Hydrogen storage capacity of Ti-doped boron-nitride and B/Be-substituted carbon nanotubes

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We investigate the hydrogen absorption capacity of two tubular structures, namely, B/Be-substituted single-wall carbon nanotube (SWNT) and Ti covered single-wall boron nitride nanotube (SWBNT) using first-principles plane wave method. The interaction of H_2 molecules with the outer surface of bare SWBNT, which is normally very weak, can be significantly enhanced upon functionalization by Ti atoms. Each Ti atom adsorbed on SWBNT can bind up to four H_2 molecules with an average binding energy suitable for room temperature storage. While the substitution process of Be atom on SWNT is endothermic, the substituted Be strengthens the interaction between tube surface and H_2 to hold one H_2 molecule.

INTRODUCTION

Safe and efficient hydrogen storage requires gravimetric density exceeding 6 wt % together with fast and reversible kinetics of absorption and desorption.[1,2] Nanostructures or porous substances having high surface to volume ratios have been favored for the high capacity storage medium.

There are several studies focused on carbon-based materials such as nanotubes,[3–8] fullerenes (i.e., C_{60}),[9,10] metal hydrides and metal-organic frameworks,[11,12] titanium metallocarbohedryne,[13,14] polyacethylene,[15] and transition-metal-ethylene complexes.[16] While the binding of hydrogen molecule on the outer surface of the bare single-wall carbon nanotube (SWNT) is very weak,[7] a single Ti atom adsorbed on (8,0) SWNT can bind up to four H_2.[8] It is found that a (8,0) SWNT can store hydrogen molecules up to 8 wt %, exceeding the minimum requirement set for practical applications. Similar storage capacity has been obtained for Ti atom adsorbed on C_{60}.[9,10] The binding of H_2 molecules has been explained by a simple Dewar-Chatt-Duncanson model.[17]

Recent analysis for carbon fullerenes revealed that the binding energy of hydrogen molecules can be enhanced significantly (0.2–0.4 eV) by substitution with B or Be atoms.[18] Furthermore, experiments showed that boron nitride nanotubes can absorb 1.8–2.6 wt % hydrogen at about 10 MPa at room temperature.[19,20] Moreover, the possibility of covering the exterior surface of single-wall boron nitride nanotubes (SWBNTs) up to 50% by hydrogen was presented.[21] A chemisorption calculation of hydrogen molecules in BN clusters showed that they would be one of the possible hydrogen storage media.[22]

Motivated with these results, we examined hydrogen storage capacity of bare and Ti adsorbed SWBNT. We also investigated the H_2 storage capacity of B- and Be-substituted SWNTs. This Brief Report will be a supplement to our results published earlier[7,8,10,16] and will further clarify the interaction between H_2 and nanotubes.

We have performed first-principles plane wave calculations[23] within density functional theory[24] (DFT) using ultrasoft pseudopotentials.[25] The exchange correlation potential has been approximated by generalized gradient approximation (GGA).[26] All structures have been treated within supercell geometry using the periodic boundary conditions with dimensions $20 \times 20 \times c_o$ [c_o is the relaxed lattice constant of nanotubes along the tube axis and is equal to 4.26 and 4.33 Å for (8,0) SWNT and (8,0) SWBNT, respectively]. In self-consistent total energy calculations the Brillouin zone is sampled in the **k** space within the Monkhorst-Pack scheme[27] by $1 \times 1 \times 15$ mesh points. A plane basis set with kinetic energy of 400 eV has been used. All atomic positions and lattice parameters are optimized by using conjugate gradient method where total energy and atomic forces are minimized. The convergence for energy is chosen as 10^{-5} eV between two ionic steps, and the maximum force allowed on each atoms is 0.05 eV/Å.

I. ABSORPTION OF H_2 MOLECULE ON BARE AND Ti COVERED (8,0) SINGLE-WALL BORON NITRIDE NANOTUBE

SWBNTs have attracted much interest since they possess unique electronic and mechanical properties. For a given chiral angle and approximately equal radii (or index n), SWBNT and SWNT[28] exhibit similar structure, such as zigzag $(n,0)$ or armchair (n,n). SWBNT can be viewed as SWNT, in which the alternating C atoms are replaced by B and N atoms. However, owing to the charge transfer between B and N (and hence induced ionic character of the B–N bonds), SWBNT exhibit physical properties which are dramatically different than those of SWNT. For example, SWBNTs have higher heat tolerance and are less likely to oxidize.[29] Moreover, SWBNTs are always semiconductor with uniform and wide band gap no matter what their radii and chirality are.[30] The experimentally synthesized SWBNTs were observed to have a diameter ranging from 0.5 to 1.2 nm.[29,31] It was also reported that synthesis of the zigzag-type SWBNT is more favorable to that of the armchair type.[32,33] Recent studies have indicated that SWBNTs can be a highly efficient medium for hydrogen storage.[19–22] It is suggested that the binding energy of hydrogen molecule on SWBNT may increase as much as 40% compared with
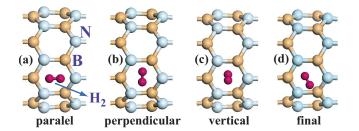
FIG. 1. (Color online) Possible H_2 absorption geometries on (8,0) SWBNT. [(a)–(c)] Various initial configurations of H_2 absorbing at hollow site. (d) Final configuration of H_2 after structure optimization.

that on SWNT due to the heteropolar bonding.[34]

We first investigate the interaction between H_2 and the outer surface of (8,0) SWBNT, which is chosen as prototype. To this end, we consider H_2 absorbed at different sites (hollow, bridge, top, etc.) with three possible initial orientations shown in Fig. 1. Upon relaxation, H_2 molecule has remained parallel to the surface oriented from B to N atom above the center of hexagon for each configuration at a distance of ~ 3.5 Å. The binding energy E_b is calculated as 50 meV. The binding is weak and physisorption and does not differ significantly from the binding of H_2 to SWNT. Consequently, absorbed H_2 molecules can be desorbed at room temperature. Earlier, Jhi and Kwon[34] calculated $E_b(H_2)$ as 100 meV for (10,0) SWBNT, where H_2 is placed above the center of hexagon at a distance of 3.0 Å. Clearly, bare SWBNTs are not suitable for hydrogen storage applications.

Next, we consider SWBNT functionalized by Ti. Ti is bound to (8,0) SWBNT surface with E_b of 1.09 eV without facing energy barrier. This displays a lower binding energy than that is obtained for SWNT (2.2 eV),[35,36] but it is still strong. Among possible adsorption sites, the most energetic one is found to be near the hollow site, where Ti atom is slightly displaced toward B and N atoms. The distances of Ti atom to the nearest B and N atoms are calculated to be 2.38 and 2.23 Å, respectively. We note that this adsorption site of Ti is different from that of SWNT. The ground state of the system is ferromagnetic with a net magnetic moment of 2.0 μ_B. According to Mulliken analysis, Ti atom donates 0.78 electron to SWBNT. Single H_2 molecule attaching to the optimized SWBNT+Ti dissociates into two H atoms as shown in Fig. 2. The H-H distance ($d_{H\text{-}H}$) increases to 3.38 Å, which was initially 0.74 Å. The ground state is still magnetic with $\mu = 2 \mu_B$. The binding energy is calculated to be 0.93 eV per H atom. This is similar to the single H_2 adsorption to Ti on SWNT,[8] where H_2 also dissociates into two H atoms with $E_b = 0.83$ eV and $d_{H\text{-}H} = 2.71$ Å. The total energy further decreases upon absorption of additional H_2 molecules. Unlike the first adsorption, subsequent hydrogen molecules do not dissociate, but their H-H bonds elongate from 0.74 to $0.84-0.90$ Å. These results are consistent with both SWNT+Ti in Ref. 8 and also elongated H-H bonds observed in metal-dihydrogen complexes.[17] The average binding energy of molecularly absorbed hydrogens is 0.46 eV, and the ground state is paramagnetic. Another possible configuration similar to that of SWNT+Ti, where four
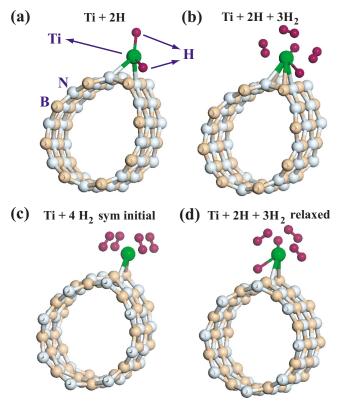

FIG. 2. (Color online) The configuration of H_2 molecules absorbing to (8,0) SWBNT+Ti system. (a) First H_2 molecule dissociates into two H atom. (b) Subsequent three H_2 are molecularly absorbed around Ti. (c) Possible (unrelaxed) symmetric configuration similar to that of SWNT+Ti with four H_2 molecularly absorbed around Ti (Ref. 8). (d) The resulting configuration occurring upon the relaxation of (c).

H_2 molecules are molecularly absorbed as shown in Fig. 2(c), is found to be metastable. Upon relaxation of the system, one H_2 dissociated as shown in Fig. 2(d). This geometry is found to be 0.5 eV less energetic than that is in Fig. 2(b). Our further study indicates that fifth H_2 cannot be bound. In order to test the stability of the system, we first increased the distance between Ti+2H+3H_2 complex and (8,0) SWBNT. After relaxation, Ti+2H+3H_2 complex returns to its initial configuration shown in Fig. 2(b). To further check the stability, the hydrogen atoms and molecules are also distorted from their equilibrium positions. Upon relaxation, equilibrium geometry is obtained indicating the stability of the system.

In order to increase H_2 storage, we consider uniform coverage of SWBNT with Ti. First, we placed eight Ti atoms per cell uniformly at the equivalent equilibrium position obtained from the optimization of single Ti atom adsorbed on SWBNT, as shown in Fig. 3(a). Unfortunately, Ti atoms dimerized when they are relaxed as illustrated in Fig. 3(b). To prevent Ti-Ti interaction leading to dimerization, we reduced the Ti coverage by placing four Ti atoms per cell as shown in Fig. 2(c). In this case, an energy barrier occurring between two Ti atoms prevented the dimerization upon relaxation. Under these circumstances, approximately 5.7 wt % (3.9 wt % if the dissociated H atoms which
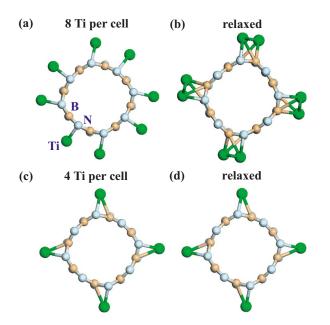
FIG. 3. (Color online) Initial and final geometries of Ti covered (8,0) SWBNT. (a) Eight Ti per cell coverage (unrelaxed). (b) Eight Ti per cell coverage upon relaxation. (c) Four Ti per cell coverage (unrelaxed). (d) Four Ti per cell coverage upon relaxation.

strongly bound to Ti atom are not counted) can be stored. The capacity may further be increased considering internal adsorption, for $(n,0)$ SWBNTs having relatively larger radius.

II. H₂ ABSORPTION ON B- AND Be-SUBSTITUTED (8,0) SINGLE WALL CARBON NANOTUBE

Earlier studies[7] reveal that the interaction of H_2 with the outer surface of SWNT is very weak. The binding energy is calculated to be ~30 meV without van der Walls (vdW) interaction and is estimated to be 50–60 meV if vdW attraction is included.[7] This interaction cannot be enhanced significantly by increasing the curvature of surface through radial deformation[7] due to the fact that H_2-SWNT distance is large. Other studies also showed that the physisorption of H_2 cannot occur in the inner wall of SWNT.[37]

It is argued that H_2 absorption energy is enhanced by B doping of fullerenes. B-doped fullerenes are known to exist experimentally. It was reported that B atoms could replace C to form $C_{54}B_6$ and $C_{48}B_{12}$ (Ref. [38]) fullerenes. It is also shown that $C_{59}B$ and $C_{58}B_2$ could be synthesized even in macroscopic quantities and are stable above room temperature.[39,40] Since SWNTs have similarities to fullerenes, it is interesting to consider B- or Be-substituted SWNTs.

As a first step [Fig. 4(a)], the substitution energy of B (or Be) in (8,0) SWNT (C_{32}) is calculated according to the expression $E_{sub} = E_T[\text{SWNT}(C_{32})] + E_T[X] - E_T[\text{SWNT}(C_{31}) + X] - E_T[C]$, where $E_T[\text{SWNT}(C_{31}) + X]$ is the total energy of the system where one of C atoms is replaced by X (X=B or Be), $E_T[\text{SWNT}(C_{32})]$ is the total energy of bare (8,0) SWNT, $E_T[X]$ and $E_T[C]$ are the free atom energies of X and carbon
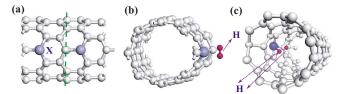

FIG. 4. (Color online) The structures of H_2 absorption on Be (or B) substituted (8,0) SWNT. (a) The final geometry of SWNT($C_{31}X$) system where one of the carbon atoms of (8,0) SWNT is replaced by X (X=B or Be). (b) External and (c) internal absorptions of H_2 molecule on SWNT($C_{31}X$) system. H_2 is molecularly absorbed for external case but dissociates into two atoms and binds to carbons for internal adsorption.

atom, respectively. Accordingly, $E_{sub}(B)$ is found to be −3.27 eV. $E_{sub} < 0$ indicates endothermic process and substitution requires energy. Next, we placed H_2 on top of substituted B atom at different initial sites as shown in Fig. 4(b) and fully relax the system. E_b is calculated as 25 meV, which is also very weak. Thus, we conclude that B substitution does not enhance H_2-SWNT interaction. It is noted that Zhao *et al.*[9] calculated $E_b = -30$ meV for B substituted fullerene (C_{36}) but obtained bonding state with $E_b = 390$ meV using local-density approximation (LDA). Our LDA calculations result to $E_b = 61$ meV for the SWNT case.

Next, we analyze the substitution of Be. $E_{sub}(Be)$ is calculated to be −9.36 eV, which is quite high indicating the adversity of Be substitution. Note, however, that due to concerted process, the energy required to substitute both B and Be into SWNT can be smaller than these substitution energies. For this case, H_2 absorption on top of Be [Fig. 4(b)] yields 0.31 eV binding energy which is significant. The Be-H distance is calculated to be 2.0 Å, and H–H bond length remained 0.77 Å. The slight elongation of H–H bond also indicates that the character of the bonding is physisorption. Attempts to absorb additional H_2 molecules have failed. In the case of internal adsorption, H_2 molecule is dissociated and H atoms are bound to C atoms in the vicinity of Be as illustrated in Fig. 4(c). Similar to the fullerene case, several Be atoms may be substituted into the (8,0) SWNT. We found that four Be atoms can be substituted without damaging the tubular structure ($C_{28}Be_4$). However, when the number of Be atom increases, the tubular form is destroyed. Each of the four substituted Be atom can bind one H_2 molecule. The average binding energy of H_2 molecules is calculated as 0.40 eV. The Mulliken analysis indicates that Be donates 1.2 electrons to the nearest three C atoms (~0.4 electron to each). The hydrogen storage capacity of $C_{28}Be_4H_8$ system is calculated to be ~2.4 wt %. The substitution of Be into fullerene (C_{36}) also significantly enhanced the absorption energy of H_2 molecules, and the binding energy was calculated to be 0.37 eV with GGA and 0.65 with LDA.[9] Note that the present binding energies of H_2 to B- or Be-substituted SWNTs calculated by GGA are consistently ~0.35 eV lower than those calculated for C_{36} fullerenes using LDA.[9]

CONCLUSION

In conclusion, using first-principles DFT calculations, we found that the interaction of H_2 with SWBNT is very weak.

However, SWBNT can be functionalized by Ti atom and single Ti can bind up to four H_2 molecules, one is dissociated and the remaining three are molecularly absorbed. Accordingly, the hydrogen storage capacity of the system ranges between 3.9 and 5.7 wt %. Our calculations also reveal interaction of H_2 with B- and Be-doped SWNTs. The substitution of both atoms is endothermic. Once Be is substituted, it significantly enhances H_2 binding. Four Be atoms can be substituted without destroying the tubular structure which reaches 2.4 wt % hydrogen storage capacity.

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