Properties of transition metal doped carbon nanotubes: a theoretical study

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Abstract

In this paper, we investigated the structural properties of Scandium (Sc) and Titanium (Ti) doped single wall carbon nanotubes (SWCNTs) using density functional theory. The doping is done on the external wall of the carbon nanotube. Our theoretical calculation shows that doping significantly affects the geometrical structure of the carbon surface. The structural optimization shows that the doping not only modifies the bonding arrangement of the neighboring carbon atoms but also introduces a planner distortion. From the simulated Density of states spectrum, it is found that the energy gap decreases when the dopant changes from Scandium (Sc) to Titanium (Ti) in the same row of the periodic table. Moreover, the Shift of the Fermi energy level also has been observed. The detailed simulation has been discussed thoroughly by using the natural bond orbital analysis, frontier molecular orbitals, partial charge distribution and the electrostatic potential surfaces.

1. Introduction

Carbon nanotube (CNT) is the name of ultrathin carbon fiber with nanometer-size diameter and micrometer-size length and was first discovered by a Japanese scientist, Sumiolijima [1]. The structure of CNT consists of enrolled graphitic sheet and can be classified into either multi-walled or single-walled CNT (MWCNT or SWCNT) depending on its preparation method. CNT is the material lying in-between fullerenes and graphite as a quite new member of carbon allotropes. It seems that a considerable number of researchers have been participating in the science of CNTs and there has been a remarkable improvement in the both experimental and theoretical studies on MWCNT and SWCNT particularly during the last couple of years. As per as the application is concern it is found that CNTs has got most active area of research in the past few decades due to their attractive mechanical, thermal, and electrical properties and various applications, including hydrogen storage[2], chemical sensors [3], and Nano bioelectronics[4], etc. Nowadays
scientists trying to enhance these properties of carbon nanotubes by incorporating different doping elements. Chen et al [5] investigated the properties of transition-metal-doped single-walled carbon nanotubes (SWCNTs) using density functional theory and found that when the dopant changed from Sc to Zn in the same row of the periodic table and from top to the bottom in the same Pt group, the energy of the highest occupied molecular orbital of the transition metal-doped SWCNTs decreases, which indicates reduced electron donating ability. Buzatu et al [6] manipulated the molecular orbital energy gap (HOMOLUMO gap) of the nanotubes by incorporating transition metal as the doping elements. They also demonstrated that multiple metal filled nanotubes could be used to construct a molecular nanotube based transistor. Dhibar et al [7] found that transition metal doping on SWCNTs will enhance its electrochemical properties of the nanocomposites which result better specific capacitance and charge/discharge rates makes them promising candidates as electrodes in super capacitors. However detailed theoretical analysis of Sc and Ti doped SWCTs haven’t found yet. In this work the effect of Sc and Ti doping on the external surface of the carbon nanotubes have been studied using natural bonding orbital analysis, Density of states, partial charge distribution, electrostatic potential, frontier molecular orbitals etc.

2. Computational Methods

The density functional theory has been applied for performing the computational simulation under Gaussian 09 software package[8]. The PBE-PBE exchange correlation functional is used which was developed by Predew, Burke and Ernzhoff [9] along with the Lan12DZ basis set. The reason for choosing the above mentioned computational scheme is that it has already been used by other researchers for the analysis of transition metals and carbon interaction [5].

An armchair (5,5) SWCNT structure is designed which consists of 100 atoms, out of those 80 atoms are carbon and 20 atoms are hydrogen. In the simulation, hydrogen atoms are added so as to avoid the dangling bonds of the SWCNT boundary and no edge effect is considered.

The geometry optimization of the undoped carbon nanotube is performed without any symmetry constraint. After that, the frequency calculation (normal mode analysis) is carried out so as to get the true optimized CNT structure. Now to get the doped CNT structure one carbon atom of the undoped carbon surface has been replaced by the dopant atom and again structure optimization has been done.

3. Results and Discussions

To obtain the most energetically favorable Sc and Ti-doped CNT structures, we considered a particular site on the carbon surface as shown in Figure 1(a). Structural distortions occur to the external wall of carbon surface when Sc and Ti used as a dopant. The Sc-C bond (~2.07 Å) is longer than to that of Ti-C(1.92 Å) and pristine SWCNT (1.44 Å). The angle between Sc and neighboring carbon, in Sc-doped CNT is found to be ~850 which is less than compare to the bond angle of carbon on the carbon surface. As a result, the position of the Sc in the doped CNT is shifted upwards. Similarly, the position of Ti is also shifted upwards and the angle between Ti and neighboring carbon is found to be ~900. The above result shows that both Sc and Ti individually effect the local bonding environment of carbon nanotube due to their difference in covalent radii (144 pm and 136 pm Sc and Ti respectively) and electro negativities (1.36 and 1.54, Sc and Ti respectively) Because of this reason both Sc and Ti cause significant planar distortion in CNTs.

The frontier molecular orbitals are significant while understanding chemical reactivity. We have shown the highest occupied molecular orbitals (HOMOs) and lowest unoccupied molecular orbitals (LUMOs) in Figure 1. When the dopant changes from Sc to Ti, It is found that the HOMO energy, along with the electron donating ability, decreases from -3.85 eV to -4.02 eV.

The geometrical parameters can be found in Table 1. Natural bonding orbital analysis shows that there is no C-Sc bond exist after doping in the case of Sc-doped CNT. However, the existence of C-Ti bond found in the case of Ti-doped CNT. The natural bond orbital type is recorded in the following Table 2 and Table 3.

<table>
<thead>
<tr>
<th>Sample Code</th>
<th>C1-X</th>
<th>C2-X</th>
<th>C3-X</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine</td>
<td>1.44</td>
<td>1.44</td>
<td>1.43</td>
</tr>
<tr>
<td>Sc-CNT</td>
<td>2.08</td>
<td>2.07</td>
<td>2.11</td>
</tr>
<tr>
<td>Ti-CNT</td>
<td>1.97</td>
<td>1.92</td>
<td>1.96</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Natural Bonding orbital</th>
<th>Occupancy</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1 – Ti</td>
<td>0.89549</td>
<td>66.26 % C1 sp&lt;sup&gt;2.87+&lt;/sup&gt; + 33.74 % Ti spd&lt;sup&gt;2.33&lt;/sup&gt;</td>
</tr>
<tr>
<td>C2 – Ti</td>
<td>0.93593</td>
<td>65.68% C2 sp&lt;sup&gt;2.5+&lt;/sup&gt; + 34.32% Ti spd&lt;sup&gt;2.59&lt;/sup&gt;</td>
</tr>
<tr>
<td>C3 - Ti</td>
<td>0.93909</td>
<td>67.68 % C3 sp&lt;sup&gt;2.61+&lt;/sup&gt; + 32.32 % Ti spd&lt;sup&gt;2.35&lt;/sup&gt;</td>
</tr>
</tbody>
</table>
Fig. 1: The doping site and frontier orbitals of the pristine, Sc- and Ti-doped SWCNTs. Orbital energies (in eV) are shown in Parentheses.
Table 3: Natural bonding orbital analysis of the pristine SWCNT.

<table>
<thead>
<tr>
<th>Natural Bonding orbital</th>
<th>Occupancy</th>
<th>Composition</th>
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<tbody>
<tr>
<td>C2-C</td>
<td>1.95841</td>
<td>49.71%C$_{2}$ sp$^{2.08}$+ 50.29% C sp$^{2.08}$</td>
</tr>
<tr>
<td>C3-C</td>
<td>1.96007</td>
<td>50.51%C$_{3}$ sp$^{1.91}$+ 49.49% C sp$^{2.10}$</td>
</tr>
<tr>
<td>C1-C</td>
<td>1.94509</td>
<td>50.01%C$_{1}$ sp$^{2.28}$+ 49.99% C sp$^{2.28}$</td>
</tr>
</tbody>
</table>

Fig. 2: Schematic illustration of the model (5, 5) pristine SWCNT with partial charge distribution.

The partial charge distribution in Figure 2 shows that Sc transfers $-0.382e$, $-0.420e$ and $-0.538e$ charge to its nearest neighbour carbon atoms. Similarly, Ti transfers $-0.343e$, $-0.388e$ and $-0.462e$ charge to its nearest neighbour carbon. It can be explained in the following way, the metallic character decreases from the left to the right in the same row of the Periodic table. Since Sc present at the left-hand side of the periodic table than comparing to Ti, so it transfers more negative charges to its neighbouring C atoms. Because of this reason Sc has got more positive charge compared to Ti. The values of partial charges are scaled according to the colored bar at the bottom. The color green indicates a positive charge and the color red, a negative charge. Darker the color (red or green), larger the magnitude of the partial charge on the atom.

Fig. 3: Density of states (DOS) of the pristine, Sc- and Ti-doped(5,5) SWCNTs. The DOS of $\alpha$ –spin and $\beta$-spin electrons are shown in the upper and lower panels, respectively. Fermi levels are marked by the vertical dotted lines.
In Figure 3 it is found that the partial density of states (PDOS) of Sc-doped CNT near the Fermi level go through significance changes the Fermi energy level shifted from -4.27 eV to higher energy -3.85 eV, but in case of Ti doped CNT the Fermi energy level shifted from -4.27 eV to higher energy -4.01 eV. Thus the result shows that Sc-doped CNTs are better electron donor compare to Ti doped CNTs.

Figure 4: Molecular electrostatic potential surface of (a) Pristine CNT (b) Sc doped CNT and (c) Ti doped CNT

Molecular electrostatic potential at a point in space around a molecule gives information about the net electrostatic effect produces at that point by total charge distribution of the molecule and correlates with dipole moments, electronegativity, partial charges and chemical reactivity of the molecules. It provides visual method to understand the relative polarity of the molecule. The distribution of electrostatic potential is shown in Figure 4 as a color overlay. Here, the values are scaled according to the colored bar at the bottom. The color blue indicates more positive portion and from yellow, to red it indicates the more negative portion of the potential surface. Such mapped electrostatic potential surface has been plotted for pristine, Sc and Ti-doped SWCNTs using the software Gauss view. The pristine carbon nanotube is found to be weakly positive on most of the outer and inner surfaces, but it is strongly positive at the two ends of the carbon nanotubes due to the presence of hydrogen.

In this case hydrogens at the carbon nanotube ends act as charge donors. Moreover, the magnitudes of both the positive and negative surface potentials associated with the basic carbon tend to be larger where the curvature is greater. However, in the case of Sc and Ti-doped CNT structures, the surface potential becomes neutral.

4. Conclusions

Density functional theory (DFT) has been employed to investigate the doping of Sc and Ti on CNT surface. Results obtained from the present study shows that there is a decreasing electron donating ability as well as decreasing HOMO-LUMO energy gap from 0.78 eV to 0.67 eV when the dopant changes from Sc to Ti in the same row of the periodic table. The lowering of HOMO-LUMO energy gap supports bioactive property of the molecule. The study of potential energy surface shows that by changing the different doping elements tubes can be designed with potential patterns tailored to specific objectives. This encouraging result could be of interest to enhance further theoretical research relaying on the experimental evidence and vice versa.

5. Acknowledgement

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6. References
