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### Ab initio study of the electronic structure of hydrogenated (3,3) and (4,4) single-wall carbon nanotubes

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#### ABSTRACT

We have studied the electronic structures of pristine and hydrogenated armchair (3,3) and (4,4) SWCNTs using (DFT/B3LYP) with 6-31 basis set. The obtained results show that the energy gap of hydrogenated SWCNTs is larger than those of pristine. Also, ionization potential and electron affinity of hydrogenated CNTs less than that for the pristine tube. Furthermore, The Fermi energy of hydrogenated CNTs smaller than pristine nanotube. The addition of hydrogen causes the distribution of charge along the length of the nanotube. Finally, the addition of hydrogen causes an increase in the highest number of DOS in the conduction and valence bands

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#### INTRODUCTION

The extraordinary mechanical properties and unique electrical properties of single-wall carbon nanotubes (SWCNT) have stimulated extensive research activities across the world since their discovery by Iijima in the early 1990s [1]. A SWCNT is a graphene sheet rolled into a cylindrical shape so that the structure is one-dimensional with axial symmetry [2]. Also, it is known that a nanotube can be metallic or semiconducting depending on their diameter and chirality [3, 4]. In recent years, CNTs has attracted great attention in many fields of technology and science and because it the most exciting quasi-1-D solids that exhibit fascinating structural, electronic, optical, electrical, and mechanical properties [5, 6]. Investigation into their properties has become one of the most active fields of modern research, these interesting properties have led to an increase in the number of investigations focused on application development in the past years. The breadth of applications for carbon nanotubes is indeed wide ranging: nanoelectronics, biosensors, detectors, quantum wire interconnects, field emission devices, composites, chemical sensors, etc. [7-9].

There is a developing interest in understanding the essentials of the interaction between hydrogenated SWNT because the probability of using SWNT for hydrogen storage. Many [10-14] studies have been performed in order to understand the mechanism of storage. Experimental results on hydrogen storage are far from uniform and have not been independently reproduced [15]. The study of side-wall functionalization of SWNT has also attracted huge attention lately because of its potential to separate semiconducting from metallic nanotubes, and grow them, even cut them in a selective way [16,17].

It is possible nowadays to study the structural and electronic properties of nanostructures in general, and carbon nanotubes in particular as well as the energetics of many-electron systems by performing fully ab initio computations The first theoretical calculation of SWCNTs electronic structure was carried out using zone folding scheme [18,19].

In this paper, we performed density functional theory (DFT) calculation to investigate the electronic structure of hydrogenated (3,3) and (4,4) SWCNTs. The DFT calculations are performed using the Gaussian 09 program [20]. Becke three parameter Lee–Yang–Parr (B3LYP) functional [21, 22] using 6-31G basis set, have been applied in the calculations.

#### 2 Computational details:

All the computational studies were carried out using DFT implemented in the Gaussian 09 programs running. All the structures generated via TubeGen 3.4 [23], which is available as source code.

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The molecular properties of the compounds have been computed by DFT using the standard 6-31G basis sets calculations in DFT were carried out with the B3LYP hybrid functional. B3LYP is one of the often-employed hybrid functional used in theoretical studies of nanotubes. The geometry optimization of the molecule is the structure at which the molecule has the minimum energy; it is performed by finding the first derivative of the energy with respect to the distance between different atoms, known as the gradient. We considered (3,3) and (4,4) SWCNTs with an open edge, the diameters of the nanotubes are 4.07, 5.43 Å, respectively. The length of optimized SWCNTs are computed to be about 15Å, and the optimized C-C bond length is found as 1.411Å, and is in close agreement with experimental value of 1.421Å [24]. Hydrogen atoms are placed on the dangling bond at both ends. The hydrogenated models consist of 90 atoms with formula of C<sub>78</sub>H<sub>12</sub> for (3,3), and 120 atoms with formula of C<sub>104</sub>H<sub>16</sub> for (4,4) SWCNTs.

## RESULTS AND DISCUSSION

### 3.1 Electronic structure:

Table 1 gives the data for pristine and hydrogenated SWCNTs nanotubes. The natural bond orbital calculations were performed to derive the highest occupied and the lowest unoccupied molecular orbital, the total energy ( $E_{\text{Tot}}$ ), energy gaps ( $E_g$ ), ionization potential (IP), electron affinity (EA) and Fermi level ( $E_F$ ).

**Table 1:** Structural and electronic properties of pristine and hydrogenated SWCNTs obtained from DFT calculations.

SWCNTs (n,m)	$E_{\text{Tot}}$ (eV)	$E_g$ (eV)	IP (eV)	EA (eV)	$E_F$ (eV)
Pristine (3,3)	-80810.02	0.292	4.739	4.446	-4.592
Pristine (4,4)	-107771.80	0.201	5.126	4.925	-5.026
Hydrogenated (3,3)	-81031.75	1.383	4.067	2.683	-3.375
Hydrogenated (4,4)	-108067.86	0.581	3.746	3.165	-3.456

We have investigated atomic and electronic structures of hydrogenated SWCNTs by density functional calculations, Table 1 shows the calculated electronic properties of hydrogenated CNTs. It can be seen that the energy gap of hydrogenated SWCNTs is larger than those of pristine. One can find that the band gap in carbon nanotubes can be changed by adding hydrogen atoms to the dangling bond of CNTs. The computed  $E_F$  for hydrogenated CNTs smaller than pristine nanotube. A similar behavior is observed for the interaction between hydrogen and (5,5) and (10,0) SWCNT using different density functional approaches reported by Barone et. al. [17], where they found that covering the (5,5) and (10,0) SWCNT with hydrogen enlarge the existing energy gap.

The IP for hydrogenated CNTs less than that for the pristine tube; this indicates that hydrogenated CNTs need small energy to become cation comparing with pristine tube. This small IP may make hydrogenated CNTs useful for high-energy particle detectors or as catalysis. The EA for hydrogenated CNTs less than that for pristine tube, i.e., adding the hydrogen atom to the dangling bond reduces the ability of the EA for hydrogenated NTs less than that for pristine tube.

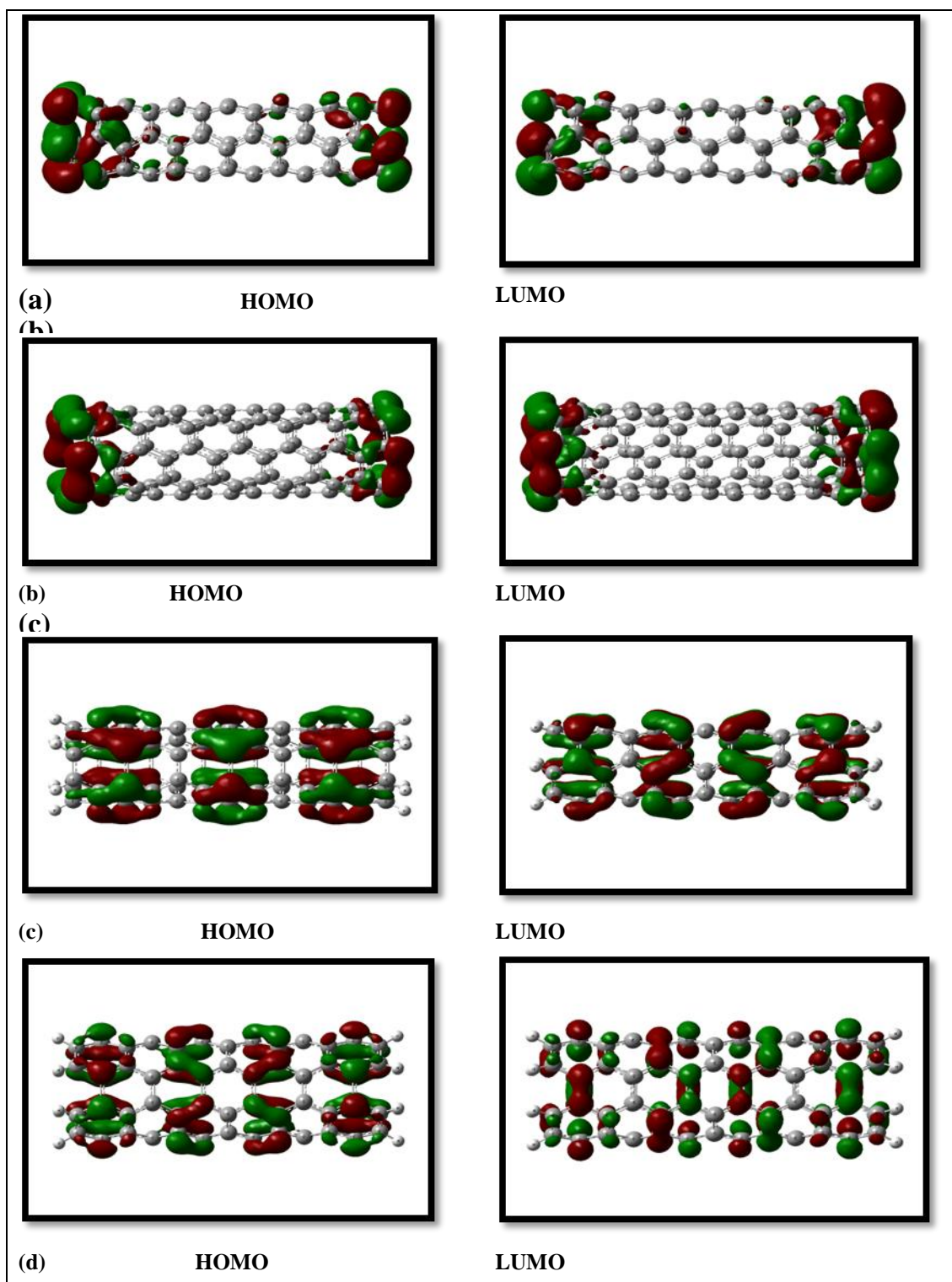
### HOMO and LUMO energies:

It is well known that the frontier molecular orbitals, the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), play an important role in chemical reactions for the reactant molecules, making the frontier orbital analysis of the CNTs necessary. In Table 2 and Figure 1, We summarize the HOMO and LUMO energy levels of pristine and hydrogenated CNTs.

It can be seen that HOMO and LUMO energy levels of hydrogenated CNTs vary little compared with those of the pristine tubes. The HOMO and LUMO energy levels of hydrogenated CNTs are smaller than those of pristine. This fact agrees with the former DFT [25].

**Table 2:** The calculated HOMO and LUMO energies of pristine and hydrogenated SWCNTs.

SWNT (n, m)	$E_{\text{HOMO}}$ (eV)	$E_{\text{LUMO}}$ (eV)
Pristine (3,3)	-4.739	-4.446
Pristine (4,4)	-5.126	-4.925
Hydrogenated (3,3)	-4.067	-2.683
Hydrogenated (4,4)	-3.746	-3.165



**Fig. 1:** HOMO and LUMO energy of: **a.** pristine (3,3), **b.** pristine (4,4), **c.** hydrogenated (3,3), **d.** hydrogenated (4,4) SWNTs.

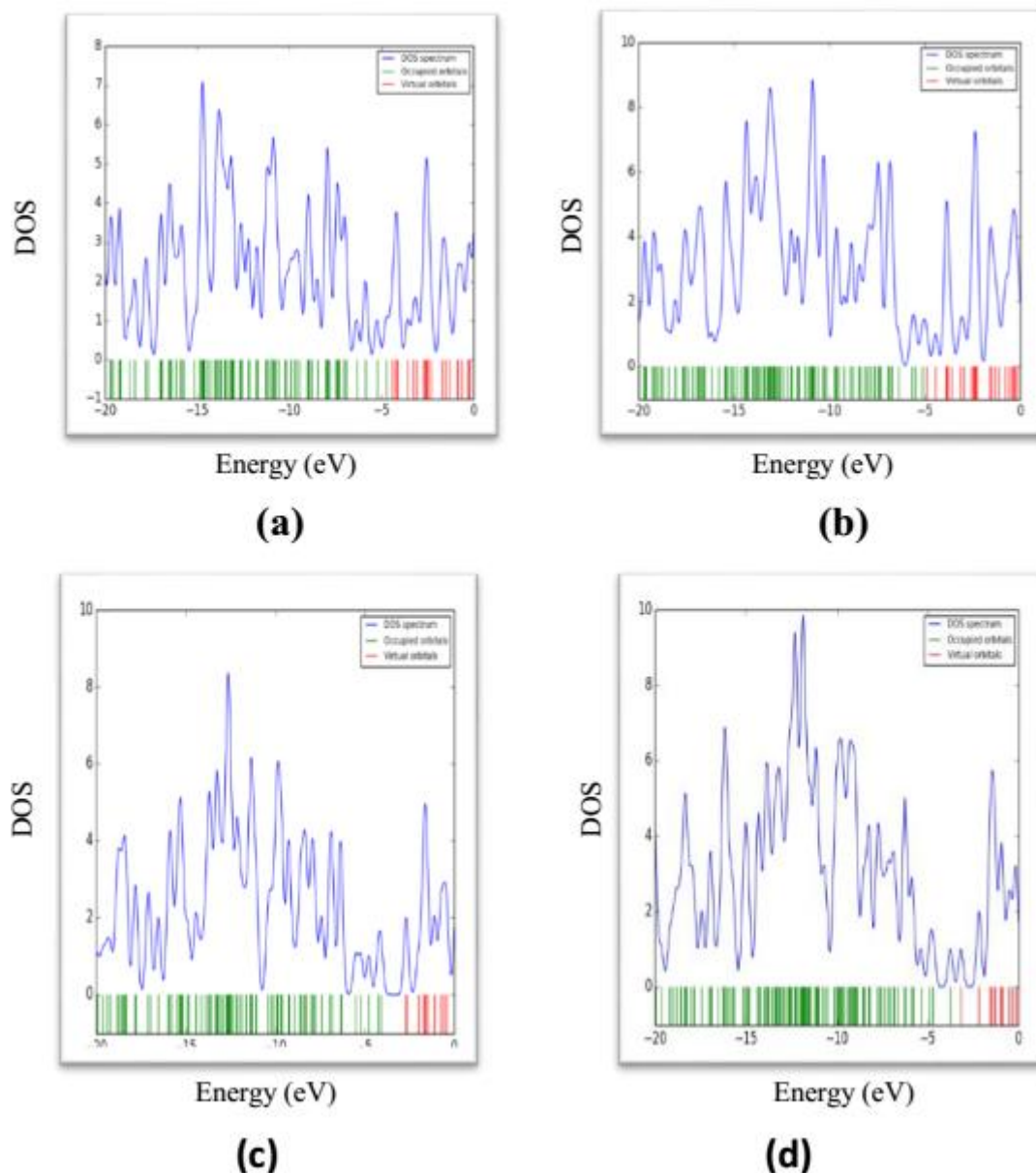
According to the Frontier molecule orbital theory, the chemical reactivity is a function of interaction between HOMO and LUMO levels of the reacting species.

High value of  $E_{\text{HOMO}}$  is likely to indicate a tendency of the molecule to donate electrons to appropriate acceptor molecule of low empty molecular orbital energy. Therefore, the energy of  $E_{\text{LUMO}}$ , indicates the ability of the molecule to accept electrons. So, the lower the value of  $E_{\text{LUMO}}$ , the more probable the molecule would accept electrons. Thus, the binding ability of the inhibitor to the semiconductor surface increases with increasing of the HOMO and decreasing of the LUMO energy values.

### 3.3 The density of states:

Density of states of pristine (3,3) and (4,4), and hydrogenated (3,3) and (4,4) SWCNTs as a function of energy level is shown in Figure 2, DOS of the optimized tube indicating that the CNTs is semiconductor. The highest number of degenerate states in the conduction and valence bands are about as 7, 9, for (3,3) and (4,4) SWCNTs, respectively. A high DOS at a specific energy level means that there are many states available for occupation. A more precise comparison for the DOS of hydrogenated CNT with the DOS of pristine shows that the addition of hydrogen causes an increase in the highest number of DOS in the conduction and valence bands for hydrogenated SWCNTs.

One can see with comparing these DOS in Figure 2, that the DOS for (3,3) and (4,4) is correlated to the particle number of hydrogen. The more the number of H atom, the stronger the peaks of DOS; especially the middle peaks are more obvious. In the figure, the shapes of the energy peaks of hydrogenated CNTs are similar, for they all have many peaks. Nevertheless, their corresponding maximum DOS values are different.



**Fig. 2:** Density of states for: **a.** pristine (3,3), **b.** pristine (4,4), **c.** hydrogenated (3,3) and **d.** hydrogenated (4,4) SWCNTs

### Conclusions:

We performed density functional theory (DFT) calculation to investigate the electronic structure of pristine and hydrogenated armchair (3,3) and (4,4) SWCNTs. It is found that the total energy increases with increasing the number of atoms. The  $E_g$  of pristine (3,3) and (4,4) SWCNTs is slightly larger than experimental results,

because the B3LYP is known to overestimate the size of band gap of semiconductors but still describes quite accurately the trend in band gap. However, the band gap in carbon nanotubes can be changed by adding hydrogen atoms to the dangling bond of CNTs. It is noticed that the majority of the molecular orbital density in HOMO and LUMO orbitals is localized along the C-C backbone. On the other hand, the DOS for (3,3) and (4,4) is correlated to the number of hydrogen. The more the number of H atom, the stronger the peaks of DOS.

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