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Hydrogen storage in boron nitride nanomaterials studied by TG/DTA and cluster calculation

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Abstract

BN nanotubes, nanocages and nanocapsules were synthesized from LaB_6 and Pd with boron powder by using an arc melting method. Thermogravimetry/differential thermogravimetric analysis of BN nanomaterials produced from LaB_6 and Pd/boron powder showed possibility of hydrogen storage of 1–3 wt%. Conditions of H_2 gas storage in $B_{36}N_{36}$ cluster, which was considered as a cap structure of $B_{99}N_{99}$ nanotube, were predicted by first principle single point energy calculations. H_2 molecules would be introduced from hexagonal rings of the cage structure. BN fullerene materials would store H_2 molecule easier than carbon fullerene materials, and its stability for high temperature would be good.

Keywords: A. Nanostructures; C. Electron microscopy; D. Microstructure

1. Introduction

Many works have been reported on carbon nanotubes [1] and nanocapsules [2] since the discovery of fullerenes [3]. Carbon nanostructures are intriguing for both scientific research and future device applications, such as cluster protection, nano-ball bearings, nano-opticalmagnetic devices, catalysis, gas storage and biotechnology [4]. Recently, several studies on boron nitride (BN) fullerene materials have been reported since they have excellent properties such as heat resistance in air, insulation, wide bandgap and structural stability [4,5]. Most of the studies on the BN fullerene materials were focused on the formation of BN nanotubes [4,6–10]. We have focused on the BN nanocapsules, nanotubes, nanocages, nanoparticles and clusters to discover new properties and structures by changing the encapsulated materials [4,9–12], and on the possibility of gas storage in BN nanocapsules [4,13,14]. Since the BN nanocapsules consist of light elements, it is believed that they can store much gas per weight [4].

The purpose of the present work is to prepare BN nanotubes, nanocapsules and nanocages, and to investigate hydrogen gas storage by thermogravimetry/differential thermogravimetric analysis (TG/DTA) and first principle calculation. LaB_6 and Pd were selected in order to take advantage of their catalytic effect to produce the BN nanomaterials. La has shown excellent catalytic properties for producing a large number of single-walled carbon nanotubes and enlarging their diameter [15], and Pd is also expected to act as a hydrogen storage material. Although gas storage of hydrogen and argon in carbon nanotubes has been reported [16,17], carbon nanotubes are oxidized at 600 °C in air [18]. On the other hand, BN are stable up to 1000 °C in air [4], which indicates the excellent heat resistance compared to the carbon materials for gas storage. To understand the formation of BN nanostructures, high-resolution electron microscopy (HREM) were carried out, which are very powerful methods for atomic structure analysis [19,20]. For the BN nanomaterials, hydrogen gas storage measurements were carried out using TG/DTA.

2. Experimental procedures

Mixture powder compacts made of boron particles (99%, 40 μm, Niraco Co. Ltd), LaB_6 particles (99%, 1 μm, Wako Co. Ltd) and Pd particles (99.5%, 0.1 μm, Niraco Co. Ltd), with the size of 3 mm in height and 30 mm in diameter were produced by pressing powder at 10 MPa. The atomic ratios of metal (M) to boron (B) were in the range of 1:1–1:10. The green compacts were set on a copper mold in an electric-arc furnace, which was evacuated down to

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2.0×10^{-3} Pa. After introducing a mixed gas of Ar 0.025 MPa and N_2 0.025 MPa, arc-melting was applied to the samples at an accelerating voltage of 200 V and an arc current of 125 A for 2 s. Arc-melting was performed with a vacuum arc-melting furnace (NEV-AD03, Nisshin Engineering Co. Ltd), and the white/gray BN nanomaterial powders were collected from surface of the bulk.

Samples for HREM observation were prepared by dispersing the materials on holy carbon grids. HREM observation was performed with a 300 kV electron microscope (JEM-3000F). To confirm the formation of BN fullerene materials, EDX analysis was performed using the EDAX system with a probe size of ~10 nm. In order to measure hydrogen gas storage in BN nanomaterials, BN nanomaterials were extracted from the obtained powder by a supersonic dispersing method based on the Stokes equation using ethanol. The Stokes equation is expressed as follows: $v = d^2(\sigma - \rho)g/18\eta$ ($h = vt$, v, sedimentation rate, η, viscosity of liquid, σ, density of particles, ρ, density of liquid, g, gravitational acceleration, d, diameter of particles, t, subsidence time, h, height of liquid). Since there is a big difference in the size and density of the produced BN nanocapsules/nanotubes and other powders, it is believed that this method would be effective for separation of BN nanomaterials. After separation of BN nanomaterials, hydrogen storage was measured by TG/DTA at temperatures in the range of 20–300 °C in H_2 atmosphere.

To search the optimized structure of $B_{99}N_{99}$ and $B_{36}N_{36}$ with H_2 molecules, semi-empirical molecular orbital calculations (PM3) were performed. The energies of $B_{36}N_{36}$ with H_2 molecules were calculated by first principle single point energy calculation using Gaussian98. In the calculation, 3-21G was used as ground function with Hartree–Fock level.

3. Results and discussion

A HREM image of a BN nanotube produced using LaB_6 powder is shown in Fig. 1(a). In Fig. 1(a), the diameter of the five-layered BN nanotube is changing from bottom to top, and amorphous patches are observed mostly at the top. A HREM image of BN nanocage produced from LaB_6/B powder is shown in Fig. 1(b), which indicates square-like shape, and four-membered rings of BN exist at the corner of the cage. The BN nanocage has a network-like structure, whose atomic arrangement is basically consistent with the $B_{36}N_{36}$ cluster structure [4,5]. BN nanocapsules with Pd nanoparticles were also produced as shown in Fig. 1(c), and Pd nanoparticles were covered by a few BN layers. In order to confirm the formation of BN nanocapsules, EDX analysis was carried out, which showed the atomic ratio of B:N ~ 1.

DTA and TG curve of BN nanomaterials produced from LaB_6 powder is shown in Fig. 2. At a temperature around 70 °C, an increase of sample weight of 0.3 mg is observed. Weight change for this sample was almost reversible, which indicates the reversibility of hydrogen adsorption. It also suggests that the hydrogen atoms would be physically absorbed. For the samples of La:B = 1:6 and Pd:B = 1:4, weight increases of 3.2 and 1.6% were observed, respectively, as listed in Table 1.

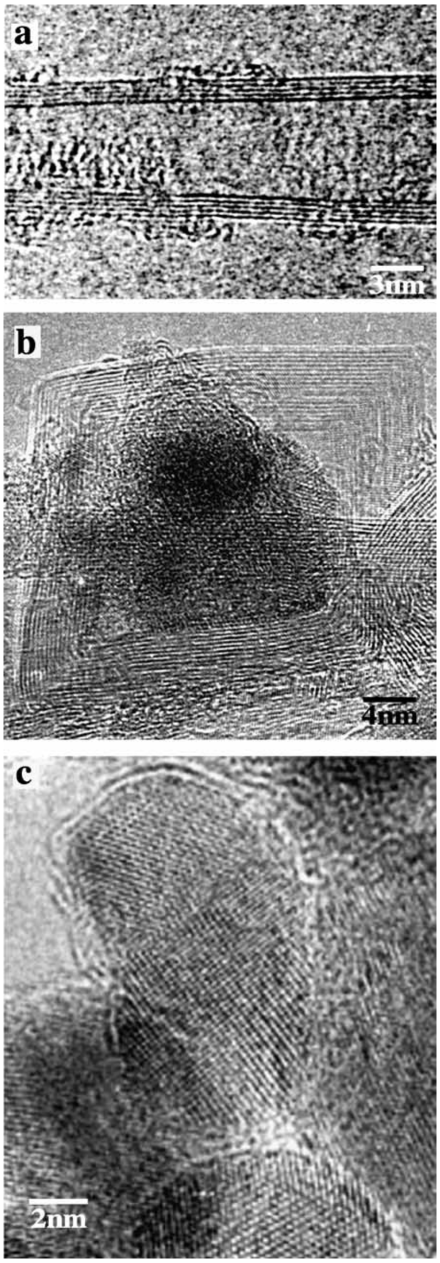

Fig. 1. HREM images of BN nanotube and BN nanocapsules produced using powder with ratios of (a) La:B = 1:6, (b) La:B = 1:7, and (c) Pd:B = 1:4.

BN nanostructures would have energy barriers for H_2 molecules to pass through tetragonal and hexagonal rings. Fig. 3 are structure models in which H_2 molecule passes from hexagonal rings of $B_{99}N_{99}$ and $B_{36}N_{36}$. Single point energies were calculated with changing set point of H_2 molecule from center of the cage at intervals of 0.1 nm. ΔE is regarded as energy barrier that is given for H_2 molecules

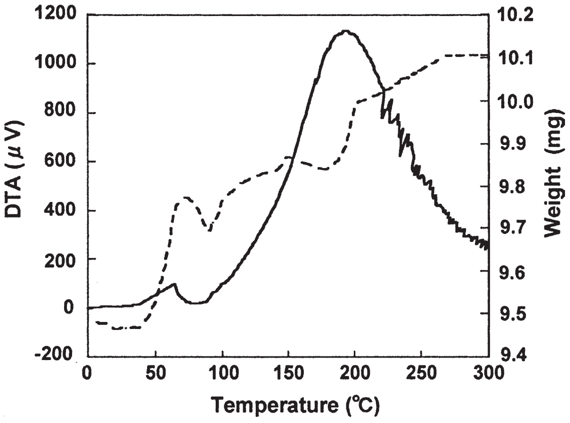

Fig. 2. DTA and TG curve of BN nanocapsules and nanotubes produced using LaB_6 powder.

Table 1
Atomic ratio of starting materials, produced structures and hydrogen storage

M:B	Nanostructures	Weight change (wt%)
La:B = 1:6	Nanotubes and nanocages	+3.2
La:B = 1:10	Nanotubes	+0.58
Pd:B = 1:4	Nanocapsules	+1.6

to pass through hexagonal rings. The ΔE of $B_{36}N_{36}$ hexagonal rings showed the smallest value of 14 eV in the present calculation, which is smaller than that of 27 eV at tetragonal rings. The ΔE of C_{60} hexagonal rings was also calculated to be 16 eV for comparison. This value is higher than that of $B_{36}N_{36}$ hexagonal rings, and the H_2 molecule would pass from hexagonal rings of $B_{36}N_{36}$ easier than from hexagonal rings of C_{60}. It is known that H_2 molecules are adsorbed on walls of single-walled carbon nanotubes over 7 MPa as an experimental result [21]. As a result of comparison of ΔE, H_2 molecules enter into $B_{36}N_{36}$ from hexagonal rings easier than tetragonal rings $B_{36}N_{36}$ and hexagonal rings of C_{60}.

A formation mechanism of BN nanotubes and nanocapsules synthesized in the present work is described below. Metal and boron particles are melted by arc-melting, and during the solidification of the liquid into metal and/or boride nanoparticles, excess boron would react with nitrogen to form BN layers at the surface of the nanoparticles. Because of electrical insulation, BN fullerene materials are usually fabricated by arc-discharge method with specific conducting electrodes such as HfB_2 and ZrB_2 [7]. The present arc-melting method from mixed powder has two advantages for BN nanomaterial production. Since the powder becomes conducting by pressing, special electrodes are not needed. In addition, ordinary, commercial arc-melting furnaces can be used. These advantages indicate a simpler fabrication method compared to the ordinary arc-discharge methods [4,22].

Although gas storages of hydrogen and argon in carbon nanotubes have been reported [16,17,23,24], there are few reports for gas storage in BN fullerene materials [4,25] and for calculations [13,14]. Weight increase of the sample in TG measurements was observed as shown in Fig. 2. It might be due to the hydrogen gas storage in the BN nanomaterials.

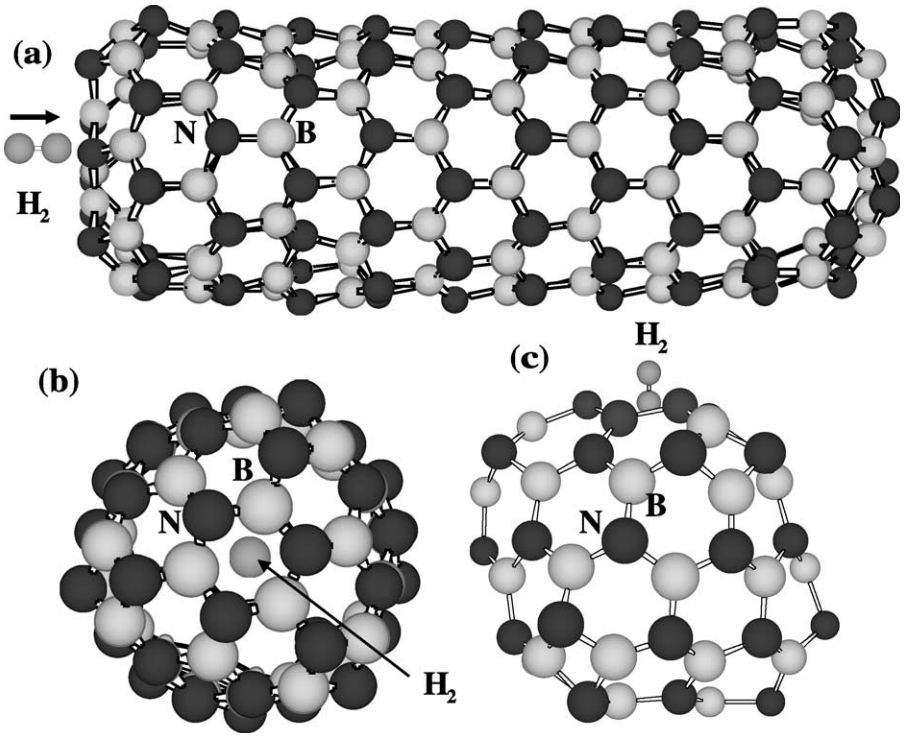

Fig. 3. Structure models that H_2 molecule passes through hexagonal rings of (a) (b) $B_{99}N_{99}$ nanotube and (c) $B_{36}N_{36}$ cluster.

Since there would be metal and boron nanoparticles in the separated BN nanomaterials even after the separation, further qualification and evaluation of the samples are needed for hydrogen storage.

Carbon fullerenes and boron nitride fullerenes are sublimed at 600 and 1000 °C, respectively. Boron nitiride fulerenes would storage H_2 molecules with smaller energy than carbon fullerenes [13,14], and would give good stability at high temperature. Boron nitride fullerene materials would be better candidate for H_2 storage materials.

4. Conclusions

HREM observation showed the formation of BN nanotubes, nanocapsules and nanocages, which were synthesized from mixtures of LaB_6, Pd, and boron powder by using an arc melting method. Although samples produced with Pd include only BN nanocapsule structures, samples produced with LaB_6 present BN nanocapsule, nanotube and nanocage structures. After separation of BN nanomaterials using ethanol, hydrogen storage was measured by TG/DTA, and the BN nanomaterials produced from LaB_6 and Pd/boron powder showed possibility of hydrogen storage of ~3 wt%. Theoretical calculation also showed H_2 gas storage in $B_{36}N_{36}$ cluster. The present work indicates that BN fullerene materials could be a one of the possible candidates as hydrogen gas storage materials.

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