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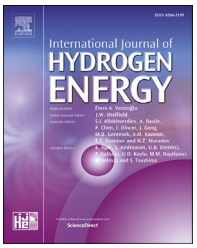

Hydrogen adsorption on single walled carbon nanotubes-tungsten trioxide composite

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ABSTRACT

In this work, hydrogen storage property of single walled carbon nanotubes-tungsten trioxide (SWCNTs-WO_3) composite is investigated. The composite is prepared and hydrogenated by electron beam (e-beam) evaporation technique. Hydrogenation is carried out during the preparation of the composite itself. The amount of hydrogen uptake by the composite is 2.7 wt%, which is due to the collective adsorption of hydrogen by CNTs and WO_3 nanostructured materials, the method of preparation and hydrogenation involved. The incorporated hydrogen is completely (100%) released in the temperature range of 175–305 °C which in turn infers that the hydrogenated composite is stable at room temperature. The stored hydrogen has the average binding energy of 0.4 eV and the nature of binding is found to be weak chemisorption. Spillover mechanism is attributed for the hydrogen uptake of the composite.

Introduction

Scientists and researchers around the world believe that, hydrogen is a potential, emission-free, additional alternate candidate for various applications [1–5]. There is growing interest in the use of hydrogen as the main fuel for stationary, mobile, and transportation applications, especially using fuel cells [6–10]. Hydrogen is not a primary source of energy as it occurs only in nature in combination with other elements, primarily with oxygen in water and with carbon, nitrogen and oxygen in living materials and fossil fuels [11–14]. Water splitting is one of the significant reaction found to produce hydrogen as a clean fuel for applications [15–18]. From the primary source to final consumer, storing energy is an essential process at several steps of the system. When the energy consumption exceeds the production capacity, the

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storage of energy is obviously required. It is also essential for all mobile and portable applications. Hydrogen storage is considered as a key technology towards hydrogen economy for the successful commercialization and market acceptance of hydrogen powered vehicles. The commercial exploitation of fuel cell technology strongly depends on the development of a viable hydrogen storage method.

A safe, efficient, and compact on-board hydrogen storage system is required to realize hydrogen powered transport applications. In the current scenario, hydrogen storage through the classical methods, such as compression and liquefaction is energy-intensive and demands heavy storage tanks. The storage of hydrogen in its solid-state form on materials is the most appropriate way to store hydrogen. There are many materials considered for the storage of hydrogen. This includes compressed gas tanks, liquid tanks, metal hydrides [19,20], liquid organic hydrides [21], carbon-based materials [22–26], high surface area sorbents [27–29], and chemical storage [30–32]. Among these, carbon nanotubes (CNTs) are considered as one of the most potential candidates for hydrogen storage [22,24,33]. Because, CNT provides some interesting properties such as, high surface area, molecular sized pores, light weight, chemical and mechanical stability [22,24,33]. Many investigations were carried out intensely for the storage of hydrogen in CNTs and CNT based materials under different conditions [34–41]. The micro-porous carbon materials showed a maximum gravimetric storage capacity of 1.3 wt% at a pressure of 10 MPa [34]. Gao et al. [35] investigated the hydrogen uptake study of pristine and Pd-Ni doped defective multi walled CNTs (MWCNTs). Pristine CNTs could only store 0.1 wt% of hydrogen at 573 K and ambient pressure. However, the oxidation treatment and subsequent loading of CNTs with Pd-Ni catalyst significantly increased the hydrogen storage capacity upto 6.6 wt%. Sankaran et al. [36] observed a maximum storage capacity of 2 wt% in boron substituted CNTs. MWCNTs impregnated with Ni nanoparticles showed a high hydrogen uptake upto 2.8 wt% under moderate temperature and pressure condition [37]. Rather et al. [38] reported a reversible hydrogen storage capacity of 0.18 wt% at 298 K and 1.6 MPa in pd embedded CNTs, which is nearly twice the storage capacity of pristine CNTs. The Pt dispersed single walled CNTs (SWCNTs) showed an enhanced hydrogen uptake upto 3.03 wt% at 125 K and 78 bar when compared to as-grown and purified SWCNTs [39]. Rashidi et al. [40] obtained a maximum hydrogen adsorption capacity of 0.8 wt% in the case of CNTs with 95% purity and the adsorption raised upto 1 wt% with some improved purified CNTs. SWCNTs functionalized with borane showed a hydrogen storage capacity of 1.5 wt% [41].

In a progress of making CNT based efficient hydrogen storage medium (HSM), recently the composite nano structures made by CNTs and metal oxide were investigated [33,42–44]. A nanotubular hybrid material containing CNTs and TiO_2 showed a hydrogen uptake of 1.04 wt% at 298 K, 22 bar and 2.5 wt% at 77 K, 25 bar [33]. In that composite, TiO_2 nanotubes alone showed 2 wt% of hydrogen storage at 77 K and 0.9 wt% at 298 K and CNTs showed 0.4 wt% under identical conditions at 77 K. The CNTs impregnated with TiO_2-nanorods and nanotubes showed a hydrogen storage capacity of 0.4 wt% at 298 K, 18 atm, which is nearly five times higher uptake than pristine CNTs [42]. The nanostructured composites, SWCNTs-SnO_2 and SWCNTs-TiO_2 exhibited a storage capacity of 2.4 and 3.2 wt%, respectively [43,44]. These reports show that there exists a synergistic effect between CNTs and metal oxide nanostructures, which leads to better adsorption/desorption of hydrogen than the individual components [33,42–44]. This paper deals with the investigation of hydrogen storage in single walled carbon nanotubes-tungsten trioxide (SWCNTs-WO_3) composite. WO_3 is an n-type semiconductor; it has been investigated for several applications ranging from smart windows, dye-sensitized solar cells, sensors to photo electrochemical (PEC) water splitting [45–47]. The interaction between WO_3 and hydrogen has been studied widely [48–52]. Interestingly, the thin film material containing MWCNTs and WO_3 has been investigated for hydrogen gas sensor applications [53].

Hence in the present experimental study, we intended to study the hydrogenation property of SWCNTs-WO_3 composite. Electron beam (e-beam) evaporation technique is one of the widely used techniques for the preparation of material containing CNTs and metal oxides such as, WO_3, SnO_2, and TiO_2 [43,44,53,54]. Therefore, we have used e-beam evaporation technique to prepare as well as hydrogenate the SWCNTs-WO_3 composite. A one step process of synthesis and hydrogenation of composite is made here i.e.; the process of hydrogenation was done during the preparation of HSM itself. In addition, WO_3 have also been prepared and hydrogenated for the comparison study. The amount of hydrogen uptake by the materials and the nature of hydrogen binding are discussed based on the characterization results.

Experimental

Materials

Commercial SWCNTs was purchased from Sigma Aldrich with the purity of >98% and used for the experiments. The expected amorphous carbon in the purchased SWCNTs was removed by heating them in a muffle furnace at 300 °C for 1 h. Further, the metal catalysts impurities were removed by washing with nitric acid and distilled water, and dried at 100 °C for 1 h. WO_3 powder with the minimum assay of 99% was purchased from Merck. Glass substrates of dimension 25 × 75 × 1.35 mm were cleaned with hot chromic acid, acetone, and distilled water by means of sonication for 30 min and used.

Composite preparation

The purified SWCNTs was mixed with WO_3 in a 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 3–4 MPa was applied to make them into pellet. Pellet with a diameter of 15 mm and a height of about 5 mm was obtained. Fig. 1 shows the schematic of preparation of pellet.

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