J|A|C|S
COMMUNICATIONS

Hydrogen Uptake in Boron Nitride Nanotubes at Room Temperature

Renzhi Ma,*,† Yoshio Bando,† Hongwei Zhu,‡ Tadao Sato,† Cailu Xu,‡ and Dehai Wu‡

National Institute for Materials Science, Advanced Materials Laboratory, Namiki 1-1, Tsukuba, Ibaraki 305-0044, Japan, and Department of Mechanical Engineering, Tsinghua University, Beijing 100084, P. R. China

Received February 25, 2002

Boron nitride (BN) is one of the most interesting materials of the III−V compounds with a potentially bright future in advanced materials design.[1] In recent years, much research interest was focused on BN nanostructures represented by BN nanotubes,[2,3] an analogue comparable to carbon (C) nanotubes in many respects. The investigations aiming to probe certain properties of BN nanotubes for potential applications are becoming more and more important.[3]

Hydrogen, the cleanest vector of energy, holds promise for solving current pollution problems with zero-emission vehicles. The use of hydrogen requires an effective, safe, and stable storage medium. Carbon nanotubes, especially single-wall tubes, are intensively studied and promoted as promising hydrogen storage materials because of their highly porous structure, light mass density, and good interaction between carbon and hydrogen molecules.[4] Recent evidence surfaced to show the feasibility of semiconducting carbon tubes as being better suited for hydrogen storage applications.[5] However, carbon nanotubes may be either metallic or semiconducting depending on tube diameter and helicity.[6] Synthesized carbon nanotubes feature highly complex electronic properties owing to their diversity in diameter and helicity. This is one of the probable reasons for the "hydrogen storage controversy" in carbon nanotubes, i.e., highly different results reported from different groups.[5,7] Conversely, BN nanotubes are semiconducting with the gap of ∼5.5 eV nearly independent of the tube diameter and helicity.[2a,2b] BN nanotubes also have a preferential nonhelical or "zigzag" orientation (the tube axes along the $[10\bar{1}0]$ direction).[8] Taking into account the chemical and thermal stability, BN nanotubes ultimately may be stable lightweight hydrogen gas accumulators. It is thus rather reasonable and of great interest to look into the hydrogen uptake capacity in BN nanotubes.

Very recently, Wang et al. reported a total hydrogen concentration of 2.6 wt % after mechanically milling h-BN powders for 80 h under a hydrogen pressure of 1.0 MPa.[9] This offers some perspective for the (de-) hydriding properties of BN. To date, there is still no investigation on the hydrogen adsorption properties of BN nanotubes. In this communication, we first experimentally measured the hydrogen uptake capacity in BN nanotubes at room temperature. We discovered that BN nanotubes, as do their carbon counterparts, provide interesting possibilities in storing hydrogen.

Two kinds of BN nanotube samples were prepared for the hydrogen adsorption measurements. They were synthesized through a chemical vapor deposition process by pyrolyzing the B−N−O precursor at ∼2000 K under N_2/NH_3 atmosphere.[10] The morphologies of the nanotubes were controlled by varying the oxygen contents in the B−N−O precursors. Specifically, multiwall nanotubes (Figure 1a, tube purity ∼80%) were obtained with $B_4N_3O_2H$ precursor (oxygen content 27%). On the other hand, bamboo-like nanotubes (Figure 1b, bamboo purity ∼90%) were produced with BN powder precursor enriched with oxygen (oxygen content ∼10%). On the basis of our TEM characterizations, multiwall nanotubes generally have a narrow diameter distribution from 10 to 30 nm and lengths of a few micrometers. The tubes are capped at each end. Usually a few nanotube are bonded together to form bundles. Bamboo-like tubes, in the conformation of joined nanobell segments,[11] occupy a slightly wider diameter range of 10−80 nm with lengths ordinarily exceeding 10 μm. There is no metal catalyst employed in producing these BN nanotubes. Therefore, our samples do not contain metal catalytic residues, which are common impurities in carbon nanotubes. A commercially available BN powder sample consisting of micrometer particles (Denka Co., Japan) was used for comparison purposes.

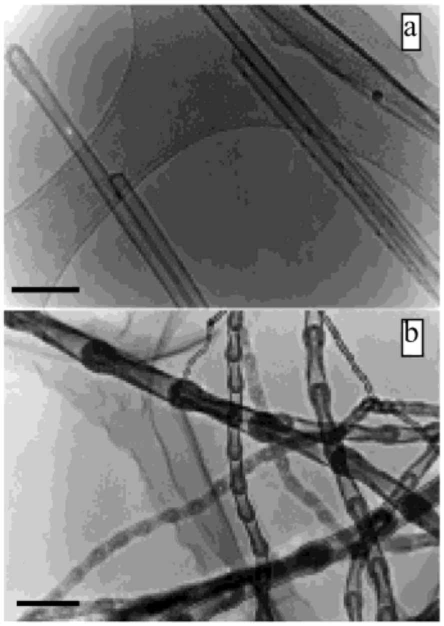

Figure 1. The morphologies of BN nanotubes: (a) multiwall nanotubes and (b) bamboo-like nanotubes. Scale bar: 100 nm.

The amount of hydrogen adsorption was measured by a gravimetric method with a Cahn D110 microbalance operated under flowing hydrogen at room temperature (293 K) and in the pressure range of 0.1−10 MPa. The BN sample, typically ∼10 mg in weight, was placed into a sample holder that was itself inserted into a pressure chamber. The chamber was evacuated and heat treatment (423 K for 2h) under vacuum was carried out. Then the sample was cooled to 293 K and high-purity hydrogen gas (99.999%) was

---

* Corresponding author. E-mail: MA.Renzhi@nims.go.jp. Fax: +81-298-51-6280.
† National Institute for Materials Science.
‡ Tsinghua University.

10.1021/ja026030e CCC: $22.00

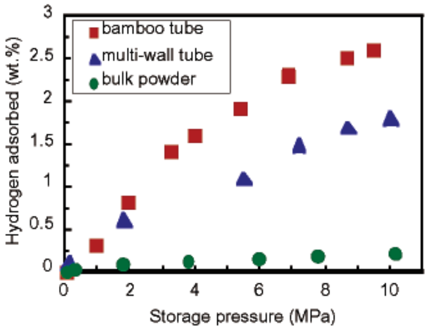

Figure 2. The hydrogen adsorption as a function of pressure in multiwall BN nanotubes and bamboo nanotubes at ∼10 MPa is 1.8 and 2.6 wt %, respectively, in sharp contrast to the 0.2 wt % in bulk BN powder. The values reported here have an error of <0.3 wt %.

admitted into the chamber. In gravimetric measurement, the moisture impurity from hydrogen is discovered to be a possible source of experimental artifact.[12] In all our experimental runs, a silica gel molecular sieve drier was employed to remove the impurities from hydrogen before admittance into the chamber. The sample weight and pressure were monitored as a function of time. For all the samples, the typical equilibration time needed for the uptake at each pressure is about 4 h. The hydrogen adsorption amount (wt %) was calculated by the mass increase divided by the sample plus adsorbed hydrogen mass. The measured results were corrected by using a reference sample that does not adsorb a measurable amount of hydrogen. The effect of moisture impurity is therefore negligible in our measurements.

Figure 2 shows the experimental isotherms of the hydrogen adsorption as a function of pressure. In general, all the isotherms exhibit the typical feature that the hydrogen adsorption amount increases monotonically with rising pressure. However, the measured values show that the multiwall and bamboo nanotube samples can adsorb hydrogen up to 1.8 and 2.6 wt %, respectively, at about ∼10 MPa, in striking contrast to the negligible 0.2 wt % weight gain in conventional BN. This confirms that BN nanotubes possess much higher hydrogen adsorption capacity than bulk BN powder. These higher uptake rates may be easily understood from their higher specific surface areas due to the nanoporous structure.

From Figure 2, it is also noticeable that BN bamboo-like nanotubes show a somewhat higher hydrogen uptake amount with higher pressure. We have observed that our BN multiwall nanotubes are usually caped at each end (Figure 1a). This feature prevents the hollow cavity of the tubes from being accessed for hydrogen molecules. The adsorption of hydrogen can thus only take place on the outside surface and interstitial sites of the tubes and bundles. On the other hand, the bamboo tubes, regarded as polymerized nanobells, usually exhibit a more defective structure and many open-edge layers on the exterior surface. The polymerized nanobell feature has been previously proposed as being helpful for adsorbing more hydrogen as verified in C nanotubes.[13] This also may be applicable to BN nanotubes and indicate the reason for the higher gravimetric hydrogen uptake capacity in the bamboo-like sample.

After the samples were returned to ambient pressure, about 70 wt % of the adsorbed hydrogen was found to be retained, suggesting the majority of the hydrogen is chemisorbed. The significantly slow equilibration time at each pressure (∼4 h) also indicates that the adsorption may be mainly a chemical interaction. The retained amount of hydrogen was released completely by subsequently heating the sample to 573 K. After the complete desorption, the hydrogen uptake capacity remained almost unchanged in the following cycle, indicating the high reversibility of the adsorption−desorption processes.

The most reported and partially reliable hydrogen uptake values for multiwall C nanotubes are around 1−3 wt %.[4d−f] The gravimetric hydrogen storage values we measured on BN nanotubes belong to this domain. Due to the capped feature of our BN nanotubes, it is reasonable to expect that more hydrogen can be stored in the inner cavities, which form the storage mechanism of C nanotubes, if opened by some post-production treatment protocols. Production and utilization of open-end or single-wall BN nanotubes for hydrogen adsorption measurements are challenges.

In summary, we have demonstrated our preliminary results that multiwall BN nanotubes can uptake 1.8−2.6 wt % hydrogen under ∼10 MPa at room temperature. Further efforts are needed for the mass production of BN nanotubes and optimization of post-production treatment protocols for a thorough investigation of the hydrogen adsorption/desorption mechanism. It is not only important with respect to the application of BN nanotubes as a possible hydrogen storage medium, but it also offers some suggestions on the design of the carbon-based hydrogen storage system.

Acknowledgment. The Science and Technology Agency (STA) fellowship supports the work carried out at the National Institute for Materials Science (Tsukuba, Japan). H.Z acknowledges the financial support from the State Key Program for Fundament Research of MOST, China (Grant No. G20000264-04).

References

(1) Paine, R. T.; Narula, C. K. *Chem. Rev.* **1990**, *90*, 73.
(2) (a) Blase, X.; Rubio, A.; Louie, S. G.; Cohen, M. L. *Europhys. Lett.* **1994**, *28*, 335. (b) Chopra, N. G.; Luyken R. J.; Cherry K.; Crespi, V. H.; Cohen, M. L.; Louie, S. G.; Zettl, A. *Science* **1995**, *69*, 966. (c) Loiseau, A.; Williaime, F.; Demoncy, N.; Hug, G.; Pascard, H. *Phys. Rev. Lett.* **1996**, *76*, 4737. (d) Han, W.; Bando, Y.; Kurashima, K.; Sato, T. *Appl. Phys. Lett.* **1998**, *73*, 3085. (e) Lourie, O. R.; Jones, C. R.; Bartlett, B. M.; Gibbons, P. C.; Ruoff, R. S.; Buhro, W. E. *Chem. Mater.* **2000**, *12*, 1808.
(3) (a) Chopra, N. G.; Zettl, A. *Solid State Commun.* **1995**, *105*, 297. (b) Srivastava, D.; Menon, M.; Cho, K. *Phys. Rev. B* **2001**, *63*, 195413.
(4) (a) Dillon, A. C.; Jones, K. M.; Bekkedahl, T. A.; Kiang, C. H.; Bethune D. S.; Heben, M. J. *Nature* **1997**, 386, 377. (b) Chambers, A.; Park, C.; Baker, R. T. K.; Rodriguez, N. M. *J. Phys. Chem. B* **1998**, *102*, 4253. (c) Liu, C.; Fan, Y. Y.; Liu, M.; Cong, H. T.; Cheng, H. M.; Dresselhaus, M. S. *Science* **1999**, *286*, 1127. (d) Cheng, H. M.; Yang, Q. H.; Liu, C. *Carbon* **2001**, *39*, 1447. (e) Darkrim, F. L.; Malbrunot, P.; Tartaglia, G. P. *Int. J. Hydrogen Energy* **2002**, *27*, 193. (f) Züttel, A.; Sudan, P.; Mauron, Ph.; Kiyobayashi, T.; Emmenegger, Ch.; Schlapbach, L. *Int. J. Hydrogen Energy* **2002**, *27*, 203.
(5) (a) Dillon, A. C.; Gilbert, K. E. H.; Alleman, J. L.; Gennett T.; Jones, K. M.; Parilla, P. A.; Heben, M. J. in Proceedings of the U.S. DOE Hydrogen Program Review, 2001 (http://www.eren.doe.gov/hydrogen/pdfs/30535am.pdf).
(6) Saito, R.; Fujita, M.; Dresselhaus, G.; Dresselhaus, M. S. *Phys. Rev. B* **1992**, *46*, 1804.
(7) Zandonella, C. *Nature* **2001**, *410*, 734.
(8) (a) Menon, M.; Srivastava, D. *Chem. Phys. Lett.* **1999**, *307*, 407. (b) Golberg, D.; Bando, Y. *Appl. Phys. Lett.* **2001**, *79*, 415. (c) Ma, R.; Bando, Y.; Sato, T.; Kurashima K. *Chem. Mater.* **2001**, *13*, 2965. (d) Lee, R. S.; Gavillet, J.; Chapelle, M. Lamy de la; Loiseau, A.; Cochon, J. L.; Pigache, D.; Thibault, J.; Willaime, F. *Phys. Rev. B* **2001**, *64*, 121405(R).
(9) Wang, P.; Orimo, S.; Matsushima, T.; Fujii, H.; Majer, G. *Appl. Phys. Lett.* **2002**, *80*, 318.
(10) (a) Ishii, T.; Sato, T.; Sekikawa, Y.; Iwata, M. *J. Cryst. Growth* **1981**, *52*, 285. (b) Ma, R.; Bando, Y.; Sato, T. *Adv. Mater.* **2002**, *14*, 366.
(11) Ma, X.; Wang, E. G.; Tilley, R. D.; Jefferson, D. A.; Zhou, W. *Appl. Phys. Lett.* **2000**, *77*, 4136.
(12) (a) Chen, P.; Wu, X.; Lin, J.; Tan, K. L. *Science* **1999**, *285*, 91. (b) Yang, R. T. *Carbon* **2000**, 38, 623. (c) Pinkerton, F. E.; Wicke, B. G.; Olk C. H.; Tibbetts, G. G.; Meisner, G. P.; Meyer, M. S.; Herbst, J. F. *J. Phys. Chem. B* **2000**, *104*, 9460.
(13) Bai, X. D.; Zhong, D.; Zhang, G. Y.; Ma, X. C.; Liu, S.; Wang, E. G. *Appl. Phys. Lett.* **2001**, *79*, 1552.

JA026030E