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One-step process of hydrogen storage in single walled carbon nanotubes-tin oxide nano composite

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ABSTRACT

Hydrogen intake study on single walled carbon nanotubes (SWCNTs)-tin oxide (SnO_2) nano composite films have been performed. The composite is prepared on glass substrates in hydrogen atmosphere by electron beam evaporation (e-beam) technique. The process of hydrogenation has been done during the preparation of hydrogen storage medium itself, as one-step process. The amount of hydrogen incorporated in the composite is found to be 2.4 wt.%. The entire (100%) amount of stored hydrogen is released in the temperature range of 200–350 °C. The stored hydrogen has weak chemical binding in the SWCNTs-SnO_2 nano composite.

1. Introduction

Hydrogen has been found as one of the possible alternative energy source by humanity as it serves as fuel [1–8]. Hydrogen is not only abundant in nature, but it is also a light and non-pollutant element. It is a challenging task to store hydrogen technologically. Nanomaterials play an important role in the curriculum of hydrogen storage. In particular, carbon nanotubes (CNTs) are one of the possible hydrogen storage media used for fuel cell applications [9,10]. There are many reports on the application of hydrogen storage on pristine and modified carbon nanostructures [11–29]. Several works are available for the measurement of hydrogen content in the hydrogenated carbon nanostructure materials such as graphene and carbon nanotubes. Subrahmanyam et al. [30] have reported the chemisorption of hydrogen in few-layer graphene and measured a storage capacity of 5 wt.% by CHN analysis. In a previous hydrogen storage study [4], we have used the CHNS analysis for the weight percentage measurement of hydrogen in SWCNTs + BH_3 complex. We found that 1.5 wt.% of hydrogen was stored in the hydrogenated SWCNTs functionalized with borane sample. Sankaran and Viswanathan [31] have used the CHN-elemental analysis to measure the composition of carbon in the synthesized carbon nanotubes sample, and also to measure the nitrogen content in the nitrogen-doped carbon nanotubes. The CNTs prepared from the zeolite showed a storage capacity of 0.2 wt.% and the nitrogen-doped CNTs showed 0.72 wt.%. The hydrogen storage capacity of CNTs prepared from the pillared clay showed 0.35 wt.% and the corresponding nitrogen-doped CNTs showed 2 wt.% [31]. Badzian et al. [32] investigated the nanostructured, nitrogen-doped carbon materials (CNTs) for

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hydrogen storage. They have used CHN analysis to measure the elemental composition of carbon, hydrogen and nitrogen. The hydrogen storage capacity of 0.7–0.8 wt.% was measured.

Recent reports showed that the nanostructured composites made up of CNTs and metal oxides are good hydrogen storage materials [33,34]. A storage capacity of 0.4 wt.% at 298 K and 18 atm was achieved using CNTs impregnated with TiO_2-nanorods and nanotubes, which was nearly five times larger uptake than pristine CNTs [33]. The adsorption isotherms of CNT-TiO_2 nanotubular hybrid material were measured at two different temperatures namely, liquid nitrogen (77 K) and room temperature (298 K). The uptake of H_2 at 298 K and 77 K were found to be 1.04 wt.% at 22 bar and 2.5 wt.% at 25 bar respectively. The TiO_2 nanotubes alone showed only 2 wt.% of hydrogen storage at 77 K and 0.9 wt.% at 298 K. CNTs showed around 0.4 wt.% of hydrogen storage under identical conditions at 77 K single handedly [34]. These reports show that there are synergistic effects existing between the CNTs and TiO_2 nanostructures, which lead to a better sorption (adsorption/desorption) for hydrogen compared to the components alone.

Tin dioxide (SnO_2) is widely used as a gas sensing material particularly for hydrogen owing to its suitable physicochemical properties including high sensitivity, fast-response time, high chemical stability and low cost [35,36]. It may be mentioned that the composite MWCNTs-SnO_2 [37,38] and SWCNTs-SnO_2 [39,40] have been reported for different gas sensor applications. Hence an attempt has been made toward fabricating the hydrogen storage system based on SWCNTs-SnO_2 nano composite system. In the present study, hydrogen storage in SWCNTs-SnO_2 nano composite film prepared by e-beam technique is reported for the first time. The structure of CNTs does not undergo any deformation during the deposition of composite (MWCNT-SnO_2, MWCNT-WO_3) using e-beam evaporation technique [41,42]. Hence, e-beam evaporation technique is adopted for the preparation of nano composite in our study. Two sets of films of pure SnO_2 and SWCNTs-SnO_2 nano composite in hydrogen atmosphere have been prepared under same experimental conditions. The hydrogen storage capacities of pure SnO_2 and SWCNTs-SnO_2 nano composite are measured. The hydrogen storage measurement in the aforementioned reports [4,30–32] involved the elemental analysis (CHN/CHNS/CHNSO) method. Hence, we have also used the same analysis for the measurement of hydrogen storage capacity of the hydrogenated samples. The hydrogen storage capacity of the nano composite SWCNTs-SnO_2 is compared with earlier reports and presented in the Discussion section. The type of binding (physical/chemical) of hydrogen with the SWCNTs-SnO_2 nano composite is discussed based on thermogravimetric analysis.

2. Experimental

2.1. Composite preparation

SWCNTs were purchased from Sigma Aldrich with the purity, >98%. SnO_2 material with the minimum assay of 99% was purchased from Merck. The SWCNTs were mixed with SnO_2 in the ratio of 1:2 by weight. This mixture was ground well for 15 min using agate mortar, and placed in a cylinder-shaped steel mold. Uni-axial pressure of 5 MPa was applied to make them into pellet. Pellet with a diameter of 15 mm and a height of about 5 mm was obtained.

2.2. Film deposition

Glass substrates of dimension 25 mm × 75 mm × 1.35 mm were cleaned with chromic acid, acetone, and distilled water by means of sonication for 30 min. The pellet was placed in water cooled graphite crucible and then evaporated on to glass substrates in hydrogen atmosphere by electron beam (Hind Hivac Model – 12A4D) at room temperature. The distance between the electron beam source and the substrate was maintained to be 20 cm. The base pressure of 6×10^{-6} mbar was created before deposition. The vacuum chamber was flushed with hydrogen gas several times before evaporation. A beam voltage of 6 kV with the beam current of 20 mA was applied. The hydrogen gas was allowed in to the chamber at a flow rate of 0.5 l/min, and the chamber pressure was maintained at 5×10^{-5} mbar. The duration of evaporation was 15 min.

2.3. Hydrogenation

The hydrogen gas allowed through a regulated valve got atomized by thermal cracking [43] produced by tungsten filament in the deposition unit. The atomized and excited molecules of hydrogen impinged on the glass substrate along with the evaporant and thereby ensure the complete hydrogenation process. Two sets of films of pure SnO_2 and SWCNTs-SnO_2 nano composite in hydrogen atmosphere were prepared under the same experimental conditions.

2.4. Characterization

The morphology of SWCNTs was studied by transmission electron microscopy (TEM). Atomic force microscopy (AFM) was used to study the morphologies of pure SnO_2 and SWCNTs-SnO_2 nano composite films. The phases of the SnO_2 thin film were studied by X-ray diffraction (XRD) technique. Energy dispersive X-ray spectroscopy (EDS) was used to validate the presence of all the elements in the SWCNTs-SnO_2 nano composite film. CHN-elemental analysis was carried out to measure the amount of hydrogen incorporated in pure SnO_2 and SWCNTs-SnO_2 nano composite films. The hydrogen desorption behavior was studied by thermogravimetric/thermal desorption spectroscopy (TG/TDS).

3. Results and discussion

3.1. Morphology analysis

The TEM image presented in Fig. 1(a) displays the presence of high quality SWCNTs with the average diameter of about 2 nm. Fig. 1(b) shows the AFM image of pure SnO_2 thin film, which comprises of uniformly distributed SnO_2 grains with the average size of around 20 nm. The surface morphology of SWCNTs dispersed in SnO_2 thin film is shown in Fig. 1(c). The AFM image reveals the inclusion of SWCNTs in SnO_2 thin film,