



Hydrogen uptake of high-energy ball milled nickel-multiwalled carbon nanotube composites



Sami-ullah Rather ^{a,b,*}, Kee Suk Nahm ^b

^a Chemical and Materials Engineering Department, King Abdulaziz University, P.O. Box 80204, Jeddah 21589, Saudi Arabia

^b School of Chemical Engineering and Technology, Chonbuk National University, Chonju 561-756, Republic of Korea

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ABSTRACT

Hydrogen uptake of Ni decorated MWCNT composites performed using Server's volumetric equipment. The maximum reversible hydrogen storage capacity exhibited by nanocomposites, measured at 298 K and hydrogen pressure of 8 MPa, was found to be ~2.27 wt.%, which is more than three times as compared to pristine MWCNTs. The enhancement of hydrogen storage capacity in coated samples as compared to pristine MWCNTs is due to the spillover of physisorbed hydrogen from metal nanoparticles to the MWCNTs. The hydrogen uptake by Ni/MWCNTs samples follows the Henry's rule, suggesting that there is no significant adsorbate–adsorbate interaction in the low-pressure region.

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1. Introduction

Hydrogen is considered as the future fuel for transport applications. Low mass density, high energy density, easy production, high abundance, and environmental friendliness make it the most convenient fuel for on-board applications. The main drawbacks of this fuel are the low volumetric density and safety. To overcome these problems, researchers start storing hydrogen in solid-state materials such as various forms of carbon, zeolites, metal-organic frameworks (MOFs), and metal hydrides [1–5]. Carbon nanotube is considered to be the most fascinating material for the hydrogen storage due to its impressive chemical stability, high surface area, highly uniform pore sizes, high stability, hollowness, and low resistivity [1,6–9]. Atomic or molecular hydrogen could be stored inside the tube-cavity, between the graphitic layers, and in the inter-spacing of carbon nanotube bundles [10,11]. Many research groups have already performed the hydrogen storage studies in carbon nanotubes such as single walled carbon nanotubes (SWCNTs) and multiwalled carbon nanotubes (MWCNTs), however, the wt.% is far from the Department of Energy (DOE) 2015 target that is 5.5 wt.% and

70 g/L at 233–358 K and 0.3–10 MPa (and ultimate 7.5% and 70 g/L) [12]. To improve hydrogen storage capacity in carbon nanotubes, various kinds of modifications were performed such as acid treatment, simple annealing, bromination, plasma etching, and KOH or NaOH activation. Such kind of modifications also includes removal of metal catalysts, and increase in both the surface area and pore volume [13–18]. Chen and Huang [17] reported that KOH activated carbon nanotubes store 4.47 wt.% of hydrogen under ambient pressure and moderate temperature, whereas unmodified carbon nanotubes store only 0.71 wt.% of hydrogen as compared to activated nanotubes performed under same experimental conditions. Torres et al. [19] reported that activation of nanostructured carbons by NaOH and KOH enhanced the storage capacity of H₂ to 2.40 and 2.70 wt.% of hydrogen at 77 K and atmospheric pressure. Though these kind of results are still far from the DOE target (7.5 wt.%), but are encouraging for researchers as they increase the hydrogen storage capacity of modified nanotubes more than 60% as compared to as produced carbon nanotube samples.

Recently researchers have started doping of transition metals into carbon nanotubes by incipient wetness-impregnation, in situ reduction, and sputtering method to increase the hydrogen storage capacity in carbon nanotubes [20,21]. The incorporation of metal into CNT is important because it dissociates the hydrogen molecule into atomic hydrogen and then spills the hydrogen called spillover mechanism to carbon nanotubes. Non-classical s-p-d hybridization and spillover mechanism makes the metal embedded carbon nanotube composites interesting due to their high hydrogen

* Corresponding author at: Chemical and Materials Engineering Department, King Abdulaziz University, P.O. Box 80204, Jeddah 21589, Saudi Arabia. Tel.: +966 26402000x68037; fax: +966 26952257.

E-mail address: rathersami@gmail.com (S.-u. Rather).

storage capacity [20–23]. Zacharia et al. [21] reported that sputtering deposition of platinum nanoparticles on the carbon nanotubes increases the hydrogen adsorption more than 40% as compared to pristine multiwalled carbon nanotubes (MWCNTs). However, metal nanoparticles only dissociate the hydrogen molecule when they are exposed to hydrogen attached to the carbon nanotubes as compared to inside the carbon nanotubes. Zhong et al. [24] reported, 2.8 wt.% of hydrogen stored in nickel-carbon nanotube composites prepared by arc-discharge method at 500 °C and 3–5 MPa of pressure. Furthermore, the Ni/graphite synthesized by arc-discharge method increases the hydrogen uptake 20% at 500 °C and 3–5 MPa and can release 2.8 wt.% of hydrogen at the same temperature. The hydrogen storage capacity of this composite decreased to 1.6 wt.% after five cycles of adsorption and desorption. The composite could store hydrogen up to 2.7 wt.% at 77 K and hydrogen pressure of 7 MPa. The capacity of 2.8 wt.% of hydrogen on Ni/CNT composite was a much appreciating work but the temperature used in this process made it more difficult to be commercially feasible. Approaching the same wt.% of hydrogen storage at room temperature will be an appreciating step towards the target (7.5 wt.%) set by the DOE.

In this paper, we present room temperature (RT) hydrogen uptake studies of Ni/MWCNT composites synthesized by high-energy ball milled method. Hydrogen storage studies were performed by automatic Sievert's volumetric apparatus at hydrogen partial pressure of 8 MPa. The hydrogen storage capacity of these materials is subsequently understood from the storage capacity contributions of pristine carbon nanotubes and that of composite measured under similar experimental conditions.

2. Materials and methods

Carbon nanotubes were first purified using the multistep purification process before ball milling nickel powder (Sigma Aldrich) with commercial multiwalled carbon nanotubes (MWCNTs) purchased from CNT Inc., Korea. MWCNTs (2 g) were introduced into a standard flask and ultrasonicated in 250 ml deionized water for 30 min. The solution was stirred with a magnetic stirrer for 30 min and heated at 100 °C for 12 h to break the network between MWCNTs and amorphous carbon and metal particles. After the sample was filtered and dried at 100 °C, the residual soot was brominated in bromine water at 90 °C for 30 min and dried. The sample was then calcinated in air at 500 °C for 45 min and the black product obtained was treated in 35% hydrochloric acid, stirring for 1 hr to remove the metal particles from carbon nanotubes at room temperature. Finally, the purified sample was washed with deionized water and dried. Purified MWCNTs (0.8 g) were mixed with Ni (0.5 g) with size less than 150 μm in an argon-filled glove box and put in a hardened steel crucible. Milling was carried out in a high-energy ball mill (SPEX 8000 Mixer) for 8 h at room temperature. The ball to powder weight ratio was 10:1. The crystal structure of Nickel/carbon nanotube composites was examined using Rigaku D/MAX 2500 X-ray diffractometer (XRD) equipped with a Cu-K α radiation source ($\lambda = 0.15418$ nm). The samples for XRD measurement were prepared by vacuum drying the nickel multiwalled carbon nanotube composite at 100 °C. Thermogravimetric analysis (TGA) was performed on a TQ50 under oxygen atmosphere using a heating ramp of 10 °C/min. Surface states of Ni/MWCNT were analyzed by X-ray photoelectron spectroscopy (XPS, AXIS-NOVA, Kratos Inc.) with Al-K α as a source of X-rays. Raman spectrum was performed in an argon atmosphere recorded using He-Ne laser at an excitation wavelength of 632 nm. Nitrogen adsorption was performed at 77 K and was carried out using a Micromeritics ASAP 2000 instrument. The micropore volume and total surface area of

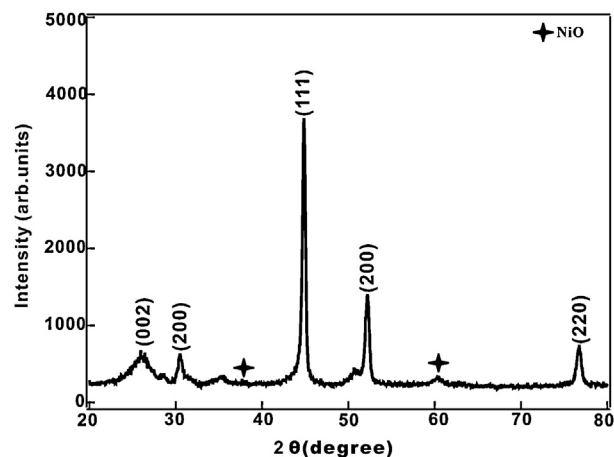


Fig. 1. X-ray diffraction profiles of Ni/MWCNTs composite synthesized by high energy ball milling method.

composite and pristine carbon nanotubes were measured using the BET method.

Transient hydrogen adsorption studies of Ni/MWCNTs material were performed by using automatic Sievert's volumetric equipment at RT and hydrogen pressure of 8 MPa. Prior to the hydrogen storage experiments, we performed the determination of the dead-volume of the system using helium gas. The determined volume was additionally cross-checked using hydrogen adsorption data of a known amount of the intermetallic alloy LaNi₅ [25]. Nearly 50 mg of sample was used in each storage experiment. Prior to each adsorption experiment, the Ni/MWCNT samples were degassed for nearly 3 h by heating at 200 °C under continuous evacuation up to 1.3×10^{-9} MPa. The gravimetric storage capacity of Ni/MWCNTs material was determined from the pressure drop of hydrogen gas using the ideal gas equation. Data acquisition for hydrogen storage was automated by interfacing the pressure transducer output to a PC via a RS-232 device. Further experimental details can be obtained from elsewhere [25].

3. Results and discussion

The crystalline structure of the Ni/MWCNTs was studied by X-ray XRD patterns [Fig. 1]. The XRD spectrum was characterized by several intense peaks between the diffraction angles of 20 and 80°.

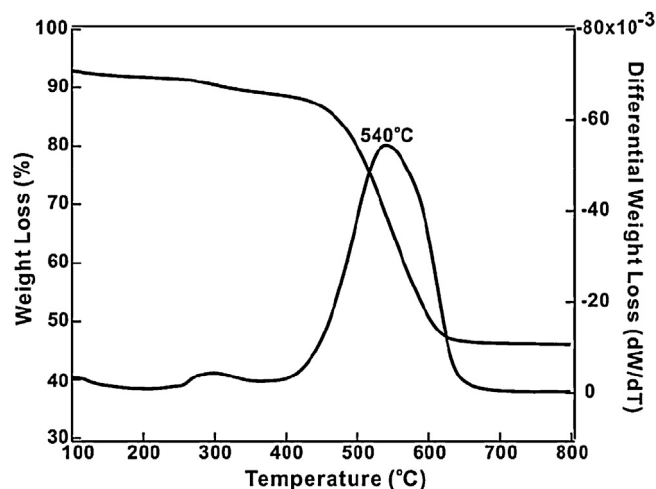


Fig. 2. Thermogravimetric data and the differential thermal plot of the Ni/MWCNTs composite material performed in an oxygen atmosphere. The heating ramp used is 10 °C/min.

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