National Conference on Recent Trends and Developments in Environmental and Basic Sciences (RTDEBS-2018)
Organized by, Faculty of Science In collaboration with
Internal Quality Assurance Cell (IQAC), Dr. S. D. D. Arts College &
Commerce & Science College, Maharashtra, India. Association with
International Journal of Scientific Research in Science and Technology
© 2018 IJSRST | Volume 4 | Issue 3 | Print ISSN: 2395-6011 | Online ISSN: 2395-602X

Interaction of Au Atom on Single Walled Carbon Nanotube: A Density Functional Study

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ABSTRACT

The interaction of Au atom on Single Walled Carbon Nanotube (8, 0) (SWCNT) has been studied using first principal of Density Functional Theory (DFT). In this study we found structural change in surface geometry of SWCNT and electronic variation in its semiconducting nature. To interpret these properties, we performed geometry optimization of pristine SWCNT and Au- SWCNT system for four different sites. Then we performed calculation for band structure (BS), density of state (DOS) and Mulliken population analysis with DMol3 code. Au atom is found chemisorbed on SWCNT on atomic site by binding distance 2.7 Å where it is physisorbed for all other sites by binding distance 2.99 Å at axial, 2.96-3.102 Å at chiral and 3.663-3.520 Å at hexagon respectively. The bond angles between C - C - C bonds were ranging from116^0 to 119.5^0 which is less than 120^0 indicates trigonal structure of bonding and prefers sp2 hybridization . Thus the properties of SWCNT can be modified by the adsorbed Au adatom by minute variation in semiconducting nature and surface geometry.

Keywords: DFT, SWCNT, Adsorption, Au Atom.

I. INTRODUCTION

Physics of nanostructure is new area of science arisen in last decade of twentieth century after discovery of fullerenes and nanotubes. It is an extension of interdisciplinary integrated modern science, now known as nanotechnology which is rapidly developing. The processing, structure and properties of nano materials are differing with their size, ranges from grain size to several hundreds of nanometers. This is main reason of researcher to develop considerable interest over the past fifteen to twenty year on this topic.

A revolution in material science and engineering is taking place as researchers find ways to pattern and characterize material at the manometer length scale. Nanomaterials with transition metal with outstanding electrical, optical, magnetic and mechanical properties are rapidly being developed for use in information technology, bio engineering and environmental applications.

A carbon nanotube (CNT) is a tubular structure made of carbon atoms, having diameter of manometer order but length in micrometers. Although this kind of structures was synthesized, studied and reported by several researchers during 1952–1989, [1–17]. Ijima's detailed analysis of helical arrangement of carbon atoms on seamless coaxial cylinders in 1991, proved to be a discovery report.[18] Since then, CNT has remained an exciting material ever. Its so-called extraordinary properties, many-fold stronger than steel, harder than diamond, electrical conductivity higher than copper, thermal conductivity higher than diamond, set off a gold rush in academic and industrial

laboratories, all over the world to find practical uses of CNTs.

Study of isolated and bundled CNTs with transition-metal atom doping shows the richness of the electronic and magnetic properties [19]. However, there is little attention paid to the physical behaviour between element and CNT. In this paper, we study the interaction between the (8, 0) CNT nuclei such as Gold (Au). We compare their electronic characteristics by computing the band structure, density of state (DOS), Binding energy, Band Gap, HOMO-LUMO energy, Homo-Lumo gap, Charge transfer. With these electronic characteristic of CNT we predict the change in its semiconducting nature. As well as we found behaviour of adsorption of Chromium on CNT with the help of Binding energy, iso-surface Charge density distribution and molecular orbital.

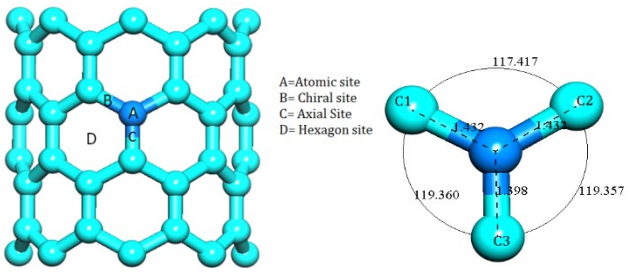
II. COMPUTATIONAL DETAILS

We have chosen (8, 0) SWCNT and Au atom model using material studio by Accelrys which is a molecular dynamics simulation software. The geometrical and electronic properties of the system were derived using quantum mechanical program code Dmol3 (Accelrys). We have also used GGA and PBE functional for optimization.

For Supercell geometries, spin unrestricted calculations were carried out with a double numeric polarized (DNP) basis set with orbital cut-off 4.4 Å. Scalar relativistic effects were included via a pseudo potential for all-electron calculations. 1 × 1 × 2 k-points were used for the Brillioun zone sampling. All the calculations were performed using boundary conditions with 64 atoms within the Supercell. The tetragonal unit cell of 20 × 20 × 8.4 Å dimensions and sufficient separation between tubes is used to avoid interaction between the tubes. The chosen cut off value leads to atomic energies with an accuracy of 0.1eV/atom, allowing calculations without sufficient loss of accuracy. The calculations were performed to find the structural and electronic properties of optimized structures. Milliken population analysis was carried out to predict the charge transfer and spin between Au-Atom and nanotubes.

We have selected (8, 0) zigzag CNT of diameter 6.26 Å and the length 8.52Å as a model to study the adsorption of gold atom. We have examined different site for adsorption of gold atom as shown in figure (1). The sites are 1) Carbon Atom (Site A), 2) Carbon-Carbon Axial Bond (site B), 3) Carbon-Carbon Chiral bond (site C) and 4) Hexagon (site D). In all calculations, the carbon nanotubes along with Au atom were first optimized to occupy their minimize energy state. For each site Au has kept at a finite distance of 3.0 Å to optimize the system to get stable structure. The binding energy (E_b) of adsorption of Au atom on nanotube for all ground state structures were calculated by $E_b = - [E_T \text{ (adsorbent + adsorbate)} - E_T\text{(adsorbent)} - E_T\text{(adsorbate)}]$.

Where E_T (adsorbent + adsorbate) is the total energy of atom and CNT system, E_T (adsorbent) is total energy of CNT and E_T (absorbate) is the total energy of atom. To verify the computational accuracy of the structure we have calculated the binding energy of CNTs, density of state, band gap Charge Density, HOMO-LUMO, Milliken population analysis for charge [20].



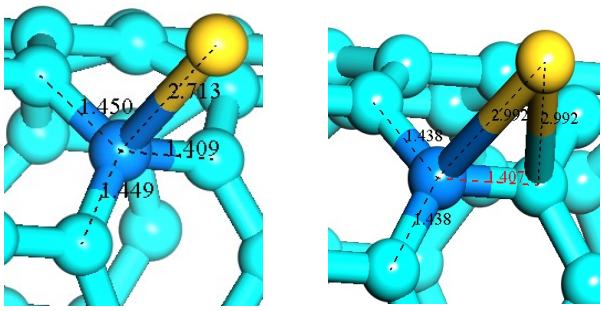
(a) (b)

Figure 1. (a) Structural model of CNT (8, 0) (b)Structural parameter at target (C_T) atom

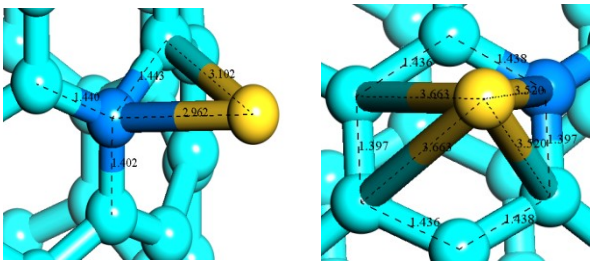
III. RESULTS AND DISCUSSION

Bond Length

The (8, 0) SWCNTs shown in Figure1, has a carbon atom arrangement with an average C-C bond length of 1.432 Å at chiral bond length and 1.398Å for axial bond length. Geometry optimization of the all four positions resulted in slight increase in bond length of chiral and axial positions of SWCNT. Figure 2 and 3 displays the modified carbon-carbon bond length and Au-SWNT bond length, result is tabulated in table 1.

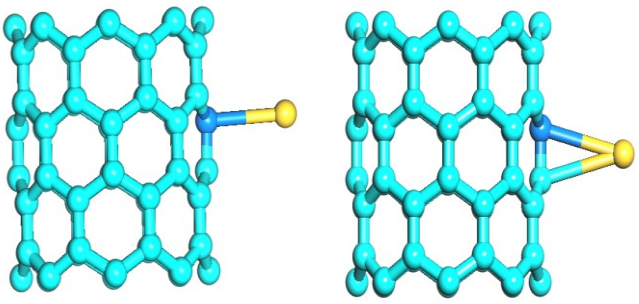


(a) Atomic bond (b) Axial bond

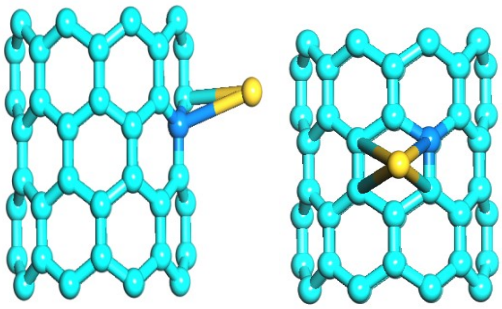


(c) Chiral Bond (d) Hexagon Bond

Figure 2. Structures with bond length in four positions



(a) (b)



(c) (d)

Figure 3. Stable geometry of Au-SWCNT
(a) Atomic bond (b) Axial Bond
(c) Chiral Bond (d) Hexagon Bond

Table 1. Shows bond length between atomic site atom C_T and adjacent carbon atom C and Gold atom Au.

Positions	Atomic bond Length (Å)	Axial Bond Length (Å)	Chiral Bond Length (Å)	Hexagon Bond Length (Å)
C_T-C_1	1.449	1.438	1.433	1.440
C_T-C_2	1.450	1.438	1.444	1.443
C_T-C_3	1.409	1.407	1.400	1.402
C_T-Au	2.713	2.991	2.962-3.102	3.663-3.520
Total	7.021	7.274	7.239-7.379	7.948-7.805

Before optimization, in the prepared model the distance of adsorption of Au adatom is about 3.0 Å from carbon atom or carbon-carbon bond. After performing Geometry optimization Au adatom get attached to carbon atom of nanotube by covalent bond of length 2.7 Å at atomic, 2.99 Å at axial, 2.96 - 3.102 Å at chiral and 3.663 - 3.520 Å at hexagon. From bond length it is observed that Au atom is chemisorbed at atomic site and physisorbed on Axial, Chiral and Hexagon site. As shown in table 1, the total length of the c-c at axial and chiral position in pure SWCNT (8, 0) is 1.432+1.432+1.398=4.262Å, but the total bond length for Au-CNT at atomic is 7.021 Å,

at axial 7.274 Å, at chiral is variable from 7.239Å to 7.379 Å and at hexagon is variable from 7.948Å to 7.805Å, The bond angles between C - C - C bonds were ranging from116^0 to 119.5^0 which is less than 120^0 indicates trigonal structure of bonding and prefers sp2 hybridization as shown in Table 2.

Table 2. Angles between target atom C_T and adjacent carbon atom C and Gold atom Au

Positions	Pure CNT (8,0)	Atomic bond Angle	Axial Bond	Chiral Bond	Hexagon Bond
C_1-C_T-C_2	117.417^0	116.664^0	116.664^0	116.664^0	117.724^0
C_1-C_T-C_3	119.36^0	119.163^0	119.163^0	118.984^0	119.186^0
C_2-C_T-C_3	119.357^0	119.156^0	119.156^0	118.885^0	119.431^0
C_3-Au-C_T			27.199	27.415^0	21.980^0, 23.080^0, 24.022^0, 39.785^0
Hybridization Nature	sp^2	sp^2	sp^2	sp^2	sp^2

A. Adsorption Energy

The Binding energy of pure (8, 0) SWCNT, molecule and Au-SWCNT were calculated. The Binding energy shown in Table 3 determines the stability of the system and the higher binding energy shows lower the stability of the system. Table 3 shows the summery of calculated binding energy of the studied system. From value of binding energy for site – A the Au atom is chemisorbed while for all other site it is physisorbed. The binding energy values are supportive to the prior statement of adsorption.

B. Charge transfer

Mulliken population analysis was used to calculate the charge transfer between the CNT and Au atom. Pristine carbon nanotube has n-type characteristics. Interaction of Au atom with CNT minutely changes its semiconducting character. Metal atoms Au gains electron from the carbon atoms. The observation Table 4 shows magnitude of partial charge transfer which is more for Site – A due to chemisorptions. The magnitudes of charge transfer for remaining sites are slightly different.

Table 3. Shows the Binding Energy values of Au atom with CNT for all sites.

Structure type	B.E in eV
Au-SWCNT(Atomic bond)	- 0.1577
Au-SWCNT(Axial bond)	- 0.1441
Au-SWCNT(chiral bond)	- 0.1142
Au-SWCNT(Hexagon bond)	- 0.1142

Table 4. Charge Transfer between CNT and Au atom

Structure type	Mulliken Charge
Au-SWCNT(Atomic bond)	0.22
Au-SWCNT(Axial bond)	0.189
Au-SWCNT(chiral bond)	0.189
Au-SWCNT(Hexagon bond)	0.16

C. Band Structure (BS), Density of State (DOS) and Energy Band Gap (BG)

The Band Structure (BS) and Density of State (DOS) of pure SWCNT is Shown in figure 4(a). The energy band gap found from BS and DOS for pure CNT is 0.701, which is competent to theoretically and experimentally reported result. Figure 4(b-e) shows BS and DOS for interaction Au atom with CNT at four different sites. BS and DOS for atomic site – A, axial bond site – C and chiral bond site – B shows there is an extra unoccupied states near conduction band. For hexagon site – D there is heavily occupied state near Fermi energy in valance band. The newly formed extra state varying from 0.234eV to 0.2629 in conduction band for interaction of Au atom with CNT is almost reduced and shifted near to Fermi level as compared to CNT. This results in reduction of band gap of CNT from 0.7eV (of pure CNT) to 0.26eV for atomic and axial bond site. For chiral bond and Hexagon position band gap reduced to 0.301eV and 0.28 respectively as shown in Table 5.

Table 5. Shows band gap values of pristine CNT and Au-CNT system

Structure type	Band gap(eV)
Pure SWCNT(8,0)	0.701
Au-SWCNT(Atomic bond)	0.258
Au-SWCNT(Axial bond)	0.259
Au-SWCNT(chiral bond)	0.304
Au-SWCNT(Hexagon bond)	0.284

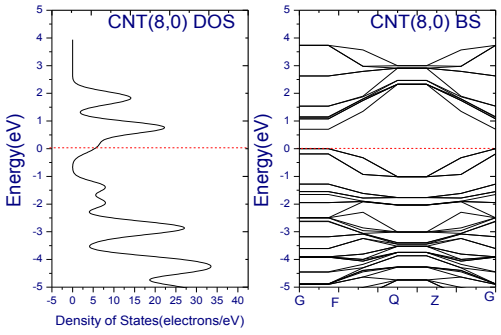


Figure 4. (a) DOS and BS of Pure CNT(8,0)

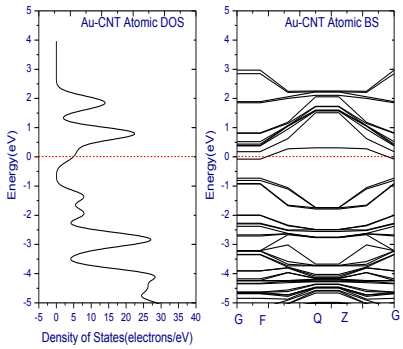


Figure 4. (b) DOS and BS of AU-CNT atomic position

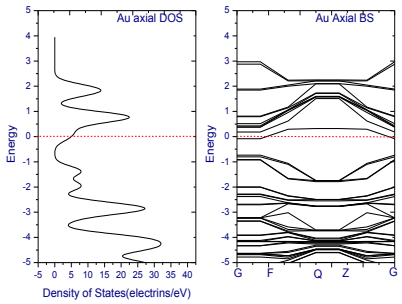


Figure 4. (c) DOS and BS of AU-CNT axial position

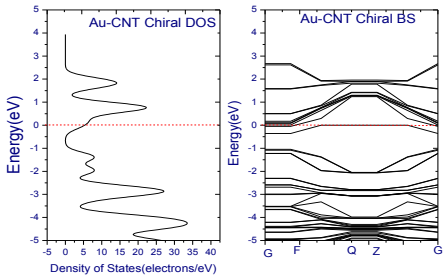


Figure 4. (d) DOS and BS of AU-CNT chiral position

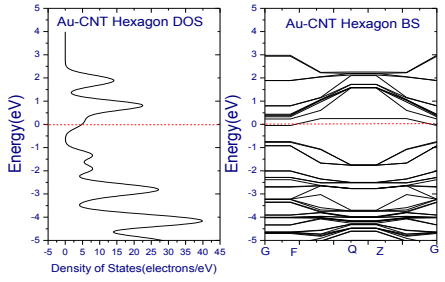


Figure 4. (e) DOS and BS of AU-CNT chiral position

IV. CONCLUSION

In this paper, we have studied the adsorption energies, stable geometries, density of states, Band Structure and Mulliken charge for interaction of Au atoms on SWCNT (8,0) using first-principles density- functional

theory. We found reduction of band gap of SWCNT from 0.7eV (of pure CNT) to 0.26eV when Au atom interacts with SWCNT. Au atom is chemisorbed on atomic site while for axial bond, chiral bond and Hexagon sites of interaction Au atom is physisorbed. The Physorption of Au atom also reduces band gap of SWCNT. After interaction we calculating Mulliken charge found that metal atoms gains electron from the surrounding carbon atoms, more amounts of electrons is gain when Au atom is interacting on atomic site. This shows that semiconducting nature of SWCNT becomes P-type.

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