

# In Situ Formation of BN Nanotubes during Nitriding Reactions

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High-yield multiwalled boron nitride (BN) nanotubes have been produced using a ball milling–annealing method. The BN nanotubes with a diameter less than 10 nm and a well-crystallized multiwalled structure were formed via an in situ nitriding reaction. The systematic investigation of the formation process at different annealing temperatures and for different times suggested that the formation of the unique multiwalled structure was attributed by a two-dimensional growth of the BN phase and a nonmetal catalytic growth.

## 1. Introduction

Boron nitride nanotubes have received increased attention due to their interesting properties such as stable insulators, a super-resistance to oxidation at high temperatures (above 800 °C), and excellent thermal conductivities.<sup>1–4</sup> BN nanotubes have been synthesized using different methods, including arc-discharge,<sup>5–7</sup> laser heating/ablation,<sup>8</sup> ball milling–annealing,<sup>9,10</sup> C nanotube substitution,<sup>11</sup> and chemical vapor deposition (CVD) method.<sup>12</sup> Among them, the ball milling–annealing method has produced such a large quantity that the BN nanotubes synthesized become commercially available. In this method, elemental boron powder is first milled in ammonia gas and subsequently annealed in a nitrogen-containing atmosphere.<sup>10</sup> The method has been used by several groups in successful synthesis of BN nanotubes. Tang et al.<sup>13</sup> found BN nanotubes and horns in a mixture of B

and Ga<sub>2</sub>O<sub>3</sub> after first ball milling for 6 h and subsequent annealing up to 1550 °C in NH<sub>3</sub> gas. Bae et al.<sup>14</sup> have also produced BN nanotubes by first ball milling of B powder and followed by annealing in NH<sub>3</sub> gas in the temperature range of 1000–1200 °C. Nanotubes in different materials have also been produced using the same method.<sup>15,16</sup> In our previous work, pure nitrogen gas was used during the annealing as the reaction gas, and the BN nanotubes produced often had a large diameter range from a few nanometers to a couple hundred nanometers.<sup>10,17</sup> In addition, different nanotubular structures (cylindrical and bamboo-like) coexist.<sup>17</sup> With variation of the annealing/growth conditions and use of different catalysts, thin BN nanotubes with diameter less than 20 nm with unique cylindrical structure or thick multiwalled cylindrical nanotubes or bamboo nanotubes with a diameter larger than 20 nm can be produced separately.<sup>17,18</sup> In this work, we report that thin BN nanotubes with a smaller diameter (less than 10 nm) and with unique multiwalled, cylindrical structure have been synthesized in a large quantity using the ball-milling and annealing method. Ammonia (NH<sub>3</sub>) gas was used during the annealing process. Influences of annealing conditions including annealing temperatures and times on nanotube formation were systematically investigated. The nanotube morphology and nanostructures were explored using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Possible catalytic effects of metal particles are discussed.

## 2. Experimental Section

Amorphous boron powder (Sigma-Aldrich) with purity of 95–97% was used as the starting material and anhydrous NH<sub>3</sub> as the

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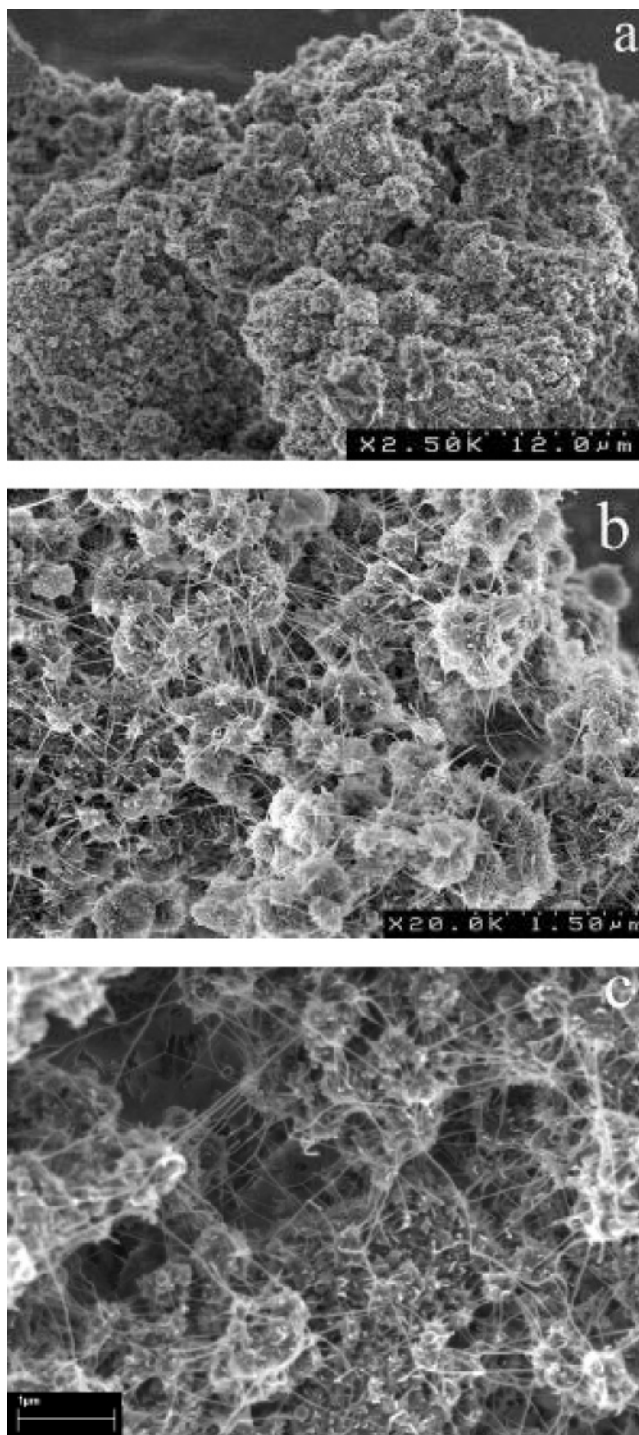
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reaction gas for both milling and annealing processes. Ball milling treatment was conducted at room temperature using a steel rotating ball mill with four hardened steel balls and a stainless steel cell.<sup>19</sup> Several grams of the boron powder were loaded into the cell and purged with NH<sub>3</sub> gas several times. A static pressure of 300 kPa of NH<sub>3</sub> gas was established prior to milling. During the milling process, some NH<sub>3</sub> gas reacted with the B powder under high-energy impacts with the formation of nanosized BN phases, which serve as nucleation structures for nanotube growth during subsequent annealing.<sup>8,17</sup> Ball milling effects, as a function of milling time and intensity, have been investigated previously;<sup>17</sup> a milling time of 150 h was used in this work. After milling, annealing was carried out under NH<sub>3</sub> gas at a flow rate of 500–1000 mL/min up to 1200 °C in a tube furnace for several hours. Milled and annealed samples were characterized using various analyzing techniques. The structures of the samples were investigated using X-ray diffraction analysis (XRD) with Co radiation ( $\lambda = 0.1789$  nm). SEM analysis was employed to examine sample morphology using both a Hitachi S4500 microscope operated at 3 kV and a Zeiss Supra 55 VP SEM instrument. Chemical contents of the element boron (B), nitrogen (N), iron (Fe), and other elements were measured using X-ray energy dispersive spectroscopy (EDS) in a JEOL (JSM6400) scanning electron microscope. To increase the measurement accuracy, powder samples were pressed into small pellets with a smooth surface before the measurement. EDS spectra were collected from a large area (100  $\mu\text{m} \times 300 \mu\text{m}$ ) of the pellet as well as from several places on each pellet, and thus an average content of each element was obtained for comparison between different samples. TEM investigations were performed using a Philips CM300 (300 kV) instrument equipped with an EDS system. BN nanotube samples were directly deposited onto copper grids coated with a holey carbon film without using any solvent to avoid any contamination. Electron energy loss spectroscopy was conducted with a JEM-3000F field-emission analytical high-resolution transmission electron microscope fitted with a Gatan Imaging Filter (GIF).

### 3. Results and Discussion

Large quantities of samples containing thin BN nanotubes were produced from amorphous boron powder after first ball milling for 150 h at room temperature in ammonia gas and then annealing in NH<sub>3</sub> gas at 1200 °C for 8 h. The SEM image taken at low magnification in Figure 1a shows a powder-like morphology of the final sample. The high-magnification image, in Figure 1b, reveals a large number of thin fibers from the surface of the aggregates/clusters. The thin nanotubes have a diameter less than 10 nm and are several micrometers long. The SEM image in Figure 1c was taken over the gap area within a cluster under a higher magnification (40 k) and it shows that thin nanotubes are also formed inside clusters, suggesting that the powder-like clusters actually consist of a large number of thin nanotubes and particles. The interesting feature is that, like thin carbon nanotubes (e.g., SWNTs), the thin BN nanotubes appear to connect to one or two particles, which possibly indicates the growth path might be due to minimized surface area.

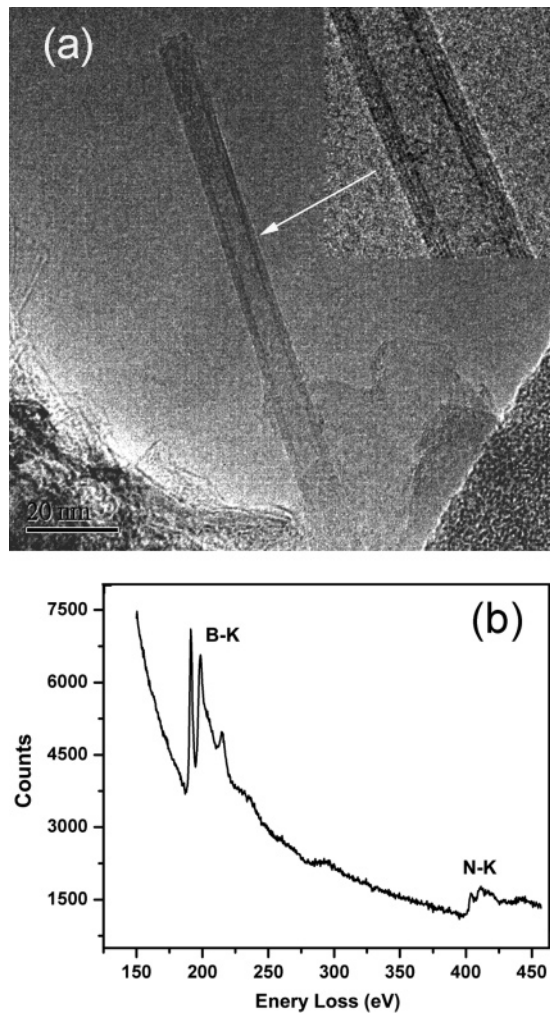
TEM observation reveals typical parallel-walled and cylindrical structure of these nanotubes as seen in Figure 2a. The clear parallel fringes on the wall area of the nanotube



**Figure 1.** SEM images taken at different magnifications from the B sample, after first ball milling for 150 h and subsequent annealing at 1200 °C for 8 h in NH<sub>3</sub>.

can be seen from the insert high-magnification image, suggesting perfect crystalline structure and a low level of structural defects. Two interesting results from the TEM analysis are as follows: (1) only multiwalled cylindrical structure is observed and no other tubular structure such as bamboo or cone-like structures is found. (2) TEM and EDS analyses over a large number of BN nanotubes do not find any Fe particles inside these thin nanotubes. Fe and Cr particles are found in the sample but outside the nanotubes. Figure 2b shows typical EELS spectra taken on a BN

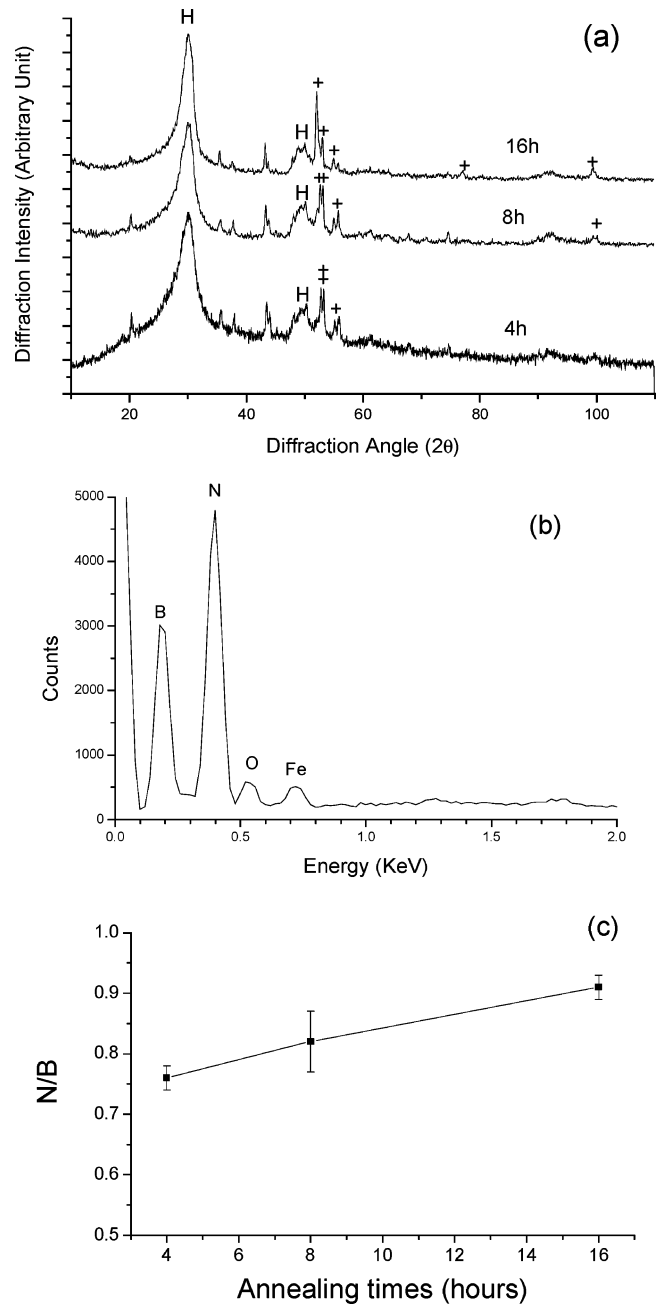
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**Figure 2.** TEM images of (a) a thin BN nanotube showing multiwalled cylindrical structures and (b) EELS spectra of a BN nanotube.

nanotube, which indicates a nanotube of BN with the presence of B and N signals and a B/N ratio of around 0.92.

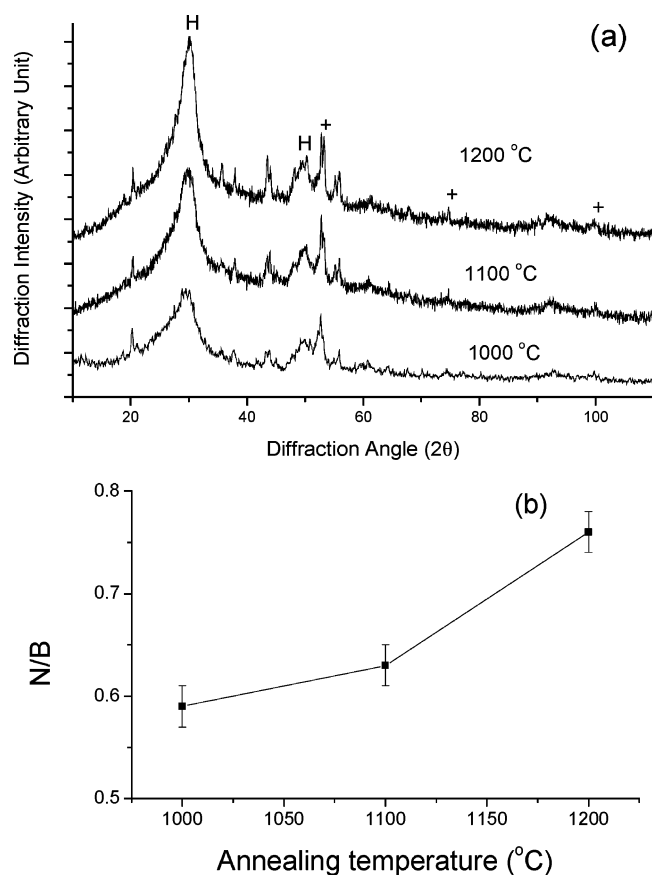
The same 150-h-milled B was annealed at 1200 °C for different times to determine the optimized condition. XRD patterns in Figure 3a were taken from the samples heated at the same temperature but for different times. The formation of BN phase during annealing is indicated clearly by the presence of BN peaks. The intensity of the BN peaks increases with increasing annealing time, suggesting a gradual nitriding reaction during annealing. The degree of nitridation was estimated using EDS analysis with an SEM on the pellet samples. Typical EDS spectra are shown in Figure 3b. Strong boron and nitrogen peaks and relatively weak peaks of oxygen and iron suggest a dominant presence of B and N and a low level of O and Fe. The average contents of B and N were measured and compared with samples heated for different times. The N/B ratio as a function of annealing time is illustrated in Figure 3c. It shows that the N/B ratio continues to increase during annealing, confirming the progress of nitriding reaction. The high N/B ratio (above 0.8) of the samples, after heating over 8 h, suggests most of the B has been nitridized to BN. A small amount of B reacts with Fe and can form FeB alloys, as suggested by XRD analysis (Figure 3a). The presence of Fe ( $4 \pm 0.5$  wt %) comes from the stainless ball and milling cell as milling



**Figure 3.** (a) XRD patterns of the same milled sample after heating at 1200 °C for 4, 8, and 16 h: H, BN; +,  $\text{Fe}_{2.12}\text{B}_{103.36}$ . (b) EDS spectra taken from the sample heated at 1200 °C for 16 h, suggesting dominant presence of B and N and low level of Fe and O. (c) Ratio of N/B as a function of annealing time. The increase of N/B ratio with increasing annealing time indicates the progress of the nitriding reaction.

contamination.<sup>9,10</sup> SEM analysis confirmed that nanotube yield increases with increasing annealing time, and BN nanotubes appear to grow longer, though not becoming coarse during extended annealing.

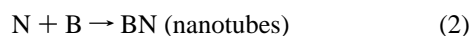
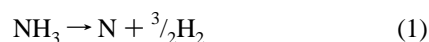
Annealing temperature is another important condition for the formation of high-yield BN nanotubes. XRD patterns in Figure 4a were taken from the samples heated at different temperatures for a similar period of time (4 h). We can see that full nitridation was not achieved at 1000 °C because the BN peaks are very broad and a weak phase as well as the high level of diffraction background is most likely associated with unreacted amorphous B. The nitriding reaction probably has a low reaction rate at 1000 °C. The



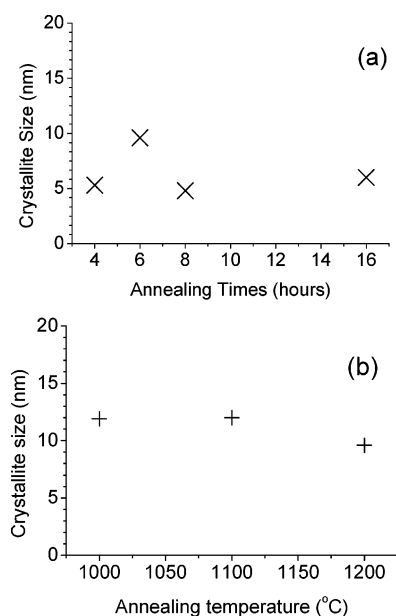
**Figure 4.** (a) XRD patterns taken from the samples annealed at different temperatures: 1000 °C, 1100 °C, and 1200 °C. H, BN; +, Fe; \*,  $\text{Fe}_{2.12}\text{B}_{103.36}$ . (b) N/B ratio as a function of annealing temperature. The increase of N/B ratio with increasing temperature suggests a fast nitriding reaction at high temperature.

diffraction intensity of the BN (002) peaks increases with increasing temperature, suggesting increased nitridation degree and reaction rate. This result is consistent with the EDS analysis results shown in Figure 4b. The N/B ratio increases as a function of annealing temperature. When the temperature increases from 1000 to 1200 °C, the N/B ratio augments from 0.59 to 0.76, suggesting a faster reaction at higher temperatures. SEM analysis revealed a higher nanotube yield in the sample heated at 1200 °C compared with that of the sample heated at 1000 °C.

The XRD and EDS results indicate a nitriding reaction between the milled B and  $\text{NH}_3$  gas during the annealing. The investigation of the influence of annealing time and temperature on the nitriding reaction also suggests that the nitriding level is associated with the nanotube yield. BN phase must be produced before any BN nanotubes are formed. The possible reactions that occurred during the annealing process are



Reaction 1 is due to the decomposition of  $\text{NH}_3$  gas as it is thermodynamically unstable at temperatures above 458 K.<sup>18</sup> When  $\text{NH}_3$  flows through a high-temperature furnace at temperatures above 1000 °C, it decomposes to N and  $\text{H}_2$  gas. The released N reacts with B to form BN, which is



**Figure 5.** Average crystallite size of the BN (002) crystals estimated from the Scherrer equation. (a) Crystal size changes as a function of annealing time and (b) crystallite size changes as a function of annealing temperature.

described in reaction 2.  $\text{H}_2$  gas might have played an important role in the nitriding reaction and the formation of BN, which can be associated with a lower N–H bond strength of 314 kJ/mol compared with a N–N bond strength of 945.3 kJ/mol.<sup>20</sup> Both reactions 1 and 2 proceed faster at higher temperatures and require a certain time period to complete.

The formation of thin BN nanotubes is also associated with special growth of the BN phases. XRD patterns in Figures 3a and 4a all show a broadened (002) BN peaks and relatively low diffraction intensity, suggesting a small crystallite size, even though EDS has confirmed that all B has been converted to BN after heating at 1200 °C for 16 h. The crystallite size of the BN phase is estimated by measuring the diffraction peak width at half-maximum (fwhm) of the (002) peak using the Scherrer equation,  $d = 0.89\lambda/(\beta \cos \theta)$  where  $d$ ,  $\lambda$ ,  $\beta$ , and  $\theta$  are the crystallite size, X-ray wavelength, the width of the peak, and the Bragg angle, respectively.<sup>21</sup> Figures 5a and 5b show the changes of the BN crystallite size under different annealing conditions. It is interesting that the crystallite size of the BN phases is around 10 nm (close to the diameter of BN nanotubes) and does not change much with the increase in annealing temperature and times. It also reveals that the thin nanotubes formed in  $\text{NH}_3$  gas maintain the same diameters and are stable under high temperatures and extended annealing. Higher annealing temperatures and longer times only improve the nanotube yield. These results might suggest that BN formation during annealing is the growth of a large number of BN (002) layers and some of them roll into nanotubes instead of formation of three-dimensional hexagonal structure under these conditions. The growth process of the thin nanotubes is controlled by the nitriding reaction instead of

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the crystal growth as in the case of the BN nanotubes formed in N<sub>2</sub> gas. They grow thicker and longer at higher temperatures or after extended annealing. These results suggest a new and very different formation mechanism of the thin BN nanotubes: in situ two-dimensional (2D) growth of thin BN nanotubes during the nitriding reaction between B and NH<sub>3</sub> gas.

Metal particles are critical catalysts for nanotube formation especially for bamboo nanotube growth in many syntheses methods,<sup>9,20</sup> but in the current case of thin BN nanotubes, metal particles do not act as catalysts as no iron particles were found inside the nanotubes by TEM observation. Indeed, noncatalytic synthesis of BN nanotubes have been reported by Lee et al.<sup>22</sup> and Tang et al.<sup>23</sup> To identify the role of metal particles, a new milling experiment using a vibration mill<sup>24</sup> with an agate bowl and an agate ball was conducted. After milling for 150 h, the milled boron powder was annealed at 1200 °C for 6 h under NH<sub>3</sub> gas. Both SEM and TEM found some thin BN nanotubes without containing any metal catalysts. EDS analysis did not detect any metal content in the sample. Detailed results on the nanotubes

produced and relevant formation mechanisms without metal catalysts will be published later.

### Conclusions

Thin boron nitride nanotubes with a diameter less than 10 nm have been produced by using a ball milling–annealing method in which amorphous boron was first ball-milled for 150 h in a NH<sub>3</sub> atmosphere and subsequently annealed in NH<sub>3</sub>. The BN nanotubes have well-defined cylindrical structures and do not contain any metal particles. No other structures such as bamboo tubes were found. It suggests that boron nitride nanotubes can be formed without metal particles acting as a catalyst. Higher yield of BN nanotubes can be achieved by using higher annealing temperatures and longer annealing times. The thin multiwalled nanotubes were formed during the nitriding reaction and due to 2D growth of BN phases.

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