

Recent Advances and Perspective on Boron Nitride Nanotubes: from Synthesis to Applications

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Abstract

Boron nitride nanotubes (BNNTs) are emerging nanomaterials with analogous structures and similarly impressive mechanical properties to carbon nanotubes (CNTs), but unique chemistry and complimentary multifunctional properties including higher thermal stability, electrical insulation, optical transparency, neutron absorption capability, and piezoelectricity. Over the past decade, advances in synthesis have made BNNTs more broadly accessible to the nanomaterials and other research communities, removing a major barrier to their utilization and research. Therefore, the field is poised to grow rapidly and see the emergence of BNNT applications for a variety of applications ranging from electronics to aerospace materials. A key challenge, that is being gradually overcome, is the development of manufacturing processes to make “neat” BNNT materials. This overview highlights the history and current status of the field, providing both an introduction to this Focus Issue – BNNTs: Synthesis to Applications – as well as a perspective on advances, challenges and opportunities for this emerging material.

Keywords: nanotubes, boron nitride nanotubes, nanomanufacturing, nanocomposites

Introduction

The history of boron nitride nanotubes (BNNTs) largely began in the mid-1990s with the first experimental realization of the nanotube form of BN in 1995¹, following close on the heels of their theoretical prediction a year earlier². That groundbreaking work, which launched the present field of BNNTs, built on the foundation of carbon nanotubes (CNTs)³ and the structural similarities between the C-C and B-N bonds. As shown in Figure 1, BNNTs and individual hexagonal-BN (h-BN) sheets have structures analogous to CNTs and graphene. This structure and the similarly strong B-N bonds give BNNTs comparably impressive mechanical properties to carbon nanotubes; however, the different composition and partially ionic bonding result in a *unique* and *complementary* suite of functional properties in comparison to CNTs (Table 1), including electrical insulation, transparency to visible light, high thermal stability, piezoelectricity, and neutron absorption.

The *uniqueness* of BNNTs stimulated early excitement and experimental activities including fundamental physics studies and small-scale chemistry research. However, while the carbon nanotube field grew rapidly over the same time period, BNNTs received limited attention (Figure 2). Notably (Figure 2a), the field grew slowly for the first half of its existence (i.e., until BNNTs reached their mid-to-late teen years) because of the relative difficulty of synthesizing BNNTs; hence, outside of particular locations [e.g., 1,4,5,6,7,8,9], BNNTs were not widely investigated. Change started in the 2010's, with the advent of synthesis approaches that could produce high-quality BNNTs, including scalable methods with gram-to-kilogram/day production capacity¹⁰, and most recently the emergence of a growing list of commercial BNNT materials. This has led to increasing activity with a growing numbers of researchers and publications, and mounting commercial activity. Now, BNNTs are a true emerging material that is accessible and available to a broad R&D community and is starting to generate commercial applications.

The *complementary* nature of BNNT properties in comparison to carbon nanomaterials including CNTs, which for some time have been produced at worldwide annual rates measured in kilotons¹¹, can be expected to drive the current phase of the BNNT field. That is particularly true for early-stage applications outside of the lab environment. While the challenges of accessing BNNT materials for research purposes has been overcome, commercial BNNTs remain costly, making CNTs (or even graphene) advantageous in cases where either type of nanomaterial can perform well—particularly so when the nanotubes are used as inclusions to improve the strength or thermal conductivity of a host material. Yet, the functional properties of BNNTs impart clear advantages, or could even be the only options where carbon nanomaterials are unsuitable, including cases where electrical insulation, high thermo-oxidative stability, or transparency to visible light are essential. BNNTs can also be advantageous over CNTs and graphene nanomaterials in that they exhibit a piezoelectric effect; furthermore, boron offers a high neutron absorption cross-section, which is absent in CNTs. Therefore, in combination with carbon nanotubes, BNNTs contribute to an expanded set of complementary, multifunctional nanotube materials beyond what can be achieved with carbon nanomaterials. For this potential to materialize on a larger scale, scientific understanding will be needed on what subset of BNNTs may produce the advantages predicated on the properties of their idealized structures. Lack of clarity on structure-property relations was a main cause of the near-collapse of CNTs in the early 2010s^{12,13}. The application potential had been hyped based

on the properties of structurally perfect single and few-walled CNTs, but initial scale up efforts produced highly defective materials that had relatively small advantages over carbon black and carbon nanofiber fillers, and hence failed to get commercial traction. Clarifying structure-property relations before embarking on extensive commercial scale-up will allow a more efficient use of resources and, likely, will mitigate or even prevent a hype-disillusionment cycle for BNNTs.

For these reasons — the emergence of BNNT manufacturing and the associated increases in material availability and researcher and commercial activity—now is a pertinent time for this Focus Issue – BNNTs: Synthesis to Applications. BNNTs have been the subject of a range of review articles, including several in recent years^{14,15,16,17,18} and exciting advances range from BNNT synthesis, to novel chemistry, to applied investigations in areas from space to medicine. The intent of this overview is not to duplicate existing and comprehensive reviews. Rather, this article serves as an introduction to the Focus Issue, highlighting recent advances to offer a current perspective and future outlook for the growing field of BNNTs.

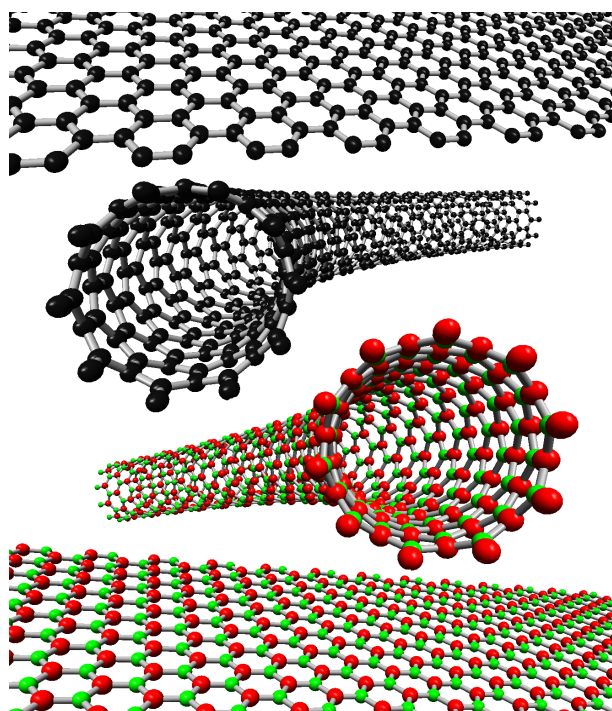


Figure 1. Ball-and-stick structural models for a single-walled BNNT and an h-BN sheet (bottom), along with a single-walled CNT and a graphene sheet (top). The alternating B and N atoms, shown in red and green, respectively, form analogous structures to those formed with C atoms, shown in black. These models, which show zigzag (10,0) nanotubes, were generated using Nanotube Modeler¹⁹.

Table 1. BNNT and CNT properties

	CNTs	BNNTs
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Electrical	Single walled CNTs: Metallic with very high ampacity, or semiconducting (0-3 eV bandgap, chirality dependent) MWCNTs: nominally metallic	Insulating (wide band-gap semiconductor, >5eV when not doped)
Oxidation resistance	Combustion between 400-600 °C	Higher (Stable up to 900 °C)
Tensile properties	High strength (e.g., 65 GPa) and stiffness (Young's modulus ~1.5 TPa)	Similarly high strength and stiffness to CNTs
Thermal conductivity	High (e.g., ~300 to 3000 W m ⁻¹ K ⁻¹)	High, but lower than CNTs due to lower isotopic purity of natural B (e.g., ~200 W m ⁻¹ K ⁻¹)
Thermal Neutron absorption cross sections	Very low; (C = 0.003 barns)	High, dominated by boron; B = 770 barns (3800 barns for enriched 10B); N < 2 barns
Optical absorption Bulk color	Absorbs across visible spectrum Black	Non-absorbing in visible spectrum White/off-white

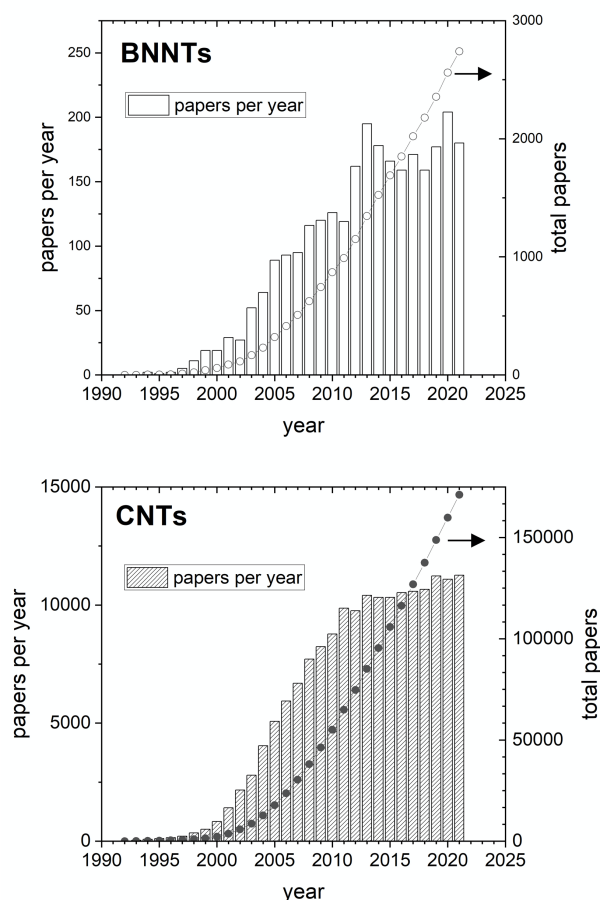


Figure 2. Comparison of (a) BNNT and (b) CNT publications based on the Scopus search engine and a title-abstract-keyword search for “boron nitride nanotube*” or “BN nanotube*” (and “carbon nanotube*”).

BNNT Highlights

In this section we highlight recent progress beginning with (1) advances in synthesis and manufacturing, which have enabled the acceleration of the BNNT field in the past decade, and followed by (2) BNNT chemistry, (3) BNNT sheets and fibers, (4) BNNT-reinforced composites, (5) biological and medical and, (6) other novel applications.

Synthesis and Manufacturing

Despite numerous efforts since their first synthesis in 1995, progress in the synthesis of high-quality BNNTs has been much slower compared to CNTs and still remains a significant challenge. The main challenges are lack of reliable BN sources that are processable at low temperatures and controlled incorporation of B and N atoms into the hexagonal lattice. Inspired by the synthesis of CNT, both low- (< 2,000 K) and high-temperature methods (> 4,000 K) have been extensively investigated for the production of BNNTs, and it is only recently that we have witnessed the advent of large-scale synthesis methods that led to successful commercialization^{10,20}. Table 2 summarizes physico-chemical properties of several BNNT materials that are currently available commercially.

Table 2. Commercial BNNT materials products based on information listed on supplier websites (BNNT LLC, Tekna, NAIeEL, BNNano, BNNT Technology LTD)²¹

Manufacturer/ Product	Method category	BNNT Type	Morphology	Purity (%BNNT)	Main impurities	Dimensions	Surface area (m ² /g)
BNNT LLC	/Raw	Few-wall, crystalline; enriched 10B/11B available	puff ball	50%	elemental B, h-BN	1-5 walls; L up to 200 um	up to 400
/Purified	Laser ablation		puff ball / powder	(99 %BN)	h-BN		
/Mat			paper	(99 %BN)	h-BN		
Tekna	/Raw	Few-wall, crystalline	fluff/powder	50%	elemental B, h-BN derivatives	d ~ 5 nm; L ~ microns	> 100
/Purified	Thermal plasma		fluff/powder	75%	h-BN derivatives		
/Buckypaper			paper	75%	h-BN derivatives		
NAiEEL	Ball-milling	Large, multiwall	powder	80%, 90%	h-BN; Mg & Fe (<1%)	d ~ 30-50 nm	unspecified
BNNano	Not specified	Few-wall, irregular surface	powder	> 90%	h-BN	d ~ 60 nm; L ~ 20 um	unspecified
BNNT LTD	Technology	Large, multiwall	powder	> 90%	unspecified	d ~ 20-100 nm; L~10-100um	unspecified

The high-temperature processes include arc discharge, laser vaporization, and thermal plasma jet methods. In these approaches, a direct BN source such as elemental B or h-BN powders can be employed and vaporized (e.g., via high-temperature plasma) to produce BNNT seeds along with effective BN precursors. BNNTs are typically grown from boron droplets (i.e., BNNT seeds) via in-flight reactions with N-containing species without metal catalysts. The inherent slow kinetics in this re-nitridation process has been largely addressed either by employing high pressure^{22,23} or by using hydrogen as a gas-phase catalyst²⁴. A high production rate approaching 20 g/h has been achieved and led to successful

commercialization of high-quality BNNTs with small diameters (~ 5 nm) and few walls (3–4 walls). A production rate of ~ 22 g/h is reported in this issue using a DC plasma process with hydrogen gas injected to form a vortex, which increases residence time in addition to forming intermediates.²⁵ The average BNNT diameter varied from ~ 10 nm to almost 20 nm in different regions of the reactor, with potential to adjust residence time to vary diameter. However, BNNTs produced in high-temperature processes are still accompanied by the production of BN impurities (e.g., a-BN, BN shells, BN flakes), necessitating additional post-purification processes for their practical applications^{26,27,28}. In this Focus Issue, Alston and co-workers²⁹ provide a comprehensive review of BNNT purification and show that improvements in both purification and purity assessment are key challenges in relation to broader use of high-temperature produced BNNTs. A recent study has employed both experimental and numerical approaches for a mechanistic understanding of BN impurity formation in a high-temperature plasma jet process, and suggested that the flow structure of the plasma jet (such as turbulence) plays a key role in the formation of BN impurities³⁰. Very recently, it was reported that BN radicals can be effectively produced from the controlled decomposition of ammonia borane in a laser ablation process. BNNTs were grown from the BN radicals via homogenous nucleation, and thus resulted in a minimal formation of B impurities³¹.

The low-temperature approach includes CVD and ball milling processes. Owing to their low processing temperatures, typical precursors include boric acid and melamine, boron powders and metal oxides, and gaseous boron-containing feedstock. The CVD process produces BNNTs with fewer impurities; however, low yields of around 1 g/h is an issue to be addressed for successful commercialization. The ball milling process has demonstrated a potential for large-scale production up to kg-scale while, in that case, low-quality of BNNTs and formation of impurities still remain challenges. Both methods usually produce BNNTs larger than 20 nm. Similar to CNT synthesis, the CVD method presents excellent opportunities for the controlled synthesis of BNNTs, including the production of vertically aligned BNNTs (VA-BNNTs). A recent review paper focussed on CVD synthesis including the effect of precursors, catalysts, and gases in the CVD process¹⁷. Although BNNT growth models are critical for catalyst design, their nucleation mechanism was less studied and still remains unknown. A recent non-equilibrium molecular dynamics (MD) simulation revealed how BNNT cap structures are created in a Ni-catalyzed CVD process³². Notably, CNT synthesis was scaled up via catalyzed CVD (floating catalyst for high-quality CNTs, supported catalyst for lower quality material); hence, improvements in BNNT CVD synthesis may be the highest-payoff pathway to scale, even though this route presently lags high-temperature synthesis in terms of productivity.

While production of high-quality BNNTs with the focus on increased yield and purity, has been the main interest in the past decade, targeted syntheses of BNNTs with specialized features provides a third challenge for BNNT synthesis (Figure 3). For example, vertically aligned BNNTs (VA-BNNTs) forests have been manufactured by using VA-CNTs as a template^{33,34}, which provides new opportunities in a wide range of applications including electronics, nanocomposites, and thermal management. The synthesis of single-walled carbon nanotubes (SWCNTs) was quickly realized at reasonable scales (e.g., in Smalley's Tubes@Rice effort); conversely, such synthesis has been achieved only in limited and small-scale reports for BNNTs (e.g.,³⁵). Notably, SWCNTs were expected to have dramatically different electrical properties (metallic to semiconducting) depending on their diameter and chirality; whereas such properties are critical for electronics, their importance was over-estimated for the area of macroscopic materials, where aspect ratio and crystallinity proved more important to attain high-level macroscopic properties³⁶. In this respect, SWCNTs and few-walled CNTs proved superior to their larger diameter, multiwalled counterparts because of their inherently higher degree of crystalline order. The optical and electrical properties of SW-BNNTs do not depend appreciably on their structure; hence there is no anticipated difference between SW-BNNTs and their few-walled counterparts. However, SW-BNNTs may also have higher crystallinity because defects cannot lock in place by chemical bonding between walls, which would be advantageous

in macroscale structures. Moreover, control of electronic/optical/adsorption properties of BNNTs by doping or creating heterostructure interfaces is of high interest for electronic or energy applications^{37,38}. Hybrid NTs such as BNNT@CNT have been demonstrated as one-dimensional van der Waals heterostructures^{39,40}, and their properties have been investigated experimentally and by first-principles modeling^{41,42,43}.

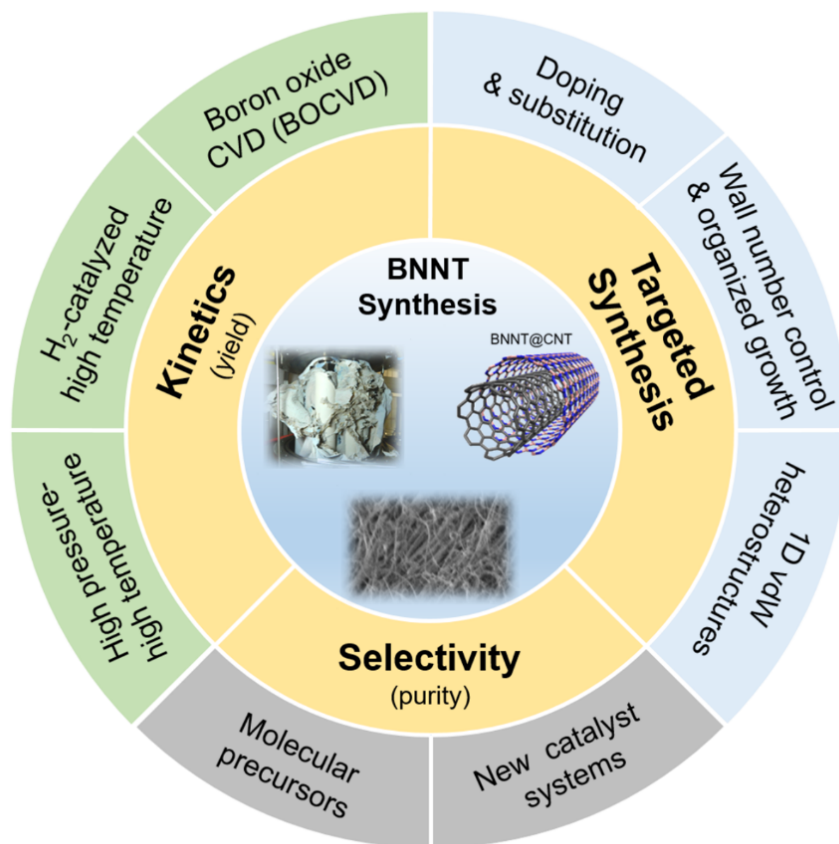


Figure 3. Current challenges (inner ring) and recent progress (outer ring) in BNNT synthesis.

BNNT Chemistry and Functionalization

Chemical processing and modification are essential to utilize BNNTs in many applications. While the B-N bond is isoelectronic with C-C, allowing the formation of analogous phases such as h-BN and BNNTs, the difference in composition and the partially ionic nature of the bonding means that BNNT chemistry differs from that developed for CNTs. Nonetheless, approaches similar to those used for CNTs have been investigated to functionalize BNNTs including surfactants, polymer wrapping, covalent functionalization and others (Figure 4), and several reviews (e.g.,^{44,45,46,47}), have addressed BNNT functionalization. Early reports used polymer wrapping⁴⁸ or covalent functionalization of BNNT edges and defects⁴⁹. Among later reports, reductive chemistry has been shown to facilitate covalent functionalization^{50,51}. The electron-

deficient boron atoms can also act as Lewis acids. For example, in this issue, BNNTs are covalently functionalized using sonolysis of a primary alcohol to form radicals that can covalently attach to the boron atoms of BNNTs⁵². Of particular importance across the BNNT field are: (1) the purification of raw BNNT materials, which contain different impurities depending on the synthesis methods, and (2) dispersion of BNNTs, which is often the critical step for the integration of BNNTs in composites. While boron impurities can be removed following chemical purification (e.g., via oxidation), other BN nanomaterials different from BNNTs are more difficult to remove due to the similarity of chemical bonds and composition and purification is generally based on selective dispersion or solubility of either the BNNTs or impurities. For example, the preferential solubility of BNNTs in chlorosulfonic acid has been employed to purify BNNTs to produce films and aerogels⁵³. In this issue, advances in BNNT purification and dispersion are addressed in comprehensive reviews by Maselugbo et al²⁹ and Smith McWilliams et al⁴⁷, respectively, and molecular dynamics simulation is employed to study interfacial interactions of poly(4-vinylpyridine) with BNNTs and h-BN with the goal to understand and improve purification of BNNTs by selective dispersion⁵⁴.

Both purification and dispersion processes are essential to producing BNNT fibers in liquid spinning methods, and the properties of nanotube assemblies and composites typically correlate with the purity and dispersion quality. Additionally, due to their ionic character, multiwalled BNNTs exhibit higher resistance to pull-out of inner walls⁵⁵ and BNNTs exhibit stronger interactions with common polymers,^{56,57} both of which give BNNTs an inherent advantage over CNTs in the area of polymer nanocomposites.

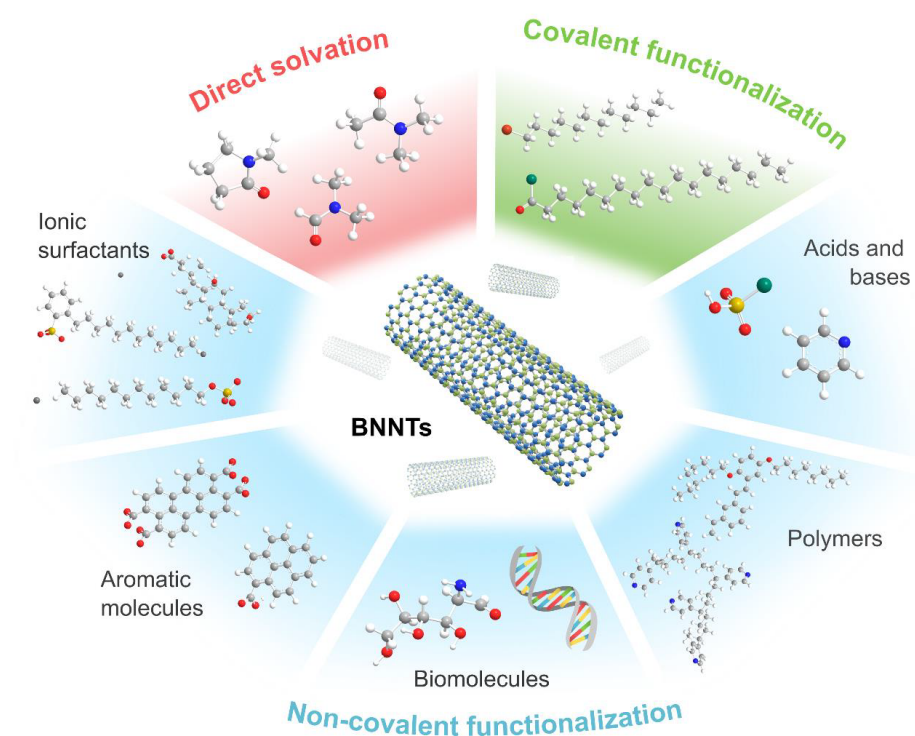


Figure 4. Approaches for chemical modification of BNNTs. Reprinted by permission from Springer Nature, Journal of Materials Research, Reference 40, copyright 2022

BNNT sheets and fibers

Similar to CNTs, direct spinning of BNNT fibers during the synthesis process can find many important applications⁵⁸. To facilitate in-flight alignment and coalescence of BNNTs from BNNT aerogels the formation of impurities must be minimized. In a recent study, BNNT fibers were formed spontaneously from the laser ablation of an ammonia borane target because of the absence of amorphous boron impurities³¹. BNNT yarns and tapes have also been collected during a CVD synthesis,⁵⁹ which can provide for continuously drawn yarns or sheets. Supported thin films also have been synthesized directly by patterning the catalyst for CVD synthesis⁶⁰ or patining using a boron ink precursor⁶¹. Along with assembly during synthesis, BNNTs have been assembled into fibers, yarns or sheets through post-synthesis processing (Figure 5). This includes twisting or compressing as-produced BNNT bundles or mats, dispersion, and filtration-based methods to produce nonwoven nanotube sheets commonly called buckypapers. Aligned BNNT films were created through surface coating using high concentration DNA-wrapped BNNTs that forms an ordered phase during drying⁶². Most recently, the first BNNT liquid crystal was reported, using high-quality BNNTs in chlorosulfonic acid, and the nematic liquid crystal domains were processed into aligned films and fibers⁶³. In addition to direct collection and liquid spinning, drawing and spinning of yarns from vertically aligned CNT arrays or forests has been used to produce CNT yarns;⁶⁴ however, there have yet to be any analagous reports showing drawable/spinnable BNNT arrays. The mechanical properties reported for BNNT assemblies to date are modest compared to the leading CNT yarn and sheet materials, but compare well to early reports for CNT fibers or to CNT buckypapers made from dispersion of similar aspect ratio CNTs. The properties of these BNNT assemblies already show promise for producing BNNT composites with high BNNT contents^{65,66} and the properties of the BNNT assemblies themselves can be expected to improve significantly as the synthesis and processing methods improve, including achieving high quality BNNTs with higher purity and longer length. In this issue, high-resolution electron microscopy is employed to study the effect of defects in purified BNNTs on alignment to form the ordered domains necessary to produce ordered assemblies by liquid-phase processing⁶⁷. Additionally, MD simulations of BN nanoribbons indicate that BNNT strength is strongly influenced by the location and orientation of preexisting cracks.⁶⁸ Such defects could reduce the strength or effective length of BNNTs, which impact performance of the assembly. BNNT production costs also will become important once these macroscopic materials attain their potential properties—these are the most cost-sensitive applications because BNNTs are used in bulk rather than as a low-concentration dispersed agent.

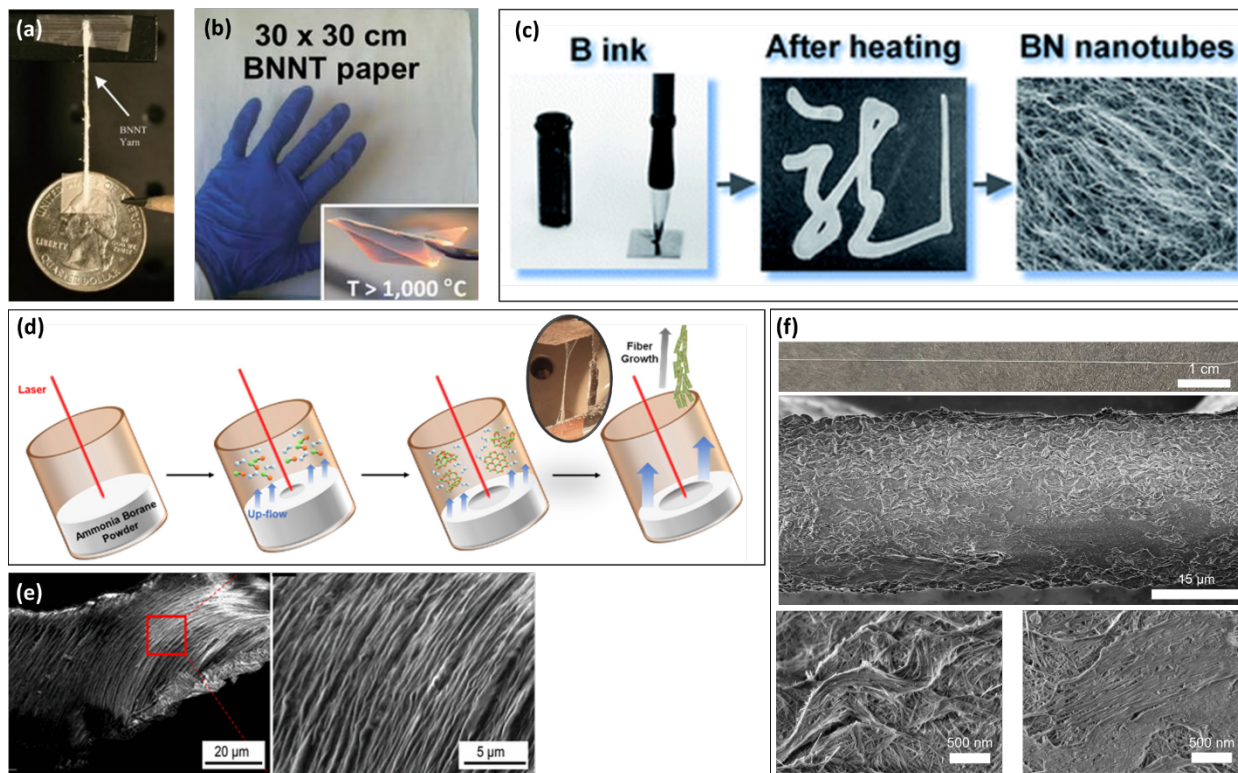


Figure 5. Examples of BNNT assemblies: (a) first BNNT yarn produced by finger twisting of as-produced BNNTs (Used with permission of IOP Science, from Ref. 22; permission conveyed through Copyright Clearance Center, Inc.), (b) BNNT buckypaper and BNNT paper airplane in a flame (Reproduced from Ref. 69 with permission from the Royal Society of Chemistry), (c) BNNT film patterned using boron ink (Used with permission of Royal Society of Chemistry, from Ref. 61; permission conveyed through Copyright Clearance Center, Inc.), (d) collection of BNNT fiber during laser synthesis (Reproduced and adapted, with permission, from Ref. 31 under a Creative Commons Licence: <http://creativecommons.org/licenses/by/4.0/>), (e) aligned BNNT-DNA film (Reprinted and adapted with permission from Ref. 62. Copyright 2019 American Chemical Society), (f) BNNT fiber produced from chlorosulfonic acid liquid crystal BNNT solution (Reproduced and adapted, with permission, from Ref. 63 under a Creative Commons Licence: <http://creativecommons.org/licenses/by/4.0/>).

BNNT-reinforced Composites

The advances in BNNT manufacturing leading to broader availability of gram-scale quantities of BNNTs achieved over the past decade, along with those for the production of BNNT assemblies (in particular fibers, films and buckypapers) and for chemically purified and modified BNNTs, have enabled increased activity in BNNT composites. BNNT composites are addressed in several recent reviews¹⁵¹⁷. Although the stronger interaction between BNNTs and polymers might ultimately make BNNTs the preferred nanotube for the mechanical reinforcement of polymers, CNTs are much more advanced in terms of synthesis, functionalization, and composite integration. Therefore, the most promising cases for BNNT composites in the short-to-medium term are those where the desired multifunctional properties make BNNTs advantageous or even render carbon-based nanomaterials unsuitable (Table 3).

In the case of multifunctional polymer nanocomposites, BNNTs have been shown to enhance the piezoelectric response of both piezoelectric and non-piezoelectric polymers^{70,71,72,73}. Additionally, the

optical properties of BNNTs allow for nanotube-reinforced polymers that remain highly transparent at modest thickness.^{74,75} This is of particular relevance for transparent coatings or adhesives, which are not achievable with CNTs due to their high absorption across the visible spectrum. Although not yet shown to offer transparent composites at bulk thicknesses, BNNT optical properties are also favorable for nanotube-reinforced dental restorative materials, where color is important to the application and the potential bioactivity and non-cytotoxicity of BNNTs may also be advantageous⁷⁶. BNNT-polymer composites are promising for substrates and packaging in particular for high power electronics where the heat dissipation challenge is increased and high electrical insulation is also needed. Composites with 10-40 wt% BNNTs have been shown to have thermal conductivities 20x higher or more than typical polymers.^{77,78,79} Relatively high loading as well as preferential alignment of BNNTs are beneficial for both mechanical and multifunctional properties. In recent years, BNNT-polymer composites have been made from BNNT papers/sheets^{65,66,80} as well as BNNT-composite fibers through composite fiber making approaches including wet spinning and electrospinning.^{81,82,83,84,85} BNNT-PAN fibers have also been converted to BNNT-enhanced carbon fiber through pyrolysis.^{84,85} While their functional properties provide nearer-term application potential, ultimately mechanical properties of BNNT-reinforced composites will also be important. In addition to exhibiting stronger interaction with polymers in comparison to CNTs^{56,57}, new MD simulations in this issue show that BNNTs are expected to interact more strongly with bismaleimide (BMI) resins – an important case for high-performance composite materials – than with either epoxy or cyanate ester resins⁸⁶. The functional properties of BNNTs also favour their application in extreme environments and use in high-temperature manufacturing processes. This includes resistance to space-based radiation and the ability to provide mass-efficient neutron shielding^{70,87,88,89,90}. Additionally, the high thermal stability of BNNTs enables high-temperature nanocomposites,⁹¹ including high application temperature and/or high fabrication temperatures needed for many metals or ceramic matrix composites. Among other examples, BNNTs have been shown to reinforce ceramics, including reducing brittle fracture and increasing the toughness of aluminium oxide ceramics produced by spark plasma sintering⁹², and to modify the dielectric properties of polymer derived ceramics for potential application as electromagnetic transparent materials in harsh conditions⁹³. BNNTs are also promising for metal composites including aluminium (e.g.,^{94,95}) and titanium (e.g.,⁹⁶), the latter showing potential for improved neutron shielding and wear for lunar applications⁹⁰. Recently, BNNTs have also been used in metal additive manufacturing, where incorporation of BNNT-decorated titanium alloy powders were employed with a laser additive manufacturing system to produce BNNT-reinforced alloys⁹⁷.

Table 3. Composites applications of BNNTs in comparison to CNTs

	Application area	CNTs	BNNTs
Both	Mechanical reinforcement	Yes	Yes
	Thermal conductivity enhancement	Yes	Yes
CNT	Electrical conductive composites	Yes	No
	Thermally conductive electrical insulators (e.g., electronics packaging)	No	Yes
BNNT	Transparent (or dye-able) composites	No	Yes
BNNTs advantageous	Neutron shielding	Negligible absorption by CNTs	Yes
	High-temperature materials processing (e.g., glass, metal & ceramic processing)	Limited by stability	Yes
	High-temperature applications (e.g., thermal barriers, fire resistance)	Limited by stability	Yes
	Biocompatible composites	Greater toxicity issue	Yes
	Piezoelectric sensing and energy harvesting	Not piezoelectric themselves	Yes

Biological and medical

Similarly to CNTs, BNNTs have shown great promise for biomedical applications. More than a decade ago, Ciofani et al. reported the first studies on the cytocompatibility of BNNTs with human neuroblastoma cells (SH-SY5Y).⁹⁸ These BNNTs were dispersed in water using polyethyleneimine and showed good viability up to concentrations of 5 µg/mL of nanotubes. After this, a variety of studies have been performed in cells as discussed in greater detail in this issue by Kodali et al.⁹⁹ The presence of impurities, BNNT concentration and exposure time have a remarkable effect on the viability of cells when exposed to this nanomaterial.

BNNTs have been explored also for drug delivery. Having a large surface area, these nanomaterials are the ideal vehicles for delivering molecules for medical treatments. For example, BNNTs coated with amine-modified silica have been used to deliver doxorubicin to prostate cells, increasing the efficiency of drug internalization and the efficacy of killing cells.¹⁰⁰ Alternatively, doxorubicin adsorbed on bare BNNTs shows a pH-dependent release and increases toxicity for HeLa and HUVECs cells when conjugated to a cancer-targeting molecule (folate). Other drugs such as tamoxifen and paclitaxel drugs were loaded in BNNTs coated with Pluronic F127 and tested against MCF-7 cells and A549 respectively, showing lower cell viability than the free drug.¹⁰¹ In addition, taking advantage of the ¹⁰B naturally present in BNNTs, Nakamura et al. have used boron neutron capture therapy to kill B16 melanoma cells.¹⁰² Other molecules have been used to cover BNNTs including single-stranded DNA,^{Error! Bookmark not defined.} plasmids,¹⁰³ N aGdF₄:Eu¹⁰⁴, for a variety of therapeutic and diagnostic applications.

The effect of BNNTs in tissue and organisms has also been studied. BNNTs composites with hydroxyapatite have improved elastic modulus, wear resistance, and osteogenesis with applications to orthopedic implants.^{105,106} The effect of BNNTs has also been studied in organisms. For example, the interaction of BNNTs with planarians have been studied showing no adverse effects.¹⁰⁷ Research in mice using ^{99m}Tc-labeled BNNTs showed that BNNTs accumulate in the liver, spleen and gut at 30 mins post-injection, and appear as well as in the kidneys and bladder; however, after 1 and 4 hours, images show a decrease of BNNTs due to clearance.¹⁰⁸ A thorough review on the toxicity of BNNTs in a variety of models is provided in this issue by Kodali et al.⁹⁹

Other novel applications

The BNNT community continues to explore and develop new applications, and what can be captured in the scope of this brief overview only scratches the surface. Hydrogen storage was first investigated relatively early in the history of BNNTs,¹⁰⁹ and there remains interest both in the storage of hydrogen and also in the addition of hydrogen to BNNTs to increase their neutron shielding capability. BNNTs also are being applied in the field of electronics, with BNNTs modified with quantum dots¹¹⁰, encapsulating atomic chains,¹¹¹ and other variations recently explored in nanoelectronics as reviewed in this issue by Zhang et al³⁸. BNNTs have also shown to be viable low-k dielectric materials¹¹² and, in printed electronics, BNNTs were recently shown to improve the performance of photosintered metal ink traces for through improved thermal management¹¹³. BNNTs also have been reported to improve the stability of encapsulated dye molecules¹¹⁴, and to be useful as carriers for high-brightness fluorophores wherein organizing dye molecules on the surface of BNNTs led to a dramatic increase in fluorescence³⁸, both of which could improve dye performance and imaging in biological applications. BNNTs, in particular in BNNT films/sheet form, can also be used as membranes such as for water filtration,^{16,18} and the high temperature stability of BNNTs can enable efficient re-use of membranes¹¹⁵. Alternatively, BNNTs have also been coated onto polymer membranes and shown potential to improve the thermal stability of separator membranes for safer lithium ion and lithium-sulphur batteries^{116,117}, representing a developing application case of BNNTs in the energy field.

Conclusions and Outlook

One could simplify BNNT history to-date by grouping it into two phases. The first phase (ca. 1995 to ~2010) was *supply-limited* and marked by a focus on synthesis methods, fundamental properties, theoretical studies, and small-scale chemistry. The second phase (~2010 to present day) has been marked by the emergence of larger-scale synthesis and commercial BNNT materials, starting a shift towards a *demand-limited* scenario with the availability of sufficient quantities of BNNTs (from a lab research perspective) to engage more researchers – including academic and industry laboratories not engaged in BNNT synthesis – and to enable increased activity in the areas such as BNNT purification and BNNT composites, where larger quantities of raw BNNT materials (e.g., > 1 g) are critical. To put this into perspective, CNTs attained the second phase starting in the mid-1990s, with Smalley's synthesis of laser-oven single-walled CNTs^{118,119} and the subsequent establishment of Tubes@Rice¹²⁰, which supplied the academic community with much of the initial studies on high-quality CNTs.

Mars-Shot?

While considering how the BNNT field will advance over its next 10 to 15 years period, it is tempting to speculate about a *Moon-shot* goal (or Mars-shot!), such as ultrastrong lightweight high-temperature composites. Such a BNNT composite would be revolutionary for multifunctional space structures; in fact, NASA continues to be a key leader in the BNNT field due in part to the unique advantages of BNNTs for space applications¹²¹, including for radiation shielding on long-duration missions (e.g., Lunar Gateway and Mars missions) and for extreme temperature cases (e.g., re-entry and for hypersonic vehicles). However, ultrastrong nanocomposite space structures based on much more developed CNT materials remain a technological challenge and an active area of research today^{122,123}. BNNTs will certainly benefit from this work that is now at the frontier of the CNT composites field. Drawing additional parallels to the progress of CNTs, it is more likely that evolutionary applications (e.g., the use of CNT powders as a better filler or additive for conductive plastics and batteries) will spur the increased demand for BNNTs needed to reach economies-of-scale. An obvious leading candidate is thermally conductive plastics for electronics packaging, which also nicely parallels the use of CNTs electrically conductive plastics. Thermal conductivities in the range of a few to $20 \text{ W m}^{-1} \text{ K}^{-1}$ are lower than typical electrical conductors but would be transformative in electrically insulating plastics, particularly in high power electronics, with high heat production rates and unmet needs for adequate electrical insulation. Reinforcement of commonly used metals would also spur large demand for BNNTs. Displacing even a tiny fraction of the aluminum alloy market with BNNT-reinforced alloys would require BNNT quantities in excess of current worldwide production capacity. Successes in these area would greatly increase the demand for BNNTs. In the medium term, the use of BNNTs as reinforcement in metal additive manufacturing (3D printing) is more likely to find niche applications. Even with recent advances in commercial BNNTs, worldwide production of BNNTs is still low and the materials are high cost. Applications where BNNT composites provide useful and unique advantages are likely to drive the increase in production volume needed to achieve viable cost points.

Particle-to-Article

Again drawing on the CNT field, where pre-formed assemblies of CNTs (i.e., buckypaper, films, tapes and yarns) have enabled some of the highest-performance CNT materials, the BNNT field is beginning to see more examples and improved properties for BNNT sheets and fibers. As for CNTs, macroscopic *articles* made of BNNTs (e.g., fibers, sheets or arrays) simplify the introduction into material manufacturing chains (relative to BNNT particles or powders) and can achieve high-content of BNNTs and BNNT alignment in composite materials, which is essential to better leverage their structural and functional properties. Much like in synthesis, the BNNT field lags by about 15-20 years the CNT area, where macroscopic CNT fibers were attained in the early 2000s¹²⁴ and properties were achieved a decade later¹²⁵. Early reports of BNNT fibers were published in the past year^{31,63}; the development of structure-processing-property relationships for BNNT fibers is now critical. As for CNTs, it will rely on improvements in BNNT purity, quality, and availability. Such anticipated improvements in BNNT assemblies will translate to broader application development, including new and improved BNNT composites with high contents of aligned BNNTs.

Understanding & Control

The recent advances in BNNT development and applications are built on ~25 years of foundational studies on BNNT growth, chemistry and properties. Fundamental research remains essential to improve understanding and control of BNNTs. Improved *in situ* assessment and diagnostics are likely to impact BNNT synthesis and manufacturing, including the less developed areas of BNNT fibers, BNNT arrays, and

doped BNNTs. Spinnable arrays, which are highly sensitive to synthesis conditions but are now fairly well-established for the case of CNTs¹²⁶, have yet to be reported for BNNTs. There is also a need for more control in terms of scalable and green methods for chemical purification and functionalization, as well as better methods to characterize BNNTs.

Standardized Methods & Standard Materials

Part of the unmet needs and challenges in comparing different BNNT studies are related to the difficulty of comparing results obtained with different BNNT materials, or even due to variability between batches of nominally the same material. While a variety of techniques are commonly used for characterizing BNNTs (i.e., electron microscopy, thermogravimetric analysis, FTIR spectroscopy, UV-vis absorption spectroscopy, Raman spectroscopy, X-ray photoelectron spectroscopy, etc.) there are currently no broadly accepted and employed methods to assess and compare BNNTs between studies. Individual studies can be performed with BNNTs from a single batch, which is advantageous for identifying trends, but this limits comparisons with other studies. Easily accessible spectroscopy-based methods using FTIR spectroscopy¹²⁷ and UV-VIS-NIR spectroscopy¹²⁸ have recently been described for assessing BNNT purity and quality; however, no method has yet proven to be broadly useful across BNNT materials or been used extensively by many groups. Therefore, the mere reporting of the purity of BNNT materials can be unclear. In addition to field-accepted methods of characterizing and comparing BNNT materials, standard reference materials (e.g., BNNT-1)¹²⁹ also have a role to play in enabling inter-lab comparison and the development of improved characterization methods for BNNTs. Notably, lack of clarity in nomenclature and characterization will hold back the growth of the field because resources—e.g., government funding, venture capital, etc.—will be scattered over a broad set of efforts with the same name yet fundamentally different properties and potential. This could lead to the same hype-disillusionment cycle that was experienced in the CNT field in the 2010s.

Strength in Diversity

Uniformity and consistency are essential in terms of standard materials and for achieving broad consensus on how to characterize, report and make comparisons between studies; however, diversity is also an advantage in finding application niches for BNNTs. In general, BNNTs are less a competitor to CNTs (or graphene and other related nanomaterials) than part of an expanded set of related nanomaterials with complementary advantages. Even within BNNTs, the current and mostly powder-like commercial materials can be expected to be suitable for some applications, while emerging macroscopic articles (buckypapers, aligned sheets and fibers, and vertical BNNT arrays) will be advantageous or necessary in other cases. Continuing to increase the number of researchers joining the field, as was done over the past decade, will be critical for adding diversity of expertise and ideas, which will push the field to new heights in ways beyond those considered here.

In summary, remarkable progress has occurred since the discovery of BNNTs, and increasing availability of BNNTs and research activity makes this an exciting time for the field. BNNTs have already earned a place as a leading nanomaterial and there is no doubt that the 2020s will see a significant growth of the field as well as the emergence of commercial applications based-on or enabled by BNNTs.

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Conflict of Interest:

The authors declare that they have no competing financial interest.

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