Abstract: Hydrogen is considered as a promising alternative energy carrier that can potentially facilitate the transition from fossil fuels to sources of clean energy because of its prominent advantages such as high energy density and environment friendly, but one of the major problems limiting the use of hydrogen for energy applications is the difficulty of storing it safely. In this work, the hydrogen storage performance of acid treated multi-walled carbon nanotubes (MWCNT)/hexagonal boron nitride (h-BN) (MWCNT/h-BN) nanocomposite is investigated. The MWCNT/h-BN nanocomposite is prepared by using drop cast method. The hydrogenation of acid treated MWCNTs and MWCNT/h-BN nano composite have been carried out using Seiverts like apparatus. The prepared nanocomposites were characterized by X-ray Diffraction (XRD), micro-Raman spectroscopy, Scanning Electron Microscope (SEM), Energy Dispersive X-Ray Spectroscopy (EDS), CHN-elemental analysis and Thermo Gravimetric Analysis (TGA). The amount of hydrogen stored in MWCNT/h-BN nanocomposite is found to be 1.6 wt. % at 100 ºC and the average binding energy of stored hydrogen is 0.48 eV.

Keywords: Acid treated MWCNT, MWCNT/h-BN nanocomposite, micro-Raman spectroscopy, Hydrogen adsorption.

Introduction

The major challenges for mankind in the upcoming years include the decreasing availability of fossil fuels and global warming that result from their ever-increasing use. Since the resultant product from the hydrogen fuel cell is water, hydrogen is the most promising and potential alternative energy carrier that can facilitate the transition from fossil fuels to sources of clean energy. The development of fuel cell power systems has enabled hydrogen to become an alternative to conventional systems. The major drawbacks associated with hydrogen fuel cell are safety, proper storage medium and lack of expected storage capacity as per US-DOE target. This necessitates for the development of safe, compact, and high capacity storage systems for molecular hydrogen.

Intensive research works on compounds like chemical hydrides, complex hydrides, and metal hydrides...
are considered as potential materials for hydrogen storage, but the reversibility of the process is still a major issue has yet to be solved. Large specific surface area materials, such as metalorganic zeolites and carbon nanotubes can store hydrogen by physisorption, but the storage capacity is very low in pristine form. A new storage material based on polymers that are able to store hydrogen has been proposed by using an HCl-treated polyaniline and polypirrole. On the contrary, people have demonstrated the inability of these polymers to store hydrogen. Nowadays, it is evident that a single pure substance cannot achieve the storage capacity and cycling stability required by technological applications. So the researchers are seeking alternative materials/methods in the preparation of hydrogen storage materials. The development of a safe and efficient storage system for usage of hydrogen is the major challenge faced by researchers all over the world.

In recent years, the synthesis of Boron-Carbon-Nitrogen (BCN) based light weight hydrogen storage medium is a hot topic, because it garnered the superior properties compare to pristine BN and carbon nanostructures. Hence, the goal of the present work is to analyze the hydrogen storage properties of acid treated MWCNTs and MWCNT/h-BN nanocomposite for the effective hydrogen storage medium in near future.

**Experimental**

The MWCNTs were kept in a tubular furnace with temperature range of 300 °C for 3 hours, then mixed with 3:1 ratio of H$_2$SO$_4$ and HNO$_3$ followed by ultasonication for 6 hours. This solution was filtered and washed with distilled water until the pH of the solution reached above 6. The resultant product was dried in vacuum oven at 100 °C for 24 hours. The obtained product was used for the nanocomposite preparation.

The MWCNT/h-BN (1:2 ratio) nanocomposite was prepared by using a drop cast method. In the synthesis, the MWCNTs and h-BN nanoparticles were grounded well for 30 min. Then the mixture was dispersed with DMF (5 mg/ml). Then the mixture was kept in an ultrasonic bath at room temperature for 3 hours. Then the dispersed solution was deposited drop by drop on glass plates and to maintain at 120 °C where DMF got evaporated and finally the MWCNT/h-BN nanocomposite deposited on the glass plates and were dried at 200 °C for 2 hours.

Hydrogen adsorption studies have been carried for the synthesized nanocomposites using a Sieverts-like hydrogenation setup. The nanocomposites were maintained in a vacuum at 150 °C for 4 hours, and the hydrogen was allowed to react with these samples at a constant flow rate of $\sim$0.5 L/min for 15 min. The equilibrium pressure of the chamber was maintained at 1 kg/cm$^2$. After hydrogenation process, the amount of hydrogen content present in the samples was estimated.

**Characterization**

Powder X-ray diffraction (XRD) pattern of MWCNTs and MWCNT/h-BN nanocomposite was recorded by X’Pert PAN analytical diffractometer with Cu anode operated at 40 kV and 30 mA. Micro-Raman measurement was carried out using Labram HR800 model spectrometer with the laser excitation of 632 nm. Scanning Electron Microscopy image was recorded using JEOL Model JSM - 6390LV. Energy dispersive X-ray spectrum (EDX) was examined by using JEOL Model JED - 2300. CHN-elemental analysis was performed to measure the quantity of hydrogen incorporated in MWCNTs and MWCNT/h-BN nanocomposite using Elementar Vario EL III model analyzer. The Thermo Gravimetric Analysis (TGA) was employed mainly to determine the desorption temperature range of hydrogen in MWCNTs and MWCNT/h-BN nanocomposite using Perkin-Elmer-Diamond model unit over the temperature range of 50-700 °C at a scanning rate of 15 °C/min.

**Results and discussion**

**Characterization**

Figure 1 shows the XRD patterns of MWCNTs and MWCNT/h-BN nanocomposite. In figure 1 (a) displays a broad peak centered at 25.7° and 43.3°, which corresponds to the (002) and (100) planes of MWCNT [12, 13]. The XRD pattern of MWCNT/h-BN nanocomposite exhibits strong diffraction peaks appeared at 27.3° and 54.4° and can be indexed to (002) and (004), respectively. This indicates that the h-BN nanoparticles are presented in MWCNT/h-BN nanocomposite. However, no significant diffraction peaks of
MWCNTs are observed in MWCNT/h-BN nanocomposite and thereby indicating that h-BN is embedded in the MWCNTs matrix and it could not be detected by X-ray diffraction.

**Figure 1** XRD pattern of (a) MWCNT (b) MWCNT/h-BN nanocomposite

Raman spectroscopy is a powerful tool for characterizing carbon and boron nitride based materials. Figure 2a shows the two significant peaks at 1325 and 1583 cm$^{-1}$. The peak at 1583 cm$^{-1}$ is designated to the tangential C-C stretching vibration, known as a graphite mode G-band and the mode at 1320 cm$^{-1}$ is attributed to the local defects that originates from structural imperfections in the MWCNTs, are named as defect mode D-band$^{16,17,18}$. Figure 2b displays one additional peak at 1340 cm$^{-1}$, which corresponds to the h-BN nanoparticles$^{19}$. Figure 2b reveals that MWCNT/h-BN features a higher $I_D/I_G$ ratio (1.1) than that of the MWCNTs (0.8), indicates the successful formation of nanocomposite.

**Figure 2** Raman spectra of (a) MWCNT (b) MWCNT/h-BN nanocomposite

The surface morphologies of MWCNTs and MWCNT/h-BN nanocomposite are investigated by SEM and are as shown in figure 3. The figure 3(a) reveals the existence of uniform distribution of high quality MWCNTs and it is clear from figure 3 (b), that the h-BN nanoparticles are homogeneously dispersed on the surface of MWCNTs.

**Figure 3** SEM Photographic of (a) MWCNT (b) MWCNT/h-BN nanocomposite

The EDX spectrum of MWCNTs (see figure 4a) shows the presence of carbon element alone. In the MWCNT/h-BN nanocomposite (figure 4b) carbon and nitrogen are alone present. The absence of any other
peak except carbon and nitrogen is an evident that no impurities are present in this nanocomposite. However, this EDX could not detect boron and it is due to the absorption of low energy X-rays by the window of the EDX detector.

![EDX spectra](image)

**Figure 4** EDX spectra of (a) MWCNT and (b) MWCNT/h-BN nanocomposite

**H₂ - Adsorption analysis**

The amounts of stored hydrogen in MWCNTs and MWCNT/h-BN nanocomposite are found to be 0.2, and 1.9 wt %, respectively, which is calculated from CHN elemental analysis.

The Raman spectra of the hydrogenated MWCNTs and MWCNT/h-BN nanocomposite are shown in figure 5. After hydrogenation, both the intensity of MWCNTs and h-BN bands decreases compared to unhydrogenated nanocomposites. This may be due to the adsorption of hydrogen by MWCNTs and h-BN nanoparticles. Thus, Raman spectra confirm the presence of hydrogen in the nanocomposite.

![Raman spectra](image)

**Figure 5** Raman spectra of hydrogenated (a) MWCNT and (b) MWCNT/h-BN nanocomposite

**H₂ - Desorption Analysis**

Figure 6 displays the thermogravimetric plot of hydrogenated MWCNT and MWCNT /h-BN nanocomposite, respectively. The spectrum corresponding to the hydrogenated MWCNT shows a weight loss of about 0.2 wt. % in the temperature range of 190 - 520 °C, which corresponds to the desorption of stored hydrogen from the sample. The TGA spectrum of hydrogenated MWCNT/h-BN nanocomposite reveals a weight loss of about 1.9 wt. % in the temperature range of 155 to 515 °C, which corresponds to desorption of stored hydrogen. The MWCNT and MWCNT/h-BN nanocomposite exhibits 100 % desorption. The binding energy of hydrogen and activation energy of desorption for hydrogenated MWCNT are 0.362 to 0.619 eV and 36.84 – 40.99 kJ/mol respectively. The binding energy of hydrogen and activation energy of desorption for hydrogenated MWCNT/h-BN nanocomposite are 0.335 to 0.616 eV, and 36.24 – 40.94 kJ/mol respectively.
In general, hydrogen can be stored in physical/chemical binding between them. Physisorption is a type of adsorption in which the adsorbate weakly binds to the surface only through Van der Waals interactions and this type of binding is stable in low temperature with the binding energy of 0.01 – 0.1 eV. On the contrary, chemisorption is a type of adsorption whereby molecules strongly bind to a surface through the formation of a chemical bond and very high temperatures are required to remove the hydrogen from the stored material. For which the binding energy falls in the range of 2-3 eV. It must be noted that the binding energy of molecular hydrogen with the adsorbent has been accepted for storage application is in-between chemisorption and physisorption. The obtained binding energy of hydrogenated MWCNT/h-BN nanocomposite lies between these ranges. Thus, the attached hydrogen in the nanocomposite forms a weak chemical bonding.

Conclusion

The absorption and desorption of stored hydrogen in MWCNT and MWCNT/h-BN nanocomposite were evaluated. Hydrogen storage capacities of MWCNT and MWCNT/h-BN were found to be 0.2 and 1.9 wt % and these samples are stable at room temperature. The hydrogen storage capacity of MWCNT/h-BN nanocomposite increases and it is due to the more adsorption sites offered by h-BN. The average binding energy of MWCNT/h-BN nanocomposite was found to be 0.38 eV and the nature of hydrogen binding is weakly chemisorbed. From the present investigation it is clear that, the MWCNT/h-BN nanocomposite is a potential candidate for hydrogen storage medium.

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