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# MODELING OF A CNT (6,0)-1gN STRUCTURE USING DFT METHOD: A STUDY OF NITROGEN-DOPING EFFECT ON IT'S STRUCTURE AND ELECTRONIC PROPERTIES

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**Abstract**

Modeling of a CNT(6,0)-1gN structure using DFT method has been carried out to study the nitrogen-doping effect on its structure and electronic properties. Geometry optimization of the structure was done using B3LYP density function. The electronic properties such as orbital energies, infrared and ultra violet spectrum, bond distances, and atomic charges were calculated.

The results show that the nitrogen-doping was affected the type of bond, bond length and bond angle between the carbon-carbon in the CNT (6,0) structure. A shift in the peak of the IR and UV spectrum was observed. The nitrogen-doping increase on the CNT (6.0) bandgap of 0.43 eV to 1.88 eV and 1.72 eV for alpha and beta electrons, respectively, and decrease electrical conductivity. The bandgap energies are in the range of the semiconductor materials.

**Key words**: CNT, nitrogen-doping, DFT, B3LYP, electronic properties, bandgap

## INTRODUCTION

Carbon nanotubes (CNTs) are carbon allotrop nanometer-sized tubular were first discovered in 1991 (1). Since the discovery to the present experimental and theoretical studies have been carried out for the development of this material. The results showed that the structure and properties of CNTs have unique and superior. CNTs have unique electrical properties, which can act as a conductor or semiconductor (2). CNT stronger than steel and diamond, and have a high thermal conductivity (3-4). Based on the uniqueness and superiority of the CNT, make it is potentially applicable in various fields and has been used as a mainstay material for future nanotechnology. In order to develop CNT, necessary to modify the structure and properties of CNTs in order to produce CNTs with the structure and properties in accordance with usability. One such is through nitrogen doping on the CNT (5). Chemical doping is an effective method to intrinsically modify the properties of the host materials. Among them, the nitrogen doping plays a critical role in regulating the electronic properties of carbon materials (6)

## RESEARCH METHOD

To investigated the effect of nitrogen doping on the structure and electronic properties of carbon nanotubes, then done modeling with doped nitrogen to Carbon Nanotubes. CNTs were

modeled a zigzag type with chirality (6.0). CNT is composed of 48 carbon atoms, and each carbon atom bonded to three other carbon atoms with $sp^2$ hybridization and at each end of the tube there are six hydrogen atoms ($C_{48}H_{12}$). Hydrogen atom aims to overcome the string dangling-bond carbon atoms. In the subsequent discussion, it was named by the pristine CNT (6.0).

Nitrogen doping on the pristine CNT (6.0) done by substituting the carbon atom in the CNT (6.0) with nitrogen atom, form a graphite-like structure, for subsequent nitrogen doped CNTs are called CNT (6.0) - 1gN. To investigated the effect of nitrogen doping on the structure and electronic properties of carbon nanotubes (6.0), were calculated parameters of the structure and electronic properties. The calculation is performed on the structure of a stable geometry (optimized).

Geometry optimization aims to obtain the stable structure of CNT (6.0), i.e structures that have the potential energy surface minimum with the smallest atomic force (like structures found in nature). During the search process performed geometry optimization with minimum energy configuration of the CNT (6.0). The procedure used is to calculate the wave function and energy on the initial geometry and then processed to look for a new geometry with lower energy. This process is repeated until the geometry with the lowest energy found. Geometry optimization procedure calculates the force on each atom by evaluating the gradient (first derivative) of the energy corresponding to the position of each atom. Berni algorithm used in each stage to select a new geometry in order to obtain the proper convergence of geometry with the lowest energy. Varying the CNT structure optimization algorithm (6.0) to change the gradient and the structure of the two repetition (iteration) are sequentially worth less than a predetermined value (convergence criteria), at this point the molecule is said to have been optimized.

Orbital energy calculations have been performed to investigate the electrical properties of nitrogen-doped CNTs. In this study we analyzed the Infra red spectroscopy and Ultra Violet to investigate the type of vibrational and electronic transitions that occur in the CNT. In the present work, all computation are carried out via the Gaussian 09 package, using Density Functional Theory (DFT) method at the B3LYP hybrid functional (7-9) with 6-31G basis set.

## RESULT AND DISCUSSION

Structure of pristine CNT (6,0) and CNT (6.0) – 1gN that is a optimization results are shown in Figure 1. Figure 1 shows a resonance bond in pristine CNT (6.0) and CNT (6.0) -1gN. This is denoted by the dashed bonds between carbon atoms. The position and value of the bond lengths and angles between atoms in the CNT is shown in figure 2 and table 1.

Figure 1 shown there are a bond resonance in pristine CNT (6.0) and CNT (6.0) -1gN. This is denoted by the dashed bonds between carbon atoms. The position and value of the bond lengths and angles between atoms in the CNT is shown in figure 2 and table 1.

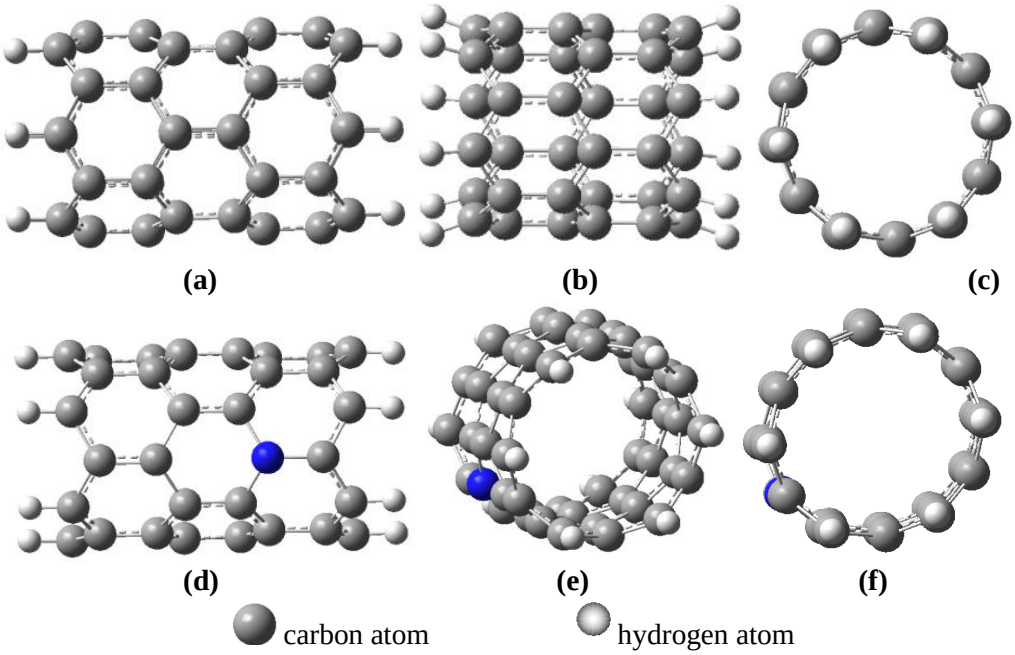



**Figure 1.** pristine CNT (6,0) and CNT (6,0)-1gN structure.
(a) pristine CNT (6,0) visible from the front. (b) pristine CNT (6,0) visible from the front ($45^0$). (c) pristine CNT (6,0) visible from the side. (d) CNT (6,0)-1gN visible from the front. (e) CNT (6,0)-1gN visible from the side ($45^0$). (f) CNT (6,0)-1gN visible from the side

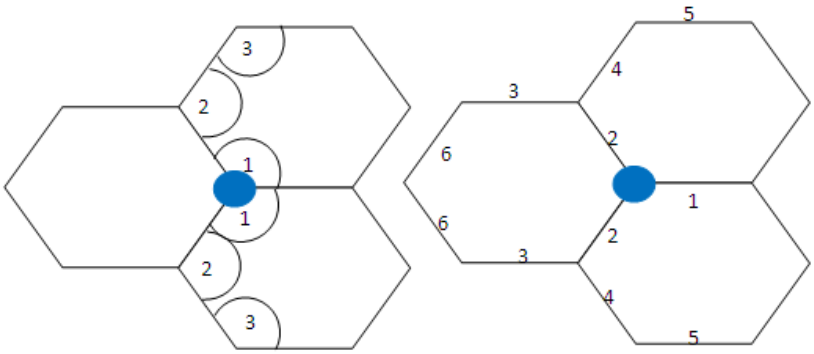



Figure 2. The position of the bond lengths and angles between atoms in the pristine CNT (6,0) and CNT (6,0)-1gN

Atoms in the blue dot is carbon atom to pristine CNT (6,0) and nitrogen atom to CNT (6.0)-1gN.

**Table 1. The bond length and bond angle in pristine and CNT (6,0)-1gN**

| number | Bond length (Å) | | Bond angle ($^0$) | |
|---|---|---|---|---|
| | Pristine | CNT (6,0)-1gN | Pristine | CNT (6,0)-1gN |
| 1 | 1.44 | 1.41 | 119.55 | 118.51 |
| 2 | 1.44 | 1.46 | 114.43 | 114.87 |
| 3 | 1.44 | 1.40 | 119.55 | 119.34 |
| 4 | 1.44 | 1.43 | - | - |
| 5 | 1.44 | 1.44 | - | - |
| 6 | 1.44 | 1.46 | - | - |

Figure 2 and Table 1 shows that the nitrogen doping on the CNT (6,0) which form the structure CNT (6.0) -1gN cause a change in the length and angle of the bond between atoms. Nitrogen doping led to increased bond length between atoms are unidirectional circular tube and decrease the bond lengths between the atoms in the direction of the axis / long tube. As an example can be seen in the bond length numbers 1, 3 and 5 (in the direction of the axis / long) as well as the number 4 and 6 (unidirectional circular tube).

Value of the structure parameter and electronic properties of pristine CNTs (6,0) and (6,0) that optimized -1gN are shown in Table 2.

Table 2. Structure parameter of pristine CNT (6,0) and CNT (6,0)-1gN

| Parameter Struktur | CNT (6,0) murni | CNT (6,0)-1gN |
|---|---|---|
| Momen dipol (Debye) | 0.00 | 0,90 |
| Diameter (Å) | 4.82 | 4,84 |

Table 2 shows that nitrogen doping on the CNT (6,0) which form the structure of the CNT (6,0) -1gN leads to changes in the diameter of the tube and the dipole moment of the CNT. Nitrogen doping on CNT (6,0) to form CNTs (6.0) -1gN have increased polarity of the CNTs of 0.00 (non-polar) to 0.90 Debye. Doping nitrogen with form a CNT (6,0) -1gN also have increased the CNT diameter of 4.82 into 4,84Å.

**Electronic Properties of Pristine CNT (6,0) and CNT (6,0)-1gN.**

The electronic properties are described by HOMO energy, LUMO energy, band gap energy and DOS (density of state).

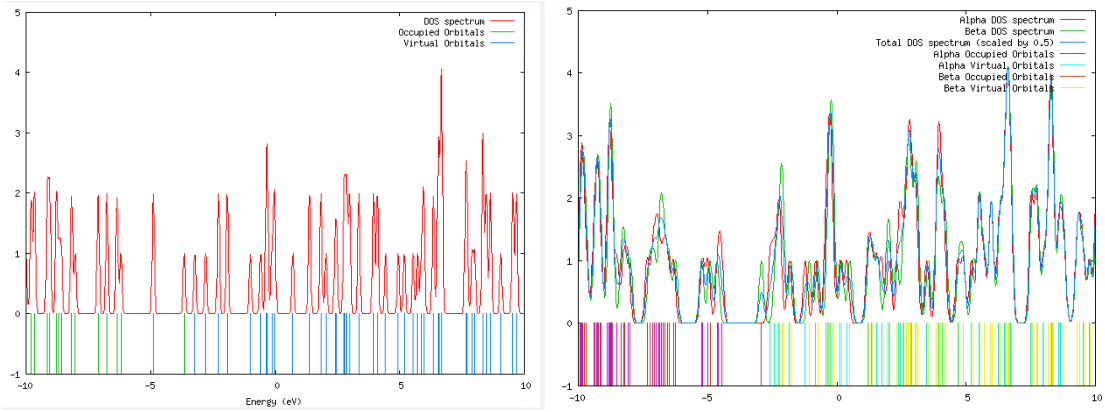



**Figure 3. DOS (*density of state*) for pristine CNT (6,0) and CNT (6,0)-1gN**

There is a difference between DOS pristine CNT (6.0) and CNT (6.0) -1gN. Differences DOS (density of states) explain that there are difference in charge density (electric current carrier) and the energy level of the carrier flow in both the CNT. The charge are the electron and hole. The difference in energy and the charge density will result in differences in the electronic properties and conductivity of the CNT. The orbital energy and the gap energy are shown in Table 2.

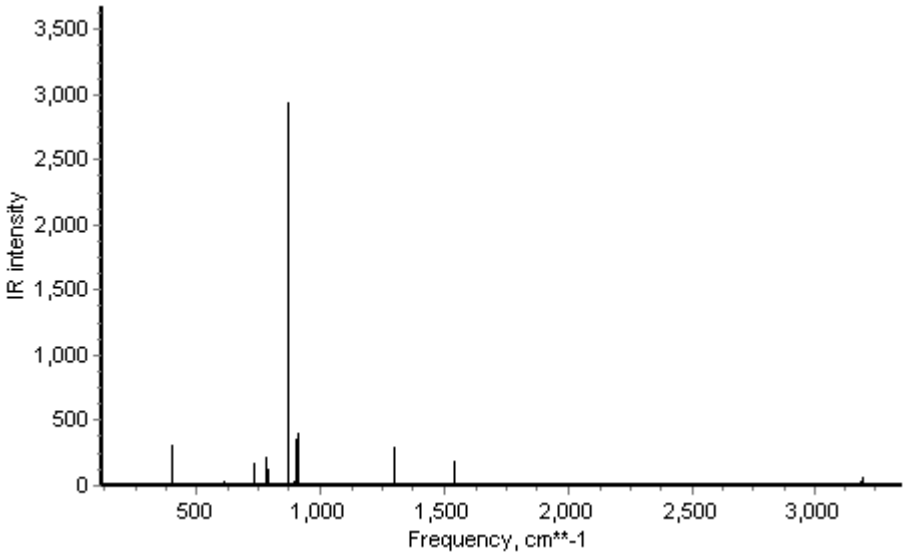
**Table 3. HOMO, LUMO and gap energy data for CNT (6,0) and CNT (6,0)-1gN**

| Symbol | pristine CNT (6,0) | CNT (6,0) -1gN | |
|---|---|---|---|
| | | Alfa | Beta |
| $E_{HOMO}$ | -3.65 | -4.46 | -4.63 |
| $E_{LUMO}$ | -3.22 | -2.58 | -2.92 |
| Eg | 0.43 | 1.88 | 1.72 |

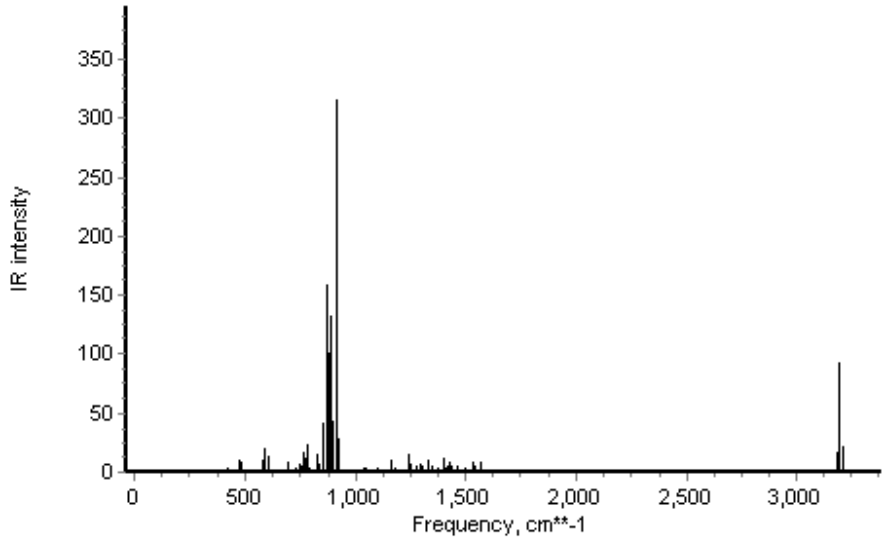
Table 3 shows that the nitrogen doping on the CNT (6,0) form a structure of CNT (6,0) -1gN decrease the HOMO energy, of -3.65eV be -4.46 and -4.63eV for alpha and beta orbitals. Instead of the nitrogen doping also increases the LUMO energy of -2.58 and -3.22 be -2.92eV for alpha and beta orbitals. Surely difference HOMO and LUMO energy levels is causing the difference in width between the HOMO and LUMO gap (energy gap). Nitrogen doping CNTs formed structure (6.0) -1gN increase energy gap 0,43eV to 1.88 and 1,72eV for alpha and beta orbitals. Gap energy value for pristine CNT (6.0) and CNT (6.0) -1gN is within the energy gap semiconductor material. CNT (6.0) -1gN called n-type extrinsic semiconductor.

**Analysis of the vibrational spectrum and electronic transitions (IR and UV).**

Infra-red radiation absorption has caused vibrations in pristine CNTs and CNT -1gN. Freqwensi maximum absorption occurs at 880.23 $cm^{-1}$ and 927.09 $cm^{-1}$ for the CNT pristine (6.0) and CNT (6.0) -1gN respectively. Spectrum vibrational and electronic transitonal shown by figure 4.



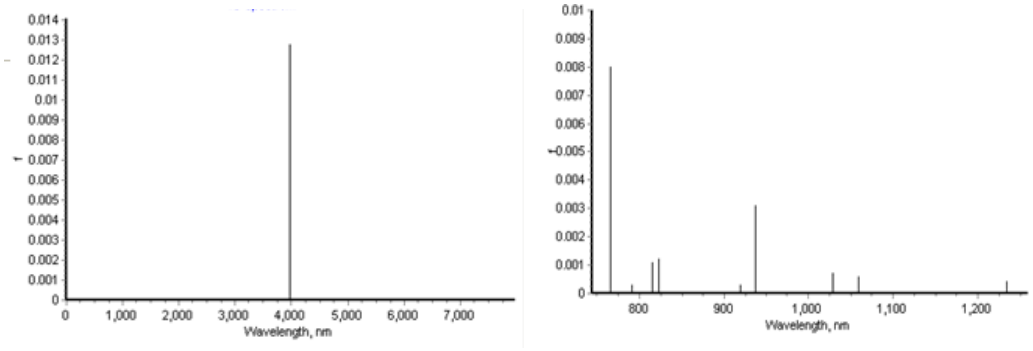

**(a)**




**(b)**

**Figure 4. Spectrum vibrational for CNT (6,0)**
**a. pristine-CNT (6,0) b. CNT (6,0)-1gN**

In pristine CNT (6,0) also occur electronic transition (singlet) from HOMO to LUMO orbitals or π bonding to the π anti-bonding by absorbing radiation with a wavelength of 3981.96 nm and 0:31 eV energy. While the CNT (6.0) -1gN experience electronic transitions with maximum absorption occurs at a wavelength of 766.84 nm.




(a) (b)

**Figure 5. Spectrum electronic transition for CNT (6,0)**
**a. pristine-CNT (6,0) b. CNT (6,0)-1gN**

## CONCLUSION AND SUGGESTION

Nitrogen doping on the CNT (6.0) can increase the diameter of 4.82 becomes 4.84 and change the dipole moment of 0.00 to 0.90Debye and increase the energy gap of 0.43 into 1.88 and 1.72 for the orbital slfa and beta respectively. Increasing the diameter and changes in the electrical conductivity of CNTs due to nitrogen doping can increase the value to the CNTs in various fields, such as the use of CNTs as adsorbent and as electronic devices.

## REFERENCES

1. S.Iijima, T. Ichibashi. Nature 363. (1993). 603.
2. R. Saito, G. Dresselhaus., MS. Dresselhaus. 1999. Psysical Properties of Carbon Nanotubes. Imperial College Press.
3. Pop E., et al., 2005, Thermal conductance of an individual single-wall carbon nanotube above room temperature. *Nano Letters* 6 (1): 96–100. arXiv:cond-mat/0512624. Bibcode:2006NanoL...6...96P. doi:10.1021/nl052145f. PMID 16402794.
4. Thostenson, Erik; Li, C; Chou, T (2005). Nanocomposites in context. *Composites Science and Technology* 65 (3–4): 491–516. doi:10.1016/j.compscitech.2004.11.003.
5. Ying Wang, Yuyan Shao, Dean W. Matson, Jinghong Li, and Yuehe Lin. Nitrogen-Doped Graphene and Its Application in Electrochemical Biosensing. American Chemical Society.. American Chemical Society. (2010). VOL. 4 NO. 4
6. Hyo-Shin Ahn, Seong Cheol Lee, Seungwu Han, Kwang Ryeol Lee, Doh Yeon Kim. Ab initio study of the effect of nitrogen on carbon nanotube growth. Nanotechnology 17 (2006) 909-912. Doi 10.1088/0957.4484/17/3/048.
7. Jaclyn D. Wiggins-Camacho and Keith J. Stevenson. Effect of Nitrogen Concentration on capacitance, Density of States, Electronic Conductivity, and Morfology of N-Doped Carbon Nanotube Electrodes. J. Phys. Chem. C. 2009. 113. No.44.
8. Ying Wang, Yuyan Shao, Dean W. Matson, Jinghong Li, and Yuehe Lin. Nitrogen-Doped Graphene and Its Application in Electrochemical Biosensing. American Chemical Society.. American Chemical Society. (2010). VOL. 4 NO. 4
9. Eduardo Cruz-Silva, Florentino Lo´ pez-Urı´as, Emilio Mun˜ oz-Sandoval, Bobby G. Sumpter, Humberto Terrones, Jean-Christophe Charlier, Vincent Meunier, Mauricio Terrones. Electronic Transport and Mechanical Properties of Phosphorus- and

Phosphorus_Nitrogen-Doped Carbon Nanotubes. American Chemical Society (2009) VOL. 3. NO. 7. 1913–1921.

10. Deep S., et.al, (2007) "Electronic properties of carbon nanotubes calculated from density functional theory and the empirical $\pi$-bond model" J Comput Electron (2007) 6: 395–400**.** DOI 10.1007/s10825-007-0147-5
11. Mirzai M., et.al, (2011).Covalent hybridization of CNT by thymine and uracil: A computational Study. J.Mol. Model (2011) 17.695-699. DOI 10.1007/s00894-010-0771-z
12. Yu Y., et.al. Theoretical Study on Electric Structure and Spectroscopic Regularies of Erhylated Single-Walled Carbon nanotubes. Russian Journal of Physical Chemistry A. (2011). Vol 85. No. 6, pp 1031-1036. ISSN 0036-0244.