Hexagonal boron nitride exfoliation and dispersion

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Abstract

Hexagonal boron nitride (hBN) research has gained traction due to its unique chemical, thermal, and electronic properties. However, to make use of these exceptional properties and fabricate macroscopic materials, hBN often needs to be exfoliated and dispersed in a solvent. In this review, we provide an overview of the many different methods which have been used for dispersing hBN. The approaches that will be covered in this review include solvents, covalent functionalization, acids and bases, surfactants and polymers, biomolecules, intercalating agents, and thermal expansion. The properties of the exfoliated sheets that are obtained and the dispersions are discussed, and an overview of the work in the field throughout the years is provided.

1. Introduction

Boron nitride (BN) nanostructures are a class of nanomaterials with unique properties that lend themselves as ideal scaffolds for many applications. In general, BN nanostructures can be described as hexagonal honeycomb-like structures formed by alternating B and N atoms, reminiscent of the structure of carbon nanomaterials (Figure 1). Given their novelty, this type of nanomaterial is vastly understudied, particularly when compared with carbon nanostructures. Since the first report of a single graphene layer through mechanical exfoliation by Geim and Novoselov,[1] interest on two dimensional nanomaterials has continuously increased. This review will highlight a two-dimensional BN allotrope, hexagonal boron nitride (hBN), which has gained broad interest in the last few years due to its morphology and unique properties.

hBN is a 2-dimensional material, similar to graphene in structure and properties, but with alternating boron-nitrogen atoms instead of carbon. It is important to note here that some authors differentiate the multilayered hBN crystal from its few layered sheets by referring to them as boron nitride nanosheets (BNNS), similar to the distinction between graphite and graphene. The polarity of the B-N bond and the particular electronic structure of this nanostructure provides hBN with unique properties not present in graphene (Table 1). For example, the atoms between successive hBN layers are stacked directly above and below each other,[2] with alternating B and N atoms in adjacent layers. This is in contrast with graphite (multilayer graphene), where hexagonal structures in successive layers are staggered.[3] Similar to graphene, hBN has a Young's modulus of about 1.0 TPa.[4] However, while the properties of graphene are significantly impacted by the degree of exfoliation, the mechanical strength of hBN remains robust even at lower levels of exfoliation.[5] For graphene, an increase in the number of layers from 1 to 8 layers decreases its mechanical strength by up to 30%. However, for hBN, its strength remains constant for stacks up to 9 layers thick.[5] Additionally, hBN is more chemically and thermally stable than graphene, with hBN being stable up to 800˚C in air while graphene begins to oxidize at 300˚C.[5] The thermal conductivity of hBN (~360 W/mK),[6] though lower than that of graphene (~2000 W/mK),[7] is also high and approaches that of copper.[8] Another major difference between hBN and graphene is their electrical conductivity. While hBN is electrically insulating due to its wide bandgap of ~5.9 eV, graphene is an electrically conductive semi-metal.[4] Finally, hBN is nearly transparent in the visible region, but a strong absorber in the UV region (ca. 205 nm) due to its wide band gap.[9]

Because of its unique properties, hBN has now been studied as a candidate for several applications. Due to its mechanical properties, hBN has been used as an additive in a variety of composite materials such as hydrogels[10], epoxy[11,12], cement[13], and ceramic oxides.[14] For instance, Chen and coworkers showed that the incorporation of 1 wt.% of hBN into epoxy increased its tensile strength by 6.6% and its Young's modulus by 5.5%.[11] Wang and coworkers also demonstrated that adding just 0.003 wt.% of exfoliated hBN into cement could improve both its compressive strength and tensile strength by up to 13% and 8%, respectively.[15] Other groups have developed hBN macromaterials, such as lightweight aerogels, foams, and membranes (Figure 2a), which can also take advantage of hBN's impressive thermal and mechanical properties (Figure 2b).[9,16,17] Additionally, hBN has been used for a variety of biomedical applications, showing promise as antibacterial coatings[18] and for neurotransmitter detection.[19] In 2018, Pandit and coworkers showed that hBN significantly reduced the viability of several strains of bacteria, including *E. coli* and *S. aureus*.[18] Nurunnabi and coworkers also indicated that a glassy carbon electrode with hydroxyl-functionalized hBN could detect very low concentrations of dopamine through changes in electrical current.[19] Furthermore, due to its thermal stability and thermal conductivity, hBN has been proposed for use in flame resistant coatings.[20–22] In 2019, Davesne and coworkers demonstrated that hBN could be conformally coated on polyurethane foam and was able to delay charring while maintaining its flexibility and appearance.[20]

It is important to point out that to process these unique nanomaterials into macroscopic functional materials, it is often necessary to produce high quality dispersions, with high quality referring to stable dispersions which contain hBN with large lateral dimensions but mostly single-layered sheets. This generally requires exfoliation of single or few-layered nanosheets from the larger hBN crystal, whose layers tend to aggregate due to attractive van der Waals interactions. The earliest techniques to achieve this were the use of common solvents,[23,24] functionalization with Lewis bases,[25,26] or the use of polymers.[27] For instance, many different solvents, including isopropanol (IPA)[28,29], N-methyl-2-pyrrolidone (NMP)[30], and tetrahydrofuran (THF)[31] have all been investigated for dispersing hBN. While these solvents are able to disperse hBN, they are not very effective at exfoliating large hBN crystals into few-layered sheets. Soon thereafter, groups tried protonation from superacids,[32] covalent functionalization through oxidation of B sites,[33–37] polymers and surfactants,[38–42] and solvent mixtures.[43] Covalent functionalization of hBN has also been studied as a way to tune the dispersibility of hBN in certain solvents or in composite materials.[33,34,36,44] Other groups have also developed procedures using acids and bases,[26,32] biomolecules,[45,46] intercalating agents,[47,48] and thermal expansion.[49,50] This review will cover each method for hBN dispersion and exfoliation and the progress that has been made towards high concentration and stable dispersions. A variety of reviews have now been published on the functionalization and applications of boron nitride nanomaterials,[51–54] and others have broadly looked at liquid-phase exfoliation of various 2D materials, including hBN.[55–60] Last year, two reviews were also published on exfoliation mechanisms for 2D materials including hBN[61] and another specifically on environmental applications of hBN.[62] This review will stand apart from others by providing an in-depth analysis of the experimental exfoliation and dispersion approaches for hBN and how they have progressed over time toward improved exfoliation (i.e. thinner sheets with larger lateral dimensions), dispersion concentration, and stability. In the next few sections, we will discuss each approach in detail. We anticipate this review will serve as a guide for new researchers in the field, as well as a reference for current researchers in the field, on how to tune the properties of hBN dispersions in order to achieve more advanced BN materials and applications.

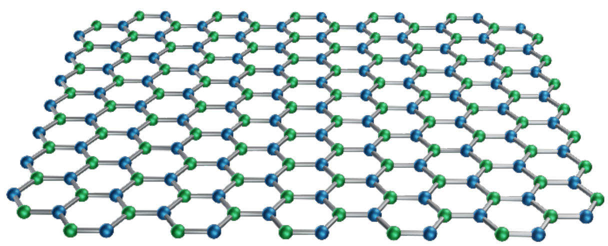

Figure 1. Schematic representations of a single hBN sheet showing the honeycomb-like structure of sp^2 hybridized, alternating boron (green) and nitrogen (blue) atoms.

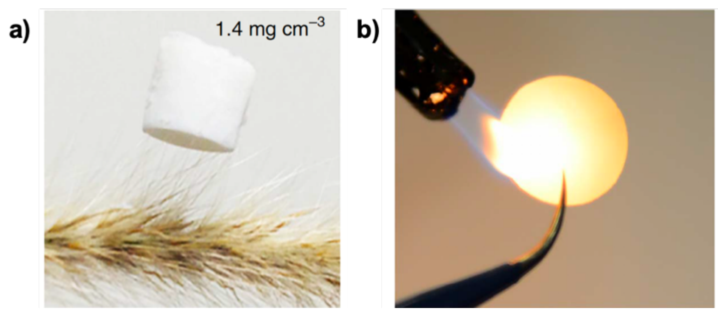

Figure 2. (a) Photo of an hBN aerogel of low density (1.4 mg/cm^3) placed on the spike of a plant. (b) Photo of a freestanding BN membrane held in a flame in ambient air. Modified from Ref [9] (W. Lei *et al. Nature Commun.* 2015, *6*, 8849.) Copyright © 2015 Springer Nature.

Table 1. Summary of material properties

Property	*Graphene*	*hBN*
Young's Modulus	0.891-1.0 TPa[63]	0.87±0.07 TPa[5]
Thermal Conductivity	~2000 W/mK[7]	~360 W/mK[6]
Electrical Conductivity	Conducting	Insulating
Oxidation Temperature (in air)	300 – 500 ˚C[64]	> 900 ˚C[65]

2. Solvents

The first reported attempts to make hBN dispersions involved its exfoliation directly in an appropriate solvent. Initially, single solvents were used, and subsequent studies expanded their approach by studying cosolvent systems. Later studies also implemented ionic liquids. Table 2 summarizes the strategies discussed in this section. For Table 2 and further tables across the manuscript summarizing the dispersion strategies, we checked the different papers and supporting pieces of information to gather the most important details, and tried to maintain the original language used by the authors.

2.1 Single solvent

Many of the initial studies on the dispersion of hBN focused on using common solvents, such as N,N-dimethylformamide (DMF), dichloroethane, N-methyl-2-pyrrolidone (NMP), or isopropyl alcohol (IPA).[23,24,66] In 2009, Zhi and coworkers dispersed hBN in DMF by using tip sonication for 10 hours.[23] They predicted the polar solvent would be ideal for overcoming the Van der Waals forces between BN layers. The dispersion obtained had hBN sheets less than 20 layers thick. These dispersions were used then to prepare composite films in polymethyl methacrylate (PMMA) for improved thermal and mechanical properties.[23] Soon thereafter, Warner and coworkers studied 1,2-dichloroethane to produce exfoliated few-layered hBN sheets.[24] In this case, the solvent was chosen for its lower boiling point and the exfoliated sheets were used for a detailed analysis of the hBN structure by transmission electron microscopy (TEM) and high resolution-TEM (HR-TEM).[24] In 2011, Coleman and coworkers conducted a systematic investigation on solvent dispersions of multiple 2D materials, establishing the framework for using the Hansen Solubility Parameter Theory in lamellar nanostructures.[66] For hBN, they found NMP and IPA were the most promising solvents, reaching concentrations of ca. 0.06 mg/mL in IPA. Finally, they used the dispersion as a filler in thermoplastic polyurethane for mechanical reinforcement.[66] From these findings, many groups have utilized IPA or NMP dispersions for further applications. For instance, Song and coworkers dispersed hBN in IPA by sonicating for 48 hours and then used the dispersion to prepare polyvinyl alcohol (PVA) composites.[28] Similarly, Xue and coworkers exfoliated hBN in IPA through a combination of heating and sonication, and the dispersed sheets were fluorinated to improve their electrical conductivity.[67] In 2016, Shang and coworkers tried to homogenize hBN in IPA using a high pressure homogenizer.[68] After 10 minutes at a pressure of 100 MPa, the dispersion concentration in IPA was improved to ~0.08 mg/mL after larger aggregates were removed, as compared to ~0.06 mg/mL for Coleman's procedure.[66,68] More recently, IPA was used to exfoliate hBN using a rotor-stator homogenizer, followed by centrifugation. Sheets were obtained with a height of 2 to 14 nm, and they were used to produce thin films by Langmuir deposition.[29] In 2013, Mutz and coworkers performed a similar study to Coleman's, investigating the Hildebrand-Scatchard Solution Theory for various BN materials (BNNTs, functionalized-BNNTS (f-BNNTs), and hBN).[31] Their results found that ethyl acetate, methanol, and acetone are good solvents for the dispersion of hBN, although they did not fully matched the predicted values (Hildebrand-Scatchard Solution Theory) for the material.[31]

Based off the Hansen Solubility Parameters and surface energy of hBN, researchers have utilized an array of other, less common, solvents such as benzyl benzoate,[69] ethylene glycol,[70] and thionyl chloride.[71] In 2011, Li and coworkers tried exfoliating hBN in benzyl benzoate with a combination of ball milling and sonication.[69] By analyzing the sample with Near Edge X-Ray

Absorption Fine Structure (NEXAFS) spectroscopy, they found that this procedure does little damage to the hBN structure.[69] Later, Huang and coworkers dispersed hBN in ethylene glycol with sonication.[70] This procedure produced ~1 nm thick hBN, as shown by TEM (Figure 3a, b) and atomic force microscopy (AFM) (Figure 3c,d). Dispersions with concentrations up to 0.5-1 mg/mL were stable for several days.[70] Finally, Sun and coworkers used thionyl chloride as an hBN exfoliation solvent.[71] After sonication for 20 hours and very light centrifugation, they could produce a dispersion yield of 20% that was stable for 9 days. They used the dispersed hBN to immobilize Pd nanoparticles for catalysis of the hydrogenation of nitro aromatics.[71]

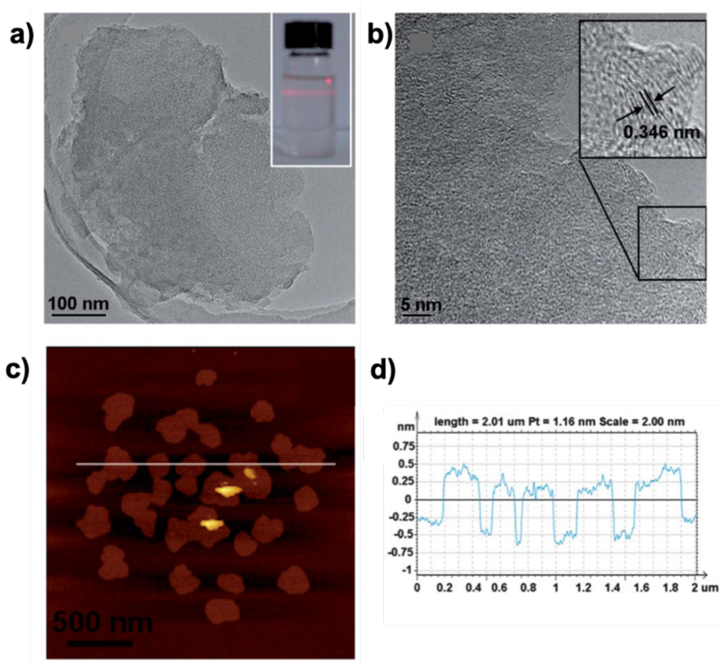

Figure 3. (a, b) TEM images of few-layer hBN sheets dispersed in ethylene glycol. (C) AFM image of the dispersion with a size of 2.5 µm x 2.5 µm. (d) Height profile plot corresponding

to the white line marked in (c). Reproduced from Ref [70] (Huang *et al. J. Mater. Chem. A*, 2013, *1*, 12192.) Copyright © 2013 with permission from the Royal Society of Chemistry.

2.2 Cosolvent Systems

Other groups have used the Hansen Solubility Parameters as a guideline for preparing mixed solvent systems with the expectation that these mixed solvents are more effective than single solvents. Many of these studies focus on alcohol/water mixtures. For instance, in 2011, Zhou and coworkers tested mixtures of ethanol and water for exfoliation and dispersion of various 2D materials.[43] They achieved their highest concentration of hBN (0.075 mg/mL) in 55 vol.% ethanol/water after 8 hours of sonication and centrifugation at 3000 rpm. Using these dispersions, they prepared thin films by electrophoretic deposition.[43] Marsh and coworkers furthered this study, examining mixtures of various alcohols or acetone in water.[72] They tested mixtures ranging from 0-100% of acetone, methanol, ethanol, 1-propanol, IPA, or *t*- butanol in water and compared the relative hBN concentration after 3 hours of sonication and 20 min centrifugation. Based on the absorbance at 400 nm, all solvent mixtures were optimal around 40-60% (w/w), with *t*-butanol performing the best and acetone performing the worst.[72] In fact, they found that increasing the dispersion concentration was directly proportional to the solvent's molecular weight. Shen and coworkers probed the surface tension of various 2D materials and tested solvent mixtures that had very similar surface tensions to the material.[73] Using this method, they found that 1:1 IPA/water is a good solvent mixture for hBN and produced well exfoliated sheets with an average thickness of 1.3 nm.[73] In 2016, the same group extended this work to more solvent combinations and analyzed both the whole surface tension and the polar to dispersive surface tension ratio.[74]

Using these properties, they determined optimized ratios of IPA/water (30:70), acetone/water (50:50), and tetrahydrofuran (THF)/water (40:60) for hBN dispersion and used the dispersions as mechanical reinforcements for polyethylene oxide (PEO) films.[74] Wang and coworkers found that by using an IPA/water ratio of 3:2 and 3 hours of sonication, they could obtain an hBN concentration of 0.3 mg/mL that was stable for 3 months.[75] In 2016, Habib and coworkers studied the *t*-butanol/water cosolvent system to better understand the role of the alcohol component.[76] Through solvent exchange experiments and simulations they found that *t*-butanol acts as a liquid surfactant, shielding the hBN from water. After 90 minutes of tip sonication in 60:40 *t*-butanol/water solution, an hBN concentration of 0.213 mg/mL was reached and the dispersion remained stable for over 18 months.[76]

Other cosolvent systems that have been applied for hBN dispersion include alkanolamines/water[77] and urea/glycerol.[78] Zhang and coworkers tested the cosolvent systems methanolamine (MEA)/water and NMP/water for optimized hBN dispersion yield and stability. They found the best results with 30 wt.% MEA in water, reaching an hBN concentration of 1.5 mg/mL that was relatively stable for 300 hours.[77] In 2019, Zheng and coworkers dispersed hBN and graphene in a 2:1 mixture of urea:glycerol with mechanical stirring.[78] They were able to produce very thin sheets (~0.7 nm) and used the exfoliated materials to form a nanocomposite that was applied as an electrode for making supercapacitors.[78]

2.3 Ionic Liquids

In 2015, Morishita and coworkers tested a variety of ionic liquids (IL): 1-butyl-3-methyl-imidazolium bis (trifluoromethylsulfonyl)imide ([bmim][Tf_2N]), 1-ethyl-3-methylimidazolium bis (trifluoromethylsulfonyl)imide ([emim][Tf_2N]), 1-ethyl-3-methylimidazolium trifluoromethanesulfonate ([emim][TfO]), 1-butyl-3-methyl-imidazolium bis (trifluoromethylsulfonyl)imide trifluoromethanesulfonate ([bmim][TfO]), 1-butyl-3-methyl-imidazolium hexafluorophosphate ([bmim][PF_6]), and 1-butyl-3-methyl-imidazolium tetrafluoroborate ([bmim][BF_4]), for hBN dispersion.[79] After 8 hours of mild bath sonication followed by centrifugation, all mixtures formed stable dispersions (Figure 4a). The f_2N and TfO liquids formed orange suspensions while the BF_4 and PF_6 liquids formed white suspensions (Figure 4b). The best dispersions were obtained from [bmim][PF_6] with a concentration of 1.9 mg/mL of hBN sheets with 1-6 layers.[79] They expanded upon this work in 2017, when they focused on [bmim][Tf_2N] and [bmim][PF_6], and used the resulting nanosheets to fabricate polymer composites.[80] Later, Sun and coworkers further explored using [bmim][PF_6], but in this case, they sonicated hBN in the IL for 30 minutes and then used a Teflon-lined autoclave with stirring to heat the sample for 12 hours.[81] They claim the shear forces, activation energy provided by the heat, and the intercalation of the IL allowed them to obtain thin nanosheets (3 nm average).[81] Finally, Du and coworkers used a different IL, 1-(3-Aminopropyl)-3-methylimidazolium bromide, to exfoliate hBN assisted by ball milling.[82] They obtained sheets with an average 3.5 nm thickness and 2 µm length, which were used to make an epoxy composite for anticorrosion coatings.[82]

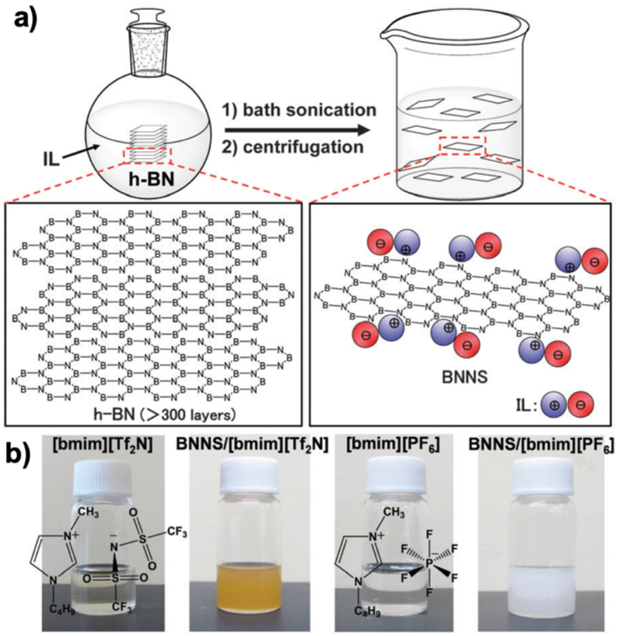

Figure 4. (a) Schematic diagram of ionic liquid-mediated exfoliation of hBN. (b) Photographs of $[bmim][Tf_2N]$, $hBN/[bmim][Tf_2N]$ supernatant, [bmim][PF6], and $hBN/[bmim][PF_6]$ supernatant. Reprinted with permission from Ref [[79]] (T. Morishita *et al. Chem. Commun.* 2015, *51*, 12068.)

Table 2: Summary of hBN dispersions exfoliated directly by solvents

Solvent	**hBN Source**	**Method of Exfoliation/Dispersion**	**Concentration**	**Thickness**	**Mean Lateral Size**	**Stability**	**Application**	**Ref**
DMF	Aldrich	Tip sonication for 10 hours, then centrifuged at 5000-8000 rpm	Not reported	7 nm at 5000 rpm (less than 20 layers), 3 nm at 8000 rpm (less than 10 layers).	Micrometer lateral dimensions	Not reported	PMMA/BNNS composites	[23]
1,2-dichloroethane	Sigma-Aldrich	Bath sonication for 3 hours, left to rest for 30 minutes	not reported	5-10 layers	micrometer sizes	not reported	Powder analysis	[24]
20 solvents studied, NMP and IPA most promising	Aldrich	Bath sonication for 1 hour, centrifuged at 500 rpm for 90 min	0.06 mg/mL in IPA	3.3 layers	0.96 µm length, 0.36 µm width	A week	Films, free standing hybrid films, polyurethane composites	[66]
IPA	Alfa Aesar	Bath sonication in IPA for 48 hours	20 mg/mL	10-20 nm	1 µm or larger	not reported	PVA nanocomposites	[28]
IPA, DMSO, NMP	Sinopharm Chemical Reagent Co. Ltd.	Heated at 50°C for 24h under stirring, bath sonication for 20 h. Stand for 2 days, and supernatant removed; centrifuged at 14000 rpm for 10 min	Not reported	3.4 nm	Not reported	2 weeks	Used for fluorination	[67]
IPA	Aladdin Reagent Co.	High pressure homogenizer under 100 mPa for 10 min at 25°C, centrifuged at 5000 rpm for 60 min; the supernatant was collected	0.083 mg/mL	6.2 nm	20-250 nm	two weeks	Powder analysis	[68]
IPA	Industrial Supply Inc.	Rotor stator homogenizer at 20000 rpm followed by centrifugation; supernatant was collected (3 variations)	0.04-0.11 mg/mL	2-14 nm	micron to sub-micron diameter	several days	Thin films by Langmuir deposition	[29]
THF, toluene, stability on acetone, bromobenzene, carbon tetrachloride,	ZYP Coatings, Inc	Bath sonicated for 20 min	0.0016 mg/mL for THF, 0.1029 mg/mL for toluene	Not reported	Not reported	ethyl acetate, methanol and acetone were most stable after 24 h,	Powder analysis	[31]

carbon disulfide, o-dichlorobenzene, DMSO, DMF, ethyl acetate, methanol, toluene, THF, water						DMSO and DMF were also good. Water and toluene were the least stable		
Benzyl benzoate	Merck	Steel milled at 150 rpm in pure nitrogen gas at 200 kPa. Diluted with benzyl benzoate and sonicated for 0.5 h, centrifuged	9% yield with 0.5 h sonication and 2000 rpm centrifugation for 1 h, 67% with 1 h and 10000 rpm for 0.5 h (starting material 0.5 g)	2.3-3.7 nm	one to several hundred nanometers of diameter	not reported	Powder analysis	[69]
Ethylene glycol	synthesized from boric acid and urea by heating in tube furnace at 900C in N_2 atmosphere	Low power ultrasonication for 30 minutes	0.5-1 mg/mL	0.8 nm	300 to 800 nm	several days	carriers to disperse noble metal nanoparticles with catalytic activity for p-nitrophenol reduction	[70]
thionyl chloride ($SOCl_2$), redispersible in IPA, ethanol, NMP, solvent transfer to 1,2-dichloroethane	Alfa Aesar, Aladdin Reagent Co.	Bath sonicated for 20 h. Stand for 24 h or centrifuge at 2000-2500 rpm for 5 min	up to 0.4 mg/mL	4.7 nm	200-300 nm	9 days	Used to immobilize Pd nanoparticles for catalysis of nitro aromatics	[71]
ethanol/water mixture	Aladdin Reagent Co.	sonicated for 8 h, centrifuged at 3000 rpm for 20 min	0.075 mg/mL at 55 vol% ethanol/water	3-4 nm	100 nm to several micrometers	a week	Thin films through electrophoretic deposition	[43]
water with methanol, ethanol, 1-propanol, IPA, acetone, or tert-butanol	Momentive	bath sonicated for 3 h, rotating the vial every 30 min. centrifugation at 3200 rpm for 20 min.	not reported	7-9 nm	Not reported	2 months	Powder analysis	[72]
1:1 IPA/water	Alfa Aesar	Bath sonicated for 4 h, centrifuged at 1000 rpm for 10 min, second centrifugation at 4000 rpm for 10 min	Not reported	1.3 nm average	Few hundred nanometers	Not reported	Powder analysis	[73]
IPA/water (30:70), acetone/water	Alfa Aesar	Bath sonicated for 4 h, centrifuged at 1000 rpm for 10 min, second centrifugation at 4000 rpm for 10 min	0.097 mg/mL for IPA/Water	2.8 nm for IPA/water	Not reported	Not reported	mechanical reinforcements for PEO films	[74]

(50:50), and THF/water (40:60)								
IPA/water 3/2 w/w	PCTP30, Saint-Gobain Ceramic Materials	Bath sonicated for 3 h. Centrifuged at 3000 rpm for 10 min.	0.3 mg/mL	500 nm.	Not reported	More than 4 months	Modified surface with polydopamine to prepare silicone composites	[75]
t-butanol and DI water 60-40 wt% ratio	not reported	Tip sonicated for 90 min, centrifuged 4 h at 3500 rpm	0.231 mg/mL	few layers thick	741 nm	over 18 months	Powder analysis	[76]
MEA or NMP in water	Aladdin Reagent Co.	Bath sonicated for 4 h at 50°C, centrifuged at 3500 rpm for 20 min, and BNNS were washed with ethanol and dried.	1.3 mg/mL	less than 5 nm	Not reported	300 hours	Reinforce epoxy resin with improved thermal and mechanical properties	[77]
2:1 urea/ glycerol	Sigma-Aldrich	Mechanical stirring at 800 rpm for 24 h, centrifuged at 5000 rpm for 25 min, supernatant was redispersed in DMF, filtered, washed, and dried.	not reported	0.7 nm	<1 µm	not reported	Supercapacitors	[78]
Ionic liquids (various)	UHP-1K, SHOWA DENKO K. K.	bath sonication for 8h, centrifuged at 3000 rpm for 20 min, supernatant was collected	1.9 mg/mL	about 4.4 layers	1.2 µm	not reported	Powder analysis	[79]
[bmim][PF_6], [bmim][Tf_2N] ILs	UHP-1K, SHOWA DENKO K. K.	Bath sonication of IL and hBN for 8h, centrifuged at 3000 rpm for 20 min, and supernatant collected	[bmim][Tf_2N] 0.30 mg/mL, [bmim][PF_6] 1.09 mg/mL	[bmim][Tf_2N] average 12 layers, [bmim][PF_6] average 16 layers	2.3-2.9 µm	not reported	Fabricate polymer composites	[80]
[bmim][PF_6] IL	Alfa Aesar Reagent Co.	Sonicated in ionic liquid for 30 min, heated at 180°C for 12 h in autoclave with stirring and centrifuge at 3000 rpm for 30 min	not reported	3 nm	3-4 µm	not reported	not reported	[81]
1-(3-Aminopropyl)-3-methylimidazolium bromide IL	Tianyuan Chemical Co.	IL was sonicated in water, hBN is added and sonicated 120 min, ball milled for 8h at 500 rpm and centrifuged at 2000 rpm for 30 min	not reported	3.5 nm average	0.5 to 2 µm	not reported	Make epoxy composite for anticorrosion coatings	[82]

3. Covalent Functionalization

Covalent functionalization is a common method for obtaining dispersed hBN in various solvents, as it offers a way to tune the polarity and hydrophilicity of the material depending on the moiety that is grafted. The majority of reported functionalization methods for hBN rely on oxidation of B sites, either by water,[33] radical addition,[34,35] common oxidizers,[36,37,83] or fluorine.[44,84] Other methods utilize reactions with amine groups in edge or defect sites[85] or reduction.[86] This section will analyze each type of covalent functionalization and how different techniques have progressed over time. A summary of the different techniques can be found in Table 3.

3.1 *Reaction with edge/defect sites*

The edges and defect sites of hBN include amino and hydroxyl groups that are available for functionalization. One of the first reported methods for the covalent functionalization of hBN sheets was through hydrolysis with water, taking advantage of these sites being prone to attack from the oxygen molecule of water.[33] Lin and coworkers reported that after 8 - 24 hours of sonication in deionized water alone, hBN sheets were exfoliated and cut, with hydroxyl groups covering the cut edges (Figure 5a). Though this method drastically reduces the lateral size of the hBN sheets (< 200 nm, Figure 5b), and mono- and few-layer (< 1 nm thick) hBN can be obtained at concentrations of 0.05 – 0.1 mg/mL.[33] The dispersed hBN sheets were filtered to produce a flexible thin film and were tested for biocompatibility with ferratin protein.[33]

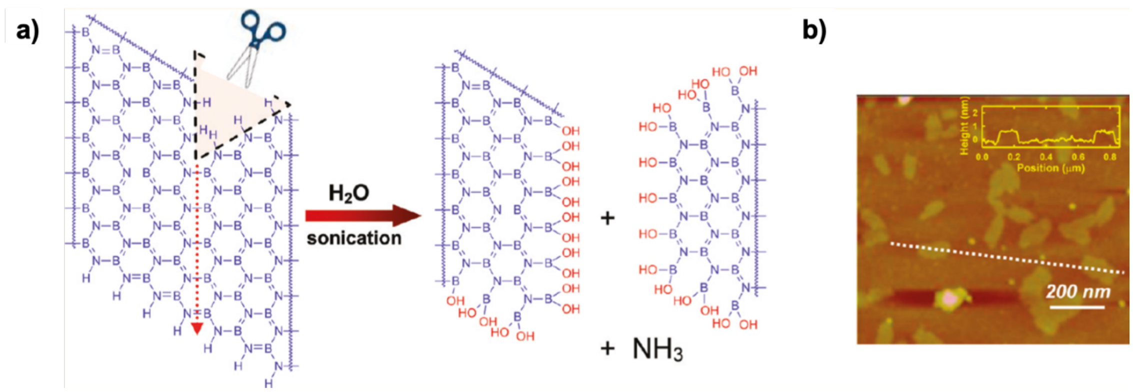

Figure 5. (a) Schematic demonstrating how sonication of hBN in water cuts and functionalizes the sheets. (b) Typical AFM topographic image showing an area populated with hBN nanosheets with feature heights less than 1 nm. (Inset: Height profile plot corresponding to the dotted line). Reprinted with permission from Ref [33] (Y. Lin *et al. J. Phys. Chem. C,* 2011, *115*, 2679-2685.) Copyright © 2011 American Chemical Society.

In 2013, Jin and coworkers also took advantage of the amino and hydroxyl group on defect sites and reacted them with methylenebis(phenyl isocyanate).[85] This molecule has an isocyanate moiety on each end, so one can attach to the hBN sheet and the other can be further reacted with other amine or hydroxyl groups. In this case, diamine diphenyl sulfone was reacted with the isocyanate, producing a highly conjugated functional group that improved hBN dispersibility in DMF and interaction with bismaleimide resin for composites.[85] The edge and defect sites are more commonly utilized for noncovalent acid-base functionalization, which will be covered in Section 4.

3.2 Radical Addition

In 2012, Sainsbury and coworkers reported oxygen radical functionalization of boron sites of hBN using di-*tert*-butylperoxide.[34] The hBN was first dispersed in NMP following a previously described procedure[66] and then reacted with di-*tert*-butylperoxide under high temperature and pressure for 12 hours, producing *t*-butoxy grafted sheets. Then, the functionalized hBN sheets (f-hBN) were stirred in piranha solution for 2 hours to remove the butyl- moieties and leave behind hydroxyl groups on the hBN surface (OH-hBN).[34] The OH-hBN is readily dispersible in water, reaching concentrations of 0.107 mg/mL (5-fold higher than pristine hBN).[34] OH-hBN was also used to prepare PVA composites and was further functionalized through a reaction with isocyanate groups in 1,6-hexamethylenediisocyanate, which enabled it to be dispersed in dichloromethane (DCM).[34] The same group followed a similar method to functionalize hBN with nitrene radicals.[35] In this case, after dispersion in NMP by previously reported methods,[66] the dispersed hBN was reacted with 4-methoxybenzyloxycarbonyl azide at 160˚C for 16 hours, producing methoxyphenyl carbamate-functionalized hBN (MPC-hBN). The addition of the MPC- moiety improved dispersibility in ethanol, chloroform, cyclohexylpyrrolidone, and DMF by 2-3 times more than pristine hBN, reaching concentrations of 0.05 mg/mL in ethanol but reduced dispersibility in IPA, THF, and toluene.[35] This reaction was then extended to attach polymer chains to the hBN surface for improved compatibility in composites. Azidopentanoic acid molecules were reacted with hBN to graft carboxylic acid groups to the surface that could then be coupled to amines or alcohols, in this case poly(bisphenol A-*co*-epichlorohydrin) (PBCE).[35] PBCE-hBN was added to a polymer matrix to improve its mechanical strength and toughness properties.[35]

In 2017, Radhakrishnan and coworkers utilized fluorine radicals to fluorinate hBN.[87] They first dispersed hBN in DMF and then added it to a solvothermal reactor with a perfluorinated polymer, Nafion. When heated to 200˚C, the polymer undergoes degradation, producing fluorine radicals, which then interact with the B-N bonds of hBN. The addition of fluorine modified the electronic band structure of hBN, and resulted in the production of a magnetic semiconductor material.[87] Moreover, the authors found extended reaction times could lead to the production of fluorinated boron nitride quantum dots.[88]

3.3 Oxidation of B Sites

As with Sainsbury's initial work,[34] many efforts toward covalent functionalization of hBN were geared toward attaching hydroxyl groups to the sheet surface. This can be accomplished either through heating or ball milling the BN powder in common oxidizing agents. In 2012, Nazarov and coworkers accomplished this by mixing hBN with hydrazine, H_2O_2, HNO_3/H_2SO_4, or oleum and heating in an autoclave at 100˚C for 30 – 40 hours.[37] The resulting hBN was dispersed in water (0.26-0.32 mg/mL) and DMF (0.34-0.52 mg/mL) and remained stable between 24 and 32 days. In 2014, Cui and coworkers heated hBN in air to 1000˚C, which was found to hydroxylate the nanosheets, as determined by Fourier-transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), and thermogravimetric analysis (TGA).[89] The hydroxylated sheets could be suspended in water without sonication with yields up to 65%. Bhimanapati and coworkers mixed hBN with $KMnO_4$ in 1:8 H_3PO_4:H_2SO_4 for 12 hours at 75˚C, and they also achieved 0.2 mg/mL dispersion in water, while also testing ethanol, acetone and IPA.[83] A modified version, adding H_2O_2 into the solution, was later used to collect hBN sheets with similar sizes, separating by centrifugation.[90] Yu and coworkers expanded upon this method, producing high quality sheets with thickness of 1.78 nm and average particle size of 486 nm, at a high exfoliation yield of 83% of the original hBN mass.[91]

In 2015, Lee and coworkers were the first to attach -OH groups to hBN through ball milling, mixing with NaOH for 24 hours.[92] In 2017, Jing and coworkers mixed BN powder with an assortment of oxidizing agents, H_2SO_4, $K_2S_2O_8$, and P_2O_5, at 80˚C for 4.5 hours, followed by H_2SO_4 and $KMnO_4$ at 35˚C for 2 hours.[93] This produced thinner and larger sheets (3 nm thick, 2-3 µm length) that were crosslinked with PVA (Figure 6a) to make biocompatible hydrogels (Figure 6b). The resulting sheets were dispersed in IPA (0.425 mg/mL) and were less than 3 nm thick. They were used as a nanofiller for polyethylene nanocomposites. Other groups followed similar procedures, but with NaClO (16 hours),[94] 2-furoic acid (2 hours),[95] or boric acid (48 hours).[96] Ball milling with NaClO produced the thinnest (0.35-1.35 nm) and smallest (50-200 nm) sheets, and were used to support silver nanoparticles for catalysis.[94] The hBN ball milled with 2-furoic acid produced the highest yield, achieving 35 mg/mL dispersion in water, which produced aerogels and thermally conductive films.[95] The sheets obtained by ball milling with boric acid were also dispersible in water, were separated by size and thickness by centrifugation, and were used to fabricate membranes.[96] Jiang and coworkers prepared boron nitride nanosheets functionalized with both -OH or -NH_2 functional groups by ball milling in the presence of sodium hydroxide with argon as a protection gas or with ammonia, respectively.[97] The shear force exfoliated the sheets while simultaneously attaching the functional groups, forming B-O-H or B-N-H bonds. The resulting nanosheets can be dispersed in water, methanol, and acetone. The highest concentrations were produced in methanol, which allows them to be used as coatings.[97] Tian and coworkers developed an exfoliation process in which hBN is ball-milled with glycine, which is highly hydrophilic.[98] Glycine was covalently attached to hBN, as shown by XPS in which a new B-O bond appeared, and stable dispersions in polar solvents, particularly water, were obtained. The dispersions were incorporated into different matrices, including epoxy resins and a cellulose-based film.[98]

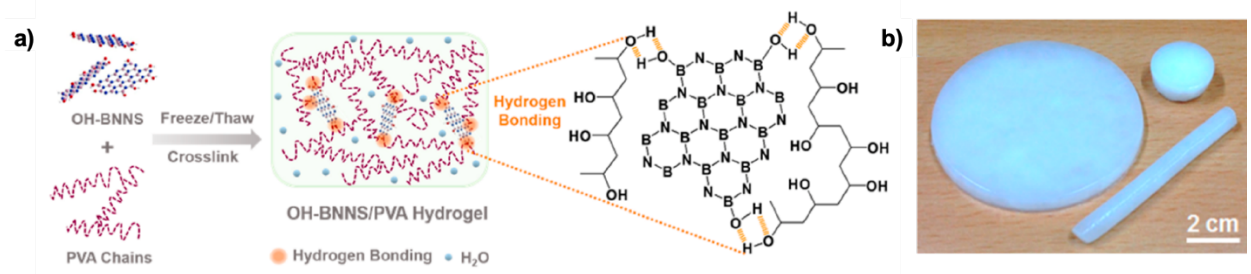

Figure 6. (a) OH-hBN/PVA interpenetrating hydrogels were fabricated by a cyclic freeze /thaw process based on the hydrogen bonding interactions between the OH-hBN and PVA chains. (b) Photo of the composite hydrogels which can be freely shaped. Reprinted with permission from Ref [[93]] (L. Jing *et al. ACS Nano,* 2017, *11*, 3742-3751.) Copyright © 2017 American Chemical Society.

In addition to hydroxyl groups, a variety of other moieties have been grafted to hBN through the oxidation of B sites. In 2012, Yu and coworkers attached amino groups to hBN sheets by reacting hBN powder with γ-aminopropyl triethoxysilane (γ-APS) under reflux for over 4 hours.[36] The amine groups could be further reacted with hyperbranched aromatic polyamide (HBP) to improve hBN dispersion in epoxy for production of epoxy composites with improved thermal properties.[36] In 2015, Kumari and coworkers oxidized hBN with H_2SO_4, $NaNO_3$, and $KMnO_4$ before functionalizing with octadecyltriethoxysilane (ODTES).[99] The long alkyl chain-grafted hBN were more dispersible in polyol ester lubricant base oil and improved the tribological properties of the lubricant.[99] Jin and coworkers did a simple low temperature oxidation of hBN at 600˚C in air to produce amorphous boron oxides on the hBN surface.[100] This procedure created B-O bonds on the surface and made the material more dispersible in ethanol.[100] In 2015, Lei and coworkers attached amine groups to B sites through ball milling in urea powder.[9] The NH_2-functionalized hBN could form very concentrated dispersions in water (30 mg/mL) that transformed into hydrogels after sitting for 2 weeks. Cryodesiccation or vacuum filtration of the dispersions could also be used to form aerogels or transparent thin membranes.[9] Finally, in 2019, Chen and coworkers ball milled hBN with sucrose crystals to produce sucrose-grafted hBN.[101] The sugar molecules covalently attached to both B (through B-O bonds) and N (through N-CH bonds). The sugar-grafted hBN could form stable dispersions in water (~10 mg/mL), DMF (~4 mg/mL), and ethanol/water mixtures (~36 mg/mL), but the lateral sizes of the dispersed particles were relatively small (100-200 nm).[101]

In 2019, two groups reported methods for attaching fluorine to B sites of hBN using ammonium fluoride. Ul Ahmad and coworkers used hydrothermal treatment of ammonium fluoride to produce fluorine free radicals that could react with B sites.[84] Alternatively, Bai and coworkers used ball milling in an ammonia fluoride aqueous solution to attach fluorine atoms.[44] The groups found that the fluorinated hBN could be used as a candidate for metal-free magnetic material[84] or as a water dispersible lubricant additive for improved friction and wear.[44] In 2021, Guan and coworkers developed boron nitride nanosheets functionalized with thiol terminated polyethyleneimine linked with poly(ethylene glycol) diacrylate (PEG).[102] The hydrophilic polymer chains allowed the BN nanosheets to disperse in water, while they were able to be detached in a reducing environment by disulfide bond cleavage. This allowed its use for loading and delivering essential oils and pesticides.[102]

3.4 Reductive conditions

Another method applied to functionalizing hBN sheets is using reductive chemistry. The Martí group demonstrated this in 2019 by using the Billups-Birch reaction between hBN and bromododecane to attach dodecyl groups to the hBN surface.[86] This reaction uses lithium in liquid ammonia to produce solvated electrons that exfoliate the hBN sheets and produce alkyl radicals.[103] After the reaction, the average f-hBN thickness decreased nearly ten-fold while the lateral dimensions remain roughly the same.[86] Moreover, alkylated hBN sheets were more dispersible in dodecane and THF and less dispersible in water and IPA than pristine hBN, showing that they have become more hydrophobic. Finally, f-hBN was filtered to produce a transparent film whose hydrophobicity was demonstrated by its contact angle measurement shown in Figure 7a and an image of a water droplet on the film in Figure 7b.[86] Later in 2023, Li and coworkers also used liquid ammonia and lithium to hydroxylate hBN by bubbling oxygen and adding water to the mixture. The obtained nanosheets are highly dispersible in water, reaching concentrations of 0.414 mg/mL, and they were used to make composited with natural rubber.[104]

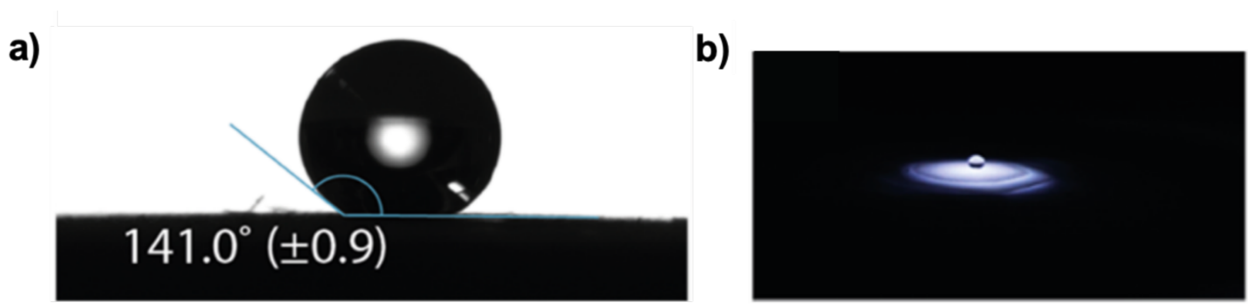

Figure 7. Water contact angle measurement of (a) fh-BN film prepared on nylon, and (b) front view of the fh-BN film with a water droplet on top and illuminated from below with an LED. Reprinted with permission from Ref [86] (C. A. de los Reyes *et al. J. Phys. Chem. C,* 2019, *123*, 19725-19733.) Copyright © 2019 American Chemical Society.

Sodium-naphtalide solutions were also used to create reductive conditions to functionalize hBN. In 2020, Sun and coworkers functionalized hBN with alkyl halides using this method. The sheets with the longest alkyl chains showed the highest concentration in dispersion, up to 0.46 mg/mL. These were used to create low density polyethylene (LDPE) composites.[105] He and coworkers used a similar method to attach methyl methacrylate to hBN, to which PMMA polymer chains were then grafted through anionic polymerization. The sheets were readily dispersible in acetone (0.194 mg/mL) and provided mechanical reinforcement for polymer composites.[106]

Table 3: Summary of hBN dispersions exfoliated by functionalization

Functionalization method	Functional group	hBN Source	Method of functionalization	Method for Dispersion	Solvent	Concentration	Thickness	Lateral Size	Stability	Application	Ref
Reaction with edge/defect sites	hydroxyl groups	UK Abrasives	bath sonication in DI water for 8 h and centrifuged at 3000 g, filtered with coarse filter paper.	same as exfoliation	water	0.05-0.1 mg/mL for 8-24 h sonication	below 10 nm	tens of nm to 1 µm	not reported	Thin films, conjugation with proteins	[33]
Reaction with edge/defect sites	amine groups	Zibo Jonye Ceramic Technologies	Sonicated in DMF, 4,4'-methylenebis(phenyl isocyanate) is added and stirred for 30 min at 70°C. Washed with DMF, then Diamine diphenyl sulfone is added and stirred at 50°C for 12 h	Stir in DMF for 30 min	DMF	not reported	not reported	Not reported	>25h	resin composites	[85]
Radical addition	hydroxyl groups	Sigma-Aldrich	Exfoliate in NMP, disperse in high pressure autoclave vessel with di-tert-butylperoxide, hydrolysis with piranha solution	Sonication for 4 h	water	0.107 mg/mL	Not reported	2-3 µm	not reported	PVA and polyurethane composites	[34]
Radical addition	nitrene radicals	Sigma-Aldrich	4-methoxybenzyloxycarbonyl azide and hBN in NMP, heated to 160°C with stirring under nitrogen atmosphere for 16 h. Filter and wash with NMP and ethanol	1 min sonication, 24 h sedimentaion	ethanol, chloroform, cyclohexyl-pyrrolidone, DMF	0.05 mg/mL in ethanol	more aggregated	Not reported	not reported	Polycarbonate composites	[35]
Radical addition	Fluorine	Sigma-Aldrich	Disperse hBN in DMF, add to solvothermal reactor with Nafion and heat to 200°C	not reported	not reported	not reported	single or bilayer	Not reported	not reported	magnetic semiconductor studies	[87]

Oxidation of B sites	Hydroxyl groups	commercial	Mix hBN and hydrazine, 30% H_2O_2, HNO_3/H_2SO_4, or oleum in autoclave at 100°C	sonicated 5 min, filtered through paper filter	water and DMF	0.26-0.32 mg/mL in water, 0.34-0.52 mg/mL in DMF	up to 3 nm, 0.6-0.7 nm thickness after centrifugation	up to 700 nm	24-26 days in water, 30-32 days in DMF for H2O2	Powder analysis	[37]
Hydroxylation	Hydroxyl groups	Alfa Aesar	hBN was heated in a tube furnace to 1000C̊ for 1 hour in air, then cooled and washed with hot water and dried	Stir in water	Water	~65%	0.69 nm	359.6 nm	Not reported	Powder for analysis	[89]
Oxidation of B sites	Sulfur functionalization	Alpha Aesar	Mix hBN with $KMnO_4$, 1:8 H_3PO_4 and H_2SO_4 is added, mixed with heating at 75°C for 12 h. Add H_2O_2 and H_2O to stop oxidation. Centrifuged and washed with water, ethanol and HCl	redispersed	ethanol, acetone, DI water, IPA	0.2 mg/mL in water	<5nm	over one micron	over 24 hours	Powder analysis	[83]
Oxidation of B sites	hydroxyl groups	UK Abrasives	hBN stirred with H_2SO_4 and $KMnO_4$ and heated at 75°C for 24 h. H_2O_2 added, washed and centrifuged with water	bath sonicated 10 min, free stand 24 h	water	83% of initial mass	1.78 nm	458 nm	> 24h	Analysis	[91]
Oxidation of B sites	hydroxyl groups	Alfa Aesar	hBN and $KMnO_4$ 1:6 are stirred with sulphuric and phosphoric acid 8:1 at 75°C for 12 hours. Frozen H_2O_2 and water are added under constant stirring, washed with water, ethanol and HCl. Centrifuged for 45 min at various rates	not reported	not reported	not reported	less than 2nm	1-3 µm controlled by centrifugation	not reported	analysis	[90]
Oxidation of B sites	Hydroxyl groups	Grade AC6004, Momentive	hBN and H_2SO_4, $K_2S_2O_8$, and P_2O_5 are stirred at 80°C for 4.5 h. Added to concentrated	Bath sonicated 1 h, centrifuged at 3000 rpm	water	0.6 mg/mL	3 nm	2-3 µm	over 6 months	biocompatible hydrogels with PVA	[93]

			H_2SO_4, and $KMnO_4$ is added under vigorous agitation for further oxidation. Heated in water bath at 35°C for 2 h while stirring. Terminated reaction by adding H_2O_2								
Oxidation of B sites	hydroxyl groups	Kojundo Korea Co.	hBN and 2M NaOH are loaded into ball mill at 200 rpm, milled for 24 h. Rinsed with HCl and washed with DI water	Sonicated for 1 h, centrifuged at 2000 rpm for 30 min	IPA	0.425 mg/mL	less than 3 nm	1.5-2 µm	one week	Nanofiller for polyethylene nanocomposites	92
Oxidation of B sites	hydroxyl groups	Sigma-Aldrich	hBN and NaClO solution are loaded in ball mill at 140 rpm and milled for 16 h. Rinsed with water and washed with ethanol	Sonicated 30 min and centrifuged at 3000 rpm for 30 min	IPA	21% yield, start 1 mg/mL	0.35-1.35 nm	50-200 nm	more than two months	Support Ag nanoparticles for catalysis	94
Oxidation of B sites	hydroxyl groups	Sigma-Aldrich	hBN and 2-furoic acid are ground in agate mortar, then ball milled for 2 h. Dissolved and washed with water	shake in water	water	35 mg/mL	2 nm	1.8 µm	1 year	aerogels and thermally conductive film	95
Oxidation of B sites	hydroxyl groups	Zibo Jonye Ceramics Techonology Co. Ltd	ball milling with boric acid at 200 rpm for 48 h. Centrifuged and washed with water	rescattering	water	12.6 mg/mL	2 nm	2.0 µm	not reported	membrane fabrication	96
Oxidation of B sites	Amine and hydroxyl groups	Momentive	hBN-NH_2 was ball milled in ammonia atmosphere (300 kPa) for 20 h; hBN-OH was prepared by ball milling in an NaOH/water solution under Ar atmosphere at 200 rpm for 20-40 h, dialyzed, then dried	powder was sonicated for 30 min in various solvents	Water, ethanol, acetone	46 ± 2 mg/mL (hBN-NH_2 in ethanol)	hBN-NH_2 ~2.8 nm and hBN-OH ~3.1 nm	600 nm (both hBN-NH_2 and hBN-OH)	up to 3 months (hBN-NH_2 in ethanol)	Powder for analysis	97

Oxidation of B sites	Glycine groups	DCEL Co.	Bath sonicated for 10 min; ball milled for 24 h at 400 rpm at room temperature under Ar atmosphere; centrifuged 2000 rpm for 20 min	redispersed by bath sonication in water for 30 min	Water	35 mg/mL	2.0 nm	1.5 µm	At least 3 months	Composite materials	[98]
Oxidation of B sites	amino groups, hyberbranched aromatic polyamide	ESK Ceramics GmbH & Co.	hBN exfoliated DMF, octadecylamine is mixed and heated at 160°C for 96 h under nitrogen. THF is added, then filtered and washed with methanol. Treated with gama-aminopropyl-triethoxysilane and grafted with 3,5-diaminobenzoic acid	sonication for 1 h	acetone	not reported	4.8 nm	1.2 µm	not reported	epoxy composites	[36]
Oxidation of B sites	hydroxyl groups, octadecyltriethoxysilane	MK Impex Canada	hBN is tip sonicated in NMP for 2 h, centrifuged at 5000 rpm for 15 min. Add H_2SO_4, $NaNO_3$, and $KMnO_4$ for oxidation and stir for 24h. Dispersed in toluene, add octadecyltriethoxysilane, reflux for 24 h under nitrogen	Not reported	polyol ester	0.25 mg/mL	5-20 nm	Not reported	10 days	improve tribological properties of lubricant	[99]
Oxidation of B sites	oxidation	Commercial	Place in furnace at 600°C for 144h	Not reported	ethanol	not reported	not reported	Not reported	48 h	analysis	[100]
	amino groups	Momentive	ball milling with urea for 20 h and washing with water	dialysis for 1 week	water	30 mg/mL	about 2.5 nm	around 100 nm	2 weeks	ultralight aerogels and freestanding membranes	[9]
Oxidation of B sites	sucrose	Qinhuangdao Eno High-Tech Material Development	ball milled with sucrose crystals for 4, 8, or 12 h. Washed with water and filtered	bath sonication for 2 h, centrifuged at 2000 for 30 min	water, DMF, 1:1 ethanol/water, IPA, THF, ethyl acetate	10 mg/mL in water, 4 mglmL in DMF, 36 mg/mL in 1:1 ethanol/water	20-10 nm	200-100 nm, dependent on ball milling time	1 month in 1:1 ethanol/water, 6 months in DMF	aerogel, PVA composite films	[101]

Oxidation of B sites	Fluorination	Commercia l	ball milled with IPA for 12, 24, or 36 h. The powder and NH_4F were mixed with water in a Teflon lined stainless steel autoclave at 190°C for 12 h, then centrifuged at 3000 rpm for 30 min	not reported	not reported	not reported	6 nm	200-500 nm	not reported	metal-free magnetic material	[84]
Oxidation of B sites	Fluorination	Commercia l	bath sonication and ball milling in ammonium fluoride aqueous solution for 10 h, then washed and centrifuged between 3000 and 6000 rpm	redispersed	water	1 mg/mL	2 nm	Not reported	>30 days	water dispersible lubricant additive	[44]
Reductive conditions	alkyl groups	Sigma-Aldrich	hBN, lithium and liquid ammonia are stirred, 1-bromododecane is added dropwise and stirred overnight, extracted in hexanes and washed and dried	bath sonication for 30 min and centrifuged at 9000 g for 30 min	water, IPA, THF, dodecane	not reported	1.2 nm	0.4 µm	not reported	thin film	[86]
Reductive conditions	hydroxyl groups	Alladin Chemical Co.	hBN and NMP were tip sonicated for 50 hrs and centrifuged for 45 min at 1500 rpm, filtered and dried. BNNSs were tip sonicated for 2 hours in THF, treated at -78°C and liquid ammonia was added. Lithium was added and stirred, O_2 was bubbled for 6h, water was slowly added with stirring, then filtered, washed and dried	Tip sonicated for 24 hrs, centrifuged at 1500 rpm for 30 min.	water	0.417 mg/mL	Not reported	200-400 nm	not reported	composited with natural rubber	[104]

Reductive conditions	alkyl groups	Alladin Chemical Co.	A sodium-naphtalide solution was added to the BNNSs and stirred for 24 hrs in an ice bath. Alkyl halides were added dropwise and stirred for 48 h at 25°C under nitrogen. O_2 was bubbled for 60 min and stirred for 12 h. Ethanol was added under vigorous stirring, followed by water and HCl neutralization. The BNNSs were extracted, filtered and dried	Tip sonicated 24 h, settled 1 week, centrifuged 5 min at 1000 rpm	chloroform, 1, 2-dichlorobenzene	0.46 mg/mL, higher with longer alkyl chains	1.5-2 nm	Not reported	not reported	LDPE composites	[105]
Reductive conditions	methyl methacrylate	Aladdin Chemical Co.	BNNS in THF were stirred for 3 hrs, and a sodium-naphthalide solution was added, and stirred in ice bath for 24 hrs, then Methyl methacrylate is added dropwise and stirred 24 hrs, followed by N_2/O_2 gas bubbled into suspension, filtered and washing	bath sonicated in acetone for 24 hrs, centrifuge at 1000 rpm 15 min	acetone	0.194 mg/mL	1.5 nm	Not reported	not reported	grafting of PMMA polymer chains, mechanical reinforcement of polymer composites	[106]

4. Acids and Bases

Another common way to modify and disperse hBN sheets is through the use of acids and bases, either in the form of Lewis bases interacting with acidic B sites or strong protic acids, such as methanesulfonic acid and chlorosulfonic acid, to protonate and exfoliate sheets. The characteristics of these dispersions are summarized in Table 4. Other acids have been applied as intercalating agents, and these will be discussed in section 7.1.

4.1 Lewis Bases

Initial works using Lewis bases for the noncovalent modification of the surface of hBN were performed by Lin and coworkers in 2010.[25,26] First, they utilized octadecylamine (ODA) and amine-terminated polyethylene glycol (PEG) as Lewis bases to form adducts with B sites by heating to 160-180˚C for 4-6 days.[26] The base-hBN adducts were readily dispersible in different solvents, including water and chloroform for PEG-hBN and THF, chloroform, DCM, and toluene for ODA-hBN. All dispersions were relatively stable at 0.01 mg/mL for up to a few months.[26] The group then attempted to increase adduct formation by ball milling the hBN with ODA to introduce defect sites.[25] They found that increasing the concentration of defect sites improves the reaction efficiency with ODA and increases the concentration of ODA-hBN that can be dispersed in THF.[25] Also in 2010, Nag and coworkers used the Lewis bases trioctylamine (TOA) and trioctylphosphine (TOP) to make dispersions of hBN in nonpolar solvents such as toluene, heptane, and benzene.[107] In 2014, Cao and coworkers used NH_3 as a Lewis base, sonicating hBN in a 3:2 mixture of NH_3:IPA for 35 hours.[108] After this process, the hBN was exfoliated into few-layered sheets and could form stable dispersions in IPA for at least a month.[108] In 2016, Kumari and coworkers tested alkylamines with different chain lengths, butylamine, ODA, and TOA for their ability to form Lewis acid-base adducts with hBN and dispersed them in mineral oil.[109] The adducts were formed by refluxing pre-exfoliated hBN (Coleman group procedure in NMP)[66] with the alkylamine in toluene for 72 hours. After studying the 3 amines, it was concluded that ODA formed the most adducts with hBN, as revealed by the weight loss in the thermal gravimetric analysis (TGA), but TOA-hBN exhibited the best dispersibility in mineral oil, reaching a concentration of 0.02 mg/mL that was stable for at least 10 days.[109]

4.2 *Strong Protic Acids*

Some very strong acids have also been applied toward the dispersion of hBN. For instance, methanesulfonic acid (MSA) was utilized by Wang and coworkers to exfoliate and disperse hBN.[32] After sonication for 8 hours, hBN concentrations of 0.2-0.3 mg/mL could be reached in MSA and the dispersions were stable for months. Moreover, after quenching in water and transferring the now exfoliated hBN sheets into organic solvents, they could produce dispersions up to 0.5 mg/mL in NMP.[32] The authors proposed that the acid protonates the hBN surface, producing a perturbation of electronic charge that induces repulsions between hBN sheets and leads to exfoliation and dispersion.[32] Later, Kaur and coworkers also used MSA in a 50% by volume mixture with N,N-dimethylformamide (DMF), where hBN was added and tip sonicated.[110] The rationale was that the ionization of DMF by MSA generates protons and hydrides, which are attracted by electrophilic boron sites, and the protons were attracted by the nitrogen atoms in hBN. Evidence of both this mechanism and the covalent functionalization of the hBN sheets was provided by FTIR and XPS. The functionalized sheets had an average size of 130-170 nm and an average of 2-5 layers.

Nafion membranes were fabricated incorporating the functionalized hBN, which presented superionic conduction.[110]

In 2016, Morishita and Okamoto extended the research of hBN dispersion to chlorosulfonic acid (CSA), which is a superacid (stronger than 100% sulfuric acid).[111] After 8 hours of sonication in CSA, the mixture was quenched with water and dried. The acid-exfoliated hBN could be redispersed in acetone, dimethyl sulfoxide (DMSO), and IPA, reaching a concentration of 0.75 mg/mL in IPA.[111] The dispersed hBN was used to prepare thermally conductive and electrically insulating composite films with PMMA.[111] Later, in 2018 Jasuja and coworkers probed the dispersion of hBN with CSA more thoroughly to better understand the mechanism (Figure 8a).[112] The authors found from X-ray photoelectron spectroscopy (XPS) measurements that the protonation occurs on the N sites, introducing aminated nitrogen sites. Additionally, by conjugating these sites to a fluorescent dye, fluorescein isothiocyanate (FITC), they could image the sheets and show that the protonation sites are distributed uniformly on the sheet surface (Figure 8b).[112] Finally, in 2021, Gudarzi and coworkers modified the exfoliation method in CSA by adding pyrene to non-covalently functionalize hBN with pyrene sulfonic acid and make the resulting dispersion more compatible in ambient conditions.[113] The resulting material consisted of large 6-7 layer sheets with a mean lateral size of 4 μm which were dispersible in various polar solvents. The dispersions were used to produce a two-layer hBN-graphene laminate through sequential vacuum filtration.[113]

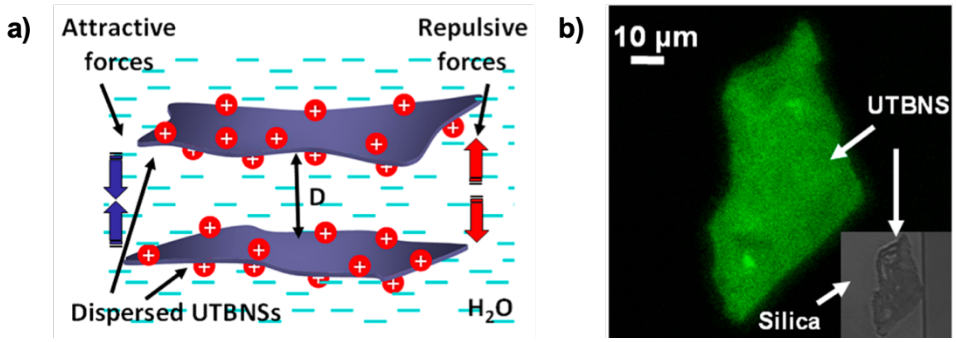

Figure 8. (a) Schematic of how protonation of ultra thin hBN sheets (UTBNSs) by CSA helps to exfoliate and electrostatically stabilize them in water. (b) Confocal image of a UTBNS covalently tagged with FITC molecules suggesting a uniform presence of protanated N atoms on its surface. The bottom right inset shows the corresponding optical image. Reprinted with permission from Ref [112] (K. Jasuja *et al. ACS Nano,* 2018, *12*, 9931-9939.) Copyright © 2018 American Chemical Society.

Table 4: Summary of hBN dispersions exfoliated by acids or bases

acid/base	hBN Source	Method of Exfoliation	Method for Dispersion	Solvent	Conc.	thickness	lateral size	Stability	Application	Ref
octadecylamine and amine-terminated polyethylene glycol	UK Abrasives	heating for 4-6 days	briefly sonicate and centrifuge at 3000 g for 10 min	THF, chloroform, methylene chloride, toluene for octadecylamine, water and chloroform for polyethylene glycol	0.5-1 mg/mL	PEG-BN 1-7 nm	tens of nm to over 1 μm	few months	Analysis	26
octadecylamine	UK Abrasives	ball milling, heating to 160-180°C for 4-6 days.	briefly sonicate and centrifuge at 3000 g for 10 min	THF	not reported	thickness of less than 5 nm	size 20-50 nm	not reported	Analysis	25
trioctylamine and trioctylphosphine	prepared from boric acid and urea	mixed in toluene and sonicated for 15 minutes	same as exfoliation	toluene, heptane, benzene	not reported	not reported	not reported	not reported	Analysis	107
ammonia	Momentive	bath sonicated in 3:2 ammonia:IPA for 35 h. Centrifuged at 3000g	Not reported	IPA	not reported	Not reported	Not reported	> 1 month	analysis	108
butylamine, octadecylamine, trioctylamine	not reported	tip sonication in NMP for 2 hours, settle overnight and centrifuged at 3000 rpm, then redispersed in toluene by sonication and mix under reflux with butylamine, octadecylamine, or trioctylamine.	Not reported	mineral oil	0.02 mg/mL with trioctylamine	Not reported	Not reported	at least 10 days.	additive for lubrication oil	109
methanesulfonic acid	Sintec Keramik Shanghai	bath sonication for 8 hours, centrifugation at 4000 rpm for 90 min	sonication for few minutes	methanesulfonic acid, NMP, DMF, DMSO	0.2-0.3 mg/ml in methanesulfonic acid, 0.5 mg/mL in NMP	<3nm	less than 500 nm	months	polymer composites	32
methanesulfonic acid	Sigma-Aldrich	50% methanesulfonic acid in DMF, tip sonicatied for 4 h.	same as exfoliation	50% methanesulfonic acid in DMF	3 mg/mL	few nanometers, 2-5 layers	130-170 nm	over 3 months	Nafion membranes with	110

		Centrifuged at 3000 rpm for 30 min							superionic conduction	
chlorosulfonic acid	Showa Denko K. K	8 hours bath sonication, quench and dry	bath sonication	acetone, DMSO, IPA	0.75mg/mL in IPA	less than 10 layers	1.3-0.5 µm	>20h	composite films with PMMA	[111]
chlorosulfonic acid	Momentive	stir for 72 h at 1500 rpm	same as exfoliation, transfer to water by dropwise quenching	chlorosulfonic acid, water	Not reported	2 nm	24.5 µm	>4 months	conjugate with fluorescent dye	[112]
chlorosulfonic acid anfd pyrene	Not reported	stir with chlorosulfonic acid/pyrene for 48 h. Wash with water.	Bath sonication and high shear mixing for 10-15 min	NMP, DMSO	0.5 mg/mL	6-7 layers	4 µm	Not reported	dielectric laminates	[113]

5. Surfactants and Polymers

Another very common method for hBN exfoliation and dispersion is using surfactants and polymers as solubilizing agents. These species are typically amphiphilic molecules composed of two parts: one can interact well with the hBN sheet and the other can make it soluble in the desired solvent. In the case of surfactants, this results in the formation of micelles when the surfactant is used at high enough concentrations (above the critical micelle concentration). Surfactants and polymers can generally be broken down into two types, ionic and nonionic. The details of these types of dispersions are summarized in Table 5.

5.1 Nonionic Surfactants and Polymers

To the best of our knowledge, the earliest polymer used for hBN exfoliation and dispersion was poly[(*m*-phenylenevinylene)-co-(2,5-dictoxy-*p*-phenylenevinylene)].[27] Han and coworkers used this polymer in 2008, demonstrating the first liquid exfoliation of hBN. After 1 hour of sonication in a polymer/1,2-dichloroethane solution (1.2 mg/10 mL), they produced 1-3 layered hBN sheets, which was extensively analyzed by TEM and HR-TEM analysis.[27]

Common polymers reported for hBN dispersion are poly(vinyl alcohol) (PVA),[40,114] polyvinylpyrrolidone (PVP),[115–119] and polydopamine (PDA).[75,120,121] In 2013, Khan and coworkers first reported using aqueous PVA solutions (20 mg/mL) for dispersing hBN through a mixture of tip sonication, bath sonication, and centrifugation.[40] The dispersions obtained resulted in hBN flakes of 1-6 layers with lateral sizes around 1.4 µm that were used to make PVA composite films with improved mechanical properties.[40] In 2017, Zhang and coworkers tested the impact of changing the hBN:PVA ratio on the formation of aerogels.[114] Moreover, many other groups have used PVA to form composites with hBN dispersed by different means.[34,93,101,120–122]

In 2014, Guardia and coworkers tested an assortment of nonionic surfactants, including PVP, Tween 80, Tween 85, Brij 30, Brij 700, Triton X-100, gum Arabic (GA), Pluronic P123, and n-dodecyl β-D-maltoside.[115] Here, the best performance was shown by PVP, with concentrations of 0.11 mg/mL of hBN with 5-25 BN layers.[115] In 2015, Ma and Spencer compared PVP to polythiophene (PT) and functionalized PTs, poly(3-thiophenezoic acid) (PTPA), poly(3-hexylthiophene-2,5-diyl) (H3PT), and poly(3-thiophene acetic acid) (P3TAA).[116] They found the best dispersions came from PVP in DMSO and H3PT in chloroform, remaining stable for at least 3 weeks in both cases. Additionally, they determined that the PTs interact with hBN sheets through π-π stacking interactions while PVP wraps or coats the sheets.[116] Bari and coworkers tested PVP-hBN dispersions in a variety of solvents.[117] After tip sonication, they could produce stable hBN dispersions in water, methanol, ethanol, IPA, chloroform, DMF, DMSO, and NMP, with NMP reaching the highest concentration (1.1 mg/mL).[117] In 2021, Chen and coworkers exfoliated hBN using PVP and probe ultrasonication with the intention of embedding quantum emitters.[119] They compared the resulting hBN nanoflakes produced from five different commercially available hBN sources, determining the one with the best optical properties and lowest impurity level.[119]

PDA was first reported for hBN dispersion in 2015 by Shen and coworkers.[120] The hBN was first dispersed in a 3:1 Tris buffer:ethanol solution containing dopamine hydrochloride, which, after stirring for 6 hours at room temperature, polymerized and coated the hBN sheets. The addition of PDA improved dispersibility in water and was used to prepare a composite film in PVA, which showed improved thermal conductivity compared to films without PDA.[120] In 2017, Wang and coworkers coated hBN (first dispersed in IPA and water as discussed in section 2) with PDA to improve its stability in water.[75] After the addition of PDA, the dispersion in water was stable for more than 4 months.[75] Later, in 2019, Ge and coworkers coated hBN with PDA to aid the production of composites with pineapple leaf microfibril cellulose and PVA.[121]

Other unique polymers have also been studied for hBN dispersion and will be discussed in chronological order below. In 2013, Liu and coworkers used a polystyrene (PS) and PMMA copolymer (P(S-*b*-MMA)) to tune the dispersibility of hBN in different organic solvents.[123] Naturally, the PS block prefers to interact with hBN through π-π interactions and PMMA extends into the solvent. In this case, the hBN is dispersible in acetone (0.078 mg/mL) and toluene (0.123 mg/mL) for at least 48 hours, but not cyclohexane.[123] Alternatively, if Cu salts are added to the mixture, PMMA will coordinate to hBN through the Cu ions and PS will extend into solution. In this case, the hBN is dispersible in cyclohexane (0.237 mg/mL), but not acetone.[123] In 2015, Zhu and coworkers studied the dispersion of hBN in Pluronic F68 (Figure 9a) and its use in combination with density gradient ultracentrifugation for thickness sorting of hBN sheets.[124] They found that using many iterations of ultracentrifugation and the density medium, iodixanol (Figure 9b), they could sort hBN into eight distinct bands of increasing thickness, ranging from 0.5-1 nm to 2.5-3.5 nm (Figure 9c). The sorted hBN sheets were used to make ultrathin films and dielectrics.[124] In 2016, Joseph and coworkers studied the use of polycarbonate (PC) for dispersion of hBN in DMF.[125] They found that after 48 hours of sonication, they could obtain dispersions containing primarily 1-2 layer hBN sheets, which were used to produce hBN ink.[125] In 2017, Muhabie and coworkers utilized adenine-functionalized polypropylene glycol (A-PPG) to disperse hBN in THF with 3 hours of ultrasonication.[126] They tested a variety of hBN:A-PPG ratios, and they obtained the highest dispersion concentration of 0.2 mg/mL with a 50:50 ratio.[126] In 2018, Ye and coworkers tested hyperbranched polyethylene (HBPE) for stabilizing hBN in a variety of solvents.[127] After optimizing the solvent, HBPE molecular weight, hBN and HBPE concentrations, and sonication time, they produced hBN dispersions in chloroform with a concentration of approximately 0.1 mg/mL. Additionally, they determined that the interactions between the hBN and HBPE occur through nonspecific CH-π interactions, and, therefore, the polymer-solvent interactions could not be too strong or hBN would not be stabilized in solution.[127] The dispersed material was used to prepare composite films and study their dielectric properties.[127] In the same year, Du and coworkers studied an alkyl ethyoxylate surfactant, Rhodoline WA9, for stabilizing hBN in water.[14] After a combination of ball milling (15 hours) and sonication (2-24 hours), they produced a slurry with a concentration of about 36.3 mg/mL that was used to make coatings on SiO_2 fibers and composites for improved mechanical strength and thermal stability.[14] Finally in 2022, Llenas and coworkers studied the exfoliation of hBN with Pluronic acid F127 using various methodologies such as ball milling, bath, and tip sonication.[128] Tip sonication produced the highest yield with 6-8 nm thick sheets, which also showed high biocompatibility and internalization in HeLa cells.[128]

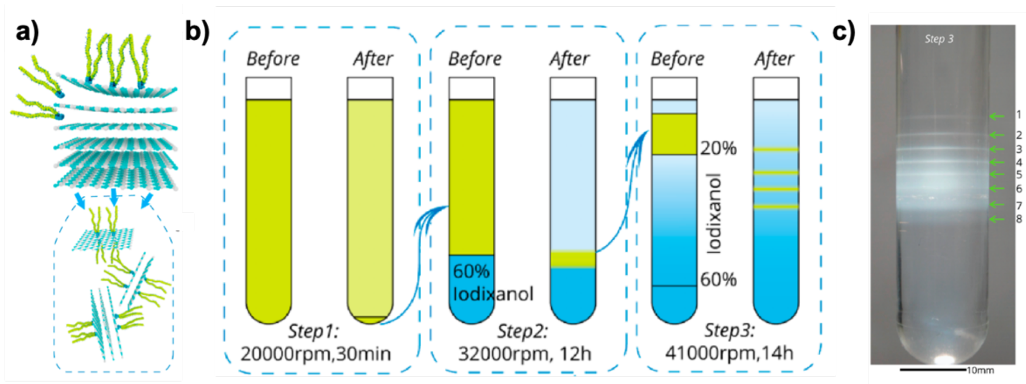

Figure 9. (a) Schematic illustration of the hBN exfoliation process using the copolymer surfactant Pluronic F68. Amphiphilic F68 exfoliates thin hBN flakes through the interaction of its hydrophobic chain segment (blue color) with the hBN surface while its hydrophilic chain segments (yellow color) stabilize the flakes in aqueous solution. (b) An illustration of the three-step process for sorting hBN according to size and thickness. (c) Eight distinct hBN bands are visible in the centrifuge tube after step 3, indicating effective sorting by thickness. Reprinted with permission from Ref [[124]] (J. Zhu *et al. Nano Lett.* 2015, *15*, 7029-7036.) Copyright © 2015 American Chemical Society.

5.2 Ionic Surfactants

Ionic surfactants are typically used to facilitate aqueous dispersions due to their amphiphilic properties. Most ionic surfactants are small molecules (smaller than polymers), but, in 2013, Lu and coworkers reported the use of an ionic polymer, poly(sodium-4-styrenesulfonate) (PSS) for hBN dispersion in water.[41] After sonicating and heating the mixture, the PSS-hBN dispersion is stable for a month without precipitation and contains hBN sheets about 3-6 layers thick. This dispersion was compared to one with a small aromatic molecule, sodium perylene-3,4,9,10-tetracarboxylate, which produced very similar results.[41]

Other reports of hBN dispersions in ionic surfactants use common surfactants such as sodium cholate (SC),[38,129] sodium dodecyl sulfate (SDS),[39] and sodium deoxycholate (SDC).[129] In

2011, Smith and coworkers tested the exfoliation of various layered compounds in aqueous SC solution using tip sonication.[38] Though the most comprehensive analysis was performed on MoS_2 dispersions, hBN also demonstrated good dispersibility in SC with well exfoliated sheets. The authors used these dispersions to prepare films by vacuum filtration.[38] Others have used the same protocol described by Smith and coworkers to exfoliate hBN for making hBN-graphene quantum dot nanocomposites for fluorescent cell imaging[130] and to study the use of optical tweezers for positioning single hBN sheets.[131] In 2012, Yao and coworkers reported the use of SDS for dispersing 2D materials through a combination of ball milling and sonication.[39] They found that after 12 hours of ball milling and 2 hours of sonication, hBN concentrations up to 1.2 mg/mL could be produced that were stable for hundreds of hours. These dispersions were also used to prepare films by vacuum filtration.[39] Finally, in 2018, Chae and coworkers tested the dispersion of hBN in SC and SDC aqueous solutions with 8 hours of sonication.[129] The hydrophobic steroid skeleton of the surfactants interacts well with the conjugated sheets. Both surfactants produced dispersions, but SC resulted in higher concentrations (2.22 mg/mL) and thinner hBN sheets (< 2 nm) than SDC (1.08 mg/mL, > 4 nm).[129] Luccherelli and coworkers worked on obtaining two types of exfoliated hBN with SC using ball milling, bath sonication, filtration, and centrifugation to obtain both sharp edged hBN sheets, and curved shaped, round edge hBN.[132] Dispersions of 1 mg/mL were prepared in water and were stable for more than 24 hours. As predicted by molecular dynamics, the rounded hBN sheets were able to create water channels across bilipid layers which can allow cross-membrane transport.[132] This procedure was later used with the addition of bile salts in the exfoliation process to study the cytotoxicity of hBN in human dendritic cells, showing that hBN has minimal toxicity on dendritic cell viability.[133]

A study in 2018 by Wang and coworkers compared ionic and nonionic surfactants for hBN dispersion, concentration, and stability in alkaline environments with the goal of using hBN to enhance Portland cement paste.[13] Here, they found that addition of the ionic surfactant SDS or nonionic surfactants PC or GA reduced the dispersion concentration compared to water alone. They did find, however, that GA-hBN dispersions are stable in alkaline cement pore solution, while the others are not.[13] Finally, they tested hBN dispersions in water alone for their impact on cement hydration and strength improvement.[13] In 2021, the Martí group performed a systematic study using nine different ionic and non-ionic surfactants to exfoliate and disperse hBN, determining the yield, sheet quality, and stability over time for the dispersions.[134] It was shown that after centrifuging at a high rate, dodecyltrimethylammonium bromide (DTAB) produced the thinnest and second largest hBN sheets within the surfactants studied, and ionic surfactants remained the most stable over time.[134]

Table 5: Summary of hBN dispersions exfoliated by surfactants or polymers

Surfactant/ Polymer	hBN Source	Method of Exfoliation	Method for Dispersion	Solvent	Concentration	Thickness	Lateral Size	Stability	Application	Ref
poly(*m*-phenylenevinylene-co-2,5-dictoxy-p-phenylenevinylene)	Not reported	1 h sonication	Same as exfoliation	1,2-dichloro-ethane	Not reported	Several layers	Several microns	Not reported	Powder for analysis	[27]
polyvinylalcohol (PVA)	Saint Gobain	Tip sonicated for 12 h and centrifuged at 1000 rpm for 45 min	Redispersed in PVA/water by tip sonicating 3.5 h and centrifuging at 500 rpm for 22 mins	Water	Not reported	3 layers	1.35 µm	Not reported	PVA composite	[40]
PVA	Aladdin Reagent Co.	hBN was stirred in PVA solution for 2 h, then frozen at -80℃ for 2 h	Same as exfoliation	Water	Not reported	Not reported	Not reported	Not reported	Composite aerogel	[114]
polyoxyethylene sorbitan monooleate (Tween 80), polyoxyethylene sorbitan trioleate (Tween 85), polyvinylpyrrolidone (PVP), polyoxyethylene (4) dodecyl ether (Brij 30), polyoxyethylene (100) octadecyl ether (Brij 700), polyoxyethylene octyl (9–10) phenyl ether (Triton X-100), gum arabic from acacia tree, Pluronic P-123 and n-dodecyl b-D-maltoside (DBDM); sodium cholate (SC)	ESK Ceramics GmbH & Co.	Bath sonicated, then centrifuged 1500 rpm for 30 min	Same as exfoliation	Water	0.05 to 0.40 mg/mL	5-25 layers	100-500 nm	At least 6 months	Liquid dispersion for analysis	[115]
PVP, polythiophene (PT), poly(3-thiophenezoic acid	Strem Chemicals	Bath sonicated for 48 h, centrifuged at 1500 rpm for 45 min, and	Same as exfoliation	IPA	Not reported	Not reported	Not reported	At least 2 weeks	Hybrid nanomaterials	[116]

(PTPA), poly(3-hexylthiophene-2,5-diyl) (H3PT), poly(3-thiophene acetic acid) (P3TAA)		left to settle for 24 h and supernatant was used								
PVP/water	Sigma-Aldrich	Tip sonicated in PVP/water solution (or organic solvent) at 10 W per hour, then centrifuged at 5000 rpm for 4 h	Same as exfoliation	Methanol, ethanol, IPA, chloroform, DMF, DMSO, NMP	Up to 1.1 mg/mL (in NMP)	Not reported	~700 nm	Not reported	Spray drying to form crumpled sheets	[117]
PVP/water	MicroLubrol, Hagen Automation, Plasma Chem, Graphene Supermarket, Sigma-Aldrich	Tip sonicated 30 h, then left to settle for 24 h and supernatant was used	Same as exfoliation	Water	Not reported	Thinnest 17 ± 15 nm (Graphene Supermarket)	Largest lateral size: 291 ± 50 nm (Plasma Chem)	Not reported	Study the optical properties of quantum emitters	[119]
PDA	Dandong Rijin Science and Technology Co.	hBN was mixed in tris-buffer solution and ethanol, then dopamine hydrochloride was added and stirred for 6 h at room temperature	Same as exfoliation	Water	Not reported	Not reported	10.4 ± 5 µm	Not reported	Composite films	[120]
PDA	Saint Gobain	Bath sonicated in IPA/water (3/2 w/w) for 3 h, then centrifuged 3000g for 10 min, vacuum filtered, and dried	Dispersed in tris buffer/ethanol with dopamine hydrochloride and stirred 6 h at room temperature	IPA/water	0.3 mg/mL	Not reported	Hundreds of nanometers to several microns	More than 4 months	Silicone composites	[75]
microfibril cellulose (MFC), polydopamine (PDA)	Boron Nitride Factory, Qingzhou	hBN was stirred and sonicated in tris buffer solution for 3 h, then stirred and sonicated another 3 h with dopamine hydrochloride. The powder was washed with water and dried	Dried powder was sonicated with MFC and water for 5 hours, filtered, and washed to form hybrid powder	Water	Not reported	Not reported	Not reported	Not reported	Composite films	[121]
P(S-b-MMA)	Sigma-Aldrich	hBN was sonicated in NMP for 24 h, then P(S-b-MMA) was added and sonicated	Redispersed in cyclohexane, acetone, and toluene	Cyclohexane, acetone, and toluene	Mostly insoluble in cyclohexane, 78 mg/L in	<5 nm	<500 nm	At least 48 h	Composite films	[123]

		another 20 h. Centrifuged at 1500 rpm for 45 min, and the supernatant was filtered, washed with chloroform, and dried			acetone, 123 mg/L in toluene					
Pluronic F68	Aldrich	Tip sonicated in PF68 for 2 hours in ice bath, then centrifuged at 10,000g for 10 mins	Same as exfoliation	Water	Not reported	<50 nm, (thinnest was 0.73 ± 0.11 nm)	Not reported	Not reported	hBN dielectric films	[124]
polycarbonate (PC)	Aldrich	hBN was bath sonicated for 24 h in DMF, then PC/DMF solution was added and sonicated 24 h. The mixture was centrifuged at 3000 rpm, then the supernatant was centrifuged again at 10,000 rpm	Same as exfoliation	DMF	Not reported	~0.85 nm	Not reported	Not reported	Printable electronic ink	[125]
adenine-functionalized polypropylene glycol (A-PPG)	Sigma-Aldrich	hBN and APPG were ultrasonicated for 3 h at 25°C in THF	Same as exfoliation	THF	0.2 mg/mL	2.73-3.5 nm	0.3-1.5 µm	Not reported	Powder for analysis	[126]
hyperbranched polyethylene (HBPE)	Aldrich	hBN, HBPE, and solvent were bath sonicated, then centrifuged at 3000 rpm for 20 min	Same as exfoliation	THF, DMF, chloroform, n-heptane, or toluene	Up to 10 mg/mL	~2 nm	200-500 nm	Several weeks	Composite films	[127]
Rhodoline® WA9	Momentive	hBN was ball milled at 300 rpm for 15 hrs	Tip sonicated at 80% of 130 W, centrifuged at 4500 rpm for 4 mins	Water	36.3 mg/mL	~56 nm after ball milling and ~19 nm after sonication (SEM), 0.7-11.3 nm (TEM);	0.5–1.0 µm	Not reported	Oxide/oxide ceramic composites (SiO_2f/SiO_2)	[14]
PF127	Merck KGaA	(1) tip sonication at either 80 or 200 W for either 8 or 24 h, or (2) ball milling in IPA and benzyl benzoate for 8 or 24 h	Same as exfoliation; (1) also centrifuged 4500 rpm, then 20,000 rpm, or (2) centrifuged at 1500 rpm,	Water, IPA, or benzyl benzoate	Tip: 11.3 wt.% for low power, 30.7 wt.% for high power; bath: 11.2 wt.% after 8 h, 25.7 wt.% after 24 h; tip sonication at low power with	(Sonication): 6-8 nm with tip sonication being slightly thinner	(Sonication): 70-225 nm for bath, 45-250 nm for tip	At least 7 days in PF127	Cytotoxicity studies	[128]

			then 4500 rpm		PF127: 28 wt.%; tip sonication at high power with PF127: decomposition; ball milling and IPA: 13 wt.% after 8 h, 29 wt.% after 24 h; ball milling and benzyl benzoate: 9 wt.% after 8 h, 21 wt.% after 24 h					
poly(sodium 4-styrenesulfonate) (PSS) or (sodium perylene-3,4,9,10-tetracarboxylate (STPB)	Alfa Aesar	hBN was suspended with a homogenizer and bath sonicated in water 10 h, then PSS or STPB were added and bath sonicated another 2 h. The mixture was heated to 80°C for 5 h then cooled and centrifuged at 3000 rpm for 30 min	Same as exfoliation	Water	0.16 mg/mL (in PSS)	2 nm	100-500 nm	1 month	Powder for analysis	[41]
Sodium cholate	Not reported	Probe sonicated for 30 min, then centrifuged	Same as exfoliation	Water	Not reported	Not reported	Not reported	Several weeks	Powder for analysis	[38]
Poly(diallyldimethylammonium) (PDDA)	Aladdin Reagent Co.	hBN was tip sonicated for 4 h and settled for 24 h, then centrifuged at 2000 rpm for 20 min. The supernatant was centrifuged again at 10,000 rpm for 10 min, washed, then sonicated in PDDA and NaCl for 30 min. Centrifuged again at 10,000 rpm for 10 min	Dispersed with graphene quantum dots by sonicating for 30 mins	Water	Not reported	Not reported	Not reported	Not reported	Cell imaging	[130]
sodium cholate	Sigma-Aldrich	Horn ultrasonicated for 30 min in ice bath, settled overnight, then centrifuged at 1500 rpm for 15 min	Same as exfoliation	Water	Not reported	Not reported	0.1–1 µm	Several months	Liquid dispersion for characterization	[131]

SDS (0.05 wt%)	Momentive	Ball milled 100 rpm for 12 h	2 h bath sonication (80 W)	Water	1.2 mg/mL	1.2-8 nm	10-500 nm	Hundreds of hours	Powder for analysis, thin film	[39]
sodium cholate or sodium deoxycholate	Sigma-Aldrich	Bath sonication for 8 h then centrifuged at either 3000g or 20,800g	Same as exfoliation	Water	Up to 2.22 mg/mL	SC: thickness <2 nm, SDC: >4 nm	SC: 100-400 nm	Less than 1 week for dispersions centrifuged at 3000g	Powder for analysis	[129]
sodium cholate	Alfa Aesar	Sharp-edged hBN was ball milled for 20 h at 100 rpm, then milled again with SC for 3 h at 100 rpm and centrifuged at 950g. Round hBN was bath sonicated for 1 h and centrifuged at 420g	Redispersed in water	Water	Up to 1 mg/mL	Sharp-edged flakes: 4.69 ± 0.05 nm; round flakes: 6 to 35 nm	Sharp-edged flakes: 342 nm; round flakes: 156 nm	More than 24 hours	Cell membrane interaction studies	[132]
sodium cholate and sodium deoxycholate	Alfa Aesar	Ball milled at 100 rpm for 20 h	Milled with bile salts at 100 rpm for 3 h	Water	1 mg/mL	TEM: single and few-layered; AFM - 5.05 ± 1.35 nm	TEM: 358 ± 166 nm; AFM: 225 ± 55 nm	Several weeks	Cytotoxicity studies	[133]
polycarboxylate (PC) based superplasticizer (Sika® ViscoCrete® 2100), SDS, gum arabic (GA)	Momentive	Tip sonication at 80 ± 5 W	Same as exfoliation, centrifuged at 1400g for 10 min	Water	0.078 ± 0.011% (3.1 ± 0.4% in terms of mass conversion)	<10 nm	Not reported	Several hours	Additive in OPC cement composite	[15]
SDS, SDBS, SC, CTAB, CTAC, DTAB, PF108, PF88, PF87	Sigma-Aldrich	Stirred 1 h, then bath sonicated 20 min; centrifuged at 100g or 8000g	Same as exfoliation	Water	2-3% (mass conversion)	Varied by surfactant; 1-18 nm,	300-900 nm	Varied by surfactant; generally 10 days or longer (for dispersions centrifuged at 8000g)	Antibacterial coating	[134]

6. Biomolecules

The mechanism of dispersion of hBN by biomolecules is similar to surfactants and polymers, only differing in the use of molecules with a biological, rather than synthetic, origin. SC and SDC are biomolecules, however they have been already reviewed in section 5.2. Interestingly, biomolecules have been extensively utilized for boron nitride nanotube (BNNT) dispersion and application in *in vivo* and *in vitro* studies. However, for hBN, biomolecules were only recently explored for dispersion studies. Table 6 summarizes the characteristics of these types of dispersions.

In 2018, two groups reported the use of alginic acid, a compound derived from sea algae, for hBN dispersion.[45,135] Wang and coworkers tested alginic acid for dispersion of 7 different C and BN nanomaterials and found that for hBN, it failed to produce a stable dispersion, with only 20% of dispersed material remaining after 7 days.[45] Chu and coworkers used the sodium salt of alginic acid and were able to reach an hBN concentration of 0.86 mg/mL in water after stirring and sonication.[135] Though their authors did not perform long-term stability studies, they were able to use the dispersions to make unsaturated polyester resin composites with improved thermal and mechanical properties.[135] In 2019, Deshmukh and coworkers tested 17 plant extracts in IPA for hBN dispersion after 24 hours of sonication.[136] They found that extracts from *panax ginseng* roots, *morus nigra* leaves, and *hovenia dulcis* stems could produce stable dispersions with ca. 5 nm thick hBN sheets that would remain stable for up to 18 days. In the same year, Wang and coworkers applied a soy protein isolate (SPI) as a natural surfactant for hBN dispersion.[137] After a combination of tip and bath sonication, they could produce a dispersion concentration of 0.65 mg/mL that was used to prepare cellulose nanofiber composite films.[137] The same year, two polysaccharides, pectin[46] and ethyl cellulose (EC),[138] were introduced for hBN dispersion. Yang and coworkers dispersed hBN in 50:50 water:IPA solutions, with pectin as a stabilizer, through a combination of stirring and ultrasonication.[46] The dispersed material was stable for at least 360 hours and was used to make pectin aerogels with improved thermal stability, mechanical properties, and flame retardancy as compared to neat pectin (Figure 10).[46] Moraes and coworkers stabilized hBN with EC through shear mixing in ethanol.[138] The exfoliated hBN was thin (about 2 nm) with small lateral sizes (< 100 nm), making it ideal for hBN ink printing. The materials were redispersed in solvents ideal for different types of printing and used to make ion-conductive printed films and printed separators for Li-ion batteries.[138]

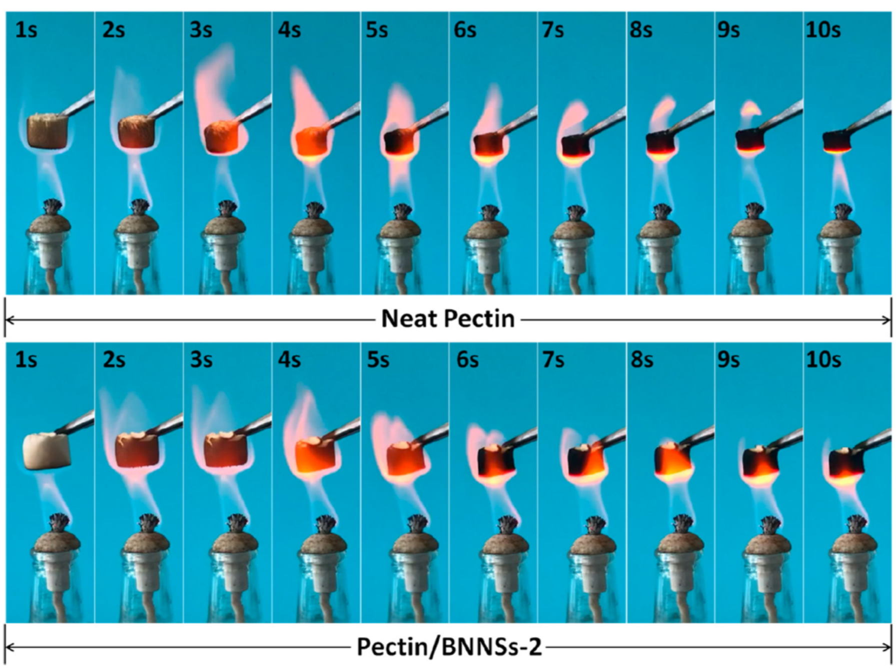

Figure 10. The burning behaviors of neat pectin and a pectin/hBN aerogel (pectin/BNNSs-2) over 10 seconds. Reprinted with permission from Ref [[46]] (W. Yang *et al. Composites Part A,* 2019, *119*, 196-205.) Copyright © 2019 Elsevier.

In 2021, Kode reported a non-covalent complexation of hBN and DNA to make dispersions in phosphate buffered saline solutions, with concentrations up to 8% in mass.[139] Quian and coworkers studied the use of flavin mononucleotide (FMN) for liquid phase exfoliation of hBN.[140] They determined that FMN self-assembles on hBN via π-π interactions and intermolecular hydrogen bonds, which was initially predicted by molecular dynamic simulations. Experimental work showed they obtained hBN sheets with an average thickness of 5.7 nm and dispersions in water with a concentration of 0.38 mg/mL.[140]

Table 6: Summary of hBN dispersions exfoliated directly by biomolecules*

Biomolecule	hBN Source	Method of Exfoliation	Method for Dispersion	Solvent	Concentration	Thickness	Lateral Size	Stability	Application	Ref
alginic acid (AA)	Sigma-Aldrich	30 min tip sonication	Same as exfoliation	Water	Not reported	Not reported	306 ± 504 nm	Less than 7 days	Microbial toxicity studies	45
sodium alginate (SA)	Not reported	Stirred and bath sonicated in SA solution for 10 h, then centrifuged at 9000 rpm for 10 min	Redispersed in water by sonicating 2 h, and centrifuged again at 1500 rpm for 10 min	Water	0.86 mg/mL	Not reported	Not reported	More than 10 hours	Layer-by-layer assembly, unsaturated polyester resin composites	135
plant extracts	Sigma-Aldrich	hBN was bath sonicated in plant extract for 24, then the solution was allowed to settle overnight before centrifuged at 15,000 rpm for 60 min	Freeze-dried hBN was redispersed in water	Water	Up to 23%	Thickness: <7 nm in *Panax ginseng*, *Morus nigra*, and *Hovenia dulcis*	77.7 nm	For PG, MN, and HD dispersions, stable for 18 days	Removal of cationic and anionic dyes, radical scavenging activity, polymer composites	136
soy protein isolate (SPI)	Dandong Rijin Science and Technology Co.	Tip sonicated for 12 h in ice bath, then 1 h in bath sonicator; centrifuged at 3000 rpm for 15 min	Same as exfoliation	Water	0.65 mg/mL	Not reported	Not reported	Not reported	Thermally conductive biocomposites	137
pectin	Aladdin Reagent Co.	hBN was sonicated and mechanically stirred for 12 h, then centrifuged at 4000 rpm for 10 min. The supernatant was tip sonicated (40% amplitude, 5 s on, 5 s off) for an additional 2 h	hBN in water was mixed with solution of pectin in water and sonicated 1 h	Water/IPA	Not reported	Not reported	Not reported	At least 360 hours	Bio-composite hydrogel	46
ethyl cellulose (EC)	Sigma-Aldrich	Dispersed in an EC/ethanol and shear mixed for 120 min at 10,230 rpm, then centrifuged at 4000 rpm for 20 min	Redispersed in EC, then dispersed in a cyclohexanone/terpineol solution at 85/15 v/v by bath sonication for 6 h	Several including ethanol, ethyl lactate	5.1 wt.% in cyclohexanone/ terpineol ink; 45 wt.% from partial evaporation	2.4 ± 1.2 nm	<100 nm	Not reported	Nanosheet ink	138
DNA	Momentive	Tip sonicated in PBS buffer with DNA (1:2 hBN:DNA ratio) for 1 h, then centrifuged at 3260g for 30 min	Same as exfoliation	Water/PBS buffer	19.04 ± 5.10 % in PBS	Not reported	Not reported	Not reported	Cell cytotoxicity studies	139

flavin mononucleotide (FMN)	Alfa Aesar	hBN was ball milled for 20 h at 100 rpm, then mixed and milled with FMN at 100 rpm for 3 h. The powder was recovered by adding water and bath sonicating for 1 h and centrifuging at 950g for 45 min	Redispersed by bath sonication in water	Water	0.380 mg/mL obtained by dialysis	151 nm (average)	5.7 nm (average)	Several weeks	Comparison to MD simulations, powder for analysis	[140]

7. Intercalating Agents

As can probably be inferred from the name, intercalating agents can populate the interlayer region between hBN sheets promoting interlaminar expansion and exfoliation. With only a couple exceptions, most intercalating agents can be broken into two categories: acids or salts. In either case, ions intercalate between neighboring hBN sheets and disrupt the interlayer interactions. A summary of these techniques can be found in Table 7.

7.1 Intercalating Acids

H_2SO_4 has been reported twice as an intercalating acid, although very different methodologies were utilized for obtaining exfoliated sheets.[141,142] In 2013, Du and coworkers reported one technique that used a combination of H_2SO_4, $KMnO_4$, and H_2O_2.[141] First, hBN was stirred for 12 hours in H_2SO_4 with $KMnO_4$. The authors propose that during this time, H^+ ions intercalate between hBN layers, increasing their spacing, while $KMnO_4$ decomposes into MnO_2 nanoparticles which can also intercalate into the, now increased, interlayer spaces.[141] After 12 hours, H_2O_2 is added to the mixture, which can remove the nanoparticles and, in the process, produce O_2 gas, which accelerates the expansion and completes the exfoliation (Figure 11). This method is effective at exfoliating hBN, producing hBN sheets approximately 2 layers thick and about 4 μm wide.[141] In 2018, Wang and coworkers also reported a method using H_2SO_4 for hBN exfoliation.[142] They stirred hBN in concentrated H_2SO_4 for 9 hours to allow the acid to intercalate between hBN sheets and then quickly poured the mixture into water, which rapidly generates heat and completes the exfoliation of hBN. Using this method, they produced dispersions with 3-6 layer hBN sheets and concentrations up to 0.195 mg/mL that were stable for over 2 weeks.[142]

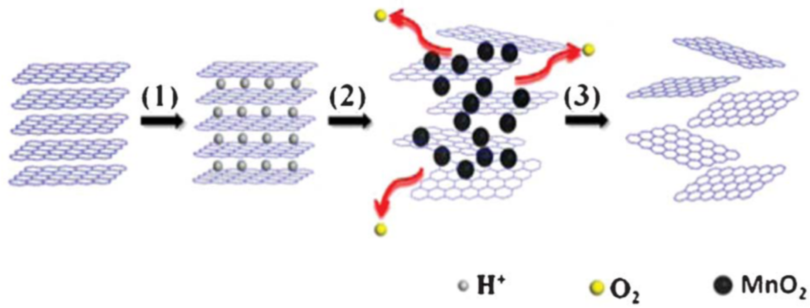

Figure 11. Scheme demonstrating the 3-step hBN exfoliation by H_2SO_4, $KMnO_4$, and H_2O_2. Reprinted with permission from Ref [[141]] (M. Du *et al. CrystEngComm,* 2013, *15*, 1782.) Copyright © 2013 The Royal Society of Chemistry.

H_3PO_4 has also been reported as an intercalating agent for hBN.[143,144] In 2013, Kovtyukhova and coworkers reported the preparation of stage 1 intercalation compounds by the thermal drying of hBN in Bronsted acids, such as H_3PO_4.[143] In 2017, these compounds were used to prepare hBN dispersions in different solvents by stirring and heating them to 120˚C for 3 hours or 45 hours, depending on the solvent.[144] Using this method, hBN could be dispersed in IPA, n-pentanol, 3-octanol, n-octanoic acid, and DMF. However, to obtain large monolayers of hBN, less polar solvents with longer alkyl chains, such as octanoic acid, were found to be optimal, while more polar solvents, such as DMF, did not produce monolayers larger than 1 µm.[144] The authors propose that formation of hydrogen bonds is necessary for stabilization of large sheets and that aprotic, polar solvents can morphologically damage the monolayers.[144]

This year, Wu and coworkers used solution-assisted ball milling with tannic acid (TA) to produce boron nitride nanosheets, using the shear forces to induce exfoliation of the hBN layers.[145] The phenyl groups of TA interrupt the π-π stacking interactions of the layers and promotes exfoliation while also acting as a stabilizer. BNNS-TA have improved hydrophilic properties, which produced a dispersion of 40 mg/mL and remained stable in water for at least a week. AFM and TEM show a thickness of about 1.5 nm and average particle size of 3.4 µm. TGA, FTIR, and XPS confirm the interactions between the TA and the BNNS. BNNS-TA were also integrated into epoxy, providing elevated thermal and mechanical properties, which were compared to commercial thermal pads for improved heat dissipation.[145]

7.2 Salts

The most common salts used for exfoliating hBN are NaOH and KOH, but, as with H_2SO_4, there are various methods to achieve this intercalation. In 2013, Li and coworkers reported exfoliation of hBN by grinding it in molten NaOH/KOH and then heating to 180˚C for 2 hours.[47] The exfoliated hBN (about 4 nm thick) could then be redispersed in water or ethanol and remained relatively stable for 1 month.[47] A very similar method was reported in 2019, but the mixture was added to water instead of using molten salts and produced a very comparable result.[146] Zhao and coworkers also used NaOH, but they prepared a concentrated solution in water, which was stirred with hBN so that Na^+ and OH^- ions could intercalate between the sheets.[147] After evaporating the water and washing excess salt, the exfoliated hBN (about 2-3 nm thick) could be dispersed in water and alcohols.[147] Finally, in 2019, another method was reported that involved dispersion in water with a Li_2SiF_6/NaOH mixture.[148] After stirring for 60 hours, hBN with lateral sizes > 1 µm and thicknesses < 5 layers were dispersed in water at concentrations up to 12.78 mg/mL. The authors proposed that the adsorption of SiF_6^{2-} to the hBN leads to interlayer expansion through electrostatic repulsion which can facilitate the intercalation of Li^+ and Na^+ cations into the interlayer space.[148] To further test this mechanism, they tried replacing the different ions and found they were all necessary for exfoliation and dispersion to take place.[148]

In addition to hydroxides, other salts composed of small cations are ideal for use as intercalating agents. In 2018, Ortiz and coworkers used $ZnCl_2$ and KCl as intercalating salts in gelatin.[48] After sonicating at 50˚C for 3 hours and burning off the gelatin, they obtained dispersion yields up to 16.3% of the starting material with 1-3 nm thick hBN sheets. Comparing the two salts, they found that KCl produced thinner sheets and larger yields, likely due to the larger size of the K^+ ion which can weaken the inter-sheet interactions more effectively.[48] Wang and coworkers investigated LiCl as an intercalating agent for hydrothermal exfoliation.[149] They dispersed hBN and LiCl in a variety of solvents and heated the mixture in an autoclave for 12 hours to yield dispersed, exfoliated hBN sheets. Of the 5 solvents tested, 1-octanol, IPA, DMF, NMP, and water, they found that IPA produced the highest concentration dispersion (4.13 mg/mL).[149] Later, LiCl and NaOH were also used in combination with high temperature treatment by first heating hBN to 800°C for 1 h to increase the interlayer distance, weaken the Van der Waals forces between them, and oxidize the hBN.[150] It was then kept in a NaOH/LiCl aqueous solution at 180°C with agitation to intercalate OH^- and Li^+. Dispersions in IPA/water remained stable for a week and were then used to spin a nanocomposite fiber with polyamide acid.[150] In 2019, a variety of salts, including sodium citrate, sodium tartrate, ammonium oxalate, and ethylenediaminetetraacetic acid disodium salt, were used as intercalating agents in NMP dispersions.[151] After hBN was sonicated in each of the salt solutions, it was found that ethylenediaminetetraacetic acid disodium salt produced the best dispersions, reaching concentrations of 1.8 mg/mL with 1-4 layer hBN sheets (36x better than NMP alone).

7.3 Other Intercalating Agents

There have been 2 intercalating agents reported that did not fit into the above categories: carbon quantum dots (CQDs)[152] and supercritical CO_2.[12] In 2016, Zhang and coworkers used CQDs, prepared from urea and citric acid, as intercalating agents for hBN dispersed in water.[152] After sonicating and heating the mixture to 60˚C for 60 hours, a concentration of 0.19 mg/mL of hBN sheets (approximately 6 nm thick) was produced and used as an aqueous lubricant.[152] In 2017, Tian and coworkers utilized supercritical CO_2 to exfoliate hBN.[12] After mixing hBN with supercritical CO_2 under high-speed stirring, the researchers rapidly depressurized the system, causing the gas to expand and break apart the interlayer interactions (Figure 12). This process was repeated 8 times and the exfoliated material was dispersed in IPA.[12] Though they could obtain a higher concentration dispersion after exfoliation, the addition of a stabilizing agent was needed to prepare stable dispersions over time. Regardless, they were able to use the exfoliated hBN sheets to make epoxy resin composites with improved thermal conductivity.[12]

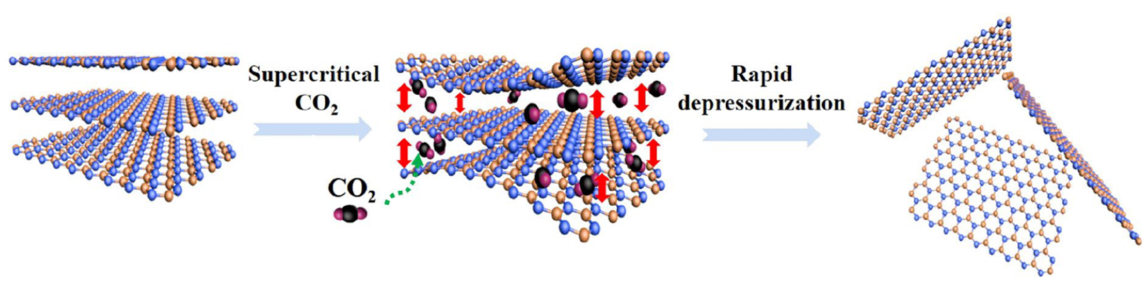

Figure 12. Schematic representation of hBN exfoliation by supercritical CO_2 depressurization. Reprinted from Ref [12] (X. Tian *et al. Scientific Reports,* 2017, *7*, 17794.) Copyright © 2017 Springer Nature.

Table 7. Summary of hBN dispersions exfoliated by using intercalating agents

Intercalating Agent	hBN Source	Method of Exfoliation	Method for Dispersion	Solvent	Concentration	Thickness	Lateral Size	Stability	Application	Ref
H_2SO_4; MnO_2 nanoparticles through in situ reaction	Alfa Aesar	hBN was stirred in H_2SO_4 and $KMnO_4$ for 12 hours, then H_2O_2 was added and centrifuged 10 min at 3000 rpm	Same as exfoliation	Concentrated H_2SO_4 (98% w/w)	Not reported	1.44 nm	4 µm	Not reported	Powder for analysis	141
H_2SO_4	Boron Nitride Factory, Qingzhou	hBN was stirred in concentrated H_2SO_4 for 9 h at room temperature, sonicated in water for 0.5 h, then centrifuged	Solid was redispersed in water, then settled overnight	Water	0.195 mg/mL	85% of sheets <5 layers thick	0.6 µm (average	At least 2 weeks	Dye adsorption	142
H_3PO_4	UK Abrasives	hBN was mixed with H_3PO_4 and kept at 120℃ on glass slides. The sample was added to solvent and stirred at high temperature for 3 h or 45 h and settled at room temperature for 40-45 days	Powder dispersed in solvent by stirring	Hexane, toluene, DMSO, NMP, IPA, n-pentanol, 3-octanol, n-octanoic acid, DMF	Not reported	Few layered	<100 nm to 3 µm	At least 3 hours	Powder for analysis	144
$HClO_4$, H_2SO_4, H_3PO_4	UK Abrasives	hBN was added to acid and stirred with glass stick then allowed to settle. Excess acid was poured away, and suspension was deposited on Si wafer and dried	Same as exfoliation	Water	Not reported	Not reported	Not reported	Not reported	Powder for analysis	143
tannic acid (TA)	Dandong Chemical Research Institute Co.	hBN was sonicated in a TA/water mixture for 10 min. The mixture was ball milled at 400 rpm and centrifuged at 2000 rpm for 10 min	hBN-TA was sonicated in ethanol for 30 min	Acetone, ethanol	40 mg/mL	1.5 nm	3.4 µm	Up to 1 month	Epoxy composites	145
molten NaOH and KOH	Alfa Aesar	NaOH and KOH were added to hBN and ground finely, placed in a PTFE-lined autoclave and heated at 180℃ for 2 h before cooling to room temperature	Dried powder was bath sonicated for 1 min, settled for 1 month	Water, ethanol	0.191% yield	4 nm per sheet, reported as <10 layers per stack	Not reported	~ 1 month	Powder for analysis	47
NaOH/KOH	Not reported	NaOH and KOH were mixed in a homogeneous reactor with hBN and placed in a PTFE-lined stainless-steel autoclave in a rotator oven for 2 h at 20 rpm at 180℃, bath sonicated 30 min,	Dispersed in base oil	Water, base oil	0.2 mg/mL in base oil	1.38-1.50 nm	0.2-0.5 µm	In base oil, less than 1 week	Tribological property assessment as hBN-based oils	146

		then centrifuged at 3000 rpm for 10 min								
NaOH	Alfa Aesar	hBN was dispersed with magnetic stirring in a saturated solution of NaOH at 30°C, then evaporated at 80℃ for 12 h	Powder was dispersed in 20 mL water, then centrifuged 30 min at 1000 rpm	Water, alcohols	Not reported	~2-4 layers with each being ~1 nm	1-2 µm	Not reported	Powder for analysis	147
Li_2SF_6/NaOH, K_2SiF_6/NaOH, and $(NH_4)_2SiF_6$/NaOH (Li^+, K^+, NH_4^+ ions)	Sigma-Aldrich	hBN was stirred in Li_2SF_6/NaOH and at 500 rpm for 60 h at 25℃, followed by centrifugation at 2000 rpm for 30 min	Redispersed in water by bath sonication	Water	12.78 mg/mL	Average 2.2 layers	Average 2.7 µm	Not reported	Thermally conductive papers	148
KCl, $ZnCl_2$	Saint Gobain	hBN was stirred in water and gelatin at 80℃, then $ZnCl_2$ and KCl were added, and the mixture was tip sonicated at 50℃ for 3 h, centrifuged at 3000 rpm for 30 min, and 600 rpm for 30 min	Same as exfoliation	Water/ gelatin solution	Not reported	1-3 nm for K^+ and 2-16 nm for Zn^{2+}	10-80 nm for K^+, 10-120 nm for Zn^{2+}	Not reported	Powder for analysis	48
Li+ through LiCl source	Ourchem	hBN was dispersed in solvent with LiCl, then placed in a Teflon-lined stainless-steel autoclave and stirred at 500 rpm for 12 h at 180℃. Centrifuged at 500 rpm for 5 min	Same as exfoliation	1-octanol, IPA, DMF, NMP, water	~55% or up to 4.14 mg/mL (in IPA)	~2 nm	~10 µm	Not reported	Photocatalytic applications for the degradation of methyl orange	149
NaOH/LiCl	Suzhou YuanTeXinCai Ltd.	hBN was heated at 800℃ for 1 h in air, then stirred with water, NaOH, and LiCl at 500 rpm for 2 h at 180℃. Bath sonicated for 30 min then centrifuged at 150g for 10 min	Same as exfoliation	Water	Up to 3.78 mg/mL	~2.58 nm	1.18 µm	At least 1 week	Nanocomposite paper	150
Sodium citrate, sodium tartrate, ammonium oxalate, potassium sodium tartrate, ethylenediaminetetraacetic acid	Aladdin Reagent Co.	hBN was mixed with the binary organic electrolyte solution and bath sonicated, then centrifuged at 1644g for 40 min. The supernatant was centrifuged again at 10,278g for 10 min and washed by repeated cycles of sonication centrifugation	Same as exfoliation	NMP	up to 1.8 mg/mL (in ethylenediaminetetraacetic acid disodium /NMP)	85% of sheets between 0.4-1.8 nm	~100 nm	Not reported	Powder for analysis	151
carbon quantum dots (CQDs)	Tianjin Heowns Biochemical Technology	hBN and CQDs were bath sonicated in water at 60℃ for 60 h, then centrifuged at 600g	Same as exfoliation	Water	0.019 wt%	0.68 nm	Not reported	Not reported	Lubricant	152
supercritical CO_2	Liaoning DCEI Co.	hBN was heated to 60℃ in a reactor, and gaseous CO_2 was cooled to liquid and transported to the reactor. The CO_2 was gasified and pressurized to 12	Treated hBN was sonicated in IPA then centrifuged at	IPA	up to 0.04 mg/mL	Between 5-9 layers	Length 1.23 µm and width 0.76 µm	20% of flakes precipitate after 24 hours	Epoxy composites	12

		MPa, stirred with a magnetic stirring rotor for 1 h at 12 rpm, then vented and collected	1500 rpm for 45 min								

8. Thermal Expansion

Some groups use increased temperatures or rapid temperature changes to break hBN interlayer interactions and obtain exfoliated sheets. This technique generally relies on rapid gasification of a liquid[10,49,50,153] or sonication at increased temperatures where stacking interactions are weakened.[154,155] Table 8 summarizes the details for these types of dispersions.

Liquid exfoliation by rapid temperature change and gasification was first demonstrated in 2016 by Rafiei-Sarmazdeh and coworkers.[49] Their method involved heating hBN to 1000-1400˚C within 30 minutes and rapidly quenching it to room temperature by using a cool aqueous solution containing 1.5 wt.% NH_4HCO_3. The hot hBN quickly evaporates the water and decomposes the NH_4HCO_3.[49] The pre-stressed hBN is then added to a water/ethanol solution and sonicated at low power for 8 hours to produce exfoliated hBN sheets (< 2 nm thick) at a concentration of about 1.5-2 mg/mL.[49] Zhu and coworkers also demonstrated a gas exfoliation procedure, first heating hBN to 800˚C for 5 minutes and then quickly immersing it in liquid nitrogen until the nitrogen gasified completely.[50] This process was repeated 10 times and then the pre-stressed hBN could be dispersed in alcohol with 30 minutes of sonication. Density functional theory calculations found that thermal expansion of the hBN layers allows nitrogen to intercalate which is followed by gas exfoliation.[50] Later, in 2018, Sun and coworkers used gasification of water to exfoliate hBN.[10] They first heated hBN to 800˚C for 10 minutes and then quickly cooled the mixture in ice water (0˚C), which rapidly gasifies the water. After repeating this process 7 times and freeze drying the resulting supernatant, the exfoliated hBN sheets (1-3 nm thick, 1-2 µm lateral) can be dispersed in water up to concentrations of 3 mg/mL.[10] Finally in 2019, Cheng and coworkers pre-impregnated hBN with oxalic acid to increase the amount of decomposing gases that can disrupt the Van der Waals interactions between the layers when exposed to 800°C temperature for 2 hours.[153] The procedure was repeated three times. AFM and TEM showed the sheets are about 2 nm thick (about 6 layers) and had a lateral size of 100-200 nm, while also indicating the crystalline structure of hBN remained after the high temperature procedure. XPS showed a partial doping of O atoms into the nanosheets during the exfoliation process. The exfoliated hBN was used as an additive in oil, which exhibited improved anti-friction performance.[153]

In 2017, Yuan and coworkers demonstrated the usefulness of thermal expansion-assisted ultrasonic exfoliation.[154] They started with hydroxylated hBN sheets, heated them to 200˚C under H_2 gas for 90 seconds, and then probe sonicated in IPA for 1 hour. With this method, they obtained a yield of about 26% of exfoliated hBN sheets (approximately 1-5 layers, 1-3 µm lateral).[154] The exfoliated hBN was used as a filler in thermoplastic polyurethane elastomer composites (TPU) for improved thermal conductivity.[154] In 2019, Tian and coworkers sonicated hBN in a 60% *t*-butanol/water solution at 82˚C and high pressure for 2 hours (Figure 13a).[155] At elevated temperature and pressure, solvent molecules could permeate hBN layers and evaporate to exfoliate hBN sheets. This procedure produced hBN sheets which were about 4-6 BN layers thick and 1-2 µm in size (Figure 13b-c).[155] In 2019, Zhu and coworkers combined a water freeze-thaw technique with PVP as a stabilizer in hopes of increasing dispersion concentration and stability.[118] In this technique, a freeze-thaw cycle in which a water/PVP/hBN mixture is strongly agitated for 12 hours at 4˚C, cooled to -26˚C for 12 hours, thawed to room temperature, and then sonicated, is repeated 30 times to obtain well exfoliated hBN sheets (1-3 layers). The final concentration in water reached 1.64 mg/mL and was stable for several months.[118] It was proposed that this method works by the PVP adsorbing to the hBN surface through strong hydrophobic and π-π interactions for stability and the water molecules intercalating between hBN sheets at 4˚C and then expanding when frozen.[118] In 2022, Zheng and coworkers also reported a solid suspension method for exfoliating hBN.[156] They suspended hBN above their solvent (DMF, NMP, ethanol, or IPA) using nickel foam, then heated the reactor vessel to 150˚C for 12 hours. They found that this solid suspension method increased contact between the solvent and hBN to promote exfoliation without mechanical agitation, resulting in relatively large nanosheets (about 1 µm diameter). The same procedure was also applied to MoS_2, WS_2, and graphene to demonstrate the versatility of this method.[156] Finally, in 2023, E and coworkers studied the mechanism of solvothermal exfoliation.[157] They first pre-treated their hBN by ball milling, then sonicated the powder in either NMP, DMF, acetonitrile, or IPA. They found that the addition of LiCl and cetyltrimethyl ammonium bromide (CTAB) during the sonication process improved the dissociation of hBN, where the Li^+ ions and CTAB were suggested to intercalate the hBN layers through cation-π interactions.[157] Furthermore, they determined that the solvothermal process causes dissociation of hBN, forming the byproducts $B(OH)_3$, $NH_4B_5O_8{\cdot}4H_2O$, and $(NH_4)_2B_{10}O_{16}{\cdot}8H_2O$ as demonstrated by XRD, XPS, and FTIR.

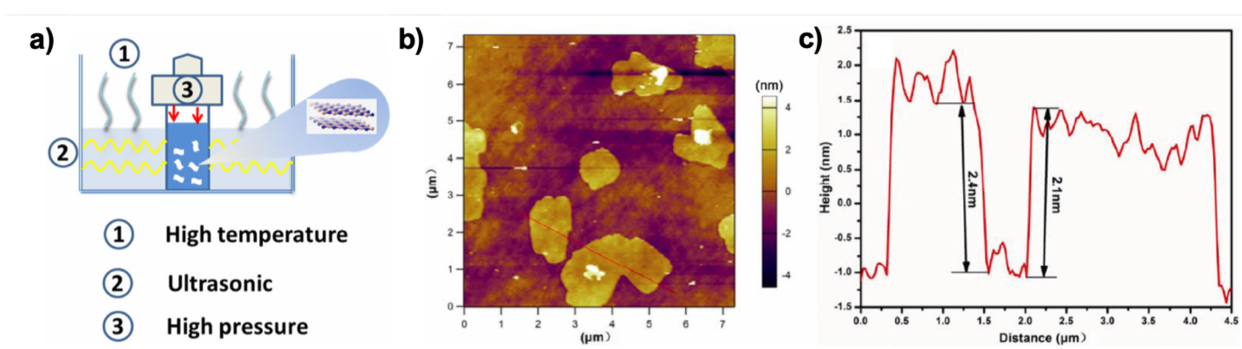

Figure 13. (a) Schematic of sonication-assisted hydrothermal method for hBN exfoliation. (b) Representative AFM image and (c) corresponding height profile of the exfoliated hBN. Reprinted from Ref [155] (Z. Tian *et al. J. Adv. Ceram.* 2019, *8*, 72-78.) Copyright © 2019 Springer Nature.

In 2018, Rizvi and coworkers described a different approach using expansion of high-pressure gas to exfoliate several 2D nanomaterials, which was named compressible flow exfoliation (CFE). This strategy presented several advantages including being a faster, continuous process and producing fewer defects on the materials.[158] The hBN is suspended in a carrier gas at high pressures and vented into IPA as the dispersion solvent for collection. They achieved concentrations of 0.075 mg/mL with an hBN sheet thickness of 2 nm and width of 350 nm, where a higher pressure in CFE resulted in better flake quality. Concentrated suspensions of hBN were mixed with a polyethylene terephthalate (PET) resin to create films by extrusion.[158] Finally, the exfoliation method based on supercritical CO_2 described in the previous section can also be classified as a thermal expansion method.[12]

Table 8: Summary of hBN dispersions exfoliated by thermal expansion

hBN Source	Method of Exfoliation	Method for Dispersion	Solvent	Concentration	Thickness	Lateral Size	Stability	Application	Ref
Aldrich	hBN was heated to 1000-1400℃ within 30 min and rapidly cooled to room temperature using NH_4HCO_3	Dispersed in water/ethanol mixture, bath sonicated for 8 h, and centrifuged at 3000 rpm for 20 min	Water, water/ethanol	Not reported	<2 nm	500 nm to 3 µm	Not reported	Powder for analysis	[49]
Sigma-Aldrich	hBN was heated to 800℃ under air, then immersed in liquid nitrogen until the liquid nitrogen gasified completely (repeated several times)	Dispersed in alcohol and sonicated 30 min, centrifuged for 10 min at 800 rpm	Alcohol	Not reported	Most <3 nm	50-500 nm	Not reported	Powder for analysis	[50]
Macklin	hBN was heated to 800℃ in air for 10 min then quickly transferred to an ice-water mixture and dried. This was repeated 3-7 times, then centrifuged at 5000 rpm for 15 min	Same as exfoliation	Polyacrylamide	Not reported	95% <4 nm	Not reported	Not reported	Composite hydrogels	[10]
Sinopharm Chemical Reagent Co. Ltd.	Oxalic acid ($H_2C_2O_4$) was added dropwise to hBN powder, then calcined at 800℃ for 2 h under nitrogen	hBN was sonicated in water for 5 min, then centrifuged at 3000 rpm for 10 min (repeated several times to give BNNS-1, BNNS-2, and BNNS-3). The supernatant was dried, and the powder was redispersed in several solvents	Ethanol, base oil	0.07 mg/mL in ethanol after 7 days	For BNNS-3, <6 nm	100-200 nm	Not reported	Oil additive as lubricant	[153]
Dandong Rijin Science and Technology Co.	hBN was stirred in NaOH at 80℃ for at least 72 h under reflux. Tt was washed with water then dried to obtain BN-OH. The furnace was flushed with Ar and heated to 200℃, then H_2 gas was introduced and BN-OH was placed in the furnace for 90 s.	Tip sonicated for 1 h in IPA then centrifuged for 30 min at 5000 rpm	IPA	Not reported	Average 3-4 layers	Average 1.6 µm	Not reported	Composite materials for thermal conductivity	[154]
Alfa Aesar	hBN and t-butanol were sonicated at 355 K in a TFE-lined stainless-steel reactor for 2 h, then centrifuged at 3500 rpm for 30 min	Same as exfoliation	t-butanol	Not reported	~2.4 nm	~1 µm	Not reported	Powder for analysis	[155]

Aladdin Reagent Co.	hBN was added to a PVA/water solution under strong agitation for 12 h at 4℃, frozen at -26℃ for 12 h, thawed, then sonicated for 30 min at 100 W (several cycles of process were repeated). The mixture was centrifuged at 3000 rpm for 30 min and the supernatant was centrifuged again at 10,000 rpm	Same as exfoliation	Water	1.64 mg/mL	<1.5 nm	350-500 nm	Not reported	Powder for analysis	118
Nanjing XianFeng Nano Co.	Solvent was added to a PTFE container with hBN above nickel foam, sealed in a stainless-steel autoclave at 150℃ for 12 h, then sonicated for 10 min. The mixture was centrifuged at 2000 rpm for 10 min	Same as exfoliation	DMF, NMP, EtOH, or IPA	Not reported	0.5-3 nm	~1 µm	Not reported	Composite polymer electrolyte film	156
Tianyuan Aviation Materials Technology Co.	hBN was ball milled for 12 h, then sonicated with LiCl and solvent for 30 min. The mixture was transferred to a stainless-steel autoclave and heated at 180℃ for 12 h, then cooled to room temperature	Same as exfoliation	NMP, DMF, MeCN, or IPA	Not reported	Not reported	~1 µm	Not reported	Powder for analysis	157
Momentive	hBN was suspended in a gas that passes through a flow compression channel, then allowed back to ambient conditions in solvent where they expand. Centrifuged at 1400 rpm for 90 min	Same as exfoliation	IPA	0.075 mg/mL	~4.2 nm	276 nm	At least 6 months	PET composites	158

9. Outlook and Conclusions

Overall, there are a wide variety of methods employed for the dispersion of hBN into solution. Depending on the desired solvent and application of the dispersion, each method can provide its own unique benefits.

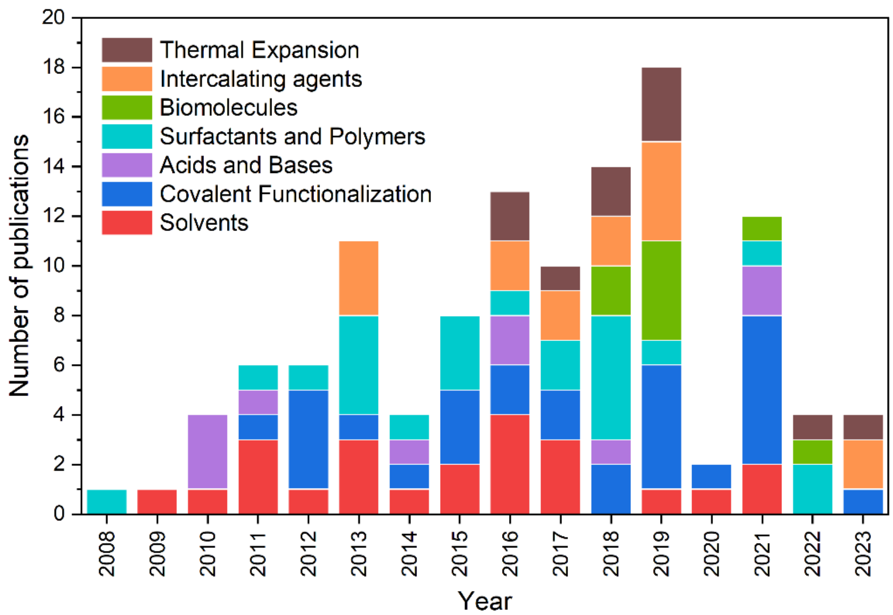

Figure 14. Publications on the exfoliation and dispersion of hBN referenced in this work, arranged by year of publication and method of exfoliation

Figure 14 shows all the publications reported in this work arranged by year and method of exfoliation. It becomes apparent that since the first report in 2008, publications on hBN exfoliation and dispersion have been steadily increasing in numbers in the past 15 years. While things slowed down during the pandemic it seems this area is again catching momentum. Some exfoliation techniques have been consistently studied and improved upon throughout the years including using solvents, covalent functionalization, and surfactants and polymers, which are also the techniques with the highest number of publications overall. For example, the first reports of hydrolysis of hBN had low concentrations of 0.05-0.1 mg/mL in water and thickness below 10 nm,[33] while reports seven years later show concentrations of up to 35 mg/mL with sheets 2 nm thin,[95] showing improvements in both concentration and exfoliation quality.

Interestingly, other techniques have seen increased interest in more recent years, such as thermal expansion, and particularly, biomolecules. Most studies using biomolecules (which begin to appear in 2018)[45,135] disperse hBN in water to produce biocompatible materials for biological applications.

Generally, works on hBN exfoliation have been consistent in reporting the morphology, thickness, and size of the sheets obtained, making it possible to compare between the works. While not all works report the concentration achieved in dispersion in the same way, primarily some report the yields from the initial amount of material while others report the concentration in dispersion, it is still possible to get a comparison of the amount of exfoliated hBN across the published literature. On the other hand, the stability of the dispersions is not always reported, in part because often times, the material is dispersed in a solvent to then immediately be integrated into another matrix, making the stability irrelevant. Nonetheless, for most cases, an important parameter is the amount of time the sheets can remain exfoliated.

When aiming to produce the largest, thinnest boron nitride nanosheets, a few trends can be observed. Solvents such as IPA and water [73], urea and glycerol [78], and ionic liquids [81] produced sheets 0.7 to 3 nm thin and 1-4 μm in lateral size. Several works that functionalized hBN with hydroxyl groups produced sheets between 2-3 nm thick and 1.5-3 μm in lateral size.[89–93,95,96] Protonating hBN with chlorosulfonic acid also produced large sheets of several micrometers in lateral size and few layers [111–113], with the largest one reported with 2nm thickness and 24.5 μm of length, obtained by stirring for 72 hours in the CSA.[112] A few more works using intercalating agents and thermal expansion consistently produced 1-2.5 nm thick sheets with lateral lengths from 0.6 μm. [12,49,141,142,144,145,147–150,154–156] Intercalating Li^+ ions produced the largest ones at 10 μm.[149]

This review shows that a wide variety of properties such as concentration, thickness, and size of the sheets can be obtained by using different methodologies. Thus, the exfoliation technique can be selected depending on the applications of the desired material. There are cases in which having a higher concentration of mostly single sheets is more important and a smaller lateral size is not relevant, while for other cases, large sheets are imperative for the application. Additionally, different exfoliation mechanisms provide better dispersions in particular solvents. For example, most biological applications require solubility in water, while to improve tribological properties of lubricants, miscibility with mineral oils is important. Therefore, it is imperative to keep the end goal of the material in mind in order to select the method of exfoliation to be employed. As the areas of application where hBN is utilized keep increasing, there is a need to continue optimizing its exfoliation and the dispersions to meet specific needs. By summarizing the research done on the exfoliation of hBN sheets, we have aimed to present the state-of-knowledge of the field and allow for a better understanding of how to control the properties of this material. This will allow us to tailor hBN for different applications and capitalize on its fullest potential.

Abbreviations

BN	boron nitride
hBN	hexagonal boron nitride
BNNS	boron nitride nanosheets
IPA	isopropanol
NMP	N-methyl-2-pyrrolidone
THF	tetrahydrofuran
PMMA	polymethyl methacrylate
TEM	transmission electron microscopy
HR-TEM	high resolution electron microscopy
PVA	polyvinyl alcohol
NEXAFS	Near Edge X-Ray Absorption Fine Structure
AFM	atomic force microscopy
PEO	polyethylene oxide
MEA	methanolamine
IL	ionic liquids
[bmim][Tf_2N]	1-butyl-3-methyl-imidazolium bis (trifluoromethylsulfonyl)imide

[emim][Tf_2N]	1-ethyl-3-methylimidazolium bis (trifluoromethylsulfonyl)imide
[emim][TfO]	1-ethyl-3-methylimidazolium trifluoromethanesulfonate
[bmim][TfO]	1-butyl-3-methyl-imidazolium bis (trifluoromethylsulfonyl)imide trifluoro-methanesulfonate
[bmim][PF_6]	1-butyl-3-methyl-imidazolium hexafluorophosphate
[bmim][BF_4]	1-butyl-3-methyl-imidazolium tetrafluoroborate
f-hBN	functionalized hBN
DCM	dichloromethane
MPC	methoxyphenyl carbamate
PBCE	poly(bisphenol A-*co*-epichlorohydrin)
FTIR	Fourier-transfom infrarred spectroscopy
XPS	X-ray photoelectron spectroscopy
TGA	thermogravimetric analysis
γ-APS	γ-aminopropyl triethoxysilane
HBP	hyperbranched aromatic polyamide
ODTES	octadecyltriethoxysilane
PEG	poly(ethylene glycol)

LDPE	low density polyethylene
ODA	octadecylamine
TOA	trioctylamine
TOP	trioctylphosphine
MSA	methanesulfonic acid
DMF	N,N-dimethylformamide
CSA	chlorosulfonic acid
DMSO	dimethyl sulfoxide
FITC	fluorescein isothiocyanate
PVP	polyvinylpyrrolidone
PDA	polydopamine
GA	gum Arabic
PT	polythiophene
PTPA	poly(3-thiophenezoic acid)
H3PT	poly(3-hexylthiophene-2,5-diyl)
P3TAA	poly(3-thiophene acetic acid)
PS	polystyrene

PC	polycarbonate
A-PPG	adenine-functionalized polypropylene glycol
HBPE	hyperbranched polyethylene
PSS	poly(sodium-4-styrenesulfonate)
SC	sodium cholate
SDS	sodium dodecyl sulfate
SDC	sodium dodecyl sulfate
SDC	sodium deoxycholate
DTAB	dodecyltrimethylammonium bromide
EC	ethyl cellulose
FMN	flavin mononucleotide
TA	tannic acid
CQD	Carbon Quantum Dots
CTAB	cetyltrimethyl ammonium bromide
CFE	compressible flow exfoliation
PET	polyethylene terephthalate

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