

# Electron Localization States in Asymmetric Shape Carbon Nanotubes Caused by Hydrogen Adsorption

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**Abstract.** In this paper, we presented pseudopotential-based density functional theory studies on energy, structure, energy band structure of hydrogenated single-walled carbon nanotube. The stability of the configuration mainly depends on hydrogen coverage. According to the adsorption energies, the stability deteriorates with the increase of the hydrogen adsorption. The cross section of configurations become various shapes such as “beetle” or “lip” appearance without the balanced effects of hydrogen atoms. We also explored the energy band structures of configurations in three typical adsorption patterns, showing that the disparate trends of energy band gap as the hydrogen atoms concentrate. For  $C_{32}H_{24}$ , the band gap may reach the large value of 2.79 eV for the adsorption pattern A configuration and reduce to be zero for the adsorption pattern C case, the values of band gap for pattern A configurations decrease, which is opposite of the pattern B configurations as the adsorption hydrogen becomes more disperse. It is deduced that the hydrogen adsorption has significant effect on the electrical properties of the carbon nanotube.

**Keywords:** carbon nanotube; hydrogen; density functional theory

## 1. Introduction

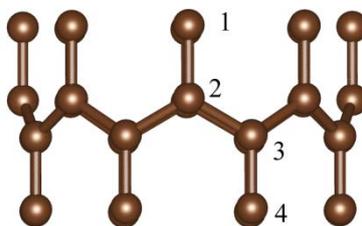
Hydrogen has been considered as one of best fuels in the future, which may be free of pollution and substitute for fossil fuels. For practical application with hydrogen, the U.S. Department of Energy (DOE) has estimated up to 6.5 mass% of hydrogen (density of 62.5 kg/m<sup>3</sup>), however, the best materials such as TiV<sub>2</sub> can storage only up to 2.6 mass% at experiment condition [1]. Recently, researches claimed that carbon nanostructure materials in the form of tubes [2-7], graphite [8], and fibers [9-11], may be used for efficient hydrogen storage. Ye et al. used high-purity single-walled carbon nanotubes and obtained 8.0mass% H<sub>2</sub> adsorption at 80 K above 100 bars [2]. Dollin et al. found that single wall carbon nanotube (SWNT) soots could absorb about 5 to 10 weight % of H<sub>2</sub> at 133 K and 300 torr [4]. Browning et al. reported that 6.5mass% hydrogen can be stored in carbon nanofibers under conditions of 120 bars pressure and ambient temperature [9]. Chambers et al. observed that at 120 atmospheric pressure and room temperature, graphite nanofibers with herringbone structure could store 67 weight % of H<sub>2</sub> [11]. Chen et al. reported a H<sub>2</sub> storage system with which H<sub>2</sub> uptake can achieve 20 weight% for Li-doped CNT 653 K or 14 weight% for K-doped CNT at room temperature [5]. But later researches revealed that the high H<sub>2</sub> uptakes in Ref. 9 were due to the impurity water present in the hydrogen feedstream rather than to H<sub>2</sub> [6-7].



Besides physisorption, chemisorption has also been proposed for hydrogen storage in carbon nanotubes. The C-H bond forms when atomic hydrogen adsorbs on SWCNT being shown by studies [12,13]. Recently, theoretical researches [14-20] reported that high coverage up to 7.5 weight% storage can be achieved through chemisorption on the nanotubes. Yang et al. found that the storage capacity of hydrogen depends on the diameters of carbon nanotubes and the hydrogen coverage up to 100% for is stable the SWCNT tube [19]. Nikitin et al. showed approximately  $5.1 \pm 1.2$  weight % hydrogenation of SWCNTs with diameters ranging from 1 to 1.8 nm has been realized, which is a reversible process [20]. The stable structures and mechanical properties of the hydrogenated nanotubes which are necessary to practical applications also are meaningful for exploration. In effect, the stability and band structure of the hydrogenated nanotubes for different adsorption pattern and hydrogen coverage is needed to be investigated. The effect of distribution of hydrogen atoms under the same adsorption pattern and coverage is interesting. This will provide the comprehensive understanding of the effect of hydrogen adsorption on the carbon nanotube.

## 2. Methods

In this paper, we investigated the structural and electrical properties of hydrogenated single-walled carbon nanotube, using SIESTA (Spanish Initiative for Electronic Simulations with Thousands of Atoms) [21-23] approach within local density approximation (LDA). On a mesh with an energy cutoff of 210 Ry, we adopted the variable cell conjugate gradient algorithm to relax the structures. We set the force convergence criterion on each atom to be  $0.005 \text{ eV/\AA}$ , and the stress tolerance was 0.01 GPa. The intertubular distance is  $10 \text{ \AA}$ , which is large enough to eliminate the interplay for neighboring carbon nanotubes. We also obtained the energy band structures of optimized geometries for different coverage in order to compare the effect of hydrogen adsorption at different levels.



**Figure 1.** Side view of the SWCNT with the sites of atomic hydrogen labelled.

Previous studies indicated that the hydrogen atoms might prefer to form dimer and chain along the axis of the tube [15, 19]. The sites of atomic hydrogen on the wall of carbon nanotube are showed in Figure 1. The hydrogen atoms trend to form hydrogen dimer [15, 19]. We focused on the specific coverage on nanotubes, considering three typical patterns: pattern A, the vertical chain pattern [24]; pattern B, the dimer pattern [24]; pattern C, the parallel polyacetylene-like chains pattern [25]. The hydrogen atoms adsorb 1-2 sites, 2-3 sites and 1-2-3-4 sites forming pattern A, pattern B and pattern C, respectively. Herein, the formulas expressing the atom number per unit of the hydrogenated SWCNTs are  $C_{28}H_8$ ,  $C_{28}H_{16}$ ,  $C_{28}H_{20}$ ,  $C_{28}H_{28}$ ,  $C_{32}H_8$ ,  $C_{32}H_{16}$ ,  $C_{32}H_{24}$ ,  $C_{32}H_{32}$ ,  $C_{36}H_8$ ,  $C_{36}H_{20}$ ,  $C_{36}H_{28}$ ,  $C_{36}H_{36}$  and so on. For  $C_{32}H_{16}$ , we considered nine hydrogenated configurations in one pattern A, one pattern B and seven pattern C configurations. The adsorption energy per hydrogen atom is defined as below

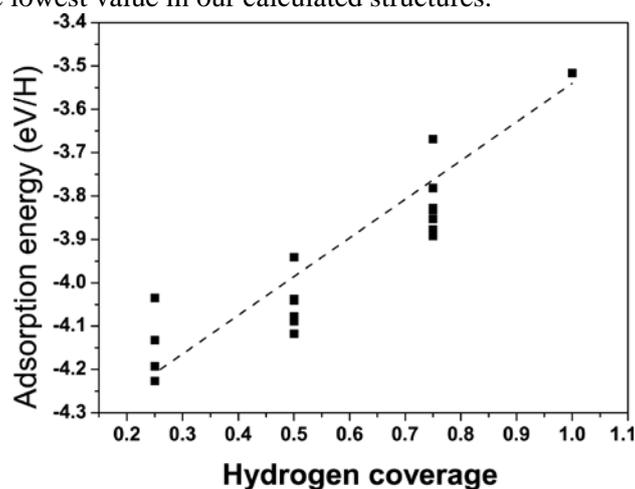
$$E_{ad} = (E_{H-SWCNT} - E_{SWCNT} - n_H E_H) / n_H$$

Where  $E_{SWCNT}$  is the total energy of carbon nanotube,  $E_H$  is the total energy of an isolated H atom,  $E_{H-SWCNT}$  is the energy of the hydrogenated nanotube,  $n_H$  is the number of hydrogen atom. The low value of  $E_{ad}$  indicates the high stability.

### 3. Results and discussion

#### 3.1. The adsorption energies and structures of the hydrogenated SWCNTs.

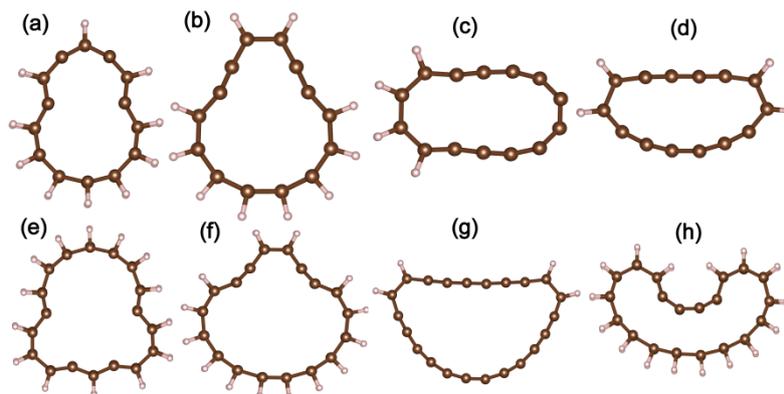
For the comparison of stability, adsorption energies per hydrogen atom of hydrogenated carbon nanotube (8,0) at different coverages are plotted in Figure 2, the dotted line shows the global tendency of the adsorption energy. We found that the length of C-H bond is 1.11-1.13 Å, the length of C-C bond ranges from 1.40 to 1.57 Å and the adsorption energies increase linearly as the hydrogen coverage increased, which is in agreement with previous reports [15], indicating the weak stability. The configurations with a small quantity of hydrogen atoms show high stability, such as C<sub>32</sub>H<sub>8</sub>, the bottom left in Figure 2, have the lowest value in our calculated structures.



**Figure 2.** The adsorption energies per hydrogen atom at three adsorption coverages

It is noted that the adsorption energies belonged to three patterns have a variation at the same coverage as shown in Figure 2. The adsorption configurations in pattern C have obvious fine performances which have presented in our studies [26, 27]. In addition, there are two transitions in pattern C configurations [26, 27] and the structures with the hydrogen atoms in disperse manner having lower adsorptions energies. It indicates that hydrogen atoms do not prefer to form clusters on the surface of SWCNT. The diameters of hydrogenated SWCNTs vary with the hydrogen coverage. For the coverage of 100%, the diameter of circular cross section of the adsorption configuration is 7.280 Å which is larger than that of fully relaxed geometry of nanotube (8,0). This is caused by the forming of C-H bond with sp<sup>3</sup> hybridization, which is in agreement with report [28], the ∠CCH bond angles ranges from 104.1o to 111.3o which are close to the ideal tetrahedral sp<sup>3</sup> bond angle of 109.5o. The hydrogen atoms are not symmetrical distributed, thus the cross section of stable configurations becomes collapsed due to the carbon atoms relatively move towards inside.

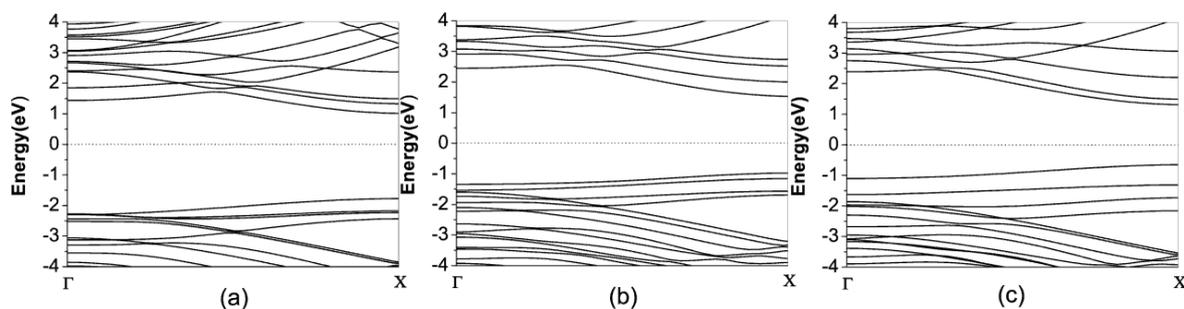
The shapes of the hydrogenated carbon nanotube are listed in Figure 3, it is seen that the structure deformation are induced by the adsorption. For high hydrogenation, the configurations in pattern A are listed in Figure 3a and Figure 3e, the configurations in pattern C are showed in Figure 3b, Figure 3f and Figure 3h, the atomic hydrogen stretches outward leading to “beetle” shape. For low hydrogenation, as shown in Figure 3c, Figure 3d and Figure 3g, the structures form in the shape of “lip”. It is deduced that the hydrogen adsorption affects obviously the structure of nanotube for all adsorption patterns. The asymmetric distribution of hydrogen atoms affects the structure largely without the balanced effects of hydrogen atoms.



**Figure 3.** The top views of the hydrogenated nanotubes for (a)  $C_{28}H_{20}$  configuration in pattern A, (b)  $C_{28}H_{20}$  configuration in pattern C, (c)  $C_{28}H_8$  configuration in pattern C with hydrogen atoms together (d)  $C_{28}H_8$  configuration in pattern C with dispersed hydrogen atoms, (e)  $C_{36}H_{28}$  configuration in pattern A, (f)  $C_{36}H_{28}$  configuration in pattern C, (g)  $C_{40}H_8$  configuration in pattern C, (h)  $C_{40}H_{32}$  configuration in pattern C.

### 3.2. The energy band structures of the hydrogenated SWCNTs.

We have presented the electrical properties of hydrogenated SWCNTs and discussed two transitions [26]. In this paper, the energy band structures of configurations in pattern A, pattern B and pattern C were investigated, the variations related with the dispersed extent of atomic hydrogen were also discussed. For example, as shown in Figure 4, the typical three band structures in pattern A with the formula as  $C_{36}H_{28}$  were chosen and plotted.

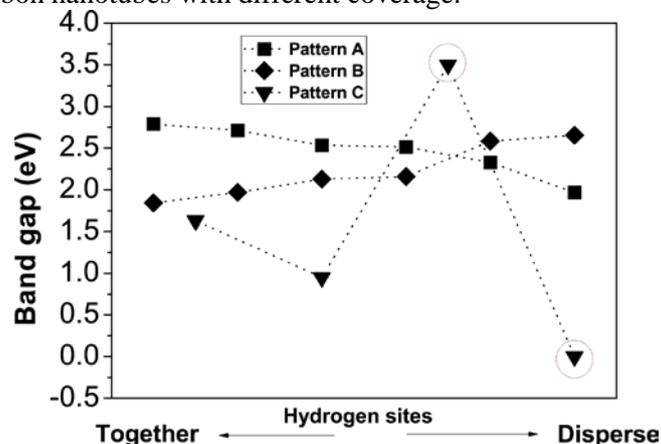


**Figure 4.** The three band structures of  $C_{36}H_{28}$  in pattern A.

Firstly, the adsorbed hydrogen atoms are gathered, the energy bands of configuration are depicted in Figure 4a, which has a band gap of 2.79 eV. The value of gap has reduced to 2.51 eV as the adsorbed hydrogen atoms divide into two parts with a small interval showed in Figure 4b. If the interval is further enlarged, the gap may continue to decrease to 1.97 eV in Figure 4c. In summary, the band gap has the largest value for configuration with hydrogen atoms together, and decreases as the hydrogen atoms are apart. The analogous results are found in all of the hydrogenated carbon nanotubes with the adsorbed manner of pattern A. But this is not applied to the case of hydrogenated carbon nanotubes in pattern B and pattern C.

Figure 5 shows the band gap values of three patterns in the formula of  $C_{32}H_{24}$ . As shown, there is an opposite tendency for pattern B configurations compared with pattern A ones. It is found that the value of band gap decreases as the hydrogen atoms are together, which is reduced from 2.66 eV for all hydrogen atoms dispersed as far as possible to 1.84 eV for the hydrogen atoms close together. For pattern C configurations, the band gap value also decreases as the degree of dispersing increases except two values signed in dotted circle in Figure 5 corresponding to the transitions [26, 27]. It is shown that the band gaps for zigzag nanotubes are sensitive to the adsorption manner and the

distribution of the atomic hydrogen. It shows that the value of band gap may be controlled by adjusting the adsorption manner or the distribution of the hydrogen in the certain adsorption manner, the gap even may be zero in pattern C configurations. The similar conclusions are obtained from the other hydrogenated carbon nanotubes with different coverage.



**Figure 5.** The band gap values of three patterns in the formula of  $C_{32}H_{24}$ .

In general, the stability of hydrogenated nanotubes deteriorates with the increasing of the hydrogen adsorption, but to some extent, the manner of adsorption may improve it. On the other hand, the electrical properties may be designed by choosing the manner of adsorption and the distribution of hydrogen atoms in forming of structure constriction. Therefore, our calculations showed that the effect of hydrogenation may be comprehensive treated in the aspects of stability and band structure.

#### 4. Conclusions

We researched the stable adsorption configurations by altering the hydrogen coverage, and found that the adsorption energy ascends with the increasing of the hydrogen adsorption, indicating the poor stability. The adsorption pattern and the distribution of the atomic hydrogen may affect the adsorption energy and structural deformation. The cross section of configurations become various shapes such as “beetle” or “lip” appearance without the balanced effects of hydrogen atoms. The electrical properties of hydrogenated nanotubes demonstrate varied trends as the distribution and adsorption pattern have altered. For  $C_{32}H_{24}$ , the band gap may reach the large value of 2.79 eV in the adsorption pattern A configuration and reduce to be zero in the adsorption pattern C case, the values of band gap for pattern A configurations decrease, which is opposite of the pattern B configurations as the adsorption hydrogen becomes more disperse. It provides the possibility that the band gap may be controlled by adjusting the adsorption pattern and the distribution of the atomic hydrogen.

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