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# Effect of Diameter on Density of States of Side Wall Functionalized Single Walled Carbon Nanotube

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**Abstract**
A carbon nanotube (CNT) is known for its unique physical, electrical, thermal, and mechanical properties. A functionalized carbon nanotube shows charge variation and this charge variation brings changes in the electronic properties when functionalized efficiently. There has been significant research done on Single walled carbon nanotube (SWCNT) to improvise the working of a CNT by end/side wall functionalizing it with some external group. Our earlier study involves the use of armchair and zigzag SWCNT functionalized with two different electronegative groups, amidogen ($NH_2$) and hydroxyl (OH). This work sheds light on CNTs of different diameters and their interaction with different electronegative groups. Electronic properties of functionalized armchair SWCNTs (2, 2), (3, 3), (4, 4) and (5, 5) are studied using Density Functional Theory (DFT) calculations with GUI of Quantum Espresso (QE) software i.e. BURAI software. Functionalization creates a potential difference across the different carbon atoms of the CNT. The Fermi level of CNT thus varies during its interaction with the functional group which can be seen via Density of States (DOS) curve. CNTs of four different sizes are considered in this work which shows a significant dependence of the nanotube diameter on the DOS curve.

**Keywords**: Carbon nanotube (CNT), Side wall functionalization, Single walled carbon nanotube (SWCNT), Amidogen ($NH_2$), Hydroxyl group (OH), Density of States (DOS), Density Functional Theory (DFT)

## 1. INTRODUCTION

The Multi walled carbon nanotube (MWCNT) was firstly recognized by Iijima in 1991 [1] and two years later Single walled carbon nanotube (SWCNT) was discovered [2]. Its demand is rapidly rising because of their potential application for future electrical and mechanical devices. The demand for nano-materials has been tremendously increasing ever since their advent. This small size and light weight nano-material is a suitable candidate for various applications such as target drug delivery [3], energy storage and molecular electronics etc.

Carbon nanotubes are rolled up graphene sheets as shown in Fig. 1. Like graphene sheets CNT have $sp^2$ type of bonding due to the orbital hybridization. This type of bonding accounts for the exceptional strength of CNTs. Its chiral indices (n, m) show whether it is metallic, semi-metallic or semiconducting in nature. Therefore it is essential to choose (n, m) indices very carefully and not lower than a certain limit [4] because CNT of very less (n, m) indices are not feasible [2]. Graphene is a semimetal with zero band gap energy and the representative members of 2D-family that have been receiving much attention in many fields, due to their remarkable physical, chemical and electronic properties [5].

Among covalent and non-covalent functionalization, covalent functionalization is of side wall or end type functionalization and end cap functionalization is more reactive than side wall functionalization [6]. In this work, single walled carbon nanotubes are considered to study the charge variations across the nanotubes length in order to interpret the effect of side wall functionalization on it. SWCNT is a single strand of cylindrical nanotube. Carbon nanotubes shows different electronic properties when chirality or size of diameter is different [7]. Different CNTs possessing different electronic properties

could engineer similar properties when functionalized with different external groups [8]. A functional group is added on the side wall of the CNT and not the open end. In this work we use amidogen ($NH_2$) and hydroxyl (OH) groups which are electronegative in nature [9-10]. Here these groups are considered to study the effect of functionalization on the electrical properties and the DOS of the carbon nanotubes. The semiconducting carbon nanotube may also behave like the metallic one and vice-versa.

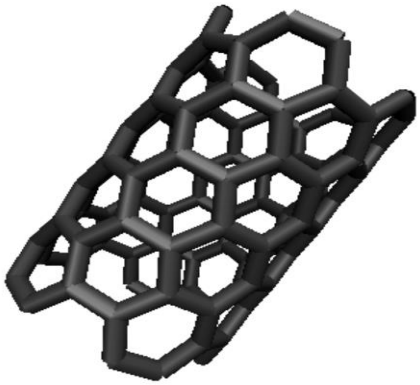

**Figure 1 Carbon nanotube (CNT) created using VMD software**

## 2. METHODOLOGY

The electronic properties of the carbon nanotubes can be studied using different methods such as Density Functional theory (DFT) calculations, Hartree Fock (HF) method, semi-empirical method, Force Field method and many others. In this work, the electronic properties of the different types of CNTs are studied using DFT calculations with Quantum Expresso software as it gives more accurate results than other methods. The aim of this study is to investigate and compare the electronic properties of CNT when interacted with Amidogen ($NH_2$) and Hydroxyl (OH) group. The flowchart shown in Fig. 2 gives the step wise procedure of the complete functionalization method and the DOS calculation of the pristine and functionalized CNT.

Four different sizes of armchair SWCNT (2, 2), (3, 3), (4, 4) and (5, 5) are used in this work to see the effect of diameter on the DOS. The physical parameters of these CNTs are as listed in Table 1. The diameter of the (2,2) SWCNT is less than 3 Å [11] and (3, 3) have diameter of the range of 4 Å. Whereas the diameter of (4, 4) and (5, 5) SWCNT is greater than 4 Å. The length of all the CNTs is 10Å. $NH_2$ and OH groups are interacting with the CNTs at one adsorption site i.e., at the side wall. Ab-initio calculations of CNT-electronegative group were performed using DFT method.

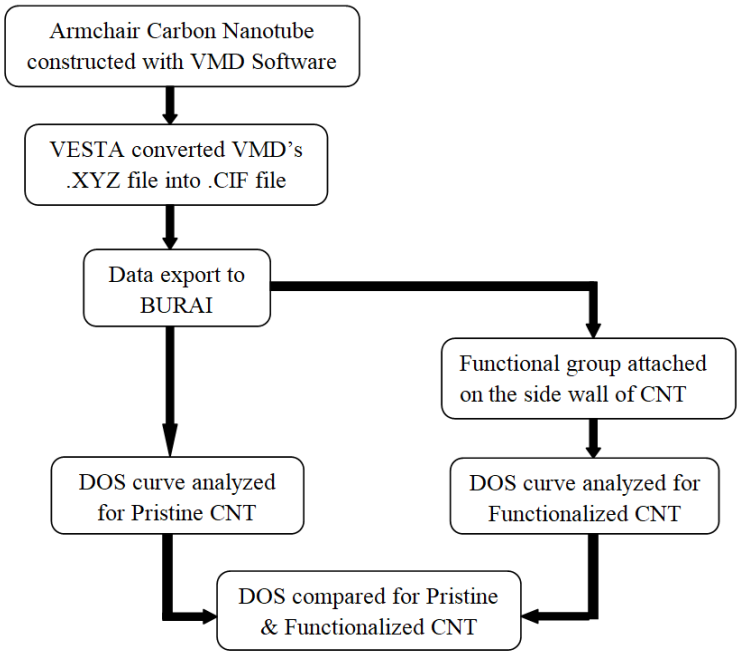


**Figure 2 Methodology used for calculating DOS**

**Visual Molecular Dynamics (VMD) Software**

The VMD software is a molecule editor and it visualizes the Graphene & CNT structure which is employed in computational chemistry, bioinformatics, molecular modelling and material science etc [12]. It is an extendable via plugin architecture and is meant for cross-platform use and is freely available. In this paper four different carbon nanotubes, (2, 2), (3, 3), (4, 4) and (5, 5) are configured using VMD software as shown in Fig.1.

**VESTA Software**

VESTA software package is distributed free of charge for scientific, academic, educational and noncommercial users [13]. It makes the crystal structure and visualizes the various types of structure created by many other software. Thus VESTA acts like a link between VMD and BURAI as it converts the VMD (.xyz) file to a (.cif) file and export it to BURAI as shown in Fig.3.

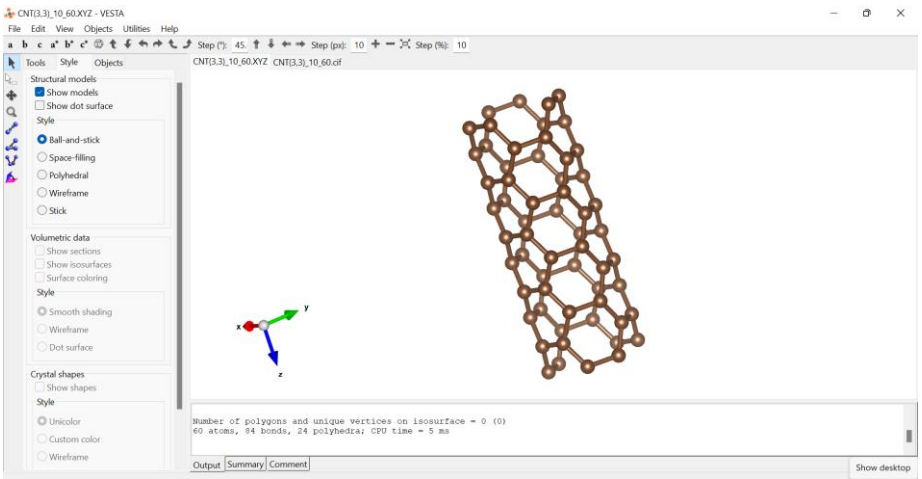

**Figure 3 (3, 3) CNT visualized with VESTA software**

**Quantum Espresso Software**

The BURAI [14] is Graphical User Interface (GUI) of Quantum Espresso software [15]. It can perform the optimization, SCF calculations and finds the density of states (DOS) and band structure of the given structure. It can also perform the molecular dynamics (MD) simulations of the material used. Quantum Espresso (QE) is a comprehensive set of Open-Source software for calculating electronic-structure data and simulating nanoscale materials. Its underpinnings include the density-functional theory (DFT), Pseudo-potentials, and plane waves etc. The pseudo-potentials used are obtained from Quantum Espresso software library. A comparative study is done between the pristine and functionalized carbon nanotube using Quantum Expresso software as shown in Fig 4.

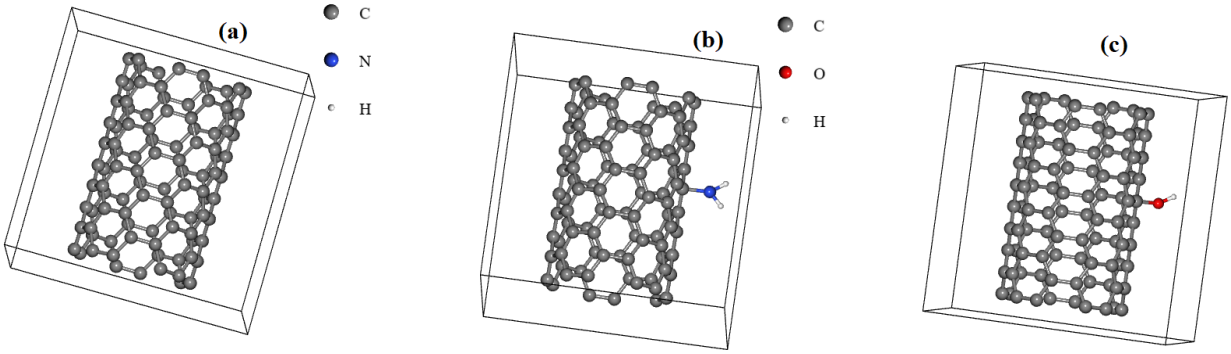


**Figure 4 Unit cell of a (5, 5) SWCNT (a) Pristine, (b) $NH_2$ Functionalized and (c) OH Functionalized**

## 3. RESULTS & DISCUSSION

In this work, we calculate the charge distribution and hence the Density of States (DOS) of Pristine and Functionalized SWCNT of finite length. Simulation is performed with Density Functional Theory (DFT) calculations using Quantum expresso software package. Electronegative groups -$NH_2$ & -OH are attached on the CNT surface which creates a partial charge at the vicinity of CNT thus creating a variation at Fermi level (at zero energy level). On the left side of Fermi level is valence band (VB) and on the right side is conduction band (CB). Functionalization changes the behavior of CNT at Fermi level i.e., between valence band & conduction band.

DOS is compared for different armchair SWCNT namely (2, 2), (3, 3), (4, 4) and (5, 5) as shown in Fig 5. The DOS is observed to be increasing as the diameter of the CNT increases from (3,3) to (5,5) SWCNT. Whereas the (2, 2) SWCNT having a diameter of less than 3 Å is observed to show an expected DOS due to the curvature effect. As already mentioned, the (3, 3) SWCNT have a diameter of the range of 4 Å whereas (4, 4) and (5, 5) are larger diameter nanotubes. Amidogen ($NH_2$) and Hydroxyl (OH) group is then attached on the surface of CNT. In all the above-mentioned cases, the results are presented and discussed giving a comparative study between pristine and functionalized SWCNT of different diameters as shown in Table 1.

**Table 1 Physical parameters of Pristine & Functionalized SWCNT**

| SWCNT | No. of Atoms | Electronic Nature | Chirality | Diameter (Å) | DOS (States/eV) | | |
|---|---|---|---|---|---|---|---|
| | | | | | P-CNT | $NH_2$-CNT | OH-CNT |
| (2, 2) | 40 | Metallic | Armchair | 2.70 | 32 | 12 | 7.2 |
| (3, 3) | 60 | Metallic | Armchair | 4.06 | 23.8 | 7.3 | 7 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| (4, 4) | 80 | Metallic | Armchair | 5.41 | 24.7 | 9 | 7.8 |
| (5, 5) | 100 | Metallic | Armchair | 6.76 | 40 | 8.4 | 8 |

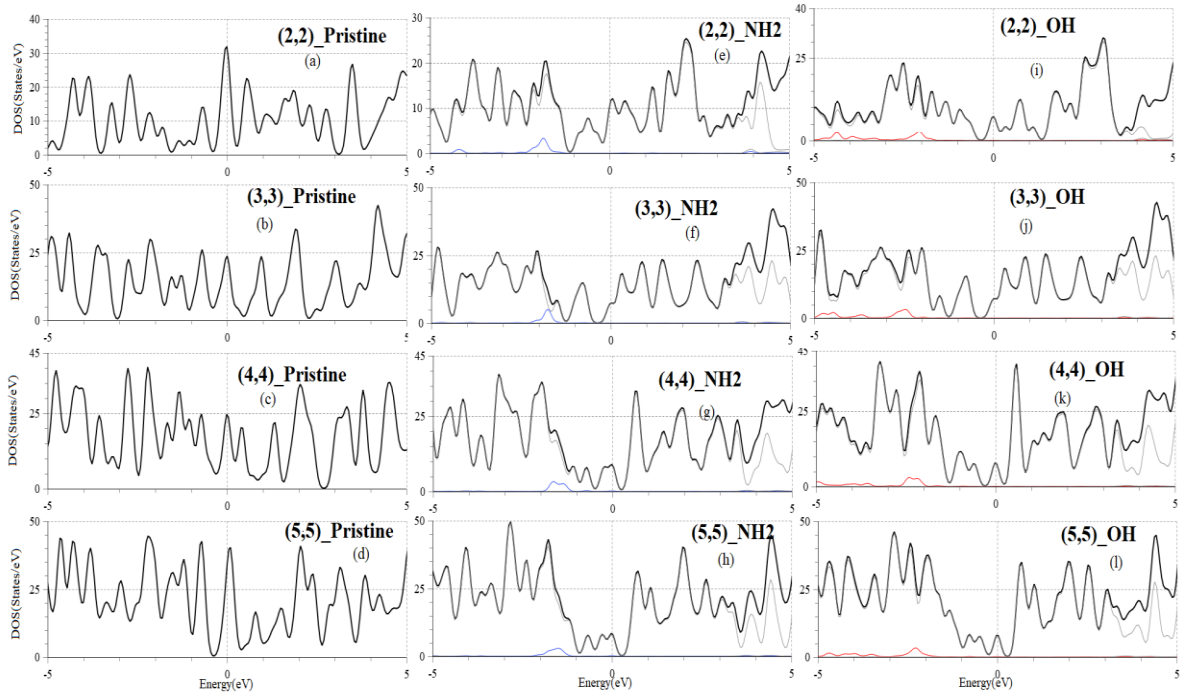


**Figure 5 DOS plots for (2, 2), (3, 3), (4, 4) and (5, 5) Pristine and Functionalized CNTs**

**Case 1) Pristine SWCNT without Functionalization**

In this case, the DOS are calculated for the pristine SWCNT prior doing any kind of side wall functionalization. The DOS is calculated for (2, 2), (3, 3), (4, 4) and (5, 5) types of carbon nanotubes using Quantum Expresso as shown in Fig 5. From the Table 1, the DOS is increasing from lower diameter to higher diameter CNTs. (2, 2) CNT is supposed to show lowest density of states but it shows the highest DOS. This is due to the curvature effect, as its diameter is less than 3 Å and neighboring atoms affects its behavior.

**Case 2) SWCNT functionalized with $NH_2$**

In this case, the SWCNT (2, 2), (3, 3), (4, 4) and (5, 5) have been side wall functionalized with electronegative group, Amidogen ($NH_2$). In this case the results obtained are different from the pristine CNT case. DOS decreases at Fermi level for all the CNTs as shown by DOS plots in Fig 5. (2, 2) SWCNT shows smaller change as compared to other CNTs due to the curvature effect resulting due to its small diameter.

**Case 3) SWCNT functionalized with OH**

In this case, the SWCNT (2, 2), (3, 3), (4, 4) and (5, 5) have been side wall functionalized with Hydroxyl (OH) group. The DOS in this case are observed to decrease less as compared to the $NH_2$ case. Both $NH_2$ & OH are electronegative groups in nature with same charge value. But the DOS observed for OH case is less than that for the $NH_2$ functionalized case as oxygen atom in OH cannot donate its electron pair as easily as nitrogen in the $NH_2$ group.

## 4. CONCLUSIONS

From the perspective of applications in the realm of nanotechnology, carbon nanotubes are significant. The interaction between two electronegative groups and CNTs of various diameters is studied in this work. The electronic properties of the pristine and side wall functionalized armchair SWCNTs (2, 2), (3, 3), (4, 4) and (5, 5) are studied using Density Functional Theory (DFT). The calculations are performed using GUI of Quantum Espresso software i.e., BURAI software. The fermi level is observed to be shifting on functionalizing the carbon nanotube with an external group. A significant variation of the nanotube diameter is observed on the DOS of the carbon nanotube. Curvature effect is observed to play an important role on the DOS of the carbon nanotube having diameter less than 3 Å.

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