

# A Facile Sulfur Vapor Assisted Reaction Method To Grow Boron Nitride Nanorings at Relative Low Temperature

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Boron nitride (BN) nanorings were synthesized using a sulfur vapor assisted solid-state method at 600 °C. The rings had typical diameters of 100–300 nm, and the shells were 5–20 nm thick and about 50 nm wide. On the basis of the characterization of X-ray powder diffraction pattern (XRD), X-ray photoelectron spectroscopy (XPS), and Fourier transformation infrared spectroscopy (FTIR) measurement, the as-prepared product was pure-phase hexagonal BN. High-resolution transmission electron microscopy (HRTEM) images proved that the nanorings were formed through the coiling of the (002) planes of hexagonal BN. A possible growth process for BN nanorings is suggested.

## Introduction

Since the discovery of carbon nanotubes,<sup>1</sup> one-dimensional materials have become the focus of intensive recent studies because of their wide potential applications in electronics, optics, and mechanics.<sup>2,3</sup> There has been a great deal of interest in the preparation and characterization of nanotubes,<sup>4,5</sup> nanowires,<sup>6,7</sup> nanorods,<sup>8,9</sup> nanocables,<sup>10,11</sup> nanofibers,<sup>12,13</sup> and nanobelt<sup>14,15</sup> in recent years.

Boron nitride (BN) is one of the most interesting non-oxide materials with a potentially bright future in advanced materials design<sup>16</sup> and exists in several forms. Hexagonal BN (hBN) and cubic BN (cBN) are the two main forms. hBN, having hexagonal structure similar to that of graphite, consists of sp<sup>2</sup>-bonded layers. The lattice constants of hBN ( $a = 2.504 \text{ \AA}$ ,  $c = 6.656 \text{ \AA}$ )<sup>17</sup> are very close to those of graphite ( $a = 2.470 \text{ \AA}$ ,  $c = 6.790 \text{ \AA}$ ).<sup>18</sup> These form the basis of growing a one-dimensional nanostructure. Furthermore, the desirable mechanical, electronic, thermal, and chemical properties of hBN make it an important material in some specific application fields of nanoscience and nanotechnology. Until now, various methods have been used for the preparation of BN one-dimensional materials, by arc discharge,<sup>19</sup> by chemical vapor deposition (CVD),<sup>20</sup> by template-based synthesis,<sup>21</sup> by co-pyrolysis method<sup>22</sup> to grow BN nanotubes, by B<sub>4</sub>N<sub>2</sub>O<sub>3</sub> precursors to grow BN nanocages,<sup>23</sup> and by synergic nitrogen source to grow BN vessel and hollow sphere nanostructures.<sup>24</sup> However, there are few reports on the synthesis of BN nanorings. Nanorings are an important category of fullerene-like structures, to which particular attention should be addressed. Also, they may have novel physical and chemical properties within these particular one-dimensional materials. In this paper, we report some novel BN nanorings synthesized through a sulfur vapor assisted solid-state reaction method at the temperature of 600 °C.

## Experimental Section

First, 0.31 g of H<sub>3</sub>BO<sub>3</sub> (A.R.), 0.17 g of Li<sub>3</sub>N (C.P.), and 0.16 g of S (C.P.) were pressed together into a pellet. The pellet was placed into a quartz tube. After being under vacuum and

charged with Ar to 1 atm, the tube was heated to 600 °C and kept for 1 h. After the growth, the sample was cooled to room temperature. The product was filtered with CS<sub>2</sub> and water to remove the byproducts, separately. Finally, the BN was obtained.

The X-ray powder diffraction (XRD) pattern was recorded on a Rigaku D max- $\gamma$ A X-ray diffractometer with Ni filtered Cu K $\alpha$  radiation. The X-ray photoelectron spectroscopy (XPS) was performed on an ESCALAB 2200-XL X-ray photoelectron spectrometer. Fourier transformation infrared spectroscopy (FTIR) measurement was carried out using a Nicolet FTIR760 infrared spectrometer. About 3–5% (in weight) samples were mixed with KBr and ground thoroughly, and then they were pressed into a thin pellet for characterization. Field emission scanning electron microscopy (FESEM) was taken on a JSEM6700F (JEOL) field emission scanning electron microscope. High-resolution transmission electron microscopy (HRTEM) images were taken with a Philips Tecnai 20U-Twin high-resolution transmission electron microscope. The accelerating voltage was 200 kV.

## Results and Discussion

**Composition of the Sample.** Figure 1 shows the typical XRD patterns of BN nanorings. All of the diffraction peaks could be indexed as hBN with lattice constants of  $a = 2.495 \text{ \AA}$  and  $c = 6.702 \text{ \AA}$ , consistent with the reported values of the literature  $a = 2.504 \text{ \AA}$ ,  $c = 6.656 \text{ \AA}$ .<sup>17</sup> The prominence of the (002) peak indicates the presence of well-stacked layered structures in hBN. No impurities such as B<sub>2</sub>O<sub>3</sub> were detected by the XRD.

The composition of the as-prepared hBN could also be derived from the XPS spectra (Figure 2). Figure 2 is a typical survey spectrum of the hBN nanorings, which indicates the presence of B and N elements. The appearance of C and O is due to the adsorption of CO<sub>2</sub> and O<sub>2</sub> onto the surface of the sample. The binding energy of B1s with 190.2 eV and that of N1s with 398.0 eV are consistent with the reference value.<sup>25</sup> Quantification of the peaks gives the atomic ratio of B to N of 1.05:1, from which we can conclude that the sample is BN. Figure 3 shows the typical FTIR spectra of the hBN nanorings, in which two strong characteristic peaks positioned at 1384 and 815 cm<sup>-1</sup> are observed. The broad peak at 1384 cm<sup>-1</sup> is a

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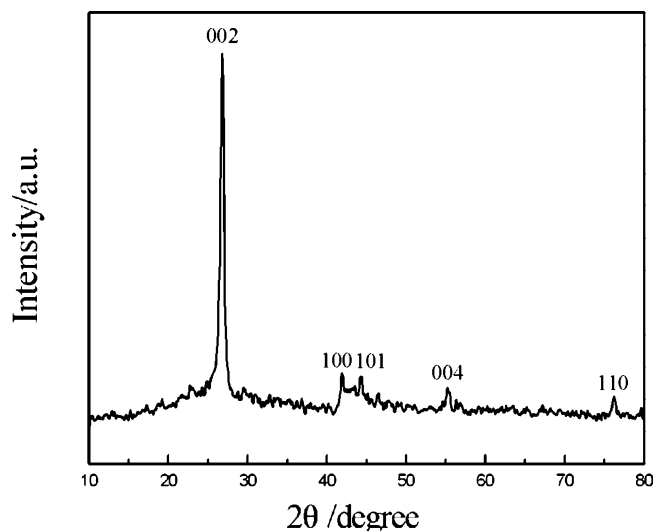


Figure 1. XRD pattern of the synthesized hBN nanorings.

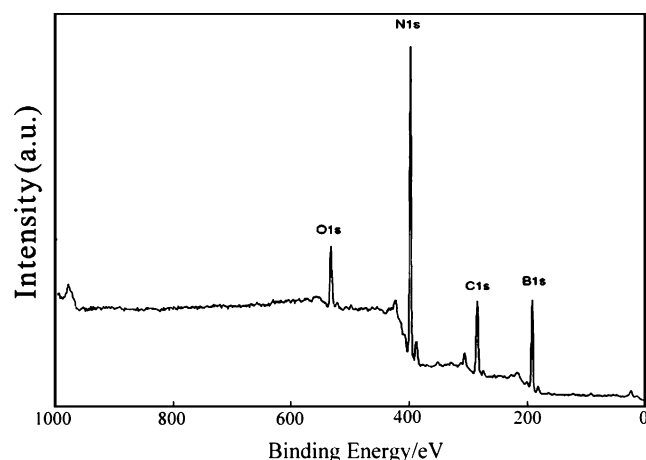


Figure 2. XPS spectra of hBN nanorings.

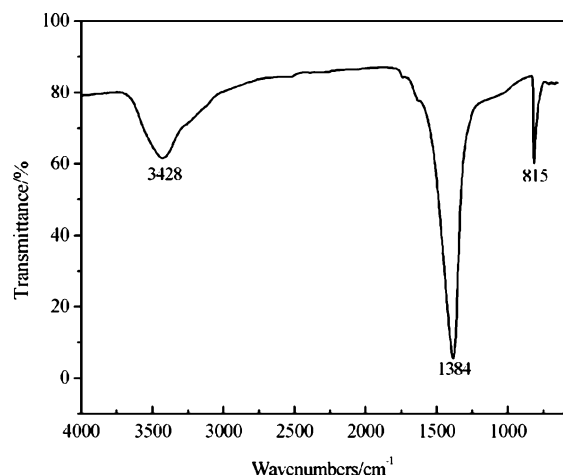


Figure 3. FTIR spectra of the obtained hBN nanorings.

stretching of the B–N bond within the basal plane of the  $sp^2$ -bonded hexagonal BN, while the absorption band of the sharp, weak peak at  $815\text{ cm}^{-1}$  could be attributed to the bending of the B–N–B bond between the basal planes.<sup>16</sup> The peak around  $3428\text{ cm}^{-1}$  can be attributed to the water molecules absorbed on the surface of BN nanorings. On the basis of the above characterization of XRD patterns, XPS, and FTIR spectra, the as-prepared product is pure-phase hBN.

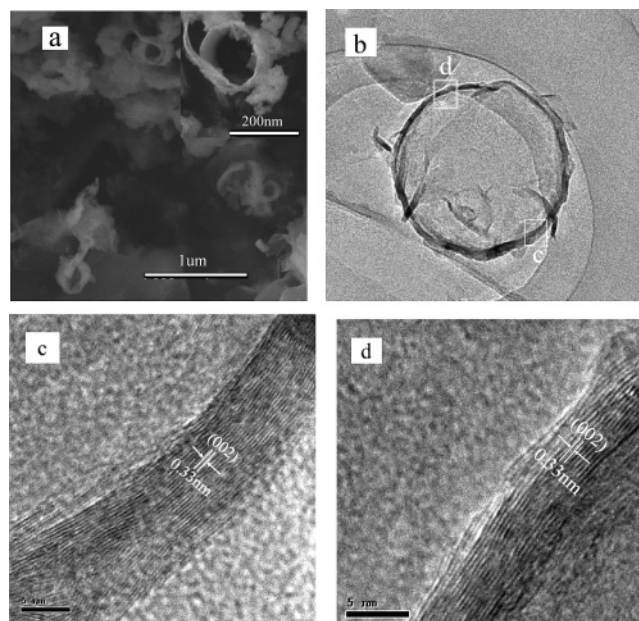


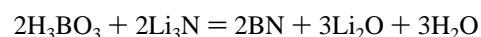
Figure 4. (a) SEM image of the as-synthesized hBN nanorings. The inset is the high magnification SEM image of a free-standing BN nanoring, showing uniform and perfect geometrical shape. The ring diameter is 100–300 nm, the thickness of the ring is 5–20 nm, and the width of the ring shell is about 50 nm. (b) TEM image of a separate nanoring. (c) and (d) HRTEM image corresponding to the separate nanoring.

**Morphologies and Structures.** FESEM, TEM, and HRTEM images of the as-synthesized hBN are shown in Figure 4. Figure 4a shows the FESEM images of hBN and exhibits its ring-like morphology. The as-synthesized hBN is composed of many nanorings. Also, two types of rings have been found in the sample. One type is that the ring has nearly circular shape. The rings have typical diameters of 100–300 nm, and the shells are 5–20 nm thick and about 50 nm wide. The inset SEM images recorded at high magnification clearly show the perfect circular shape of the complete rings. The other type is that the ring is not entirely closed.

Figure 4b shows the TEM image of a separate hBN nanoring. The ring diameter is about 300 nm, and the thickness is 15 nm. Figure 4c and d shows the lattice images of the parts marked with c and d in Figure 4b. The interplanar spacing of 0.33 nm corresponds to the distance between the (002) planes of hBN. This indicates that nanoring is formed through the coiling of the (002) planes of hBN.

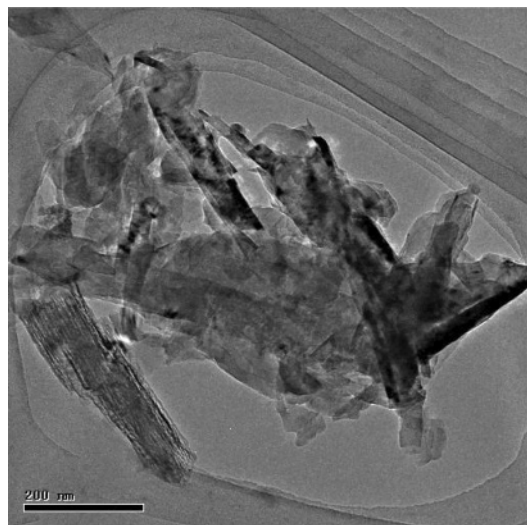
From the above analysis about the nanorings, we suggest a possible growth mechanism of BN nanoring as follows.

(1) The formation of hBN belts: hBN can be synthesized through the reaction between  $\text{H}_3\text{BO}_3$  and  $\text{Li}_3\text{N}$  without sulfur added at the same reaction conditions as the above. The reaction could be described by the following equation:

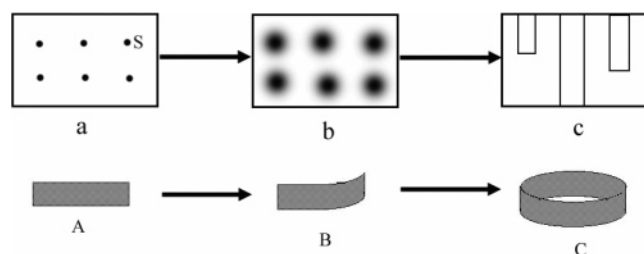


Although we can obtain hBN through this equation, the morphology of the products is very different from that of nanoring. In these reaction conditions, most of the particles of the product are belt or sheet structures (as shown in Figure 5).

(2) Growth mechanism of hBN nanoring: In many ways analogous to carbon, boron nitride forms both hard, diamond-like  $sp^3$ -bonded phases and softer, graphite-like  $sp^2$ -bonded phases. hBN is a layered structure that is similar to graphite with the exception that hexagonal rings of the basal planes in



**Figure 5.** TEM image of the hBN nanobelts through the reaction between  $\text{H}_3\text{BO}_3$  and  $\text{Li}_3\text{N}$ .



**Figure 6.** A possible growth process of hBN nanorings: (a) a pellet; (b) S vapor expand in the pellet; (c) holes left in the pellet; (A) a hBN nanobelt; (B) a curved belt under the force of the S vapor; (C) a nanoring.

hBN are positioned directly above each other and rotated  $180^\circ$  between alternate layers. Also, there are van der Waals interactions between the layers. Thus, the structures such as tubes and rings are basically determined by the layer structures of hBN. Under certain conditions, pieces of graphite sheet would have many dangling bonds; they would have little reason to remain flat, and the physical tendency to reach the lowest energy level would induce the sheets to eliminate their dangling bonds by curling up.<sup>26</sup> The interaction of the lamellar interlayers could be diminished from the edges, and the rolling process could proceed. According to the previous research about graphite,<sup>27</sup> the graphite layers could curl with the assistance of various driving forces. Thus, we conclude that the hBN nanorings may be formed by the rolling of the lamellar hBN structures with the assistance of the driving forces. We find that belt or sheet structures of hBN could only be gained through the reaction between  $\text{H}_3\text{BO}_3$  and  $\text{Li}_3\text{N}$  without S added. However, when S was added in the reaction, the hBN nanoring can be obtained. Thus, S plays an important role in the formation of hBN nanoring. Figure 6 shows a possible growth process for hBN nanorings. The reactants including  $\text{H}_3\text{BO}_3$ ,  $\text{Li}_3\text{N}$ , and S were pressed together into a pellet (Figure 6a). When the temperature was raised, S can turn into vapor in the pellet and the vapor

will expand in the sealed system (Figure 6b). The expanding vapor can provide a momentary driving force for rolling of the hBN layers (Figure 6A and B). Furthermore, after the vapor escaped from the pellet, some holes are left in the pressed pellet (Figure 6c). The hBN belts can encircle along this hole and form a ring structure (Figure 6C).

## Conclusions

In summary, hBN nanorings of 100–300 nm in diameter, 5–20 nm in thickness, and 50 nm in width were synthesized by a sulfur vapor assisted solid-state method at 600 °C. The nanoring was formed through the coiling of the (002) planes of hexagonal BN. Sulfur plays an important role in the formation of hBN nanoring. The sulfur vapor can provide a momentary driving force for rolling of the hBN layers when sulfur sublime. Furthermore, the hBN belts can encircle along the holes that were left after the sulfur vapor escaped and form a ring structure.

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