



Characterization and hydrogen storage in multi-walled carbon nanotubes grown by aerosol-assisted CVD method



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ABSTRACT

The characterization and hydrogen storage capacity of multi-walled carbon nanotubes (MWCNTs) have been studied in the present work. MWCNTs with high purity and bulk yield were achieved from a mixture of camphor/alcohol on a Ni/zeolite support by aerosol-assisted chemical vapor deposition (AACVD). The morphology, surface quality and structure of MWCNTs were characterized by transmission electron microscopy (TEM). Crystallinity and defects of the MWCNTs were studied by Raman spectroscopy and thermo gravimetric analysis (TGA). Hydrogen storage properties of MWCNTs were investigated using a quartz crystal microbalance (QCM). Values between 1.2 and 2.0 wt.% of adsorbed H₂ were reached depending on the exposure pressure. The results also showed that the remaining zeolite present in the as-prepared MWCNT powder adsorbs hydrogen, allowing better adsorption performance of the CNT12 and CNT13 samples. The hydrogen adsorption behavior of CNTs is significantly affected by their structural and morphological characteristics.

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1. Introduction

Carbon nanotubes (CNTs) are among the most interesting materials in current nanotechnological research, due to their low chemical activity, high aspect to ratio, high mechanical strength, and conductivity [1]. There have been extensive reports in recent years to demonstrate the growth of CNTs under different conditions [2–4]. Among CNTs synthesis methods, chemical vapor deposition (CVD) is the most suitable and economic method at low temperatures and ambient pressure when compared with laser, or arc process [5]. However, these methods are associated with a low yield and the formation of many undesired products [5]. On the other hand, aerosol assisted chemical vapor deposition (AACVD) offers more opportunities to obtain larger amounts of CNTs. Using AACVD, various inorganic porous materials were also investigated as support materials by researchers in producing single- and multi-walled CNTs [2,3]. These studies showed that the resulting structure, the morphology and applications are dependent on the experimental conditions [2,3]. The applications for CNTs have enormous potentials such as novel nanoscale electronic devices, electron field emitters, energy storage and energy conversion devices, sensors, and lithium ion

batteries [4–7]. Recently, attention has focused on carbon-based materials due to the usage of CNTs as a safe hydrogen storage medium [5,8–11]. To date, many studies have revealed that hydrogen storage capacity is enhanced by added metals to carbon structures, such as Fe, Ni, Co, Cu, Au, Ag, Pt, Ca, Li, K, Al and Pd [3,5,12–14] or by using CNT-based composites [15–17]; however, the properties of hydrogen storage in these materials is still being researched at a basic level. Actually, the reproducibility of the reported hydrogen storage capacity of CNTs is poor, and the mechanism of how hydrogen is stored in CNTs remains unclear [8]. Liu et al. pointed out that certain amount of hydrogen (less than 1.7 wt.% under a pressure of ~12 MPa and at room temperature) can be stored in CNTs [8], which indicate that CNTs cannot fulfill the benchmark of 6.5 wt.% set by the U.S. Department of Energy (DOE) for hydrogen storage systems [8,13,18]. Recently, very low values of hydrogen storage capacity of CNTs started to emerge, in particular, those experimentally obtained at room temperature. The reproducibility of the reported high hydrogen capacity of CNTs is poor, and the mechanism of how the hydrogen is stored in CNTs remains unclear [8]. However, experimental studies on hydrogen storage of CNTs and CNT-based hybrid structures, as well as, the hydrogen adsorption mechanism and hydrogen adsorption sites are studied [5,13].

In the present work, synthesis of MWCNTs has been obtained in an AACVD process under nitrogen and argon flow, and their hydrogen adsorption capacity at room temperature under different loading pressures were studied. Zeolite is investigated as a suitable support for

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growing CNTs and storing hydrogen, allowing better adsorption performance in between carbon nanotubes. Transmission electron microscopy (TEM), thermal gravimetric analysis (TGA) and Raman spectroscopy were used to evaluate the structure, grade of graphitization and quality characteristics of MWCNTs.

2. Experimental details

2.1. Preparation of MWCNT

MWCNTs were synthesized using an aerosol-assisted CVD method. Approximately 2.0 g of camphor, mixed with 10 mL of isopropyl alcohol were placed in an ultrasonic nebulizer. Pure nitrogen (N₂) and argon (Ar) gas were used to transport the precursor mist generated in the atomization chamber to a horizontal quartz tube (length: 50 cm, diameter: 3.0 cm) inserted in a furnace. For CNT12 and CNT13 samples, nickel particles were used as catalyst impregnated in zeolite (molecular sieve: alkalimetal aluminum silicate/calcium, Chromatograph grade, linde/Coast engineering laboratory/Redondo Beach CA-USA). While for CNT11, only nickel particles were employed, as shown in Table 1. The mist (camphor mixed with alcohol) was pyrolyzed over catalyst-impregnated zeolite at 800 °C under a flow of 1 L/min for 20 min. When the system was cooled naturally to room temperature (RT), the blackened zeolite was collected for characterization.

2.2. Sample characterization

Structural characterization was done with a high-resolution transmission electron microscope (HRTEM, Tecnai F20 FEG-S/TEM) operated at 200 kV. TEM samples were ultrasonically dispersed in isopropyl alcohol and then collected in an ultrathin holey carbon-coated Cu grid. Thermogravimetric analysis (TGA) of blackened zeolite was performed with a TA Instruments, TGA Q50, under nitrogen gas and heated from room temperature (RT) to 800 °C with the heating rate of 10 °C/min. Micro-Raman spectra were recorded at RT on a LabRam 010 from ISA using a He–Ne laser with wavelength of 632.8 nm at 5.5 mW. The Raman system uses a backscattering geometry, where the incident beam is linearly polarized and the spectral detection unpolarized. The objective lens of the microscope was an Olympus Mplan10× (numerical aperture 0.9).

As-prepared MWCNT powders grown by aerosol-assisted CVD were deposited at RT on top-face of a microbalance quartz crystal (QC) used as support-substrate. The powder was dispersed in isopropyl alcohol using an ultrasonic bath for 7 min. The suspension formed was deposited using a dropper onto the QC and then dried to room air at RT. Then, the QC was located in the head of a quartz crystal microbalance system (from MDC model SQM-310) placed inside a vacuum chamber. The chamber was pumped down to 7×10^{-6} Torr using turbo and rotatory pumps. A gate valve placed between the chamber and the turbo pump to isolate the chamber from the vacuum, allowed pressurizing with hydrogen gas injecting it through a needle valve. The mass changes upon hydrogen adsorption were determined by in-situ monitoring of the changes in the resonance frequency of the QC as function of time while the sample was exposed to hydrogen for 8 min. After H₂ exposure, the chamber was again pumped down to 7×10^{-6} Torr, the process was repeated by injecting hydrogen until reaching a higher pressure. Increasing pressures between 3 and 45 Torr (measured with a capacitive gauge, Baratron from MKS instruments) were used in the different

hydrogenation cycles for studying the pressure effect on the hydrogen storage behavior at RT of the MWCNTs.

The relationship between the mass added to the QC due to the H₂ adsorption by the CNTs and the shift in its resonance frequency, Δf , is represented by the Sauerbrey's equation [19–21]:

$$\Delta f = -\frac{2f^2}{A\sqrt{\rho} \times \mu} \Delta m$$

where f is the QC resonant frequency, ρ is the density, μ is the shear modulus of the QC and A is the area covered by the mass. This equation indicates that a negative variation of the resonance frequency is due to a mass gain. Details about the use of this equation and method for the determination of mass gained by a QC can be found in [22] where a study of hydrogen absorption in films and Pd clusters using a microbalance quartz crystal system was reported.

3. Results and discussion

Apart from the first studies on the synthesis of CNTs, there are plenty of reports using thermal decomposition of many hydrocarbons on zeolites (such as Y-type high-silica zeolite (HSZ-390HUA), or aluminophosphate crystals (AFI)) as mesoporous substrates or support [2]. However, it is difficult to compare the present results with those reported, because the CVD method presents more sensitive parameters and conditions (temperature, flow, gas carrier) on CNTs production. However, from the viewpoint of the present research, the results obtained using camphor/alcohol as precursor material, are comparable with other results in the production of CNTs on a large scale. Most precursors used for the synthesis of CNTs are derived from hydrocarbons such as methane, ethane, acetylene, benzene, ethanol, as well as some alkyl chains (C₁₂ and C₁₆ alkanes) [23] which have been used as carbon sources of CNT synthesis. However, these precursors do not exhibit a high performance in the synthesis of CNTs.

Comparing camphor (C₆H₁₆O) with the most commonly used CNT precursors, Kumar et al. [2,3] reported mass production of CNTs from camphor using CVD, and established the growth condition of MWCNTs and SWCNTs using Fe–Co catalyst impregnated in zeolite support. MWCNTs were grown at a temperatures as low 550 °C, whereas SWCNTs were grown at 900 °C. These studies confirm that SWCNTs or MWCNTs can be selectively grown by proper selection of catalyst materials and their concentration [3].

Based on the above, it was found that for the synthesis of CNTs using a mixture of camphor/alcohol, the performance is dependent on the catalyst materials, gas carrier, and support used. TEM micrographs of the MWCNTs are shown in Figs. 1 and 2. Fully growth of MWCNTs was obtained when N₂ was used as gas carrier (Fig. 1). Fig. 2 shows TEM images of MWCNTs made by AACVD using argon as gas carrier. These images clearly reveal that the formed products are nanotubes with average diameters of 20 nm and 200 nm for CNT12 and CNT13, respectively. As shown in Fig. 1(a–d), Ni particles were attached on the tips of the CNTs, indicating the formation of graphene shells around the Ni particles and the continuous movements of the Ni particles produced the CNTs. While in Fig. 2(a–d), the CNTs presented chain structures when they were synthesized with argon. Ni-filled CNTs and their chain structures were formed, as shown in Fig. 2(a). Some defects are observed on the graphitic layers. Furthermore, most of the outer surface of the tube

Table 1
Experimental condition, intensity ratio of Raman spectra and hydrogen storage capacity of MWCNTs.

Sample	Catalyst	Support	Carrier gas	Intensity ratio (I _D /I _G)	Intensity ratio (I _C /I _G)	H ₂ storage capacity (wt.%)
CNT11	Ni	–	N ₂	1.02	0.50	1.5
CNT12	Ni	Zeolite	N ₂	0.77	0.82	1.7
CNT13	Ni	Zeolite	Ar	0.63	0.84	2.1

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