J. Iran. Chem. Soc., Vol. 4, No. 4, December 2007, pp. 431-437.

JOURNAL OF THE
Iranian
Chemical Society

The Effect of Atomic Hydrogen Adsorption on Single-Walled Carbon Nanotubes Properties

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(Received 20 September 2006, Accepted 3 March 2007)

We investigated the adsorption of hydrogen atoms on metallic single-walled carbon nanotubes using *ab initio* molecular dynamics method. It was found that the geometric structures and the electronic properties of hydrogenated SWNTs can be strongly changed by varying hydrogen coverage. The circular cross sections of the CNTs were changed with different hydrogen coverage. When hydrogen is chemisorbed on the surface of the carbon nanotube, the energy gap will be appeared. This is due to the degree of the sp^3 hybridization, and the hydrogen coverage can control the band gap of the carbon nanotube.

Keywords: Carbon nanotube, *Ab initio* molecular dynamics, Atomic hydrogen adsorption

INTRODUCTION

Hydrogen has been known as an ideal energy carrier but achieving efficient storage has not been easily possible yet. In the beginning, metal alloys were used as storage tanks but they are expensive and heavy for commercial production focused on mobile applications [1]. In recent years, it has been shown that carbon nanotubes (CNTs) have sufficient gas storage capacity due to their chemical stability, large surface area, hollowness, and light mass.

Pederson and Broughton suggested that CNTs should be able to draw up liquids by capillarity [2]. In 1991, Dillon *et al.* showed that the hydrogen would condense inside SWNTs [3]. Two years later, Liu *et al.* reported that this storage can take place at room temperature [4]. At the same time, Chen *et al.* achieved the high storage capacity of alkali-doped carbon nanotubes [5]. Subsequently a lot of experimental efforts were performed to improve the hydrogen storage capacity of single-walled carbon nanotubes (SWNTs). There are many useful theoretical studies that give insight into the adsorption procedures. In late 1998, Darkrim *et al.* investigated the influence of tube diameter on the hydrogen storage capacity using Grand Canonical Monte Carlo (GCMC) simulation [6]. In 1999, Johnson *et al.* studied the hydrogen adsorption in neutral tubes or positively and negatively charged SWNTs using a classical simulation method [7,8]. Williams *et al.* simulated the H_2 physisorption using GCMC [9]. The dependence of the results on the intermolecular potential used for H-C interaction is a notable disadvantage of classical simulations and this shows that it is better we use the *ab initio* methods for these systems [1].

Since 2001, the quantum picture has been introduced into the molecular dynamics study of hydrogen in SWNTs. In the first research using this method, a quantum mechanical molecular dynamics simulation of H_2 adsorption on a two dimensional lattice of armchair (9,9) SWNTs was carried out

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*Corresponding author. E-mail: sjalili@kntu.ac.ir by Cheng *et al.* [10]. A mixed quantum mechanics/molecular mechanics (QM/MM) model was used for investigating the nature of molecular hydrogen adsorption in pure and alkali-metal-doped SWNTs. The results revealed that the charge transfer from the alkali metal to the tube polarizes the H_2 molecules and this charge induce dipole interaction is responsible for higher hydrogen uptake of the doped tubes [11]. Gülseren *et al.* showed that electronic and atomic structures of CNTs undergo dramatic changes with hydrogen chemisorption by first principle calculations [12]. In a number of researches, Density Functional Theory (DFT) was used to study the interaction of atomic and molecular hydrogen with SWNTs [13,14,15].

It has been shown that physical and chemical properties of a SWNT can be changed by the adsorption of foreign atoms or molecules. For example, upon exposure to molecules such as NO_2 or O_2, small gap semiconducting SWNT can be changed to a metallic, while a metallic tube remains metallic. Adsorption of H_2 or NH_3 does not change charge carriers and conductivity in metallic and semiconducting SWNTs [16].

The theoretical studies on hydrogen storage in SWNTs were classified into two different categories. The first group (classical modeling) investigates the physisorption of molecular hydrogen into the tube where the molecular hydrogen does not dissociate and has the advantage of the temperature dependence of the simulations. The second group (*ab initio* calculations) deals with atomic hydrogen chemisorbed on the tube walls and has the advantage of showing the nature of the interaction [1]. Chemical functionalization of CNTs can change the atomic and electronic properties of nanotubes and may enhance the performance in hydrogen storage of secondary batteries and supercapacitors. It is clear that atomic hydrogen that approach to the CNT prefer to bind to the tube walls and not enter to the tube interior. Sidewall functionalization of the SWNTs by atomic hydrogen leads to transforming electronic structures from metallic to semiconducting. Thus, a systematic study is essential for the atomic and electronic structures of hydrogen-chemisorbed SWNTs in terms of hydrogen coverage [15].

In this paper, atomic structures and electronic properties of hydrogenated SWNTs have been investigated using *ab initio* molecular dynamics method.

Table1. Structural Parameters for (3,3), and (5,5) Carbon Nanotubes

(n,m)	(3,3)	(5,5)
Chiral vector C_h*(Å)*	12.78	21.313
Translational vector T *(Å)*	2.46	2.46
CNT radius r_t *(Å)*	2.06	3.39
CNT Supercell $a\times b\times c$ *(Å^3)*	10×10×7.38	10×10×7.38

METHOD

We studied (3,3) and (5,5) armchair nanotubes in the presence of various adsorption patterns of atomic hydrogen. The unit cell of each tube contains 12 and 20 carbon atoms, respectively. Our supercells include 36 atoms for (3,3) SWNT, and 60 atoms for (5,5) SWNT, corresponding to three unit cells along the tube axis. The lattice constants of the supercell are a = b = 10 Å in the *x* and *y* directions, and along the axis of tube (*z* direction), c, is taken to be equal to translational vector. Calculated structural parameters for them are presented in Table 1. First, the C-C bond length was constrained at 1.42 Å, and then the structure was optimized. After optimization, hydrogen atoms are placed about 1.12 Å (similar to 1.1 Å of CH_4 molecules) away from the top of the C atoms. Then, tubes with different patterns of hydrogen atoms are fully relaxed. An energy cutoff of 60 Ry was chosen. The BLYP was employed for the exchange and correlation functional. For calculation of the band structure, 21 K-points along the tube axis were used. The calculations were performed with CPMD 3.9.1 program [17].

TRANSFORMATION OF SWNT GEOMETRY

From previous analysis of stability of many hydrogen adsorption patterns, the pair formation of hydrogen adsorbed is more favorable than the separated one [15,18]. Thus, we considered only the pair adsorption for hydrogen coverage. On the armchair SWNT wall, carbon bonds are perpendicular to the tube axis or are oriented by 30° from the tube axis. At low coverage we observed that C-C perpendicular bonds were broken if two hydrogen atoms are attached to these carbons.

These results indicate that all types of hydrogenated structures are not stable at low coverage and the CNTs may be destroyed at the beginning step of hydrogen adsorption. We considered various types of hydrogen adsorption patterns at same coverage, and searched for most stable ones. For instance, different positions of four hydrogen atoms with respect to (5,5) SWNT are shown in Fig. 1. According to their energies, configuration shown in Fig. 1a is more preferable. Thus, in this paper we limit our calculations to the special stable atomic structures.

Cross sections of fully relaxed geometry of hydrogenated (5,5) tubes at several adsorption patterns are displayed in Fig. 2. The coverage, θ, was specified as ratio of the number of hydrogen atoms to the number of carbon atoms ($\theta = N_H/N_C$). All bond lengths are given in unit of Å. At θ = 0.1 and 0.2 the circular cross section of pure (5,5) tube becomes elliptical. While the cross section at θ = 0.3 and 0.5 are triangular and polygonal, respectively. The symmetry of the hydrogenated CNTs are changed from polygonal to perfect circular shape by increasing coverage from θ = 0.5 to θ = 1.0. The bond angles near the hydrogen positions prefer to have values close to the ideal tetrahedral bond angle (109°). This verifies that hydrogen is chemisorbed on carbon and the sp^2 hybridization of C-C bond in the CNT wall transfer to the sp^3 hybridization.

From Fig. 3, it can be seen that the circular cross section of pure (3,3) tube changes by increasing hydrogen coverage similar to that at (5,5) tube. At θ < 0.5 the cross sections are elliptical, while they are triangular and circular at θ = 0.5 and 1.0, respectively.

For full coverage at θ = 1.0, three different configurations (i.e., arch, zigzag and inside) were considered, due to the positions of hydrogen atoms with respect to SWNT (Fig. 4). Zigzag and arch configurations have stable geometry. The inside configuration is unstable and hydrogen atoms break off from the SWNT wall and H_2 molecules form inside the CNT.

Adsorption and Strain Energy

First, we studied adsorption energy and stability of the structures. The adsorption energy per hydrogen atom is defined as

$$E_{ad} = \{E_{tot}(CNT-H) - E_{tot}(CNT) - n_H E(H)\}/n_H \qquad (1)$$

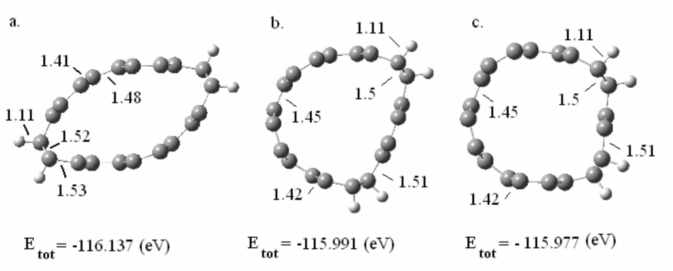

Fig. 1. Cross sections of various types of four hydrogen atoms on the (5,5) tubes, and their total energies.

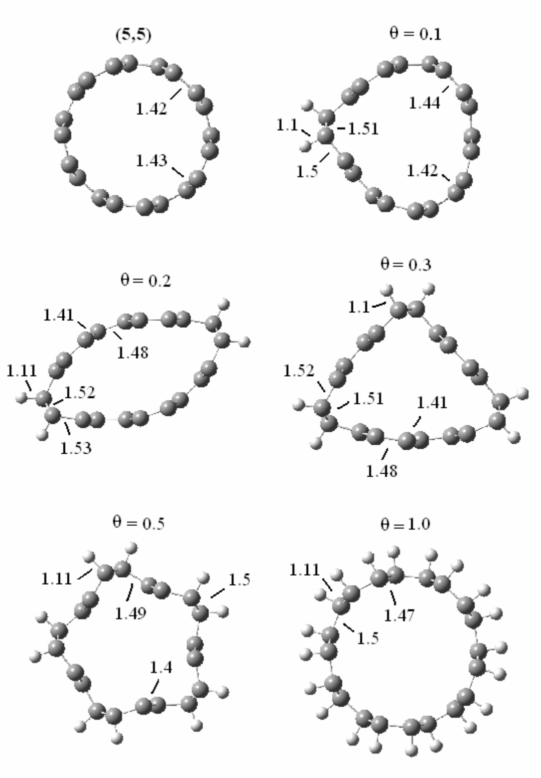

Fig. 2. Cross sections of the hydrogenated (5,5) tubes with various adsorption patterns.

where $E_{tot}(CNT\text{-}H)$ is the total energy of the hydrogenated CNT, $E_{tot}(CNT)$ and $E(H)$ are the total energy of the pure CNT and atomic hydrogen. n_H is the number of hydrogen atoms. By definition, negative E_{ad} value corresponds to the stable structure.

The strain energy, which is the C-C bond distortion energy

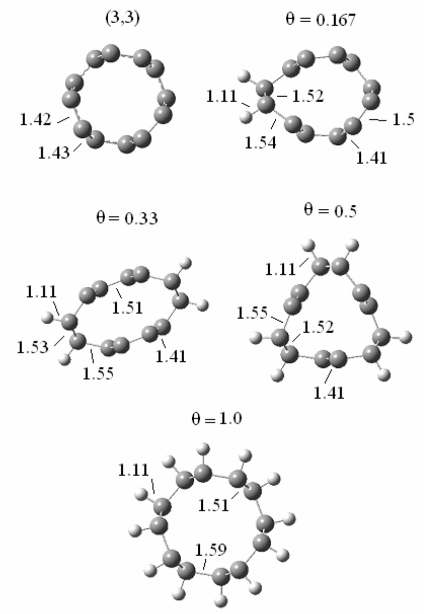

Fig. 3. Cross sections of the hydrogenated (3,3) tubes with various adsorption patterns.

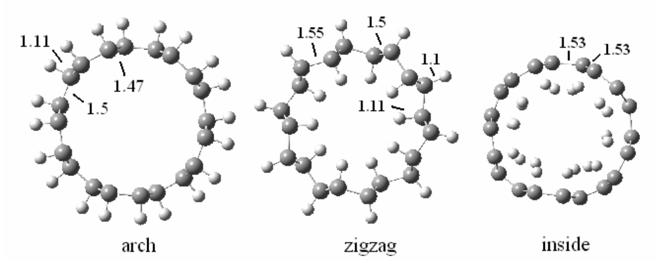

Fig. 4. Cross sections of the hydrogenated (5,5) tubes with full coverage.

upon adsorption [19], is calculated by:

$$E_s = E_{tot}(strained\ CNT\ without\ H) - E_{tot}(ideal\ CNT) \qquad (2)$$

In Fig. 5, E_{ad} and E_s for different hydrogen coverage are shown. The strain energy indicates that the sp^3 hybridization is the main factor for the obtaining energy. The difference between strain energies of small (3,3) SWNT corresponding to the two coverages of θ = 0.167 and 0.33 is a small value of 0.03 eV. The observed minimum can be related to the instantaneous interaction of adsorbed hydrogens in the selected structure of the small (3,3) SWNT and this is not observed for other carbon nanotubes [15,19]. Usually, the strain energy increases by increasing the hydrogen coverage [15].

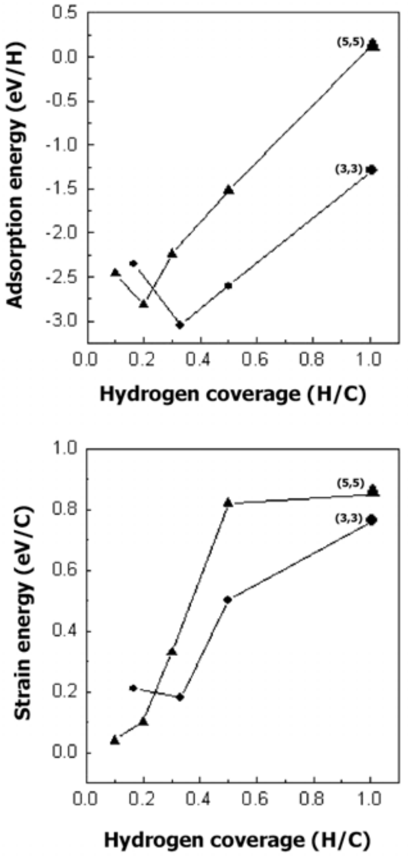

Fig. 5. Hydrogen adsorption energy and strain energy.

It is believed that the adsorption energy contains the effects of both bond energy and strain energy [19]. There is a minimum in E_{ad}, which can be explained as follows. By increasing the hydrogen coverage, the number of sp^3 hybridizations is also increased; thus, adsorption energy decreased. Meanwhile, by increasing hydrogen coverage the repulsion between hydrogens is increased and, thus, the adsorption energy also increased. These effects result in a minimum.

Electronic Structures

A SWNT is defined by a cylindrical graphene sheet. The remarkable electronic properties of SWNTs can be deduced by the surprising electronic properties of graphene [20]. The analysis based on the zone-folding approximation indicates that the (n,n) armchair CNTs are always metal. Whereas, the (n,0) zigzag CNTs are generally semiconductor and are only metal if n is an integer multiple of three [20]. The (3,3) and (5,5) armchair CNTs are metal as suggested by our simulation results. The band structures of (5,5) and (3,3) SWNTs are presented in Figs. 6 and 7, respectively. Crossing the π valence and π^* conduction band at the Fermi level clarifies the metallic behavior of these tubes.

Electronic band structures of hydrogenated (5,5) tubes for different coverage are shown in Fig. 6. The hydrogenated tubes show metallic behavior at $\theta < 0.5$. At these coverage levels, hydrogen adsorption breaks the symmetry, and highly degenerate states in the conduction band are split into singlets. At half coverage, $\theta = 0.5$, a large band gap of about 2.47 eV at Γ point is found by removing π states near the Fermi level. For $\theta = 0.5$, Park *et al.* reported a large band gap opening of nearly 3.07 eV using DFT calculations [15]. By increasing coverage from $\theta = 0.5$ to 1.0, the band gap is reduced to 0.7 eV. At full coverage with zigzag configuration, the band gap (3.8 eV) is much more than that in arch-type (0.7 eV). A band gap of 1.0 eV for full hydrogenated (5,5) tube is known to be underestimated in LDA calculation [21]. In the arch and zigzag- type, Lee *et al.* clearly observed the band gaps of 1.63 eV and 2.63 eV, respectively [14]. Thus, converting the SWNT with hydrogen can lead to transformation of the CNT from metallic to insulator by enhancing the sp^3 hybridization. In our previous study [16], we found that H_2 adsorption does not have a significant influence on the electronic structures of metallic SWNTs and, therefore, the inside type exhibits metallic behavior.

In the case of (3,3) SWNTs, the band gap shows a similar trend (Fig. 7). Hydrogenated (3,3) SWNTs are metal at lower coverages than $\theta < 0.5$. The enhanced hydrogen coverage transform electronic properties from metallic to semiconducting. The largest band gap observed at half coverage is about 2.98 eV. The band gap at full coverage in arch and zigzag-types are 2.81 eV and 3.66 eV, respectively (Fig. 8). Thus, the band gap opening seems to be more serious.

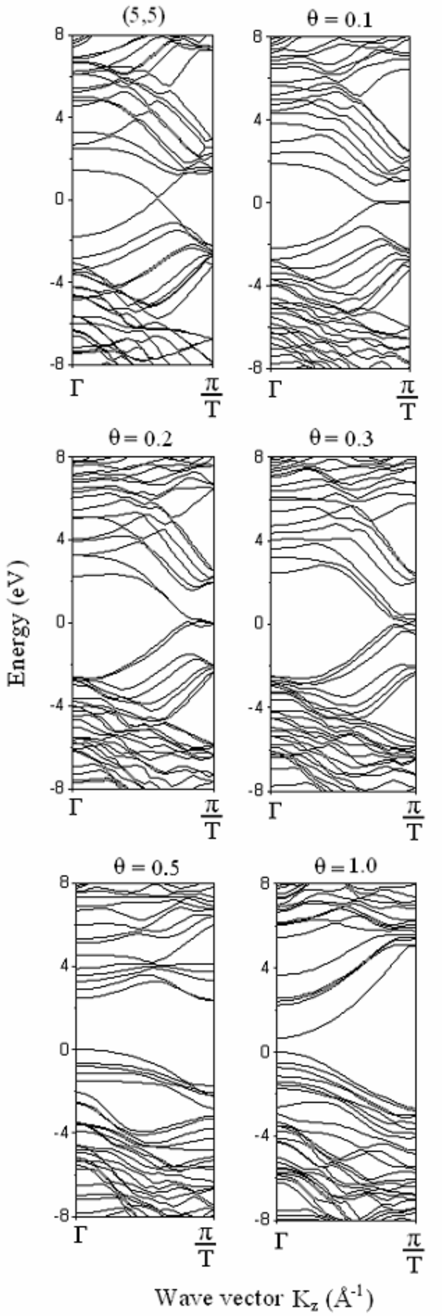

Fig. 6. Electronic band structures of hydrogenated (5,5) carbon nanotubes (The Fermi level is at 0 eV).

It is clear from Jeong *et al.* observations [21] that the electronic structure is significantly modified and transformed from metallic to semiconducting or insulating. Experimental values of the band gaps of hydrogenated SWNT range from 1.88 to 4.4 eV (Note that the patterns of hydrogenation

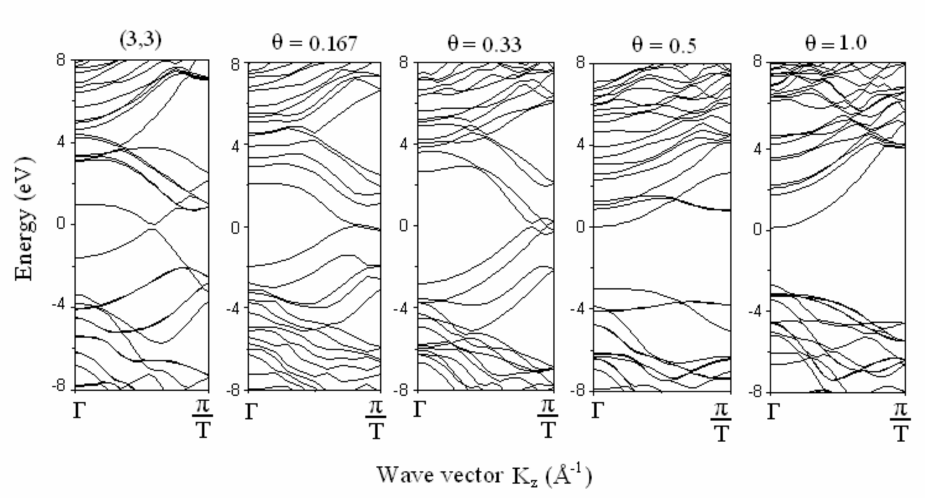

Fig. 7. Electronic band structures of hydrogenated (3,3) carbon nanotubes.

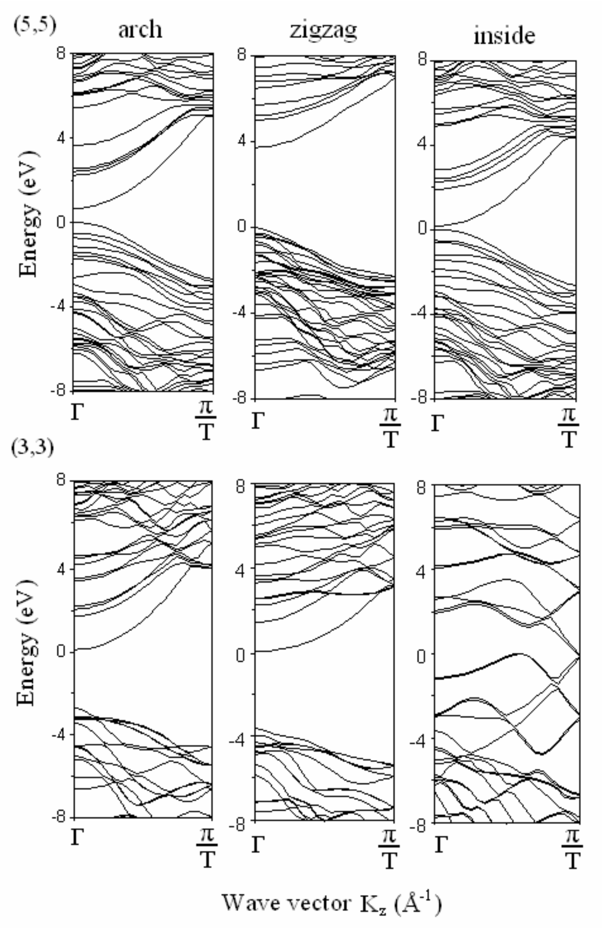

Fig. 8. Electronic band structures of hydrogenated (5,5) and (3,3) carbon nanotubes with full coverage.

obtained in the experiment is not clear). Our calculated band gaps are close to the experimentally observed values.

CONCLUSIONS

In conclusion, it was found that stability of hydrogenated SWNTs is depend on the adsorption patterns. The band gap of the SWNTs can be controlled by hydrogen coverage and degree of sp^3 hybridization. Strictly, the band gap has opened up after chemisorption of the hydrogen atoms, due to the enhance sp^3 hybridization. The metallic CNTs become insulating with enhanced the hydrogen coverage.

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