Dispersion and Individualization of Boron Nitride Nanotubes

Ashleigh D. Smith McWilliams [▽,a], Cecilia Martínez-Jiménez [▽,a], Kevin R. Shumard [▽,a], Matteo Pasquali [a,b,c,e], Angel A. Martí*[a,c,d,e]

a. Department of Chemistry, Rice University, Houston, Texas 77005, USA
b. Department of Chemical and Biomolecular Engineering, Rice University, Houston, Texas 77005, USA
c. Department of Materials Science and Nanoengineering, Rice University, Houston, Texas 77005, USA
d. Department of Bioengineering, Rice University, Houston, Texas 77005, USA
e. Smalley-Curl Institute for Nanoscale Science and Technology, Rice University, Houston, Texas 77005, USA

* Corresponding author: amarti@rice.edu

Abstract

Boron nitride nanotubes (BNNTs) have attracted significant attention due to their outstanding properties such as high thermal stability, high tensile strength, and lightweight. The use of BNNTs to generate macroscopic materials and composites, as well as their use in biological and electronic applications require their effective dispersion in a variety of solvents. In this review, we explore the work generated in the area of BNNT dispersions, highlighting the different approaches that have been taken. Topics that will be covered in this review include covalent functionalization, acids and bases, polymers, biomolecules, aromatic molecules, ionic surfactants, and solvents without additives. The properties of these dispersions will be discussed in light of the dispersion obtained, properties and/or materials made, and will culminate with an outlook of the field, outstanding challenges and future directions.

1. Introduction

Boron nitride (BN) nanomaterials compose a relatively new and vastly understudied class of materials. They are structural analogs of carbon nanomaterials, coming in as many allotropes, but with different, complementary properties. The B-N bond is isoelectronic with the C-C bond, allowing for a variety of BN materials with analogous structures to carbon. Nonetheless, due to the distinctive composition of BN materials, their properties markedly differ from their carbon counterparts. In particular, boron nitride nanotubes (BNNTs) have gained general interest in the last few years due to their morphology and properties.

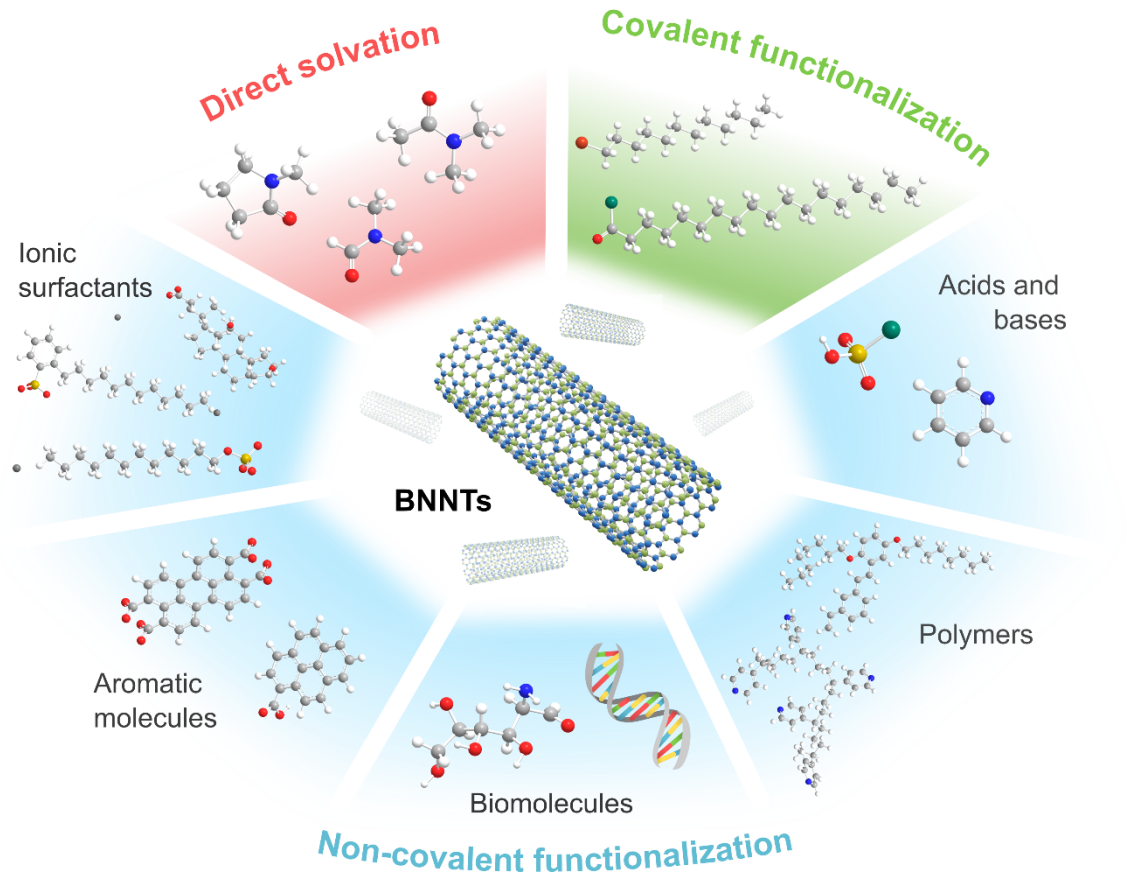

Figure 1. Schematic representations of a BNNT showing the honeycomb-like structure of sp^2 hybridized, alternating boron (blue) and nitrogen (light green) atoms, and representations of the different types of dispersions methods reported.

BNNTs are structural analogs of carbon nanotubes (CNTs) and can be rationalized as rolled-up sheets of hexagonal boron nitride (hBN), which possess a honeycomb-like structure of sp^2 hybridized, alternating boron and nitrogen atoms (Figure 1). BNNTs were successfully predicted by Rubio et al.[1] before they were synthesized, a year later, by Zettl and coworkers.[2] The change in chemical makeup imprints BNNTs with distinctive properties from those of CNTs (Table 1), similar to the case between hBN and graphene. While the mechanical strength of both species

is high, ~ 1 TPa,[3],[4] BNNTs are much more chemically and thermally stable, not oxidizing in air until temperatures past 800 °C,[5],[6] while CNTs begin oxidizing at temperatures as low as 400 °C.[7] Though the thermal conductivity of BNNTs (~200 W/mK) is lower than that of CNTs (300-1000 W/mK), Chang and coworkers found that using isotopically pure ^{11}BNNT could improve their thermal conductivity to be equal to that of CNTs.[8] Finally, the most striking difference between the two materials is their electrical conductivity, with CNTs demonstrating conducting or semiconducting properties, depending on tube chirality, while BNNTs maintain a uniform wide band gap of ~5-6 eV,[9] making them electrically insulating regardless of structure.

Table 1. Summary of material properties

Property	*CNT*	*BNNT*
Young's Modulus	1.8±1.4 TPa[4]	1.22±0.24 TPa[3]
Thermal Conductivity	300-1000 W/mK[8]	~200 W/mK[8]
Electrical Conductivity	Conducting/ Semiconducting	Insulating (~5-6 eV)[9]
Oxidation Temperature (in air)	400 °C [7]	> 800 °C [6],[7]

The unique properties of BNNTs make them top candidates for many applications. In the field of materials science, BNNTs' mechanical strength, thermal stability, and thermal conductivity make them useful prime materials for a variety of composites.[10]–[23] (Figure 2a-b) For example, Zhi and coworkers have prepared BNNT/polystyrene (PS) composite films.[22] These films remained transparent to visible light, and the addition of 1 wt. % BNNTs increased

the elastic modulus of the film by ~21% and made the films more stable to oxidation.[22] Similarly, in 2020, Chang and coworkers reported the addition of pyridine-attached BNNTs (Py-BNNTs) in composites of a variety of materials.[23] They found that adding 20 wt. % Py-BNNTs to epoxy improved the thermal conductivity by 69.6%. In addition, they found that adding 2 wt. % Py-BNNTs to polyvinyl alcohol (PVA) increased the tensile strength by 75.3%.[23] These properties have been utilized in other BNNT materials, as well, such as films[24]–[26] and mats.[27] Another important area for BNNT applications is in nanomedicine. Since BNNTs are commonly considered noncytotoxic in most cell lines, they have been proposed for many biomedical applications, such as imaging and drug delivery.[28]–[41] (Figure 2c) For instance, Ciofani and coworkers conjugated the dye Oregon Green to BNNTs in order to image them in cells and track their cellular uptake.[28] Additionally, Allard and coworkers used BNNTs to encapsulate fluorescent dyes, showing shifts in their photophysical properties, and used them for fluorescent microscopy imaging of *D. Pulex*.[40] Alternatively, Emanet and coworkers noncovalently linked Doxorubicin, a common cancer drug, to BNNTs grafted with folate, a cancer cell targeting group, in an attempt to deliver the drug and release it inside cancer cells.[39] In addition to encapsulation for imaging, several groups have demonstrated endohedral complexes that have potential applications in optoelectronics, nanothermometry, and catalysis. [40],[42]–[45] For instance, the Zettl group has taken advantage of capillary forces and demonstrated a wet chemistry approach to filling with noble metals (Pd, Ag, Pt, Au), a transition metal (Co), and a post transition metal (In)[42] and Qin et al. has loaded BNNTs with tellurium(Te).[46] Other important uses for BNNTs include sensing applications,[47]–[49] hydrogen storage,[50],[51] space radiation shielding,[52] and coatings for nanowires,[53],[54] among others.

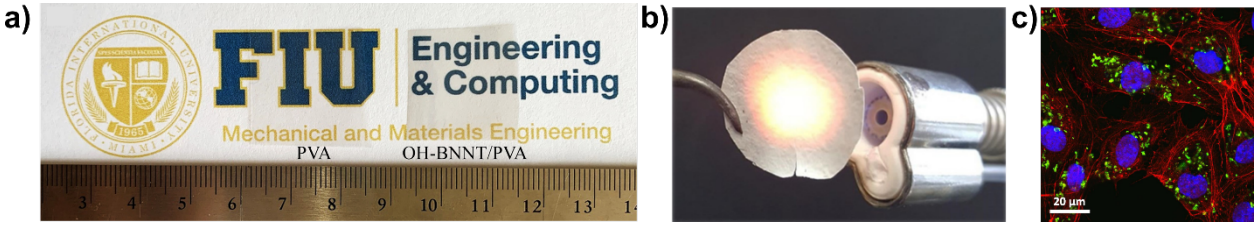

Figure 2. (a) Pure polyvinyl alcohol (PVA) film and 1%wt OH-BNNT/PVA film, showing they are both transparent. Reprinted with permission from Ref [26] (X. Lu et al. Polym. Compos. 2020, 41(12), 5182.) Copyright © 2020 John Wiley & Sons. (b) Thermally regenreable ultrafiltration membrane using debundled BNNTs with P4VP. Reprinted with permission from Ref [20] (H. Lim et al. J. Membr. Sci. 2018, 551, 172.) Copyright © 2018 Elsevier Inc. (c) Confocal image showing fluorescently labeled functionalized BNNTs in green internalized by fibroblasts. Reprinted with permission from Ref [28](G. Ciofani et al. Colloid Interface Sci., 2012, 374(1), 308.) Copyright © 2012 Elsevier Inc.

Obtaining the expected macroscopic materials and advanced applications from these exciting nanomaterials relies, in most cases, on the ability to prepare uniform, stable dispersions of these nanoarchitectures in solution. In addition, it often requires breaking apart the nanotube network, as well as, separating BNNTs from BN and other impurities, to produce individualized BNNTs stabilized in solution. Specifically, dispersing BNNTs in a liquid solvent requires disrupting intertube interactions and, most commonly, using an agent to improve their wettability in the desired solvent. The earliest attempts to disperse and individualize BNNTs utilized noncovalent functionalization with polymers[16],[17],[55] or covalent functionalization of BNNT edges and defect sites.[17] Soon thereafter, groups turned to biomolecules[56] and other dispersing agents, such as Lewis bases[57] and aromatic molecules.[58] More recently, some studies have been done that focus on tailoring the solvent itself to obtain BNNT dispersions without the use of a wettability agent.[59],[60] This review will cover each type of BNNT dispersion and the advances that have

been made toward increased dispersion concentration and stability. Many good reviews have been published on the synthesis, functionalization, and applications of BNNTs,[5],[47],[52],[61]–[65] including a mini-review published in 2020 focused on theoretical studies of BNNT dispersion and functionalization.[66] To complement these, this review will provide an in-depth analysis of experimental dispersion techniques for BNNTs (Figure 1), and how they have evolved over time. We hope this work will serve as a guide for continued studies toward the achievement of novel, timely, and advanced BNNT devices and applications.

2. Covalent Functionalization

Attempts at covalently functionalizing BNNTs can be generally broken down into 4 types of reactions: functionalization of amine groups in defect sites and edges (Section 2.1), oxidation of boron sites (Section 2.2), radical addition (Section 2.3), and reduction (Section 2.4). Here, we will describe functionalization methodologies based on the chemistry used. A summary is presented in Table 2.

2.1. Functionalization of Amine Groups in Defect Sites and Edges

Some of the first attempts at covalent functionalization of BNNTs focused on functionalizing defect sites and tube edges where free amine groups can be found. Zhi and coworkers found that these amine groups could be functionalized with an acyl chloride using a simple reflux reaction.[67] In particular, they reacted the BNNTs with stearoyl chloride, attaching long aliphatic chains, and making the BNNTs dispersible in many organic solvents, such as chloroform, N,N-dimethylacetamide (DMAc), tetrahydrofuran (THF), dimethylformamide (DMF),

acetone, toluene, and ethanol. In fact, they could reach concentrations of > 0.5 g/L of functionalized BNNTs in DMAc.[67] This group later utilized the same reaction conditions to attach other acyl chloride moieties, including naphthoyl chloride, butyryl chloride, and chloroacetyl chloride.[10],[68] First, they studied how grafting functionalities such as napthoyl, butyryl, and stearoyl to the BNNT surface could be used to tune its electronics.[68] Though the dispersibility of the functionalized BNNTs was not analyzed in this case, the addition of these moieties is expected to impact BNNT dispersion ability. Additionally, they attached Cl groups, using chloroacetyl chloride, that could in turn be utilized to graft polymers, polystyrene (PS) or polymethylmethacrylate (PMMA), through an atom transfer radical polymerization (ATRP).[10] Though this investigation was focused on the production of polymer composites, the authors did find that PS functionalized BNNTs were more easily dispersible in organic solvents, such as DMAc and chloroform.[10]

More recently, in 2016, Kalay and coworkers utilized the same reaction between amine groups in defect sites and edges and an acyl chloride group to attach an oligo peroxide to the BNNT surface.[69] This peroxide reacted with N-isopropylacrylamide (NIPAM) to polymerize it, producing poly(N-isopropylacrylamide)-grafted BNNTs. After adding the polymer, the f-BNNTs were dispersible in water and some organic solvents, including dioxane and dichloroethane. Moreover, since poly(N-isopropylacrylamide) is a thermo-responsive polymer, the authors propose using the f-BNNTs in biomedical applications, such as for smart surfaces or nanocarriers.[69]

Other reactions that have been performed on the amine sites available on raw BNNTs include S_N2 alkylation[70] and an isocyanate reaction.[11] For the first, Zhi and coworkers dispersed BNNTs into ionic liquids by grinding and then performed the S_N2 reaction with 1-bromoicosane.[70] Again, dispersibility studies were not performed, however the authors indicate that these functionalized BNNTs show dispersibility in organic solvents and were not dispersible in water. In 2012, Zhou and coworkers reacted free amine groups in BNNTs with isophorone diisocyanate, adding isocyanate groups to the BNNT surface.[11] These NCO-functionalized BNNTs could be individualized in chloroform or further reacted with 2-chloroethanol, 1-pyrenyl methanol, and p-chloroaniline, among others. Finally, f-BNNTs could be dispersed more easily in PVA and hydroxypropyl methylcellulose to make composite films.[11]

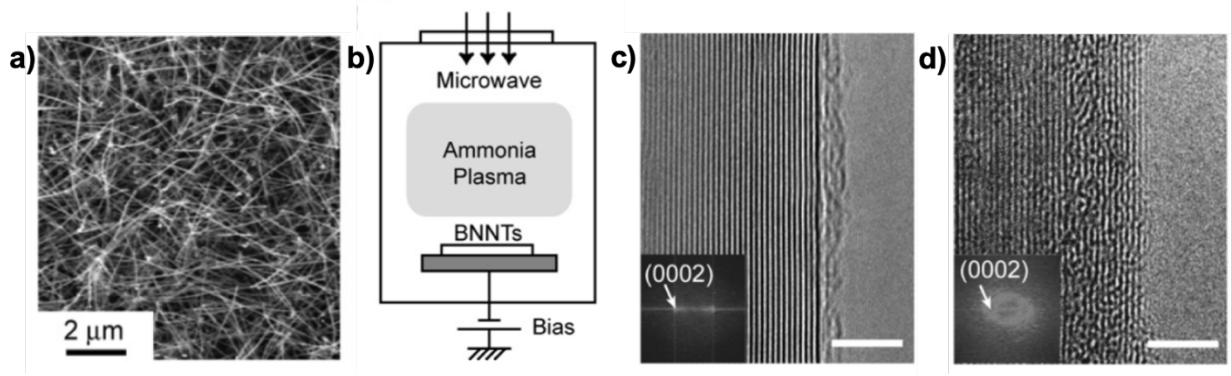

Figure 3. (a) Typical SEM image of pristine BNNTs on Si substrate as a specimen for plasma treatment. (b) Schematic illustration of the microwave plasma system used in this study. HR-TEM images and Fourier transform images of the wall of a (c) pristine BNNT with a clear tube edge and (d) ammonia plasma-treated BNNT with rough edges. Scale bar 4 nm. Reprinted with permission from Ref **[71]** (T. Ikuno *et al. Solid State Commun.* 2007, *142*, 643-646.) Copyright © 2007 Elsevier.

In order to increase the accessibility to amine groups, researchers have established methods to increase defect sites through plasma treatment[71]–[73] and ball milling.[12] The Zettl

group first used ammonia plasma treatment to increase defect sites, and therefore, free amines on the BNNT surface (Figure 3).[71] The added amine groups made the BNNTs highly dispersible in chloroform and their dispersions were stable up to 7 days. After plasma treatment, f-BNNTs were coupled with 3-bromopropanoyl chloride,[71] and, later, mercaptopropionic acid, through 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC) coupling.[72] Dai and coworkers further studied the use of controlled plasma treatments to tune functionalization and defect creation in the BNNTs.[73] Through a combination of Ar, O_2, and N_2 + H_2 plasmas, they were able to add carbonyl and amide functionalities to the BNNT surface.[73] Additionally, Iannitto and coworkers developed an in-flight plasma treatment wherein ammonia gas injection temporarily fluidized the BNNTs.[74] This allowed for a more complete coverage of the added amine on the surface of the BNNTs. Fourier Transform Infrared Spectroscopy (FTIR) and Thermogravimetric Analysis (TGA) data demonstrate that while the plasma of ammonia creates several free radicals (·H, ·NH, ·NH_2), it is NH_3 which is bound to the BNNTs due to its low binding energy and removal at 250 °C. Owing to the hydrogen bonding capability of the amine group, the tubes were able to be individualized and dispersed well in water, while remaining stable over time. By using a solvent free, nonthermal method for attaching amine, they provide a much-needed proof of concept for addends of other functional groups. Finally, in 2011 Singhal and coworkers ball-milled BNNTs in NH_4HCO_3 to increase defect and amine sites.[12] The added amines improved the BNNT dispersibility in an Al matrix, which was used to make BNNT-Al composites.[12]

2.2. Oxidation of Boron Sites

Another commonly utilized method of covalently functionalizing BNNTs is through the oxidation of boron sites generally using hydrogen peroxide[13],[14],[31] or strong acids.[28]–[30],[75] One of the first examples of this was reported by Zhi and coworkers in 2009, when they reacted BNNTs with H_2O_2 at high temperatures and pressure, adding hydroxyl moieties to the BNNT surface.[13] This reaction improved the dispersibility of BNNTs in water, producing dispersions with concentrations > 0.25 g/L that were stable for at least 2 days. Additionally, esterification reactions were performed between the hydroxylated BNNTs and either perfluorobutyric acid or thioglycolic acid to further modify the BNNT properties and make them better for polymer composites.[13] The same group later silanated the hydroxyl groups with 3-aminopropyltrimethoxysilane (KBM 903), leaving a free amine group for reaction with polyhedral oligosilsesquioxane to produce epoxy nanocomposites.[14] In 2015, Emanet and coworkers used a similar method to add hydroxyl groups by refluxing the BNNTs in H_2O_2 for 48 hours, and then reacted the f-BNNTs with carbohydrates such as glucose, lactose, or starch, using a glutaraldehyde linker.[31] These BNNTs could be dispersed in cellular medium and were investigated for cellular uptake and biocompatibility.[31]

An alternative to using hydrogen peroxide for boron oxidation, is to utilize another well-known oxidizer, nitric acid. In 2012, Ciofani and coworkers sonicated BNNTs in 65% nitric acid to add hydroxyl groups to the surface.[28] The hydroxyl groups were then reacted with 3-aminopropyltriethoxysilane (APTES), leaving free amino groups on the surface. While these silanated BNNTs could be dispersed in aqueous media, the stability was significantly improved by

further conjugation to Oregon Green, a fluorescent dye.[28] The group utilized these dye-conjugated BNNTs to perform biocompatibility and confocal imaging studies,[28] and later, linked the dye to transferrin protein to get a more targeted cellular uptake.[29] The same group, in 2015, used the same nitric acid procedure to add hydroxyl groups to the surface, which they then reacted with folic acid, to coat the BNNTs in folate.[30] These f-BNNTs could be dispersed in aqueous media and used for cell viability studies and imaging, with the goal to use them as a tool for cancer treatment.[30] More recently, da Silva and coworkers oxidized BNNTs with a 3:1 mixture of sulfuric and nitric acid, which were then grafted to a polymer, to make a water/ethanol dispersible hybrid hydrogel that could be used for drug delivery.[75] The polymer grafting was accomplished through the addition of a crosslinking agent, triethylene glycol dimethacrylate, which could then polymerize a mixture of NIPAM and methacrylic acid (MAA) to produce a hybrid BNNT-Poly[(NIPAM-co-MAA] system.[75]

More recently, in 2020, two new methods of oxidation were demonstrated. First, Lu was able to show that hydroxylation is possible via sonication.[26] The researchers showed that tip sonication for 45 minutes resulted in a dispersion that, after freeze drying, still had a strong peak at 3000-3600 cm^{-1} region of the infrared (IR) spectrum, due to the addition of hydroxyl groups on the BNNT surface. Because this method is free from organic solvents, there is a lot of interest in its use, particularly in the biomedical space. A challenge that this method presents, however, is that the researchers clearly demonstrated other damage to the tubes such as unzipping or formation of nanoribbons. Again in 2020, Mapleback and coworkers found that using milder sonication in combination with ozonation also resulted in oxidation at boron sites.[76] They found that dispersion in water was much easier after this process, most likely due to the ability for

hydrogen bonding to occur. Interestingly, they noted that ozonation results in 'cleaning' of the surface of the tubes and allowed for further functionalization using polyethylenediamene, which was used for electrophoretic deposition of BNNT films. The work of both groups provides a new methodology of functionalization that does not rely strictly on corrosive materials such as nitric acid or hydrogen peroxide.

2.3. Radical Addition

Another method recently utilized for BNNT covalent functionalization is radical addition reactions. Ejaz and coworkers first reported this in 2014, when they used bis(4-bromomethylbenzoyl)peroxide, a peroxide that breaks down into free radicals at 105 °C, to attach brominated benzyl groups to the BNNT surface.[77] They propose that the free radicals react with localized π double bonds of the aromatic rings in edges and defect sites. The f-BNNTs were mixed with glycidyl methacrylate or styrene and ATRP was initiated using 4-methyl-benzyl bromide, to form a polymer-BNNT composite.[77] Lin and coworkers used a similar mechanism, but with lauroyl peroxide and dicumyl peroxide, which underwent thermal decomposition by refluxing in chloroform for 8 hours.[15] They propose that the free radicals react with B sites of BNNTs, as was seen with the H_2O_2 oxidation reactions described above. These f-BNNTs form stable dispersions in chloroform, 0.25 mg/mL and 0.33 mg/mL for Lauryl- and Cumyloxy-BNNTs, respectively, for up to 3 days.[15] The hydroxylated BNNTs were also used to produce polycarbonate composites for mechanical testing, which resulted in 8% and 12% increases in tensile strength, respectively.[15]

2.4. Reducing Conditions

Another method applied to covalently functionalize BNNTs is chemical reduction. Shin and coworkers first reported the reduction of BNNTs using a sodium naphthalide solution, coating the BNNTs in negative charges that could react with 1-bromohexane.[78] In 2018, the Martí group reported the use of the Billups-Birch reaction to functionalize BNNTs with dodecyl groups.[79] This reaction uses lithium in liquid ammonia to produce solvated electrons that can react with bromododecane to functionalize BNNTs. Dispersions of the f-BNNTs were tested in an array of solvents, such as water, THF, and dodecane. These tests indicated that solvents containing long carbon chain worked better to disperse these functionalized BNNTs.[79] Moreover, heating the BNNTs up to 600 °C removed the carbon chains and yielded pristine BNNTs as confirmed by both TGA and atomic force microscopy (AFM). [79] In a later publication, the Martí group also demonstrated the importance of using a glass stir bar for this reaction, as Teflon can outcompete and even deplete dodecane in the functionalization reaction.

Table 2: Summary of characteristics of BNNT dispersions prepared by functionalization

Molecule Used	*Method of functionalization*	*BNNT synthesis method / source*	*Method of dispersion*	*Dispersion solvent*	*Stability*	*Application*	*Ref.*
Functionalization of Amine Groups in Defect Sites and Edges							
Stearoyl Chloride	Mixing	CVD Method	Stirring at 100 °C and annealing	Chloroform, DMF	-	Powder for characterization	[67]
Chloroacetyl Chloride followed by Polystyrene or PVP	ATRP	BOCVD Method	Stirring at 120 °C and annealing	Chloroform, DMF.	-	Powder for characterization	[10]
Naphthoyl chloride, butyryl chloride, and stearoyl chloride	-	CVD Method	-	-	-	Powder for characterization	[68]
Oligoperoxide followed by NIPAM	Peroxide attached, then PNIPAM functionalization	CVD Method	Sonication and centrifugation	Dioxane and dichloroeth-ane	-	Powder for characterization	[69]
Isophorone diisocyanate followed by 2-chloroethanol, 1-pyrenyl methanol, benzyl alcohol, p-chloroaniline, glycine methyl ester, trifluoroacetic acid, PVA, or HPMC	-NCO functionalization	CNT Replacement	Stirring, Sonication, and Centrifugation	THF	-	Powder for characterization	[11]

Ionic Liquids followed by 1-bromoicosane attachment	Ionic liquids facilitated S_N2 reaction to attach icosane moiety	CVD Method	Mortar and Pestle and Centrifugation	Organics (unlisted)	-	Powder for characterization	[70]
Amines	Microwave plasma induced amination	CVD Method	Sonication	Chloroform and water	7 days	Dispersions for characterization and alternate functionalization	[71]
Amines followed by MPA or butyryl chloride	Amine mediated functionalization	CVD Method	Sonication	Water	-	Dispersions that can interact with gold nanoparticle passivating layer	[72]
Amines	RF Plasma induced amination	Boron ink method	-	-	-	Powder for characterization	[73]
Amines	RF Plasma induced amination	HABS Method	Sonication	Water	At least 2 hrs	Powder for characterization	[74]
Amine Functionalized Aluminum Matrix	Amine Ball milling	Ball-milling and annealing	Stirring, Sonication, and Drying	Ethanol	-	Powder for characterization	[12]
Oxidation of Boron Sites							
Hydroxide followed by perfluorobutyric acid or thioglycolic acid	Hydroxide mediated functionalization	BOCVD Method	Heating under reflux	Water	-	Polycarbonate or polyvinyl butyral matrices	[13]
Hydroxide followed by POSS	Hydroxide mediated functionalization	BOCVD Method	Stirring, Reflux	Toluene	-	Epoxy	[14]

Hydroxide followed by Glucose, Lactose, or Starch	Hydroxide mediated functionalization	CVD Method	Heating under reflux, Centrifugation, and Sonication	Bovine Serum Albumin Solution	-	Cell Uptake Studies	[31]
Hydroxide followed by APTES	Hydroxide mediated functionalization	Annealing Method (Nano and Ceramic Materials Research Center, Wuhan Institute of Technology, China)	Tip Sonication and Centrifugation	PBS	-	Cell Viability Studies	[28]
Hydroxide followed by APTES followed by Transferrin	Hydroxide mediated functionalization	-	Tip Sonication and Centrifugation	PBS	-	Cell Viability Studies	[29]
Hydroxide followed by Folate	Hydroxide mediated functionalization	CVD Method	Tip Sonication, stirring, and centrifugation (freeze-dried)	PBS	-	Cell Uptake Studies	[30]
Hydroxide followed by TEGDMA and MAA-NIPAM	Hydroxide mediated functionalization	CVD Method	Sonication	Acetone	-	Gel	[75]
PVA	Mixing	From BNNT, LLC	Sonication and Drying	Water	-	Film	[26]
Ozone followed by Polyethyleneimine	AOP	From BNNT, LLC	Sonication and centrifugation	Water	6 months	Film	[76]

Radical Addition							
BBMBPO initiator followed by Glycidyl methacrylate or Styrene	ATRP	BOCVD Method	Sonication and centrifugation	various	-	Powder for characterization	[77]
Hydrogen peroxide, Lauroyl peroxide, and dicumyl peroxide	Mixing	Hydrogen Assisted BNNT Synthesis (HABS) Method	Sonication and centrifugation with autoclave (hydroxide) or heating under reflux (Lauroyl and dicumyl peroxides)	Acetone, Chloroform	3 days	Polycarbonate films	[15]
Reducing Conditions							
1-bromohexane	Reductive alkylation	HABS Method	Stirring	Water and methanol	-	Powder for characterization	[78]
1-bromododecane	Billups-Birch reductive aklylation	From BNNT, LLC	Stirring, Sonication, and Centrifugation	THF, IPA, MEK, Dodecane, Cetane	-	Dispersions for characterization	[79]

3. Non-covalent Functionalization

Non-covalent functionalization encompasses a wide array of approaches for enhancing dispersibility via association of molecules to the surface of tubes, without being directly bound. Functionalization relies on intermolecular forces such as wrapping of tubes, π-π stacking, and amphiphilic interactions. This will be divided into 5 distinct classes of molecules: polymers (Section 3.1), biomolecules (Section 3.2), aromatic molecules (Section 3.3), ionic surfactants (Section 3.4), and acids and bases (Section 3.5). A summary is presented in Tables 3-7.

3.1. Polymers

Another early method for dispersing BNNTs into solution was through noncovalent functionalization with polymers. In this section we will go through reports of polymers that were utilized to produce stable dispersions of BNNTs. Biopolymers will be discussed in section 3.2, and polymers used solely for the production of polymer composites will not be included. Dispersions have been achieved using non-aromatic (Section 3.1.1), aromatic (Section 3.1.2), and block co-polymers (Section 3.1.3), and their details are summarized in Table 3.

3.1.1. Non-aromatic polymers

Non-aromatic polymeric functionalization takes advantage of the nonpolar nature of BNNTs generally by wrapping long chains around the BNNTs. This association to the tubes mediates the environment around the tube in order to promote dispersion. In 2005, two reports

of BNNT dispersion in polymers were published, both being non-aromatic polymers.[16],[55] In the first, Xie and coworkers utilized an amine-terminated polyethylene glycol, PEG1500N, to disperse BNNTs in water.[55] The BNNTs and PEG were heated to 100 °C for 3 days under an N_2 atmosphere, after which unreacted PEG could be removed by dialysis and unreacted BNNTs removed by low-speed centrifugation. Control experiments revealed that the amine group was necessary to produce stable dispersions, so the authors proposed an acid-base interaction between the amine groups and boron sites of the BNNTs, which has been corroborated with hBN.[55] Soon after, Zhi and coworkers reported the dispersion of BNNTs in organic solvents, such as chloroform, DMAc, and THF, through wrapping with the polymer poly[m-phenylenevinylene-co-(2,5-dioctoxy-p-phenylenevinylene)] (PmPV).[16] This polymer has a helical structure that can interact with BNNTs through π-π interactions. This method of BNNT dispersion was used to prepare a composite film,[16] and, in a later publication, to purify BNNTs from other BN impurities produced during BNNT synthesis.[17]

Polymer dispersions have also been prepared with the goal of studying the photophysics of BNNT hybrids. For instance, Huang and coworkers obtained BNNTs-zinc phthalocyanines hybrids, in which the zinc phthalocyanines served as organic π-electron donors. [80] The authors used polyvinylpyrrolidone (PVP) to wrap the BNNTs and make aqueous dispersions and studied the electron transfer between them and BNNTs through steady state absorption, transient absorption, steady state photoluminescence, and time resolved photoluminescence.

Ciofani and coworkers first reported using polymers to disperse BNNTs in aqueous media to test their cytocompatibility in cells by working with polyethyleneimine (PEI) in 2008.[36]

Dispersions of BNNTs wrapped with PEI in PBS were stable for up to 1 month, with only a 5% decrease in concentration over that time. The dispersions were tested for cell uptake and cytocompatibility in human neuroblastoma cells, finding the BNNTs to be nontoxic.[36] Additionally, in a future report, the PEI was conjugated to carboxyl-protected quantum dots to enable in vitro imaging studies.[81]

In 2021, De los Reyes and coworkers used non-aromatic polymer ethyl cellulose to individualize and disperse BNNTs in organic solvents and showed that solution-processing can be less destructive than other treatments used for purification of BNNTs. [82] Dispersions were mostly stabilized through CH-π and OH-π interactions, and after centrifugation, the BNNTs were mostly isolated from other BN impurities, obtaining a purer material. They showed their highest dispersibility in benzyl alcohol. [82]

3.1.2. Aromatic polymers

Aromatic polymers have been used to disperse BNNTs, mainly by taking advantage of the interactions between each other through π-π stacking. In 2010, Velayudham and coworkers produced BNNT dispersions in chloroform using poly(p-phenylene-ethynylene) (PPE), a ferrocene-conjugated PPE, and polythiophene (PT) with the goal of preparing composites.[18] The interactions between the polymers and BNNTs were probed with UV-Vis spectroscopy, nuclear magnetic resonance (NMR), photoluminescence, and lifetime measurements. The authors determined that all polymers adsorb to the BNNTs through π-π interactions, with the PPEs aligning along the vertical axis of the nanotube and PT wrapping around it.[18] Dispersions

in chloroform reached concentrations of ~0.30 mg/mL for the PPEs and ~0.22 mg/mL for PT, and were stable for up to 6 months, as long as chloroform could not evaporate. Additionally, composite films of self-aligned BNNTs were prepared by dropping the dispersion on a silicon substrate and holding it vertically, absorbing solvent with a Kimwipe.[18] Later, Gao and coworkers tested 5 water-soluble polymers: a conjugated poly(p-phenylene) ((-)PPP), poly(xylylene tetrahydrothiophenium chloride) (PXT), poly(sodium styrene sulfonate) (PSS), poly(sodium vinyl sulfonate) (PVS), and poly(sodium acrylate) (PAA) to prepare BNNT dispersions.[83] These five polymers were chosen to test the impact of conjugated π-electrons on dispersion ability, with (-)PPP having extend conjugation, PXT and PSS having a phenyl group, and PVS and PAA containing no conjugation. As expected, the more conjugated system dispersed the most material, with (-)PPP dispersing almost 3x more material than PXT.[83] The PXT-dispersed BNNTs were used to prepare a superhydrophobic coating by depositing on a Si wafer and then thermally treating the film at 240 °C for 6 hours, converting PXT to poly(p-phenylene vinylene).[83]

In 2015, Fernandez-Yague and coworkers studied the dispersibility of polydopamine (PD) coated BNNTs in water and buffer, where PD also binds to the BNNTs through π-π interactions.[84] PD-BNNT dispersions in water, ~20 μg/mL, were stable for up to 2 months and dispersions in buffer were utilized to test BNNT cytotoxicity in osteoblasts.[84] The same year, Martinez-Rubi and coworkers dispersed BNNTs in chloroform using poly(3-hexyl-thiophene) (P3HT) and studied its photophysical properties.[85] The BNNTs formed a stable dispersion with a concentration of 0.2 mg/mL for weeks with only trace sedimentation. Due to the photophysics of the polymer, the addition of BNNT changes the solution color from orange to purple, shown in

photos and the absorption spectra (Figure 4). Using UV-Vis and polarized excitation fluorescence microscopy, they were able to determine that π-π interactions between the BNNTs and the polymer induce planarization of the polymer along the tube axis, which produces the color change.[85]

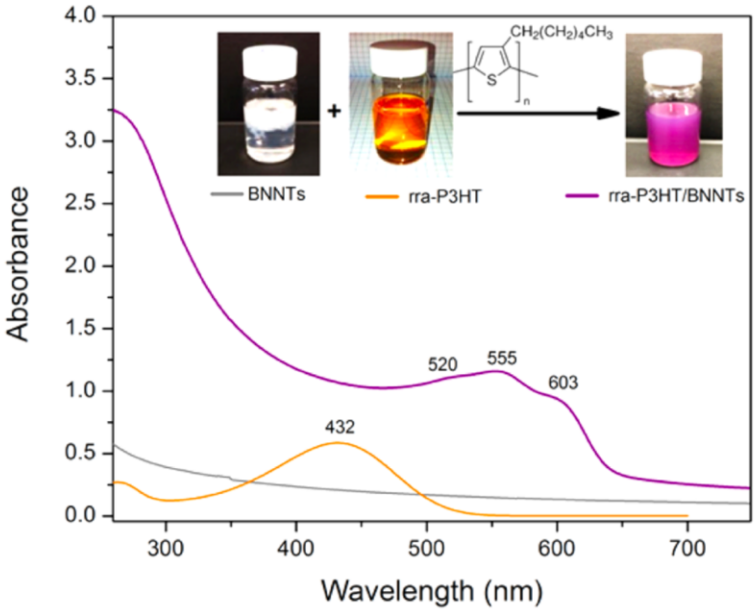

Figure 4. Photos and absorption spectra of BNNT (0.2 mg/mL), rra-P3HT solution, and rra-P3HT/BNNT suspensions in $CHCl_3$ (rra-P3HT to BNNT weight ratio = 0.08). Reprinted with permission from Ref **[85]** (Y. Martinez-Rubi *et al. J. Phys. Chem. C,* 2015, *119*, 26605-26610.) Copyright © 2015 American Chemical Society.

In 2018, Lim and coworkers dispersed BNNTs in various alcohols, finding the optimum proportion of poly(4-vinylpyridine) (P4VP) to effectively individualize and stabilize the nanotubes.[20] The dispersion in methanol was stable for at least 7 days, and was then filtered to prepare a composite film that could be used as a water filtration membrane.[20] More recently, they worked on adding the dispersion to glycerol diglycidyl ether, which is an epoxy

where P4VP is soluble and can interact with the BN surface to prepare BNNT-hBN-epoxy composites.[86] Later, Lee and coworkers explored the ability of P4VP to disperse BNNTs more easily than hBN, in order to remove hBN impurities.[87] Dispersions in methanol were centrifuged to remove larger impurities, and methanesulfonic acid was added to the supernatant, removing the P4VP from the BNNTs and causing them to aggregate. These aggregates were collected by filtering and washing to obtain purified BNNTs. While nanosized flakes were not fully removed, the process provides more insight into using solution-processing methods for BNNT purification.[87]

A two-step in-situ polymerization process was also studied in 2020 to disperse BNNTs in aqueous solution.[88] Cetyltrimethylammonium 4-vinylbenzoate was used by the authors to disperse BNNTs in water, and a free radical polymerization was performed to permanently fix the polymer layer adsorbed to the surface of the BNNTs. The material was able to produce highly stable (>1 year) dispersions in water.[88]

The interactions between BNNTs and aromatic homopolymers have also been investigated by Rice and coworkers in 2020, where poly(2,7-carbazole)s PC35 and PC92 dispersed BNNTs by stretching along the nanotube and forming highly ordered J-aggregates.[89] Dispersions were the most stable in THF and were used to fabricate a film by electrophoretic deposition to build capacitors, as well as composites with PMMA. In 2021, two polyfluorenes, poly(9,9-dioctylfluorenyl-2,7-diyl) (PFO) and poly(9,9-dioctylfluorenyl-2,7-diyl)-alt-co-(6,6-[2,2bipyridine]) (PFO-BPy), were reported for the individualization and dispersion of BNNTs.[90] These polyfluorenes wrap around the nanotube structure, showing significant bathochromic

shifts in their absorption and emission spectra, which is attributed to strong π-π interaction between the fluorenes and the BNNTs. The Stokes shift was larger for PFO-BPy than for PFO, indicating differences between the interactions of both polymers. These findings contribute to the understanding of the interaction between conjugated polymers and BNNTs.[90]

3.1.3. Block co-polymers

Block co-polymers have been used to disperse BNNTs acting like surfactants, in which they generally have hydrophobic sections interacting with the structure and hydrophilic sections interacting with the solvent.

In 2011, Horváth and coworkers utilized a polyoxyethylene sorbitan monooleate (Tween 80) to disperse BNNTs in aqueous cell media to test their cytocompatibility in different cell types.[37] They produced dispersions at concentrations of 20, 2, and 0.2 μg/mL and found that those < 20 μg/mL were stable for at least 5 days. The dispersed BNNTs were determined to be toxic in several of the cell lines tested.[37] In 2014, Nithya and coworkers compared two different Pluronic block copolymers and PEI for dispersibility of BNNTs in water.[38] After removing aggregated BNNTs and excess polymer, they found the best dispersion was prepared with Pluronic F127, followed by PEI, and Pluronic P123. The dispersions were utilized for antibacterial studies against E. coli and S. aureus, and cytotoxicity studies in human liver cells.[38]

Lee and coworkers dispersed BNNTs in water with methoxy-poly(ethylene glycol)-1,2,-distearoyl-sn¬-glycero-3-phosphoethanolamine-N conjugates (mPEG-DSPE), which, after 2 hours of sonication, formed stable dispersions for months.[19] The DSPE chains are fatty acids that can wrap around BNNTs, while the hydrophilic mPEG stabilizes the BNNTs in water. The authors also tested dispersions in mPEG and DSPE separately, finding that DSPE could disperse some BNNTs, using the phosphate groups for water stabilization, but mPEG alone could not disperse BNNTs as it had no way to interact with the nanotube surface.[19] The dispersed BNNTs were used to form monolayer composite films by coating on a Si substrate and evaporating water.[19]

Some studies have been performed to report the optimal dispersion conditions with block-co polymers. In 2014, Zeng and Liu performed such optimization with BNNT dispersions in ethanol solutions of PVP and Triton X100.[91] They tested the dispersions in polymer concentrations of 0-5 wt.% and tracked their stability over 50 hours by UV-Vis, finding the optimal polymer concentrations to be 2 wt.% PVP and 3 wt.% Triton X100.[91] In 2019, Jeon and coworkers optimized BNNT dispersions in two Pluronic block copolymers, Pluronic P85 and Pluronic F127, in water.[92] After optimizing sonication time and centrifugation rate and time, they produced ~5 wt.% BNNT dispersions that were stable for at least 1 month.[92] Also in 2019, the Martí group studied 4 polymers from the Pluronic series, Pluronic F108, Pluronic F87, Pluronic L81, and Pluronic 17R4, for their ability to disperse BNNTs.[93] Among the 4 polymers tested, it was found that the highest molecular weight and most hydrophilic polymer, Pluronic F108, dispersed the most material and was capable of dispersing individualized nanotubes. These results were compared to dispersions with ionic surfactants, which will be discussed in more detail in section 3.4.[93]

Table 3: Summary of characteristics of BNNT dispersions prepared with polymers

Polymer	*BNNT synthesis method / source*	*Method of dispersion*	*Dispersion solvent*	*Stability*	*Application*	*Ref.*
PEG_{1500N}	Carbon nanotube substitution reaction	mixing	water and organic solvents	-	-	[55]
PmPV	CVD method	Sonication and centrifugation.	chloroform, DMAc, THF	-	-	[16]
PmPV	BOCVD method	Sonication and centrifugation.	chloroform, DMAc, THF	-	Purification	[17]
PVP	-	-	water	-	Photophysical studies of π electron donors and BNNTs	[80]
PEI	Ball milling and annealing, from Australian National University	Mixing, stirring at 70 °C, and sonication. Centrifugation.	PBS	-	*In vitro* testing on human neuroblastoma cell line	[36]
PEI	Ball milling and annealing, from Australian National University	Stirring at 70 °C, sonication. Centrifugation	PBS	-	Conjugate with quantum dots, track uptake by living cells	[81]
Polymer Ethyl Cellulose	Induction Plasma torch method from Tekna Advanced Materials Inc.	Sonication and centrifugation	acetone, benzyl alcohol, butanol, ethanol, methanol,	-	Purification	[82]

			propanol, THF, toluene			
PPE, ferrocene-conjugated PPE, PT	Thermal CVD	Sonication and centrifugation	chloroform, methylene chloride, THF	6 months	Self-organized composite films	[18]
((-)PPP), PXT, PSS, PVS, PAA	-	Sonication and centrifugation	water	-	superhydrophobic surfaces	[83]
PD	HTP, from BNNT, LLC.	BNNTs dispersed with Tris-HCl and SDBS by tip sonication and centrifugation. Dopamine hydrochloride added, stirred and centrifuged	water, PBS	-	Study cytocompatibility in vitro with cultured human osteoblasts	[84]
P3HT	Thermal plasma process	Bath sonication	chloroform	Weeks	Dispersion, demonstrate use off polarized excitation fluorescence microscopy	[85]
P4VP	From BNNT, LLC	Bath sonication	methanol	7 days	Composite film for water filtration	[20]
P4VP	From BNNT, LLC	Bath sonication	methanol	-	BNNT-hBN-expoxy composite	[86]
P4VP	High-temperature inductively coupled plasma facility at Jeonbuk National University	Bath sonication and centrifugation	methanol	-	purification, remove hBN impurities	[87]

CTVB	RF Plasma Process	Vortexing (after freeze drying wrapped BNNTs)	water	>1 year	-	[88]
Poly(2,7-carbazole)s	HABS method	Bath sonicated, centrifugation, filtration	THF, chloroform	>1 year (THF)	simple capacitors and PMMA composites	[89]
PFO, PFO-BPy	Plasma technique, supplied by High-Enthalphy Plasma Research Center at Jeonbuk National University	Tip sonication, centrifugation	toluene, chloroform	-	Fabrication of devices through dose-controlled, floating evaporative self-assembly.	[90]
Tween 80	BOCVD method	Sonication and stirring	water, cell culture medium	-	Assess in vitro cytotoxicity with four cell lines	[37]
P123, F127, PEI, ammonium olate	CVD method	Stirring at 70 °C, sonication. Centrifugation	PBS	-	Evaluation antibacterial activity and cytotoxicity in four different cell types	[38]
mPEG-DSPE	Growth vapor trapping (GVT)	Sonication and centrifugation	water	>24h	Composite films, biomedical applications	[19]
PVP, Triton X-100	CVD method	Bath sonication	ethyl alcohol	>10 days	-	[91]
Pluronic P85, Pluronic F127	High-Enthalpy Plasma Research at Chonbuk National University	Sonication and centrifugation	water	>1 month	-	[92]
Pluronic F108, F87, L81, 17R4	From BNNT, LLC	Sonication and centrifugation	water	>1 month	-	[93]

3.2. Biomolecules

Another popular method for dispersing BNNTs is through the use of biomolecules. These can be broken down into 5 general sections based on the type of biomolecule used: DNA (Section 3.2.1), proteins or peptides (Section 3.2.2), saccharides (Section 3.2.3), mononucleotides (Section 3.2.4). The details of each dispersion are summarized in Table 4.

3.2.1. DNA

One of the first biomolecules used for BNNT dispersion was Salmon DNA, as reported by Zhi and coworkers in 2007.[56] After sonication for 3 hours, the DNA wraps around BNNTs and can produce up to a 0.2 wt.% BNNT solution in water that remains stable for at least a few hours. UV-Vis and cathodoluminescence measurements revealed that the DNA interacts with BNNTs through π-stacking interactions. The BNNTs can be recovered by heating and washing with boiling water and the BNNT-DNA dispersion can be filtered to produce a BNNT mat with some nematic ordering.[56] In 2019, Kode and coworkers dispersed BNNTs in a variety of short single-stranded DNA sequences.[25] They found that $(GT)_{20}$ single-stranded DNA formed the best dispersion, which was stable for more than 12 months when stored at 4 °C. Membrane filtration was used to purify the dispersion from non-BNNT species and solvent evaporation was used to prepare an aligned BNNT film (Figure 5).[25] In 2021, Kode and coworkers were able to further demonstrate the use of DNA as a good dispersant, this time with a cosolvent system.[94] Using herring DNA (bp<50), they wrapped BNNTs and showed the highest dispersion concentration using cosolvent systems of alcohol and water. At 50% isopropanol/water, the mixtures they could achieve were of greater concentrations than with surfactant-wrapped BNNTs. Interestingly, they did molecular

dynamics calculations that indicate that the alcohol acts similar to a surfactant by aligning at the electronic double layer and widening it, which contributes to the greater stability of the dispersion.

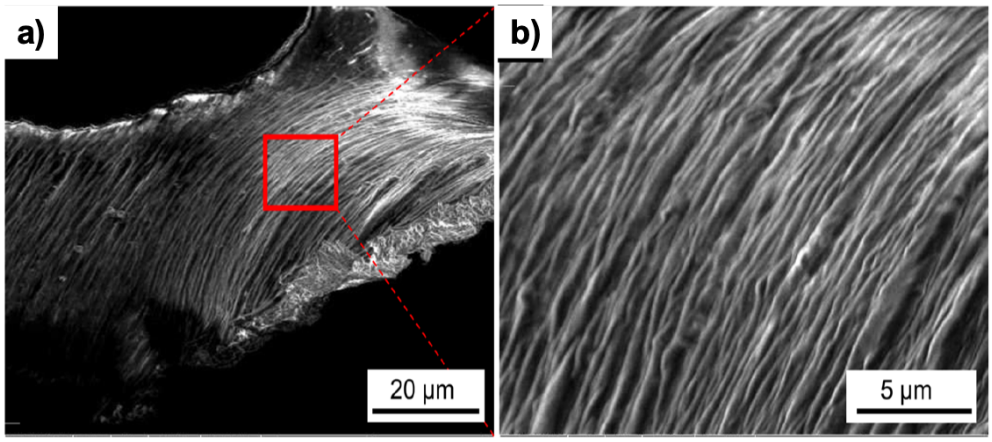

Figure 5. (a) SEM image of an aligned DNA-BNNT film formed by solvent evaporation of purified dispersions of BNNTs:DNA = 1:0.75 mass ratio (≈11.5 mass % of DNA-BNNT hybrids) without applied shear. (b)Surface morphology of the film showing the alignment of densely packed nanotube bundles. Reprinted with permission from Ref [25] (V. Kode *et al. ACS Appl. Nano Mater.* 2019, *2*, 2099-2105.) Copyright © 2019 American Chemical Society.

3.2.2. Proteins and Peptides

Another type of biomolecule that can individualize and disperse BNNTs groups proteins and peptides. In 2008, Ciofani and coworkers prepared BNNT dispersions using the positively charged protein poly-L-lysine (PLL).[32] This protein could be conjugated with fluorescent quantum dots for imaging and functionalized with folate for cell targeting. 50 µg/mL BNNT dispersions in PBS were used for uptake and cytocompatibility studies in human glioblastoma multiforme cells,[32] normal human fibroblasts,[32] and C2C12 cells.[95] Later, Gao and coworkers used the B3 peptide (HWSAWWIRSNQS) for BNNT aqueous dispersion.[96] This peptide

has an α-helical conformation that enables it to wrap around the BNNT and interact through π-π interactions. When the sequence is modified to reduce the α-helix conformation, the peptide can no longer disperse the nanotubes.[96]

3.2.3. Saccharides

Saccharides are a third type of biomolecule used to disperse BNNTs. Perhaps due to the many variations of polysaccharides and their similarities to synthetic polymers, they are one of the most predominant biomolecular dispersion agents reported. In 2009, Chen and coworkers used glycodendrimers, with a pyrene group at the dendrimer focal point, to disperse BNNTs in water.[33] Though a maximum dispersion concentration was not reported, the dispersions were stable in water for weeks at a time. Since the pyrene focal point was used to interact with the BNNT through π-π interactions, the glycans could be tuned for conjugation of fluorescent dyes or to bind to cell surfaces.[33] In 2010, Ciofani and coworkers first reported the use of glycol-chitosan to disperse BNNTs in PBS.[34] These dispersions were stable for many weeks and were used to test the cell viability.[34] The same group later tested these dispersions for compatibility in human vein endothelial cells[97] and their effects on stem cell biology and tissue regeneration in planarians.[98] Later, Gao and coworkers investigated BNNT dispersions in gum arabic, dextran, dextran sulfate, amylose, and amylopectin.[35] They found gum arabic produced the best dispersions, reaching a maximum concentration of 22 μg/mL. Additionally, they were able to immobilize proteins onto the wrapped BNNTs.[35] Later, the same group used gum arabic dispersed BNNTs to test cytocompatibility in human endothelial and neuron-like cells.[99]

In 2013, Lau and coworkers tested another array of polysaccharides: hyaluronic acid, chitosan, chitosan phosphorylcholine, and rhodamine-labeled chitosan phosphorylcholine.[100] The BNNTs were first dispersed in glycine, which served as a linker between the polysaccharides and BNNTs, and then the polysaccharide solution was added. After washing away free polysaccharide, hexane was added to the BNNT dispersion in water to produce an oil/water interface where the BNNT-polysaccharide hybrids formed a film. This process made the polysaccharide covering of the BNNTs more uniform and the dried film could be readily redispersed in water.[100] All of the produced dispersions, except with hyaluronic acid, were stable for extended periods of time as long as glycine was used.[100] In 2016, Rocca and coworkers coated BNNTs with pectin derived from apples and dispersed them in water.[101] These dispersions remained stable after several months, as confirmed by zeta potential measurements, and were tested for cytocompatibility in macrophages.[101] Finally, in 2018, Wang and coworkers studied alginic acid for the dispersal of 7 carbon and boron nitride nanomaterials, including BNNTs and hBN, in water and cell media.[102] They found, through zeta potential, absorbance, and dynamic light scattering (DLS) measurements, that the BNNT dispersions remained stable for at least 7 days and that stability improved with increased BNNT outer diameter.[102]

In 2013, Ferreira and coworkers compared the polysaccharide chitosan, the monosaccharide glucosamine, and the polymer PEG_{1000} to see which produced the best dispersion in water.[103] Dispersions were prepared by refluxing the BNNTs and dispersion agent in ethanol for 6 hours, centrifuging the hybrids out of solution, and redispersing them in water with brief sonication. Tracking the amount of material grafted by TGA and the stability of the dispersion with zeta potential, they found that glucosamine produced the best dispersions and these were stable

for at least 8 days, while the others were not.[103] The dispersed BNNTs were used for biocompatibility and cytotoxicity studies.[103]

3.2.4. Mononucleotides

Mononucleotides are the fourth type of biomolecule that has been utilized for BNNT dispersion. These interact with BNNTs through π-π interactions to stabilize them in aqueous solution.[104],[105] In 2011, Gao and coworkers first reported the use of flavin mononucleotide (FMN) for BNNT disentanglement and dispersion.[104] They could disperse individualized or small bundles of BNNTs with lengths up to 8 μm using this method. Additionally, they found that the pH and temperature dependence of FMN fluorescence, when free in solution, disappears when it is adsorbed to the BNNT.[104] Later, the same group tested an assortment of nucleotides for BNNT dispersion: adenosine 5'-mono-, di-, and triphosphate, guanosine, guanosine 5'-mono-, di-, and triphosphate, uridine 5'-monophosphate, and cytidine 5'-monophosphate.[105] After characterizing the relative dispersion concentration by UV-Vis absorbance, they found that all monophosphates performed better than the di- and triphosphates and that guanosine produced the best dispersion overall. Additionally, they attached CdS quantum dots to the nucleotide for fluorescence imaging.[105]

Table 4: Summary of characteristics of BNNT dispersions prepared with biomolecules

Biomolecule	*BNNT synthesis method / source*	*Method of dispersion*	*Dispersion solvent*	*Stability*	*Application*	*Ref.*
ssDNA	From BNNT, LLC	Sonication and centrifugation	Water	-	Film	[25]
PLL + Folate	Ball-milling and Annealing (Australian National University, Canberra, Australia)	Tip sonication and centrifugation	Phosphate-buffered solution	-	Cell Proliferation Studies	[32]
Glycodendrimer (labeled as G-2)	CVD method	Sonication and centrifugation	Phosphate-buffered solution	Weeks	Cell Viability Studies	[33]
Glycol-chitosan	Annealing Method (Nano and Ceramic Materials Re-search Center, Wuhan Institute of Technology, China)	Sonication and centrifugation	Phosphate-buffered solution	-	Cell Proliferation Studies	[34]
Gum Arabic, dextran, dextran sulfate, amylose, and amylopectin	CVD method	Tip sonication and centrifugation	Water	-	Dispersion for Characterization	[35]
Thiol-Modified DNA	CVD method	Stirred at 90 °C and sonicated	Water	-	Liquid Crystals	[56]
DNA (surfactant exchange)	BNNT, LLC	Sonication and centrifugation	Water/Alcohol (MeOH, EtOH,	-	Dispersions for Characterization	[94]

			and IPA at various concentrations)			
PLL	Ball-milling and annealing (Australian National University, Canberra, Australia)	Tip sonication and centrifugation	Phosphate-buffered solution	-	Cell Viability and Uptake Studies	[95]
Short Peptide (B3 (HWSAWWIRSNQS))	CVD method	Tip sonication and centrifugation	Water	-	Dispersions for Characterization	[96]
Glycol-chitosan	Annealing Method (Nano and Ceramic Materials Research Center, Wuhan Institute of Technology, China)	Tip sonication and centrifugation	Phosphate-buffered solution	-	Cell Viability Studies	[97]
Gum Arabic	CVD Method	Sonication and centrifugation	Phosphate-buffered solution	-	Animal Cell Studies	[98]
Gum Arabic	CVD Method	Tip sonication and centrifugation	Phosphate-buffered solution	-	Cell Viability Studies	[99]
Glycine exchanged with hyaluronic acid, chitosan, chitosan phosphorylcholine, or rhodamine-B-labeled chitosan phosphorylcholine	BOCVD Method	Sonication and centrifugation	Water	-	Films	[100]

Pectin	CVD Method	Tip sonication and centrifugation	Phosphate-buffered solution	several months	Cell Viability Studies	[101]
Alginic Acid	From Sigma Aldrich	Tip sonication and centrifugation	Water	7 days	Cell Viability Studies	[102]
Flavin Mononucleotide	CVD Method	Tip sonication and centrifugation and dialysis	Water	-	Dispersions for Characterization	[104]
Nucleotides (AMP, ADP, ATP, GMP, GDP, GTP)	CVD Method	Tip sonication and centrifugation and dialysis	Water	-	Dispersions for Characterization	[105]
Glucosamine, Polyethylene Glycol, or Chitosan	CVD Method	Sonication and centrifugation	Phosphate-buffered solution	7 days	Cell Viability Studies	[103]

3.3. Aromatic Molecules

Another type of dispersing agent often utilized encompass aromatic molecules, which can interact with BNNTs through π-π stacking interactions and contain a polar moiety, such as a carboxylic acid, to stabilize them in water. A summary of the reported dispersions using this technique is shown in Table 5. In 2008, Wang and coworkers first demonstrated this with perylene-3,4,9,10-tetracarboxylic acid tetrapotassium salt (PTAS).[58] After stirring and sonicating BNNTs in a 1mM solution of PTAS, the authors obtained BNNT concentrations of ~0.3 mg/mL in water. Since the carboxylic acid moieties make the hybrids dispersible in aqueous solution, the system is pH-responsive and can exhibit binding to aqueous metal ions.[58] Additionally, after vacuum-annealing the dispersion, they generated graphitic C species on the BNNT surface, making the material a p-type semiconductor.[58] Later, Kim and coworkers tested a variety of aromatic molecules, to see what properties were most important for BNNT dispersion.[106] The molecules tested were 9-naphthalenecarboxylic acid (NCA), 9-anthracenecarboxylic acid (ACA), 1-pyrenecarboxylic acid (PCA), 1-aminopyrene (AP), and 1-hydroxypyrene (HP), to investigate the impact of the extended aromatic system and/or different polar dispersing groups, on the molecule's ability to disperse BNNTs. They found that PCA dispersed the greatest concentration of material, ~17 μg/mL, followed by ACA and AP, which had pretty similar dispersions, then HP, and, finally, NCA, which dispersed almost none.[106] Moreover, AFM and TEM images demonstrated that PCA and ACA produced dispersions of individualized tubes, while NCA and AP gave small bundles. These results indicate that dispersion is improved by increasing the number of aromatic rings and using a more polar group for water stabilization, i.e. a carboxylic acid performs better than amine or hydroxyl groups.[106] Finally, Emanet and coworkers used

Doxorubicin (Dox), a common cancer drug, to disperse BNNTs in PBS.[39] In this case, Dox contains a mixture of amino, carbonyl, ether, and hydroxyl groups that can stabilize the BNNTs in solution. The group studied how pH impacted Dox loading and release profiles, hoping to make a system that would release the drug once it was inside the cell. They found that at lower pH, as would be found in lysosomes of cells, Dox release increases.[39] Finally, they loaded folate on the Dox-BNNTs, for specific cell targeting and tested cellular uptake and toxicity.[39]

Table 5. Summary of characteristics of BNNT dispersions prepared with aromatic molecules

Aromatic molecule	*BNNT synthesis method / source*	*Method of dispersion*	*Dispersion solvent*	*Stability*	*Application*	*Ref.*
PTAS	CVD Method	stirring and sonication	water	-	B-C-N/BN coaxial nanotubes	[58]
NCA, ACA, PCA, AP, HP	CVD Method	sonication and centrifugation	methanol and water	-	-	[106]
Dox	synthesized from colemaite using Fe_2O_3 as catalyst	stirring and centrifugation	PBS	-	cancer drug nanocarriers	[39]

3.4. Ionic Surfactants

Surfactants are another type of dispersing agent for BNNTs. These molecules contain a polar head group attached to a nonpolar tail and will aggregate into micellar structures when their concentration is above the critical micelle concentration. Dispersions with surfactants that have been studied are summarized in Table 6. Yu and coworkers first reported the use of the surfactant ammonium oleate for making BNNT dispersions in 2009.[107] They found that they could produce dispersions of individualized BNNTs that were relatively stable for several months and still contained individual BNNTs after 60 days.[107] Ammonium oleate was later used by Nithya and coworkers in 2014 and compared to many polymers (see Polymers section 3.1).[38] In 2012, Zheng and coworkers utilized sodium dodecylbenzenesulfonate (SDBS) to individualize and disperse BNNTs for radial elasticity measurements.[108] The Martí group performed a systematic study of 4 different ionic surfactants, sodium dodecyl sulfate (SDS), cetyltrimethylammonium bromide (CTAB), dodecyltrimethylammonium bromide (DTAB), and cetyltrimethylammonium chloride (CTAC), and 4 polymers, Pluronic F108, Pluronic F87, Pluronic L81, and Pluronic 17R4, for BNNT dispersion.[93] Here, it was found that the high molecular weight, nonionic polymer, Pluronic F108, dispersed the most material , but that ionic surfactants were more selective for BNNTs over impurities. Additionally, it was found that cationic surfactants and nonionic polymers produced individualized BNNTs in the dispersion, while anionic surfactants dispersed small bundles. AFM and Cryo-TEM images can be seen for SDS, CTAB, and Pluronic F108 dispersions in Figure 6.[93]

Finally, UV-Vis and DLS measurements determined that all dispersions were stable for at least a month.[93]

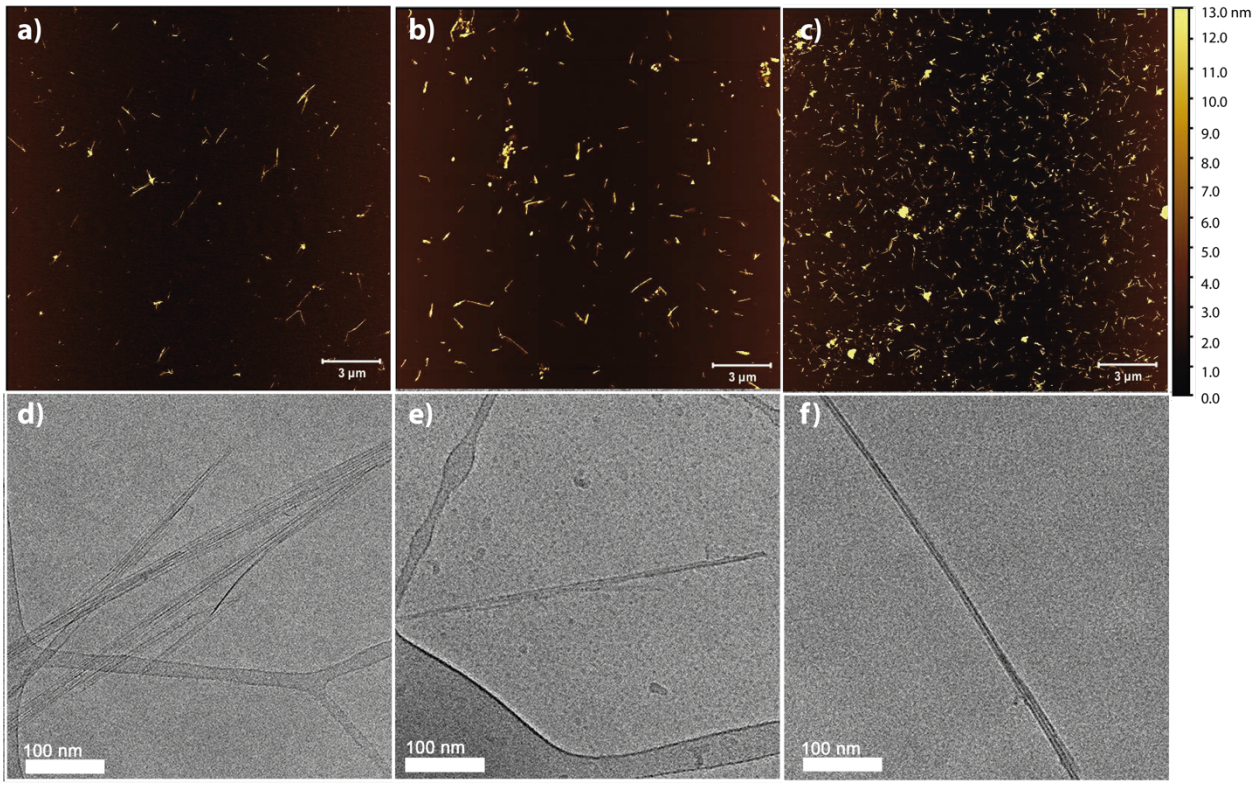

Figure 6. Representative AFM (a-c) and cryo-TEM (d-f) images of BNNT dispersions in SDS (a, d), CTAB (b, e), and Pluronic F108 (c, f). Reproduced from Ref. **[93]** with permission from the Royal Society of Chemistry. (A. D. Smith McWilliams *et al. Nanoscale Adv.* 2019, *1*, 1096-1103.)

In addition, in 2020, the Martí group also synthesized fluorescent surfactants linking together a fluorescent dye and an alcohol.[109] One of the synthesized surfactants, composed of Eosin Y and a ten-carbon chain, was used to disperse and individualize BNNTs, and they were able to be imaged using standard fluorescence microscopy. BNNTs dispersed with a fluorescent surfactant composed of Rhodamine with a 12-carbon chain were also imaged to study their

diffusion in aqueous solutions using fluorescence microscopy. Association between the surfactant and the BNNT helped provide better imaging contrast, allowing to determine their rotational and translational diffusion. [110]

In 2021, Ko and coworkers reported the purification and length fractionation of BNNTs using gel column chromatography.[111] They first studied the dispersion efficiency of several different surfactants, in which bile salts sodium cholate (SC) and sodium deoxycholate (DOC) showed the best efficiency and no visible aggregates. Aqueous SC was used as the dispersant and eluent for the chromatography studies, in which early fractions produced the longest BNNTs, with the shortest BNNTs and impurities at the end. Likewise, this year several surfactants were studied by Khoury and coworkers to make dispersions that were later used to add the BNNTs to polyvinyl alcohol and produce fibers by wet spinning. [112] They also determined DOC produced the most nanotubes in dispersion (about 0.57 mg mL^{-1} of DOC-BNNTs), and were stable for weeks stored at 4 °C.

Table 6. Summary of characteristics of BNNT dispersions prepared with ionic surfactants

Ionic surfactant	*BNNT synthesis method / source*	*Method of dispersion*	*Dispersion solvent*	*Stability*	*Application*	*Ref.*
ammonium olate	ball milling and annealing	ultrasonication and settling	water	60 days	-	[107]
SDBS	Pressurized vapor/ condenser (PVC) method	sonication	water	-	-	[108]
SDS, CTAB, DTAB, CTAC, Pluronic F108, F87, L81, 17R4	From BNNT, LLC	Sonication and centrifugation	water	>1 month	-	[93]
Eosin Y surfactant	From BNNT, LLC	bath sonication	water	-	Fluorescence microscope imaging	[109]
Rhodamine B surfactant + CTAC	From BNNT, LLC	tip sonication	water	-	Fluorescence microscope imaging and diffusion tracking	[110]
SDS, SDBS, SC, DOC	High-Enthalpy Plasma Research Center at Chonbuk National University	tip sonication and centrifugation	water	-	Purification	[111]
SDC, SDS, TTAB, LSZ	From BNNT, LLC.	bath sonication, tip sonication and centrifugation	water	-	Fiber spinning with PVA	[112]

3.5. Acids and Bases

Though less commonly used than other methods, acids and bases have also been well established as effective BNNT dispersing agents. In particular, Lewis bases and strong protic acids have been utilized for this purpose, as they can interact with boron sites or protonate nitrogen sites respectively. A summary of each dispersion type is presented in Table 7.

3.5.1. Lewis Bases

Since the boron sites in BNNTs are inherently electron-deficient, they can be exploited as Lewis acids for functionalization with dispersing agents. In 2007, Pal and coworkers first used this method, where BNNTs interacted with trioctylamine, trioctylphosphine, and tributylamine.[57] After warming a mixture of base and BNNTs to 70 °C for 12 hours, the BNNTs could produce stable dispersions in toluene or other nonpolar solvents at room temperature.[57] In 2020, Chang and coworkers reported the dispersion of BNNTs using pyridine as their Lewis base.[23] After tip sonicating BNNTs in pyridine and then centrifuging them out of solution, the BNNTs can be redispersed in water, THF, DMF, methanol, and acetone. These dispersions, monitored by Turbiscan, were stable and uniform after 24 hours in all solvents and after 1 week in ethanol.[23] The pyridine-BNNT hybrids were used to prepare composites with polydimethylsiloxane (PDMS), epoxy, and PVA fibers, and were utilized as an agent for nanofluids, in order to improve their thermal conductivity and/or tensile strength.[23]

3.5.2. Protic Acids

The Pasquali group has pioneered the use of the superacid chlorosulfonic acid (CSA), for BNNT dispersion.[60],[113] In 2017, they found that stirring BNNTs in CSA could individualize and disperse them, likely through protonation of nitrogen sites.[60] Cryogenic Transmission Electron Microscopy (Cryo-TEM) images showed the BNNTs were individualized and filled with acid.[60] In 2018, they demonstrated the use of CSA for purification of BNNTs from hBN and B particles.[113] Additionally, using the purified dispersions, they could prepare BNNT films, mats and aerogels [113] This year, they reported on the formation of liquid crystal domains by using CSA to dissolve highly pure BNNTs at concentrations above 170 ppmw (Figure 7a), which can be processed into aligned films and fibers, as shown in Figure 7 b and c. [114]

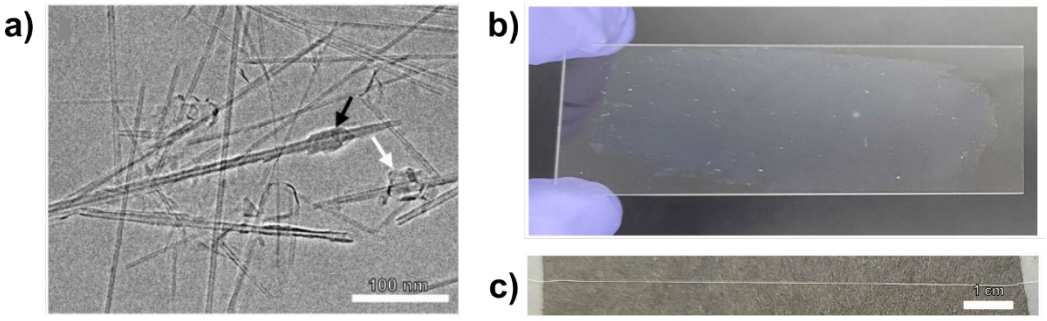

Figure 7. a)Cryo-TEM image of highly purified BNNTs in CSA. b) BNNT film made from BNNT solution in CSA deposited on a glass slide. c) Segment of fiber made from highly purified BNNTS. Reprinted with permission from Ref **[114]** Material from: Simonsen Ginestra, C. J. et. al., Liquid Crystals of Neat Boron Nitride Nanotubes and their Assembly into Ordered Macroscopic Materials, *Nature Commun.,*13 (3136), published 2022, Copyright © 2022 Springer Nature.

Table 7. Summary of characteristics of BNNT dispersions prepared with acids or bases

Acid or Base	*BNNT synthesis method / source*	*Method of dispersion*	*Dispersion solvent*	*Stability*	*Application*	*Ref.*
trioctylamine, trioctylphosphine, tributylamine	Carbon nanotube substitution	Mix at 70 °C for 12 hours and sonication	Toluene, non-polar solvents like benzene	long periods of time	-	[57]
pyridine	RF-ICP system, from Tekna Plasma Systems, INC	tip sonication and centrifugation	water, THF, DMF, methanol, acetone, ethanol	24 hours, 1 week for ethanol	Prepare composites with PDMS, epoxy, and PVA fibers	[23]
CSA	High temperature Pressure (HTP) from National Institute of Aerospace / NASA Langley Research Center	mixing	CSA	-	-	[60]
CSA	HTP supplied by NASA	mixing, speed-mixing, centrifugation	CSA	-	purification, make thin films, mats, and aerogels	[113]
CSA	From BNNT, LLC	speed-mixing, sonication	CSA	-	fibers	[114]

4. Direct Solvation

Finally, a few methods have been explored for dispersing BNNTs directly into solvents without the use of a dispersing agent. These reports either utilize Hansen or Hildebrand Solubility Parameters to help determine the dispersion solvent.

In 2013, Mutz and coworkers first tried to study the Hildebrand Solubility Parameters of different BN species with static light scattering and refractometry.[115] They found that these parameters are not great indicators for the dispersion of larger particles and materials.[115] In 2016, Tiano and coworkers also explored solubility parameters, finding that Hansen solubility parameters could provide a better indication for dispersion results.[59] Following this method, after comparing results from 16 different solvents, they determined DMAc, DMF, acetone, and N-methyl-2-pyrrolidone (NMP) were all good solvents for the dispersion of BNNTs, with DMAc producing the most uniform and stable dispersions and reaching a concentration of 0.25 mg/mL after mild sonication.[59] Utilizing the parameters outlined by Tiano and coworkers, Snapp and coworkers showed the viability of using THF to mediate the dispersion of BNNTs in polydimethylsiloxane, which has similar Hansen parameter values to BNNTs for dispersion and hydrogen bonding forces, but a very different value for intermolecular forces.[116] More recently, in 2020, a further investigation of Hansen parameters and solvent dispersibility was provided by Torres Castillo and coworkers.[117] They confirmed that DMAc and DMF are good solvents, but added that ethanol and isopropyl alcohol should also be considered good solvents. Interestingly, acetone and NMP are much lower on their list as compared to Tiano and coworkers. Torres Castillo attributes this to the fact that the material they studied went through

a round of purification, so the Hansen parameters determined for BNNTs were different than what Tiano and coworkers were using. Further investigation into this needs to be considered, as methods for purification are constantly evolving.

5. Outlook and Conclusions

In summary, there are a wide variety of methods employed for the dispersion of BNNTs into solution. Due to differences in structures and properties of aiding agents and solvents, very different approaches must often be taken to achieve stable dispersions of each species. BNNTs are not very wettable in most solvents and need to be individualized from the nanotube network and often, other BN impurities. Molecules that can wrap around the BNNT surface, such as biomolecules, polymers, and surfactants, tend to be ideal for preferentially dispersing BNNTs over other species.

As researchers work to propel this area of study forward, a large area of consideration has been and continues to be material quality. Although a variety of synthesis[2],[6],[118],[119] and purification[17],[25],[120]–[122] methods have been developed, production of BNNTs in bulk results in the formation of other BN impurities, such as hBN, BN cages, cubic BN, or B particles, that can be extremely difficult to remove due to similarities in their properties to those of BNNTs.[123],[124] This also presents a significant challenge in differentiating the impurities in any sort of bulk measurement. Generally, qualitative techniques are the standard method for determining the quality of material, so most researchers will include TEM or SEM images as an indication of purity. There have been a few attempts at giving a more quantitative component to

the evaluation of quality using bulk techniques such as TGA, FTIR, Raman, XPS, and ^{11}B NMR. [125],[126] These methods have proven useful for determining certain characteristics such as boron oxide or boric acid content. However, the challenge with these techniques is that it is particularly difficult to differentiate between the various allotropes of BN impurities, which is compounded, as mentioned above, by the fact that different synthesis methods produce different impurities. Furthermore, there is presently no bulk method for determining the morphology of individual BNNTs, like there is with the chirality-dependent fluorescence for semiconducting CNT [127] or the RBM region in Raman for CNTs.[128] There is some indication that extensional rheology can be used for aspect ratio determination, though this is highly specialized. [114]

Moreover, any methodology for dispersion must consider that the type of impurity present in the sample can impact the overall dispersibility of the material. For instance, large BN cages may hold together BNNT aggregates making it much more difficult to break apart a large nanotube network. On the other hand, hBN impurities may wrap around smaller bundles of BNNTs, impeding the individualization of those nanotubes. Furthermore, the techniques for purification vary as much as those for dispersing BNNTs. Dispersion and purification techniques that work well for one type of material may be ineffective for another, due to differences in the impurities present in each. These impurities can be related to the different BNNT production method employed, such as chemical vapor deposition (CVD) or the pressurized vapor/condenser (PVC) method. Another consideration is that as large-scale BNNT manufacturers work to improve the quality of their product, the types and quantities of these impurities change, meaning the material used in early studies of BNNT dispersions may no longer be available today, and the ones in use today may behave differently. Due to these differences in material quality, which are sometimes vast,

reproduction of results and continued growth from the current state-of-knowledge in BNNT dispersion will rely heavily on researchers developing a uniform method for reporting the type of BNNT material used in their study. Therefore, the application of a single dispersion technique to various types of BNNT materials could provide much more insight into how different impurities impact dispersion quantity and quality.

Another key area that needs to be addressed for BNNT dispersion research is the assessment of the dispersions. As can be seen from the studies presented in this review, there is not a consensus on what constitutes a dispersion, let alone any method for determining the quality of such a dispersion. Often, the application will determine the necessary properties of the mixture. Some studies work on determining characteristics of the dispersions, such as their concentration or stability, while others focus on preparing a dispersion that works for their desired application without consideration of other properties. This second approach is useful for their specific end goal, but there is lost information regarding the characteristics of the dispersions prepared. A more systematic approach to the assessment of BNNT dispersions will give us, as a community, more information on how different synthesis methods compare in the dispersed final product. The primary characteristics that we have identified in this review are individualization of tubes, concentration, and stability. Individualization of tubes helps to create a homogenous dispersion, which provides a more uniform distribution of material and, for most applications, will maximize the properties sought after. As shown in some works, this can be determined by imaging samples of the dispersions through AFM or more specialized techniques like Cryo-TEM. [60],[93],[106],[111],[114] Concentration will help to compare different synthesis methods and solvents used to better standardize dispersants and provide insight into trends. Getting the final

concentration of BNNTs has been obtained through UV-Vis by calculating the extinction coefficient, or by mass conversion. [84],[93],[106],[112] Control over the concentration of BNNTs in solution is necessary for processing dispersions into macroscopic materials. Stability of the dispersion can provide insight into the thermodynamics or kinetics of the dispersed BNNTs in a particular solvent and is related to the quality of the dispersion. The stability of the dispersion is addressed in some of the works by measuring the amount of time it takes for BNNTs to settle out, while others have relied on zeta-potential or UV-Vis absorbance. This might not be as important if the dispersion is integrated right away within another matrix for the application or made into a macroscopic material. Most procedures include a centrifugation or settling step to retain only what is stable in the dispersion, so having a standard for this will also help to identify trends.

An additional consideration that needs to be discussed is regarding the mechanical dispersion techniques utilized. There is significant variance in the methods used for mechanically dispersing the material such as stirring, grinding/milling, tip sonication, bath sonication, and heating under reflux. With each of these, there is some amount of energy being imparted to the system and therefore some chemistry can happen, as outlined throughout this review. Indeed, several researchers rely on this chemistry to functionalize the tubes in order to promote the dispersion they are intending. The challenge here is that, again, there is not a systematic evaluation of the effect a particular method will have on the final dispersion. As such, we have outlined each method in the tables in this review to help identify this as a necessary variable that needs consideration. Standardization of mechanical dispersion, just as standardization of analysis of dispersion, will better enable the community to identify trends.

It is important to stress that the ultimate applications of the BNNTs is paramount, so some or all these characteristics may not be important based on the application. For example, those working to utilize BNNTs for biomedical applications, such as drug delivery or imaging, can work with smaller yields of well-dispersed material,[32],[39],[41],[129]–[131] and prefer aqueous media. On the other hand, others who want to achieve industrial-scale production of BN materials and composites must focus their efforts on increasing the dispersion yield substantially. Furthermore, we must keep in mind the feasibility, cost, and safety concerns associated with scaling up their procedure to an industrial scale. Finally, if removal of the dispersing agent would be required in the end product, one must consider how this can be achieved without damaging the material's final structure or properties.

There is no doubt that the contributions from a broad range of scientists to develop methods for BNNT dispersion have provided a solid foundation for understanding these materials. These initial studies will certainly foster the continued development of these techniques until they can be applied at an industrial scale. The knowledge obtained will lead to better-informed decisions on the type of dispersion needed for particular applications, ultimately making applications such as drug delivery, exceptionally strong and thermally stable materials, and advanced electronic devices using BNNTs feasible and accessible to everybody.

Acknowledgments

We acknowledge the financial support from the National Science Foundation (CHE-1807737 and CHE-2108838) and AFOSR (FA9550-19-1-7045). C.M.-J. acknowledges support from CONACyT (Mexico, No. 710115).

Abbreviations

((-)PPP)	poly(p-phenylene)
ACA	9-anthracenecarboxylic acid
AFM	Atomic Force Microscopy
AP	1-aminopyrene
APTES	(3-aminopropyl)triethoxysilane
ATRP	Atom transfer radical polymerization
BN	Boron Nitride
BNNTs	Boron nitride nanotubes
BOCVD	Boron oxide chemical vapor pressure
CNTs	Carbon nanotubes
Cryo-TEM	Cryogenic Transmission Electron Microscopy
CSA	Chlorosulfonic acid
CTAB	cetyltrimethylammonium bromide
CTAC	cetyltrimethylammonium chloride
CVD	chemical vapor deposition
DLS	Dynamic light scattering
DMAc	N,N-dimethylacetamide
DMF	N,N-Dimethylformamide
Dox	Doxorubicin
DSPE	1,2,-distearoyl-sn--glycero-3-phosphoethanolamine-N
DTAB	dodecyltrimethylammonium bromide
EDC	1-ethyl-3-(3-dimethylaminopropyl)carbodiimide
f-BNNTs	Functionalized boron nitride nanotubes

FMN	Flavin mononucleotide
FTIR	Fourier Transform Infrared Spectroscopy
HABS	hydrogen assisted BNNT synthesis
hBN	Hexagonal boron nitride
HP	1-hydroxypyrene
HTP	High temperature pressure
HR-TEM	High resolution transmission electron microscopy
IR	Infrarred
MAA	Methacrylic acid
mPEG	methoxy-poly(ethylene glycol)
NCA	9-naphthalenecarboxylic acid
NIPAM	N-isopropylacrylamide
NMP	N-methyl-2-pyrrolidone
NMR	Nuclear magnetic resonance
P3HT	poly(3-hexyl-thiophene)
P4VP	poly(4-vinylpyridine)
PAA	poly(sodium acrylate)
PBS	Phosphate buffered solution
PCA	1-pyrenecarboxylic acid
PD	polydopamine
PDMS	Polydimethylsiloxane
PEG	Polyethylene glycol
PEI	polyethyleneimine
PFO	poly(9,9-dioctylfluorenyl-2,7-diyl)
PFO-BPy	poly(9,9-dioctylfluorenyl-2,7-diyl)-alt-co-(6,6-[2,2bipyridine])
PLL	Poly-L-lysine

PMMA	Polymethylmethacrylate
PmPV	poly[m-phenylenevinylene-co-(2,5-dioctoxy-p-phenylenevinylene)]
PPE	poly(p-phenylene-ethynylene)
PS	Polystyrene
PSS	poly(sodium styrene sulfonate)
PT	polythiophene
PTAS	perylene-3,4,9,10-tetracarboxylic acid tetrapotassium salt
PVA	Polyvinyl alcohol
PVC	pressure/vapor condenser
PVP	polyvinylpyrrolidone
PVS	poly(sodium vinyl sulfonate)
PXT	poly(xylylene tetrahydrothiophenium chloride)
Py	Pyridine
RBM	radial breathing mode
RF-ICP	high radio frequency induced coupled plasma
rra-P3HT	Regiorandom- poly(3-hexyl-thiophene)
SC	Sodium chocolate
DOC	sodium deoxycholate
SEM	Scanning electron microscopy
SDS	sodium dodecyl sulfate
TGA	Thermogravimetric Analysis
THF	Tetrahydrofuran

Author Contributions

▽ A.D.S.M., C.M.-J. and K.R.S. contributed equally to this manuscript.

Notes

The authors declare no competing financial interest.

References

[1] A. Rubio, J. L. Corkill, and M. L. Cohen, Phys. Rev. B 49(7), 5081 (1994), https://doi.org/10.1103/PhysRevB.49.5081.

[2] N. G. Chopra, R. J. Luyken, K. Cherrey, V. H. Crespi, M. L. Cohen, S. G. Louie, and A. Zettl, Science 269(5226), 966 LP (1995).

[3] N. G. Chopra and A. Zettl, Solid State Commun. 105(5), 297 (1998), https://doi.org/10.1016/S0038-1098(97)10125-9.

[4] M. M. J. Treacy, T. W. Ebbesen, and J. M. Gibson, Nature 381(6584), 678 (1996), https://doi.org/10.1038/381678a0.

[5] C. H. Lee, S. Bhandari, B. Tiwari, N. Yapici, D. Zhang, and Y. K. Yap, Molecules 21(7), 922 (2016), https://doi.org/10.3390/molecules21070922.

[6] D. Golberg, Y. Bando, Y. Huang, T. Terao, M. Mitome, C. Tang, and C. Zhi, ACS Nano 4(6), 2979 (2010), https://doi.org/10.1021/nn1006495.

[7] Y. Chen, J. Zou, S. J. Campbell, and G. Le Caer, Appl. Phys. Lett. 84(13), 2430 (2004), https://doi.org/10.1063/1.1667278.

[8] C. W. Chang, A. M. Fennimore, A. Afanasiev, D. Okawa, T. Ikuno, H. Garcia, D. Li, A. Majumdar, and A. Zettl, Phys. Rev. Lett. 97(8), 085901 (2006), https://doi.org/10.1103/PhysRevLett.97.085901.

[9] X. Blase, A. Rubio, S. G. Louie, and M. L. Cohen, Europhys. Lett. 28(5), 335 (1994).

[10] C. Zhi, Y. Bando, C. Tang, H. Kuwahara, and D. Golberg, J. Phys. Chem. C 111(3), 1230 (2007), https://doi.org/10.1021/jp066052d.

[11] S.-J. Zhou, C.-Y. Ma, Y.-Y. Meng, H.-F. Su, Z. Zhu, S.-L. Deng, and S.-Y. Xie, Nanotechnology 23(5), 055708 (2012), https://doi.org/10.1088/0957-4484/23/5/055708.

[12] S. K. Singhal, A. K. Srivastava, R. Pasricha, and R. B. Mathur, J. Nanosci. Nanotechnol. 11, 5179 (2011), https://doi.org/10.1166/jnn.2011.4182.

[13] C. Y. Zhi, Y. Bando, T. Terao, C. C. Tang, H. Kuwahara, and D. Golberg, Chem. – Asian J. 4(10), 1536 (2009), https://doi.org/10.1002/asia.200900158.

[14] X. Huang, C. Zhi, P. Jiang, D. Golberg, Y. Bando, and T. Tanaka, Adv. Funct. Mater. 23(14), 1824 (2013), https://doi.org/10.1002/adfm.201201824.

[15] S. Lin, B. Ashrafi, K. Laqua, K. S. Kim, and B. Simard, New J. Chem. 41(15), 7571 (2017), https://doi.org/10.1039/C7NJ00193B.

[16] C. Zhi, Y. Bando, C. Tang, R. Xie, T. Sekiguchi, and D. Golberg, J. Am. Chem. Soc. 127(46), 15996 (2005), https://doi.org/10.1021/ja053917c.

[17] C. Zhi, Y. Bando, C. Tang, S. Honda, K. Sato, H. Kuwahara, and D. Golberg, J. Phys. Chem. B 110(4), 1525 (2006), https://doi.org/10.1021/jp054941f.

[18] S. Velayudham, C. H. Lee, M. Xie, D. Blair, N. Bauman, Y. K. Yap, Sarah. A. Green, and H. Liu, ACS Appl. Mater. Interfaces 2(1), 104 (2010), https://doi.org/10.1021/am900613j.
[19] C. H. Lee, D. Zhang, and Y. K. Yap, J. Phys. Chem. C 116(2), 1798 (2012), https://doi.org/10.1021/jp2112999.
[20] H. Lim, B. L. Suh, M. J. Kim, H. Yun, J. Kim, B. J. Kim, and S. G. Jang, J. Membr. Sci. 551, 172 (2018), https://doi.org/10.1016/j.memsci.2018.01.030.
[21] C. Zhi, Y. Bando, C. Tang, S. Honda, K. Sato, H. Kuwahara, and D. Golberg, Angew. Chem. Int. Ed. 44(48), 7929 (2005), https://doi.org/10.1002/anie.200502591.
[22] C. Zhi, Y. Bando, C. Tang, S. Honda, H. Kuwahara, and D. Golberg, J. Mater. Res. 21(11), 2794 (2006), https://doi.org/10.1557/jmr.2006.0340.
[23] M. S. Chang, M.-S. Jang, S. Yang, J. Yu, T. Kim, S. Kim, H. Jeong, C. R. Park, and J. W. Jeong, Nano Res. (2020), https://doi.org/10.1007/s12274-019-2612-4.
[24] L. Li, L. H. Li, S. Ramakrishnan, X. J. Dai, K. Nicholas, Y. Chen, Z. Chen, and X. Liu, J. Phys. Chem. C 116(34), 18334 (2012), https://doi.org/10.1021/jp306148e.
[25] V. R. Kode, M. E. Thompson, C. McDonald, J. Weicherding, T. D. Dobrila, P. S. Fodor, C. L. Wirth, and G. Ao, ACS Appl. Nano Mater. 2(4), 2099 (2019), https://doi.org/10.1021/acsanm.9b00088.
[26] X. Lu, P. Nautiyal, J. Bustillos, A. Loganathan, C. Zhang, Y. Chen, B. Boesl, and A. Agarwal, Polym. Compos. 41(12), 5182 (2020), https://doi.org/10.1002/pc.25785.
[27] W. Hao, C. Marichy, and A. Brioude, Environ. Sci. Nano 4(12), 2311 (2017), https://doi.org/10.1039/C7EN00811B.
[28] G. Ciofani, G. G. Genchi, I. Liakos, A. Athanassiou, D. Dinucci, F. Chiellini, and V. Mattoli, J. Colloid Interface Sci. 374(1), 308 (2012), https://doi.org/10.1016/j.jcis.2012.01.049.
[29] G. Ciofani, S. Del Turco, G. G. Genchi, D. D'Alessandro, G. Basta, and V. Mattoli, Int. J. Pharm. 436(1), 444 (2012), https://doi.org/10.1016/j.ijpharm.2012.06.037.
[30] T. H. Ferreira, A. Marino, A. Rocca, I. Liakos, S. Nitti, A. Athanassiou, V. Mattoli, B. Mazzolai, E. M. B. de Sousa, and G. Ciofani, Int. J. Pharm. 481(1), 56 (2015), https://doi.org/10.1016/j.ijpharm.2015.01.048.
[31] M. Emanet, Ö. Şen, Z. Çobandede, and M. Çulha, Colloids Surf. B Biointerfaces 134, 440 (2015), https://doi.org/10.1016/j.colsurfb.2015.07.036.
[32] G. Ciofani, V. Raffa, A. Menciassi, and A. Cuschieri, Nanoscale Res Lett 4, 113 (2008), https://doi.org/10.1007/s11671-008-9210-9.
[33] X. Chen, P. Wu, M. Rousseas, D. Okawa, Z. Gartner, A. Zettl, and C. R. Bertozzi, J. Am. Chem. Soc. 131(3), 890 (2009), https://doi.org/10.1021/ja807334b.
[34] G. Ciofani, S. Danti, D. D'Alessandro, S. Moscato, and A. Menciassi, Biochem. Biophys. Res. Commun. 394(2), 405 (2010), https://doi.org/10.1016/j.bbrc.2010.03.035.
[35] Z. Gao, C. Zhi, Y. Bando, D. Golberg, M. Komiyama, and T. Serizawa, RSC Adv. 2(15), 6200 (2012), https://doi.org/10.1039/C2RA20765F.
[36] G. Ciofani, V. Raffa, A. Menciassi, and P. Dario, J. Nanosci. Nanotechnol. 8(12), 6223 (2008), https://doi.org/info:doi/10.1166/jnn.2008.339.
[37] L. Horváth, A. Magrez, D. Golberg, C. Zhi, Y. Bando, R. Smajda, E. Horváth, L. Forró, and B. Schwaller, ACS Nano 5(5), 3800 (2011), https://doi.org/10.1021/nn200139h.
[38] J. S. M. Nithya and A. Pandurangan, RSC Adv. 4(60), 32031 (2014), https://doi.org/10.1039/C4RA04846F.

[39] M. Emanet, Ö. Şen, and M. Çulha, Nanomed. 12(7), 797 (2017), https://doi.org/10.2217/nnm-2016-0322.
[40] C. Allard, L. Schué, F. Fossard, G. Recher, R. Nascimento, E. Flahaut, A. Loiseau, P. Desjardins, R. Martel, and E. Gaufrès, Adv. Mater. 32(29), 2001429 (2020), https://doi.org/10.1002/adma.202001429.
[41] J. Niskanen, I. Zhang, Y. Xue, D. Golberg, D. Maysinger, and F. M. Winnik, Nanomedicine Lond 11(5), 447 (2016), https://doi.org/10.2217/nnm.15.214.
[42] T. Pham, A. Fathalizadeh, B. Shevitski, S. Turner, S. Aloni, and A. Zettl, Nano Lett. 16(1), 320 (2016), https://doi.org/10.1021/acs.nanolett.5b03874.
[43] C. Tang, Y. Bando, D. Golberg, X. Ding, and S. Qi, J. Phys. Chem. B 107(27), 6539 (2003), https://doi.org/10.1021/jp034310q.
[44] T. Cui, X. Pan, J. Dong, S. Miao, D. Miao, and X. Bao, Nano Res. 11(6), 3132 (2018), http://dx.doi.org.ezproxy.rice.edu/10.1007/s12274-018-1975-2.
[45] M. Zarghami Dehaghani, B. Bagheri, A. Nasiriasayesh, A. H. Mashhadzadeh, P. Zarrintaj, N. Rabiee, M. Bagherzadeh, S. Habibzadeh, O. Abida, M. R. Saeb, H. W. Jang, and M. Shokouhimehr, ACS Omega 5(49), 32051 (2020), https://doi.org/10.1021/acsomega.0c05080.
[46] J.-K. Qin, P.-Y. Liao, M. Si, S. Gao, G. Qiu, J. Jian, Q. Wang, S.-Q. Zhang, S. Huang, A. Charnas, Y. Wang, M. J. Kim, W. Wu, X. Xu, H.-Y. Wang, L. Yang, Y. Khin Yap, and P. D. Ye, Nat. Electron. 3(3), 141 (2020), https://doi.org/10.1038/s41928-020-0365-4.
[47] S. Kalay, Z. Yilmaz, O. Sen, M. Emanet, E. Kazanc, and M. Çulha, Beilstein J. Nanotechnol. 6(1), 84 (2015), https://doi.org/10.3762/bjnano.6.9.
[48] Y. Yu, H. Chen, Y. Liu, L. H. Li, and Y. Chen, Electrochem. Commun. 30, 29 (2013).
[49] A. L. M. Reddy, B. K. Gupta, T. N. Narayanan, A. A. Martí, P. M. Ajayan, and G. C. Walker, J. Phys. Chem. C 116(23), 12803 (2012), https://doi.org/10.1021/jp210597m.
[50] Z. Ahadi, M. Shadman, S. Yeganegi, and F. Asgari, J. Mol. Model. 18(7), 2981 (2012).
[51] A. L. M. Reddy, A. E. Tanur, and G. C. Walker, Int. J. Hydrog. Energy 35, 4138 (2010).
[52] A. L. Tiano, C. Park, J. W. Lee, H. H. Luong, L. J. Gibbons, S.-H. Chu, S. Applin, P. Gnoffo, S. Lowther, H. J. Kim, P. M. Danehy, J. A. Inman, S. B. Jones, J. H. Kang, G. Sauti, S. A. Thibeault, V. Yamakov, K. E. Wise, J. Su, and C. C. Fay, Nanosensors Biosens. Info-Tech Sens. Syst. 2014 9060, 51 (2014), https://doi.org/10.1117/12.2045396.
[53] Y. Li, P. S. Dorozhkin, Y. Bando, and D. Golberg, Adv. Mater. 17(5), 545 (2005), https://doi.org/10.1002/adma.200401266.
[54] K. E. Walker, G. A. Rance, Á. Pekker, H. M. Tóháti, M. W. Fay, R. W. Lodge, C. T. Stoppiello, K. Kamarás, and A. N. Khlobystov, Small Methods 1(9), 1700184 (2017), https://doi.org/10.1002/smtd.201700184.
[55] S.-Y. Xie, W. Wang, K. A. S. Fernando, X. Wang, Y. Lin, and Y.-P. Sun, Chem. Commun. No. 29, 3670 (2005), https://doi.org/10.1039/B505330G.
[56] C. Zhi, Y. Bando, W. Wang, C. Tang, H. Kuwahara, and D. Golberg, Chem. – Asian J. 2(12), 1581 (2007), https://doi.org/10.1002/asia.200700246.
[57] S. Pal, S. R. C. Vivekchand, A. Govindaraj, and C. N. R. Rao, J. Mater. Chem. 17(5), 450 (2007), https://doi.org/10.1039/B614764J.
[58] W. Wang, Y. Bando, C. Zhi, W. Fu, E. Wang, and D. Golberg, J. Am. Chem. Soc. 130(26), 8144 (2008), https://doi.org/10.1021/ja8020878.

[59] A. L. Tiano, L. Gibbons, M. Tsui, S. I. Applin, R. Silva, C. Park, and C. C. Fay, Nanoscale 8(7), 4348 (2016), https://doi.org/10.1039/C5NR08259E.
[60] O. Kleinerman, M. Adnan, D. M. Marincel, A. W. K. Ma, E. A. Bengio, C. Park, S.-H. Chu, M. Pasquali, and Y. Talmon, Langmuir 33(50), 14340 (2017), https://doi.org/10.1021/acs.langmuir.7b03461.
[61] C. Y. Zhi, Y. Bando, C. C. Tang, Q. Huang, and D. Golberg, J. Mater. Chem. 18(33), 3900 (2008), https://doi.org/10.1039/B804575E.
[62] C. Zhi, Y. Bando, C. Tang, and D. Golberg, Mater. Sci. Eng. R Rep. 70(3), 92 (2010), https://doi.org/10.1016/j.mser.2010.06.004.
[63] G. Ciofani, S. Danti, G. G. Genchi, B. Mazzolai, and V. Mattoli, Small 9(9–10), 1672 (2013), https://doi.org/10.1002/smll.201201315.
[64] Z. Gao, C. Zhi, Y. Bando, D. Golberg, and T. Serizawa, Nanobiomedicine 1, 7 (2014), https://doi.org/10.5772/60000.
[65] D. Zhang, S. Zhang, N. Yapici, R. Oakley, S. Sharma, V. Parashar, and Y. K. Yap, ACS Omega 6(32), 20722 (2021), https://doi.org/10.1021/acsomega.1c02586.
[66] M. Foroutan, S. J. Fatemi, and S. M. Fatemi, J. Nanostructure Chem. (2019), https://doi.org/10.1007/s40097-019-0305-x.
[67] C. Zhi, Y. Bando, C. Tang, S. Honda, K. Sato, H. Kuwahara, and D. Golberg, Angew. Chem. Int. Ed. 44(48), 7932 (2005), https://doi.org/10.1002/anie.200502846.
[68] C. Zhi, Y. Bando, C. Tang, and D. Golberg, Phys. Rev. B 74(15), 153413 (2006), https://doi.org/10.1103/PhysRevB.74.153413.
[69] S. Kalay, Y. Stetsyshyn, V. Lobaz, K. Harhay, H. Ohar, and M. Çulha, Nanotechnology 27(3), 035703 (2016), https://doi.org/10.1088/0957-4484/27/3/035703.
[70] C. Zhi, Y. Bando, W. Wang, C. Tang, H. Kuwahara, and D. Golberg, J. Phys. Chem. C 111(50), 18545 (2007), https://doi.org/10.1021/jp076980s.
[71] T. Ikuno, T. Sainsbury, D. Okawa, J. M. J. Fréchet, and A. Zettl, Solid State Commun. 142(11), 643 (2007), https://doi.org/10.1016/j.ssc.2007.04.010.
[72] T. Sainsbury, T. Ikuno, D. Okawa, D. Pacilé, J. M. J. Fréchet, and A. Zettl, J. Phys. Chem. C 111(35), 12992 (2007), https://doi.org/10.1021/jp072958n.
[73] X. J. Dai, Y. Chen, Z. Chen, P. R. Lamb, L. H. Li, J. du Plessis, D. G. McCulloch, and X. Wang, Nanotechnology 22(24), 245301 (2011), https://doi.org/10.1088/0957-4484/22/24/245301.
[74] R. Iannitto, H. Shin, Y. Martinez Rubi, B. Simard, and S. Coulombe, ACS Appl. Nano Mater. 3(1), 294 (2020), https://doi.org/10.1021/acsanm.9b01952.
[75] W. M. da Silva, G. A. A. Monteiro, P. L. Gastelois, R. G. de Sousa, W. A. de A. Macedo, and E. M. B. Sousa, Nano-Struct. Nano-Objects 15, 186 (2018), https://doi.org/10.1016/j.nanoso.2017.09.014.
[76] B. J. Mapleback, N. Brack, L. Thomson, M. J. S. Spencer, D. A. Osborne, S. Doshi, E. T. Thostenson, and A. N. Rider, Langmuir 36(13), 3425 (2020), https://doi.org/10.1021/acs.langmuir.0c00018.
[77] M. Ejaz, S. C. Rai, K. Wang, K. Zhang, W. Zhou, and S. M. Grayson, J. Mater. Chem. C 2(20), 4073 (2014), https://doi.org/10.1039/C3TC32511C.
[78] H. Shin, J. Guan, M. Z. Zgierski, K. S. Kim, C. T. Kingston, and B. Simard, ACS Nano 9(12), 12573 (2015), https://doi.org/10.1021/acsnano.5b06523.

[79] C. A. de los Reyes, K. L. Walz Mitra, A. D. Smith, S. Yazdi, A. Loredo, F. J. Frankovsky, E. Ringe, M. Pasquali, and A. A. Martí, ACS Appl. Nano Mater. 1(5), 2421 (2018), https://doi.org/10.1021/acsanm.8b00633.
[80] Q. Huang, A. S. D. Sandanayaka, Y. Bando, C. Y. Zhi, R. Z. Ma, G. Z. Shen, D. Golberg, J. C. Zhao, Y. Araki, O. Ito, and L. Gao, Adv. Mater. 19(7), 934 (2007), https://doi.org/10.1002/adma.200602058.
[81] G. Ciofani, V. Raffa, A. Menciassi, and A. Cuschieri, Biotechnol. Bioeng. 101(4), 850 (2008), https://doi.org/10.1002/bit.21952.
[82] F. D. De los Reyes, T. Fujieda, A. Takeuchi, T. Kawai, and Y. Nonoguchi, Nano Sel. 2(8), 1517 (2021), https://doi.org/10.1002/nano.202000265.
[83] Z. Gao, K. Fujioka, T. Sawada, C. Zhi, Y. Bando, D. Golberg, M. Aizawa, and T. Serizawa, Polym. J. 45(5), 567 (2013), https://doi.org/10.1038/pj.2012.170.
[84] M. A. Fernandez-Yague, A. Larrañaga, O. Gladkovskaya, A. Stanley, G. Tadayyon, Y. Guo, J.-R. Sarasua, S. A. M. Tofail, D. I. Zeugolis, A. Pandit, and M. J. Biggs, Bioconjug. Chem. 26(10), 2025 (2015), https://doi.org/10.1021/acs.bioconjchem.5b00257.
[85] Y. Martinez-Rubi, Z. J. Jakubek, M. B. Jakubinek, K. S. Kim, F. Cheng, M. Couillard, C. Kingston, and B. Simard, J. Phys. Chem. C 119(47), 26605 (2015), https://doi.org/10.1021/acs.jpcc.5b09049.
[86] H. Lim, Md. A. Islam, M. M. Hossain, H. Yun, M. J. Kim, T. H. Seo, J. R. Hahn, B. J. Kim, and S. G. Jang, Langmuir 36(20), 5563 (2020), https://doi.org/10.1021/acs.langmuir.0c00664.
[87] S.-H. Lee, M. Kang, H. Lim, S. Y. Moon, M. J. Kim, S. G. Jang, H. J. Lee, H. Cho, and S. Ahn, Appl. Surf. Sci. 555, 149722 (2021), https://doi.org/10.1016/j.apsusc.2021.149722.
[88] S.-H. Kang, S.-W. Jeon, S. Y. Moon, Y.-J. Yoon, and T.-H. Kim, J. Phys. Chem. Lett. 11(11), 4511 (2020), https://doi.org/10.1021/acs.jpclett.0c01177.
[89] N. A. Rice, W. J. Bodnaryk, I. Tamblyn, Z. J. Jakubek, J. Lefebvre, G. Lopinski, A. Adronov, and C. M. Homenick, J. Polym. Sci. 58(13), 1889 (2020), https://doi.org/10.1002/pol.20200164.
[90] I. Yu, Y. Jo, J. Ko, S. Y. Moon, S. Ahn, and Y. Joo, ACS Appl. Mater. Interfaces 13(10), 12417 (2021), https://doi.org/10.1021/acsami.1c02315.
[91] X. J. Zeng and W. L. Liu, IET Micro Nano Lett. 9(9), 569 (2014), https://doi.org/10.1049/mnl.2014.0129.
[92] S.-W. Jeon, S.-H. Kang, J. C. Choi, and T.-H. Kim, Polymers 11(4), 582 (2019), https://doi.org/10.3390/polym11040582.
[93] A. D. Smith McWilliams, C. A. de los Reyes, L. Liberman, S. Ergülen, Y. Talmon, M. Pasquali, and A. A. Martí, Nanoscale Adv. 1(3), 1096 (2019), https://doi.org/10.1039/C8NA00315G.
[94] V. R. Kode, K. R. Hinkle, and G. Ao, Langmuir 37(37), 10934 (2021), https://doi.org/10.1021/acs.langmuir.1c01309.
[95] G. Ciofani, L. Ricotti, S. Danti, S. Moscato, C. Nesti, D. D'Alessandro, D. Dinucci, F. Chiellini, A. Pietrabissa, M. Petrini, and A. Menciassi, Int. J. Nanomedicine 5, 285 (2010).
[96] Z. Gao, C. Zhi, Y. Bando, D. Golberg, and T. Serizawa, J. Am. Chem. Soc. 132(14), 4976 (2010), https://doi.org/10.1021/ja910244b.
[97] S. Del Turco, G. Ciofani, V. Cappello, M. Gemmi, T. Cervelli, C. Saponaro, S. Nitti, B. Mazzolai, G. Basta, and V. Mattoli, Colloids Surf. B Biointerfaces 111, 142 (2013), https://doi.org/10.1016/j.colsurfb.2013.05.031.

[98] A. Salvetti, L. Rossi, P. Iacopetti, X. Li, S. Nitti, T. Pellegrino, V. Mattoli, D. Golberg, and G. Ciofani, Nanomed. 10(12), 1911 (2015), https://doi.org/10.2217/nnm.15.46.
[99] G. Ciofani, S. Del Turco, A. Rocca, G. de Vito, V. Cappello, M. Yamaguchi, X. Li, B. Mazzolai, G. Basta, M. Gemmi, V. Piazza, D. Golberg, and V. Mattoli, Nanomed. 9(6), 773 (2014), https://doi.org/10.2217/nnm.14.25.
[100] Y.-T. R. Lau, M. Yamaguchi, X. Li, Y. Bando, D. Golberg, and F. M. Winnik, J. Phys. Chem. C 117(38), 19568 (2013), https://doi.org/10.1021/jp4073729.
[101] A. Rocca, A. Marino, S. Del Turco, V. Cappello, P. Parlanti, M. Pellegrino, D. Golberg, V. Mattoli, and G. Ciofani, Biochim. Biophys. Acta BBA - Gen. Subj. 1860(4), 775 (2016), https://doi.org/10.1016/j.bbagen.2016.01.020.
[102] Y. Wang, M. Mortimer, C. H. Chang, and P. A. Holden, Nanomaterials 8(2), 76 (2018), https://doi.org/10.3390/nano8020076.
[103] T. H. Ferreira, D. C. F. Soares, L. M. C. Moreira, P. R. O. da Silva, R. G. dos Santos, and E. M. B. de Sousa, Mater. Sci. Eng. C 33(8), 4616 (2013), https://doi.org/10.1016/j.msec.2013.07.024.
[104] Z. Gao, C. Zhi, Y. Bando, D. Golberg, and T. Serizawa, ACS Appl Mater Interfaces 3(3), 627 (2011), https://doi.org/10.1021/am1010699.
[105] Z. Gao, T. Sawada, C. Zhi, Y. Bando, D. Golberg, and T. Serizawa, Soft Matter 7(19), 8753 (2011), https://doi.org/10.1039/C1SM06141K.
[106] D. Kim, T. Sawada, C. Zhi, Y. Bando, D. Golberg, and T. Serizawa, J. Nanosci. Nanotechnol. 14, 3028 (2014), https://doi.org/10.1166/jnn.2014.8579.
[107] J. Yu, Y. Chen, and B.-M. Cheng, Solid State Commun. 149(19–20), 763 (2009), https://doi.org/10.1016/j.ssc.2009.03.001.
[108] M. Zheng, C. Ke, I.-T. Bae, C. Park, M. W. Smith, and K. Jordan, Nanotechnology 23(9), 957103 (2012), https://doi.org/10.1088/0957-4484/23/9/095703.
[109] A. D. S. McWilliams, S. Ergülen, M. M. Ogle, C. A. de los Reyes, M. Pasquali, and A. A. Martí, Pure Appl. Chem. 92(2), 265 (2020), https://doi.org/10.1515/pac-2019-0219.
[110] A. D. Smith McWilliams, Z. Tang, S. Ergülen, C. A. de los Reyes, A. A. Martí, and M. Pasquali, J. Phys. Chem. B 124(20), 4185 (2020), https://doi.org/10.1021/acs.jpcb.0c03663.
[111] J. Ko, H. M. Kim, S. Y. Moon, S. Ahn, S. G. Im, and Y. Joo, Chem. Mater. 33(12), 4723 (2021), https://doi.org/10.1021/acs.chemmater.1c01165.
[112] J. F. Khoury, J. C. Vitale, T. L. Larson, and G. Ao, Nanoscale Adv. 4(1), 77 (2022), https://doi.org/10.1039/D1NA00677K.
[113] M. Adnan, D. M. Marincel, O. Kleinerman, S.-H. Chu, C. Park, S. J. A. Hocker, C. Fay, S. Arepalli, Y. Talmon, and M. Pasquali, Nano Lett. 18(3), 1615 (2018), https://doi.org/10.1021/acs.nanolett.7b04335.
[114] C. J. S. Ginestra, C. Martínez-Jiménez, A. Matayaho Ya'akobi, O. S. Dewey, A. D. Smith McWilliams, R. J. Headrick, J. A. Acapulco, L. R. Scammell, M. W. Smith, D. V. Kosynkin, D. M. Marincel, C. Park, S.-H. Chu, Y. Talmon, A. A. Martí, and M. Pasquali, Nature Commun. 13(3136) (2022), https://doi.org/10.1038/s41467-022-30378-5.
[115] M. Mutz, E. Eastwood, and M. D. Dadmun, J. Phys. Chem. C 117(25), 13230 (2013), https://doi.org/10.1021/jp400874f.

[116] P. Snapp, C. Cho, D. Lee, M. F. Haque, S. Nam, and C. Park, Adv. Mater. 32(43), 2004607 (2020), https://doi.org/10.1002/adma.202004607.
[117] C. S. Torres Castillo, C. Bruel, and J. R. Tavares, Nanoscale Adv. 2(6), 2497 (2020), https://doi.org/10.1039/D0NA00136H.
[118] M. W. Smith, K. C. Jordan, C. Park, J.-W. Kim, P. T. Lillehei, R. Crooks, and J. S. Harrison, Nanotechnology 20(50), 505604 (2009), https://doi.org/10.1088/0957-4484/20/50/505604.
[119] T. H. Ferreira, P. R. O. Silva, R. G. Santos, and E. M. B. Sousa, J. Biomater. Nanobiotechnology 02(04), 426 (2011), https://doi.org/10.4236/jbnb.2011.24052.
[120] H. Chen, Y. Chen, J. Yu, and J. S. Williams, Chem. Phys. Lett. 425(4–6), 315 (2006), https://doi.org/10.1016/J.CPLETT.2006.05.058.
[121] D. M. Marincel, M. Adnan, J. Ma, E. A. Bengio, M. A. Trafford, O. Kleinerman, D. V. Kosynkin, S.-H. Chu, C. Park, S. J. A. Hocker, C. C. Fay, S. Arepalli, A. A. Martí, Y. Talmon, and M. Pasquali, Chem. Mater. 31(5), 1520 (2019), https://doi.org/10.1021/acs.chemmater.8b03785.
[122] M. S. Amin, B. Atwater, R. D. Pike, K. E. Williamson, D. E. Kranbuehl, and H. C. Schniepp, Chem. Mater. 31(20), 8351 (2019), https://doi.org/10.1021/acs.chemmater.9b01713.
[123] Y. Martinez Rubi, Z. J. Jakubek, M. Chen, S. Zou, and B. Simard, ACS Appl. Nano Mater. 2(4), 2054 (2019), https://doi.org/10.1021/acsanm.9b00057.
[124] H. Harrison, J. T. Lamb, K. S. Nowlin, A. J. Guenthner, K. B. Ghiassi, A. D. Kelkar, and J. R. Alston, Nanoscale Adv. 1(5), 1693 (2019), https://doi.org/10.1039/C8NA00251G.
[125] H. Cho, S. Walker, M. Plunkett, D. Ruth, R. Iannitto, Y. Martinez Rubi, K. S. Kim, C. M. Homenick, A. Brinkmann, M. Couillard, S. Dénommée, J. Guan, M. B. Jakubinek, Z. J. Jakubek, C. T. Kingston, and B. Simard, Chem. Mater. 32(9), 3911 (2020), https://doi.org/10.1021/acs.chemmater.0c00144.
[126] M. S. Amin, T. E. Molin, C. Tampubolon, D. E. Kranbuehl, and H. C. Schniepp, Chem. Mater. 32(21), 9090 (2020), https://doi.org/10.1021/acs.chemmater.0c03609.
[127] R. B. Weisman, S. M. Bachilo, and D. Tsyboulski, Appl. Phys. A 78(8), 1111 (2004), https://doi.org/10.1007/s00339-003-2461-5.
[128] Q. Cheng, S. Debnath, E. Gregan, and H. J. Byrne, Appl. Phys. A 102(2), 309 (2011), https://doi.org/10.1007/s00339-010-5997-1.
[129] J. Peng, S. Wang, P.-H. Zhang, L.-P. Jiang, J.-J. Shi, and J.-J. Zhu, J. Biomed. Nanotechnol. 9(10), 1679 (2013), https://doi.org/info:doi/10.1166/jbn.2013.1663.
[130] T. Lu, L. Wang, Y. Jiang, Q. Liu, and C. Huang, J. Mater. Chem. B 4(36), 6103 (2016), https://doi.org/10.1039/C6TB01481J.
[131] X. Li, N. Hanagata, X. Wang, M. Yamaguchi, W. Yi, Y. Bando, and D. Golberg, Chem Commun 50, 4371 (2014), https://doi.org/10.1039/c4cc00990h.