Physica E 60 (2014) 75–79

Contents lists available at ScienceDirect

Physica E

journal homepage: www.elsevier.com/locate/physe

Reversible hydrogen storage in functionalized single-walled carbon nanotubes

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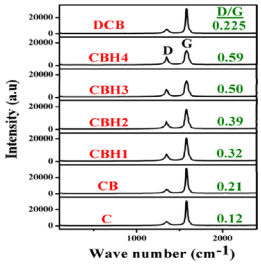
HIGHLIGHTS

- Functionalized SWCNTs shows a storage capacity of 4.77 wt% at 50 °C.
- Entire (100%) stored hydrogen is released in the temperature range of 90–125 °C.
- Hydrogenation and dehydrogenation is stabilized and are reproducible.
- Deterioration level of the sample is only of ~2.3%.
- Storage capacity achieved here is close to the US DOE target.

GRAPHICAL ABSTRACT

Functionalized SWCNTs shows a maximum hydrogen storage capacity of 4.77 wt% at 50 °C and the entire (100%) stored hydrogen is released in the temperature range of 90–125 °C



ARTICLE INFO

Article history:
Received 12 August 2013
Accepted 12 February 2014
Available online 20 February 2014

Keywords:
Single-walled carbon nanotubes
Functionalization
Borane
Hydrogen
Storage capacity
Dehydrogenation

ABSTRACT

In this work, functionalized carbon nanotubes (CNTs) based hydrogen storage medium has been designed by the facile drop-casting method. Initially, the commercial single-walled carbon nanotubes (SWCNTs) were purified by standard methods and functionalized with borane (BH_3). The morphology of SWCNTs was imaged by transmission electron microscopy (TEM). The energy dispersive spectroscopy (ED) shows that the purified SWCNTs are free from elemental impurities. The functional groups in the functionalized SWCNTs were analyzed by fourier transform infra-red spectroscopy (FTIR). Then, the functionalized SWCNTs were hydrogenated in a Seivert like hydrogenation setup for different time duration. Elemental analysis (CHN) combined with thermo gravimetric/thermal desorption spectroscopy (TG/TDS) measurements were used to quantify the amount of hydrogen stored in the functionalized SWCNTs. A maximum hydrogen storage capacity of 4.77 wt% is achieved at 50 °C and the entire (100%) stored hydrogen is released in the temperature range of 90–125 °C. The amount of hydrogen stored in functionalized SWCNTs increases with increasing hydrogenation duration. The entire hydrogenation and dehydrogenation process was probed by Raman and CHN-elemental analyses. The whole hydrogenation and dehydrogenation experiments were stabilized and they were repeatable. The achieved hydrogen storage capacity in this investigation is close to the US DOE target.

1. Introduction

Hydrogen is emerging as a green fuel for transportation applications [1,2]. The storage and delivery of hydrogen remains

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http://dx.doi.org/10.1016/j.physe.2014.02.006
1386-9477

a subject of technological importance in recent times. Storage of hydrogen in the form of gas under high pressure and liquid at cryogenic temperatures has basic problems associated with leakage, safety and storage capacity. On the other hand, solid-state materials provide an alternative choice for hydrogen storage, but the interaction between hydrogen and host material involved either strong interaction (covalent or ionic) or weak (van der Waals forces) interaction. Materials like metal hydrides, metal organic frameworks, clathrates and other nanostructures could not provide the combined advantages of high gravimetric storage capacity, reliability, and suitable kinetics for applications [3–6]. The nanostructures based on carbon have attracted the scientific community as one of the possible materials for hydrogen storage [7–10]. In the group of various carbon nanostructures, carbon nanotubes (CNTs) are widely investigated potential hydrogen storage material [11–17]. The remarkable properties of CNTs such as hollowness, cylindrical shape, interstitial sites, and nanometer scale diameter and porosity make them as one of the interesting candidates for hydrogen storage [17]. The initial hydrogen storage work of Dillon et al. [18] in SWCNT bundles led to extensive investigation of CNTs for hydrogen storage. Consequent investigations of hydrogen storage in CNTs indicated that, bare CNTs are not suitable material for the storage of hydrogen [19–23]. The reason is that, the nature of interaction between hydrogen molecules and CNTs involved physisorption (van der Waals interaction), and hence the stored hydrogen is stable only at lower temperatures. The modification of CNTs by the addition of atoms or molecules could lead to enhanced interaction between hydrogen and CNTs which resulted in higher storage capacity [24–29]. Further, it is pointed out that, the functionalization of SWCNTs with transition metal atoms itself occupies more weight percentage on SWCNTs [30] and also they forms strong metal hydrides while hydrogenation [31,32].

In this work, a hydrogen storage medium (HSM) based on SWCNTs, capable of storing and releasing hydrogen in the temperature range suitable for fuel cell applications has been designed. Here, the modification of SWCNTs is made by means of functionalizing them with BH_3. The simulation studies [27] based on density functional theory (DFT) carried out by our group indicated that, functionalization of SWCNTs with BH_3 enhances the binding energy of hydrogen molecules and thereby increases the storage capacity. Hence, we have chosen BH_3 for the functionalization of SWCNTs. Moreover, it is decided to conduct the hydrogenation experiment just above room temperature, because hydrogen storage at very lower temperatures and pressure conditions is not viable for mobile applications. The functionalized SWCNTs were hydrogenated for different time duration. Further, the hydrogenated samples were annealed to check desorption of hydrogen. The amount of hydrogen uptake and desorption temperature range have been measured. The binding energy of hydrogen and the nature of hydrogen binding are estimated based on the characterization results. The whole hydrogenation and dehydrogenation experiments were repeated to examine the reproducibility.

2. Experimental

2.1. Materials

SWCNTs were purchased from Sigma Aldrich with the purity of $>98\%$. The chemical reagents of Merck products with 99% purity were used for experiments. The expected amorphous carbon in the purchased SWCNTs was removed by heating them to 300 °C for 1 h. Then, the metal catalyst impurities were removed by washing with nitric acid and distilled water, and dried at 100 °C for 1 h. Alumina substrates were cleaned with ethanol, acetone and distilled water by means of sonication for 30 min (alumina substrates were taken as it will not react while heating).

2.2. Methods

The purified SWCNTs dispersed in 2-propanol (ultrasonicated for 1 h in the ratio of 5 mg/ml) were deposited on alumina substrates maintained at 70 °C using simple drop cast method. After deposition, the substrates were annealed at 300 °C for 1 h to remove any impurities. $LiBH_4$ was used as the precursor for BH_3. $LiBH_4$ mixed with di-ethyl ether in a ratio of 25 mg/ml was drop casted over the surface of SWCNTs. Then the substrates were annealed at 275 °C (decomposition temperature of $LiBH_4$) for 1 h which yields borane. The released BH_3 reacts with SWCNTs and forms a complex, SWCNT+BH_3 [25]. This complex acts as a hydrogen storage medium (HSM). The weight percentage of the hydrogen present in the functionalized sample was estimated using CHN-elemental analysis. This is one of the widely used standard techniques for the composition measurement of elements such as carbon, hydrogen and nitrogen as well as hydrogen storage capacity [33–37]. Then the functionalized samples were loaded in the Seivert like hydrogenation setup [33] and hydrogenated for different time duration by maintaining the substrate temperature at 50 °C and the hydrogen flow rate of $\sim$0.5 l/min, and then the samples were left in the chamber to attain room temperature. After hydrogenation, the hydrogen content present in the sample was again estimated using CHN-elemental analysis. The storage capacities are calculated as the difference of hydrogen content in the samples before and after hydrogenation experiment and the results are presented in Table 1. Further, the hydrogenated samples were annealed to check desorption of hydrogen. In this process, the hydrogenated samples were annealed at 200 °C for 30 min in a furnace. The temperature was controlled by a digital PID (proportional–integral–derivative) controller. After annealing, the samples were left in the furnace to reach room temperature.

2.3. Characterization

The morphology of SWCNTs was analyzed by transmission electron microscopy (TEM) using JEOL JEM 2100 model unit with an accelerating voltage of 200 kV. Energy dispersive X-ray spectrum (EDS) of SWCNTs was recorded using JEOL-MODEL 6390 unit with an accelerating voltage of 5 kV. FTIR spectra were recorded over the range 4000–450 cm^{-1} using Shimadzu model (FTIR-8400S, CE) spectrometer at room temperature with a resolution of 1 cm^{-1}. Raman measurements were carried out in Renishaw InVia model spectrometer with the laser excitation of 514 nm. CHN-elemental analysis was performed using Elementar Vario EL III model analyzer. The thermo gravimetric/thermal desorption spectroscopy (TG/TDS) measurements were carried out using Perkin Elmer-Diamond model unit over the temperature range, 40–800 °C at a scanning rate of 10 °C/min.

Table 1
Hydrogen adsorption and desorption characteristic parameters.

Sample index	H_2 flow duration (min)	H_2 (wt %)	T_m (°C)	E_d (kJ/mol)	E_B (eV)
CBH1	30	3.277	121	20.66	0.310
CBH2	35	3.785	113	20.11	0.302
CBH3	40	4.345	111	19.97	0.300
CBH4	45	4.770	107	19.69	0.287