{b+\frac{c-d}{f+(-1)^l(2n-m)}+\frac{a}{d}}{d} + S^i \quad (2)$$

From curve fitting we get the values of the constants as follows s=.3911 and s=.0645 respectively for mode 1 and mode 2 nanotube. And i=0 for outer tube and i=1 for inner tube. However for our purpose we have ignored the shifting factor s in this equation and taken the interaction effect into account in our algorithm for finding the chirality. Thus the values of other constants follows: For mode 1 a=-0.05533; b=0.4023; c=-0.9921; f=-10.75; k=2.2. And for mode 2 a =-0.3272; b=7.014; c= -2.359; k=0.1571, f=0.

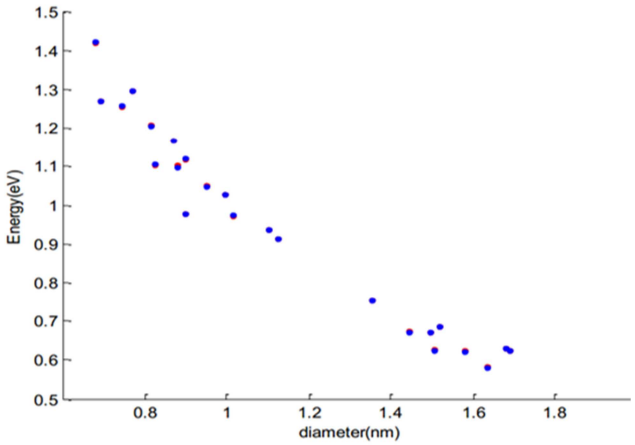

Fig. 3. Optical Transition energy vs Diameter plot. Red dot are experimental value [17] and Blue dot are values found from the developed equation.

From the above observation it is evident that the developed equation would accurately estimate the Band gap and RBM frequency for a particular DWNT's inner and outer wall.

c. Chirality:

Using Resonant Raman Spectroscopy for finding the chirality of CNT is pretty commonplace. Similar work has been done to assign the chirality of SWNT. However here we represent the modifications required to use this method in characterizing DWNT.

From the radial breathing mode frequency of Raman spectroscopy we will get the diameter of both the inner and outer tube using equation (1). The higher frequency will belong to the inner tube and lower frequency will belong to the outer tube. We can also estimate the diameter difference of the tube from these frequencies using only the inverse relation between the diameter and RBM frequency. For each tube diameter would be as follow:

$$d = 0.078.\sqrt{n^2 + m^2 + mn} \quad (3)$$

From the resonant optical transition energy of the inner and outer tube two more equations will be formed:

$E_{11}(s) = k.(b + \frac{c-d}{f+(-1)^l(2n-m)} + \frac{a}{d})/d$, which yields

$$2n - m = (f - \frac{c-d}{E_{11}(S) * \frac{d}{k} - b + \frac{a}{d}})$$

$2n_1 - m_1 = (-10.75 - \frac{-0.9921-d}{E_{11}(S)*\frac{d}{2.2}-0.4023+\frac{0.05533}{d}})$=a1 (from mode 1 equation) (4)

$2n_2 - m_2 = (\frac{-2.359-d}{E_{11}(S)*\frac{d}{0.1571}-7.014+\frac{0.3272}{d}})$ = a_2 (from mode 2 equation) (5)

So if we solve two sets of equations (i) and (ii) we will get two sets of chiralities n1 and m1 for both the tube. Again by solving (i) and (ii) we will get n2 and m2. Now if mod (n1-m1, 3) = 1 and n1>m1 n=n1 and m=m1. But if mod (n2-m2, 3) = 2 and n2>m2 then n=n2 and m=m2. And the procedure will be the same for both inner and outer tube provided that their respective equation is used while solving for the chirality.

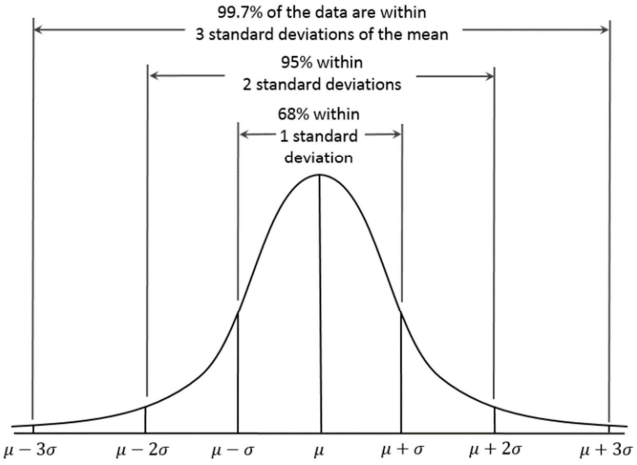

Fig. 4. A typical normal distribution and percentage of data within the standard deviation from the mean.

An algorithm was also developed to make the chirality assignment more robust. By this algorithm little bit of error in diameter and transition energy due to interaction effect between the tubes and other second order effect will not affect the chirality assignment. An approximation of the algorithm was that the error resulted in finding the

experimental optical transition energy was normally distributed. As the percentage of error between the experimental data and the data resulted from our equation is very small even if the errors does not follow a fully normal distribution that fact would not eventually result in a major error in the assignment.

The probability of finding a data within three standard deviation of the mean is 99.7%. So if the first calculation's result does not match any of the two chirality assignment condition then the optical transition energy was changed by one standard deviation or any threshold value of the error in both positive and negative directions one after another. In this work this procedure was repeated six times until one of the condition of the assignment process was met.

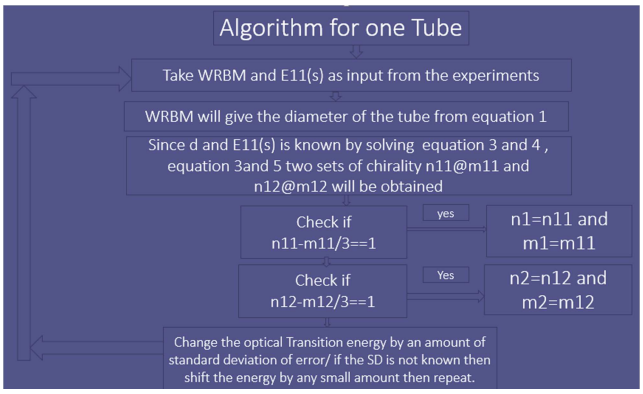

Fig. 5. A Flow Chart of the Algorithm used to solve the chirality of DWNT from the developed Equations.

No. of test	Chirality	Tube	W_{rbm} (cm^{-1})	Energy (eV)	(n1, m1)	(n2, m2)	(n, m)	Correct/ wrong
1.	(8,3)	Inner	304.86	1.298	(5,6)	(8,3)	(8,3)	Correct
	(17,4)	Outer	155.92	.626	(9,13)	(17,4)	(17,4)	Correct
2.	(6,5)	Inner	314.72	1.256	(6,5)	(5,6)	(6,5)	Correct
	(13,9)	Outer	157.07	.6697	(13,9)	(11,9)	(13,9)	Correct
3.	(8,7)	Inner	232.62	.972	(8,7)	(8,8)	(8,7)	Correct
	(15,8)	Outer	150.27	.624	(15,8)	(10,13)	(15,8)	Correct
4.	(11,1)	Inner	260.47	.979	(11,1)	(5,7)	(11,1)	Correct
	(18,5)	Outer	144.14	.583	(18,5)	(10,15)	(18,5)	Correct
5.	(8,4)	Inner	285.21	1.105	(8,4)	(5,6)	(8,4)	Correct
	(11,9)	Outer	174.48	.752	(10,11)	(11,9)	(11,9)	Correct
6.	(7,5)	Inner	286.76	1.209	(6,7)	(7,5)	(7,5)	Correct
	(21,1)	Outer	139.73	.6291	(13,13)	(21,1)	(21,1)	Correct
7.	(10,2)	Inner	270.82	1.169	(6,8)	(10,2)	(10,2)	Correct
	(14,7)	Outer	163.46	.673	(14,7)	(9,12)	(14,7)	Correct
8.	(9,4)	Inner	260.1	1.119	(6,7)	(9,4)	(9,4)	Correct
	(20,3)	Outer	139.29	.624	(13,12)	(20,3)	(20,3)	Correct
9.	(8,6)	Inner	251.82	1.05	(7,7)	(8,6)	(8,6)	Correct
	(13,2)	Outer	216.71	.938	(8,9)	(13,2)	(13,2)	Correct
10.	(6,4)	Inner	344.16	1.42	(5,6)	(6,4)	(6,4)	Correct
	(17,4)	Outer	155.39	.626	(17,4)	(9,13)	(17,4)	correct
11.	(7,3)	Inner	342.32	1.27	(7,3)	(4,5)	(7,3)	Correct
	(11,1)	outer	263.4	.979	(11,1)	(5,7)	(11,1)	Correct
12.	(7,6)	Inner	266	1.1043	(7,6)	(6,6)	(7,6)	Correct
	(20,3)	Outer	139.17	.624	(13,12)	(20,3)	(20,3)	Correct
13.	(6,5)	Inner	318.64	1.256	(6,5)	(5,5)	(6,5)	Correct
	(11,3)	Outer	237.9	1.0265	(7,8)	(11,3)	(11,3)	Correct

Fig. 6. A summary of the results obtained in solving the chirality of DWNT from the developed equations and algorithm.

Using this technique the chirality of several semiconducting inner and outer tube was successfully assigned whose diameter was within the range of 0.8-1.65 nm. Outside this range the interaction and the curvature effects becomes too large or too small respectively.

4. Conclusions

DWCNT will replace SWNT due to its various advantages thermally and electrically. However, characterization and fabrication of DWNT has been the real challenge in this field. Thus this work will provide a perfect platform for improving the characterization of Double walled carbon nanotube.

From that observation of experimental data an empirical relation was developed between RBM frequency and Diameter of the nanotube with minimum error. This relation was used to predict the diameter of the tube correctly. Later by solving the diameter and first optical transition energy chirality of DWNTs was successfully assigned.

However, there might still be some issue which was not properly addressed here. Assuming the diameter of the nanotube to be constant may result in some error. Actual percentage of the error resulting from that variation remains something to be explored in future work.

References

[1] A. Kasuya, Y. Sasaki, Y. Saito, K. Tohji, Y. Nishina: Evidence for size dependent discrete dispersions in single-wall nanotubes, Phys. Rev. Lett. 78, 4434 (1997).

[2] S. Reich, J. Maultzsch, C. Thomsen, P. Ordej´ on: Tight-binding description of graphene, Phys. Rev. B66, 035412 (2002).

[3] S. Reich and C. Thomsen, Phys. Rev. B 62, 4273 (2000).

[4] R. Saito, G. Dresselhaus, and M. S. Dresselhaus, Physical Properties of Carbon Nanotubes (Imperial College Press, London, 1998).

[5] X. Blase, L. X. Benedict, E. L. Shirley, S. G. Louie: Hybridization effects and metallicity in small radius carbon nanotubes, Phys. Rev. Lett. 72, 1 878 (1994).

[6] P. M. Rafailov, H. Jantoljak, C. Thomsen: Electronic transitions in single walled carbon nanotubes: A resonance Raman study, Phys. Rev. B61, 16 179 (2000).

[7] J. D. Correa, A. J. R. da Silva, and M. Pacheco, "Tight-binding model for carbon nanotubes from ab initio calculations," J. Phys.: Condens. Matter, Vol. 22, No. 7, pp. 275503, 2010.

[8] S. Reich, J. Maultzsch, and C. Thomsen, "Tight-binding description of graphene,"Phys. Rev. B, Vol. 66, No. 3, pp. 035412, 2002.

[9] H. Zeng, H. F. Hu, J. W. Wei, Z. Y. Wang, L. Wang, and P. Peng, "Curvature effects on electronic properties of small radius nanotube," Appl. Phys. Lett., Vol. 91, No. 3, pp. 033102, 2007.

[10] P. Y. Yu, M. Cardona: Fundamentals of Semiconductors (Springer-Verlag, Berlin 1996.

[11] P. K. Valavala, D. Banyai, M. Seel, and R. Pati, "Selfconsistent calculations ofstrain-induced band gap changes in semiconducting (n, 0) carbon nanotubes,"Phys. Rev. B, Vol. 78, No. 23, pp. 235430, 2008.

[12] Jamal, G. R. A. et al.: Elec. Engg., Instn. Engrs., Bangladesh, 37 (II), December 2011.

[13] D. Graf, F. Molitor, K. Ensslin, C. Stampfer, A. Jungen, C. Hierold, L. Wirtz, Raman imaging of graphene, Solid State Communications 143 (2007).

[14] Henrard, L.; Herna dez, E.; Bernier, P.; Rubio, A. Phys. ReV. B 1999, 60, R8521.

[15] Rao, A. M.; Chen, J.; Richter, E.; Schlecht, U.; Eklund, P. C.; Haddon, R. C.; Venkates waran, U. D.; Kwon, Y.-K.; Toma ek, D. Phys. ReV. Lett. 2001, 86, 3895.

[16] Minggang Xia, Shengli Zhang, Xianjun Zuo, Erhu Zhang, Shumin Zhao, Jian Li, Lei Zhang, Yachao Liu, and Run Liang PHYSICAL REVIEW B 70, 205428 (2004).

[17] Daisuke Shimamoto, Hiroyuki Muramatsu, Takuya Hayashi, Yoong Ahm Kim, Morinobu Endo, Jin Sung Park, Riichiro Saito, Mauricio Terrones, and Mildred S. Dresselhaus Applied Physics Letters 94, 083106 (2009).

[18] B. W. Smith, M. Monthioux, and D. E. Luzzi, Nature London 396, 323 1998.

[19] H. Yorikawa and S. Muramatsu, "Chirality-dependence of energy gaps of semiconducting nanotubules", Solid State Communications, Vol 94, Issue 6, Pages 435-437, May 1995.

[20] M. S. Strano, S. K. Doorn, E. H. Haroz, C. Kittrell, R. H. Hauge and R. E. Smalley, "Assignment of (n, m) Raman and Optical Features of Metallic Single- Walled Carbon Nanotubes", Nano Lett., Vol. 3, No. 8, pp. 1091-1096, 2003.

[21] Y. Lian, Y. Maeda, T. Wakahara, T. Akasaka, S. Kazaoui, N. Minami, N. Choi and H. Tokumoto, "Assignment of the Fine Structure in the Optical Absorption Spectra of Soluble SingleWalled Carbon Nanotubes", J. Phys. Chem. B, 107, 12082-12087, 2003.

[22] J. Lefebvre, S. Maruyama and P. Finnie, "Photoluminescence: science and applications", Topics in Applied Physics, Vol. 111, pp. 287-319, 2008.

[23] Raman Characterization and Tunable Growth of Double-Wall Carbon Nanotubes, Lijie Ci, Zhenping Zhou, Xiaoqin Yan, Dongfang Liu, Huajun Yuan, June 2, 2003.

[24] Identification of the constituents of double-walled carbon nanotubes using Raman spectra taken with different laser-excitation energies, Feng Li, S. G. Chou, Wencai Ren, J. A. Gardecki, 28 November 2002.

[25] Assignment of the chiralities of double-walled carbon nanotubes using two radial breathing modes, Minggang Xia, Shengli Zhang, Xianjun Zuo, Erhu Zhang, Shumin Zhao, 23 November 2004.

[26] G. D. Mahan, Phys. Rev. B65, 235402 2002.

[27] R. Pfeiffer, Ch. Kramberger, F. Simon, H. Kuzmany, September 24, 2013.

[28] Sihan Zhao, Tomoya Kitagawa, Hisanori Shinohara, Ryo Kitaura, Phys. Rev 10.1007/s12274-014-0515, June 13, 2014.