Conversion from carbon nanotubes to boron nitride nanotubes and boron nitride-carbon nanotubes

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**CONVERSION FROM CARBON NANOTUBES
TO BORON NITRIDE NANOTUBES AND
BORON NITRIDE-CARBON NANOTUBES**

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CONVERSION FROM CARBON NANOTUBES TO BORON NITRIDE NANOTUBES AND BORON NITRIDE-CARBON NANOTUBES

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Abstract

Boron nitride nanotubes (BNNTs) have excellent mechanical, thermal properties as well as large bandgap and high oxidation resistance. Based on these properties, BNNTs are proposed to be candidate for diverse applications including reinforcement, field emitter, biological sensor and polyer wrapping. Owing to the remarkable properties of BNNTs and the many applications that such nanotubes might enable, the growth methodology of high quality BNNTs is a critical subject studied by many in the past two decades. Due to the similarities with carbon nanotubes (CNTs), many of the BNNTs synthesis techniques were adopted from its carbon counterparts, such as arc-discharge method, chemical vapor deposition, laser ablation, ball milling and carbon nanotube-substitution reaction methods. However, these methods often encounter various drawbacks such as high temperature growth and insufficient yield, restricting many of its potential applications. In the M.Eng program, a relatively low temperature method (900 °C) to convert carbon nanotubes (CNTs) into their BNNTs equivalent was developed. This conversion technique preserves the geometrical structure of the nanotubes and produces the longest vertically aligned BNNTs arrays to date (4mm in height). Additionally hybrid boron nitride-carbon nanotubes (BNCNTs) and cone-stacking structured BNNTs were successfully synthesized. Moreover, the mechanism of the conversion process and discussed the differences in formation of multi-wall vs cone-stacking BNNTs structure have also been examined. Lastly, the optical bandgap of converted boron nitride-carbon nanotubes has successfully been tuned. This work thus demonstrates a simple synthesis method to explore the combination of both CNTs as well as BNNTs and will be of great interest to many in the field.

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Chapter 1

Introduction

1.1 Motivation

Boron Nitride Nanotubes (BNNTs) are nanotubes with similar hexagonal structure as carbon nanotubes (CNTs), with its alternating B and N atoms in substitution with C. [10, 11, 12, 13] Owing to the same honeycomb atomic configuration as CNTs, BNNTs have similar excellent mechanical properties (i.e. Young's modulus of 1.2 TPa [14, 15]) and remarkable thermal conductivity [16, 17]. In addition, due to the binary nature of BNNTs, its sublattice symmetry is broken, leading to a large bandgap of more than 5 eV [18] and thus electrically insulating [19]. Moreover, BNNTs' bandgap is also independent of the diameter and chiralities of the nanotubes [10, 18], differing from its carbon counterpart. Besides, the strong covalent bonding between B and N allows BNNTs to possess excellent chemical stability [20] and a much higher oxidation resistance of up to 800 °C in air and 2800 °C in inert atmosphere. [21]. Furthermore, BNNTs have excellent piezoelectricity [22, 23]. As such, BNNTs are very attractive and promising for a wide range of applications. It has been applied as protective capsules for environmental-sensitivity nanoparticles from oxidation and contamination by the surrounding [24]. It is also a promising candidate for structural reinforcement [25] and as a nanofiller to enhance the thermal conductivity of polymeric films and fibers [26]. Furthermore, BNNTs have also found to be useful in other prospective applications, include gas absorbents,

spintronic devices as well as interconnects for nanoscale electronics, radiation stoppers. In addition, it has been predicted that by integrating BNNTs with CNTs, its superlattices and isolated CNTs/BNNTs junctions could produce itinerant ferromagnetism and spin polarization. [27]

However, synthesis of BNNTs is still a challenging task and mostly, the synthesis approaches for BNNTs are adopted from techniques for CNTs growth, such as arc-discharge method, [14] chemical vapor deposition (CVD), [28, 29, 30] laser ablation, [31] ball milling [32] and other high temperature and plasma enhanced processes. While some of these methods could produce large quantity of BNNTs, the geometry and the quality of the BNNTs may not be suitable for electronics, reinforcement and medical applications [11, 25, 33]. Thus far, for BNNTs, the highest quality was obtained from CVD [28, 30]. Yet, there is still a need for high temperature growth condition and sometimes, dangerous precursors (i.e. borazine) are involved. On the other hand, the development for CNTs growth is well advanced for the past 2 decades, with commercial CVD systems and mass production of CNTs readily available. [34] Therefore, instead of revising on the current techniques for CNTs growth and redeveloping them for BNNTs, a more straightforward alternative would be to transform CNTs directly into BNNTs via a direct chemical conversion approach. Previously, it has been reported that by reacting CNTs with B₂O₃ in N₂ environment, CNTs could convert into Boron Nitride-Carbon nanotubes (BNCNTs) and subsequently, into BNNTs [35, 36, 37]. This process is initiated by O₂ etching on the surface of the CNTs with some remnant O₂ in the chamber and followed by B and N substitutions in these defect sites. [35, 36, 37] However, there are two drawbacks about this method. One is that residuals of carbon are often found in the resultant BNNTs and the other is that high temperature environment is necessary (beyond 1500 °C). This would impose challenge to the thermal stability of the CNTs during the conversion process. [38]

Therefore, we need to find a new way to synthesize BNNTs that lowers the required temperature and is high-quality and suitable for large scale synthesis.

1.2 Objectives

The major objectives of my M.Eng project are to look for a new method to synthesize BNNTs. Details are listed below:

- To look for a new method that requires a lower temperature yet still produce BNNTs with high quality.
- To apply this method to long aligned nanotubes.
- To justify the existence of stacked-cup BNNTs and study the method of its synthesis.
- To study the mechanism of this new method and optimize it.

1.3 Major Contribution for this Thesis

The major contribution of my M.Eng project are listed as following.

- A new approach to synthesize BNNTs is proposed. Previous methods for growing BNNTs either require high temperature and strict conditions, such as CVD method, etc. or produce BNNTs with low quality, such as ball milling method. Our method reduces required temperature to 900 °C, due to the introduction of hydroxyl groups so that the energy to excite carbon atoms is reduced. Furthermore, converted BNNTs perform the same structure as prepared CNTs and the synthesis of CNTs is mature nowadays, therefore this method can produce high-quality BNNTs easily. Lastly, because the condition it needs is not strict, this conversion

method can be extended to large-scale synthesis of BNNTs. Also, the conversion process is controllable and the composition of C in the BN matrix (or vice versa) can be tailored to produce BNCNTs composites. The synthesis of high aspect ratio BNCNTs is of significant interest due to its unique anisotropic properties with tunable electrical/thermal characteristics. Due to the highly compatible nature of BN and C, this work provides a direct linkage between the CNTs and BNNTs communities and allows the exploration for the hybridization of both.

- Long aligned BNNTs (around 4 mm) were synthesized by this method. The approaches of growing CNTs are very mature nowadays and the converted BNNTs process the same structure with prepared CNTs. We, therefore, used water assisted CVD system to produce super growth of aligned CNTs and then prepared them for conversion. After the same conversion process, aligned BNNTs are successfully obtained. There are several advantages of vertically aligned nanotubes as compared to those which are not aligned. For example, it can be readily incorporated into applications such as aligned BNNTs or BNCNTs membrane mimicking protein channels selecting specific ions and also as efficient metal-free electrocatalysts for the oxygen reduction reaction. Furthermore, this also enables patterning of BNNTs/BNCNTs array which could be integrated for other applications.
- Both multi-wall and stacked-cup BNNTs can be synthesized, selected by the concentration of hydroxyl groups introduced to CNTs. The mechanisms for these two structures are also discussed. Stacked-cup nanotubes provide more extra space from exposed edges, and thus they have other promising applications different from normal-wall nanotubes, such as ion storage and diffusion, which is realized in stacked-cup CNTs and predicted in stacked-cup BNNTs. In this M.Eng project, I successfully converted CNTs to both multi-wall and stacked-cup BNNTs. The

mechanism of conversion of single wall is calculated by functional density theory while the outside-to-inside mechanism of conversion of multi-wall BNNTs is justified by EELS result. Furthermore, the occurrence of stacked-cup structure is explained consistently by the mismatch and fragmentation of BN nucleations, similar to the growth of stacked-cup CNTs.

- This method together with longest aligned BNNTs and stacked-cup BNNTs have been written into a academic paper. The authors includes me (first author), Siu Hon Tsang, Roland Yingjie Tay and my supervisor Edwin Hang Tong Teo (corresponding author). And this paper has been submitted.
- The optical bandgap of BNC nanotubes can be tuned. When the concentration of carbon in BNC nanotubes is sufficiently low, instead of merely superposition of BNNTs and CNTs, there will be some emergent properties. One remarkable property is the red shift of the UV-Vis absorption spectrum, due to the impaired conjugation effect of the surrounding carbon. Therefore, by applying different reaction time for the conversion process, BNC nanotubes with different concentration of carbon, hence different optical bandgap, can be obtained. In this M.Eng project, we successfully tuned the bandgap of BNC nanotubes from 5.7 eV to 4.8 eV.

1.4 Organization

This thesis is organized as below:

- Chapter 1 introduces the motivation, objectives as well as the major contributions of this thesis.
- Chapter 2 reports the literature review on the properties, applications of BNNTs as well as its synthesis approach. Finally the characterization techniques used in this project are covered.

- Chapter 3 describes the experimental plan and setup for this M.Eng project including functionalization, CVD for conversion reaction and the details of characterization.
- Chapter 4 reports the major finding of BNNTs and BNC nanotubes, especially with long aligned arrangement, and their characterization, including physical properties, Raman spectra and XPS results.
- Chapter 5 covers the discovery of stacked-cup BNNTs, study and discuss the mechanism for the synthesis of multi-wall and stacked-cup BNNTs.
- Chapter 6 shows the possibility for tuning electrical properties of BNNTs and its relation with the concentration of carbon atoms.
- Chapter 7 summaries the findings of this project and recommends some future directions based on the current discoveries of this M.Eng project.

Chapter 2

Literature Review

2.1 Structure and Properties

2.1.1 Boron Nitride Nanotubes

BNNT is a 1D material with sp^2 -hybridized alternating boron and nitrogen atoms which are covalently bonded in a hexagonal structure as illustrated in Fig. 2.1 [39, 40]. With this unique structure, BNNTs have excellent mechanical, optical and thermal properties as

Figure 2.1: Structural model of a multi-walled BNNT with BN bond length of 1.44 Å.

Figure 2.2: (a) Scanning electron microscopy image of purified boron nitride nanotubes grown at 1,500 °C and (b) Comparative thermogravimetric analysis curves of BNNTs and CNTs. [1]

well as a wide bandgap. The axial Young's modulus for a multi-wall BNNT was measured to be 1.18 TPa and the experimental value is consistent with the calculation based on tight-binding method [15, 41, 42]. According to diverse calculation methods, it is shown that phonon mean free path in BNNTs is the same as that in CNTs [43], and thus have high thermal conductivity [44, 45]. However, the experiment found that the thermal conductivity of pure BNNTs is only 18 W/mk, which is lower than bulk hexagonal boron nitride at room temperature [46, 47, 48]. BNNTs also have a large bandgap of around 5 eV, which is predicted and confirmed by calculation [10, 49] and experiment [50, 51, 52]. What's more promising is the thermal stability in air. As shown in Fig. 2.2, compared to CNTs, BNNTs are much more stable in air and stay unoxidized until 1,100 °C [53, 54].

2.1.2 Stacked-cup Nanotubes

Different from the aligned-wall structure in multi-wall BNNTs, there is another kind of nanotube that has a distinct morphology of wall structure, stacked-cup nanotubes [55, 56, 57]. The sketch of stacked-cup nanotubes is shown in Fig. 2.3. The first successfully synthesized nanotubes with stacked-cup structure are stacked-cup carbon nanotubes [58].

Figure 2.3: Sketch of stacked-cup nanotubes.

Stacked-cup nanotubes are hollow inside as multi-wall BNNTs, but their walls are made up of stacked snowflakes with cone shape.. In the case of stacked-cup carbon nanotubes, the nanoflake is graphene flake with open edges [58], the TEM images of which is shown in Fig. 2.4.

Because of the open edges and extra room between each flakes, it is predicted that stacked-cup nanotubes are promising in ion store and molecule carrier [59, 60, 61]. As for stacked-cup carbon nanotubes, [61] reported that stacked-cup carbon nanotubes are candidate materials for lithium-ion battery anodes, delivered a stable capacity of $310 \text{ mAh } g^{-1}$ at a rate of C/2 to 300 cycles. Also stacked-cup nanotubes expose the edge of nanoflake on its surfaces, and thus the surface state is active [62, 63, 64, 65], in which case it can be easily modified by the method of functionalization or thermal treatments to introduce new chemical bondings. Both functionalizing and dispersing stacked-cup nanotubes are performed less costly than normal nanotubes [58].

The stacked-cup BNNTs are also predicted to be one of the candidates for atomic and gas absorbent [66], similar with carbon nanotubes. Cone angles of stacked-cup BNNTS is calculated to be lower than that of stacked-cup carbon nanotubes, which results from the different stacking of BN layers from graphene layers [58].

2.1.3 BNC nanotubes

Instead of nanotubes consisting of pure carbon atoms or pure boron nitride, BNC nanotubes consist of both of them. BNC nanotubes recently attract much attention because of some extraordinary properties compared to CNTs and BNNTs [67, 68]. BNC nanotubes are predicted to process higher chemical and thermal stabilities than those of carbon nanotubes [36]. Additionally, BNC nanotubes are promising candidates as emitters for flat panel displays [69], photoluminescent materials, high temperature transistors, lightweight electrical conductors as well as high temperature lubricants [70].

Figure 2.4: (a)-(c) HRTEM images and enlarged HRTEM images of stacked-cup carbon nanotubes.

Figure 2.5: HRTEM image of a multi-wall BNNT capsule for Pt nanoparticles with size of 2 nm.(Golberg et al. 2010, unpublished results)

2.2 Applications of BNNTs

The direct possible application of BNNT is based on the excellent thermal properties and chemical stability. BNNTs can be applied as protective capsules for most of types of particles and nanomaterials, some of which might be unstable in oxidation condition, or can be contaminated by environment. Fig. 2.5 illustrates BNNTs capsule for nanosized catalytic Pt particles. Also, other applications of multi-wall BNNTs as protective shields for various functional nanomaterials, such as semiconducting nanowires [24, 71, 72], magnetic nanorods [73, 74, 75], and luminescent nanomaterials [76, 77], have also been successfully published.

Multi-wall BNNTs were also discovered to be promising candidate for the reinforcement material [25, 78, 79, 80, 81] and furthermore BNNTs can increase the thermal conductivity of existing polymeric films and fibers [26, 82, 83]. The resulted stress and elastic modulus of applied polymeric fibers can be greatly enhanced up to 30% to 50%

Figure 2.6: PH sensor of BNNTs with Ag nanoparticles.

by loading with small amount, compared to original materials, of BNNTs, only 1 to 3% heavier than previous. [25]

What's more, BNNTs can be used as field emitters [84, 85, 86] and pH sensors [87]. In 2009, the sensors with several micrometers were fabricated. This sensor consisted of biotin-fluorescein functionalized multi-wall BNNTs. Inside the BNNTs, there were nanosized Ag particles (Fig. 2.6) [88]. Original pH dependent photoluminescence and Raman signals, interacted with fluorescein molecules, were increased by surface enhanced resonance on decorated Ag nanoparticles with the average diameter of 20 nm). This total mechanism allowed these novel nanosystems to be applied as plausible three-dimensional pH mapping probes. Specially, the spatial resolution of the pH sensor was decided by the diameter of laser beam and the diameter of BNNTs.

Additionally, BNNTs based material is potential in biosensing of different kinds of bacterium and viruses [89]. In 2014, Panchal, et al. studied the possible application of BNNTs in detecting microorganisms based on the resonant frequency shift BNNTs performed after the adsorption of different kinds of bacterium or viruses which were counted as additional mass to the BNNTs-based sensor system. According to the finite

element method (FEM)-based results, by using the single-wall BNNTs of smaller length and diameter the sensitivity can be greatly enhanced.

Last but not least, BNNTs are theoretically predicted to be promising in carrying out some of the significant functions of biological ion channels [90], in which case BNNTs were suggested to have potential for being sensitive biosensors, antibiotics, or filtration devices. There are other prospective applications of BNNTs, including gas adsorbents [91, 92], spintronic devices [93, 94], UV lasers [95, 96], high resistivity substrates [97], as well as interconnects [98] for nanoscaled electronics, radiation stoppers [99], functional sensors [100, 101] and reinforcing agents for functional airspace materials [11].

2.3 Fabrication of BNNTs

The synthesis of BNNTs is much more difficult than that of CNTs, Nevertheless, some approaches are similar with the growth of CNTs due to the similar structure which some methods requires distinct equipment and procedure.

2.3.1 Arc-discharge Method

The first synthesis of BNNTs is arc-discharge method, which is similar to that for synthesis of CNTs [14]. A h-BN rod is used as the anode while a copper electrode is set as the cathode. After the power is on, h-BN rod is sublimated by arc discharge and some residue containing BNNTs will appear on the copper cathode. Another different arc-discharge method is to use hafnium diboride (HfB_2) as electrode and synthesize in nitrogen atmosphere [12].

2.3.2 Chemical Vapor Deposition

The first successful synthesis of BNNTs using CVD method is reported in 2000 [28]. They used borazine ($\text{B}_3\text{N}_3\text{H}_6$) as precursor for nitrogen and boron resources. The chemical

reaction is demonstrated as follows:

There are many materials that can be used as catalyst and NiB was found to be the most effective one. After the whole system was heated up to 1,100 °C and hold for half an hour, white deposits were found on the substrate and confirmed to be BNNTs. Recent advance of CVD growth of BNNTs shows that floating nickelocene can also be used as catalyst and produce double-walled BNNTs [102], also hazardous borazine can be replaced by ammonia and boric acid but higher temperature of 1,300 °C and RF inducting furnace are required [30].

2.3.3 Laser Ablation

Laser ablation method is another successful approach to synthesize BNNTs [31]. The material that is exposed to laser includes pure hexagonal boron nitride and catalysts such as nickel and cobalt with size of nanoscale. After being heat up to around 1,200 °C, the material is ablated by pulsed excimer laser with optimized wavelength of 248 nm. At last product can be collected on Cu collector. The quality of resulted product is poor, which contains amorphous boron nitride besides BNNTs with diameters of several nanometers. The main resulted BNNTs contains walls with number less than four, specially in inert gas such as Ar and He. With strict conditions and poor quality, laser ablation is not an ideal method for BNNTs synthesis.

2.3.4 Ball Milling

Ball milling is also an approach to synthesize BNNTs [21, 103]. The reported number of stainless iron milling vessels used in the setup of ball milling is four. Pure boron powder is preloaded in each of the vessel. After putting normal steel balls inside the vessels, the pressure is increased to thousands of pascals (300,000 Pa as reported) meanwhile inner

space of the vessels are filled with ammonia. After that, the resulted product is annealed isothermally at 1,200 °C for 16 h while instead of ammonia, system is filled with nitrogen gas. Lastly, the original boron power will be changed to BNNTs with the efficiency of 65–85% [103]. Although the yields of ball milling method is high, the condition is strict, including long time and high temperature and the quality is poor.

2.3.5 CNT-substitution Reactions

CNT-substitution reactions is also a promising method for synthesis of BNNTs. Instead of direct growth, this method uses CNTs as catalyst, in other word template, and during reaction, boron atoms and nitrogen atoms will replace carbon atoms based on the chemical formula below:

CNT-substitution reaction is carried out in a CVD system. Instead of boron power, B_2O_3 powder with lower saturated vapor pressure is used and mixed with CNTs. The CVD system is then heated up to 1,500 °C with ammonia as precursor and kept for around 0.5 hour. After the reaction, besides BNNTs, amorphous carbon and boron nitride are also found. In order to get rid of byproducts including amorphous carbon, product is annealed under air in 550 °C. Although this method produces BNNTs with high quality, it requires very high temperature and relatively cumbersome procedures.

2.3.6 Problems of Current Method

Currently, CVD and ordinary carbon nanotube-substitution reaction methods require high temperature from 1100 C to 3000 C, which prevent large-scale synthesis and industrial application of BNNTs, such as reinforcement for large-scale material [25]. Also, arc-discharge method, laser ablation and ball milling methods produce BNNTs with low

quality, which prevents their application from emitters, reinforcement and medical areas [11].

Furthermore, up to now, the synthesis method for BNNTs produce BNNTs with relatively large diameters of 50 nm [11], which prevents their industrial application from nanoscaled capsules [26]. It is still necessary to find a method to finely control or decrease the diameters of BNNTs. Actually, certain functionalized properties and specially a defect structure of BNNTs (such as stacked-cup BNNTs) may be related to their diameters and structure. Thus, the advance of different structure may provide BNNTs with new properties and more portential applications. [11]

2.4 Conversion of Graphene to hexagonal boron nitride (h-BN)

Graphene is typical conductor while h-BN is insulator, and furthermore their hybrids hexagonal boron carbonitride are promising as a semiconductor [104]. reports a direct conversion from hexagonal carbon lattice of graphene to h-BN which has the same hexagonal structure using chemical method, which inspires this thesis.

The substitution reaction for graphene is carried out in a quartz tube with furnace at around 1100 °C. Pristine Graphene is grown on copper foils first. After that, it is transferred onto silicon wafer substrates and then loaded into a quartz tube and then furnace. Solid boric acid powder is also preloaded in a boat inside the tube as boron source. The tube is then pumped down to around 60 mTorr with Ar gas for half an hour. After that, the whole quartz tube is heated up to 1,000 °C in 40 min and then kept at that temperature for the conversion reaction. Boric acid is heated up to 300 °C – 600 °C separately to release boron. At the same time ammonia gas flows at 50 sccm as nitrogen source. Normally a conversion of half an hour leads to a 50% conversion of graphene, and graphene will be fully converted to h-BN in around two hours. [104]

2.5 Characterization

2.5.1 Raman Spectroscopy

Raman Spectroscopy had been used to identify crystalline materials by lattice vibration. For BNNTs, peaks ranging from 1,364 to 1,370 cm^{-1} are assigned to the E_{2g} phonon mode, shown in Fig. 2.7. The same phenomenon appear in h-BN thin film as shown in Fig. 2.8. The intensity of the peaks gets progressively weaker and the peaks are blue shifted of up to 4 cm^{-1} due to the hardening of E_{2g} as the number of layers decreases [3]. With the intensity and shift of peaks being proportional to the number of layers, N, Raman is often used in a preliminary characterization of the quality and number of layers of h-BN. For monolayer h-BN, the peak is blue shifted because of the hardening of E_{2g} due to shorter B-N bonds which implies compressive stress caused by the stretching of the film. Interestingly, for bi-layers, red shift of around 2 cm^{-1} occurs due to random strain caused during cleavage. It is reported that the variations in peaks observed for monolayer (1,368 to 1,370 cm^{-1}) and bi-layers (1,363 to 1,367 cm^{-1}) are caused by the variations in strain of the film.

2.5.2 Ultraviolet-visible (UV-vis) Spectroscopy

UV-vis spectroscopy bases on the absorption or reflectance of light varying from ultraviolet to visible region.

Here, UV-vis is often used to determine the optical band gap (OBG) of a material. In the case of BNNTs, BNNTs usually diverse in IPA or ethanol. Fig. 2.9 shows the absorbency spectrum of the BNNTs with a peak at 225 nm [4]. To calculate the OBG, the absorption spectrum is converted to Taucs plot. The derived absorption coefficient α is defined as

$$\alpha = \frac{a(E - E_g)^{1/2}}{E}$$

Figure 2.7: Raman spectra excited at 229 nm on (a) a BNNT-rich area in a standard TEM carbon grid, (b) a particle of h-BN on the same grid, and (c) highly crystalline powder h-BN. [2]

Figure 2.8: Raman spectra of mono to few layers h-BN [3].

Figure 2.9: (a) SEM image of the film of BNNTs with small diameters and TEM image showing a well-crystallized multi-wall structure; (b) PL spectra from the BNNT film at 10 and 293 K after vacuum annealing. [4]

where a is a constant, E is the photon energy and E_g is the optical bandgap. Thus a plot of $a^2 E^2$ versus E would yield a straight line around absorption peak with the E axis intercept equal to bandgap E_g . The bandgap measure in Fig. 2.9 is around 5.5 eV.

2.5.3 Fourier Transform Infrared Spectroscopy (FTIR)

Differing from UV-vis spectroscopy, FTIR is based on the absorption or reflection of light in infrared spectrum. A FTIR spectrometer can simultaneously collect the data of samples with high spectral resolution over a wide frequency range, which is significantly advantageous over a dispersive spectrometer which can only measure intensity over a comparatively narrow range of frequency in real time.

FTIR is used here to detect the hydroxyl groups attached to CNTs. A typical FTIR absorption spectra is shown in Fig. 2.10 where there is a strong peaks for all curves around $3,430 \text{ cm}^{-1}$, which stands for hydroxyl groups [105]. The segments around $2,950$ and $2,830 \text{ cm}^{-1}$ are attributed to the asymmetric (aCH_2) and symmetric (sCH_2) stretching of CH bond. In functionalized multi-wall nanotubes, the peak at $1,384 \text{ cm}^{-1}$ is due to COH stretching vibrations and the peak at $1,043 \text{ cm}^{-1}$ is due to CO stretching vibrations [106, 107].

Figure 2.10: FTIR spectra corresponding to (a) multi-wall carbon nanotubes, (b) acid functionalized multi-wall carbon nanotubes, (c) solar exfoliated graphene, (d) PDPA functionalized graphene, and (e) graphene multi-wall carbon nanotube composite. [5]

2.5.4 Scanning Electron Microscopy (SEM)

SEM is one of the kinds of electron microscope that demonstrate images of object by scanning it with a focused beam of electrons in real time. During scanning, the electrons have interaction with molecules as well as atoms in the scanning object, reflect various detectable signals that consist of various information about the surface profile of the object as well as its composition. The focused electron beam is usually scanned in a raster scan pattern, and therefore the location of spot from of the electron beam, together with the reflected signals can produce an image of the object. The finest resolution of typical SEM can be better than one nanometer. What's more, object can be observed in different vacuum condition including high vacuum, low vacuum and at a wide range of cryogenic or elevated temperatures. [108]

SEM is used as a primary characterization tool which is especially useful to determine

Figure 2.11: Scanning electron microscopy images of as-grown BNNTs at (a) low and (b) high resolution. [6]

the presence of BNNTs. It is used to determine the length and diameter roughly of the as-grown BNNTs. A typical SEM image of BNNTs is shown in Fig. 2.11.

2.5.5 Transmission Electron Microscopy (TEM)

TEM is also a kind of electron microscopy technique as SEM. However, in TEM, a focused beam of electrons is transmitted through an ultra-thin sample, instead of scanning as in SEM. After the interaction with molecules and atoms in the sample as it passes through, an image is produced based on the detectable signals. TEM can produce images at a greatly higher resolution than normal light microscopes because of the short de Broglie wavelength of moving electrons compared with light. Owing to that, TEM can be used to detect the fine details, even atomic configuration.

TEM is by far the only method to reveal the structure of BNNTs and the number of its walls. The inter-wall distance is measured to be around 0.34 nm [109], which is close to very ideal h-BN of 0.333 nm. A typical TEM image of BNNTs is shown in Fig. 2.12. Furthermore, TEM can be used to determine the morphology of nanotubes, including single/multi-wall, bamboo-like and stacked-up nanotubes. An TEM image of stacked-up CNTs is shown in Fig. 2.13 [110].

Figure 2.12: Representative HRTEM images of (a) multi-wall [7] and (b) single-walled [8] BNNT bundles. The inset in (b) depicts an individual single-walled BNNT with a BN nested octahedral fullerene encapsulated within.

2.5.6 X-ray Photoelectron Spectroscopy (XPS)

XPS is a kind of quantitative spectroscopic technique that is sensitive to the surface of samples. XPS is capable of measuring the elemental composition as well as bond types within a material. Spectra of XPS can be detected by irradiating a sample with a focused beam of X-rays and in the mean time detecting the number of escaping electrons and measuring their kinetic energy from the surface (about 0 to 10 nanometers depth) of the sample being analyzed.

XPS is use to determine the BNNTs' composition and its bonding properties. As shown in Fig. 2.14 [9], based on peak fitting, we can divide the high-resolution XPS spectrum of boron into boron-carbon and boron-nitrogen bond which peak at 189.6 eV and 191.5 eV respectively. Also, carbon peak in Fig. 2.14[c] can also be fit into the peaks of carbon-nitrogen and carbon-boron, carbon-carbon and carbon-oxygen, which peak at 286.2 eV, 283.6m 284.6 and 288.5 respectively. Furthermore, the high-resolution XPS

Figure 2.13: TEM image of stacked-cup CNTs.

spectrum of nitrogen can be divided into nitrogen-boron, nitrogen-carbon which contains graphitic type and pyridinic type both, and they peak at 397.4 eV, 398.5 and 399.8 eV respectively.

Figure 2.14: (a)XPS survey spectrum of VA-BC₂NNTAs. (bd) High-resolution XPS spectra of B 1s, C 1s, and N 1s of VA-BC₂NNTAs, respectively. [9]

Chapter 3

Experiment

Experiments are divided into three parts. The first part is to introduce hydroxyl group by exposing to oxygen plasma. Secondly, the conversion reaction is carried out in CVD system and last is characterization methods.

3.1 Functionalization

To trigger the reaction of conversion, it is necessary to introduce hydroxyl groups to carbon atoms on CNTs beforehand. There are mainly two methods to accomplish it. One is to use nitric acid and sulfuric acid to oxidize CNTs for around 8 hours. However, the long time oxidation will damage CNTs too much that their quality is unsuitable for conversion reaction. Furthermore, to convert aligned CNTs, CNTs need to stick to alumina substrate with metal catalyst, in which case long time exposition in acid will destroy this structure. The other method is to expose CNTs in oxygen plasma, which takes only around tens of seconds and maintains the structure of original CNTs. Therefore plasma method was applied to introduce hydroxyl groups to CNTs. In order to test the role concentration of hydroxyl groups play in conversion, two recipes were used for functionalization, The power and the duration for these two recipes were 150 W, 15 s and 200 W, 30 s respectively. As for the flow rate of oxygen, both of these recipes

Figure 3.1: FTIR spectra of (a) pure CNTs, (b) functionalized CNTs with $< 1\%$ OH groups and (c) functionalized CNTs with $> 4\%$ OH groups.

used flow rate of 30 sccm. The resulted concentrations of hydroxyl groups are shown in Fig. 3.1.

3.2 Conversion Reaction

The conversion reaction is carried out in thermal CVD system at relatively low temperature. The whole setup is illustrated in Fig. 3.2. Black CNT powder, functionalized with hydroxyl group, is located on an 1 cm by 1 cm silicon wafer and then loaded into

Figure 3.2: Schematic layout of CVD system.

quartz tube. Boron acid powder is loaded as well as boron precursor under ambient pressure. The tube is installed to the furnace with CNT inside but boron acid outside the furnace. The tube is firstly heated up to 150 °C and hold for 30 min to get rid of the oxygen absorbed by CNTs. After that the tube is heated up to 830 °C in 90 min under atmosphere pressure with 300 sccm argon gas flow. The system is then keep at 830 °C for 10 min meanwhile boron acid is heated up to around 500 °C and ammonia gas flows at 5 sccm as nitrogen source. During this process, the conversion is triggered. After that, temperature is increased to 900 °C and kept at 900 °C for 20 min for further conversion. At last, the tube is cooled down to room temperature naturally. After the whole process is finished, black powder can be observed to change to white one, which is BNNT. To obtain BNC nanotubes, the conversion process should be terminated during 900 °C. The boric acid need to be cooled down first and ammonia keeps flow for 5 more min in order to react with boron oxide residue in CNTs until they are fully reacted. After that the temperature of the system is reduced to room temperature. And powder with color varying from black to gray could be observed. After the conversion, amorphous carbon and unconverted CNTs can be removed by annealing the product in atmosphere at around 500 °C.

3.3 Characterization

Scanning electron microscopy (SEM, LEO 1550 Gemini) was used to characterize CNTs, BNCNTs and BNNTs and observe their alignment. Fourier Transform Infrared Spectroscopy (FTIR, Shimadzu IR Prestige-21) is used to characterize the relatively concentration of OH groups in CNTs. Raman spectroscopy (WITec) with laser excitation wavelength of 532 nm was used to determine the vibration mode of CNTs, BNCNTs, BNNTs and the quality of the BNNTs and BNC nanotubes at room temperature. Transmission electron microscope (TEM, JEOL 2100) was operated with an acceleration voltage of 200

kV, to determine the atomic arrangement and walls. X-ray photoelectron spectroscopy (XPS) was used to characterize the elemental composition of carbon, boron as well as nitrogen constituent of BNNTs and BNC nanotubes. Ultraviolet-visible spectroscopy ((UV-Visible; Shimadzu UV-2450) was used to detect the absorption spectra of BNNTs and BNC nanotubes. Electron energy loss spectroscopy (EELS, Tecnai G2 F20 X-Twin) was applied to determine the spacial distribution of carbon, nitrogen and boron atoms in BNC nanotubes in order to study the mechanism of multi-wall nanotubes conversion.

Chapter 4

Transition: From Carbon Nanotubes to Boron Nitride-Carbon Nanotubes and Boron Nitride Nanotubes

In this chapter, we report a relatively low temperature (900 °C) chemical substitution process to obtain CVD equivalent quality of BNCNTs, BNNTs and BN stacked-cup nanostructure (akin to the stacked-cup structure reported for CNTs [58]). This process is fully compatible with CVD CNTs synthesis method and we demonstrate the conversion of highly-dense, vertically aligned CNTs into BNNTs and obtained the longest vertically aligned BNCNTs and BNNTs reported thus far (around 4 mm). This conversion reaction is a continuous process, in which case the concentration of carbon atoms decreases as reaction time goes while that of boron and nitrogen atoms increase and vice versa. Therefore, we can get BNC nanotubes with certain percentage of carbon theoretically. The concentration of carbon, however, is not proved to be linear to reaction time. Furthermore, conversion process is not conducted uniformly among the whole CNTs sample. For the reasons stated above, what we can get is BNC nanotubes with certain average percentage of carbon.

Figure 4.1: Image of vertically aligned CNTs and their SEM image which shows their alignment.

4.1 CNTs and Functionalized CNTs

Pristine aligned CNTs were synthesized with water assisted CVD method (also known as supergrowth [111]) in a commercial CVD system (Aixtron Blackmagic setup). After

Figure 4.2: Raman spectra of (a) CNTs without being functionalized and (b) functionalized CNTs.

Figure 4.3: FTIR spectra of (a) pure CNTs, (b) functionalized CNTs with $< 1\%$ OH groups and (c) functionalized CNTs with $> 4\%$ OH groups.

being functionalized by oxygen plasma (see Chapter 3), CNTs in black before conversion are shown in Fig. 4.1, with the length of around 4 mm. In order to visualize the defect caused by hydroxyl groups, the Raman spectra of CNTs before and after functionalization are shown in Fig. 4.2. Obviously in Fig. 4.2(a), G peak, corresponding to peak of $1,580\text{ cm}^{-1}$, is stronger than D peak, $1,347\text{ cm}^{-1}$. After functionalization, in Fig. 4.2(b), D peak, conversely, is stronger than G peak, which indicates defects, in this case hydroxyl groups, are introduced into CNTs.

The existence of hydroxyl groups is justified by FTIR spectra, which is shown in Fig. 4.3. Clearly, with different time and power (150 W, 15 s and 200 W, 30 s respectively) during which CNTs were exposed to oxygen plasma, we can get functionalized CNTs with different concentration of hydroxyl groups. Blue line in Fig. 4.3(b) corresponds to less than 1% of OH groups and green line in Fig. 4.3(c) stands for CNTs with more than 4% of OH groups.

Figure 4.4: Image of gray BNC nanotubes and its SEM image which shows the alignment.

4.2 BNC Nanotubes

BNC nanotubes were synthesized in 1994 [112, 113] for the first time and its unique electrical property attracts many attention (see Chapter 2). When the conversion process was terminated before full conversion, BNC nanotubes, with color of gray compare to black pristine CNTs before conversion, were obtained, as shown in Fig. 4.4. The SEM image of Fig. 4.4 shows that converted BNC nanotubes remained their alignment inherited from pristine CNTs.

There are two possible paths for the conversion process. One starts from CNTs, and then converted to BNC nanotubes, finally to BNNTs. The other starts from CNTs as well, however, in the transient state, it is coaxial BNNTs and CNTs (which is the mixed of BNNTs and CNTs) instead of BNC nanotubes, and finally to BNNTs. Therefore, to justified the existence of BNC nanotubes, the existence of carbon-nitrogen or carbon-

Figure 4.5: The 1s core level XPS (X-ray photoelectron spectroscopy) spectra of BNC nanotubes with carbon concentration of 20% of (a) C 1s, (b) B 1s and (c) N 1s. The peak in (a) can be divided into peaks corresponding to C-C bond, C-N bond and C-OH bond. The peak in (c) can be divided into N-B bond and N-C bond.

boron bonds needs to be proven existence, which requires XPS technique.

The XPS results of converted BNC nanotubes are demonstrated in Fig. 4.5, the peaks of C-N bonds can be observed, which indicates the existence of BNC nanotubes. However, the puzzle for the lack of C-B bond remains unsolved. The most probable reason why there is no C-B bond in XPS results is the surplus of ammonia. The precise control of solid boric acid precursor is difficult, thus after the termination of conversion process, there were many boric acid and boron oxide residues in nanotubes sample. To get rid

of these residues, ammonia flow was kept to continue so that the residues could totally react with ammonia to convert nanotubes, in which case the amount of nitrogen was much more than that of boron. Therefore strong C-N peak exists in XPS results instead of C-B peak.

4.3 Converted BNNTs and Transition Process

Full conversion is finished within two hour. After that, aligned CNTs in black are converted to aligned BNNTs in white, as shown in Fig. 4.6. The average length of aligned BNNTs is around 4 mm, which is consistent with the length of pristine CNTs. Also from the SEM image of converted BNNTs, alignment of nanotubes was successfully inherited from original CNTs to converted BNNTs, which enriches the possible applications of this

Figure 4.6: Image of gray BNC nanotubes and its SME image which shows the alignment.

Figure 4.7: The 1s core level XPS spectra of (a) carbon, (b) boron and (c) nitrogen. The red, green and blue lines are associated with CNT, BNC nanotubes and BNNT respectively.

method. Viewing the whole transition process, nanotubes are converted originally from CNTs, and then to intermediate state, BNC nanotubes, and eventually to BNNTs. To demonstrate the transition process, three samples from these three states were selected to be representatives, in which case, the intermediate state (BNC nanotubes) were synthesized in the same method as BNNTs but only have 10 min reaction time and stop 10 min after temperature reaches 830 °C.

In order to visualize the transition process, XPS spectra with C peaks at 284 eV, B peaks at 190 eV and N peaks at 398 eV are shown in Fig. 4.7, in which the different composition of carbon, boron and nitrogen in CNT, intermediate state of BCN nanotubes and BNNT can be easily observed. Red curve and blue curve correspond to 100% CNT and 100% BNNT respectively. Green curve corresponds to intermediate BNC nanotubes

Figure 4.8: Raman spectra of CNT before conversion (green), which contains D and G peaks, the intermediate state, BNC nanotubes (red), which contains a weak G peak and a peak at $1,362\text{ cm}^{-1}$ and BNNT after conversion (blue) which peaks at $1,370\text{ cm}^{-1}$.

with around 40% of carbon. From XPS results, it can be seen that the composition of C reduced from 100% for CNTs (red) to 40% for BNCNTs (green) and 0% for BNNTs. Whereas for B and N, their composition increases as the CNTs are being converted into BNNTs. The ratio between B:N is also found to be approximately 1:1 for both BNCNTs and BNNTs. As shown in Fig. 4.7, the efficiency for conversion at the beginning is high that it took around 10 min to have 60% CNTs converted and less than 30 min to convert 100%. This result also indicates that the composition ratio between carbon, boron and nitrogen in BNC nanotubes can be tuned by conversion parameters such as reaction time and furnace temperature as well as precursor temperature. Here the different composition is mainly due to the different reaction time. Furthermore, XPS result shows that the reduction of carbon composition is not linear with time since the rate is higher at the beginning.

These three states were also characterized by Raman spectroscopy. In the Raman

Figure 4.9: UV-absorption spectra of (a) pristine CNTs, (b) BNC nanotubes and (c) converted BNNTs.

spectra of Fig. 4.8 (a), green line represents functionalized CNT with D peak ($1,347 \text{ cm}^{-1}$) and G peak ($1,580 \text{ cm}^{-1}$). There were OH groups which were introduced into CNTs and acted as defects, which explains the fact that D peak is stronger than G peak. The Blue represents BNNT after conversion with peak at $1,370 \text{ cm}^{-1}$ and full width at half maximum (FWHM) of 30 cm^{-1} , which corresponds to E_{2g} mode of h-BN. The resulted spectrum of converted BNNTs shows that the crystal quality by this method is good. The red curve is BNC nanotubes, the same as those in XPS characterization. A weak peak of G mode can also be observed in red curve. Besides the weak G peak, a peak at $1,362 \text{ cm}^{-1}$ is observed. This peak at $1,362 \text{ cm}^{-1}$ is superposed by D mode of from sp^2 carbon ($1,347 \text{ cm}^{-1}$) and E_{2g} mode of h-BN ($1,370 \text{ cm}^{-1}$), an indication for the existence of both C and hBN domains. The red spectrum indicates that the Raman spectrum of BNC nanotubes is merely the superposition of it of CNTs and of BNNTs. And the

comparative strength and position of peaks will change according to the composition ratio of carbon, boron and nitrogen.

Fig. 4.9 shows the UV-visible absorption spectrum of CNTs, BNC nanotubes and BNNTs, respectively. Due to the π -plasmon, a broad peak at around 270 nm is observed from the CNTs array. For BNC nanotubes, superposition of 2 peaks is being observed at 220 nm and 270 nm, contribution from both hBN and C domains. As for BNNTs, only one peak at 220 nm is observed, which is consistent with CVD-growth BNNTs [114].

This chapter reports the successful conversion from pristine CNTs, to BNC nanotubes and to converted BNNTs. There are several implications pertaining to the direct conversion process of obtaining high quality BNNTs from CNTs. First and foremost, the temperature of obtaining BNNTs in the entire process (i.e. 650 °C for the growth of CNTs and 900 °C for the conversion process) is significantly lower than most of current CVD BNNTs processes, which is typically in the range of 1500°C. This implies that the substitution process can be easily integrated with most of the CNT CVD systems, including commercial setups. Also, as the techniques of obtaining CNTs are more developed than those for BNNTs, a direction conversion process also provide an alternative to obtain structural architecture that has been well studied for CNTs growth but not for BNNTs, such as the highly dense, vertical aligned CNTs via supergrowth process. In addition, the conversion process also provide a controllable approach of obtaining BNCNTs, a composite nanotube that is consists of domains of BN and C.

Chapter 5

Morphology: Multi-wall vs. Stacked-cup BNNTs and Their Mechanisms

This chapter reports the successful synthesis of both multi-wall and stacked-cup BNNTs, also describes and discusses the role OH groups play during conversion and the effect due to the different compositions of OH groups. Similar to CNTs, BNNTs can perform different morphologies in terms of wall structure. But previously, only single/multi-wall BNNTs were observed. There is one kind that can be observed in CNTs and predicted in BNNTs only, stacked-cup structure. The schematic graph of multi-wall and stacked-cup BNNTs are shown in Fig. 5.1. Multi-wall BNNTs consist of aligned walls paralleled to the axis of nanotubes while the aligned walls in stacked-cup BNNTs tilt to have certain degree with the axis.

As mentioned in Chapter 3, OH group is necessary to initiate the reaction process and it also has a major role in controlling the resultant morphology of the BNNTs. This is because the required energy for N to substitute functionalized C is much lower than with pristine C and hence, the substitution of N at C-OH sites is preferred. Table 5.1 calculated by density functional theory [104] makes the effect of OH groups more clear. The energy for nitrogen to substitute carbon on pristine CNTs is very high (2.75 eV).

Although the introduction of OH groups increases the energy for boron to substitute pristine carbon (from 1.04 eV to 2.89 eV), it can significantly reduce the required energy for nitrogen to -1.0 eV. With this embedded nitrogen, the energy for subsequent boron to substitute is also reduced to only 0.01 eV. Therefore, Oh group plays a crucial part in this conversion method.

Therefore, the conversion process is initiated by the substitution of N with C-OH sites and therefore, there is a direct implication on the conversion process with the dosage of OH attachment and the crystalline structure of the nanotubes. To observe this correlation, 2 sets of CNTs have exposed to oxygen plasma at different dosages (150 W at 15 seconds 200 W at 30 seconds) and their corresponding FTIR results are shown in Fig. 5.2 (b) and Fig. 5.2 (c). As observed in the FTIR spectra, the broad dip at around 3400 cm^{-1} corresponds to OH group attachment and the difference in the intensity of the dip between the 2 prepared samples is about 3 times, corresponding to their oxygen plasma exposure.

To examine the microstructural quality of BNNTs obtained from the conversion process with different OH attachment dosage, transmission electron microscopy (TEM) is used. Fig. 5.3 (a) shows the pristine CNTs after oxygen plasma treatment. The CNTs are all multiwall, with the number of walls varying between 5 to 20 layers. Fig. 5.3 (b) shows the TEM image of a BNNT corresponds to the lower OH dosage, after the conversion

Figure 5.1: Schematic graph of (a) multi-wall BNNTs and (b) stacked-cup BNNTs.

Figure 5.2: FTIR spectra of (a) pure CNTs, (b) functionalized CNTs with $< 1\%$ OH groups and (c) functionalized CNTs with $> 4\%$ OH groups.

site	E_{sub} (eV)				
	N	B	BN	BNH ₂	BNH ₄
pristine	2.75	1.04	2.78	1.76	1.16
hydroxyl	-1.0	2.89	-	-	-
vacancy	-11.27	-14.3	-	-	-
embedded N	-	0.01	0.72	0.54	-0.07
embedded B	1.27	-	0.82	0.49	-0.12

Table 5.1: Substitution energy for B, N and BN related pairs to replace corresponding carbon atoms at different locations in CNTs.

process. A distinctive multiwall nanotube structure can still be seen, with an inter-wall spacing of 0.34 nm, in agreement with CVD grown BNNTs. [115] This result indicates that for low dosage of OH attachment, the microstructure of the BNNT is still highly crystalline. Importantly, the inner tube diameter of the converted BNNT is identical to the inner tube diameter of CNTs before the conversion (i.e. 7-10nm); this suggests that the conversion process is by substitution and not by the growth of BN encapsulation on CNTs and subsequently, the etch off of the C content. This is because for the latter, the inner tube diameter of the BNNTs will be conformal to the outer tube diameter of the CNTs and not to the inner tube.

As for the case of higher dosage of OH attachment, the TEM image of the resultant

Figure 5.3: TEM image of (a) CNT before conversion; (b) BNNT after conversion of CNT with less OH groups and (c) stacked-cup BNNT after conversion of CNT with more OH groups.

BN structure is shown in Fig. 5.3 (c). From the TEM image, it can be seen that the microstructure is still tubelike; however, the walls of the nanotube are now consisting of flakes and stacked orderly in an upward manner. These observations show that with higher dosage of OH group attachment, a new BN structure is being evolved, akin to a cone-stacking structure.

5.1 Multi-wall BNNTs and Their Mechanism

The process of conversion to multi-wall BNNTs, which corresponds to CNTs with lower hydroxyl concentration, was calculated by density functional theory [104]. Fig. 5.4 illustrates the conversion process for CNTs with low OH concentration. Fig. 5.4 (a) shows the schematic of a CNT with an OH group (in green) attached to 1 of the C atoms (in gray). At the beginning of the conversion process, functionalized C atoms (i.e. OH group attached) tend to be substituted by N atoms while B atoms remain unfavorable, as shown in Fig. 5.4 (b). After the formation of N nucleation, the substitution of neighboring C

atoms around the N nucleation by B atoms or BN pairs becomes much easier, as shown in Fig. 5.4 (c). These substitution processes continue and the whole nanotube will be converted into BNCNTs (with increasing ratio between BN:C) and lastly, into BNNTs, as shown in Fig. 5.4 (d)-(e).

Since the conversion process occurs in the entire multiwall structure while OH group are mostly attached onto the outermost wall. In order to have more insight into the conversion mechanism, electron energy loss spectroscopy (EELS) is being used to provide an elemental mapping of a BNNT in the intermediate stage of the conversion process. The EELS mapping of a BNCNT is shown in Fig. 5.5 (b), obtained from a portion of the nanotube seen at the TEM image at Fig. 5.5 (a) (i.e. within the green box). In the EELS mapping, blue and red dots represent B and N, respectively, and green dots correspond to C. It can be seen that the outer walls are mainly consisting of B and N with the concentration of C increasing toward the inner walls of the tube. This means that the CNT is now encapsulated with BNNT by the substitution process. From this result, it can be seen that the conversion process is not homogenous across the entire nanotube but more

Figure 5.4: Schematic for the conversion from CNTs to BNNTs. C, N, B atoms and OH groups are denoted in gray, red, blue spheres and green-white pair, respectively. (a) OH group is being attached onto the surface of CNT. (b) C with OH attachment is being substituted by N atom. (c) B atoms substitution occurs at the neighboring site (d) BN domain nucleates and expands. (e) BN domain expands further and the CNT is fully converted to BNNT.

Figure 5.5: EELS mapping of BNCNTs (the intermediate stage of the conversion process) (a) TEM image of the BNCNT and the green box indicates the area where the EELS mapping was taken. (b) EELS mapping of the BNCNTs, green dots corresponds to C, blue and red dots correspond to B and N, respectively.

favorable to occur at the outer tubes, because of the higher concentration of OH group. However, despite the low or even negligent amount of OH attachment in the inner tubes of the CNTs (resulting from the oxygen plasma treatment), the conversion process is not terminated at the outer wall and does indeed eventually convert the whole nanotube. This is because there would be a certain amount of hydroxyl groups diffusing into the inner walls of CNTs due to the open tips and vacancy defects, which are originated from growth or caused during plasma treatment. Additionally, besides oxygen plasma treatment, the disassociation of boric acid also provides a secondary OH source [104], which will diffuse through the opening of the nanotubes and allow the conversion process to continue toward inner walls.

5.2 Stacked-cup BNNTs and Their Mechanism

For the case of cone-stacking BNNTs that is obtained with high concentration of OH groups, the formation of the microstructure originates from the mismatch of BN nucle-

Figure 5.6: Schematic for the formation of cone-stacking BNNTs. C, N, B atoms and OH groups are denoted in gray, red, blue spheres and green-black pair respectively. (a) Two OH groups is functionalized on a segment of CNT. (b) C atoms with OH group attached are replaced by N atoms and leading to two nucleation. (c) The two BN nucleations grow and their edges are mismatched to each other. (d) Segment splits at the mismatched edge. (e) Edges of these two BN nucleation form stacked structure.

ation and is analogous to the growth of stacked-cup carbon nanofibers [116]. Fig. 5.6 illustrates the conversion process for CNTs with high OH concentration. To simplify, Fig. 5.6 (a) shows the schematic of a CNT with 2 OH groups (in green) attached to 2 of the C atoms (in gray). As before, functionalized C atoms tend to be replaced by N and form 2 nucleations while B atoms remain inactive, as shown in Fig. 5.6 (b). These 2 nucleations expand as subsequent substitutions, similar to the case of multi-wall BNNTs. However, as the conversion proceeds further, the boundary between these two adjacent BN nucleations might be mismatched due to the asymmetry of B and N atoms, as shown in Fig. 5.6 (c). In this case, the wall of nanotube will be split at the edge between the 2 BN patches, as shown in Fig. 5.6 (d). Subsequently, the edges tend to stack in order to occupy the lower energy states and hence lead to a cone-stacking BNNT, as shown in Fig. 5.6 (e).

Stack-cup structure occurs when two areas, which result from hydroxyl groups, of BN on CNT do not match with each other due to the atom asymmetry of h-BN. Therefore, pure converted BNNTs occur when the concentration of hydroxyl groups is low and

hence the number of BN areas is low. There is no certain transition point for these two structures. However, an interval between pure BNNTs and highly stack-cup BNNTs exists, where the degree of how BNNTs being destroyed by stacked-cup structure. Nevertheless, for applications, we need only pure BNNTs or stack-cup structure instead of intermediate structure.

Chapter 6

BNC Nanotubes and Their Electrical properties

This chapter reports the tuning bandgap property of BNC nanotubes that this conversion method enables. When the concentration of carbon in BNC nanotubes is sufficiently low, there will be some emergent properties. Due to the impaired conjugation effect of the surrounding carbon when the BN concentration is increased, the optical bandgap for BN nucleation in BNC nanotubes will be increased as the conversion proceeds.

The measurements of converted BNNTs, BNC nanotubes with different concentration of C as well as CNTs were carried out. The results are shown in Fig. 6.1. Since they are direct bandgap semiconductors, the absorption coefficient α satisfies Tauc relation [117]

$$\alpha = \frac{a(E - E_g)^{1/2}}{E}$$

where a is a constant, E is the photon energy and E_g is the optical bandgap. $\alpha = A/t$, where A is the optical absorbance and t is the length of nanotubes. Thus a plot of $\alpha^2 E^2$ versus E would yield a straight line around absorption peak with the E axis intercept equal to bandgap E_g . Therefore as shown in Fig. 6.1, the measured bandgaps of converted BNNTs and BNC nanotubes with carbon concentration of 7%, 15% and 20% are 5.70 eV, 5.40 eV, 5.00 eV and 4.80 eV respectively, which is consistent with calculation [118]. Interestingly, Fig. 6.1(d) illustrates that there are three parts in the

Figure 6.1: Ultraviolet-visible absorption spectrum of (a) BNNTs after conversion, (b) BNC nanotubes with carbon concentration of 7%, (c) BNC nanotubes with carbon concentration of 15%, (d) BNC nanotubes with carbon concentration of 20%, (e) BNC nanotubes with carbon concentration of 40%, (f) CNT before conversion. Measured bandgaps for (a)-(d) are 5.70 eV, 5.40 eV, 5.00 eV and 4.80 eV respectively.

spectrum of BNC nanotubes, a bump around 270 nm and two slopes which correspond to C, BN and interaction between C and BN [119]. Although Taucs plot to extract the optical bandgap (OBG) is widely used for solid thin films, it can be applied to estimate the OBG for nanotubes as well [120, 121, 122, 123]. In general, the effective length of nanotubes responsible for photon absorption is shorter than the total length, which results in the underestimation of the absorption coefficient. As such, the gradient of the slope of Taucs plot is decreased, which results in lower estimated OBG. Nevertheless, the doping effects of C in BNNTs are reflected in the shift in optical absorption. The trend of increasing concentration of C with bandgap lowering is observed on the BNCNTs samples.

Chapter 7

Summary and Future Work

7.1 Summary

7.1.1 Conversion of functionalized CNTs to BNC nanotubes and BNNTs

A new approach to synthesize BNNTs is proposed. Previous methods for growing BNNTs either require high temperature and strict conditions, such as CVD method, etc. or produce BNNTs with low quality, such as ball milling method. Our method reduces required temperature to 900 °C, due to the introduction of hydroxyl groups so that the energy to excite carbon atoms is reduced. Furthermore, converted BNNTs perform the same quality as prepared CNTs and the synthesis of CNTs is mature nowadays, therefore this method can produce high-quality BNNTs easily. Lastly, because the condition it needs is not strict, this conversion method can be extended to large-scale synthesis of BNNTs. Also, if conversion process is aborted before full conversion, gray product is observed. From Raman spectroscopy and TEM results, it could be determined to be either coaxial CNT/BNNT or BNC nanotubes. After that, the peak of C-N bond is observed in XPS result and red shift is shown in UV-Vis spectrum, we determine that BNC nanotubes can be converted using this method.

7.1.2 Synthesis of long vertically aligned BNNTs

Long aligned BNNTs (5 mm) were synthesized by this method. The approaches of growing CNTs are very mature nowadays and the converted BNNTs process the same structure with prepared CNTs. We, therefore, used water assisted CVD system to produce super growth of aligned CNTs and then prepared them for conversion. After the same conversion process, aligned BNNTs are successfully obtained.

7.1.3 Synthesis of two kinds of BNNTs, multi-wall and stacked-cup

Both multi-wall and stacked-cup BNNTs can be synthesized, selected by the concentration of hydroxyl groups introduced to CNTs, and also discuss their mechanism. Stacked-cup nanotubes provide more extra space from exposed edges, and thus they have other promising applications different from normal-wall nanotubes, such as ion storage and diffusion, which is realized in stacked-cup CNTs and predicted in stacked-cup BNNTs. In this M.Eng project, CNTs were converted to both multi-wall and stacked-cup BNNTs. The mechanism of conversion of single wall is calculated using functional density theory by Gong et al. [104] while the outside-to-inside mechanism of conversion of multi-wall BNNTs is justified by EELS result. Furthermore, the occurrence of stacked-cup structure is explained consistently by the mismatch and fragmentation of BN nucleations, similar to the growth of stacked-cup CNTs.

7.1.4 Tuning the optical bandgap of BNC nanotubes

The optical bandgap of BNC nanotubes can be tuned. When the concentration of carbon in BNC nanotubes is sufficiently low, instead of merely superposition of BNNTs and CNTs, there will be some emergent properties. One remarkable property is the red shift of the UV-Vis absorption spectrum, due to the impaired conjugation effect of the

surrounding carbon. Therefore, by applying different reaction time for the conversion process, BNC nanotubes with different concentration of carbon, hence different optical bandgap, can be obtained. In this M.Eng project, the bandgap of BNC nanotubes was successfully tuned from 5.7 eV to 4.8 eV.

7.2 Future Work

Based on the discovery in my M.Eng project, there are several recommendations to further exploration of related research topic.

- To investigate thoroughly the mechanism of the conversion reaction. Further theoretical study on related subject is recommended.
- To tune the optical bandgap of BNC nanotubes furthermore. Due to the impaired conjugation effect, the bandgap of converted BNC nanotubes now can be tuned from 5.7 eV to 4.8 eV. However, when the concentration of carbon in BNC nanotubes keeps increases, this impaired conjugation effect becomes weak and the superposition begins to dominate. The study on lowering the optical bandgap further more for more electrical applications is recommended to conduct in the future.
- To discover more applications for this conversion method. Aligned BNNTs has been converted already. But the structure, morphology and position arrangement of CNTs are diverse. Therefore this method can be applied to more areas that are needed to be studied further.

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