Section A -Research paper

END/SIDE WALL FUNCTIONALIZATION OF SINGLE WALLED CARBON NANOTUBE USING MOLECULAR ORBITAL PACKAGE FOR DRUG DELIVERY PURPOSE

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Abstract

Carbon nanotubes serve many important purposes when designed efficiently. Prior work show how single walled carbon nanotubes (SWCNT) can be used as nanomotors. There has been significant research done on SWCNTs to improvise the working of CNT as nanomotors by end/side wall functionalizing it with some external group attached to it. Our earlier study involved the use of zigzag (5, 0)@(15, 0) double walled carbon nanotube (DWCNT) end functionalized with amidogen group. In this work, we have used a (5, 5) armchair SWCNT such that a potential difference is developed on the walls of CNTs due to end/side wall functionalization. This would enhance the effectiveness of CNTs as a nanomotor. The SWCNT has been end and side wall functionalized with groups such as COOH (carboxylic acid), NH_2 (amidogen) and OH (hydroxyl) groups which opens door for a comparative study between the charge variation due to end functionalization & side wall functionalization. Carbon nanotube with side wall functionalization shows a more amplified variation in the charge value as compared to end functionalized tube. The average charge of the entire CNT is enhanced due to the functionalization process and a charge spike can also be seen on the carbon atom where the functional group is attached. This type of a configuration achieved would be helpful for the application of these carbon nanotubes in the field of nanomotors which can further be used in the drug delivery purposes.

Keywords: "Amidogen (NH2)", "Carbon nanotube (CNT)", "Carboxylic acid (COOH)", "End functionalization", "Hydroxyl (OH)", "Molecular orbital package (MOPAC)", "Side wall functionalization", "Single-walled carbon nanotube (SWCNT)", "Translation Vector (Tv)", "Visual Molecular Dynamics (VMD)".

1. Introduction

The demand for nanomaterials has been tremendously increasing ever since their advent. It is not surprising since the size and light weight of nanomaterials make them a suitable candidate for various applications such as energy storage, molecular electronics, and targeted drug delivery etc. One of the most impressive is the carbon nanotubes [1], which are well discussed in this paper.

1.1 Carbon Nanotubes

Carbon nanotubes are cylindrical structures made from rolling up of graphene sheets. CNTs, like graphene sheets, have sp^2 type of bonding due to orbital hybridization. This type of bonding accounts for exceptional strength of CNTs. If chiral indices (n, m) are extremely small, the structure described will be a molecule which can obviously not be called a "tube", and may be unstable. It is, therefore, essential to choose (n, m) very carefully and not lower than a certain limit [2].

Currently, bulk nanotubes are being majorly used which is nothing but a mass of unorganized fragments of CNTs. Though individual tubes have a better tensile strength [3], but such composites yield strengths sufficient for many applications.

CNTs can be classified further based on their level of segregation. It is quite obvious that when CNTs are formed they formed as intertwined tubes that are later on separated from one another. Here, we have used single walled carbon nanotubes (SWCNTs) [4] to study charge variation across the nanotubes in order to interpret the effect of end functionalization and side wall functionalization (discussed in sections 2 & 3). SWCNT is a single strand of cylindrical nanotube.

1.2 End Functionalization

As the name itself suggests, end functionalization [5–8] means attaching a functional group to the CNT. The functional group includes –COOH, $-NH_2$, -OH, $-SO_2H$, $-C_5H_4N$, etc. This can be better understood when studied according to the position where the group is attached. The end functionalized SWCNT is created with AVOGADRO software is as shown in Figure 1.

End wall functionalization is observed on the open tube ends. Dissolution of CNTs in organic solvents requires the introduction of a hydrophobic substituent onto the carboxylic groups. Major approaches include amidation or esterification. Functionalization with different amines has been widely investigated to obtaining soluble CNTs, via covalent bonds and ionic bonds. This opens doors for CNTs to be used as nanomotors and antioxidants [9].

1.3 Side Wall Covalent Functionalization

Covalent chemical functionalization on the side wall of the CNT is another viable route to soluble materials. The functional group is added on the side wall of the CNT, i.e., along the sides of the tube and not the open end. In this work, we have used three of the functional groups COOH, NH_2 and OH on the side walls of the single walled carbon nanotubes to study their effect on the carbon nanotubes.

A comparative study is done between the end functionalization and side wall functionalization. The side wall functionalized SWCNT is created with MOPAC software as shown in Figure 2.

Figure 1 End functionalized (5, 5) SWCNT created on AVOGADRO software

Figure 2 Side wall functionalized (5, 5) SWCNT created on MOPAC software

1.4 Translation Vector

Experimentally, it is not feasible to calculate charge on an isolated grain sized nanostructure. On the other hand, simulations can be done on such nanostructures but such results cannot lead to a solution for real life situations. It therefore becomes a necessity to repeat those structures to a few microns size at least to get the results that are in good agreement with the experiments. Repeating these nanotubes over and over again up to a few microns is a very tedious job and to which MOPAC software comes with a solution of using a translation vector Tv.

A translation vector Tv, can be understood as a vector quantity that enables us to move across a symmetric structure with the help of a few known parameters. This is given by:

$\vec{T}$=m$\vec{a}$+n$\vec{b}$+o$\vec{c}$,

Where m, n, o $\in \mathbb{Z}$ and $\vec{a}$, $\vec{b}$, $\vec{c}$ are the unit translation vectors.

In this case, we do not want to translate along just a unit cell, i.e., carbon atom but the whole nanometric CNT. The translation vector for the same can be given as:

$\vec{T}$= 12.502 + m$\vec{a}$

Where 12.502 is the fixed parameter, m $\in \mathbb{Z}$, $\vec{a}$ is the length of SWCNT with chiral indices (5, 5) and length 15Å.

Translation vector has resulted in uniform and symmetric results owing to the repetition of single unit of CNT. This makes the results well explainable and understandable.

2. Methodology

In this section we describe the details of the software used for this study. We primarily used two softwares as mentioned below.

2.1 AVOGADRO Software

The AVOGADRO software [10] is a molecule editor and visualizer which is used in computational chemistry, molecular modeling, bioinformatics and material science. It is designed for cross platforms and is extensible via plugin architecture. In this work we use Avogadro software extensively to prepare the structure of SWCNT required for the charge calculations.
The structures of (5, 5) SWCNT as prepared with this software are as shown in Fig.3.

2.2 MOPAC Software

"Molecular Orbital PACkage" (MOPAC) [11] is a computational software which is based on the concepts of quantum chemistry theory. It involves the concepts of thermodynamics and makes use of some advanced mathematics. MOPAC software is used for the study of molecular structures and processes, as well as solid state physics problems, based on Dewar and Thiel's NADO approximation. The semi-empirical Hamiltonians MNDO (13), AM1 [13], PM3 [14], PM6, RM1, MNDO-d, and PM7 are used in the calculations of the electronic part. This electronic part is used to obtain the heat of formation and its derivative with respect to molecular geometry and the molecular orbital. With the help of these results MOPAC can calculate the thermodynamic properties, isotopic substitution effects, vibrational spectra and force constants for ions, molecules, polymers and radicals etc.

In the MOPAC program a data-file is created which depicts a molecular system and specifies the desired calculations and outputs. The user then recommends MOPAC to perform the calculations using the mop input data file. Various keywords are also used to perform different types of calculations in the MOPAC. A translation vector 'Tv' is also used to extend the structure to infinite length. Finally, one can extract the desired quantitative results of the system using other plotting software from the output files created by MOPAC.

In this work, we calculate the charge distribution on the surface of an infinite length SWCNT for three different cases and compared the results as follows: Case 1) SWCNT with no end/side wall functionalization, Case 2) COOH group attached to one end of the SWCNT and on the side wall of SWCNT, Case 3) NH_2 group attached to the end of the SWCNT and on the side wall and Case 4) OH group attached to one end of the SWCNT and on the side wall . These four different configurations are studied in detail in order to understand the effect of end/ side wall functionalization on the surface of these nanotubes by groups -COOH, -NH_2 and -OH. The results are compared in each case with the SWCNT with no end/side wall functionalization case and also the comparison between the results of end functionalized & side wall functionalized SWCNT has been done. This end/ side wall functionalization is useful in the application of SWCNT as nanomotors as discussed in Section 2 & Section 3.

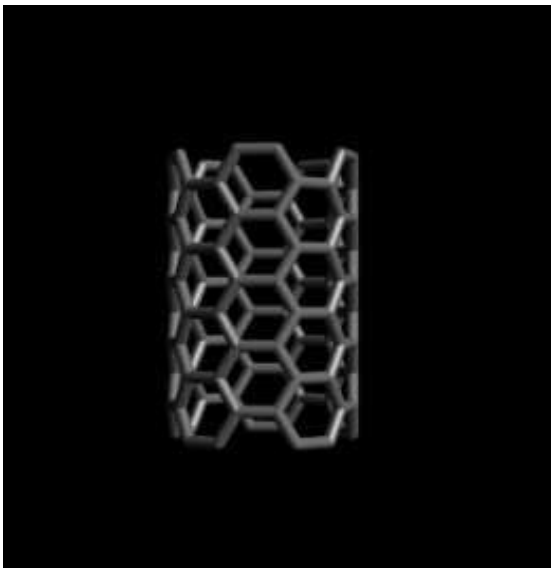

Figure 3 (5, 5) SWCNT created on AVOGADRO software

3. Results & Discussion

In this section, we will discuss our results for four different cases as follows: Case 1) SWCNT where charge calculations are done without doing any functionalization Case 2) SWCNT end and sidewall functionalized with COOH group Case 3) SWCNT end and side wall functionalized with NH_2 group and Case 4) SWCNT end and side wall functionalized with OH group. In all of the above-mentioned cases, the results are presented and discussed giving a comparative study between end functionalization & side wall functionalization.

Case 1) SWCNT without Functionalization

In this case, the charge calculations are done on the SWCNT prior doing any end/side wall functionalization. The SWCNT shows a symmetric charge distribution throughout the length as seen in Fig. 4 & 5. The charge value is observed to be ranging between [-0.25, 0.25] in the case of SWCNT. This symmetric behavior in the values of charge distribution is seen due to the translation vector used which creates an infinitely long repetition unit as discussed in Section 3 under the heading methodology. The results so obtained are in good agreement with the earlier work [6,7].

Case 2) SWCNT functionalized with COOH

2.1) End Functionalization

Here, the SWCNT (5, 5) has been end functionalized with COOH as seen in Fig.6. The charge on carbon atoms close to the attached group is observed to be decreased significantly on the CNT with value ranging between [-0.45, 0.06] on SWCNT as seen in Fig. 6. The effective charge is seen to be increased as well as distributed. Due to high charge accumulation resulting from the electronic repulsion towards the end of the CNT which is in proximity with the COOH group and this accounts for the dip in charge value on SWCNT on atom number 87 and overall symmetrical increase in charge values throughout. This is because COOH is much more electronegative compared to the atoms nearby.

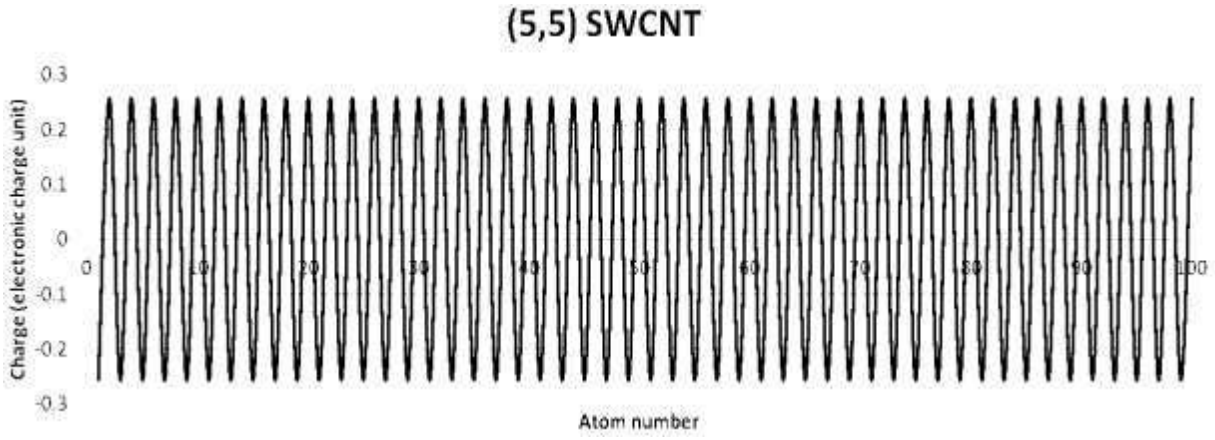

Figure 4 Charge on each atom of (5, 5) SWCNT

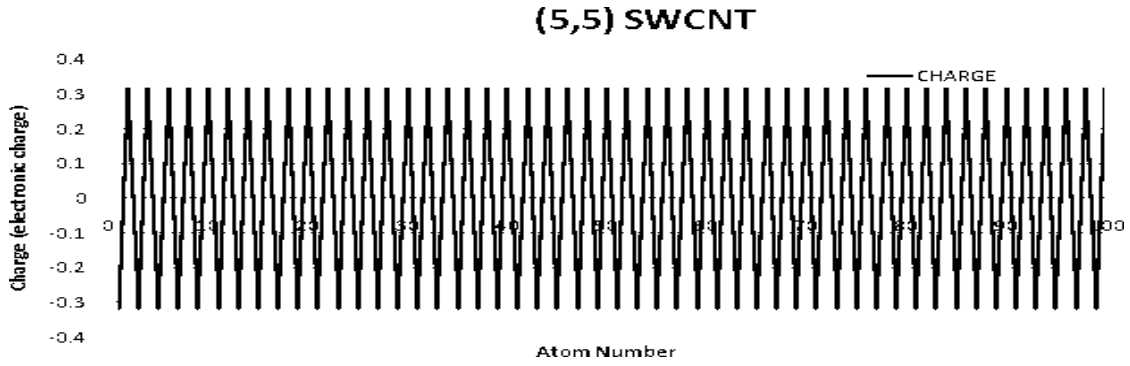

Figure 5 Charge on each atom of (5, 5) SWCNT as calculated by MOPAC Software

2.2) Side Wall Functionalization

Here, the SWCNT (5, 5) have been side wall functionalized with COOH as seen in Fig. 2. The side wall functionalization with COOH has slightly different effect on SWCNT as it has due to end functionalization. The charge on carbon atoms close to the attached group is observed to be increased significantly with value ranging between [-0.61, 0.28] on SWCNT as seen in Fig. 6. The effective charge is seen to be increased as well as distributed.

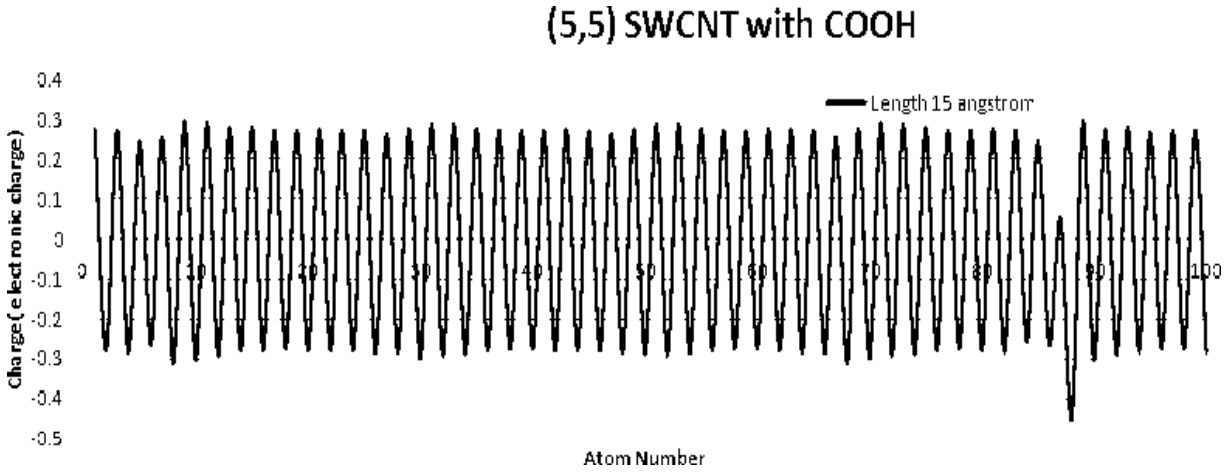

Figure 6 Charge on each atom of (5, 5) SWCNT with COOH (end functionalized) as calculated by MOPAC software

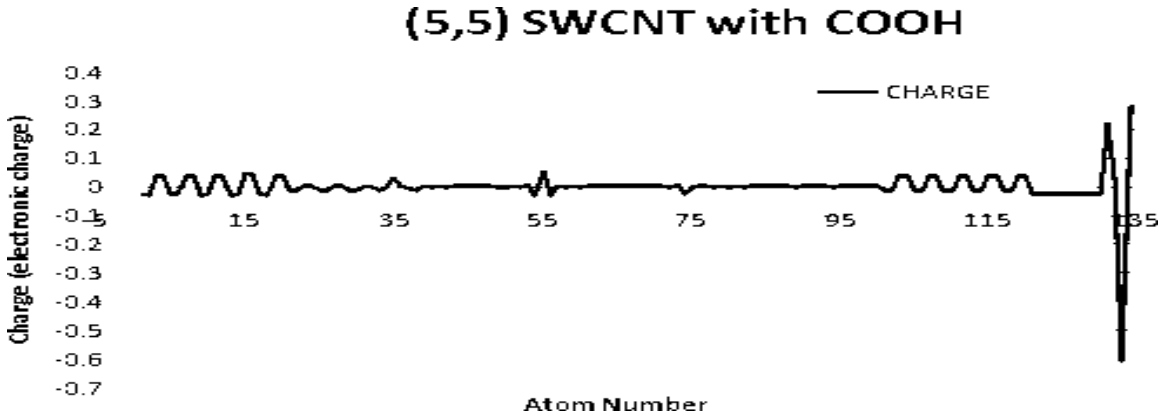

Figure 7 Charge on each atom of (5, 5) SWCNT of COOH (side wall functionalized) as calculated by MOPAC software

Case 3) SWCNT functionalized with NH_2

3.1) End Functionalization

In this case, the SWCNT (5, 5) has been end functionalized with NH_2 group. The charge is observed to be increased significantly on the carbon rings lying close to the attached group of the CNT with value between [-0.39, 0.22] on SWCNT as seen in Fig. 8. The effective charge is seen to be decreased. This overall decrease in charge values is seen because amidogen has an electron withdrawing tendency. This result is in good agreement with other works done on zigzag CNTs [5,6].

3.2) Side Wall Functionalization

In this case, the SWCNT (5, 5) have been side wall functionalized with NH_2 (amidogen) group. The charge is observed to be increased on the carbon rings lying close to the attached group and charge of entire CNT is increased with value between [-0.71, 2] as seen in Fig. 9. Because amidogen is electropositive, the carbon atom where amidogen is bonded will show charge 2. These results are different from the end functionalization.

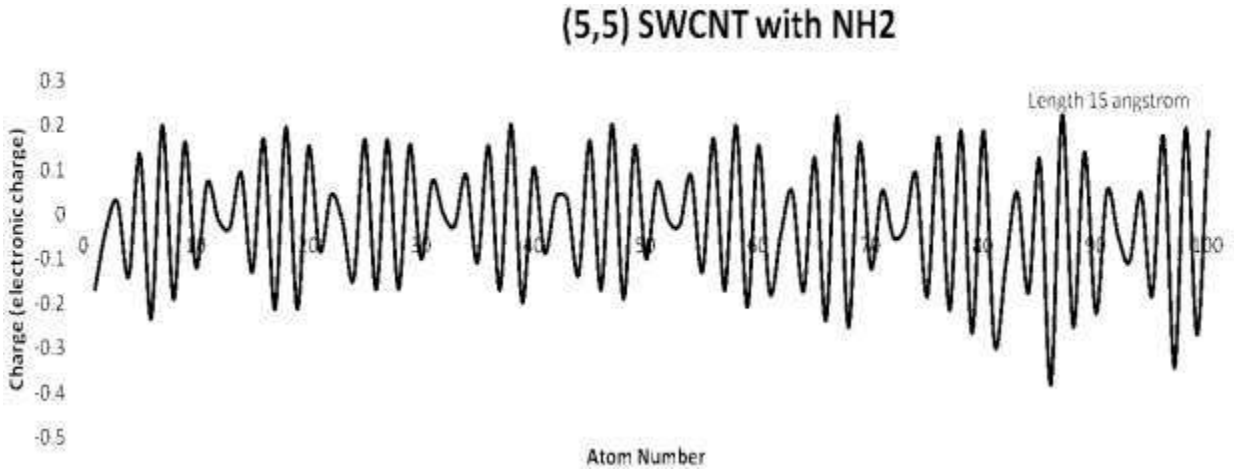

Figure 8 Charge on each atom of (5, 5) SWCNT with NH_2 (end functionalized) as calculated by MOPAC software

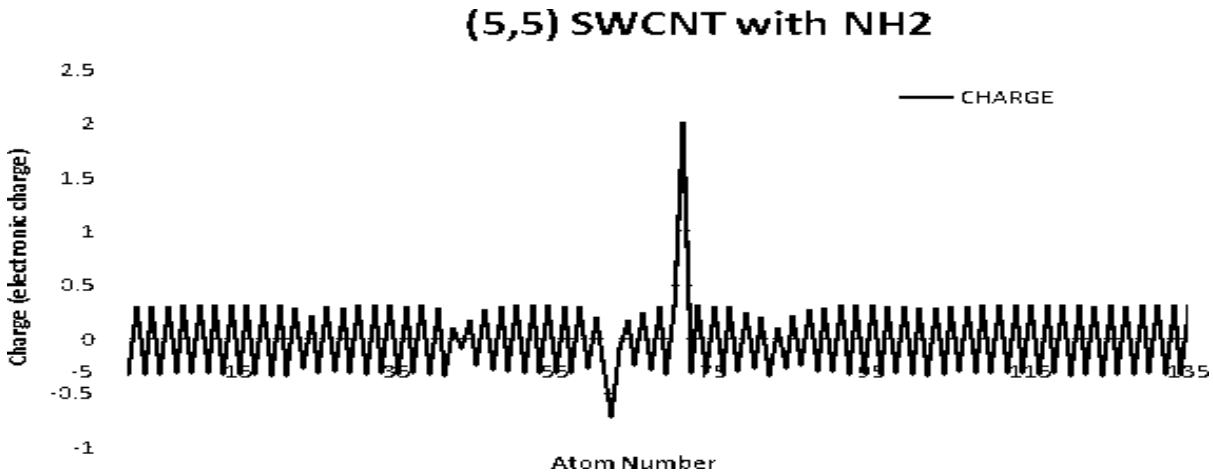

Figure 9 Charge on each atom of (5, 5) SWCNT of NH_2 (side wall functionalized) as calculated by MOPAC Software

Case 4) SWCNT functionalized with OH

4.1) End Functionalization

In this case, the SWCNT (5, 5) has been end functionalized with OH group. The charge values close to the atom where the group OH is attached are observed to decrease to as low as [-0.35, 0.06] in the case of SWCNT as seen in Figure 10. An almost symmetric charge distribution is

seen in the SWCNT apart from the first atom in the chain, the spike in charge value is majorly due to the end effects and high accumulation of charge because of the electronic repulsion from the OH group. The overall charge values decrease here as OH is a strong electronegative group and it is towards the end of the nanotube. Small peaks are observed which could be because of the end effects.

4.2) Side Wall Functionalization

In this case, the SWCNT (5, 5) has been side wall functionalized with OH group. The charge values close to the atom where the group OH is attached are observed to decrease to as low as [-0.51, 0.35] in the case of SWCNT as seen in Figure 11. An almost symmetric charge distribution is seen in the SWCNT apart from the atom where OH is attached and at the carbon atom number 76th, the spikes in charge value is majorly due to the group attached at side wall and high accumulation of charge because of the electronic repulsion from the OH group. Because OH is a strong electronegative group and is located on the nanotube's side wall, the overall charge values decrease. The overall results for all the cases can be summarized as in Table 1.

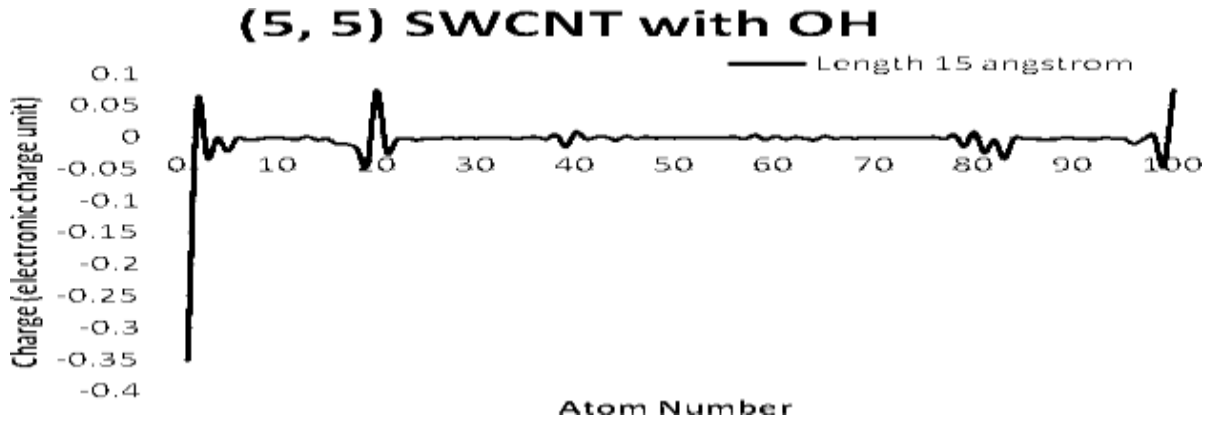

Figure 10 Charge on each atom of (5, 5) SWCNT with OH (end functionalized) as calculated by MOPAC software

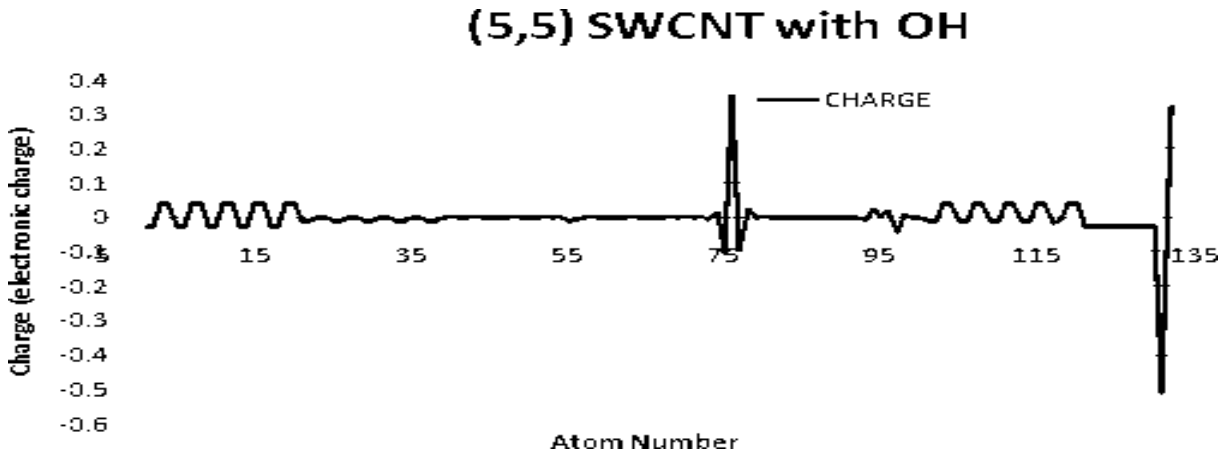

Figure 11 Charge on each atom of (5, 5) SWCNT with OH (side wall functionalized) as calculated by MOPAC software

Table 1 Comparative study of charge variation values on the surface of SWCNT-End & Side Wall Functionalized

Type of Carbon Nanotube	Nature of the attached group	Charge values on SWCNT (electronic charge unit) on the carbon atom lying close to attached group	Charge values on SWCNT (electronic charge unit) on the carbon atom lying close to attached group
Without functionalization	No group attached	[-0.25, 0.25]	[-0.31, 0.31]
		End functionalized	Side wall functionalized
Functionalized with COOH	Electron giving	[-0.45, 0.06]	[-0.61, 0.28]
Functionalized with NH_2	Electron withdrawing	[-0.39, 0.22]	[-0.71, 2.00]
Functionalized with OH	Strong Electron giving	[-0.35,0.06]	[-0.51,0.35]

4. Conclusions

Carbon nanotubes are important from the point of view of application in the field of nanomotors. Nanomotors require opposite charges on the opposite ends of the carbon nanotube for their fully

functional forms. End functionalization can be used to add an external group on the surface of a carbon nanotube. When functionalized with external groups such as COOH, NH_2 & OH, a single walled carbon nanotube shows significant variation in its charge values. Carbon nanotube with side wall functionalization shows a more amplified variation in the charge value as compared to end functionalized tube. This work suggests that the CNT can be modified to be served as nanomotors depending on the functional group attached on it. The charge values on the carbon nanotube without end functionalization were observed to be in good agreement with the other works. An experimental study with similar results holds a great potential towards the creation of nanomotors which can prove to be a boon to mankind.

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