



Boron nitride nanotubes

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ABSTRACT

This article presents an overview of the up-to-date developments in boron nitride nanotubes (BNNTs), including theory, fabrication, structure, physical properties, chemical functionalization and applications. Soon after the discovery of carbon nanotubes, BNNTs were theoretically predicted, followed by their successful fabrication by arc-discharge in 1995. Subsequently, various methods were developed for the BNNT synthesis, although till now, the growth of highly pure single-walled BNNTs at large quantities remains a challenge. The physical property investigations reveal that BNNTs exhibit a stable wide band gap, superb mechanical strength, high thermal conductivity, ultra-violet light emission, etc. All these properties build up the solid basis for their future technological applications. Chemical modification is also a decent approach to adjust the BNNTs properties. In recent years the yield of multi-walled BNNTs has reached the grams level, that can allow their detailed chemical functionalization studies. So far, many kinds of functionalizations through different weak interactions and covalent bonding were developed. These treatments improved BNNT dispersions in solvents and extended their fields of applications. Moreover, some application-related studies on multi-walled BNNTs, such as composites fabrication, hydrogen storage, biocompatibility, and mechanical, and electrical breakdown tests have also been started in recent years.

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1. Introduction

1.1. Boron nitride nanotube studies

A boron nitride nanotube (BNNTs) can be imagined as a rolled up hexagonal BN layer or as a carbon nanotube (CNTs) [1] in which alternating B and N atoms entirely substitute for C atoms (Fig. 1). Similar to CNTs, BNNTs have chiralities, an important geometrical parameter, but for them, the chiralities do not play an important role in determining electrical properties [2,3].

In 1981, Ishii et al. reported on a discovery of one-dimensional BN nanostructures, which possess bamboo-like structure. These were named BN whiskers [4]. However, the nanoscaled BN with a perfect tubular structure was firstly theoretically predicted only in

1994 [5,6] and then experimentally synthesized by arc-discharge in 1995 [7]. In the following few years, most works were focused on the synthesis of BNNTs followed by their structural characterizations. A variety of methods, such as laser ablation [8], chemical vapor deposition (CVD) [9], ball-milling [10], substitution reaction [11] were invented and adopted to synthesize BNNTs. These synthesis methods provided BNNTs with different purity, diameters and structures in order to meet the requirements for detailed physical property investigations. However, for chemical studies of BNNTs, large quantities of highly pure BNNTs were not available, thus the related works appeared only later, during 2003–2005 [12–15]. The real applications of BNNTs are still far from the market, but some Laboratory level explorations have successfully been carried out, e.g. polymeric and ceramic composites [16–18], hydrogen storage [19], etc., have been demonstrated. Actually, compared with a limited number of experimental works, more papers were published in regard of theory. The studied topics included BNNTs' electronic structure [6], property tuning [20,21], hydrogen storage [22], magnetic properties [23], molecular dynamic simulations [24], etc. Fig. 2 shows a rough statistics for the categories of papers published with respect to BNNTs so far. Most works are on the theoretical and synthetic studies, while investigations on chemistry and applications are rather few due to difficulties in obtaining high-quality massive samples suitable for these kinds of researches.

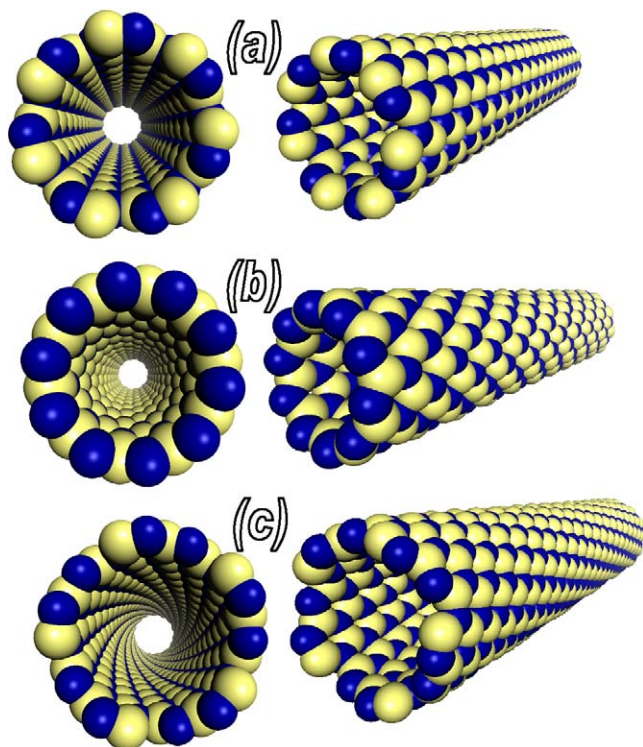


Fig. 1. Atomic models of (a) (7, 7) arm-chair BNNT; (b) (10, 0) zig-zag BNNT and (c) (10, 5) chiral BNNT.

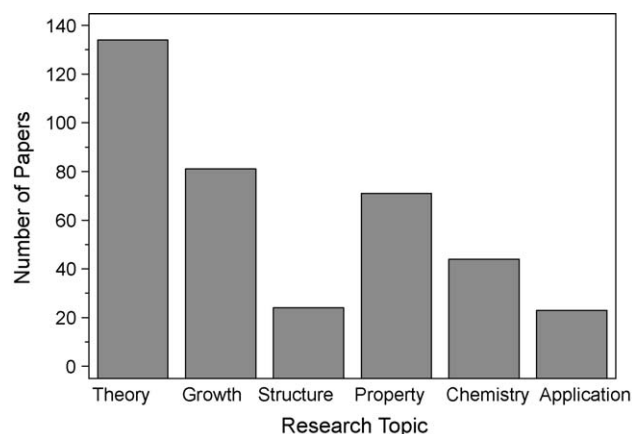


Fig. 2. Statistics of papers on BNNTs published.

1.2. BNNT vs CNT

BN is a binary compound made of Group III and Group V elements in the periodic table. However, due to its specific structure, properties and polymorphism similarities, BN is much closer to the C system compared to other conventional Groups III–V compounds. Here we briefly compare BNNTs with CNTs as summarized in Table 1 [3,25–27]. The detailed description of BNNTs' properties will be presented in the following sections.

BN materials are isoelectronic with their all-carbon analogues but possess local dipole moments due to a difference in electronegativity of B and N atoms. The B–N bond contains a significant ionic component. This polarity can remarkably alter both molecular and solid-state electronics as well as optical properties of the system by modifying the character of the frontier molecular orbitals [2,25,26]. The obvious and most appealing difference between BNNTs and CNTs is their visible appearance: BNNTs are pure white (sometimes slightly yellowish due to N vacancies) while CNTs are totally black, as shown in Fig. 3. The band gap of BNNTs has been reported to be between 5.0 and 6.0 eV independent to tube chirality. This provides good electrical insulation [6,28–30], while CNTs can be a metal or a narrow band-gap semiconductor [31]. This discrepancy in electronic structure results in different luminescence emission: BNNTs have violet or ultraviolet luminescence under excitation by electrons or photons [32–37], while CNTs can emit infrared light and the wavelengths depend on their chiralities [38–41]. Moreover, originating from the symmetry difference, BNNTs have only one strong Raman active phonon mode at 1370 cm^{-1} [2,42], whereas CNTs possess a nominal G band at 1580 cm^{-1} and a defect-induced D band at 1350 cm^{-1} [43]. Both tube types have radial breathing modes (RBM), but the frequencies are slightly different [27].

Both BNNTs and CNTs have superb mechanical properties: the Young's modulus of CNTs has been predicted to reach a TPa level. The BNNTs' Young's modulus is a bit lower, around 0.7–0.9 TPa, according to the theoretical calculations [27,44]. However, experimentally, both BNNTs and CNTs' Young's moduli varied in samples fabricated by different methods [45–48]. Sometimes the BNNTs' data are even better than for CNTs due to a higher synthesis temperature and better crystallization. In regard of thermal properties, CNTs were calculated to have astonishingly high thermal conductivity (6000 W/mK) [49]. For BNNTs the two theoretical papers gave two totally different predictions: one computed a value higher than CNTs [50], the other—a lower one, down to hundreds of W/mK [51]. A recent experimental work has revealed that at a similar diameter, BNNTs thermal conductivity is

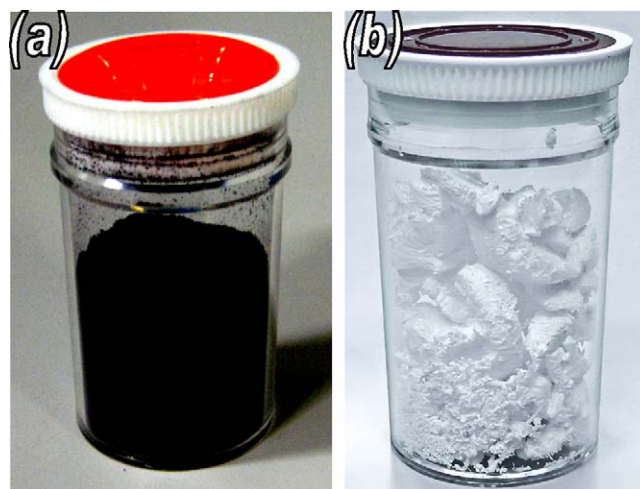


Fig. 3. Images of (a) CNTs and (b) BNNTs exhibiting totally different appearance.

comparable with that of CNTs [52]. Besides that BNNTs possess better thermal and oxidation stability than CNTs [53–55].

To sum up, on one hand, both tube types may be used in similar applications due to property similarities, for example, for the mechanical reinforcement or thermal conductivity improvement of matrix materials, etc. On the other hand, the differences are obvious: BNNTs are basically electrically insulating, whereas CNTs are conductive. This causes discrepancy of their usages. For instance, BNNTs are suitable fillers for insulating materials [56], while CNTs are usually used to improve electrical conductivity of polymers [57–60]. In some cases both tube types were used in optical devices, they may work in different wavelength ranges.

2. Theoretical investigation

2.1. Electronic structures

The BNNTs were first theoretically predicted and subsequently their electronic structures were investigated by a tight binding method [5]. All BNNTs were found to be semiconducting materials with direct or indirect band gaps larger than 2 eV. BNNTs with larger diameters have a larger band gap, with a saturation value corresponding to the band gap of a hexagonal BN, as shown in Fig. 4. It should be noted that the total energy calculations were lacked due to limitations of tight binding method. The subsequent studies based on local-density-functional (LDA) calculations proved

Table 1
Properties of BNNTs vs CNTs.

Materials	Bonding	Electronic structure	Luminescence	Raman active mode	Young's modulus (TPa)	Thermal conductivity (W/mK) at room temperature	Thermal stability
CNTs	Covalent bonds; bonding length: $1.400\text{--}1.463\text{ \AA}$ [2,25–26]	Metallic or semiconducting, dependent on chiralities [31]	Infrared (wavelength: $800\text{--}1700\text{ nm}$) [38–41]	G band: 1580 cm^{-1} ; D band: 1350 cm^{-1} ; [43] RBM model: (10, 10) CNT, 171.0 cm^{-1} [2]	1.09–1.25 [44] 0.84–0.99 [2] (theoretical) 0.27–0.95 [45] (experimental)	~ 6000 (theoretical, SWCNT); [49] >3000 (experimental, MWCNT, $D \sim 14\text{ nm}$); [52] ~ 1000 (experimental, MWCNT, $D \sim 10\text{ nm}$); [52] ~ 300 (experimental, MWCNT, $D \sim 35\text{ nm}$) [52]	Depends on sample, roughly between 500 and $700\text{ }^{\circ}\text{C}$ [53]
BNNTs	Covalent bonds with ionic component; bonding length: $1.437\text{--}1.454\text{ \AA}$ [2,25–26]	$5.0\text{--}6.0\text{ eV}$ band gap, independent of chiralities [6,32]	Violet and/or ultraviolet (wavelength $220\text{--}460\text{ nm}$) [32–36]	A_1 tangential mode: 1370 cm^{-1} ; [42] RBM mode: (10, 10) BNNT, 153.0 cm^{-1} [2]	0.784–0.912; [44] 0.71–0.83 [2] (theoretical); 0.5–0.7; [46,47] 1.22 ± 0.24 [48] (experimental)	$>\text{CNTs}$ (theoretical); [50] $\sim 180\text{--}300$ (theoretical, SWBNNT); [51] $\sim 180\text{--}300$ (experimental, MWBNNT, $D \sim 35\text{ nm}$) [52]	High, up to $800\text{--}900\text{ }^{\circ}\text{C}$ in air [54,55]

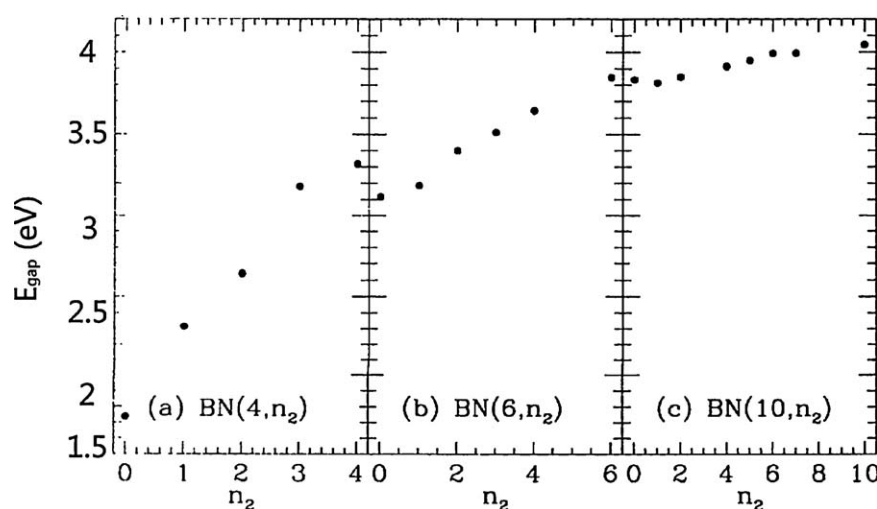


Fig. 4. Evolution of calculated tight-binding band gap for (n_1, n_2) BNNTs as a function of n_2 for (a) $n_1 = 4$, (b) $n_1 = 6$, and (c) $n_1 = 10$. For large n , the gap is fairly independent of n_2 . Reproduced with permission from [5].

that it is energetically more favorable to fold a hexagonal BN sheet into a BNNT than to form a CNT from a graphite sheet [6]. Moreover, more fine details regarding the electronic structures were revealed. In one hand, according to band-folding analysis, BNNTs are large-gap semiconductors, with a direct gap for $(n, 0)$ tubes and an indirect gap for (n, n) tubes. On the other hand, strong hybridization effects can take place because tube curving reduces the BNNT's band gap remarkably. For the $(n, 0)$ BNNTs, than $n > 12$ (diameter > 0.95 nm), the hybrid state was found not to play any role in determining tube gaps. The gaps are stable at around 4 eV according to LDA. It is well-known that LDA may underestimate the band gap, thus, this value is reasonable. In another calculation using density functional theory, the band gaps of BNNTs were eventually saturated at 5.03 eV with an increase in diameter [61–65].

Various methods have been developed to tune the electronic structure of BNNTs, including physical methods, such as applying electric field [66–71,20] or strain [72,73], or chemical methods, such as doping [74–89], introducing defects [21,78,81,90,91] or surface modification [22,75,76,90,92–121]. The methods and species chosen and related references are summarized in Table 2. Physical methods could directly reduce the band gap of BNNTs, while chemical methods were found to tune the band gap by introducing localized energy levels inside the gap. For example, by applying an 0.2 V/Å electric field, the band gap of a (12, 12) BNNT was directly reduced from 4.5 eV to about 2.5 eV [67], whereas F-doping induced an unoccupied localized state in the gap of BNNTs [79]. In addition, chemical modification methods of BNNTs were sometimes found to enrich the properties of BNNTs, for instance, polarization field was induced by chemical adsorption [94] or ferromagnetism appeared in doped BNNTs, etc. [88,121].

For electronic structure of multi-walled BNNTs (MWBNTs) [mainly double-walled BNNTs (DWBNTs)] the hybridization between π and σ states of inner and outer tubes exists [122–125]. This effect leads to the top valence and bottom conduction bands localization on the outer and inner tubes, respectively. The band gap of DWBNTs is slightly narrower than that of the inner tubes. This is because the downward shifts of the π states of the inner tube are larger than those of the outer tube. Moreover, in the inter-wall region the peculiar charge redistribution is induced by the near-free-electron states of BNNTs [124]. The fluorine doping can significantly modify the DWBNTs' inter-wall interactions and thus both tube walls turn into effective conducting channels. This leads to a remarkably improved electrical transport in them [125].

There are strong interactions between electrons and holes in BNNTs [126,127]. The excitonic effects were indeed shown to be

more important in BNNTs than in CNTs. Bright and dark excitons in BNNTs alter the optical response qualitatively. For example, the absorption spectrum of the (8, 0) BNNT is dominated by a peak at 5.72 eV, due to an exciton with a binding energy of 2.3 eV. The binding energy for the first excitonic peak is more than 3 eV in the (2, 2) tube, which will fast converge to around 2.1 eV of the hexagonal single BN sheet due to strongly localized nature of this exciton. This is consistent with the results by the Louie's group [126]: a 2.3 eV binding energy for a (8, 0) BNNT.

2.2. Other theoretical issues

Various issues of BNNTs were investigated by theoretical methods, including hydrogen storage [22,95–99,102,107,108,112,113,117,128], magnetism [23,88,129–140], phonon characteristics [141–148], stability [149–158], molecular dynamics [24,159–167], field-electron emission [168], scanning tunneling microscopy simulation [169], electron transport [170], symmetry breaking [171], work function [172], spin-splitting [173–175] and quantum computing [176,177]. Some theoretical topics which were intensively investigated, such as hydrogen storage and magnetism, had been closely related to experiments and applications, as presented in the following sections. Here we only choose one example which clearly shows the difference between BNNT and CNTs.

Molecular dynamics simulations were used to investigate BNNTs' thermal and structural stability, as well as the interactions between molecules and BNNTs. An interesting discovery is that, a very thin BNNT, namely (5, 5) BNNT with a diameter of 6.9 Å, has been found to transport water, while the (5, 5) CNT was not able to do so due to much larger energy barrier [165]. The Van der Waals interactions between water molecules and nitrogen atoms reduced the energy barrier effectively. According to this, thin BNNTs were proposed as promising candidates for a synthetic aquaporin-1 water channel. Further studies revealed that Stone-Wales defects in a BNNT might induce phase transition of water, that is, a transition between the liquid-like and vapor-like phases [24].

3. Fabrication

In this section, we will review the growth methods developed for BNNTs. The main characteristics of each method are summarized in Table 3. Moreover, growth mechanism and purification methods will also be briefly discussed. It is noted that there have been only few works with respect to the latter topic.

Table 2

Methods used to modify BNNTs theoretically.

Methods	Species	References
Defects	Stone–Wales defects	[90,91]
	N and/or B vacancies	[21,78]
	B antisite (B_N), N antisite (N_B)	[21,81]
Doping	C	[74,78,85]
	Si	[75,82,89]
	Pt	[76]
	F	[77,79,86,125]
	O	[78,88]
	Cs	[80]
	P, As, Sb, In, Ga, Al	[81]
	V, Cr, Mn	[84,87]
	Ti	[108]
Surface functionalization and absorption	CO, NO	[74,90]
	Formaldehyde molecule	[75]
	Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, and Zn, Pd, Pt	[93]
	H	[22,76,90,94,96–99,102,104–108,112,115,117,119,177]
	Tetracyano-p-quinodimethane, tetrafluorocyno-p-quinodimethane, Tetrakis(dimethylamino) ethylene, anthracene, tetrathia-fulvalene	[100]
	Naphthalene group, alkyl chain, Li, $-COCF_3$	[101]
	Dichlorocarbene	[103]
	Fe	[154]
	O, O ₂ , H ₂ O	[90,112,115,119]
	NH ₂ , NH ₃	[90,111,119,120]
	Metalloporphyrin MP (M = Fe, Co, Ni, Cu, and Zn) complexes	[114]
	N ₂	[115,119]
	Heavy carbenes	[116]
	Ni	[115]
	CH ₄ , CO ₂ , NO ₂ , F	[119]
		[119,121]
Others	Electric field	[20,66–68,71]
	Strain	[73]

3.1. Growth mechanism

The growth mechanism theory-oriented studies have been much fewer than experimental works [180–186]. Here we summarize some molecular dynamic results and phenomenological growth models which can provide instructions for optimizing and controlling the growth of BNNTs. They are as follows: (1) BNNTs with different chiralities may have very different growth mechanism [180]: the open-ended zig-zag BNNTs tend to close into amorphous-like caps, preventing further growth; whereas the formation of squares in the arm-chair BNNTs traps the tip into a flat cap, which then can revert into the further growth of a hexagonal network by incorporating incoming atoms. This discrepancy comes from the higher stability of B–N bonds compared to B–B and N–N bonds. (2) In case of BNNTs grown by laser vaporization, a root-growth model was proposed [183]. The growth of BNNTs was due to surface diffusion along the external surfaces, thus, the nanotube lengths were limited by the corresponding diffusion lengths. (3) In case of using metal catalysts, the metals with stronger metal–B and metal–N energy bonds may produce thinner BNNTs. The formation enthalpies of BN from respective borides or nitrides can be considered as the key factor in such catalyst design [186].

3.2. Arc-discharge

BNNTs were firstly fabricated by arc-discharge between a BN-packed tungsten rod and a cooled copper electrode [7]. A product was MWBNNTs with inner diameters of the order of 1–3 nm. The metal particles in the BNNTs tips were proposed to reflect the possible scenario for the BNNT nucleation and growth. In the following-up improved experiments using HfB₂ as electrodes, SW- and DWBNNTs were synthesized [187–189]. Different from CNTs (for whose graphite rods are always used as electrodes), since the BN materials are insulating, they are not suitable for electrodes. Thus, in most experiments, conductive boron compounds, such as ZrB₂, YB₆, were used instead [185,190,191] and N₂ was used as a protection gas and a nitrogen source. The boron compounds can serve as catalysts during the growth. BNNTs fabricated by arc-discharge possess good crystallization due to a high growth temperature (~3000 K).

Table 3

Summary of growth methods of BNNTs.

Methods	Temperature (°C)	Catalyst	B source	N source	Comments	References
Arc-discharge	~3500	No catalyst; or Ni, Co; or Y; or Zr	h-BN; or HfB ₂ ; or B; or YB ₆ ; or ZrB ₂	h-BN; or N ₂	High crystallization; SWBNNTs and MWBNNTs; impurities: BN onions, cages, etc.	[7,185–191]
Laser ablation	~1200; or 5000	No catalyst; or Ni, Co	h-BN; or c-BN	h-BN; or c-BN	High crystallization; SWBNNTs and MWBNNTs; impurities: BN cones, etc.	[8,183,192–199]
Template synthesis	1000; or 750; or 1580; or 500–600	No catalyst; or MoO ₃ as promoter	B ₂ O ₃ ; or B ₃ N ₃ H ₃ Cl ₃ ; or BH ₃ NH ₃	NH ₃ ; or N ₂ ; or B ₃ N ₃ H ₃ Cl ₃ ; or BH ₃ NH ₃	CNT or porous alumina anodic as template; controllable morphology, carbon in lattice	[11,200–213]
Auto-clave	600; or room temperature	Mg; or Fe	Mg(BO ₂) ₂ ; or B; or NH ₄ BF ₄	NH ₄ Cl; or N ₂ ; or NH ₄ BF ₄	Bad quality; low yield; impurities: BN cages, B, etc.	[214–217]
Ball-milling	1000–1200	Fe; or Cr; or Ni	B	NH ₃	MWBNNTs; large yield; low purity; impurities: B; h-BN; BN fiber, etc.	[218–225]
CVD and chemical synthesis	1500; or 1100; or 1200; or 600; or 800	Co; or Ni; or NiB; or Nickelocene; or Fe; or Ga; or Li	B; or B ₂ H ₆ ; or BH ₃ NH ₃ ; or BN; or B ₂ O ₃ ; NaBH ₄ ; or H ₃ BO ₃	NH ₃ ; or BH ₃ NH ₃ ; or N ₂ ; or NH ₄ Cl; or urea	MWBNNT; quality varies based on the specific method; high yield (grams level) available	[9,177,178,216,217,226–246]
Other methods	4000; or 3700; or 600	No catalyst	BN; or B	BN; or N ₂	High crystallization; impurities: BN webs; amorphous phase, etc.	[247–249]

3.3. Laser ablation

Golberg et al. [8] for the first time adopted laser ablation to grow BNNTs. Single crystal cubic BN targets were used as precursors. A CO₂ laser was focused onto the target edge to heat it up to 5000 K and to obtain MWBNNTs in the melted layer. In the following experiments [183,192–199], *h*-BN was also used as a precursor and both SWBNNTs [183] and MWBNNTs were synthesized by this method. Fabricating BNNTs by ablation can be achieved without catalysts [194]. However, using Co or Ni as catalysts was found useful to get longer tubes with a reduced number of atomic layers. The BNNTs prepared by laser ablation usually possess perfect crystallization. However, the purity of a product by laser ablation is not satisfying: except BNNTs, BN cones, onions and amorphous boron flakes can be easily found.

Very recently, a new technique named pressurized vapor/condenser method has been developed [199] that seems to be a very promising method for the large scale growth of BNNTs. This method is actually an improved laser ablation process. The boron vapor is generated by heating target materials over 4000 °C by a high-powered laser. The target materials can be hot-pressed BN, cold-pressed BN, amorphous B powders and cast B. Pressured N₂ (2–20 times of the atmosphere pressure) was used as a nitrogen source. A condenser made of BN, B, stainless steel, copper, niobium and tungsten was used to trigger homogeneous nucleation. Hundreds of milligrams of few-walled BNNTs are available using this synthetic route.

3.4. Template synthesis

Two kinds of template syntheses were used for the BNNTs fabrication: CNTs' substitution reaction [11,200–210] and porous alumina filter membrane [211–213] template synthesis. In case of the former, CNTs are reacted with B₂O₃, and nitrogen or NH₃ is used as a protection gas and a nitrogen source [11]. The obtained product is mainly B_xC_yN_z nanotubes. A subsequent oxidation was designed to remove extra carbon. However, it should be noted that this carbon in the tube lattice cannot be removed easily, thus, the final product is BNNTs doped with carbon. Metal oxide, such as MoO₃ was found to effectively increase the yield of BNNTs [204]. The advantage of this method is that the morphology of starting CNTs can be maintained in BNNTs, for example, SWBNNTs [207] and aligned BNNT ropes [206] can be synthesized by using corresponding CNTs morphologies.

BNNTs were also synthesized using pores inside porous alumina [211]. 2,4,6-Trichloroborazine was decomposed at 700–950 °C to fill the pores of alumina with BN materials. A product exhibited tubular structures with an average diameter of 280 nm. However, detailed studies revealed a polycrystalline structure of the obtained BNNTs.

3.5. Auto-clave

Due to high crystallization temperature of BNNTs, an auto-clave was thought not to be suitable apparatus for the growth of BNNTs. However, some special auto-claves were adopted [214–217]. In one experiment, a mixture of Mg(BO₂)₂·H₂O, NH₄Cl, NaN₃ and a Mg powder in an autoclave was heated at 600 °C for 20–60 h [214]. BNNTs with diameters 30–300 nm and lengths up to 5 μm were obtained. The BNNTs fabricated by this method had special morphologies showing thin walls and large inner spaces. The Mg powder was proposed to be a catalyst for the growth of BNNTs. In other experiments, it was found that Co or Fe could work as catalysts, and boron or NH₄BF₄ could be the boron source, while the N source was usually NH₄Cl or NaN₃ [216,217]. Due to a safety problem, a temperature below 600 °C was adopted in all the experiments.

3.6. Ball-milling

Chen et al. [218] were first to develop this method to synthesize BNNTs. They used ball-milling of a hexagonal BN powder to generate highly disordered or amorphous nanostructures, followed by annealing at a temperature up to 1300 °C. BNNTs and bamboo-like BN nanostructures were obtained. No specific catalysts were used. Fe species coming from a stainless-steel container were proposed to be effective catalysts for the BNNTs' growth. The yield ratio of pure BNNTs was rather low as the products were mixed with a large amount of amorphous materials. Subsequently, experiments were designed to improve the quality and purity of ball-milled BNNTs by using a boron powder as the precursor, introducing NH₃ as a protection gas during ball-milling and optimizing annealing conditions [219–225]. The characteristics of BNNTs produced by this method were indeed improved. The yield of BNNTs was increased and their diameters were reduced to less than 10 nm. However, the purity of the samples still remained low. A very recent paper has revealed that highly pure bamboo-like BN nanostructures and BN nanowires can be fabricated by this method, while for BNNTs, the purity remains an issue.

3.7. Chemical vapor deposition and chemical synthesis

It is difficult to separate a CVD method from the chemical syntheses. Some experiments were not employing the standard CVD method, however a typical CVD process might partially be involved [9,178,179,216,217,226–246]. Many works adopted this method. The process might go just by a simple annealing of FeB particles under protection of a nitrogen gas [243], or a complicated design of floating catalysts was required [231]. The main characteristics of this method are summarized in Table 3.

The initial CVD growth of BNNTs was reported by Lourie et al. [9]. Borazine was used as a precursor and Co, Ni, NiB and Ni₂N particles were found to be effective catalysts. The growth temperature was 1000–1100 °C, which had been common in most CVD growths of BNNTs. Yap and co-workers [236] realized a low temperature (600 °C) growth of BNNTs by a plasma enhanced pulsed-laser deposition. It is surprising that the BNNTs have been claimed to possess good crystallinity. To meet the demands of large-scale synthesis of highly pure BNNTs, our group has developed a CVD method using boron and metal oxide as the reactants (BOCVD) [226,233,234]. This method separates a boron precursor (boron powder plus metal oxide) from the as-grown BNNTs during the growth. This preserves BNNTs from contamination by the precursors and guarantees their ultimate purity, as displayed in a SEM image (Fig. 5). Various metal oxides were found to be effective for the BNNTs' growth. A mixture of MgO and FeO or MgO and SnO was found to be the best [234]. So far, grams level of BNNTs can be fabricated by this method. Also significant efforts were made to realize world-first kilogram level growth. Another promising CVD method for the mass production of BNNTs has recently been developed utilizing a floating catalyst. This might be further optimized toward realization of a continuous growth of BNNTs [231].

3.8. Other methods

There were a few other reported methods to fabricate BNNTs, but no consecutive works were then presented to confirm their validity. This is perhaps due to bad samples qualities or extremely low yields etc. For example, Shimizu et al. [247,248] developed a plasma jet method to produce BNNTs. The authors used an arc plasma jet to bombard a BN sintered disk. The purity of a product was poor, however, the crystallization of tubes was perfect. Bengu

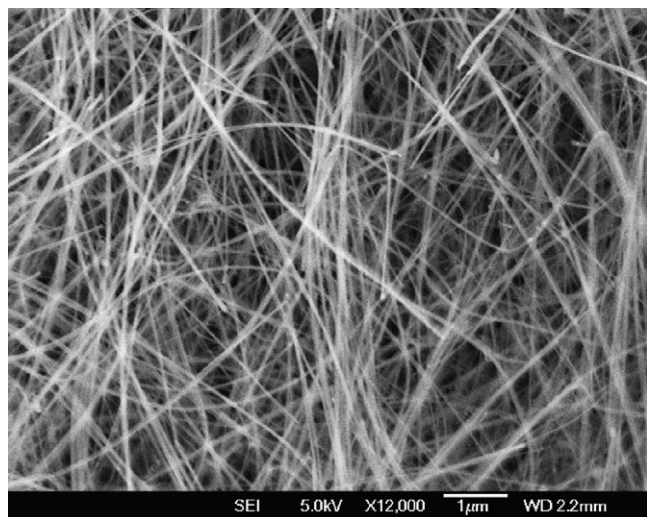


Fig. 5. SEM image of BNNTs produced by BOCVD method. The tube length can be up to tens of micrometers.

and Marks [249] used low-energy electron-cyclotron resonance plasma to grow a limited number of SWBNNTs and investigated their structures by transmission electron microscopy (TEM).

3.9. Purification of BNNTs

Only few works have been related to purification of BNNTs [250–253]. This might be due to specific impurities of BNNTs which are usually stubborn, such as BN particles, very thick BN fibers, boron, etc. Similar to CNTs, an acid was used to remove metal catalysts from BNNTs. For other impurities two methods were developed. One is to convert BN nanoparticles to water soluble B_2O_3 by partial oxidation [251]. This technique utilizes the difference in anti-oxidation ability of BN particles and BNNTs. The other method is to adopt centrifugation separation utilizing the geometry and weight difference of impurities and BNNTs [252,253]: an impure BNNTs sample is dispersed in a solvent, followed by selective centrifugation to remove large size particles.

4. Structure

4.1. Modeling

A theoretical work by generalized tight-binding molecular dynamics reveals that unlike CNTs, BNNTs possess a wave-like or “rippled” surface in which B atoms rotate inward to an approximately planar configuration, whereas the N atoms move outward into a corresponding pyramidal configuration [254]. More interestingly, it was found that a zig-zag BNNT may favor a flat end, while in an arm-chair tube the conical tube closure is more energetically favored and a “chiral” tube may have the amorphous end. This discovery made it possible to find out the chirality of BNNTs by simply checking TEM images of the BNNTs’ ends. The fact that flat ends are seen in the experiments much more frequently than the conical ends indicates more abundant production of “zig-zag” tubes compared with “arm-chair” ones. However, the exact relationship between chirality and tip morphology has not been verified as yet because of very few relevant experimental works [188].

A (5, 0) zig-zag BNNT was considered to be the smallest stable BNNT, as documented by the first-principle calculations performed by Xiang et al. [255]. The strain energy of a BNNT depends only on its radius, but not on its chirality. A formula $E_{\text{strain}} = 2.89938/$

$R^{2.09481}$ was found to fit the strain energy of a BNNT, where the units of energy and radius are in eV and Å, respectively. The smallest BNNT was proposed by comparing the formation energies of the BNNT and BN strip. It was found that for $n \geq 5$, the (n, 0) zig-zag tubes are more stable than zig-zag strips, but for $n < 5$ the relationship is reversed. Thus, from the energy point of view, the smallest stable BNNT is a (5, 0) zig-zag nanotube with a diameter of about 4.0 Å.

As far as the defects of BNNTs are concerned [256–261], it is widely accepted that the adjacent pentagon–heptagon pairs (called Stone–Wales defects) in BNNTs generate less favorable homoelemental bonds, such as B–B and N–N bonds, and the high energy of the frustrated B–B and N–N bonds make BN systems structurally unstable [180]. However, it has also been revealed that the Stone–Wales defects may appear in BNNTs to reduce a high stress caused by the geometrical strains [260]. Moon and Hwang [261] claim that the tetragon–octagon pairs are favored only in the flat BNNTs caps and BN clusters during the growth. But the formation energy of the tetragon–octagon pairs in BNNTs is significantly higher, by 7–10 eV, than that of the pentagon–heptagon pairs. Therefore, the pentagon–heptagon pairs are energetically more favorable than the tetragon–octagon pairs, even though they may introduce B–B and N–N bonds in the tube. These results were also supported by the calculations of Dumitrica et al. [153] and Bettinger et al. [262].

4.2. Morphology

Similar to CNTs, BNNTs can form multi-walled or single-walled tubes. Loiseau et al. [188] presented a series of BNNTs with a varying number of walls, including SWBNNT. The tubes were grown by arc-discharge in that case, as shown in Fig. 6 (the SWBNNT shown here is a single tube, while in other cases, the tubes may be bundled [207]). The spacing between layers is about 0.34 nm (in another work, it is between 0.38 and 0.42 nm [263]), which is larger than the interplanar distance of 0.333 nm in a bulk hexagonal BN. The wall of SWBNNT is imaged by waved fringes, which is actually a common phenomenon for SWBNNTs synthesized by various growth methods [187,264–267]. This may result from the incomplete ordering during preliminary steps of the growth process or defects induced by the post-growth electron irradiation under TEM observations. Actually, as discussed above, in BNNTs the B and N atomic planes are slightly shifted in the direction perpendicular to the tube axis [254]. Therefore, the so-called “lip-lip” interactions between adjacent layers of BNNTs are stronger than those in multi-walled CNTs [268], which is important for stabilizing BNNTs. Thus, the SWBNNTs are considered to be less energetically favorable than MWBNNTs and CNTs. A recent study reveals that under electron beam irradiation, vacancy defects can easily form in BNNTs [266]. Moreover, once a vacancy forms, the formation energy for a subsequent neighboring vacancy becomes close to zero. Clustering of multiple vacancies is energetically favorable and leads to extended defects which can locally change the tube diameter and chirality.

Most BNNTs prepared by arc-discharge have closed ends [187], while the open ends or ends with catalyst particles are commonly observed for BNNTs grown by other methods [242,264,269–272]. For closed ends, a flat tip imaged as fringes perpendicular to the tube axis is most typical, as shown in Fig. 7. These tips are very specific compared with those in CNTs, which are typically cone-like [1]. This observation is consistent with the results of molecular dynamic simulations [254], as discussed above. The typical flat ends were proposed to correspond to triangular facets, which result from the three 120° disclinations in a hexagonal BN network.

Another typical morphology of BNNTs is so-called double-helix structure exhibiting regular dark and bright spots on the side walls

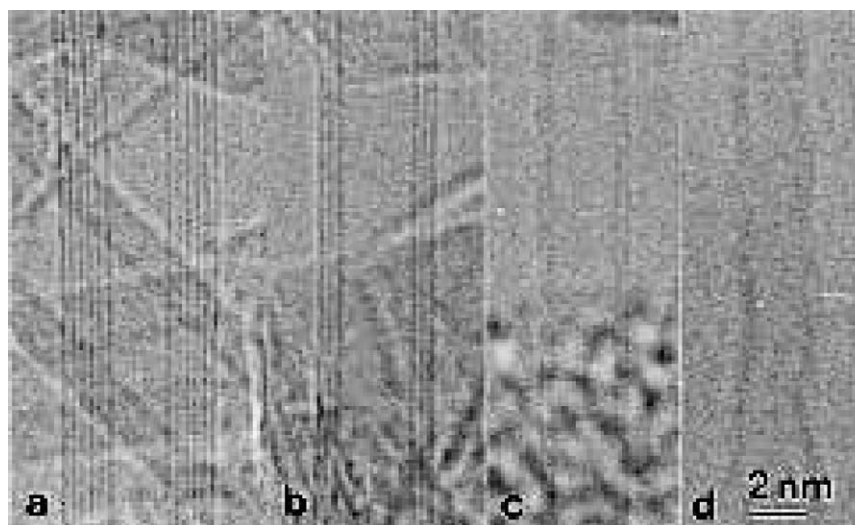


Fig. 6. High-resolution TEM images of typical BNNTs produced by arc-discharge, containing, respectively: (a) six, (b) three, (c) two, and (d) one layers. Reproduced with permission from [188].

of the tubes, as shown in Fig. 8. BNNTs possessing this kind of structure are usually grown by the BOCVD method [233,237,230]. A detailed study of this structure was presented by Celik-Aktas et al. [273]. A double-helix structure was explained as follows: the helix I is made up of polygonized highly crystalline hexagonal BN, and helix II is associated with circular tubes having less regular wall spacing.

4.3. Atomic order

Intensive investigations of BNNTs by high-resolution TEM and electron diffraction successfully uncovered their two important features [263,265,269,270,274,275]: the chirality and atomic stacking in MWBNNTs.

Theoretical investigations of the chirality preference of BNNTs give contradictory results: Blase et al. [180] revealed that armchair BNNTs are preferred, while Menon and Srivastava [254] claimed that zig-zag tubes are more energetically favorable. The

experimental works on BNNT chirality totally adopted the experimental diffraction methods developed for CNTs and the results were found to depend on the samples. Golberg et al. [54,204,206,270,276–279] reported that BNNTs made through a CNTs substitution reaction and laser heating possess preferential zig-zag chirality. In a detailed study of chirality of SWBNNTs and DWBNNTs produced by laser vaporization [263], among 121 tubes investigated, there were 12% of the zig-zag tubes, while chiral angles for other tubes uniformly distributed from zig-zag (0°) to armchair (30°). Also, no correlation of chiral angles for the constituent tubes in the concentric double-walled BNNTs was observed. However, in the Celik-Aktas et al.'s study of MWBNNTs fabricated by BOCVD methods [275], most tubes exhibit electron diffraction patterns similar to Fig. 9a, rather than Fig. 9b. It should be noted that there are two sets of hexagonal diffraction spots from each wall of one nanotube depending on its chirality. Thus, Fig. 9a shows a very narrow range of chiral angle distribution in different layers of a MWBNNT. This indicates that the structure of MWBNNTs is dominated by a single chirality for the whole tube. This is significantly different from the case of multi-walled CNTs, in which chirality of each layer is independent of other layers [280–282]. Celik-Aktas et al. [275] also did not find obvious chirality preference for the MWBNNTs.

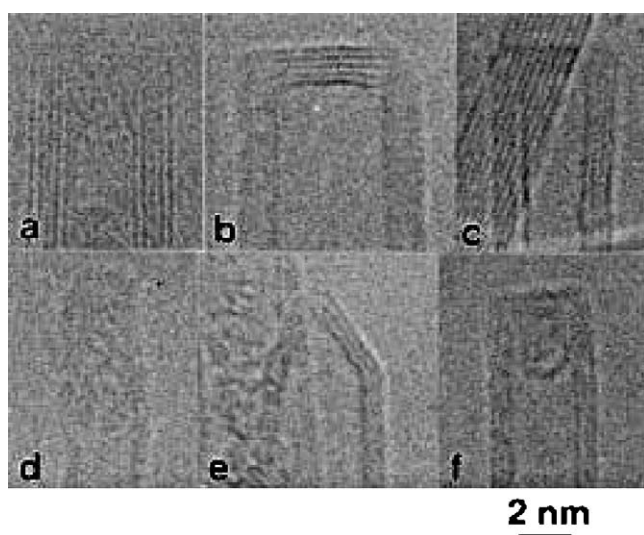


Fig. 7. High-resolution TEM images of tip-ends of BNNTs produced by arc-discharge. (a)–(c) Flat tips of tubes with various diameters and number of layers. (d) Amorphous-like termination of a SWBNNT. (e) Conically shaped end. (f) Not-empty tube end, filled presumably with an amorphous BN material. Reproduced with permission from [188].

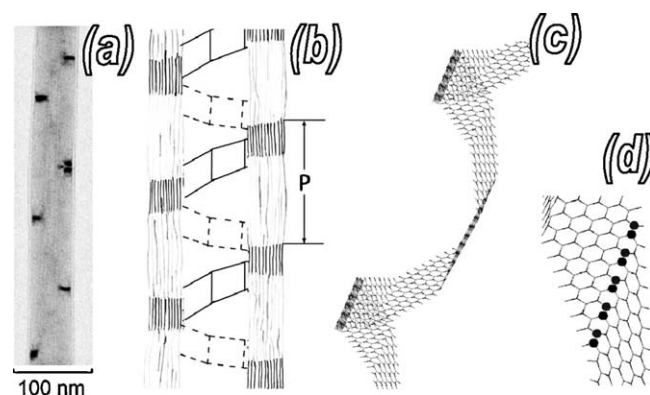


Fig. 8. (a) Typical TEM image of a multi-walled BNNT grown by BOCVD method. (b) Schematic of the proposed structure model for the BNNT shell. (c) Atomic structure model of a hexagonal helix in the case of a zigzag tube. (d) Line defects of a sp^3 bond in BN joining two facets. Reproduced with permission from [273].

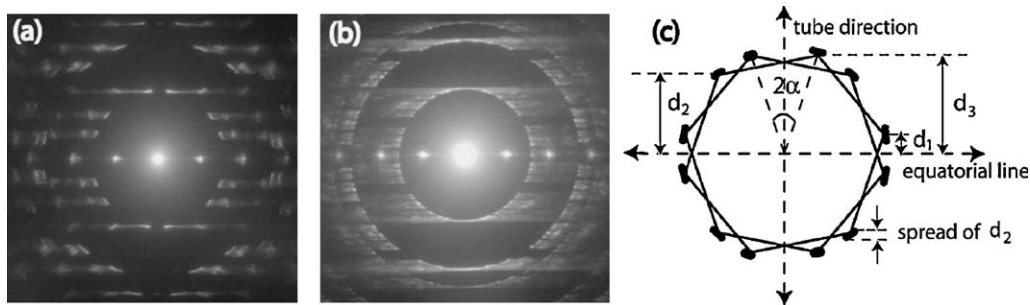


Fig. 9. (a) Typical electron diffraction pattern from a MWBNNT ($\alpha = 9^\circ$). The diffraction pattern was recorded from a tube of 33 walls. (b) An example of multi-helix diffraction pattern. This particular diffraction pattern shows the highest degree of randomness observed in BNNTs so far. The tube had as many as 37 walls. (c) Schematic for chiral angle measurement. Ratios of d_1 , d_2 , and d_3 are used to calculate the average chiral angle. Reproduced with permission from [275].

The atomic stacking of MWBNNTs was deduced from the high-resolution TEM images. For the BNNTs produced by an arc-discharge method, when the B and N atoms were alternately stacked (similar to hexagonal BN), the calculated images matched the experimental results very well [265]. However, in case of BNNTs grown by a CNTs substitution reaction, Golberg et al. [270] found coexistence of hexagonal and rhombohedral stackings within the tube shells. A competitive crystallization of *h*-BN and *r*-BN domains was proposed to explain the formation of these special structures.

5. Physical properties

5.1. Electrical properties

In spite of structure similarity, BNNTs possess totally different electronic structures with CNTs. With a constant wide band gap at 5.0–6.0 eV, unmodified BNNTs can be considered as insulating materials. A dielectric constant of 5.90 was predicted by theoretical calculations [71], which is universal for all BNNTs, regardless of their radius and chirality. As mentioned in Section 2.1, various methods were suggested to effectively modify the band structure of BNNTs. However, so far, only doping and applying electric field have experimentally been realized [283–285], while others methods are only deduced by theoretical calculations.

Actually, no perfect BNNTs can be fabricated experimentally. Radosavljevic et al. [286] confirmed that SWBNNTs made by laser ablation are intrinsically *p*-doped. The authors used a prototype BNNT field-effect transistor set-up (FETs) to confirm this. It was

also found that unlike tunneling domination in CNT FETs [287], the current injection in BNNTs near room temperature is controlled by thermionic emission over the Schottky barriers at the contacts. The barrier height is determined to be in a 250–300 meV range for the Ni–BNNT junctions.

Doping BNNTs by fluorine and carbon was found to effectively improve transport property of BNNTs [283,288]. Tang et al. [283] observed that the resistivity of BNNTs could be decreased from $\sim 300 \Omega\cdot\text{cm}$ to $0.2\text{--}0.6 \Omega\cdot\text{cm}$ by fluorine doping. Golberg et al. [289] tested transport properties of individual BNNTs doped with carbon. Instead of pure insulating and metallic behaviors of pure BNNT and pure CNT, respectively, the C-doped BNNTs exhibited well-defined semiconducting characteristics. These works implied that doping can be an effective way to modify band structure of BNNTs, which is consistent with the theoretical predictions.

Bai et al. [290] found the first signs of a piezoelectric behavior in MWBNNTs through experimental verification of a deformation-driven electrical transport in such tubes, as shown in Fig. 10. Fig. 10(a) and (b) indicates that the insulating character of an individual BNNT can dramatically be changed under tube bending. A notable current of several tens of nA may be detected passing through the tube. The transport was found to be reversible, and almost entirely disappeared after tube reloading. The transport was also found to be bias-sign sensitive (a positive to a negative range sweeping or vice versa), that is, a sort of hysteresis existed for the *I*–*V* curves taken on deformed BNNTs. A spontaneous polarization was proposed to explain this phenomenon [291]: when the directions of an applied field and a polarization field are

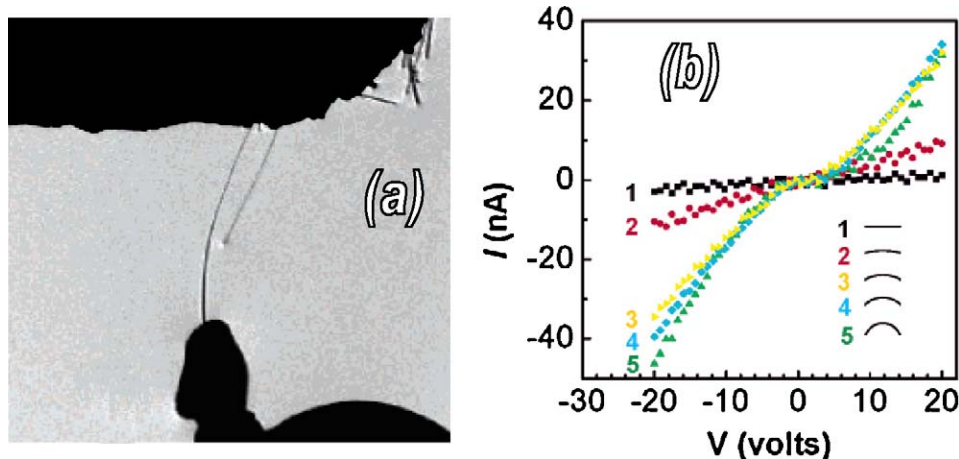


Fig. 10. (a) Bending of a BNNT mounted in a STM-TEM sample holder. (b) Serial representative *I*–*V* curves along with an increase in a BNNT bending curvature, the inset shows an approximate BNNT curvature. Reproduced with permission from [290].

coincident the carrier transport is smooth; while when these directions become opposite the transport is obstructed.

To sum up this section, BNNTs are mainly insulating materials. Under doping they may exhibit a typical semiconducting behavior. As a constant wide-band gap semiconductor with a tunable band gap, BNNTs still have a potential to function in nanoelectronic devices, especially under high temperature and hazard environments. However, doping of BNNTs seems to be difficult, so far, only few works have been reported. The researchers need to find an easy and controllable way to modify BNNTs.

5.2. Mechanical properties

The elastic properties of BNNTs have theoretically been investigated in many works [44,46–48,292–296]. Slightly different results were presented but all calculated values indicate a very high, but slightly smaller Young's modulus than for CNTs, as shown in Table 4 [44]. Compared with the numbers of ~ 1.22 – 1.25 TPa in CNTs, BNNTs possess a Young's modulus ranging from 0.837 to 0.912 TPa. The yield strength is also slightly smaller than that of CNTs. However, the theoretical works by Dumitrica and Yakobson [295] have shown that relative to CNTs, the BNNTs yield defects have lower activation but higher formation energies. This leads to an interesting phenomenon of strength crossover for these two important tube types (CNTs vs BNNTs) under different conditions: at moderate temperatures CNTs are stronger, while at high temperatures (or extremely long deformation times) the situation is reversed and BNNTs become more thermomechanically stable.

Chopra and Zettl [48] tested Young's modulus of single MWBNNTs synthesized by arc-discharge. The nanotubes were claimed to be highly crystalline with very few defects. By observing a thermal vibration amplitude of a cantilevered BNNT in TEM, an axial Young's modulus of 1.22 ± 0.24 TPa was elucidated, which is even higher than the theoretical values. In another experiment done by Suryavanshi et al. [46], a well established method, electric-field-induced resonance was adopted and an average effective elastic modulus of 722 GPa was documented for MWBNNTs grown by the BOCVD method. Instead of these indirect methods, Golberg et al. [47] used an integrated TEM-atomic force microscope (AFM) piezo-driven holder to directly test the elastic modulus. The values of 0.5–0.6 TPa were found for MWBNNTs grown by the BOCVD method. This data is

Table 4

Structural and elastic properties of nanotubes obtained from the tight-binding calculations. Young's modulus values given in parentheses were obtained from first-principles calculations. Reproduced with permission from [44].

$B_xC_yN_z$	(n,m)	D_{eq} (nm)	σ	Y_s (TPa nm)	Y (TPa)
C	(10,0)	0.791	0.275	0.416	1.22
	(6,6)	0.820 (0.817)	0.247	0.415 (0.371)	1.22 (1.09)
	(10,5)	1.034	0.265	0.426	1.25
	(10,7)	1.165	0.266	0.422	1.24
	(10,10)	1.360	0.256	0.423	1.24
	(20,0)	1.571	0.270	0.430	1.26
	(15,15)	2.034	0.256	0.425	1.25
BN	(10,0)	0.811	0.232	0.284	0.837
	(6,6)	0.838 (0.823)	0.268	0.296 (0.267)	0.870 (0.784)
	(15,0)	1.206	0.246	0.298	0.876
	(10,10)	1.390	0.263	0.306	0.901
	(20,0)	1.604	0.254	0.301	0.884
	(15,15)	2.081	0.263	0.310	0.912
Bd	(5,0)	0.818	0.301	0.308	0.906
	(3,3)	0.850	0.289	0.311	0.914
	(10,0)	1.630	0.282	0.313	0.922
	(6,6)	1.694	0.279	0.315	0.925
BC_2N II	(7,0)	1.111	0.289	0.336	0.988
	(5,5)	1.370	0.287	0.343	1.008

close to the theoretical values considering a number of defects existing in the tubes.

The only theoretical work on plastic deformation of BNNTs has revealed an unexpected weakness of $(n, 0)$ BNNTs [297]. The (n, n) BNNTs have comparable plastic limits to those of CNTs with similar wrapping angles. However, the $(n, 0)$ BNNTs have much smaller elastic limits against bond rotations. In the $(n,0)$ BNNTs bond rotation defects induced by plastic deformation quickly lead to bond breaking and thereby cause the tubes to be substantially weaker than would be expected from their purely elastic response.

5.3. Wetting properties

BNNT films were fabricated and used for water contact angle tests by the Yap's group [298]. BNNT films were found to be significantly more hydrophobic than BN thin films. The advancing water contact angles measured for BNNT films were of 145 – 160° compared to 44 – 52° for BN films. This difference is proposed to be induced by weak adhesion due to a small diameter of BNNTs and their low packing density in bundles. Upon compression a flat BNNT film surface morphology presents a smaller water contact angle of $\sim 135^\circ$ by reducing the area of a drop base in contact with the air pockets formed in between the fibers.

Yum and Yu [299] investigated wetting properties of an individual BNNT. A standard Wilhelmy method was adopted to analyze the interactions between BNNT and various liquids, including bromonaphtalene (non-polar liquid), poly(ethylene glycol), glycerol and water (polar liquids). The measured contact angles of a BNNT were comparable with CNTs but slightly larger [300]. Water showed certain fluctuations in forming contacts with a BNNT: both partial wetting and non-wetting behaviors were observed. The surface tension of BNNTs was calculated to be 27 mN m^{-1} , which is close to that of CNTs, i.e. 27.8 mN m^{-1} .

5.4. Thermal stability

BNNTs possess ultimately high resistance to oxidation [54,55,301,302]. In air, BNNTs are very stable up to at least 700°C . Highly crystalline and low-defect BNNTs may be stable up to 900°C with only the tube caps being oxidized [55]. Thermogravimetric analysis (TGA) reveals an increase in weight at 800 – 900°C due to oxidation. The exact temperature depends on a sample [29,54]. Fig. 11 shows a comparison of anti-oxidation ability of BNNTs fabricated by BOCVD and CNTs fabricated by CVD methods. Marked oxidation for BNNTs starts from 900 to 950°C the CNTs have a sharp decrease in weight at around 500°C . However, it should be noted that the anti-oxidation properties of

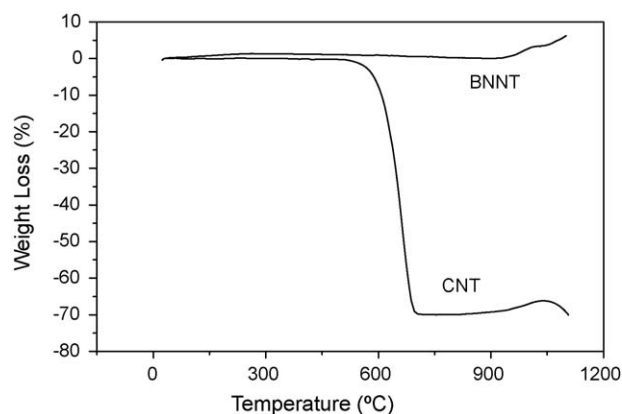


Fig. 11. Thermogravimetry (TGA) results of BNNTs and CNTs in air indicating much higher anti-oxidation ability of BNNTs.

both BNNTs and CNTs are strongly related to the tube structure perfection [54,55]. Obvious oxidation of arc-discharge grown CNTs takes place at around 700 °C [54]. No studies on arc-discharge grown BNNTs, which are thought to possess perfect structures and low defect concentrations, are available in the literature.

A very recent work by Xu et al. [302] reveals that due to partially ionic nature of the B–N bond, a strong electric field can remarkably decrease the breakdown temperature of individual MWBNNTs. BNNTs can be decomposed at 1000–1700 °C, which is much lower than 3000 °C for a bulk h-BN. The strong local electric field up to 0.28 and 0.80 V/nm was proposed to be responsible for the lower decomposition temperature: the ionicity of the B–N bond makes B atoms and N atoms feel a different force in the electrical field, thus, the action of this Coulomb force is to try to separate the B–N bonds.

5.5. Magnetic properties

Magnetism of BNNTs was treated theoretically. The O [137], C [23], V [131], Cr, Mn [87], Ge [136], F [132], Be [138] and H [129] doping were found to induce magnetism in BNNTs. The saturated magnetic moment was predicted to range from 1 to 3.98 μ_B per doping atom varying from element to element. The main part of magnetic moments comes from the doping atoms other than B and N atoms. It is interesting that C doping of BNNTs may result in an anti-ferromagnetically ordered semiconducting state, while B and N doping in CNTs gives a non-magnetic state [23]. This stresses the difference of electronic structure of BNNTs and CNTs. The reason why doping induced magnetism in BNNTs was not addressed experimentally might be due to strict restrictions for doping sites. For example, spontaneous magnetization is found in the H-BNNTs with two H atoms on two B atoms, next to each other, whereas no magnetism is observed when two H atoms are adsorbed on two neighboring N atoms or on two neighboring B and N atoms [129].

Ferromagnetism has never been experimentally observed [303]. Magnetic properties of MWBNNTs were investigated by electron paramagnetic and nuclear magnetic resonances and compared with the results for a h-BN powder [304–306]. All BN samples contained intrinsic paramagnetic defects assigned to the electrons trapped at the nitrogen vacancies. The quadrupole coupling constant and asymmetry parameter of BNNTs were close to those of h-BN. Also a very similar local symmetry of the B site and charge distribution over the B–N bond in BNNTs and h-BN were revealed. These facts explain why MWBNNTs hold very similar electronic properties to h-BN.

5.6. Thermal conductivity

It is an attractive point that BNNTs, electrically insulating materials, possess very high thermal conductivity [307]. Thermal conductivity of CNTs was demonstrated to be due to electrons and phonons, while for BNNTs, it is exclusively due to phonons [308]. Some theoretical works even predicts that, different from higher thermal conductivity of graphite compared to h-BN, BNNTs' thermal conductivity may be higher than for CNTs', i.e. 6000 W/mK [49,308,309]. However, this is only a speculation without detailed calculations. In another theoretical work done by Stewart et al. [51], a thermal conductivity of ~ 200 W/mK was obtained for a (8, 0) SWBNNTs. Isotopically pure ^{11}B BNNTs may have a 50% increase in thermal conductivity. This data is consistent with the experiments performed by the Zettl's group, as shown in Fig. 12 [310]. However, a big problem is that the latter experiments were performed on MWBNNTs with diameters of ~ 40 nm, and it has been known that with an increase of the nanotube's diameter, the thermal conductivity can be dramatically decreased. This is because instead of all-layers heat transport in bulky materials, only few shells are involved in thermal transport in nanotubes

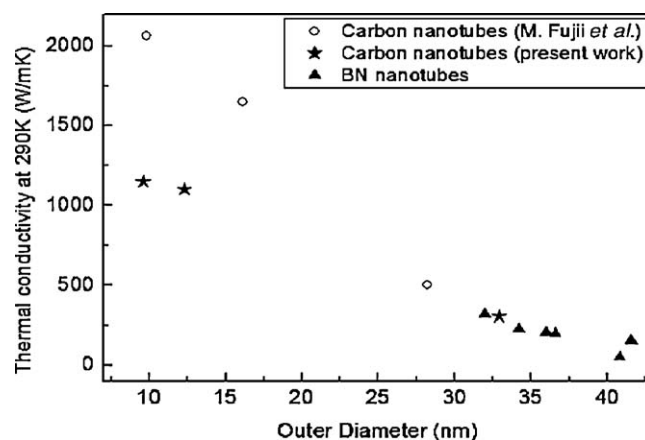


Fig. 12. Thermal conductivity of BNNTs at 290 K vs outer diameter. Data shown by open circles are from Ref. [311]. It should be noted that the data for CNTs and BNNTs by this work maybe comparable because the experimental condition are same. Reproduced with permission from [52].

[312]. For CNTs' with a diameter of around 40 nm, the thermal conductivity was also only ~ 300 W/mK, in contrast to the theoretical value of 6000 W/mK for a single-walled CNT. Thus, it is believed that natural BNNTs have fairly high, but slightly smaller thermal conductivities compared to CNTs of the same diameter, whereas isotopically pure ^{11}B BNNTs rival CNTs. Moreover, it was shown that similar to a variety of one-dimensional systems, the room temperature thermal conductivity of BNNTs does not obey the Fourier's empirical law for thermal conduction [308].

There were other two works where thermal conductivity of BNNTs was experimentally tested. Chang et al. measured thermal conductivity of a BNNTs' mat, a very low value of ~ 1.5 W/mK at room temperature was obtained due to an extremely high interfacial thermal resistance [313]. A simple route was established to roughly estimate thermal conductivity of individual BNNTs and a range of 120–960 W/mK was found. In another work performed by Tang et al. [314], a BNNTs mat was detected to have thermal conductivity of 4 W/mK, whereas it can be up to ~ 14 W/mK for a mat consisting of bamboo-like structured BN fibers.

5.7. High pressure phase transition

Two theoretical studies dealt with the deformation and phase transitions in BNNTs bundles. Guerini et al. [315] investigated a transformation of a bundle consisting of (16, 0) BNNTs under pressure from 0 to 4 GPa. A discontinuous reduction of volume was observed at 1 GPa, and a symmetry-breaking transition was confirmed, similar to the case of CNTs. In calculation by Hao et al. [316] it was demonstrated that a unique sp^2 – sp^3 – sp^2 transition and a series of new BN crystal phases appeared under high pressure. However, the condition of appearance of these transitions was critical: the BNNTs in the bundle should be arranged according to the so-called an antiparallel polar bonds rule. This might be the reason that so far this unique transition has not been observed in the experiments.

High-pressure experiments were performed on BNNTs under monitoring by Raman spectroscopy or X-ray diffraction. The samples were all made by the BOCVD method. However, contradicting results were obtained. In case of Raman studies [317,318], BNNTs were detected to undergo an irreversible phase transition, possibly to an amorphous phase, at a much lower pressure of ~ 12 GPa, as compared to ~ 51 GPa in CNTs. This was explained due to ionic nature of the B–N bonds. By contrast, in X-ray diffraction studies [319], a w-BN phase appeared at 3.2 GPa and then up to 19.1 GPa the sample remains crystalline.

5.8. Optical properties

Compared with other property investigations of BNNTs, a significant amount of works dealt with theoretical and experimental analysis of BNNTs' luminescence and absorption. As mentioned in Section 2.1, recent theoretical works have revealed that the absorption behavior is strongly related to excitonic effects in BNNTs [318]. However, most of theoretical works on optical properties of BNNTs were based on band structure calculations [320–326]. The dependence of luminescence and absorption spectra on BNNTs' chiralities and external transverse field was demonstrated [327,328].

Lauret et al. [32] investigated optical absorption of SWBNNTs fabricated by a laser ablation method. Two optical transitions at 4.45 and 5.5 eV were observed and attributed to the SWBNNTs' transitions. The nature of these lines was discussed and two interpretations were proposed. One explanation is that these optical transitions occur between the van Hove singularities in the one-dimensional density of states of SWBNNTs. However, another explanation, attributing the 4.45 eV line to an exciton looks more plausible. More information was not provided because the experiments were performed at room temperature other than low temperature [329].

The studies on photoluminescence and cathodoluminescence showed that BNNTs are an effective violet and ultra-violet light emission material. The emission peaks mainly depend on samples. The following peaks were found: ~230, ~279, ~338, ~460 nm [34–37,330–342]. The explanations were complicated for different peaks, including band-gap transitions [330,341], excitonic effects [333], or O-center emission [34] in different papers. Other important conclusions drawn under the luminescence experiments are as follows: (1) time-resolved photoluminescence demonstrated that a charge recombination process in BNNTs is dominated by the fast recombination occurring within individual

BN layers, and the slower decay process is due to the charge transfer and recombination across different BN layers [35]. (2) A phonon replica structure of cathodoluminescence of natural BNNTs and $^{10}\text{BNNTs}$ revealed isotopic effect of B in BNNTs [334]. (3) Chen et al. [331] reported a tunable light emission of Eu-doped bamboo-like BN structures, the broad emission band was shifted by adjusting Eu concentration in BN fibers.

6. Modification

As for all wide band gap semiconductors, modification can effectively tune BNNTs' electronic structure and expand their applications. However, due to the chemical inertness and poor wetting properties [299], experimental modifications of BNNTs have been much fewer than theoretical investigations, as summarized in Table 2. Fig. 13 shows the experimental strategies currently developed for modification of BNNTs. These will be described separately in the following sections.

6.1. Doping

Only F [283], Eu [331,343] and C [74,78,85,344] were successfully doped into BNNTs. BF_3 and NH_3 were used as precursors for the growth of F-doped BNNTs, and MgCl_2 was adopted as a catalyst [283]. The F-doped BNNTs possess a collapsed structure and improved electrical conductivity. However, discrepant conclusions were made in regard of F-doped BNNTs: it was not fully clear were they *p* type or *n* type semiconductors [77,79,86]. Eu-doped BN bamboo-like fibers were produced by a ball milling method using a mixture of B and Eu as precursors [331]. The Eu doping was claimed to induce a dramatic change of luminescence properties of BNNTs. Carbon doping was predicted to continuously tune BNNTs' electronic structure. Golberg et al. [346] prepared a series of BN nanotubes doped with carbon (they can also be called

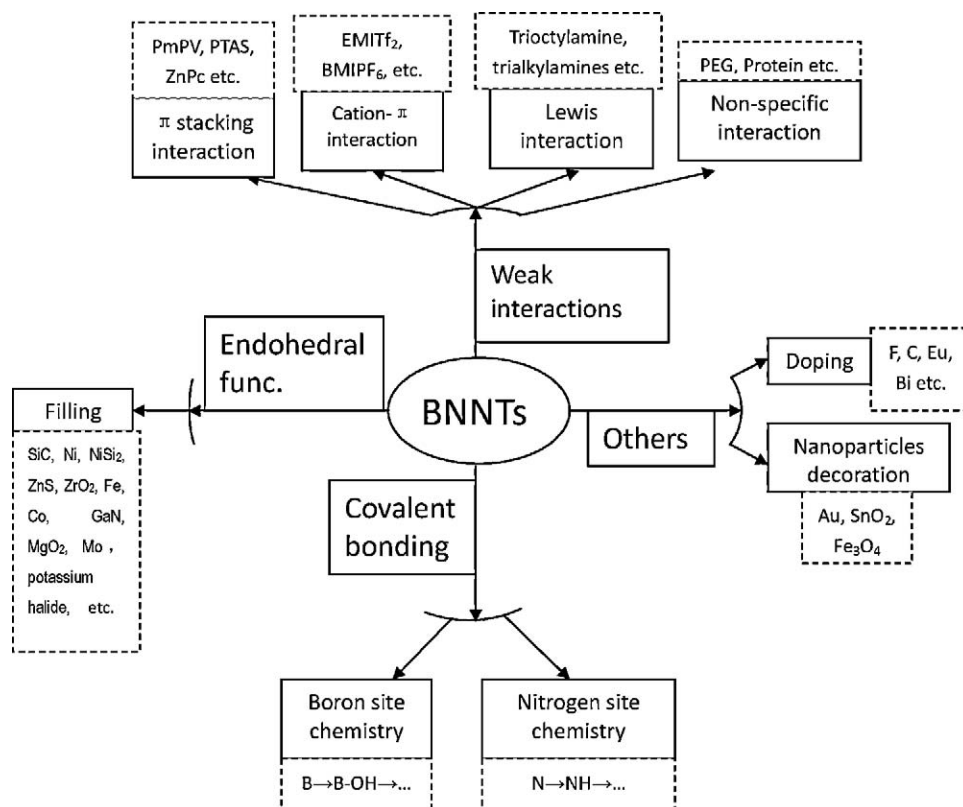


Fig. 13. Schematic diagram of chemistry with BNNTs.

BCN nanotubes) by controlling a reaction time. The detailed chemical composition analysis revealed that the tubes maybe homogeneous BCN NTs or phase separated BN-C NTs depending on the synthesis conditions.

Since doping has been proved to be a powerful tool to tune properties of semiconductors, more effective doping methods are supposed to be developed for BNNTs. However, challenges exist. For example, controlling the concentration of a dopant is an extremely difficult project. Currently, even carbon doping to BNNTs cannot be well controlled. This also makes it is difficult to study properties of doped BNNTs. On the other hand, some experiences gained under doping of various BN materials can be used as a reference. For example, C and O doping to BN has been shown to be an effective method to tune luminescence properties of BN nanoparticles [345], similar methods should be developed for BNNTs.

6.2. Filling

Various materials were filled in BNNTs, including metals and semiconductors, as summarized in Table 5 [347–366,208]. Due to poor BNNT wetting, most of the well-established filling methods for CNTs using capillarity or wet chemistry were not effective [347]. Thus, most filled BNNTs were produced during a high temperature growth. The filling processes were not under control and in some cases, the filled BNNTs were only occasionally observed in the samples. The property and application studies on filled BNNTs were rather rare, only the electron field-emission of SiC-filled BNNTs [351] and a molecular oxygen generator by MgO₂-filled BNNTs [364] were demonstrated. However, in principle and theoretically, the filled BNNTs can be rather useful. For example, metal-filled BNNTs can be a nanoscale “lacquered wire”, and C₆₀-filled BNNTs can work as a special nanoswitch [366].

Due to superb structural stability and chemical inertness BNNTs can be a unique nanosize test tube for chemical reactions. The related studies will be a challenge for BNNTs' fillings in the future. Moreover, drugs deliveries may be accomplished within the BNNT cavities, which may have potential applications in a novel branch of the nanomedicine.

6.3. Nanoparticles decoration

BNNTs' potential applications can be extended by functionalizing them with different nanoparticles. Some nanoparticles, such as SnO₂, Au, Fe₃O₄, were attached to the surfaces of BNNTs due to intrinsic non-specific interactions [12,36,369]. The interaction between BNNTs and SnO₂ nanoparticles is very strong it is easy to obtain BNNTs fully covered with SnO₂. Detailed studies reveal that the characteristic lattice distances of both BNNTs and SnO₂ have been slightly changed due to the strong interactions between them, which may due to the formation of Sn–N bonds or electrostatic tube/particle interactions [369]. The other nanoparticles can only partially cover BNNTs. To improve the interactions between nanoparticles and BNNTs, some special methods were developed. For example, Sainsbury et al. [368] prepared BNNTs fully covered with Au particles through utilizing the S–Au chemistry: firstly the tubes were functionalized with a S-containing compound, followed by the Au nanoparticle attachment. Very recently, Huang et al. [370] developed an ethanol-thermal process and successfully attached uniformly distributed Fe₃O₄ nanoparticles on the BNNT surfaces. The magnetic properties of the obtained nanocomposites were studied and magnetism-driven manipulation of BNNTs was demonstrated.

One potential application of nanoparticles decoration is to combine the diverse functional properties of nanoparticles themselves with the large surface area of BNNTs. However, most works on nanoparticle decoration on BNNTs have been performed on multi-walled structures with relatively low surface areas. Nevertheless these studies are still useful for understanding the general BNNT-nanoparticles bonding mechanisms. Follow-up studies on single-walled BN tubes and subsequent application prospect elucidations are awaited in the future.

6.4. Weak interactions

Different from carbon's delocalized π electronic structure, BNNTs possess a localized π electronic structure that results in electrically insulating properties [371]. Though it is so, the π electronic structure enables BNNTs to interact with materials

Table 5
Summary of filling works on BNNTs.

Filled materials	Method	Comments	References
SiC	B + SiO ₂ and NH ₃ as precursor, on Ni covered graphite, at 1500 °C; or Si + In ₂ O ₃ in a BN crucible, at 1600 °C under CH ₄ ; or B ₂ O ₃ powder covered with CNTs was placed close to SiO ₂ and Si mixture, at 1753 K under N ₂	All BNNTs are filled, BN layers are curled; electrically insulating; improved anti-oxidation ability and reduced turn-on fields for field-emission of SiC nanowires	[347,351,353,367]
Ni, NiSi ₂	B + MgO and NH ₃ as precursor, Ni, and Si as substrate, at 1100–1300 °C	Only some BNNTs are partially filled	[348]
ZrO ₂	ZrB ₂ powder reacts with NH ₄ Cl under mixture of N ₂ and NH ₃ gases	All BNNTs are filled, BN layers are curled	[349]
ZnS	B–N–O precursor, ZnS whiskers, at 1700 °C under N ₂ ; or ZnS placed above B–N–O precursor at 1600 °C under N ₂ /NH ₃ atmosphere	BN-coated ZnS nanoarchitectures	[352,363]
KCl, KI, KBr	BNNTs sealed in evacuated quartz ampoules together with KI, KCl, or KBr, respectively, heated at 670–740 °C	Ex situ filling, well-defined morphology	[354]
Fe	Fe ₄ N and B mixture heated up to 1000 °C under N ₂ ; or FeB nanoparticles as catalysts, ball-milling water-free FeCl ₃ and NaBH ₄ , followed by annealing in argon at 500 °C	Fe particles and wires occasionally observed filled in BNNTs	[357,358,360–361]
Fe–Ni alloy and Co, Mo, Y	Preliminary filling of C-based nanotubes with MoO ₃ or pure metal (Fe–Ni, Co), followed by C to BN conversion	Most BNNTs are filled by clusters and/or wires	[358,361,362,365]
GaN	Ga ₂ O ₃ , Ga, and B powder as precursor, iron oxide as catalyst, at 1100 °C under NH ₃	BN layers are curled, some nanotubes are filled	[359]
Yttrium	Arc-melting method in an Ar/N ₂ gas mixture from YB ₆	Very few BNNTs are filled	[362]
Si–SiO ₂	SiO powder placed above B–N–O precursor at 1200 °C under Ar atmosphere to synthesize Si–SiO ₂ nanocables, then heated to 1600 °C under N ₂ /NH ₃ atmosphere to sheath the cables with BN	Si/SiO ₂ /BN structure	[363]
MgO ₂	B + MgO at 1300 °C under NH ₃ . BNNTs crystallized on an Mo substrate	Nanoscale oxygen generators confirmed with TEM	[364]
C ₆₀	BNNTs sealed in an evacuated quartz ampoule together with obtained C ₆₀ powder heated to between 550 and 630 °C for 24–48 h	Well-defined morphology	[355,366]

through π stacking interactions [14,372–374] and cation– π interactions [375]. Moreover, electrostatic interactions, interactions between Lewis acids and bases [376,377], and some non-specific interactions [13,378–381] were also used to modify BNNTs.

Soluble BNNTs were obtained by Xie et al. [13] by using an amine-terminated oligomeric poly(ethyleneglycol) (PEG1500N) to interact with BNNTs. The functionalized BNNTs well dispersed in water. The interactions between B sites on BNNTs with amino groups in PEG1500N were suggested to be behind this phenomenon, however more details were not presented. In addition, non-specific interactions were also used to bind various proteins and DNA [379,381] on the surfaces of BNNTs, or wrap BNNTs with polymers, such as poly(vinyl pyrrolidone) (PVP) [373] to improve BNNTs' solubility or fabricate hybrid materials. It is believed that the cause of the non-specific interactions may be electrostatic interactions, or interactions due to surface polarization of BNNTs.

The interactions based on π electronic structure could be π stacking interaction or cation– π interaction. The π stacking interaction was used to wrap BNNTs with polymers, such as poly[m-phenylenevinylene-co-(2,5-dioctoxyp-phenylenevinylene)] (PmpV) [14] and polyaniline in order to improve BNNTs solubility in organic solvents or to form composites. Some dyes, such as zinc phthalocyanine [372] and perylene-3,4,9,10-tetracarboxylic acid tetrapotassium salt (PTAS) [374], can strongly interact with BNNTs and induce dramatic variations in optical properties of dyes due to a charge transfer. It was proposed that BNNTs can more effectively interact with molecules having π electronic structure than CNTs. However, no exact evidences were presented so far. In addition, BNNTs were found to interact with some ionic liquids, such as 1-ethyl-3-methylimidazolium trifluoromethanesulfonate (EMITf₂) and 1-butyl-3-methylimidazolium hexafluorophosphate (BMIPF₆) [375] to form a gel with new molecule ordering through cation– π interactions.

The vacant *p*-orbitals of the B atoms distributed in the BNNTs' lattice may exhibit the behavior of a Lewis acid, which interact with the electron lone-pair of the phosphorus or nitrogen atoms (Lewis base). This was demonstrated by Pal et al. [376] by checking interactions between BNNTs and Lewis bases, such as alkylamines and phosphines. The Lewis bases functionalized BNNTs were found to be well dispersed in various organic solvents.

The above mentioned experiments were all carried out on MWBNNTs. A very recent experiment revealed that SWBNNTs might possess different accessibility to molecules: PEG1500N or trioctylphosphine, which were proved to effectively interact with MWBNNTs, did not interact with SWBNNTs [377]. The reason is still unclear. Maguer et al. [377] developed a versatile method to functionalize BNNTs utilizing a new family of Lewis bases—the quinuclidines. Subsequently, a series of quinuclidine derivatives with different molecular chains were synthesized. These interacted with both SWBNNTs and MWBNNTs successfully. For example, a quinuclidine bearing a lipophilic chain could induce solubilization of BNNTs in organic solvents, while glycine-grafted quinuclidine was used to make water soluble BNNTs.

6.5. Covalent bonding

The covalent bonding chemistry of BNNTs was only developed in recent years. The novelty of BNNTs' chemistry is that it may go on either N sites and/or B sites [90,111]. This may result in different modifications of BNNTs' properties. The N site chemistry is mainly relied on amino group chemistry [15,101,368,381,382], the self-formed amino groups may appear during the growth or there may exist deuterogenic amino groups. The present authors for the first time reported a chemical reaction between the –COCl groups in stearoyl chloride and amino groups on the BNNTs [15]. This reaction was used to connect long alkyl chains to BNNTs. The

modified BNNTs were well dispersed in common organic solvents. The similar method was adopted to connect short alkyl chains and naphthalene groups to BNNTs, or even graft polymer chains on BNNTs, in the frame of an atom transfer radical polymerization approach [382]. However, since the amino groups utilized in the above-mentioned experiments were self-formed during the growth, the achieved concentration was rather low. Ikuno et al. [381] developed a method to increase concentration of active N sites through a NH₃ plasma treatment. The amino group concentration was effectively enriched followed by thiol-functionalization of BNNTs and self-assembly of gold nanoparticles on them.

The B site covalent chemistry was only recently demonstrated by the present authors. Since most of the organic chemistry was based on the C and N species, the B chemistry was much less popular [383]. In our studies, we found that B sites could be activated by oxidizing BNNTs in H₂O₂ at high temperature and high pressure conditions. Hydroxyl groups were attached on B sites of BNNTs and the hydroxylated BNNTs could be well dispersed in water upon sonication opposed to hydrophobic properties of pristine BNNTs. More importantly, the B-site-activated BNNTs can be starting materials for further modification through hydroxyl groups, e.g. an esterification reaction with carboxyl groups can be performed. Thus, it was proposed that this chemical route could be a universal way to activate BNNTs for various chemical functionalizations.

The chemistry of BNNTs is still in its early stage. General strategies for multi-step chemical modifications have still been not established. Actually, unlike CNTs, for which one can use many organic chemical reactions as the references, modifications of BNNTs, especially on their B sites are very difficult, since the latter are not common chemically active sites in organic chemistry. At the current stage, most works are devoted to a design of modifications methods for BNNTs instead of designing the final products. This explains why the functions of functionalized BNNTs have not been properly demonstrated. Moreover, even after surface modifications, although the BNNTs' dispersibility in many solvents can be improved, it is still difficult to obtain high concentration solution of BNNTs, which is primary important for applications, such as composite materials fabrication, etc. As having been revealed, SWBNNTs may exhibit different surface chemical properties compared with MWBNNTs. Therefore, understanding the mechanisms and developments of new functionalization methods for SWBNNTs are the challenging tasks.

7. Application

No real applications of BNNTs were developed so far. One reason is that as for any nanosize materials, the Society needs some time to understand the truly intrinsic properties. The other reason is that till now the scientists cannot control the BNNTs' synthesis and properties well. However, some investigations on BNNTs are closely related to applications, such as hydrogen storage, biocompatibility tests, composite materials fabrication, etc. These will be presented in the following sections.

7.1. Hydrogen storage

As an important potential application for nanomaterials, the hydrogen storage of BNNTs was intensively studied by theoretical calculations. However, totally different results were obtained due to different models and calculation methods adopted. Some reports claimed that both physisorption and chemisorption are not energetically favored, thus, BNNTs are not good candidates for hydrogen storage [177]. The other reports stated that hydrogen storage capacity of BNNT arrays is obviously much better than for

CNTs, and can reach and/or exceed the commercial standard presented by the US Department of Energy [22]. Thus, to date, it is difficult to make a well-established judgment on hydrogen storage capacity of BNNTs using only theory. However, an accordant conclusion can be made, e.g. the defects, doping, and/or deformation of BNNTs may remarkably improve their ability to absorb hydrogen [112].

In the pioneering experiment by Ma et al. [19] a 1.8 wt.% hydrogen uptake was recorded for BNNTs at 10 MPa, and the bamboo-structured BN fibers had a 2.6 wt.% hydrogen capacity. This is a remarkable increase compared to a value of 0.2 wt.% for a commercial powder. Chemical absorption was proposed to be the main absorption mechanism. Subsequently, Oku and Kuno [306,384] also found that a mixture of BNNTs and BN cages can absorb hydrogen up to ~3 wt.%. Tang et al. [179] synthesized BNNTs with collapsed structures. The latter had a specific area up to 789 m²/g compared with conventional values for BNNTs of 254 m²/g. These collapsed BNNTs were reported to possess 4.2 wt.% hydrogen absorption ability at 10 MPa. Instead of a gravimetric method adopted in the above-mentioned experiments, Chen et al. [385] used an electrochemical measurement to test hydrogen accumulation in BNNTs and a disappointing result of only ~0.25 wt.% of hydrogen absorption was obtained. However, BNNTs are still supposed to possess a higher chemical activity than a conventional BN powder. The rather modest data is thought to be due to a normal atmosphere of 0.1 MPa used in the latter experiments. The experimental studies on BNNTs' hydrogen storage are still very few, and similar to theoretical works, discrepant results have been reported. There have still no detailed and comprehensive studies in regard of BNNTs' hydrogen storage.

7.2. Nanofillers for composites

The exciting properties of BNNTs, such as high elastic modulus [47] and high thermal conductivity [49,310,313] make them advantageous for novel nanofillers in composite materials to obtain mechanical reinforcement, high thermal conductivity and a low coefficient of thermal expansion in a matrix. BNNTs composite studies were only initiated in recent years because the above-mentioned difficulties in the high-yield synthesis of pure BNNTs. So far, polymeric [16,56,382,386–389] and ceramic composites [17,390] were fabricated, however, the metal composites were not demonstrated as yet.

The present authors initiated the works on polymeric composites of BNNTs [16]. BNNTs were firstly used to realize the mechanical reinforcement. It was shown that BNNTs can effectively improve the elastic modulus of polystyrene and polymethyl methacrylate (PMMA) [16,382,389] by ~20% with only a 1 wt.% fraction of BNNTs. Better mechanical reinforcement could be achieved with the help of a surfactant, such as PmPV, which was found to improve both dispersibility and interfacial interaction between BNNTs and a polymer. Following this idea, hydroxylated BNNTs were used to reinforce polycarbonate (PC) and polyvinyl butyral (PVB) [383]. Compared with pristine BNNTs, hydroxylated BNNTs were demonstrated to be more effective. Up to more than 30% improvement of elastic modulus was recorded for both polymers, compared with around 20% improvement with

pristine BNNTs. The improvement of yield strength was also documented. It should be noted that with the covalently modified BNNTs, the mechanical properties achieved are fairly close to those predicted in theoretical models. Thus, it is suggested that BNNTs are strongly bonded to a polymer matrix and the external tensile load is transmitted from a matrix to BNNTs through the interfacial shear stresses.

The published data with respect to the mechanical reinforcement using BNNTs are comparable with the CNTs' data. Actually, the quality of nanofillers determines the resultant mechanical reinforcement achieved. For CNTs, discrepant results were reported because the CVD-grown CNTs possess much more defects compared with arc-discharge grown CNTs. Therefore, much modest reinforcement was obtained when CVD-grown CNTs were used as fillers [391]. So far, BNNTs utilized for the reinforcement have mostly been grown by the BOCVD method at a temperature up to 1500 °C. Such tubes possess the elastic modulus of 0.5–0.7 TPa [290]. The good quality of the nanotubes guarantees a decent improvement of the mechanical properties. However, till now, only MWBNNTs were adopted for testing, they possess a rather low aspect ratio (100–300). It is believed that with thinner BNNTs, somewhat better results can be achieved.

A novelty of BN materials compared with C materials is that BN materials are electrically insulating, but similarly to C, they possess the high thermal conductivity [310]. Therefore, another important application of BNNTs as nanofillers is relied on their use for creation of new thermo-conductive insulating polymeric composites. BNNTs were firstly used to improve thermal conductivity of PMMA [372]. With a 10 wt.% BNNTs fraction, the thermal conductivity of PMMA was improved ~3-fold. Very recently, four polymers were embedded with a high fraction of BNNTs via a filtering-absorbing method [56]. It was shown that more than 21-fold improvement of thermal conductivity can be achieved, as shown in Table 6. Moreover, it was demonstrated that the coefficients of thermal expansion of these polymers were dramatically reduced while decent break-over voltage and hardness were kept.

BNNTs' polymeric composites can be novel packaging materials. As indicated above, they can be efficient for electronic devices. The high thermal conductivity can help heat-releasing, which allows high performance of a device. Moreover, due to a wide band gap of BNNTs, polymeric composites with low BNNTs' fraction can keep decent transparency. Thus, they can be used as effective packaging materials for organic photovoltaic devices, as demonstrated by Ravichandran et al. [386].

To date only two papers have been published in regard of ceramic–BNNTs composites [17,390]. The robustness of BNNTs to oxidation is a solid advantage for the fabrication of BNNTs ceramic composites. Bansal et al. [17] firstly used BNNTs synthesized by ball-milling to fabricate barium calcium aluminosilicate glass composites. The addition of 4 wt.% BNNTs increases the glass strength up to 90% and the fracture toughness up to 35%. Huang et al. [390] investigated mechanical properties of Al₂O₃-BNNTs and Si₃N₄-BNNTs composites. No obvious Vickers hardness and Young's modulus improvement were revealed. However, it was observed that BNNT small additions had been able to dramatically enhance a high-temperature superplastic deformation (SPD) of Al₂O₃ and Si₃N₄, which was explained in line with the microstructure

Table 6
Thermal conductivity improvement of polymeric composites of BNNTs. Reproduced from with permission from [56].

Polymers	BNNTs' fraction (wt.%)	Pure polymer (W/mK)	Polymer–BNNTs composites (W/mK)	Improvement (multiple)
Polyvinyl butyral	18	0.24 ± 0.03	1.81 ± 0.08	7.5
Polystyrene	35	0.18 ± 0.01	3.61 ± 0.21	20.1
Polymethyl methacrylate	24	0.15 ± 0.03	3.16 ± 0.26	21.1
Polyethylene vinyl alcohol	37	0.17 ± 0.04	2.50 ± 0.05	14.7

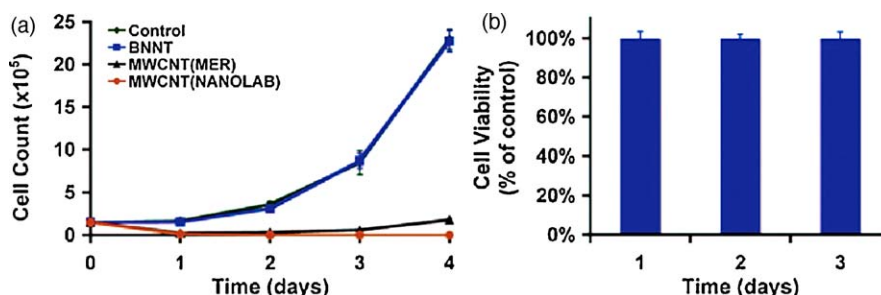


Fig. 14. BNNTs are not cytotoxic. (a) BNNTs do not inhibit HEK 293 cell proliferation, while CNTs are shown to induce apoptosis in HEK 293 cells; (b) BNNTs have no effect on cell viability. HEK 293 cells were cultured with BNNTs or with media alone. Cell viability is expressed as the percentage of viable cells compared to untreated controls. Error bars represent the standard deviation for three replicates. Reproduced with permission from [397].

variations at grain boundaries and interactions between the BNNTs and a matrix.

7.3. Bio-compatibility and applications

For a nanomaterial, biocompatibility should be considered prior to any practical applications. Ciofani et al. [392–396] initiated the first biocompatibility tests on BNNTs [392–396]. In their experiments, PEI-coated BNNTs were used for *in vitro* tests on a human neuroblastoma cell line [392,393]. The results indicated very good cell viability up to a concentration of 5.0 $\mu\text{g}/\text{ml}$ of BNNTs in the cell culture medium. At a higher concentration, a moderate toxicity was noticed, which was assigned to PEI coating instead of BNNTs themselves. Subsequently, Ciofani et al. [394–396] confirmed the complete cytocompatibility of poly-L-lysine coated BNNTs with both glioblastoma and primary fibroblast cells. Chen et al. [397] used pristine BNNTs for *in vitro* tests although the authors formed aggregates in the culture media. The experimental results for BNNTs do not appear to inhibit cell growth or induce apoptotic pathways in the HEK 293 cells. In contrast, CNTs have been shown to induce apoptosis in the cells, as shown in Fig. 14. The work by Chen et al. [397] documented that the surface of functionalized BNNTs may have glycodendrimers capable of interacting with proteins and cells. Moreover, BNNTs could deliver DNA oligomers to the interior of cells with no apparent toxicity. These studies demonstrated relevant safety of BNNT, which may have potential applications in the biological systems where the toxicity of CNTs is a problem.

Explorations of BNNTs' bio-applications have just been started and very few works have been done. A recent experiment demonstrated that small molecules could be translocated across the cell membrane of human neuroblastoma cells by using a very low electrical field in the presence of BNNT mediated electroporation. Thus BNNTs were proposed to act as small probes able to enhance cell permeabilization [398]. In another experiments, folate-functionalized BNNTs were demonstrated to act as B delivery agents to malignant glioblastoma cells [394].

Actually, the biocompatibility and bio-applications of inorganic nanomaterials have become hot topics in recent years. However, due to natural complexity of nanomaterials, frequently, the discrepancies in results are obtained during different experiments on the same kind of a nanomaterial. For example, CNTs with different impurities exhibit different biocompatibilities [399]. The intrinsic properties of CNTs have even been hidden in some experiments due to those impurities. Therefore, we believe that more experiments should be performed on BNNTs with different preparation histories to confirm their intrinsic properties.

7.4. Other applications

Although very few papers explored other possible applications of BNNTs (and some of them are solely based on theoretical

studies) some interesting results were demonstrated. For example, Huang et al. [400] designed a submicrometer-sized pH sensor based on biotin–fluorescein-functionalized MWBNNTs. The sensing mechanism is based on pH-dependent photoluminescence and Raman signals in fluorescein molecules attached on BNNTs. Lee proposed a gigahertz oscillator made of DWBNNTs. Higher frequencies than for an CNT oscillator were predicted [401]. Belonenko and Lebedev [176] showed that BNNT intercalated with alkali metal atoms and alkaline-earth metal ions can be used as two qubit cells for a quantum computer. It was documented that the antiferromagnetic state of a linear chain of intercalated atoms and ions had turned out to be energetically more favorable. In the Zettl's group experiments, a robust thermal transport against bending was found for CNTs, as well as for BNNTs. Based on this discovery, these nanotube system were proposed to be excellent and robust phonon waveguides [402].

8. Summary

Current studies have demonstrated that the following issues of BNNTs are in the present agenda.

1. Various growth methods have been developed for fabrication of BNNTs, including arc-discharge, laser ablation, template synthesis, CVD, chemical reaction, ball-milling and others.
2. The morphology and structure of BNNTs varies from sample to sample. In addition to standard tubular structures, the special features may include the cross-sectional polygonization and double helix structure appearance.
3. A wide BNNT band gap of around 5.0–6.0 eV may be tunable by functionalization, doping, and applying electric field.
4. Excellent mechanical properties, high thermal conductivity, superb thermal and anti-oxidation stabilities, good biocompatibility and effective light emission are the key selling points of BNNTs.
5. A variety of chemical methods through weak interactions and covalent bonding have been developed to obtain functionalized and dispersible BNNTs.
6. Some preliminary applications, such as polymeric and ceramic composites, and sensors have been demonstrated.

However, despite the many advantages mentioned, still many problems exist. High quality BNNT samples are still difficult to fabricate in large quantities, compared with a kilograms level growth of CNTs. This hinders the progresses of studies in regard of BNNTs' chemistry and applications. The constant wide band gap results in electrical insulation, which makes it difficult to develop realistic electrical applications. Although many methods were predicted by theoretical calculations to modify BNNTs' properties effectively, they are rarely realized experimentally. Therefore, at a current stage, the two issues are fundamental for the BNNTs' studies: one is to find an

effective way to synthesize kilograms level highly pure BNNTs, the other is to develop a method to effectively and reliably tune the BNNTs' electronic structure.

As far as the future applications of BNNTs are concerned, the following issues might be attractive based on their intrinsic properties. The good biocompatibility of BNNTs and novel surface chemical properties are able to make BNNTs useful in nanomedicine applications. However, a long-fiber-structure may be a disadvantage. Thus, short BNNTs and BNNTs' derivatives may be more practical in bio-applications. Fortunately, according to current studies, BNNTs are not so difficult to be shortened. BNNTs with perfect straight morphologies and high mechanical strength may be used as tips of a scanning probe microscope. Although BNNTs are not highly conductive, the chemical inertness of BNNTs makes it useful for probing some special materials. In addition, dedicated doping of BNNTs may open the door to novel and diverse applications. For example, C-doped BNNTs with the adjustable band gap may be used in many kinds of semiconductor devices. In addition, applications employing high thermal conductivity of BNNTs are also highly anticipated.

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