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Comparative Study of Hydrogen Adsorption on Carbon and BN Nanotubes

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The physisorption and chemisorption of hydrogen in BN nanotubes, investigated by density functional theory (DFT), were compared with carbon nanotubes. The physisorption of H₂ on BN nanotubes is less favorable energetically than on carbon nanotubes; BN nanotubes cannot adsorb hydrogen molecules effectively in this manner. Chemisorption of H₂ molecules on pristine BN nanotubes is endothermic. Consequently, perfect BN nanotubes are not good candidates for hydrogen storage by either mechanism. Other strategies must be utilized if BN nanotubes are to be employed as hydrogen storage media such as utilizing them as supporting media for hydrogen-absorbing metal nanoclusters.

1. Introduction

The efficient storage of hydrogen is vital for its utilization as a future energy carrier. Although many alloys are capable of storing hydrogen reversibly,¹ the gravimetric storage capacity is too low for practical purposes. The current goal of the U.S. Department of Energy (DOE) is a capacity of >6.5 wt % at ambient temperature and pressure. To achieve this goal, hydrogen storage media should have large surface areas and suitable binding energies. Carbon nanotubes are attractive candidates for high-capacity hydrogen storage media, partly due to their ultrahigh surface area/weight ratio. Consequently, a large number of experimental and theoretical studies of hydrogen storage in nanotube-based materials have been reported.² However, data on the hydrogen storage capacity of carbon nanotubes are still in dispute³ because some experiments are not reproducible.⁴

Hydrogen trapping in nanotube-based materials originates either from van der Waals (vdW) interactions (physisorption or molecular adsorption, binding energies ~2.3 kcal/mol (~0.1 eV)) or from covalent C–H bond formation (chemisorption or atomic adsorption, binding energies of individual H atoms in the 46.1–69.1 kcal/mol range (2–3 eV) have been computed⁵). Obviously it is difficult to obtain high hydrogen storage capacity only by physisorption; however, chemisorption (especially at defect sites) is also ill-suited for hydrogen storage if the binding energies are too large. Accordingly, much recent research has focused on obtaining intermediate binding energies between H₂ and nanotubes (4.6–6.9 kcal/mol (0.2–0.3 eV) range), which allow both adsorption of molecular hydrogen and its release under conditions suitable for practical applications.

The discovery of carbon nanotubes opened many opportunities for developing novel one-dimensional nanomaterials.⁶ This

interest now extends to boron nitride (BN) nanotubes, which represent group III–V compounds with tubular structures.⁷ The substantial ionicity of BN nanotubes is responsible for many of its properties, which differ from their carbon analogues. For example, BN nanotubes are semiconductors with wide band gaps weakly dependent on the diameter, helicity, and the number of tube walls.^{7a} Similar to carbon nanotubes, BN nanotubes are also regarded as possible hydrogen storage media. It has been reported recently that BN nanotubes can take up 1.8–2.6 wt % hydrogen under ~10 MPa at room temperature⁸ and that collapsed BN nanotubes (i.e., richer in defects) exhibit an even higher hydrogen storage capacity (4.2 wt %).⁹ The large hydrogen uptake of BN nanotubes is attributed primarily to chemisorption.¹⁰ Although hydrogen storage in BN-related materials has been studied theoretically,^{7j,10,11} important questions have not yet been answered. What are the differences between hydrogen adsorption in BN and in carbon nanotubes? How does the nanotube–hydrogen interaction depend on the tube diameter? We have performed density functional theory (DFT) computations with periodic boundary conditions (PBC) to address these questions.

2. Computational Methods

All electron periodic boundary conditions (PBC) DFT calculations were carried out by employing the generalized gradient approximation (GGA) with the PW91 functional¹² and the double numerical plus polarization (DNP) basis set^{13a} using the DMol program package.¹³ Self-consistent field (SCF) calculations were carried out with a convergence criterion of 10^{−6} a.u. on the total energy and the electron density. To ensure high quality results, the real-space global orbital cutoff radius was chosen to be as high as 5.5 Å in the computations. However, it should be noted that the quantities reported here have not been corrected for zero-point vibrational and thermal energies (e.g., to ambient temperatures), nor has entropy (which favors dissociation) been considered.

Second-order Møller–Plesset (MP2) and CCSD(T) computations were performed on model systems, H₂ physisorbed

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TABLE 1: Optimized Nearest Distances between H₂ and the Ring Centers of Benzene and Borazene (Å), and Physisorption Energies of H₂ on Benzene and Borazene (kcal/mol) at Different Theoretical Levels (H₂ is Perpendicular to the Benzene or Borazene Ring Plane)

	distance		physisorption energy	
	H ₂ -benzene	H ₂ -borazene	H ₂ -benzene	H ₂ -borazene
PW91	2.986	2.998	-0.86	-0.59
PBE	3.000	2.524	-0.34	-0.38
MP2	3.000	2.994	-1.12	-0.60
CCSD(T)			-0.87 ^{a,b}	-0.62 ^a

^a Based on single point energies at the CCSD(T)/cc-pVTZ/MP2/6-311+G** level. ^b This value is close to that obtained at CCSD(T)/cc-pVTZ level (0.95 kcal/mol), see ref 15.

benzene and borazene, to validate the performance of the computational methods employed to study weak interactions, using the Gaussian 03 program.¹⁴ Dispersion contributions are not treated well by current DFT theory, but MP2 includes both (weakly) overlapping densities and dispersion interactions, and CCSD(T) serves as the current “golden standard” for computational chemistry. Our evaluations show that the PW91 functional performs more satisfactorily than the PBE functional in reproducing MP2 and CCSD(T) structures and energies of H₂ physisorption on the model systems (Table 1). Therefore, the PW91 functional was used to compare the H₂ physisorption in carbon and BN nanotube systems. Note that our goal is not to predict hydrogen physisorption energies with high accuracy due to the insufficiency of GGA or LDA (local density approximation) DFT levels to describe the long-range dispersion interactions. However, our results at uniform levels allow comparisons of hydrogen physisorption on C and BN nanotubes and provide insights to help understand experimental findings.

The nomenclature of BN (*n,m*) nanotubes is similar to the C (*n,m*) nanotubes. As BN nanotubes are known experimentally to adopt zigzag structures,^{7d,7f,16} only models for zigzag tubes were computed, and the results were compared with their carbon analogues. One-dimensional PBC was applied along the tube axis to simulate infinitely long (rather than truncated) nanotube systems. Interactions between individual hydrogen atoms or molecules and their one-dimensional periodic images were avoided in our computational supercell models, which include two unit cells of the zigzag tube (for example, supercell length *c* = 8.45 Å for a (9,0) BN nanotube). For comparison, we also studied the hexagonal BN graphitic sheet and used a 4 × 4 supercell on the graphene plane, as shown in Figure 1.

Moreover, PBC computations on BN double-walled nanotube (DWNT) models were performed by employing the PW91 functional and the ultrasoft pseudopotential by Vanderbilt¹⁷ using a plane-wave pseudopotential VASP code.¹⁸ The energy cutoff for the plane-wave basis is 360 eV. The supercell models are similar to those used in the Dmol computations. Five *k* points were employed for sampling the one-dimensional Brillouin zone to optimize the geometric structures and compute the adsorption energies.

3. Results and Discussion

3.1. Physisorption of H₂ Molecule on (9,0) Carbon and BN Nanotubes. The thermodynamic driving force is measured by the hydrogen adsorption energies on nanotubes. The hydrogen physisorption energy is defined as the difference between the total energy of the complexed species (H₂-host) and the sum of the energies of the separated host and a H₂ molecule. The physisorption energy ($E_{\text{physisorption}}$) of one H₂ molecule on the sidewall of a single-walled nanotube (SWNT) is calculated

as follows:

$$E_{\text{physisorption}} = E_{\text{host-H}_2} - E_{\text{host}} - E_{\text{H}_2} \quad (1)$$

By our definition, $E_{\text{adsorption}} < 0$ in eq 1 corresponds to exothermic adsorption leading to minima stable toward dissociation into SWNT and molecular H₂. Endothermic energies, $E_{\text{adsorption}} > 0$, mean that the adsorption is unstable energetically relative to the separated host model and molecular H₂. Note that entropy, which favors dissociation, has not been considered, so that eq 1 does not represent the full thermodynamics at finite temperatures.

At the PW91 level, the physisorption energies of a H₂ molecule above the hexagon surfaces on (9,0) carbon and BN nanotubes were calculated to be -0.63 and -0.30 kcal/mol, respectively. The computed physisorption energy in a (9,0) carbon nanotube is comparable to those reported previously for graphenes and SWNTs with various methods.^{5a,19} For comparison, these physisorption energies between the H₂ molecule and (9,0) carbon and BN nanotubes at the PBE level were -0.40 and -0.08 kcal/mol, respectively. Clearly PBE tends to give small adsorption energy for vdW interaction, in agreement with the trend found for the model molecules (Table 1). Thus, we can conclude that the H₂ physisorption energy in BN nanotubes is smaller than that in carbon nanotubes, but both are miniscule.²⁰ Considering entropy, H₂ would not bind to BN nanotubes at realistic temperatures. Understandably, the uptake of hydrogen in BN nanotubes, found experimentally, was attributed primarily to chemisorption.¹⁰

3.2. Chemisorption of a H Atom on (9,0) Carbon and BN Nanotubes. We used a hydrogen atom, rather than a H₂ molecule, as an initial chemisorption model. On this basis, the hydrogen atom chemisorption energy ($E_{\text{chemisorption}}$) is defined as the difference between the total energy of the bound host-H and the sum of the energies of the separated host and an individual H atom (eq 2):

$$E_{\text{chemisorption}} = E_{\text{host-H}} - E_{\text{host}} - E_{\text{H}} \quad (2)$$

As with H₂ physisorption, the chemisorption energies were computed for a single H atom binding at different sites on the nanotube wall. Figure 2 summarizes the optimized structures and the associated energies for H chemisorption on (9,0) carbon and BN nanotubes.

As reported previously,^{5a} a H atom prefers to attach to a carbon atom, with the formation of a C-H bond (Figure 1a). As with other chemical functionalizations of carbon nanotubes,²¹ the hybridization of the carbon changes from sp² to sp³. Likewise a H atom is chemisorbed preferentially at a boron or a nitrogen on the outside wall of a (9,0) BN tube (Figure 2b and c), with the formation of a B-H or a N-H bond. The B-H distance (*r* = 1.31 Å) is substantially longer than that of a typical B-H bond (ca. 1.19 Å), the deformation of the NBN angles (114.3°, 114.3°, and 116.0°) at the boron center toward tetrahedral (109.5°) is only modest, and the BN bond lengths (1.46, 1.51, and 1.51 Å) are shorter than typical single BN bond values (e.g., 1.567 Å in the sp³-hybridized cubic BN phase).²² These structural features point to a rather weak B-H bond. Indeed, the H atom binding energy at the boron site, while exothermic, is only -6.54 kcal/mol (Figure 2c).

As with carbon nanotubes, hydrogen atom chemisorption at N deforms the BN tube in the adsorption region more strongly. The length of the N-H bond (1.05 Å) is normal, and the bond angles involving the H-adsorbed N atom (102.2°, 110.5°, and 110.5°) are essentially tetrahedral. The BN lengths (1.55, 1.42,

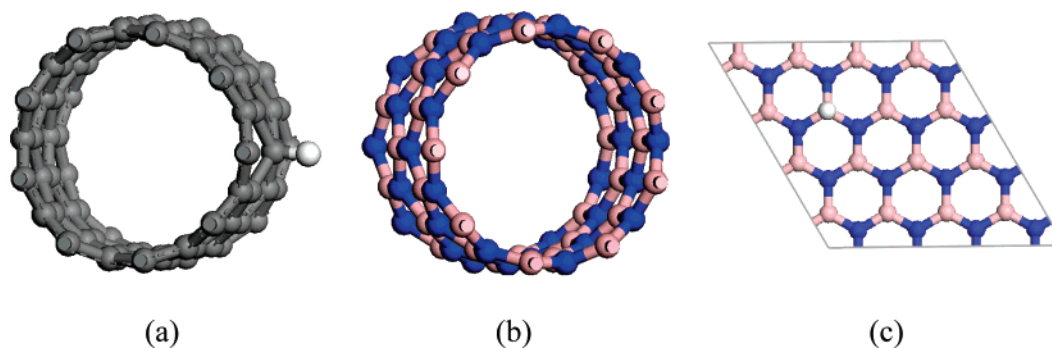


Figure 1. Schematic representations of models used in this investigation: (a) a H-bound (9,0) carbon nanotube, (b) a pristine (9,0) BN nanotube, and (c) a hexagonal BN graphitic sheet with a H bound to a B atom. C, B, N, and H atoms are denoted by black, orange, blue, and white colors, respectively.

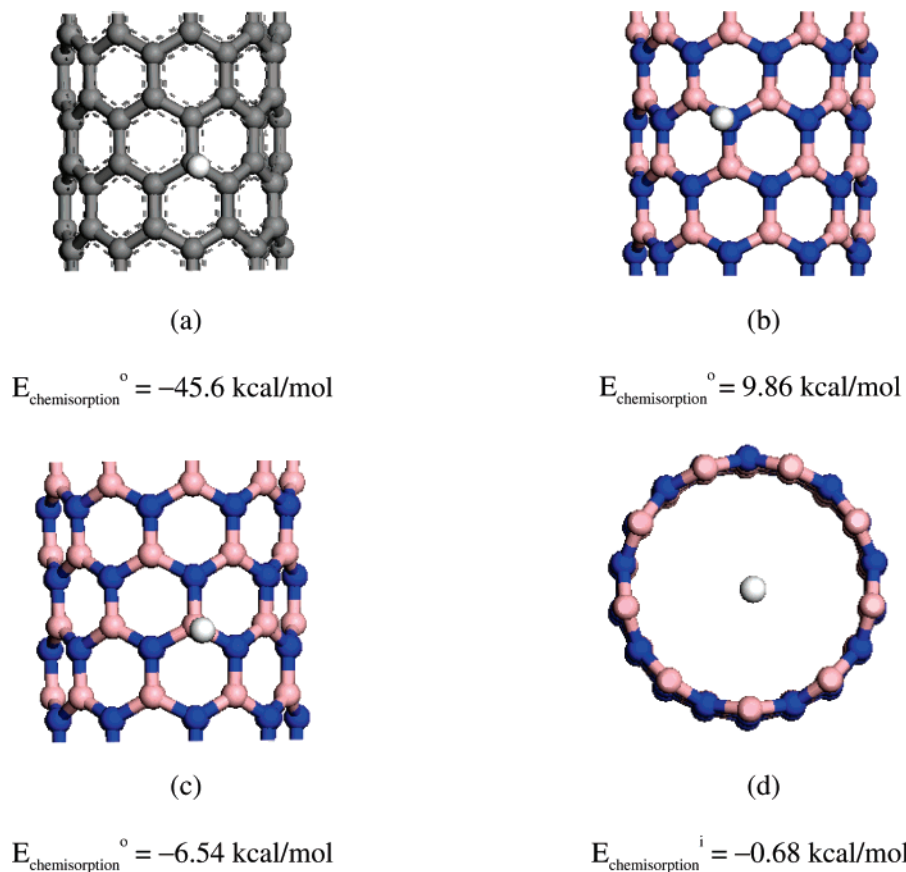


Figure 2. Chemisorption sites of a single hydrogen atom on (9,0) SWNT's. (a) At the outer wall (o) of the carbon nanotube, (b) at N, and (c) at B on the outside of the BN nanotube; (d) shows the optimum position of the hydrogen adsorbed inside (i) the BN tube.

and 1.51 \AA) are close to those reported by Yang et al.^{11e} for the sp^3 -hybridized N and are significantly longer than the B–N bond length of $1.42\text{--}1.45 \text{ \AA}$ in the perfect nanotube with sp^2 hybridization. Nevertheless, the exohedral N–H binding energy actually is *endothermic* (9.86 kcal/mol , Figure 2b). The N–H bond is metastable. The H only remains attached to N during optimization because an energy barrier toward dissociation exists.

A hydrogen atom, set initially near a boron or a nitrogen inside the BN (9,0) tube wall moves toward the center of the tube upon full geometry optimization (as shown in Figure 2d). This is due to the repulsion associated with the strong curvature effect of nanotubes.^{21b,23}

Therefore, the lowest-energy configuration of H attachment is to a boron atom from the exohedral side, as reported by Yang et al.^{11e} for an (8,0) BN tube: the exohedral H atom binding

energies were predicted to be -7.38 kcal/mol at B and 6.69 kcal/mol at N. The electron deficient character of boron results in a stronger interaction with hydrogen than that with nitrogen. Note that even the most favorable binding energy of a H atom to the (9,0) BN tube (-6.54 kcal/mol) is nearly an order of magnitude less than that to the (9,0) carbon tube (-45.6 kcal/mol , Figure 2a).

When two hydrogen atoms are chemisorbed in (9,0) carbon nanotubes, they prefer to bind to two adjacent carbon atoms because this only would saturate one C–C π bond and disrupt the tube structure modestly.^{5a} Similarly, in the BN tube, two hydrogen atoms prefer binding locations at two adjacent B and N atoms.^{11d} As with single H atom adsorption, the chemisorption exothermicity of two hydrogen atoms on (9,0) BN tubes (-85.26 kcal/mol) is much less than that on (9,0) carbon tubes (-109.09 kcal/mol).

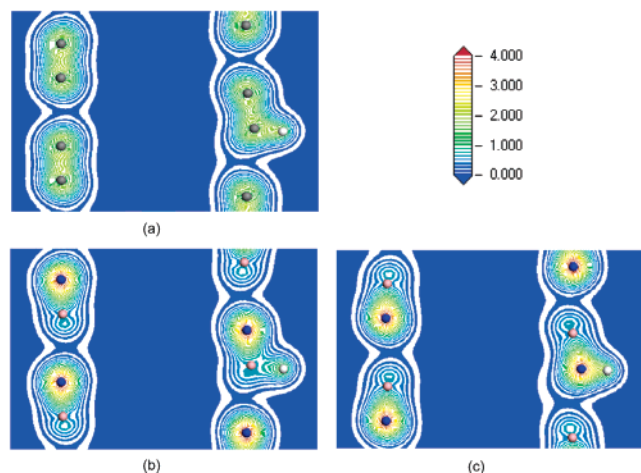
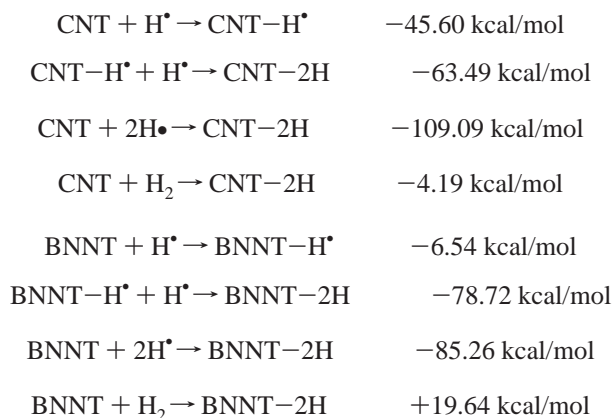


Figure 3. Contour plots of the electron density for chemisorption of a single hydrogen atom (a) at a C atom in the (9,0) carbon nanotubes, (b) at a B atom, and (c) at a N atom in (9,0) BN nanotubes. Plots (a), (b), and (c) are all obtained from the cross-section (yz plane) along the axis (z direction) of the tube including the adsorbed hydrogen atom. In each figure, the side of the wall without H adsorption is on the left, and the side with H adsorption is on the right.

It is important to emphasize that no H atoms are present in hydrogen gas because the binding energy of the H_2 molecule is -104.90 kcal/mol (at the PW91 level employed in this work). Consequently, H_2 cannot be *chemisorbed* by pristine (9,0) BN nanotubes because this is *endothermic* by nearly 20 kcal/mol. In contrast, the chemisorption of H_2 by a pristine (9,0) carbon nanotube is predicted here to be *exothermic* by -4.19 kcal/mol. For a better comparison, the reaction energy data for both C and BN nanotubes are summarized below:



This exothermic H_2 binding energy is in the desired energy range of $0.2-0.3$ eV for hydrogen storage and seems to indicate that single-walled carbon nanotubes (SWCNTs) hold promise for hydrogen storage in the gas phase. However, this is not realistic considering the rather small diameter of (9,0) SWCNTs. Note that the binding energies of SWCNTs decrease with increasing the tube diameters,^{21b,23} for example, (10,0) SWCNTs (at GGA level)^{5a} were computed to have endothermic H_2 binding energy. Thus, chemisorption of H_2 molecules on carbon nanotubes with normal diameters is not favorable.

3.3. Electronic Structure of Hydrogen Chemisorbed on (9,0) Carbon and BN Nanotubes. The computed electron densities of the single H atom-chemisorbed carbon and BN nanotubes are summarized in Figure 3a–c. Each contour plot refers to the cross section in a yz plane along the tube z axis passing through the adsorbed hydrogen atom. The red area

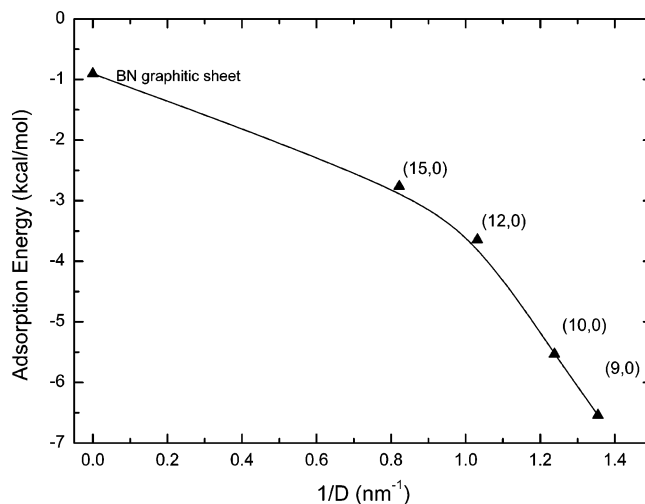


Figure 4. Chemisorption energies of H above the B atom in BN graphitic sheet and nanotubes as a function of the inverse of tube diameters (D). The chemisorption energies of H at a B atom increase gradually with decreasing the BN tube diameter. H chemisorption on BN graphitic sheet shows very low adsorption energies, i.e., -0.90 kcal/mol at a B atom as shown and 19.1 kcal/mol at a N atom (not shown in the plot).

denotes a region with high electron density; the overlap indicates covalent bonding between atoms.

Significant overlap of electron density between C and H occurs when the H atom is chemisorbed at a C atom in carbon nanotubes (Figure 3a). The BN nanotubes display the “lop-sided” densities characteristic of a considerable degree of ionic B–N bonding (Figure 3b and c). There is some overlap between N and H chemisorbed at N in BN nanotubes (Figure 3c). The same is found for BH when H is adsorbed at a B atom (Figure 3b). Because hydrogen can transfer more electron density to the electron-deficient boron, the B site is more favorable than the N site for single hydrogen atom chemisorption.

3.4. Hydrogen Chemisorption on BN Nanotubes with Various Diameters and a BN Graphitic Sheet. Chemisorption energies of H for the optimal boron sites in a BN graphitic sheet and for nanotubes with various diameters are shown in Figure 4. As discussed above, exohedral nanotube adsorption is more favorable than endohedral adsorption because of the curvature effect;^{21b,23} a H bound to the convex surface results in less skeletal distortion. The H atom chemisorption energies at B decrease smoothly with increasing BN tube diameters, approaching the limit of the graphitic sheet. The chemisorption energy of a H on a BN graphitic sheet is negligibly small, -0.90 kcal/mol at B, and is even *substantially endothermic* (19.1 kcal/mol) at a N atom.

When a H atom is chemisorbed at the B site of BN graphitic sheet, the newly formed B–H bond length is 1.34 Å, and the B–N bond lengths and NBN angles involving the H-adsorbed B atom are 1.49 Å and 117.5° , respectively. Likewise, when a H atom is adsorbed at a N site, the newly formed N–H bond length is 1.08 Å, and the B–N bond lengths and BNB angles involving the H-adsorbed B atom are 1.55 Å and 109.6° , respectively. The above results indicate the same deformation in local structure as found in the (9,0) BN nanotube (see above); both are attributed to the greater p character of the hybridization at B and especially at N after a H atom is chemisorbed.

3.5. Hydrogen Chemisorption on BN Double-Walled Nanotubes (DWNT). To mimic the hydrogen chemisorption behavior in BN multiwalled nanotubes (MWNT), we investigated the hydrogen chemisorptions in BN double-walled nano-

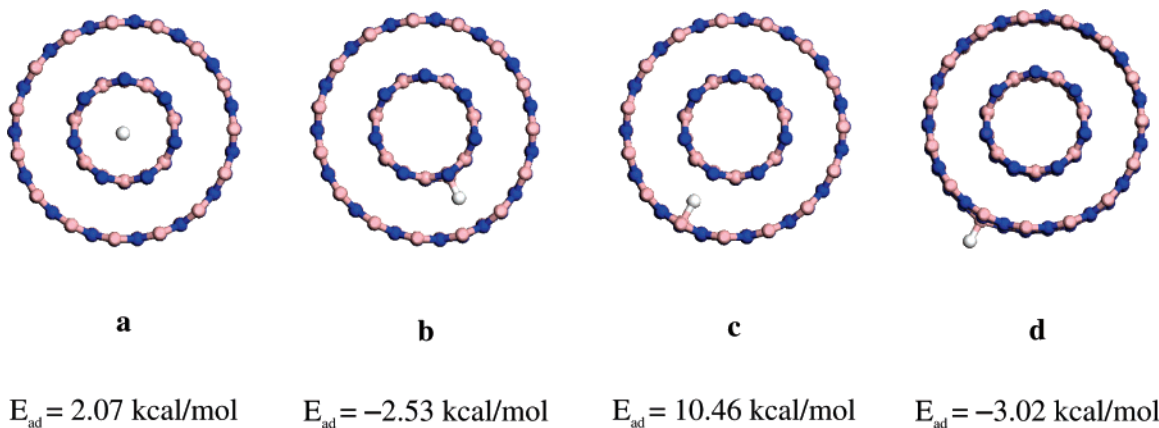


Figure 5. Hydrogen chemisorption in (7,0)@(15,0) BN double-walled nanotubes. The most stable adsorption site for hydrogen is on top of B atoms outside the outer (15,0) BN nanotube.

tubes (DWNT). BN (7,0)@(15,0), one of the most favorable BN DWNTs,²⁴ was chosen as the DWNT model. After full structural relaxation, the interwall distance is computed to be about 3.23 Å, comparable to the previous theoretical and experimental results.^{7b,8,24}

No significant changes in geometric structure have been found for hydrogen chemisorption at various sites in the BN (7,0)@(15,0) DWNT (Figure 5) compared with the same sites in the isolated BN (7,0) and (15,0) SWNTs, respectively. Because of the curvature effect as shown in Figure 4, hydrogen prefers to be chemisorbed energetically to the B sites of the outer surface of (7,0) BN SWNT among various sites in (7,0) and (15,0) BN SWNTs. However, for (7,0)@(15,0) BN DWNTs, the most energetically favorable site for H chemisorption is on top of the B sites on the outer surface of the DWNT, i.e., the outer wall of (15,0) BN tubes (Figure 5d); the related binding energy (−3.02 kcal/mol per H atom) is close to that when H is attached to a B atom outside the isolated BN (15,0) tube (−2.65 kcal/mol per H atom using VASP, comparable to the Dmol result (−2.76 kcal/mol, Figure 4)). The repulsion between the hydrogen atom and the BN tube wall is mainly responsible for the less negative H chemisorption energy on the outside wall of a thinner (7,0) tube inside the DWNTs. Further, considering the difficulties for H atoms to penetrate the tubewalls into the intertube region, H atoms tend to adsorb on top of B atoms in the outer tube wall of BN DWNTs (and even MWNTs).

3.6. Experimental Implications. Our computations show that hydrogen physisorption and chemisorption are both weaker in BN than in carbon nanotubes. According to the latest critical measurements,^{4b,c} no carbon nanotube has hydrogen storage above 0.2 wt %. How then is the rather large hydrogen storage (up to 4.2%)^{8,9} in BN tubes reported recently to be understood?

Yang et al.'s^{11d} extensive study of hydrogen storage on zigzag (8,0) BN tubes showed that, at low coverage, the H₂ adsorption energy increases when the number of the adsorbed H's is larger. However, at 50% coverage, i.e., about 4 wt % H storage, the hydrogen adsorption energy (−4.35 eV) is still 0.21 eV (4.8 kcal/mol) *smaller* than the H₂ bond energy. Hence, the chemical reaction between H₂ molecules and BN nanotubes is endothermic. Hence, hydrogen molecule storage by chemisorption is not to be expected, at least in pristine BN nanotubes. The same conclusion holds for hydrogen molecule storage in carbon nanotubes.^{5a,19b}

Note that the synthesized BN nanotubes generally have much larger diameters^{8,9} (10 nm in ref 8). Considering the size dependence discussed above, the pure pristine BN tubes used experimentally should have much lower hydrogen-binding

energies than those of our model systems. Ma et al.⁸ reported that, under pressure, multiwalled BN nanotubes (without any metal catalysts) take up 1.8–2.6% hydrogen, 70% of which was ascribed to chemisorption. Tang et al.⁹ reported up to 4.2 wt % hydrogen uptake in collapsed BN nanotubes. Ma and Tang's experiments correspond to 15.1–18.2% and around 50% hydrogen coverage on the BN SWNT surfaces, respectively. To achieve such high hydrogen uptake in BN MWNTs, the hydrogen coverage should be much higher (even over 100%).

How can H₂ chemisorption take place in BN nanotubes? This is the key question. The hydrogen storage reported by Ma⁸ and Tang⁹ cannot be explained by using the simple pristine BN nanotube models. Local defects and deformations as noticed in ref 9 should play an important role in enabling hydrogen chemisorption because the dangling bonds in defect nanotubes can offer strong binding sites and enhance the dissociation of H₂ on BN nanotubes.^{11f} Moreover, the defects may also enhance the H₂ physisorption (as in carbon nanotubes²⁵). However, the BN nanotubes in ref 8 do not have many defects; the mechanism of the hydrogen chemisorption is still a mystery. One possible explanation, analogous to that proposed in carbon nanotubes,²⁶ is that the high H₂ pressures can facilitate dissociative chemisorption in the interstitial region on the exterior of BN nanotubes. Another plausible rationalization is that realistic nanotube bundles may be very different from the model of homogeneous nanotubes packed into perfect arrays.²⁷

Another reasonable possibility for the high hydrogen storage reported by Tang⁹ is that the platinum cluster contaminants in the BN tube samples may serve as sites for hydrogen storage.²⁸ Such nanotubes serve as the supporting media for the metal clusters. The reaction between H₂ molecules with Pt clusters is exothermic, and the high H–H bond energy is overcome by the even greater energy of two H–Pt (bulk) bonds. The possibility of hydrogen adsorption on metal contaminant was also proposed by Hirscher²⁹ to explain Heben's controversial experiments, which claimed that single-walled carbon nanotubes can store up to 8 wt % hydrogen at room temperature and moderate pressure.³⁰ Recently, Kang et al.³¹ suggested that hydrogen dissociative catalysts (such as Ni, Co, and Pt) be used to enhance the hydrogen storage and showed that multiwalled carbon nanotubes (MWCNTs) with 6 wt % of Ni nanoparticles can take up approximately 2.8 wt % hydrogen at moderate temperatures and pressures (0.9 wt % higher than in Ni-free MWCNTs).

However, the basic endothermicity of reactions between H₂ molecules and pristine nanotubes is not changed by mechanistic considerations. Hydrogen adsorption at the metals themselves,

instead of enhanced hydrogen chemisorption on nanotubes, can be a better interpretation for the 0.9 wt % higher hydrogen storage in the nanotubes containing Ni particles.³¹ It would be very interesting to examine the function of platinum clusters in Tang's experiments.⁹ The above arguments show that H₂ physisorption is too weak in BN nanotubes, and it is difficult to achieve hydrogen chemisorption unless dangling bonds in the defect tubes are employed; however, the chemisorbed hydrogen in defect tubes can only be released at high temperatures, which limits practical applications.

Do these pessimistic conclusions mean that we have reached a dead end in utilizing BN nanotubes (and carbon nanotubes) as hydrogen storage media? The answer is definitely *no*. Even though nanotubes themselves may not be able to adsorb hydrogen effectively, they may serve as supporting systems for hydrogen-absorbing metals or alloys, especially clusters (as in Tang's experiment⁹), because BN nanotubes are chemically inert and thermally stable and can protect and stabilize the active metal clusters. Recently, Yildirim and Ciraci³² predicted that up to 8 wt % hydrogen storage can be achieved in titanium-decorated SWCNTs due to the strong binding between titanium and hydrogen. Moreover, Zhang et al.³³ predicted that some organometallic buckyballs, such as C₄₈B₁₂[Sch]₁₂, can store up to 9 wt % hydrogen under mild conditions; Kang et al.³⁴ predicted that Ni-dispersed fullerenes can take up 6.8 wt % H₂; Sun et al.³⁵ predicted that coating C₆₀ with isolated transition metal atoms (e.g., Sc and Ti) can lead to hydrogen storage capacities up to 8 wt % hydrogen. It seems very likely that metal- or alloy-coated BN nanotubes can function similarly. Nanotubes can also be used as additives to enhance hydrogen storage abilities of other materials. A recent example is Dehouche et al.'s³⁶ demonstration that SWCNTs can function as catalysts for improving the hydrogen absorption and desorption properties of Ti/Zr-doped NaAlH₄.

4. Conclusion

The physi- and chemisorption of hydrogen in (9,0) carbon and BN nanotubes were compared by means of density functional theory (DFT) computations employing periodic boundary conditions. Both physisorption and chemisorption of hydrogen in BN nanotubes are less favorable energetically than in carbon nanotubes. BN nanotubes cannot adsorb hydrogen molecules effectively by physisorption. Chemisorption of H₂ molecules on pristine BN nanotubes is endothermic. Consequently, perfect BN nanotubes are not good candidates for hydrogen storage. Thus, BN nanotubes cannot store hydrogen effectively, providing that only physi- and chemisorption mechanisms are considered. Alternative strategies have to be employed to use nanotube systems as hydrogen storage media, such as utilizing them as supporting media for hydrogen-absorbing metal nanoclusters.

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