

Catalyzed Collapse and Enhanced Hydrogen Storage of BN Nanotubes

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Immense efforts were undertaken worldwide to investigate synthesis, structure, properties, and potential applications of carbon nanotubes since these novel materials had been discovered in 1991.¹ Applications in field emitters² and storage devices for hydrogen³ have been proposed and have given rise to much controversy. However, although BN nanotubes were successfully synthesized⁴ shortly after the discovery of carbon nanotubes, only a few investigations of the practical applications⁵ of BN nanotubes have been reported to date. This is mainly due to the fact that there is no reliable method to produce bulk amounts of BN nanotubes. Although the carbon nanotube-substitution method⁶ can provide the mass quantity of BN nanotubes, it is considerably difficult to fully remove the starting carbon from final products. In fact, except for a few methods,⁷ the low quantities of BN nanotubes (usually carbon contaminated) synthesized so far restrict the detailed characterization of physical and chemical properties.

Recently, we synthesized BN nanotubes in a high yield via the CVD method using a novel precursor mixture of B₂O₂ and Mg vapors.⁸ The only possible contamination source, Mg, was evaporated and transported far from the reaction area. Therefore, although the formation mechanism of nanotubes warrants further investigation, the synthesized product exhibits a considerably high purity with respect to carbon contamination. Most importantly, this simple and reproducible method allows us to prepare BN nanotubes which are available in gram amounts during a single run, paving the way of thorough investigations of BN nanotubes practical applications.

The novel morphology of BN nanotubes with a collapsed structure described here was unexpectedly discovered during the study of defects existing in pure BN nanotubes. The collapse causes the enlargement of a specific surface area of BN nanotubes and remarkably enhances their hydrogen storage capacity.

Five hundred and eight milligrams of BN nanotubes synthesized via the above method was tiled on the surface of a platinum plate (25 × 25 × 0.05 mm³, purity 99.99%), pinned with another platinum plate of the same size, and then placed into a BN boat held in a conventional furnace. The platinum plates were pretreated in acetone and diluted HCl solution. After being heated at 1500 °C for 6 h under a high-purity argon flow, 516 mg of a sticky product was collected. Figure 1a shows a typical transmission electron microscopy (TEM) image of the BN nanotubes after the treatment. The one-dimensional nanotubular morphology of the starting BN nanotubes is basically maintained, as displayed in the TEM image, because the inner areas of the collapsed nanotubes exhibit apparently bright contrast. All wall layers are fractured and protrude outward forming a hairlike structure. High-resolution TEM examinations

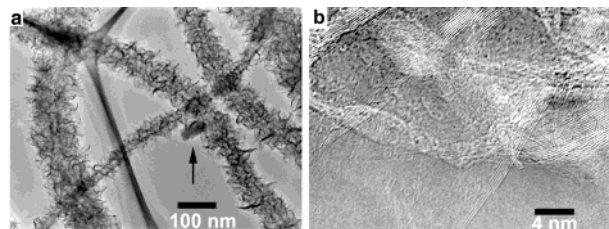


Figure 1. (a) TEM image of BN nanotubes after heating at 1500 °C for 6 h in the presence of platinum; the arrow points to a platinum nanoparticle. (b) High-resolution TEM image of the collapsed BN nanotubes.

(Figure 1b) depict that the disordered BN layers are in fact composed of highly crystallized BN fragments. Energy-dispersion X-ray analysis and electron energy loss spectra further confirm the stoichiometric BN composition, without traces of carbon, platinum, and oxygen in the collapsed BN nanotubes.

The specific surface areas of the BN nanotubes with or without the platinum-assisted heat treatment were measured during nitrogen gas adsorption on the basis of the BET adsorption isotherms. The structural collapse significantly increases the specific area of BN nanotubes from 254.2 to 789.1 m²/g.

The mass gain of approximately 1.6% after heating treatment should be attributed to the platinum contamination, which does not incorporate into BN nanotubes but exists as discrete metal particles. An occasionally observed platinum particle is marked with an arrow in Figure 1a.

Further experiments were carried out to elucidate the mechanism of collapse. When graphite or BN plates were used to pin BN nanotubes and treated at the same conditions as described above, no noticeable morphology changes were observed. However, when the starting BN nanotubes were mounted onto some noble metal plates (tungsten, molybdenum, and niobium were tested in our experiments), fully or partially collapsed BN nanotubes were observed. These experimental results indicate that the collapse of BN nanotubes was accomplished due to the metal catalysts. Our TEM observations also indicate that the metals rarely led to collapse of BN nanobamboo.⁹

The hydrogen uptake experiments were carried out under ambient temperature and pressure ranging from 2 to 11 MPa. The hydrogen adsorption amount was defined as the ratio of the mass gain and the mass of the starting BN plus adsorbed hydrogen; this was measured by a gravimetric method. After being dried in an argon flow for 8 h at 150 °C, the BN nanotubes with and without platinum catalytic treatment, typically 200 mg in weight, were placed into a stainless steel vacuum system. After the system was degassed to better than 10⁻⁵ Pa, a hydrogen gas of 99.999% purity, after further purification by passage through a liquid nitrogen trap and then by a silica gel drier, was introduced into the chamber until a desired

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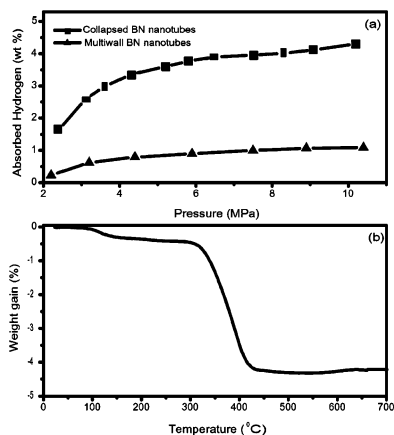


Figure 2. (a) Gravimetric storage capacity at room temperature as a function of the hydrogen pressure for the collapsed BN nanotubes and the starting nanotubes with complete structure. (b) TGA spectrum of the hydrogen release of the collapsed BN nanotubes after hydrogen uptake under 10.2 MPa for 4 h.

pressure was achieved. The equilibration time for hydrogen uptake at each pressure was usually fixed at 4 h. The sample was then transferred into a microbalance at atmospheric pressure to measure the weight changes. Desorption isotherms could be measured by moving the absorbed sample into a thermogravimetric analyzer (TGA), in which a constant flow of approximately 30 sccm of highly purified argon was used as a purging and protecting gas. The temperature was increased from room temperature to 700 °C linearly at a rate of 2 °C/min. Selected replicate experiments and the hydrogen uptake of the activated carbon were conducted to determine the reproducibility and reliability of the measurements. The maximum error of hydrogen uptake values was less than 10%.

Figure 2a shows the measured storage capacity as a function of the gas pressure at ambient temperature for the multiwalled BN nanotubes and the collapsed BN nanotubes catalyzed by the platinum metal. Although both isotherms exhibit the monotonically increasing amount of hydrogen absorption with the applied pressure, the hydrogen uptakes were approximately saturated when the gas pressure is larger than 6 MPa. At about 10 MPa, the multiwalled BN nanotubes can absorb 0.9 wt % of hydrogen, which is smaller than 1.8 wt % reported previously.^{5b} The discrepancy may be attributed to the measurement details. In fact, the amounts of hydrogen uptakes in our investigations were measured at ambient pressure. Therefore, the weight gain was the portion remaining inside the nanotubes after the hydrogen environment was removed. It means that about 50% of the absorbed hydrogen was already desorbed when lowering the hydrogen partial pressure to nearly atmospheric conditions, despite the fact that hydrogen uptake strongly depends on the diameter and nanoporous density. The absorbed amount in the collapsed BN nanotubes exceeded that of the raw multiwalled nanotubes by a factor of ~ 4 . The measured value at ~ 10 MPa is 4.2 wt %. This confirms that the collapsed surfaces of BN nanotubes effectively increase the hydrogen adsorption capacity due to the high specific surface area.

Obviously, the magnitude of the hydrogen absorption, after removing the hydrogen pressure, cannot be interpreted in terms of physisorption both inside the tube and in the interstitial channels of BN nanotubes. It is due to the fact that physisorbed hydrogen is too weakly bound and could not lead to such large sorption at room temperature.¹⁰ It is worth noting that the theoretical and experimental investigations on hydrogen uptake of carbon nanotubes have

suggested that a chemical absorption process may be involved.^{11–13} The observed large hydrogen uptake in our experiment is likely primarily due to the chemisorption nature. Our TGA measurements clearly display the absorption mechanism. Figure 2b is the TGA curve of the collapsed BN nanotubes after hydrogen uptake under ~ 10 MPa for 4 h. Two apparent weight losses occurred in the ranges from 80 to 140 °C and from 300 to 450 °C, and 5% and 95% absorbed hydrogen amounts were released, respectively, corresponding to these two ranges. Accordingly, we believe that the enhancement of hydrogen storage in the collapsed BN nanotubes is a direct consequence of the increasing numbers of dangling bonds due to the surface collapse.

In summary, the present study has shown that the morphology of BN nanotubes could be strongly modified by a post-production treatment procedure: heating pure BN nanotubes in the presence of platinum. The method results in a nearly full collapse of the BN nanotube walls and consequently forms crystalline and disordered hairlike BN nanotube fragments. Although the metal-catalyzed growth mechanism is somewhat speculative, the open tube walls could effectively increase the number of channels for hydrogen uptake. As a result, collapsed BN nanotubes possess a higher hydrogen adsorption capacity than do any multiwalled nanotubes of conventional morphology.

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Supporting Information Available: Comparative hydrogen uptake for the collapsed BN nanotubes and activated carbon, TEM images of as-prepared and platinum-thermal treated BN nanotubes (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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