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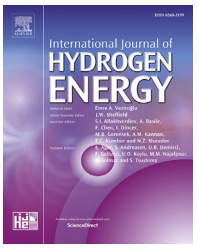

Synthesis and characterization of MWCNT impregnated with different loadings of SnO_2 nanoparticles for hydrogen storage applications

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ABSTRACT

Multi-walled carbon nanotubes (MWCNTs) loaded with different wt % of tin oxide (MWCNT: SnO_2) nanocomposites have been synthesized by impregnation method and their hydrogen uptake capacity is investigated. The hydrogen storage capacity of MWCNT: SnO_2 (3 wt %), MWCNT: SnO_2 (5 wt %), MWCNT: SnO_2 (7 wt %) and MWCNT: SnO_2 (9 wt %) composites is found to be 2.03, 1.95, 0.94 and 1.59 wt % respectively. The enhanced hydrogen storage capacity is due to Sn–O–C bond formation and summative adsorption of hydrogen by MWCNT and SnO_2 nanoparticles. Moreover, physical/chemical properties of composites are examined by Fourier transform infrared spectroscopy, scanning electron microscopy, energy dispersive X-ray spectroscopy, and X-ray diffraction, thermogravimetric and Raman analyses. Hydrogen adsorption and desorption behavior of the composites are analyzed using Raman and thermogravimetric analyses. The stored hydrogen is desorbed in the temperature range of 183 °C-536 °C.

Introduction

Hydrogen, a future fuel with high energy density and zero CO_2 emission during combustion has drawn much consideration as a successor for petroleum derivatives in mobile and stationary applications in the near future [1–8]. Despite being a versatile energy carrier, hydrogen is still not being used on par with conventional fuels due to the difficulties in storage and utility at ambient conditions [4–7]. To overcome the bottleneck, several solid-state materials [8–20] such as metal-organic frameworks (MOFs) [9], metal hydrides [10], clathrate hydrates [11] and carbon-based materials [12–19] have been widely investigated. Among these materials, carbon nanotubes (CNTs) have attracted much importance as solid-state hydrogen storage medium due to their properties such as lightweight, hollowness, high surface to volume ratio and high stability [12–14,18,19]. Following the report of Dillon et al. [19] on the high hydrogen storage capacities (5–10 wt %) in hollow cylinder SWCNTs, extensive research

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has been focused on increasing the hydrogen storage efficiency of CNTs. Hirscher et al. [20] has focused on the conflicting results of hydrogen storage in CNTs and has found that pristine CNTs have negligible hydrogen storage capacity (less than 0.4 wt %) at ambient conditions. This is due to the existence of weak van der Waals interaction between CNTs and hydrogen [21,22]. Afterwards, several advancements have been made to enhance the hydrogen storage capacity of CNTs through surface modification by anchoring it with metals and metal oxides such as Li-MWCNT [23], Pt-MWCNT [24,25], V-CNT [26], Pd- CNT [26], Ti-CNT [27], Y-SWCNT [28], Pt-SWCNT [29] and MWCNT/h-BN (hexagonal boron nitride) [30] which provide activation sites for incoming hydrogen molecule. Moreover, considerable attention has been paid to increase the surface area, pore size, defects and chemical functionalization of MWCNT/SWCNT treated with HNO_3 [31] and bases such as KOH and NaOH [32].

Recent reports demonstrate that the nanostructured composites comprising CNTs and metal oxides are potential hydrogen storage materials [33–39]. Hydrogen storage capacity of 3.2 wt % is achieved with SWCNT-TiO_2 composite [33]. Rather et al. [34] have accomplished the H_2 uptake capacity of 0.4 wt % at 298 K and 18 atm in the case of carbon nanotubes impregnated with TiO_2 nanorods/nanotubes and have reported that the hydrogen storage capacity is five times higher than that of the bare CNT. Noroozi et al. [35] have examined the hydrogen storage capacities of pristine SWCNTs and SWCNTs impregnated with titanium dioxide (SWCNT-TiO_2), zirconium oxide (SWCNT-ZrO_2) and zinc oxide (SWCNT-ZnO) composites employing a purpose-built Sievert's like apparatus and observed the hydrogen storage capacity of 0.08 wt %, 0.40 wt %, 0.31 wt % and 0.25 wt % respectively at room temperature. Larijani et al. [36] observed hydrogen storage capacities of 0.45 wt %, 0.12 wt %, and 0.40 wt % in SWCNT-TiO_2, enriched PdO-SWCNT and enriched Pd-SWCNT respectively at room temperature under 30 atm pressure of H_2. Silambarasan et al. [37] have reported that the hydrogen storage capacity of SWCNT functionalized with SnO_2, WO_3 and TiO_2 at 100 °C is 1.1 wt %, 0.9 wt % and 1.3 wt % respectively. In a one-step process, Silambarasan et al. [38] have demonstrated a higher hydrogen storage capacity of 2.4 wt % in SWCNT-SnO_2 thin films deposited by electron-beam evaporation technique followed by hydrogen exposure in an e-beam chamber. Further studies revealed that metal oxide nanoparticles functionalized on the surface of the CNTs are well known for their catalytical dissociation of hydrogen molecules on the surface of CNTs through spillover mechanism [40–42]. Review of literature shows that SWCNT: SnO_2 and MWCNT: SnO_2 composites prepared by various methods such as electron beam evaporation [43], sol-gel [44], hydrothermal [45], chemical route [46–49], vapor phase method [50], thermal evaporation [51] and electro-spinning [52] have found wide application in the field of Li-ion batteries [47], gas sensors [48] and as well as hydrogen storage [37,38] as a result of their superior properties such as, high chemical stability, large surface to volume ratio, fast response time and abnormal variation in the properties at nanoscale [53]. Most of the literature reports on hydrogen storage capacity reveal that the storage is due to the surface modification of SWCNT with various metal oxides and metals [33–39]. However, the lack of consistent literature studies on MWCNT based metal oxide composites as hydrogen storage systems has triggered our interest to pursue the present work.

In the present work, we have made an attempt for the first time to investigate the hydrogen storage capacity of MWCNTs impregnated with different weight percentage of SnO_2 synthesized by simple and cost-effective wet impregnation method. The hydrogen storage properties of pristine MWCNT, SnO_2, and MWCNT impregnated with different wt % of SnO_2 are studied. In addition, we have investigated the influence of various concentrations of SnO_2 impregnation on MWCNTs on their structural, morphological, spectral and thermal properties. The thermogravimetric analyzer is employed to investigate the hydrogen desorption properties of these composites.

Experimental methods

Materials

Multi-walled carbon nanotubes with a diameter in the range of 110–170 nm and length of 5–9 μm (assay ≥ 90%) were purchased from Sigma Aldrich. The precursor tin chloride dihydrate ($SnCl_2 \cdot 2H_2O$) was procured from Merck with purity ≥ 99.9%. The materials were used as received without further purification.

Preparation of MWCNT: SnO_2 nanocomposites

MWCNTs loaded with various concentrations of SnO_2, (MWCNT: SnO_2) nanocomposites, were prepared by simple wet impregnation method by taking MWCNTs as a base material and $SnCl_2 \cdot 2H_2O$ as a precursor for SnO_2. The MWCNTs suspension was prepared by ultrasonicating 50 mg of pristine MWCNT in 75 ml of double distilled water for 1 h in bath sonicator followed by probe sonication for about 15 min. The calculated amount of $SnCl_2 \cdot 2H_2O$ was dissolved in 25 ml double distilled water so as to yield 3 wt %, 5 wt %, 7 wt % and 9 wt % of SnO_2 in the precursor solutions and subjected to constant stirring for about 30 min in separate experiments. In the synthesis process of MWCNT: SnO_2 nanocomposites, the as-prepared aqueous solutions of $SnCl_2 \cdot 2H_2O$ was added drop by drop into the MWCNT suspension prepared via sonication and then heated to 90 °C to evaporate the water. The black precipitate obtained after the complete removal of the solvent was dried at 110 °C for 24 h to eliminate the hydroxyl group and other impurities present in the synthesized nanocomposites. The MWCNT: SnO_2 nanocomposites synthesized using a different concentration of the $SnCl_2 \cdot 2H_2O$ solution is named as MWCNT: SnO_2 (3 wt %), MWCNT: SnO_2 (5 wt %), MWCNT: SnO_2 (7 wt %) and MWCNT: SnO_2 (9 wt %). SnO_2 nanoparticles were also prepared separately following the above procedure and their properties were studied and compared with those of the MWCNT composites. The schematic illustration of the synthesis of MWCNT: SnO_2 nanocomposites is shown in Scheme 1.

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