

Final Report

**Title: Investigation of hydrogen storage in Single Walled Carbon
Nanotubes for fuel cells - 2**

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14. ABSTRACT Single walled carbon nanotubes (SWCNTs) dispersed in 2-propanol are deposited on the alumina substrate using drop caste method. The deposited SWCNTs are characterized using the techniques SEM, EDS and FTIR. Then the SWCNTs are functionalized with BH3 using LiBH4 as the precursor. FTIR, XPS and CHNS techniques are use to confirm the functionalization. The functional groups are identified from FTIR studies. The various elements present in the functionalized SWCNTs are identified from XPS and CHNS studies. The functionalized samples are hydrogenated and the hydrogen storage capacity of these samples is estimated. The SWCNT deposition, functionalization with BH3 and hydrogenation are carried out successfully for the first time. The SWCNTs have been successfully functionalized with BH3 as predicted theoretically using LiBH4 as the precursor. From XPS studies, the presence of Li, B, and O are observed in our sample. Presence of BH3 is confirmed using FTIR studies. The hydrogen storage capacity of the functionalized SWCNTs is found to be 1.5 wt% at 50? C. Hydrogenation depends upon various parameters which are to be optimized to achieve maximum hydrogen storage capacity.								
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Abstract:

Single walled carbon nanotubes (SWCNTs) dispersed in 2-propanol are deposited on the alumina substrate using drop caste method. The deposited SWCNTs are characterized using the techniques SEM, EDS and FTIR. Then the SWCNTs are functionalized with BH_3 using LiBH_4 as the precursor. FTIR, XPS and CHNS techniques are use to confirm the functionalization. The functional groups are identified from FTIR studies. The various elements present in the functionalized SWCNTs are identified from XPS and CHNS studies. The functionalized samples are hydrogenated and the hydrogen storage capacity of these samples are estimated. The SWCNT deposition, functionalization with BH_3 and hydrogenation are carried out successfully for the first time.

Objectives:

As per our theoretical investigations [1] carried out previously, the single walled carbon nanotube functionalized with lightweight and electron deficient molecule, borane exhibited high hydrogen storage capacity of about 11.5 wt% (theoretical). The binding energy $/\text{H}_2$ also lies in the energy range which is recommended for an ideal hydrogen storage medium. Experiments are carried out to confirm the theoretical predictions and practical applicability of this system. CNT deposition , Functionalization of CNT with BH_3 and Hydrogenation are the experiments carried out. At each stage the samples are characterized to confirm the successful completion of the experiments.

Introduction:

It is predicted theoretically that functionalization of CNTs with complex metal hydrides, containing lithium, aluminum and boron can be used as a storage medium for hydrogen and they offer several benefits over other (metal atoms, ions, molecules) by means of storing hydrogen [2]. Out of these hydrides, BH_3 is found to be more suitable than the other metal hydrides. Functionalization with BH_3 enhances the binding energy of hydrogen molecules as well as the storage capacity [1].

The single walled carbon nanotubes coated with Borane ($\text{CNT}+\text{BH}_3$) exhibited higher hydrogen storage capacity (11.5 wt%). The H_2 desorption temperature is 306 K. Hence this system qualifies as a hydrogen storage medium (HSM) for fuel cells operating at room temperature or above. The following experiments are carried out to confirm these results and to check the suitability of $\text{CNT}+\text{BH}_3$ as a practicable HSM. The ultimate goal is to prepare CNT samples functionalized with BH_3 and hydrogenate them. The samples are characterized at various stages and finally the hydrogen storage capacity is estimated.

Experiments:

CNT deposition:

25mg of single walled CNTs were taken and mixed with 5 ml of 2-propanol in a 50 ml round bottom flask. It was then kept in an ultrasonic bath at room temperature for 1 h to allow the CNTs to be dispersed uniformly. Because of their very high surface energy the CNTs have a tendency to aggregate together and to disperse them sonication is necessary, The substrates are cleaned with ethanol and acetone by means of sonication for 15 min. The dispersed CNT solution is then deposited drop wise on the substrates maintained in air ~ 60°C using a micro pipette. The solvent from each drop was allowed to evaporate before the next drop was added. After deposition the sample is subsequently heated to 300°C for 1 h to remove the impurities and amorphous carbon.

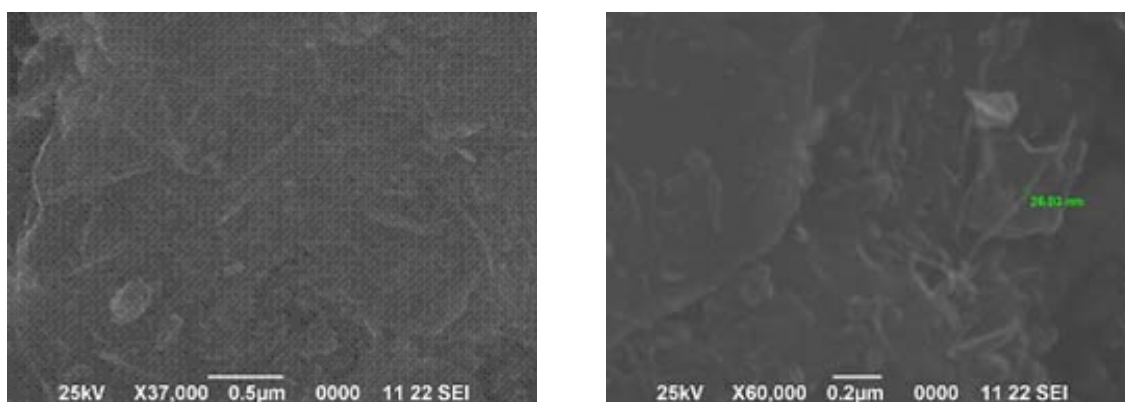


Figure 1 SEM image of purchased SWCNT

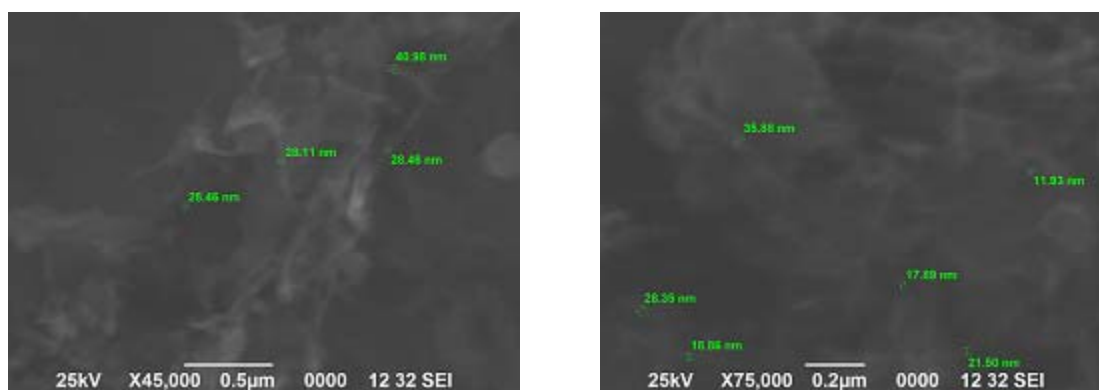


Figure 2 SEM image of SWCNTs after sonication

Characterization Results:

The morphology of the purchased SWCNT and dispersed SWCNT in 2-propanol after sonication for 1 h are analyzed by scanning electron microscopy (SEM) and the images are shown in Figs. 1 and 2. The scanning electron microscope (SEM) image provides the morphology and the particle size of the samples. The average diameter of SWCNTs is estimated to be 22 nm.

After CNT deposition the total wt % of the material in the substrates is measured through Energy Dispersive X-ray (EDAX) analysis. The EDAX spectrum is shown in Fig.3. The wt% of carbon is present in our sample is 66.29. The remaining 33.71 wt% of oxygen present in the sample may be due to CNT deposition in open atmosphere.

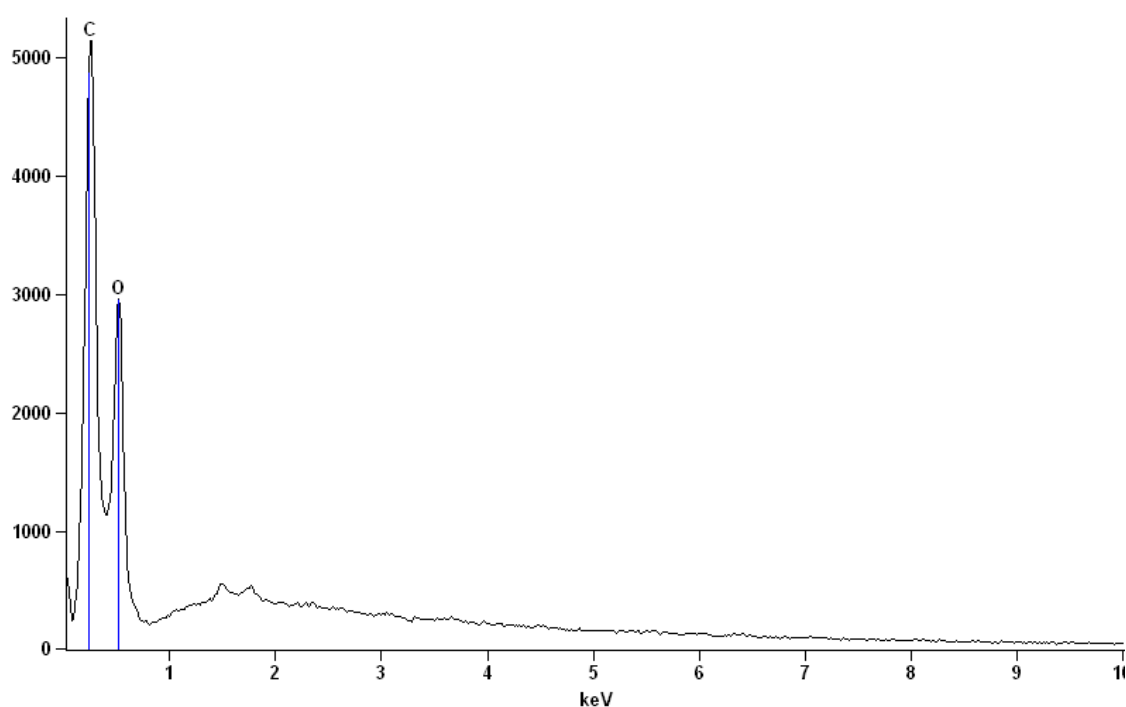


Figure 3 EDAX analysis

Fig. 4 shows the FTIR spectrum of SWCNT deposited on alumina substrates in the range $4500-500\text{cm}^{-1}$. A broad absorption peak at 3436cm^{-1} is attributed due to the hydroxyl group. This might have resulted from water during the purification. The Peaks at 1575cm^{-1} , 1631cm^{-1} are due to C=C stretching and isolated stretching modes of vibrations respectively. A small peak at 1402cm^{-1} is due to C-H deformation vibration. Peak at 1240cm^{-1} is assigned to C-C stretching vibration .

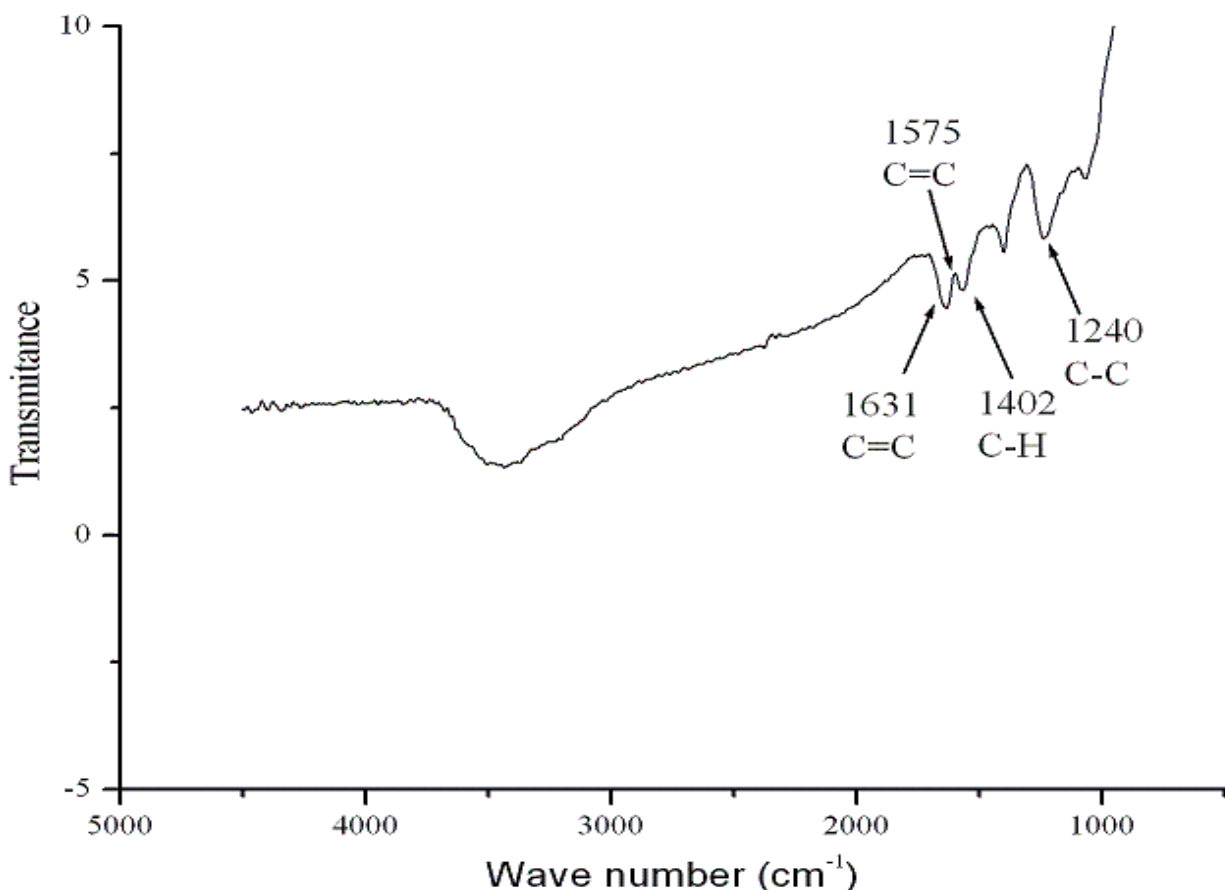
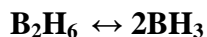


Figure 4 FTIR image of SWCNT

Functionalization of CNT with BH₃:

The next task is to functionalize the SWCNT with BH₃. BH₃ can be deposited on the SWCNTs using LiBH₄ precursor. Lithium borohydride LiBH₄, yields diborane on heating. Generally boranes are the compounds comprising boron and hydrogen. The parent member BH₃ is called borane and it dimerizes to form diborane, B₂H₆. Diborane is a colorless gas at room temperature. It has been reported that at room temperature there is no isolated monoborane, BH₃. It is in equilibrium mixture with B₂H₆:



But at very low pressure and at a temperature of about 200 °C, a small fraction of B₂H₆ is cleaved into BH₃. So there is a definite possibility of producing borane. Since BH₃ remains in equilibrium mixture with B₂H₆, we can use **B₂H₆ ↔ 2BH₃** to functionalize the SWCNTs. Depending upon their interaction with SWCNTs they will remain as such or split up into BH₃ molecules. On higher coverage of BH₃ molecules on SWCNTs we can observe dimerization of BH₃ molecules, which leads to the formation of B₂H₆ or it can remain as BH₃. Moreover diborane is metastable at normal pressures up to 50°C, definitely it will decompose into 2BH₃ molecules. The existence of B₂H₆ as itself or as 2BH₃ depends upon temperature and pressure in which our system (SWCNTs) is maintained. 125 mg of LiBH₄ in 5ml of Di ethyl ether was drop casted over

the SWCNT deposited on alumina substrates of dimension 19mmx19mmx0.65mm (alumina substrate was taken as it will not react during a heating process). Then the substrates are subsequently heated to 275°C for 1h.

Characterization Results:

From the FTIR studies we can determine the functional groups from the peaks in the spectrum. Also it provides information on the dispersion of BH_3 and B_2H_6 on SWCNTs after functionalization. If the stretching bonds corresponding to BH_3/CNT are more then naturally the reactivity of BH_3 and CNT is more. Fig. 5 shows the FTIR spectrum of SWCNT functionalized with LiBH_4 in the range $4500\text{-}500\text{cm}^{-1}$. In addition to the peaks for the hydroxyl group, C=C stretching modes, C-C stretching vibration, a new absorption peak at 2355 cm^{-1} occurs due to asymmetric B-H stretching in Borane B-H_3 complexes. The peaks at 2387 and 1182 cm^{-1} have been assigned to stretching and bending mode of B-H bond in the BH_3 group respectively. The presence of BH_3 in the functionalized sample is confirmed by this FTIR study. The absorption peaks corresponding to C-H bonds are usually observed between $2800\text{-}3100\text{ cm}^{-1}$. In our case it is observed at 3080 cm^{-1} . Our experimental result reveals that there is a bond between one of the hydrogen atoms in BH_3 and carbon in the SWCNTs. This is in agreement with our theoretical results[2].

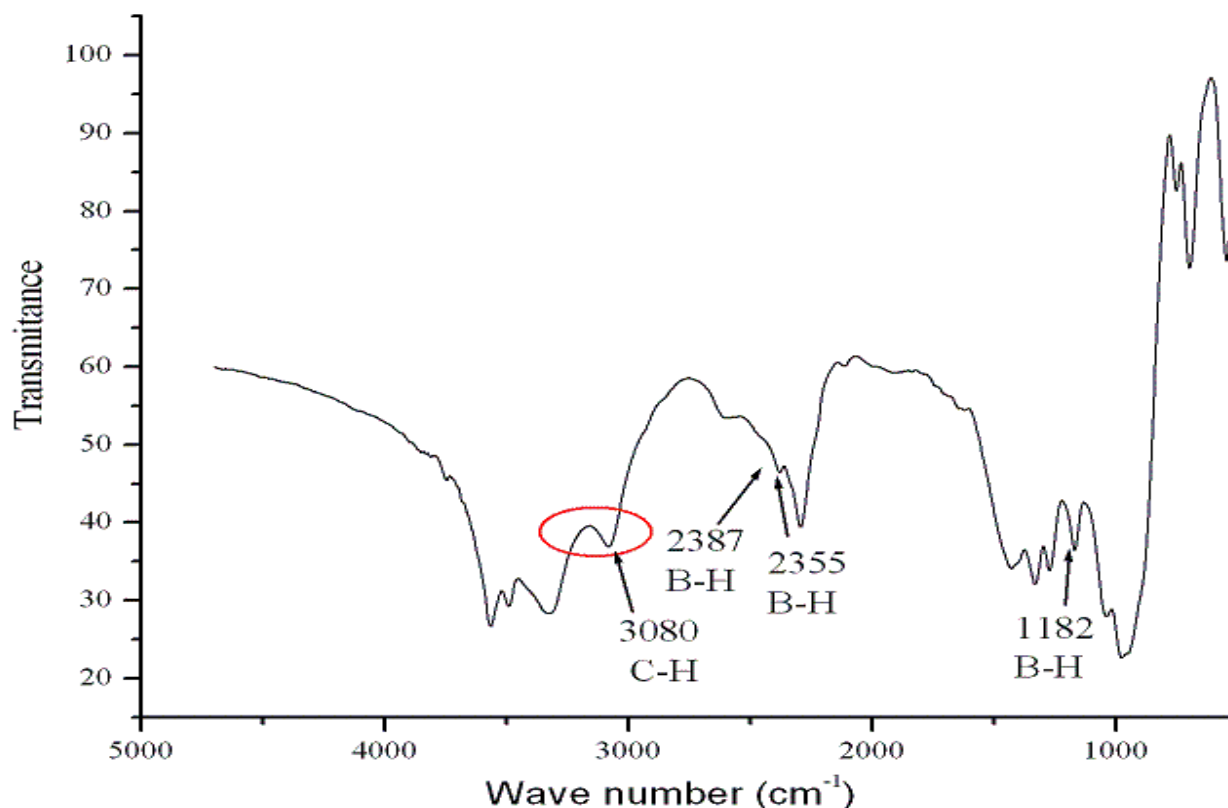


Figure 5 FTIR image of SWCNT functionalized with LiBH_4

After functionalization, the weight percentage of the elements carbon, hydrogen present in the sample were analyzed using CHNS and XPS analysis. The major elements of an organic substance, namely, carbon, hydrogen and nitrogen are commonly determined using commercially available CHN and CHNS analyzers, in which organic substance undergoes oxidative decomposition and the subsequent reduction. We have performed CHNS study. Approximately 7mg of the mixture of SWCNT functionalized with LiBH_4 was used for this study. The wt% of various elements are: 11% for C, 0.25% for S, 0.31% for H and nitrogen is not present in our sample. Also X-ray photoelectron spectroscopy study is carried out to find the other possible elements present in the sample. The full survey spectrum of our sample is shown in Fig. 6.

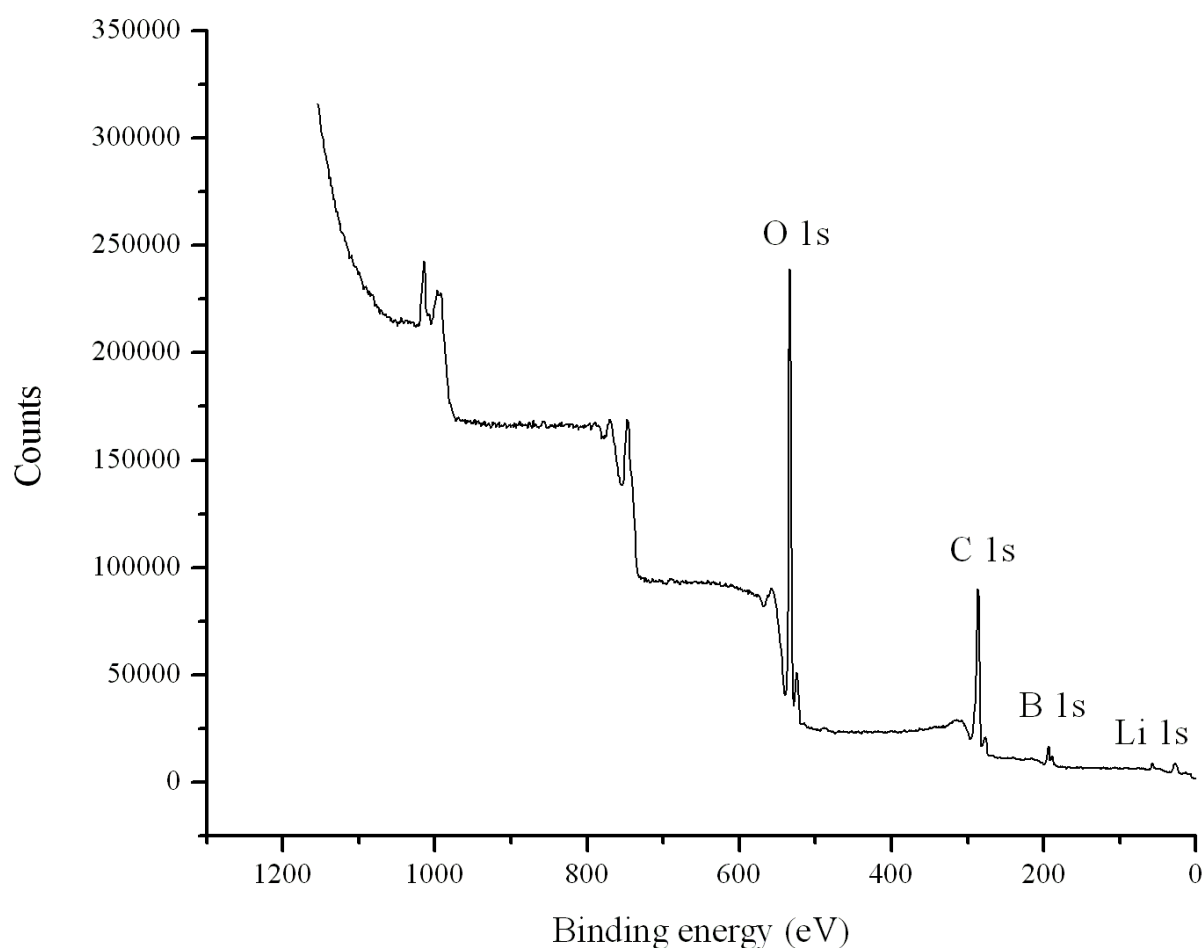
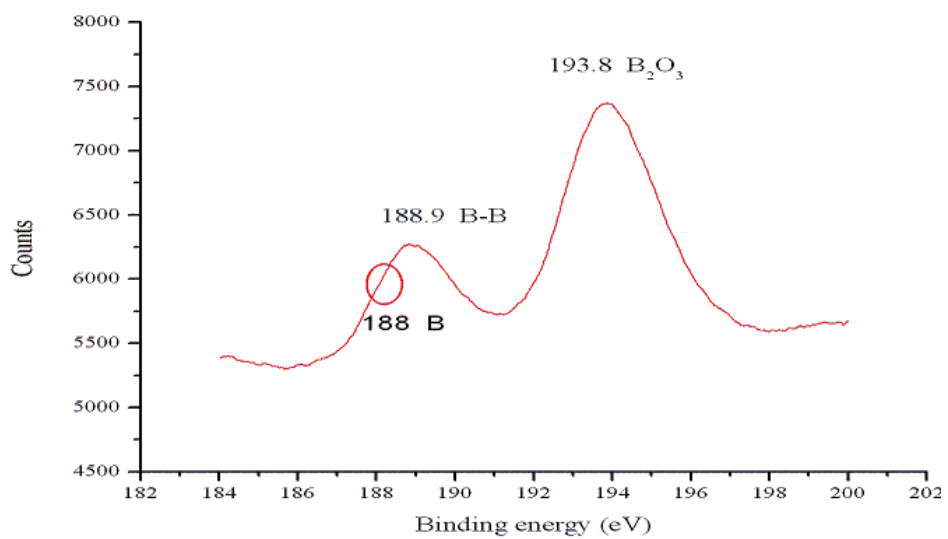
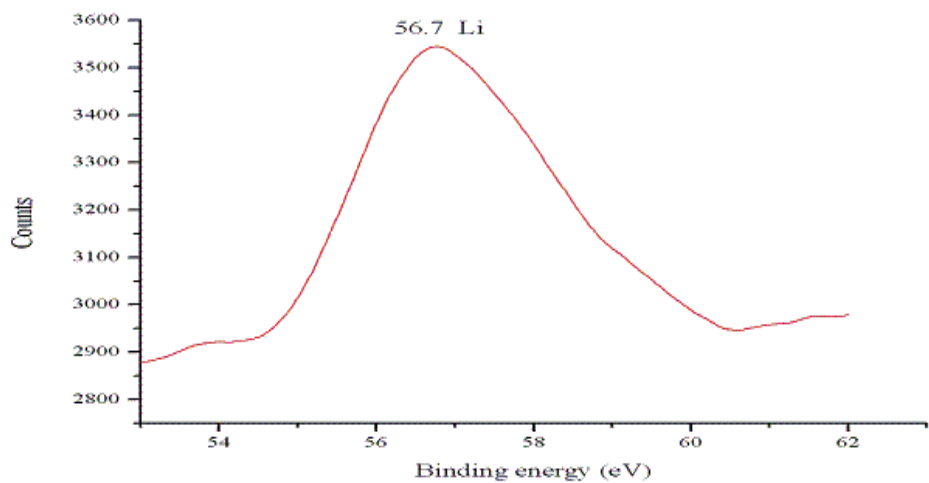


Figure 6 XPS survey spectrum

The Li 1s, B 1s, C 1s, O 1s regions of the XPS spectrum are displayed individually in Fig.7. The Li 1s spectra is the broad peak in the range 53-62 eV. The B 1s spectrum shows two components at 188.9 eV and 193.8 eV. The lower binding energy component is assigned to boron atoms bonded only to the other boron atoms, whereas the higher energy component represents the oxidized boron. The C 1s component at 286.3

eV is assigned due to C-O or C-OH bond [8], a small peak at 290.9 eV is due to Li_2CO_3 . The main O 1s component is assigned to boron oxide .



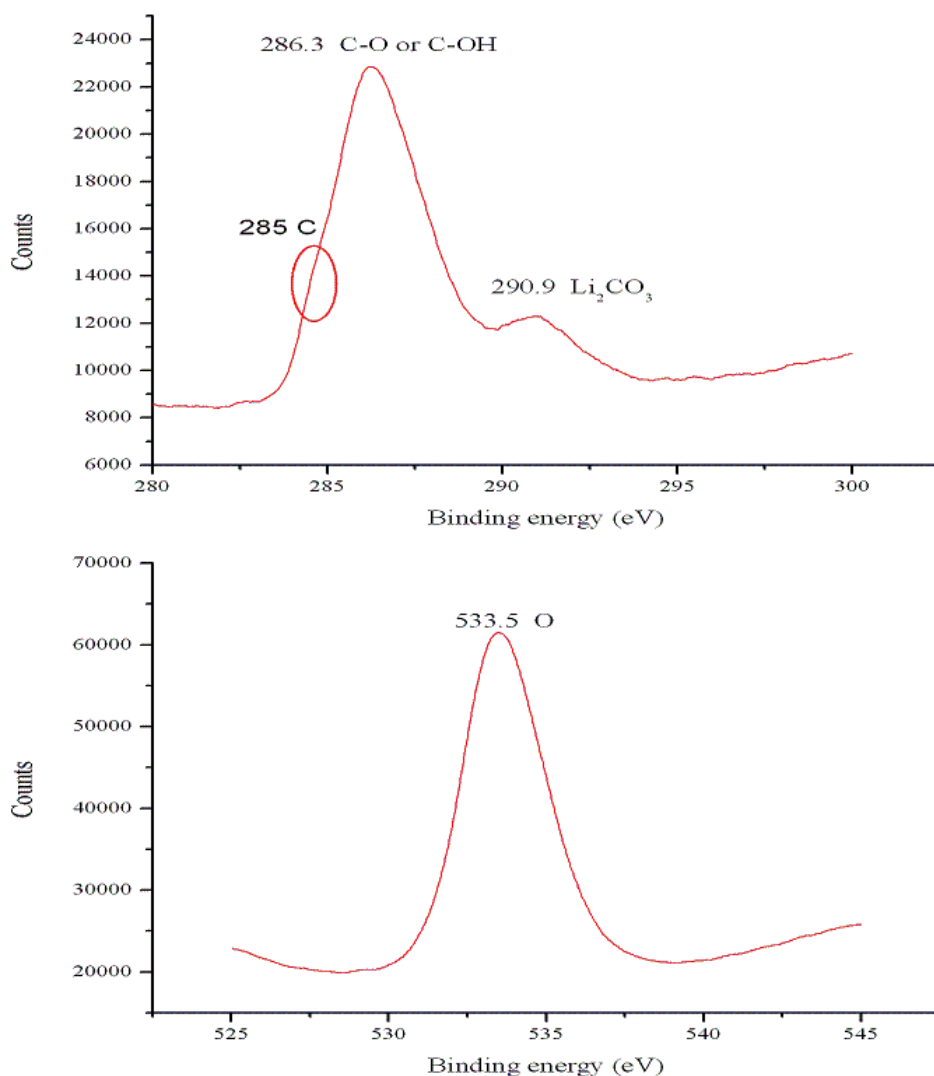


Figure 7 XPS of Li, B, C, O

Hydrogenation:

The functionalized sample is loaded in the Seivert like hydrogenation setup and hydrogenated as detailed below. One of the functionalized samples is loaded in the hydrogenation setup (Fig.8). The sample is maintained at certain predetermined temperature for certain time duration and the hydrogen flow is allowed for certain time. The sample is left in the chamber to attain the room temperature. After the hydrogenation the hydrogen content present in our sample is estimated using CHNS elemental analysis and a wt% is observed. This process is repeated for various samples under various conditions. This observation confirms the stable hydrogenation process carried out in the hydrogenation setup.

Hydrogenation setup

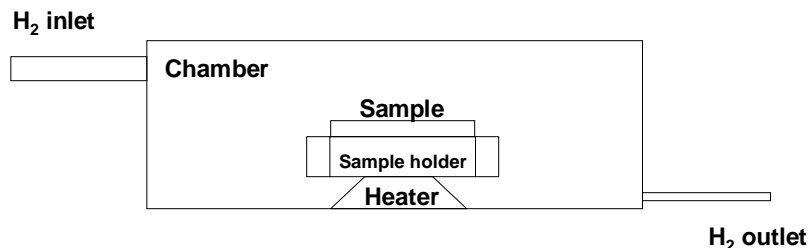


Figure 8 A schematic diagram of hydrogenation setup

Results and Discussion:

i) The CNT is deposited successfully on the substrate and annealed.

After CNT deposition the total wt % of the material in the substrate is measured through Energy Dispersive X-ray (EDAX) analysis. The wt% of carbon present in our sample is 66.29. The remaining is oxygen (33.71 wt%). The FTIR is used to determine the functional groups from the bands in the spectrum. In the FTIR spectrum (Fig. 4) of SWCNT coated on alumina substrates, a broad absorption peak at 3436 cm^{-1} is attributed due to the hydroxyl group. This might have resulted from water during the purification. The peak at 1631 cm^{-1} is due to C=C stretching modes of vibration. Absorption at 1240 cm^{-1} is assigned to C-C stretching vibration.

ii) Functionalization of Carbon nanotubes with BH_3 is achieved.

The FTIR spectra of SWCNTs functionalized with LiBH_4 are shown in Fig. 5. The higher the BH_3 dispersion, the higher is its reactivity with SWCNT. If the stretching bonds corresponding to BH_3/CNT are more than naturally the reactivity of BH_3 and CNT is more. In addition to the above peaks the new absorption peak at 2355 cm^{-1} occurs due to asymmetric B-H stretching in Borane complex. The peak at 1182 cm^{-1} has been assigned to the bending mode of B-H bond in the BH_3 group.

X-ray photoelectron spectroscopy is used to find the elements present in our sample. The full survey spectrum for our functionalized sample is shown in Fig. 6. The lower binding energy component is assigned to boron atoms bonded only to the other boron atoms [16], whereas the higher energy component represents the oxidized boron. The C 1s component at 286.3 eV is assigned to C-O or C-OH bond. A small peak at 290.9 eV is due to Li_2CO_3 . The main O 1s component is assigned to boron oxide. The deconvoluted XPS spectra (Fig. 7) show the individual components. The hydrogen storage capacity of the hydrogenated samples is estimated using CHNS elemental analysis in the machine - Elementar Vario EL III – GERMANY.

iii) Hydrogen storage in functionalized samples is confirmed.

After the hydrogenation, the hydrogen content present in our sample is estimated using CHNS elemental analysis and the following wt% of hydrogen is observed. This observation confirms the stable hydrogenation process carried out in the hydrogenation setup.

Time of heating (min)	Temperature of the substrate (°C)	Flow rate (liter/min)	Duration (Min)	Storage capacity (wt %)	CNT/LiBH ₄ in mg
40	100	1	4	0.68	3/12
100	100	3	20	0.53	3/16
100	100	3	20	0.54	2/10
100	100	3	20	0.63	3/16
100	100	1	20	0.87	3/12
100	50	3	20	1.5	3/12

There is lot of scope for improvement since there are five parameters involved and are to be optimized for the maximum hydrogen storage.

Work that may be performed in the future as follow on:

In the present phase of the project we are getting interesting results. Even though we got the expected results, we encountered with the following problems,

- i. In the present phase two chemical depositions methods viz. CNT deposition on the substrate and Functionalization of CNT with LiBH₄ are carried out in the open atmosphere. As a result about 30% of atmospheric oxygen is getting incorporated along with CNT.
- ii. The two successive chemical deposition methods are time consuming.

To avoid these problems, one can deposit CNT on the substrate under suitable vacuum condition, in the future as follow on. But CNT alone cannot be deposited (as the structure of CNT is destroyed), so one has to mix metal oxide with CNT and vacuum deposit. This will result in a composite thin film. By this process one can achieve two things, first, one gets a stable and strong base material, second one gets a

sample with larger surface area. When these composite thin films are functionalized with BH_3 one will have a practicable hydrogen storage medium. After hydrogenation it can be used in a fuel cell.

Vacuum deposition is faster than chemical deposition. Also the CNTs may get deposited with their axis perpendicular to the plane of the substrate. These will enhance the sites for functionalization and hydrogen adsorption which will in turn increase hydrogen storage capacity and the practical applicability of the system.

Summary/ Conclusions:

The SWCNTs have been successfully functionalized with BH_3 as predicted theoretically using LiBH_4 as the precursor. From XPS studies, the presence of Li, B, and O are observed in our sample. Presence of BH_3 is confirmed using FTIR studies. The hydrogen storage capacity of the functionalized SWCNTs is found to be 1.5 wt% at 50°C . Hydrogenation depends upon various parameters which are to be optimized to achieve maximum hydrogen storage capacity. Surely, we will be able to achieve the DOE target in the near future..

Almost 85% of the goals set was met.

References:

- [1] K. Iyakutti, Y. Kawazoe, M. Rajarajeswari, and V. J. Surya,. Aluminum hydride coated single-walled carbon nanotube as a hydrogen storage medium. *Int. J. Hydrogen Energy* 34 (2009) 370-375.
- [2] V. J. Surya, K. Iyakutti, M. Rajarajeswari and Y. Kawazoe, Functionalization of single-walled nanotube with borane for hydrogen storage. *Physica E* 41 (2009) 1340-1346.

Appendix

A. Personal Supported: i) D. Silambarasan

ii) Dr. V. Vasu

iii) V.J. Surya

B. Publications:

- i) Experimental investigation of Hydrogen storage in single walled carbon nanotubes functionalized with borane - D. Silambarasan, V.J. Surya, V. Vasu and K. Iyakutti
Submitted to International Journal of Hydrogen Energy
- ii) First principles investigation on carbon nanostructures functionalized with borane: An analysis on their hydrogen storage capacity- V. J. Surya, K. Iyakutti, V. Prasanna Venkatesh, H. Mizuseki and Y. Kawazoe , Submitted to Physica E
- iii) Role of electric field on desorption of chemisorbed hydrogen from carbon nanostructures, SWCNT and C₆₀. V. J. Surya, K. Iyakutti, H. Mizuseki and Y. Kawazoe
Submitted to the ACCMS-VO5 Conference to be held at IMR, Sendai, Japan during 10-13 Dec.2010.
- iv) Hydrogenation in SWCNTs Functionalized with Borane -D. Silambarasan, V. Vasu, V. J. Surya and K. Iyakutti, ccepted for presentation in the 55th DAE Solid State Physics Symposium 2010 to be held at Manipal University , Manipal 576104, Karnataka, India during Dec. 26-30, 2010.
- iv) Computation Of Interaction Potential Of Adsorbates On Zigzag SWCNTs - Application To Functionalization And Hydrogen Storage - I. Lakshmi, D. Silambarasan, V. J. Surya, M. Rajarajeswari, K. Iyakutti, H. Mizuseki And Y. Kawazoe
Accepted for publication in International Journal of Nanoscience – 2010

C. Interactions:

i. Participation/presentations at meetings ,Conferences, Seminars, etc.

- a) Investigation of hydrogen storage in carbon based nanostructures coated with lightweight hydride, BH₃ – K. Iyakutti , The fourth general meeting of Asian Consortium on Computational Materials Science – Virtual Organization held at IMR, Sendai, Japan, Jan 12 -14, 2010.
- b) Hydrogen Storage in Single Walled Carbon Nanotubes Coated with Hydrides – Theoretical and Experimental Investigations – K. Iyakutti , The fourth Indo-US Rountable on Alternate Energy, held at NIAS-IISc, Bangalore, India.

ii. Technological Application

If we achieve hydrogen storage capacity of 5.5 wt% (the US DOE standard set a year ago) then SWCNT functionalized with BH₃ will be a good hydrogen storage medium for Fuel Cells.

D. Inventions: None

E. Honors/ Awards : None

F. Archival Documentation: PDF of the Preprint of the submitted paper is attached to the Report