Insight into BN Impurity Formation during Boron Nitride Nanotube Synthesis by High-Temperature Plasma

Keun Su Kim, Gabriela Sigouin, Hyunjin Cho, Martin Couillard, Mary Gallerneault, Se Youn Moon, Hun Su Lee, Myung Jong Kim, Se Gyu Jang, and Homin Shin

ABSTRACT: The high-temperature plasma process has demonstrated great potential in growing high-quality boron nitride nanotubes (BNNTs) with small diameters (~5 nm) and few walls (3–4 walls) and led to successful commercialization with a high production rate approaching 20 g/h. However, the process is still accompanied by the production of BN impurities (e.g., α-BN, BN shell, BN flakes) whose physicochemical properties are similar to those of BNNTs. This renders the post-purification process very challenging and thus hampers the development of their practical applications. In this study, we have employed both experimental and numerical approaches for a mechanistic understanding of BN impurity formation in the high-temperature plasma process. This study suggests that the flow structure of the plasma jet (e.g., laminar or turbulent) plays a key role in the formation of BN impurities by dictating the transport phenomena of BNNT seeds (e.g., B droplets), which play an important role in BNNT nucleation. We discussed that the turbulence enhances the radial diffusion of B droplets as well as their interparticle coagulation, which leads to a significant reduction in the population of effective BNNT seeds in the BNNT growth zone (T < 4000 K). This results in the generation of unreacted BN precursors (e.g., B-N-H species) in the BNNT growth zone that eventually self-assemble into BN impurities. Our numerical simulation also suggests that a higher thermal energy input makes the flow more turbulent in the BNNT growth zone due to the elevated velocity difference between the plasma jet and ambient cold gas. This finding provides critical insight into the process design that can suppress the BN impurity formation in the high-temperature plasma process.

1. INTRODUCTION

Boron nitride nanotubes (BNNTs) are a class of one-dimensional (1D) nanostructure. Structurally, BNNTs are very similar to the better-known carbon nanotubes (CNTs), yet composed of hexagonal B-N networks. Due to the structural similarity, both BNNTs and CNTs exhibit extraordinary mechanical properties, while BNNTs are electrical insulators with many other attractive characteristics, including optical and infrared transparency, greater thermal stability (up to 900 °C in the air), neutron radiation shielding, as well as piezoelectricity. Therefore, BNNTs have been highly regarded as promising multifunctional materials and are poised to revolutionize materials technologies in a wide range of areas such as defense, aerospace, automotive, electronics, and biomedical sectors. Among various BNNT applications, the development of BNNT-reinforced nanocomposites has been one of the most dynamic research areas in the past decade. Thanks to their structural stability, chemical inertness, and lightweight, BNNTs hold a unique position as a filler material in the development of lightweight structural materials for extreme conditions. Many notable progresses have been reported so far for the fabrication of BNNT-polymer, -metal, -glass, and -ceramic nanocomposites. Since broader availability of BNNTs is essential for the full realization of their potential in such applications, a significant amount of effort has also been devoted to the research on their large-scale synthesis with high quality and purity.

Among various synthesis routes, recent notable progress has been achieved by high-temperature processes, including laser and thermal plasma processes. Thanks to their high temperatures and strong gradients in the thermofluid field, small diameter nanotubes are produced exclusively with high crystallinity. In particular, the thermal plasma process enabled the continuous processing of feedstock at large scales.
and thus led to the recent commercialization of BNNT.\(^\text{28}\) The thermal plasma process is based on the vaporization of feedstock containing boron species to produce B droplets that serve as nucleation sites for BNNT growth (Figure 1).\(^\text{6}\) It was proposed that BNNTs are produced from boron droplets via reactions with N-containing species, such as \(\text{N}_2\) (e.g., \(2\text{B} + \text{N}_2 \rightarrow 2\text{BN}\)).\(^\text{6}\) Historically,\(^\text{20}\) the BNNT growth by thermal plasma was largely deterred by the slow reaction kinetics of this nitridation process because it usually requires activation of \(\text{N}_2\) molecules into more reactive species (e.g., \(\text{N}\) radicals, vibrationally excited \(\text{N}_2\) (\(\nu\)) or \(\text{N}_2^+\) ions) to achieve a reasonable reaction rate. Thermal plasmas are capable of producing such species,\(^\text{27}\) yet they are stable only at high temperatures and recombined or de-excited into stable \(\text{N}_2\) molecules again at temperatures below 5000 K. Therefore, they are not available for the BNNT growth that takes place at a temperature range between 2300 and 4000 K.\(^\text{6}\) This challenge was largely addressed in our previous works,\(^\text{6,25}\) where hydrogen was introduced as a gas-phase catalyst that effectively stabilizes excited B or N species produced at high temperatures into B-N-H species (e.g., BH and NH radicals). These species are effective BN precursors due to their relatively weak bond strengths (e.g., BH bond, 314 kJ/mol) compared to \(\text{N}_2\) molecules (945 kJ/mol) and stability in the temperature range suitable for BNNT growth. The presence of such species turned out to significantly expedite the nitridation process of B droplets, resulting in a high-yield growth of BNNTs.\(^\text{25}\)

Despite the significant progress in improving the reaction kinetics, the plasma process still suffers from the production of BN impurities, indicating that the selectivity of the nitridation reaction needs to be further improved toward BNNTs. Those impurities are mainly amorphous BN (\(\alpha\)-BN) or turbostratic BN (\(\beta\)-BN) by-products and have very similar physicochemical properties to those of BNNTs. Therefore, it is not an easy task to separate them from as-produced BNNTs via post-purification methods. A method of multiple washes with various solvents has been reported,\(^\text{29}\) yet the whole process is chemical- and time-intensive. Treatments at very high temperatures (\(>900^\circ\text{C}\)) in the presence of water\(^\text{30}\) or halogen species (e.g., \(\text{Cl}_2\) or \(\text{Br}_2\))\(^\text{31}\) seem to be efficient alternatives obviating the necessity of the solvent washing step. However, such harsh processing conditions may cause serious damage or loss of BNNTs, resulting in a considerable yield and quality reduction. A more elegant solution would be if one could reduce or suppress the formation of such BN impurities during synthesis through a mechanistic understanding of their formation. However, the relevant study has been plagued by extreme synthesis conditions such as high temperature and its strong gradient, and thus still remains elusive. In the previous study of graphene synthesis by an induction thermal plasma, Pristavita et al. reported that the absence of recirculation eddies at the entrance of the reactor greatly improves uniformity in the particle size distribution and also suppresses the production of volatile compound impurities.\(^\text{32,33}\) Based on numerical simulation, they suggested that the long residence time of the particles trapped in the colder recirculation zones is responsible for the formation of volatile compounds. A geometry that eliminates recirculation eddies was proved to completely eliminate such impurities in the product. Although this is important progress in graphene synthesis and also provides some insight for other nanomaterial syntheses by thermal plasmas, a similar study on the BN system is limited.

In this study, we have employed both experimental and numerical approaches to understand the formation of BN impurities in the thermal plasma synthesis of BNNTs. First, a parametric study on a variety of plasma operating conditions (e.g., pressure, input power, gas flow rate) has been performed with optical emission spectroscopy (OES) to identify the key operating parameter, which dictates the formation of BN impurities. Through various materials evaluation techniques, including field emission scanning electron microscopy (FE-SEM), high-resolution transmission electron microscopy (HR-TEM), thermogravimetric analysis (TGA), and Fourier transform infrared (FT-IR) spectroscopy, our experimental study found that the formation of BN impurities is strongly affected by the thermal energy input (i.e., plasma power) with the existence of an optimum range, where the production of BN impurities is minimized. To understand our experimental findings, a numerical study via computational fluid dynamics (CFD) simulation was performed.

2. METHODS

2.1. BNNT Synthesis and Optical Emission Spectroscopy. BNNTs were synthesized by the hydrogen-assisted BNNT synthesis (HABS) method, as described in our previous work.\(^\text{6}\) Briefly, for the stable plasma generation, a commercial RF induction plasma torch (Tekna PS-50, Tekna Systems, Inc.) composed of a five-turn coil and a ceramic tube with an internal diameter of 50 mm was employed (Figure S1). In the parametric study, the plasma power was varied from 30 to 50 kW at an RF frequency of \(~3\) MHz (Lepel Corp.) while the gas flow rates were fixed: 3 slpm of carrier gas (Ar); 30 slpm of central gas (Ar); and 25/135/60 slpm of sheath gas (Ar/N\(_2\)/H\(_2\)). All of the synthesis experiments were preceded by a 1 h reactor preheating cycle and lasted with h-BN powder (99.5%, avg. 70 nm, MK-hBN-N70, M K Impex Corp.) injection for 4 h. In the presence of a high-temperature plasma jet, strong gradients, and fast materials transformation, stable feeding of feedstock is crucial to achieving reliable BNNT production.
The powder was released from a twin-screw powder feeder (K-Tron) and carried by argon gas (3 slpm) to the plasma torch. The powder was injected into the plasma jet through an injection probe located on the top of the plasma torch. The feed rate was about 0.8−1.0 g/min. The reaction products were collected from the collection chamber and characterized without further purification or treatment. To verify the chemical species generated, optical emission spectra were measured at \( Z = 0.38 \) m from the bottom of the plasma torch during the synthesis. A modular spectrometer (JAZ-EL200-XR1, Ocean Optics, with 1.7 nm FWHM resolution) was employed for the measurement over a wavelength range from 200 to 1025 nm. The emission light was collected through a hole in the graphite liner and transported to the spectrometer by an optical fiber (QMMJ-55-UVVIS-200/240-2PCBL-0.25, OZ Optics Ltd., with a core size of 200 \( \mu \)m). During the synthesis run, the temperature of the graphite liner was continuously monitored using a C-type thermocouple and measured as about 1000 °C, which is much lower than the sublimation temperature of graphite (4000 K). Accordingly, emissions from \( \text{C}_2 \) swan or \( \text{CH} \) band were not observed in our experiments. It has also been confirmed in our previous study that the carbon contamination by the presence of the graphite liner is not significant in our process.\(^6\)

### 2.2. Materials Characterization

Morphology of the BNNT samples produced under different conditions was analyzed by SEM (Hitachi, S-4700) and HR-TEM (FEI Titan cubed 80-300). The SEM samples were mounted on aluminum stubs using carbon tapes without gold coating. Each sample was analyzed with a 2 kV, 5 \( \mu \)A probe current at a working distance of 8 mm. TEM samples were prepared by dispersing a few milligrams of the as-produced samples in deionized water using bath sonication for 10 min. The solutions were deposited on a 200 mesh TEM copper grid coated with lacey carbon, and images were acquired at 300 kV. TGA (NETZSCH TG 209 F1 Iris) was carried out by heating a \( \sim 10 \) mg sample under an air atmosphere to 950 °C at a rate of 10 °C/min. The molecular structure of BN impurities was characterized by Fourier transform infrared (FT-IR) spectroscopy using an Agilent Cary 630 FT-IR spectrometer, with a diamond attenuated total reflectance (ATR) cell as the sample interface.

![Figure 2](https://acsomag.org/images/2021/27418-27429/27420.png)

Figure 2. BNNT samples synthesized with different plasma powers of 30, 35, 40, 45, and 50 kW. (a) Photos of the BNNT samples showing a morphology change with the plasma power. (b)−(f) SEM images of the BNNT samples. The sample produced at 35 kW exhibits the most clean and aligned BNNTs among the samples. (g) SEM image of unvaporized h-BN collected from the sample produced at 30 kW. The inset is its photo. The scale bar is 1 \( \mu \)m.
2.3. Thermo fluid Simulations. The thermo fluid fields inside the reactor were calculated using an in-house plasma code coupled with Ansys-Fluent. The plasma generation model was developed based on the magneto-hydrodynamic (MHD) theory that comprises conservation equations for mass, momentum, and energy, coupled with a set of Maxwell’s equations (Figure S1). To investigate turbulence effects, the Reynolds stress model was adopted. Although a more sophisticated turbulence model based on three-dimensional transient simulation may be needed for capturing multiscale eddies and their dynamic behaviors, such models are complicated and also computationally expensive. For this reason, the traditional turbulence models (e.g., k-ε model, RNG k-ε model, and Reynolds stress model) have also been widely employed in the modeling of various nanomaterials synthesis by thermal plasmas and provided important tools for analysis of turbulent phenomena with reasonable computational costs. Thermodynamic and transport properties of plasma gases (e.g., density, specific heat at constant pressure, viscosity, thermal conductivity, electrical conductivity, and radiation losses) were calculated under the local thermodynamic equilibrium (LTE) assumption. A particle-in-cell (PIC) approach was employed to simulate the injection and vaporization of h-BN feedstock in the plasma jet; however, subsequent chemical reactions that lead to the formation of BN precursors and nucleation of BNNTs were not taken into account due to the total lack of thermodynamic, transport, and reaction data for some B-N-H-containing species at high temperatures (1000–10 000 K). All of the simulations were carried out with several typical assumptions: (i) the plasma and the reaction stream are in an LTE state; (ii) the plasma is optically thin; (iii) two-dimensional axis-symmetry is assumed; and (iv) the electric charge effects are neglected. It is noted that assumptions (ii) and (iv) may not be valid if nucleation and growth of nanoparticles are considered. In the presence of a dense particle cloud, the plasma is not optically thin anymore, and the emission from the plasma can be absorbed by particles, potentially decreasing the radiative heat transfer. This may have an effect on the nucleation and growth of BNNTs by affecting the energy balance. In the thermal plasma process, particles are often charged either negatively by the free electrons in the plasma or positively by the electron emission mechanism such as thermionic emission, thus experiencing the Coulomb force from others. The details of charge balance on the surface will affect not only BNNT agglomeration but also their nucleation and growth. More details on the governing equations, computational domain, and boundary conditions can be found in the Supplementary Information (see Figure S2, Tables S1 and S2).

3. RESULTS AND DISCUSSION

3.1. Effect of Thermal Energy Input on the Formation of BNNTs and BN Impurities. A parametric study was performed on the plasma operating conditions of plasma power, reactor pressure, and gas flow rate, and it found that plasma power has the strongest effect on the macroscopic morphology (e.g., fibril- or sheet-like) of the BNNT sample produced. However, no significant change in the yield was observed for the power range considered. Although accurate purity assessment in a quantitative fashion is crucial for process optimization, the lack of reliable methods for the evaluation of BNNT materials is the current significant challenge. A high-temperature treatment can be employed to selectively remove impurities from the sample for BNNT purity evaluation; however, it has been demonstrated that complete removal of BN impurities without etching of BNNTs is currently not achievable. Thus, our discussion on purity is largely based on microscopy analysis. Figure 2a shows the morphologies of the BNNT samples produced with different plasma powers. At both low (30 kW) and high powers (50 kW), sheet-like
materials were produced, while more fibrous materials were produced in the intermediate power ranges (35−45 kW). The fibrous materials contain more BNNTs in a bundled form, as evident from their SEM images (Figures 2c−e and 3), while the sheet-like materials mainly consist of individualized BNNTs with more particulate impurities (Figure 2b,f). Those impurities seem to prevent BNNTs from bundling with each other. The low purity obtained with the low plasma power can be explained by its insufficient thermal energy in achieving the complete vaporization of the feedstock (i.e., h-BN powder). The sample is largely dominated by the unvaporized h-BN feedstock, as shown in Figure 2g. With the high power (e.g., 50 kW), additional thermal energy is available for the generation of abundant BNNT precursors from the complete vaporization of the feedstock. However, this sample also contains many nonfibrous particles (Figure 2b) similar to the sample produced at the low input power (Figure

Figure 4. Characterization of the BNNT samples synthesized with different plasma powers. (a) TGA graphs. (b) DTG graphs showing that the amorphous BN content increases as the plasma input power increases. (c) FT-IR spectra of h-BN feedstock and BN impurities separated by solvent wash. The peaks related to N−H and B−H bonds suggest that the BN impurities are B-N-H compounds. (d) BN impurity extracted by water wash. (e) SEM image of the BN impurity extracted. (f) SEM image of the h-BN powder (i.e., feedstock). The scale bar is 2 μm.

Figure 5. TEM analysis of the BNNT samples synthesized. (a)−(c) TEM images of the sample produced at 35 kW. (d) Size distributions of the boron particles (>50 nm) in the BNNT sample produced at 35 kW. (e)−(f) TEM images of the sample produced at 50 kW. The images show more impurities with polydisperse B particles (dotted white circles). (g) HR-TEM image of the BN impurities in the sample produced at 50 kW. The image exhibits the typical turbostratic nature of the BN impurities. (h) Size distributions of the boron particles (>50 nm) in the BNNT sample produced at 50 kW.
which is intriguing (see Figure S3 for higher magnification).

Further characterization was performed to better understand the nature of the impurities produced with the high plasma power. Figure 4a,b show the TGA and DTG graphs of the samples, respectively. The mass loss below 200 °C is mainly attributable to the desorption of water or organic vapors adsorbed from the air. It was discussed that the presence of defect sites on BN materials (e.g., α- or t-BN) and/or dangling functionalities facilitate such adsorption. A larger mass loss was observed with the sample produced with the high power, implying a higher content of defective BN materials in this sample. The broad peaks from 650 to 800 °C in the DTG graphs are due to the oxidation of elemental boron particles. The boron particles serve as nucleation sites (i.e., seeds) of BNNTs in this plasma process. This peak intensity decreases as the plasma power increases, indicating lower B contents in the samples produced at high powers. The event around 900 °C might be associated with the oxidation of defective BN by-products, such as α- or t-BNs because crystalline h-BN materials (e.g., feedstock or BNNTs) start to oxidize from 950 °C. It is interesting to see that the intensity of this peak strongly depends on the plasma input power. A high plasma power, this peak becomes more intense, suggesting a higher content of BN by-products (e.g., α- or t-BNs) in the sample. As the plasma power decreases, this peak becomes weaker, indicating a lower content of BN by-products, while the peak at 950 °C becomes stronger, implying that more crystalline BN impurities, such as untreated or partially-treated h-BN feedstock, are present in the sample. Both peaks are weak in the samples produced under the intermediate power range (35−40 kW), which is in line with the SEM observation. The molecular structure of the BN by-products was investigated using FT-IR spectroscopy. Figure 4c shows the FT-IR spectrum clearly shows absorption peaks corresponding to h-BN-like materials (e.g., B3N3 ring-like structure) such as the in-plane B-N stretching mode at 1390 cm⁻¹ and the out-of-plane B-N-B bending mode at 780 cm⁻¹. However, peaks associated with N-H and B-H bonds also appear near 3200 and 2260 cm⁻¹, respectively. This indicates that the BN by-products are defective BN materials passivated with hydrogen atoms, as illustrated in Figure 4c.

The detailed structural characteristic of the as-synthesized samples was also investigated by TEM. Figure 5a–c shows TEM images of the sample produced at 35 kW. A large quantity of BNNTs is observed with particulate impurities whose size ranges from 10 to 100 nm. Those impurities are mostly B particles produced from the dissociation of the feedstock, as shown in Figure 5b (arrows). The presence of other types of impurities with an irregular shape is also evident from Figure 5b (in a dotted circle), but their population is not high. The high-resolution TEM (HR-TEM) image (Figure 5c) confirms BNNTs have a tubular structure with a few walls (2−5 walls) and form bundles because their surfaces are relatively clean without attachment of large-sized impurities. The small debris on the tube surfaces might be from the sample
preparation. Figure 5e−g shows TEM images of the sample produced at 50 kW. Its low magnification image (Figure 5e) presents more impurities compared to the sample produced at 35 kW. BNNTs are also heavily coated with impurities, as indicated with arrows in Figure 5e. In this sample, B particles larger than 150 nm are often observed (see dotted circles in Figure 5e), broadening their size distribution, as shown in Figure 5d,h. Since the size of B particles plays an important role in the nucleation of BNNT,6,22,42 the increased polydispersity may have affected the growth of BNNTs. The crystallographic structure of the BN impurities observed in Figure 5f was also studied using HR-TEM. The impurities are composed of defective layers, which are stacked in random orientation (Figure 5g). The average distance between adjacent fringes is about 0.34 nm, corresponding to the d-spacing of the (002) plane of h-BN; thus, those impurities are typical turbostratic BNs.43,44

The main observation in the materials characterization is that the high-thermal energy input promotes the formation of α- or t-BN impurities and also increases the polydispersity of B particles, which may have an adverse effect on the nucleation of BNNTs. A plausible explanation for this new finding was further investigated in the next section using optical emission spectroscopy (OES) and numerical simulations via CFD simulations.

3.2. Thermofluid Field Analysis. The BNNT growth mechanism by thermal plasma includes homogeneous nucleation (e.g., B droplet formation), interparticle coagulation (e.g., B droplet growth), and heterogeneous nucleation (e.g., BNNT nucleation via interaction between B droplets and B-N-H species), which are largely dictated by the transport phenomena such as convection, diffusion, and thermophoresis in microsecond to millisecond time scales.68 Therefore, an understanding of the thermofluid fields (e.g., species, temperature, velocity, and turbulence fields) is very important for process optimization.

To investigate the effect of the plasma power on the generation of chemical species, emission spectra were measured at Z = 0.38 m from the top of the plasma torch and presented in Figure 6. In all cases, both atomic B (249.7 nm) and H (Hα at 656.2 and Hβ at 486.1 nm, respectively) lines46 were observed along with molecular emission bands from the BH (A1Π−X1∑, (0,0) and (1,1) bands at 433.1 nm and 436.7 nm) and NH (A3Π−X3∑, (0,0) and (1,1) bands at 336.0 nm and 337.0 nm) radicals,47 which are known as good BN precursors.25,48 Their intensities vary with plasma power, as their concentrations strongly depend on the plasma temperature. As the input power decreases, the intensity of the atomic B line decreases rapidly, as indicated in Figure 6e (in a dotted circle), which implies insufficient B vapor generation due to the poor evaporation of feedstock or rapid B droplet formation due to faster cooling of the plasma jet. The nucleation of B droplets from their vapors occurs at 4200 K.25,48 The OES measurement clearly shows that the thermofluid fields are largely affected by the plasma power and thus are studied in detail by numerical simulations.

Figure 7 shows the temperature and velocity fields inside the reactor calculated for different plasma powers ranging from 30

Figure 7. Thermofluid field analysis of BNNT synthesis by a high-temperature plasma process. (a) Temperature fields calculated with plasma powers of 30, 35, and 50 kW. (b) Velocity fields calculated with plasma powers of 30, 35, and 50 kW. (c) Axial temperature profiles. Z is the axial distance from the bottom of the plasma torch. (d) Axial velocity profiles. (e) Radial temperature profiles calculated at Z = 0.38 m. The dotted line indicates the temperature corresponding to the B droplet nucleation temperature. R is the radial distance from the reactor axis. (f) Radial velocity profiles calculated at Z = 0.38 m. (g) Residence times calculated with different plasma powers.
to 50 kW. In the simulation, the injection of h-BN feedstock and its subsequent vaporization were considered; however, dissociation of BN vapors, nucleation of B droplets, and the BNNT growth from their precursors have not been considered due to the complexity and lack of thermodynamic and reaction data. Since unvaporized h-BN feedstock was observed in the sample produced at 30 kW plasma power, we have investigated the evaporation efficiency using the numerical simulation. Unlike the experimental observation, our simulation predicted complete vaporization of feedstock for all of the cases. This is probably because dissociation of BN vapors into elemental B and N was not considered. Since the dissociation process takes additional energy from the plasma, the simulated plasma temperature inside the torch might be higher than that of the actual one, and thus a complete decomposition of feedstock was predicted.

With an insufficient thermal energy input (e.g., 30 kW), the plasma temperature cools down fast through the heat exchange with the reactor walls, as shown in Figure 7a,c,e. The predicted temperature at $Z = 0.38$ m already reaches the B nucleation temperature (4200 K) in the 30 kW case, which is in line with the OES measurement, where the atomic B line (249.7 nm) almost disappeared (Figure 6e). Such shrinkage of the high-temperature zone may lead to incomplete treatment of the feedstock and is supported by the SEM observation (Figure 2g). With additional thermal energy input, the high-temperature zone expands in both axial and radial directions, which is favorable for BNNT growth, providing more BNNT precursors through the complete vaporization of feedstock. This also lengthens the BNNT growth zone with the potential to extend the in-flight BNNT growth time.

However, it should be noted that the BNNT growth time is a function of both the growth zone length and the residence time of precursors. More thermal energy input usually accelerates the plasma jet toward the reactor exit due to the volume expansion (Figure 7b,d,f). Upon increasing the plasma power from 30 to 50 kW, the maximum plasma velocity increased from 29 to 59 m/s near the torch exit, as shown in Figure 7b,d. The elevated jet speed decreases the residence time of the BNNT precursors in the BNNT growth zone, and thus they may not have enough time to grow BNNTs. As shown in Figure 7g, the residence time estimated for the high power case (e.g., 50 kW, $t_{res} = 0.087$ s) is much shorter than that of the low power case (e.g., 30 kW, $t_{res} = 0.135$ s). The extra thermal energy input can extend the BNNT growth zone further; however, it also shortens the residence time of the precursors in the growth zone due to the increased plasma velocity. This may limit the effective growth of BNNTs. Thus, our simulation suggests that in the low power case (e.g., 30 kW), the BNNT growth is largely limited by the low vaporization efficiency of the feedstock and the small BNNT growth zone, while the short residence time in the BNNT growth zone would be the limiting factor in the high power case (e.g., 50 kW). This may explain to some extent why the polydispersion of B particles is enhanced as the plasma
power increases and its potential impact on the BNNT growth. A more fundamental mechanism should be elucidated.

3.3. Effects of Turbulence on BN Impurity Formation.

The turbulence in nanomaterial synthesis usually enhances the exchange of mass, momentum, and energy among precursors and thus significantly alters the transport phenomena in the nucleation of nanomaterials and their subsequent growth.\textsuperscript{49,50} The RF plasma torch is generally known to produce a stable and laminar plasma jet, thanks to the absence of the arc fluctuation prevailing in the DC plasma torch.\textsuperscript{50} However, the plasma jet always interacts with the ambient cold gas downstream of the torch nozzle, which makes the flow fluid-dynamically unstable. This dynamic flow usually leads to a complex distribution of nanoparticles in morphology and composition.

To study the effects of thermal energy input on turbulence, the ratios of turbulent to laminar viscosity ($\mu_t/\mu_l$) are calculated\textsuperscript{11} for different plasma powers and presented with the effective BNNT growth zones (i.e., $2300 \text{ K} < T < 4200 \text{ K}$) in Figure 8a–c. Higher ratios indicate that the transport phenomena are largely dictated by the turbulent process. In all cases, the plasma cores and high-temperature zones ($T > 5000 \text{ K}$) exhibit less turbulent behavior because the gas viscosity (i.e., laminar or molecular viscosity) in those regions is one order higher than that at room temperature.\textsuperscript{50} The flow can be relaminarized by the increased gas viscosity at high temperatures despite the large velocity difference between the plasma jet and ambient gas (i.e., source of the turbulence). The intermediate or low-temperature regions become more turbulent as the relaminarization effect diminishes, as indicated in Figure 8d. It should be noted that although most of the BNNT precursors are formed at high temperatures, BNNTs do not grow until the temperature reaches the low to intermediate ranges ($2300 \text{ K} < T < 4200 \text{ K}$)\textsuperscript{2525} where the turbulence effect becomes important. It is highly likely that the turbulence may affect the BNNT growth. With the low thermal energy input (e.g., 30 kW), the flow still remains laminar in the BNNT growth zone, even though the turbulence is initiated around the boundary layers (Figure 8e). The turbulence was not fully developed at the center until the flow reached the end of the growth zone because the velocity difference between the plasma jet and ambient gas is not significant at the boundary (Figure 7d). However, as the plasma jet is further accelerated with more thermal energy input, a large velocity difference between the plasma jet and ambient cold gas takes place at their boundary layers, intensifying the turbulence (Figure 8f,g). At 50 kW, the turbulence is now strong enough to be fully developed even from the entrance of the BNNT growth zone (Figure 8g). Higher viscosity ratios near 10 prevail in the whole BNNT growth zone, indicating that the turbulence effect must be taken into account properly to understand the BNNT growth. Our key finding from the numerical simulations is that a higher thermal energy input makes the flow more turbulent in the BNNT growth zone due to the elevated velocity difference between the plasma jet and ambient cold gas.

Such fluctuation of the flow may enhance the radial diffusion of B droplets (e.g., eddy diffusion) just formed from their vapors,\textsuperscript{49,50,52} and thus reduces their concentration in the BNNT growth zone (Figure 4b). Since B droplets serve as active sites for BNNT nucleation, such diffusional loss is not favorable for the abundant nucleation of BNNTs. The turbulent flow also promotes the growth of particles via more frequent collisions (i.e., interparticle coagulation) because the collision frequency is a function of the local velocity gradient.\textsuperscript{49,50,52} Such agglomeration of particles not only reduces the B droplet concentration at downstream but also enhances the polydispersity in their size distribution. The latter would be a plausible explanation of our TEM observation, where higher thermal energy inputs (i.e., more turbulent flow) promote the polydispersity of B particles (Figure 5h). Large B droplets (e.g., >100 nm) formed by multiple coagulation processes are less reactive, eventually being unproductive BNNT seeds. Thus, both the radial
diffusion and interparticle coagulation enhanced by the turbulence may lead to a significant reduction in the number of effective BNNT seeds available in the growth zone. Consequently, more B-N-H precursors will remain unreacted in the BNNT growth zone. Those unreacted B-N-H precursors might be a direct source of the formation of α- or t-BN impurities as the temperature cools down further.

Recently, Krstic and Han reported numerical simulations of clusterization or agglomeration processes of molecular precursors containing B, N, and H at various temperatures from 1500 to 6000 K, using quantum-classical molecular dynamics (QCMD) based on the density-functional tight-binding (DFTB) quantum mechanics. Their main finding is that various BN nanostructures, including nanocages, nano-flakes, and α- and t-BNs can self-assemble in free space simply from B-N-H species without the presence of pre-existing catalyst nanoparticles. Their simulations predict that hydrogen-containing BN molecular precursors are mostly effective in self-assembling into BN nanostructures compared to other atomic precursors or BN radicals. They also found that a temperature around 2000 K is the most productive temperature for their self-assembly, promoting the formation of h-BN networks. This previous study strongly suggests that unconsumed B-N-H precursors in our plasma process have a good potential to form BN impurities as the temperature cools down to 2000 K. Since the turbulent flow produces more unreacted B-N-H species as discussed above, one could expect more BN impurity formation under a turbulent environment.

The overall mechanism proposed in this study is illustrated in Figure 9. In the early stage of the process, nanometric B droplets are formed and transported to the BNNT growth zone to serve as BNNT nucleation sites; however, in the presence of turbulence (Figure 9a), the flow instability promotes radial diffusion as well as interparticle coagulation of B droplets via more frequent collisions. The number density of B droplets subsequently decreases, and their size distribution also becomes polydisperse as more large-sized particles (>100 nm) are produced. Since large B particles are less reactive, such change leads to a significant reduction in the number of effective BNNT seeds in the BNNT growth zone. Consequently, many of the B-N-H species remain unreacted and then cluster to form initial α-BN fragments. Such BN impurities eventually turn into t-BNs through annealing in the plasma. The BNNT surfaces are coated with those BN impurities that hinder the coalescence of individual BNNT into bundles. Consequently, the BNNTs produced are entangled randomly and form a nonwoven membrane with a sheet-like morphology. The growth mechanism in a laminar flow is illustrated in Figure 9b. In this case, the radial diffusion and the B droplet growth via coagulation are relatively mild; thus, more small B droplets are available in the BNNT growth zone. Those are highly efficient BNNT seeds and thus facilitate the nucleation of BNNTs through the reaction with B-N-H precursors. A majority of B-N-H precursors are consumed for the BNNT growth, resulting in an abundant BNNT production with fewer BN impurities. The surfaces of BNNTs are relatively clean, so BNNTs can coalesce into aligned bundles through intermolecular forces such as van der Waals force. The final product collected exhibits a fibrill-like morphology due to its aligned bundled structure.

The growth mechanism discussed here is consistent with our experimental observation. With a low energy input, BNNT growth is largely limited by a low vaporization efficiency of the feedstock and a small BNNT growth zone due to its insufficient thermal energy. While a high energy input can improve the vaporization efficiency and growth zone length, the flow becomes more turbulent due to the elevated jet speed that promotes the formation of BN impurities from B-N-H species rather than BNNTs. This is a plausible explanation why an optimum power range exists in our experiments. The high energy input has several advantages in the BNNT synthesis, including better vaporization efficiency and high-throughput treatment of feedstock and is, therefore, more suitable for industrial scale processes. To fully take advantage of the high-thermal energy environment, the turbulence must be minimized. One could employ a torch nozzle with a larger diameter to decrease the plasma jet speed. A reactor design that avoids abrupt changes in geometry at the entrance of the reactor would also be desirable for the elimination of recirculating eddies that usually intensify turbulence. As such, one could maintain a laminar flow in the BNNT growth zone while operating at high plasma powers. Due to the difficulty of the flow measurements in the high-temperature plasma, our effort was placed on the development of a numerical model for studying the turbulence phenomena in the RF plasma process. Experimental measurements such as mean velocity measurement or visualization of jet fluctuation using Schlieren photography or particle tracking velocimetry (PTV) can provide greater details on the flow structure, thus being of particular interest for further optimization of the process.

The PTV technique has been widely used in thermal plasma spray coating and materials synthesis. Since the PTV technique is a noninvasive method, it can be applied to both plasma core and jet boundary without thermal damage. To overcome the emission from plasma, a pulse laser or lamp with a specific wavelength can be employed for the scan, and the plasma emissions can be effectively removed using a filter that passes only the light from the laser or lamp.

4. CONCLUSIONS

In the thermal plasma synthesis of BNNTs, the re-nitridation of B droplets by N-containing species is an important step that largely determines the yield and purity of BNNT products. In our previous study, it was shown that the rate of this reaction can be dramatically improved by introducing hydrogen as a gas-phase catalyst; however, the selectivity of the reaction toward BNNTs demands refinement to achieve high purity.

This study suggests for the first time that the flow structure of the plasma jet such as turbulence plays a key role in the formation of BN impurities in the BNNT synthesis by governing the transport phenomena of BNNT seeds such as boron droplets. We discussed that the turbulence enhances the radial diffusion of B droplets as well as their interparticle coagulation, which leads to a significant reduction in the population of effective BNNT seeds in the BNNT growth zone, and thus promotes the formation of BN impurities from the surplus B-N-H species. Our numerical simulation also suggests that a higher thermal energy input makes the flow more turbulent in the BNNT growth zone due to the elevated velocity difference between the plasma jet and ambient cold gas. Our findings can bring new aspects or insight in terms of BNNT synthesis and purity enhancement.
The authors are grateful to M. Plunkett and D. Ruth for their assistance in the BNNT synthesis experiments.

**REFERENCES**

1. Rubio, A.; Corkill, J. L.; Cohen, M. L. Theory of graphitic boron nitride nanotubes. *Phys. Rev. B* 1994, 49, S081–S084.

2. Golberg, D.; Bando, Y.; Tang, C. C.; Zhi, C. Y. Boron nitride nanotubes. *Adv. Mater.* 2007, 19, 2413–2432.

3. Rao, C. N. R.; Govindaraj, A. Synthesis of inorganic nanotubes. *Adv. Mater.* 2009, 21, 4208–4233.

4. Arenal, R.; Wang, M. S.; Xu, Z.; Loiseau, A.; Golberg, D. Young modulus, mechanical and electrical properties of isolated individual and bundled single-walled boron nitride nanotubes. *Nanotechnology* 2011, 22, No. 265704.

5. Blase, X.; Rubio, A.; Louie, S. G.; Cohen, M. L. Stability and band gap constancy of boron nitride nanotubes. *Euro. Phys. Lett.* 1994, 28, 335–340.

6. Kim, K. S.; Kingston, C. T.; Hrdina, A.; Jakubinek, M. B.; Guan, J.; Plunkett, M.; Simard, B. Hydrogen-catalyzed, pilot-scale production of small-diameter boron nitride nanotubes and their macroscopic assemblies. *ACS Nano* 2014, 8, 611–620.

7. Chen, Y.; Zou, J.; Campbell, S. J.; Le Caer, G. Boron nitride nanotubes: Pronounced resistance to oxidation. *Appl. Phys. Lett.* 2004, 84, 2430–2432.

8. Kim, K. S.; Jakubinek, M. B.; Martinez-Rubi, Y.; Asrafari, B.; Guan, J.; O’Neill, K.; Plunkett, M.; Hrdina, A.; Lin, S.; Dénommée, S.; Kingston, C.; Simard, B. Polymer nanocomposites from free-standing, macroscopic boron nitride nanotube assemblies. *RSC Adv.* 2015, 5, 41186–41192.

9. Kang, J. H.; Sauti, G.; Park, C.; Yamakov, V. I.; Wise, K. E.; Lowther, S. E.; Fay, C. C.; Thibeault, S. A.; Bryant, R. G. Multifunctional electroactive nanocomposites based on piezoelectric boron nitride nanotubes. *ACS Nano* 2015, 9, 11942–11950.

10. Ye, S.; Cheng, C.; Chen, X.; Chen, X.; Shao, J.; Zhang, J.; Hu, H.; Tian, H.; Li, X.; Ma, L.; Jia, W. High-performance piezoelectric nanogenerator based on microstructured P (VDF-TrFE)/BNNTs composite for energy harvesting and radiation protection in space. *Nano Energy* 2019, 60, 701–714.

11. Xu, X. G.; Ghamsari, B. G.; Jiang, J. H.; Guibard, L.; Andreev, G. O.; Zhi, C.; Bando, Y.; Golberg, D.; Berini, P.; Walker, G. C. One-dimensional surface phonon polaritons in boron nitride nanotubes. *Nat. Commun.* 2014, 5, No. 4782.

12. Levchenko, I.; Xu, S.; Teel, G.; Mariotti, D.; Walker, M. L. R.; Keidar, M. Recent progress and perspectives of space electric propulsion systems based on smart nanomaterials. *Nat. Commun.* 2018, 9, No. 879.

13. Cifani, G.; Raffa, V.; Menciassi, A.; Cuschieri, A. Boron nitride nanotubes: an innovative tool for nanomedicine. *Nano Today* 2009, 4, 8–10.

14. Zhi, C.; Bando, Y.; Terao, T.; Tang, C.; Kuwahara, H.; Golberg, D. Towards thermoconductive, electrically insulating polymeric composites with boron nitride nanotubes as fillers. *Adv. Funct. Mater.* 2009, 19, 1857–1862.

15. Nautiyal, P.; Rudolf, C.; Loganathan, A.; Zhang, C.; Boesl, B.; Agarwal, A. Directionally aligned ultra-long boron nitride nanotube induced strengthening of aluminum-based sandwich composite. *Adv. Eng. Mater.* 2016, 18, 1747–1754.

16. Nautiyal, P.; Zhang, C.; Loganathan, A.; Boesl, B.; Agarwal, A. High-temperature mechanics of boron nitride nanotube "Buckypaper" for engineering advanced structural materials. *ACS Appl. Nano Mater.* 2019, 2, 4402–4416.

17. Bansal, N. P.; Hurst, J. B.; Choi, S. R. Boron nitride nanotubes-reinforced glass composites. *J. Am. Ceram. Soc.* 2006, 89, 388–390.

18. Jia, Y.; Ajayi, T. D.; Morales, J.; Chowdhury, M. A.; Sauti, G.; Chu, S. H.; Park, C.; Xu, C. Thermal properties of polymer-derived ceramic reinforced with boron nitride nanotubes. *J. Am. Ceram. Soc.* 2019, 102, 7584–7593.
(19) Kim, J. H.; Pham, T. V.; Hwang, J. H.; Kim, C. S.; Kim, M. J. Boron nitride nanotubes: synthesis and applications. *Nano Converg. 2018*, *S*, No. 17.

(20) Kim, K. S.; Kim, M. J.; Park, C.; Fay, C. C.; Chu, S. H.; Kingston, C. T.; Simard, B. Scalable manufacturing of boron nitride nanotubes and their assemblies: a review. *Semicond. Sci. Technol. 2017*, *32*, No. 013003.

(21) Rao, R.; et al. Carbon nanotubes and related nanomaterials: critical advances and challenges for synthesis toward mainstream commercial applications. *ACS Nano 2018*, *12*, 11756–11784.

(22) Smith, M. W.; Jordan, K. C.; Park, C.; Kim, J. W.; Lillehei, P. T.; Crooks, R.; Harrison, J. S. Very long single- and few-walled boron nitride nanotubes via the pressurized vapor/condenser method. *Nanotechnology 2009*, *20*, No. 505604.

(23) Cho, H.; Kim, J. H.; Hwang, J. H.; Kim, C. S.; Jang, S. G.; Park, C.; Lee, H.; Kim, M. J. Single- and double-walled boron nitride nanotubes: controlled synthesis and application for water purification. *Sci. Rep. 2020*, *10*, No. 7416.

(24) Fathalizadeh, A.; Pham, T.; Mickelson, W.; Zettl, A. Scaled synthesis of boron nitride nanotubes, nanoribbons, and nanoconocochs using direct feedstock injection into an extended-pressure, inductive coupled thermal plasma. *Nano Lett. 2014*, *14*, 4881–4886.

(25) Kim, K. S.; Couillard, M.; Shin, H.; Plunkett, M.; Ruth, D.; Kingston, C. T.; Simard, B. Role of hydrogen in high-yield growth of boron nitride nanotubes at atmospheric pressure by induction thermal plasma. *ACS Nano 2018*, *12*, 884–893.

(26) Kim, M.; Lee, Y. H.; Oh, J. H.; Hong, S. H.; Min, B. I.; Kim, T. H.; Choi, S. Synthesis of boron nitride nanotubes using triple DC thermal plasma reactor with hydrogen injection. *Chem. Eng. J. 2020*, *395*, No. 125148.

(27) Kim, K. S.; Kim, T. H. Nanofabrication by thermal plasma jets: From nanoparticles to low-dimensional nanomaterials. *J. Appl. Phys. 2019*, *125*, No. 070901.

(28) http://www.tekna.com/boron-nitride-nanotubes (last accessed date September 10 2020).

(29) Guan, J.; Kim, K. S.; Jakubinek, M. B.; Simard, B. pH-Switchable Water-Soluble Boron Nitride Nanotubes. *ChemistrySelect 2018*, *3*, 9308–9312.

(30) Marincel, D. M.; Adnan, M.; Ma, J.; Bengio, E. A.; Trafford, M. A.; Kleinerman, O.; Kosynkin, D. V.; Chu, S. H.; Park, C.; Hocker, S. J.; Fay, C. C.; Arepalli, S.; Marti, A. A.; Yeshayahu, T.; Pasquali, M. Scalable purification of boron nitride nanotubes via wet thermal etching. *Chem. Mater. 2019*, *31*, 1520–1527.

(31) Cho, H.; Walker, S.; Plunkett, M.; Ruth, D.; Iannitto, R.; Martinez-Rubi, Y.; Kim, K. S.; Homenick, C. M.; Brinkmann, A.; Couillard, M.; Dénommée, S.; Kingston, C.; Simard, B.; et al. Scalable gas-phase purification of boron nitride nanotubes by selective chlorine etching. *Chem. Mater. 2020*, *32*, 3911–3921.

(32) Pristavita, R.; Mendoza-Gonzalez, N. Y.; Meunier, J. L.; Berk, D. Carbon blacks produced by thermal plasma: the influence of the reactor geometry on the product morphology. *Plasma Chem. Plasma Process. 2010*, *30*, 267–279.

(33) Pristavita, R.; Mendoza-Gonzalez, N. Y.; Meunier, J. L.; Berk, D. Carbon nanoparticle production by inductively coupled thermal plasmas: controlling the thermal history of particle nucleation. *Plasma Chem. Plasma Process. 2011*, *31*, 851–866.

(34) Kim, K. S.; Moradian, A.; Mostaghimi, J.; Alinejad, Y.; Shahverdi, A.; Simard, B.; Soucy, G. Synthesis of single-walled carbon nanotubes by induction thermal plasma. *Nano Res. 2009*, *2*, No. 800.

(35) Trelles, J. P.; Chazelas, C.; Vardelle, A.; Heberlein, J. V. R. Arc plasma torch modeling. *J. Therm. Spray Technol. 2009*, *18*, 728–752.

(36) Shigeta, M. Simulating turbulent thermal plasma flows for nanopowder fabrication. *Plasma Chem. Plasma Process. 2020*, *40*, 775–794.

(37) Gonzalez, N. Y. M.; Morsli, M. E.; Proulx, P. Production of nanoparticles in thermal plasmas: a model including evaporation, nucleation, condensation, and fractal aggregation. *J. Therm. Spray Technol. 2008*, *17*, 533–550.

(38) Colombo, V.; Ghedini, E.; Gherardi, M.; Sanibondi, P.; Shigeta, M. A two-dimensional nodal model with turbulent effects for the synthesis of Si nano-particles by inductively coupled thermal plasmas. *Plasma Sources Sci. Technol. 2012*, *21*, No. 025001.

(39) Boulos, M. I.; Fauchais, P.; Pflender, E. *Thermal Plasmas, Fundamentals and Applications*; Plenum: New York, 1994.

(40) Feucht, S.; Kellett, M.; Malloy, D.; Molter, T.; Willis, W. S.; King’ondu, C.; Suib, S. L. Pyrolytic decomposition of ammonia borane to boron nitride. *Inorg. Chem. 2011*, *50*, 783–792.

(41) Fazen, P. J.; Rensmen, E. E.; Beck, J. S.; Carroll, P. J.; McGhie, A. R.; Sneddon, L. G. Synthesis, properties, and ceramic conversion reactions of polyborazylene - A high-yield polymeric precursor to boron nitride. *Chem. Mater. 1995*, *7*, 1942–1956.

(42) Arenal, R.; Stephan, O.; Cochin, J. L.; Loiseau, A. Root-growth mechanism for single-walled boron nitride nanotubes in laser vaporization technique. *J. Am. Chem. Soc. 2007*, *129*, 16183–16189.

(43) Yang, H.; Iwamoto, C.; Yoshida, T. Peculiar deformation characteristics of turbostratic boron nitride thin film. *Thin Solid Films 2005*, *483*, 218–221.

(44) Zhong, B.; Zhang, X.; Xia, L.; Yu, Y.; Wen, G. Large-scale fabrication and utilization of novel hexagonal/turbostratic composite boron nitride nanosheets. *Mater. Des. 2017*, *120*, 266–272.

(45) Shigeta, M.; Murphy, A. B. Thermal plasmas for nano-fabrication. *J. Phys. D: Appl. Phys. 2011*, *44*, No. 174025.

(46) NIST. Atomic Spectra Database. https://www.nist.gov/pml/atomic-spectra-database. (Last accessed Sept 14, 2021).

(47) Pease, R. W. B.; Gaydon, A. G. The Identification of Molecular Spectra; Chapman and Hall: London, 1965.

(48) Khрабry, A.; Kaganovich, I. D.; Yatom, S.; Vekselman, V.; Радич-Периц, Ј.; Родман, J.; Райтсес, Y. Determining the gas composition for the growth of BNNTs using a thermodynamic approach. *Chem. Phys. Chem. 2019*, *21*, 13268–13286.

(49) Colombo, V.; Gherardi, E.; Gherardi, M.; Sanibondi, P.; Shigeta, M. A two-dimensional nodal model with turbulent effects for the synthesis of Si nano-particles by inductively coupled thermal plasmas. *Plasma Sources Sci. Technol. 2012*, *21*, No. 025001.

(50) Shigeta, M. Turbulence modelling of thermal plasma flows. *J. Phys. D: Appl. Phys. 2016*, *49*, No. 493001.

(51) Kim, K. S.; Park, J. M.; Choi, S.; Kim, J.;Hong, S. H. Comparative study of two-and three-dimensional modeling on arc discharge phenomena inside a thermal plasma torch with hollow electrodes. *Phys. Plasmas 2008*, *15*, No. 023501.

(52) Shigeta, M. Modeling and simulation of a turbulent-like thermal plasma jet for nanopowder production. *IEEJ Trans. Electr. Electron. Eng. 2019*, *14*, 16–28.

(53) Kristic, P. S.; Han, L.; Irle, S.; Nakai, H. Simulations of the synthesis of boron-nitride nanostructures in a hot, high pressure gas volume. *Chem. Sci. 2018*, *9*, 3803–3819.

(54) Pflender, E.; Fincke, J.; Spores, R. Entrainment of cold gas into thermal plasma jets. *Plasma Chem. Plasma Process. 1991*, *11*, S29–543.

(55) Kawajiri, K.; Sato, T.; Nishiyama, H. Experimental analysis of a two-dimensional nodal model with turbulent effects for the synthesis of Si nano-particles by inductively coupled thermal plasmas. *Plasma Sources Sci. Technol. 2012*, *21*, No. 025001.

(56) Damiani, D.; Tarlet, D.; Meillot, E. A particle-tracking-velocimetry (PTV) investigation of liquid injection in a DC plasma jet. *J. Therm. Spray Technol. 2014*, *23*, 340–353.