3d Transition metal decorated B–C–N composite nanostructures for efficient hydrogen storage: A first-principles study

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Abstract. Ti decorated BC₄N nanotube has been studied using first-principles density functional approach, to explore the storage of molecular hydrogen. It combines the advantages of carbon nanotube, together with the thermal stability of BN nanotube. The local structural unit of BN₃ and NB₃ linked with B–N bonds are responsible for the extra stability of BC₄N nanotube as compared with CNT. While the host carbon nanotube is metallic, the substitutional doping of B and N with a large enough concentration (33%) turns it to semiconducting. Endohedral decoration, although energetically favourable, encounters a rather high barrier height of ~4 eV, as obtained from our nudge elastic band calculation of the minimum energy path. Exohedral Ti@BC₄N can bind up to four H₂ molecules. For full Ti coverage, the system can absorb up to 5.6 wt% of hydrogen. *Ab initio* molecular dynamics simulation reveals that at 500 K hydrogen gets released in molecular form. We believe that this novel composite nanotube, functionalized by Ti atoms from outside, serves as a promising system for hydrogen storage.

Keywords. Hydrogen storage; B–C–N composite nanotube; density functional; electronic structure; molecular dynamics.

1. Introduction

Hydrogen is considered to be one of the best alternative and renewable fuels (Schlappbach and Züttel 2001; Züttel 2003, 2004) because of its abundance, easy synthesis, and nonpolluting nature when used in fuel cells. 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 favourable thermodynamics (Schlappbach and Züttel 2001). 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 Department of Energy, USA (DOE Report), 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 requirements. Alternative options, by utilizing suitable solid state hydriding and dehydriding reactions in low-Z complex hydrides are being extensively studied, 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 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 (Darkrim *et al* 2002; David 2005; Jacoby 2005; Orimo *et al* 2007; Sakintuna *et al* 2007; Wolverton *et al* 2008).

Particularly promising from the point of view of hydrogen storage are porous materials such as clathrates (Hu and Ruckenstein 2006; Struzhkin *et al* 2007), zeolites (Logar and Kaucic 2006), metal–organic frameworks (Rowsell and Yaghi 2005; Hirscher and Panella 2007) and various carbon based nanostructures, such as fullerenes and nanotubes (Dillon and Heben 2001; Meregalli and Parrinello 2001; Williamson *et al* 2004). These cage-like structures have high stability, light weight (leading to high gravimetric efficiency), large surface-to-bulk ratio and possibility of functionalization with appropriate metals. Hence these systems serve as ideal materials for storage of molecular hydrogen endohedrally or exohedrally. We shall briefly discuss in the next section the advantages as well as shortcomings of single walled carbon nanotubes (CNT) (Dillon *et al* 1997) and their isoelectronic counterparts such as boron nitride nanotubes (BN–NT) (Ma *et al* 2002) for hydrogen storage.

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2. Hydrogen storage in CNT and BN–NT

Early experiments on carbon nanotubes are not so encouraging since the hydrogen storage capacity reported are less than 1% or so (Tibbetts *et al* 2001; Shiraishi *et al* 2003). Kajiura *et al* (2003) measured the hydrogen storage capacity of five types of commercially available carbon materials with different nanostructures at up to 8 MPa at room temperature. Using an apparatus where the error in the gravimetric density was less than 0.04 wt%, they reported the highest storage capacity to be 0.43 wt%. Recent theoretical study indicates that high hydrogen content in the pure carbon nanotubes cannot be achieved through physical sorption (Blase *et al* 1994). More recently, Yildirim and Ciraci (2005) have shown from their first principles calculations that functionalizing the CNT with suitable transition metal atoms could lead to high capacity hydrogen storage (~8 wt%) along with the possibility of some interesting hydrogen desorption of the system. However, tendency of a normal CNT to get oxidized around 600°C, rejects the practical possibility of using this TM functionalized CNT as far as high capacity hydrogen storage is concerned.

Because of these shortcomings of carbon nanotube, efforts have been shifted towards non-carbonic materials composed of light elements such as B and N. B–N nanostructures are analogous to their carbon counterparts and offer many advantages. For example, B–N nanotubes are stable up to 1000°C. In addition to their heat resistance in air and structural stability, B–N nanotubes are semiconducting with wide bandgaps (5.5 eV) that is nearly independent of tube diameter or helicity. With the advancement in synthesis techniques, many novel forms of B–N nanostructures, such as nanotubes (Chopra *et al* 1995; Ma *et al* 2002), bamboo-like wires (Oku *et al* 2004a), nanocages (Oku *et al* 2004b), and nanocapsules (Oku and Narita 2002) have been discovered. Furthermore, several authors have also studied the hydrogen uptake and reversibility issues of B–N nanostructures (Ma *et al* 2002; Narita and Oku 2002; Oku and Narita 2002; Oku *et al* 2004a, b). However, if we look at the practical implementation of these kinds of structures for hydrogen storage, these have limited success. This is because of (a) the stability of most of these cage like B–N nanostructures at room temperature (Sun *et al* 2005) and (b) the abnormally high hydrogen-desorption temperature from the B–N nanotubes for its extra thermal stability (Ma *et al* 2002).

3. B–C–N composite nanotube: Motivation and a wish list of properties

Is it possible to exploit the thermal stability of BN nanotube, together with the advantages of Ti functionalized CNT? The aim of the present work is precisely to achieve

this by designing a Ti functionalized B–C–N nanocomposite, viz. BC₄N nanotube, as a possible H-storage material. B_xC_yN_z nanostructures have been studied both experimentally and theoretically (Weng-Sieh *et al* 1995; Sen *et al* 1998). Recently, BC₄N nanotubes have been experimentally synthesized (Raidongia *et al* 2008) and found to be semiconducting in nature with a very high thermal stability. The local structural unit of BN₃ and NB₃ linked with B–N bonds are responsible for the extra stability, as compared to its host carbon nanotube. While the host carbon nanotube is metallic, the substitutional doping of B and N with a large enough concentration (33%) turns it to a semiconductor. The synthesis, characterization and various properties of BC₄N nanotubes are described in detail by Raidongia *et al* (2008). What we have done is to explore how to functionalize it for storage of molecular hydrogen (Bhattacharya *et al* 2008).

Incidentally, there have been earlier studies of transition metal doped carbon nanotubes (Yagi *et al* 2004), but the motivation was to understand magnetism that got manifested in this system. However, in order to utilize functionalized nanotubes for efficient hydrogen storage, we have to address several open questions e.g.: (i) Does transition metal prefer to stay in exohedral or endohedral position of the nanotube? (ii) What is the energy barrier for the transition metal to enter into or escape from the nanotube? (iii) What happens when more transition metals are decorated in different hexagonal faces of the nanotube? (iv) How the binding energy of H₂ changes during addition of more H₂ in the TM-doped BC₄N nanotube both in exohedral and endohedral position? (v) As more H₂ are stored, what are the changes in the geometry and electronic structure of the nanotube? (vi) Lastly, from the hydrogen storage point of view, what is the effect of the temperature on the stability of this kind of B–C–N composite nanotube? In this work, we provide a detailed study to address these questions for this novel BC₄N nanotube, and see if the storage efficiency can be improved significantly.

4. Computational details

Electronic structure and total energies were calculated with the Vienna *ab initio* simulation package (VASP) (Kresse and Hafner 1994; Kresse *et al* 1996), based on DFT (Hohenberg and Kohn 1964; Kohn and Sham 1965). Projector-augmented wave (PAW) potentials (Blöchl 1994) 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 (Perdew and Wang 1992; Perdew *et al* 1992) exchange–correlation potential. The *k*-points mesh was generated by the Monkhorst–Pack (Monkhorst and Pack 1976) 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 (Pulay 1980; Press *et al* 1986), atomic forces were converged to less than 0.001 eV/Å by conjugated gradient (CG) minimization. We also performed *ab initio* molecular dynamics (MD) simulations in order to investigate the stability of the optimized structures and desorption of hydrogen molecules from Ti@BC₄N nanotube.

5. BC₄N nanotube

5.1 Ground state structure

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 investigated to be semiconducting with varying energy gaps, and all are nonmagnetic (Raidongia *et al* 2008). Since nanotubes with larger bandgap are likely to show stronger hydrogen adsorption (Yildirim and Ciraci 2005), we have chosen for our model study, the (6,6) armchair BC₄N nanotube that shows the largest bandgap (~1.0 eV) in this family. The accuracy of our computational tool was tested by relaxing this (6,6) armchair nanotube structure, that resulted in the optimized diameter of 8.3 Å, which is in good agreement with the available experimental value (Raidongia *et al* 2008). Further, to take into account the different chemical orderings of hexagons, we have cho-

sen the length of the nanotube to be 14.9 Å. The corresponding supercell that we constructed for our simulation studies contains 24 B, 96 C and 24 N atoms (figure 1a).

The thermal stability of BC₄N nanotube is very high, ~900°C (Raidongia *et al* 2008). Selective substitution of C atoms by B and N (figure 1b) make this system more stable compared to the well-known CNT. Such a composite carbon based nanotube is expected to retain the advantages of CNT, and at the same time avoid the possibility of oxidation of normal CNT. However, pure BC₄N nanotube is not a good hydrogen storage medium as it can store only up to 0.7 wt% of hydrogen (Raidongia *et al* 2008).

Therefore, we have tried to dope a 3d transition metal, like Ti, which had earlier been used to decorate other fullerene and nanotube surfaces (Yildirim and Ciraci 2005; Barman *et al* 2008) 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 amongst all 3d transition metals from hydrogen storage point of view (Shevlina and Guo 2006).

5.2 Endo- vs exo-hedral 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 the B–C–N hexagonal faces, the mean number of valence electrons is 4 and a Ti atom also has exactly the same number of valence electrons. We placed Ti on the different hexagonal faces of the BC₄N nanotube either exohedrally or 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 positions at different hexagonal sites for BC₄N nanotube. Endohedral position turns out to be energetically favourable compared to exohedral, and amongst 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 Ti@BC₄N 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

Figure 1 (Colour online). (a) Ball and stick model of pure BC₄N nanotube and (b) BN₃ and NB₃ connection with a BN bond. Pink ball = B, blue ball = N, dark ash ball = C.

help of nudge elastic bands (NEB) method where we tried to move a Ti atom slowly from outside to inside of the BC_4N nanotube in six steps. We found that the approximate barrier height is 4 eV/Ti atom (figure 2). This signifies that, it is energetically costly to substitute a Ti atom inside the nanotube.

5.3 H-storage in $\text{Ti@BC}_4\text{N}$

The results of adsorption of hydrogen in molecular form have been summarized in table 2 both for exohedral and endohedral positions (figure 3). It is to be noted from table 2 that in exohedral and endohedral $\text{Ti@BC}_4\text{N}$, each of the Ti+ ion can get attached to 4 H_2 molecules. In the endohedral case, the last H_2 molecule gets physisorbed with Ti atom with a very weak binding energy value of

Table 1. Binding energy values and number of inequivalent hexagons for different adsorption sites of Ti atoms both in exohedral and endohedral positions of BC_4N nanotube. Different hexagon faces have been designated as $\text{B}_{n_1}\text{C}_{n_2}\text{N}_{n_3}$ with $n_1 + n_2 + n_3 = 6$. N_{hex} is the number of inequivalent hexagons (total 57) in BC_4N nanotube of length, 14.9 Å.

Different hexagonal faces N_{hex}		Binding energy (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	-1.57
2N-1B-3C	9	-1.81	-1.52
1B-1N-4C	6	-2.07	-1.70

Figure 2. Barrier height for Ti atom to move from outside to inside of the BC_4N nanotube as calculated by nudge elastic band (NEB) method (see text for details). The estimated barrier height is ~4 eV.

~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 $\text{Ti@BC}_4\text{N}$ nanotube with consecutive H_2 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 H_2 molecule. But from our NEB results we may infer that endohedral Ti decoration is practically a difficult task. So in order to increase the weight percent for hydrogen storage, we have decorated this BC_4N nanotube exohedrally with Ti atoms on all the 6C hexagonal sites and optimized the geometry of the decorated structure. The final optimized structure is shown in figure 4a. We infer from this that since each Ti atoms can adsorb 4 H_2 molecules, altogether 72 H_2 molecules can be adsorbed by this system with an estimated 5-60 wt% of hydrogen storage. Now a fully relaxed self-consistent calculation on $\text{Ti}_{18}\text{@BC}_4\text{N}+72\text{H}_2$ is computationally quite demanding. So we have checked with two adjacent Ti atoms, i.e. $\text{Ti}_2\text{@BC}_4\text{N}$ and found that this system can adsorb 8 H_2 molecules (figure 4b). With this result, we can conclude that the final Ti decorated BC_4N system can adsorb up to 5-60 wt% of hydrogen.

5.4 Electronic structure

In figure 5 we have illustrated the partial density of states of pure BC_4N , $\text{Ti@BC}_4\text{N}$ and $\text{Ti@BC}_4\text{N}+n\text{H}_2$ [$n = 1, 2, 3, 4$], 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 BN_3 and NB_3 linked with B-N bonds (figure 1b) is the main reason of 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 6a), 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 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 $\text{Ti@BC}_4\text{N}$) becomes de-populated in $\text{Ti@BC}_4\text{N}+4\text{H}_2$ at the cost of the H-1s peak to grow (see figure 5). This is also apparent from the molecular orbital plot of $\text{Ti@BC}_4\text{N}+4\text{H}_2$ where we can clearly see that we need two unoccupied d-orbital, one for molecular bonding with hydrogen and the other to bind the metal to the nanotube (figure 6b).

Figure 3 (Colour online). Consecutive adsorption of H_2 molecules in (a) exohedral $\text{Ti@BC}_4\text{N}$ nanotube and (b) endohedral $\text{Ti@BC}_4\text{N}$ nanotube. Pink ball = B, blue ball = N, dark ash ball = C, light ash ball = Ti, white ball = H.

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

Table 2. Binding energy values for H_2 adsorption in exo- and endo-hedral $\text{Ti@BC}_4\text{N}$ nanotubes.

BE (eV) for exohedral molecular H_2 adsorption		BE (eV) for endohedral molecular H_2 adsorption	
System	BE value (eV/ H_2 molecule)	System	BE value (eV/ H_2 molecule)
$\text{Ti@BC}_4\text{N}+1\text{H}_2$	−0.66	$\text{Ti@BC}_4\text{N}+1\text{H}_2$	−0.48
$\text{Ti@BC}_4\text{N}+2\text{H}_2$	−0.67	$\text{Ti@BC}_4\text{N}+2\text{H}_2$	−0.63
$\text{Ti@BC}_4\text{N}+3\text{H}_2$	−0.58	$\text{Ti@BC}_4\text{N}+3\text{H}_2$	−0.18
$\text{Ti@BC}_4\text{N}+4\text{H}_2$	−0.40	$\text{Ti@BC}_4\text{N}+4\text{H}_2$	−0.04

Table 3. Bond length details of Ti–C, Ti–H and H–H in 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

Figure 5 (Colour online). Partial densities of states projected on to the individual constituents for (i) BC₄N, (ii) Ti@BC₄N, (iii) Ti@BC₄N+1H₂, (iv) Ti@BC₄N+2H₂, (v) Ti@BC₄N+3H₂ and (vi) Ti@BC₄N+4H₂.

5.5 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+4H₂ sys-

tem which is heated in steps first from 0–300 K and then from 300–500 K with 1 fs time step using Nose algorithm (Nose 1984). We have noticed that at 300 K the system remains stable with all four H₂ molecules attached on Ti atom in Ti@BC₄N nanotube, whereas hydrogen starts desorbing from Ti@BC₄N nanotube at a temperature around 500 K (figure 7). By carrying out *ab initio* mole-

Figure 6 (Colour online). (a) 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 and (b) Ti- d orbital hybridized with the $1s$ orbitals of 4H_2 complex and the $2p$ orbitals of 6C carbon hexagon, in $\text{Ti@BC}_4\text{N}+4\text{H}_2$.

Figure 7 (Colour online). Desorption of hydrogen from $\text{Ti@BC}_4\text{N}+4\text{H}_2$ at 500 K.

cular dynamics (MD) to this 153 atoms system for 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 H_2 molecules without breaking the Ti–C bonding from the host system $\text{Ti@BC}_4\text{N}$ at a relatively moderate temperature around 500 K.

6. Conclusions

In summary, we investigated the ground state structure and stability of exohedral as well as endohedral Ti-decorated (6,6) armchair BC_4N nanotube which can be considered as an amalgam of carbon and B–N nanotubes. Each sitting on 6C hexagonal face of the nanotube absorbs

up to 4 H_2 molecules. The entire structure remains stable up to 500 K where H_2 comes out without breaking the Ti–C bonding. The desorption temperature and kinetics are quite favourable, at the same time, the gravimetric efficiency corresponding to full Ti coverage turns out to be $\sim 5\text{--}6$ wt%. Thus Ti-decorated BC_4N nanotube shows more promise than conventional carbon nanotube and boron nitride nanotube for the purpose of H_2 storage in a nanostructure material.

Currently we are exploring the possibility of jacking up the gravimetric efficiency to ~ 8 wt%, retaining the desorption characteristics in tact, by flattening the nanotube and forming a graphene-like planar structure with TM decoration on both sides (Bhattacharya *et al*, to be published). While hydrogenation of graphene has already been suggested by earlier workers (Sluiter and Kawazoe 2003; Boukhvalov *et al* 2008), such a novel Ti-decorated planar BC_4N structure is expected to yield a breakthrough in the area of hydrogen storage in nanomaterials.

Acknowledgements

The authors would like to thank Prof. Umesh V. Waghmare for many helpful discussions, and to Dr Mousumi Upadhyay-Kahaly for providing the structural details of (6,6) BC_4N nanotube.

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