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Bulk Storage Capacity of Hydrogen in Purified Multiwalled Carbon Nanotubes

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The as-prepared and purified multiwalled carbon nanotubes (MWNTs) with a mean outer diameter of 5.1 nm were employed for hydrogen storage measurements. Compared with the as-prepared sample, the purified one has a much higher gravimetric hydrogen storage capacity. Then the purified MWNTs were cold-compacted into a cylinder for volumetric hydrogen storage measurements. The gravimetric and volumetric hydrogen storage capacities of the bulk sample reach 6.3 wt % and 31.6 kg/m^3 at room temperature under an equilibrium pressure of 14.8 MPa, respectively. In addition, the microstructure including surface structure and pore texture of MWNTs were investigated by electron transmission microscopy, high-resolution electron transmission microscopy, cryogenic nitrogen adsorption, and X-ray photoelectron spectroscopy. It is considered that the structural modification may be determinant for the improvement of the hydrogen storage capacity of MWNTs.

1. Introduction

The ever-growing demand for energy and rising concern of environmental pollution caused by the use of conventional fossil fuels, call for new and clean fuels. Among all kinds of energy sources, hydrogen is the best choice as a clean fuel. The advantages of hydrogen as energy sources lie in the fact that its byproduct is water, and it can be easily regenerated. Unfortunately, owing to the lack of a suitable storage system satisfying a combination of both volume and weight limitations, the use of hydrogen energy technology has been restricted from automobile application. Therefore, to implement hydrogen energy for electrical vehicles, the first step is to look for an economical and safe hydrogen-storage medium. Recent reports on very high and reversible adsorption of hydrogen in nano-structured carbon materials such as carbon nanotubes,[1−3] graphite nanofibers,[4,5] and alkali-doped nanotubes[6] have stimu-lated many experimental works[7−11] and theoretical calcula-tions[12,13] worldwide. Experimental results demonstrate that nanostructured carbon materials have relatively high gravimetric hydrogen storage capacity; however, owing to the low apparent density of carbon nanotubes and nanofibers, one doubts whether their volumetric hydrogen storage capacity could meet the volumetric target value of the U.S. Department of Energy's (DOE) hydrogen plan,[14] which requires a system-volume efficiency (the ratio of stored hydrogen to system volume) of 63 kg H$_2$/m^3 for a practical hydrogen fuel cell-driven vehicle.

In this study, multiwalled carbon nanotubes (MWNTs) with a mean outer diameter of 5.1 nm were synthesized using the floating catalyst method,[15] and were purified with a multistep procedure.[16] The purified MWNTs were cold pressed into a cylinder, and then the cylinder was subjected to hydrogen adsorption measurements. Moreover, the relationship between the pore structure and hydrogen storage capacity of the MWNTs was also preliminarily discussed.

2. Experimental Section

2.1. Preparation of MWNTs. Multiwalled carbon nanotubes were synthesized by catalytic decomposition of hydrocarbons using a floating catalyst method with a horizontal reaction chamber.[15] Benzene was used as carbon source and ferrocene as catalyst precursor. The carrier gas was hydrogen and it flowed into the reaction chamber with the carbon source and catalyst precursor. The synthesis of MWNTs was performed in the temperature range of 1050−1150 °C, and for 45 min. The diameter distribution of the MWNTs obtained from typical TEM images is shown in Figure 1. According to Figure 1, the ratio of the MWNTs with outer diameters of 4−7 nm is greater than 70%, and the Gaussian fit of the diameter distribution indicates that the mean diameter of the MWNTs is 5.1 nm.

2.2. Purification of MWNTs. The as-prepared MWNTs were purified by a procedure that was reported elsewhere.[16] The procedure for purifying the MWNTs briefly includes: (a) about 1 g of the raw material was introduced into a flask and ultrasonicated in 250 mL of deionized water for 30 min. (b) The mixture was stirred with a magnetic stirrer for 30 min and heated at 100 °C for 12 h, to break the network between MWNTs, amorphous carbon, and the metal particles (Fe). (c) After the sample was filtered and dried at 100 °C, the residual soot was bromined in bromine water at 90 °C for 30 min and dried. (d) The sample was then heated in air at 500 °C for 45 min. (e) The black product obtained was treated in hydrochloric acid to remove the catalyst particles at room temperature. (f) Finally, the purified sample was washed with deionized water and dried. Some of the purified sample was cold pressed into a cylinder at a forming pressure of 60 MPa, and the density of the bulk sample was 0.47 g/cm^3. Owing to many oxygen functional groups were generated on the surface of MWNTs in the process of purification, which would strongly chemisorb water and oxygen molecules and subsequently prevent hydrogen from accessing the internal structure,[17] the sample was therefore heated at 1000 °C in argon atmosphere before hydrogen storage experiments.

2.3. Hydrogen Storage Measurements. Hydrogen adsorption studies were performed in a custom-built unit[3] consisting of a copper sample cell, and a hydrogen reservoir connected with a high-pressure valve. Prior to the hydrogen storage, experiments were conducted to make sure that the system was leak free.
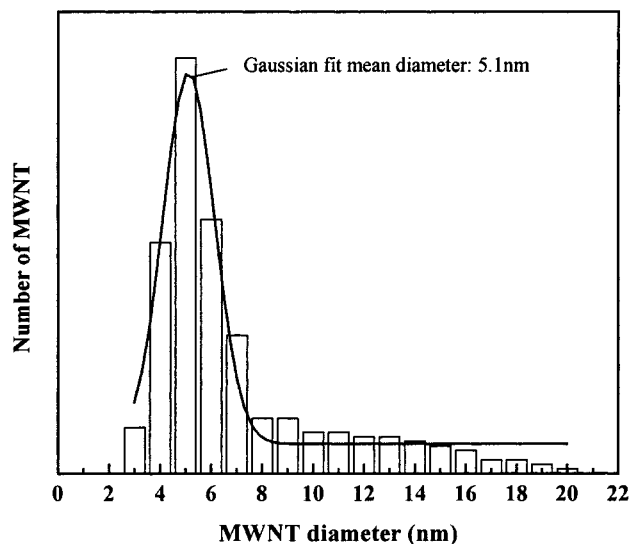

Figure 1. Diameter distribution of the MWNTs using data obtained from TEM images.

Calibration of the unit was conducted as follows: the empty copper cell was evacuated to about 10^{-2} Torr at the temperature of 300 °C for 3 h. When the copper cell was cooled to room temperature (keeping constant at 23 °C), high-purity hydrogen (99.999%) at a pressure of 14.9 MPa was introduced via a hydrogen purifier into the copper cell. The pressure would decrease to an equilibrium pressure, and keep constant for 12 h. And the difference between the start pressure and equilibrium pressure was taken as P_1. After the calibration, the pretreated bulk MWNT sample was introduced into the copper sample cell, and then followed the above procedure. The drop of the system pressure from an initial value was measured (P_2). The gravimetric and volumetric capacities of hydrogen stored in the MWNTs were calculated according to the difference between P_2 and P_1, taking into account of the compressibility factor of hydrogen at the working pressure.

For comparison, the as-prepared MWNTs, purified but unshaped MWNTs, LaNi$_5$, and NdNi$_5$ were used for hydrogen storage measurements with the same method.

2.4. Characterization of MWNTs. Characterization of the MWNTs in the as-prepared and purified state was conducted. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) were used to identify and characterize the morphology of the product obtained. TEM specimens were prepared by sonicating the product in alcohol, then dipping a TEM sample grid into the dispersion. To check the chemical modification, the as-prepared and purified samples were analyzed by X-ray photoelectron spectroscopy (XPS). Nitrogen adsorption isotherms of the MWNT samples were measured at 77.5 K by an ASAP 2010 volumetric sorption analyzer with an additional option for micropore analysis. The volume of adsorbed nitrogen at 77.5 K was measured as a function of the equilibrium pressure over a range from 10^{-5} Torr to the saturation vapor pressure. Prior to the adsorption measurements, the samples were outgassed under vacuum at 573 K for 3 h. The pore size distributions (PSD) of the samples were obtained by analyzing the isotherm with BJH equation.

3. Results and Discussion

Hydrogen storage capacities of various kinds of MWNTs as well as LaNi$_5$ and NdNi$_5$ were summarized in Table 1. The hydrogen storage capacities of LaNi$_5$ and NdNi$_5$ are 1.4 wt %

at the equilibrium pressure of 12.4 and 14.6 MPa, respectively. The adsorption capacity of NdNi$_5$ is consistent with that reported by Lundin et al.,[18] which indicates that our experimental system and method are reliable. It can be seen that the gravimetric hydrogen storage capacity of the purified MWNTs is much higher than that of the as-prepared one, which implies that the purification process is very important for the hydrogen storage performance of our materials. Figure 2 shows the bulk MWNTs cylinder that was compressed under a pressure of 60 MPa in a stainless steel die without any binder. We can see that the purified MWNTs used in the present work possess a quite good forming ability. It is worthy to note that compaction under high-pressure exerts little effect on the hydrogen storage capacity of the MWNTs, and the bulk one shows a similar gravimetric hydrogen storage capacity (6.3 wt %) to that of the unshaped purified MWNTs (6.5 wt %). As the apparent density of the bulk MWNT cylinder was 0.47 g/cm³, the volumetric hydrogen storage density was calculated to be 31.6 kg/m³, which is close to 50% of the goal (63 kg/m³) of the DOE Hydrogen Plan. If the apparent density of the bulk MWNT cylinder increased to 0.8−1 g/cm³, its volumetric hydrogen storage density would come close to the goal of the DOE Hydrogen Plan.

The experimental results show that the hydrogen storage capacity of the purified carbon nanotubes was greatly improved compared with that of the as-prepared counterpart. We consider that this improvement could be largely accounted for the removal of the impurities, oxygen-containing functionalities, and adsorbed species in the MWNTs.

TEM images of the as-prepared and the purified MWNTs were shown in Figure 3. The as-prepared one (as shown in Figure 3a) contains not only numerous nanotubes, but also a considerable amount of iron particles, amorphous carbon and multishell carbon nanocapsules. About 50 wt % impurities coexist with MWNTs according to the TEM observations and thermogravimetric experimental results. Figure 3b presents the typical TEM image of the purified MWNTs. There is little trace of amorphous carbon, multishell carbon nanocapsules and metal particles in the purified sample. Furthermore, many caps at the tips of the purified MWNTs were disconnected and the ends were opened, and most of the catalyst particles that were embedded in the tips of the MWNTs were also removed. Figure 4 presents a typical HRTEM image of a purified nanotube, and we can observe that graphite layers are not perfect, but full of defects.
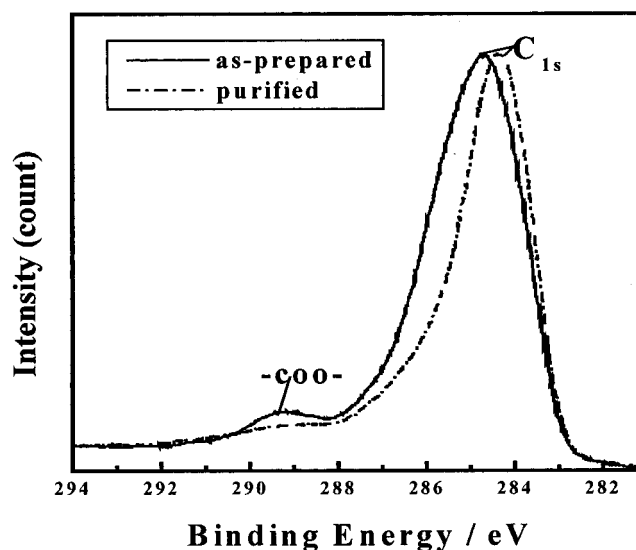
Assuming that the amorphous carbon, carbon nanospheres and the iron particles have no ability of storing hydrogen in the as-prepared sample, the calculated hydrogen storage capacity for 100% MWNTs from the measured capacity (2.0 wt%) of the as-prepared sample with a purity of about 50 wt % would be only 4 wt %, which is yet much lower than the measured capacity (6.5 wt %) of the purified one. Therefore the increase of hydrogen storage capacity of the purified MWNTs may be attributed to purification, the opening-up of the ends, and the exposure of more surfaces of the MWNTs. By opening the ends of MWNTs, the hydrogen could more easily enter into the hollow core of the MWNTs. The discontinuous layers rather than ideal structure as observed by HRTEM (shown in Figure 4) would act as adsorption centers and provide the access for hydrogen to be stored between the graphite layers. Due to the removal of the amorphous carbon and carbon nanospheres adhered on the surface of the MWNTs, larger outer surface area of MWNTs was exposed to hydrogen, which is also partly responsible for the improvement of hydrogen adsorption.

Capacity of Hydrogen in Carbon Nanotubes

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TABLE 1: Hydrogen Storage Capacity of Various Samples

sample type	sample weight (g)	equilibrium pressure (MPa)	gravimetric hydrogen storage capacity (wt %)	volumetric hydrogen storage capacity (kg/m^3)
as-prepared MWNTs	0.7281	14.1	2.0	
purified MWNTs	0.2580	14.5	6.5	/
purified and formed MWNT cylinder	0.2394	14.8	6.3	31.6
LaNi$_5$	1.1761	12.4	1.4	
NdNi$_5$	1.0241	14.6	1.4	/
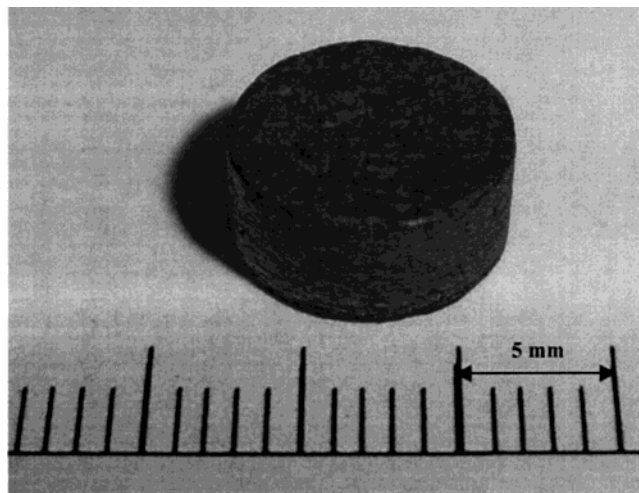
Figure 2. Photo of the bulk MWNTs compacted under a pressure of 60 MPa without binder.
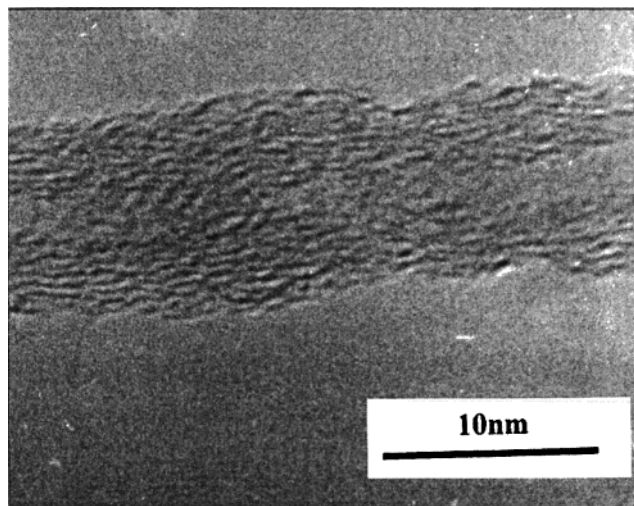
Figure 4. HRTEM image of the purified MWNT, indicating the outer graphite layers are not perfect, but full of defects.
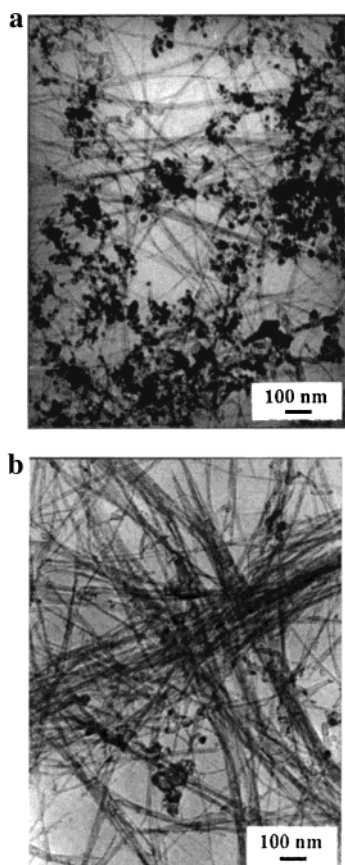
Figure 3. TEM images of (a) the as-synthesized MWNTs and (b) the purified MWNTs.

Figure 5. C$_{1s}$ photoelectron spectra of the as-prepared MWNTs (solid curve) and the purified MWNTs (dashed curve).

XPS spectra of C$_{1s}$ of the as-prepared and purified samples around 284.5 eV are shown in Figure 5. The as-prepared sample has a relatively wide C$_{1s}$ peak, and a clear peak observed in the range of high electron binding energy (289.0−289.4 eV), which is associated with carboxyl carbon. The purified sample has much narrower C$_{1s}$ peak around 284.4 eV and no notable peak in the range of high electron binding energy, which reveals that the sample is in a simpler chemical state. We consider that this simple chemical state of C and lower oxygen-contained groups correspond to the higher hydrogen storage capacity of the purified carbon nanotubes. There are two possible reasons that could explain the above results. One is the elimination of impurities (having no ability of storage hydrogen) contributing to more complicated chemical states and wider C$_{1s}$ peak. The other is the removal of oxygen-containing functional groups from the surface of MWNTs and the liberation of carbon surface for hydrogen adsorption during the purification process.
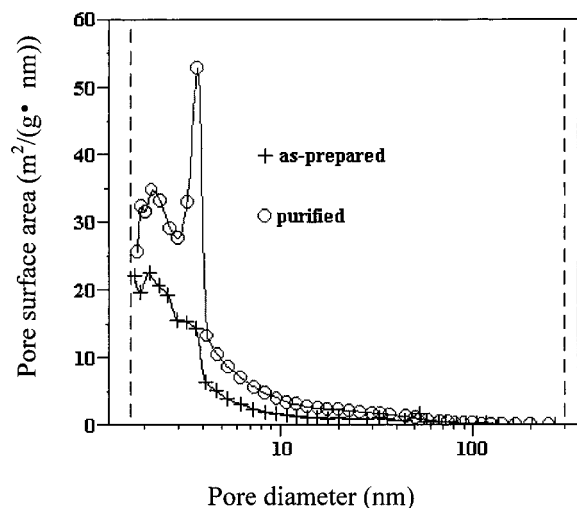
Figure 6. Pore size distribution of MWNTs in the as-prepared and the purified states before hydrogen storage.

The pore size distribution curves of the as-prepared and purified carbon nanotubes are shown in Figure 6. Both samples show two similar major peaks around 1.5–2.0 and 2.5–3.0 nm, corresponding to the innercavity diameter obtained by the TEM image. It should be noted that the two peaks for the purified sample is much stronger than those of the as-prepared one, indicating a significant increase of the pore volume and gives a proof of the removal of the tips of MWNTs during the purification process. There is no doubt that the increase of pore volume and the opening of MWNT tips provide more access for hydrogen adsorption in the carbon nanotubes, resulting in a great improvement of the hydrogen storage capacity of the purified MWNTs.

4. Conclusions

The volumetric and gravimetric hydrogen storage capacities of the as-prepared and the purified MWNTs were investigated. It was found that the purified MWNTs with mean outer diameter of 5.1 nm can be compressed into a bulk form without any binder and the compaction under high-pressure exerts little effect on their gravimetric hydrogen storage capacity. The experi-

mental results show that the purified MWNTs had opened tips, simpler chemical state, larger micropore volume and then much higher hydrogen storage capacity than the as-prepared MWNT product. The volumetric and gravimetric hydrogen storage capacities of the formed purified MWNTs bulk were 6.3 wt % and 31.6 kg/m^3, respectively. Furthermore, the microstructural and surface characterizations reveal that pore structure and surface modification are important for the improvement of hydrogen uptake capacity of MWNTs.

References and Notes

(1) Dillon, A. C.; Jones, K. M.; Bekkedahl, T. A.; Kiang, C. H.; Bethyne, D. S.; Heben, M. J. *Nature* **1997**, *386*, 377.
(2) Ye, Y.; Ahn, C. C.; Witham, C.; Fultz, B.; Liu, J.; Rinzzler, A. G.; Colbert, D.; Smith, K. A.; Smalley, R. E. *Appl. Phys. Lett.* **1999**, *74*, 237.
(3) Liu, C.; Fan, Y. Y.; Liu, M.; Cong, H. T.; Cheng, H. M.; Dresselhaus, M. S. *Science* **1999**, *286,* 1127.
(4) Chambers, A.; Park, C.; Baker, R. T. K.; Rodriguez, N. M. *J. Phys. Chem. B* **1998**, *102*, 4253.
(5) Fan, Y. Y.; Liao, B.; Liu, M.; Wei, Y. L.; Lu, M. Q.; Cheng, H. M. *Carbon* **1999**, *37*, 1649.
(6) Chen, P.; Wu, X.; Lin, J.; Tan, K. L. *Science* **1999**, *285*, 91.
(7) Ahn, C. C.; Ye, Y.; Ratnakumar, B. V.; Witham, C.; Bowean, R. C.; Fult, J. B. *Appl. Phys. Lett.* **1998**, *73*, 3378.
(8) Strobel, R.; Jorissen, L.; Schliermann, T.; Trapp, V.; Schutz, W.; Bohmhammel, K.; Wolf, G.; Garche, J. *J. Power Sources* **1999**, *84*, 221.
(9) Ye, Y.; Ahn, C. C.; Witham, C.; Fultz, B.; Liu, J.; Rinzler, A. G.; Colbert, D.; Smith, K. A.; Smalley, R. E. *Appl. Phys. Lett.* **1999**, *74*, 2307.
(10) Lee, S. M.; Park, K. S.; Choi, Y. C.; Park, Y. S.; Bok, J. M.; Bae, D. J.; Nahm, K. S.; Choi, Y. G.; Yu, S. C.; Kim, N. G.; Frauenheim, T.; Lee, Y. H. *Synth. Met.* **2000**, *113*, 209.
(11) Zhu, H. W.; Chen, A.; Mao, Z. Q.; Xu, C. L.; Xiao, X.; Wei, B. Q.; Liang, J.; Wu, D. H. *J. Mater. Sci. Lett.* **2000**, *19*, 1237.
(12) Darkrim, F.; Levesque, D. *J. Chem. Phys.* **1999**, *109*, 4981.
(13) Lee, S. M.; Lee, Y. H. *Appl. Phys. Lett.* **2000**, *76*, 2877.
(14) Hynek, S.; Fuller, W.; Bentley, J. *Int. J. Hydrogen Energy* **1997**, *22*, 601.
(15) Fan, Y. Y.; Li, F.; Cheng, H. M.; Su. G.; Yu, Y. D.; Shen, Z. H. *J. Mater. Res.* **1998**, *13*, 2342.
(16) Hou, P. X.; Bai, S.; Yang, Q. H.; Liu, C.; Cheng, H. M. *Carbon* Accepted for publication.
(17) Park, C.; Anderson, P. E.; Chambers, A.; Tan, C. D.; Hidalgo, R.; Rodriguez, N. M. *J. Phys. Chem. B* **1999**, *103*, 10572.
(18) Lundin, C. E.; Lynch, F. E.; Magee, C. B. *J. Less-Common Met.* **1977**, *56*, 19.