

1D and 2D Boron Nitride Nano Structures: A Critical Analysis for Emerging Applications in the Field of Nanocomposites

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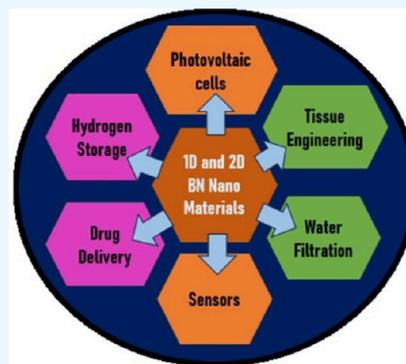
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ABSTRACT: Boron nitride (BN) with its 1D and 2D nano derivatives have gained immense popularity in both the field of research and applications. These nano derivatives have proved to be one of the most promising fillers which can be incorporated in polymers to form nanocomposites with excellent properties. These materials have been around for 25 years whereas significant research has been done in this field for only the past decade. There are many interesting properties which are imparted to the nanocomposites wherein thermal stability, large energy band gap, resistance to oxidation, excellent thermal conductivity, chemical inertness, and exceptional mechanical properties are just a few worthy of mention. Hexagonal boron nitride (h-BN) was selected as the parent material by most researchers reviewed in this paper through which 2D derivative Boron nitride nanosheets (BNNS) and 1D derivative Boron nitride nanotubes (BNNTs) are synthesized. This review will focus on the in-depth properties of h-BN and further will concisely focus on BNNS and BNNTs for their various properties. A detailed discussion of the addition of BNNS and BNNTs into polymers to form nanocomposites, their synthesis, properties, and applications is followed by a summary determining the most suitable synthesizing processes and the materials, keeping in mind the current challenges.



1. INTRODUCTION

Nanoscience is the modification of particles at the nano level wherein the properties of the material can be enhanced at macro level. These structures have proved to have extreme potential mechanically, electrically, optically, and thermally which can be further utilized in exceptional applications. Nanoscience, with its top-down approach, has gained immense popularity with its ability to achieve extensive variations in the properties of the materials.¹ Variations in terms of physical, electrical, and mechanical properties with varying particle size have led to immense applications in various fields such as the automotive, defense, aerospace, construction, and electronics industries, etc.^{2–6} Another upcoming field in materials is polymers, in the form of composites, polymer matrix composites, nanocomposites, etc.⁷ The dispersion of nano materials into the composites or forming a thin film on the polymer are a few methods which lead to materials with enhanced properties.^{8,9}

Nano materials seem to be one of the most discussed fillers both in the field of research and in their applications in industry, especially BN. BN consists of an equal number of boron (B) and nitrogen (N) atoms and shares a similar structure with graphite. However, it differs in its bonding, as the N atomic nucleus and B atoms combine to form a strong sigma^{10,11} bond through an sp² orbital. This bonding imparts a partially ionic character due to the electron pairs in sp² hybridized BN and weak van der Waals forces between

adjacent B and N atoms of different layers, giving rise to anisotropic properties. BN exists in four crystalline forms, namely hexagonal BN (h-BN), cubic BN (c-BN), rhombohedral BN (r-BN), and wurtzite BN (w-BN). The key distinction among these phases lies in their hybridization: h-BN and r-BN are dense phases with sp² hybridization, while c-BN and w-BN are low-density phases with sp³ hybridized BN bonds.¹² Particularly intriguing is h-BN, as it shares a structural resemblance to graphite.¹³ BN nanomaterials can be categorized into different dimensions: zero-dimensional (0D) such as nanospheres; one-dimensional (1D) like nanotubes, nanofibers, and nanoribbons; and two-dimensional (2D), including thin films and nanosheets. Figure 1 depicts the exfoliation of h-BN to form BNNTs and BNNS.¹⁴ h-BN has proved to have excellent thermal stability and can withstand high temperatures without significant structural changes. It has a high decomposition temperature of around 900–1000 °C in an inert atmosphere. It is an excellent electrical insulator even at high temperatures and extreme conditions. In addition, h-

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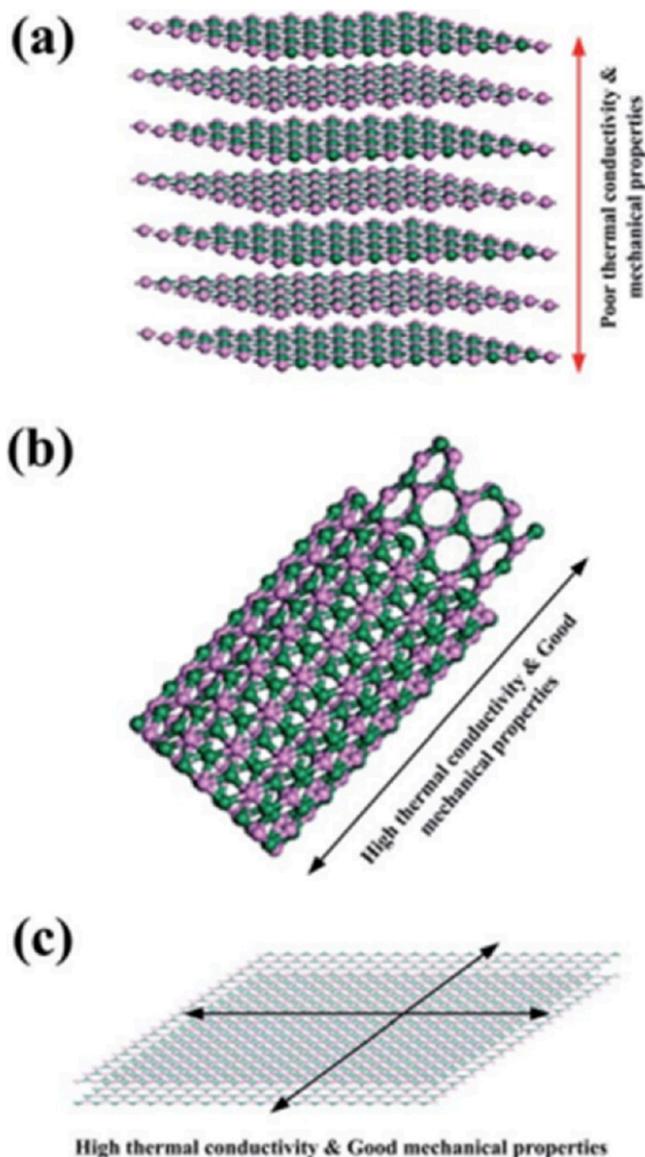


Figure 1. (a) High performance h-BN showing poor thermal conductivity and mechanical properties across vertical layers. (b) BNNTs with high thermal conductivity and good mechanical properties. (c) BNNS showing high thermal conductivity and good mechanical properties like BNNTs. Adapted/reprinted with permission from ref 29. Copyright (2014) Royal Society of Chemistry.

BN is transparent in the ultraviolet, visible, and infrared regions of the electromagnetic spectrum, making it useful for applications in optics and photonics. As a result, h-BN shows great promise as a scaffold for diverse functional materials with numerous potential applications. These applications encompass electronics^{15,16}, sensors^{17,18}, hydrogen storage^{19,20}, health-related technologies^{21,22}, as well as water and gas separation^{23–28}.

2. HEXAGONAL BORON NITRIDE

Boron nitride in its basic form is quite like graphite, with boron and nitride atoms placed alternatively replacing the carbon atoms.³⁰ This compound was prepared in 1840 with boric acid and potassium cyanide as base materials. Boron nitride due to its analogous behavior to graphite has become quite a popular research subject wherein B–N ionic bonding leads to a

comparable difference in the properties. Boron nitride is immiscible in water and exhibits tremendous chemical and thermal stability, high electrical resistivity, and thermal conductivity with a low dielectric constant.^{11,31,32} Incorporation of BN to polymers has proven to improve its wear resistance. There are many nano derivatives that can be synthesized from the parent BN-like boron nitride ribbons, nanotubes, nano powder, and nanosheets. This paper will mainly focus on incorporation of boron nitride nanosheets (BNNS) and nanotubes (BNNT) to form transparent nanocomposites.

2.1. Boron Nitride Nano Sheets (BNNS). The two-dimensional nano derivative from h-BN is the BNNS as shown in Figure 2(a,b). These are analogous to graphene and can be

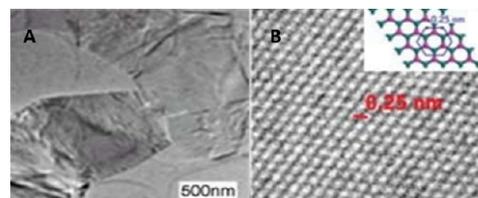


Figure 2. (a) BNNS sample under SEM with 500 nm magnification. (b) TEM image of BNNS keeping the electron beam perpendicular to the (002) plane, showing BNNS with a fringe separation of approx. 0.25 nm. Adapted/reprinted with permission from ref 34. Copyright (2009) Wiley.

produced in bulk via two main methods of preparation. BNNS can be prepared by either micro milling h-BN and sonicating with assisted exfoliation or by growing the same on or without a substrate via chemical vapor deposition method.³³ The main considerations while synthesizing BNNS is to monitor the size, shape, thickness, density, and alignment of the BNNS (Figure 3).

2.2. Boron Nitride Nanotubes (BNNT). Since the discovery of carbon nanotubes (CNTs), a constant stir was created to intensify the experimentation process on similar structures.^{36–38} The major concern depicted with CNTs was the variation in electrical properties with a slight variation in the chirality or tube diameter. As a wide-range of properties could be achieved due to this feature, the implementation of CNTs for various applications became intricate as the diameter and the chirality of the tubes were difficult to monitor. This led to the development of BNNT. Their structure is like that of graphite wherein B and N replace the carbon atoms forming an sp^2 trigonal planar structure.³⁹ Their first discovery was with an inner diameter of 1–3 nm (Figure 4) and length up to 200 nm with an energy gap of 5.5 eV.⁴⁰ BNNTs exhibit similar structures as CNTs with their properties independent of the diameter of the tube (Figure 5), their chirality, the number of tubes, and the resistance to oxidation at elevated temperatures. This suggests the implementation of BNNTs for various applications wherein thermal and chemical stability are basic criteria, such as in nanocomposites, NEMS, biomedical uses, and many more.^{40–44}

2.3. Synthesis of BNNTs. One of the first methods through which BNNTs were synthesized is the arc discharge method wherein BNNTs were grown through using cooled copper and BN packed tungsten as electrodes.⁴⁶ Many successful attempts were made after this wherein some modified the above method like the modified arc discharge method^{47–50} and the rest were different, such as autoclav-

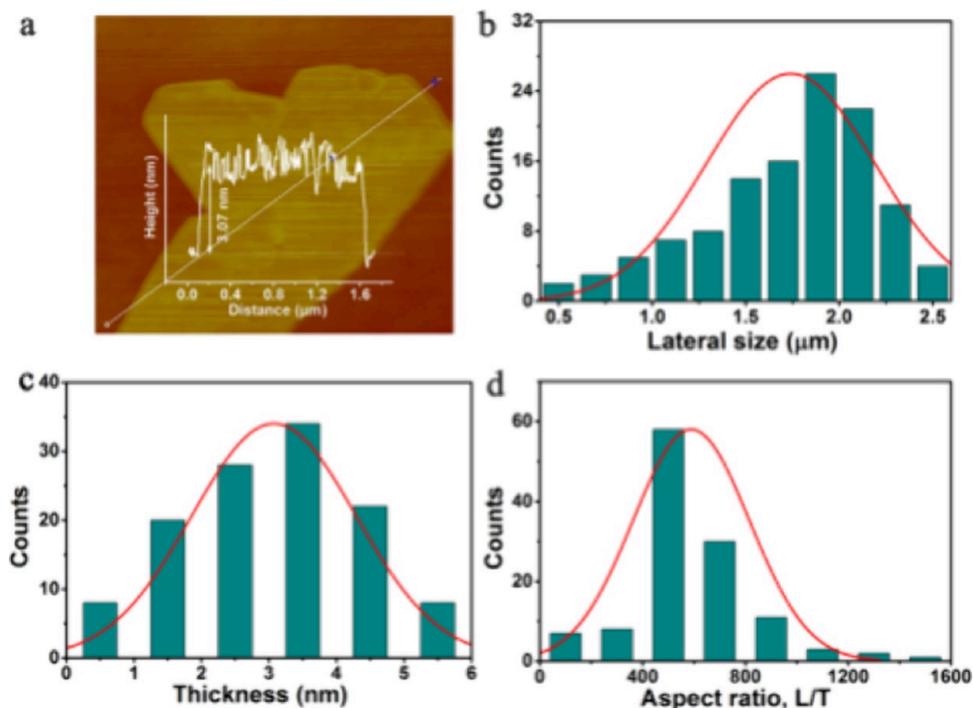


Figure 3. (a) AFM images of BNNS, (b) histograms of measured values for nanosheets length, (c) histograms of measured values for nanosheets thickness, and (d) aspect ratio (length/thickness). Adapted/reprinted with permission from ref 35. Copyright (2018) Nature.

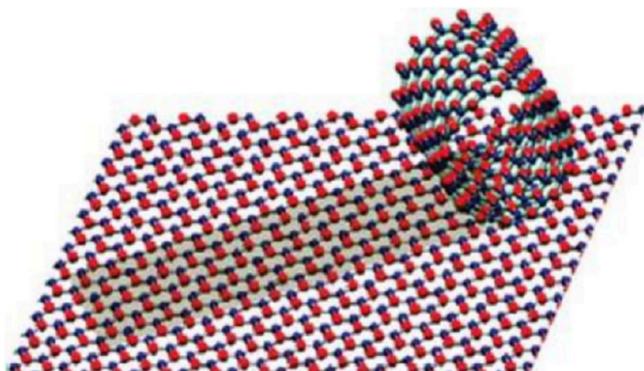


Figure 4. BNNT with alternating boron and nitrogen atom rolled hexagonal lattice. Adapted/reprinted with permission from ref 30. Copyright (2010) American chemical society.

ing^{51–53}, template synthesis,^{54–56} plasma jet method,^{57,58} laser ablation^{59–63} ball milling,^{64–67} chemical vapor deposition,^{68–72} etc. Some of the methods through which controlled synthesis and mass production of BNNTs are achieved are discussed as follows.

2.3.1. Thermal Annealing and Chemical Vapor Deposition. One of the most successful methods is the boron oxide-assisted chemical vapor deposition (BOCVD)^{73,74} as it was able to produce BNNTs in gram yields. A vertical induction furnace is used in this process where a BN crucible is placed in the bottom with boron and magnesium oxide loaded in the crucible. This is heated to 1300 °C forming boron oxide and magnesium vapors which are further reacted with ammonia in an argon-controlled chamber at low temperatures. This separates boron from boron oxide and promotes the growth of highly pure BNNTs. This method was further enhanced by Zhi et al.⁷⁵ to produce BNNTs with further reduced impurities⁷⁶ producing grams of it at the laboratory level.⁷⁷

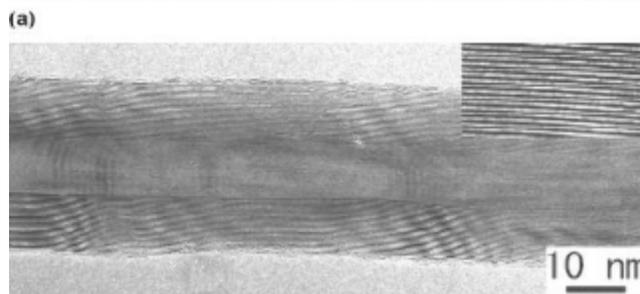
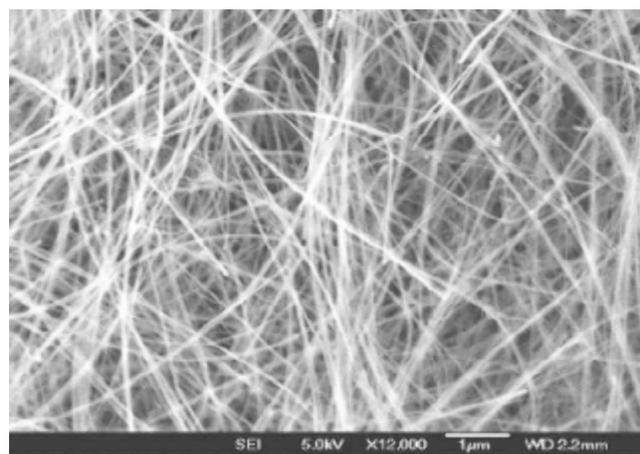


Figure 5. (a) The typical scanning electron microscope (SEM) image of BNNTs synthesized by BOCVD (bottom-up chemical vapor deposition) method. (b) The high-resolution transmission electron microscope (TEM) image of BNNTs synthesized by BOCVD method. The inset shows an enlarged portion of a BN tubular wall, providing a closer view of the nanotube structure. Adapted/reprinted with permission from ref 45. Copyright (2006) Springer.

Nevertheless, the commercialization and practical application of BNNTs in the industry face obstacles due to their comparatively lower production rate and the requirement for specialized chamber designs (Figure 6).

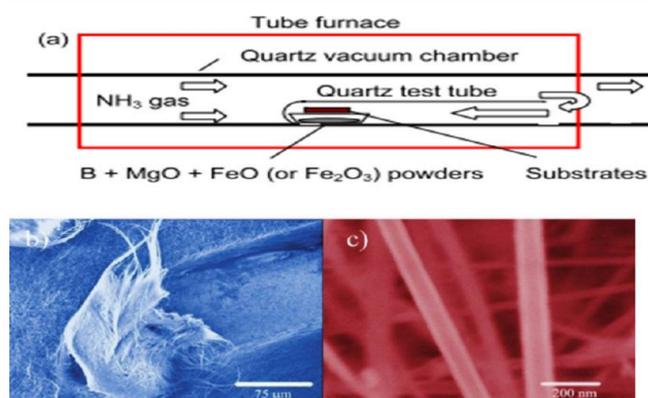


Figure 6. (a) The experimental setup used for BNNT growth in a horizontal tube furnace. Adapted from ref 78. (b) SEM image showcasing the tubular structure of BNNTs with amorphous free side walls. (c) SEM image of hollow dense BNNT structure. Adapted/reprinted with permission from ref 79. Copyright (2010) ACS Publication.

Lee et al. presented a successful method for producing high-purity BNNTs using a conventional resistive tube furnace at 1200 °C.⁷⁸ The key aspect of this technique is the application of catalytic chemical vapor deposition (CCVD), where a closed-end quartz test tube is utilized to trap and confine the growth vapors, facilitating the formation of BNNTs. This approach is referred to as the growth vapor trapping (GVT) approach. By incorporating catalytic nanoparticles (MgO, Fe, Ni) coated on Si substrates, the GVT growth of BNNTs can be precisely controlled through the vapor–liquid–solid (VLS) process. This controlled approach differs significantly from the original BOCVD method, where BNNTs are formed through spontaneous nucleation/condensation. Furthermore, they achieved a breakthrough by demonstrating patterned growth of BNNTs on a Si substrate using CVD for the first time.⁷⁹ The CCVD/GVT method is highly effective in producing BNNTs with exceptional quality and purity at specific, predetermined locations. Moreover, the GVT approach offers the advantage of easy reproducibility in various research laboratories, as the setup is relatively simple and straightforward.⁸¹ The BNNT films display superhydrophobic characteristics attributed to two main factors. First, their nanoscopic surface roughness, as depicted in Figure 7, contributes to the creation of a water-repellent surface.⁸² Additionally, the films exhibit reduced surface energy caused by the formation of adsorbates, further enhancing their superhydrophobic properties.⁸⁰

Another approach for the synthesis of BNNTs, first introduced by Chen et al. in 1999 involves the high-temperature ball milling process.⁸³ Over time, this method has been further developed and refined by incorporating boron ink.^{84–87} The process entails ball milling boron powder under an N₂/NH₃ atmosphere for an extended duration, which can be up to 150 h. Subsequently, the milled boron powder is mixed with ferric nitrate (Fe(NO₃)₃) and cobalt nitrate (Co(NO₃)₂) in ethanol to create B ink. The B ink is then subjected to treatment with N₂/NH₃ at temperatures ranging from 1000

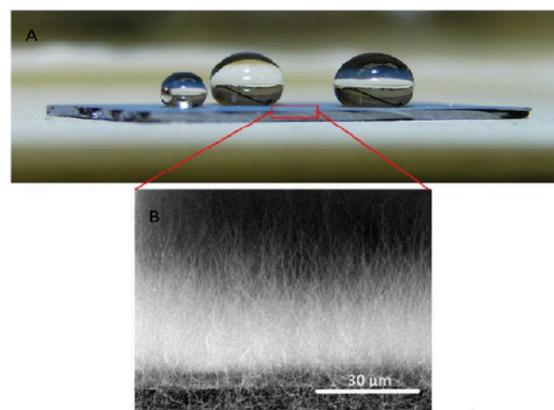


Figure 7. (a) A photograph demonstrating the superhydrophobic nature of a BNNT film produced by CCVD. (b) A zoom-in cross-sectional view of BNNTs grown on a silicon substrate, revealing the vertical alignment of the BNNTs on the substrate surface. Adapted/reprinted with permission from ref 80. Copyright (2012) ACS Publication.

°C to 1300 °C for several hours to facilitate the conversion into BNNTs. Additionally, B ink can be applied onto various surfaces to deposit BNNTs.⁸⁶

2.3.2. Laser Vaporization with Pressurized Vapor/Condenser Method. Since 1996, the laser ablation or laser evaporation technique has been employed for the growth of BNNTs, drawing inspiration from the growth process of carbon nanotubes (CNTs) followed by the work of many researchers.^{88–91} In 2005, Yap et al. achieved a significant breakthrough by demonstrating the first successful patterned growth of BNNTs on substrates using iron catalysts and pulsed-laser deposition of a BN target.⁹² This catalytic pulsed-laser deposition (PLD) approach enabled the formation of fine BNNTs with diameters ranging from ~10 to 20 nm, at relatively low substrate temperatures of about 600 °C.

In 2007, Arenal et al. reported a root-based growth mechanism for single-wall BNNTs through laser heating under N₂ at 1 atm.⁸⁸ A notable advancement in the synthesis of BNNTs was achieved in 2009 through a modified laser evaporation technique.⁹³ This method, later referred to as the high temperature/high pressure (HTP) method, utilized the pressurized vapor/condenser (PVC) approach. In this process, a high-powered laser, either a 1 kW free-electron laser with a wavelength of 1.6 μm or a kW-class CO₂ laser with a wavelength of 10.6 μm, was used to vaporize a boron (or BN) target within a chamber filled with high-pressure nitrogen (pressure ranging from 2 to 20 bar). The intense laser vaporization resulted in the production of a hot boron vapor stream at temperatures of approximately 4000 °C, which then condensed into liquid boron droplets, serving as nucleation sites. These boron droplets, aided by the elevated nitrogen pressure, rise upward and rapidly form BNNTs. To promote the growth of BNNT fibrils, a cooled metal wire is introduced through the boron plume in the chamber, acting as a condenser. The condenser can be made from various materials such as BN, B, stainless steel, copper niobium (Cu–Nb), and tungsten (W), in different shapes like wires, sheets, ribbons, and rods. The production rate typically ranges from 20 to 120 mg/h. The resulting BNNTs appear as tube bundles and an entangled network of fibrils (Figure 8).

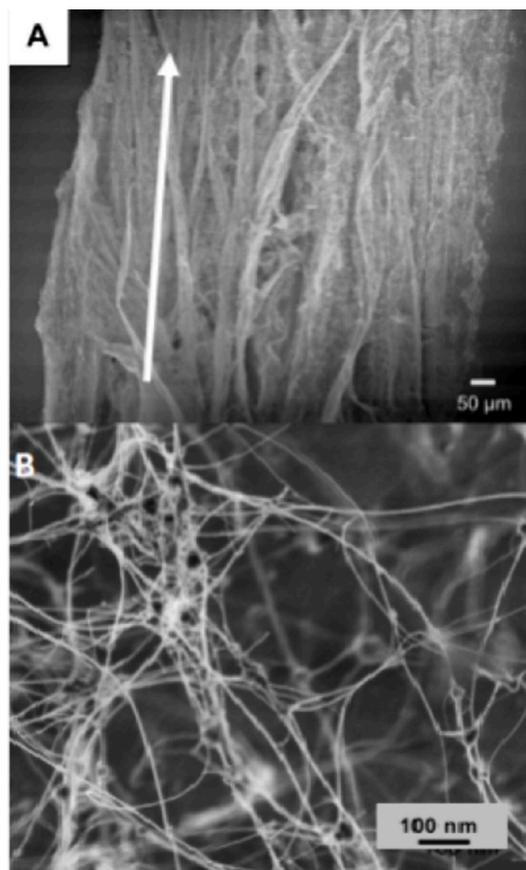


Figure 8. (a) SEM image of BNNT fibrils produced by the pressurized vapor/condenser method (PVC). The white arrow indicates the growth direction, which is parallel to the BNNT fibrils. (b) SEM image of the entangled network of BNNTs also produced using the pressurized vapor/condenser method (PVC). The short arrow highlights a round, solidified boron droplet present within the network. Adapted/reprinted with permission from ref 94. Copyright (2009) IOP Science.

Recently, the PVC/HTP method has undergone further modifications, introducing a new high-pressure chamber with a pressure of 1000 psi or 68 atm. This upgraded setup utilizes a 2.5 kW diffusion-cooled CO₂ slab laser as the energy source.⁹⁵

2.3.3. Large Scale Synthesis by Inductive Thermal Plasma Method. The torch method was utilized for large-scale synthesis of small-diameter BNNTs, measuring approximately 5 nm, at an impressive rate of 20 g/h. The process involved feeding solid hexagonal boron nitride (h-BN) powder, along with N₂ and H₂ gases, into a high-temperature induction plasma with temperatures exceeding 8000 K and operating at

atmospheric pressure.⁹⁶ The high-temperature plasma decomposed all the precursor materials into their constituent elements (B, N, and H), leading to the condensation of nanosized boron droplets downstream of the reactor, where the temperature gradient was notably large at 105 K/s. These boron droplets served as nucleation sites for the formation of BNNTs.

It was claimed that hydrogen gas played a crucial role in this process by acting as a catalyst. It formed an intermediate H–B–N species, which hindered the recombination of N radicals generated from the N₂ feedstock or from the dissociation of h-BN.

A similar technique using inductively coupled plasma for BNNT synthesis was independently reported in 2014.⁹⁷ In this method, a customized extended pressure inductively coupled plasma (EPIC) system was constructed, capable of producing plasma with power ranging from 40 to 50 kW. By flowing N₂ gas at a rate of 50 L per minute, a N₂ plasma plume was generated. Boron feedstock, such as amorphous boron or h-BN powder, was injected into the plasma plume at rates ranging from 100 mg/min to 1700 mg/min, using N₂ as the carrier gas at pressures varying from 14.7 to 75 psi absolute. Under high N₂ pressure, molten boron droplets formed within the plasma plume, which reacted with N₂ to create BNNTs, resulting in a remarkable growth rate of 35 g per hour.⁹⁷

2.4. Synthesis of BNNS. Borazine was used to grow one ever BNNS kind of structure on a metal substrate.⁹⁸ The two most prominent methods, mechanical and chemical exfoliation, are used to form BNNS.⁹⁹ The former utilized a Scotch tape to peel the layers of the BN sample^{100–102} or exfoliate BN and further ultrasonicate to achieve BNNS layers,^{34,103} whereas the latter utilizes molten hydroxides for the same.¹⁰⁴ This review will briefly discuss the methods of synthesizing BNNS.

1. **Mechanical Exfoliation:** This method involves direct by applying forces in the material causing mechanical exfoliation^{105–107} and other exfoliation techniques use shear forces which reduce the size.^{86,108} Ball milling is a highly effective approach for exfoliating bulk h-BN material into few-layered sheets. Urea is found to be one of the most popular mixtures of h-BN as the smaller molecules of urea can easily penetrate the interlayer defects of h-BN assisting efficient exfoliation.^{109,110}

It is noteworthy (Figure 9) that the thickness of BNNS has a direct relation with the properties whereas the thickness of the BNNS is defined by the method of synthesizing and further the time duration for which processes like ball milling are performed of the BNNS is defined by the method of synthesizing and further the time duration for which processes like ball milling are performed, low-energy ball milling and integration with sonication have been used to obtain high-yield

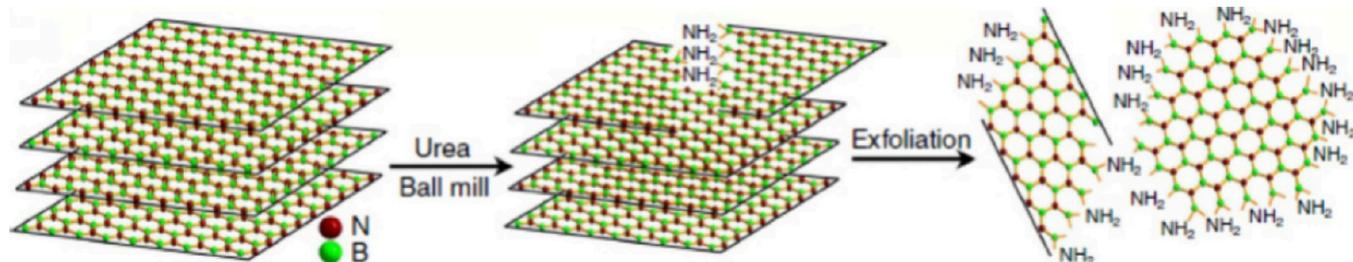


Figure 9. Urea assisted ball milling. Adapted/reprinted with permission from ref 99. Copyright (2022) Chemistry Europe.

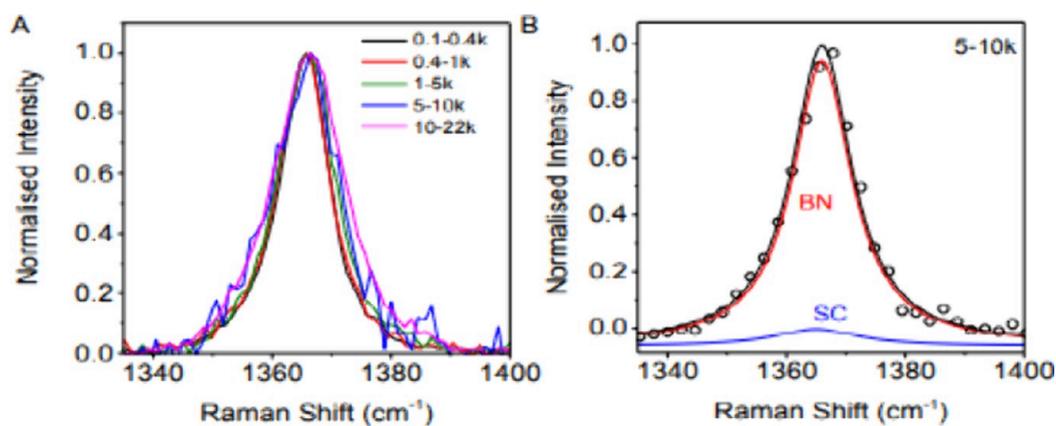


Figure 10. (a) Results of Raman Spectroscopy based ranging for different sizes and (b) results of Raman spectroscopy for BNNS dispersed normal to the maxima peak at G Band Frequency. Adapted/reprinted with permission from ref 111. Copyright (2018) ACS Publication.

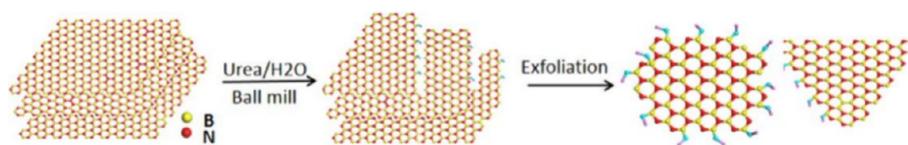


Figure 11. Schematic representation of BNNS from h-BN via ball milling. Adapted/reprinted with permission from ref 117. Copyright (2019) IOP Science.

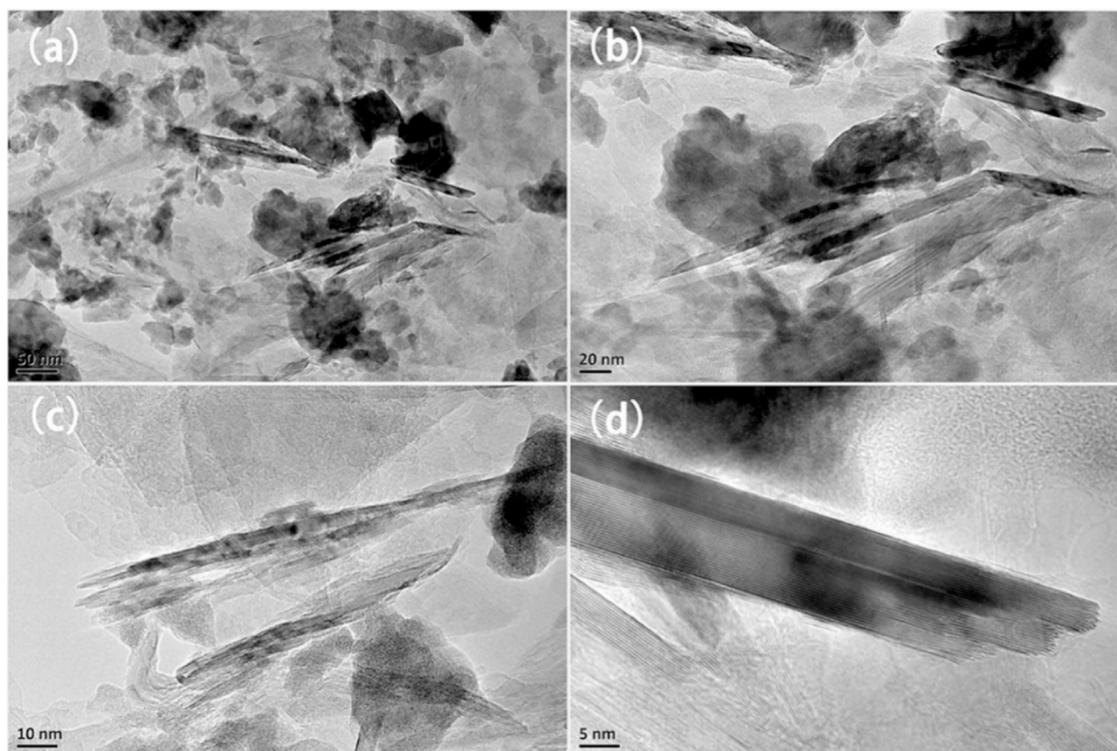


Figure 12. TEM images of ball milled commercial h-BN sample to BNNS under (a) 5000× magnification, (b) 12 500× magnification, (c) 25 000× magnification, and (d) 50 000× magnification. Adapted/reprinted with permission from ref 118. Copyright (2021) ACS Publications.

and high-quality BNNS⁸⁷ (Figure 10). The BNNS achieved after the process of ball milling wherein organic dispersion solvents are used can lead to successful exfoliation of h-BN, but the milling is not homogeneous and isotropic in a particular direction.⁹⁹ In some cases, the XRD results done on the ball milled sample show an increase in the width of the peak suggesting the presence of defects and many petite samples of

BNNS which is also confirmed with the help of SEM and TEM¹⁰⁹ (Figure 11). Recently BNNS exfoliated via utilizing thionyl chloride as the liquid medium have found their way into applications wherein large lateral dimensions of BNNS are needed.^{112–114} These BNNS obtained are not suitable for nanocomposite films fillers wherein high thermal transport is the prime criteria.^{110,115,116} The above research supports the

effectiveness of the method of ball milling as the mechanical forces break more inter layer bonds due to weak Vander walls forces than intra layer bonds. To further improve the quality of BNNS obtained from this process by regulating the mechanical forces applied and by selecting appropriate dispersing agents resulting in high aspect ratios and better lateral dimensions.⁹⁹ Figure 12 highlights the TEM imaging of the ball milled BNNS sample.

2. Liquid Exfoliation: BNNS can be successfully obtained using different solvents. Many researchers have experimented with the same to produce the results wherein solvents such as 1,2-dichloroethane,¹¹⁹ water,¹²⁰ sodium dodecyl sulfate (SDS)–water solutions,¹²¹ *N,N'*-dimethylformamide (DMF)³⁴, sulfonic acid, and methanesulfonic acid¹²² have been used to exfoliate h-BN to BNNS. The selection of solvents is essential for effective exfoliation which forms the basic criteria for the output of BNNS obtained and the Hansen solubility parameter (HSP)¹²³ theory is used to understand their functions in h-BN exfoliation. Liquid exfoliation uses effective exfoliation agents like isopropyl alcohol (IPA). IPA is one of the most effective solvents. The surface energy of IPA is very similar to that of nanosheets which in turn reduces the van der Waals forces of attraction between

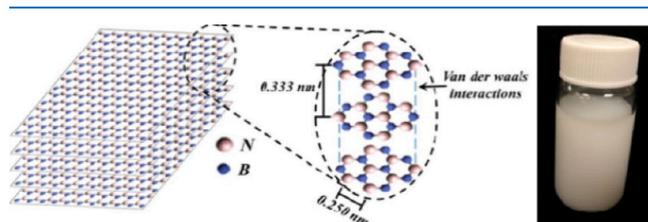


Figure 13. Crystal Structure representation of h-BN on the left. Aqueous solution of BNNS obtained from sonication of h-BN in IPA on the right. Adapted/reprinted with permission from ref 99. Copyright (2022) Chemistry Europe.

the interlayered sheets of boron nitride thereby reducing the energy required for exfoliation (Figure 13).^{99,124,125}

Furthermore, epitaxial growth of monolayer h-BN has been demonstrated on preferred substrates like Pt,^{111,126} Ru (001), and Ni^{111,127} using borazine as the precursor. Many of the solvents are excluded due to their high cost, toxicity, and high boiling point. One of the important conclusions derived was that the surfactants play a major role in the stabilization of the aqueous solution and a minor role in the process of exfoliation.⁹⁹ Many have discussed the use of polymers like polybutadiene, poly(styrene-*co*-butadiene), poly(vinyl chloride), poly(vinyl acetate), PMMA, etc. in water or organic solvents for the process of exfoliation. The results for the same have been found up to the mark wherein many hurdles were observed. The main is the extraction of these added polymers from the exfoliated samples.^{128–131} Out of all the above stated exfoliations, isopropanol (IPA) is found to have the maximum efficiency out of all the solvents.⁹⁹

3. Chemical Vapor Deposition (CVD): Growing a single layer of Epitaxial h-BN can be achieved on substrates like Pt,¹¹¹ Ru (001), and Ni¹¹¹ by adsorption and decomposition of borazine.¹³² Traditionally, Cu and Ni foils are one of the most popular choice of substrate for

the growth of two-dimensional hexagonal boron nitride (h-BN) due to their cost-effectiveness and excellent catalytic properties.^{133,134} Further experimentation have led to identification of many substrates, including Pt,^{135,136} Ni and Cu.^{137,138} Wang et al.⁹² achieved the preparation of a triangular monolayer single crystal h-BN measuring 20 nm by thermal annealing Cu foils, and the size of the h-BN varied depending on the annealing time.

2.5. Properties of BNNS and BNNT. Boron nitride therefore due to its analogous behavior as graphite has become a quite popular research subject wherein B–N ionic bonding leads to a comparable difference in various properties of the two materials.

2.5.1. Electrical Properties of BNNTs and BNNS. One of the most discussed properties of boron nitride materials is the wide band gap which further induces an internal electrical insulation in the material.^{139–142} Polarization effects of BNNTs (Figure 6) have proven to drastically increase the adhesion between the nano tubes and the matrix polymer which show much more promising results than CNTs.¹⁴³ This adhesion has further increased the interfacial bond between the nano tubes and the matrix polymer forming a composite with higher mechanical strength than that with CNTs.

The defects and the edge effects of the matrix polymer make BNNS the most superior 2D dielectric material.^{144,145} A similar internal electrical insulation is observed in BNNS as well, which continues to perform the best until excessive defects or excessive edge effects hamper the same.

Therefore, both of the filler derivations of BN can be preferred in polymer composites to enhance dielectric properties.

2.5.2. Thermal Properties of BNNTs and BNNS. Both of the nano derivatives of the BN structure show excellent resistance to oxidation at higher temperatures with exceptional structural stability. BNNTs can withstand a temperature of 800 °C and monolayer BNNS can withstand temperatures up to 850 °C in air.^{146–148} BNNTs and BNNS therefore are two of the most preferred fillers wherein high-performance oxidation resistant coatings are required.¹⁴⁹

A direct relation was observed between the increase in the oxidation at slightly lower temperatures when the number of layers of BNNS are increased.¹⁵⁰ A drastic decrease in BNNTs decomposition temperature can be observed at 1000 °C to 1700 °C when placed in a sturdy electric field as it hampers the partial ionic bonds.¹⁵¹

A major difference between the predicted thermal conductivity and the actual experimental thermal conductivity is observed. The thermal conductivity of BNNTs was predicted to be 6000 WmK⁻¹^{152–154} wherein the experimental results^{155–157} proved the results to be around 200 WmK⁻¹ for MWBNNT with a 40 nm diameter.

A direct relation between the diameter of the BNNTs and thermal conductivity is observed where reduced diameter will have higher is the thermal conductivity therefore single walled nano tubes have higher thermal conductivity than multiwalled nanotubes and CNTs (Figure 14). An interfacial thermal resistance drastically reduces the thermal conductivity if BNNTs are used collectively.^{158,159}

BNNS have demonstrated a varied range of thermal conductivities in various experiments with no concrete results.^{160,161} One of the key factors observed to play a role in the determination of a relatively lower thermal conductivity

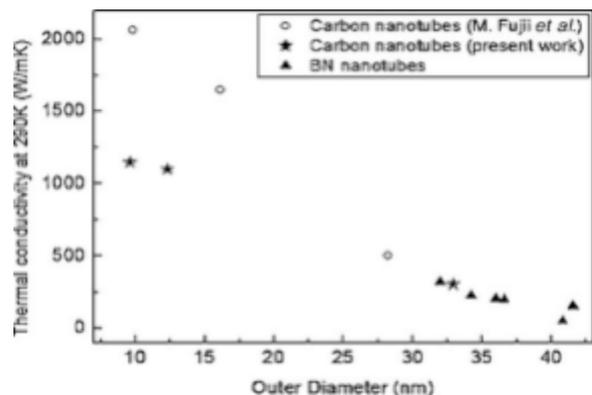


Figure 14. Graph displaying the thermal conductivity of BNNTs (boron nitride nanotubes) at 290 K (Kelvin) in comparison to their outer diameter. Adapted/reprinted with permission from ref 156. Copyright (2006) *Phys. Rev. J.*

than their carbon counterpart is molecular dynamics. A strong phonon scattering restriction is observed between the layers of BNNS which can be improvised by isotopic enrichment.^{162,163}

Even with ambiguous results single layered BNNTs and BNNS improve the thermal conductivity when used as fillers in polymers for thermally conductive and electrically insulating composites.

2.5.3. Mechanical Properties of BNNTs and BNNS. BNNTs and BNNS both seem to exhibit excellent mechanical properties in terms of Young's modulus. Theoretical values of 0.837–0.912 are reported^{164–168} further due to larger scattering BNNTs seem to perform better in extreme deformation conditions and at high temperatures. A range of data in terms of Young's modulus is observed which seems to vary with the method of synthesis adopted. A similar result is seen in the case of BNNS wherein the method adopted for synthesis varied the bending modulus.^{169–171} The mechanical properties in the case of BNNS seem to also depend on the sheet thickness wherein the increase in the thickness of the sheet size decreases the bending modulus. This is due to the stacking defects within the layers of BNNS. Therefore, thin BNNTs and BNNS are preferred when a reinforcement option is to be considered in polymers for optimum mechanical results.

2.5.4. Optical Properties of BNNTs and BNNS. The constant energy band gap with less impurities imparts the white color to both these Nano derivatives of BN.¹⁷² Both of these show photoluminescence and cathodoluminescence under UV light.^{173–177} The method of synthesis is responsible for the optical properties wherein the wavelength emitted depends on the method of synthesis. With increasingly thinner the BNNS sheets, better investigation of the quantum properties can be made.

UV radiation is one of the emissions received on the earth's surface via the Sun. The spectrum of UV radiation is further subdivided into the three categories of UVA (315–400 nm), UVB (280–315 nm), and UVC (100–280 nm). Out of which UVB is largely blocked by glass but more than 50% of UVA can penetrate through glass. These radiations are classified according to their wavelength wherein the shorter the wavelength, the more harmful they become. There are many factors that determine the impact of UV radiation such as time of the year and of the day, latitude, altitude, clouds, and haze etc.¹⁷⁹

Incorporation of both BNNS and BNNTs in composites or as thin films can lead to transparent polymers which can be used to shield for UV blocking (Figure 15). Channelizing the property of the BNNS by coating the polymers will be the focus of this paper.

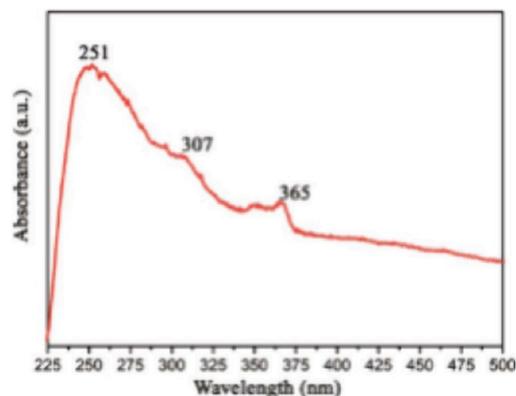


Figure 15. UV spectroscopy of BNNS. Adapted/reprinted with permission from ref 178. Copyright (2018) IOP Science.

3. NANOCOMPOSITES AND THEIR SYNTHESIS METHODS

Nanocomposites are composite materials in which at least one of the constituents has nanometric dimensions. The matrix is generally the base, and the strength is provided nanometrically. Nanofillers are added to improve various physical properties like the mechanical, thermal, and physicochemical properties of the resulting materials.^{180–184} The process of nanocomposite synthesis involves ensuring the uniform distribution of nanofillers within a polymer or ceramic matrix. Nanocomposites are categorized based on the types of nanofillers and matrix materials employed. Specifically, two main classes of BN nanocomposites are discussed here, determined by the chosen matrix material: polymer-based and ceramic-based nanocomposites. This paper focuses on polymer based nanocomposites.

3.1. Polymer Based Nanocomposites. Polymer-based nanocomposites consist of a polymer matrix that acts as a base for the material and nanofillers, such as BN nanomaterials, as reinforcements. Polymers possess appealing properties like being lightweight, ease of processing, corrosion resistance, ductility, and cost-effectiveness. Additionally, they exhibit gas barrier properties, heat resistance, and fire resistance.^{185,186} However, their main drawback lies in their low thermal and electrical conductivities.¹⁸⁷ By incorporating nanofillers as reinforcing agents into a polymer matrix, the resulting nanocomposite's properties are significantly enhanced. As mentioned previously, nanofillers can be categorized into three classes based on their dimensionality: 0D (spherical particles), 1D (nanotubes and fibers), and 2D (nanosheets). The selection of the reinforcement material depends on the intended application. When reinforcing a polymer matrix, several crucial factors come into play:

- (i) The properties of the polymer itself.
- (ii) The characteristics and the percentage by weight of the nanofiller added reinforcement.
- (iii) The average particle size, orientation, and distribution of the nanofillers added to the polymer matrix.¹⁸⁸

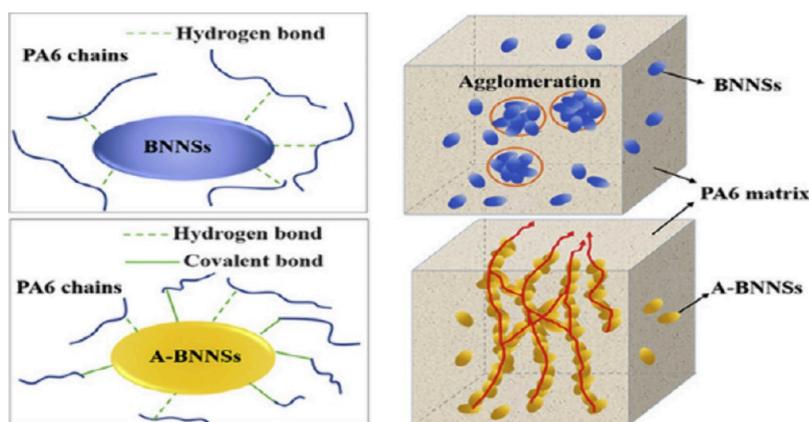


Figure 16. Nanocomposites depicted in the image are composed of nylon-6 (PA6) along with hexagonal boron nitride nanosheets (h-BNNS) or amino-functionalized h-BNNS (A-BNNS). Adapted/reprinted with permission from ref 190. Copyright (2018) ACS Publications.

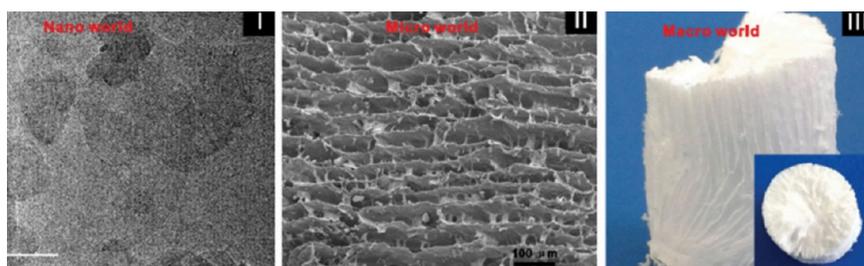


Figure 17. Hierarchical structures of the free-standing 3D-BNNS aerogel are depicted as follows: (I) Transmission electron microscopy (TEM) image of the BNNS. (II) Scanning electron microscopy (SEM) image of the 3D-BNNS aerogel, captured from a direction perpendicular to the ice growth. (III) Photograph of the 3D-BNNS aerogel. Adapted/reprinted with permission from ref 192. Copyright (2015) Wiley.

3.2. Synthesis of Polymer Based Nanocomposites.

Polymer Nanocomposites are manufactured using various methods, which can be broadly categorized into four main routes: melt intercalation/blending, in situ polymerization intercalation, template synthesis, and solvent mixing. Additionally, more recently, sonication and high-shear mixing have been suggested as alternative techniques to produce (bio)-nanocomposite materials. In this review, the emphasis will be on the techniques employed to create polymer-based nanocomposites utilizing BNNTs and BNNS as nanofillers to improve their properties.

3.2.1. Melt Intercalation/Blending. Melt intercalation stands out as the most widely utilized method for synthesizing thermoplastic polymer-based nanocomposites. This approach typically involves three main steps: first, annealing the polymer matrix at high temperatures, followed by the addition of nanofillers, and finally, blending the composite to achieve a uniform distribution.¹⁸⁹ For example, h-BN can be integrated into a polymer matrix through the preparation of thermoplastic polyurethane (TPU) nanocomposites containing nano-h-BN. This is accomplished by melt blending using a corotating twin-screw extruder, and then forming thin TPU/h-BN films via hot pressing techniques.

In their study, Wang et al.¹⁹⁰ enhanced the thermal conductivity and mechanical properties of nylon-6 (PA6) through a two-step process (Figure 16). They first performed surface functionalization of BN nanosheets (BNNS) with amino groups, followed by melt blending with PA6. As a result of the amino functionalization, the BN nanosheets were better dispersed in the polymer matrix compared to nonfunctionalized BNNS as shown. This significant improvement in

dispersion led to a nearly 10-fold increase in thermal conductivity and thermal stability of the PA6/A-BNNS nanocomposites.

3.2.2. In-Situ Polymerization. This technique allows efficient dispersion of nanofillers within the polymer matrix. Typically, nanomaterials are combined with a neat monomer or a monomer solution, and the mixture is then polymerized using heat, radiation, or an organic initiator. This method offers several advantages for preparing BN/polymer-based nanocomposites, especially the formation of strong interactions between BN nanoparticles and the polymer matrix through covalent bonds. Additionally, it helps to suppress particle aggregation by enabling the controlled growth of polymer chains around the nanoparticles. However, further research is required to address the solvent removal process in this method.¹⁰

3.2.3. Template Synthesis. Templating is a technique used in the production of nanostructured materials. It utilizes a pre-existing pattern or template as a guide to shape the nanomaterials for the synthesis process. This method imparts precise control over the size, shape, and arrangement of nanomaterials, resulting in well-defined and tailored nanostructures with enhanced properties for various applications. The method of templating is commonly used to synthesize nanomaterials with well-defined size, shape, and configuration. This process involves three main steps: (i) creating building blocks, (ii) assembling building blocks guided by templates, and (iii) removing the template if necessary.¹⁹¹

Zeng et al. described a method for developing 3D-BNNS networks using an ice-templated approach. First, anisotropic freezing was done by using liquid nitrogen as a cryogen and

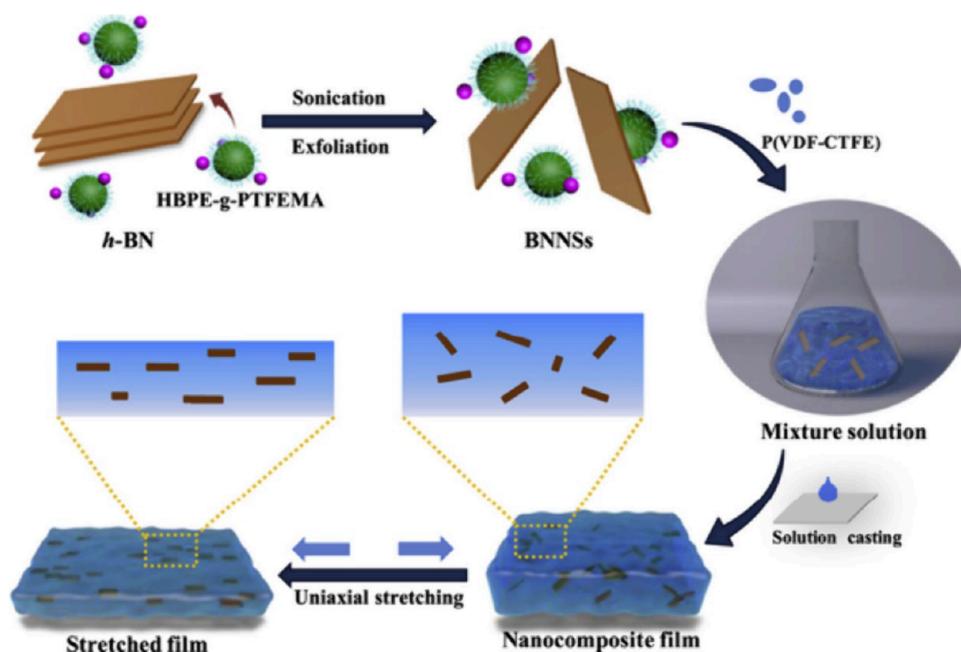


Figure 18. Process involves exfoliating BNNS in dimethylformamide (DMF) using a fluoro-hyperbranched polyethylene-*graft*-poly(trifluoroethyl methacrylate) (HBPE-*g*-PTFEMA) as a stabilizing agent. Preparation of Stretched BNNS/P(VDF-CTFE) Nanocomposite Film: This process entails creating a nanocomposite film composed of BNNS embedded in a poly(vinylidene fluoride-chlorotrifluoroethylene) (P(VDF-CTFE)) polymer matrix. To achieve the desired orientation of BNNS within the film, the material is uniaxially stretched at a constant temperature, allowing for controlled alignment of the nanosheets along the direction of deformation. Adapted/reprinted with permission from ref 197. Copyright (2020) IOP Science.

pouring a nonfunctionalized BNNS (NF-BNNS) aqueous slurry into a Teflon mold. During the freezing process, the suspended NF-BNNS and poly(vinyl alcohol) (PVA) were expelled from the growing ice crystals, allowing for precise directional ice growth (Figure 17). The frozen samples were then freeze-dried to obtain the BNNS aerogel scaffolds. These aerogel scaffolds were then sintered to form 3D-BNNS aerogels, which were subsequently immersed in an epoxy solution matrix. The resin infiltrated the aerogel scaffold, resulting in the formation of 3D-BNNS aerogel nanocomposites.¹⁹²

The emulsion templating approach for producing nanocomposites is particularly intriguing due to several advantages it offers. One significant benefit is that this method circumvents the need for multiple sintering steps, streamlining the fabrication process. Additionally, it eliminates the use of harmful solvents, making it a more environmentally friendly and safer approach.¹⁹³

3.2.4. Solvent Mixing. The solvent mixing method is an effective technique for dispersing nanofillers, especially layered materials, into polymer matrix nanocomposites. Nanofillers, often in a layered structure, are exfoliated by intercalating an organic compound into their interlayer spaces. This process results in the dispersion of well-separated plate-like particles. The exfoliated material is then dispersed in a solvent and mixed with a polymer solution. The polymer chains intercalate into and displace the solvent within the layered material. After removing the solvent, a multilayered structure is obtained, with the polymer chains trapped within the exfoliated material. The resulting nanocomposites exhibit reinforcement due to the large contact surface area between the polymer matrix and the exfoliated material.¹⁰

Using the polymer intercalation approach, BN-based polymer nanocomposites can be prepared, leading to improved

thermal conductivity and mechanical strength.¹⁹⁴ Due to their 2D structure, BNNS possess the advantage of easy orientation along the plane within polymer matrices. This characteristic has been leveraged to fabricate nanocomposites with enhanced thermal conductivity using the polymer intercalation method. Song et al.¹⁹⁵ demonstrated the production of composite films by dispersing BNNS in polymers, resulting in nanocomposites with excellent thermal transport performance comparable to polymer/graphene nanocomposites. Similarly, Morishita et al.¹⁹⁶ developed NF-BNNS/thermoplastic polymer composite films through a straightforward wet-process method. NF-BNNS were exfoliated from h-BN by physically adsorbing chlorosulfonic acid on the h-BN surfaces via sonication. The NF-BNNS were then dispersed in acetone and mixed with a poly(methyl methacrylate)/acetone solution. The nanocomposite film was obtained by spreading the solution onto a glass support.

Furthermore, employing the same strategy of nanofiller alignment, poly(vinylidene fluoride-chlorotrifluoroethylene) (P(VDF-CTFE)) nanocomposites with BNNS oriented in parallel within the polymer matrix were prepared by casting. Initially, h-BN was exfoliated using fluoro-hyperbranched polyethylene-*graft*-poly(trifluoroethyl methacrylate) as a polymer stabilizing agent to prevent nanosheet aggregation. The resulting BNNS were then dispersed in dimethylformamide and added to a P(VDF-CTFE) matrix, leading to the formation of BNNS/P(VDF-CTFE) nanocomposite films. To further control the nanosheet orientation along the direction of deformation, the films were uniaxially stretched at a constant temperature (Figure 18).¹⁹⁷ This approach allows for the manipulation of nanosheet orientation, leading to enhanced properties and tailored performance of the nanocomposite films.

Table 1. Comparison Between BNNTs and BNNS with Additional Properties

sr. no.	properties	BNNT	BNNS
1	color	white	white
2	bonding	covalent bonds with ionic component	covalent bonds with ionic component
3	electronic structure	5.0–6.0 eV band gap independent of chirality	5.0–6.0 eV band gap independent of chirality
4	mechanical properties	Youngs modulus: 0.784–0.912 TPa; 0.71–0.83 TPa (theoretical)	2D elastic modulus: 22–510 Nm ⁻¹ (with thickness up to 1–2 nm)
5	thermal conductivity (WmK ⁻¹) at room temperature	single wall: 180–300 multi wall: 180–300	300–2000 theoretical 40 experimental
6	thermal stability	high up to 800–900 °C in air	superior to graphene
7	wetting properties and hydrophobicity	poor	water repelling, anticorrosive, and self-cleaning properties

4. PROPERTIES OF BNNT AND BNNS REINFORCED POLYMER NANOCOMPOSITES

Isentropic and Homogenous reinforcing of fillers into matrix polymers requires thorough dispersion of the fillers with no coagulation for even stress distribution for which mixing of the fillers in the matrix polymer becomes a crucial step. For filler reinforcement the critical area of evaluation is the boundary between the reinforcement and the matrix polymer. This region is where the stress transfer from the matrix polymer takes place to the filler and depending on the adhesion between the two this can lead to an isotropic material with a better interfacial interaction and dispersibility. In the case of immiscible materials like BNNTs additional functionalization is required for an appropriate adhesion between the matrix polymer and this filler.

Functionalizing BNNTs by covering them with amine terminated oligomeric polyethylene glycol (PEG1500N)¹⁹⁸ or poly[*m*-phenylenevinylene-*co*-2,5,-dioxyp-phenylenevinylene) (PmPV).⁷³ An electrostatic interaction between Boron with amine sites in the case of PEG1500N is observed whereas interaction between PmPV with the π stacking present on the surface of BNNTs have proved relatively weak but one in which the interaction can be channelized for various applications. This functionalization has proved to improve the dispersibility of BNNTs across the matrix polymers with a better and stronger interfacial interaction.^{45,148} This has further led to improving the overall properties of the matrix polymers with BNNTs as the reinforcements. A study of the molecular dynamics of BNNTs functionalized with PmPV reinforced polystyrene (PS) and polythiophene (PT) shows better and stronger molecular interactions than CNTs in the same.^{199–201}

BNNS have shown high miscibility with various solvents thereby reducing the requirement for additional functionalization before utilizing them in polymer applications. There are additional functional groups attached to them which increase their dispersibility when dispersed via sonication. h-BN, the parent material for the majority of all derivatives, exhibits exceptional mechanical properties thereby imparting the same to the derivatives BNNS and BNNTs, making them a suitable option for mechanical reinforcements. Addition of 1% of BNNTs to polystyrene by weight increases the mechanical strength by 7%. These can be further enhanced by using PmPV as a surfactant.⁴⁵

A few parameters were observed wherein the dispersibility of BNNTs, interfacial interactions between the polymer, and the transparency of the polymer seems to be affected directly by the percentage of BNNTs added.

Properties achieved by BNNS, however, depend on the thickness of the BNNS achieved. The most common method

of preparation is via exfoliation of h-BN powder and further using sonication centrifugation technique²⁰² to fabricate various BNNS based transparent composites. Addition of 0.3% BNNS by weight to PMMA increased the strength by 11% and elastic modulus by 22%. Creating a colloidal solution in various solvents was tested¹⁰³ which with the addition of just 0.12% by weight increased the properties of PVA by 40% in comparison to the pure polymer. In addition to this, various factors affect the properties imparted to the polymers by BNNS. Uniaxial drawing, strain induced exfoliation, method of preparation of BNNS, and the alignment of the BNNS are just some of the factors which directly increase the efficiency of the mechanical reinforcement especially in case of BNNS.^{202–204}

Thermal conduction with electrical insulation is an exceptional property possessed by h-BN materials and their derivatives, which makes them an apt choice for thermally conductive insulating polymer composites. The nano derivatives of h-BN form an advantageous option for reinforcing polymers (the values of the same are discussed in Table 1). Exceptional properties are observed along the lattice plane (002) which exhibits very high thermal conductivity, whereas the thermal conductivity in the other lattice plane is not the same, leading to high thermal conductivity in h-BN. This effect is additionally maximized when the size is in nanometers, as the thickness of the low thermal conducting lattice planes can be reduced. The small size may encourage connection between two particles forming a conductive pathway thereby increasing the thermal conduction in the polymer itself.

PVF composite film with BNNTs 10% by weight can increase the thermal conductivity of the polymer up to 250%.²⁰⁵ Similar experiments were conducted by incorporating BNNS manufactured by sonication exfoliation and exfoliating h-BN to give nano BNNS in PMMA³⁴ and PVA. BNNS exfoliated via ball milling, with urea as the solvent are functionalized BNNS as they possess improved stability while dispersing in an aqueous solution.²⁰⁶ Reduction in the coefficient of thermal expansion was observed. It is extremely important to increase the dispersibility interaction between the filler and the polymer, especially at the grain boundary of the filler. This affects the thermal conductivity of the polymer composite in addition to the size and shape. The interaction can be increased by adding a surface modification for any filler loading.^{205,207–210} To improve the homogeneity along a particular direction, the filler orientation and alignment play a very important role. Various processing methods help in increasing the orientation and alignment of the filler, including the electric field application and the magnetic field application in the case of BNNS.^{211–214} Whereas in the case of BNNTs,

polymer composite fibers can be aligned during the fabrication process via electrospinning.²¹⁵

Many experiments have also established a correlation between the thermal diffusivity and the alignment of entrenched BNNS in nanocomposites which is valid when the percentage of BNNS added is higher than 10% by weight²¹⁶ (Figure 19). Some of the other researchers have also

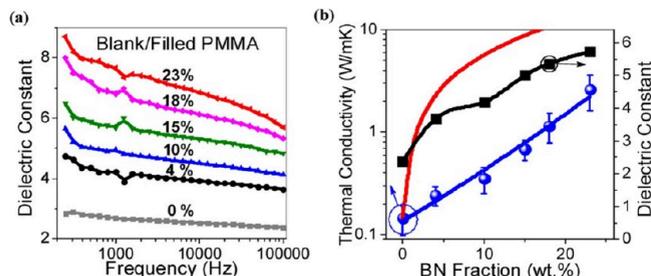


Figure 19. (a) Dielectric constants varying with frequency for pure PMMA and PMMA/BN composite materials. (b) The dielectric constant (measured at 10^6 Hz) and thermal conductivity show an increasing trend as the BN fraction in PMMA/BN composites increases. The blue curve represents the fit to experimental data using the Agari model, while the red curve indicates the theoretical upper limit of thermal conductivities according to a parallel model. Adapted/reprinted with permission from ref 176. Copyright (2012) Springer.

suggested the presence of defects induced during exfoliation of BNNS have proved favorable. These BNNS when incorporated as fillers improve the dispersion of filler in the matrix polymer by reducing the thermal resistance offered by the matrix polymer to BNNS at the interface.^{99,217,218}

5. APPLICATIONS OF NANOCOMPOSITES IN VARIOUS SECTORS

BN nanocomposites are employed to augment the strength and toughness of the matrix material, creating materials that combine the advantageous properties of both components. In the following sections, we will review the key applications of nanostructured BN and BN-based nanocomposites, with a specific focus on their significance in the fields of energy, environment, and health.

5.1. Energy Applications. **5.1.1. Transistors and LED.** This is in terms of Thermal Management wherein BN-based nanocomposites are utilized in electronic devices, such as transistors and LEDs, to enhance thermal conductivity and dissipate heat efficiently. Due to its exceptional thermal properties, BN has garnered significant attention in research for the development of innovative nanocomposites. Single-layer h-BN possesses an impressive theoretical thermal conductivity of approximately 1700 to $2000 \text{ Wm}^{-1} \text{ K}^{-1}$.¹⁰ High power electronic devices face the issue of excessive heat generation at the junction thereby reducing the efficiency and lifespan of the device. A recent study has suggested that utilizing BNNTs as a filler reduces the heat generation as their thermal conductivity is high thereby these acts as a heat sink source.²¹⁹

Reducing the size of field effect transistors (FET) have faced a lot of shortcomings like current leakage, high contact resistance, etc.²²⁰ This was resolved by incorporating BNNTs in FETs without using any semiconductor material. This was achieved by creating a quantum tunnel between BNNT

decorated gold quantum dots.²²¹ Additionally, iron nanoparticles coated with BNNTs were also utilized providing flexible tunnelling channel with bending angles up to 75° .²²² Exploiting the tubular shape of the BNNTs researchers have filled atomic chains inside with tellurium. These tellurium atoms are covalently bonded with each other inside the chain and stacked on one another using van der Waals forces. The experimentation successfully proved the FET channelling of length up to 100 nm and are therefore categorized as semiconducting materials with high ampacity (Figure 20).^{220,223}

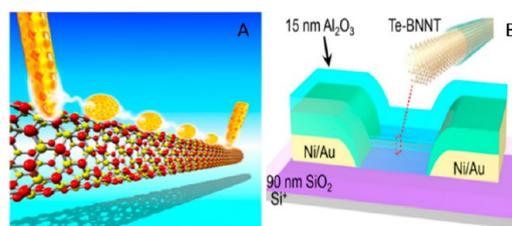


Figure 20. (a) Transistors formed by connecting atomic chains inside BNNTs and (b) transistors formed without using semiconductors. Adapted/reprinted with permission from ref 220. Copyright (2021) ACS Publications.

Channelizing the evenness and atomically smooth surfaces and the presence of free dangling bonds and charge traps on the surface of 2D h-BN, many researchers have experimented with these materials for FET devices for high mobility.²²⁴ One of the researchers fabricated in plane and vertical graphene/h-BN heterostructure device for FET via benzoic acid resulting in electron and holes in graphene $15000 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ at room temperature.²²⁵ Whereas a monolayer h-BN film formed via PECVD at 500°C for the graphene/h-BN FET device reveals exceptional quality and even multilayer graphene/h-BN films are favorable for FET applications.^{224,226}

5.1.2. Energy Storage and Capacitors. BNNS have seemed to find their way into sustainable yet efficient energy storage devices like dielectric capacitors, electrochemical capacitors, and commercial batteries. Dielectric capacitors are one of the most preferred due to their high power density, larger operating voltage, and better life with more efficiency. The recent advancements in the field of dielectric capacitors using poly(vinylidene fluoride) (PVDF) as the dielectric film and by further incorporating BNNS into the polymer composite not only increases the dielectric strength but also the overall performance of the capacitor. The E_b value reported is as high as $\sim 1200 \text{ MVm}^{-1}$ with a very low dielectric loss ($\sim 2.5 \times 10^{-4}$) and excellent electrical insulation. BNNS was added to many more polymers like ferroelectric terpolymer, cross-linked divinyltetram-ethylsiloxane-bis(benzocyclobutene), reporting excellent results. Therefore addition of BNNS-added polymers to form nanocomposites delivers better overall efficiency than ceramics.²²⁴

5.1.3. Thermal Energy. In nanocomposites, the improvement in thermal conductivity is achieved by minimizing the interfacial thermal resistance between the nanofillers and the polymer or ceramic matrices. By reducing this resistance, heat transfer within the nanocomposite becomes more efficient, leading to enhanced thermal conductivity.^{227,228} Notably, the thermal conductivity of nanocomposites depends on factors such as the type of polymer matrix used, and the concentration of fillers incorporated. Optimizing these parameters is crucial

for tailoring the thermal properties of the nanocomposite material to meet the specific application requirements.

PVA/BN films have been found to exhibit higher thermal conductivities at lower BN loads compared to epoxy/BN composites, as demonstrated in the study conducted by Song et al.¹⁹⁵ This finding has sparked further research interest in utilizing PVA as a potential polymer matrix for BN nanocomposites. For instance, Zhang et al.²²⁹ developed h-BN/PVA composites using a vacuum filtration technique, followed by wetting the PVA. During the wetting process, some h-BN fillers diffuse through the polymer matrix, creating pathways for heat conduction. This diffusion phenomenon reduces the time needed for polymer infiltration and, in turn, enhances the thermal conductivity of the resulting nanocomposite. This research showcases the potential of PVA as an effective polymer matrix for BN nanocomposites, where the unique interaction between PVA and BN fillers can lead to improved thermal properties which can be a great choice for batteries, electronic chips, mechanical and automotive cooling systems, and 5G.

5.1.4. Solar Cells. Nanocomposites play a significant role in enhancing the multifunctionality and efficiency of solar cells, serving as protective and photoactive layers or as surfaces for solar panels.¹⁸⁴ Introducing few-layered h-BN between graphene and *n*-Si has been shown to enhance the performance of Gr/Si Schottky junction solar cells. h-BN acts as an effective electron-blocking and hole-transporting layer, reducing interface recombination and improving cell performance.²³⁰

Perovskites have emerged as promising materials for solar cells due to their high absorption coefficients and processability at low temperatures.²³² However, their main drawback lies in their poor environmental stability.²³³ Encapsulating perovskites using h-BN materials can greatly improve their stability. Seitz et al.²³⁴ evaluated double-sided encapsulation with h-BN (h-BN/perovskite/h-BN) to provide long-term stability to 2D perovskites based on phenethylammonium lead iodide. By leveraging the insulating behavior and inertness of h-BN, heterojunction solar cells have been developed. Cho et al.²³¹ prepared MoS₂/WSe₂ heterojunction solar cells with an h-BN passivation layer using a polydimethylsiloxane (PDMS)-mediated deterministic transfer process. The power conversion efficiency of their h-BN/MoS₂/WSe₂ heterojunction solar cells (Figure 21) was improved by approximately 74% compared to unmodified h-BN material. This improvement was attributed to the reduced recombination rate at the junction and surface of the semiconductor regions, leading to enhanced overall solar cell performance.

5.1.5. Hydrogen Storage. Hydrogen (H₂) is a highly attractive renewable energy resource, but its generation and storage for practical applications remain challenging.²³⁵ Low-dimensional BN nanophase materials have shown significant promise in H₂ uptake capacity due to their strong interactions with heteropolar BeN bonds and partial H₂ chemisorption.^{236,237} Highly porous BN microbelts have been synthesized through a one-step, template-free reaction between boric acid-melamine precursors and ammonia at moderate conditions. These microbelts possess a high specific surface area of 1488 m²g⁻¹. H₂ sorption analysis demonstrated that BN microbelts exhibit reversible H₂ uptake ranging from 1.6 to 2.3 wt % at 77 K and relatively low pressure (1 MPa).²³⁸

Salameh et al.²³⁹ has developed mesoporous monolithic (3D) BN structures using a template-assisted PDC (polymer-derived ceramics) route. These BN monoliths feature a

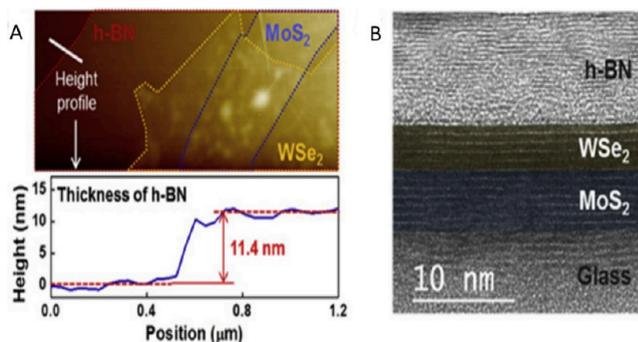


Figure 21. (A) Top, AFM image of the MoS₂/WSe₂/h-BN heterostructures. This image allows for a nanoscale visualization of the arrangement and morphology of the materials in the heterostructure. (B) False-color high-resolution TEM image that illustrates the cross-section of the heterostructure. This image offers detailed insights into the atomic arrangement and interfaces between the MoS₂, WSe₂, and h-BN layers, providing a clear view of their stacking arrangement and crystal structure. Adapted/reprinted with permission from ref 231. Copyright (2019) ACS Publications.

mesoporous network with a specific surface area ranging from 584 to 728 m² g⁻¹ and display gravimetric H₂ storage capacity of up to 8.1%. Furthermore, BN nanocomposites have potential applications in H₂ production. Methods have been developed to increase H₂ production using different sources, such as photocatalysis or electrocatalysis^{240,241} (Figure 22).

Hydrogen storage affinity was observed by Ti/BNNT as the binding energies of both is similar. Ti can attach up to 7 hydrogen molecules in the quasi-molecular form as Ti is catatonically functionalized and B–N surface bonds are heteropolar in nature.²⁴² It has been observed that BNNTs can take up to 2.6% of dopants, defects, or any surface imperfections which might aid improvement in the electrical properties.^{243,244} This can be achieved when BNNTs defect sites are modified with a transition metal specifically for hydrogen storage. Ti dopants can modify the electronic properties of BNNTs by affecting their charge transfer behavior.^{242,245}

5.1.6. Electrochemical Devices. BN-based nanocomposites have emerged as an interesting choice for use in electrochemical devices.²⁴⁶ Researchers like Idrees et al. and Wan et al.^{247,248} have focused on polymer-derived ceramics (PDC)-based nanocomposites as stable electrodes for Li-ion batteries (LIB) and other electrochemical applications. The combination of PDCs with other nanomaterials, such as carbon nanotubes,^{249,250} graphite,²⁵¹ and BN,²⁵² leads to structural modifications that enhance their properties, making them promising candidates for potential applications in LIB and supercapacitors. For instance, David et al.²⁵² demonstrated that integrating exfoliated BNNS into SiCN (silicon carbonitride) significantly increases the charge capacity of free-standing SiCN-based LIB electrodes. Similarly, Singh et al.²⁵³ investigated how Li⁺ insertion capacity could be enhanced by incorporating various loads of BNNTs into SiOC (silicon oxycarbide) ceramics. The presence of BNNTs in the composite affected the free carbon phase within the SiOC matrix, resulting in improved electrochemical performance.

The versatility and tunability of BN-based nanocomposites make them attractive for developing advanced electrode materials with enhanced electrochemical properties, paving the way for more efficient and durable electrochemical devices.

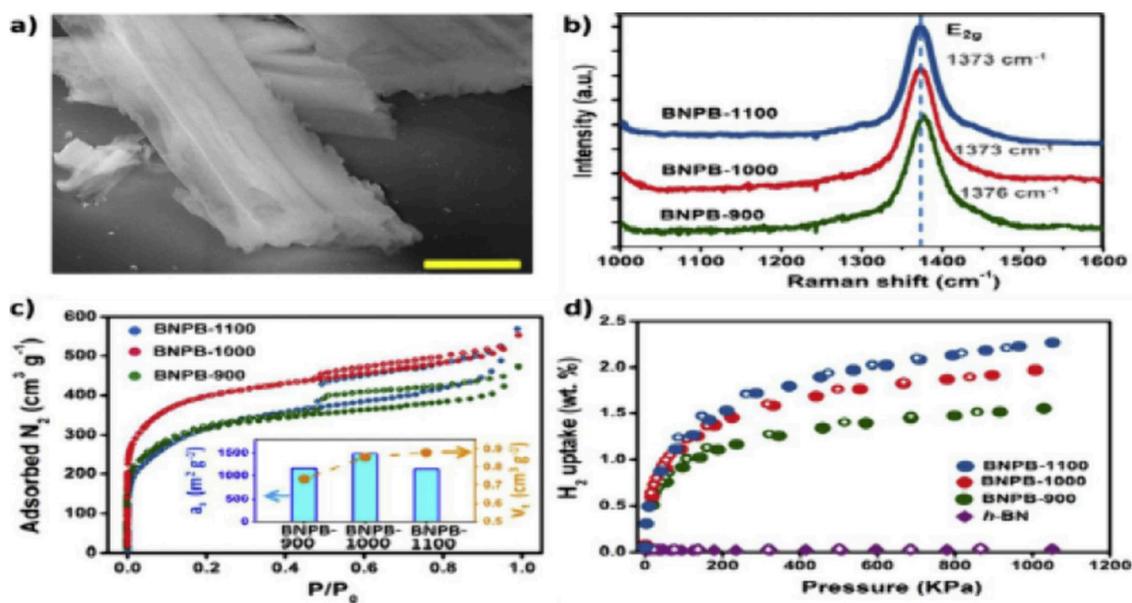


Figure 22. (a) Tilted view of isolated porous structures, clearly revealing the belt-shaped morphology of the BN micro belts. The scale bar indicates a length of 1 mm, giving an idea of the size of the structures. (b) Raman spectra of BN porous micro belts prepared at different temperatures, namely 900 °C, 1000 °C, and 1100 °C. Raman spectroscopy provides information about the structural and chemical characteristics of the BN micro belts. (c) Nitrogen adsorption–desorption isotherms of BN porous micro belts prepared at the same temperatures mentioned earlier. These isotherms provide insights into the porosity and surface area of the BN micro belts. The inset in this panel summarizes the Brunauer–Emmett–Teller (BET) surface areas and total pore volumes for the obtained samples. (d) H₂ adsorption–desorption isotherms of the BN porous micro belts at 77 K and 1 MPa. This data showcases the H₂ uptake capacity of the BN micro belts under specific conditions. Adapted/reprinted with permission from ref 238. Copyright (2013) ACS Publications.

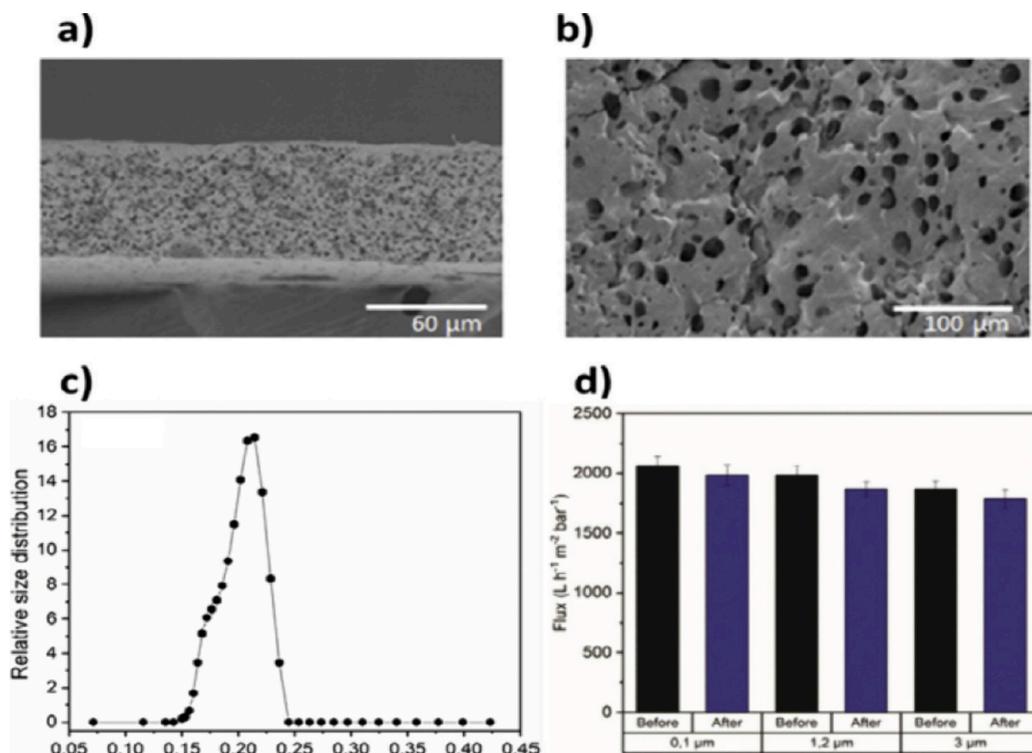


Figure 23. (a) View of the cross-section of the h-BNNS/PVA membrane nanocomposite. It reveals the internal structure and layering of the membrane (b) Surface SEM photograph displaying the top view of the h-BNNS/PVA membrane nanocomposite, providing insight into the morphology and surface characteristics of the material. (c) Plot representing the relative pore size distribution of the h-BNNS/PVA membrane. It gives information about the distribution of pore sizes within the nanocomposite membrane (d) Corresponding flux values of the h-BNNS/PVA membrane nanocomposite before and after conducting particle rejection tests. Flux is the rate of fluid flow through the membrane, and the tests are performed to evaluate the membrane's effectiveness in rejecting particles from the fluid. Adapted/reprinted with permission from ref 28. Copyright (2018) RSC Publications.

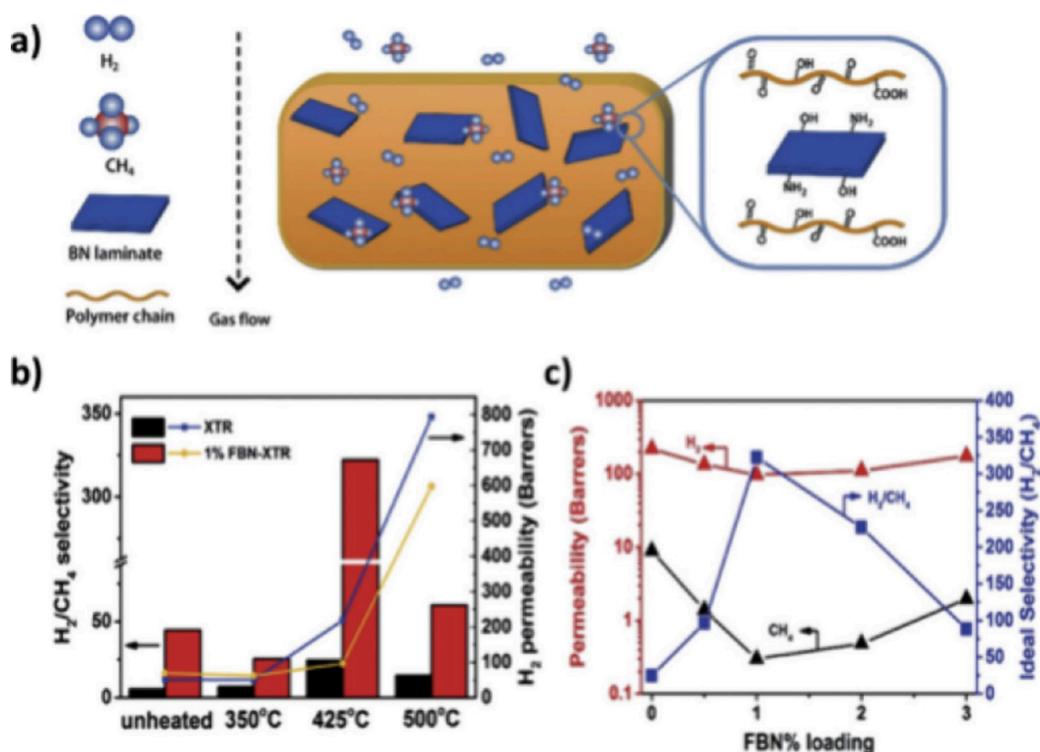


Figure 24. (a) Schematic representation of the FBN-XTR membrane structure and the process of selective gas permeation through the membrane. This provides an overview of how the membrane functions in separating different gases. (b) H₂ permeability and H₂/CH₄ selectivity of 1 wt % FBN-XTR and pure XTR membranes at different thermal rearrangement temperatures. It shows the relationship between the membrane composition and gas separation performance. (c) Gas permeability and selectivity of membranes with various FBN loads, specifically for the H₂/CH₄ gas pair, at a temperature of 258 °C and pressure of 1 bar. It demonstrates how the gas separation performance varies with different FBN loadings in the membrane. Adapted/reprinted with permission from ref 261. Copyright (2018) Wiley online library.

5.2. Environmental Applications. 5.2.1. Water Purification.

Environmental applications are available in terms of water purification wherein BN nanocomposites are used in filtration systems for efficient water purification, owing to their high surface area and tunable porosity. Novel BN-based materials have shown great potential for applications in water technologies, especially in water purification processes. BN nanotubes (BNNTs) have exceptional adsorption properties, making them highly effective for sorbing pollutants like oil and organic solvents from heavy industries and for water purification.^{254–256}

Researchers have also fabricated BN-based nanocomposites specifically for water purification using templating methods. Gonzalez Ortiz et al.²⁸ developed innovative h-BN nanosheet (h-BNNS) and poly(vinyl alcohol) (PVA) based nanocomposites. They created porous membranes by casting a homogeneous h-BNNS/PVA dispersion onto a glass support, followed by coagulation in a water bath to remove the solvent and form the porous structure. The h-BNNS/PVA nanocomposite membranes were then tested for permeability to pure water and particle rejection (Figure 23). The results showed high pure water permeability values of approximately 2000 L h⁻¹ m⁻² bar⁻¹ and a rejection efficiency of around 76% for particles of about 0.1 mm in size. BN-based nanocomposites offer promising solutions for efficient water purification, providing opportunities for addressing environmental challenges and advancing water treatment technologies.

5.2.2. Gas Separation. Gas separation technologies play a crucial role in chemical industries due to their clean and energy-efficient nature, along with high transport selectiv-

ity.^{257,258} Nanocomposites made from polymeric materials have garnered extensive research attention due to their numerous advantages, including being lightweight, having process flexibility, and being cost-effective.²⁵⁹ The potential applications of hexagonal boron nitride (h-BN) in gas separation have been theoretically explored, particularly for separating H₂ and CH₄ gases. h-BN has demonstrated excellent H₂/CH₄ selectivity (>105 at room temperature) and low adsorption energies (around 0.1 eV) for both H₂ and CH₄ on monolayer membranes.²⁶⁰ This makes h-BN an attractive candidate for gas separation applications. In practice, functionalized BN nanosheets (FBN) have been incorporated as fillers in thermally rearranged polyimide (XTR) to tailor the gas transport and mechanical properties, resulting in an FBN-XTR nanocomposite (Figure 24). FBN-XTR membranes have been employed for H₂ separation, showing superior H₂/CH₄ separation performance compared to state-of-the-art membranes.²⁶¹

By leveraging the unique properties of h-BN and incorporating it into polymeric matrices as nanocomposites, researchers are paving the way for the development of advanced gas separation membranes with improved selectivity and efficiency in chemical industries.

5.3. Applications in Field of Health. BN nanocomposites show great promise in advancing technologies and addressing challenges in these critical areas, making significant contributions to the energy sector, environmental sustainability, and advancements in healthcare. Their stability, flexibility, size, shape, low toxicity, and biodegradability make BN an ideal candidate for nanocarriers. For efficient drug delivery,

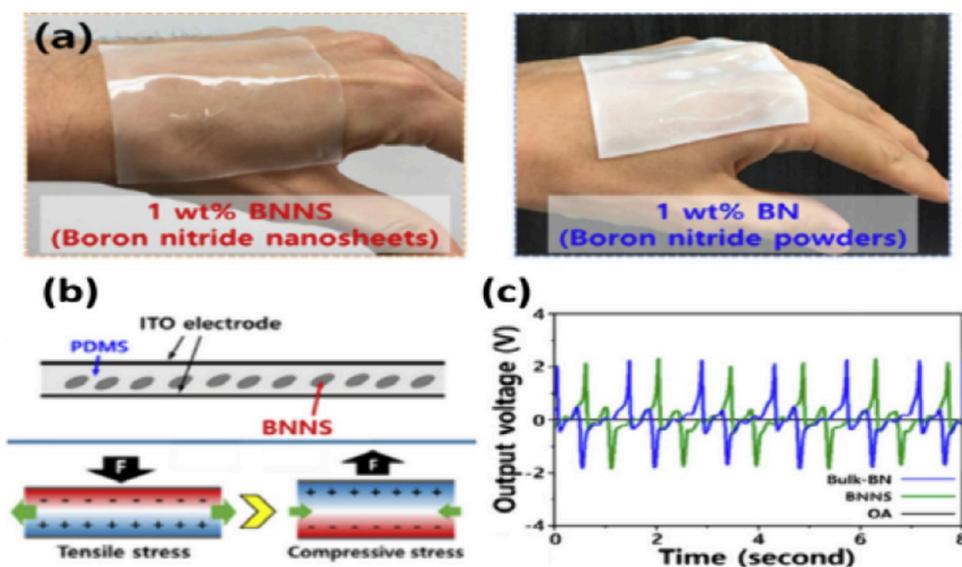


Figure 25. (a) Transparent BNNS with 1% BNNS by weight addition and addition of Boron nitride by 1% by addition by weight. (b) Mechanism of TFPS design. (c) Voltage signals of BNNS, h-BN, and OA samples utilized in a PDMS composite device with mechanical vibration infused. Adapted/reprinted with permission from ref 266. Copyright (2018) Science Direct.

nanoparticles should be small enough to travel through blood vessels and penetrate tissues, while also being large enough to avoid being filtered out through endothelial fenestrations (pores in the endothelial cells of blood vessels). BN nanoparticles can be synthesized in various sizes, allowing for optimization of drug loading and delivery.²⁶²

By leveraging these characteristics, BN nanocomposites can be engineered to transport and release therapeutic agents effectively, offering a promising avenue for targeted drug delivery and improved treatments in the medical field. The advancement of sensing technologies, particularly wearable biomedical electronic devices, and novel sensing functionalities like fluorescence or colorimetric detection methods, has witnessed rapid growth in recent years. Consequently, there is a significant focus on designing and producing functional nanocomposite materials with specific physicochemical properties to create sensors, leading to a prominent area of research.²⁶³

In the pursuit of new sensing functionalities, researchers have developed nanosized copper sulfide (CuS) dispersed on the surface of BN nanosheets (BNNS-CuS) through a straightforward solvothermal process. This unique sensing material, BNNS-CuS, has been utilized for the visual detection of total cholesterol in human serum. The study demonstrated that BNNS-CuS devices exhibit high selectivity toward cholesterol, with a linear detection range of 10 to 100 mM and a detection limit as low as 2.9 mM.²⁶⁴

These findings showcase the potential of BN nanocomposites in sensor development and their ability to offer precise and sensitive detection capabilities for various applications, including biomedical sensing and diagnostics. Biomedical imaging can be done by BN nanocomposites. These are utilized as contrast agents in biomedical imaging techniques, enabling enhanced imaging and diagnostics. BN-based nanocomposites are explored for drug delivery applications, facilitating targeted and controlled drug release.

BNNS have great potential for use as reinforcement in nanocomposite materials or scaffolds for tissue engineering and regenerative medicine. This is due to their ability to improve

the mechanical and thermal properties of the materials without adversely affecting the properties of the polymer used. A study conducted by Nagarajan et al.²⁶⁵ involved the synthesis of gelatin/h-BNNS bionanocomposites through the process of electrospinning. Subsequently, the nanocomposites were cross-linked to enhance their stability in aqueous media. The use of BNNS in such bionanocomposites can significantly enhance the overall properties of the materials, making them well-suited for tissue engineering applications where mechanical integrity and biocompatibility are critical factors. By combining BNNS with biocompatible polymers like gelatin, researchers are paving the way for innovative approaches in regenerative medicine and tissue repair. These advancements hold great promise for the development of novel biomaterials that can promote tissue regeneration and healing (Figures 25 and 26).

5.4. Radiation Absorption and Neutron Shielding.

Whenever cosmos radiation interacts with any matter in space it leads to the generation of neutrons which further lead to the destruction of the space equipment and can also damage the health of astronauts. NASA has shown that an isotope of ^{10}B

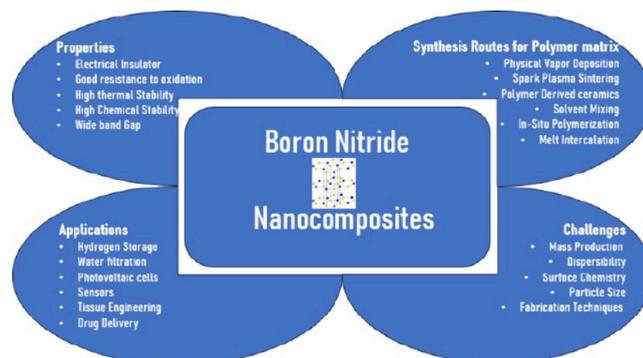


Figure 26. An overview of the current obstacles faced by BN nanocomposites, including the types and properties of BN nanostructures, approaches for synthesizing polymer- and ceramic-based nanocomposites, and their diverse applications and potential opportunities.

formed BNNTs when incorporated in a polyamide film composite increases the neutron absorption by 120%.²⁶⁷ Hydrogen containing nanotubes are a recent area of research interest as they improve the radiation shielding from solar particle events and galactic cosmic radiation.²⁶⁸ They have shown a higher affinity to store zero dimensional particles due to their high hydrogen binding energy and high surface area.^{269–274}

6. CONCLUSIONS AND FUTURE OUTLOOK

1D and 2D h-BN nanostructures have promising applications in various fields. The growth of high quality and bulk production is still a challenge. h-BN composites with other materials have evolved rapidly because their performance and properties can be tailored. The research incorporating h-BN nano derivatives to form polymer composites is still in its nascent stage whereas the results of the same have proved to be extremely promising.

There are many difficulties observed in the preparation, structural analysis, and parameters measurements of BNNTs. The first BNNT was discovered almost 25 years ago but only over the past decade has significant work been observed. For any mass applications of BNNTs the yield and the purity form the most critical hurdle that must be overcome by the researchers of today. Many routes of synthesis through which BNNTs can be synthesized are discussed above. They form the perfect filler as they have an added advantages of electrically insulating properties, high resistance to oxidation, and much more as discussed above.

An additive advantage in terms of BNNS can be achieved with liquid exfoliation of h-BN for mass production which can be incorporated in polymer composition, but the yield and thickness is still a concern. A recent advancement yielding an increased filler fraction of BNNS has led to very high in-plane thermal conductivity in polymer composites. This property is a directional property which makes the thermal conductivity in the perpendicular direction of the filler alignment very low. One of the vast and most unexplored areas of interest are the solvents of exfoliation. Since all the methods mostly involve the use of solvents many researchers can focus on the criteria of dispersion, and furthermore, the sample selected from a nonhomogeneously dispersed solvent leads to inaccurate experimentation. BNNS can form stable solutions rather than precipitates but is not correlated to the well dispersion, defects in the layers, or any other details related to the exfoliation process. The additional validation of the results is usually done by TEM where the sample created is so small with only a few BNNS present at the cross-section. Therefore, this extensive experimental validation may make comparing the data received by XRD and the multiple nanoscale images of the TEM with the bulk results based on assumption. Attaching hydroxyl groups on the boron end, reacting them with the hydroxyl group, and then hydrogenating the nitrogen group and further reacting it with the amino group improves the dispersibility of the fillers in the nanocomposites.

A varied area of research in terms of BN nanostructures has not been utilized, therefore considering the availability of utilizing BNNS, due to their similar properties to BNNTs and better availability, BNNS incorporated polymer nanocomposites may represent a preferable option for researchers to use in the areas of optical properties, transparent polymers, radiation properties, biocompatibilities, electronic packaging, thermal management of energy, hydrogen fuel cells, photovoltaic

packaging, and many more. There are many methods of making these nanocomposites but selecting the appropriate method and fine-tuning it is crucial, depending on the specific target application, composition, and dispersion requirements. Achieving a uniform dispersion of nanofillers within polymer matrices is a fundamental prerequisite for obtaining the desired mechanical and physical characteristics in nanocomposites. The properties of these nanocomposites are also influenced by the chemistry of the polymer matrix and the nature of the nanofillers used. The interfaces between the polymer matrix and nanofillers can significantly impact the effectiveness of load transfer. Therefore, surface functionalization of nanofillers plays important role in improving their dispersion and enhancing the interfacial adhesion between the matrix and fillers, thereby optimizing the overall performance of the nanocomposite material, a key factor toward high performing nanocomposites.

There are a few challenges which can be observed in the journey of BN nanostructures, namely the lack of mass production of these structures as all of these results have proved to be extremely successful, making these materials very expensive. The materials have not been fully explored due to the mass production issues. This further leads to limitations in testing when it comes to experimentation and iterating the percentage of fillers to check for properties at various stages. The percentage addition of BN nanostructures above 5% by weight has also shown agglomeration at various sites of the polymer, leading to anisotropic properties in terms of thermal, mechanical, electrical, etc. Moreover, this also leads to poor interfacial properties among the fillers and polymer composite. The ionic bond of B–N elements restricts the initiation of chemical reactions in the case of any surface modification. Furthermore, the distribution of 1D and 2D nano structures among the other materials like polymers is critical. The grain boundary condition between the filler and the polymer at the interface and a homogeneous distribution of the fillers throughout the polymers are the primary conditions to produce BN nanostructure incorporated polymer composites. The selection of the exfoliation process and the quality of BNNS depends on the application. There are a few applications which may allow leverage for slight defects. There are shortcomings related to the validation of BNNS via XRD and TEM wherein the intricate exfoliated BNNS mixtures lead to either peak broadening or even shifting of the peak depending on the quality of exfoliation. With all the review articles referred to in this paper, a crucial challenge identified for the researchers working in the field of BNNS and BNNTs is to define a set of parameters which defines what high quality nanomaterials are by creating a benchmark. This can be shared across the community, making reproduction of the results easier via modifying exfoliation processes and processing parameters. Thus, these also act as the future areas wherein researchers can explore the range of work.

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Notes

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