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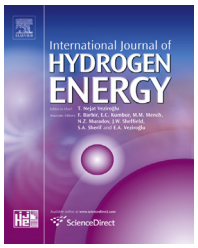

# Investigation of single-walled carbon nanotubes-titanium metal composite as a possible hydrogen storage medium

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ABSTRACT

The present experimental work deals with the investigation of hydrogen uptake study of single-walled carbon nanotubes (SWCNTs-Ti)-titanium metal composite. The mixture containing SWCNTs and Ti powder is made into tablet by cold pressing. The composite has been prepared and hydrogenated by evaporating the tablet in hydrogen ambient on glass substrates using electron beam (EB) evaporation technique. Efficient hydrogen uptake of 4.74 wt.% is achieved with the composite and the adsorbed hydrogen posses the average hydrogen binding energy of 0.4 eV. The obtained hydrogen uptake is due to the cumulative adsorption of hydrogen by CNTs and Ti nanostructured materials. The physical properties are characterized by transmission electron microscopy (TEM), atomic force microscopy (AFM), X-ray diffraction study (XRD), scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS) and Raman analysis. Hydrogenation and dehydrogenation behavior of the composite are studied using CHN-elemental analysis and thermo gravimetric/thermal desorption spectroscopy (TG/TDS) studies, respectively. The stored hydrogen is found to be 100% reversible in the temperature range of 160–310 °C.


## 1. Introduction

Hydrogen is a potential emission-free alternative fuel, which can reduce dependence on fossil fuels and significantly reduce the green house gases [1,2]. The cautious storage and delivery of hydrogen are the problems associated with the relatively advanced storage methods such as high-pressure gas or liquid etc. The storage of hydrogen on nanostructures has potential advantages over those methods. The properties such as high surface area, molecular sized pores, light weight, chemical and mechanical stability offered by carbon nanotubes (CNTs) make them as one of the better aspirants for the storage of hydrogen [3–5]. Initially in 1997, Dillon et al. [6] have reported the study of hydrogen storage on CNTs. Following that remarkable work, intensive research has been carried out on CNTs to store hydrogen [7–10]. Rzepka et al. [7] have investigated the hydrogen storage capability of micro porous carbon materials and they obtained a maximum gravimetric storage capacity of 1.3 wt.% at a pressure of 10 MPa. Hydrogen adsorption on crystalline ropes of single-walled carbon nanotubes (SWCNTs) has been examined by Ye et al. [8] and more than 8 wt.% of hydrogen was stored at pressures higher than 40 bar at 80 K. Simulation study based on density functional theory (DFT) investigated by Arellano et al. [9] have

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reported the interaction of molecular and atomic hydrogen with (5, 5) and (6, 6) SWCNTs. The physisorbed hydrogen molecule has the binding energies in the range of 0.04–0.07 eV. Cabria et al. [10] have studied the adsorption of molecular hydrogen on the outer surface of (5, 5), (6, 4), (8, 1) and (16, 2) CNTs using DFT calculations and achieved the hydrogen adsorption of 14.3 wt.% with the hydrogen binding energies between 40 and 80 meV. Even a higher storage capacity had been achieved in most of those studies, the nature of interaction between hydrogen molecules and CNTs involved physisorption (van der Waals interaction) and it indicates that bare CNTs are not an eligible material for hydrogen storage [7–13]. Basically, the weak binding of hydrogen releases easily at low temperatures, while the strong binding of hydrogen requires high temperature to release. However, it has been shown that the addition of metal species with CNTs enhances the binding energy of hydrogen as well as the storage capacity (than CNTs) via two processes namely, i. Providing multiple sites for adsorption and, ii. Electron charge transfer between metal and carbon atoms [14–17]. Moreover, the hydrogenated CNT-metal complex systems are reported to be stable at room temperature [14–16]. Chen et al. [18] have found a higher binding energy of hydrogen in Li doped CNT (0.18 eV) than undoped CNT (0.025 eV) using DFT calculations and Yang et al. [19] have measured the hydrogen storage capacity of 2.5 wt.% in Li doped CNTs experimentally. Lipson et al. [20] have discussed electrochemical loading of SWCNTs encapsulated by thin Pd coating leading to a storage capacity of 8–12 wt.% in ambient conditions. A maximum storage capacity of 2 wt.% has been observed by Sankaran et al. [21] in boron substituted CNTs. Hydrogen storage properties of multi-walled CNTs (MWCNTs) impregnated with Ni nanoparticles showed a high hydrogen uptake upto 2.8 wt.% under moderate temperature and pressure condition [22]. Rather et al. [23] have observed a maximum 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. Shelvin et al. [14] have performed ab initio DFT simulations on hydrogen storage in CNT (8, 0) via defect-modulated titanium doping and reported a high hydrogen storage capacity of 7.1 wt.%. The Pt dispersed single-walled CNTs (SWCNTs) prepared by Reddy and Ramaprabhu [24] have showed an enhanced hydrogen uptake upto 3.03 wt.% at 125 K and 78 bar when compared to as-grown and purified SWCNTs. Reyhani et al. [15] have compared the hydrogen storage capacities of pure and metal nanoparticles (Ca, Co, Fe, Ni, and Pd) decorated MWCNTs and found increase in storage capacity in metal decorated MWCNTs.

The complexity with light elements such as Li, Be, B, Na and Al is that the hydrogen bind either strongly (covalent or ionic interactions) or weakly (van der Waals interactions) to the host material [28]. The metals such as Pt, Pd and Ti are the most investigated candidates to enhance the hydrogen storage capacity of CNTs [23–27]. Among them, the heavy transition metals Pt and Pd are not good candidates for the molecular absorption, because these metals showed the formation of classical metal hydride cluster ($PtH_4$, $PdH_4$), which has not bound to the nanotubes [28]. Moreover, the Pd-CNT shows the hydrogen storage capacities measured in experiments to be typically ~0.5 wt.%, depending on the storage condition [23,25–27]. On the other hand, the light transition metal, Ti showed a storage capacity of 8 wt.%, which is higher than Pt and Pd [29]. Moreover, the study of interaction between metals such as Au, Al, Fe, Ti, Ni and Pd and SWCNTs has also denoted that Ti interact strongly with the sidewall of nanotubes through the partial covalent bonding while the other metals Au and Al interact weakly with SWCNTs through van der Waals forces [30]. Hence, the combinations of Ti metal with CNTs for hydrogen storage lead us for the present investigation with high interest.

Thus, aim of the present study is focused on the investigation of hydrogen storage in SWCNTs-Ti composite. The electron beam (EB) evaporation technique is used to prepare and hydrogenate the SWCNTs-Ti composite simultaneously for the first time. EB evaporation is one of the widely used techniques for the preparation of composites such as MWCNT-$SnO_2$ [31], MWCNT-$WO_3$ [32] and SWCNT-$SnO_2$ [33]. Hence, we have also used the EB evaporation technique. The amount of hydrogen uptake, desorption temperature range, binding energy and the nature of hydrogen binding are discussed based on the characterization results.

## 2. Experimental

### 2.1. Materials preparation

SWCNTs were purchased from Sigma Aldrich with >98% purity. The Ti metal powder with >99% assay was purchased from Merck. The expected amorphous carbon and metal impurities present in the purchased SWCNTs were removed by the standard heating and acid washing procedures. Glass substrates of dimension $25 \times 75 \times 1.35$ mm$^3$ were cleaned with chromic acid, acetone and distilled water by means of sonication for 30 min. SWCNTs were mixed with Ti metal powder in the ratio of 1:2 by weight and ground well for 30 min using an agate mortar. The mixture was placed in a cylinder-shaped steel mould and an uni-axial pressure of 4–5 MPa was applied to make them into tablet. Tablet with the diameter of 15 mm and a height of 5 mm was obtained.

### 2.2. Composite preparation

The tablet was placed in water cooled graphite crucible and then evaporated in hydrogen atmosphere by electron beam (Hind Hivac Model-12A4D) on glass substrates. The substrates were kept at a distance of 20 cm from the electron beam source. The chamber base pressure was $5 \times 10^{-6}$ mbar. The vacuum chamber was flushed with hydrogen gas several times before evaporation. A beam voltage of 6 kV with the beam current of 30 mA was applied. The hydrogen gas was allowed into the chamber till the pressure reduced to $5 \times 10^{-5}$ mbar. The duration of evaporation was 15 min.

### 2.3. Hydrogenation

The hydrogen gas allowed through a regulated valve got atomized by thermal cracking produced by the tungsten filament in the deposition unit [33,34]. The atomized and excited molecules of hydrogen impinged on the substrates along with the evaporant and thereby ensure the complete