Indian Journal of Chemistry
Vol. 47A, June 2008, pp. 808-814

Nitrogen-containing carbon nanotubes as a possible hydrogen storage medium

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Received 4 March 2008; revised 7 May 2008

Nitrogen containing carbon nanotubes have been synthesized using a variety of templates. The hydrogen absorption capacity of these materials has been evaluated. The study shows that it is necessary to stabilize nitrogen in the carbon nanotube framework for reproducible hydrogen uptake. The role of nitrogen is to activate gaseous molecular hydrogen and its subsequent transport to the carbon surface by "spill-over" process. Nitrogen sites, in addition to its catalytic role, can also contribute to net hydrogen storage.

IPC Code: Int. Cl.^{8} B01J20/20; B82B3/00; C01B31/02

Hydrogen economy essentially depends on hydrogen storage. The choice of an appropriate medium to store hydrogen has not yet been rationalized and it has been posing challenges to the scientific community for the past several decades. In the search for hydrogen storage media, solid matrices appear to be a promising option. Among all the possible choices, storage by carbon materials appears to be an appropriate option. Indeed, the reports of high storage capacity (up to 67 weight %) with less reproducibility have been reported[1-4]. It has been shown that pure carbon surface cannot activate hydrogen molecule which is clear from the inelastic neutron scattering experiments[5,6]. The binding strength of hydrogen to carbon is about 5 kJ/mol, regardless of the type of carbon materials. Modification of carbon surface has been advocated as one of the methods for hydrogen activation. Though, the addition of metal or metal oxides enhances the hydrogen storage capacity to a certain extent the retrieval of hydrogen requires higher temperatures[7,8]. Preparation of carbon materials in different forms and phase purity seems to enhance the storage capacity. However, the preparation methods of such materials involve complicated processes, and the materials with the same morphology and properties are not reproducible[9-11]. We propose that hetero-atoms like N, P, S and B may be able to act as the alternate centers for hydrogen activation, and the activated hydrogen may be able to migrate to the carbon surface more easily. The choice of hetero-atoms has been made on the basis of various parameters like the redox behavior of the hetero-atom and the feasibility of incorporation of the hetero atom in the carbon nanotube framework. Even among various hetero-atoms, N, P, S and B differ significantly in their behavior. Our recent theoretical result using density functional theory (DFT) and experimental result proves that the boron substituted carbon nanotubes has higher hydrogen absorption than the pure carbon[12-14].

The template synthesis method has been widely used for preparing micro- and nano-structured materials, which involve the synthesis of the desired material within the pores of a membrane to generate nanotubes of uniform diameter. Combination of chemical vapor deposition (CVD) and template synthesis methods has been reported for the synthesis of highly aligned, uniform, hollow and open-ended CNTs (suitable for filling with other materials) with diameters ranging from 20 to 200 nm. The template synthesis method has several advantages such as controlling composition, morphology and the size of the nanotubes[15-17]. Nitrogen-containing carbon nanotubes have been prepared by template synthesis using nitrogen containing polymer precursors such as polyacrylonitrile and polypyrrole[18, 19]. However, no specific methodology has been formulated to have control over the amount of nitrogen content in the carbon nanotubes.

In the present work, hydrogen absorption activity of nitrogen-containing carbon nanomaterials is compared with those of pure carbon nanomaterials. Nitrogen containing carbon nanomaterials have been prepared by template-assisted method using various templates such as zeolite, clay, and alumina membrane. The prepared nitrogen containing carbon nanotubes have been characterized by X-ray diffraction (XRD), Raman spectroscopy, scanning electron microscopy (SEM), transmission electron microscopy (TEM), and low pressure and high pressure hydrogen absorption measurements. The variation of template and the carbon precursor causes differences in the morphology and also the environment of nitrogen, which has relevance towards hydrogen storage application is examined. This work is exploratory in nature, and gives the path towards enhancing the hydrogen storage capacity. Only further detailed studies can substantiate the feasibility.

Materials and Methods

All the chemicals used were of analytical grade. Pyrrole (Sisco Research Laboratory) was distilled under vacuum prior to use. Ferric chloride hexahydrate, *p*-toluene sulfonic acid, 48% HF (Merck) were used as received. Acetylene (99.95%), hydrogen (99.98%) and argon (99.99%) gases were used with no further purification. Alumina template membranes (0.2 µm pore diameter and 60 µm thick) were obtained commercially (Whatman Anodisc Membrane Filters, Whatman Inc). H-zeolite-Y (Sud Chemie Pvt. Ltd., India) and Na-montmorillonite were used for the preparation of Al-pillared clay. $AlCl_3 \cdot 6H_2O$ (S.D. Fine-Chem Ltd., India) was used as source of aluminum ion for the preparation of Al-pillared clays. For the hydrogen absorption experiments, helium (99.99%) and hydrogen (99.98%) were purified using a liquid nitrogen trap and activated carbon trap prior to experiments.

Preparation of nitrogen containing carbon nanotubes (NCNT1) using polypyrrole as carbon source

Polypyrrole (PPY) coatings were applied by a reaction coating approach[20] by suspending alumina template membrane in an aqueous pyrrole (0.1 *M*) solution containing 0.2 *M* ferric chloride hexahydrate. *p*-Toluene sulfonic acid (0.2 *M*) was added slowly and polymerization was carried out for 3 h. This led to the black coating of polypyrrole on the template membrane. The surface layers were removed by polishing with fine neutral alumina powder and then ultrasonication for 20 min to remove the residual alumina used for polishing. The polypyrrole coated alumina membrane was characterized by IR-spectroscopy. The characteristic –NH-stretching frequencies were observed at 1540, 1460 and 1312 cm^{-1} for polypyrrole and matched with those reported in literature[21]. The membrane was then dried and placed in a quartz boat and carbonized in Ar atmosphere at 1173 K for 6 h. The resulting carbon/alumina composite was immersed in 48% HF for 24 h to remove the template. The residue was thoroughly washed with distilled water to remove traces of HF and dried at 373 K for 10 min (NCNT1).

Preparation of carbon nanotubes (CNT1) without nitrogen content

Polyphenyl acetylene was used as carbon source for the preparation of carbon nanotubes[22] without hetero-atoms, Since it contained only carbon-hydrogen bonds. The polyphenyl acetylene/alumina composite was prepared by adding 10 ml of 5% *w/w* polyphenyl acetylene in dichloromethane to the alumina membrane, applying vacuum from the bottom. Suction was applied to ensure that the polymer solution penetrates inside the pores of the membrane. The rest of the procedure is simiar to the method described above.

Preparation of carbon nanotubes by chemical vapor deposition (CVD) method

Calcined H-Y-Zeolite (CNT2 and NCNT2) and Al-pillared clay (CNT3 and NCNT3) were used as the template. Acetylene was employed as carbon precursor for the preparation carbon nanotubes and pyridine was chosen as nitrogen source in combination with acetylene for NCNT. The carbonization was carried out at 1173 K. The subsequent procedure is similar to the procedure described above.

Characterization of carbon nanotubes

The prepared NCNTs were characterized by powder X-ray diffraction using Shimadzu XD-D1 X-ray diffractometer with Ni-filtered Cu Kα radiation (λ =1.5418 Å). Shimadzu FT-IR 8400 series was used for IR studies in the range of 400 cm^{-1} to 4000 cm^{-1}. Elemental analysis of the CNTs was made using Perkin Elmer CHN analyzer after the removal of template. Transmission electron micrographs were recorded with a JEOL-JEM 100SX microscope, working at a 100 kV accelerating voltage. TEM sampling grids were prepared by placing 2 µl of the sample dispersed in ethanol solution on a carbon-coated grid and the solution was evaporated at room temperature. Scanning electron micrographs were obtained using Philips XL 30 instrument.

Volumetric high pressure hydrogen absorption measurement was made using custom-built volumetric and Seivert's apparatus as described in our earlier work[14]. The experiments were repeated under the same conditions at various pressures.

Results and Discussion

Template assisted synthesis of CNTs and NCNTs

The scanning electron micrographs of CNT1 and NCNT1 are shown in Fig. 1 (a & b, respectively). The formation of well oriented CNTs bundles with tubular nature can be clearly seen. The length of the CNTs is ~ 50-60 µm with open mouth at both the ends.

The TEM images of CNT1 and NCNT1 (Fig. 1, c and d, respectively) after the carbonization at 1173 K for 6 h show hollow tubes with slight deformation at the end of the tube caused by the ultrasonication and vigorous HF treatment. The micrograph also indicates the formation of cylindrical, hollow and transparent tubes. The outer diameter of the tube is less than 200 nm, which is less than the channel diameter of the template used (also seen is a layer of amorphous carbon on the wall of the tube). The carbon nanotubes produced by this method are not completely graphitic in nature as those produced by arc-discharge process. Thus, their disordered structure is quite typical of fibers or nanotubes produced by decomposition of hydrocarbons, as is evident from the amorphous carbon on the wall of the carbon nanotube.

X-ray diffraction studies on CNT1 and NCNT1 are shown Fig. 2a. A predominant peak at 2θ = 25.6° corresponds to (002) plane. This indicates the graphitic nature of the carbon of NCNT1, whereas CNT1 shows a broad peak. The peak at 2θ = 43.7° corresponding to (100) plane of graphite is shown in the XRD pattern of both CNT1 and NCNT1. Usually the Raman spectra of sp^2 carbon materials are laser energy dependent and the frequency of the disorder induced D-band is observed between 1250 and 1450 cm^{-1}. The D-band is activated in the first order scattering process by the presence of in-plane substitutional hetero-atoms, vacancies, grain

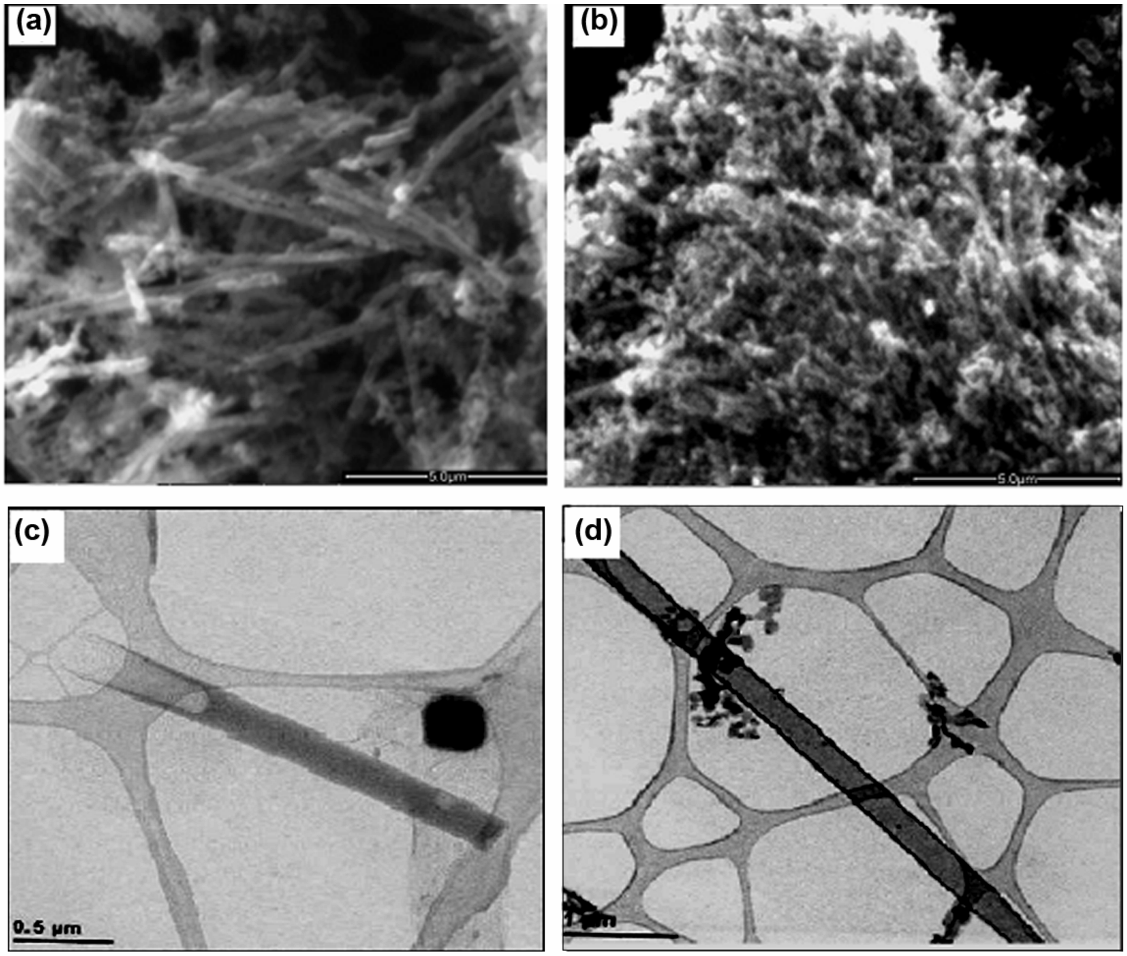

Fig. 1—(a-b) SEM images of carbon nanotubes CNT1 and NCNT1, and, (c-d) TEM images of CNT1 and NCNT1 respectively.

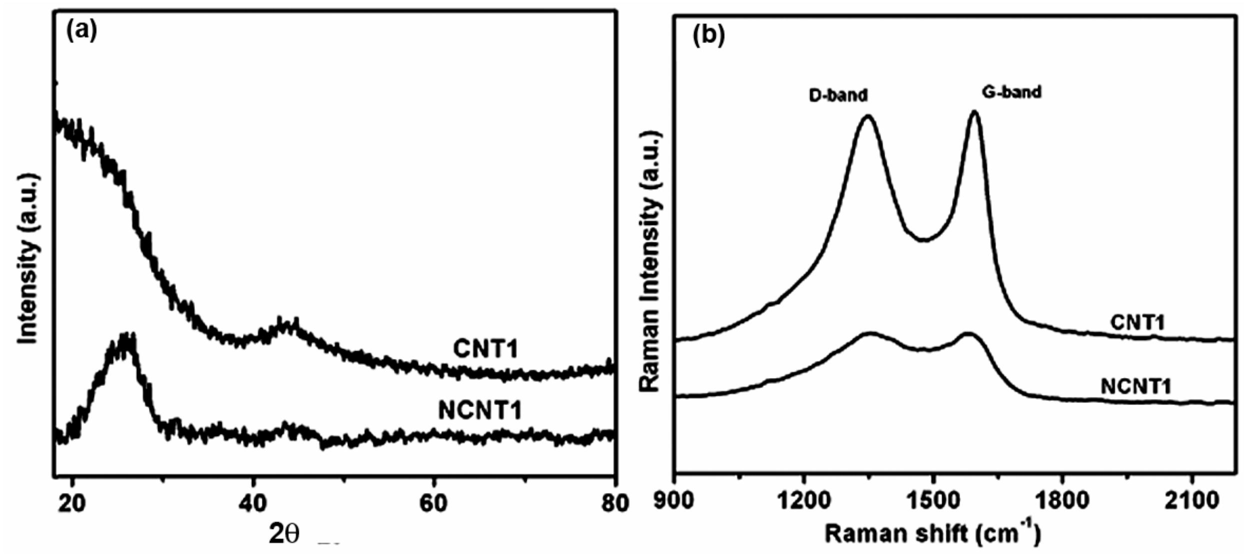

Fig. 2—(a) XRD pattern of CNT1 and NCNT1, and (b) Raman spectra of CNT1 and NCNT1 prepared from alumina membrane as template.

boundaries or other defects and by finite size effect, all of which lower the crystalline symmetry of the quasi-infinite lattice. The Raman spectra (Fig. 2b) of the carbon nanotubes prepared from the alumina membrane template with polymer as the carbon precursor show sharp D and G bands at 1345 and 1595 cm^{-1} respectively with equal intensity. SEM and TEM analysis show a well aligned tubular morphology. Due to the tubular morphology, the peaks are sharp and distorted. NCNT1 shows broad peak with high full-width half-maximum (FWHM) as compared to pure carbon nanotubes (CNT1), due to the substitutional effect of nitrogen in the carbon nanotubes.

Carbon nanotubes prepared by using zeolite as template (CNT2 and NCNT2) and clay (CNT3 and NCNT3) as template show graphitic nature of the carbon nanomaterials from X-ray diffraction analysis. Predominant (200) reflections at 2θ = 24.1° and (100) reflection of graphite at 44.7° are observed. Raman spectrum showed well resolved D-band characteristic peak due destabilization of graphitic plance[23]. The FWHM and the intensity of the D-band are higher than the G-band in NCNT2 compared to CNT2. This signifies greater disorderliness upon nitrogen substitution in the carbon nanotubes.

The SEM and TEM analysis shows more amorphous and fibrous nature. Usually carbon nanotubes produced by CVD method leads to the formation of nanotubes with disordered structure, amorphous carbon and fibers[24,25]. Similar observation can be seen in the TEM images for the prepared samples. Since no catalyst has been used for the synthesis of carbon nanotubes, it is worth mentioning that the nanotubes produced by template synthesis under normal experimental conditions are almost free from impurities.

Elemental analysis was carried out to confirm that whether the nitrogen has really present in the carbon nanotube framework. From the results, it is clear that nitrogen has been incorporated in the carbon framework and its amount (%) fluctuates for different carbon sources. In the template synthesis, it has been shown that carbon nanotubes prepared from polypyrrole (NCNT1) show a maximum of 6.4% of nitrogen content in the sample. The carbon nanotubes prepared using pyridine as nitrogen source, NCNT2 and NCNT3, show 2.5 and 1.8% of nitrogen, respectively.

Determination of hydrogen storage capacity

Evolved gas analysis (EGA) has been carried out to study the hydrogen activation on the pure carbon nanotube (CNT1) and nitrogen containing carbon nanotubes (NCNT1) prepared from alumina membrane template. The traces of evolved gas from the nitrogen containing carbon nanotubes (NCNT1) are shown in Fig. 3a. It is seen from the trace that a species of trace corresponding to mass of 17 was evolved which indicates the formation of ammonia. The evolution of ammonia was observed above 473 K showing that nitrogen present in the carbon network in CNT is capable of becoming a hydride at room temperature. During recycle of the sample, there is decrease in ammonia formation (Fig. 3b), indicating a stoichiometric nature of the reaction. However, the evolved gas traces from the pure carbon nanotube (CNT1) show (Fig. 3c) the signal at a background level. This confirms that nitrogen in the carbon nanotubes can play an important role in the hydriding process. It is presumed that nitrogen atomic sites may be the active sites where hydrogen atoms are generated from the activation of hydrogen molecule similar to those of metallic sites (catalytic sites). If these activated hydrogen atoms were to spill over to the carbon surface then improvement in hydrogen storage capacity is achievable. The reason for activation of hydrogen at nitrogen sites may be due to the favorable free energy of formation at these sites. The subsequent migration to carbon sites may be due to the favorable redox potential values of various species that can be formed. The redox potential of NH and NH_2 species may be suitable for producing hydrided carbon species such as CH, CH_2, and CH_3. Formation of ammonia was also independently established by other chemical tests such as spectrophotometry.

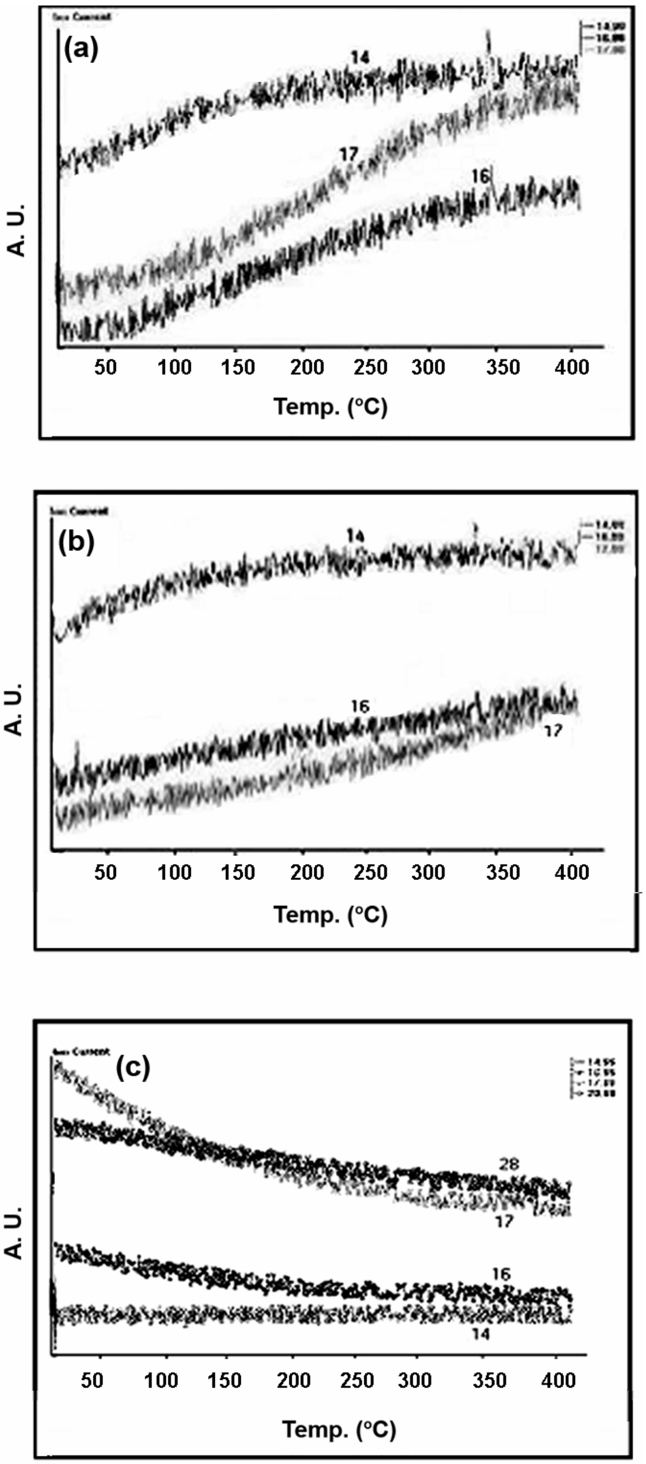

Fig. 3—(a) EGA profile of nitrogen containing CNT; number present in the figure represents the mass number of N, NH_3 and N_2, (b) EGA profile of nitrogen containing CNT after recycling, and, (c) EGA profile of pure CNT prepared from polyphenyl acetylene

By an independent method, the evolved gas analysis experiment has been carried out where the experimental conditions were similar to the evolved gas analyzer. The sample was initially evacuated and then heated to 393 K for 4 h. The hydrogen gas was then charged with atmospheric pressure and subsequently heated to 673 K followed by cooling to room temperature. After reaching room temperature the sample was heated slowly and the gas evolved was flushed using dil. H_2SO_4 solution, by hydrogen as the carrier gas. The acid solution was tested for ammonia. The evolution of ammonia was ascertained by spectrophotometry using Nessler's reagent. A standard calibration plot has been made with various concentrations of ammonium chloride which was used as ammonia source. By comparison with the calibration plot, the amount of ammonia evolved from the NCNT1 sample is found to be 0.085 ml/mg of gas phase volume. After the reaction, the samples were analyzed for nitrogen content by CHN analysis. The sample shows 4.3% of nitrogen against the nitrogen content in the 6.6%. From this result the total amount of ammonia evolved corresponds to one-third of the total nitrogen content in the sample. Theoretically, one can predict the weight % of hydrogen from the amount of ammonia evolved. It is estimated that CNTs containing 20% of nitrogen is capable of taking up about 1 wt% of hydrogen[23]. If this hydrogen could be transported to the carbon skeleton, it may be possible to achieve the Department of Energy (DOE) standards of hydrogen storage capacity in heteroatom containing CNTs.

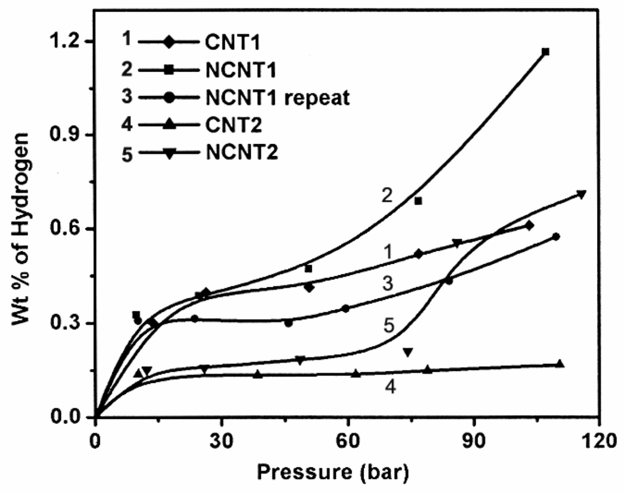

Fig. 4—High pressure hydrogen absorption activity of carbon nanotubes prepared from alumina membrane and zeolite templates. [1, CNT1; 2, NCNT1; 3, NCNT1 repeat; 4, CNT2; 5, NCNT2].

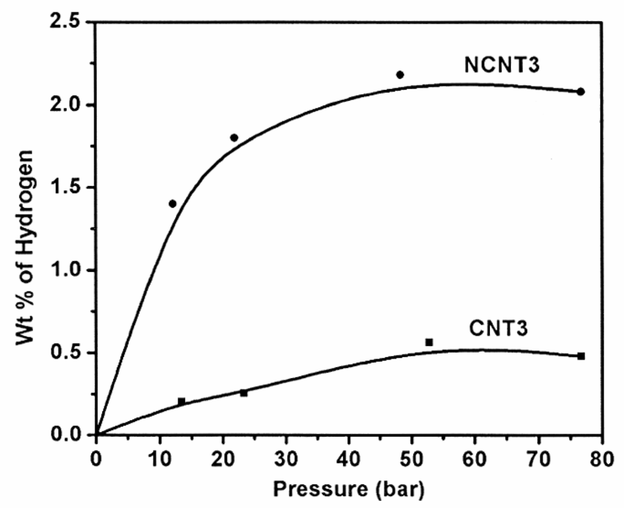

Fig. 5—High pressure hydrogen absorption activity of carbon nanotubes prepared from clay template (CNT3 and NCNT3).

Hydrogen absorption capacity

High pressure hydrogen absorption measurements show that hydrogen absorption increased with increase in pressure. The hydrogen storage capacity of nitrogen containing carbon nanotubes prepared from alumina membrane (NCNT1) was maximum (1.2 wt%) at 100 bar hydrogen pressure (Fig. 4). However, in the second cycle, NCNT1 shows reduced hydrogen uptake of 0.6 wt%. This further confirms the role of nitrogen in hydrogen activation and its subsequent absorption. This is revealed from both the EGA and high pressure absorption experiments authenticating the role of nitrogen in hydrogen activation. The maximum hydrogen storage capacity of the carbon nanotubes prepared from the zeolite as template is 0.2 wt% for CNT2 while NCNT2 showed hydrogen storage capacity of 0.72 wt%.

The hydrogen storage capacity of carbon nanomaterials prepared from the pillared clay template (CNT3 and NCNT3) showed a maximum storage capacity of 0.35 wt% for pure CNTs and 2 wt% for NCNT3 (Fig. 5). There is no reduction in hydrogen storage capacity in the second and third cycles which indicates strong interaction between nitrogen in carbon network. It can be justified by the peculiar structural features of clay templated NCNTs (or) due to the efficient nitrogen incorporation in the CNTs matrix.

The above study shows that nitrogen-containing carbon nano-materials are amenable to hydrogen absorption compared to pure carbon materials. Results confirms that nitrogen atoms in carbon matrices act as the active centers and these active sites should be made catalytic in nature by adopting and devising suitable preparation methods. Surface engineering techniques should be employed to achieve high hydrogen storage capacity. The heteroatom substitution in the carbon nanotubes opens up another avenue in the search for materials for hydrogen storage.

Acknowledgement

We thank Council of Scientific and Industrial Research (CSIR), New Delhi, India for the fellowship to one of us (MS) and DST Government of India for financial support.

References

1 Dillon A C, Jones K M, Bekkedahl T A, Kiang C H, Bethune D S & Heben M J, Nature, 386 (1997) 377.
2 Hynek S, Fuller W & Bentley J, Int J Hydrogen Energy, 22 (1997) 601.
3 Chambers A, Parks C, Baker R T K & Rodriguez N.M, J Phys Chem B, 102 (1998) 4253.
4 Liu C, Fan Y Y, Liu M, Cong H T, Cheng H M & Dresselhaus M S, Science 286 (1999) 1127.
5 Schimmel H G, Kearley G J, Nijkamp M G, Visser C T, de Jong K P & Mulder F M, Chem Eur J, 9 (2003) 4764.
6 Ren Y & Price D L, Appl Phys Lett, 79 (2001) 3684.
7 Yang R T, Carbon, 38 (2000) 623.
8 Hirscher M, Becher M, Haluska M, Dettlaff-Weglikowska U, Quintel A, Duesberg G S, Choi Y M, Downes P, Hulman M, Roth S, Stepanek I & Bernier P, Appl Phys A, 72 (2001) 129.
9 Ansón A, Lafuente E, Urriolabeitia E, Navarro R, Benito A M. Maser W K & Martínez M T, J Phys Chem B, 110 (2006) 6643.

10 Lee J W, Kim H S, Lee J Y & Kang J K, Appl Phys Lett, 88 (2006) 143126.

11 Hirscher M , Becher M, Haluska M, Quintel A, Skakalova V, Choi Y M, Dettlaff- Weglikowska, Roth S, Stepanek I, Bernier P, Leonhardt A & Fink J, J Alloys Comp, 330 (2002) 654.

12 Sankaran M & Viswanathan B, Carbon, 44 (2006) 2816.

13 Sankaran M, MuthuKumar K & Viswanathan B, Ful. Nanotubes Carbon Nanostruc, 13 (2005) 43.

14 Sankaran M & Viswanathan B, Carbon, 45 (2006) 1628.

15 Parthasarathy R V, Phani K L N & Martin C R, Adv Mater, 7 (1995) 896.

16 Martin C R, Science, 266 (1994) 1961.

17 Kyotani T, Tsai L F & Tomita A, Chem Mater, 8 (1996) 2109.

18 Stephan O, Ajayan P M, Colliex C, Redlich Ph, Lambert J M, Bernier P & Lefin P, Science, 266 (1994)1683.

19 Glerup M, Steinmetz J, Samaille D, Stéphan O, Enouz S, Loiseau A, Roth S & Bernier P, Chem Phys Lett, 387 (2004)193.

20 Rajesh B, Thampi K R, Bonard J M, Xanthopoulos N, Mathieu H J & Viswanathan B, J Phys Chem B, 107 (2003) 2701.

21 Selampinar F, Akbulut U, Yalçin T, Süzer S & Toppare L, Syn Metals, 62 (1994) 201.

22 Rajesh B, Karthikeyan S, Bonard J M, Thampi K R & Viswanathan B, Eurasian Chem Tech J, 3 (2001) 11.

23 Sankaran M & Viswanathan B, Prep Pap-Am Chem Soc, Div Fuel Chem, 51 (2006) 803.

24 Colomer J F, Bister G, Willems I, Konya Z, Fonseca A, Van Tendeloo G & Nagy J B, Chem Comm, (1999)1343.

25 Ci L, Xie S, Tang D, Yan X, Li Y, Liu Z, Zhou W & Wang G, Chem Phys Lett, 349(2003)734.