Hydrogen storage in aligned carbon nanotubes

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Aligned carbon nanotubes (CNTs) with diameters of 50–100 nm, synthesized by plasma-assisted hot filament chemical vapor deposition, were employed for hydrogen adsorption experiments in their as-prepared and pretreated states. Quadruple mass spectroscopy and thermogravimetric analysis show a hydrogen storage capacity of 5–7 wt% was achieved reproducibly at room temperature under modest pressure (10 atm) for the as-prepared samples. Pretreatments, which include heating the samples to 300 °C and removing of the catalyst tips, can increase the hydrogen storage capacity up to 13 wt% and decrease the pressure required for storage. The weight gains were measured after the samples moved out of the hydrogen environment. The release of the adsorbed hydrogen can be achieved by heating the samples up to 300 °C. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1341224]

Recently, the use of carbon nanotubes for hydrogen storage has attracted more and more attention because of their high storage capability and potential application in the next generation energy source. Different types of nanotubes (single and multi-wall), as well as nanofibers, have been studied for this purpose. In the experimental reports published, high hydrogen pressure (up to 100 atm),[1,2] subambient temperature[3,4] and alkali-metal doping[5] are applied to achieve hydrogen adsorption. In this letter, we introduce a simple hydrogen storage method for carbon nanotubes (CNTs) at room temperature under moderate pressure (2–10 atm.). Different pretreatments of the CNTs have been adopted to increase the H_2 uptake capability to 13 wt%. Quadruple mass spectroscopy (QMS) and thermogravimetic analysis (TGA) were used to study H_2 desorption properties.

The synthesis of aligned CNTs by plasma-assisted hot filament chemical vapor deposition has been reported previously.[6,7] In this study, thin stainless steel wafers (0.1 mm in thickness), 10×10 mm in size were used as substrates to grow uniformly distributed CNTs. Usually, the weight gain of one substrate was around 1 mg with an average CNT length of 10 μm, which can be obtained after a 20 min growth under nitrogen and 3 vol % methane. The synthesized CNTs were then moved to a stainless steel vacuum system for H_2 storage experiments. This system is connected to a mechanical and turbo pump, with a base vacuum of 1×10^{-6} Torr, and is equipped with a QMS. The H_2 uptake experiment was carried out as the following: after the system was pumped to 1×10^{-6} Torr, the valves connected to the pumps were closed and high purified H_2 (99.999%) was let into the chamber until the desired pressure (2–10 atm.) was reached. The substrate was installed on a substrate holder that could be heated up to 500 °C. The hydrogen pressure was usually maintained for 2 h. Then the sample was moved to a microbalance (accuracy of 0.01 mg) at atmospheric pressure to measure the weight variation. The samples can be analyzed by QMS or moved to the TGA (Perkin-Elmer 7 series system), which analyzes weight change against heat treatment. Highly purified nitrogen (99.999%) was used as the purging gas in TGA. The purging lasted for 2 h, and then the temperature was increased from room temperature to 300 °C linearly at a rate of 5 °C/min.

Figure 1(a) shows a scanning electron microscopy (SEM, Hitachi S-4000) picture of the CNTs synthesized on stainless steel substrate. Aligned CNTs with diameters of 50–100 nm and densities of 10^8–10^9/mm^2 have been obtained. A catalyst particle decorates at the growth end of each tube. The distribution of CNTs on the substrate surface is very uniform, in contrast to the bundle-like growth of CNTs on nickel substrate.[7] Transmission electron microscopy (TEM, JEOL 2100) observation of the tube [Fig. 1(b)] indicates that graphite layers are open ended on the body of the tube.

All of our hydrogen adsorption experiments were performed at room temperature. Hydrogen pressure (2 atm) was used at first for the synthesized CNTs without any treatment. There was no obvious weight gain observed even after 24 h storage. When 10 atm H_2 pressure was applied, the three samples we measured, showed 5.7, 6.6, and 6.7 wt% gain, respectively, after 2 h adsorption.

A heating pretreatment of the sample was used to identify its effect on hydrogen storage. After the synthesized

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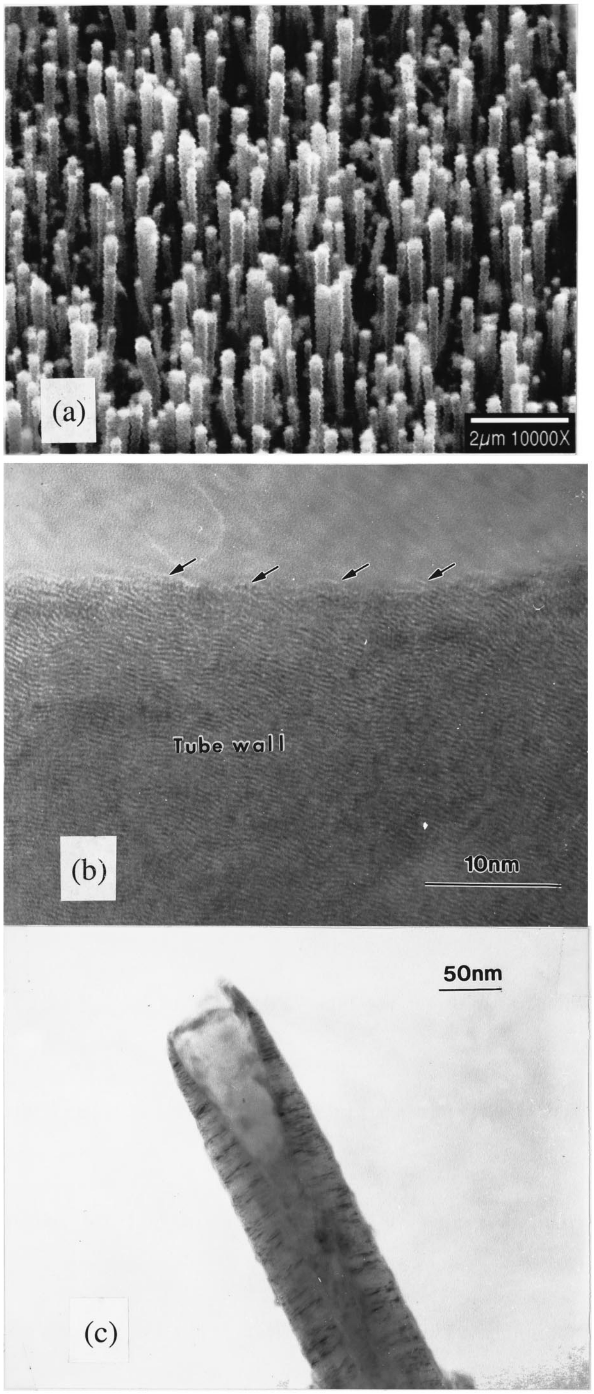

FIG. 1. (a) SEM picture of the CNTs synthesized by plasma-assisted CVD; (b) TEM picture of the tube wall structure, which indicates that there are open-ended layers; (c) catalyst removed CNTs.

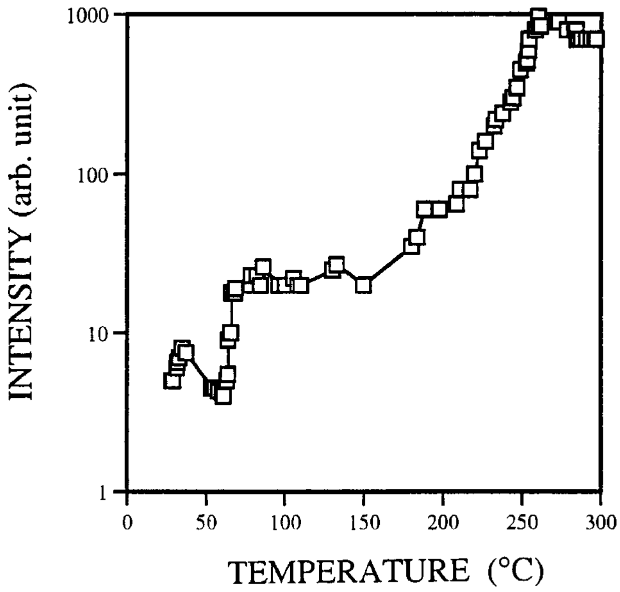

FIG. 2. QMS measurement of the released hydrogen intensity during the heating process under 1×10^{-6} Torr.

CNTs were installed in the storage chamber and pumped to 1×10^{-6} Torr, they were heated to 300 °C for 2 h and then cooled down to room temperature. The hydrogen was then let into the chamber and maintained at 2 atm. A weight gain of 4.7%, 6.8%, and 7.8% was obtained, respectively, for the three samples after 2 h adsorption.

For the catalyst-capped nanotubes, the hydrogen is expected to be stored between the graphite layers with a layer distance of 0.34 nm. The open-ended layers observed by TEM [Fig. 1(b)] would contribute to this. If the catalyst can be removed, more hydrogen would be expected to be stored in the hollow center of the tubes, which is the storage mechanism for the single-wall CNTs.[2,3] The synthesized CNTs were immersed in 69.5% nitric acid (HNO_3) for 3 min to eliminate the catalyst particles decorated on the growth end of the tubes and then rinsed in distilled water for 24 h. TEM observation [Fig. 1(c)] of the treated samples shows that most of the particles were removed. The treated samples were then baked at 300 °C for 4 h under 1×10^{-6} Torr to remove the adsorbed water moisture on the CNTs surface. The four catalyst-free samples present a H_2 uptake of 8.8, 9.1, 9.4, and 13.8 wt%, respectively, at room temperature under 10 atm. This is higher than the above mentioned results and indicates that the central hole can contribute to the hydrogen storage for the multi-wall CNTs.

QMS was first used to identify the hydrogen release during the heating process. After the hydrogen storage experiment was performed, the system was pumped to 1×10^{-6} Torr, and the valve connected to the QMS system was then opened. The sample was heated to 300 °C at a rate of 5 °C/min, and intensities of the released gases were measured during this process. Figure 2 shows a QMS result of the hydrogen release. An intensive increase of hydrogen intensity has been obtained during the heating process. Meanwhile, the intensities of oxygen, nitrogen and water were not observed to have such a big variation. This result strongly supports that the released gas was hydrogen.

The more quantitative measurement was performed by TGA. Figure 3(a) is the result of an as-prepared carbon nanotube sample without hydrogen uptake. There is no apparent weight loss during the heating process to 300 °C. Figure 3(b) shows the sample with hydrogen storage at room temperature under 10 atm for 2 h (a weight gain of 0.06 mg, with a weight percent of 6.5). An apparent weight decrease occurred at 120 °C and the weight kept decreasing during the following heat treatment. There is no more weight loss after 250 °C and the total weight loss coincides very well with the weight gain of hydrogen adsorbed (i.e., the weight gain has disappeared). Figure 3(c) gives a result of the sample with the catalyst tips free. The result was similar to that with

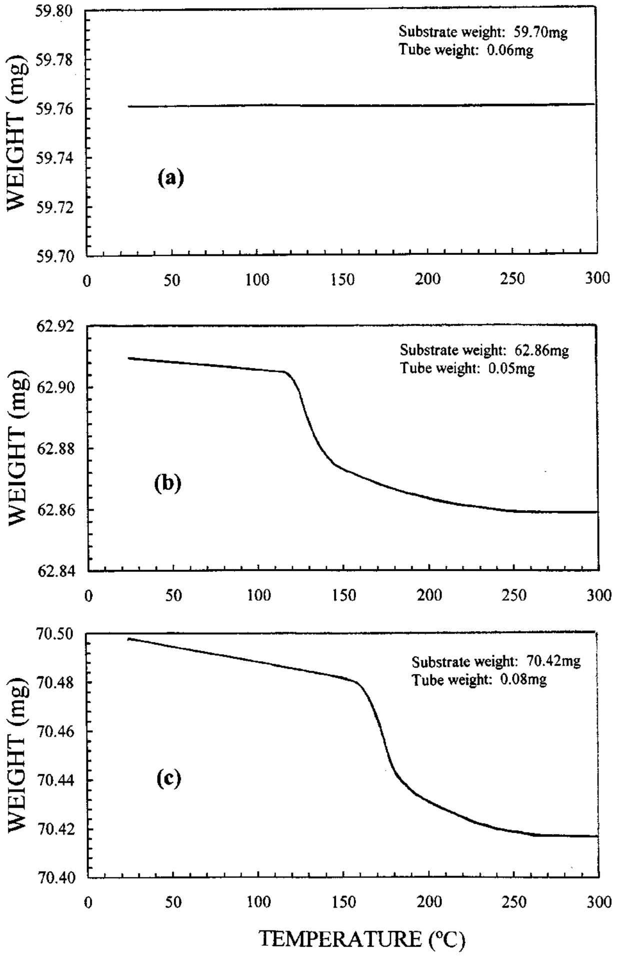

FIG. 3. TGA spectra of the hydrogen release: (a) as-prepared sample without hydrogen uptake; (b) as-prepared sample stored at room temperature under 2 atm hydrogen; (c) catalyst-free samples stored at room temperature under 10 atm.

spectrum (b), but the obvious weight loss occurred at 160 °C.

The QMS and TGA results indicate that the hydrogen has been adsorbed by carbon nanotubes and can be released during heating treatment above room temperature. Compared with other results of the multi-wall nanotubes,[2,5] we did not use high pressure and alkali-metal doping to achieve the high hydrogen uptake. The reason may be attributed to the structure of our nanotubes (open end of the layers on the body) and their alignment. What should be mentioned is that the weight gain measured in our experiment was the portion remaining inside the nanotubes after they were moved out of the hydrogen environment. According to the results obtained by Chambers *et al.*[1] and Liu *et al.*,[2] a major fraction of the stored hydrogen (up to 80%) was released after the lowering of the pressure to nearly atomospheric conditions. Therefore, we can speculate that the actual hydrogen uptake capability in the hydrogen environment will be higher than what we measured.

The structure of our synthesized CNTs is different from the ideal CNTs with concentric cylinder structure. They are similar to that reported by Chambers *et al.*,[1] which is cone shaped, but with a very small cone angle [less than 5°, which can be seen from Fig. 1(b)]. The open-ended graphite sheets can be expected as the major channel for the hydrogen encapsulated when the growth end is decorated by catalyst particle. The catalyst-free CNTs do show their higher storage capability in our experiments. The alignment and straight growth of CNTs are important to maintain this structure for the whole tube with less stress and deformation, as well as the high efficiency adsorption due to the higher exposure surface area of the CNTs. The high purity of the CNTs is also important, which can be identified from the effect of heating treatment in our experiments.

A high hydrogen uptake has been obtained in aligned multi-wall nanotubes. This is a simple, effective and easily controlled process. The synthesis of CNTs on alloy wafers containing catalysts (Fe, Co, and Ni) by plasma-assisted CVD has great potential for large-area growth and continuous production for industry applications. Meanwhile, the quality and quantity of the CNTs are more controllable.

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