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Facile Synthesis of High-Quality Nano-Size ^{10}B-Enriched Fibers of Hexagonal Boron Nitride

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Abstract: The interesting properties of hexagonal boron nitride (h-BN) and its potential uses in thermo-structural advanced applications have been limited or restricted by its inherent brittleness, which can easily be eliminated by its fibers (h-BN) in nanoscale dimensions. The current study is based on the synthesis of nanoscale ^{10}B-enriched fibers of h-BN (^{10}BNNFs) from ^{10}B in the precursors instead of B in two-hour annealing at 900 °C and one-hour growth at 1000 °C. All of the ^{10}BNNFs are randomly curved and highly condensed or filled from ^{10}h-BN species with no internal space or crack. XRD peaks reported the ^{10}h-BN phase and highly crystalline nature of the synthesized ^{10}BNNFs. ^{10}h-BN phase and crystalline nature of ^{10}BNNFs are confirmed from high-intensity peaks at 1392 (cm^{-1}) in Raman and FTIR spectroscopes.

Keywords: enriched-boron; annealing; growth-duration; synthesis; ^{10}BNNFs

1. Introduction

Nanofibers have a large surface area and porous structure due to which it has characteristic properties suitable for a variety application in the field of environmental sciences, automotive industries, smart textile and biomedical, etc. [1].

Boron nitride (BN) is an important material known as an artificial non-oxide ceramic. Hexagonal or cubical are the most commonly available phases of BN. Both of these polymorphs have interesting properties: high-temperature stability, high electric insulation, the low dielectric constant, large cross-section for thermal neutron and resistance to oxidation at high temperature, etc.[2–4]. Among all polymorphs of BN, hexagonal boron nitride (h-BN) is more interesting due to its stability and ease of synthesis or production. However, the inherent brittleness is the only drawback of h-BN which restricts its use in thermos structural advanced applications [2,5]. The brittleness issue can be resolved by preparing h-BN in fibers. Afterward, it can be used as composite materials. Such composites have all the interesting properties of nanoscale materials of h-BN. However, the first step in making such composites is the synthesis of h-BN fibers (BNFs), which are commercially not available in the market [5]. Because of this goal, many researchers have focused on developing a reliable technique for producing fibers of h-BN. Nanosize fibers of h-BN (BNNFs) were claimed with boron oxide as a precursor. For the increased spin ability, polyvinyl butyral (PVB) was added to the solution. The pyrolyzation of the as-formed product resulted in the synthesis of BNNFs with a diameter under 100 nm [6]. Next time, electrospun polyacrylonitrile (PAN) was coated with boron oxide solutions to form BNNFs [7]. Oxygen contents in the final product was one of the very serious issues related to the above techniques. Polyborazine/polyacrylonitrile blend solutions were also used as precursors for the synthesis of BNNFs [8]. The health-risky nature of the precursors and the complexity of the experimental procedure were some of the main problems associated with the above technique. Boric acid and melamine-based polymeric precursors had been used to synthesize BNFs with lengths in the range of 200–500 μm and diameters of 1–2 μm. The adopted procedure was claimed to be cost-effective, simple, and notified to form pure BNFs [2]. However, unlike the claim, the procedure was found to be complex and lengthy with carbon- and nitrogen-based compounds as impurities in the final product. The as-found impurities were almost impossible to eliminate even at a higher temperature of 1600 °C.

Regardless of the pros and cons of the above techniques, a simple and cost-effective technique was needed to synthesize fibers of h-BN. The fibers of h-BN needed to be not only pure and nanoscale but also ^{10}B-enriched.

^{10}B is one of the stable isotopes of Boron, which has a thermal neutron cross-section of 3840b. The daughter nuclei of ^{7}Li and ^{4}He are produced when a thermal neutron is captured by ^{10}B according to the nuclear reactions given as below [9,10]:

$$^{10}B + n \rightarrow {}^{7}_{3}Li + {}^{4}_{2}He \qquad 2.792\ \text{MeV (ground state) } 6\ \% \tag{1}$$

$$^{10}B + n \rightarrow {}^{7}_{3}Li + {}^{4}_{2}He \qquad 2.310\ \text{MeV (excited state) } 94\ \% \tag{2}$$

^{10}B-enriched nanofibers of h-BN (^{10}BNNFs) are large bandgap semiconductors. The emitted daughter's nuclei when accelerated into the semiconductor layer of ^{10}BNNFs produce electron-hole pairs. These pairs, when detected by their respective electrodes, can be shown in the form of electrical signals. Thus, ^{10}BNNFs can be a potential element in solid-state neutron detectors like ^{10}BNNTs [11] and other nuclear feeding activities. In this reference, it can also be a useful material in boron neutron capture therapy (BNCT), biomedical and drug delivery, etc.

The method for the synthesis of ^{10}BNNFs in the current study can be traced back to the Boron oxide chemical vapor deposition (BOCVD) technique for the synthesis of BNNTs. In BOCVD, Boron (B) and Magnesium oxides (MgO) were developed as carbon-free precursors for the synthesis of BNNTs in high quality [12]. The BOCVD precursors for the BNNTs synthesis were further developed by the addition of iron oxides (FeO). As a result, the mixture of B, MgO, and FeO was developed as effective precursors. The precursors resulted in the synthesis of high-quality of BNNTs [13]. The as-introduced precursors were obtained in nano-size with γ-Fe_2O_3 instead of FeO. Such a precursor's mixture has successfully been optimized for the synthesis of nanotubes, nanowires, nanosheets, and microtubes, etc., of h-BN [14]. The optimization also resulted in a simple technique for the synthesis of BNFs. The work on the synthesis of BNNTs showed that the replacement of B by ^{10}B resulted in enriched boron nitride nanotubes (^{10}BNNTs) [15]. The logics of ^{10}BNNTs and BNFs lead to the synthesis of enriched boron (^{10}B) nitride nanofibers. The detail of the methodology thus developed for the synthesis of ^{10}BNNFs is given in the next section.

2. Materials and Methods

A 100 mg mixture of Magnesium oxides (MgO) and Iron Oxides in a 1:1 ratio is uniformly mixed with enriched Boron (^{10}B) powder of 100 mg in weight. The mixture is put in an alumina boat and annealed in the Argon atmosphere at 900 °C for 2-hours. Afterward, the annealed mixture in the boat is partially covered via a few Silicon (Si) substrates and pushed inside one end closed quartz tube already placed in the quartz tube chamber (beneath the heating filament) of the horizontal tube furnace. The furnace is seal closed and afterward flushed with Argon gas with a flow rate of 100 sccm. Consequently, the furnace is programmed to heat the precursor's mixture with a heating rate of 10 °C/min. During heat-up, Argon gas flow (100 sccm) is maintained as a source of an inert atmosphere. In such a condition, the precursor's mixture is heated up to 800 °C [16]. At 800 °C, NH_3 (200 sccm) is introduced into the system as a reactive gas. Under such a condition, the precursor's mixture is further heated up to 1000 °C. Growth of the final material was assumed to occur at 1000 °C. Therefore, 1000 °C is fixed as the final temperature. At the final temperature, the system is maintained for 1-hour to complete the growth. Subsequently, the reactive gas (NH_3) flow is stopped whereas the inert (Argon) atmosphere was maintained till the system was brought to room temperature.

3. Results and Discussions

B, MgO, and FeO were introduced as effective precursors for the synthesis of BNNTs [13]. The replacement of enriched Boron (^{10}B) in the precursors with MgO and γ-Fe_2O_3 in the precursors resulted in the synthesis of enriched Boron nitride nanotubes (^{10}BNNTs)[15]. Along with the precursors, variations in the experimental parameters have also been found to play a crucial role in the synthesis of different nano (10^{-9}) or micro (10^{-6}) structures of hexagonal boron nitride (h-BN)[14,17]. As a strategy, experimental procedures were successfully optimized in two stages of annealing and growth duration. As a result, a technique was developed for the synthesis of micron-scale fibers of h-BN [18]. In that technique, the precursor's mixture (B, MgO, and γ-Fe_2O_3) was first annealed (in the inert atmosphere) for two hours at 900 °C. Afterward, the annealed mixture was first softened in the Argon atmosphere up to 800 °C. The growth was initiated at 800 °C with NH_3 as a reactive gas and then continued for two hours at 1000 °C [18]. In the present work, the goal was to synthesize not only fibers of h-BN in nano-size but also ^{10}B-enriched. Therefore, changes had to be brought not only in precursors but also in the experimental parameters. As for precursors, ^{10}B was introduced as a precursor with MgO and γ-Fe_2O_3 instead of Natural B whereas, for the reduction of size, the growth duration was reduced to one hour instead of two. The rest of the procedure remains the same as for the synthesis of micron size BNFs [18]. The changes result in the synthesis of high-quality nano-size ^{10}B-enriched fibers of h-BN (^{10}BNNFs). Figure 1 shows the as-synthesized ^{10}BNNFs characterized by Field emission scanning electron microscopy (FESEM). Figure 1a shows a relatively lower magnification micrograph of the as-synthesized ^{10}BNNFs. All of the ^{10}BNNFs are randomly curved and dispersed at the top of the Si-substrate. In general, the ^{10}BNNFs create a view of cooked noodles from the top. All the ^{10}BNNFs are of variable size or diameter in the range of greater than 20 nm and smaller than 100 nm. The smaller size ^{10}BNNFs lay among or beside larger size ^{10}BNNFs. Some of them seem to stick with others and form clusters. The region with a cluster-like appearance is further magnified and viewed in higher magnification as shown in Figure 1b. In a higher magnification micrograph, most of the ^{10}BNNFs seem isolated. A cluster-like appearance is a place in the micrograph where a higher density of smaller size ^{10}BNNFs is present. Both smaller and larger size ^{10}BNNFs have a variable diameter and randomly curved morphology with an average length of greater than five microns. No other species or morphologies can be seen in higher magnification. To internally look into the structure, the ^{10}BNNFs sample is analyzed with the help of a high-resolution transmission electron microscope (HRTEM).

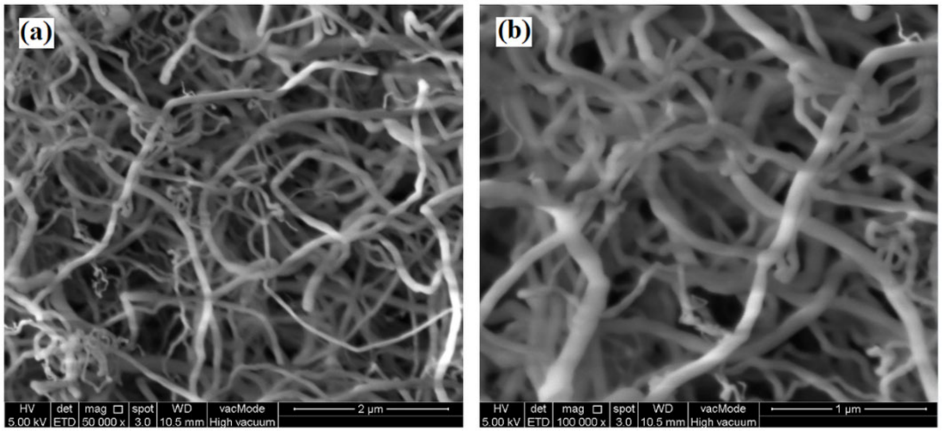

Figure 1. FESEM shows the apparent structure and morphology of the as-synthesized ^{10}B-enriched fibers of h-BN (^{10}BNNFs) in (**a**) low and (**b**) higher magnification.

Figure 2a shows an individual ^{10}BNNF from the as-synthesized ^{10}BNNF sample. The ^{10}BNNF looks like a round and solid concrete pillar, which is highly condensed or filled with no internal space or crack. The HRTEM shows a non-uniform or rough outer surface of the as-synthesized ^{10}BNNF. The rough or non-uniform outer surface confirms the non-uniform or variable diameter of ^{10}BNNF in the sample. To further confirm this fact and others, another ^{10}BNNF is arranged on the TEM copper grid and characterized via HRTEM. The micrograph of this ^{10}BNNF is shown in Figure 2b**.** It shows that the ^{10}BNNF is curved from various points. These curves in the structure confirm the curved morphology of the ^{10}BNNFs shown in Figure 1 via FESEM. Besides this, the ^{10}BNNF has a solid or condensed structure. However, the condensation of the ^{10}h-BN species in the current ^{10}BNNF is different from the one shown in Figure 2a. Unlike the previous, the ^{10}h-BN species in the current ^{10}BNNF seems to be condensed from out to inside. As a result of this condensation, the ^{10}BNNF attains a rope-like morphology. Some crack-like spots can also be seen near the center. However, these are not the cracks. These are the points where ^{10}h-BN species from different directions meet and construct the final morphology. All the condensed species have visible lattice fringes with an interlayer spacing of ~ 0.34 nm, as shown in the inset on the upper right hand of Figure 2b. According to the available literature, these layer spacings are the characteristics of the h-BN lattice with a highly crystalline nature [19].

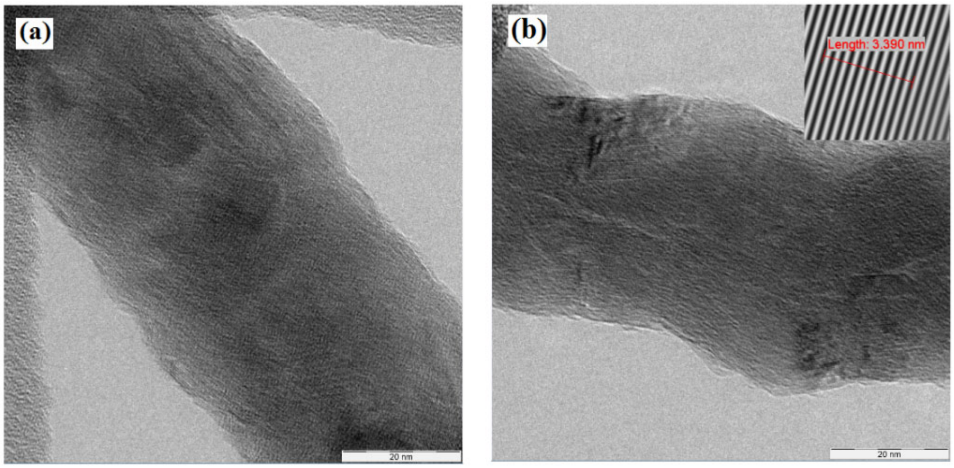

Figure 2. HRTEM micrographs show (**a**) a highly condensed or filled ^{10}BNNF with no internal space or crack, (**b**) curved ^{10}BNNF from various points with ^{10}h-BN species condensed from out to inside. The inset on the upper right-hand corner shows the interlayer spacing.

The possible plan for the formation (during different growth stages) of ^{10}BNNF due to condensation of ^{10}h-BN species is shown via a sketch in Figure 3 The sketch shows (a) the formation, (b) attraction or assembling (c) condensation, and finally (d) deposition of condensed ^{10}h-BN species on Si substrate forming ^{10}BNNF.

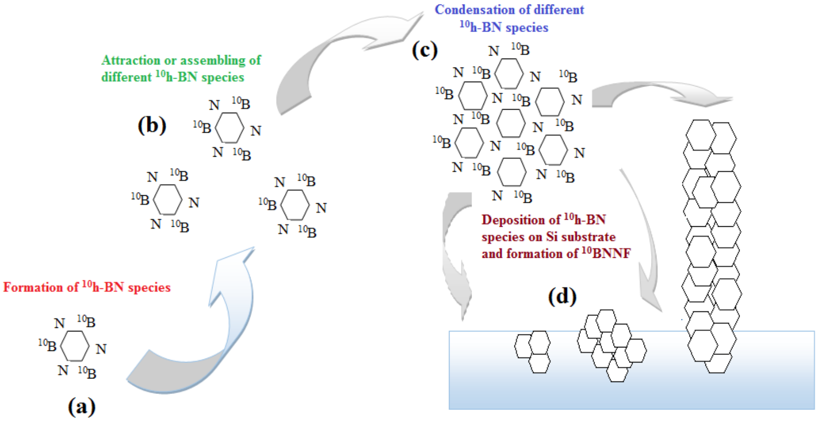

Figure 3. A sketch showing different growth stages (**a**–**d**) of the as-synthesized ^{10}BNNFs.

The compositions, crystalline nature, and phase of the as-synthesized ^{10}BNNF sample are checked with X-ray diffraction (XRD). The as-obtained XRD pattern is shown in Figure 4. The peaks in the XRD pattern are spotted at different 2-theta values of 26.7°, 41.8°, 43°, 55°, 76.2°. The sharp and high-intensity peak at 26.7° stands for (002) planes in ^{10}h-BN with a highly crystalline nature. The peaks with lower intensities reported at 41.8°, 43°, 55°, 76.2° correspond to (100), (101), (004) and (110) planes in ^{10}h-BN [13,20]. The intensities of the peaks on one side indicate the crystalline nature of the sample and on the other side reflect the higher number of planes in that particular sample. Based on this logic, the majority of planes present in the current ^{10}BNNF sample are (002).

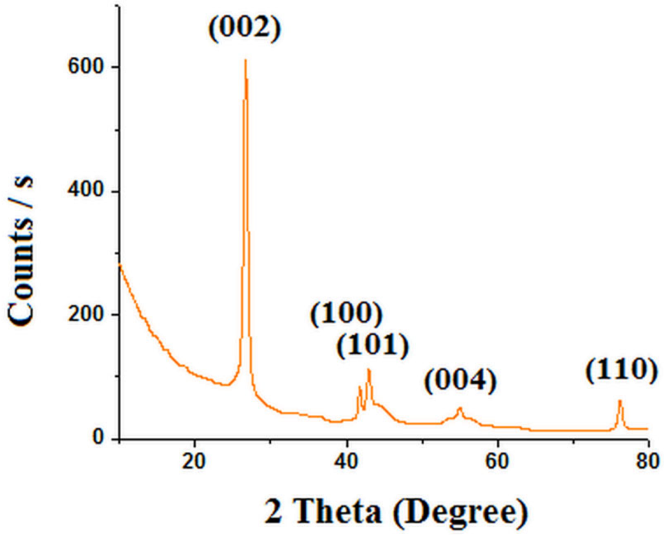

Figure 4. The as-obtained XRD pattern shows peaks for ^{10}h-BN contents of the as-synthesized ^{10}BNNFs.

Non-destructive Raman spectroscopy was used to further check the contents, phase, and crystalline nature of the synthesized ^{10}BNNFs. Raman spectroscopy of the sample is carried out in the spectral range of 800–1600 (cm^{-1}) with a laser beam with a wavelength of 514 nm. The obtained Raman spectrum of the sample is displayed in Figure 5. The spectrum shows a high-intensity peak in the displayed spectrum in 1392 (cm^{-1}). This high-intensity peak according to the available literature corresponds to the E_{2g} mode of vibrations in ^{10}h-BN (with B–10 content) or ^{10}BNNFs [15,21]. During Raman spectroscopy of the sample, a small peak can also be seen in the spectrum at 1150 (cm^{-1}). Such a lower intensity peak in the spectrum can be assigned to the formation of boric acid. It might have been formed due to sample exposure to oxygen in the air or $^{10}B_2O_3$ contents in the sample with laser interaction during Raman spectroscopy [22].

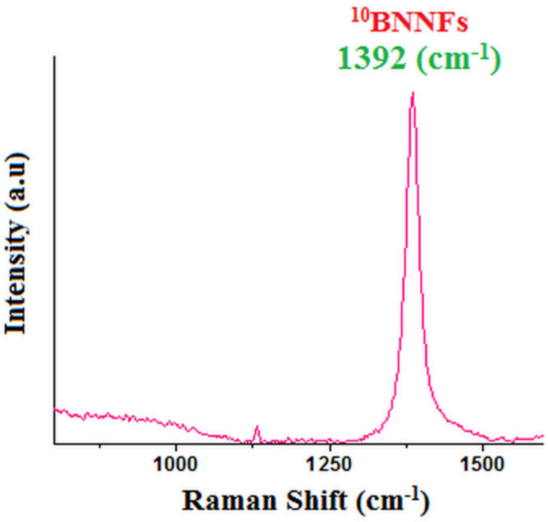

Figure 5. The spectrum shows a high-intensity peak in the displayed Raman spectrum at 1392 (cm^{-1}) for the synthesized ^{10}BNNFs sample.

Fourier transformed infrared (FTIR) spectroscopy of the ^{10}BNNF sample is performed in the spectral range of 400–3500 (cm^{-1}). The as-obtained FTIR spectrum is shown in Figure 6. The FTIR spectrum shows a lower intensity peak at 800 (cm^{-1}). It is a weak absorption and corresponds to an out-of-plane R-mode. In this mode of vibrations, Boron and Nitrogen atoms move radially in or outward. Along with lower intensity, a higher intensity peak was also spotted in the FTIR spectrum at 1392 (cm^{-1}). It is a strong absorption corresponds to in-plane stretching in ^{10}h-BN. In this mode, the atoms vibrate along longitudinal or tube axis called L-mode [21].

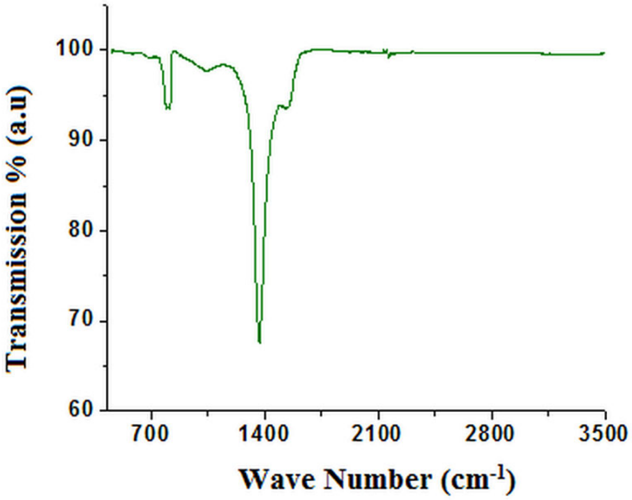

Figure 6. FTIR spectrum shows peaks correspond to "R" and L-mode of vibrations in ^{10}h-BN.

4. Conclusions

As the use of B, MgO, and γ-Fe_2O_3 as precursors mixture worked for the synthesis of nanotubes, nanowires, nanosheets, and microtubes, etc., of hexagonal boron nitride with different experimental parameters. Likewise, the same precursor's mixture with two hours annealing and two hours growth duration resulted in micron size fibers of hexagonal boron nitride. This is because the ^{10}B-enriched boron nitride nanotubes can be synthesized by using ^{10}B instead of B in precursors with MgO and γ-Fe_2O_3. Similarly, the same precursor's mixture (^{10}B, MgO, and γ-Fe_2O_3), with a growth duration of one hour instead of two, resulted in enriched nanoscale fibers of h-BN. ^{10}B enrichment, nanoscale properties, and semiconductor nature enable ^{10}BNNFs a potential material to be used as a sensing element in solid-state neutron detectors, BNCT and biomedical applications, amongst others

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References

1. Salles, V.; Bernard, S.; Brioude, A.; Cornu, D.; Miele, P. A new class of boron nitride fibers with tunable properties by combining an electrospinning process and the polymer-derived ceramics route. *Nanoscale* **2010**, *2*, 215–217.
2. Hou, X.; Yu, Z.; Chou, K.-C. Facile synthesis of hexagonal boron nitride fibers with uniform morphology. *Ceram. Int.* **2013**, *39*, 6427–6431.
3. Economy, J.; Anderson, R. Boron nitride fibers. *J. Polym. Sci. Part C Polym. Symp*. **1967**, *19*, 283-297.
4. Paine, R.T.; Narula, C.K. Synthetic routes to boron nitride. *Chem. Rev.* **1990**, *90*, 73–91.
5. Toury, B.; Bernard, S.; Cornu, D.; Chassagneux, F.; Letoffe, J.-M.; Miele, P. High-performance boron nitride fibers obtained from asymmetric alkylaminoborazine. *J. Mater. Chem.* **2003**, *13*, 274–279, doi:10.1039/B207476A.
6. Qiu, Y.; Yu, J.; Rafique, J.; Yin, J.; Bai, X.; Wang, E. Large-scale production of aligned long boron nitride nanofibers by multijet/multicollector electrospinning. *J. Phys. Chem. C* **2009**, *113*, 11228–11234.
7. Qiu, Y.; Yu, J.; Yin, J.; Tan, C.; Zhou, X.; Bai, X.; Wang, E. Synthesis of continuous boron nitride nanofibers by solution coating electrospun template fibers. *Nanotechnology* **2009**, *20*, 345603.
8. Bernard, S.; Ayadi, K.; Berthet, M.-P.; Chassagneux, F.; Cornu, D.; Letoffe, J.-M.; Miele, P. Evolution of structural features and mechanical properties during the conversion of poly [(methylamino) borazine] fibers into boron nitride fibers. *J. Solid State Chem.* **2004**, *177*, 1803–1810.
9. Li, J.; Dahal, R.; Majety, S.; Lin, J.; Jiang, H. Hexagonal boron nitride epitaxial layers as neutron detector materials. *Nucl. Instrum. Methods Phys. Res. Sect. A Accel. Spectrometers Detect. Assoc. Equip.* **2011**, *654*, 417–420.
10. Reed, B.C. *The Physics of the Manhattan Project*; Springer: Berlin/Heidelberg, Germany, 2010.
11. Ahmad, P.; Khandaker, M.U.; Amin, Y.M.; Khan, G.; Ramay, S.M.; Mahmood, A.; Amin, M.; Muhammad, N. Catalytic growth of vertically aligned neutron sensitive 10Boron nitride nanotubes. *J. Nanopart. Res.* **2016**, *18*, 25, doi:10.1007/s11051-016-3326-0.
12. Tang, C.; Bando, Y.; Sato, T.; Kurashima, K. A novel precursor for synthesis of pure boron nitride nanotubes. *Chem. Commun.* **2002**, 1290–1291, doi:10.1039/B202177C.
13. Zhi, C.; Bando, Y.; Tan, C.; Golberg, D. Effective precursor for high yield synthesis of pure BN nanotubes. *Solid State Commun.* **2005**, *135*, 67–70.
14. Ahmad, P.; Khandaker, M.U.; Khan, Z.R.; Amin, Y.M. Synthesis of boron nitride nanotubes via chemical vapour deposition: A comprehensive review. *Rsc Adv.* **2015**, *5*, 35116–35137, doi:10.1039/C5RA01594D.
15. Ahmad, P.; Khandaker, M.U.; Amin, Y.M. Synthesis of highly crystalline multilayers structures of 10BNNTs as a potential neutron sensing element. *Ceram. Int.* **2015**, *41*, 4544–4548, doi:10.1016/j.ceramint.2014.11.150.
16. Ahmad, P.; Uddin Khandaker, M.; Mohd Amin, Y.; Amin, M.; Imran Irshad, M.; Ud Din, I. Low temperature synthesis of high quality BNNTs via argon supported thermal CVD. *Ceram. Int.* **2015**, *41*, 15222–15226, doi:10.1016/j.ceramint.2015.08.102.
17. Ahmad, P.; Khandaker, M.U.; Amin, Y.M.; Muhammad, N. Synthesis of Highly Crystalline Multilayered Boron Niride Microflakes. *Sci. Rep. UK* **2016**, *6*, 21403.
18. Ahmad, P.; Khandaker, M.U.; Amin, Y.M.; Muhammad, N.; Khan, G.; Khan, A.S.; Numan, A.; Rehman, M.A.; Ahmed, S.M.; Khan, A. Synthesis of hexagonal boron nitride fibers within two hour annealing at 500 °C and two hour growth duration at 1000 °C. *Ceram. Int.* **2016**, *42*, 14661–14666, doi:10.1016/j.ceramint.2016.06.089.
19. Huang, Y.; Lin, J.; Tang, C.; Bando, Y.; Zhi, C.; Zhai, T.; Dierre, B.; Sekiguchi, T.; Golberg, D. Bulk synthesis, growth mechanism and properties of highly pure ultrafine boron nitride nanotubes with diameters of sub-10 nm. *Nanotechnology* **2011**, *22*, 145602.
20. Cai, P.; Chen, L.; Shi, L.; Yang, Z.; Zhao, A.; Gu, Y.; Huang, T.; Qian, Y. One convenient synthesis route to boron nitride nanotube. *Solid State Commun.* **2005**, *133*, 621–623.
21. Han, W.Q.; Yu, H.G.; Zhi, C.; Wang, J.; Liu, Z.; Sekiguchi, T.; Bando, Y. Isotope effect on band gap and radiative transitions properties of boron nitride nanotubes. *Nano Lett.* **2008**, *8*, 491–494.
22. Arenal, R.; Ferrari, A.C.; Reich, S.; Wirtz, L.; Mevellec, J.Y.; Lefrant, S.; Rubio, A.; Loiseau, A. Raman spectroscopy of single-wall boron nitride nanotubes. *Nano Lett.* **2006**, *6*, 1812–1816.