

EFFICIENT AND FACILE SYNTHESIS OF HYDROXY-FUNCTIONALIZED HEXAGONAL BORON NITRIDE NANOSHEETS BY ION-ASSISTED LIQUID PHASE EXFOLIATION METHOD

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Keywords	Abstract
Hexagonal boron nitride Nanosheets Functionalization Liquid phase exfoliation Probe sonication	Hexagonal boron nitride (h-BN) nanosheets have attracted significant attention due to their unique mechanical, thermal, and electronic properties. Their biocompatibility, thermal conductivity, chemical stability, and versatility make them indispensable in cutting-edge technologies. Hydroxy-functionalized h-BN nanosheets (h-BNNS-OH) exhibit immense potential in various applications, including electrochemical energy storage, drug delivery systems, and heat spreaders in thermal management systems. This study focuses on the hydrothermally ion-assisted liquid-phase exfoliation of h-BN powder to produce few-layer h-BNNS-OH. The exfoliation process involves hydrothermal treatment of bulk h-BN in the presence of concentrated aqueous solution of KOH and NaOH at 180 °C, followed by sonication for dispersion of h-BNNS-OH in water. Characterization of h-BNNSs was performed using powder X-ray diffraction (XRD), Raman spectroscopy, Fourier-transform infrared spectroscopy (FTIR), transmission electron microscopy (TEM), scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS). The resulting exfoliated h-BNNSs are hydroxyl-functionalized on their surface. This study demonstrates the effectiveness of the successive execution of the hydrothermal treatment in the presence of excess alkali metal hydroxides and probe sonication as a facile and efficient exfoliation process, resulting in dispersions of h-BNNS-OH in water with remarkably high stability (beyond 9 weeks) and high product yield (17 %) at only one exfoliation cycle.

İYON DESTEKLİ SIVI FAZLI EKFOLYASYON YÖNTEMİYLE HİDROKSİ FONKSİYONLU HEKZAGONAL BOR NİTRÜR NANOTABAKALARIN ETKİN VE KOLAY SENTEZİ

Anahtar Kelimeler	Öz
Hekzagonal bor nitrür Nanotabakalar Fonksiyonlandırma Sıvı faz ekfoliasyonu Prob sonikasyonu	Hekzagonal bor nitrür (h-BN) nanotabakalar, sahip oldukları sıra dışı mekanik, termal ve elektronik özellikler sayesinde son yıllarda önemli bir araştırma konusu haline gelmiştir. Biyoyumlulukları, yüksek ısıl iletkenlikleri, üstün kimyasal kararlılıkları ve çok yönlü yapıları, bu malzemeleri ileri teknoloji uygulamalarında vazgeçilmez kılmaktadır. Hidroksi grupları ile fonksiyonlandırılmış h-BN nanotabakalar (h-BNNS-OH'lar), elektrokimyasal enerji depolama, ilaç taşıma sistemleri ve termal yönetim uygulamalarında ısı yayıcı olarak kullanılma potansiyeli açısından dikkat çekmektedir. Bu çalışmada, h-BN tozunun hidrotermal olarak iyon destekli sıvı faz ekfoliasyonu yöntemiyle birkaç katmanlı h-BNNS-OH'ların sentezi amaçlanmıştır. Ekfoliasyon sürecinde, hacimli h-BN, konsantre sulu KOH ve NaOH çözeltisi varlığında 180 °C'de hidrotermal işleme tabi tutulmuş, ardından elde edilen ürün, sulu dispersiyon formunda h-BNNS-OH elde edilmesi amacıyla sonikasyona maruz bırakılmıştır. Üretilen h-BNNS'lerin karakterizasyonu; Fourier dönüşümlü kızılötesi spektroskopisi (FTIR), Raman spektroskopisi, taramalı elektron mikroskobu (SEM), enerji dağılımlı X-ışını spektroskopisi (EDS), X-ışını kırınımı (XRD) ve geçirimli elektron mikroskobu (TEM) teknikleri kullanılarak gerçekleştirilmiştir. Elde edilen h-BNNS'lerin yüzeylerinin hidroksil grupları ile fonksiyonlandırıldığı belirlenmiştir. Bu çalışma, fazla miktarda alkali metal hidroksit varlığında gerçekleştirilen ardışık hidrotermal işlem ve problu sonikasyonun, yalnızca bir ekfoliasyon çevrimi ile yüksek stabiliteye (9 haftadan daha uzun süre) ve yüksek ürün verimine (%17) sahip sulu h-BNNS-OH dispersiyonlarının elde edilmesi için etkili ve uygulanabilir bir ekfoliasyon yöntemi olduğunu ortaya koymaktadır.

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1. Introduction

Hexagonal boron nitride (h-BN) is a two-dimensional (2D) material composed of layers that exhibit sp^2 hybridization. Its structural configuration resembles that of graphite, featuring systematically stacked planes of boron nitride hexagons (Meziani et al., 2022). h-BN is characterized by the covalent bonding of alternating boron and nitrogen atoms into hexagonal layers, which are interconnected by relatively weak van der Waals forces. A key difference lies in the nature of the B-N covalent bonds, which exhibit polarity and partial ionic character due to the differing electronegativities of boron and nitrogen. In contrast to graphene, which features a uniform distribution of π electrons, h-BN displays diminished electron delocalization within its π bonds, as the lone pair electrons in the p_z orbitals of nitrogen atoms are more localized (Lei et al., 2021). These distinctive structural attributes of h-BN confer properties such as electrical insulation, high thermal conductivity, excellent chemical stability, exceptional resistance to oxidation, and hydrophobic characteristics, facilitating its use in applications including high-temperature crucibles, dielectric layers, anti-wear and corrosion coatings (Ren, Cui, Pu, Xue and Wang, 2017). A typical h-BN crystal exhibits a substantial particle size, a limited specific surface area, inherent chemical resistance, and no molecular binding sites on its surface. These characteristics hinder the ability of h-BN to effectively interact with other materials (Kim et al., 2020). Consequently, the chemical inertness of h-BN poses challenges for its functionalization.

h-BN nanosheets (h-BNNSs), often referred to as "white graphene" (de los Reyes et al., 2019), is a 2D material known for its remarkable properties, including high thermal conductivity (Cai et al., 2019), excellent chemical stability (Lei et al., 2021), mechanical robustness (Zhi, Bando, Tang, Kuwahara and Goldberg, 2009), thermal stability and electrical insulation (Li et al., 2015). Due to these outstanding properties, h-BNNSs are recognized as a highly promising inorganic material of the 21st century, offering a wide array of potential applications that include sectors like aerospace and healthcare technologies. Ultra-thin layers of h-BN have attracted substantial attention from researchers for a wide range of applications, including but not limited to nanoelectronics, photonics, heat spreaders, biomedical fields, anti-corrosion coatings, catalysis, separators of rechargeable batteries, and solid-state electrolytes (de Moraes et al., 2020; Fu et al., 2017; Zhang, Feng, Wang, Yang and Wang, 2017).

The exceptional configuration of h-BNNSs, which are atomically thin, imparts unique characteristics that distinguish them from other 2D materials. For instance, the mechanical response of few-layer BNNSs to indentation is markedly different from that of few-layer

graphene, the most thoroughly investigated 2D material. While graphene experiences a significant decline of more than 30% in mechanical strength as the number of layers rises from one to eight, the strength of BNNSs tends to remain relatively uniform regardless of the number of layers (Cai et al., 2024). Nevertheless, the potential of single or few-layer h-BNNSs for technological applications has been significantly limited due to the low efficiency in their production (Sun et al., 2016).

2. Literature Review

The crystalline structure of h-BNNSs is characterized by a layered arrangement with a hexagonal lattice, similar to pristine h-BN. The hydroxyl functionalization introduces slight modifications in interlayer spacing, enhancing its chemical reactivity and dispersibility in various matrices. The nanosheets typically exhibit a thickness of a few nanometers, corresponding to one to a few atomic layers, and lateral dimensions in the micrometer range. Morphologically, h-BNNSs are smooth and uniform, with sharp edges that facilitate integration into composite materials and interfaces. The diverse applicability of h-BNNSs underscores the need for scalable and efficient production methods capable of delivering high-quality, functionalized nanosheets (Gautam and Chelliah, 2021). The incorporation of hydroxyl groups into boron nitride (BN) materials has become a focal point of research aimed at improving their performance in micro- and nanoscale applications. This surface hydroxylation modifies the inherent properties of BN, facilitating an expansion of its potential uses across various fields (Ren, Stagi and Innocenzi, 2021).

Conventional methods such as chemical vapor deposition (CVD) and mechanical exfoliation face limitations in scalability and control over the number of nanosheets (Gautam and Chelliah, 2021). Liquid-phase exfoliation, particularly hydrothermal methods combined with ultrasonication, provides a promising route to overcome these challenges (Kong et al., 2024). Sonication is widely regarded as the predominant mechanical force employed in liquid exfoliation. The ultrasound process involves the formation and collapse of bubbles, which produce microjets and vibrational waves (Tan et al., 2017). Despite this method's ease of use and cost-effectiveness, its exfoliation efficiency, when applied independently, is remarkably low. As a result, it is commonly used as a secondary process in conjunction with other liquid-phase exfoliation methods, including intercalant-assisted exfoliation. This technique involves the introduction of selected ions or organic molecules into the layers, forming intercalation compounds that expand the spacing between layers and considerably diminish the interactions among them (Yang, Zhang and Xie, 2016).

Goni et al. reported 44% yield for dispersion of -OH functionalized h-BNNS by 12 h probe sonication time using very dilute solutions of 2-propanol (IPA) by repeating the liquid exfoliation procedure by 5 cycles (Goni, Chemelli and Uhlig, 2021). Other researchers synthesized hydroxylated h-BNNSs through a process of liquid exfoliation facilitated by molten hydroxide, utilizing bulk h-BN powder with lateral sizes ranging from 4-7 μm as the starting material. The yields of these syntheses were only below 10% at one exfoliation cycle. Using h-BN nanopowder and preparation of aqueous h-BN with alkali hydroxides may shorten the sonication time and increase the yield at one cycle (Fu et al., 2017; Wang et al., 2018).

In this study, h-BNNS with hydroxyl functionalization were synthesized by liquid phase exfoliation method in two main steps: i) hydrothermal treatment of h-BN nanopowder in the presence of hydroxides and ii) dispersion in water by using probe sonication. Utilizing this technique facilitates the production of h-BNNS-OH with more than 70% increase in the yield at only a single cycle while keeping the exfoliation time much shorter.

3. Materials and Methods

3.1. Materials

h-BN nanopowder with average particle sizes of 65-75 nm and 790 nm were purchased from Nanografi, Türkiye. Potassium hydroxide (KOH) and sodium hydroxide (NaOH) were commercially sourced from Tekkim, Türkiye. Hydrophilic polyvinylidene difluoride (PVDF) membrane filter (0.22 μm pore size) used in vacuum filtration was supplied from Merck Millipore. Deionized water (DI, resistivity $\geq 18 \text{ M}\Omega\cdot\text{cm}$) was employed in the dispersion of h-BNNSs in probe sonication.

3.2. Exfoliation and Functionalization of h-BN Nanopowder

12.71 g of KOH, 14.34 g of NaOH and 100 mL of distilled water are mixed in a PTFE dish. 5.01 g of h-BN powder is added to this solution and mixed vigorously. The resulting mixture was transferred to a stainless steel reactor, and the sealed reactor was heated to 180 $^{\circ}\text{C}$ in the oven and kept at this temperature for 2 h to facilitate chemical interaction, weakening the Van der Waals forces between the h-BN layers. After the hydrothermal treatment, the autoclave was cooled down to room temperature. The solid content is taken into a beaker with 500 mL of distilled water to dissolve excess hydroxides. At this point, the pH of the suspension is around 13-14. Then, the suspension is vacuum filtered and washed multiple times with DI water until the pH of the supernatant is between 5-6. This washing procedure ensures the removal of residual alkali reagents and any byproducts formed during the hydrothermal process. The white solid is then dispersed into 500 mL of DI

water and sonicated by a probe sonicator (Bandelin Sonolpuls HD 4400) for 10 min. The parameters for probe sonication are 0.5 s on/ 0.5 s off pulses, 75 % Amplitude (300 W). After probe sonication, the dispersion is centrifuged at 2000 rpm for 30 minutes to separate unexfoliated bulk material, and the supernatant containing exfoliated h-BN nanosheets is collected. A sample from the dispersion is taken to a small bottle and set aside in order to follow dispersion stability over time. The supernatant is then filtered by vacuum filtration, and the white solid is dried in the oven at 80 $^{\circ}\text{C}$ for 12 h and then dried further at 80 $^{\circ}\text{C}$ under vacuum.

Only changing the probe sonication time to 30 and 60 min, the aforementioned exfoliation procedure was repeated to evaluate the influence of probe sonication time on yield and morphology of h-BNNSs. The h-BNNS-OH obtained from probe sonication times of 10, 30 and 60 min were named as h-BNNS-OH-10, h-BNNS-OH-30 and h-BNNS-OH-60, respectively.

3.3. Characterizations

The structural and chemical characterizations of the fabricated h-BNNSs were performed by means of various techniques. XRD patterns were measured from 5–80 $^{\circ}$ 2 θ by powder X-Ray Diffraction (XRD, PANalytical Empyrean, PIXcel 1D Detector, Cu K α) for crystalline and chemical phase analyses. The Fourier transform infrared (FTIR, Perkin Elmer Spectrum Two) spectra were recorded in KBr mode to demonstrate the covalent bonding of -OH groups to the exfoliated h-BNNS. The range of wavelengths analyzed was from 4000 to 400 cm^{-1} , with a step size of 1 cm^{-1} . The samples in the powder form were completely dried before the preparation of their KBr pellets. The Raman spectra of h-BN and h-BNNS-OH were obtained utilizing a laser with 785 nm excitation in a Renishaw InVia Raman microscope. The surface morphology and elemental composition of the produced materials were analyzed using a Hitachi Regulus 8230 Field Emission Scanning Electron Microscope (FE-SEM) in conjunction with energy-dispersive X-ray spectroscopy (EDS), operating at a voltage of 10 kV. The characterization of the morphology of the exfoliated h-BNNS was conducted through Transmission Electron Microscopy (TEM, JEOL JEM 1220).

4. Results and Discussion

With an aim to produce a few layer h-BNNSs by efficient route, liquid-phase exfoliation of h-BN into h-BNNS-OH was done according to the scheme given in Figure 1. Presumably, homogeneous dispersion of h-BN in an aqueous concentrated solution of NaOH and KOH prior to the heating in autoclave increases the amount of partially exfoliated h-BN precursor, making the probe sonication step more efficient. The initial treatment of h-BN powder with highly concentrated aqueous solution

of alkali hydroxides aimed to facilitate the intercalation of K^+ , Na^+ , and OH^- ions into the interlayer regions of h-BN, a process motivated by the elevated chemical potential. Specifically, K^+ and Na^+ ions first adhere to the surface of h-BN before migrating into the spaces between neighboring BN lattices, resulting in the wrinkling or curling of the upper BN layer. The infiltration of supplementary ions into the interlayer space results in the detachment of the partially exfoliated h-BNNS from their original structure, a phenomenon attributed to the functionalization of boron nitride with hydroxyl groups. This phenomenon increases the interlayer distance at the edges of the BN layer, thereby promoting the further incorporation of alkali ions (Fu et al., 2017). At the end of the liquid-phase exfoliation, -OH functionalized h-BNNSs are successfully dispersed in DI water, while the unexfoliated h-BN lacks oxygen on its surface, which prevents it from forming a suspension and causes it to settle in water (Yuan et al., 2024).

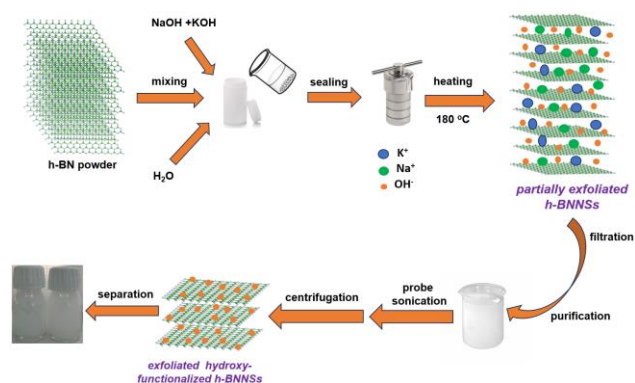


Figure 1. Schematic illustrating the fabrication of hydroxy-functionalized h-BNNS by hydrothermal ion-assisted liquid exfoliation method.

To evaluate the influence of sonication time on the yield and morphology of h-BNNS-OH, the fabrication procedure was performed by varying the sonication time at 10, 30, and 60 min. Starting with the bulk h-BN nanopowder, parameters of probe sonication were kept constant for each sonication period in order to reproduce the results and see the effect of sonication time.

The investigation into the crystalline nature of the fabricated h-BNNS-OH products was performed via powder X-ray diffraction (XRD) analysis, as depicted in Figure 3. The resulting XRD patterns demonstrate a highly crystalline structure, characterized by a prominent and sharp peak at $2\theta = 26.9^\circ$, which corresponds to the (002) plane of the hexagonal phase of boron nitride. Additionally, the four other weaker peaks with a slight broadening present in the patterns are associated with the (100), (101), (102), and (004) planes, observed at 2θ angles of 41.9° , 44.0° , 50.3° , and 55.2° , respectively (Sun et al., 2016). The peak positions

observed in BNNSs were nearly identical to those found in pristine h-BN powder. Comparison of the XRD spectra of h-BN nanopowder, h-BNNS-OH-10, h-BNNS-OH-30 and h-BNNS-OH-60 reveals that the peaks in all materials exhibit consistency in terms of diffraction angle and shape. This observation indicates that the exfoliation process through ion-assisted liquid phase exfoliation employing probe sonication did not compromise the crystalline structure of the original material. Consequently, h-BNNS-OH preserved the high crystalline integrity characteristic of bulk h-BN (Fu et al., 2017; Guerra, Wan, Degirmenci, Sloan, Presvytis and McNally, 2018; Rana, et al., 2021). Moreover, the amplified XRD patterns in the inset reveal that the intensity of the (004) peaks for OH-BNNSs is remarkably high when using the (100) plane as a baseline. It is commonly understood that exfoliation occurs predominantly on the (002) plane, which results in an increased number of (002) planes. When OH-BNNSs are randomly dispersed, they typically align with their largest facets. These largest facets represent the preferred orientations, namely the (002) or (004) planes, during X-ray diffraction (XRD) measurements. Thus, the XRD results further substantiate the effectiveness of the exfoliation process (Yuan et al. 2024).

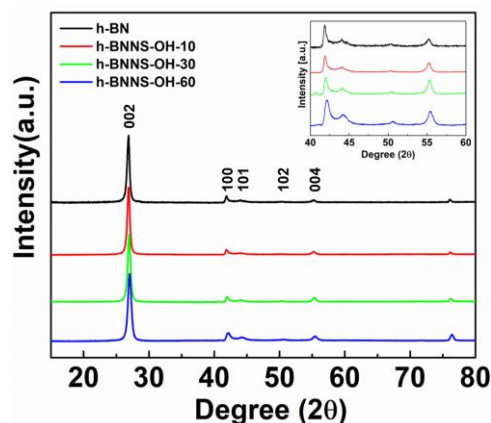


Figure 2. XRD patterns of pristine h-BN nanopowder, h-BNNS-OH-10, h-BNNS-OH-30 and h-BNNS-OH-60.

Figure 3 shows that Raman spectra of pristine h-BN powder and h-BNNS-OH produced through 10, 30 and 60 min probe sonication periods exhibit characteristic G band with a prominent E_{2g} peak at $\sim 1369\text{ cm}^{-1}$, which is indicative of the in-plane vibrational mode of h-BN (Gorbachev, Riaz, Nair, Jalil, Britnell, Belle, Hill, Novoselov, Watanabe, Taniguchi, Geim and Blake, 2011). The sharpness and intensity of the peak for all probe sonication times suggested minimal structural defects. The hydroxy-functionalized h-BN nanosheets exhibited no significant changes in Raman features, affirming that functionalization did not compromise the structural integrity (Rana et al., 2021; Wang, Li, Marsden, Bissett and Young 2021).

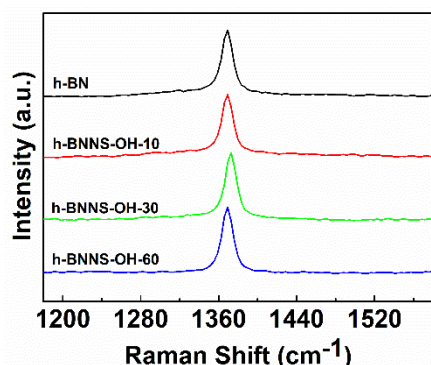


Figure 3. RAMAN spectra showing E2g peak for h-BN nanopowder, h-BNNS-OH-10, h-BNNS-OH-30 and h-BNNS-OH-60.

As shown in Figure 4, FTIR spectra exhibited characteristic absorption bands at 1379 cm^{-1} (B-N stretching mode) and 808 cm^{-1} (B-N-B bending mode) for h-BN and the exfoliated h-BNNSs. In the spectrum of h-BNNS-OH-10, the appearance of broad O-H stretching band at 3440 cm^{-1} confirmed the presence of surface hydroxyl groups, validating the functionalization process (Fu et al., 2017). Hydrothermal exfoliation did not lead to the formation of extra functional groups on the h-BNNS-OH surface, which can be attributed to the significant chemical stability of h-BN (Kong et al., 2024). This structural modification is critical for improving the chemical reactivity and dispersion of the nanosheets. On the other hand, the O-H stretching band was not significant in the case of h-BNNS-OH-30 and h-BNNS-OH-60.

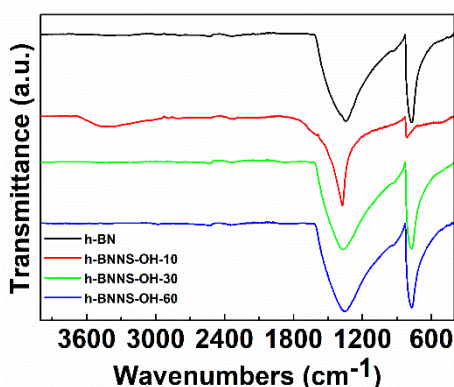


Figure 4. FTIR spectra of h-BN nanopowder, h-BNNS-OH-10, h-BNNS-OH-30 and h-BNNS-OH-60.

The scanning electron microscopy (SEM) images of the pristine h-BN powder before exfoliation, as depicted in Figure 6a-b, reveal characteristic layered structures characterized by their smooth surfaces and well-defined edges. Figure 6c-d illustrate the SEM images and the associated energy-dispersive spectroscopy (EDS) elemental mapping of the dispersed h-BNNS-OH on a silicon substrate. For h-BNNS-OH with 10 min sonication time, SEM analysis demonstrated that the exfoliated nanosheets exhibited lateral dimensions ranging from 60 to 200 nm. The nanosheets displayed

uniform and smooth surfaces and sharp edges, indicating successful exfoliation (Fu et al., 2017; Kong et al., 2024). The EDS elemental mapping depicted in Figure 5e-g indicates the presence of boron and nitrogen in the h-BNNS-OH, which was synthesized through a sonication process lasting 10 minutes. Concurrently, the oxygen detected is derived from the -OH surface functional groups on the h-BN sheets (Rana et al., 2021).

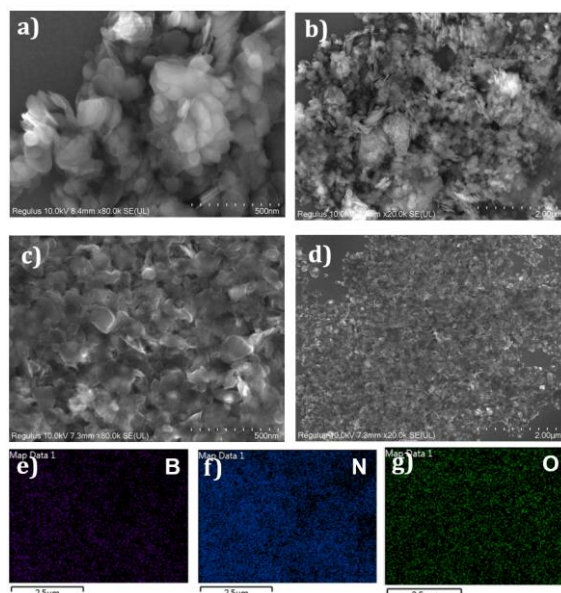


Figure 5. SEM images of (a)-(b) h-BN, (c)-(d) h-BNNS-OH-10, EDS elemental mapping images of (e) boron (B), (f) nitrogen (N), and (g) oxygen (O) in h-BNNS-OH-10.

On the other hand, SEM images of the liquid exfoliation procedure with longer sonication times (30 and 60 min) indicate significant reduction in lateral size and uniformity (Figures 6 and 7). In addition, they clearly reveal that longer sonication times result in less uniform size distribution. However, in their EDS mapping images (Figures 6c-e and 7c-e), it is seen that the structures contain only boron (B), nitrogen (N) and oxygen (O). It is understood from the SEM and EDS images that h-BNNS-OH nanosheets were obtained.

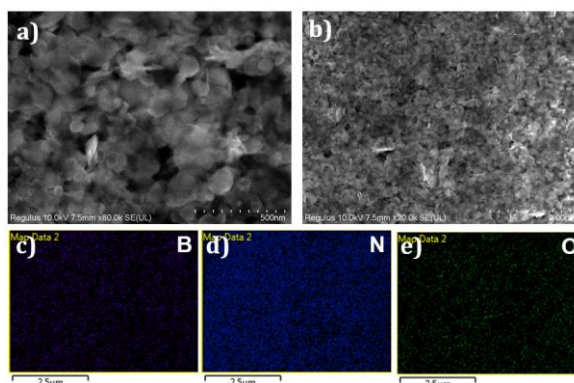


Figure 6. SEM images of h-BNNS-OH-30 (a-b), and EDS elemental mapping images of (c) boron (B), (d) nitrogen (N), and (e) oxygen (O) in h-BNNS-OH-30.

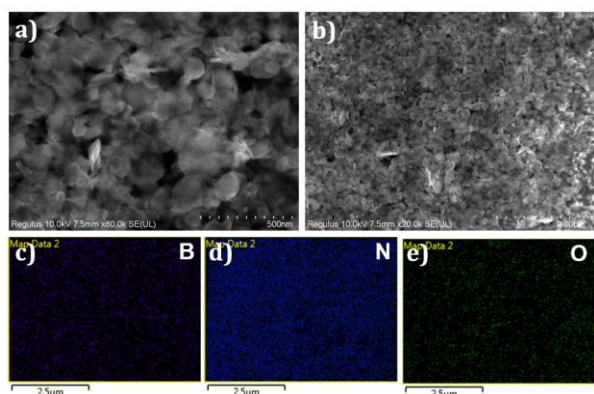


Figure 7. SEM images of h-BNNS-OH-60 (a-b), and EDS elemental mapping images of (c) boron (B), (d) nitrogen (N), and (e) oxygen (O) in h-BNNS-OH-60.

Figure 8 presents TEM images of hydroxyl functionalized h-BNNS, revealing that after the exfoliation process, the h-BNNSs take on a two-dimensional, sheet-like configuration similar to graphene. The presence of semi-transparent layers suggests the existence of very thin layers, which are observed alongside thicker flakes, as demonstrated by the darker areas in panels a to c. Especially, the nanosheets obtained via 10 min sonication time are exceptionally flat, with no evidence of bending or folding, and the edges are free from defects (Figure 8a). This suggests that the chemical exfoliation technique including 10 min probe sonication has resulted in minimal alteration to the nanosheets' structure (Guerra et al., 2018). Relative contrast of the layers in TEM images qualitatively showed thickness variations across the h-BN nanosheets. The semitransparent layers give the evidence about obtaining few-layer h-BNNSs. Also, the BNNSs exhibit a crumpled or pleated configuration and appear semitransparent when exposed to the electron beam, indicating their inherent ultrathin sheet-like nature (Figure 8 a).

To guarantee that the products obtained are exclusively h-BNNS-OH, the yields of different probe sonication times were assessed using the same purification and separation procedure. At the end of dispersion by probe sonication, the dispersion was filtered to obtain h-BNNS-OH in the solid form. The solid was dried in the oven at atmospheric pressure and then under vacuum. The dried product was then weighed. The yield of exfoliated h-BNNS was calculated based on the starting amount of bulk h-BN powder for each experiment. For sonication periods of 10, 30 and 60 min, the exfoliation procedure was performed twice and the average yields were calculated as 17, 19 and 22%, respectively. At the end of the evaluation, yield vs sonication time was plotted as shown in Figure 9, which shows that as the sonication time increases, the yield of liquid-phase exfoliation increases. Nevertheless, the increase in the yield is not directly proportional to the time. The hydrothermal alkali salt pretreatment-assisted

exfoliation method achieves an average yield of 17 % at single exfoliation cycle via only 10 min probe sonication, which is considerably greater than the yields typically observed in prior research employing molten-salt liquid-phase exfoliation technique, where yields are usually below 10% at one cycle despite much longer sonication times (Fu et al, 2017).

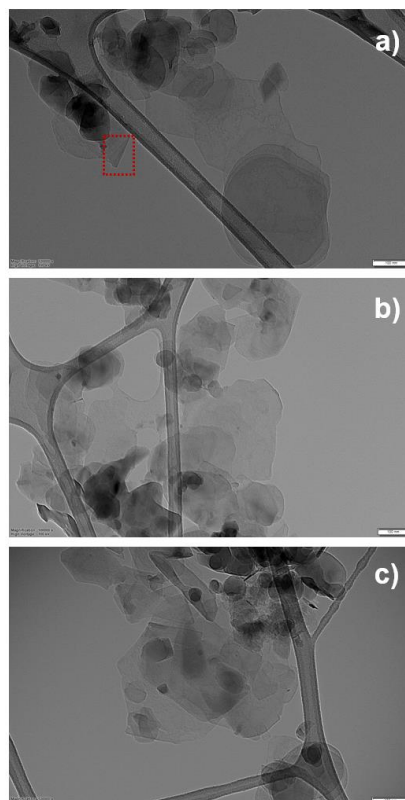


Figure 8. TEM images of h-BNNS-OH samples of a) h-BNNS-OH-10, (b) h-BNNS-OH-30, and (c) h-BNNS-OH-60.

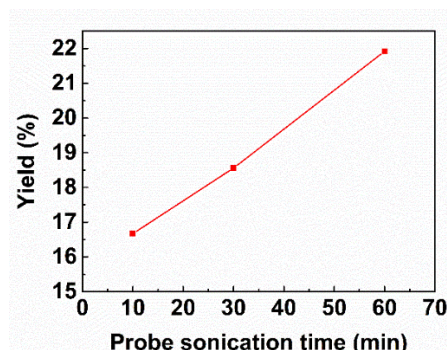


Figure 9. Percent yield of h-BNNS-OH vs. sonication time.

In order to evaluate the stability of h-BNNS-OH dispersions in DI water, samples collected at the end of the centrifugation step corresponding to sonication periods of 10, 30, and 60 min were monitored weekly. High dispersion stability was observed for all sonication

periods beyond 9 weeks, according to the photos taken after 1, 6, and 9 weeks (Figure 10).

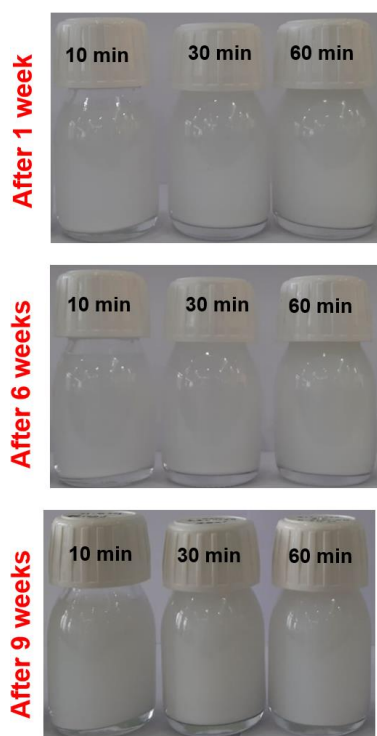


Figure 10. Dispersion stability of h-BNNS-OH with sonication periods of 10, 30 and 60 min after 1, 6 and 9 week

5. Conclusions

This study presents a robust two-step approach for the production of high-quality, hydroxyl-functionalized h-BN nanosheets. Hydrothermal exfoliation in a concentrated KOH and NaOH solution, followed by ultrasonic probe treatment, effectively reduced the thickness of h-BN nanopowder while introducing hydroxyl groups on the nanosheet surfaces. Utilization of this strategy facilitates the synthesis of the h-BNNS-OH with a yield of 17 % in only a single cycle, surpassing the yields associated with the vast majority of liquid-phase exfoliation methods that have been reported thus far. Chemical and morphological characterization results confirmed the nanosheets' high purity, uniform morphology, and functionalization. Our future work will focus on exploring additional functionalization strategies to further expand the application possibilities of h-BNNS.

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Author Contributions

In this study, Gulsah YAMAN UZUNOĞLU contributed to scientific literature research, article creation, experimental design, analysis, preparation, and writing of the article results.

Conflict of Interest

There is no conflict of interest with any person/institution in the prepared article.

References

- Cai, Q., Li, L.H, Mateti, S., Bhattacharjee, A., Fan, Y., Huang, S., & Chen, Y.I. (2024). "Boron Nitride Nanosheets: Thickness-Related Properties and Applications." *Advanced Functional Materials* 34(40): 2403669. DOI: <https://doi.org/10.1002/adfm.202403669>
- Cai, Q., Scullion, D., Gan, W., Falin, A., Zhang, S., Watanabe, K., ... Li, L.H. (2019). "High thermal conductivity of high-quality monolayer boron nitride and its thermal expansion." *Science Advances* 5(6): eaav0129. DOI: <https://doi.org/10.1126/sciadv.aav0129>
- de los Reyes, C. A., Hernández, K., Martínez-Jiménez, C., Walz Mitra, K.L., Ginestra, C., Smith McWilliams, A. D., Pasquali, M., ... Martí, A. A. (2019). "Tunable Alkylation of White Graphene (Hexagonal Boron Nitride) Using Reductive Conditions." *The Journal of Physical Chemistry C* 123(32): 19725-19733. DOI: <https://pubs.acs.org/doi/10.1021/acs.jpcc.9b05416>
- de Moraes, A. C. M., Hyun, W. J., Luu, N. S., Lim, J.-M., Park, K.-Y., & Hersam, M. C. (2020). "Phase-Inversion Polymer Composite Separators Based on Hexagonal Boron Nitride Nanosheets for High-Temperature Lithium-Ion Batteries." *ACS Applied Materials & Interfaces* 12(7): 8107-8114. DOI: <https://pubs.acs.org/doi/10.1021/acsami.9b18134>
- Fu, L., Wang, T., Yu, J., Dai, W., Sun, H., Liu, Z., ...Lin, C.-T. (2017). "An ultrathin high-performance heat spreader fabricated with hydroxylated boron nitride nanosheets." *2D Materials* 4(2): 025047. DOI: <https://iopscience.iop.org/article/10.1088/2053-1583/aa636e>
- Gautam, C. & Chelliah, S. (2021). "Methods of hexagonal boron nitride exfoliation and its functionalization: covalent and non-covalent approaches." *RSC Advances* 11(50): 31284-31327. DOI: <https://doi.org/10.1039/D1RA05727H>
- Griffin, A., Harvey, A., Cunningham, B., Scullion, D., Tian, T., Shih, C.-J., ... Coleman, J. N. (2018). Spectroscopic Size and Thickness Metrics for Liquid-Exfoliated h-BN. *Chemistry of Materials*, 30(6), 1998-2005. DOI: <https://doi.org/10.1021/acs.chemmater.7b05188>

- Goni, F., Chemelli, A. & Uhlig, F. (2021). "High-Yield Production of Selected 2D Materials by Understanding Their Sonication-Assisted Liquid-Phase Exfoliation." *Nanomaterials* 11(12): 3253. DOI: <https://doi.org/10.3390/nano11123253>
- Gorbachev, R. V., Riaz, I., Nair, R. R., Jalil, R., Britnell, L., Belle ...Blake, P. (2011). "Hunting for Monolayer Boron Nitride: Optical and Raman Signatures." *Small* 7(4): 465-468. DOI: <https://doi.org/10.1002/sml.201001628>
- Guerra, V., Wan, C., Degirmenci, V., Sloan, J., Presvytis, D. & McNally, T. (2018). "2D boron nitride nanosheets (BNNS) prepared by high-pressure homogenisation: structure and morphology." *Nanoscale* 10(41): 19469-19477. DOI: <https://doi.org/10.1039/C8NR06429F>
- Kim, M., Moon, S.W., Kim, G., Yoon, S. I., Kim, K., Min, S. K. & Shin, H. S. (2020). "Effect of Pt Crystal Surface on Hydrogenation of Monolayer h-BN and Its Conversion to Graphene." *Chemistry of Materials* 32(11): 4584-4590. DOI: <https://doi.org/10.1021/acs.chemmater.0c00736>
- Kong, X., Chen, Y., Yang, R., Wang, Y., Zhang, Z., Li, M., ...Yu, J. (2024). "Large-scale production of boron nitride nanosheets for flexible thermal interface materials with highly thermally conductive and low dielectric constant." *Composites Part B: Engineering* 271: 111164. DOI: <https://doi.org/10.1016/j.compositesb.2023.111164>
- Lei, Y., Pakhira, S., Fujisawa, K., Liu, H., Guerrero-Bermea, C., Zhang, T., ... Terrones, M. (2021). "Low temperature activation of inert hexagonal boron nitride for metal deposition and single atom catalysis." *Materials Today* 51: 108-116. DOI: <https://doi.org/10.1016/j.mattod.2021.09.017>
- Li, Q., Chen, L., Gadinski, M. R., Zhang, S., Zhang, G., Li, H. U., ... Wang, Q. (2015). "Flexible high-temperature dielectric materials from polymer nanocomposites." *Nature* 523(7562):576-579. DOI: <https://doi.org/10.1038/nature14647>
- Meziani, M. J., Sheriff, K., Parajuli, P., Priego, P., Bhattacharya, S., Rao, A.M., ...Sun, Y.-P. (2022). "Advances in Studies of Boron Nitride Nanosheets and Nanocomposites for Thermal Transport and Related Applications." *ChemPhysChem* 23(1): e202100645. DOI: <https://doi.org/10.1002/cphc.202100645>
- Rana, P., Dixit, R., Sharma, S., Dutta, S., Yadav, S., Sharma, A., ... Sharma, R. K. (2021). "Enhanced catalysis through structurally modified hybrid 2-D boron nitride nanosheets comprising of complexed 2-hydroxy-4-methoxybenzophenone motif." *Scientific Reports* 11(1): 24429. DOI: <https://doi.org/10.1038/s41598-021-03992-4>
- Ren, J., Stagi, L. & Innocenzi, P. (2021). "Hydroxylated boron nitride materials: from structures to functional applications." *Journal of Materials Science* 56(6): 4053-4079. DOI: <https://doi.org/10.1007/s10853-020-05513-6>
- Ren, S., Cui, M., Pu, J., Xue, Q. & Wang, L. (2017). "Multilayer Regulation of Atomic Boron Nitride Films to Improve Oxidation and Corrosion Resistance of Cu." *ACS Applied Materials & Interfaces* 9(32): 27152-27165. DOI: <https://doi.org/10.1021/acsami.7b06425>
- Sun, W., Meng, Y., Fu, Q., Wang, F., Wang, G., Gao, W., ... Lu, F. (2016). "High-Yield Production of Boron Nitride Nanosheets and Its Uses as a Catalyst Support for Hydrogenation of Nitroaromatics." *ACS Applied Materials & Interfaces* 8(15): 9881-9888. DOI: <https://doi.org/10.1021/acsami.6b01008>
- Tan, C., Cao, X., Wu, X.-J., He, Q., Yang, J., Zhang, X., ... Zhang, H. (2017). "Recent Advances in Ultrathin Two-Dimensional Nanomaterials." *Chemical Reviews* 117(9): 6225-6331. DOI: <https://doi.org/10.1021/acs.chemrev.6b00558>
- Wang, W., Li, Z., Marsden, A.J., Bissett, M.A. & Young, R.J. (2021). "Interlayer and interfacial stress transfer in hBN nanosheets." *2D Materials* 8(3): 035058.
- Wang, T., Wang, M., Fu, L., Duan, Z., Chen, Y., Hou, X., ... Yu, J. (2018). "Enhanced Thermal Conductivity of Polyimide Composites with Boron Nitride Nanosheets." *Scientific Reports* 8(1): 1557. DOI: <https://doi.org/10.1038/s41598-018-19945-3>
- Yang, W., Zhang, X. & Xie, Y. (2016). "Advances and challenges in chemistry of two-dimensional nanosheets." *Nano Today* 11(6): 793-816. DOI: <https://doi.org/10.1016/j.nantod.2016.10.004>
- Yuan, F., Guan, Q., Dou, X., Yang, H., Hong, Y., Xue, Y., ... Qin, Y. (2024). High-yield synthesis of hydroxylated boron nitride nanosheets and their utilization in thermally conductive polymeric nanocomposites. *RSC Advances*, 14(30), 21230-21240. doi:10.1039/D4RA02329C
- Zhang, K., Feng, Y., Wang, F., Yang, Z. & Wang, J. (2017). "Two dimensional hexagonal boron nitride (2D-hBN): synthesis, properties and applications". *Journal of Materials Chemistry C*, 5(46), 11992-12022. DOI: <http://dx.doi.org/10.1039/C7TC04300G>
- Zhi, C., Bando, Y., Tang, C., Kuwahara, H. & Golberg, D. (2009). "Large-scale fabrication of boron nitride nanosheets and their utilization in polymeric composites with improved thermal and mechanical properties." *Advanced Materials* 21(28): 2889-2893. DOI: 10.1002/adma.200900323

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