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## Hetero-atoms as activation centers for hydrogen absorption in carbon nanotubes

### B. Viswanathan <sup>\*</sup>, M. Sankaran

National Centre for Catalysis Research, Indian Institute of Technology Madras, Chennai-600 036, India

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### ABSTRACT

Carbon materials should have specific centers for hydrogen adsorption/absorption. The role of heteroatom substitution in carbon nanotubes as an activator has been identified by Density Functional Theory. The effect of various hetero-atoms like nitrogen, phosphorus, sulphur and boron for hydrogen activation and their geometrical positions has been recognized as the one of the possible reasons for easy hydrogenation. Experimentally, nitrogen and boron containing carbon nanotubes have been synthesized by using template method. The hydrogen absorption capacity of these materials has been evaluated. It is shown that, there is a need to stabilize nitrogen in the carbon nanotube framework for reproducible hydrogen uptake. In case of boron containing carbon nanotubes, two different chemical environment of boron facilitates hydrogen interaction. They exhibit a maximum of 2 wt% of hydrogen storage capacity at 80 bar and 300 K. This configuration has a bearing in hydrogen sorption characteristics.

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#### 1. Introduction

22All the three components of the hydrogen economy, namely, production, storage and application of hydrogen have been posing 23challenges to the scientific community for the past several decades. At 24present, storage of hydrogen in solid matrices appears to be the 25appropriate option. The desirable storage capacity for viable commercial 26exploitation of hydrogen as energy source is at least 6.5 wt.% as originally 27postulated by United States-Department of Energy (US-DOE). However, 28any figure up to 67 wt.% has been claimed as possible storage capacity in 29solids especially in carbon based materials [1-4]. This has led to a variety 30 of investigations dealing with modification of carbon materials like 31 metal loading, preparing carbon materials in various geometrical forms, 32 and phase purity and addition of metal oxides [5,6]. However, none of 33 these studies have unambiguously established that carbon nanomater-34 ials can store hydrogen to the extent required by the original US-DOE 35 standards at ambient conditions. This situation is critical, demanding 36 definite and exploratory solutions from practicing scientists. The 37 essential questions that require immediate attention are: 38

- (i) Are the carbon materials appropriate for solid state hydrogen storage?
  - (ii) If this was to be true, what types of materials or treatments for the existing carbon materials are suitable to achieve the desirable levels of hydrogen storage?
- (iii) What are the stumbling blocks in achieving the desirable storage of hydrogen in solid state?

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 (iv) Where does the lacuna lie? Is it in the theoretical foundation of 46 the postulate or is it in our inability to experimentally realize the 47 desired levels of storage?

Against this background, the need for an activator for hydrogenation 49 in carbon materials is realized, which should be easily hydridable than 50 carbon and facilitate migration of the dissociated hydrogen to 51 equipotential carbon surface has been realized. While considering 52 these aspects, hetero-atoms like N, P, S and B seem to be promising 53 activators due to their properties like higher redox potential than that of 54 carbon and the lower standard free energy of formation of hydrides. 55 Therefore, the present study is to establish the role of heteroatom in the 56 carbon materials for hydrogen storage by means of theoretical and 57 experimental methodologies. 58

In this study, the importance, gradation and the geometrical positions 59 of hetero-atom substitution in carbon nanotubes for hydrogen activation 60 were studied theoretically. To study the activation of hydrogen by the 61 hetero-atoms, we apply a combined Universal Force Field (UFF) and 62 Density Functional Theory (DFT) methods. In the later stage, DFT method 63 has been utilized to study the reaction mechanism by using simple 64 clusters chosen from the reactive part of the carbon nanotube (CNT) for 65 accurate results. In correlation to theoretical results, experiments were 66 carried out to show the role of hetero-atoms for hydrogen activation. 67 Pure CNTs and hetero-atom containing carbon nanotubes (HCNTs) were 68 prepared by using various templates such as zeolite, clay and alumina 69 membranes. The prepared CNTs are characterized by X-ray diffraction 70 (XRD), Raman spectrum, infrared spectroscopy (IR), cross polarization 71 magic angle spinning nuclear magnetic resonance (CP MAS NMR), 72 transmission electron microscopy (TEM) and high pressure hydrogen 73 adsorption measurements. The variation of template and the car-74 bon precursor causes differences in the morphology. The chemical 75

<sup>\*</sup> Corresponding author. Fax: +91 4422575245. E-mail address: bvnathan@iitm.ac.in (B. Viswanathan).

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**Fig. 1**. (a) The side view of the UFF optimized CNT (4, 4) cluster taken for the study, where the terminal positions are saturated with hydrogen (b) Top view of the heteroatom (arrow indicated ball) containing CNT cluster with the hydrogen molecule interaction (c). Hydrogen interaction with the boron atoms substituted in the adjacent positions of the CNT. (d) Hydrogen interaction with the alternate positions of the CNT (the arrow indicated are boron atom).

environment of nitrogen and boron and their relevance towards
hydrogen storage application is also examined in correlation to theoret ical results.

#### 79 2. Computational methods

80 For the theoretical calculations the model has been constructed with three arm chair type (4, 4) carbon nanotubes, which form a 3.65 Å inter 81 82 tubular space as shown in Fig. 1. The substitution of hetero-atoms carried out at the edge positions of the nanotube, which show the minimum 83 potential energy for the cluster. Computations using DFT have been 84 85 carried out on the optimized configuration obtained using UFF 1.02 parameter. Cerius2 software was used for the force field calculations and 86 87 the single point energy calculations on the optimized configurations obtained from force field have been carried out using Gaussian 03 with 88 Becke's three parameter hybrid function with LYP correlation function 89 (B3LYP) and 6-31G (p, d) as basis set. The total energy, H–H bond 90 distance as well as the dissociation energy of hydrogen were obtained 91 from these calculations. To study the reaction mechanism, a simple 92 cluster model with 14 carbon atoms has been chosen. The cluster model 93 94 is the terminal and reactive part in the SWNT for the hydrogen interaction and hydrogenation [7,8]. The cluster was fully optimized 95 with Density Functional B3LYP method with 6-31G (p, d) basis set. All 96 the DFT calculations were performed using Gaussian 03 in a cluster of 97 IBM Linux machine. 98

#### 99 3. Experimental section

100 3.1. Synthesis of pure, nitrogen and boron containing carbon nanotubes

Pure carbon nanotubes (CNT1) were prepared by using polyphenylacetylene polymer as the carbon source by using alumina membrane as template. The composite was then carbonized by heating in Ar atmosphere at 1173 K for 6 h at a heating rate of 10 K/min. This resulted in the deposition of carbon on the channel walls of the membrane. The

carbon/alumina composite was then placed in 48% hydrofluoric acid 106 (HF) to free the nanotubes. The tubes were washed with distilled water 107 to remove HF [9]. For nitrogen containing CNTs (NCNT1) preparation 108 polypyrrole has been used. Polypyrrole (PPY) coatings were applied by a 109 reaction coating approach by suspending alumina template membrane 110 in an aqueous pyrrole (0.1 M) solution containing 0.2 M ferric chloride 111 hexahydrate. The membrane was then dried and placed in a quartz boat 112 and carbonized in Ar atmosphere at 1173 K for 6 h. The resulting carbon/ 113 alumina composite was immersed in 48% HF for 24 h to remove the 114 template. The residue was thoroughly washed with distilled water to 115 remove traces of HF and dried at 373 K for 10 min (NCNT1). Boron 116 containing CNTs (BCNT1) were prepared by using the boron containing 117 polymer as the carbon precursor. Stable cross linked  $\pi$ -conjugated 118 organoboron polymer prepared by hydroboration polymerization of 1,4-119 divinylbenzene and diborane in THF medium under nitrogen atmo- 120 sphere. The polymer/alumina composite membranes have been 121 carbonized at 900 °C for 6 h in Ar atmosphere. The carbon/alumina 122 composite was treated with 48% HF for 24 h to remove the template and 123 washed with distilled water followed by drying at 100 °C (BCNT1). 124

Other CNTs were prepared by chemical vapour deposition (CVD) 125 method by using H-zeolite Y (CNT2, NCNT2 and BCNT2) and Al-pillared 126 Clay (CNT3, NCNT3 and BCNT3) as template. Acetylene (5 ml/min) has 127 been used as a carbon source and for boron source in-situ generation of 128 borane gas by the addition of conc. H<sub>2</sub>SO<sub>4</sub> to the NaBH<sub>4</sub> in THF medium. 129 For the nitrogen source pyridine was chosen and bubbled through inert 130 gas reaction chamber, carbonized at 900 °C in Ar atmosphere. The 131 carbon/zeolite and carbon/clay composite have been treated with 48% 132 HF for 24 h and the undissolved carbon has been washed with distilled 133 water and dried at 100 °C. In the present case metal or metal oxide 134 catalyst were not used and this will avoid the presence of metal 135 impurities in carbon nanotubes and facilitates the study of the effect of 136 heteroatom alone. The prepared materials have been characterized by 137 various techniques like XRD, IR, TEM, SEM, Raman, MAS-NMR, and 138 hydrogen adsorption activity. Table 1 represents the detail about the 139 preparation and characterization of the samples prepared. 140

Synthesis of heteroatom substituted carbon nanotubes

Template	Carbon materials	Carbon source	Technique	Morphology
Alumina membrane	CNT1	Polyphenylacetylene (PPA)	Filtration	Tubular
	NCNT 1 (6.4%)	Polypyrrole (PPY)	In-situ polymerization	
	BCNT1	Organoboron polymer		
Zeolite	CNT2	Acetylene	CVD	Tubes and fibers
	NCNT2 (2.5%)	Acetylene + pyridine		
	BCNT2	Acetylene+borane gas		
Clay (pillared)	CNT3	Acetylene	CVD	Tubes and fibers
	NCNT3 (1.8%)	Acetylene + pyridine		
	BCNT3	Acetylene+borane gas		

t1.13 Number in bracket represents the percentage of nitrogen content by carbon, hydrogen, and nitrogen (CHN) analysis.

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#### 141 **4. Results and discussion**

#### 142 4.1. Theoretical section

The total energy, hydrogen bond distance and the dissociation 143energy of hydrogen molecule obtained are given in Table 2. The points 144 that emerge out of the results are: (i) Hydrogen activation has been 145favored by a decrease in the hydrogen dissociation energy in the case of 146 147 substitution of hetero-atoms like N, P and S. The dissociation energy of hydrogen in its free state is 4.76 eV, and remains unaltered when it is 148 149placed in between the pure carbon nanotubes (4.51 eV). Whereas it is altered to 0.13, 0.22 and 2.33 eV for S, N, and P substituted CNTs 150151respectively. Though the calculated dissociation energy values are 152unrealistically small, they definitely indicate that the dissociation of hydrogen molecule is a facile process on heteroatom substituted carbon 153 nanotubes. Even though the calculated dissociation energy is small, the 154process of hydrogen storage may involve other barriers including mass 155 transport and hence could not be achieved at such low energies. 156

The lowering of this dissociation energy of hydrogen molecule can be 157explained on the basis of redox potential values of the respective redox 158couples involved. For instance, redox potentials of hetero-atoms are 159higher than that of carbon  $(S/S^{2-}, N/N^{3-}, P/P^{3-}, C/C^{4-}$  are respectively, 160 161 0.171, 0.057, -0.111 and -0.132 V vs Standard Hydrogen Electrode (SHE). The same fact can be further independently supported by the Ellingham 162 diagram which indicates that free energy of formation of N-H bond is 163 more favorable than that of C–H bond [7]. 164

The bond length of the hydrogen molecule is elongated in 165166 heteroatom substituted CNT compared to that of pure CNT, indicating that there is considerable amount of activation of hydrogen molecule in 167 heteroatom containing CNTs. (ii) Substitution of boron atom in the CNT 168 shows interesting results. Single boron substitution cannot activate the 169170hydrogen molecule. Two boron atoms are essential for the hydrogen 171activation. The dissociation energy of hydrogen for single boron 172substitution is 5.95 eV where as when two boron atoms are substituted in adjacent positions the dissociation energy is reduced to 3.88 eV. It is 173further decreased to 0.28 eV when two boron atoms are substituted in 174 the alternate positions. This implies substitution of boron at alternate 175 positions is more favorable for hydrogen activation rather than 176 substitution at adjacent positions. It can be substantiated that boron-177 boron bond length is the key factor for hydrogen-hydrogen bond 178 activation. Substitution of B at alternate position seems to be favorable 179180 for the activation of hydrogen, where in bonding appears to be similar to that of diborane [8]. 181

Calculation of transition state parameters show that the reaction
proceeds from one minimum to another minimum via an intermediate
maximum. The movement of hydrogen from the heteroatom can be

Bond length and dissociation energy of hydrogen on the CNTs calculated using B3LYP with 6-31 g(p, d) basis set on the UFF optimized structure

t2.3	Substitution	Total energy (Hartrees)	Bond length H <sub>1</sub> –H <sub>2</sub> (Å)	Dissociation energy (eV)
t2.4	Hydrogen	-1.175	0.708	4.76
t2.5	CNT	-3686.5502	-	-
t2.6	CNT+H <sub>2</sub>	-3687.7161	0.776	4.51
t2.7	N CNT	-3702.5908	-	-
t2.8	N CNT+H <sub>2</sub>	-3703.5989	0.835	0.22
t2.9	P CNT	-3989.1694	-	-
t2.10	P CNT+H <sub>2</sub>	-3990.2550	0.815	2.33
t2.11	S CNT	-4046.0020	-	-
t2.12	S CNT+H <sub>2</sub>	-4047.0067	0.817	0.13
t2.13	B CNT	-3671.7254	-	-
t2.14	B CNT+H <sub>2</sub>	-3672.9440	0.818	5.95
t2.15	2B CNT (adjacent)	-3658.6666	-	-
t2.16	2B CNT (adjacent)+H <sub>2</sub>	-3659.8092	0.913	3.88
t2.17	2B CNT (alternate)	-3659.3491	-	-
t2.18	2B CNT (alternate)+H <sub>2</sub>	-3660.3594	0.928	0.28

Table 3

4.2

Transition state optimized parameters of the cluster and the value of the activation energy calculated by B3LYP with 6-31 g(p, d) basis set

							49.0
Substitution	Ea I (eV)	Ea II (eV)	H <sub>1</sub> -H <sub>2</sub> (Å)	Х–Н (Å)	$C-H_1^a$ (Å)	C-H <sub>2</sub> <sup>a</sup> (Å)	t3.3
CNT cluster	10.02	-	0.71	-	-	-	t3.4
N CNT cluster	3.84	4.58	1.45	1.11	1.70	1.94	t3.5
P CNT cluster	3.81	3.99	1.51	1.61	1.27	2.33	t3.6
S CNT cluster	3.65	4.85	1.50	1.75	1.24	2.40	t3.7
2B CNT cluster (adjacent)	2.22	2.98	1.95	1.31	2.59	2.72	t3.8
2B CNT cluster (alternate)	1.5	2.33	2.95	1.47	1.47	2.34	t3.9
Where $F_{a} = F$ (transition state	-E (react	ant)					t3.10

<sup>a</sup> Shortest C–H bond distance.

conceived by the transition state theory calculation. The activation 185 energy ( $\Delta E_a$ ) for this process has been obtained using the calculated 186 parameters and the results are given in Table 3. 187

From the results, it is clear that the energy for the activation of 188 hydrogen in the first transition state is lower for the heteroatom 189 containing CNT compared to pure CNT. In addition, subsequent transfer 190 of hydrogen to carbon is a facile process in the presence of heteroatom. 191 Boron containing CNT with boron atom located at alternate positions 192 show considerable reduction in the overall activation barrier compared 193 to the system with boron located at adjacent positions. These results 194 support the contention that hetero-atoms are the appropriate sites for 195 hydrogen activation. In recent results it has been shown that high 196 hydrogen in the carbon frame work [10]. These results further support the 198 present theoretical calculations.

The present studies thus have shown that hydrogenation of CNTs 200 requires activation centers and the heteroatom containing CNTs are able 201 to activate the hydrogen in a facile manner compared to pure CNTs. For 202 the effective hydrogenation and hydrogen storage these hetero-atoms 203 should be incorporated geometrically and chemically into the carbon 204 network. 205

P. Experimental section	206
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Carbon nanomaterials have been prepared by using various tem- 207 plates such as zeolite, clay and alumina membranes as per the details 208 given in Table 1. The prepared carbon nanomaterials have been 209 characterized by XRD, Raman, SEM, TEM and hydrogen absorption 210 measurements. Volumetric hydrogen absorption measurements have 211 been carried out using custom built volumetric and Seivert's apparatus. 212 All the hydrogen absorption measurements have been carried out at 213 room temperature. The experiments have been repeated under the 214 same conditions for various pressures. The compressibility factor of 215 hydrogen has been utilized. 216

Template aided synthesis of nitrogen containing carbon nanotubes 217 using alumina membrane as the template yielded well-aligned carbon 218 nanotubes (NCNT1) and gives a maximum of 1.2 wt.% hydrogen storage. 219 However, in the consecutive cycle the value decreased to 0.6 wt.% due to 220 reduction of nitrogen concentration. Nitrogen containing carbon 221 nanomaterials produced by clay as the template (NCNT3) showed a 222 maximum of 1.75 wt.%. The maximum storage capacity retained even 223 after three cycles. Thus the nitrogen atoms in carbon nanotubes act as 224 the active centre and these active sites should be made catalytic in 225 nature by adopting \_\_\_\_\_ devising suitable preparation methods [11,12]. 226

The importance of gradation and the geometrical positions of boron 227 substitution in carbon nanomaterials for hydrogen activation through 228 DFT have been analyzed (refer theoretical section). Preparation and 229 characterization of boron containing carbon nanomaterials by different 230 methods and their structural morphology and also the chemical 231 environments of boron and their relevance towards hydrogen storage 232 application are studied. The variation of template and the carbon 233 precursor causes difference in the morphology and also the chemical 234 environments of boron. <sup>11</sup>B CP MAS NMR experiments have been carried 235

t3.1

 $\pm 3.11$ 

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Table 4

Comparison of hydrogen storage capacity and their morphology variation due to templates used in preparation of carbon nanotubes



out to determine the environment of boron in the carbon network. Boron 236containing carbon nanotubes prepared with polymer precursor using 237alumina membrane as template show different boron chemical environ-238239ments and structural morphology. There are two different chemical environments in which boron is present in the carbon nanotube prepared 240by polymer route (BCNT1). A maximum of 2 wt.% of hydrogen storage 241 capacity has been achieved, whereas BCNT produced by other method 242 showed multiple environments for boron and exhibited a hydrogen 243 244storage capacity of 0.2 wt.% only. These results correlate with the 245theoretical studies, that differences in the chemical environment alter the hydrogen absorption activity [13,14]. Comparison of hydrogen storage 246capacity and their morphology variation due to templates used in 247preparation of carbon nanotubes are tabulated in Table 4. 248

#### 5. Conclusions 249

The significant conclusions arrived at from these studies are heteroatom-250containing carbon nanomaterials are amenable to hydrogen absorption 251compared to pure carbon materials. It confirms that, these hetero atoms 252in carbon matrices act as the active centers and these active sites should 253be made catalytic in nature by adopting and devising suitable preparation 254methods. The heteroatom substitution in the carbon nanotubes opens up 255256another avenue in the search for materials for hydrogen storage. 281

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