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Theoretical studies on Chirality for Graphene

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Abstract— These Graphene can be obtained from the parent molecule graphite by laser evaporation or laser chemical vapor deposition methods (LCVD) on a SiC substrate or similar substrates. The symmetry of the molecule determines its chirality. Using a microprocessor, a control of the diameter (*d*) and the chiral angle (θ) will result in the formation of graphene without any agglomerates. The various values of integers (*n*, *m*) are time-averaged using a software program and its chirality (*ch*) have been determined for low values of (*n*, *m*) such as (1, 2) (2, 1), (1, 3) respectively. We conclude that (2, 1) or (1, 2) are the (*n*, *m*) values for which non-agglomerated graphene structure can be generated. Higher values of (*n*, *m*) will lead to agglomeration.

We find that there are twice as many as basis points or there are hexagonal cells, for a given (*n*, *m*). The chirality angle (θ) increases when m value increases and decreases with the *m* value, or the chirality angle (θ) is directly proportional to *m* value.

We generated rolled hexagonal, planar unrolled and cubic nanotube lattices. The nearest neighbor (C-C) bonding distance is maintained at 1.421Å. The angle between chirality and translation vector $\vec{T}$ increases gradually with increasing (*n*, *m*) values. *n*=1 required 7 cycles for convergence and *n*=2 required 9 cycles for convergence. The value of C-C bond increases with n value. The tubule radius and height increases with (*n*, *m*) value.

Index Terms— chirality, agglomeration, LCVD – Laser Chemical Vapour Deposition, Chiral angle, substrate, translational vector, nearest neighbour

1 Introduction

Graphene is made out of carbon atoms arranged on a honeycomb (hexagonal) structure. It is obtained from graphite, a three dimensional (3D) allotrope of carbon. Graphenes can be compared to benzene rings stripped out of hydrogen atoms. In fact, Graphite is made out of stacks of graphene layers which are weakly coupled by Van der Waals forces. Wallace [1] in 1946 first gave the band structure of graphene and showed its semi- metallic behavior.

Graphene has a structural flexibility which is seen from its electronic properties. The sp^2 hybridization between one *s* orbital and two *p* orbitals leads to a trigonal planar structure with a formation of a σ bond between carbon atoms that are separated by 1.421 Å. It is the σ bond that is responsible for the robustness of its lattice structure. The structure of graphene, made out of carbon atoms is a triangular lattice with a basis of two atoms per unit cell. It is the π bond that is responsible for control of conductivity.

Owing to structural and electronic flexibility, graphene can be tailored chemically in different ways. We can deposit metal atoms on top of it [2], or we can deposit molecules on it [3].

Intercalated compounds are also possible [4]. Geim and Novoselov [5] have given a complete history of the 'rise of Graphene'. Also, we can incorporate nitrogen and boron in its structure [6]. It has potential applications in the field of electronics, superconductors, in batteries, etc. Several workers [7-15], have expressed difficulty in producing non-agglomerated carbon nanotubes. Here we have made an attempt to understand the theoretical basis for non-agglomeration of CNT's.

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2 Chiral Vector

The structure of single-wall carbon nanotube (except for cap region on both ends) is specified by a vector of original hexagonal (also called honeycomb) lattice called the chiral vector. The chiral vector corresponds to a section of nanotube perpendicular to the tube axis. In figure 1, the unrolled hexagonal lattice of the nanotube is shown, in which OB is the direction of the nanotube axis, and OA corresponds to the chiral vector C_h.

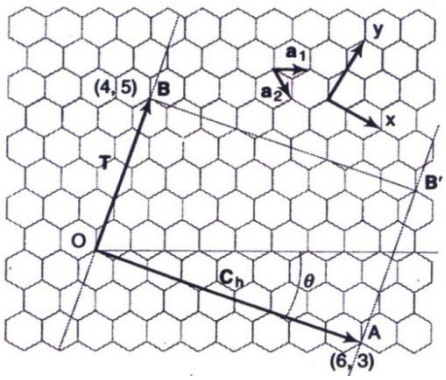

Fig.1. Chiral vector in a hexagonal lattice

By considering the crystallographically equivalent sites O, A, B and B′, and by rolling the honeycomb sheet so that points O and A coincide (and points B and B′ coincide), a paper model of carbon nanotube can be constructed. The vector OB defines another vector namely translational vector, *T*. The rectangle generated by the chiral vector C_h and translational vector *T*, i.e., the rectangle OAB′B in the figure is called the unit cell for the nanotube. The chiral vector of the nanotube is defined as,

$$C_h = na_1 + ma_2$$

where *n, m* are integers $(0 \le |m| \le n)$ and a_1, a_2 are the unit vectors of the hexagonal lattice. In figure 2, a_1 and a_2 can be expressed using the Cartesian coordinate (*x, y*) as

$$a_1 = \left(\frac{3}{2} a_{cc}, \frac{\sqrt{3}}{2} a_{cc} \right) \quad (1)$$

$$a_2 = \left(\frac{3}{2} a_{cc}, -\frac{\sqrt{3}}{2} a_{cc} \right) \quad (2)$$

Here, a_{cc} is the bond length of carbon atoms. For graphite a_{cc} = 1.42 Å .This same value is often used for nanotubes. But, a_{cc}=1.44 Å is a better approximation for nanotubes. It should really depend on the curvature of the tube. A slightly larger value for more curvature is known.

We see from equations (2) and (3), that the lengths, a_1, a_2, i.e., $|a_1|, |a_2|$ are both equal to $\sqrt{3} a_{cc} = a$. Therefore, *a* is the unit length and this is also the lattice constant. Hence a_1, a_2 can be expressed in terms of lattice constant.

$$a_1 = \left(\frac{\sqrt{3}}{2}, \frac{1}{2} \right) a \quad (3)$$

$$a_2 = \left(\frac{\sqrt{3}}{2}, -\frac{1}{2} \right) a \quad (4)$$

Length of chiral vector is the peripheral length of the nanotube

$$L = |C_h| = a\sqrt{n^2 + nm + m^2} \quad (5)$$

The angle between the vectors C_h and a_1 is called chiral angle, θ. It denotes the tilt angle of the hexagons with respect to the direction of the nanotube axis, and it specifies the spiral symmetry. The chiral angle is defined by taking the inner product of C_h and a_1, to yield an expression for cos θ:

$$\cos\theta = \frac{C_h \cdot a_1}{|C_h||a_1|} = \frac{2n + m}{2\sqrt{n^2 + nm + m^2}} \quad (6)$$

From this expression it can be shown that the chiral angle,

$$\theta = \tan^{-1}\left[\frac{\sqrt{3} m}{2n + m} \right] \quad (7)$$

The tube diameter is then given by

$$d_1 = \frac{L}{\pi} = \frac{a}{\pi}\sqrt{n^2 + nm + m^2} \quad (8)$$

The translational vector, *T*, which is perpendicular to the chiral vector, is expressed as

$$T = \frac{[(2m + n)a_1 - (2n + m)a_2]}{d_R} \quad (9)$$

The length *T* is the unit lattice length along the tube axis direction:

$$T = \frac{\sqrt{3} C_h}{d_R} = \frac{3 a_{C-C}\sqrt{n^2 + nm + m^2}}{d_R} \quad (10)$$

Here, $d_R = \begin{cases} d \text{ if } n - m \text{ is not a multiple of } 3d \\ 3d \text{ if } n - m \text{ is a multiple of } 3d \end{cases}$

and *d* is the highest common division of (*n,m*).

The number of hexagons in a unit cell is given by:

$$N = \frac{2(n^2 + nm + m^2)}{d_R} \quad (11)$$

Figure 2 below shows a real space lattice of graphene.

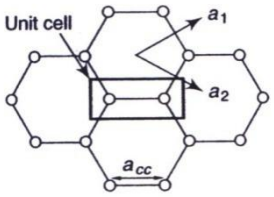

Fig. 2. Real Space Lattice of Graphene

3 Analysis

In order to find out a solution for non-agglomerated carbon nanotubes we have used a web-accessible nanotube structure generator, namely TubeGen online-version 3.4 [16]. When the chiral angle is kept as low as possible then the surface area generated will be large and will result in non-agglomeration. The graphene molecule is known to occupy a large surface area for a given volume, like a sphere. The chiral vector (*n, m*) values have to be as low as possible, with the condition that *n*=*m* will produce "armchair" configuration, *m*=0 will produce a "zigzag" configuration and we are looking for a "chiral" configuration only. i.e. (*n*≠*m*) and (*m*≠0) [17].

The equation governing the relation for the cell gutter parameters $\hat{a}_1, \hat{a}_2$ and $\hat{a}_3$ the tubule translation vector *T* is, $T = n\hat{a}_1 + m\hat{a}_2$. Generally, graphene being a flat mono layer of carbon atoms, tightly packed into a two-dimensional (2D) honeycomb (hexagonal) lattice and serves as the basic building block for graphite materials for all dimensionalities. Graphene can be wrapped up into 0 Dimension fullerenes, 1 Dimension nanotubes or stacked as 3 Dimensional Graphite.

$\hat{a}_1, \hat{a}_2$ are basically unit vectors. *n, m* are integers. The analysis is done in Gaussian mode, the measuring units in Angstrom (1 Å $= 10^{-10}$ m) and the lattices are hexagonal, planar unrolled, and cubic. Whether it is Hexagonal, or cubic or planar unrolled, the angle between chiral vector (*ch*) and tubule translation vector (*T*) remain same value for a given (*n, m*). In our case, we have chosen (1, 2), (2, 1), (2, 2) and (1, 3). (2, 2) happens to be arm-chair configuration which is ruled out for an agglomeration-free structure. This leaves with (1, 2), (2, 1) and (1, 3) (*n, m*) values. The angles for these (*n, m*) values between (*ch*) and (*T*) are 25.857°, 154.143° and 30.9609° respectively. For all these three (*n, m*) values, the nearest neighbor bonding distance is 1.421 Å(C-C). We predict that (2, 1) whose angle formation between (C_h) & (*T*) vector is 154.143° (an obtuse angle) should have larger surface area while folding for a given bond length and hence most suitable contender for non-agglomerated graphene structure.

The second point is that, the chiral angle for hexagonal, cubic and planar unrolled structures are 40.8934° (1,2), 19.1066° (2,1), 30° (2,2) and 46.1021° (1,3), respectively. Taking away the (2,2)

arm-chair configuration leaves us with three choices namely (1,2), (2,1) and (1,3). The lower the value of the (*ch*) angle, lesser will be the tubule diameter *d*, given by $d = \frac{a}{\pi}\sqrt{n^2 + nm + m^2}$ and hence greater will be the *T* (Tubule translation vector) value; $T = \frac{\sqrt{3}Ch}{d}$. When the lattice length (*T*) increases, the number of hexagons in a unit cell will increase giving rise to better electrical conductivity. The (*n, m*) values (2, 1) whose chiral angle (*ch*) is 19.1066° (2, 1) is ideal for non-agglomerated graphene. In terms of number of sub-cells, both (1, 2) and (2, 1) have the same number, namely 14 sub-cells, irrespective of the Hexagonal, planar unrolled or cubic structures. (3, 1) has 26 sub cells which will increase the chances for agglomeration because of the density of (C-C) bonds. The basis points are twice as much as their number of sub-cells respectively irrespective of whether they have hexagonal, planar (unrolled) or cubic structures.Tables 1,2 and 3 below give the (*n,m*) values for (1,2), (1,3) and (2,1) respectively.

Table 1 Chirality (1,2) 28 basis points

	a_1	a_2	a_3
C	1.094104	0.000000	-5.680817
C	0.207600	1.074228	-5.399064
C	0.630415	0.894227	-2.96459
C	-0.261656	1.062356	-4.057834
C	-1.092705	-0.055327	-3.776081
C	-0.674828	-0.861204	-4.869325
C	0.717514	-0.825977	-4.587573
C	0.942019	0.556475	-0.530116
C	0.197674	1.076099	-1.62336
C	-1.019043	0.398267	-1.341607
C	-0.968954	-0.508127	-2.434851
C	0.315043	-1.047766	-2.153099
C	0.997599	-0.449288	-3.246342
C	1.087442	0.120556	1.904358
C	0.622133	0.900009	0.811114
C	-0.765612	0.781602	1.092867
C	-1.092147	-0.065412	-0.000377
C	-0.143005	-1.084718	0.281375
C	0.725109	-0.819318	-0.811868
C	0.936842	0.565148	3.245588
C	-0.377121	1.027056	3.527341
C	-1.022676	0.388842	2.434097
C	-0.575825	-0.930317	2.71585
C	0.324702	-1.044812	1.622606
C	-0.772796	0.774501	4.868571
C	-0.907065	-0.611799	5.150324
C	-0.132985	-1.085993	4.05708
C	1.041031	-0.336630	4.338832

Table 2 Chirality (1,3) 52 basis points

	a_1	a_2	a_3
C	1.450462	0.000000	-7.727607
C	0.810853	1.202646	-7.322905
C	1.269941	0.700777	-4.945224
C	0.504175	1.360017	-5.944346
C	-0.845805	1.178327	-5.539644
C	-1.410029	0.340086	-6.538766
C	-1.070231	-0.979002	-6.134064
C	-0.171241	-1.440318	-7.133187
C	1.098506	-0.947166	-6.728484
C	1.44977	0.044807	-2.567543
C	1.068723	0.980648	-3.566665
C	-0.215653	1.434341	-3.161963
C	-1.099963	0.945474	-4.161085
C	-1.39885	-0.383482	-3.756383
C	-0.809001	-1.203893	-4.755505
C	0.545948	-1.343793	-4.350803
C	1.290983	-0.661212	-5.349926
C	1.398258	0.385634	-1.188984
C	0.461921	1.374943	-0.784282
C	-0.548015	1.342952	-1.783404
C	-1.419861	0.296366	-1.378702
C	-1.268861	-0.702731	-2.377824
C	-0.126665	-1.444921	-1.973122
C	0.847617	-1.177024	-2.972245
C	1.037919	1.013195	1.593399
C	0.124441	1.445114	0.594277
C	-1.128645	0.911043	0.998979
C	-1.449699	-0.047038	-0.000143
C	-0.771425	-1.228309	0.404559
C	0.21786	-1.434007	-0.594563
C	1.310793	-0.621016	-0.189861
C	1.385678	0.428645	3.971081
C	0.769533	1.229495	2.971958
C	-0.589239	1.325382	3.37666
C	-1.311747	0.618998	2.377538
C	-1.246547	-0.741592	2.78224
C	-0.459805	-1.375652	1.783118
C	0.883573	-1.150278	2.18782
C	1.420316	-0.294180	1.188697
C	1.245404	0.743510	5.349639
C	0.07974	1.448268	5.754341
C	-0.885342	1.148916	4.755219
C	-1.447554	-0.091799	5.159921
C	-1.036358	-1.014791	4.160799
C	0.262055	-1.426593	4.565501
C	1.130046	-0.909305	3.566378
C	-0.26425	1.426188	7.1329
C	-1.330243	0.578181	7.537602
C	-1.385016	-0.430777	6.53848
C	-0.417089	-1.389200	6.943182
C	0.591279	-1.324473	5.94406
C	1.428726	-0.250164	6.348762

Table 3 Chirality (2,1) (28 basis points)

	a_1	a_2	a_3
C	1.094104	0.000000	-5.680817
C	1.094058	-0.010101	-1.905112
C	0.997599	0.449288	-3.246342
C	-0.251837	1.064727	-3.528095
C	-0.674828	0.861204	-4.869325
C	-0.973604	-0.499160	-5.151078
C	1.001705	0.440059	0.529362
C	0.725109	0.819318	-0.811868
C	-0.666848	0.867397	-1.093621
C	-0.968954	0.508127	-2.434851
C	-0.682750	-0.854937	-2.716604
C	-0.261656	-1.062356	-4.057834
C	0.993409	-0.458479	-4.339586
C	0.732642	0.812589	2.963836
C	0.324702	1.044812	1.622606
C	-0.964221	0.517051	1.340853
C	-1.092147	0.065412	-0.000377
C	-0.271453	-1.059895	-0.282130
C	0.197674	-1.076099	-1.623360
C	0.334334	1.041770	5.398310
C	-0.132985	1.085993	4.057080
C	-1.091497	0.075492	3.775327
C	-1.022676	-0.388842	2.434097
C	0.187731	-1.077878	2.152344
C	0.622133	-0.900009	0.811114
C	-0.772796	-0.774501	4.868571
C	0.613797	-0.905714	4.586819
C	0.936842	-0.565148	3.245588

4 CONCLUSION

From our theoretical analysis on graphene, we conclude that the (*n, m*) values, namely, (2, 1) or (1, 2) are the chosen two sets of numbers to get a non-agglomerated graphene that can be generated. Higher values of (*n, m*) will lead to agglomeration.

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REFERENCES

[1] Wallace, P.R., 1947, Phy. Rev. 71, 622.
[2] Ostinga., JB., H.B. Heersche, X. Liu, A. Morpuzo and L.M.K. Vanderspyen, 2008, Nature Mater 7, 151.
[3] Dressalhaus, M.S., Dresselhaus, G, Eklunch. PC, "Science of Fullerenes and carbon nanotubes", Academic Press: San Diago, CA, 1995; pp 760.
[4] Tanuma, S., H. Kanimura, 1985, Graphite intercolated compounds: Progrss of research in Japan (World Scientific, Singapore).
[5] Geim, A.K and Novoselov, K.S., (2007), "The rise of Graphene", Nature materials 6(3): 183-191.
[6] Scientific American September 2001 which contain a number of articles on nanotechnology.
[7] Maeda, Y, S. Kimram M. Kanda, M. Harashima and others, J. Am. Chem, Proc, 127 (2005), p. 10287.
[8] Wang, H.M., and others, Applied Physics Letters, 96, 023107 (2010).
[9] Yomigki Yoon and Sayeef Salahuddin, Applied Physics Letters, 96, 013510 (2010).
[10] Thomas Svensson and Zhijianshen, Applied Physics Letters, 96, 021107 (2010).
[11] Tan. WD., C.Y. Su, R.J. Kniza, GQ. Xia, LJ. Li, DY Tang, Applied Physics Letters, 96, 031106 (2011).
[12] Kim. KS, Y. Zhao, H. Jang, S.Y. Lee, J.M. Kim, K.S. Kim, J.H. Ahu, P. Kim, Y. Chao, B.H. Hong, Nature (London) 457, 706 (2009).
[13] Yong-Won Song, Sung-Yeon Jang, Won-Suk Han, Mi-Kyang Bae, Applied Physics Letters, 96, 051122 (2010).
[14] Mcclure, J.W., Phy. Rev., 112, 715 (1958).
[15] Nano computing by V.Sahni and D.Goswami,Tata McGraw Hill co.Ltd, New Delhi-8(2008).
[16] Tubegen online version 3.4 (web interface, http://turin.nss, udel.edu/research/ tubegenonline.html) Frey J.T., and D.J. Doren, University of Delaware, Newark DE, 2005.
[17] Introduction to nanotechnology by Charles. O. Poole JV., Frank K. Surens, Wiley InterScience, John Wiley and sons Inc., Replika Press Pvt. Ltd, India