

**Boron Nitride Nanomaterials:
From Fabrication to Characterization**

by

Luhua Li

April 2010

A thesis submitted for the degree of

Doctor of Philosophy

of

The Australian National University



THE AUSTRALIAN NATIONAL UNIVERSITY



by

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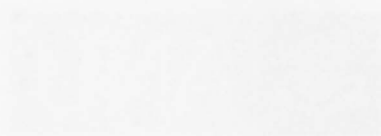
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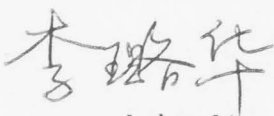
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Declaration

This thesis is an account of the research that I performed during the academic program for the degree of doctor of philosophy. To the best of the author's knowledge, this thesis contains no material previously published by another person, except where due reference is made in the text. This thesis contains no material which has been accepted for the award of a degree or diploma in any other university.



Luhua Li

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Abstract

Boron nitride nanotubes (BNNTs) and ultra thin BN sheets are two of the most important next generation nanomaterials. The synthesis and study of them are of both fundamental interest and technological importance. Improved methods of fabricating BNNTs and ultra thin BN sheets are presented in this thesis together with studies that characterize their properties and indicate potential applications.

The production of high purity BNNTs in large quantities has been a major obstacle inhibiting the broad study and application of BNNTs. A new approach, involving a liquid boron (B) ink, has been developed to produce higher purity and larger quantities of BNNTs. In the new method, the ball milled B particles are homogeneously mixed with ethanol and metal nitrate in an ultrasonic bath. The ink-like liquid mixture, or B ink, is annealed in nitrogen containing gas to synthesize 0.5g of high purity BNNTs at one time. This significant invention has brought the practical application of BNNTs one step closer. As an example, bulk sized (not film shaped) BNNT reinforced polyurethane (PU) composites have been produced.

The growth of nanotube films on various substrates and surfaces is vital for a range of applications. However, unlike the sophisticated carbon nanotube (CNT) film production, patterned growth of BNNTs over large areas had not previously been achieved. The new B ink method also overcomes this obstacle by providing a simple but powerful way to grow BNNT films on different substrates. It is demonstrated that the ink can be directly painted/brushed, sprayed, or even inkjet printed on different substrates with any desired pattern and the ink layer is converted to a film of high density BNNTs by the annealing. This is the first method capable of growing BNNTs on non-flat or complex surfaces. Because the coating method involves direct growth of nanotubes, the BNNT films have strong adhesion to the substrate, which is very desirable for practical applications and a number of potential applications of such coatings are demonstrated.

The larger quantities and particularly the higher purity of the BNNTs grown have enabled new properties of BNNTs to be discovered. For example, for the first time, single deep ultraviolet (DUV) emission at 225nm (5.51eV) has been found from BNNTs with a

cylindrical multiwall structure and diameters smaller than 10nm. This finding suggests that BNNTs can work as nanoscale DUV light emitters opening up potential applications in miniaturized optic and optoelectronic devices as well as in biomedical analysis and treatment. In addition, many intriguing anti-wetting properties have been demonstrated for these BNNT films.

In addition to BNNTs, the ball milling method was modified to allow ultra thin BN sheets to be produced in large quantities. Investigations have shown that small sheets, as thin as 2nm, can be produced, and the in-plane structure of the sheets remains largely intact. Interestingly, the thin BN sheets exhibit better DUV luminescence than the un-milled *h*BN particles.

List of publications

L. H. Li, C. P. Li, and Y. Chen, *Synthesis of boron nitride nanotubes, bamboos and nanowires*. Physica E **40**(7), 2513, 2008.

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List of Abbreviations

AAO	anodic aluminium oxide
AFM	atomic force microscope
BNNTs	boron nitride nanotubes
BPR	ball to powder weight ratio
CFM	conductive force microscopy
CL	cathodeluminescence
CNTs	carbon nanotubes
CVD	chemical vapour deposition
DMA	dynamic mechanical analyser
DUV	deep ultraviolet
EDS	energy-dispersive x-ray spectroscopy
EELS	electron energy loss spectroscopy
EFM	electrostatic force microscopy
EXAFS	extended x-ray absorption fine structure
FWHM	full width at half maximum
HRTEM	high resolution transmission electron microscopy
KPFM	kelvin probe force microscopy
LEDs	light-emitting diodes
MFM	magnetic force microscopy
NEXAFS	near edge x-ray absorption fine structure
PEY	partial electron yield
PFM	piezo force microscopy
PL	photoluminescence
SAED	selected area electron diffraction
SEM	scanning electron microscopy
SPM	scanning probe microscope
SRPES	spin resolved photoelectron spectroscopy
STM	scanning tunnelling microscopy
TEM	transmission electron microscopy
TFTs	thin-film transistors

TGA	thermogravimetric analysis
TIM	thermal interface materials
VUV	vacuum ultraviolet
XPS	x-ray photoelectron spectroscopy
XRD	x-ray diffraction

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Chapter 1

Introduction to boron nitride materials

Boron nitride nanotubes (BNNTs) and BN nanosheets are two of the most important next generation materials. The synthesis and study of them are of both fundamental interest and technological importance. They exhibit many unique properties unavailable in their carbon counterparts, carbon nanotubes (CNTs) and graphene. However, the synthesis of large quantities of pure BNNTs, the growth of patterned BNNT films on substrates and the mass production of ultra thin BN sheets are still a long way behind those of CNTs and graphene layers. Therefore, more effective BNNT and thin BN sheet synthesis methods are needed for the exploration of both their intrinsic properties and new applications. In chapter 1, the introduction of the synthesis and properties of BNNTs and BN nanosheets are presented.

1.1 Hexagonal boron nitride

Boron nitride is a synthetic III-V chemical compound having equal numbers of boron (B) and nitrogen (N) atoms. BN can have hexagonal, cubic and sometimes even wurtzite, crystalline forms. The most common form of BN is *h*BN, sometimes called α -BN. It consists of layers of hexagonal lattices of alternating B and N atoms. The B and N are covalently bound within the lattice, while the layers are weakly bound by van de Waals forces. Between layers, B atoms are located directly above or beneath N atoms, and vice versa for N atoms. The in-plane lattice spacing of *h*BN is 0.25nm and the interlayer distance is 0.333nm [1]. The structure of *h*BN is the cause of most of the anisotropies in its properties.

*h*BN usually has the low density of 2.1-2.2g/cm³ (theoretically 2.27g/cm³) [2] and is quite stable with excellent resistance to thermal shock. It does not decompose until 1000°C in air, 1400°C in vacuum and 2800°C in inert gases, and is not soluble in most acids. *h*BN is a widely used high temperature lubricant in both industry and daily life. A special advantage is that its lubricity comes directly from the BN layers not from gas or water molecules so that *h*BN can even be used in vacuum. The thermal expansion of *h*BN is very low and the thermal conductivity can reach 600W/mK (in plane) [2].

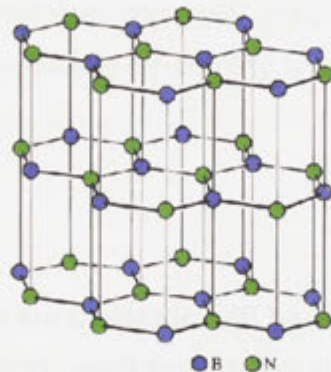


Figure 1.1 Layered structure of *h*BN, where blue colored balls represent B atoms and green ones represent N atoms.

*h*BN has high electrical resistivity, which is very different from graphite. The difference in electrical conductivity between *h*BN and graphite can be of the order of 10¹⁸. The main reason for this is the different electron delocalisation in the two materials. From the band structure point of view, the valence and conductive bands of graphite cross each other at the Fermi level, while for *h*BN, the two bands do not overlap [3]. So graphite can be viewed as a semimetal and *h*BN is a wide bandgap semiconductor. Therefore, *h*BN is usually used as an electrical or charge sealing material and an electronic substrate material. The bandgap of *h*BN was not explicitly known until very recently: when single crystals of *h*BN were produced and found to have a direct bandgap of 5.9eV [4, 5]. This discovery makes *h*BN promising for deep ultraviolet optoelectronic applications, such as light-emitting diodes (LEDs) and laser light sources.

1.2 Atomically thin BN sheets

Graphene, a single layer of graphite, has aroused intense research interest. Because *h*BN is isostructural to graphite, it is also interesting to explore the properties of a monolayer or

atomically thin sheets of *h*BN. Small quantities of BN monolayers can be exfoliated or etched from *h*BN particles, in a similar way to produce graphene [6-8]. However, the quantity is too small for researches and applications. Many large quantity production methods proposed for graphene, such as Hammer's and related methods [9, 10] or the chemical modification methods [11], are not directly usable on *h*BN. Hitherto there have been only two bulk quantity methods developed for production of atomically thin BN sheets. One is substrate growth by chemical vapour deposition (CVD) [12, 13] and the other is solution exfoliation under sonication [14].

In 1995, Nagashima et al reported the epitaxial growth of a monolayer of BN on a Ni(111) substrate by the decomposition of borazine ($B_3N_6H_3$) at 700-800°C [12]. In striking contrast to the strong modification of the band structure of graphene when grown on Ni(111), the bond between the BN monolayer and the Ni(111) substrate is much weaker. Hence, the BN monolayer on a Ni(111) substrate should be more like an isolated free-standing film [15]. This decomposition method is still being used to grow a BN monolayer on transitional metal substrates [16]. More recently, Song et al sublimated ammonia borane (BNH_6) at 120-130°C and then thermally treated by Ar/ H_2 gas glow to grow BN sheets with a few number of layers on copper foil [13]. The problem for the BN sheets grown on substrate by CVD methods is that they cannot be used in many applications, such as fillers in composites,

The solution exfoliation method was first proposed for production of atomically thin graphite sheets [17], and then was found to work on *h*BN as well. During the process, *h*BN particles were ultrasonicated in a liquid which has a similar surface tension to *h*BN so that ultrathin BN sheets can be exfoliated [14]. The BN sheets produced this way usually have smaller sizes than those produced by CVD method, but with better crystallinity. Although the BN sheets produced by solution exfoliation can be easily used in preparing composites [14], a serious problem for this method is that most of the BN sheets are more than ten layers thick, which may directly affect the desirable properties.

Because of the lack of materials, there have been few experimental studies of BN monolayers [6-8, 12, 15] and most of the properties are still largely based on theoretical calculations.

1.3 Boron nitride nanotubes

1.3.1 The history of BNNTs

CNTs, first discovered in 1991 by Iijima [18], are seamless cylinders of graphitic carbon with nanosized diameters. The CNTs reported by Iijima had cylindrical multiwalled structure and the existence of single walled CNTs was confirmed two years later [19]. Although *h*BN and graphite have a very similar structure, the first non-carbon nanotubes were not BNNTs but metal dichalcogenide nanotubes: tungsten disulfide (WS_2) nanotubes [20]. It was three years after the discovery of CNTs that the existence of BNNTs was theoretically proposed [21, 22]. In 1995, cylindrical BNNTs were successfully synthesized in the laboratory [23]. It is worth noting that since the discovery of BNNTs, the number of research publications on BNNTs has grown linearly with those for CNTs and especially in recent years, the number of theoretical papers related to BNNTs has vastly increased [24]. This reflects the importance of BNNTs as an alternative to CNTs.

1.3.2 The structures and characterizations of BNNTs

BNNTs can be viewed as *h*BN layers rolled into tubes. Single walled BNNTs have different chiralities depending on the rolling axis [19, 25]. As an example, Figure 1.2 shows a monolayer of *h*BN with two chiral vectors n and m . When $n=m$, the single walled BNNT is called an armchair nanotube; when $n=0$, it is a zigzag nanotube; and in all other cases, they are called chiral. In the case of CNTs, the chiralities are quite important, because they determine the electrical properties. For example, armchair CNTs and those tubes with $n-m$ being an integer exactly divisible by 3 are metallic. The other CNTs are semiconductors. This property of CNTs sounds attractive; however, there is usually no preferable growth chirality for CNTs and the separation of metallic and semiconducting CNTs is very challenging [19, 26, 27]. In contrast, the electrical properties of BNNTs are independent of their chirality and diameter [21]. Almost all BNNTs have a wide bandgap of around 6eV, except those with diameters less than 1nm [21, 28, 29]. The bandgap of these very fine BNNTs is depressed by about 1eV owing to the sp^3 hybridization [21]. Usually, the chirality of individual BNNTs can be determined by high-resolution transmission electron microscopy (HRTEM) as well as selected area electron diffraction (SAED) [27].

Single walled BNNTs are not easy to synthesize, although they may form at the same time as multiwalled tubes at small percentages [30-32]. This difficulty is mainly caused by the strong interaction among BN layers due to the ionic character of the BN bonding [33]. In

comparison, the synthesis of single walled CNTs is much easier [34, 35], because the carbon atoms only have the same chemical bond.

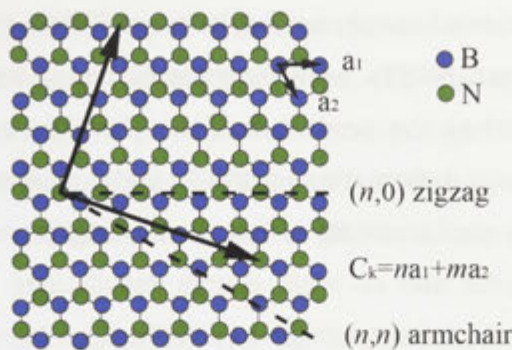


Figure 1.2 A single layer of hBN with vector number n and m to show the chirality of a single walled BNNT.

BNNTs and CNTs have different closures at the tip. CNTs end with a hemispherical part of a buckyball structure. For high quality BNNTs, rectangular or square shaped flat caps, presumably formed by a combination of square, pentagonal, or pentaline shapes, are normally found on the tip [36-38]. This difference can be attributed to the different topological defects that can arise with C-C and B-N bonds [33]. In addition to cylindrical multiwalled BNNTs, BNNTs with a bamboo-like structure can also be formed [39, 40].

1.3.3 The properties of BNNTs

BNNTs and CNTs have many similar properties. For example, the mechanical strength, the thermal conductivity and the surface tension are quite similar. On the other hand, BNNTs also possess some unique properties that cannot be found in their carbon counterpart. For instance, BNNTs have better high temperature stability than CNTs; the wide bandgap of BNNTs is much less dependent on the chirality and diameter; and BNNTs may have strong piezoelectric properties.

In spite of hBN being brittle, BNNTs have superb stiffness and bending flexibility along the axial direction [41]. This can be mainly attributed to the tubular structure and the strong sp^2 bonding. Unlike the mechanical studies of CNTs, which were pioneered by theoretical calculation [42], the study of the mechanical properties of BNNTs was started by practical experiments. The elastic property of an individual multiwalled BNNT was determined from its thermal vibration amplitude inside a HRTEM at 27°C, with its axial Young's modulus

being found to be 1.22TPa [43]. This value is in the same range as the measured Young's modulus of CNTs (0.4-4TPa) [44], but almost one order of magnitude higher than that of other known insulating fibres. Later, the elastic modulus of BNNTs was more systematically measured using the electromechanical coupling between BNNTs and an applied electric field in a TEM. In total, eighteen BNNTs were individually tested and the average value was 722GPa [45], which matched the predictions from the tight-binding and first-principle calculations [42]. The plastic deformation of BNNTs under axial compression is anisotropic due to the relative radial displacements of boron and nitrogen atoms, as shown by tight-binding molecular dynamics and *ab initio* energy calculations [46]. Similar to the CNT system, the defects with the lowest energy in BNNTs were formed by Stone-Wales bond rotations during deformation. However, more energy is required for the formation of this dislocation in BNNTs than in CNTs [47]. So, although a BNNT has slightly lower mechanical properties than a CNT, the thermodynamic yield limit of BNNTs should be higher under constant strain or in a high temperature environment. Because of these excellent mechanical properties, BNNTs have been put into different materials to produce nanocomposites [48, 49].

BNNTs have better thermal and chemical stability than CNTs. In general, CNTs can be oxidized at 400-500°C in air and totally burnt out at about 700°C [50-52]. In contrast, the oxidation of BNNTs starts at 600-950°C and the burning-out happens above 1200°C [52, 53]. The oxidation process in BNNTs is associated with the formation of B_2O_3 and the evaporation of nitrogen gas [53]. The oxidation temperature of BNNTs is highly dependent on the structure or the density of defects in the tube, as the oxidation happens first at the defects. For example, at 600°C the BNNTs with bamboo-like structures may first start to oxidize at the connection points on the surface of the nanotubes, where a relatively higher density of defects is present and then the oxidation spreads along the wall direction [53]. On the other hand, well crystallized cylindrical BNNTs will not react with oxygen (O_2) until 950°C and the oxidation usually starts from the tips where most of the defects occur [54].

CNTs are well known for their unprecedented thermal conductivity [55-57]. When graphite is rolled up into a nanotube, the phonon confinement can dramatically reduce phonon scattering, which cannot occur in bulk materials. The theoretically calculated thermal conductivity of CNTs is 6000W/mK. But as thermal conductivity is very sensitive to defects as well as, in the case of a nanotube, the diameter of the nanotube [57], the measured values are much smaller, usually of the order of several hundred W/mK. The thermal conductivity of BNNTs is of the same order as that of CNTs due to the same phonon dispersion relation

[58], although *h*BN has lower thermal conductivity than graphite. It is worth noting that BNNTs have the biggest thermal conductivity boost of any known material from changes in the isotopic content. BNNTs with more than 99.5% ^{11}B can have a thermal isotope effect of about 50% [59], which gives rise to even better thermal conductivity than most CNTs. Recent theoretical studies found that this giant boost was mainly because the presence of ^{11}B can enormously increase the phonon transport at high frequencies [60, 61]. The calculations also predicted that much higher thermal conductivity can be realized for BNNTs. All these results bring a bright future for the use of BNNTs as dielectric thermal conductors.

Due to the wide bandgap of close to 6eV [21, 28, 29], BNNTs are usually insulators. Field emission and contact current-voltage measurements on a single double-walled BNNT have been done with the help of a piezoelectric driven stage in TEM [62, 63]. The results showed BNNTs and CNTs had similar current densities in field emission, though the turn-on voltage of BNNTs was twice that of CNTs and no electric conductivity was measured from BNNTs even at 10V. Nevertheless, the electrical properties of BNNTs can be modified by introducing an electric field [64, 65], doping with C [66], coating with gold [67], applying a deformation [68], or functionalizing the surface [69]. After these conductivity alternations, BNNTs can be useful in molecular electronic devices [41].

BNNTs are very promising deep ultraviolet (DUV) light emitters. Their second harmonic generation and electro-optical efficiency, in particular, are much larger than those of *h*BN, and their photoluminescence (PL) quantum yields surpass those of CNTs [24]. DUV light is defined as light of wavelength between 10 and 300nm. As the luminescence properties of a material are closely related to its bandgap, various optical studies of BNNTs have been conducted in order to determine the bandgap of BNNTs. For example, electron energy loss spectroscopy (EELS) [70, 71], tunnelling spectroscopy [72] and optical absorption [73] of BNNTs have been conducted. These experiments gave bandgap values in the range of 4.5-5.8eV, which are in roughly good agreement with the theoretical calculations [21]. Some of these experiments also indicated that the luminescence of BNNTs was related to strongly bound excitons and the excitonic effects in BNNTs were much more prominent than those in *h*BN. In spite of the already known large bandgap of BNNTs, only near UV (300-400nm) luminescence was detected from BNNTs in early research: both PL and cathodeluminescence (CL) studies showed a broad luminescence band peaking at 315-375nm and no DUV emission [74-77]. These results were possibly due to either low excitation energies or the poor crystallinity of the BNNTs used. For example, most of the PL studies at that time used excitation wavelengths with smaller energies than the bandgap of

BNNTs. It was not until 2006 that the first DUV light emission from BNNTs was reported [78-80]. However, compared to the broad peak around 300nm, this DUV emission was still very weak at room temperature. Until now many intrinsic luminescence properties of BNNTs are still unknown and there has not been any report showing BNNTs can have single DUV light emission similar to single crystal *h*BN [4, 5] .

BNNTs have similar surface tension and wetting properties to CNTs. The wetting properties of BNNTs have been measured using the Wilhelmy method. An individual 40nm diameter BNNT was mounted on a BNNT cantilever of 200nm diameter and immersed into four different liquids [81]. An atomic force microscope (AFM) was employed to measure the wetting force in each liquid. The surface tension of this BNNT was deduced to be 26.7mN/m and the contact angle between BNNT and water was about 85° in spite of both partial wetting and non-wetting being observed. These values are quite similar to those of CNTs [82], but much larger than those of *h*BN mainly because the positive Laplace pressure introduced by high surface curvature and the nanoscale size can exceed the adhering disjoining pressure and cause the water film on the cylindrical surface to become unstable [83]. The author of Ref. [81] also calculated the dispersive and polar components of the surface tension of the BNNT: $\gamma^d = 22.5\text{mN/m}$, and $\gamma^p = 4.3\text{mN/m}$. These results are important not only for the fundamental understanding of the surface properties of BNNTs, but also for the potential use of BNNTs in applications, such as the fillers in composites or anti-wetting coating. Despite of these fundamental studies of individual BNNT, the wetting properties of BNNT films under different conditions are almost unexplored.

1.3.4 The large quantity synthesis of BNNTs

Although many methods have been demonstrated to be capable of synthesizing BNNTs, the production of high purity BNNTs in large quantities is still challenging. This section briefly summarizes the synthesis methods of BNNTs.

Cylindrical BNNTs were first produced using a plasma arc-discharge method [23], a similar way to that used to successfully fabricate carbon fullerene (C-60) [84]. In this method, a hollow tungsten electrode with an inserted pressed *h*BN rod and a copper electrode were used as anode and cathode, respectively. Helium gas was chosen as the environmental gas. Multiwalled cylindrical BNNTs with lengths of ~200nm were observed in the dark-grey soot deposited on the cathode after a dc current was applied. Metal particles were found on the

tips of all BNNTs. This arc-discharge method was further modified by using a tantalum (Ta) electrode to fabricate much longer BNNTs, whose B:N ratio was almost equal to 1 [37]. Tubes with and without metal particles were observed in the sample. It was the first time that closed square and open triangular caps were found on the tip of BNNTs. In both previous methods no nitriding reaction was involved, because *h*BN was used as the starting material and no B-N rebonding was required. Later, nitrogen gas and ammonia gas were introduced into the arc-discharge method to react with metal borides to form BNNTs. One advantage of using metal boride is that it can enormously increase the conductivity of the electrode. For example, the arc-discharge method using a hot pressed hafnium diboride (HfB_2) electrode and nitrogen as the reaction gas successfully produced single walled BNNTs for the first time [36]. The yield of the arc-discharge method was improved by using a specially made electrode. In the process, boron powder together with metal particles were first melted to form ingots and then the ingots were mechanically shaped into electrodes for BNNT production [85]. A majority of nanotubes produced by this method were double walled and self-assembled into bundles and ropes.

The high energy and high temperature in the arc-discharge method ensure the production of highly crystalline BNNTs with single or double walls and flat caps on the tip. However, the BNNTs produced in this way are usually accompanied by a large number of BN particles and the production quantity is also low. The limitation of the usable electrode types is definitely an important reason for this, because the electrodes have to be conductive, but *h*BN, boron and most boron compounds are electrical insulators [86].

Laser heating was the second method used to successfully produce cylindrical BNNTs. In this method, *c*BN placed in a diamond anvil cell was heated by a high powered CO_2 laser beam to more than 5000°C in nitrogen gas [87]. Under the heat, the *c*BN either first transformed to *h*BN and then melted or directly melted to form BNNTs. Multiwalled BNNTs with high crystallinity predominated in the product and the B:N ratio was ~ 0.93 . In another report, pure *h*BN was used as a target and ablated with a CO_2 laser. The estimated temperature during the ablation process was 3130°C [31]. Although double and multiwalled BNNTs were also present in the product, single walled BNNTs without catalyst predominated. The majority of these single walled BNNTs were of zigzag configuration. This preference was in line with the theoretical prediction. Subsequently, a furnace was used to provide extra heat during the laser ablation. In the so called oven laser ablation method, the laser beam was focused on a hot pressed plate containing *h*BN and Ni/Co metal powders in a thermal furnace that can heat the sample up to 1200°C in an argon, nitrogen or helium

atmosphere [88]. The inert gas atmospheres, argon or helium, produced mainly single walled BNNTs. Double or triple walled BNNTs were formed if N_2 gas was used. The product had a light grey colour and most BNNTs had metal catalysts on the tip. More recently, a laser with high repetition rate and short pulse was employed for BNNT production [89]. This kind of laser allowed a much higher ablation rate on the target, so a higher yield of BNNTs was possible. However, the BNNTs produced in this way had widely varying diameters and number of walls. Like the arc-discharge method, the laser ablation method is able to produce high quality BNNTs owing to the high temperature involved, but a large number of BN particles and nanocones are always present in the products.

Chemical vapour deposition (CVD) had produced BNNTs with a bamboo-like structure before the discovery of cylindrical BNNTs [40]. In this method, diborane (B_2H_6) mixed with NH_3 or N_2 gas came into contact with different metal borides, such as HfB_2 , zirconium boride (ZrB_2), titanium diboride (TiB_2), vanadium boride (VB_2), niobium boride (NbB_2) and tantalum boride (TaB_2) at $1000^\circ C$ for 2h. These BN filaments and nanotubes had diameters of 10-100nm and lengths of 1-10 μm . Then, $B_xC_yN_z$ nanotubes also with bamboo-like structures were produced by pyrolysing acetonitrile (CH_3CN) and boron trichloride (BCl_3) at $900-1000^\circ C$ for 1.5h in the presence of micro-sized Co particles [90]. However, there was only ~10wt.% of $B_xC_yN_z$ nanotubes in the product. Similar results were obtained when borane (BH_3) with N,N-dimethylmethanamine ($N(CH_3)_3$) and pyridine (C_5H_5N) over Co powder was pyrolysed at $1000^\circ C$ [91]. BNNTs were deposited on a silicon wafer covered with a thin layer of silicon dioxide (SiO_2/Si) if volatile borazine ($B_3N_3H_6$) was heated up to $1000-1100^\circ C$ for 0.5h with Co, Ni, NiB and Ni_2B catalysts [92]. Still, only bamboo-like BNNTs were obtained. Cylindrical BNNTs with quite straight walls were produced by heating melamine ($C_3N_6H_6$) and diborate (H_3BO_3) in N_2 atmosphere at the higher temperature of $1700^\circ C$ for 2h without adding any metal catalyst [93]. Interestingly, the amorphous BN particles of bulbous shape were acting as catalysts. Other compounds such as ammonium fluoroborate (NH_4BF_4), potassium borohydride (KBH_4), boron trifluoride etherate ($(C_2H_5)_2OBF_3$) and trimethyl borate ($C_3H_9BO_3$) were also used in CVD methods and high pressure, novel catalysts and other assisted conditions were sometimes required [94-97]. In general, the BNNTs produced by CVD have low crystallinity which confines the applications of them.

The substitution reaction method and the template directed growth methods are alternative methods for preparing BNNTs. The first substitution attempt reported used CNTs as templates to react with boron oxide (B_2O_3) in N_2 gas at $1500^\circ C$ [98]. During heating, CNTs

were first oxidized, and then B and N atoms positioned themselves in the vacancies. The product had a grey colour. Although the produced BNNTs had similar diameters and lengths to the original CNTs, the BNNTs showed a better degree of crystallization than the starting CNTs and the chiralities of the nanotubes were changed after the substitution reaction [99]. This method was further modified by adding MoO_3 and V_2O_5 into B_2O_3 . This resulted in well aligned BNNTs in rope form and Mo metal particles were found on both the nanotube tips and between the nanotube walls, possibly due to the high temperature used. It is worth noting that the substitution method usually leaves C residues in the BNNTs, although there has also been a report claiming that the electron energy loss spectroscopy (EELS) analysis did not find any C in the product [98]. One attempt to reduce the amount of C residues was to use higher temperature [54]. Besides using CNT templates, BNNTs have also been successfully produced using anodic aluminium oxide (AAO) and mesoporous silica as templates [100, 101]. Impurities and bad crystallinity are still two major problems of the substitution and template methods.

In 1999, Chen et al. found that ball milling prior to annealing could dramatically reduce the required annealing temperature [32, 102, 103]. At first, *h*BN powder was used as the starting material, which was ball milled in a rolling mill with several hard steel balls in N_2 gas at 300kPa pressure [102]. The ball milled *h*BN powder was annealed in N_2 gas at up to 1300°C . Both cylindrical and bamboo-like BNNTs were obtained. Because no chemical reaction was required during annealing, as the starting phase was BN, a solid-state nucleation and growth process was involved. Then, the method was modified to use B powder as the starting material, which was ball milled in similar equipment but in NH_3 gas [103, 104]. During ball milling, B particles were repeatedly ground under mechanical impacts to form nanosized particles full of structural defects and the reaction between NH_3 and the B powder can create some BN nucleation sites. The ball milled powder was then heated in N_2 or NH_3 gas to produce BNNTs at different temperatures. Annealing in N_2 gas at $1200\text{-}1300^\circ\text{C}$ usually resulted in larger diameter bamboo-like BNNTs and steel catalysts introduced by ball milling were found at the tip of tubes [104]. Annealing in NH_3 at 1300°C produced cylindrical BNNTs with much more uniform diameter and no catalyst was found [105]. The different structures produced in different gases was related to the different nitriding reaction rates [106]. Thanks to the large capacity of the ball milling facilities, for the first time large quantities of BNNTs were available for commercial applications. ^{10}B enriched and rare-earth doped BNNTs were also successfully produced using the ball milling and annealing method [107, 108]. Although the ball milling and annealing method

has advantages over other methods of BNNT synthesis, there is a need to improve nanotube yield. This is one major objective of this research.

To summarize, although various methods are able to produce microscopic quantities of BNNTs, the demand for high purity BNNTs not only at large scale but also with high crystal quality has not been satisfied. This difficulty limits the practical applications of BNNTs.

1.3.5 Growth of BNNT films on a substrate

Many applications require the nanotubes to be coated or, even better, grown on a substrate. The coating of single walled and multiwalled CNTs on different substrates has been routinely achieved using CVD methods [109-111]. However, patterned coating of BNNTs over a large area has not yet been achieved. Although BNNT coatings could be produced by the CVD method [92, 93], as mentioned previously, the synthesis of BNNTs was not very efficient due to their high thermal and chemical stability. So the quality and density of BNNTs in the coating were not satisfactory. To overcome this problem, the catalytically-enhanced plasma-assisted CVD method was introduced [112, 113], but only limited improvements were obtained. In 2005, Gan et al. developed another route, in which a thin hBN layer was sputtered onto a SiO₂/Si wafer using a radio-frequency magnetron, and then this layer was thermally annealed in NH₃ for 1h to transform it into a BNNT film [114]. However, a large number of the SiO₂ and B₂O₃ aggregates were still present in the film. In the same year, a plasma-enhanced pulsed-laser deposition technique was proposed for growing BNNTs on a substrate at the relatively low temperature of 600°C [115]. A negative substrate bias voltage was introduced by nitrogen plasma to accelerate the positive ions and let BN vapour propagate towards the substrate surface. Small BNNT clusters were formed, but the density of nanotubes produced in this way was very low. It is urgent to develop a large scale and high purity film coating method for BNNTs on different substrates with even complicated shapes.

1.4 Objectives of the thesis

The aims of this thesis were: i) to further improve the ball milling and annealing method for the production of BNNTs with higher purity and in larger quantities; ii) to develop a new method to grow high density and high purity BNNTs and BN nanowires on different substrates; iii) to explore the luminescence properties of different BN nanomaterials,

including BNNTs, BN nanowires and BN nanosheets; iv) to test the superhydrophobic properties of the films of BNNTs; v) to develop a high-yield and highly-efficient method to produce atomically thin BN sheets.

1.5 Thesis structure

This thesis has the following structure. An introduction to BN materials is presented in Chapter 1. It includes the synthesis, characterization and properties of *h*BN crystals, the monolayer of *h*BN and BNNTs. The equipment and techniques needed to synthesize and characterize BNNTs and BN nanosheets are set out in Chapter 2.

The large quantity synthesis of BNNTs with high purity and ultra thin BN sheets, the growth of BNNT films on different surfaces and the investigation of the properties and applications of BNNTs or BNNT films are discussed in the following chapters. A new method of producing high purity and high density of BNNTs in large quantities is presented in Chapter 3. This innovative boron (B) ink method enables the large scale synthesis of BNNTs and the fabrication of bulk quantities of reinforced composites. The mechanical properties of the composites are also presented in this chapter. In addition to allowing bulk quantities of BNNTs, the new method has also enabled the growth of BNNT films on different substrates, which has been presented in Chapter 4. This unique and versatile method can grow securely attached BNNTs on both flat substrates and, for the first time, non-flat objects with complex shapes. This coating method can also produce BN nanowire films on a steel substrate. The adhesion force between the BNNT film and the substrate is measured and potential applications of the BNNT coating are demonstrated. The novel properties of the grown BNNT films have been explored. The PL properties are presented in Chapter 5. The high purity and good crystallinity of the BNNTs in the film produced by the B ink method made it possible, for the first time, to observe single deep ultraviolet (DUV) emission. The wetting properties of the BNNT films are presented in Chapter 6. Both superhydrophobicity and hydrophobicity are observed on the as-grown BNNT films. The superhydrophobic and hydrophobic films exhibit different drop retraction behaviour during evaporation, drop impact behaviour and self-cleaning efficiencies. Investigations of methods for producing large quantities of atomically thick BN sheets by the ball milling method are presented in Chapter 7. Interestingly, stronger DUV emission was observed from the milled BN nanosheets than from the initial *h*BN particles. The conclusions and future directions from this work are presented in Chapter 8.

Chapter 2

Experimental techniques

A wide range of equipments and analysis techniques were used in the synthesis and characterization of BNNTs and thin BN sheets. They are briefly introduced in this chapter.

2.1 Synthesis equipments and techniques

2.1.1 Ball milling

Ball milling is an essential step in the production of BNNTs and thin BN sheets. Ball milling is a technique that grinds material by mechanical impacts between the milling balls and the milling vial. This technique was originally developed to produce nickel and iron based superalloys [116]. Then its application spread to the synthesis of other equilibrium or non-equilibrium alloys, amorphous powders and nanoparticles. There are different types of milling equipment, each with unique working principle. The ball milling conditions, including the milling media, the ball to powder weight ratio, the controlling agent, the rotating speed or vibration frequency, the milling time and the milling temperature, also crucially affect the products [116].

In the research presented in this thesis, two kinds of ball milling facilities were used. For BNNT synthesis, a large number of defects need to be introduced into the B particles, so a purpose-built vertical rolling mill was used, shown schematically in Figure 2.1. The rolling mill can create strong compressional forces via ball impacts, which can break crystal structure and induce defects or semi-amorphous structure. Before ball milling, four 25.4mm

diameter bearing steel balls together with 2g of B powder were placed in the steel milling vial. Then the vial was sealed and dehydrated NH_3 gas at 300kPa pressure was introduced. The vial was driven with a rotor at speed $\sim 155\text{rpm}$ for 100-150h. During milling, the combination of the vial rotation and the external magnet (NdFeB) lifted the balls and then allowed them to fall freely, causing strong impacts with the powder.

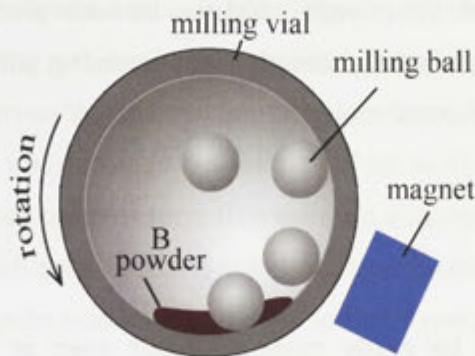


Figure 2.1 Schematic diagram of the purpose-built vertical rolling ball mill (side view).

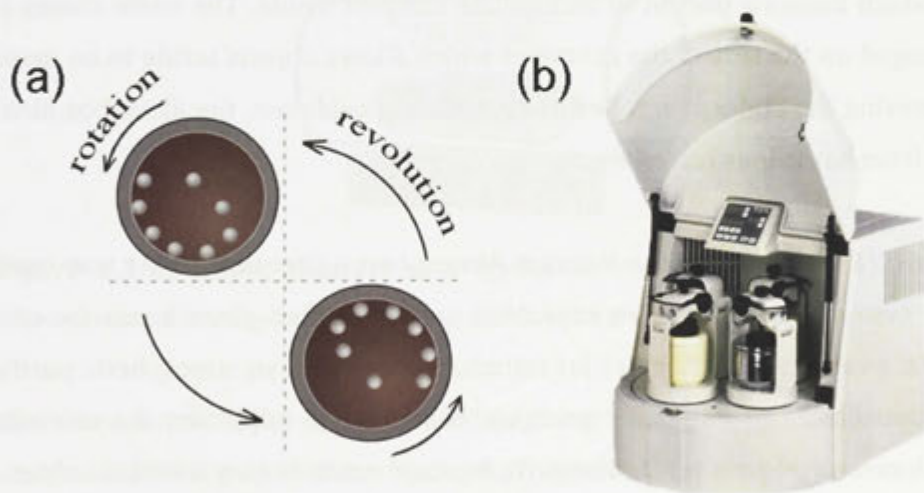


Figure 2.2 (a) Schematic diagram of the horizontal planetary ball mill with two vials being used simultaneously (top view); (b) A photo of the Fritsch Pulverisette 5 horizontal planetary ball mill.

To exfoliate BN nanosheets, a planetary mill was used. It was named because its vial and ball movements resemble the orbital characteristics of our planetary system. During operation, the vials rotate about both their own and a central axis. When the directions of these two centrifugal forces are different, the balls can run down the vial wall and exert impacts. A schematic drawing of the system, with two vials being running simultaneously, is shown in

Figure 2.2a. A planetary mill is effective at producing shear forces, which can have a strong peeling-off effect.

In the experiments reported here, a four-station horizontal planetary mill (the Fritsch Pulverisette 5, Germany, shown in Figure 2.2b) was used. A large number of steel balls of smaller diameter (12.7mm) were used to reduce the force of the impacts but increase the milling efficiency. Various liquid controlling agents, including water, ethanol, dodecane and benzyl benzoate, were tested. These vials could also be made airtight and purged with inert gas (e.g. N_2 at 200kPa) to prevent the sample from oxidizing. After ball milling, the sample was either at the bottom of the vial or on the vial wall.

2.1.2 Glove Box

The milled B powder can be easily oxidized in air even at room temperature. After oxidization, it becomes much less chemically reactive and is no longer usable to produce BNNTs. So an inert atmosphere is required to handle and store the ball milled B powder. A glove box can provide such an environment. A glove box is a sealed container, filled with inert gas, which allows a person to manipulate samples inside. The name comes from the gloves arranged on the side of the container which allows objects inside to be manipulated without breaking the atmosphere. Besides preventing oxidation, the glove box also isolates the person from hazardous materials.

A MO-M Dri-Train glove box (the Vacuum Atmospheres Company, USA) was used in this work. This system consists of two separated inert gas filled glove boxes for conducting experiments, a vacuum antechamber for introducing samples, an atmospheric purifier and a pressure controller. The automatic pressure controller is important for minimizing the oxygen and moisture levels inside the glove box and controls two solenoid valves: one for introducing inert gas and the other to evacuate the glove box atmosphere. Usually, the oxygen and moisture levels in the glove box are as low as one part per million. The operation procedure for this glove box is described below. In order to open the vacuum antechamber and place the sample inside, the antechamber should first be filled with inert gas. Next, the antechamber is pumped down for several minutes so that it can be refilled with the inert gas from the glove box without contaminating its atmosphere. Lastly, the sample is transferred into the glove box container for operation. The antechamber needs to be pumped down again to ensure that no air enters the container. When the sample needs to be removed, the inverse procedure should be followed.

2.1.3 Thermal annealing

Three horizontal tube furnaces were used in the annealing processes to either produce BNNTs or reduce organic solvents. These furnaces are a Lindberg/Blue M STF 54233C (USA), a Carbolite CFM 14/2 (England) and a Jetlow two-zone furnace (Australia). All these furnaces operate and work similarly (Figure 2.3). The furnace boxes have silicon carbide heating elements and an integrated controller to regulate the working temperature. For two of these furnaces, the heating rate can be adjusted by a programmable controller. Cylindrical hollow spaces are left between the heating elements to accommodate high purity alumina or quartz heating tubes. The quartz tubes can withstand up to 1100°C and the alumina tubes can be used at much higher temperature. However, an alumina tube has relatively poorer resistance to thermal shock than a quartz tube, so rapid heating was done using a quartz tube. The heating tubes can be sealed at both ends so that a reaction or protecting gas can be passed through the heating zone. The heating tubes can be sealed at both ends so that a reaction or protecting gas can be passed through the heating zone.



Figure 2.3 Schematic diagram of a typical horizontal furnace with heating elements and a heating tube containing an alumina crucible and the sample.

Among the three furnaces, the Carbolite CFM 14/2 has the highest rate of heating, which is more suitable for BNNT growth in nitrogen gas. The Jetlow two-zone furnace has the highest working temperature (up to 1600°C), so it is used for high temperature heating, such as the annealing of B powder in NH_3 to produce small cylindrical BNNTs. The Lindberg/Blue M STF 54233C has the largest annealing capacity; hence it is usually used for large quantity synthesis.

2.2 Characterization techniques

2.2.1 X-ray powder diffraction

X-ray diffraction (XRD) is an important method for characterizing the crystallographic structure of a sample. The spectrum depends on the Bragg diffraction condition:

$$n\lambda = 2d \sin \theta \quad (2.1)$$

Where, n is an integer, λ is the wavelength of the x-ray, d is the interplanar spacing, and θ is the incident angle of the x-ray into the lattice plane. Therefore, each crystal with a unique interplanar spacing gives a unique spectrum. The pattern can be compared with the standard database to determine the crystal phases. Based on the peak position and shape, XRD is capable of detecting the crystallite size, the preferred orientation and the stress in a crystal [117]. A Philips 3020 analytical x-ray spectrometer with Co target at a working voltage of 40kV and current of 30mA was used for all the XRD measurements. The wavelength of Co radiation is 0.1789nm.

2.2.2 Scanning electron microscopy

Scanning electron microscopy (SEM) is vital for visualizing the morphology and topography of the synthesized nanomaterials. It can image the sample surface by scanning it with a high energy electron beam. The interactions between the electrons and the sample surface lead to secondary electrons. This signal is collected to form a high-resolution image with a large depth of field [118]. It is better for the SEM sample to be electrically conductive for the best imaging quality. For non-conductive samples, the charging from the accumulation of electrons on the sample surface reduces the resolution. Lowering the accelerating voltage may help to decrease the charging effect, but the imaging resolution is compromised.

Several field emission SEMs were used in this work, including a Hitachi S4500, Hitachi 4300 SE/N, Zeiss UltraPlus, Zeiss Supra 55P and a LEO 1530. For image acquisition, the accelerating voltage was usually set to 3kV. As BN materials are almost non-conductive, the samples needed to be coated with a thin layer of conductive metal, e.g. gold or gold and palladium alloy, to alleviate the charging effect. The coating was prepared by using a dc magnetron sputterer (Emitech K575X, USA) under argon atmosphere. The coating thickness can be controlled by adjusting the vacuum level, the sputtering time and the sputtering current. All these parameters can be pre-set on the instrument panel.

2.2.3 Transmission electron microscopy

Transmission electron microscopy (TEM) is a powerful tool for checking the micro-structure and crystallography of a material. It enables the study or imaging of an ultra thin section by passing an electron beam through it. The interaction between the material and the electrons can be magnified and imaged, e.g. by film, CCD or CMOS camera. The resolution of TEM is usually high enough to examine the atomic arrangement. Selected area electron diffraction (SAED) can also be performed on most TEMs. The SAED pattern is caused by the diffracted electrons passing through a crystalline material [119].

A Philips CM300 TEM with a thermo-emission gun (LaB₆ filament) operating at 300kV was used to analyse the structure of BNNTs and obtain crystallographic information of the thin BN sheets. Additional crystallographic information was obtained from SAED patterns. The TEM samples were prepared by dropping a tiny amount of material dispersed in solvent onto a carbon coated copper grid. BNNTs were dispersed in ethanol under gentle ultrasonic bath conditions. The ball milled BN sheets in the liquid controlling agent could be directly used to prepare TEM samples. To remove the solvent, the grid was heated to 100-200°C.

2.2.4 Energy-dispersive x-ray spectroscopy

The chemical compositions were obtained by energy-dispersive x-ray spectroscopy (EDS). EDS measurement uses x-rays emitted when electrons in an outer shell relax by filling in an electron hole in an inner shell after high energy electron excitation has been applied to the specimen surface. The energies of the emitted x-rays depend on the element and the number of the x-rays can indicate the quantity of the element (in standardized measurement). The spectrometer can record both the energy and the number of the x-rays. The detectable elements for EDS range from boron to uranium [118]. The Hitachi 4300 SE/N is connected to an Oxford cold stage and INCA Energy 350 EDXA and the Zeiss UltraPlus is connected to a similar cold stage and INCA Energy 450 EDXA system. The chemical composition could be measured qualitatively or quantitatively. For both measurements the BN sample was coated with a thin layer of platinum, and the accelerating voltage was 15kV. Quantitative analysis was achieved by correcting to standard spectra.

2.2.5 Optical microscopy

Two optical microscope systems were used in this work: the dissecting Wild M400 photomicroscope equipped with a Spot Flex 14bit CCD camera and the Olympus BX51M with a ColorView DP12 CCD camera.

2.2.6 Thermogravimetric analysis



Figure 2.4 Photo of the Shimadzu 50 TGA instrument.

Thermogravimetric analysis (TGA) uses the precise measurement of the variation in sample weight during temperature changes in a chosen atmosphere. Its sensitivity comes from the electromagnetic force controller which constantly adjusts the electric current to continuously keep the microbalance in equilibrium. The current change can be converted into an accurate weight change. TGA is widely used to determine the characteristics of materials, e.g. the degradation point of a polymer, the decomposition point of an organic solvent or the progress of a chemical reaction. In my research, TGA was used to monitor the nitriding reaction of the B ink and the decomposition process of benzyl benzoate. All these TGA investigations were done using a Shimadzu 50 TGA instrument (Japan) (Figure 2.4). The sensitivity of this instrument is 0.0001mg, and the temperature range is from room temperature to 1500°C. The sample weight can be monitored in two measurement ranges: 20mg and 200mg. For the test, the specimen was placed into an alumina crucible (~0.3μL) which sat on a platinum pan. The reaction chamber was purged with nitrogen or inert gases during measurements.

2.2.7 Photoluminescence spectroscopy with a synchrotron radiation source

In order to excite BNNTs and thin BN sheets which have wide bandgaps ($\sim 6\text{eV}$), a high energy radiation source is a prerequisite. Commercial desktop photoluminescence (PL) spectroscopes can hardly provide enough high energy radiation. Therefore, the PL measurements were conducted using synchrotron radiation at the high flux vacuum ultraviolet (VUV) PL spectroscopy of the National Synchrotron Radiation Research Center, Taiwan (NSRRC). The Taiwan synchrotron consists of an injector, a booster ring, a storage ring, a transport line and a number of beamlines. A schematic diagram of the Taiwan synchrotron is shown in Figure 2.5. Electrons are accelerated in the linear accelerator (LINAC) followed by the booster ring, and then sent through the transport line to the storage ring. The storage ring allows the electrons to circulate for hours emitting synchrotron light. The beamlines can channel the synchrotron light to various experiments. Synchrotron radiation has a huge range of applications, for example, x-ray imaging, diffraction, scattering and tomography, extended x-ray absorption fine structure (EXAFS), spin resolved photoelectron spectroscopy (SRPES), biological crystallography, chemical dynamics and photoluminescence.

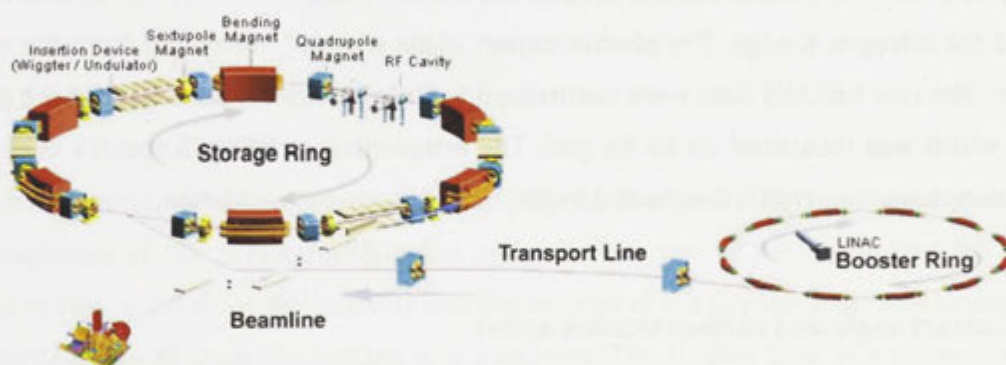


Figure 2.5 Schematic diagram of the Taiwan synchrotron facility.

The synchrotron in Taiwan began operation in 1993 and is classed as a third generation light source. The circumference of the storage ring is 120m, and the storage energy is 1.51GeV. There are 34 beamlines around the storage ring. BL03A1 was used for the PL measurements, covering photon energies from 4eV to 40eV. It collects 50mrad of the horizontal radiation and uses a six-metre cylindrical grating monochromator (6m-CGM) with an incident angle of 70° . The maximum energy resolving power can reach 45000. The light spot on the sample is smaller than $0.45\text{mm} \times 0.2\text{mm}$. The luminescence photons are collected via a photomultiplier tube (Hamamatsu R943-02) by scanning a monochromator (Jobin-Yvon HR320, France) with a 0.32m focal length and a 1200grooves/mm grating, and counted by a dual channel photon counter (Stanford SR400, USA) linked to a PC via an IEEE-

488 interface. The sample is placed in a vacuum chamber at 10^{-7} - 10^{-9} Torr and can be cooled down to 10K with a water cooled compressor.

2.2.8 Near edge x-ray absorption fine structure spectroscopy

Near edge x-ray absorption fine structure (NEXAFS) is a powerful spectroscopic tool for probing the structure of a material. It is highly sensitive to bond angles, bond lengths and the presence of adsorbents. A NEXAFS spectrum records the emission of Auger electrons from valence molecular orbitals. They arise from the excitation of electrons from a core level to partially filled or empty states and the decay of the core hole states [120].

The NEXAFS spectrum of the thin BN sheets were taken in an ultrahigh vacuum chamber attached to the bending-magnet beam line 24A1 at NSRRC, Taiwan. It is equipped with a microchannel plate detector for NEXAFS measurement and a low-energy ion gun for sample bombardment with low-energy argon or nitrogen ions (0.2 to 5keV). The NEXAFS spectra were recorded in the surface-sensitive partial electron yield (PEY), with a cut-off kinetic energy of 100eV for measurements around the boron K-edge or 300eV for measurements around the nitrogen K-edge. The photon impact angle was 40° , measured from the sample surface. The raw NEXAFS data were normalized to the photoelectron current of the photon beam, which was measured on an Au grid. The broadening of NEXAFS spectra in the low-resolution measurements is dominated by the monochromator resolution.

2.2.9 Contact angle and surface tension meter

An optical contact angle and surface tension meter (CAM 101, KSV, Sweden) was used to measure the surface and wetting properties of the BNNT films grown on substrate. Figure 2.6 shows a photo of the instrument, which includes a digital CCD camera with 50mm focal length, an adjustable sample stage and a monochromatic LED light source. The CAM 101 software controls the camera settings, such as the frame interval and pre-set frame number, and automatically calculates the contact angle, drop volume, drop contact diameter, drop height and three parameters of the fitting quality. The Young-Laplace equation, circle, polynomial or Bashforth/Adams model is optional for the curve-fitting of the drop profiles captured by the camera. This instrument is able to measure the static contact angle, the advanced and receded contact angles, the surface/interfacial tension of liquid, and the free surface energy and elasticity of the liquid interface. The accuracy of the contact angle measurement can be down to 0.1° . The highest frame interval of the camera is 33ms. The

liquid dispenser is changeable. In my research, either a flat headed stainless steel needle (gauge 24, exterior size 0.565mm) or a glass capillary tube with a 60 μ m exterior diameter tip was used. In order to get the most accurate results, the system needs to be first calibrated using a 4mm diameter stainless steel ball. This instrument is in a conditioned laboratory with constant temperature and humidity (20 $\pm$ 2°C, 65 $\pm$ 2%).



Figure 2.6 Photo of the optical contact angle and surface tension meter (CAM 101).

2.2.10 Scanning probe microscopy

A Cypher scanning probe microscope (SPM) (Asylum Research, USA) was used to measure the roughness of the pressed *h*BN pellet and the thickness of the ball milled BN sheets. Photos in Figure 2.7 show the exterior and the interior of the Cypher SPM. SPM usually uses a physical probe to scan the surface of a specimen. The Cypher SPM is a state-of-art and multi-functional instrument. It integrates atomic force microscopy (AFM), conductive force microscopy (CFM), electrostatic force microscopy (EFM), kelvin probe force microscopy (KPFM), magnetic force microscopy (MFM), Piezo Force Microscopy (PFM) and scanning tunnelling microscopy (STM). The Cypher SPM is controlled by IGOR Pro coded software.

The Cypher SPM is the highest resolution AFM in the world. Its topographical mapping resolution can reach 60pm. Figure 2.8 shows a schematic diagram of the working mechanism of the Cypher AFM. It measures height changes by raster-scanning a sample surface using an ultra-sharp cantilever tip which is usually made of silicon or silicon nitride. A laser light is focussed on the back of the tip and the reflected light can be used to monitor its deflection or oscillation. The sample is placed on a piezoelectric crystal scanner that can move in the X-Y plane, and another piezoelectric crystal is connected to the cantilever to

manage the Z axis movement. The piezoelectric crystal that connects to the cantilever compensates changes in the cantilever deflection or oscillation by applying a reverse force to the cantilever. The voltage that is applied to this piezoelectric crystal is recorded and transferred into height data. However, the height data acquired in this way is not always accurate because of the nonlinearity of any piezoelectric crystal due to hysteresis effects. This inaccuracy could be very serious when the height of a surface varies by more than tens of micrometres. Traditionally for a more accurate result, several closed looped scans need to be done to reduce the hysteresis of the piezoelectric crystal. However, this method only gives a tiny improvement in accuracy. The Cypher AFM provides a better way to solve this problem by using a Nano Positioning System (NPS) sensor, which can accurately trace the height change even over the tens of micrometres range. There is also a drawback that this NPS sensor may slightly reduce the resolution. The AFM is also equipped with an optical lens and CMOS camera to more easily locate the area of interest for scanning. This optical system, quite different from the traditional AFM, is independent of the cantilever system so that higher resolution can be achieved. With a special cantilever holder, this AFM is also able to map in a liquid environment.



Figure 2.7 Photographs of the exterior (left) and the interior (right) of the Cypher scanning probe microscope.

There are two scanning modes for AFM operation: contact/DC mode and tapping/AC mode. These two modes actually use the same Z axis feedback movement to measure the height and the difference is whether the tip is in continuous or oscillating contact with the specimen surface. Contact mode is not suitable for soft surfaces and liquid environments and may easily wear out the sharp tip. Tapping mode can be subdivided into attractive and repulsive modes and which mode is used is mainly determined by the distance between the tip and the surface and by the tip amplitude.

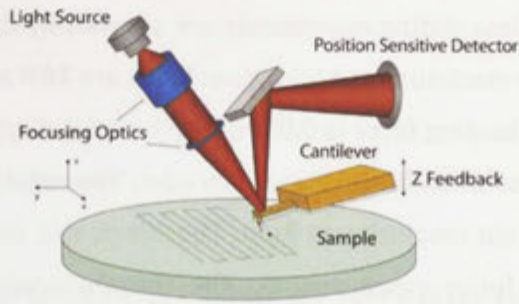


Figure 2.8 Schematic diagram of the working mechanism of the Cypher AFM.

The other functions of the Cypher SPM use a similar feedback response to the tip deflection or oscillation to measure different properties of the material surface, for example, magnetism, surface potential, or piezoelectricity. However, in these cases, the magnetic, electrostatic or piezoelectric force between the cantilever tip and the specimen surface is used to control the deflection or oscillation of the cantilever. So these measurements require special cantilevers, for instance, a cantilever with a conductive or magnetic tip.

2.2.11 Universal mechanical testing system

The compression tests of the BNNT reinforced polyurethane composites were conducted on an Instron 4505 (USA). It can do uniaxial tensile and compression tests. The system has one fixed and one moving crosshead and can apply a load force of up to 100kN. The testing speed ranges from 0.001 to 1000mm/min, and the accuracy of the load is $\pm 0.5\%$. The data acquisition rate is up to 500Hz. The extensometers in the system can precisely measure changes in length. For measurement, the specimen is either clamped by the jaws or placed between two flat cylindrical steel blocks. The testing environment, including the temperature and humidity, is also measured on site.

2.2.12 Dynamic mechanical analysis

The adhesion force of a BNNT film to its substrate was measured by a Q800 dynamic mechanical analyser (DMA) (TA Instruments, USA) (Figure 2.9a). DMA is a thermoanalytical technique that can measure the mechanical, thermal stability and viscoelastic properties of a material as a function of time, temperature or force. Different materials, such as polymers, fibres and some light metal films, are compatible with this instrument. A non-contact and

linear drive motor is connected to a set of air bearing slides to provide a precise static or oscillatory force. Frictionless sliding movements are allowed by the air bearing thanks to a pressurized gas flow. The maximum and minimum loads are 18N and 0.0001N, respectively, and the resolution of the loading force is 0.00001N. The axial displacement of the specimen is monitored by a high resolution linear optical encoder. The measurable specimen length is 0.5 μ m-10mm and the strain resolution is 1nm. Therefore, this instrument is very suitable for accurate and small force measurement. The thermocouple and the flow-in liquid nitrogen pipe can create a wide range of testing temperatures from -150 to 600°C. The three specimen clamps make it suitable for tension, 3-point bending, and compression tests. The film tension clamp was used in the BNNT film adhesion measurement (Figure 2.11 b).

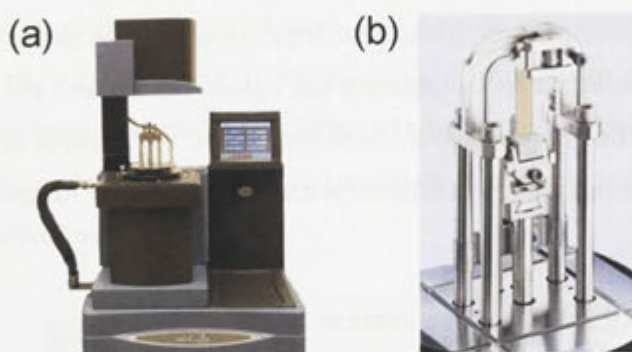


Figure 2.9 (a) Photograph of the Q800 dynamic mechanical analyser from TA Instruments; (b) photograph of the film tension clamp.

2.2.13 X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) is a commonly used technique that can quantitatively identify elements (except hydrogen) and provide information on the chemical state of the surface. XPS measures the kinetic energy of all the collected electrons, including both photoelectrons and Auger electrons. The measurement depth of XPS is approximately 5-10nm. XPS instruments usually consist of an x-ray source, a sample holder in a vacuum chamber and a photoelectron detector [121].

XPS measurements of the thin BN sheets were performed in the Laboratory for Surface and Materials Science, the Department of Physics at the University of Rijeka, Croatia, using a laboratory XPS system (SPECS, Germany) with monochromatic Al K α x-rays of 1486.74eV.

Chapter 3

Large-scale synthesis of boron nitride nanotubes and their reinforced composites

3.1 Introduction

Boron nitride nanotubes (BNNTs) are attracting more and more attention in the wake of the great enthusiasm for carbon nanotube (CNT) research. BNNTs not only have superior thermal conductivity and similar mechanical properties to CNTs [45, 58], they also exhibit some unique properties that cannot be found in CNTs. For example, BNNTs are more stable at high temperature and less chemically reactive than CNTs [52, 122]. They have a uniform wide bandgap close to 6eV [21, 29] and provide excellent radiation shielding due to the presence of the ^{10}B isotope [107]. Therefore, BNNTs are promising composite fillers that can not only greatly improve the mechanical properties and thermal conductivity of the composite, but also help meet high temperature and electrical insulating requirements. BNNTs are found to have luminescence in the deep ultraviolet (DUV) range [123] and a giant Stark effect [124], which make them potential candidates for optoelectronic applications. A recent theoretical study also predicts that BNNTs could enable faster and more effective desalination [125].

Various synthesis techniques have been proposed in the past decade to produce BNNTs, including arc-discharge [23], laser ablation [126], chemical vapour deposition (CVD) [92], high-temperature chemical processes [127, 128], and the ball milling and annealing method [102, 104]. The ball milling and annealing method was first proposed by Prof. Ying Chen at

the Australian National University in 1999 [102, 104]. It has successfully produced BNNTs, BN nanorods and BN nanowires in much larger quantities than the other methods and made commercial application of BNNTs possible for the first time [129-132]. Recently, the longest BNNT (over 1mm) has been produced using this method [133]. In this chapter, a liquid B ink method is demonstrated, which is based on the ball milling and annealing method. The new method can greatly enhance the yield and density of BNNTs in product. The yield of BNNTs in the new process is comparable to that of CNTs produced in the CVD process. This improvement is mainly due to the addition of nitrate and ethanol to the ball milled B particles.

The large scale synthesis of high purity BNNTs makes the practical use of BNNTs possible. As an example, BNNTs were put into polyurethane (PU) at different volume contents to produce bulk sized (not film) composites. Compressive modulus and hardness of the composites were measured.

3.2 Experimental

Fine B particles were first produced by intensive ball milling. Amorphous B powder of 2g (95%-97%, Sigma-Aldrich) was sealed in a steel milling vial with four hardened steel balls with diameter of 25.4mm. The ball to powder weight ratio (BPR) was 132:1. Anhydrous ammonia (NH_3) as reaction gas was purged into the vial and a static pressure of 300kPa was established prior to the milling treatment. The ball milling process lasted for 150h with a rolling mill at 155rpm rotating speed to ensure the formation of nanosized B particles with metastable structures [102, 134]. B ink was prepared by mixing the ball milled B particles with ferric nitrate (98%, Sigma-Aldrich) or cobalt nitrate (98%, Sigma-Aldrich) in ethanol solution under 1h ultrasonic bath. The ink-like solution was then poured into a crucible and isothermally annealed using a horizontal tube furnace at temperatures between 1000 and 1300°C for several hours in different atmospheres: nitrogen with 5% hydrogen ($\text{N}_2+5\%\text{H}_2$) at gas flow rate of 0.1L/min or NH_3 at 0.3L/min. During the annealing, the B particles reacted with the N containing gas via the chemical reaction: $\text{B} + \text{N} \rightarrow \text{BN}$, and were transformed into BNNTs.

A neat PU as well as two BNNT reinforced PU composites at 0.5vol.% and 2vol.% were produced. For the composites, 0.2g and 0.77g BNNTs produced in $\text{N}_2+5\%\text{H}_2$ at 1100°C were dispersed in acetone (6.25g, Merck AR grade) for 2h under ultrasonic bath. A bench-top

ultrasonicator (Model 28x, Neytech) was used at power 80W. Fifteen grams of polyurethane prepolymer (TGI-PPG prepolymer, Airthane PPT-80A, Air Products and Chemicals) were dissolved in each of the BNNT acetone solutions. Magnetic stirring at 40°C homogeneously mixed the BNNT with the prepolymer and eliminated the acetone solvent via evaporation. Next, 3.75g of hardener (aromatic diamine, Lonzacure MCDEA-GS, Air Products and Chemicals) was melted at 95°C and poured into each of the prepolymers plus BNNT samples. Further stirring was conducted in vacuum to mix the prepolymer with the hardener and remove any entrained air. The mixtures were moved into cylindrical moulds and held for 24h in vacuum at room temperature. All samples were pre-cured at 40°C in air for 8h and post-cured at 100°C in air for 15h. The final cylindrical composites had a diameter of 31.5mm and heights of 16-20mm. The neat PU sample was produced at the same time following a similar procedure.

Samples were analysed using the following methods. Nanotube phases were investigated using Philips 3020 X-ray Diffraction (XRD) machine. A Hitachi 4300SE/N Scanning Electronic Microscope (SEM) at 3kV was employed to examine nanotube and composite morphology. The elemental composition of the nanotubes was measured using X-ray energy dispersive spectroscopy (EDS) attached to the SEM. Transmission Electron Microscope (TEM) investigations were performed using a Philips CM300 (300kV) instrument. Thermogravimetric analysis (TGA) was conducted with a Shimadzu TGA-50 instrument. The Rockwell hardness was measured at various locations on the polished composite surfaces with a 1/2inch diameter steel sphere under 60kg load (HRR). The hardness results are averages from at least five measurements at different locations. The compression tests were done with an Instron 5500R1186 machine at 28°C and 22% humidity. The crosshead speed was 2mm/min and maximum load was ~2kN.

3.3 Results and Discussion

The major difference between the old ball milling and annealing method and the new B ink method is that ethanol and metal nitrate, such as $\text{Fe}(\text{NO}_3)_3$ or $\text{Co}(\text{NO}_3)_2$, are added to the ball milled B particles to form B ink prior to annealing. The initial idea was that a solvent, like ethanol, could help not only reduce the oxidation of the ball milled B particles but also spread the B particles evenly in the crucible so that more of them could have contact with the reaction gas and effectively convert to BNNTs. Although adding ethanol was found to slightly increase the yield of BNNTs, the purity of the product was still not satisfactory. The

next thought was adding nitrate to enhance the growth of BNNTs, because catalysts, like nitrate, had been widely known to be essential for the formation of nanotubes. As a result, the purity of the BNNT product was dramatically improved. The BNNTs produced by the B ink method showed a similar structure to those produced using old ball milling method. So the main purpose of the study is to explain this dramatic purity improvement after adding ethanol and nitrate.

3.3.1 Large quantity synthesis of BNNTs

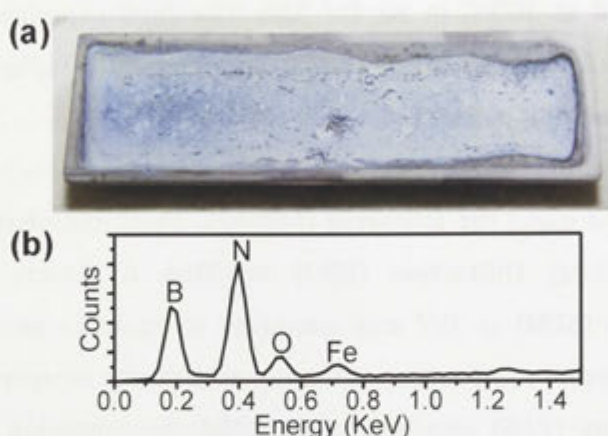


Figure 3.1 (a) Photo of a slightly bluish white BNNT layer in an alumina crucible produced by the B ink annealing method. The top inner size of the crucible is 68mm x 19mm; b) EDS spectrum showing elements B and N dominate the sample, along with some O and Fe.

The new B ink annealing method allows BNNTs to be produced both in large quantities and higher yield. The photo in Figure 3.1a shows a layer of fluffy materials covering the bottom of a ceramic combustion boat (size: 68mm × 19mm). It is worth noting that the colour of the product (slightly bluish white) was totally different from that of the BNNT samples produced using the old ball milling and annealing method (dark brown). Because the colour of BN is white and the colour of B particles is dark brown, this indicates that enormously more B particles underwent a nitriding reaction to form BN. So the colour of the BNNT product already suggests high purity of BNNTs in the product (also proved by SEM, which will be shown later). The EDS spectrum in Figure 3.1b reveals that the annealed sample was predominantly elements B and N, along with some O and Fe impurities. The Fe was from both the ball milling process and the $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ added to the B ink. Larger quantities of BNNTs can be produced by using bigger crucibles. For example, 0.5g of BNNTs was

synthesized in a rectangular stainless steel boat of 100mm × 40mm. The morphologies and structures of the materials are discussed below.

The diameter and structure of BNNTs can be adjusted by adopting different annealing atmospheres and temperatures, similar to the old ball milling and annealing method [104, 133, 134]. BNNTs with cylindrical structure and small diameters were synthesized by annealing in NH_3 gas. In this process, 0.034M $\text{Co}(\text{NO}_3)_2$ ethanol solution was chosen to prepare the B ink, because Co is an effective catalyst for both NH_3 decomposition and BNNT growth [135]. But note that other nitrates are also able to produce similar BNNTs. The SEM image in Figure 3.2a shows a high density of small tubes obtained after the annealing in NH_3 at 1300°C for 6h. The tube lengths are mainly 3-5 μm . Investigation by TEM (Figure 3.2b) showed that they have small diameters in the range of 2-10nm and a well-crystallized, multi-walled cylindrical structure.

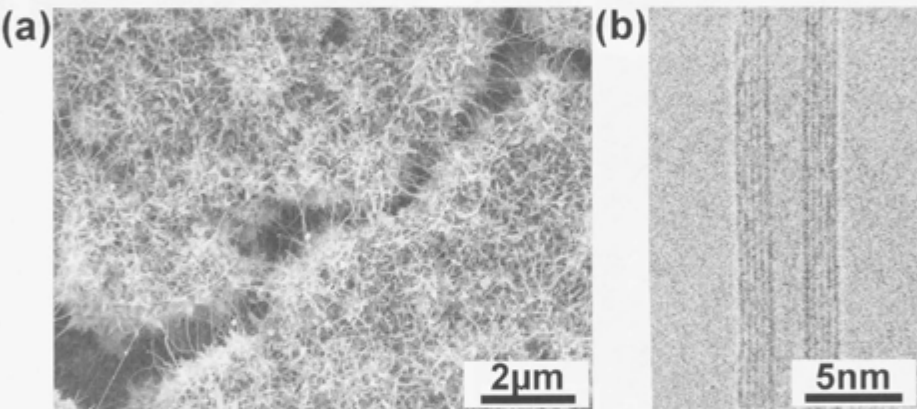


Figure 3.2 (a) SEM image of the BNNTs produced with $\text{Co}(\text{NO}_3)_2$ in NH_3 gas at 1300°C; b) TEM image revealing small diameter and cylindrical structure of a nanotube.

When B ink (with 0.02M $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ethanol solution) was annealed at 1000-1100°C for 3-4h in $\text{N}_2 + 5\% \text{H}_2$ gas, longer BNNTs with larger diameters were produced. The SEM image in Figure 3.3a reveals a high density of nanotubes with lengths of 100-200 μm . The longest BNNT found by SEM observation was more than 300 μm (Figure 3.4). The tube diameters are in the range of 50-80nm. Although the majority of the nanotubes grew in random directions (Figure 3.3a), well-aligned BNNTs were often found at the edge of the boat (Figure 3.3b), which is believed to be caused by the gas flow during annealing [136, 137]. TEM analysis revealed that most of the tubes had a bamboo-like structure and usually contained metal catalyst on the tip (Figure 3.3c). The detailed structural information and growth mechanism of the bamboo-type tubes have been reported previously [102, 104, 108]. The formation of different tubular structures is related to the different annealing atmospheres and

temperatures [106]. That is to say that the structure or the size of BNNTs is more related to the annealing conditions rather than what kind of nitrate is added. In fact, experiments showed that $\text{Fe}(\text{NO}_3)_3$, $\text{Co}(\text{NO}_3)_2$, $\text{Al}(\text{NO}_3)_3$ and $\text{Mg}(\text{NO}_3)_2$ all gave the same structure of nanotubes if the annealing conditions were the same, although the diameters of nanotubes may be slightly different.

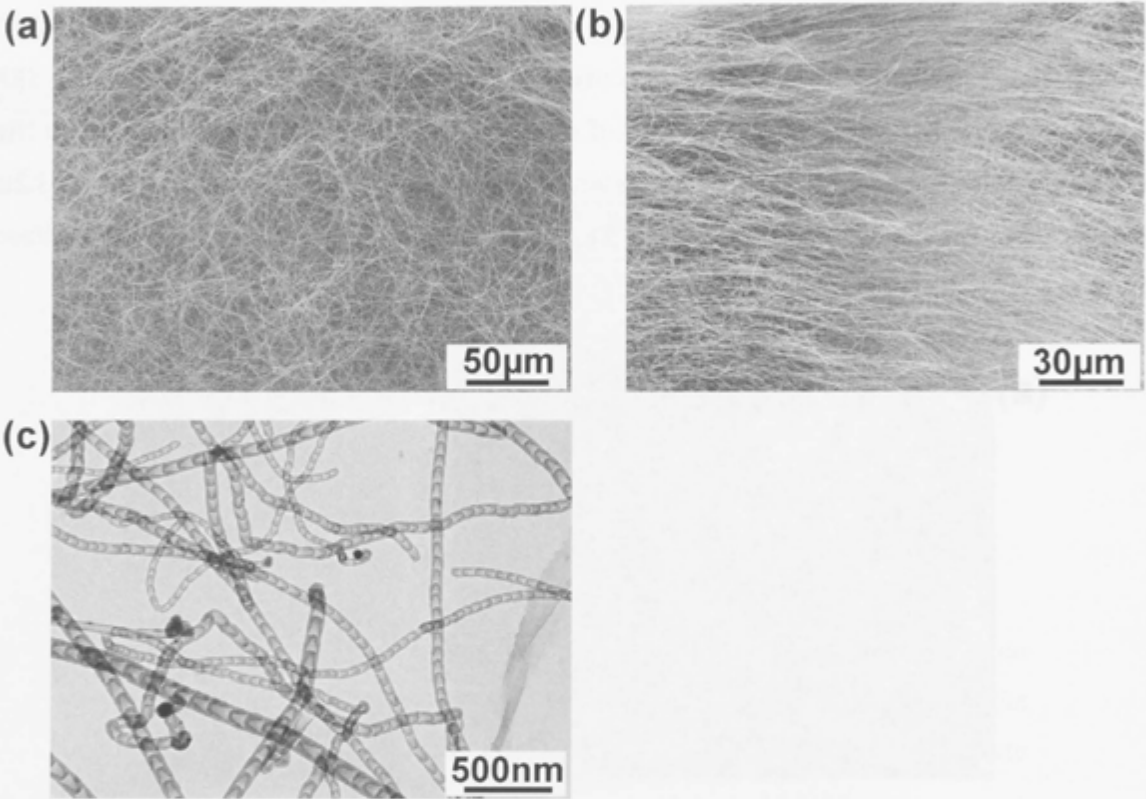


Figure 3.3 (a) SEM image showing high purity BNNTs produced with $\text{Fe}(\text{NO}_3)_3$ in $\text{N}_2+5\%\text{H}_2$ gas at 1100°C ; (b) SEM image showing the aligned BNNTs found near the crucible edge; (c) TEM image showing most of these nanotubes have a bamboo-like structure with a metal catalyst on the tip.

The B ink annealing method can produce larger quantities of BNNTs than the arc-discharge and laser ablation methods [23, 126]. The density of nanotubes produced by the new method is higher than those from the CVD method [92] and the increased yield overcomes a drawback of the chemical method reported by Singhal et al. [128]. The new method can also produce different sized BNNTs with different structures by varying the annealing conditions.

3.3.2 The role of metal nitrate

TGA was used to investigate the roles of both ethanol and nitrate in the annealing process. The TGA curve in Figure 3.5a shows the weight change of B ink during heating in $N_2+5\%H_2$ gas. In the analysis, 0.1M $Fe(NO_3)_3 \cdot 9H_2O$ ethanol solution was used to prepare the B ink (100mg B powder in 1mL solution) and the heating rate was $20^\circ C/min$. Because of the similar catalytic effects from metal nitrates for nanotube growth [138, 139], only $Fe(NO_3)_3$ was used in this analysis. In the curve, three different stages corresponding to three different physical and chemical changes in the B ink during the annealing can be seen. The first stage is from room temperature to $145^\circ C$, in which the weight of the sample plummeted dramatically from 48.5 to 5.6mg. This rapid weight loss was caused by ethanol evaporation. The next stage is from 145 to $400^\circ C$. During this stage, nitrate, $Fe(NO_3)_3$, thermally decomposed to metal oxide, Fe_2O_3 , which was further reduced into nanosized metal particles that acted as catalysts to assist the nanotube growth [140, 141]. The last stage is from 400 to $1100^\circ C$, where the weight of the sample rebounded due to the nitriding reaction between B particles and N_2 gas with the formation of BN phases.



Figure 3.4 SEM images showing a BNNT greater than $300\mu m$ in length (arrowed).

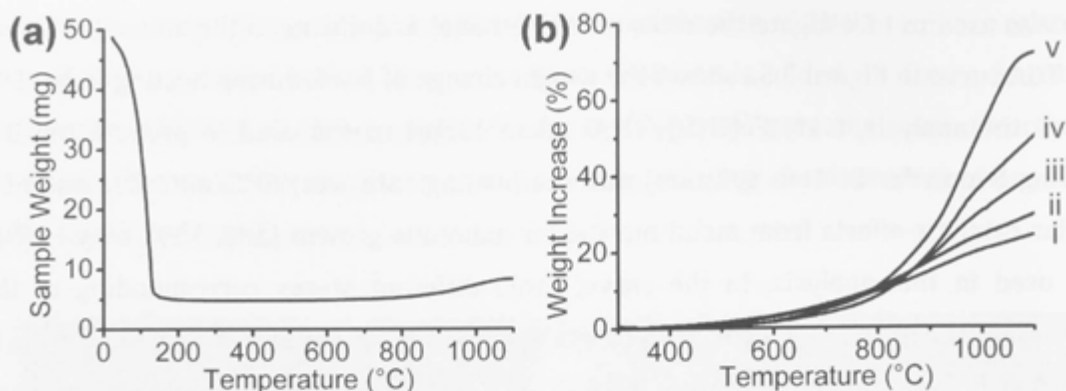


Figure 3.5 a) TGA curve showing the B ink weight change during annealing to 1100°C in $N_2+5\%H_2$ gas; b) five TGA curves comparing the nitriding reaction rates of: (i) ball milled dry B particles; (ii) ball milled B particles with pure ethanol; (iii) B ink with 0.013M $Fe(NO_3)_3 \cdot 9H_2O$ ethanol solution; (iv) B ink with 0.04M $Fe(NO_3)_3$ ethanol solution; and (v) B ink with 0.1M $Fe(NO_3)_3$ ethanol solution. All B inks were prepared by adding 100mg of ball milled B particles to 1mL of solution.

Metal nitrate plays an essential catalytic role in the high-yield synthesis of BNNTs. In the ball milled B powder, small steel particles, 2.09at.% Fe, are formed from the high energy collisions between the milling vial and balls during ball milling. So even if no nitrate is added to the ball milled B particles, these metal particles can still act as catalysts to grow BNNTs [104, 134]. However, they are not numerous or efficient enough to transform all the B particles to BNNTs. The nanosized metal particles decomposed from the nitrate added in the B ink can compensate for this deficiency, as shown below. The nitriding reaction rates of five samples: (i) ball milled dry B particles only, (ii) ball milled B particles with pure ethanol added, (iii), (iv) and (v) B ink prepared using 0.013M, 0.04M and 0.1M $Fe(NO_3)_3 \cdot 9H_2O$ ethanol solution, were compared (Figure 3.5b). In the TGA curves, the percentage weight gain is based on the minimum weight of each sample during annealing. For the ball milled dry B particles and the B particles with pure ethanol, the weight gains were only 24.7% and 30.2% during annealing. In contrast, there were much larger weight gains for the B ink with added $Fe(NO_3)_3$, and the weight gain increased with increased concentration of nitrate. The B ink with 0.013M, 0.04M and 0.1M $Fe(NO_3)_3 \cdot 9H_2O$ showed weight increases of 40.2%, 50.9% and 73.2%, respectively. The increased weight gains seen by TGA mean faster rates of nitriding. The rate of nitriding is important for the formation of BNNTs, because fast nitriding is prone to the formation of BNNTs while the slow nitriding is more likely to form BN particles. For example, if a heating rate of 5°C/min was used, almost only BN particles resulted. Therefore, metal nitrate is the main reason for the improvement in the nanotube yield.

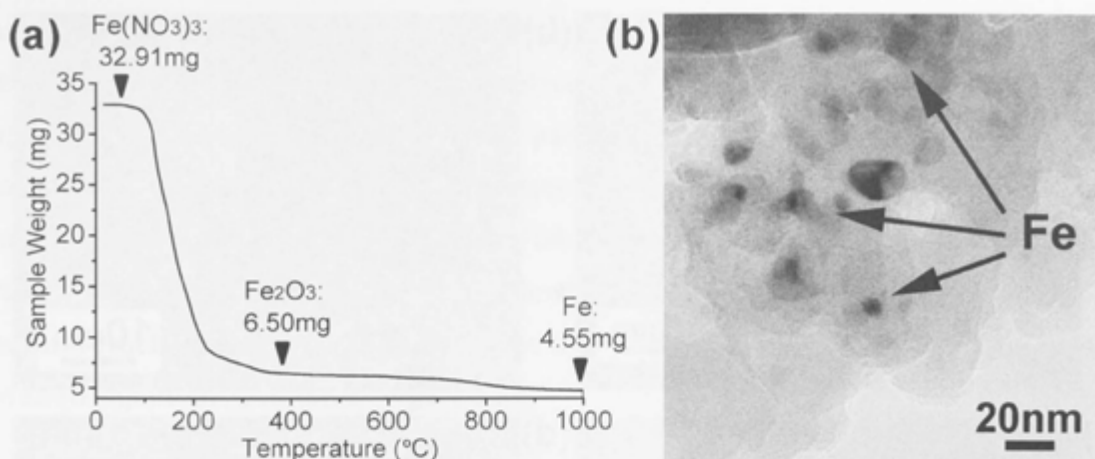


Figure 3.6 (a) TGA curve of $\text{Fe}(\text{NO}_3)_3$ annealed in $\text{N}_2+5\%\text{H}_2$ up to 1100°C with the critical phase indicated; (b) TEM image of B ink after 800°C annealing in $\text{N}_2+5\%\text{H}_2$ gas; the small dark dots with diameter 5-10nm are Fe catalysts decomposed and reduced from $\text{Fe}(\text{NO}_3)_3$.

The detailed TGA investigation of the heating process of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in $\text{N}_2+5\%\text{H}_2$ gas revealed that most of the $\text{Fe}(\text{NO}_3)_3$ thermally decomposed to Fe_2O_3 at 350°C , and then these oxides were largely reduced by H_2 into Fe particles at around 850°C (Figure 3.6a). The TEM image (Figure 3.6b) shows the Fe particles (dark) reduced from the B ink after annealing at 800°C in $\text{N}_2+5\%\text{H}_2$ are as small as 5nm, while the 20nm particles could be steel particles from ball milling or the agglomeration of Fe decomposed from $\text{Fe}(\text{NO}_3)_3$. These Fe particles created more reaction sites for nitriding and acted as seeds for nanotube growth. The highest yields of BNNTs were produced when 0.08 to 0.2mg $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was added to 1mg of ball milled B powder. Figure 3.7 compares the products from different B inks containing different percentages of $\text{Fe}(\text{NO}_3)_3$. All the samples were annealed in $\text{N}_2+5\%\text{H}_2$ gas at 1100°C for 3h. It can be qualitatively seen that if less $\text{Fe}(\text{NO}_3)_3$ is added, the yield of BNNTs is lower because there is still not enough catalyst; and if too much is added, particle impurities are found in the product, due to the loss of the catalytic function of the large Fe particles [142, 143].

3.3.3 The role of ethanol

Although most of the ethanol evaporated below 145°C , it still slightly enhanced the BNNT growth. TGA (Figure 3.5b) shows that even by adding pure ethanol into the B particles without nitrate, there was still a bigger weight gain than for the dry B particles. The role of ethanol can be explained as follows. Firstly, ethanol can help to break up the agglomerates of

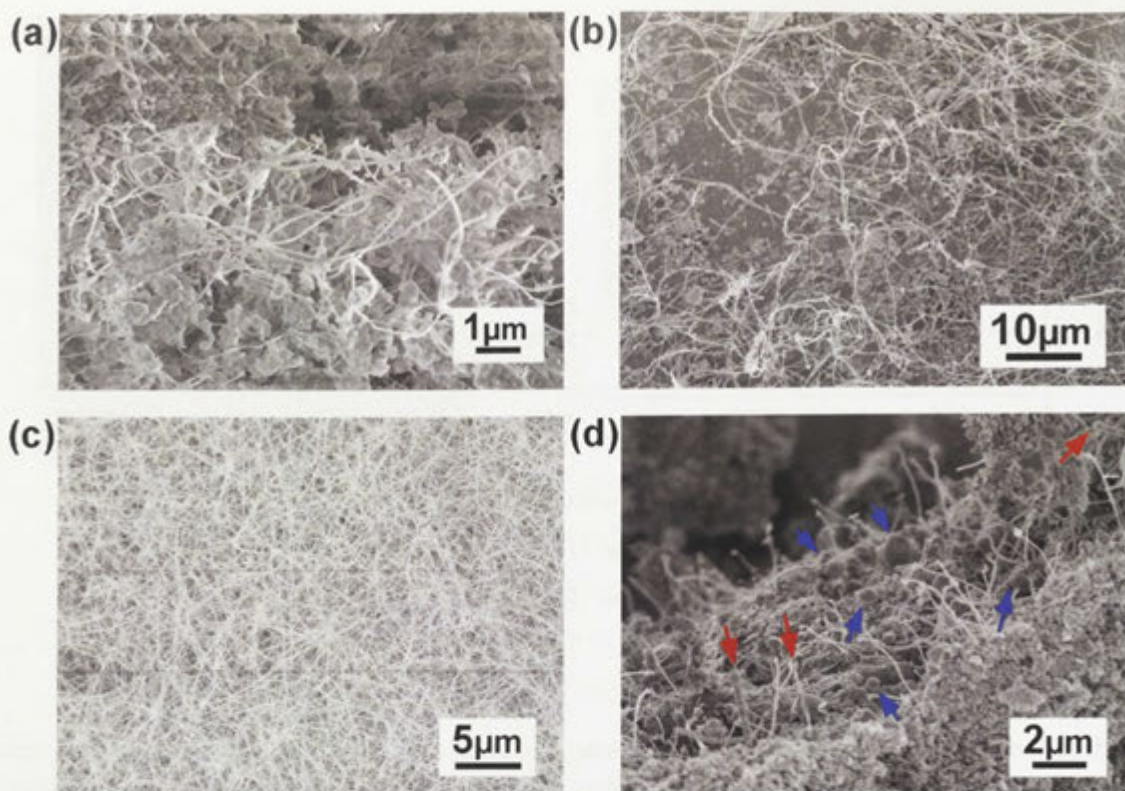


Figure 3.7 SEM images of the BNNTs produced by using B inks with different amount of $\text{Fe}(\text{NO}_3)_3$. (a) There were more particles than BNNTs in the product when ball milled B particles with pure ethanol without adding any $\text{Fe}(\text{NO}_3)_3$ was used in annealing; (b) improved density of BNNTs when 0.04mg $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was added to every mg of ball milled B (still not enough $\text{Fe}(\text{NO}_3)_3$), but there were still particulate contaminants; (c) very high density of BNNTs when 0.2mg $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was added to every mg of ball milled B (within the optimum range); (d) low density of BNNTs produced when 0.29mg $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was added to every mg of ball milled B (too much $\text{Fe}(\text{NO}_3)_3$). The big round Fe particles were found in the product (blue arrows), which had almost lost their catalytic function; while a small number of BNNTs grew up with big catalysts on the tip (red arrows). Charging effect affected the quality of some of the images.

B particles during the mixing aided by ultrasonication. The nanosized B particles normally agglomerate into large clusters under the ball impacts during milling. The agglomeration slows down the nitriding reaction, and hence reduces nanotube yield. The ultrasonic treatment in ethanol can break these large agglomerates into loose B particles giving better contact with the reaction gas so that an enhanced rate of nitriding was achieved during annealing. Secondly, ethanol helps to protect the metastable B particles from oxidation. The ball milling process produces the metastable disordered B structures that are highly reactive in air even at room temperature. The oxidation of these structures may cause them to lose their chemical reactivity. The ethanol can cover the surface of these ball milled

particles preventing the oxidation. Thirdly, ethanol assists homogeneous mixing of the nitrates with the nanosized B particles. Metal nitrates are solid, so without liquid it is impossible to evenly mix them with the B particles. In addition, ethanol does not leave C contamination in BNNTs, if excessive volumes are avoided (because a high heating rate is required for the formation of BNNTs). TGA (Figure 3.5a) shows that ethanol can be evaporated away at low temperature (below 145°C), and thus it is not involved in any chemical reactions at high temperature. The EDS analysis of the final BNNT products does not show significant C residues (Figure 3.1b).

Besides ethanol, water was also tried for the preparation of B ink. However, the synthesis result was not as good as when ethanol was used. This is because although water can also play the mixing role, it does not evaporate as quickly as ethanol during annealing, which means that water is more likely to remain in the sample and be involved in the high temperature reaction. Other organic solvents were not tried mainly because the solvent itself is not directly involved in the reaction. So, ethanol, non-toxic and easy to evaporate, is good enough.

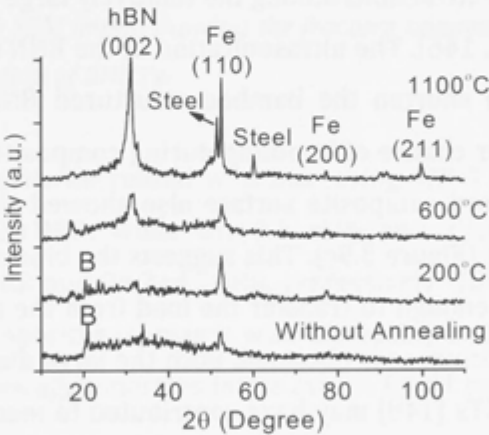


Figure 3.8 XRD patterns showing increased hBN formation process with increasing temperature.

The metastable disordered B structures produced by the ball milling treatment can react with the nitrogen containing gas at a relatively lower temperature to form BN phases [102, 104]. The XRD spectra of the B ink annealed at different temperatures in Figure 3.8 clearly show the formation and increase of the BN phases with increased annealing temperature. At room temperature, there were only disordered B structures. The (002) BN phase appeared at 600°C. At 1100°C, this peak became dominant. The crystal sizes of hBN phases at these temperatures were 70 and 99nm, estimated from the Scherrer equation. The XRD results

confirm the weight gains in TGA were caused by the nitriding reaction or the BN phase increase between 400 and 1100°C. Because the ball milled B particles are preferable for growing one-dimensional BNNTs with the presence of metal catalysts at lower growth temperatures [106, 107, 144], high density of BNNTs can be synthesized in large quantities.

3.3.4 BNNT reinforced polyurethane composite

The BNNTs synthesized in $N_2+5\%H_2$ gas were added to PU to produce composites. Two composites with 0.5vol.% and 2vol.% of BNNTs, along with one neat PU, were prepared using the same conditions (Figure 3.9a). Figure 3.9b compares the compressive stress-strain curves of the three samples. Compared to the neat PU, the 0.5vol.% BNNT filled composite shows a 38.2% enhancement in compressive modulus. The compressive moduli of the neat PU and the 0.5vol.% BNNT reinforced composites are 19.85MPa and 27.43MPa, respectively. SEM investigation on several fracture surfaces of the composites revealed that the 0.5vol.% BNNT composite, as a whole, had a good dispersion of nanotubes, though some agglomerations were also found. This may be because of the low volume percentage of nanotubes used, the small attractions among the relatively large nanotubes and the impacts from ultrasonication [145, 146]. The ultrasonication of the BNNTs in solvent could not only separate BNNTs but also shorten the bamboo structured BNNTs [147]. The shortened BNNTs have a much lower chance of bundling during composite synthesis [146, 148]. The observation of the fractured composite surface also showed that most BNNTs tended to break rather than pull out (Figure 3.9c). This suggests the binding between BNNTs and the polymer matrix is strong enough to transfer the load from the matrix to the nanotubes so that the mechanical enhancement is obtained. Both the large diameter and the geometrical shape of the bamboo BNNTs [148] may have contributed to mechanical interlocking or the non-covalent bonding between nanotubes and matrix [149].

However, the 2vol.% BNNT reinforced composite exhibited a lower compressive modulus value of 21.1MPa. This deterioration is mainly caused by the agglomeration of nanotubes. As the volume content of nanotubes in the matrix increases, the chance of agglomeration increases dramatically due to the large surface area of nanotubes [146]. These agglomerates can cause voids and adhesion defects in the composite [150]. The SEM image (Figure 3.9d) shows an example of voids and defects due to the agglomerations of BNNTs. During fracture, the crack propagated along the interface between two nanotubes and polymer as well as the voids caused by the crossing of the two tubes.

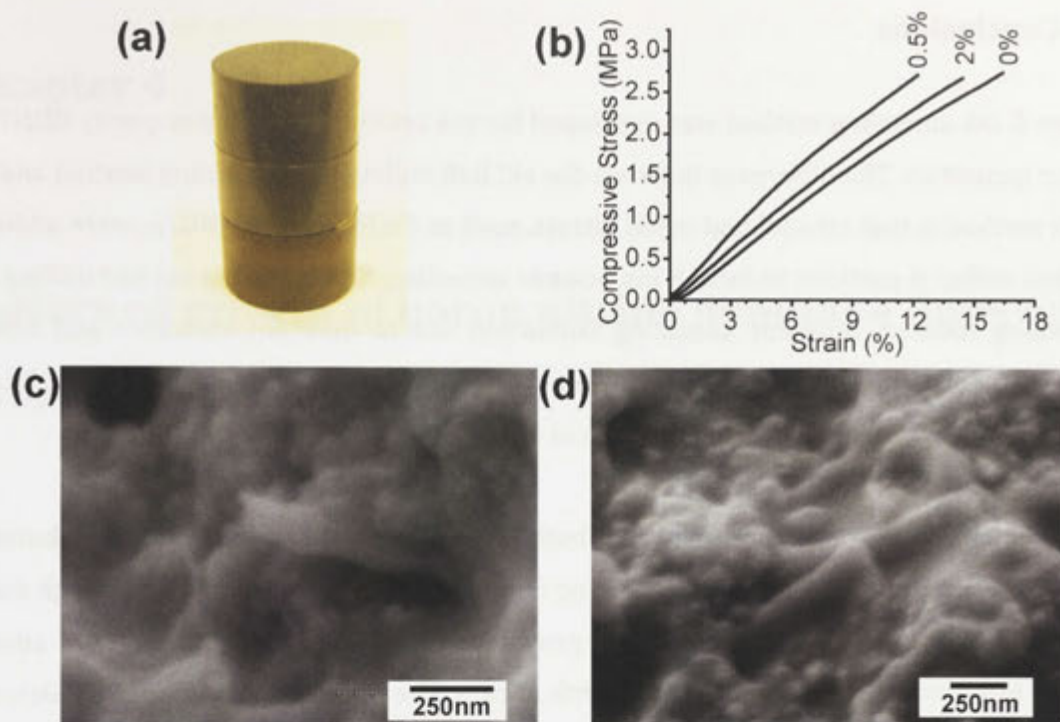


Figure 3.9 (a) A photo showing from bottom to top: neat polyurethane, 0.5vol.% and 2vol.% BNNT reinforced composites; (b) the stress-strain curves of the neat polymer, and two BNNT reinforced composites; (c) SEM image showing a broken BNNT on the fractured surface; (d) SEM image showing the fracture happened on voids and defects due to the agglomeration of BNNTs.

The hardness of the composite decreased with increasing BNNT content. The neat PU had Rockwell hardness $80.7 \pm 2.1 \text{HRR}$, while the 0.5vol.% and 2vol.% BNNT reinforced PU composites had $79.1 \pm 1.9 \text{HRR}$ and $76.2 \pm 4.2 \text{HRR}$, respectively. This is probably because the number of voids in the composites increases with increasing nanotube content [151]. This trend is consistent with more agglomerates in the 2vol.% BNNT reinforced composite.

The production of the BNNT reinforced composites was mainly to demonstrate a potential application of the large quantity synthesis of BNNTs by the B ink method. In order to better understand the compressive modulus and hardness changes with the content of BNNTs in the matrix, it would be desirable to quantify the density of voids in the composites. It would also be desirable to functionalize the nanotubes to improve the wetting properties and to allow stronger bonding between the fillers and the matrix. However, these are beyond this study.

3.4 Conclusions

A new B ink annealing method was developed for the production of higher purity BNNTs in larger quantities. The difference between the old ball milling and annealing method and the B ink method is that ethanol and metal nitrate, such as $\text{Fe}(\text{NO}_3)_3$ or $\text{Co}(\text{NO}_3)_2$, were added to the ball milled B particles to form B ink prior to annealing. Similar to the old ball milling and annealing method, different annealing conditions led to different structure and size of BNNTs: small diameter cylindrical multiwalled BNNTs were produced in NH_3 at 1300°C ; and bamboo structured BNNTs were produced in $\text{N}_2+5\%\text{H}_2$ at $1000-1100^\circ\text{C}$.

Systematic investigations confirmed that both the metal nitrate and ethanol contributed to the significant improvement in the nitriding reaction and were essential for the high purity synthesis of BNNTs. Mainly, the nitrate provided extra metal catalysts and the ethanol helped to intimately mix the B particles with nitrate. The optimum amount of $\text{Fe}(\text{NO}_3)_3$ was determined to be 0.08-0.2mg of $\text{Fe}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$ added to every 1mg of ball milled B powder.

The B ink annealing method provided adequate BNNTs for various applications. Bulk quantities of BNNT reinforced PU composites at different volume contents could be prepared and the compressive moduli of the composites were measured. Results showed that the composites had better compressive modulus but lower hardness than the neat PU.

** Most of the work presented in this chapter was done by author and the TEM investigations were done by group members.*

Chapter 4

Patterned growth of boron nitride nanotube films on substrates

4.1 Introduction

It has been demonstrated that the growth of carbon nanotube (CNT) films on various substrates and surfaces is vital for applications, such as nanoscale functional devices [152, 153], antifouling surfaces [154], bioapplications [155, 156] and thermal interface materials (TIM) [157, 158]. The growth of boron nitride nanotubes (BNNTs) on various substrates is also important due to many of their special or unique properties. For example, a BNNT film may be used in building optoelectronic devices [73, 159]. In the past decade, BNNTs in powder form have been produced by several groups [23, 104, 160-163]. However, there are only a few reports on the growth of BNNT films on flat substrates [112-115], either by chemical vapour deposition (CVD), radio-frequency magnetron or plasma-enhanced pulsed-laser deposition techniques. However, both the density and the purity of the BNNT films produced by these methods are low. In addition, the patterned growth of BNNTs over a large area as well as on complex non-flat surfaces has not been achieved yet.

The boron (B) ink method described in Chapter 3 enables high-density BNNT films with any desired pattern to be grown on, and firmly attached to, the chosen surface. The B ink, a mixture of nanosized B particles, metal nitrate catalyst and ethanol, is first painted, sprayed, or inkjet printed onto the substrate surface, depending on the desired result, and then annealed in a nitrogen containing gas so that the ink layer is converted into a BNNT film. This is the first method capable of growing BNNTs on complex non-flat surfaces and greatly

broadens the potential application of BNNTs. Several possibilities have been examined. It is demonstrated that a needle given an internal BNNT coating could greatly enhance microfluidic transport; a BNNT coated mesh can efficiently separate oil and water on a microlitre scale; and a coated screw could be used to minimize wear at the interface. The B ink painting method can be easily scaled up thanks to the large capacity of the ball milling facilities.

4.2 Experimental

Ball milling was conducted in a vertical rotating high-energy ball mill. Several grams of amorphous B powder (95%-97%, Fluka) were sealed in a steel milling vial with four hardened steel balls with diameter of 25.4mm in anhydrous ammonia (NH_3) at 300kPa. The milling experiment lasted for 150h at ambient temperature. Then the milled sample was unloaded and mixed with nitrate in ethanol within an airtight bottle in the inert gas filled glove box for subsequent mixing in a ultrasonic bath under power of 80W. The painted substrate was annealed in a horizontal tube furnace at 950-1300°C in $\text{N}_2+15\%\text{H}_2$ with flow rate of 0.1L/min or NH_3 gas with rate of 0.3L/min.

The possibility of applying the ink via commonly available inkjet printers, as opposed to just painting the ink onto a surface using a brush, was also investigated. A Canon BJC 210 inkjet printer with cartridge of BC-02 or BX-02 model was used. A new cartridge was opened, emptied and cleaned with ethanol. Two steel meshes located between the ink containing chamber and nozzles were removed. Dilute B ink (50mg/mL B in 0.035M $\text{Co}(\text{NO}_3)_2 \cdot 9\text{H}_2\text{O}$ ethanol solution) was used to allow it pass through the ink supply tunnel of cartridge and the nozzles. B ink was directly poured into the ink containing chamber of the cartridge and several minutes were needed to let ink ooze through the ink supply tunnel. Printing was successfully tested on two different substrates: thin stainless steel sheet and silicon dioxide covered silicon (SiO_2/Si). The stainless steel sheet was thin enough to be bent and accepted by printer, just like a piece of normal paper. SiO_2 wafer was cut into small pieces (about 20mm x 10mm) and glued onto paper for printing. The coating patterns were designed using Microsoft Word software. All the printing work was done in air. The coated substrates were annealed at temperature of 1100°C in $\text{N}_2+15\%\text{H}_2$ atmosphere for 30mins.

The potential of the method for growing BNNTs on complex shapes was tested using a steel mesh, a steel needle and a screw. The steel mesh (with wires of $\sim 150\mu\text{m}$ in diameter) was thoroughly brushed with the B ink (83.3mg/mL of B in 0.03M $\text{Fe}(\text{NO}_3)_3$ ethanol). The brushed mesh was hung over an alumina boat and heated at 1100°C for 1h in $\text{N}_2+15\%\text{H}_2$ gas, so that both sides of the mesh could contact with the reaction gas and thus be totally covered by BNNTs. The steel needle (outer and inner diameter ~ 510 and $\sim 260\mu\text{m}$, respectively), cut from a syringe, was totally immersed into B ink (62.5mg/ml of B in 0.04M $\text{Co}(\text{NO}_3)_3$ ethanol) so that the ink also covered the needle's internal channel. The screw had a diameter of 0.9mm and the thread spacing of $200\mu\text{m}$. The ink was brushed on the screw.

The strength of the bonding of the BNNT films to steel surface was tested by a Q800 DMA (TA Instruments, USA) equipped with a standard tension clamp for the adhesion test. The resolution of the loaded force is 0.00001N. Double-sided Scotch tape (1cm x 1cm) was attached to a relatively thick BNNT film to avoid the tape directly contacting the substrate, and the other side of the tape was fixed to a thin rectangular stainless steel sheet (thickness 0.14mm). The coated substrate and the stainless steel sheet were fixed to the tension clamps. A shear force (in controlled force mode) was applied to pull the tape away from the BNNT film. The starting force and the rate of force increase were 0.001N and 0.5N/min, respectively.

To show the potential applications of the BNNT films, wetting properties were analyzed. The contact angles were measured using an optical contact angle and surface tension instrument (CAM 101, KSV) in a conditioned laboratory ($20\pm 2^\circ\text{C}$, $65\pm 2\%\text{RH}$). The contact angles and drop volumes were automatically calculated by software which uses the Young-Laplace equation to curve-fit drop profiles captured by a camera. The images showing paraffin oil drops (LabChem, density $0.87\text{g}/\text{cm}^3$) passing through the BNNT coated mesh were recorded at a frame interval of 33ms.

Hitachi 4300SE/N and Hitachi 4500 FESEM scanning electronic microscopes at 3kV were employed to examine sample morphology and x-ray energy dispersive spectroscopy (EDS) was conducted in 4300SE/N instrument at 15kV. TEM investigations were performed using a Philips CM300 (300kV) microscope.

4.3 Results and Discussion

The B ink painting method, as illustrated in Figure 4.1, consists of four steps. (a) Nanosized and chemically active B particles are produced by milling of amorphous B powder. (b) The ball milled B particles are homogenously mixed with ethanol and a small amount of ferric (or any other metal) nitrate to form an ink-like solution (B ink) under ultrasonic bath. (c) The B ink is painted, sprayed or inkjet printed to create a thin layer of B ink in desired pattern on the substrate. (d) The B ink covered substrate is annealed at 950-1300°C in $N_2+15\%H_2$ or NH_3 gas which converts the B layer into a high purity BNNT film.

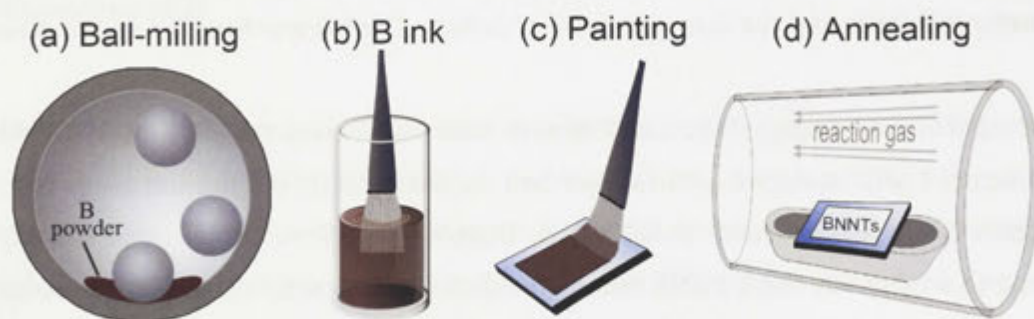


Figure 4.1 Schematic diagram showing the four steps involved in the B ink coating method. (a) Ball milling of B powder in NH_3 to produce nanosized B particles; (b) mixing ball milled B particles, metal nitride and ethanol to form B ink; (c) painting the B ink on the substrate; (d) annealing of the painted substrate in a nitrogen-containing atmosphere to grow the BNNT film.

Figure 4.2 shows a BNNT thin layer formed on a stainless steel substrate using the B ink painting method. The photo in Figure 4.2a shows the B ink (62.5mg/mL of B in 0.04M $Fe(NO_3)_3 \cdot 9H_2O$ ethanol solution) being brushed on a stainless steel substrate using a painting brush. A complicated pattern (a traditional Chinese calligraphic dragon character) was chosen to demonstrate the flexibility and ease of use of the method. After annealing of the painted substrate at 1100°C in $N_2+15\%H_2$ atmosphere, a light bluish white layer was formed on the painted surfaces (Figure 4.2b). The SEM image of the right-bottom corner of the calligraphy pattern reveals the BNNT film was only grown at the ink brushed area (Figure 4.2c). The chemical composition was determined by EDS (Figure 4.2d). Fe and Ni come from both substrate and catalysts. The enlarged image in Figure 4.2e shows the high purity and density of nanotubes with diameters in the range of 50-80nm. Regular BNNT patterns were produced by mask coating, in which B ink was brushed on the un-covered areas of mask before annealing (Figure 4.3). In this example, B ink was brushed on the substrate through a tape mask and then annealed at 1100°C in $N_2+15\%H_2$ gas for 0.5h.

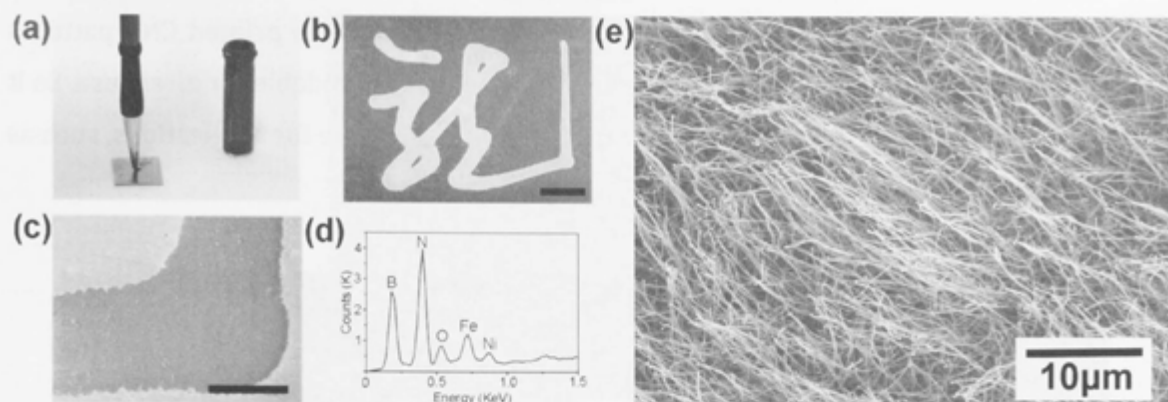


Figure 4.2 Patterned BNNT film produced by B ink method. (a) A photo showing the process of B ink brushed on a steel substrate surface using a painting brush; (b) optical microscopic photo of a white BNNT pattern on the substrate after annealing, scale bar 5mm; (c) SEM image of part of the BNNT film taken from the right-bottom of the pattern, scale bar 500μm; (d) EDS spectra recorded from the white BNNT film; (e) SEM image at higher magnification showing pure and high-density BNNTs in the film.

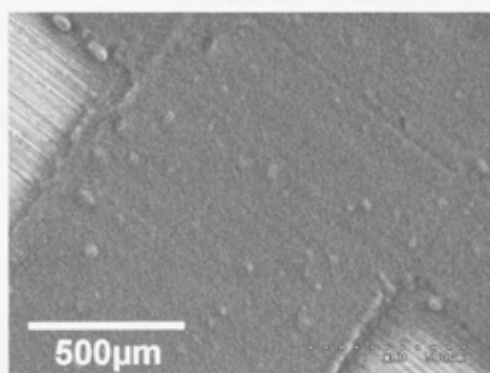


Figure 4.3 SEM image showing a BNNT film pattern created by the B ink mask coating method.

Inkjet printing is an economical coating method for repeatedly depositing materials in complex patterns. It has been used to fabricate organic integrated circuits [164-167], silicon thin-film transistors (TFTs) [168] and three-dimensional biological structures [169]. Most inkjet printers use either piezoelectric or thermal mechanism to eject droplets of liquid. Recently, the electrohydrodynamically driven jet printer was invented to achieve submicron resolution [170]. Chemically functionalized CNTs have been dispersed in solvent and inkjet printed on different substrates. One obvious advantage of this printing process is that it can deposit CNT patterns even on non-thermal durable substrates. However, some properties of CNTs may be changed during functionalization and the adhesion between the printed CNTs

and substrate is usually poor. In order to improve the adhesion, the printed CNT patterns can be covered with a polymer film, but the CNTs are no longer available for direct use. So it is also important to be able to directly grow nanotubes on substrate for applications, such as field emission and heat transfer.

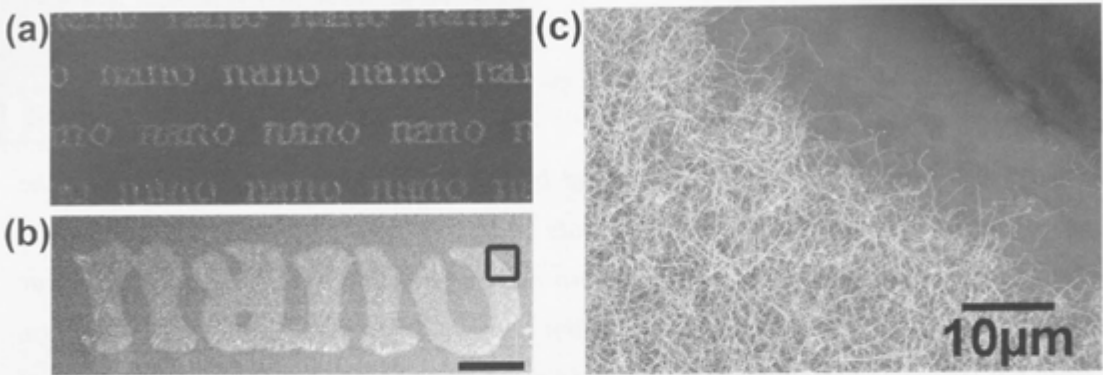


Figure 4.4 BNNT films produced by B ink printing. (a) Optical microscope photo of inkjet printed arrays of BNNTs forming the word “nano”; (b) SEM image of one word in “Times New Roman” font, scale bar 500μm; (c) higher magnification SEM image of the top right of the letter “o”, indicated by the square.

B ink is compatible with inkjet printing and able to print and grow BNNTs directly on a substrate, because of the fineness of the B particles (average size 45 nm). Figure 4.4a shows an optical microscope photo of BNNTs forming repeated lines of the word “nano” on a SiO₂/Si substrate. A commercial office inkjet printer with a dilute B ink (50mg/mL of B in 0.035M Co(NO₃)₂·6H₂O ethanol) were used and the annealing was conducted at 1100°C in N₂+15%H₂ for 0.5h. Figure 4.4b shows a SEM image of one group of letters in ‘Times New Roman’ font of font size “5”. A higher magnification SEM image from the edge of the letter “o” (indicated by the square) shows that only the ink printed area has BNNTs (Figure 4.4c). By using a high resolution jet printing device [170], it is believed that the B ink printing method is able to replicate any BNNT pattern with micron resolution.

The BNNT film thickness (nanotube length and density) can be controlled by the amount of ink, that is, the thickness of the ink layer painted on the substrate. Painting or brushing usually resulted in films with a thickness of 5-40μm. Spraying a diluted B ink (e.g. 30mg/mL of B in 0.02M Fe(NO₃)₃·9H₂O ethanol solution) produced a sparse array of BNNTs (Figure 4.5).

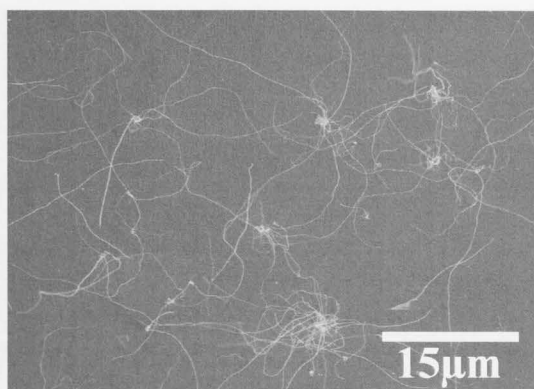


Figure 4.5 SEM image of the low density or sparsity of BNNTs on SiO₂/Si substrate by spraying dilute B ink.

Similar to the B ink annealing described in Chapter 3, the BNNTs produced in N₂+15%H₂ atmosphere at 1100°C usually have diameters 40-80nm and bamboo-like structure (Figure 4.6). Cylindrical BNNTs with similar diameters could also be formed (Figure 4.6), probably due to the higher heating rate during annealing, which led to higher migration or precipitation rates of BN in the catalyst [171]. The reason that the cylindrical BNNTs were not formed in the large quantity synthesis process may be because it was hard to heat a large amount of B ink rapidly, in contrast to the small amount of ink used in the painting/coating process. Very thin cylindrical BNNTs with diameters less than 10nm can be produced by annealing in NH₃ at 1300°C (Figure 4.7) [107]. The growth mechanisms of different BNNT structures in different atmospheres have been discussed before [106].

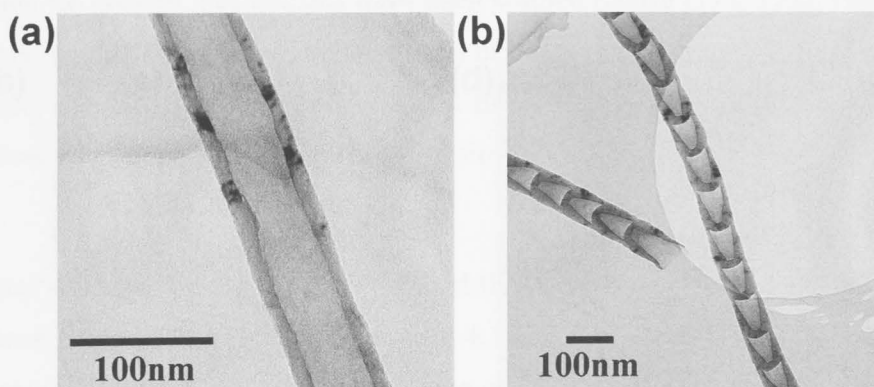


Figure 4.6 (a) TEM image of a BNNT with cylindrical structure; (b) TEM image of two bamboo-like structured BNNTs.

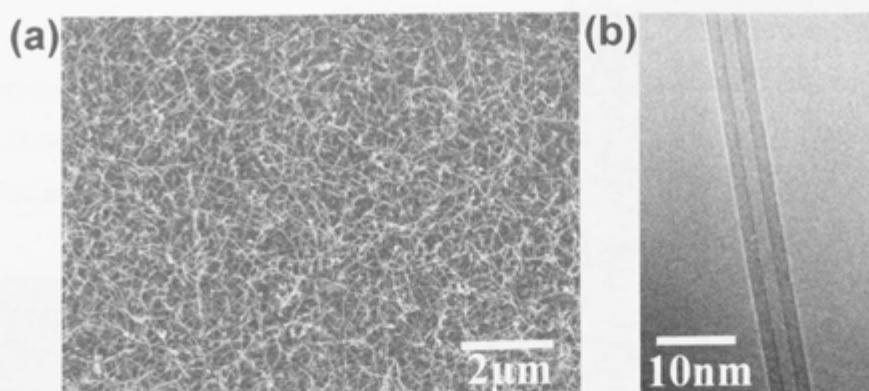


Figure 4.7 (a) SEM image of BNNTs with small diameters and cylindrical structure grown on SiO₂/Si substrate; (b) a corresponding TEM image of a BNNT in the film.

In addition to the nanotubes, high density BN nanowires can be also formed on a stainless steel substrate by heating the ink in a N₂+15%H₂ atmosphere at 1100°C. The SEM picture (Figure 4.8a) shows a high-density of nanowires with average diameter of 50-80nm and some large wires of ~100nm diameter. The typical nanowire structure can be seen from the TEM picture in Figure 4.8b. A polycrystalline phase is revealed by the TEM image in Figure 4.8c. The high-resolution TEM image (Figure 4.8d) shows the nanowire has a well-crystallized local structure. BN nanowires were often found on stainless-steel substrates, especially when a thin layer of B ink was coated on the surface. The reason for the formation of the BN nanowires is still not clear, but the stainless steel surface probably acted as an additional catalyst for the growth of BN layers, which has been found in another case using a different precursor [130].

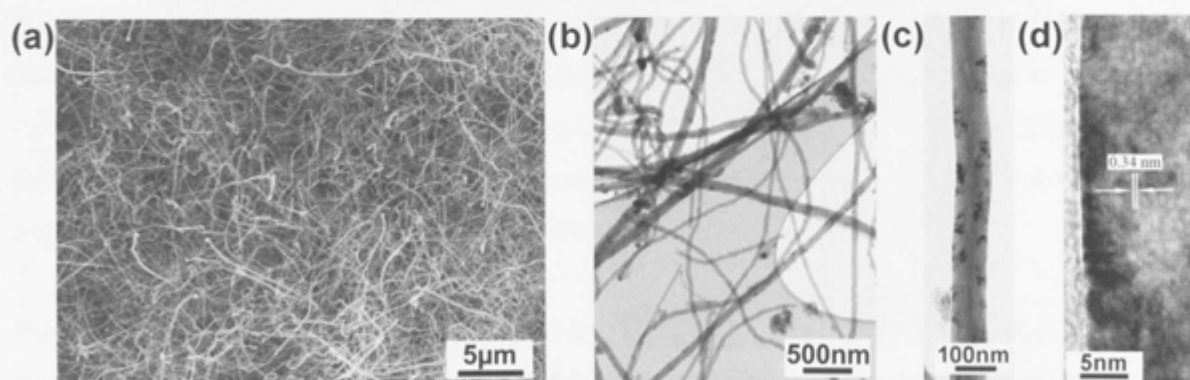


Figure 4.8 (a) SEM image showing high density of BN nanowires formed on stainless steel substrate; (b) TEM image showing their nanowire structure; (c) TEM image of one single nanowire with polycrystalline structure; (d) HRTEM image showing graphite-like layers from a local area of the nanowire.

The use of different nitrates in preparing B ink (e.g. $\text{Fe}(\text{NO}_3)_3$, $\text{Co}(\text{NO}_3)_2$, $\text{Mg}(\text{NO}_3)_2$, or $\text{Cu}(\text{NO}_3)_2$) did not show a big influence on the size, length or structure of BNNTs. As mentioned in Chapter 3, the added nitrate provides more catalyst for nanotube growth and the ethanol not only makes the BNNT film coating possible but also slightly enhances the nitriding reactions between the ball milled B particles and the reaction gas. As a result, the high-density BNNT films were achieved.

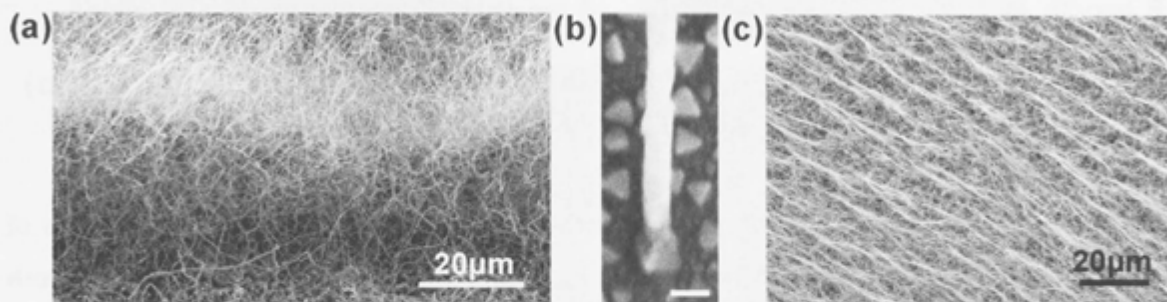


Figure 4.9 (a) Cross-sectional view of partly erect BNNTs in the film; (b) a BNNT securely attached to the steel substrate via a catalyst particle; (c) SEM image of BNNT film after high-pressure air blowing at a short distance.

The grown BNNT films are firmly attached to the substrate. BNNTs can have one end connected to the surface (Figure 4.9a), because the coating involves nanotube growth during annealing. In some case, the tubes appear to be attached via a metal particle, as shown in the SEM image of Figure 4.9b, although tip growth was also found in the sample. Both root and tip growth mechanisms have been studied before [172, 173]. The attachment strength between BNNTs and the substrate was firstly tested by blowing the film with an air gun at a short distance. After high-pressure air blowing, most nanotubes remained and the strong air flow aligned the tubes to the air flow direction (Figure 4.9c).

The adhesion strength between a 1cm^2 area of the BNNT film and the steel substrate was also measured using a DMA [174, 175]. Figure 4.10a shows the set-up of the measurement. A typical stress-strain curve is shown in Figure 4.10b, in which the Scotch tape was completely detached from the BNNT film at a shear stress of 4.75kPa. The average failure shear stress from five BNNT films (all on steel substrates) was $4.67 \pm 0.35\text{kPa}$. After the tape was pulled off, there was still a white layer of BNNTs left on the substrate, which indicates that the tape did not have direct contact with the substrate and the tape could only pull off some of the BNNTs in the films.

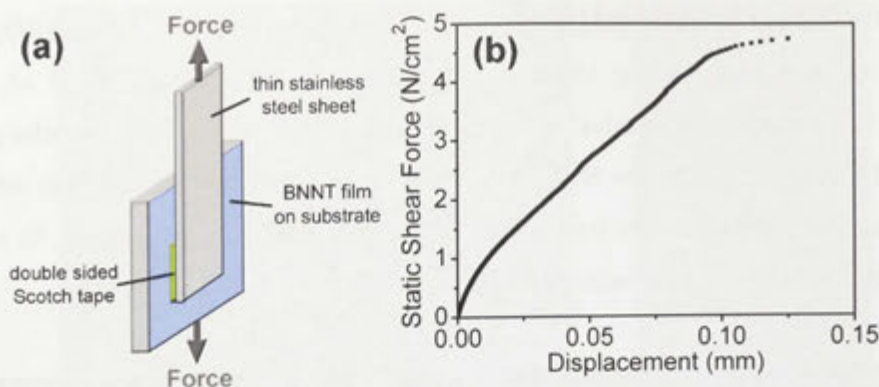


Figure 4.10 (a) A schematic diagram showing the set-up of the adhesion test by DMA; (b) the stress-strain curve of 1cm² BNNT film under static shear force.

Another important advantage of the B ink method is that it can grow BNNTs on objects of various and complex shapes. SEM images in Figure 4.11a and b show a steel mesh homogeneously coated with BNNTs. The mesh was thoroughly brushed with the B ink and, after annealing at 1100°C in N₂+15%H₂ gas for 1h, both sides were covered by a high density of BNNTs without blocking the small square openings. Figure 4.11c and d show BNNTs were grown on both the external and internal surfaces of a steel syringe needle. This was accomplished by first immersing the needle in the ink and then placing it along the gas flow direction during annealing so that erect BNNTs even grew on the surface of its internal channel. Figure 4.11e and f show BNNTs standing on both the threads and the gaps of a tiny screw. These examples demonstrate that BNNTs can be delicately grown on any irregularly shaped object, as long as the B ink can reach and cover its surface.

Coating of BNNTs on non-flat objects opens up many new applications. Here, three potential applications are briefly described. A BNNT covered needle (Figure 4.11c and d) could be very useful in microfluidic devices [176]. Due to the huge surface roughness of the BNNT film that enables the Cassie state [177], the as-grown BNNT films can be superhydrophobic [178, 179]. Because of the superhydrophobicity, when fluid flows through such a BNNT coated needle, the adsorption onto the channel surface and the frictional drag can be greatly reduced, allowing better performing microfluidic devices. A detailed study of the superhydrophobic properties of the BNNT films will be presented in Chapter 6. In contrast to the super anti-wetting to water, the BNNT films are extremely wettable to oil. In general, if a solid has surface tension larger than a quarter of the surface tension of an oil, the solid is wettable to the oil [180]. The surface tension of an individual BNNT with diameter of 40nm has been measured to be 26.7-27.0mN/m [81] and most oils have surface tensions of 20-30

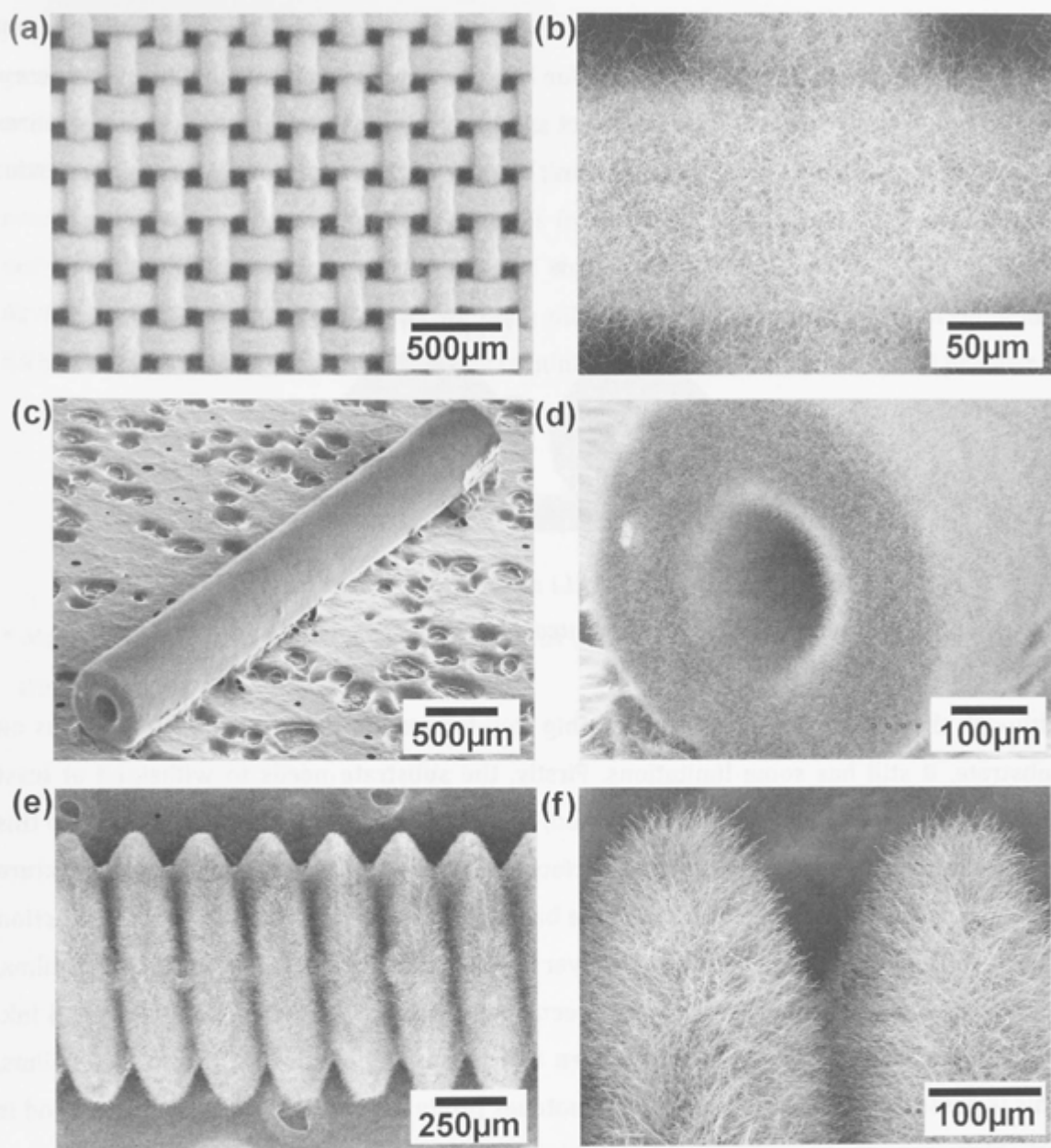


Figure 4.11 SEM images of BNNTs grown on the surfaces of irregularly-shaped objects: (a), (b) woven steel mesh of wires of $\sim 150\mu\text{m}$ diameter; (c), (d) steel syringe needle with outer diameter $\sim 510\mu\text{m}$ and inner diameter $\sim 260\mu\text{m}$; (e), (f) steel screw of 0.9mm diameter and the thread spacing of $200\mu\text{m}$.

mN/m [180]. So BNNTs are inherently wettable to oil. In addition, the huge roughness of the BNNT film can further increase this wettability, according to the Wenzel equation [181]. As a result, the contact angle of the BNNT film to paraffin oil was found to be $\sim 5^\circ$ (measured at 1s after drop dispense). The combined superhydrophobicity and superoleophilicity of the BNNT coated mesh (Figure 4.11a and b) opens up exciting possibilities such as the separation of water and oil in microlitre volumes [182]. Figure 4.12a shows that the coated mesh is impermeable to water so that a water drop can sit on it with contact angle of 161° .

While Figure 4.12b shows that a paraffin oil drop can pass through the same mesh in just 0.3s. A third possible application area is for low friction coatings. A BNNT film on a screw (Figure 4.11e and f) has the potential to act as a solid lubricant [183, 184], which minimizes wear even in vacuum or at high temperature, because of the excellent tribological properties of hBN materials.

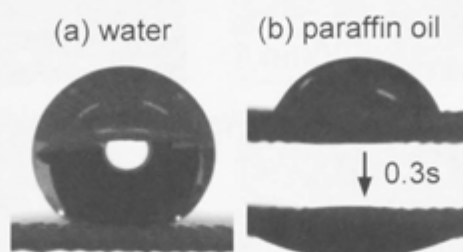


Figure 4.12 (a) A water drop ($7.2\mu\text{L}$) on the BNNT coated mesh; (b) a paraffin oil drop passing through the BNNTs coated mesh in 0.3s.

Although the B ink painting method is a big step-forward in the growth of BNNT films on substrate, it still has some limitations. Firstly, the substrate needs to withstand at least 1000°C to be able to be used in this method, as high temperature annealing is used. So this method cannot be applied to polymer surfaces. Secondly, because of the high temperature used, the substrate must not react with the ball milled B particles, catalysts and the reaction gas. It was found that Si (without a SiO_2 layer on the surface) could not produce BNNT films, probably due to a chemical reaction between Si and one or more components in the B ink. Thirdly, the B ink method has not yet been able to produce vertically aligned BNNT films. This is possibly because the density of nanotubes produced by the B ink painting method is not high enough to provide mutual support or the BNNTs are not formed very synchronously as is the case of CVD growth of vertically aligned CNTs.

4.4 Conclusions

The unique and innovative B ink painting method can effectively grow BNNTs on different surfaces. A high-density and firmly attached BNNT film with any desired pattern can be easily accomplished by first painting, mask coating, spraying or inkjet printing the B ink at desired locations and then thermally annealing the ink layer in a nitrogen-containing atmosphere. Because of the large capacity of the ball-milling facility, the preparation of B ink can be easily scaled-up. No pre-deposition of catalyst is required, as the ink already contains catalyst. The size and nanostructure of BNNTs are dependent on the thermal annealing

process. Due to the invention of the B ink painting method, for the first time, BNNTs can be grown on the surface of objects with irregular or complicated shapes. A fine mesh, tiny tube and small screw were successfully coated with BNNTs, which indicates that any irregularly shaped object can be coated with BNNT film if the B ink can reach and cover its surface. This new method opens up many new applications for BNNT films. It was briefly shown that a needle with BNNT coating inside the channel could enable better performing microfluidic devices; a BNNT covered mesh can separate oil from water on a microlitre scale; and a BNNT film on a screw gives a possible way to minimize wear and solve interfacial problems.

** Most of the work presented in this chapter was done by author and the TEM investigations were done by group members.*

Chapter 5

Photoluminescence of boron nitride nanotube films

5.1 Introduction

Boron nitride nanotubes (BNNTs) have a wide bandgap larger than gallium nitride (GaN) and not very sensitive to tube diameter and chirality changes [21]. So they are potential candidates for DUV light source. However, the exact bandgap and optical properties of BNNTs are still in dispute. Till now, only strong and broad 300-330nm light emission along with weak DUV emission has been detected from BNNTs [75, 77, 78, 80]. These luminescence spectra are similar to those from polycrystalline *h*BN powders [185] and *h*BN thin films [186]. Because single DUV emission can only be obtained from single crystal *h*BN [4, 5], this may indicate that the DUV emission is still highly dependent on the quality and purity of BNNTs. On the other hand, nanotubes can be easily contaminated by atmospheric gases (oxygen or moisture) due to their huge surface area. This has been found to dramatically change the electronic properties of carbon nanotubes (CNTs) and those of nanosized III-nitride crystals [187-189] and subsequently affect their luminescence properties [187, 190]. Unfortunately, the effect of this gas adsorption has not been considered previously in the luminescence measurements of BNNTs before. In this chapter, the results of photoluminescence measurements on the high purity films of BNNTs with different structures and on BN nanowires are reported. All of these samples were prepared using the new B ink painting method described in Chapter 4. A single DUV light emission at 225nm (5.51eV) (without the broad peak around 300nm) was detected from BNNTs with a well crystallized structure and of small diameter, but not from the bamboo structured

BNNTs and the BN nanowires which showed strong near 300nm band. The resolved excitonic sub-bands in the DUV emission suggest BNNTs and BN nanowires have quite similar excitonic recombinations to hBN.

5.2 Experimental

The photoluminescence measurements were conducted using the high flux vacuum ultraviolet (VUV) beamline BL03A1 of the National Synchrotron Radiation Research Center (NSRRC), Taiwan. Synchrotron radiation can provide sufficiently high energy photons for the excitation of BN materials in high vacuum (10^{-7} - 10^{-9} Torr). All the PL measurements used an excitation wavelength of 175nm, except where otherwise stated. The luminescence photons were collected via a photomultiplier tube (Hamamatsu R943-02) by scanning a monochromator (Jobin-Yvon HR320) with a 0.32m focal length and a 1200grooves/mm grating, and counted by a dual channel photon counter (Stanford SR400) linked to a PC via an IEEE-488 interface. All PL curves were corrected for the sensitivity of the photomultiplier tube using the sensitivity curve found in Figure 5.1.

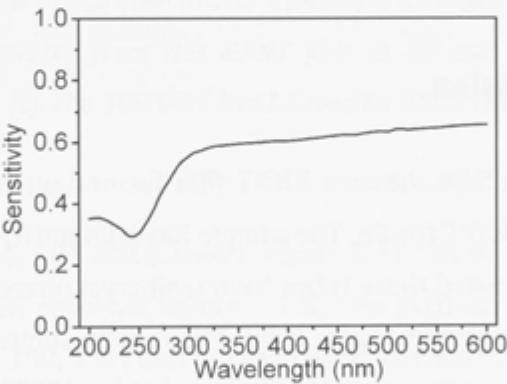


Figure 5.1 The sensitivity curve of the Hamamatsu R943-02 photomultiplier tube.

The synchrotron PL measurement requires an adequate large quantity of samples. The B ink coating method was used to produce high purity BNNT and BN nanowire films for the measurements. In brief, nanosized B particles were first prepared through the ball milling treatment in dehydrated ammonia (NH_3) gas at room temperature. Then, the milled B particles were dispersed in ethanol together with a small amount of metal nitrate to form B ink. After an ultrasonic treatment for homogenous mixing, the B ink was brushed on a silicon wafer covered with a layer of silicon dioxide (SiO_2/Si) substrate, which was produced by oxidizing Si (400) in high purity oxygen (O_2) at 1100°C for 3h. The painted ink with substrate was immediately heated inside a horizontal tube furnace in a nitrogen-containing

atmosphere to activate the nanotube growth. The films of BNNTs of different diameters and structures were produced under different growth conditions for PL measurement. Detailed information regarding the growth of BNNT and BN nanowire films can be found in Chapter 4.

For comparison, a layer of BN nanoparticles was also grown on a Si/SiO₂ substrate. The particle layer was produced by annealing the B ink in NH₃ gas at 1300°C for 3h, but at a much lower rate of temperature increase of 5°C/min. So, only BN particles were formed. The loose powder-like BNNTs were synthesized using the old ball milling and annealing method, in which the ball milled dry B particles were annealed in NH₃ at 1300°C for 8h. Because no nitrate and ethanol was added, the purity of the product was much lower (there were a high percentage of BN particles in product).

A Shimadzu TGA-60 analyser was used to monitor the sample weight change during annealing in Argon (Ar). Before annealing, the BNNTs were flushed by Ar for 1h to remove atmospheric gas. The rate of temperature increase was 5°C/min and the gas flow rate was 50mL/min during heating.

5.3 Results and Discussion

The SEM image in Figure 5.2a shows a BNNT film formed on the SiO₂/Si substrate after annealing in NH₃ gas at 1300°C for 3h. The sample has high purity BNNTs with diameters of 3-10nm. TEM analysis revealed these tubes have well-crystallized cylindrical structure and 2-10 layers of walls (see insert in Figure 5.2a). Figure 5.2b shows the PL spectra from this film at 10K and room temperature after the film was held at 150°C for 16h in vacuum (about 10⁻³Torr) to remove any adsorbed gas on the nanotube surface. Both spectra exhibit strong single DUV light emission peaked at 225nm and the broad near 300nm band is not present, which has not been previously reported for BNNTs. The position of the 225nm peak does not change from 10 to 293K. The full width at half maximum (FWHM) of the DUV bands are 30.6nm (0.77eV) and 31.8nm (0.81eV) at 10 and 293K, respectively. It is proposed that the unusually large FWHMs are mainly due to the strong excitonic effects in BNNTs. The asymmetric shapes of the DUV bands suggest the existence of several sub-bands. The 10K PL spectra with excitation wavelength of 135nm revealed at least four sub-bands (which does not exclude the possibility that more sub-bands may exist) and they are centred at 212, 220,

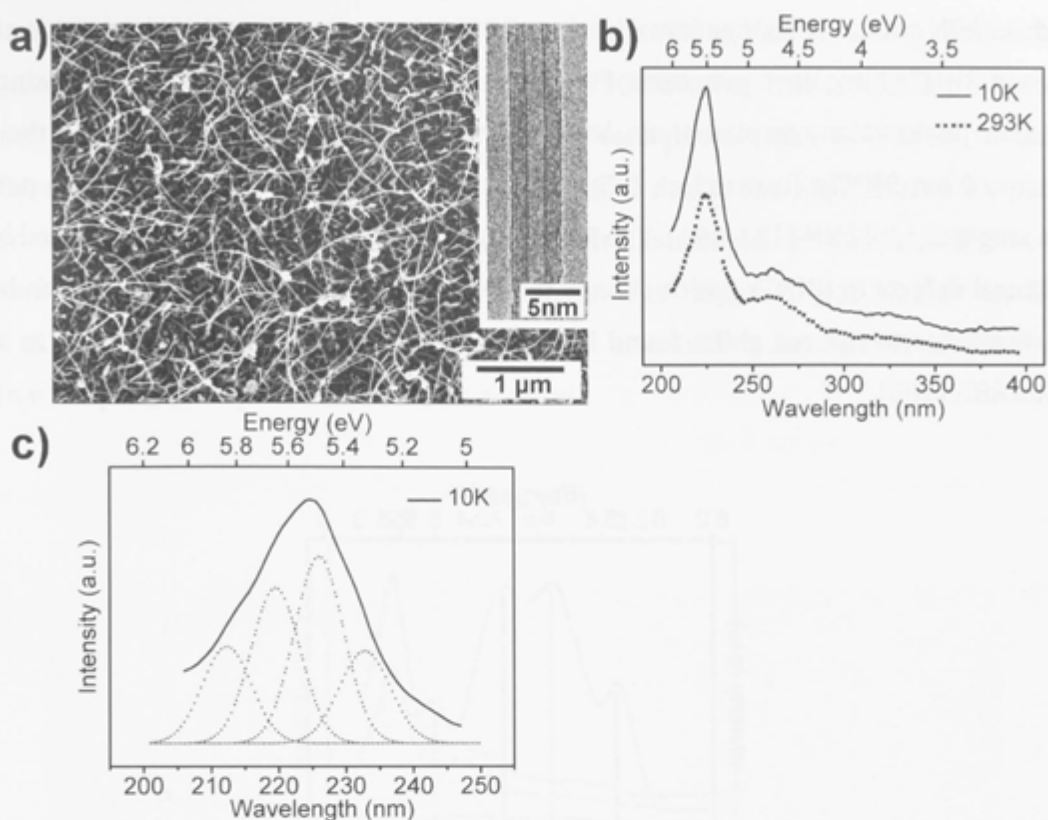


Figure 5.2 (a) SEM image of the film of small diameter BNNTs produced in NH_3 by the B ink method, and TEM image (the insert) showing a well defined multiwall cylindrical structure; (b) PL spectra from this BNNT film at 10 and 293K after the vacuum annealing cleaning; (c) The 10K DUV band Gaussian-fitted with sub-bands at 212, 220, 226 and 234nm.

226 and 234nm (5.85, 5.64, 5.49 and 5.30eV) (Figure 5.3). The sub-band positions at around 226 and 234nm have been reported before [123]. The excitons in BNNTs are so strongly bound and localized [123, 159, 191] that one-dimensional confinement effects should not be displayed in our multiwalled BNNTs which have diameters larger than 1nm. So regarding excitonic effects, our BNNTs can be viewed as $h\text{BN}$. Then it is not surprising to see the centres of these sub-bands are coincident with some of those detected from the single crystal $h\text{BN}$ [4] and high quality $h\text{BN}$ powder at low temperatures. It indicates BNNTs have very similar bandgap values to $h\text{BN}$, consistent with many recent theoretical and experimental findings [71, 123, 191]. We show below that, similar to the case of $h\text{BN}$ [192-195], the 212nm sub-band was only found on well crystallized and small diameter cylindrical BNNTs after being cleaned in vacuum at high temperature, which implies that it may be due to self-trapped Frenkel excitons; the 220nm sub-band is also sensitive to crystal quality as it was not found on the bamboo structured BNNTs; and the 226 and 234nm bands may relate to bound excitons induced by various structural defects. The origins of the sub-

bands in *h*BN still need further investigation and this is the first time that the origins of sub-bands in BNNTs have been proposed. Figure 5.2c shows the 10K DUV band fitted using four Gaussian peaks. Many explanations have been proposed for the red shift of the DUV emission from BNNTs (centred at 225 to 235nm) compared to the 215nm peak position from single crystal *h*BN [123, 191]. The fitting suggests that this shift is mainly caused by the structural defects in BNNTs which change the intensities of the 226 and 234nm sub-bands. This is similar to the red shifts found in polycrystalline *h*BN compared to those in single crystal *h*BN [185].

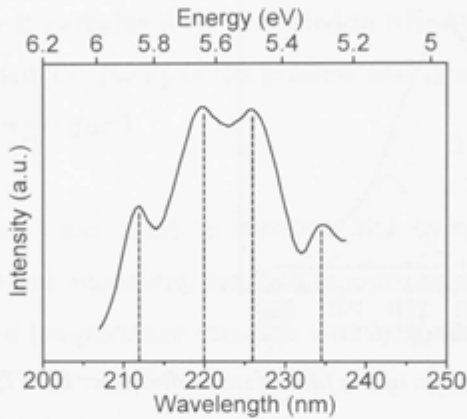


Figure 5.3 The DUV emission at 10K from the small sized cylindrical BNNT film with excitation wavelength 135nm.

Besides the strong DUV emission at 225nm, there are also two very weak bands at around 265nm (4.78eV) and 320nm (3.78eV). The first weak band is probably due to bound excitons caused by structural defects. Evidence for this comes from the studies of a deformed single crystal *h*BN [192, 196]. After deformation, the 215nm peak shifted to 227nm and a background-like slope appeared in the 250 to 310nm range. The weak band at 320nm may be due to impurities [123, 197]. The contribution to the spectra from the SiO₂/Si substrate is very small (Figure 5.4).

To confirm that the luminescence spectra were from BNNTs rather than nanosized BN particles which might exist in the thin film, the PL of a layer of nanosized *h*BN particles was also measured. The thin film of BN particles was coated on a SiO₂/Si substrate using similar annealing conditions but with a much slower heating rate. In contrast to the spectra of the BNNT film, a broad peak at around 316nm was observed for the particles with much weaker DUV light emission at around 233nm (Figure 5.5). Therefore, the luminescence signals shown in Figure 5.2b must predominantly come from BNNTs. The loose powder-like BNNTs

(not coated on the substrate) produced by the old ball milling and annealing method were also investigated. They were produced in NH_3 at 1300°C using ball milled dry B particles without adding any nitrate and ethanol [198]. These powder-like BNNTs show similar luminescence to the *h*BN particles (Figure 5.6). This is due to the high level of BN particle impurities in the powder-like BNNT sample, though this sample also contains BNNTs with the same cylindrical structure and small diameter. This suggests that high purity BNNT films, as produced by the B ink method, are crucial to achieving strong DUV light emission and that BN particle impurities need to be avoided.

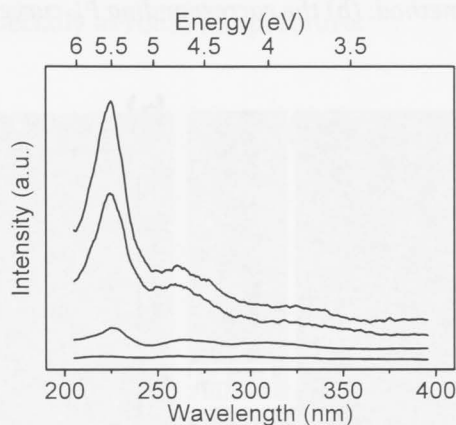


Figure 5.4 PL spectra of, from top to bottom: the cylindrical BNNT film at 10K, the cylindrical BNNT film at 293K, Si/SiO₂ substrate at 10K, and Si/SiO₂ substrate at 293K. All PL measurements were conducted under the same conditions with the same sampling time. The intensities shown are absolute values but the baselines of top three spectra have been shifted upwards.

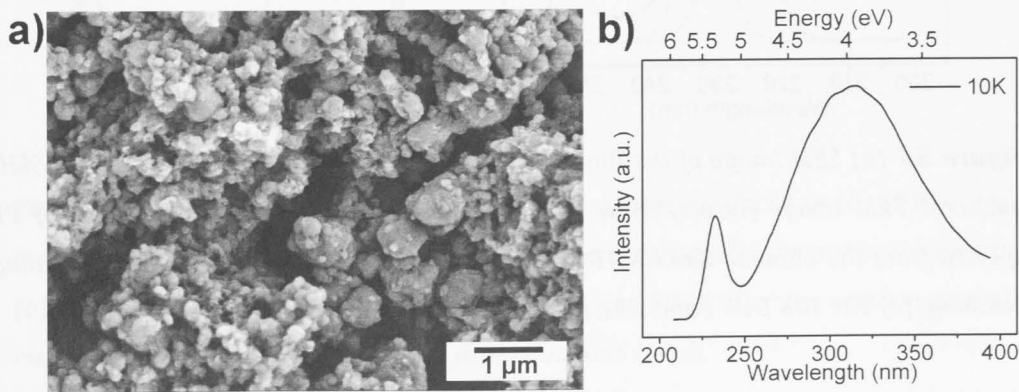


Figure 5.5 (a) SEM image of the nanosized BN particles coated on a SiO₂/Si substrate; (b) 10K PL spectrum of the BN particles.

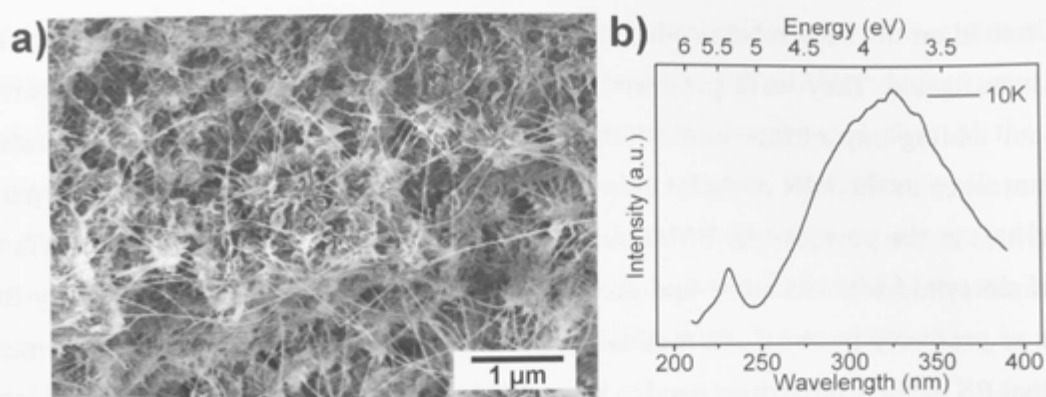


Figure 5.6 (a) SEM image of the loose powder-like BNNTs produced by the old ball milling and annealing method; (b) the corresponding PL curve at 10K.

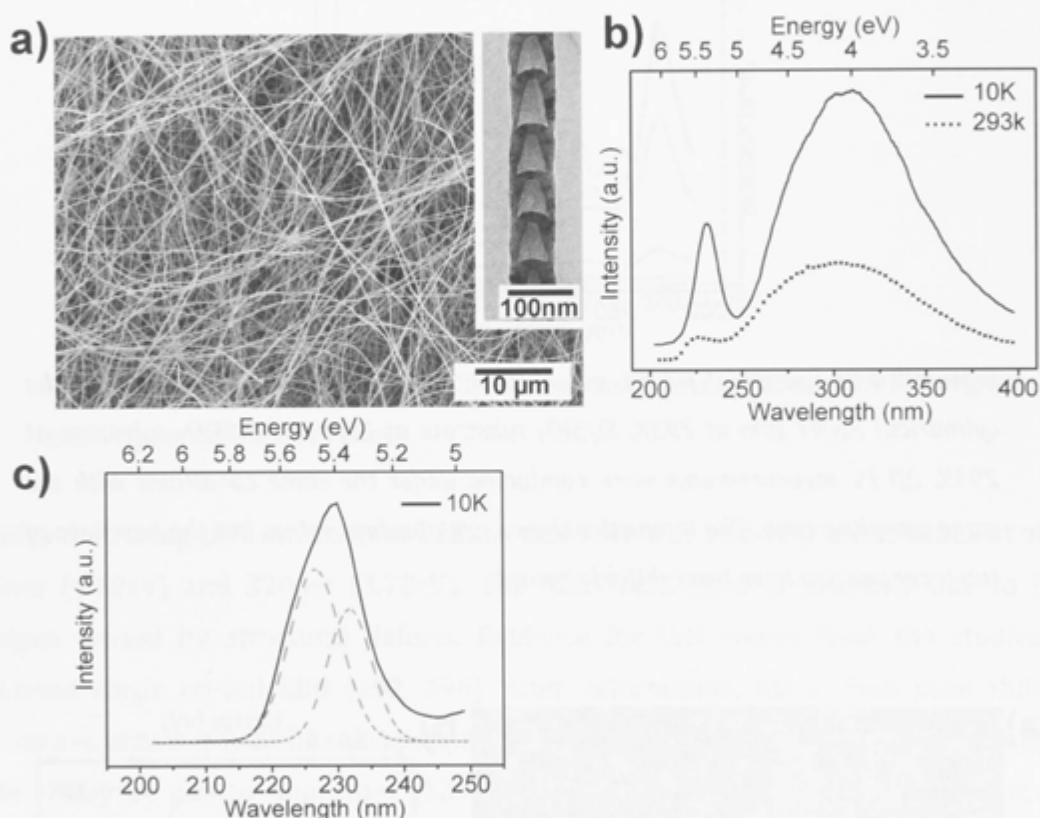


Figure 5.7 (a) SEM image of the film of large diameter BNNTs produced in N_2 -15% H_2 gas, and TEM image (insert) showing a thick-walled bamboo-like structure; (b) PL spectra from the bamboo-like BNNT film at 10 and 293K after the vacuum annealing cleaning; (c) The 10K DUV band with fitted Gaussian bands.

A film of BNNTs of larger diameters and bamboo-like structure was also tested for its DUV emission. The SEM image in Figure 5.7a shows such a high purity BNNT film on a SiO_2/Si substrate, also produced by the B ink method. They were produced in N_2 +15% H_2 gas at 1100°C for 0.5h and have a bamboo-like structure and diameters of 50-80nm (see insert in

Figure 5.7a). Figure 5.7b shows the 10 and 293K PL spectra of the film after the same vacuum annealing treatment. At both temperatures the DUV emission at 229nm (5.41eV) is not as prominent as the broad 306nm band. The fitting shows that the DUV emission is only comprised of 226 and 234nm sub-bands (Figure 5.7c). The other two sub-bands centred at 212 and 220nm seen in the small cylindrical BNNTs are not present. As there are many more defects in the bamboo-like nanotubes, this is evidence that the 227 and 233nm sub-bands are related to structural defects, such as dislocations and stacking faults, and the 212 and 220nm sub-bands are sensitive to crystalline quality. This nature of the DUV emission from bamboo-like BNNTs means that they have lower DUV luminescence yields than cylindrical BNNTs [79], especially at room temperature.

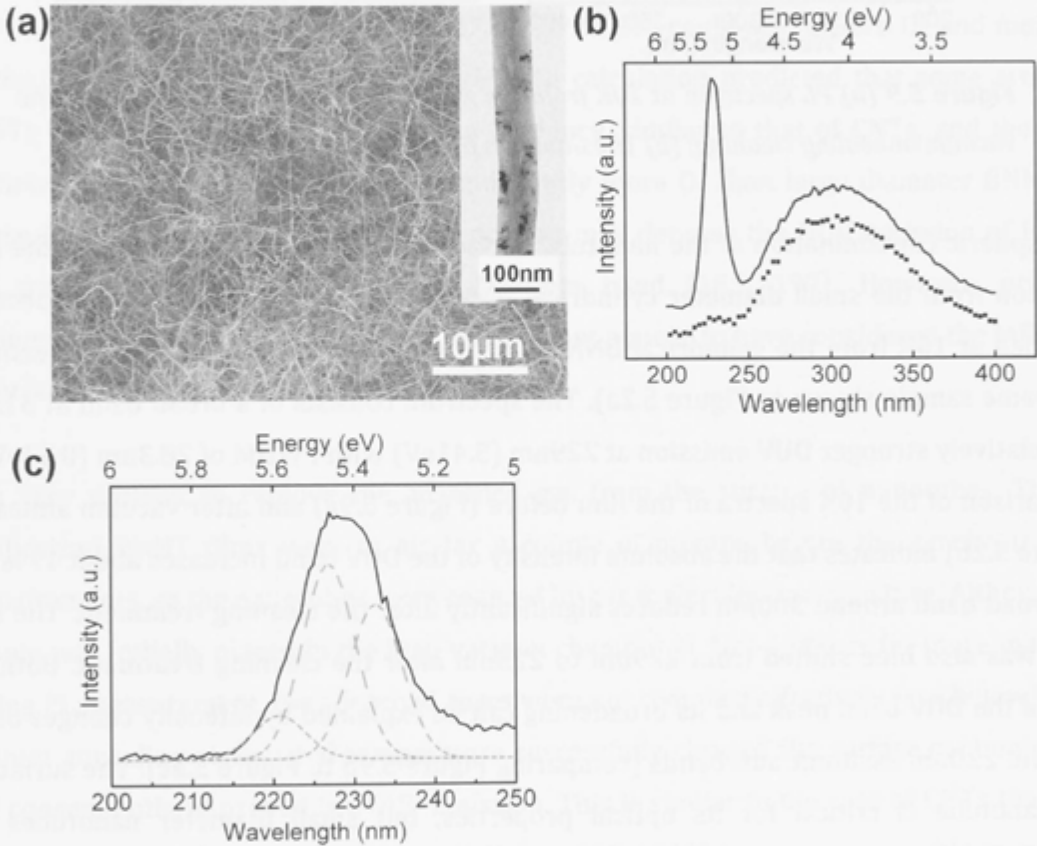


Figure 5.8 (a) SEM image of the film of BN nanowires produced in $N_2+15\%H_2$ gas on steel substrate, and TEM image (insert) showing a polycrystalline nanowire structure; (b) PL spectra from the BN nanowire film at 10 and 293K after the vacuum annealing cleaning; (c) The 10K DUV band with fitted Gaussian bands.

The PL spectra from the BN nanowires coated on a steel substrate after vacuum annealing are shown in Figure 5.8. It can be seen that at room temperature the BN nanowires show very similar emission to the bamboo-like BNNT film. However, at 10K, the DUV emission

from the BN nanowires is much stronger (Figure 5.8b). Fits to the 10K DUV band show that the 226 and 234nm sub-bands still dominate the DUV emission, but a very weak 220nm sub-band is also present.

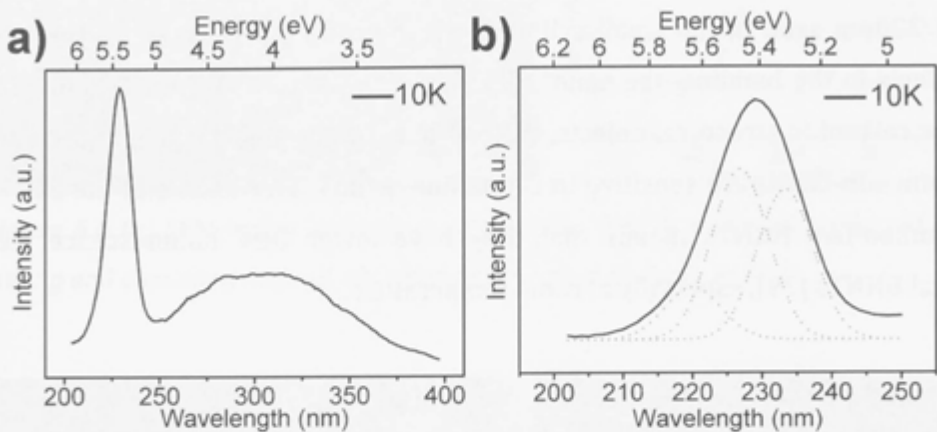


Figure 5.9 (a) PL spectrum at 10K from the small cylindrical BNNT film before the vacuum annealing cleaning; (b) The Gaussian fittings of its DUV band.

Atmospheric contamination of the nanotube surface can have a strong impact on the light emission from the small diameter cylindrical BNNTs. Figure 5.9a shows the PL spectrum recorded at 10K from the cylindrical BNNT film without the vacuum annealing treatment (the same sample shown in Figure 5.2a). The spectrum consists of a broad band at 315nm and relatively stronger DUV emission at 229nm (5.41eV) with FWHM of 28.3nm (0.44eV). A comparison of the 10K spectra of the film before (Figure 5.9a) and after vacuum annealing (Figure 5.2b) indicates that the absolute intensity of the DUV band increases about 17% and the broad band around 300nm reduces significantly after the cleaning treatment. The DUV band was also blue shifted from 229nm to 225nm after the cleaning treatment. Both the shift of the DUV band peak and its broadening can be explained by intensity changes of the 212 and 220nm excitonic sub-bands (comparing Figure 5.9b to Figure 5.2c). The surface of the nanotube is critical for its optical properties, but small diameter nanotubes are particularly prone to adsorb oxygen and other molecules on their surface [187, 199]. So the self-trapped exciton band emerged only after the surface contamination was removed. The same vacuum annealing treatment, however, made much less improvement in the DUV emission of the large diameter bamboo-like nanotubes (Figure 5.10) and the BN nanowires. This is probably due to the lower gas adsorption efficiency of large nanotubes [200] as well as the greater number of defects existing in the bamboo-like tubes and the nanowires.

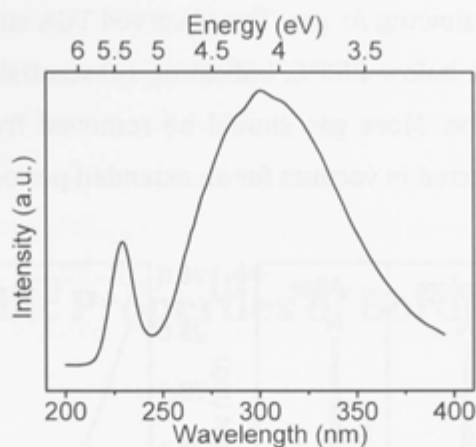


Figure 5.10 PL spectra at 10K from the bamboo BNNT film before vacuum annealing.

The results indicate, similar to CNTs [187, 199], BNNTs could also adsorb O_2 and moisture on the surface on exposure to air. An *ab initio* calculation predicted that some armchair BNNTs would have a strong oxygenation tendency, similar to that of CNTs, and the small diameter BNNTs are likely to adsorb significantly more O_2 than large diameter BNNTs or coarse hBN crystals [194, 200]. The adsorption may depress the DUV emission of BNNTs and partly contribute to the broad 300 nm band [185, 197]. However, previous luminescence analyses conducted on BNNTs do not appear to have considered the influence of surface contamination.

It is very difficult to remove the adsorbed gas from the surface of nanotubes. The as-synthesized BNNT films were in air for a couple of months before the synchrotron PL measurements, so the nanotubes were covered by gas molecules and moisture. Although the sample was initially placed in the high vacuum chamber at 10^{-7} - 10^{-9} Torr for more than 24h during PL measurement, the adsorbed gases were not removed effectively (see below). Only vacuum annealing at elevated temperature successfully cleaned the surface contamination and consequently improved the DUV emission. This is similar to the case of CNTs that high vacuum was not effective and only annealing at 110-150°C in vacuum was able to remove oxygen (O) efficiently from their surfaces [187].

The cleaning effect of the vacuum annealing treatment was checked by using x-ray energy dispersive spectroscopy (EDS) to semi-quantitatively examine the change in O content of the BNNT film before and after the vacuum annealing. The spectra in Figure 5.11a show a significant decrease in O signal strength after the treatment and the estimated reduction in O content is about 60%. TGA was also used to monitor the degassing process of BNNTs

during heating to 500°C in flowing Ar gas. The observed TGA curve (Figure 5.11b) shows a weight drop of about 1.5% below 250°C, indicating substantial desorption of oxygen and moisture from the nanotube. More gas should be removed from BNNT if the annealing cleaning treatment is conducted in vacuum for an extended period.

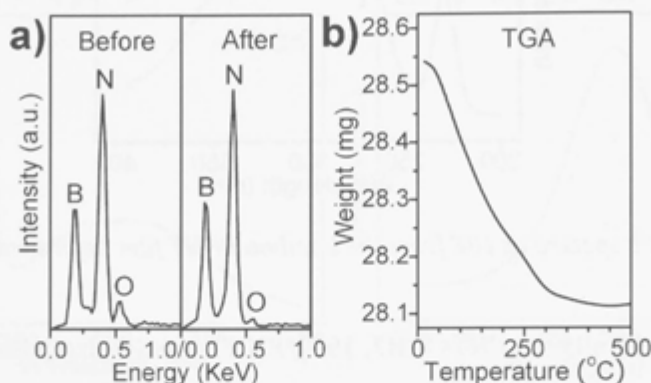


Figure 5.11 (a) EDS spectra of film of small diameter cylindrical BNNTs before and after the vacuum cleaning, showing a decrease in the O content of the film; (b) TGA curve showing the weight loss of the BNNTs after heating in Ar.

5.4 Conclusions

For the first time, a single DUV emission at 225nm (5.51eV) was realized from BNNTs with small diameters and a cylindrical multiwall structure. As comparison, the bamboo structured BNNTs and BN nanowires only show weak DUV emission and strong near 300nm band. Detailed investigation of the sub-bands existing in the DUV bands showed the DUV light emission of BNNTs and BN nanowires are very sensitive to the crystallinity and BNNTs and BN nanowires should have similar excitonic structure and bandgap as *h*BN, probably due to the strongly bound and localized excitons in BNNTs and BN nanowires. Results also show that the luminescence of BNNTs, especially those with small diameters, is more sensitive to atmospheric contaminations adsorbed on their surfaces. So besides the impurities, these adsorptions may also contribute to the near 300nm band shown in BNNTs. These results suggest BNNTs have strong luminescence in DUV range and high potential to be used in miniaturized optoelectronic devices.

** Most of the work presented in this chapter was done by author. The TEM investigations were done by group members and one of the PL results was done by collaborators.*

Chapter 6

Superhydrophobic Properties of Boron Nitride Nanotube Films

6.1 Introduction

The lotus has been a sacred symbol in many cultures since ancient times, mainly due to the purity and un-attachment it represents. Water drops run easily off its leaves and carry dirt with them. This extreme resistance to wetting, or superhydrophobicity, is usually characterized by a water contact angle larger than 150° and hysteresis smaller than 10° [201]. Less marked anti-wetting properties are only termed hydrophobicity. Superhydrophobicity is highly desirable for numerous applications, such as water repellent and self-cleaning coatings [202], microfluidic lab-on-a-chip systems for chemical, biological and medical analyses [176] and a low water friction surface for ocean freighters [203]. The contact angle of the lotus leaf can reach 170° due to its cutin and lipid covering as well as its hierarchical micro and nano double structure [204, 205]. The latter is crucial for achieving superhydrophobicity, as chemical composition alone can only give hydrophobicity with contact angle less than 120° [177].

One well-known property of *h*BN is its low wettability to molten metals and polymers [206, 207]. Because of its excellent lubricity at both low and high temperatures (up to 900°C) [2], *h*BN powder is widely used as a refractory material in foundry and polymer processing. However, *h*BN is wettable to water [208]. Boron nitride nanotubes (BNNTs) can be viewed as *h*BN sheets rolled up into seamless tubes of nanosized diameter. They inherit many excellent properties from *h*BN, such as high thermal conductivity and good stability at high

temperature [52, 53, 59, 209]. BNNTs also acquire some properties not available from *h*BN, such as high elastic modulus [45]. With their small diameter and high curvature, BNNTs should have better anti-wetting properties than *h*BN, due to the positive Laplace pressure that makes liquids on nanotubes unstable [83]. Superhydrophobicity has already been observed for thin films of BNNTs grown on substrate [178], mainly due to nano-roughness of the film surface. In this chapter, the wetting properties, including contact angle and contact angle hysteresis, critical transition pressure, pH effect, drop impact and self-cleaning efficiency, of as-grown BNNT films were investigated in detail.

6.2 Experimental

6.2.1 Young's contact angle of *h*BN

The Young's contact angle of *h*BN was estimated by measuring the water contact angle on pressed *h*BN pellets. The pellets were prepared by pressing *h*BN particles ($<10\mu\text{m}$, UKAbrasive, USA) under 10ton load using a pellet maker (Spectropress, Chemplex Industries Inc., USA). The pellets were round and of 13mm diameter. An atomic force microscope (AFM) (Asylum Research, USA) was used to measure the roughness of the pellet surface. The average roughness was determined from ten topographic mapping results (scanning size of $30\mu\text{m} \times 30\mu\text{m}$ and with tapping mode).

6.2.2 Synthesis of BNNT films

The BNNT films coated on substrates were produced by the following B ink method. Nanosized B particles were first prepared by ball milling amorphous B powder (95%-97%, Fluka) in ammonia gas (NH_3) at 300kPa for 150h. The ball milled B particles were then dispersed into cobalt nitrate ($\text{Co}(\text{NO}_3)_2$) ethanol solution in an ultrasonic bath for 1h. The resultant B ink was brushed onto stainless steel substrates. Finally, the substrate with ink was annealed in nitrogen with 15% hydrogen ($\text{N}_2+15\%\text{H}_2$) reaction gas at 1100°C from 0.5 to 3h to form BNNT films.

6.2.3 Contact angle measurements

All contact angle measurements were conducted in a conditioned laboratory ($20\pm 2^{\circ}\text{C}$, $65\pm 2\%\text{RH}$). An optical contact angle and surface tension instrument (CAM 101, KSV) equipped with a digital CCD camera (lens 50mm, highest frame interval 33ms) was used. The contact angle, drop volume and drop contact diameter were automatically calculated by the software which used the Young-Laplace equation to curve-fit drop profiles captured by the camera. Before each measurement, the system was calibrated using a 4mm diameter stainless steel ball. For measurement of equilibrium contact angle (θ_e), a flat-headed stainless steel needle (gauge 24, exterior diameter 0.565mm) coated externally with a thin layer of paraffin wax (mp $53\text{-}57^{\circ}\text{C}$, Sigma-Aldrich) was used to dispense deionised water drops at a constant volume $\sim 10\mu\text{L}$ onto the films. Slight vibrations were applied to the films to help drops reach an equilibrium state. For measurement of the advanced contact angle (θ_a), a glass capillary tube with a $60\mu\text{m}$ exterior diameter tip was used to gradually add water into the drops. For measurement of the receded contact angle (θ_r), the drops ($\sim 10\mu\text{L}$) were allowed to evaporate in the laboratory environment and their profiles were automatically captured at one frame per minute. The contact angles under pressure were obtained by altering the drop volumes from 0.1 to $30\mu\text{L}$ and the volumes were converted into drop diameters for the pressure calculation. For the critical transition pressure, the films were submerged in deionised water at different depths (10-100cm) for 1min and subjected to small vibrations. The contact angles were measured immediately after the films were removed from the water without drying. The pH effect on contact angles was measured using diluted sulfuric acid (H_2SO_4) (98%, Merck) and sodium hydroxide (NaOH) pellets (Ajax FineChem) dissolved in deionised water. All contact angle values were average results from 5-10 measurements.

6.2.4 Drop impact and self-cleaning tests

The dynamic response of drops falling on the BNNT films was revealed by capturing images at one frame per 33ms. Water drops with diameter $\sim 2\text{mm}$ were released from a height of 5mm (the height of the needle tip). For self-cleaning tests, copper particles ($<10\mu\text{m}$, Sigma-Aldrich) were sprayed on the BNNT films. The self-cleaning efficiency was determined by the rolling off of drops with or without initial kinetic energy. Drops without initial kinetic energy were static drops placed on the films and then rolled off by tilting the films at $5\text{-}20^{\circ}$. Drops with initial kinetic energy were drops released from 10mm above films tilted at 40° . The cleaning efficiencies were estimated from both optical microscope and scanning electron microscope (SEM) images.

6.2.5 Characterization techniques

Zeiss Supra 55VP and Leo 1530 instruments were used to investigate the surface morphologies of the BNNT films and their cleaning effects. The values of fractional area (f_s) were illustrated by using a SEM image analysis technique in which Photoshop software was used to only retain pixels above the threshold brightness 212 in the SEM images [178, 210]. X-ray energy dispersive spectroscopy (EDS) attached to a Hitachi 4300SE/N SEM was used for the examination of the chemical composition of the nanotubes. An Olympus BX51M optical microscope with a camera (DP12, ColorView) attached was used to acquire particle cleaning images.

6.3 Results and Discussions

6.3.1 Young’s contact angle of hBN

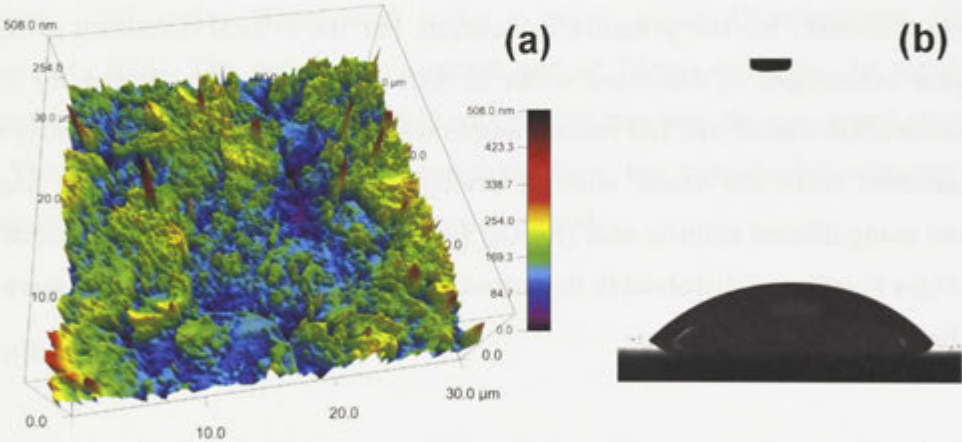


Figure 6.1 (a) 3D AFM image showing part of the hBN pellet surface; (b) photo of a 9.74μL water drop on the hBN pellet with contact angle 50.4°.

The Young’s contact angle of hBN was measured first to examine its wetting properties. Figure 6.1a shows a typical AFM image of the hBN pellet surface. The average roughness was 1.028 ± 0.017 . The average contact angle of the water drop to the pellet was $50.0\pm5.9^\circ$ (Figure 6.1b). According to the Wenzel equation [211]:

$$\cos \theta^* = r \cos \theta \tag{6.1}$$

where θ^* represents the contact angle of a drop on a surface, r is the roughness of this surface, and θ is Young's contact angle on a perfectly flat solid surface. Therefore, θ of hBN is estimated to be 51.3° . It means hBN is wettable to water.

6.3.2 Superhydrophobic BNNT films

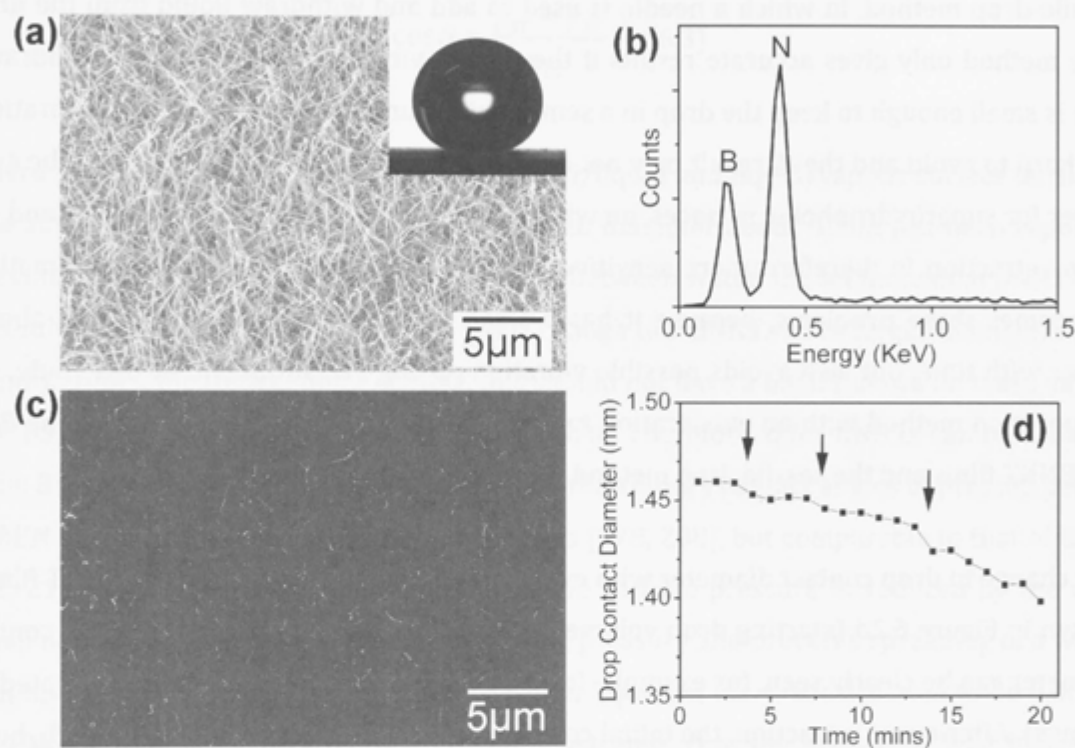


Figure 6.2 (a) SEM image of the semi-erect BNNT film tilted at 30° , the insert shows an almost round $9.85\mu\text{L}$ drop on the film; (b) EDS spectra confirms these are BNNTs; (c) processed SEM image for estimating the contact area between this BNNT film and drop; (d) drop contact diameter change during evaporation with the arrows indicating the baseline retraction movements of the drop.

BNNT films produced in $\text{N}_2+15\%\text{H}_2$ by the B ink method were firmly adhered to the substrates. In total, eight BNNT films produced under similar synthesis conditions but with different annealing time were tested for their wetting properties. Among these samples, four BNNT films gave relatively high equilibrium contact angles (θ_e), $171.7\pm4.2^\circ$, $169.1\pm3.8^\circ$, $167.8\pm3.6^\circ$, and $167.4\pm5.9^\circ$. These are rather high values compared to some of the reported results from as-grown CNT and BNNT films [154, 178, 212, 213]. Figure 6.2a shows the SEM image of the BNNT film (30° tilted) with θ_e larger than 170° . It can be seen that most BNNTs are semi-erect, i.e. self-standing but tilted or bent, on the substrate. They are not vertically aligned because of the lack of mutual support due to the relatively low nanotube density.

These BNNTs are 2-6µm long. The inset in Figure 6.2a is a typical image of a drop (9.85µL) sitting on this film. EDS confirmed the expected chemical composition of the nanotubes (Figure 6.2b).

The contact angle hysteresis of the film was measured by the evaporation method. Various techniques have been applied for θ_a and θ_r measurements [214], but the most popular is the sessile drop method, in which a needle is used to add and withdraw liquid from the drop. This method only gives accurate results if there is no vibration and the water withdrawal rate is small enough to keep the drop in a semi-equilibrium state. In reality, small vibrations are hard to avoid and the θ_r result may not be accurate [214]. The inaccuracy could be even larger for superhydrophobic surfaces, on which drops are able to move more freely and the drop retraction is therefore more sensitive to small vibrations. The evaporation method overcomes these problems, because it has a small water withdrawal rate that is almost linear with time, but also avoids possible vibration during measurement. In this study, the evaporation method with an evaporation rate of ~0.12µL/min was used to determine θ_r of the BNNT films and the sessile drop method was used for comparison.

The change in drop contact diameter with evaporation time for this semi-erect BNNT film is shown in Figure 6.2d (starting drop volume 9.40µL). The sudden retractions of the contact diameter can be clearly seen, for example, from 3 to 4min, and from 7 to 8min (indicated by arrows). After every retraction, the initial contact angle (θ_o) should be smaller than θ_a , but a little bigger than θ_e (in fact, the difference between θ_a and θ_e for this film is very small, $1.52\pm0.68^\circ$, determined by a glass capillary tube with micro-sized tip). Here, we assume that $\theta_o \approx \theta_e$. Since the value of θ_r is related to the size of the drop [181, 214], we turned to the differences between the contact angles after one retraction and before the next, that is, $\theta_o - \theta_r$. Therefore, the hysteresis can be calculated from the sum: $(\theta_a - \theta_e) + (\theta_o - \theta_r)$, which is 3.8° for this film (2.7° by the sessile drop method). The other three films showed similar hysteresis values. So these four BNNT films are superhydrophobic.

The large contact angle and small hysteresis suggest a Cassie state, in which the drop sits partly on BNNTs and partly on air. The Cassie-Baxter equation can be applied [211, 215]:

$$\cos \theta^* = f_s \cos \theta - (1 - f_s) \quad (6.2)$$

where θ^* represents the contact angle of a drop on a composite surface with solid and air; f_s is the fractional area of a drop sitting on solid; and θ is Young's contact angle on a perfectly flat solid surface. Here, the Young's contact angle of flat BNNT walls, rather than *h*BN, should be used, because the wetting property of a nanotube could differ enormously from that of bulk material. θ on flat BNNT walls can be calculated from Young's equation [213]:

$$\cos \theta = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}} \quad (6.3)$$

where γ_{SV} , γ_{SL} and γ_{LV} are the solid/vapour, solid/liquid and liquid/vapour surface tensions. The surface tension of a multiwalled BNNT with diameter about 40nm has been reported previously, 26.7mN/m, and the surface tension between water and an individual BNNT was 25.8mN/m or theoretically 21.1mN/m [81]. Though our BNNTs have larger diameters (40-80nm), from a theoretical point of view, this should not have a big influence on these values [81, 83]. Water has a surface tension of 72.2mN/m. Therefore, θ for BNNTs can be deduced to be 85.6-89.3°. This value is much larger than the Young's contact angles of pressed pellets of *h*BN particles and of directly grown *h*BN films [178, 208], but comparable to that of CNTs [82, 213]. This value arises because the positive Laplace pressure introduced by the very small nanotube diameter opposes the disjoining pressure and prevents spreading of a water film on the tube surface [81, 83]. Then based on Equation 6.2, f_s is calculated to be 0.0097-0.0103. In addition, f_s may be qualitatively illustrated from the processed SEM image by counting the percentage of pixels above a pre-set brightness threshold. A processed SEM image (non-tilted) of this film (Figure 6.2c) clearly shows that predominantly the tips of the semi-erect BNNTs have contact with the drop, which leaves most of the drop sitting on air. However, water did not seep or penetrate into the film, even during the lengthy drop evaporation measurement.

6.3.3 Hydrophobic BNNT films

The other four BNNT films have relatively smaller θ_e : 159.5±2.7°, 158.6±3.5°, 155.7±7.2°, and the lowest 149.0±2.7°. Microscopic investigations found these films had different BNNT arrangements. The SEM image of Figure 6.3a shows the surface of the BNNT film (tilted 30°) with $\theta_e = 159.5^\circ$, and the insert is a typical image of a drop (10.05µL) on its surface. Unlike the randomly tilted semi-erect BNNTs in the superhydrophobic films (Figure 6.2a), BNNTs in these films are prostrate. The BNNTs are lying down because the BNNTs in these films are

much longer (15-50 μm) so that their stiffness cannot sustain their own weight (Figure 6.3a). The different lengths of BNNTs in the different films are caused by different annealing time used. The prostrate films were annealed for more than 0.5h, while the semi-erect films were annealed for less than 0.5h. The processed SEM image (also treated by the same SEM image analysis technique) of this film (Figure 6.3b) reveals that the drop is sitting on the prostrate BNNT walls instead of their tips, which gives rise to a larger f_s . From Equation 6.2, f_s for this film is 0.0588-0.0626, which is about six times that of the semi-erect film with θ_e above 170° (Figure 6.2a).

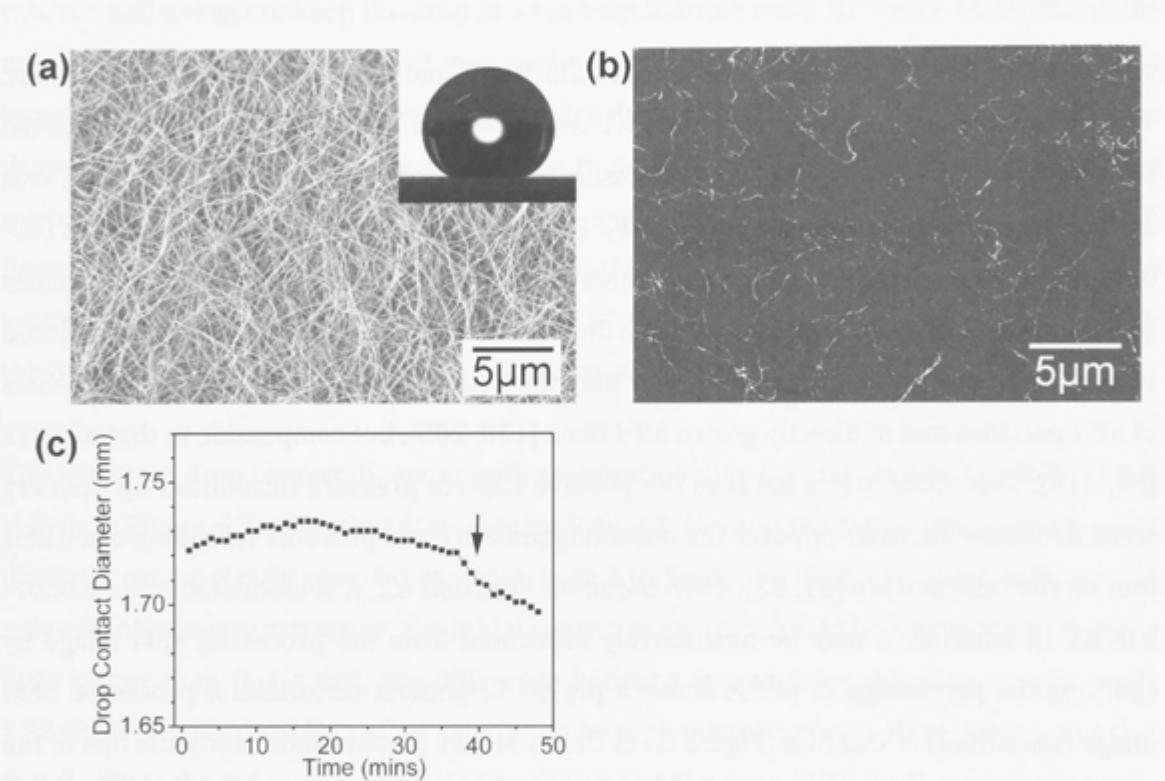


Figure 6.3 (a) SEM image of the prostrate BNNT film tilted at 30°, the insert shows a 10.05 μL drop on the film; (b) processed SEM image suggesting a larger contact area between BNNTs and drop on this film; (c) drop contact diameter change during evaporation with the arrow indicating the baseline retraction movement of the drop.

The evaporation method was also used to measure the hysteresis of the prostrate BNNT film. Figure 6.3c shows the change in drop contact diameter with evaporation time (starting drop volume 10.98 μL). One intriguing observation is that the contact diameter for this film increased slightly at first (until 18min), and then decreased (from 19 min) during evaporation. This was different from the continually decreasing drop contact diameter observed for the semi-erect BNNT film (Figure 6.2d). This observation appears unusual, but was observed to some degree on all the prostrate BNNT films. The most likely explanation is

that the drop was slowly spreading on the prostrate BNNTs without seeping. This phenomenon can be described by the transition from the initial contact angle to the equilibrium contact angle on individual BNNTs. The initial contact angle on a single BNNT (θ_i) is the instant contact angle when the liquid just contacts the BNNT without spreading. If this initial state is not thermodynamically favoured, water will spread to form a saturated state, which is defined by the equilibrium contact angle on a single BNNT. In fact, the contact angle of a single BNNT measured by the Wilhelmy method was an equilibrium value [81]. The initial contact angle on a fibre-like material can be estimated by [83]:

$$\cos \theta_i = 1 + \frac{1}{\gamma(a + d_0)} \int_{l_0}^{\infty} (a + h)\Pi(h)dh \quad (6.4)$$

where γ represents the surface tension of water, a is the radius of fibre or nanotube (average $\sim 30\text{nm}$ for our BNNTs in the film), d_0 is the Born repulsion length $\sim 0.158\text{nm}$, and $\Pi(h)$ is the disjoining pressure. For practical calculations [216]:

$$\Pi(h) = \frac{2d_0^2 S_d}{h^3} + \frac{S_p}{l_0} \exp\left(\frac{d_0 - h}{l_0}\right) \quad (6.5)$$

where h is the liquid film thickness on solid fibre, l_0 is the correlation length $\sim 0.6\text{nm}$, S_d and S_p are the apolar and polar components of the initial spreading coefficient (S_i) [217]. S_d can be calculated from: $S_d = \gamma_S^d - \gamma_{SL}^d - \gamma_L^d$, in which γ_S^d , γ_{SL}^d , γ_L^d are the apolar components of the surface tensions of BNNTs, between BNNT and water, and of water. $\gamma_S^d = 22.5\text{mN/m}$, $\gamma_L^d = 21.8\text{mN/m}$, and $\gamma_{SL}^d = 0.0055\text{mN/m}$ calculated from $\left(\sqrt{\gamma_S^d} - \sqrt{\gamma_L^d}\right)^2$ [81, 218]. So S_d is 0.7mN/m . Then $S_p = S_i - S_d = -72.6\text{mN/m}$. Consequently, θ_i for water on an individual BNNT is 90.9° . It means that when a dry BNNT has contact with a drop, water spontaneously spreads on its wall until the equilibrium contact angle reaches 85° . This explains why the observed contact diameter increases on the prostrate BNNT film during evaporation. However, as was observed, this spreading process was very slow and inconspicuous, probably due to both the small difference between the initial and equilibrium water contact angles on BNNT and the near to non-wetting property of BNNT. In spite of the slight spreading, no catastrophic seeping was found on all four of the prostrate films.

The hysteresis values of the prostrate films are much larger. The film shown in Figure 6.3a has a hysteresis of 17.1°, measured by the evaporation method (13.1° by sessile drop method). Figure 6.3c shows the change in contact diameter of a drop on this film during evaporation. The drop retraction movements were much slower. In Figure 6.3c, the retraction happened at 37min and continued for about 5mins. This is totally different from the quick retractions observed on the semi-erect film. These differences are mainly due to the larger fractional contact areas and different three phase contact line structures of the prostrate BNNT films [219]. The hysteresis result from the film shown in Figure 6.3a is representative of the four prostrate BNNT films. Therefore, these films can be regarded as only hydrophobic, not superhydrophobic.

For vertically aligned CNTs and Si spikes, the contact angle usually increases with increasing nanotube length or spike height, until a constant contact angle value is reached [220, 221]. However, for non-aligned nanotube films, or our BNNT films, the nanotube length could have a negative effect on wettability, because extra length may change the nanotube arrangement, especially for nanotubes with small diameters (easier to lie down). For the B ink method, the length of BNNTs mainly depends on the annealing time, if other synthesis conditions are the same. In order to control the tube length to achieve semi-erect BNNTs and obtain superhydrophobicity, the annealing time should be no longer than 0.5h.

Small diameter BNNT films produced in NH₃ at 1300°C by the B ink method, in contrast, hardly showed stable hydrophobicity, as water drops easily seeped into the films.

6.3.4 Pressure effect and critical transition pressure

If a drop in the Cassie state has a larger contact angle than that of a drop in the Wenzel state on the same surface, then the transition from Cassie to lower energy Wenzel state may occur [222], but the energy barrier needs to be overcome first, by means of pressure or force. This energy barrier can determine the stability of the superhydrophobicity in the Cassie state. Since the Young's contact angle of BNNT is slightly below 90° (as shown previously), the BNNT films may become hydrophilic once the Cassie state irreversibly transits to the Wenzel state. So, the effect of pressure on the contact angles and the critical transition pressures of these BNNT films should provide useful information [203].

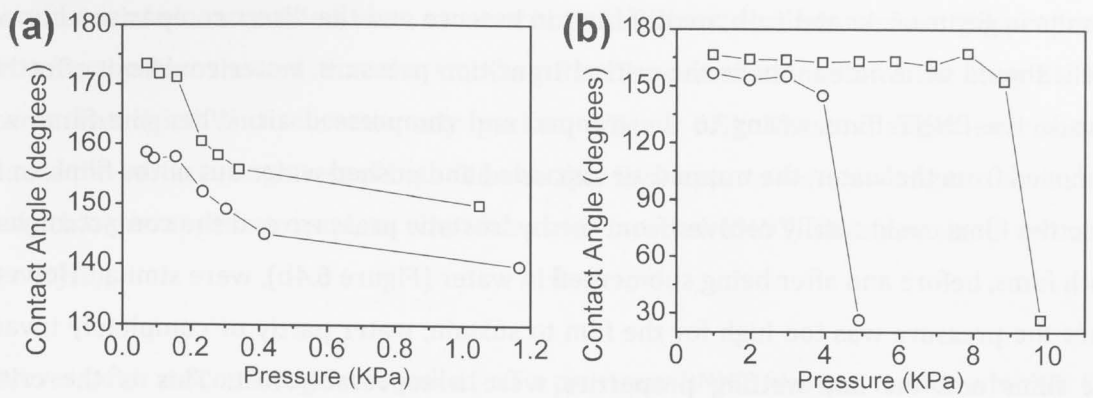


Figure 6.4 (a) Contact angles of the semi-erect (square) and the prostrate (round) BNNT films under various pressures exerted by different sized drops; (b) contact angles after the semi-erect (square) and prostrate (round) BNNT films were submerged in water at different depths to estimate the critical transition pressure.

Various small pressures could be applied to the BNNT films by modifying the sizes of drops statically sitting on films. For a drop with diameter smaller than its capillary length (2.73mm for water), the pressure that the drop exerts on the film surface can be estimated to be roughly the same as the internal pressure of the drop [181, 223]. The internal pressure of the drop can be calculated from Laplace's law [181]:

$$\Delta P = \frac{2\gamma}{R} \quad (6.6)$$

where γ is the surface tension of water and R is the diameter of the drop. So the smaller the drop, the higher is the pressure on the film [181]. Figure 6.4a shows the contact angles of the two kinds of BNNT film (Figure 6.2a and 6.3a) using different sized drops. The contact angles of both films decreased synchronously with increasing pressure. At around 1kPa, θ_e for the semi-erect and the prostrate BNNT films dropped to 150.5° and 141.1°, respectively. This was because the pressure slightly squeezed water into the cavities between nanotubes and thereby increased f_s . However, for both films at 1kPa, the drops are still in, or mostly in, the Cassie regime.

To further increase the pressure in order to estimate the critical transition pressure, the films were submerged in deionised water at different depths. Figure 6.4b shows the measured contact angles of the two films immediately after they were removed from the water. These results represent the wettability of each film after the hydrostatic pressure was released, or in other words, the recoverability of their wettability from pressure. So the

results in Figure 6.4a and 6.4b are different in essence and the direct comparison between them should be avoided. Above the critical transition pressure, water could not effectively invade the BNNT films owing to the trapped and compressed air. When the films were removed from the water, the trapped air expanded and pushed water out of the films. In this case the films could totally recover from the hydrostatic pressure and the contact angles of both films, before and after being submerged in water (Figure 6.4b), were similar. However, once the pressure was too high for the film to sustain, water partly or completely invaded the films and the anti-wetting properties were irrecoverably lost. This is the critical transition pressure. At about 5kPa, the prostrate BNNT film was completely wetted with $\theta_e = 26.3^\circ$ and the Wenzel state formed. For the semi-erect film, the critical transition pressure was about 10kPa. At about 4kPa for the prostrate BNNT film and at 8-9kPa for the semi-erect film, water was found to partially penetrate a few small areas, but the water invasion at these pressures was still not dramatic enough to completely transit the Cassie states to Wenzel states. These small areas still showed contact angles $>110^\circ$, indicating that the transition into Wenzel states on both BNNT films was not straightforward. Instead, coexistent Cassie and Wenzel states were formed first. The coexistent states were much less stable because only a little extra hydrostatic pressure could force complete transition. The main reason for the different critical transition pressures found on the semi-erect and prostrate films appears to be the different cavity size in the two films. The processed SEM images (Figure 6.2c and 6.3b) show that the prostrate BNNT film has larger micro-cavities than the semi-erect film because the drop supporting areas for the semi-erect BNNT film are more evenly arranged. According to the Laplace equation (Equation 6.6), the liquid invasion pressure is inversely proportional to the pore size, so less pressure is required for water to invade the prostrate BNNT film. The different nanotube arrangement (prostrate or semi-erect) may also partly contribute to the different critical pressures.

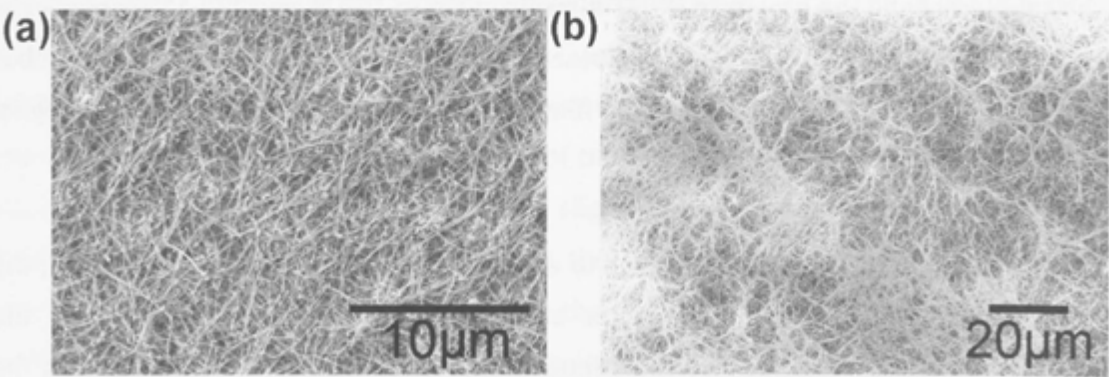


Figure 6.5 SEM images of water intruded (a) semi-erect BNNT film, (b) prostrate BNNT film.

After the invaded water dried, most areas of both films had lost their non-wetting property. SEM investigation showed that the standing BNNTs were flattened and the long BNNTs became entangled and more densely packed (Figure 6.5). These changes enormously reduced the surface roughness of both films so that Cassie states were no longer sustainable. These changes appear to explain why the water-invaded BNNT films remained wettable after drying.

However, after a Scotch tape was pulled off a prostrate BNNT film (no matter whether the film had been water invaded or not), the film suddenly became superhydrophobic. For example, by sticking tape onto the water-invaded prostrate film (Figure 6.5b) and then mechanically pulling the tape off, the film suddenly had $\theta_e = 169.3 \pm 4.8^\circ$ and hysteresis of several degrees. This dramatic change appears to have arisen because the long nanotubes on the film surface being removed by the tape and the new surface now had high roughness and low fractional area (Figure 6.6).

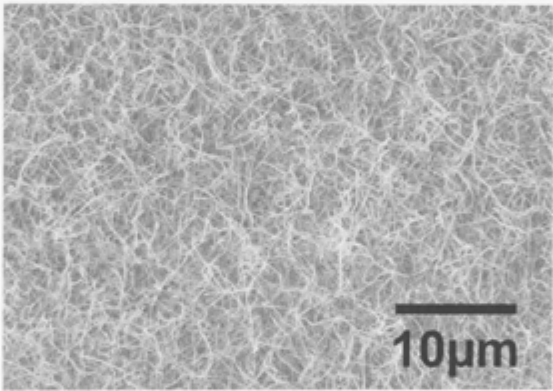


Figure 6.6 SEM image showing the water penetrated prostrate BNNT film after a Scotch tape was pulled off.

6.3.5 pH effect

Because of the chemical inertness of BNNTs and the small fractional area of the films, even strongly acidic and basic conditions do not affect the anti-wetting properties of BNNT films [178]. For the semi-erect BNNT film, θ_e showed little change with variations in the pH of the drop, although a slight decrease in θ_e was observed at pH 11-14 (Figure 6.7a). For the prostrate BNNT film, θ_e values were affected slightly more by strongly acidic and basic drops, and the standard deviation of the contact angle results was also larger (Figure 6.7b). The pH value showed a bigger influence on the prostrate film mainly because it had larger f_s .

The lower critical transition pressure of the prostrate film may also make it less stable and more easily affected by chemicals.

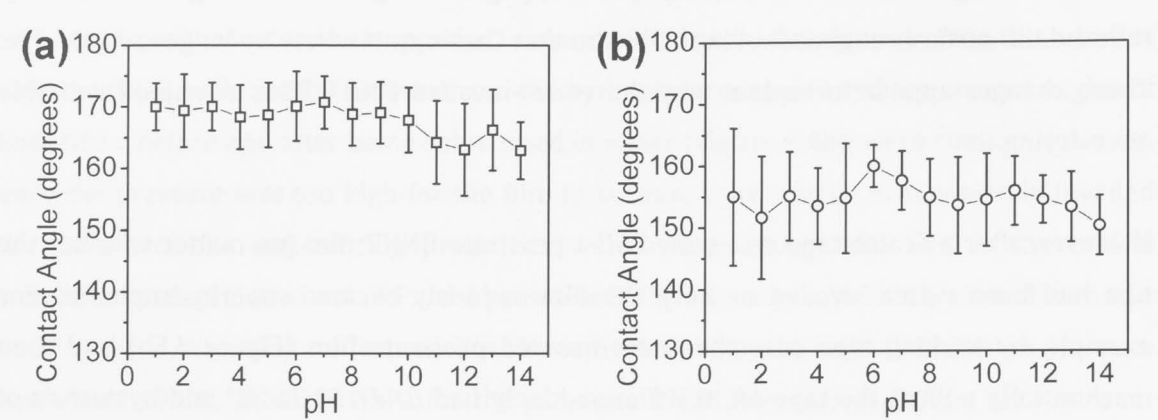


Figure 6.7 Effect of drop pH variations on the contact angle of, (a) the semi-erect BNNT film (square); (b) the prostrate BNNT film (round).

6.3.6 Drop impact

The dynamic behaviour of free falling drops on impact with these two BNNT films was also investigated. The drop impacting velocity, calculated from the drop release height, was 0.23m/s. The drop diameter was 2.1mm. The corresponding Weber number (*We*) can be calculated [224]:

$$We = \frac{\rho v^2 R}{\gamma} \tag{6.7}$$

where ρ is the density of water, v is the impacting velocity, R is the diameter of the drop, and γ is the surface tension of water. Then *We* for this drop was 1.6. Because of the small *We* used, no splashing occurred on either film. However, the drops showed totally different behaviours on two kinds of film. For the semi-erect BNNT film (Figure 6.8a), the drop completely rebounded from the surface several times before, in most cases, bouncing off the film. Images in Figure 6.8a were able to be captured only after the film was delicately adjusted to be level to try and retain the drop on the film, but the drop still jumped out of the camera’s focus. The estimated restitution coefficient (ϵ) for the first bounce off this film was 0.79. During the drop impact, kinetic energy was transferred via the liquid surface tension, the contact angle hysteresis and the drop oscillation [224]. Water may also intrude into the film and dissipate some energy [225]. This possibility can be estimated by calculating the

maximum drop impact pressure exerted on the film. If the propagation of compressional waves, viscosity and surface tension are all neglected, we can estimate [226]:

$$P_{\max} = \rho v_{\max}^2 \quad (6.8)$$

where $P_{\max}$ is the maximum impact pressure, ρ is the density of water, and $v_{\max}$ is the impacting velocity of the water drop. Note this estimate is too small for rigid solid surfaces, but suitable for nonhomogeneous surfaces [227]. The maximum pressure from the falling drop was about 67Pa. The likely effect of this pressure can be determined by referring to Figure 6.4a and 6.4b. It can be seen this pressure was too small to cause penetration of water into the film because of the trapped and compressed air.

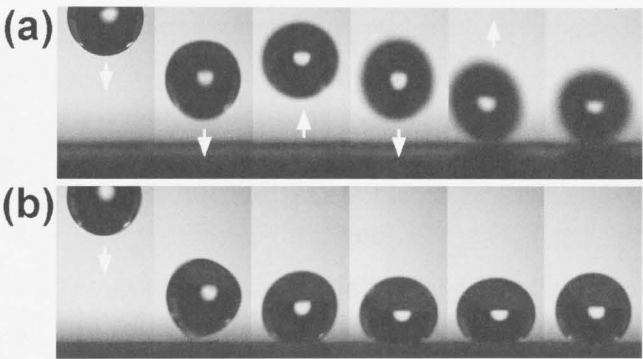


Figure 6.8 The dynamic behaviour of a free falling drop on, (a) the semi-erect BNNT film; (b) the prostrate BNNT film with the arrows indicating the direction of movement of the drop.

For the prostrate BNNT film (Figure 6.8b), the drop hardly showed any rebound. Instead, it was pinned and then pulsated on the film. The lack of bounce on this film can be partly blamed on its higher hysteresis, yet, it should not be the only reason, because a surface with contact angle 160° and hysteresis 30° can still show bounce with high elasticity [224]. Water intrusion is unlikely to be a major reason either, because: (1) the estimated maximum drop pressure is also too small for this film, as the previous calculation showed; (2) the drop kept its round shape and did not show a dramatic increase in the receded angle during the retraction phase (when the drop moved upwards); and (3) the contact angle after the drop stabilized on this film showed similar values to those measured by the sessile method. Another possible reason for the lack of bounce may be the deformation of the film surface caused by the drop impact. For the prostrate film, long BNNTs lie loosely on each other and there are a great number of voids in the film. These voids allow the nanotubes to move

(compressively) when the drops impinge on them. However, the same deformation does not appear to occur on the semi-erect BNNT films.

6.3.7 Self-cleaning efficiency

One important application of a superhydrophobic surface is to provide self-cleaning and anti-coating function [205, 221, 228]. The self-cleaning effect of both kinds of film was tested by rolling off drops with and without initial kinetic energy. Irregularly shaped copper particles were homogeneously sprayed on two films for the cleaning tests (Figure 6.9a). The size of these particles was 2-10 μ m, according to SEM. The cleaning efficiencies were first tested by tilting the BNNT films with static drops sitting on them (drops without initial kinetic energy). The semi-erect film showed almost perfect cleaning along the drop rolling-off path. These areas looked almost fleckless under an optical microscope (Figure 6.9b). SEM revealed only a very small number of particles with sizes $\sim$ 2 μ m still left on this film (Figure 6.10a). The estimated percentage of particles remaining was <2.5%. In contrast, about 50% of particles remained on the prostrate BNNT film after a similar cleaning process (Figure 6.9c and Figure 6.10b). It took three to four static drop cleaning passes to remove most of particles off this film. Hydrophobic surfaces can still show self-cleaning because the contaminating particles can be trapped and carried in front of the fast rolling-off drop without re-depositing [205]. Self-cleaning happens only if the total adhesion force between the particle and the film surface (van der Waals forces) is overcome by the particle-water adhesion force. The particle-water adhesion force is the same for both films, but the adhesion force between the particle and BNNT film is related to f_s [228]. Higher f_s usually means higher particle-film adhesion, which makes cleaning more difficult. In cleaning tests, both films could allow fast rolling-off drops when tilted, but their different f_s resulted in distinctly different cleaning efficiencies. Drops with small initial kinetic energy were also used for cleaning tests. The drops were released from 10mm height to impinge on a 40° tilted BNNT film (impacting velocity about 0.44m/s). Even for the prostrate BNNT film, most of the copper particles were successfully removed by just one drop. The drop with higher kinetic energy could introduce higher impact pressure on the film surface and lead to higher adhesion forces between water and particles.

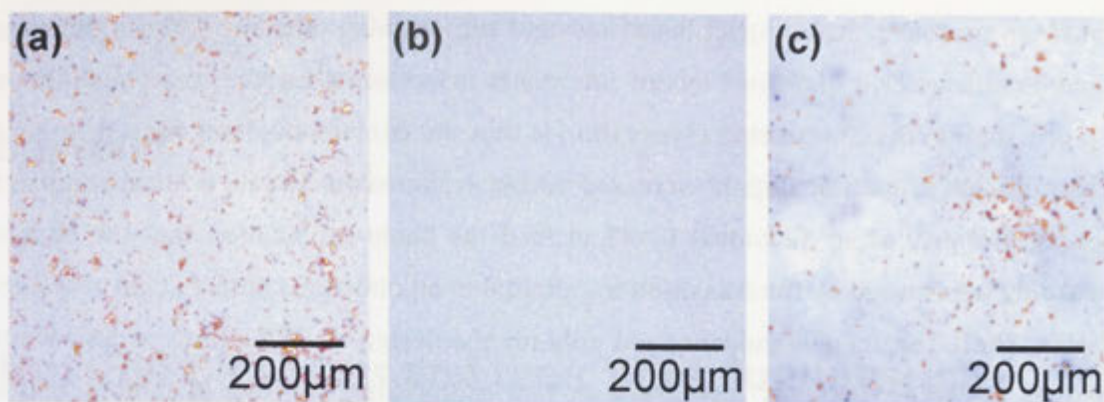


Figure 6.9 (a) Optical microscope image of copper particles smaller than $10\mu\text{m}$ (red dots) spread on BNNT film for the self-cleaning test; (b) the semi-erect BNNT film thoroughly cleaned after a static drop rolled off; (c) still many particles left on the prostrate BNNT film after the same cleaning.

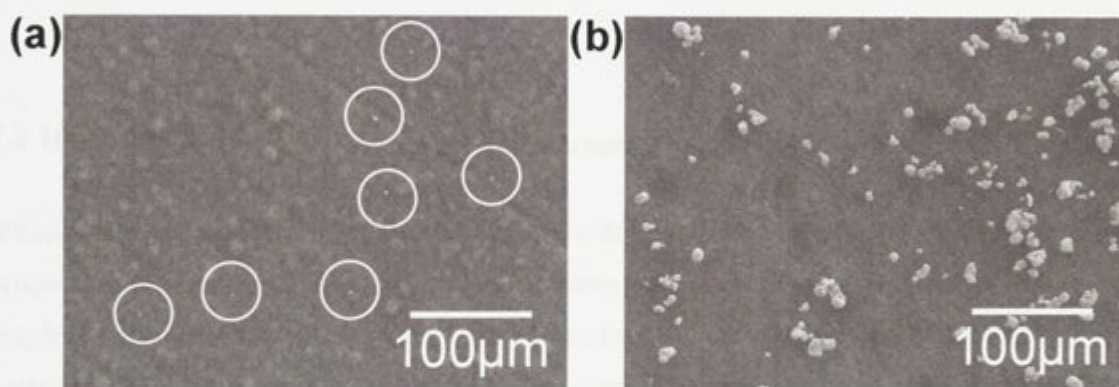


Figure 6.10 SEM images of, (a) semi-erect BNNT film, (b) prostrate BNNT film, after cleaning by a drop without initial kinetic energy. The red circles highlighted the $\sim 2\mu\text{m}$ sized copper particles scarcely left on the semi-erect film.

6.4 Conclusions

A non-aligned semi-erect BNNT film synthesized by the B ink method showed superhydrophobicity with contact angle above 170° and hysteresis less than 4° . This anti-wetting property was stable over a large range of drop sizes and the critical pressure for transiting from Cassie state to Wenzel state was estimated to be around 10kPa. The low fractional contact area (f_s) and huge roughness created by the semi-erect BNNT film were two of the main reasons for achieving superhydrophobicity. However, longer growing times led to prostrate BNNT films, on which only hydrophobic behaviour was observed. The superhydrophobic and hydrophobic BNNT films showed distinct drop retraction behaviour during evaporation; a different pressure effect on contact angle; and different critical

transition pressure, drop impact behaviour and self-cleaning efficiency. These differences could be satisfactorily explained by the differences in fractional surface area, roughness and compressibility. One interesting observation is that the contact diameter for a drop on the prostrate BNNT film first slightly increased during evaporation. The theoretical study of the wetting property of an individual BNNT yielded the likely explanation that the observed spreading was caused by the transition from initial to equilibrium contact angle of water on BNNTs. These results give guidance not only for the design of BNNT films as anti-wetting coatings to water, but may also assist in fabricating films for use in molten polymer processing, as BNNTs are more stable than their counterpart carbon nanotubes at high temperatures.

** All of the work presented in this chapter was done by author.*

Chapter 7

Ultra thin BN sheets and their photoluminescence

7.1 Introduction

When a layered material is exfoliated into two-dimensional (2D) sheets, some exceptional properties may emerge. The most obvious example is graphene, a single atomic layer of graphite. In graphene, the quasiparticles, like electrons and holes, behave like relativistic particles [229, 230] and scattering only happens at the edge of a graphene sheet [231]. Graphene also shows unprecedented mechanical strength [232] and excellent thermal conductivity [233]. Because of these properties, graphene has aroused intense interest as a matter of fundamental science and possible commercial application since the discovery of free-standing graphene in 2004 [234]. Hexagonal boron nitride (*h*BN) shares the same layered structure as graphite, but there has not been much large quantity synthesis or many investigations into the properties of atomically thick BN sheets [6, 8, 14].

Ball milling is a widely used technique capable of inducing chemical reactions, forming non-equilibrium phases and producing nanoparticles at large-scale [116]. Although ball milling is usually a violent process which destroys crystal structure and introduces a great number of defects [104, 235-237], Janot et al. and Antisari et al. have found that by carefully controlling the milling conditions, ball milling was also able to cleave large graphite particles into thinner sheets while maintaining the in-plane crystal structure [238, 239]. However, these two brief reports did not answer many basic questions, such as what are the optimum

milling conditions to reduce the layer thickness, what is the minimum sheet thickness that can be produced and what kind of defects can be introduced during milling.

In this chapter, a study of the use of ball milling method to efficiently produce BN sheets with atomic thickness in large quantities is presented. In these experiments, a planetary mill with a large number of small steel balls was used to maximize the cleaving effect while minimizing the force of impacts on the in-plane layer of BN. Benzyl benzoate was used as the milling agent. The effect of other milling agents, including water, ethanol and dodecane, has also been examined. A range of techniques, including scanning electron microscopy (SEM), x-ray energy dispersive spectroscopy (EDS), x-ray diffraction (XRD), transmission electron microscopy (TEM), near-edge x-ray absorption fine structure (NEXAFS), x-ray photoemission spectroscopy (XPS), atomic force microscopy (AFM) and photoluminescence (PL), were used to characterize the ball milling produced thin BN sheets.

7.2 Experimental

A four-station horizontal planetary mill (Fritsch Pulverisette 5, Germany) was used to reduce the thickness of *h*BN particles. 0.5g of *h*BN powder (Merck) and 6mL benzyl benzoate (Sigma-Aldrich) were placed in a steel milling vial (inner diameter of 100mm) with 50 steel balls (diameter of 12.7mm). The sealed vial was purged with pure nitrogen (N_2) gas at a pressure of 200kPa. The rotation speed was 150rpm. Small amounts of paste were taken out after different milling times. The samples were diluted with benzyl benzoate and centrifuged (Eppendorf 5424 with standard rotor, Germany) at 376rcf (2000rpm) for 1h or 9391rcf (10^4 rpm) for 0.5h to remove the large particles.

A Hitachi S4500 SEM operated at 3kV was used for morphology investigations. EDS attached to a Hitachi 4300SE/N SEM was used for the examination of the change of carbon content in the product. A Cypher AFM (Asylum Research, USA) was used to measure the thickness of the ball milled sheets. In both SEM and AFM investigations, the specimens were prepared by depositing small droplets of the benzyl benzoate liquid containing BN sheets on Si (400) wafers and heating up to 200°C in air. A Philips 3020 XRD diffractometre was used to analyse the phases in samples. The specimens for XRD were prepared by mixing the initial *h*BN powder or the ball milled samples with ethanol and then spreading the paste on glass substrates. TEM investigations were performed using a Philips CM300 (300kV). A Shimadzu TGA-60 analyser was used to monitor the evaporation of benzyl benzoate in argon (Ar) gas.

The rate of temperature increase was 1°C/min and the gas flow rate was 50mL/min during heating. XPS measurements were performed in the Laboratory for Surface and Materials Science, the Department of Physics, the University of Rijeka, Croatia, using a laboratory XPS system (SPECS) with monochromatized Al K α x-rays of 1486.74eV.

Both PL and NEXAFS measurements were conducted at National Synchrotron Radiation Research Center (NSRRC), Taiwan. The samples were prepared by spreading the paste of ball milled sheets on Si substrate and annealing at high temperature. Other detailed experimental information on the PL measurements can be found in Chapter 5. All PL spectra were corrected for the sensitivity of the photomultiplier tube (Figure 5.1). The NEXAFS spectra were taken in an ultrahigh vacuum chamber attached to the bending-magnet beam line 24A1, equipped with a microchannel plate detector for NEXAFS measurement and a low-energy ion gun for sample bombardment with low-energy argon or nitrogen ions (0.2 to 5keV). The NEXAFS spectra were recorded in the surface-sensitive partial electron yield (PEY) mode, with a cut-off kinetic energy of 100eV for measurements around the B K-edge or 300eV for measurements around the N K-edge. The photon impact angle was 40°, measured from the sample surface. The raw NEXAFS data were normalized to the photoelectron current of the photon beam, measured on an Au grid. The broadening of NEXAFS spectra in the low-resolution measurements is dominated by the monochromator resolution.

7.3 Results and discussion

7.3.1 The initial hBN particles

The initial hBN particles (before ball milling) have plate-like shapes and a high diameter to thickness ratio, both of which are typical characteristics of materials with hexagonal structure (Figure 7.1a). The particle widths are 0.3-1 μ m, and the thickness ranges from 20 to 110nm. Figure 7.1b shows the TEM image of the particles at low magnification. Electron diffraction (not shown) confirms that (002) planes are preferentially aligned along the top surface of each plate. Higher magnification TEM edge-on images of the particles show that the many plates are closely attached to each other (Figure 7.1c and d). These attachments are more likely to be derived from the crystal growth, rather than pure physical stacking. In Figure 7.1c, the whole stack of plates shows a similar dark contrast in the bright-field image, indicating that the crystalline orientations of all the plates in the stack are nearly identical.

However, the contrast within each particle is not homogeneous and in the form of stripes. This can be interpreted as evidence for the deviation of their structures from perfect single crystals due to the presence of planar defects, such as stacking faults or dislocations. Figure 7.1d shows another typical example of the planar defects in the crystals (arrowed).

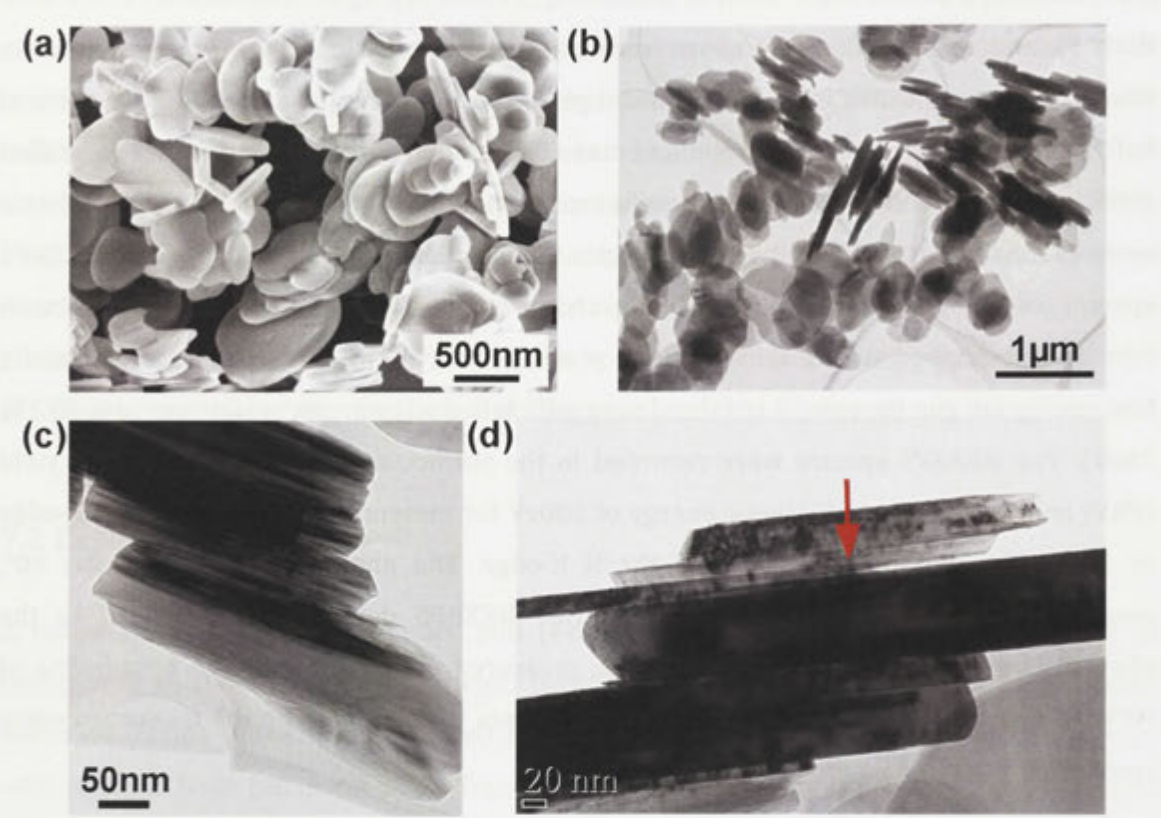


Figure 7.1 (a) SEM image of the initial hBN particles; (b) TEM image of the initial particles at low magnification; (c) and (d) higher magnification TEM edge-on images of the particles with a planar defect arrowed.

7.3.2 The thin BN sheets produced by ball milling

After planetary milling in benzyl benzoate, most of the hBN particles were successfully reduced to thin sheets. Figure 7.2a shows a SEM image of the sheets ball milled for 15h and then centrifuged at 376rcf for 1h. The sheets are smaller and thinner, although some relatively big particles are still present. These big particles can be removed by centrifuging at higher *g*-forces. The SEM image in Figure 2b shows that only sheets with quite uniform small thickness remained after the centrifugation in benzyl benzoate at 9391rcf for 0.5h. These sheets have diameters of several hundred nanometres and thicknesses of several nanometres. Figure 7.2c shows an AFM image of three BN sheets on a Si substrate. The

height trace curves of these sheets (Figure 7.2d) show that the sheets labelled (1), (2) and (3) are 3.7, 2.4 and 2.3nm thick, respectively. Even thinner sheets may exist. The bright-field TEM image in Figure 7.2e shows a group of overlapping sheets. Some extremely thin

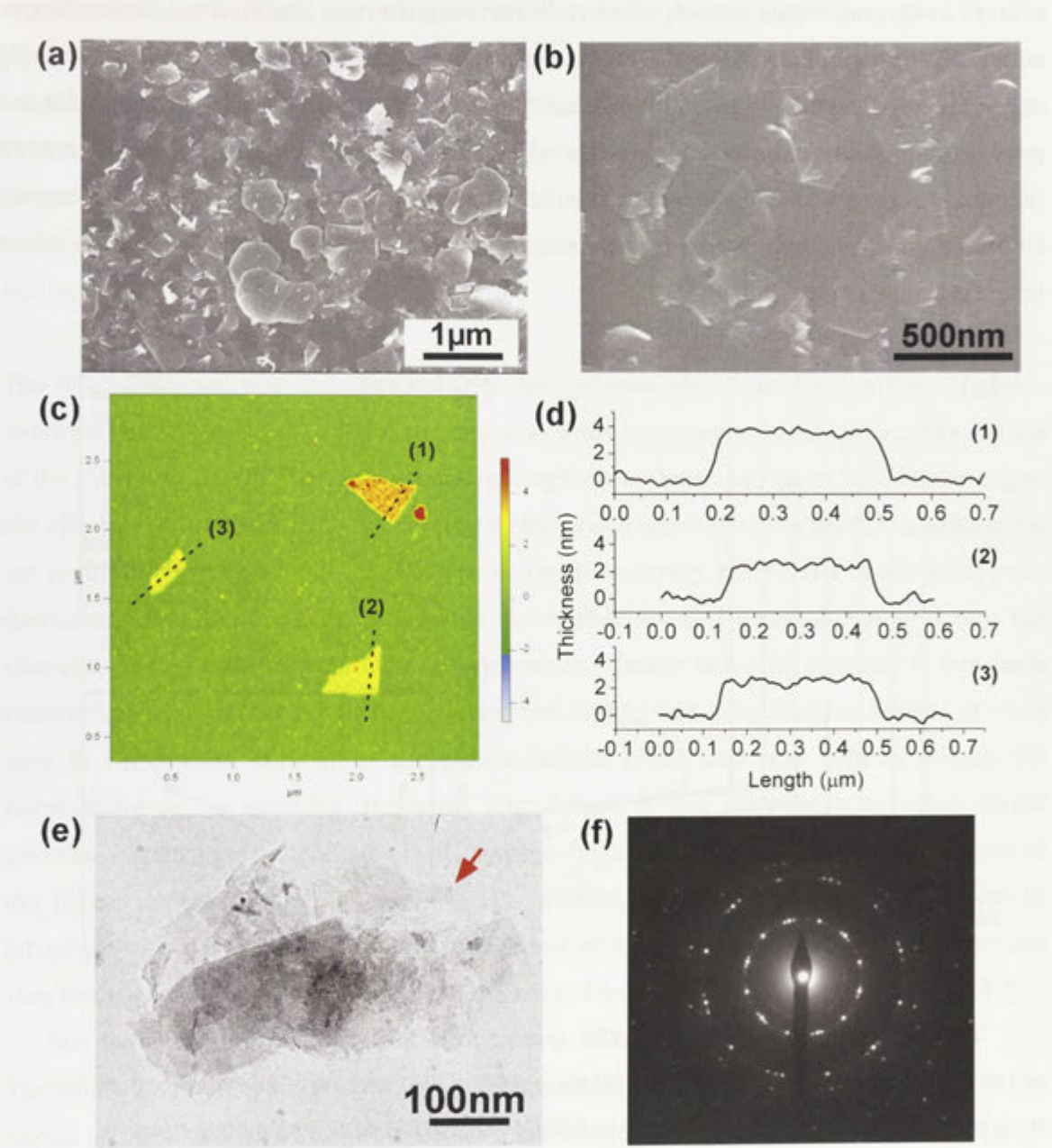


Figure 7.2 (a) SEM image of thin BN sheets after ball milling in benzyl benzoate for 15h and centrifugation at 376rcf for 1h; (b) SEM image of ultra thin BN sheets after centrifugation at 9391rcf for 0.5h; (c) AFM image showing three BN sheets on Si substrate; (d) the height trace curves of the three sheets indicating their thickness are close to 2nm and widths are several hundred nanometres; (e) TEM image of the sheets, with a very thin sheet arrowed; (d) the corresponding electron diffraction pattern.

sheets are also noticeable (arrowed). The corresponding electron diffraction pattern (Figure 7.2f) confirms that the (002) planes have little damage. Careful investigation of the pattern reveals that it consists of several sets of dots with six-fold symmetry and these sets are rotated at various angles to each other. A diffraction pattern of this kind can be due to two reasons: (1) overlapping sheets disoriented relative to each other by a shift and rotation; (2) stacking faults existing within an individual sheet. However, the TEM investigation did not provide enough evidence to reliably judge which one is the major cause. The isolation of an individual sheet on a TEM grid over a hole in the amorphous carbon film seems challenging. Orienting a single sheet parallel to the electron beam in the TEM column to obtain a lattice image is an even more difficult task.

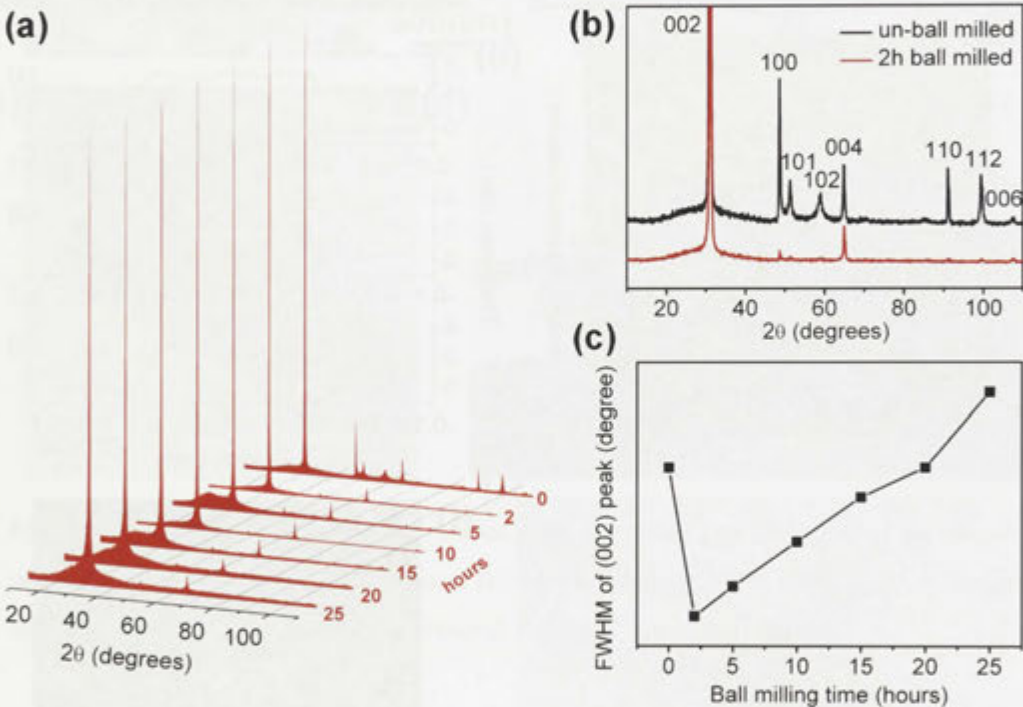


Figure 7.3 (a) The normalized XRD spectra from hBN particles after different ball milling times in benzyl benzoate; (b) the enlarged XRD spectra of un-milled and 2h ball milled BN particles; (c) the change in FWHM of the (002) peak with milling time.

The normalized XRD spectra of hBN particles ball milled in benzyl benzoate for different times are compared in Figure 7.3a. From the XRD results, the most dramatic change had happened after just 2h of ball milling. In order to show the peak intensity changes more clearly, the XRD spectra of the initial powder and the 2h ball milled sample are enlarged in Figure 7.3b. It can be seen that the intensities of the (004) and (006) peaks had only slightly decreased after 2h of ball milling. The (004) peak still existed after 25h of milling and the (006) peak was present till 20h of milling. This indicates that the ball milling did not

dramatically influence the short range order of the BN crystals in the c-direction [240]. In other words, the in-plane structure was little affected. The (100), (101), (102), (110) and (112) peaks, in contrast, almost disappeared after 2h milling. As the short range order of the crystal was mostly intact, the disappearance of these peaks should be caused by the preferential orientation of the ball milled BN sheets on substrate (the (002) plane parallel to the substrate surface), due to both the dramatically reduced thickness and the high diameter to thickness ratio of the milled sheets. This preferential orientation has already been demonstrated in the SEM and TEM images (Figure 7.2a and e). The XRD results show that most particles were successfully cleaved into thinner sheets within the first 2h of ball milling.

The (002) XRD peak position was almost unchanged even after 25h of ball milling. This also confirms that the in-planar crystal structures at short range were largely intact. The change of the FWHM of the (002) peak with ball milling time is shown in Figure 7.3c. Interestingly, the effective reduction of both the crystal thickness and size during the first 2h of milling did not result in a broadening of the (002) peak. On the contrary, the FWHM of the (002) peak decreased after 2h of milling. A possible explanation for this unusual change is that the cleavage during ball milling released microstrains inside the *h*BN crystals. It has been reported previously that the cleavage during ball milling was more likely to happen at weak sites in the crystal, such as at the planar defects [238], and may help to release the microstrains in the particles. However, after longer milling times such an effect would decrease because the high efficiency of cleavage during the first 2h would consume most of the planar defects in the *h*BN particles. In addition, the extended ball milling began to introduce new defects into the sheets. Together with the effect due to decreasing crystal size, this can explain why the (002) peak broadened from 2 to 25h of milling (Figure 7.3c).

The NEXAFS spectra from the un-milled *h*BN particles and the 15h ball milled sheets in the region of the B K-edge at the π^* resonance are compared in Figure 7.4. The main peak at around 192eV after ball milling in benzyl benzoate is broader than that of the initial particles. This indicates that there was slightly more amorphous structure after ball milling. The two small peaks located at higher energy are more pronounced and also slightly shifted compared to the un-milled particles, indicating more B-C-N bonds or more nitrogen vacancies in the ball milled sheets. However, the increase in both the amorphous content and the B-C-N bonds or nitrogen vacancies is not dramatic.

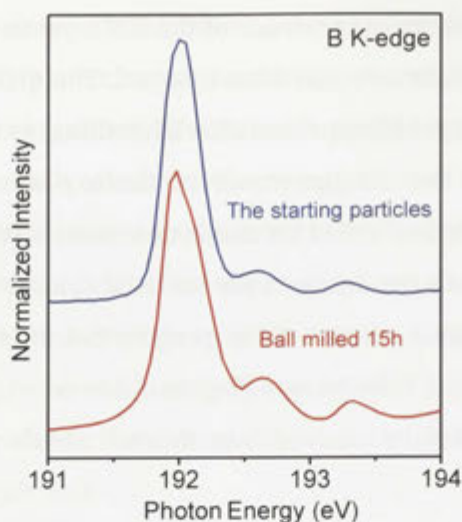


Figure 7.4 The NEXAFS spectra in the region of B K-edge near the π^* resonance from PEY measurements. Blue line: the initial hBN particles (un-milled) and red line: the sheets ball milled for 15h in benzyl benzoate.

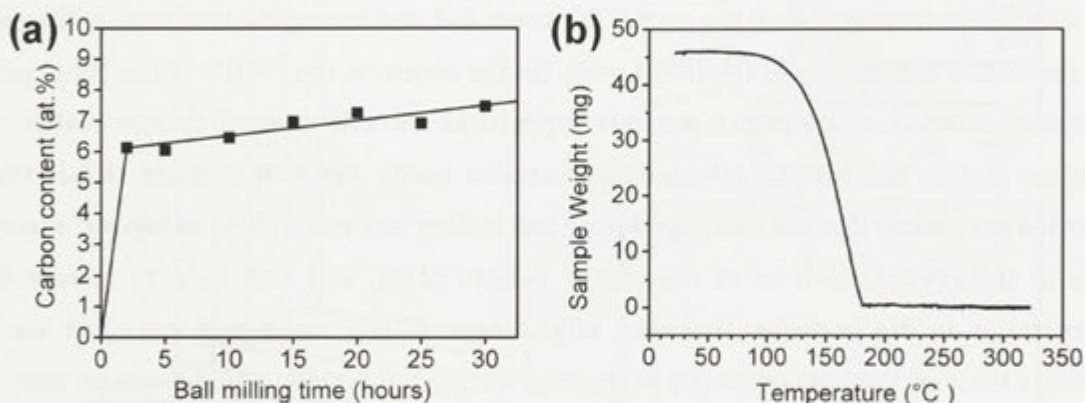


Figure 7.5 (a) EDS results showing that the carbon content of the vacuum heated sheets increases linearly with the increase in ball milling time; (b) TGA curve showing that benzyl benzoate evaporates at 160°C.

It was found that benzyl benzoate could not be completely removed from the milled sheets even after heating in vacuum. Figure 7.5a shows the carbon contents of the ball milled sheets after vacuum heating ($<10^{-5}$ torr) at 500°C for 3h. It can be seen that the carbon content increased almost linearly with milling time, although TGA shows that benzyl benzoate evaporates at 160°C. A possible explanation for the increasing carbon content is that benzyl benzoate can be trapped between the stacking sheets [17], which possess huge surface areas. The number of sheets increases with ball milling time; hence more inter-sheet area is available to retain benzyl benzoate. As a result, the longer milled sheets show a higher carbon content. On the other hand, these C residues are mostly physically absorbed

on the sheets, as evidenced from the XPS results. The normalized XPS spectra from the initial *h*BN particles and the vacuum heated sheets produced by 15h ball milling in benzyl benzoate are compared in Figure 7.6. Compared to the initial particles, the ball milled sheets show only a moderate increase in the number of B-C-N₂ and B-N-O bonds. This result is consistent with the NEXAFS result that only a small amount of carbon bonds were introduced by ball milling.

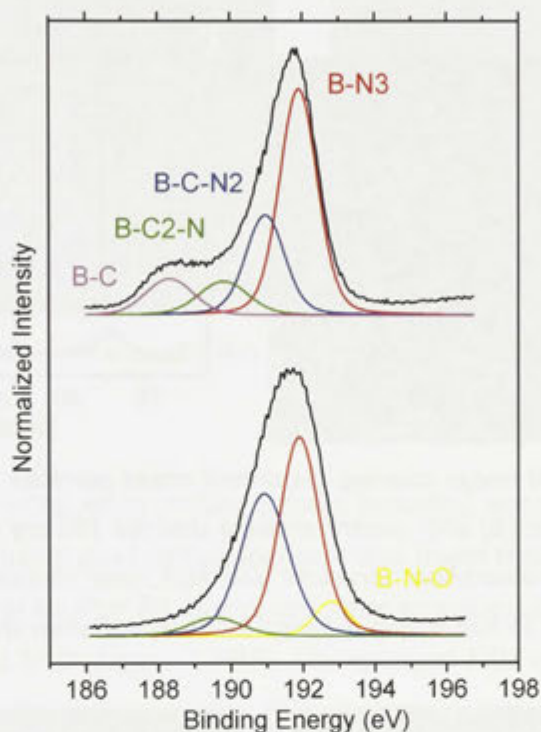


Figure 7.6 The normalized XPS spectra from the initial *h*BN particles (top) and the 15h ball milled sheets after vacuum heating (bottom) with fits to different bonds (the B-C bond may be due to surface contamination of the *h*BN particles).

7.3.3 Suitable milling conditions and exfoliation mechanism

The efficient exfoliation of the *h*BN particles while retaining their in-planar crystal structure requires favourable milling conditions. The first step is to choose a suitable mill. Most kind of mills use a strong collision force to grind material [104, 235-237]. A planetary mill, on the other hand, mainly produces shear forces, which suits the exfoliation purpose. However, planetary milling in dry conditions still causes severe damage to the crystal structure of a material. For example, when the *h*BN particles were dry ball milled in the same planetary mill, round and semi-amorphous particles were produced (Figure 7.7). Therefore, a liquid controlling agent must be used during milling. A liquid agent can work as a lubricant to

reduce the damage on particles and make the shear force gentler [238, 241]. Under the gentle shear force and due to the strong in-plane sp^2 bonding and the weak van de Waals inter-plane bonding in hBN crystals, the thin BN layers were either mechanically cleaved off (Figure 7.8a) or peeled off from the surfaces of the large hBN particles (Figure 7.8b). The use of the small steel balls (diameter of 12.7mm) can also help to minimize the damage to the in-plane crystal structure and the relatively large number of these balls makes the milling more efficient.

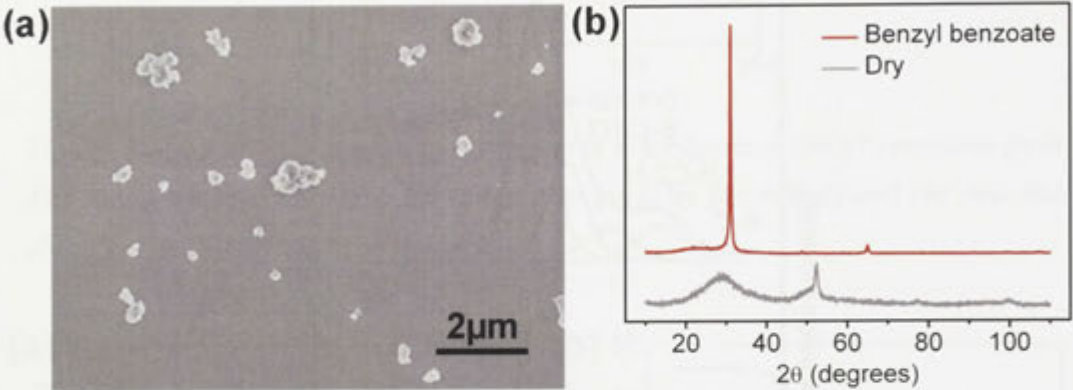


Figure 7.7 (a) SEM image showing the almost round particles after dry planetary ball milling for 15h; (b) XRD spectra showing that the 15h dry ball milled product (grey) has a semi-amorphous structure and high steel contamination, while the products from the 15h ball milling in benzyl benzoate still show strong hBN phases.

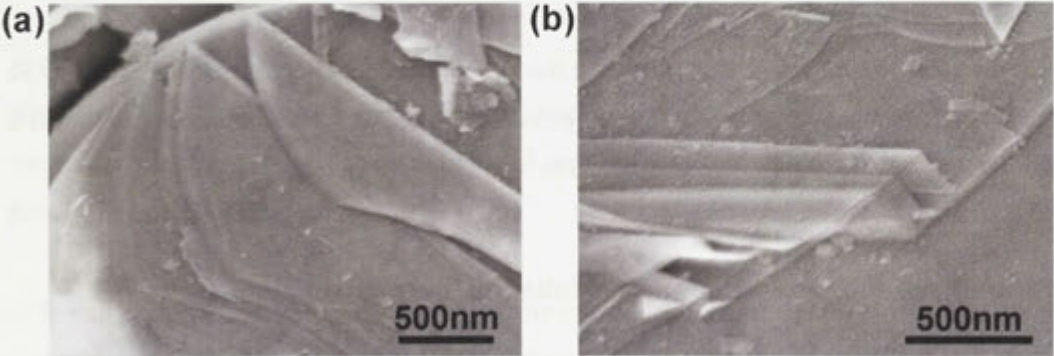


Figure 7.8 SEM images showing the two exfoliation mechanisms during ball milling: (a) cleavage from the edge of the hBN particles by shear force; (b) peeling off thin sheets from the top surface by shear force.

7.3.4 The change of milling media and agent

A nylon vial and fifty nylon balls were also tried for the production of thin BN sheets in ethanol. The majority of particles remained large after 15h milling and centrifugation at

376rcf for 1h (Figure 7.9a), though many thin BN sheets with quite straight edges were also found (Figure 7.9b). The widths of the relatively thin sheets were usually two to five times larger than those produced in benzyl benzoate using steel milling media, but they were also thicker (normally 7-12nm). These differences are caused by the lower density and hardness of the nylon balls which lead to milder impacts on the BN particles.

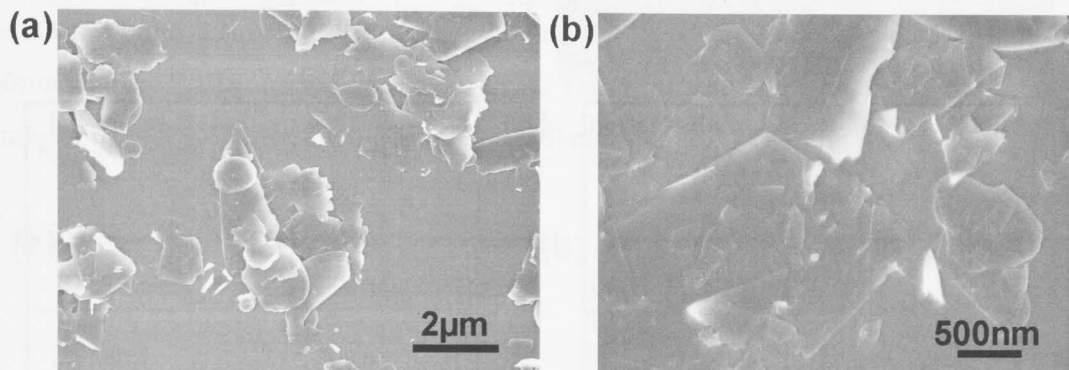


Figure 7.9 SEM images showing the thin BN sheets produced by ball milling in ethanol after centrifugation.

The effects on milling using other milling agents, including water, ethanol and dodecane, were also investigated using steel milling media. It was found that ball milling in ethanol or water usually resulted in smaller BN sheets and more structural damage, according to both SEM (Figure 7.10a) and XRD (Figure 7.10b). The enlarged XRD spectra show that after 2h ball milling in ethanol, there were similar changes in peak intensities to those for benzyl benzoate (Figure 7.10c). However, after 15h of ball milling in ethanol, the BN particles had much more damage, since the (004) peak totally disappeared and the amorphous phase began to appear (Figure 7.10d). These differences are caused by the lower viscosity of ethanol and water relative to benzyl benzoate and dodecane, so a smaller lubricant effect or larger milling force results in more structural damage occurring. Another feature of the XRD spectra from the ethanol milled samples is the strong peak from steel contamination (Figure 7.10d). The EDS results show that the milling in water and ethanol gave much more steel contamination (Figure 7.11). Dodecane and benzyl benzoate both gave good exfoliation results, but benzyl benzoate is better for preventing the aggregation or rejoining of thin BN sheets by becoming physically attached to the newly cleaved BN sheets, due to its similar surface tension to BN and graphite [17].

7.3.5 Photoluminescence of the milled BN sheets

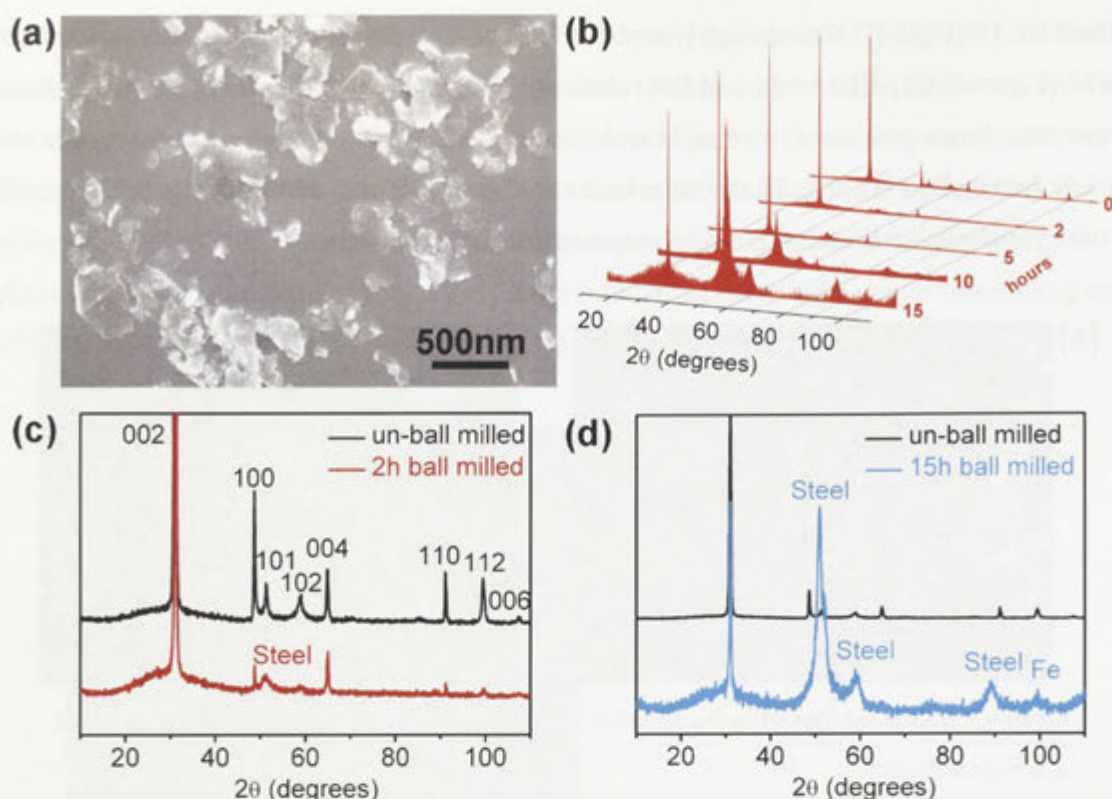


Figure 7.10 (a) SEM image of the BN sheets produced by 15h ball milling in ethanol; (b) XRD spectra from the sheets ball milled for different times in ethanol; (c) the enlarged XRD spectra from the initial hBN particles and the 2h ethanol ball milled sheets; (d) the enlarged XRD spectra from the initial hBN particles and the 15h ethanol ball milled sheets.

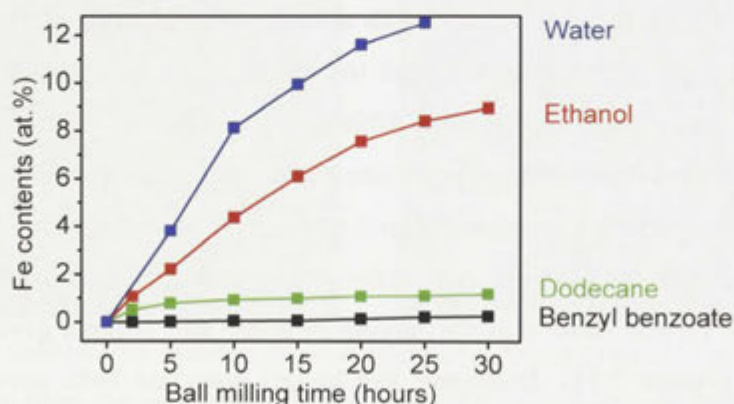


Figure 7.11 A comparison of the Fe content of the ball milled BN sheets using different agents.

The room-temperature PL from the initial hBN powder and the sheets produced by ball milling in benzyl benzoate for different times and annealed in vacuum are compared in Figure 7.12a. Roughly, ball milled BN sheets show a similar luminescence profile to the

initial particles: a DUV peak at around 224nm and a broad band near 300nm. However, the relative intensity of these two bands changed dramatically after ball milling. For the initial *h*BN particles, the 300nm band is almost twice as intense as the DUV band. Yet, after only 2h of milling, the DUV emission has become relatively stronger. The strongest DUV emission is obtained after 15h of ball milling. After that, the relative intensity of the 300nm band increases with increasing ball milling time. For example, for the sheets ball milled for 30h, the 300nm band has become almost as strong as the DUV band and a new peak at round 340nm (Figure 7.12a, arrowed) has emerged. This new peak is highly likely to relate to the damage or defects created by the extended ball milling.

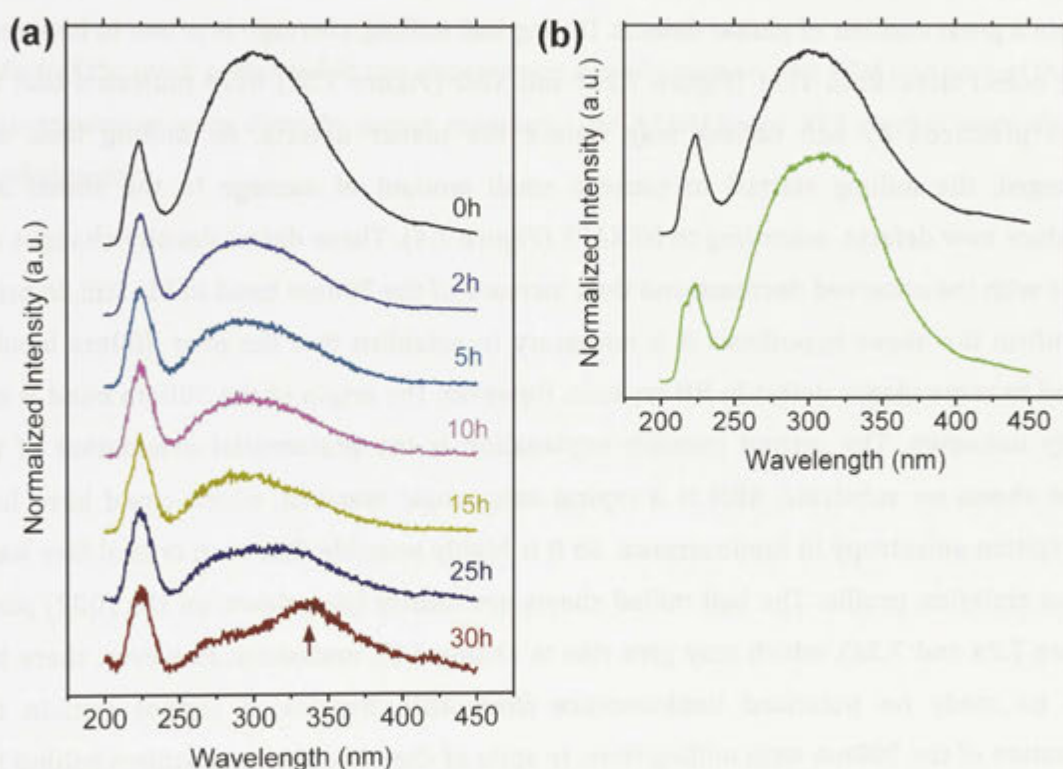


Figure 7.12 (a) The room-temperature PL spectra from the un-milled *h*BN particles and the sheets produced after different hours of ball milling in benzyl benzoate and annealed in vacuum ($<10^{-5}$ torr) at 500°C for 3h, a new peak (arrowed) at around 340nm appeared after 30h of ball milling; (b) comparison of the room-temperature PL spectra from the un-milled *h*BN particles (black) and a sample prepared by vacuum annealing a mixture of un-milled *h*BN particles and benzyl benzoate (green).

The observed decrease in relative intensity of the 300nm band with milling is not related to the addition of benzyl benzoate to the *h*BN particles, the ultrasonication, or the annealing in vacuum, because a comparison sample, produced by first mixing the un-milled *h*BN powder with benzyl benzoate in an ultrasonic bath and then annealing at 500°C in vacuum, showed

increased 300nm emission (Figure 7.12b). This increased 300nm emission is possibly due to benzyl benzoate residues and the increased contribution of the 215nm sub-band to the DUV peak is probably due to the vacuum annealing. The increase in carbon impurities in the sheets after ball milling (Figure 7.4 and 7.6) is unlikely to be the reason for the observed PL change either, because it should lead to stronger 300nm emission [123, 197].

So these intensity changes in PL must come from the ball milling and two possible explanations are as follows. The first possibility is that the decrease in the density of planar defects in the short-time ball milled BN sheets leads to the decreased intensity of the 300nm band. The TEM images (Figure 7.1c and d) have revealed that the initial *h*BN particles contain a great number of planar defects. During ball milling, cleavage is prone to happen at these defect sites. Both TEM (Figure 7.2d) and XRD (Figure 7.3c) have indicated that the sheets produced by ball milling may reduce the planar defects. As milling time was prolonged, the milling started to cause a small amount of damage to the sheets and introduce new defects, according to NEXAFS (Figure 7.4). These defect density changes are in line with the observed decrease and then increase of the 300nm band in PL. Still, in order to confirm the above hypothesis it is necessary to establish that the near 300nm band is related to some planar defect in BN crystals. However, the origin of the 300nm band is still largely unknown. The second possible explanation is the preferential orientation of the milled sheets on substrate. *h*BN is a typical anisotropic material, which could have high polarization anisotropy in luminescence. So it is highly possible that each crystal face has a unique emission profile. The ball milled sheets are mostly lying down on the (002) plane (Figure 7.2a and 7.3a), which may give rise to changed PL emissions. However, there has been no study on polarized luminescence from *h*BN. Besides, it cannot explain the fluctuation of the 300nm with milling time. In spite of the uncertain mechanism behind the relative intensity change after ball milling, ball milled *h*BN sheets are more desirable than the initial particles in DUV light emission applications.

7.4 Conclusions

Planetary ball milling can be an effective method to produce ultra thin sheets of BN if suitable milling conditions are chosen. Benzyl benzoate was found to be a better milling agent than water, ethanol, or dodecane. After only 2h of milling, the majority of the large BN particles were effectively cleaved. Ultra thin BN sheets with widths of hundreds of nanometres and only a few nanometres thick were found after centrifugation. Various

investigations indicated that in spite of the thickness reduction, ball milling did little damage to the in-planar structure of the sheets and introduced a very small amount of point defects. The thin BN sheets produced by this method showed better DUV emission than the unmilled particles. Besides BN, this ball milling method should be applicable to any other layered materials, such as graphite, because it uses mechanical peeling and cleaving to produce thin layers.

** Most of the work presented in this chapter was done by author. The TEM and part of the EDS investigations were done by group members; the NEXAFS and XPS studies were done by collaborator.*

Chapter 8

Concluding remarks

8.1 Summary

A liquid boron (B) ink method has been invented based on the old ball milling and annealing method to produce higher purity and larger quantities of BNNTs. In the new ink method, high energy ball milling is first used to prepare nanosized B particles in ammonia (NH_3) gas. The repeated mechanical impacts introduce a great amount of defects in the B particles, along with the formation of some BN nucleation sites and steel nanoparticles. Then the ball milled B particles are homogeneously mixed with ethanol and metal nitrate under ultrasonic bath. The ink-like liquid mixture, or B ink, is annealed in nitrogen containing gas to synthesize BNNTs. During annealing, the B particles act as soot for nanotube growth and the steel particles and the added metal nitrate serve as catalysts. The annealing in nitrogen plus hydrogen gas enables the production of 0.5g of 100-200 μm long BNNTs mostly with bamboo-like structure and diameters of 40-80nm at one time. The annealing in ammonia gas results in high crystalline cylindrical nanotubes with diameters smaller than 10nm. Investigations show that the added metal nitrate acting as extra catalyst particles dramatically boosts the yield and purity of nanotubes in the products and ethanol mainly helps the intimate mixing between the B particles and the nitrate. This significant progress in the fabrication of large quantities of BNNTs opens up the door for practical applications. As an example, bulk sized (not film shaped) BNNT reinforced polyurethane (PU) composites were produced. The mechanical tests showed that the compressive modulus of the 0.5vol.% BNNT reinforced composite improved by 38.2%.

The new B ink method also provides a simple way to grow BNNT films on different substrates. The ink can be directly painted/brushed, sprayed, or even inkjet printed on

different substrates with any desired pattern, and then the annealing converts the ink layer to a high density of BNNT film. In addition, a high density of BNNTs of high purity can, for the first time, be grown on objects with complex shapes. As examples, BNNTs were homogeneously grown on a steel mesh, a steel syringe and a tiny screw. Because the coating method involves direct nanotube growth, the BNNT films have strong adhesion to the substrate, as shown by measurement using a dynamic mechanical analyser (DMA). The coating parameters, such as the nanotube density and the film thickness, can be controlled by the density of the ink or the ink coating method used. Small diameter cylindrical and bamboo-like BNNTs can be produced as well as cylindrical BNNTs and BN nanowires with diameters of 40-100nm. The high purity BNNT films show many new properties and applications.

Photoluminescence (PL) measurements have shown that BNNTs with a small cylindrical multiwall structure (diameters <10nm) can have single deep ultraviolet (DUV) emission peaked at 225nm (5.51eV). On the other hand, the bamboo-like tubes only have relatively weak DUV luminescence but intense emission near 300nm. It is the first time that a single DUV emission has been detected from BNNTs. An examination of the resolved excitonic subbands in the DUV emission suggests that BNNTs have quite similar excitonic recombinations to *h*BN. It was also found that the luminescence from the small diameter BNNTs is more easily affected by atmospheric contamination than bulk sized *h*BN.

Both superhydrophobicity and hydrophobicity are observed on the as-grown BNNT films produced by the B ink method. The non-aligned semi-erect BNNT films can have a contact angle larger than 171° and hysteresis smaller than 4°. This anti-wetting property is stable over a large range of drop sizes and the critical pressure for the transition from Cassie state to Wenzel state is estimated to be around 10kPa. The low fractional contact area and huge roughness created by the BNNT film are two of the main reasons for achieving superhydrophobicity. If the as-grown BNNTs are prostrate (bent over), only hydrophobicity is observed. The superhydrophobic and hydrophobic BNNT films exhibit distinct drop retraction behaviour during evaporation, drop impact behaviour and self-cleaning efficiencies. The possible reasons for these differences are the different fractional surface area, roughness and compressibility for these two kinds of films.

In addition to BNNTs, BN sheets with atomic thickness are also important for both fundamental science and practical application. Planetary ball milling in benzyl benzoate is found to be an effective way to produce BN sheets in large quantities and the in-plane

structure of these sheets is largely intact. Sheets as thin as 2nm are found in the product. Various characterization techniques, including scanning electron microscopy (SEM), x-ray diffraction (XRD), transmission electron microscopy (TEM), near-edge x-ray absorption fine structure (NEXAFS), x-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM) are used to show that ball milling did little damage to the in-planar structure of the sheets and introduced a very small amount of point defects into the sheets. Interestingly, the thin sheets show better DUV luminescence than the un-milled hBN particles, as the relative intensity of the broad band near 300nm dramatically reduces.

8.2 Future directions

The results of this study point in a number of directions for future work. Some possibilities are suggested below.

In the large quantity synthesis of BNNTs, although nitrate, or extra catalysts, was added to achieve a better yield of BNNTs, the Fe particles in the B powder formed from the impact during ball milling still contributed largely to the BNNT growth. It would be very interesting to find whether the structure and size of BNNTs can be changed if only nitrate-derived catalyst particles were involved in the formation of BNNTs. It would be especially interesting to know whether, when a $N_2+5\%H_2$ atmosphere is used, only cylindrical tubes (without bamboo structured tubes) can be produced. However, the removal of the Fe particles from the ball milled B powder is not straight-forward. Firstly, contamination is inevitable during ball milling. Even if other milling media is used, such as tungsten carbide (WC), the debris of the milling media can still act as catalysts for BNNT growth [242]. Secondly, acid cannot be used to remove the Fe particles, because the B particles can react with acid and convert to other compounds not suitable for BNNT synthesis.

For improved composites, stronger bonding between BNNTs and matrix should lead to bigger improvements in mechanical properties. The functionalization of the surface of BNNTs is definitely worth trying as a means to both change the wetting properties of BNNTs and to help form chemical bonds between BNNTs and the matrix. In addition, the use of small diameter cylindrical BNNTs, which are stronger than the bamboo tubes, should be tested. However, finer nanotubes are usually more difficult to disperse, so a more effective dispersion method is a must for the production of fine BNNT reinforced composites.

In future it would be worth trying to produce vertically aligned BNNTs on a substrate, because it could open up further applications. The main problem to achieve this is how to continuously deposit small amounts of B ink on the substrate during annealing, similar to the way a carbon-containing gas is continuously introduced in the CVD method for producing vertically aligned CNTs. One possible route towards this is, instead of painting B ink on the substrate, to continuously transport evaporated B ink into the high temperature reaction chamber (at more than 1000°C). The evaporated ethanol can continuously bring the nanosized B particles to react with the reaction gas and to deposit on the substrate. In this way, BNNTs may grow into a vertical forest. However, it is not known whether the ethanol will leave C contamination in the BNNT product.

Further investigation on the luminescence of BNNTs and BN nanowires is desirable. Although this study resolved four possible DUV sub-bands, it is highly possible that more sub-bands exist. In order to resolve the other DUV sub-bands, a synchrotron PL system with higher resolution than the VUV photoluminescence in NSRRC, Taiwan is needed. In addition, the origins of these DUV sub-bands are also of scientific interest and important to the practical application. Time resolved PL will help to find these origins. But the VUV system in NSRRC, Taiwan is not very useful in this sense. In regard to the near 300nm band, there is still a lack of direct evidence what chemical impurity or impurities lead to the presence of this band. So, detailed chemical analyses are required to establish a relationship between chemical impurities and intensity of the near 300nm band.

In the study of wetting properties of BNNT films, it was found that the erect BNNT film, although superhydrophobic, could not sustain pressure above 10kPa, which can highly limit its practical application. So how to make the surface of the BNNT film mechanically stronger is critical. One obvious solution is protecting the film with a thin layer of hydrophobic polymer. By doing this, the film can sustain pressure much larger than 10kPa [243] and still remain superhydrophobic. As mentioned previously, *h*BN particles are a widely used refractory material in foundry and polymer processing. So the wetting properties of the BNNT films to molten metals or polymers are worth studying, especially since this property of BNNTs has never been investigated. Besides, the B ink method can homogeneously grow BNNT films on outline-giving non-flat surfaces, which can be very useful in foundry and polymer processing.

It would also be interesting to change the wetting properties of BNNTs or BNNT films, as in some cases, such as using BNNTs as fillers in composites, BNNTs or BNNT films need to be

wettable. There should be several ways to change their wetting properties. For example, chemical and plasma functionalization, both are easy to realize and could give rise to interesting results.

Future work is needed to further reduce the thickness of the sheets by optimizing ball milling conditions, because a monolayer or few layers thick sheet of BN or carbon is of more scientific interest. Besides, because of this large quantity synthesis method, the ultra thin sheets can be directly used to enhance composites. More applications can be expected after more characterization and property measurements are done on these ultra thin sheets.

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