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Hydrogen adsorption in defected carbon nanotubes

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Abstract Recently there has been lot of interest in the development of hydrogen storage in various systems for the large-scale application of fuel cells, mobiles and for automotive uses. Hectic materials research is going on throughout the world with various adsorption mechanisms to increase the storage capacity. It was observed that physisorption proves to be an effective way for this purpose. Some of the materials in this race include graphite, zeolite, carbon fibers and nanotubes. Among all these, the versatile material carbon nanotube (CNT) has a number of favorable points like porous nature, high surface area, hollowness, high stability and light weight, which facilitate the hydrogen adsorption in both outer and inner portions. In this work we have considered armchair (5,5), zig zag (10,0) and chiral tubes (8,2) and (6,4) with and without structural defects to study the physisorption of hydrogen on the surface of carbon nanotubes using DFT calculations. For two different H_2 configurations, adsorption binding energies are estimated both for defect free and defected carbon nanotubes. We could observe larger adsorption energies for the configuration in which the hydrogen molecular axis perpendicular to the hexagonal carbon ring than for parallel to C–C bond configuration corresponding to the defect free nanotubes. For defected tubes the adsorption energies are calculated for various configurations such as molecular axis perpendicular to a defect site octagon and parallel to C–C bond of octagon and another case where the axis perpendicular to hexagon in defected tube. The adsorption binding energy values are compared with defect free case. The results are discussed in detail for hydrogen storage applications.

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Keywords Carbon nanotube · Hydrogen adsorption · Defects · Chiral · Achiral

Abbreviations

CNT	Carbon Nanotube
DFT	Density Functional Theory
SWCNTs	Single Walled Carbon Nanotubes
H_2	Hydrogen molecule
H	Hydrogen atom
E_{ads}	Adsorption binding energy
1 Å	$= 10^{-10}$ m
1 eV	$= 1.602 \times 10^{-19}$ J
O	Octagon
P	Pentagon

1 Introduction

Ever since the discovery of Carbon Nanotubes (CNTs), vigorous research is going on to explore the tremendous potential of these nanostructures in diverse fields of applications such as flat panel display, microelectronic devices, chemical and electromechanical sensors and fuel cell (Sinnot et al. 2001). One of the recent researches on CNT focuses on its hydrogen storage capacity for several electronic and automotive power sources. These nanomaterials are predicted to be a suitable choice due to its lightweight, high mechanical strength, porous nature and nano size (Gulseren et al. 2001). Between the two possible ways of adsorption like chemisorption and physisorption, latter proves to be a stable and efficient process for hydrogen in carbon nanotubes (Alonso et al. 2004).

Both experimental and theoretical studies exist on the adsorption of molecular and atomic hydrogen in carbon nanotubes (Dillon et al. 1997; Arellano et al. 2002). In spite of

numerous publications on CNT as hydrogen storage material still there is lack of consensus on the reported values of storage capacity in these nanostructures, which makes the adsorption study an essential and significant one to get a clear data on various parameters. Hence by considering specific type of samples and studying the adsorption characteristics may reveal the suitable tube parameters like diameter, defects and chirality for optimizing the storage capacity in nanotubes.

Several theoretical works based on simulation studies were published on the hydrogen adsorption in single walled carbon nanotubes (SWCNTs). These works considered SWCNTs without any structural defects. Cracknell, in his work has observed that the H_2 adsorption is more inside the tube due to curvature effect (Cracknell 2002) and it has also been reported that the doped CNTs show an improved storage capacity of hydrogen. In their model calculation on adsorption, it has been reported that the possibility of high adsorption in these novel materials is approximately of the order of 6.5 wt%.

Single walled carbon nanotubes proved to have better storage performance over other nanostructures like activated carbon of larger surface area indicating the active role of curvature and porous nature of CNTs apart from chirality (Poirier et al. 2004). There exists literature on adsorption studies on hydrogen and Aluminum atom in SWCNTs with various diameters using the density functional calculations in which it was shown that H_2 could not be adsorbed in to the inner wall of the nanotube contradicting the previous claim (Tada et al. 2001). Lot of research is going on the bundle of SWCNTs with adsorption sites as grooves, interstitial channels, outer surface of bundle, and inner part (pore) of the tube. The observed adsorption binding energies (E_{ads}) are ordered as E_{ads} (channels) > E_{ads} (grooves) > E_{ads} (pores) > E_{ads} (surface) (Pradhan et al. 2002a). In an extensive study on the interaction of molecular and atomic hydrogen with SWCNTs, Alonso and his group have reported the DFT calculations for physisorption with armchair tubes (Alonso et al. 2004). Using ab initio methods Krasheninnikov et al. have studied the adsorption and migration of carbon adatoms on zigzag carbon nanotubes (Krasheninnikov et al. 2004). During the adsorption process the possible positions of hydrogen molecule (commonly referred as H_2 configuration) on the outer surface of carbon nanotube are, above Carbon–Carbon bond (X), above carbon ring with molecular axis parallel (Y) and above carbon ring with molecular axis perpendicular to nanotube wall (Z). This is clearly shown in Fig. 1 for a typical carbon nanotube (Arellano et al. 2002). Extensive research on the issue of hydrogen adsorption for different configurations at various adsorption sites in the presence of defects becomes necessary to look in to the possible ways of improving the storage capacity, especially at the time, when the carbon nanotubes

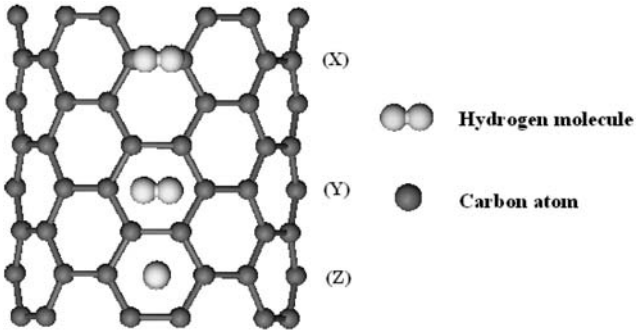

Fig. 1 Three different configurations of hydrogen molecule above a carbon–carbon bond (X) and above a hexagon with the molecular axis parallel (Y) and perpendicular (Z) to the nanotube wall

are emerging as a most suitable material for energy storage and fuel cell applications.

We have considered achiral carbon nanotubes (5,5), (10,0) and chiral tubes (8,2), (6,4) and estimated the adsorption binding energies (E_{ads}) of hydrogen molecule with two suitable configurations. In order to study the role of structural defects on hydrogen adsorption, we have introduced defects like pentagon and octagon in the hexagonal structure of the carbon nanotubes and calculated E_{ads} for different configurations with respect to these defect rings. To the best of our knowledge, so far no work has been done on hydrogen adsorption in defected carbon nanotubes either theoretically or experimentally. For the defect free case we have compared our result with Alonso et al. and found to be in good agreement. The computational details for calculating the physisorption binding energies and the method of construction of nanotubes of various types are given in detail in the next section.

2 Computation details

We have performed the DFT calculations for evaluating the adsorption binding energy of hydrogen molecule on outer surface of opened single walled chiral and achiral carbon nanotubes. The difference in electronegativity between hydrogen and carbon atom affects the nanotube-adsorbate interaction, so as to avoid this the dangling bonds at the stem ends were not saturated with H. The total energy of the system was estimated through simulation by means of Kohn sham equation. We have included the electron exchange and correlation effects through Generalized Gradient Approximation (GGA) with Perdew, Burke and Enzerhof (PBE) approach that are suitable for adsorption energy calculations. Another widely used approximation is Local Density Approximation (LDA) which is followed by Alonso et al. and also by several others (Alonso et al. 2004; Arellano et al. 2002; Pradhan et al. 2002b). It is still a controversy whether the GGA or LDA could describe correctly

Table 1 Number of carbon atoms and unit cells for carbon nanotube simulation

Type of tube	Number of unit cells	Number of C atoms present in CNT		Tube length (Å)	Number of defects
		Without defect	With defect		
(5,5)	5	100	98	14.6	2P, 1O
(10,0)	3	120	118	12.2	2P, 1O
(8,2)	2	112	110	13.7	2P, 1O
(6,4)	1	152	150	17.2	2P, 1O

P—Pentagon, O—Octagon

the Van der Waals interaction between H_2 and carbon nanotube surface as observed by Seung and Young in their recent work on hydrogen adsorption (Jhi and Kwon 2004). For fast computation we have chosen minimal basis (MIN) as numerical basis set with global orbital cut off 3.5 Å. From the well known expression for calculating the molecular adsorption binding energies, E_{ads} are obtained for various cases of our study.

$$E_{ads} = E_{CNT} + E_{Hydrogen} - E_{CNT+Hydrogen} \quad (1)$$

where E_{CNT}, $E_{CNT+Hydrogen}$, and $E_{Hydrogen}$ are total energy of free carbon nanotube, CNT with adsorbate and single hydrogen molecule respectively.

For the present work we have considered five unit cells of (5,5) armchair tube with 100 carbon atoms and three unit cells of (10,0) zig zag tube with 120 atoms as achiral type tubes. The diameter values of (5,5) and (10,0) are 6.8 Å (1 Å $= 10^{-10}$ m) and 7.81 Å respectively. It is known that the chiral angle is 30° for armchair metallic type and 0° for zig zag semiconducting tube.

For the case of chiral nanotube we have constructed two unit cells of (8,2) with 112 atoms and single unit cell of (6,4) with 152 atoms having chiral angles 10° and 23°. All these tubes are taken to have tube length approximately ranging from 12 Å to 17 Å. These details are shown in Table 1.

To study the role of structural defects on hydrogen physisorption on carbon nanotubes, defects like pentagon and octagon are inserted in the normal hexagonal structure of CNTs. Such an insertion of defects slightly deforms the tube as expected. Calculations are performed on the adsorption binding energies by taking the 'defect rings' as adsorption sites. The binding energy values are also estimated at the hexagon site in the defected tubes for comparison. Computations are repeated for different hydrogen configurations. The results for various cases are analyzed and their significance is discussed in the next section.

3 Results and discussion

In this section we discuss the construction and adsorption binding energy values of single hydrogen molecule for the two cases of carbon nanotubes namely with and without defects.

3.1 Without defect

We have considered two achiral and two chiral tubes of metallic and semiconducting types. As a first case hydrogen molecule is placed above the carbon-carbon bond of hexagonal structure with molecular axis parallel to C–C bond (configuration (X) in Fig. 1). We have observed that the adsorption binding energy of H_2 on (5,5) tube is 0.072 eV with H_2 molecule separation (D) 6.316 Å from nanotube axis. This result is slightly greater than 0.068 eV of Alonso et al. using LDA calculations (Alonso et al. 2004). This difference is due to the consideration of strong exchange correlation effects through GGA calculations, which is reasonable for metallic type tubes. The zig zag tube (10,0) exhibits higher binding energy value 0.095 eV than other types and it may be due to its larger diameter. In the case of chiral nanotubes, (8,2) gives adsorption binding energy 0.093 eV, whereas (6,4) tube exhibits a value of 0.077 eV, which is very close to that of (5,5) tube. This we attribute it to more or less the same diameter of (6,4) and (5,5). Here we could observe that the chirality does not affect the physisorption as already observed by Alonso et al. in their simulation studies. These results are shown as a part of Table 2.

We have considered another interesting configuration (Z) in which the hydrogen molecule is placed with its molecular axis perpendicular to the hexagonal ring. Fig. 2(a) shows H_2 adsorbed (8,2) and Fig. 2(b) shows hydrogen adsorbed (6,4) tube for the configuration (Z). Since the molecule is able to fit better into the electron density valley that exists on the center of the hexagons, this configuration is known to be most stable of all three configurations discussed so far in this paper. The estimated adsorption binding energy values along with separation for this configuration are given in Table 2.

From Table 2 we could observe for all types of tubes, the separation value decreases for configuration (Z) compared to configuration (X), which reflects in the E_{ads} values. We could observe an increase of 0.19 eV, 0.17 eV, 0.15 eV and 0.18 eV (for (5,5), (10,0), (8,2) and (6,4) respectively) in adsorption binding energies for (Z) configuration over that of (X). This trend shows that the perpendicular to carbon ring configuration (Z) is more stable than parallel to C–C bond configuration (X) as expected from the previous studies. Another interesting point observed for configuration (Z) is that

Table 2 Separation values (D) and adsorption binding energies calculated for two different configurations in defect free carbon nanotubes

Type of CNT	Hydrogen molecule configuration			
	Molecular axis parallel to C–C bond of hexagon		Molecular axis perpendicular to hexagon	
	Separation* (Å)	E_{ads} (eV**)	Separation (Å)	E_{ads} (eV)
(5,5)	6.316	0.072 (0.068#)	5.626	0.262
(10,0)	6.915	0.095	6.105	0.263
(8,2)	6.486	0.093	5.646	0.243
(6,4)	6.287	0.077	5.778	0.255

*Separation refers the distance from tube axis to H_2 molecule

**$\text{eV} = 1.602 \times 10^{-19}$ J

#Adsorption binding energy value observed by Alonso et al. through LDA approach

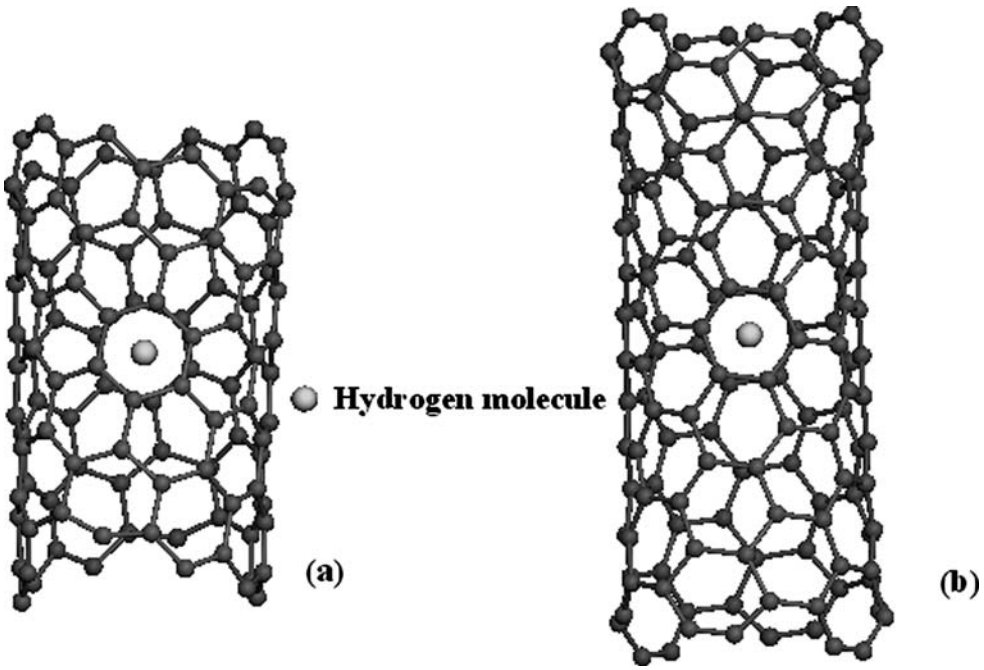

Fig. 2 Configuration (Z) at hexagonal ring of (**a**) (8,2) and (**b**) (6,4) chiral carbon nanotubes

E_{ads} comes out to be the same for armchair and zig zag type unlike for the configuration (X).

3.2 With defect

The presence of structural defects such as pentagon and octagon play a significant role in the electrochemical properties like adsorption on the nanotubes. Several literature works exist on the study of adsorption in defect free carbon nanotubes and most of these are for symmetric type only. Here, in this paper we have taken both chiral and achiral type for our study. To see the effect of structural defects on the H_2 adsorption in carbon nanotube one octagon and two pentagons are inserted in the hexagonal structure of all types of tubes considered here. Figure 3 shows hydrogen adsorption for configuration (X) with respect to octagon introduced in (a) (8,2) and (b) (6,4) carbon nanotube and Fig. 4 shows hydrogen adsorption for configuration (Z) with respect to octagon in defected (6,4) chiral carbon nanotube.

Adsorption binding energies for configuration (X) and (Z) with respect to octagon at higher curvature and for configuration (Z) with respect to hexagon in defected tube are calculated as mentioned above where E_{CNT} in (1) now refers to total energy of defected tube. The graph shown in Fig. 5 gives the binding energy changes as a function of separation for configuration (X) with respect to octagon in defected (5,5) and (10,0). For all types of tubes, the separation value (D) decreases with respect to octagon compared to defect free tubes confirming the role of defects on the physisorption phenomena. The observed adsorption binding energies and the corresponding separation values for configuration (X) with respect to octagon are shown in Table 3.

It is claimed that the value of adsorption binding energy has to be around 0.2 to 0.3 eV for possible techno-

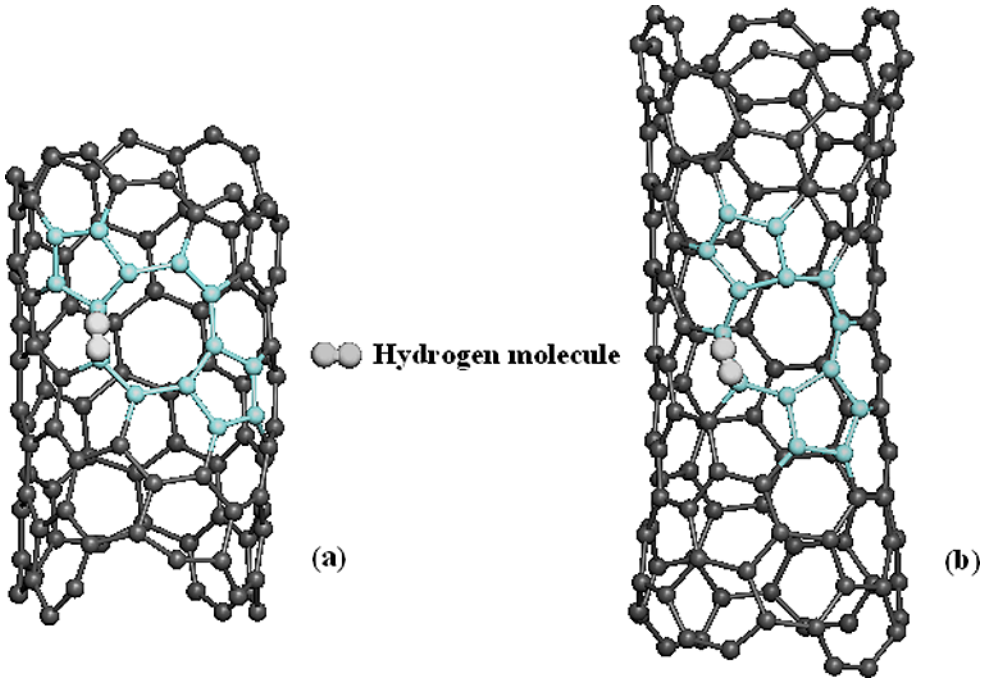

Fig. 3 Defected (**a**) (8,2) and (**b**) (6,4) nanotubes for configuration (X) with respect to octagon at higher curvature. *Light colored portion* indicates the presence of octagon and pentagons in the nanotube

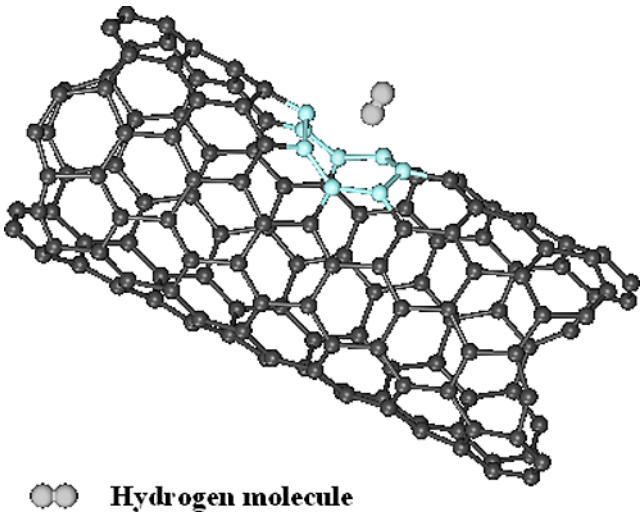

Fig. 4 Defected (6,4) carbon nanotube for configuration (Z) at octagon. *Light colored portion* indicates the presence of octagon in the nanotube

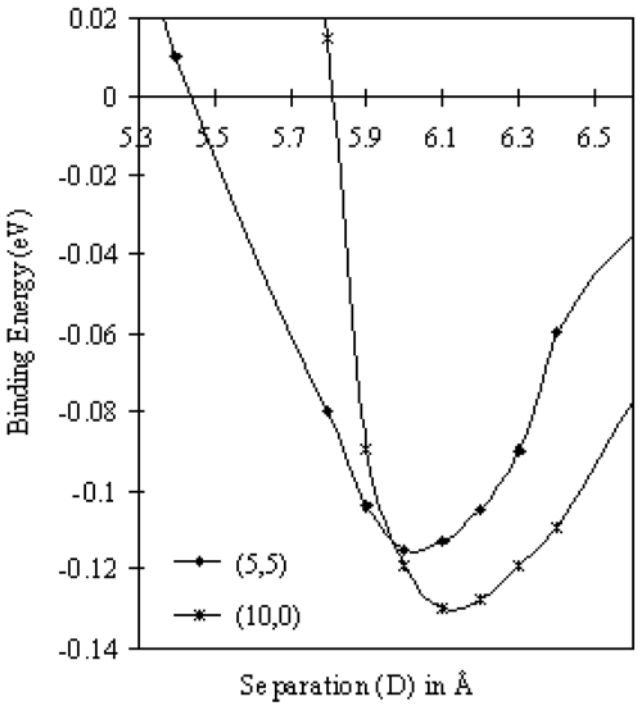

Fig. 5 Binding energy variation of H_2 as a function of separation for configuration (X) with respect to octagon in defected (5,5) (*filled diamond*) and (10,0) (*asterisk*) carbon nanotubes

logical applications such as Fuel cells. Here we discuss the results corresponding to the octagon defects in carbon nanotubes. For (8,2) tube with respect to configuration (X) our results show 50.54% increase in adsorption binding energy compared to defect free case while there is an increase of 55.84% for (6,4) tube. Similarly we could observe for defected (5,5) armchair tube 59.72% and 36.84% for defected (10,0) zig zag semiconducting tube. In reference (Pradhan et al. 2002b), it was reported that the defect induced disorder in nanotubes might enhance the physisorption binding energy of H_2 molecules. Our results agree very well with this observation although there are no experimental values to compare the data.

We have also considered the configuration (Z) in which hydrogen molecule interaction is perpendicular to the carbon ring. For this configuration we have considered two

Table 3 Separation values (D) and E_{ads} for configuration (X) with respect to octagon at higher curvature

Type of CNT	Diameter (nm)	Separation (Å)	E_{ads} (eV)
(5,5)	0.677	6.031	0.115
(10,0)	0.781	6.154	0.130
(8,2)	0.716	6.025	0.140
(6,4)	0.681	5.856	0.120

Table 4 Separation values (D) and E_{ads} for configuration (Z) with respect to octagon and hexagon in defected tubes

Type of CNT	Hydrogen molecule configuration			
	Molecular axis perpendicular to octagon		Molecular axis perpendicular to hexagon*	
	Separation (Å)	E_{ads} (eV)	Separation (Å)	E_{ads} (eV)
(5,5)	4.969	0.247	4.874	0.287
(10,0)	5.603	0.250	5.775	0.269
(8,2)	5.376	0.248	5.558	0.238
(6,4)	5.157	0.244	5.230	0.256

*Here we would like to mention that we have considered the hexagonal ring in presence of octagon and pentagons

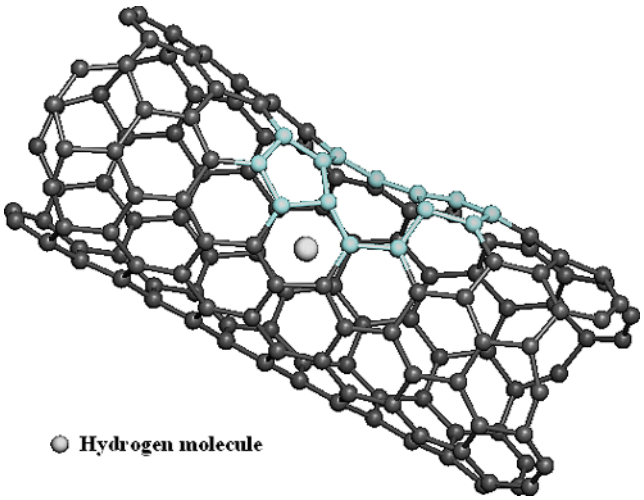

Fig. 6 Defected (6,4) carbon nanotube for configuration (Z) at hexagon nearer to octagon. *Light colored portion* indicates the presence of octagon in the system

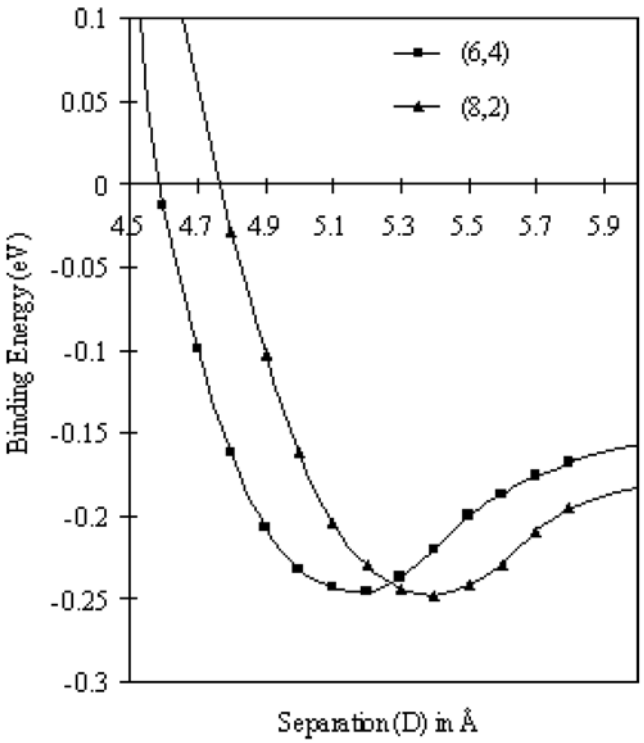

Fig. 7 Binding energy variation of H_2 as a function of separation for configuration (Z) at octagon in defected (6,4) (*filled square*) and (8,2) (*filled triangle*) carbon nanotubes

kinds of carbon rings, one in the form of octagon and another hexagon in the defected tubes. Figure 6 shows (6,4) tube for configuration (Z) at hexagonal ring in presence of octagon. Figure 7 shows a graph between separation and binding energies for this configuration at octagonal ring in defected (6,4) and (8,2) CNTs. The estimated adsorption binding energy values and the corresponding separation for equilibrium adsorption for both hexagonal and octagonal rings are given as Table 4.

In this part we discuss first the configuration (Z) corresponding to hexagon in defected nanotube. There is not much appreciable change in adsorption binding energies for this site between defect free and defected tubes. It is interesting to note that there is a difference of 0.031 eV in adsorption energies of (5,5) and (6,4) indicating the effect of chirality on the hydrogen adsorption in the presence of defects unlike in the defect free case.

Next we discuss the configuration (Z) with respect to octagonal ring. The calculated adsorption binding energies are lower than that at hexagonal ring for the present case discussed in the previous paragraph. When we compare the values with that of defect free case we could observe a decrease of the order of 0.01 eV for all type of tubes except for (8,2) tube where there is an increase in binding energy. Comparison of Table 2 (defect free case) and Tables 3 and 4 for the variation in E_{ads} indicates the role of defects on hydrogen adsorption in single walled carbon nanotubes, which is the main result of our present study.

4 Conclusion

In conclusion we could say that defects have an important contribution to the adsorption mechanism of single walled carbon nanotubes of different types and sizes. There is a considerable increase in the adsorption binding energy of the order of 50% due to the presence of structural defects in CNTs, which will definitely affect the hydrogen storage capacity in carbon nanotubes. This result may prove to be an interesting one that needs more attention on the aspect of physisorption in chiral single walled carbon nanotube and also other nanostructures. Work is under progress on this issue.

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