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ab initio study of the exo-hydrogenated single wall carbon nanotubes

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ABSTRACT

Stability of the fully exo-hydrogenated zigzag (n,0) and armchair (n,n) single wall carbon nanotubes (C_nH_n) is studied using first-principles calculations. Zigzag and armchair carbon nanotubes (CNTs) were found to be different in electronic and atomic structures with respect to chemical hydrogenation. It was noted that the binding energy of hydrogenated carbon nanotubes revealed an approximately inverse proportionality behaviour with their diameter. Moreover, each single hydrogen atom was attached to nanotube by an exothermic process. The similar diameter exo-hydrogenated zigzag nanotubes were found to be energetically more favourable than armchair nanotubes. The calculated values of band gaps in small hydrogenated zigzag CNTs were found to be higher in both types of hydrogenated CNTs. These findings were important for particular functionalization of hydrogenated carbon nanotubes and improve the understanding to separate similar diameter zigzag and armchair nanotubes from each other through chemical functionalization.

1. Introduction

Over the past three decades, some major issues are facing by the world, which include decreasing the supply of fossil fuels and increase in the rate of global warming with climate change. The key solution to these problems lies in developing new methods of energy production and utilization of hydrogen and its storage [1]. Hydrogen can be used efficiently for an alternate and renewable source because it can be extracted from water. The beneficial and productive storage of hydrogen for mobile applications is still a vital challenge for the scientific and industrial community [2]. Considerable amount of work has been done on carbon as hydrogen storage. Carbon has major utilization for a catalyst support and in fuel cell electrodes [3]. In 1997, Dillon et al. performed the first study of using the Single Wall Nanotube (SWNT) as hydrogen storage material. It was reported a storage of 10 wt.% of hydrogen in SWNT, this was measured using the temperature desorption programme [4]. However, Schimmel et al. [5] reported the storage capacities of carbon materials upto 2.5 wt. % due to adsorbing the large amount in pores of carbon nanotubes. After these study, researchers mainly focused to use carbon nanotubes for hydrogen storage purposes. Nikitin et al. [6] found that hundred percent hydrogenated SWCNT with diameter 2 nm could be stable at room temperature along with hydrogen storage capacity of about 7 wt.%. Park et al. [7] reported the atomic and electronic structures of hydrogen–chemisorbed single wall CNTs. In their study, they investigated relative stability of various hydrogen adsorption geometries with surface coverage. Hydrogen adsorption and storage were calculated in pristine and cobalt doped single walls CNTs using DFT and suggested that transition metal atoms can increase exo-hydrogenation [8]. The band gap of carbon nanotubes also changed with hydrogen coverage and is independent of metallicity of nanotubes. This may be caused by sp^3 hybridization in hydrogenated CNTs [9,10]. In all studies reported previously about chemisorbed hydrogenated carbon nanotubes [11,12], C—H bond formation, binding energies and band gaps were not systematically and properly studied using density functional theory. Therefore, this report gives insight into the smaller to larger diameters carbon nanotubes for hydrogen storage purposes. This report can be helpful to investigate hydrogen release temperature of hydrogenated CNTs. Further, this study also leads to researchers for band gap opening in hydrogenated CNTs for their optoelectronic applications.

2. Computational method for structural properties

Carbon nanotubes [13] show interesting structural and electronic properties with wide variety of technological applications especially storage of hydrogen. Absorption capacity of nanotubes to store hydrogen varies from 10 wt.% to 0.4 wt.% as reported by different researches [14–16]. Study of hydrogen chemisorption in nanotubes still

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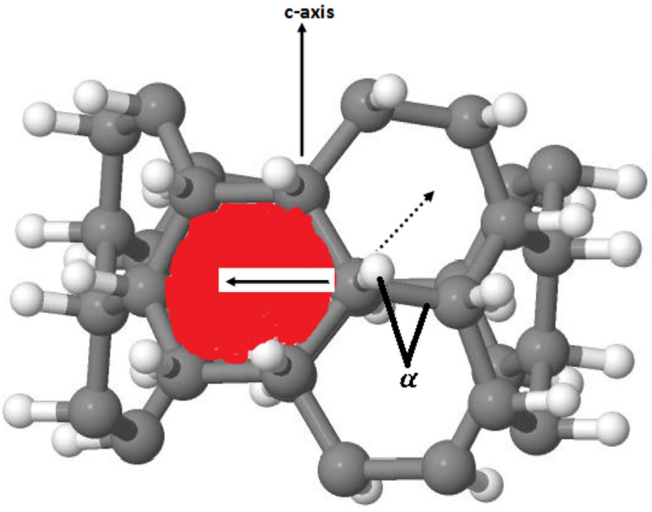

Fig. 1. The arrows show rotation of C—H bond along symmetry directions for optimization of CNT (4,4)H structure.

needs better understanding of hydrogen and nanotube systems [17]. In order to calculate binding energy, initial geometries were generated using the TubeGen tool [18] based on the hexagonal unit cell geometry. The single hydrogen atom was attached externally with each carbon atom to form C—H bond of value 1.10 Å. This study is based on the assumption that all carbon atoms in a nanotube are hybrid with hydrogen atoms from outside as shown in Fig. 1. The cut-off energy of 540 eV is used in these calculations. The Brillouin zone was sampled using a Monk-Pack [19] grid of 1 × 1 × 20 of k-points. An ultrasoft pseudopotential [20] was used along with a GGA-PBE functional [21] to perform these calculations and on the fly (OTF) pseudopotentials were generated by CASTEP code [22] based on density functional theory [23,24]. For pseudopotential, cut-off radii $r_{c,H}$ and $r_{c,C}$ have values of 0.423 Å and 0.741 Å respectively. The H—H atom distance for any two hydrogenated CNTs was arranged in the range of 6–9 Å to make sure isolated hydrogenated CNTs. The CNT (4,4)H structure was tested to consider C—H rotation along high symmetry directions as shown in Fig. 1. Single point energy calculations were done to find out optimum orientations of CNT (4,4)H. The local C—C—H bond angle (α_{CCH}) curves in Fig. 1 are tilted about c-axis in armchair CNTs to obtain optimum bond angles. Arrows indicate possible directions of rotations of C—H bond.

Hydrogen atoms were shifted by small displacement along z-axis and structures were relaxed to ensure the equilibrium orientation of bonds along z-axis. The hydrogenated CNTs were fully relaxed by optimizing all the positions along tube axis until maximum force and stress are less than 0.05 (eV/Å) and 0.1 GPa and each atom was moved less than 10^{-3}Å as in Fig. 2. The H—H distance between two CNTs was calculated in the range of 6–9 Å in order to generate isolated hydrogenated CNTs as shown in Fig. 3.

Similarly, optimum orientation was also obtained for hydrogenated zigzag CNT (4,0)H along c-axis when C—H bond tilted along the positive and negative directions. Fig. 4 shows the geometry optimized structure of CNT(4,0)H for tilted C—H bond along z-axis. The single point calculations were carried out to find the optimum bond angle for CNT (4,0)H as shown in Fig. 5.

3. Binding energy calculations for exo-hydrogenated CNTs

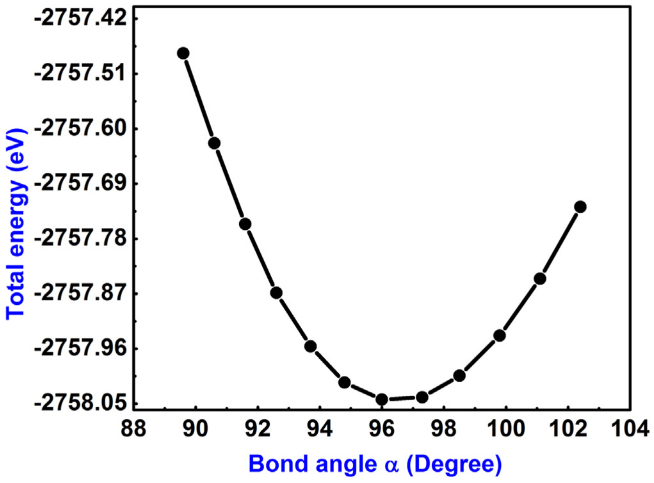

Fig. 2. Energy minimization curve of CNT (4,4)H by rotation of C-H bond along high symmetry direction.

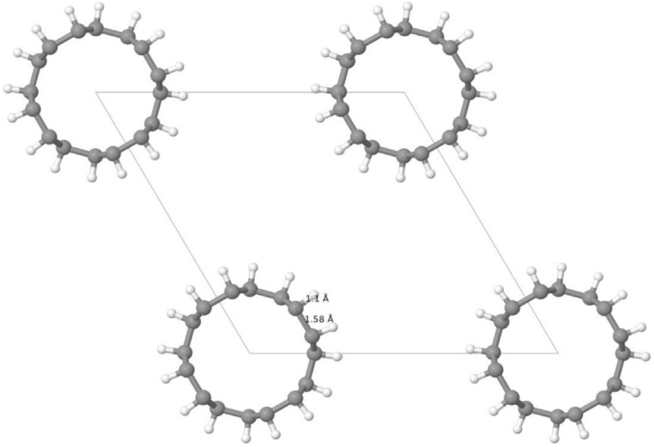

Fig. 3. The H-H distance represents the separation of geometry optimized structure of CNT(4,4)H.

The bond lengths and bond angles given in Table 1 can be determined for the optimized pristine zigzag and armchair nanotubes structures. The C—C bonds of two kinds were calculated in both types of zigzag and armchair CNTs. In first type C—C bond length ($\mathbf{d_{CC}}$) was found to increase with increase in diameters and in the second type $\mathbf{d_{CC}}$ was observed to decrease with increasing diameters of zigzag CNTs. On the other hand, $\mathbf{d_{CC}}$ lengths of both types were observed to decrease with an increase in diameters (D) for armchair CNTs. The calculated C—C—C bond-angles in both zigzag and armchair CNTs were increased with the increase in diameters of CNTs.

The hydrogenated zigzag (n,0) and armchair (n,n) CNTs were geometrically optimized. The binding energy per hydrogen was calculated using relation [25]:

$$E_B(n) = (E(CNT) - E(CNT + nH))/n + E(H) \tag{1}$$

In equation (1), E(H) is the energy of an isolated single H atom and its calculated value in present study is about E(H) = −13.584 eV. Upon hybridization, value of the original C—C bond length was found to increase from 1.42 to 1.62 Å, which is typical for an sp^3 structure. From Table 2, it is seen that C—C bond length stretches more in armchair carbon nanotubes than zigzag CNTs due to hydrogenation. The increase in C—C bond length from its original value was found to be about 9–12% for zigzag CNTs and about 10–15% in arm chair CNTs. Both C—C and C—H bond lengths found to be weakly dependent on diameter of nanotubes. It is also observed that value of C—H bond length decreases with increase in diameters of CNTs.

On the other hand, local C—C—H bond angles (α_{CCH}) in arm chair CNTs deviated more than the ideal tetrahedral bond angle of 109.5°. It was observed that C—C—H bond angles (α_{CCH}) in zigzag CNTs are found to be closer to optimum value of tetrahedral sp^3 bonding than those of