A Preliminary Study on the Chiral Vector Approach in Determining the Optimum Structure of Carbon Nanotubes and its Correlation to the Chemical Potential Energy Using Avogadro

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Abstract: In this study, the following quantitative properties of carbon nanotubes were explored: the chiral vectors, which are numbers that describe the carbon nanotubes' structure, and properties such as chemical potential energy. The objective of this study is to simulate various carbon nanotube structures with chiral vectors that range from (0-3) and find a relation between these chiral vectors and the chemical potential energy. Using the software Avogadro, 12 carbon nanotubes with different chiral vectors (n, m) were simulated. These carbon nanotubes were of different lengths to keep the number of atoms in the molecules as close to 100 as possible. Avogadro was also used to calculate the theoretical chemical potential energy of these molecules. Using multiple correlation to analyze the simulations' data, an R2 value of 0.632 was obtained, which indicates a small positive linear association between them.

Key Words: carbon nanotubes; chiral vectors; chemical potential energy

1. INTRODUCTION

1.1. Background of the Study

Scientists have been studying carbon nanotubes (CNTs) for the past two decades because of their superior mechanical and electrical properties. In terms of structure, CNTs are a sheet of graphene rolled into a tube. CNTs can be classified as single-walled CNT (SWCNT), double-walled CNT (DWCNT), or multi-walled CNT (MWCNT), depending on the number of carbon-layers in their sidewalls (Schnorr & Swager, 2011).

An SWCNT is a hollow cylinder made up of covalently bonded carbon atoms arranged in a hexagonal pattern. Because of its atomic structure and unique carbon bond properties, the SWCNT has remarkable mechanical and electrical properties (Gao et al., 2021).

Additionally, different types of SWCNTs can be identified, except for their length, by the orientation of the tube axis relative to the carbon network. They are represented by the indices of their chiral vector, n and m (Schnorr & Swager, 2011). The CNT is an armchair when the chiral indices, n and m, are equal. On the other hand, the CNT is zigzag when either n or m is 0. Moreover, the CNT is chiral when their chiral indices are neither of these two (Kaushik & Majumder, 2015). Depending on their composition, CNT may also have metallic or semiconducting properties. The CNT is metallic if n - m = 3q (where q is an integer and n>m) and semiconducting if not (J. Liu et al., 2017). The n and m integers precisely define nanotube chirality and specify the electronic band structure. Hence, the chirality of carbon nanotubes has a significant impact on their electronic properties (Tune et al., 2012).

Further studies show that CNTs have received much interest because they are great at lowering resistance and improving the electrochemical efficiency of composite cathodes (Qin et al., 2014), which is the positive electrode of a battery (Battery University, 2020). Moreover, incorporating CNT into sulfur cathode gives rise to advanced electrodes with improved discharging capacity and cycling performance (L. Zhu et al., 2014).

Furthermore, as seen in batteries and electrochemical pseudocapacitors, energy storage technologies are based on the conversion of chemical potential energy to electrical energy, with the energy being stored in the form of chemical potential energy (C. Liu et al., 2016), which is the energy stored in the chemical bonds of a substance that can be absorbed or released due to a change of the particle number of the given species (CK-12 Foundation, 2021).

Consequently, in this study, the researchers focused on the SWCNT's structure, chiral vectors, and chemical potential energy.

Based on existing literature, no studies have been found regarding the use of virtual simulation to investigate the chemical potential energy of a CNT. Furthermore, no studies have been found describing the effects of changing a CNT's chiral vectors to its chemical potential energy. Despite the lack of existing studies, a molecular editor helped gather the necessary data in this research. Avogadro by

Avogadro Chemistry was the molecular editor used in this study.

This study aims to fill the gap in analyzing the relationship between chiral vectors and the chemical potential energy of CNTs, as this has not been determined in the existing literature. The study would enable future researchers to better determine the optimal CNT structure in possible energy-related applications such as battery electrodes (X. Liu et al., 2012).

1.2 Research Objective

This paper's main objective is to simulate a carbon nanotube structure using different chiral vectors to find a carbon nanotube structure that will yield the highest chemical potential energy with the same number of atoms. Existing literature was the basis for finding the optimal structure. Furthermore, the study aims to determine the relationship between the structures and the chemical potential energy.

1.2.1 Specific Objectives

a. To accomplish this task, the researchers aim to do the following:
b. Find the chiral vectors and make the pairings needed in building the CNT structure with a set number of 100 atoms
c. Simulate different carbon nanotube structures with varying chiral vectors and get their chemical potential energy
d. Sort data according to the structure that has the highest energy
e. Use correlation to figure out the relationship between the chiral vectors and the energy

1.3 Scope and Limitations

This research was limited to only SWCNT structures as their electrical properties are significantly higher than those of (MWCNTs) (Zaytseva & Neumann, 2016). In addition to having a simpler structure and higher electrical characteristics than MWCNTs, SWCNTs are the most studied classification of CNTs both experimentally and theoretically (Laird et al., 2015). As this research was limited to single-walled carbon nanotubes, the researchers did not tackle the effects of varying numbers of walls. Moreover, the number of atoms was only normalized to see if a structure change was the cause and not the size of the molecules increasing. Hence, the researchers have limited the CNT's structure to have only 100 atoms each or 102 if 100 is not possible. Lastly, chiral values used were only from a range of 0-3.

1.4 Significance of the Study

This study contributes to the body of knowledge regarding carbon nanotubes' structures and their implications about their chemical potential energy that may be converted into other forms of energy, such as electrical energy. With the growing need for sustainable energy, this research may serve as a constituent in further research applying carbon nanotubes into batteries. In turn, this study could hopefully reveal new ways to use carbon nanotubes as a material viable for sustainable energy. The data and information gathered can also provide additional resources for future researchers. Furthermore, using simulation prevents unnecessary effort and laborious work. Lastly, since the simulation is in a virtual environment, it is cheaper and requires lesser materials and equipment than actual laboratory work.

2. METHODOLOGY

2.1. Research Design

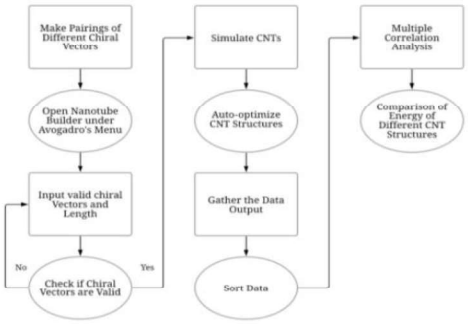

Figure 1. *Flowchart of Methodology*

Figure 1 was used as the flowchart for the entire methodology. The researchers have chosen Avogadro as the visualizer and simulator for the experiment, based on Hanwell et al. (2012). The virtual carbon nanotube (CNT) was built with varying chiral vector and length values using the "Nanotube Builder" available in Avogadro. This option was accessed through the "Build Menu" found in the Toolbar. The builder takes in input for chiral vectors n and m as well as length. The researchers tested different combinations of chiral vectors and length values using different CNT shapes as some chiral vector pairings are not possible.

This study made use of quantitative data, which was collected from Avogadro. After the researchers inputted the chiral vectors n and m, the output was three different types of CNT structures: zigzag, armchair, and chiral. After the CNTs were built, they used Avogadro's auto-optimization, which automatically optimized the CNT's geometry according to the inputted values of chiral vectors and

length. The final output was the final structure of the base CNT and its chemical potential energy.

The researchers only used Avogadro and had no other participants aside from themselves. Furthermore, the researchers only used the simulator mentioned above and mathematical means and tools to acquire their data. Thus, no ethical issues were violated in this study.

2.2. Data Collection Method

The primary data collected were the carbon nanotubes' structures based on the manipulated chiral vectors and the chemical potential energy produced that was determined by the CNT structure. The data was collected from the various simulations that were run in Avogadro. Each simulation had different chiral vector pairs (n,m). These values were selected by choosing a maximum value for the chiral vectors and producing every possible carbon nanotube with chiral vector values less than or equal to the chosen value. In this case, the chosen value was 3, which theoretically gives 16 different (n,m) pairs. However, there are certain (n,m) pairs that are not possible, these being (0,0), (0,1), (1,0), and (1,1). This is because either n or m has to be greater than 1. With this limitation in mind, 12 carbon nanotubes were simulated: (0,2), (0,3), (1,2), (1,3), (2,0), (2,1), (2,2), (2,3), (3,0), (3,1), (3,2), and (3,3), with the lengths modified to keep the number of atoms in the carbon nanotubes as close to 100 as possible to normalize the data as best as possible. After each simulation, the carbon nanotubes' geometries were further optimized. Once these geometries were as optimized as the software would allow, Avogadro automatically calculated and displayed the theoretical chemical potential energy (kJ/mol) produced by the setup.

Energy output in Avogadro's "Calculate Energy" is computed by a variation of the "force field," called Merck Molecular Force Field or MMFF94. MMFF94 is designed to deal with condensed-phase processes in molecular dynamics simulation and molecular geometry optimization in proteins and other biological systems (H. Zhu, 2014).

Avogadro uses the variant MMFF94s (Cornell & Hutchison, 2015). The "s" stands for static as this variant is better suited for time-averaged static molecular geometry (H. Zhu, 2014).

All simulations were done using an AMD Ryzen 5 3550H CPU, Nvidia GeForce GTX 1650 GPU, and 16GB of DDR-2400 RAM.

2.3 Data Collection Instruments

Avogadro is a free, open-source, and cross-platform molecule editor developed by Avogadro Chemistry. The program is written in C++, but Python scripts can be used as extensions to add functionality. Avogadro supports multithreading for rendering and computation, which can reduce wait times on processors with multiple cores. However, GPUs cannot be used for hardware acceleration (Hanwell et al., 2012).

Avogadro has a robust feature set that allows it to create many different types of molecules, including a Nanotube Builder that can create different nanotubes depending on the parameters. It can also optimize molecules' geometry through the Optimize Geometry tool, which gives proper bond angles and lengths. The Auto Optimize tool also does this but continuously. Lastly, it can also calculate the energy of a system through its Calculate Energy function (Cornell & Hutchison, 2015).

2.4 Data Analysis

After collecting data, the researchers analyzed the chiral vectors used in creating the structure and energy produced by the carbon nanotubes and the structure of the CNT that was determined by the chiral vector. A chiral vector pair vs. energy graph was created to easily visualize the trend between the two variables and compare the difference in the energy output of different chiral vector pairs. The statistical tool used was a multiple correlation between the chemical potential energy and the chiral vectors that affect the structure of the CNT structure. A corresponding scatter plot was also used to visualize further the correlation between the two chiral vectors and energy. The unstandardized predicted value of the energy was used to account for the two chiral vectors, the independent variables. This was then plotted against the energy to create the scatter plot. The unstandardized predicted value was calculated after the equation of the line was determined since it is the value that the model predicted for the dependent variables (Penn State Eberly College of Science, 2018). To do this, the researchers opted to use Microsoft Excel and IBM SPSS Statistics to help analyze their data.

3. RESULTS AND DISCUSSION

3.1 Simulation Results

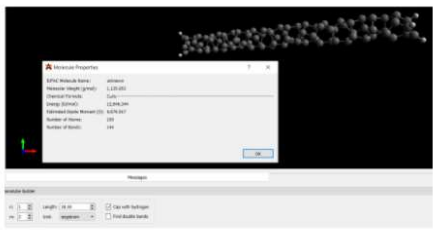

Figure 2. *CNT with chiral vectors (1,2)*

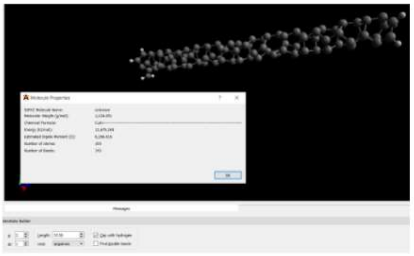

Figure 3. *CNT with chiral vectors (2,1)*

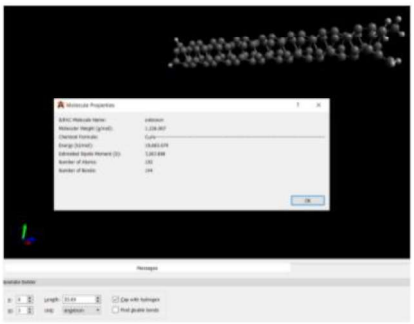

Figure 4. *CNT with chiral vectors (0,3)*

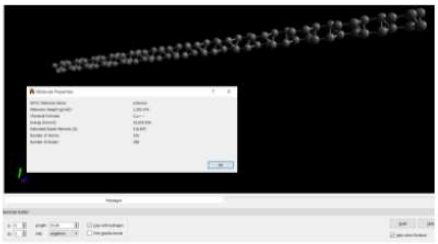

Figure 5. *CNT with chiral vectors (0,2)*

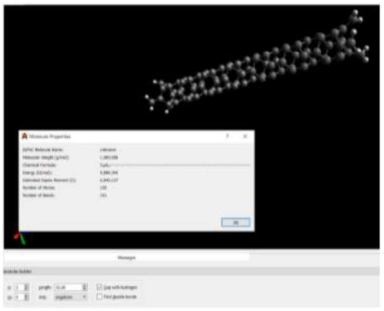

Figure 6. *CNT with chiral vectors (3,0)*

Figure 7. *CNT with chiral vectors (2,0)*

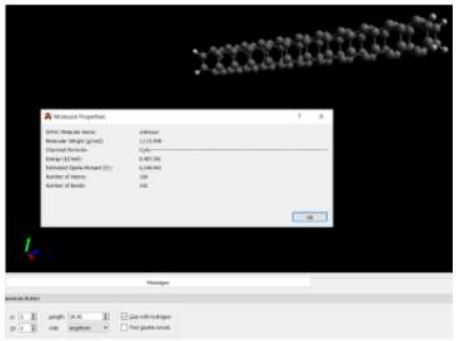

Figure 8. *CNT with chiral vectors (2,2)*

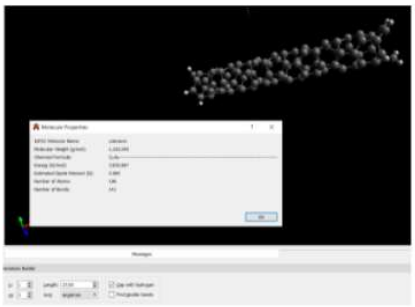

Figure 9. *CNT with chiral vectors (1,3)*

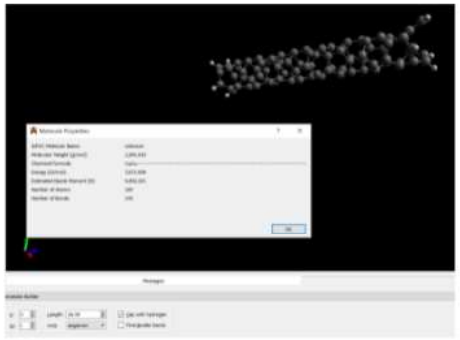

Figure 10. *CNT with chiral vectors (3,1)*

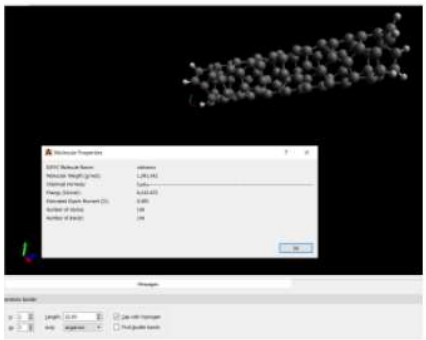

Figure 11. *CNT with chiral vectors (2,3)*

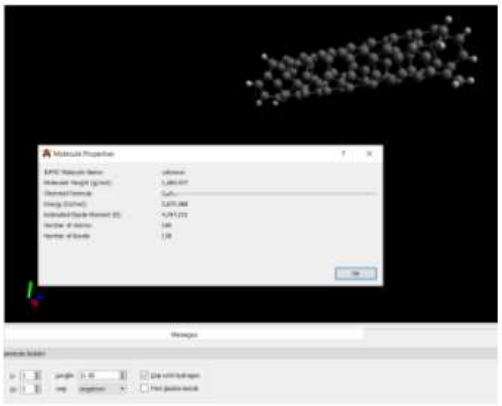

Figure 12. *CNT with chiral vectors (3,2)*

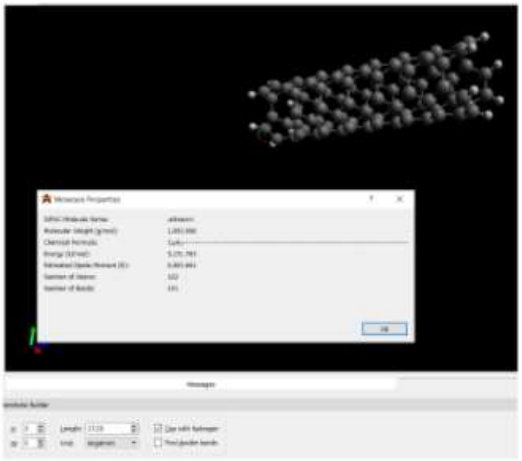

Figure 13. *CNT with chiral vectors (3,3)*

Figures 2-13 show each simulation of CNT with data regarding chiral vectors n and m, classification, number of atoms, number of bonds, CNT length (angstrom), molecular weight (g/mol), and chemical potential energy (kJ/mol). The structures are all set to 100 atoms except for some structures that have 102 because, as explained before, the next shortest value would be 96.

3.2 Primary observations

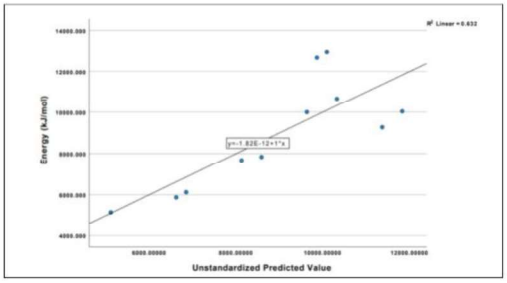

Figure 15. *Linear regression of Energy vs. Unstandardized Predicted Value*

In Table 1, the information about the CNTs with different structures and chiral vectors is displayed.

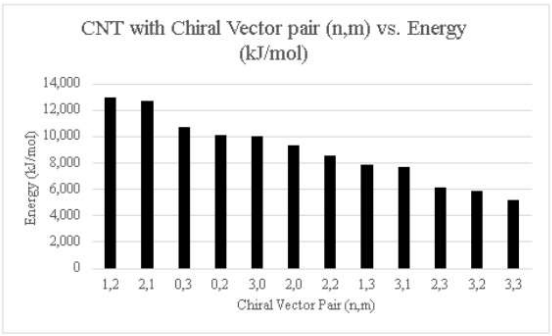

Figure 14. *Bar graph comparing the energy values of each CNT*

In previous research by Jing Liu et al. (2017), it was stated that CNTs that follow the trend of n - m = 3q, where q is an integer, are the most conductive while others are only semiconductive.

It can be seen in Figure 14 that two of the simulated CNTs were chiral and have the most energy, given that they have the same number of atoms. CNTs with (1,2) and (2,1) yield 12,946.344 kJ/mol and 12,675.248 kJ/mol respectively. These CNTs do not follow the trend indicated by the previous research in the previous paragraph. They both exceed two thousand kJ/mol more than the third-highest energy CNT, the (0,3). Moreover, it can be seen that different CNT structures produce different energy outputs, especially with the two armchair structures that have a difference of 3335.618 kJ/mol even though they have the same structure and the same number of atoms. Lastly, there is no obvious pattern that can be seen in the produced data. As the CNTs were made to have 100 atoms, with a few exceptions, it can be seen that the number of bonds, length, molecular weight, and energy are very different from one another and do not follow a specific trend.

3.3 Statistical Analysis

Figure 15 shows the scatter plot corresponding to the correlation between the two chiral vectors and the energy. The y-axis represents chemical potential energy (dependent variable), while the x-axis represents the two chiral vectors (independent variable). The dependent variable's unstandardized predicted value was used to account for the two independent variables and was plotted against the dependent variable. This produced an R2 value of 0.632, consistent with the R2 value in Table 2.

This R2 value of 0.632 is positive, which shows a small positive linear association between them (Kiernan, 2014).

4. CONCLUSIONS

Chiral vectors that range from (0-3) were paired up and used to make carbon nanotubes. Using the software Avogadro, only 12 carbon nanotubes with different chiral vectors were simulated successfully, which are (0,2), (0,3), (1,2), (1,3), (2,0), (2,1), (2,2), (2,3), (3,0), (3,1), (3,2), and (3,3). Since CNTs can only be made if one chiral vector is at least greater than 1, chiral vector pairs (0,0), (0,1), (1,0), and (1,1) are not possible inputs to create a CNT. Results were then sorted with the CNT, with the highest amount of energy being the first. Chiral CNTs with (1,2) and (2,1) yielded the highest energy of 12,946.344 kJ/mol and 12,675.248 kJ/mol, respectively. Using multiple correlation to analyze the simulations' data, an R^2 value of 0.632 was obtained, which indicates a small positive linear association between them.

In conclusion, this study showed the relationship between the chiral vectors and the chemical potential energy of CNTs. Further simulations can be made by identifying other structures not limited to CNTs. Another recommendation is to obtain the average for each structure and compare it to other literature on what applications it can be utilized.

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6. REFERENCES

Battery University. (2020, November 20). BU-104b: Battery Building Blocks – Battery University. Batteryuniversity.com. https://batteryuniversity.com/learn/article/bu_104b_building_blocks_of_a_battery

CK-12 Foundation. (2021). CK12-Foundation. CK-12 Foundation; CK-12 Foundation. https://flexbooks.ck12.org/cbook/ck-12-chemistry-flexbook-2.0/section/17.1/primary/lesson/chemical-potential-energy-chem

Cornell, T., & Hutchison, G. (2015). Learning Avogadro The Molecular Editor. Wustl.edu. https://dasher.wustl.edu/chem430/software/avogadro/learning-avogadro.pdf

Gao, M., Bian, L., & Liang, X. (2021). Analysis for thermal properties and some influence parameters on carbon nanotubes by an energy method. Applied Mathematical Modelling, 89, 73–88. https://doi.org/10.1016/j.apm.2020.07.041

Hanwell, M. D., Curtis, D. E., Lonie, D. C., Vandermeerschd, T., Zurek, E., & Hutchison, G. R. (2012). Avogadro: An advanced semantic chemical editor, visualization, and analysis platform. Journal of Cheminformatics, 4(8). https://doi.org/10.1186/1758-2946-4-17

Kaushik, B. K., & Majumder, M. K. (2015). Carbon nanotube based VLSI interconnects: Analysis and design. SpringerBriefs in Applied Sciences and Technology, 9788132220466, i–iv. https://doi.org/10.1007/978-81-322-2047-3

Kiernan, D. (2014, January 16). Chapter 7: Correlation and Simple Linear Regression. Geneseo.edu; Open SUNY Textbooks. https://milnepublishing.geneseo.edu/natural-resources-biometrics/chapter/chapter-7-correlation-and-simple-linear-regression/

Laird, E. A., Kuemmeth, F., Steele, G. A., Grove-Rasmussen, K., Nygård, J., Flensberg, K., & Kouwenhoven, L. P. (2015). Quantum transport in carbon nanotubes. Reviews of Modern Physics, 87(3), 703–764. https://doi.org/10.1103/RevModPhys.87.703

Liu, C., Neale, Z. G., & Cao, G. (2016). Understanding electrochemical potentials of cathode materials in rechargeable batteries. Materials Today, 19(2),

109–123. https://doi.org/10.1016/j.mattod.2015.10.009

Liu, J., Lu, J., Lin, X., Tang, Y., Liu, Y., Wang, T., & Zhu, H. (2017). The electronic properties of chiral carbon nanotubes. Computational Materials Science, 129, 290–294. https://doi.org/10.1016/j.commatsci.2016.12.035

Liu, X. M., Huang, Z. dong, Oh, S. woon, Zhang, B., Ma, P. C., Yuen, M. M. F., & Kim, J. K. (2012). Carbon nanotube (CNT)-based composites as electrode material for rechargeable Li-ion batteries: A review. Composites Science and Technology, 72(2), 121–144. https://doi.org/10.1016/j.compscitech.2011.11.019

Penn State Eberly College of Science. (2018). 2.1 - What is Simple Linear Regression? | STAT 462. Psu.edu. https://online.stat.psu.edu/stat462/node/91/

Qin, G., Ma, Q., & Wang, C. (2014). A porous C/LiFePO4/multiwalled carbon nanotubes cathode material for Lithium ion batteries. Electrochimica Acta, 115, 407–415. https://doi.org/10.1016/j.electacta.2013.10.177

Schnorr, J. M., & Swager, T. M. (2011). Emerging applications of carbon nanotubes. Chemistry of Materials, 23(3), 646–657. https://doi.org/10.1021/cm102406h

Tune, D. D., Flavel, B. S., Krupke, R., & Shapter, J. G. (2012). Carbon nanotube-silicon solar cells. Advanced Energy Materials, 2(9), 1043–1055. https://doi.org/10.1002/aenm.201200249

Zaytseva, O., & Neumann, G. (2016). Carbon nanomaterials: Production, impact on plant development, agricultural and environmental applications. Chemical and Biological Technologies in Agriculture, 3(1), 1–26. https://doi.org/10.1186/s40538-016-0070-8

Zhu, H. (2014, April 28). Implementation and application of the MMFF94 force field. Unl.edu. https://digitalcommons.unl.edu/cgi/viewcontent.cgi?article=1047&context=chemistrydiss

Zhu, L., Zhu, W., Cheng, X. B., Huang, J. Q., Peng, H. J., Yang, S. H., & Zhang, Q. (2014). Cathode materials based on carbon nanotubes for high-energy-density lithium-sulfur batteries. Carbon, 75, 161–168. https://doi.org/10.1016/j.carbon.2014.03.049