A Review of Chirality Finding Techniques of DWCNT

Adnan Siraj Rakin¹
Farjana Snigdha²

¹Department of Electrical and Electronic Engineering, University of Central Florida, USA
Email: adnansirajrakin@knights.ucf.edu  Tel: 3219470327
²Department of Electrical and Electronic Engineering, Bangladesh University of Engineering Technology, Bangladesh
Email: snigdha152buet@gmail.com  Tel: 01710281183

ABSTRACT

Double Walled Carbon Nanotube has shown remarkable electrical and mechanical properties. However, their characterization has been a great challenge. Different techniques previously existed for finding the chirality of carbon nanotube. But implementing those techniques for double walled carbon nanotube represents various challenges due to interaction between the tubes and change in the optical and electrical properties. In this work, for the first time we represent a complete overview of the possible techniques proposed in finding the chirality of Double walled carbon nanotube. Additionally we compare their relative advantages and disadvantages taking accuracy, feasibility and other factors into account.

Keywords: Chirality, Characterization, Nanotube, Double walled.

DOI: 10.20448/308.3.1.6.14
Copyright: This work is licensed under a Creative Commons Attribution 3.0 License
Funding: This study received no specific financial support.
Competing Interests: The authors declare that they have no competing interests.
History: Received: 13 February 2018/ Revised: 26 February 2018/ Accepted: 2 March 2018/ Published: 5 March 2018
Publisher: Online Science Publishing
1. INTRODUCTION

Carbon nanotube has interesting properties and potential applications as both single walled and multi walled nanotube are widely investigated. For proper understanding of electronic properties of SWNTs and MWNTs systems, it is essential to study electronic and structural properties as a function of its constituent graphene wall. Examining structural correlations between two adjacent layers on MWNTs, it is found that for low bias, transport is predominantly governed by the outermost shell, while for high bias, the current is carried by a combination of outer and inner shells \[1, 2\]. The commensurability of two adjacent layers in MWNTs have been investigated theoretically \[3, 4\].

Though Scanning tunneling microscopy (STM) and spectroscopy (STS) validated chiral model for SWNT \[5\] for MWNT neither chiral indices of inner shell nor transport properties can be determined by these processes. To identify if the sample is metallic or semiconducting, transport measurements can be controlled through a gate. By atomic force microscopy outer radius and length can be roughly identified so number of tubes in a rope can be determined, but measurement of chiral indices cannot be estimated. In order to have information on both transport properties and detailed structure on the same tube simultaneously for both SWNT and MWNT is of fundamental importance. For this a good choice is in situ transport measurement in transmission electron microscope (STM). When an atomic point is contacted by high resolution (HR) its quantification of conductance in conjunction with local structure is successfully proved by Wildoer, et al. \[5\]. Wang, et al. \[6\] measured successfully the quantification of conductance of thick multiwalled nanotubes and their low magnification images. Practically by HR to identify chiral indices is very difficult. Oppositely, the selected-area electron diffraction(SAED) in a TEM has access to these indices for a SWNT \[7\] and to an estimation of these indices for unique helicity bundles \[8\] and for MWNT \[9\].

In this paper, we represent different characterization techniques for double walled carbon nanotube and their relative implications. In the next section an overview of the electrical and optical structure of double walled carbon nanotube is presented. A comparative representation of different techniques for finding chirality of DWCNT is demonstrated in section III.

2. ELECTRICAL AND OPTICAL PROPERTIES

Multi-walled carbon nanotubes (MWCNT) consist of multiple rolled layers (concentric tubes) of graphene. Basically, coaxially placed set of SWCNTs of different radii forms an MWCNT as shown in Fig.1. Cylindrically nested layers of MWCNT can be visualized as rolled-up graphene sheet. The chirality of the layer is represented by a pair of coefficients \((n, m)\) of lattice vectors \(a_1 \) and \(a_2 \) in the chiral vector, \(Ch\). For example, the chiral vector for zigzag type nanotubes is \((n, 0)\) and for armchair type nanotubes is \((n, n)\). The chirality of these nested layers is different due to their structural independence of one another.

![Fig-1. A multi-walled carbon nanotube \[10\].](image)

The distance between adjacent graphene sheets in graphite is 0.34 nm which is considered to same as spacing of two neighboring layers in MWCNT \[11\]. Each carbon atom is connected to three neighboring carbon atoms by covalent bond within the atomic layer of a graphene sheet. Three sp2 orbitals on each carbon form s-bonds to three other carbon atoms. One 2p orbital remains unhybridized on each carbon, which is perpendicular to the plane
of carbon ring and combine to form the p-bonding networks \cite{10}. Van der Waals force is the interaction between neighboring layers. The atomic interactions between the neighboring layers are the van der Waals forces.

![Inter-graphene layer spacing in graphite \cite{10}](image1.jpg)

Empirical tight-binding model is widely used for describing electronic band structure of graphene \cite{12}. Both 1st-Principle calculation and zone folding approximation are used for calculating electronic band structures of carbon nanotubes \cite{13}. Shifting the electronic band towards the Fermi level is due to curvature mixing in the plane $\sigma$ and out of plane $\pi$ states of graphene \cite{14}. One of the easiest way to calculate band gap of semiconducting SWCNT is using TB model with the nearest-neighbor approximation though it has limitation of overall quantitative predictions of the electronic energies. Van-Hove related transition energies $E_{ii}$ is used to approximate the absorption spectrum \cite{11}. The band gap of semiconducting SWCNT with chirality $(n, m)$ is:

$$E_{ii} = \frac{\Upsilon_0}{d}$$

Where, $i = 1, 2, 3, 4\ldots$ denotes first, second, third and fourth and so on transition energy from band to band. It is true for SWCNT except for very small diameter where curvature effect dominates its properties \cite{15}.

An electron and a hole in a crystal can form a bound state called an exciton. This excitonic effect is an important optical property need to be considered. After proposition from different authors to modify linear relationship of transition energy with diameter of SWCNT, correction of $\Upsilon$ was also proposed to include curvature effect \cite{16}. Jamal, G. R. A. et al modified the value of $\Upsilon$ showing it has a relation with chirality \cite{17}. The red shift in the exciton energy levels in CNT is due to dielectric media around CNT dielectric screening of coulomb interaction which also reduce the 2D short-range interactions. For outer wall protection, screening effect may be dominant in the inner tube \cite{18}. As this effect has influence on inner tube which shifts the energy so in the equation of SWCNT a constant factor is incorporated for this effect. So, a modified SWCNT equation can be estimated combining all these effects in the equation \cite{19}.

3. CHARACTERIZATION METHODS

Different researchers around the world have investigated different chirality assignment techniques for SWCNT \cite{20}. Similar methods are investigated by researchers for DWCNT.
a) Rayleigh Scattering Based Technique:

Rayleigh Scattering based technique is applied upon object which is smaller in diameter than the wavelength of elastic light scattered from it. This elastic light scattering is called Rayleigh Scattering. The scattering intensity is enhanced when the frequency of light is in resonance with an electronic transition of the object. For both metallic and semiconducting nanotubes, transition energies can be probed during applying this technique. For very first time, performing fluorescence spectroscopy experiment band gap luminescence from SWCNTs is observed by Bachilo, et al. [21] in 2002. In the experiment, they observed fluorescence emission near first optical transition and after it the light absorption at photon energy equal to second optical transition. Following this process the chirality of DWCNT is successfully extracted [21]. In many works, experimental evidence of interlayer coupling is mentioned [22]. So, Raman and Rayleigh scattering process has significant effect in finding chirality.

b) Scanning Tunneling Microscopy:

Scanning Tunneling Microscopy can provide evidence of modified electronic structure with respect to their single wall counterpart. This resultant in the discovery of the contribution originating from the inner tube to the local density of states of the double-walled system which justifies previous theoretical calculations. Moreover, inner tube chiral index could be found from the van Hove singularities present in the tunneling spectra [23].

For the case when outer tube is semiconducting and inner tube is metallic, interlayer interaction effects the energy dispersion relation which shows anti crossing of energy bands and splitting for both the tubes. However, their combination does not alter the electronic properties of each tube. This assumption was used to calculate the DOS for the tubes listed in figure 4. By comparing it to our experimental tunneling spectra we can identify the ones whose singularities would create the extra peak. Thus, the chirality pairs (11,5) and (12,3), provide the best match to the experimental data, as the constituent peaks of these spectra could account for most of the extra peaks observed in the STS spectra in the DWNT sample.

![Fig-3. a) TEM image of double- and triple-walled carbon nanotubes and (b) STM image of an isolated nanotube showing an opened end covered by amorphous carbon, as a result of acid refluxing [23].](image-url)

<table>
<thead>
<tr>
<th>n</th>
<th>m</th>
<th>diameter (nm)</th>
<th>chiral angle (deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>7</td>
<td>0.96</td>
<td>30</td>
</tr>
<tr>
<td>8</td>
<td>8</td>
<td>1.1</td>
<td>30</td>
</tr>
<tr>
<td>9</td>
<td>6</td>
<td>1.03</td>
<td>23.4</td>
</tr>
<tr>
<td>9</td>
<td>9</td>
<td>1.23</td>
<td>30</td>
</tr>
<tr>
<td>10</td>
<td>4</td>
<td>0.99</td>
<td>16.1</td>
</tr>
<tr>
<td>10</td>
<td>7</td>
<td>1.17</td>
<td>24.1</td>
</tr>
<tr>
<td>11</td>
<td>2</td>
<td>0.96</td>
<td>8.2</td>
</tr>
<tr>
<td>11</td>
<td>5</td>
<td>1.12</td>
<td>17.8</td>
</tr>
<tr>
<td>12</td>
<td>3</td>
<td>1.09</td>
<td>10.9</td>
</tr>
<tr>
<td>12</td>
<td>6</td>
<td>1.26</td>
<td>19.1</td>
</tr>
<tr>
<td>13</td>
<td>1</td>
<td>1.07</td>
<td>3.7</td>
</tr>
<tr>
<td>13</td>
<td>4</td>
<td>1.22</td>
<td>13</td>
</tr>
<tr>
<td>14</td>
<td>2</td>
<td>1.20</td>
<td>6.6</td>
</tr>
<tr>
<td>15</td>
<td>0</td>
<td>1.19</td>
<td>0</td>
</tr>
</tbody>
</table>
Fig-4. list of chirality and their relative parameter [23].

<table>
<thead>
<tr>
<th>n</th>
<th>m</th>
<th>diameter (nm)</th>
<th>chiral angle (deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>7</td>
<td>0.96</td>
<td>30</td>
</tr>
<tr>
<td>8</td>
<td>8</td>
<td>1.1</td>
<td>30</td>
</tr>
<tr>
<td>9</td>
<td>6</td>
<td>1.03</td>
<td>23.4</td>
</tr>
<tr>
<td>9</td>
<td>9</td>
<td>1.23</td>
<td>30</td>
</tr>
<tr>
<td>10</td>
<td>4</td>
<td>0.99</td>
<td>16.1</td>
</tr>
<tr>
<td>10</td>
<td>7</td>
<td>1.17</td>
<td>24.1</td>
</tr>
<tr>
<td>11</td>
<td>2</td>
<td>0.96</td>
<td>8.2</td>
</tr>
<tr>
<td>11</td>
<td>5</td>
<td>1.12</td>
<td>17.8</td>
</tr>
<tr>
<td>12</td>
<td>3</td>
<td>1.09</td>
<td>10.9</td>
</tr>
<tr>
<td>12</td>
<td>6</td>
<td>1.26</td>
<td>19.1</td>
</tr>
<tr>
<td>13</td>
<td>1</td>
<td>1.07</td>
<td>3.7</td>
</tr>
<tr>
<td>13</td>
<td>4</td>
<td>1.22</td>
<td>13</td>
</tr>
<tr>
<td>14</td>
<td>2</td>
<td>1.20</td>
<td>6.6</td>
</tr>
<tr>
<td>15</td>
<td>0</td>
<td>1.19</td>
<td>0</td>
</tr>
</tbody>
</table>

Fig-5. Experimental and calculated DOS for (18,10) corresponding to the outer tube and calculated DOS for two possible chirality for the inner tube, (12,3) and (11,5) [23].

c) Raman Spectroscopy:

Raman Spectroscopy and Resonant Raman scattering both have advantage over other processes due to their ability to probe semiconducting and metallic nanotubes [24]. Both these tools are widely used characterization tools for carbon nanotubes. To predict chirality of double walled carbon nanotube, this method has been used by Adnan and Monimuzzaman where they have used their own developed Raman equation and software generated data [25, 26].

In radial breathing mode, due to incident of light we get a frequency of Raman Spectroscopy. With the help of the developed equation using this frequency we can estimate diameter of both inner and outer tube [25]. Here the higher frequency is belonged to inner tube and lower one for the outer tube. Also, there is an inverse relation equation between the diameter and RBM frequency, using it the diameter difference of the tube from these frequencies can be estimated. We can form two equations from resonant optical transition energy one for inner tube and other for outer tube [26]. An algorithm was also developed which would make the chirality assignment more robust as well [19, 20].
Fig-6. A summary of the results obtained in solving the chirality of DWNT from the developed equations and algorithm [19].

After forming all these equations [26] we can solve these equations to estimate the chirality of DWCNT using the developed algorithm successfully [19].

d) Electron Diffraction Method:

Electron diffraction examination can help in determining chiral indices of individual DWCNTs, when it is formed by arc discharge method. Study of statistical analysis is used for structural correlation between inner and outer tube of DWCNTs. But this process has some error in the interlayer distance between inner and outer tubes. The interlayer distances during the experiment were in the range of 0.34–0.38 nm [20]. Using photoluminescence excitation spectroscopy based technique, chirality of Single walled carbon nanotubes (SWCNTs) can be estimated quite fast and easily. In comparison to Raman scattering this process skips the laborious analysis which is required for extracting Raman resonance profiles. But photoluminiscence probes have its limitation of applicable only for
semiconducting nanotubes, in contrast of which Raman and Rayleigh scattering is applicable for both semiconducting and metallic carbon nanotubes [27].

![Diagram](image)

**Fig-7.** Procedure to determine chiral indices of a DWNT using ED [20].

Though PL method has its advantages, it is not effective for DWCNT due to the interaction factor. Rayleigh scattering based technique has its edge over PL method being able to probe the transition energies of a nanotube independent of the tube’s metallic or semiconducting character. While comparing with Raman spectroscopy, Rayleigh scattering is faster one and has access to transitions in metallic nanotubes. Although having all these benefits, the process has some experimental condition as generally its signal strength is very low. To entirely suppress probable scattering background from nearby scatterer, it requires a sample geometry and a bright light source [27]. The best process to estimate chirality specially for DWCNT is Raman scattering along with different algorithm and equation [19]. On the other hand, Electron diffraction is reliable in finding chiral indices of large diameter tubes. But Electron diffraction cannot be applicable for nanotube ensembles as it can probe one nanotube at a time. Some other improved techniques has been implemented recently though. K. Liu et al [28] have
introduced an improved method in this regard. This would provide complete chirality profiling of SWNT. However we would be skeptic of their effectiveness in DWNT. Showed very recently that Rayleigh scattering is improved by interface dipole enhancement effect which was shown by which might result in their application for finding the chirality of DWNT.

4. CONCLUSION
Carbon Nanotube after all these years of research was expected to be in full swing in terms of their application in electronic, optical and mechanical devices. However, the challenges associated with their fabrication and characterization remains one of the major setbacks. Double walled carbon nanotube is expected to be more effective in application with a greater in characterization. In this work, we have summarized some of the best efforts towards achieving that goal. We presented a comparative analysis of different methods currently in use for DWNT characterization. Future work in this field would certainly make the accuracy in predicting the chirality of DWNT even more feasible and practical.

REFERENCES


*Online Science Publishing* is not responsible or answerable for any loss, damage or liability, etc. caused in relation to/arising out of the use of the content. Any queries should be directed to the corresponding author of the article.