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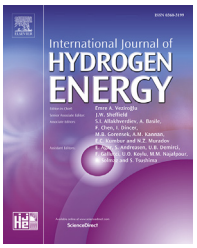

Hybrid laser ablation and chemical reduction to synthesize Ni/Pd nanoparticles decorated multi-wall carbon nanotubes for effective enhancement of hydrogen storage

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ABSTRACT

Simultaneous laser ablation and chemical reduction processes are introduced here to decorate the multi-wall carbon nanotubes with metal nanoparticles (palladium and nickel) in order to enhance the hydrogen storage capacity. This lucidly elevates the abundance of metal nanoparticles, as well as creating more nano cavities in the carbon nanotubes leading to an effective surface enlargement. Transmission electron microscopy, X-Ray diffraction and microprobe as well as the thermal gravimetric analyses support the findings how to alter the size, shape, structure, elemental analysis and the population of nanoparticles dispersed around the carbon nanotubes. The pore size and surface morphology of the nanotubes are inspected based on Brunauer–Emmett–Teller and Barret–Joyner–Halenda analyses. Furthermore, the volumetric method is employed to investigate the hydrogen trapping within the carbon nanotubes of interest. The results attest that more metal nanoparticles are populated around the carbon nanotubes by making use of this hybrid method. The hydrogen content is measured to be 8.6% (2.5%) in nanoparticles decorated multi-wall carbon nanotubes having palladium (nickel) 67% (25.3%) by weight.

Introduction

Porous walls in the molecular dimensions can adsorb large quantities of gases owing to their attractive potentials [1]. In this regard, the carbon nanotubes (CNTs) [2] are known as a good candidate for the hydrogen storage. Many theoretical and experimental attempts were made to validate that CNTs have a high capacity for the adsorption and storage of several gas species such as hydrogen, oxygen, argon and methane [3–5]. Pederson and Broughton suggested that CNTs with few nanometers diameter are able to uptake fluids via capillarity. This effect has been demonstrated for low-surface-tension liquids in large-diameter and multi-wall carbon nanotubes (MWCNTs) too [6,7]. Dillon et al. have discovered that CNTs show a storage capacity of 5–10% by weight at room temperature. The energy of hydrogen absorption in CNT cavities resembles to be higher than graphite [8], since then many workers have reported the hydrogen storage in CNTs [9–14]. The experimental results attest that CNTs can store hydrogen atoms/molecules according to the absorption events and capillary properties. These unique properties make them suitable as super absorbent materials to act as nano reactors [15–17]. Hydrogen storage of 4.2 wt% at room temperature in

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the single wall carbon nanotubes (SWNTs) is achieved by a semi-continuous hydrogen arc-discharge method [18]. Ye et al. asserted that the hydrogen adsorption on crystalline ropes of carbon (SWCNTs) exceeds 8 wt % above 40 bar at 80 K [19]. Chen et al. delineated the adsorption of 14 and 20 wt % of hydrogen via K and Li-decorated CNTs at atmospheric pressure and 200–400 °C respectively [20]. Furthermore, hydrogen intake up to 13 wt % is realized using the aligned MWCNTs [21]. Mortazavi et al. have studied the hydrogen storage properties of MWCNTs, grown via various catalysts, emphasizing the micro pore effect on hydrogen storage [22]. Moreover, the metal and metal oxide nanoparticles (NPs) have attracted much attention [23–29] to enhance the hydrogen storage in the decorated CNTs including various metal NPs such as: Fe, Co, Ca [30], Ni [30–33], Mg [34], Cu [35], Ag [36], Pt [37,38], Li [39,40], Na [41], Pd [42–46], Ti [47] and their metal oxide [48,49]. One of the main setbacks of the CNTs arises from the inaccessibility of internal cavities and the corresponding surface areas due to the blockage of the nanotubes. One makes attempt to increase the absorption events in the internal cavity by opening the head or creating extra cavities in the CNTs walls [50]. The process of purifying and binding metals to MWCNTs leads to improve the hydrogen trapping. In addition, the incomplete structures and micro cavities have been created in CNTs, which strongly affect the hydrogen storage properties [51]. Yoo et al. demonstrated that these structures act as the absorption centers [52]. Recently, we have separately examined a couple of methods based on the pulsed laser ablation in liquid (PLAL) and chemical reduction to synthesize Pd-NPs in order to attach the MWCNTs [53]. Despite Nd:YAG laser at 1064 nm is employed for the laser ablation, however the excimer and CO_2 lasers at UV/FIR wavelengths have previously found diverse applications [54,55]. Here, the volumetric method was employed to assess the hydrogen content based on the pressure change measurement. Furthermore, the decoration of MWCNTs with metal NPs (Pd, Ni) is performed using simultaneous laser ablation and chemical reduction. The aim is to investigate the impact of NPs on the properties of Ni-MWCNTs and Pd-MWCNTs for the purpose of the hydrogen storage enhancement. The hydrogen trapping improves with the amount of metal nanoparticles, as well as the population of nano cavities over MWCNTs surface. Furthermore, transmission electron microscopy (TEM), X-Ray diffraction (XRD) techniques, X-ray microprobe analysis (XPMA) and thermal gravimetric analysis (TGA/DTA) support the findings how to alter the size, shape and the structure of NPs dispersed around MWCNTs samples. The pore size and surface morphology of the nanotubes are inspected based on Brunauer–Emmett–Teller (BET) and Barret–Joyner–Halenda (BJH) analyses. Moreover, the follow-up of hydrogen adsorption/desorption events are well carried out utilizing the volumetric technique.

Experimental

Purification of MWCNTs

The purification process of MWCNTs is similar to Ref [53]. At first, 100 mg of MWCNTs, having 30–50 nm dia and ~20 μm length is heated for 1 h at 400 °C under the oxygen ambient and then is cooled down to the room temperature. Afterwards, 100 mg of the oxidized MWCNTs are floated in 3 M HF (Merck) for 24 h at room temperature. Subsequently, the MWCNTs are immersed in 3 M nitric acid (Merck) at the boiling temperature (~90 °C) for 6 h in the case of reflux. Then, the MWCNTs are rinsed several times with the deionized water. Finally, the purified samples are dried in an oven at 100 °C at the atmospheric pressure for 24 h.

Decoration of MWCNTs

Previously, the metal NPs are attached to MWCNTs using the separate methods i.e. laser ablation and chemical reduction treatments [53]. Here, the synchronous laser ablation and chemical reduction methods contribute to anchor MWCNTs via metal NPs. The decoration is carried out as below: 100 mg of the purified MWCNTs is dispersed in 50 mL of deionized water and sonicated for 15 min. Then, a certain amount of the salt of interest, such as palladium chloride ($PdCl_2$)/nickel chloride ($NiCl_2$) are added to the solution. The suspension is placed on a magnetic stirrer for 60 min. On the other hand, the metal solid target (99.9%, Aldrich) is situated at the bottom of the irradiation chamber, as to 4 mm of suspension covers the whole target surface. A Q-switched Nd:YAG laser is exploited at 1064 nm with 10 ns duration, 5 Hz repetition rate and 50 mJ energy/shot. The laser beam is focused through a quartz lens ($f = 15$ cm) to ~ 1 mm^2 spot size on the target beneath the suspension. A magnetic stirrer is used to homogenize the suspension during the process. The hydrazine solution is slowly added dropwise to the solution, while the laser shot hits the metal target inside the solution. The experiments are carried out for 90 min exposure times under metal chloride medium. Then, the modified MWCNTs will be separated from the suspension using a centrifuge (5000 rpm). Afterwards, MWCNTs are rinsed in the deionized water for several times. Finally, the samples are dried in an oven at ambient condition for 24 h at 100 °C, as shown in Fig. 1.

Hydrogen storage in metal-NPs decorated MWCNTs

The volumetric technique is employed as shown in Fig. 2 to deal with the hydrogen storage measurements [53]. At first, 100 mg of metal-MWCNTs is placed in a steel cylindrical chamber, equipped with a thermocouple, to measure the temperature. The chamber is initially evacuated using a rotary pump down to a base pressure of 10^{-2} mbar. Under this pressure, the metal-MWCNTs (Pd and Ni) are heated up to 300 °C, keeping constant for 1 h. Meanwhile, the undesired gas molecules that may be present within the bulk of the MWCNTs are significantly degased. The chamber pressure remains invariant during the degasing process. Then, the MWCNTs are cooled down to the ambient temperature. Furthermore, the hydrogen gas is injected into the chamber allowing to remain for 8 h, while the pressure chamber is elevated up to 1.5 bar. The ambient temperature is kept ~25 °C at the constant pressure (~1.5 bar) during the storage time. Then, the temperature notably decreases using the liquid nitrogen. Afterwards, the hydrogen remnant is evacuated by reducing the pressure down to 10^{-2} mbar. Finally, the vacuum

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