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Hydrogen Storage in Ti-Decorated BC₄N Nanotube

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Received: August 14, 2008; Revised Manuscript Received: September 25, 2008

We report an extensive first-principles investigation of a both exohedral and endohedral Ti decorated BC₄N nanotube for hydrogen storage. The results reveal that an endohedral capping of Ti is energetically favorable compared to exohedral capping, albeit marginally by ~ 0.1 – 0.4 eV/Ti atom. However, this endohedral insertion process is difficult since it requires overcoming of a rather high energy barrier of ~ 4 eV/Ti atom, as obtained from our nudge elastic band calculation of the minimum energy path. We observe that the exohedral Ti@BC₄N can bind up to four hydrogen molecules with successive energies of adsorption lying in the range of ~ 0.4 – 0.7 eV. We further predict that, at high Ti coverage, the system can absorb up to 5.6 wt % of hydrogen. After establishing the adsorption of hydrogen molecules on the Ti@BC₄N nanotube, we have performed molecular dynamics simulation to understand the desorption behavior. It is observed that at 300 K the system remain stable with all four H₂ attached with Ti, while at 500 K hydrogen gets released in molecular form from the Ti@BC₄N nanotube without breaking the cage. This investigation underscores the potential of Ti-decorated BC₄N nanotube as a promising candidate material for hydrogen storage.

1. Introduction

For the advancement of hydrogen storage as fuel cell technologies, storing safe and cost-effective pure hydrogen is the biggest challenge as it must meet the basic requirements of high gravimetric and volumetric density together with fast kinetics and favorable thermodynamics.¹ For commercial applications, it is necessary to develop novel materials that can reversibly store molecular hydrogen with a gravimetric efficiency of 6 wt % (the target set by the DOE, Department of Energy, U.S.A.), and at the same time possess acceptable desorption kinetics under ambient conditions. Presently, the methods for storage of hydrogen as compressed gas or in the liquid form do not meet the practical requirement. Alternative options, by utilizing suitable solid state hydriding and dehydriding reactions in low-Z complex hydrides, are being extensively studied,² albeit with limited success so far.

Desorption of hydrogen at a moderate temperature is, in some sense, more important than adsorption on it. Any light metal is known to adsorb hydrogen to reasonably high wt %. However, on metal surfaces, hydrogen undergoes dissociative chemisorptions, which results in the strong metal–hydrogen bonds. This is the primary reason why all of these metal hydrides, where hydrogen is attached in atomic form, show slow kinetics for adsorption and desorption processes. Storage of hydrogen in molecular form is advantageous due to its fast kinetics as well as low binding energy that could lead to the possibility of desorption of hydrogen molecule at low temperature. Significant

attention is being focused on nanostructured materials, such as fullerenes and nanotubes especially of carbonic compounds, as possible candidate structures for hydrogen storage.^{3–5} The nanotubes, due to their high surface-to-bulk ratio, constitute a class of materials that presents a great potential for this clean energy alternative. Most of the work in previous studies has focused on carbon and boron-nitride nanotubes, which are isoelectronic but show significant differences in terms of stability or electronic structures. The hydrogen storage capacity in the carbon nanotube is ~ 0.2 wt %, ⁶ whereas in B–N nanotubes and B–N cages, the capacity reaches up to 2.6 and 4 wt %, respectively.^{7,8} Recent calculations based on molecular dynamics simulation revealed that, even though B–N cages can adsorb up to 4 wt % of hydrogen, it is not practically usable as the structure breaks up even at room temperature (300 K).⁸ On the other hand B–N nanotubes serve better thermal stability as they are very much stable even at temperatures up to 1000 °C but fail when desorption of these systems is taken into account. Ciraci and Yildirim showed that transition metal decorated carbon nanotubes not only can adsorb up to 8 wt % of hydrogen but also are well capable of showing some interesting desorption.⁹ However, extensive work has not yet been done on desorption kinetics of TM doped carbon nanotube, and the available literature is sufficient to accept carbon nanotubes as a better option than B–N nanotubes from the desorption point of view. However, because a carbon nanotube gets oxidized at a temperature around 600 °C, the search for a better media that simultaneously possesses the thermal stability of BN nanotube and desorption of carbon nanotube continues. This motivates us toward extensive investigation on transition metal doped B–C–N nanocomposites for hydrogen storage. Extensive work has already been started on B–C–N [B_xC_yN_z] nanostructures both experimentally and theoretically.^{10,11}

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In particular, BC₄N nanotubes are nonmagnetic insulators with very high thermal stability.¹² The most stable structure is a graphitic network containing BN₃ and NB₃ units connected by a B–N bond. With the doping of a transition metal on it, storage capacity can be improved significantly. Although calculations on transition metal doped carbon nanotubes have been performed,¹³ the main motivation was to understand magnetism in this system. However, for utilizing the doped nanotubes for the purpose of hydrogen storage, there are several open questions e.g.: (1) Does transition metal prefer to stay in exohedral or endohedral position of the nanotube? (2) What is the energy barrier for the transition metal to enter into or escape from the nanotube? (3) What happens when more transition metals are decorated in different hexagonal faces of the nanotube? (4) How does the binding energy of H₂ change during addition of more H₂ in the TM-doped BC₄N nanotube both in exohedral and endohedral position? (5) As more H₂ is stored, what are the changes in the geometry and electronic structure of the nanotube? (6) Lastly, from the hydrogen storage point of view, what is the effect of the temperature on the stability of this nanotube? In this work, we provide a detailed study for these questions by using a BC₄N nanotube as an example.

2. Computational Details:

Electronic structure and total energies were calculated with the Vienna ab initio simulation package (VASP),¹⁴ based on DFT.^{15,16} Projector-augmented wave (PAW) potentials¹⁷ were employed for the elemental constituents; viz. H, B, C, N, and Ti potentials which contained one, three, four, five, and four valence electrons, respectively. The GGA calculation was performed with the Perdew–Wang^{18,19} exchange-correlation potential. The *k*-points mesh was generated by the Monkhorst-Pack²⁰ method and all results were tested for convergence with respect to the mesh size. In all calculations, self-consistency was achieved with a 0.1 meV convergence of total energy. For high precision calculation we used a cutoff energy of 400 eV for plane wave basis. For obtaining the optimized ground-state geometry,^{21,22} atomic forces were converged to less than 0.001 eV/Å by conjugated gradient (CG) minimization. We also perform ab initio molecular dynamics (MD) simulations in order to investigate the stability of the optimized structures and desorption of hydrogen molecules from a Ti@BC₄N nanotube.

3. Results

3.1. Pure BC₄N Nanotube. The ground-state structures of BC₄N nanotubes having different chirality, viz. (6,0) and (8,0) zigzag nanotubes, and (6,6) armchair nanotube, have been reported to be semiconducting with varying energy gaps, and all are nonmagnetic.¹² Ciraci et al. had shown⁹ that a nanotube with significant band gap shows strongest adsorption toward hydrogen. In the case of a BC₄N nanotube, the (6,6) armchair nanotube shows the largest band gap (~1.0 eV), and hence in our present study, we have chosen this as our basic reference system. The accuracy of our computational method was tested by relaxing the (6,6) armchair nanotube structure, and we found that the optimized diameter of the nanotube is 8.3 Å, which is in good agreement with the available experimental value.¹² Further, to take into account the different chemical orderings, we have chosen the length of the nanotube to be 14.9 Å. The corresponding supercell that we constructed contains 24 B, 96 C, and 24 N atoms.

The thermal stability of the BC₄N nanotube is very high ~900 K.¹² The presence of B and N makes this system more stable compared to the well-known carbon nanotube. In order to

TABLE 1: Binding Energy Values and Number of Inequivalent Hexagons for Different Adsorption Sites of Ti Atoms Both in Exohedral and Endohedral Positions of the BC₄N Nanotube^a

different hexagonal faces	<i>N</i> _{hex}	binding energy in eV/Ti atom	
		endohedral	exohedral
6C	18	−2.49	−2.18
1B-5C	3	−2.30	−1.87
1N-5C	6	−2.04	−1.92
2B-1N-3C	6	−2.20	−2.04
2B-2N-2C	9	−1.95	−0.157
2N-1B-3C	9	−1.81	−1.52
1B-1N-4C	6	−2.07	−1.70

^a Different hexagon faces have been designated as B_{*n*}C_{*n*}N_{*n*} with *n*₁ + *n*₂ + *n*₃ = 6. *N*_{hex} is the number of inequivalent hexagons (total 57) in BC₄N nanotube of length 14.9 Å.

incorporate B and N, we selectively substitute some of the C atoms from the carbon nanotube to form this BC₄N nanotube. Such a composite carbon-based nanotube is expected to retain the advantages of a carbon nanotube and, at the same time, avoid the possibility of oxidation of normal carbon nanotube. It has been found that unlike carbon nanotube BC₄N nanotube is not good hydrogen storage medium as it can store only up to 0.7 wt % of hydrogen.¹² Therefore, we have tried to dope a 3d transition metal, like Ti, which had earlier been used to decorate other fullerene and nanotube surfaces^{9,23} and thereby increase the wt % for hydrogen storage. The specific choice of Ti rather than any of its 3d transition metals counterparts, viz. Sc, V, Cr, Mn, Fe, etc., is because of the fact that Ti serves the best as a dopant among all 3d transition metals from hydrogen storage point of view.²⁴

3.2. Endo- vs Exohedral Ti@BC₄N Nanotube. We have first tried to understand the preferred position of Ti on different hexagonal faces of BC₄N nanotube. It is to be noted that for all of the B–C–N hexagonal faces, the mean number of valence electrons is 4 and a Ti atom also has exactly the same number

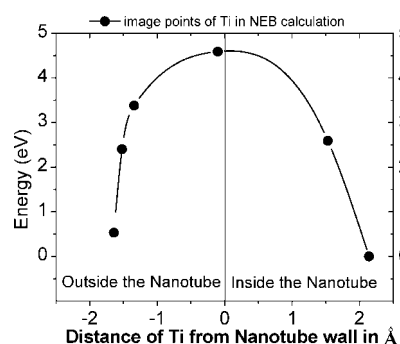


Figure 1. Barrier height for Ti atom to move from outside to inside of the BC₄N nanotube as calculated by the NEB method (see text for details). The estimated barrier height is ~4 eV.

TABLE 2: Binding Energy Values for H₂ Adsorption in an Exo- and Endo-Hedral Ti@BC₄N Nanotube

BE in eV for exohedral molecular H ₂ adsorption		BE in eV for endohedral molecular H ₂ adsorption	
system	BE value in eV/H ₂ molecule	system	BE value in eV/H ₂ molecule
Ti@ BC ₄ N + 1 H ₂	−0.66	Ti@ BC ₄ N + 1 H ₂	−0.48
Ti@ BC ₄ N + 2 H ₂	−0.67	Ti@ BC ₄ N + 2 H ₂	−0.63
Ti@ BC ₄ N + 3 H ₂	−0.58	Ti@ BC ₄ N + 3 H ₂	−0.18
Ti@ BC ₄ N + 4 H ₂	−0.40	Ti@ BC ₄ N + 4 H ₂	−0.04

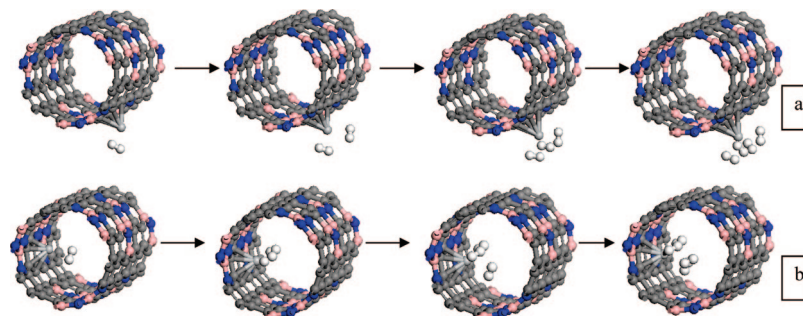


Figure 2. Consecutive adsorption of H_2 molecules in (a) an exohedral $\text{Ti@BC}_4\text{N}$ nanotube and (b) an endohedral $\text{Ti@BC}_4\text{N}$ nanotube. pink ball = B, blue ball = N, dark gray ball = C, light gray ball = Ti, white ball = H.

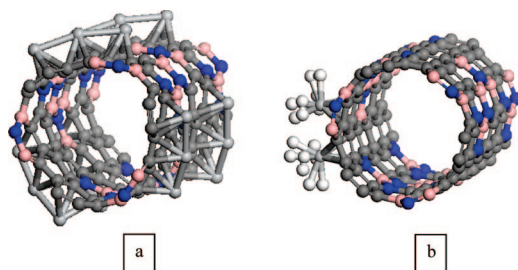


Figure 3. (a) Ball and stick model for optimized structure of $\text{Ti}_{18}\text{@BC}_4\text{N}$. (b) Two Ti atoms placed on the two neighboring 6 C hexagonal faces of BC_4N nanotube, along with 4 H_2 molecules adsorbed on each Ti, to form $\text{Ti}_2\text{@BC}_4\text{N} + 8 \text{H}_2$.

of valence electrons [4]. Thus, we placed Ti on each of the different hexagonal faces of the BC_4N nanotube both exohedrally and endohedrally and subsequently optimized the geometry of the entire structure. Table 1 summarizes the binding energy of a Ti atom both for exohedral and endohedral position

at different hexagonal sites for the BC_4N nanotube. Endohedral position turns out to be energetically favorable compared to exohedral, and among all the hexagonal faces the 6C hexagonal face (i.e., with all six carbon atoms in the hexagonal ring) is energetically most stable (see Table 1). As far as the site preference of the Ti is concerned, the on-top and bridge positions are unstable. This has been verified by fixing the initial position of Ti on top or bridge site of the nanotube, which on relaxation shows that Ti eventually moves to the nearest 6C hexagon site. In order to ascertain the exohedral versus endohedral Ti-capping in $\text{Ti@BC}_4\text{N}$ nanotube, a crucial factor is the energy barrier that the Ti atom has to cross while going from “outside” to “inside” of the nanotube or vice versa. That means even though Ti prefers energetically endohedral rather than exohedral position, a complete understanding is lacking unless and until one can find the actual barrier height required for Ti atom to enter inside the nanotube. In order to estimate this barrier height for a Ti atom, we have carried out a detailed study with the help of

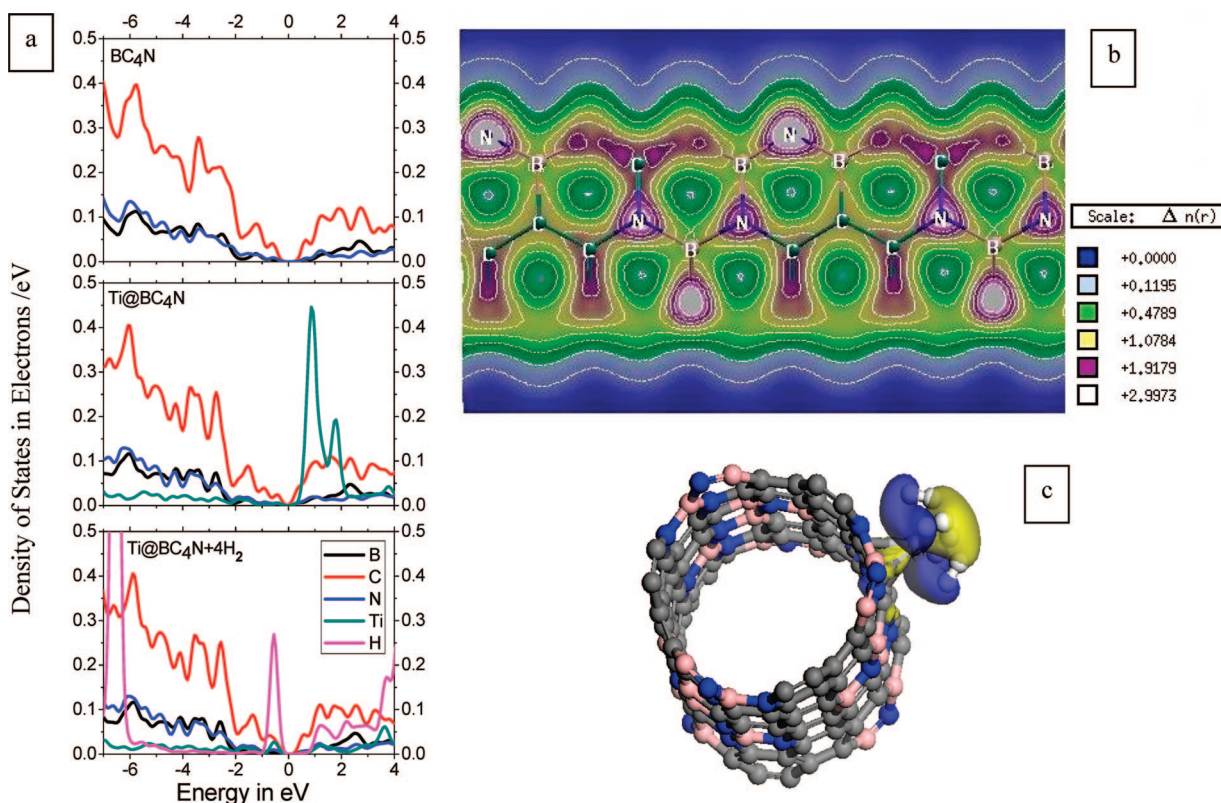


Figure 4. (a) Partial densities of states projected on to the individual constituents for (i) BC_4N , (ii) $\text{Ti@BC}_4\text{N}$, and (iii) $\text{Ti@BC}_4\text{N} + 4 \text{H}_2$. (b) Charge density contour plot for pure BC_4N nanotube, (010) plane, showing the B–N, B–C, and C–N bonds in comparison with the C–C π bond. (c) Ti-d orbital hybridized with the 1s orbitals of the 4H_2 complex and the 2p orbitals of 6C carbon hexagon, in $\text{Ti@BC}_4\text{N} + 4 \text{H}_2$.

TABLE 3: Bond Length Details of Ti–C, Ti–H, and H–H in the Ti@BC₄N Nanotube

consecutive number of Hydrogen adsorption at Ti@BC ₄ N	consecutive adsorption of H ₂ molecules in exohedral Ti@BC ₄ N nanotube			consecutive adsorption of H ₂ molecules in endohedral Ti@BC ₄ N nanotube		
	Ti–C distance (Å)	Ti–H distance (Å)	H–H distance (Å)	Ti–C distance (Å)	Ti–H distance (Å)	H–H distance (Å)
Ti@BC ₄ N+1H ₂	2.31 2.22 2.31 2.20 2.30 2.48	1.98	0.82	2.38 2.26 2.17 2.22 2.37 2.32	2.04	0.80
Ti@BC ₄ N+2H ₂	2.31 2.24 2.35 2.26 2.32 2.48	1.95 1.94	0.83 0.83	2.33 2.34 2.64 2.29 2.32 2.16	1.87 1.87	0.87 0.87
Ti@BC ₄ N+3H ₂	2.33 2.31 2.40 2.24 2.32 2.50	1.83 1.93 1.85	0.88 0.88 0.82	2.34 2.35 2.30 2.31 2.34 2.18	2.05 1.88 1.88	0.79 0.85 0.84
Ti@BC ₄ N+4H ₂	2.31 2.30 2.43 2.27 2.32 2.51	1.93 1.91 1.93 1.91	0.82 0.83 0.82 0.83	2.35 2.35 2.30 2.30 2.34 2.19	4.51 2.08 1.87 1.88	0.75 0.79 0.85 0.84

Nudge elastic bands (NEB) method²⁵ where we tried to move a Ti atom slowly from outside to inside of the BC₄N nanotube in six steps. We found that the approximate barrier height is 4 eV/Ti atom [Figure 1]. This signifies that it is energetically costly to substitute a Ti atom inside the nanotube.

3.3. H Storage. The results of adsorption of hydrogen in molecular form have been summarized in Table 2 both for exohedral and endohedral positions [Figure 2]. It is to be noted from Table 2 that, in exohedral and endohedral Ti@BC₄N, the Ti atom can be attached with 4 H₂ molecules each. In the endohedral case, the last H₂ molecule gets physisorbed with Ti atom with a very week binding energy value ~0.04 eV, while for the exohedral case the binding energies lie exactly in the energy window desired for hydrogen storage. The bond length details for both exohedral and endohedral Ti@BC₄N nanotube with subsequent H₂ addition is given in Table 3, where the Ti–H distance is referred to as the distance between Ti atom and nearest H atom of the H₂ molecule. However, from our NEB results, we may infer that endohedral Ti decoration is practically difficult task. So in order to increase the weight percent for hydrogen storage, we have decorated this BC₄N nanotube exohedrally with Ti atoms on all of the 6C hexagonal sites and optimized the geometry of the decorated structure. The final optimized structure is shown in [Figure 3a]. We infer from this that, since each Ti atoms can adsorb 4 H₂ molecules, altogether 72 H₂ molecules can be adsorbed by this system with an estimated 5.60 wt % of hydrogen storage. Now a fully relaxed self-consistent calculation on Ti₁₈@BC₄N + 72 H₂ is computationally quite demanding. So we have checked with two adjacent Ti atoms, i.e., Ti₂@BC₄N and found that this system can adsorb 8 H₂ molecules [Figure 3b]. With this result, we can conclude that the final Ti decorated BC₄N system can adsorb up to 5.60 wt % of hydrogen.

3.4. Electronic Structure. In Figure 4a we have illustrated the partial density of states of pure BC₄N, Ti@BC₄N, and Ti@BC₄N + 4 H₂ respectively. We notice from this that while the host carbon nanotube is metallic, the substitutional doping of B and N with a large enough concentration (33%) can make it semiconducting. Therefore, we may consider this B–C–N composite nanotube as an interface of two well-known nanotubes viz. carbon nanotube and B–N nanotube. The local structural unit of BN₃ and NB₃ linked with B–N bonds is the main reason for it to have an extra stability as compared with its host carbon nanotube. This difference in the nature of bonding is obvious from the charge density contour plot (Figure 4b) which shows the variation in the electron densities between the C–C bond vis-à-vis B–C, N–C, and B–N bonds.

After Ti-doping, we see the significant contribution of Ti-3d in the unoccupied level. That means the Ti atom is in the cationic state and can accept electrons from other atoms as well. We may notice just below the Fermi level some hybridization between Ti and C atoms. As hydrogen molecules are added one after another, the vacant d orbital of Ti gets gradually filled up, and as a result of that, the unoccupied states of Ti⁺ (as shown in DOS of Ti@BC₄N) become depopulated in Ti@BC₄N + 4 H₂ at the cost of the H-1s peak to grow. This is also apparent from the molecular orbital plot of Ti@BC₄N + 4 H₂ where we can clearly see that we need two unoccupied d-orbitals, one for molecular bonding with hydrogen and the other to bind the metal to the nanotube [Figure 4c].

3.5. Desorption Kinetics. A very important issue for a material to be used for hydrogen storage is its desorption kinetics and thermal stability at higher temperature. In order to test system stability and hydrogen desorption, we have performed

ab initio molecular dynamics (MD) simulation on Ti@BC₄N + 4 H₂ system which is heated in steps first from 0–300 K and then from 300 to 500 K with 1 fs time step using the Nose algorithm.²⁶ We have noticed that at a temperature of 300 K the system remains stable with all four H₂ molecules attached on Ti atoms in the Ti@BC₄N nanotube, whereas hydrogen starts desorbing from the Ti@BC₄N nanotube at a temperature around 500 K (see the Supporting Information for details). By carrying out ab initio molecular dynamics (MD) to this 153 atoms system for a 5.5 ps MD run, we get statistically meaningful values for desorption temperature. It does suggest that the system is quite stable at room temperature and it is possible to extract H₂ molecules without breaking the Ti–C bonding from the host system Ti@BC₄N at a relatively moderate temperature around 500 K.

4. Conclusion

In summary, we investigated the ground-state structure and stability of an exohedral as well as endohedral Ti-decorated (6,6) armchair BC₄N nanotube which can be considered as an amalgam of carbon and B–N nanotubes. Each Ti⁺ ion sitting on 6C hexagonal face of the nanotube absorbs up to 4 H₂ molecules. The entire structure remains stable up to 500 K where H₂ comes out without breaking the Ti–C bonding. The desorption temperature and kinetics are quite favorable, and at the same time, the gravimetric efficiency corresponding to full Ti coverage turns out to be ~5.6 wt %. This Ti-decorated BC₄N nanotube shows more promise than conventional carbon and boron nitride nanotubes for the purpose of H₂ storage in a nanostructure material.

Acknowledgment. The authors thank Dr. Mousumi Upadhyay-Kahaly for providing the structural details of (6,6) BC₄N nanotube and Prof. Umesh V. Waghmare for many helpful suggestions and discussions.

Supporting Information Available: 1. Figure containing a plot of average Ti–H bond length versus time step of MD

simulation run. 2. Two movie clips (consists of 10 snap shots) of our MD simulation run at temperatures of 300 and 500 K. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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JP807280W