

RESEARCH PAPER

A Green Chemistry Approach for Facile Synthesis of Functionalized Boron Nitride Nanosheets

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ABSTRACT

The lack of a high-yield, renewable and low-cost synthesis method limits the potential applications of boron nitride with impressive characterizations. In this study, a facile method is developed for the preparation of chemically functionalized boron nitride nanosheets (BNNSs) by considering the quantity and quality of chemical materials involved in the synthesis process. The proposed green method is a suitable and high-efficiency method for replacing other production methods of BNNSs. Ultrathin BNNSs is produced by chemical reactions and subsequent liquid exfoliation. The possibility of chemical reaction is the highest at the defect sites especially at the upper/lower surfaces as well as the edge of bulk material. Due to hydroxyl functional groups that are coupled to the surface during the synthesis, the obtained products can well be dispersed in polar solutions such as water, ethanol, acetone and isopropyl alcohol. AFM, TEM, and SEM techniques are utilized to confirm the quality of the used method and illustrated that the produced-BNNSs have minimum thicknesses in the range of 1–5.6 nm and with lateral sizes ranging from 0.8–2.5 μm . The existence of functional groups and the structure of the BNNSs are verified by FTIR, EDX, XPS, XRD and Raman analyses. It was seen that the hexagonal structure was retained during the functionalization procedure. One can expect that the functionalization and sonication process introduces functional groups onto the surface of BNNSs. By this method, the obtained yield of BN dispersion is improved up to 17-20%.

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INTRODUCTION

As a structural analogue of graphite, hexagonal boron nitride (hBN) has recently been attracting a growing attention, both theoretically and experimentally [1, 2]. Some of the unique properties of hBN are remarkable thermal stability (up to 2950°C), mechanical strength, and intrinsic electrical insulation due to its large band gap of 5.9 eV [3-6]. Owing to these superior properties, hBN

has been strongly considered as a solid lubricant at high temperatures [7, 8], UV-light emitters [9, 10], coating materials [11] and fillers in composite materials [12-14]. However, compared to the growing graphene in various areas, studies on boron nitride nanosheets (BNNSs) are slow to occur due to difficulty in handling, complexity, high cost and especially low efficiency of preparation methods [15].

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Micromechanical cleavages, mechanical exfoliation via etching and lithium ion intercalation are among methods of producing high quality nanosheets. The use of above mentioned methods is limited to fundamental studies due to low productivity and complicated processes. The methods like ball milling [16, 17], chemical vapour deposition (CVD) [18-21] and chemical reaction [22-24] have been proposed relatively better efficiency than other methods, however the disadvantages of such expensive compounds, complex chemical process, high equipment cost, high operation vacuum and low lateral dimensions of obtained-BNNSs affect its extensive and practical application in large scale. Liquid-phase exfoliation and chemical functionalization are the two most effective and simple methods for synthesis of mono- and few-layers BN nanosheets. However, the low process yield of each strategy alone limits the potential uses of nanosheets. Liquid-phase exfoliation of hBN has been carried out by sonicating of the bulk hBN in various organic solvents such as N,N-dimethylformamide (DMF) [25, 26] methane sulfonic acid (MSA) [27] and aqueous and alcoholic solution [1, 15, 22, 28-30]. The maximum concentration was obtained only about 2.5% even after intense sonication in aqueous solution. On the other hand, functionalization of hBN was successfully presented for the first time by Connell et al. [31], however, the obtained BN-monolayers have dimensions less than 100 nm. Moreover, the high efficiency of this process (10-20%) was obtained in extended working time (~6-8 days) that would reduce the performance. There have been various literatures to investigated functionalization approach, but in addition to low yield, the use of organic and aggressive reactants is challenging [32, 33].

To the best of our knowledge, we found that combining of the two types of methods mentioned above is an efficient chemistry and cost-effective synthesis route for increasing the yield of produced-BNNSs while maintaining the quality of the nanosheets. In this paper, for the first time (as far as authors know) a green and cost-effective method for the exfoliation of hBN flakes by oxidative treatment with H_2O_2 as oxidant and subsequent liquid exfoliation of functionalized BN is reported. The oxidative exfoliation of bulk hBN to nanosheets with the aid of H_2O_2 can be considered to be one of the green synthetic processes with

highest yield. The present method has advantages such as: (1) water as a by-product; (2) an organic solvent-free system; (3) high yield and purity of obtained-BNNSs, and (4) simple, inexpensive and safe method.

MATERIALS AND METHODS

Hexagonal boron nitride (purity of 98%) was supplied by Merck Company. Hydrogen peroxide (30wt. %) was purchased from Samin Chemicals Company and used as received without any further purification. Ethanol (purity of 96%) was provided from Bidestan Company and used without more purification.

Apparatus

An ultrasonic bath (Wiseclean, 290 W) and a centrifuge (MSE mistral 1000) were used in the synthesis procedure. Energy dispersive X-ray (EDX) analysis was done on the Oxford Instruments X-Max 80. As-obtained BNNSs were dried for 24 hours in an electric oven at 100 °C to extract any remaining water out and then were mixed with KBr to make the pellets. Fourier Transform Infrared (FTIR) spectra were recorded on a Perkin-Elmer IR-843 spectrometer. Raman spectra were recorded using a TakRam P50COR10 Raman Microscope at $\lambda = 532$ nm laser excitation. X-ray Photoelectron spectrometer (XPS) (Bestec, Al K_{α} radiation (1486.6 eV), working at a pressure of 10^{-10} mbar), was used to study the surface. Peak deconvolution was performed to decompose XPS peaks that overlap with each other by using Origin software. Transmission Electron Microscopy (TEM) images were taken by Philips CM300, working at 300 kV and operating at 293 K. Atomic Force Microscopy (AFM) was applied in ambient condition using a DualScope™ 95 Scanning Probe Microscope (SPM) scanner in non-contact mode. The morphology of the BN flakes was evaluated using Field Emission Scanning Electron Microscopy (FESEM) Hitachi S-4160 at an accelerating voltage of 30 kV. The spacing of boron nitride lattice was monitored using X-Ray diffraction (XRD) (Stoe, Stady-up Diffractometer), Cu K_{α} radiation, $\lambda=1.5406$ Å and step size= 0.2 (2 θ).

Exfoliation of hBN to BNNSs

Functionalized-BN nanosheets were synthesized from pristine hBN powder. In order to create additional defects, hBN was grated in an agate mortar and pestle for about 15 min and then

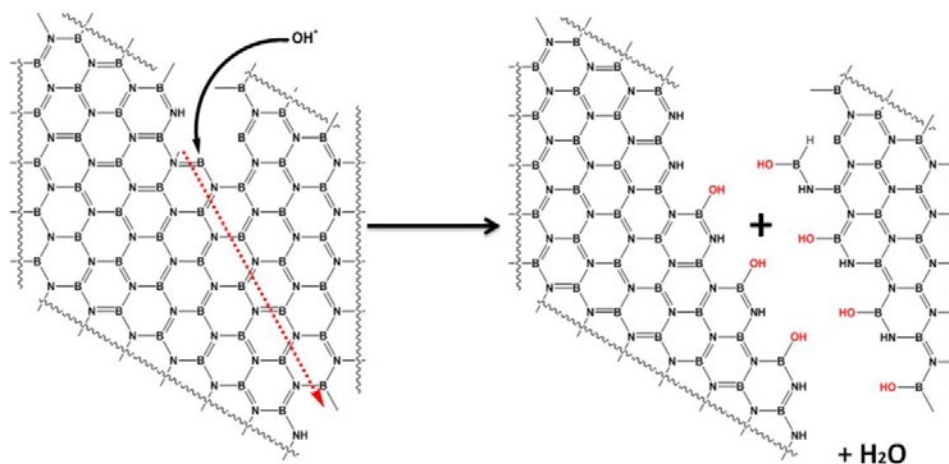


Fig. 1. A typical scheme showing that cutting of hBN start from hole defect site with the arrow as the cutting direction

heated to 400–500°C for degasification. After that, a certain amount of grounded hBN was added to 200 ml solution of H_2O_2 in a round-bottom flask, sonicated for 5 min and refluxed at 100°C for 24 h with continuous stirring to create hydroxyl functional groups. During the reflux, H_2O_2 would thermally decompose to give H_2O . After cooling, the flakes dispersed in water as solvent was sonicated in a low-power sonic bath for 1.5 h. The precipitate large-size hBN flakes were removed by centrifuge at 3000 rpm after 20 min. The top two thirds of the centrifuge container solution was considered as suspended nanosheets and collected for further analysis. The supernatant was filtered through a cellulose acetate filter (with pore size 0.2 μm) and repeatedly washed with deionised water and ethanol to remove the traces of untreated peroxide and then dried to obtain pure BNNSs.

RESULTS AND DISCUSSION

H_2O_2 is known as a cheap and important green oxidant that contains a high percentage of active oxygen and produces water during its reactions, so it has played an important role in environmental protection in the chemical industry [34, 35]. Currently, a high fraction of industrial H_2O_2 is produced by anthraquinone oxidation process [34]. The cost of production of H_2O_2 has continued to decrease with the development of technology and increasing efficiency of production process.

Since boron is an element with inherent electron deficiency, boron-containing materials are susceptible to saturate the coordination sphere and its valence shell in chemical reactions.

Therefore, the empty p-orbit of boron is easily attacked by radicals and nucleophiles such as water which causes it to hydrolysed [18, 36–38]. During the reaction, boron-nitrogen bonds at the defect sites and the surfaces might be attacked by active radicals of H_2O_2 (Fig. 1). Because of the existence and high activity of the active hydroxyl groups, the exposed hBN flakes have boron edges containing hydroxyl groups. Under prolonged periods, hydroxyl groups are not only intercalate between BN layers but also hydrolysis breaks apart large hBN sheets into smaller ones and produces few-layered nanosheets with decreased lateral sizes.

The use of H_2O_2 as an oxidant makes the proposed method environmentally friendly. Since it does not release any toxic compounds during reaction and the only by product is water molecules, BNNSs can disperse in aqueous dispersion; consequently the solution is free from any pollution. During sonication, the shock waves produced by the cavitation of bubbles created by ultrasonic waves help to separate the functionalized BN flakes and lead to formation of thinner nanosheets [39, 40].

Taking the above-mentioned facts into consideration, in the current work an attempt was made to exfoliate the hBN by functionalization. The whole synthesis process includes steps taken which is displayed in Fig. 2. It is clear that the production yield of each stages is different, but the final output yield of combined method used being in the range of 17–20% is higher than the process yields performed on many other solvents [25, 27, 30, 31, 41, 42] and especially significantly more

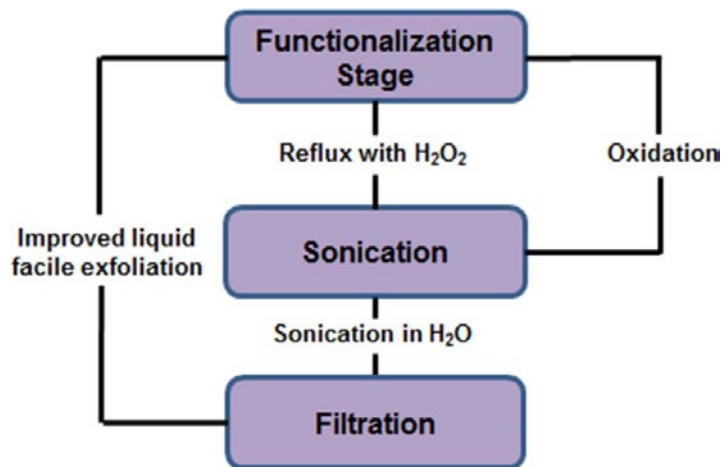


Fig. 2. Different stages for BNNSs synthesis, namely intercalation by oxidation and exfoliation by ultra-sonication

than the yield achieved (2.5-5%) by sonication systems of hBN in water [1]. It should be noted that although this method has an acceptable potential for large-scale production of BNNSs, considering the yield, dimensions and quality BN nanosheets can still be improved.

EDX spectroscopy is an analytical technique to identify the chemical composition of the samples. EDX spectrum (Fig. 3) confirms the chemical composition of hBN and BNNSs, indicating that boron and nitrogen are the main components, while carbon and oxygen elements were found only in traces. The presence of C and O is because of carbon contaminations in conjunction with BN materials and moisture absorption from atmosphere. Although these elements are identifiable with the EDX system, but quantitative analysis of light elements such as boron cannot be estimated correctly [41, 43].

In addition to EDX, XPS was also used to characterize the chemical composition of the materials. XPS studies were performed to analyse hBN and BNNSs surfaces (Fig. 4). Full XPS spectra of pristine hBN and BNNSs distinctly show the appearance of B, N, O and C which is in agreement with EDX data (Fig. 4a-b) [28]. The atomic ratio of B, N, and O is estimated to be 1.02:1:0.2 in BNNSs, indicating ideal chemical stoichiometry of B to N. It also shows that about 9 wt.% oxygen has been added to BNNSs while before oxidation the atomic ratio of O was 4 wt.% only. This indicates that some oxygen-containing groups have been introduced during the process.

Fig. 4c-f summarizes the results of B 1s, and N1s XPS spectra of hBN and BNNSs. Gaussian fit was

employed to deconvolute the component peaks. As shown in Fig. 4c and 4d, the deconvolution of the asymmetric B 1s peaks shows the presence of two types of chemical bonding of boron atoms in the structure: (i) the nitrogen-boron bond is a characteristic of hBN (at 190.3 eV) and (ii) chemical bond of boron atoms with oxygen (at 191 eV) which is on the basis of the binding energies reported for B 1s [30, 41, 44].

A structure similar to the structure of boronic acid is proposed for hydroxyl groups bonded to boron atoms. This arrangement causes blue-shift of B 1s peak. It should be noted that the chemical environment greatly affects the position of XPS peaks. Due to the bonding energy and different bond length of B-O with the structure of $B(OH)_3$, the probability of the boron bonding to hydroxyl groups is reasonable [45].

The high-resolution scans of N 1s for hBN and BNNSs were analysed to investigate the possible bonding that has been shown in Fig. 4e and 4f, respectively. Based on FWHM and symmetry of the peaks, only one kind of bond for nitrogen can be suggested. The sub-peak specified at 398.2 eV is related to the B-N bond, which confirms the presence of hexagonal BN structure.

The oxidation of the BN was obvious due to its oxidizability and oxidizing of peroxide. Therefore, one can expect that the functionalization and sonication process graft functional groups onto the surface of BNNSs. Fig. 5 shows the FTIR transmittance spectrum of hBN and BNNSs. Prior to treatment, hBN spectrum has two characteristic peaks related to B-N in-plane stretching and B-N-B out of plane bending that were observed at 1380

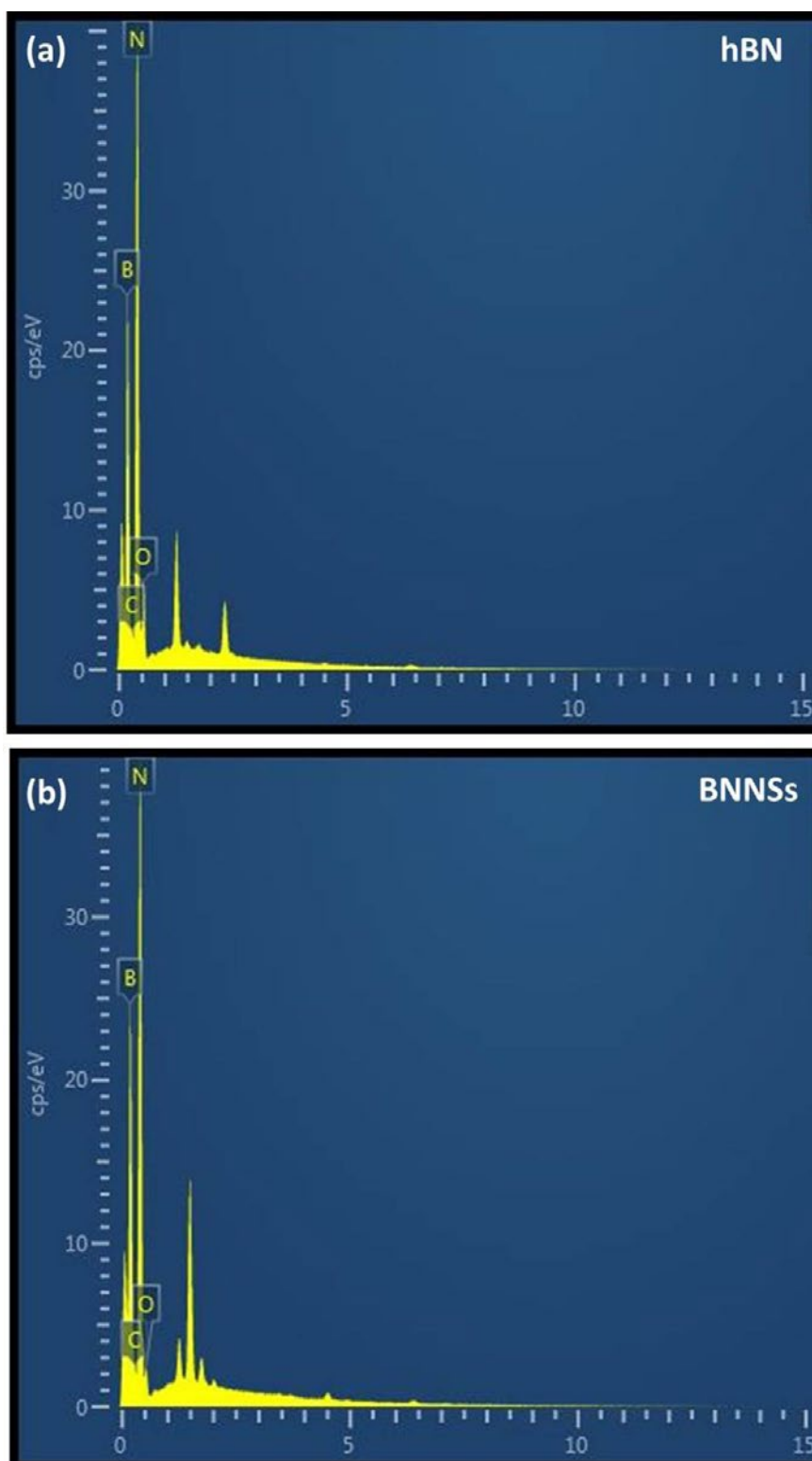


Fig. 3. EDX analysis of hBN (a) and BNNSs (b)

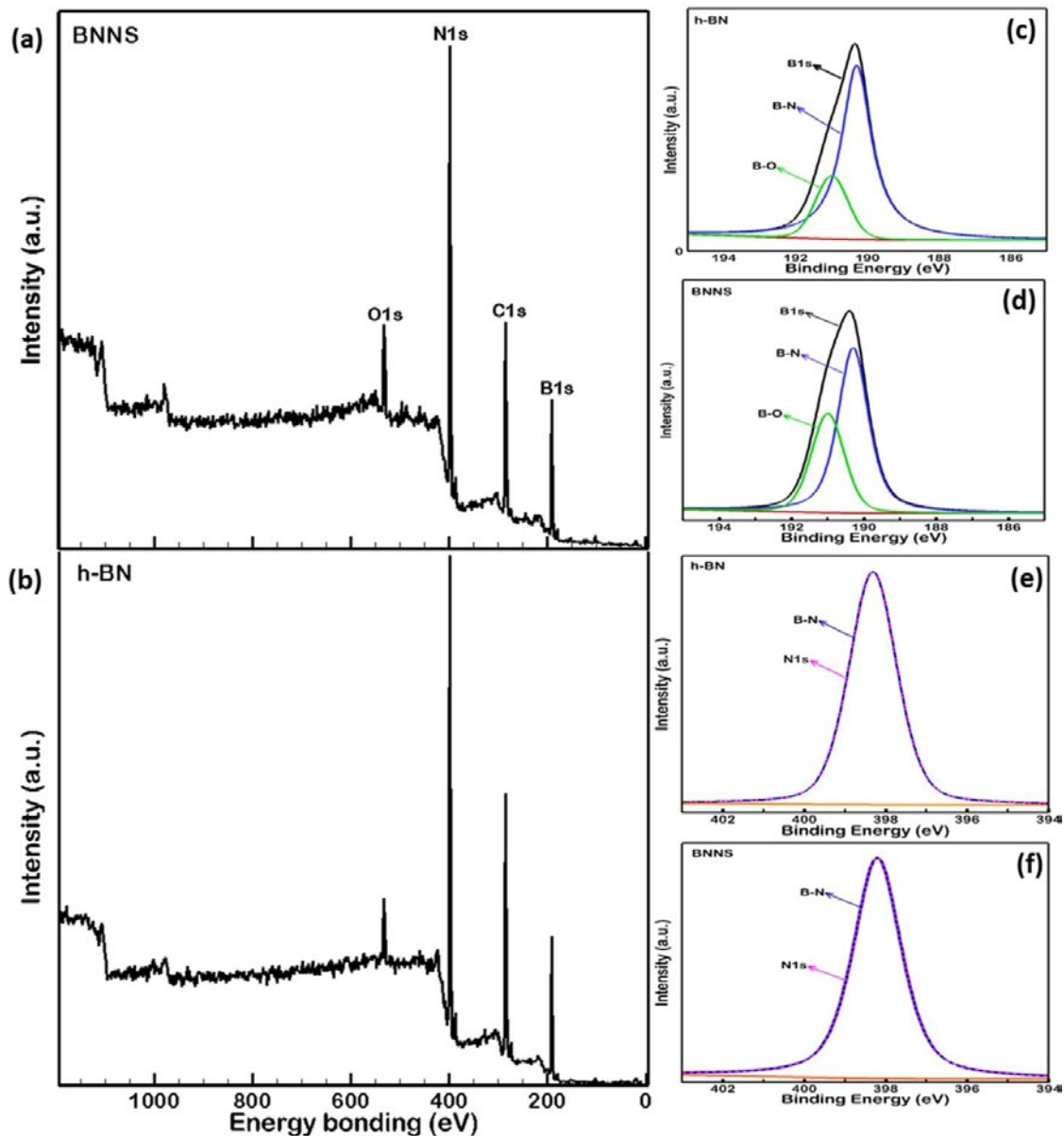


Fig. 4. XPS full spectra of pristine hBN (a) and BNNSs (b). B 1s (c) and N 1s (e) peaks of pristine hBN, and the B 1s (d) and N 1s (f) peaks of BNNSs

cm^{-1} and 815 cm^{-1} , respectively.

In the Raman spectrum of BNNSs (Fig. 5c) is observed a peak at 1366.78 , indicating intrinsic E_{2g} vibration that is characteristic spectroscopic signatures of hBN [32, 33, 46]. In addition to characteristic peaks of hBN, IR spectrum of BN nanosheets was demonstrated a relatively broad band around 3450 cm^{-1} , probably due to the presence of hydroxyl groups in the structure and the resulted stretching vibration, which is

consistent with the reported spectroscopic data [25, 47]. Due to the loss of the physical water in the sample preparation stage, the presence of a broadband at this wavelength indicates that chemical bonds of hydroxyl groups are formed with the surface by reacting to the surface boron groups. The small B-O out of plane bending vibration is visible at 1130 cm^{-1} on the shoulder of B-N stretching peak. The weak B-O-H bending vibration at 851 cm^{-1} overlapped by B-N-B

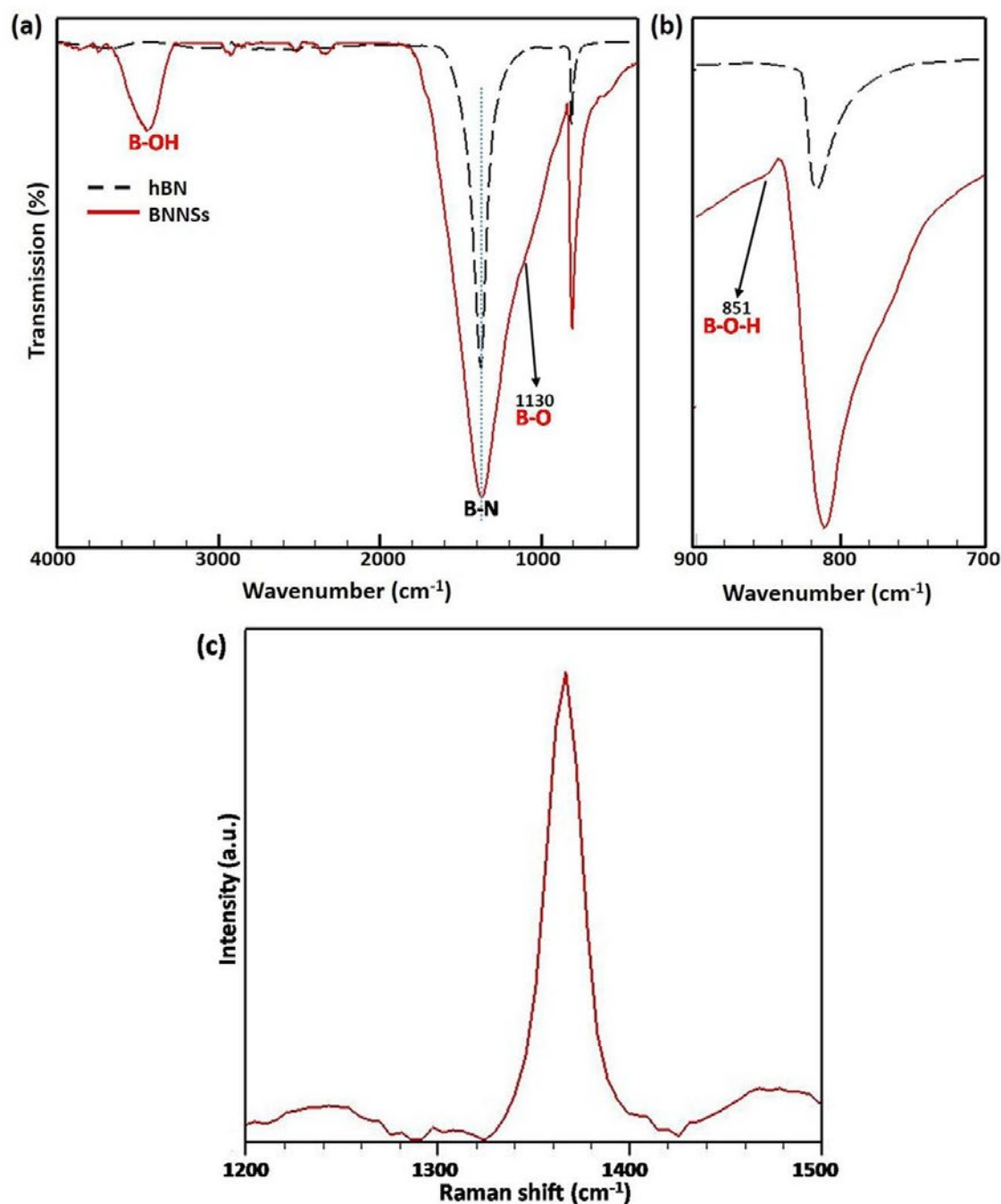


Fig. 5. (a) FTIR transmittance spectra of the BN before and after functionalization (Black; hBN, Red; BNNs). (b) The figure shows the close-up of the spectra in the 900-700 cm⁻¹ range for clarity. (c) Raman spectrum (532 nm excitation) of as-obtained BNNs powder

vibration can be seen (Fig. 5b). These peaks which are observed only in the presence of hydroxyl groups on the surface authenticate our claim for successful functionalization.

It is essential to determine the exfoliation state of the used and obtained materials. First the state of the pristine hBN powder was examined. The diverse shaped flakes with lateral size of <2.5 μm

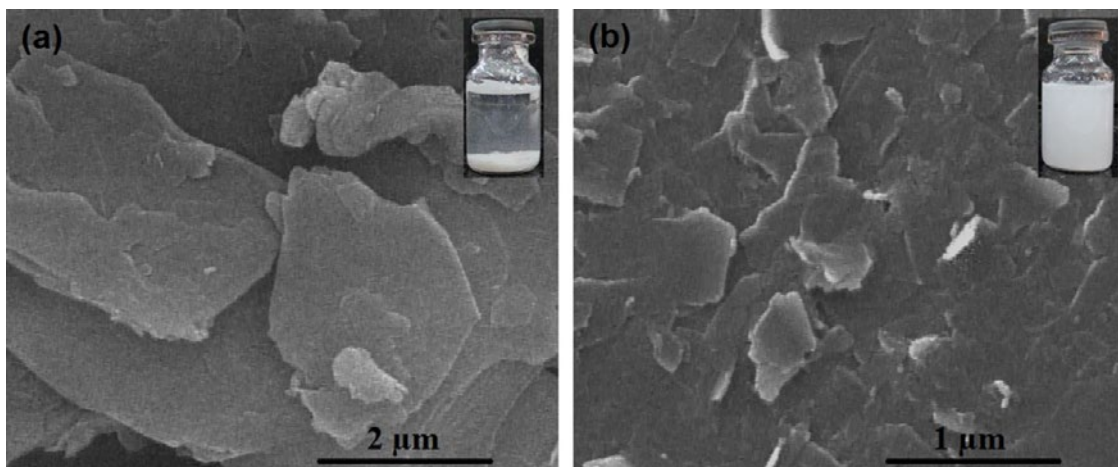


Fig. 6. SEM images of hBN powder before treatment, an inset of a photograph showing the hBN dispersed in H₂O (a), and BNNs after sonication recovered as a precipitate after centrifugation, an inset of a photograph showing the exfoliated products dispersed in H₂O standing for one week (b)

and thickness in tens of nanometres are evident in the recorded images by FESEM (Fig. 6a). After centrifugation, it's clear that both lateral sizes and thickness of the exfoliated-products are reduced. The obtained nanosheets are smaller in size compared to the original powder, with lateral size measured in the range of 500 nm to 2 μm, and the decreased thickness is not accurately measurable by SEM image [48] (Fig. 6b). Clearly, it can be concluded that the applied procedure was capable to separate the layers from each other and to produce BN nanosheets. The two upper insets in Fig. 6a and 6b show hBN and BN nanosheets, both dispersed in water. Interestingly, while the hBN is insoluble in water, BNNs is soluble due to its hydroxyl groups. It was observed that the milky solution of the BNNs can stay stable for a long period of time. BNNs are too thin and too light to precipitate; it also shows the qualified laminating of the bulk BN has taken place by the presented method. In addition, hydroxyl groups create electrostatic hindrance so that it makes stable nanosheets. Due to hydrophobicity [21, 49-51], most of hBN particles are not dispersed in water completely rather they are gathered on the top of the water. Due to being heavy, some of hBN flakes precipitate to the bottom of the bottle and the solution looks transparent [21, 49, 50].

The semi-transparent BNNs can clearly be distinguished through the TEM characterizations (Fig. 7), illustrating small thickness. The lateral size of BN nanosheets is usually bigger than 800 nm.

The TEM images show some BNNs with different lateral sizes, along with folding, they are overlapped in some places. The curled edges are observed in most two dimensional (2D) nanosheets, which helps to detract the free surface and dangling bond energies and to improve the stability of nanosheets [16].

The lateral dimension of most BN nanosheets captured by AFM is between 900 nm and 2.5 μm (Fig. 8) which corroborates well with the TEM and SEM results (Fig. 6 and 7). Cross-sections of two typical BN nanosheets show step heights of ~1-5.6 nm, indicating that they consist of about 1-14 layers. Considering this, it is essential that BN monolayers be placed several angstroms above the substrate, so that the thickness of ~1 nm is considered for one layer by AFM [1, 52, 53]. Depending on the dead space between the sheet and the substrate, this height value is ascribed to a single layer of BN. Even if the theoretical thickness is considered 0.333 nm for a single-layer, the distortion of height profile (causing the offsetting of AFM tool between the sheets and substrate) leads to a difference of 1 nm at the measured height [54, 55].

X-Ray diffraction (XRD) patterns of hBN and BNNs give us detailed data on the structural information (inter-lamellar or d-spacing) of the prepared nanosheets. hBN structure is verified by observing diffraction peaks of pristine powder (Fig. 9, black). A series of defined peaks are located at $2\theta = 26.962^\circ$, 41.798° , and 55.266° , with d-spacing

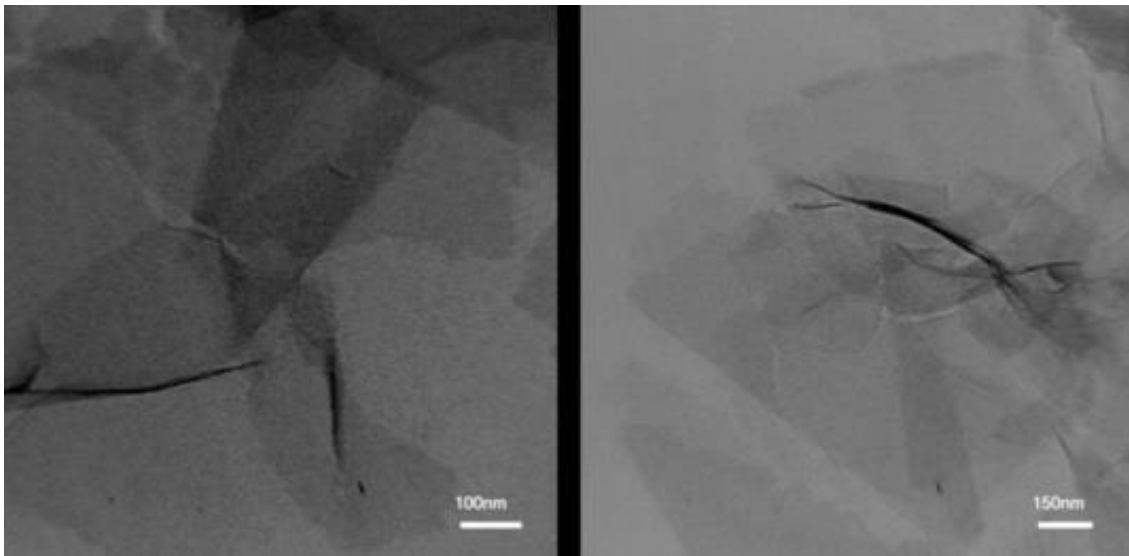


Fig. 7. TEM images of as-exfoliated BNNs

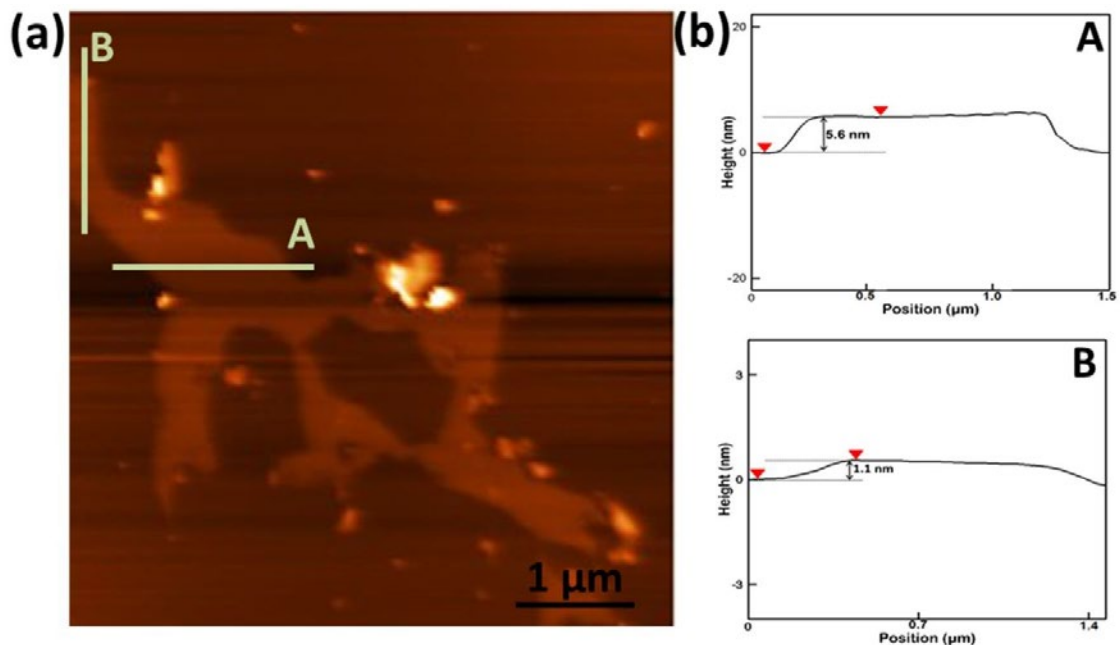


Fig. 8. A representative AFM image of BNNs and the related height profiles

of 3.307, 2.161, and 1.662°A, related to the (002), (100), and (004) planes of hBN, respectively.

The relative increase in Full Width at Half Maximum (FWHM) of (002) plane from 0.1968 for the pristine powder to 0.2640 for BNNs, the Scherrer broadening, confirms the exfoliation of hBN and the reduction of crystallite sizes. The exfoliated BNNs pattern also has distinct changes compared to hBN. The decreased intensity of

(002) peak, shifting to lower angle, $2\theta = 26.760^\circ$, related to a d-spacing of 3.328 Å, determines the exfoliation of starting hBN. The presence of hydroxyl groups and their intercalations between layers increases the spacing of the BN layers. This result illustrates that the crystallite structure of boron nitride is maintained despite the negligible disruptions in lattice and in the presence of hydrogen peroxide as an oxidizing agent.

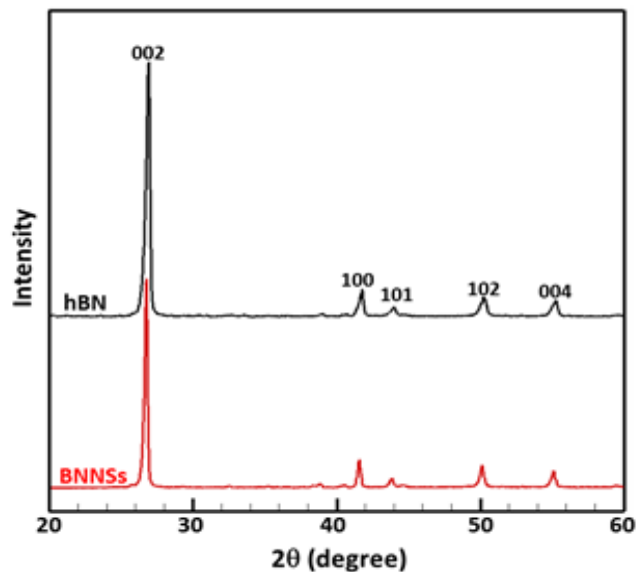


Fig. 9. XRD pattern of hBN and as-produced BNNs

CONCLUSIONS

The ability to substitute a difficult and lengthy solvent-based approach to produce boron nitride nanosheets with a moderate treatment of H_2O_2 is presented. Compared to previous studies, this green process resulted in a relative increase in efficiency (17-20%) and a better quality of BNNs. The results demonstrate that in the presence of green agent and aqueous solvent, the as-produced nanosheets are not only oxidized but also layered-crystallographic structure is maintained. This is an important achievement because the structural defects have negative effect on intrinsic properties and thus potential applications of boron nitride materials. The scalability of this method and the dispersion of BNNs into polar/non-polar solvents by more functionalization strategies are keys to their processing and application in the industry and medicine with lower cost and less environmental impact.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

REFERENCES

- Lin Y, Williams TV, Xu T-B, Cao W, Elsayed-Ali HE, Connell JW. Aqueous Dispersions of Few-Layered and Monolayered Hexagonal Boron Nitride Nanosheets from Sonication-Assisted Hydrolysis: Critical Role of Water. *The Journal of Physical Chemistry C*. 2011;115(6):2679-85.
- Nguyen BH, Nguyen VH. *Advances in graphene-based optoelectronics, plasmonics and photonics. Advances in Natural Sciences: Nanoscience and Nanotechnology*. 2016;7(1):013002.
- Wang J, Ma F, Sun M. Graphene, hexagonal boron nitride, and their heterostructures: properties and applications. *RSC Advances*. 2017;7(27):16801-22.
- Palla P, Uppu GR, Ethiraj AS, Raina JP. Bandgap engineered graphene and hexagonal boron nitride for resonant tunnelling diode. *Bulletin of Materials Science*. 2016;39(6):1441-51.
- Gonzalez Ortiz D, Pochat-Bohatier C, Cambedouzou J, Bechelany M, Miele P. Exfoliation of Hexagonal Boron Nitride (h-BN) in Liquid Phase by Ion Intercalation. *Nanomaterials*. 2018;8(9):716.
- Rafiei-Sarmazdeh Z, Morteza Zahedi-Dizaji S, Kafi Kang A. Two-Dimensional Nanomaterials. *Nanostructures: IntechOpen*; 2020.
- Song L, Ci L, Lu H, Sorokin PB, Jin C, Ni J, et al. Large Scale Growth and Characterization of Atomic Hexagonal Boron Nitride Layers. *Nano Letters*. 2010;10(8):3209-15.
- Li X, Yin J, Zhou J, Guo W. Large area hexagonal boron nitride monolayer as efficient atomically thick insulating coating against friction and oxidation. *Nanotechnology*. 2014;25(10):105701.
- Vuong TQP, Cassabois G, Valvin P, Rousseau E, Summerfield A, Mellor CJ, et al. Deep ultraviolet emission in hexagonal boron nitride grown by high-temperature molecular beam epitaxy. *2D Materials*. 2017;4(2):021023.
- Chejanovsky N, Kim Y, Zappe A, Stuhlhofer B, Taniguchi T, Watanabe K, et al. Quantum Light in Curved Low Dimensional Hexagonal Boron Nitride Systems. *Scientific Reports*. 2017;7(1).
- GÖKmenoğlu C, Özmeriç N, ÇAKAL G, DÖKmetaş N, Ergene C, Kaftanoğlu B. Coating of titanium implants with boron nitride by RF-magnetron sputtering. *Bulletin of Materials Science*. 2016;39(5):1363-70.
- Zhang N, Zhang T, Kan H, Wang X, Long H, Zhou Y. The Research of the Synthesis Mechanism and Synthesis

- Process of High Crystallinity Globular h-BN. *Journal of Inorganic and Organometallic Polymers and Materials*. 2015;25(6):1495-501.
13. Bao J, Edwards M, Huang S, Zhang Y, Fu Y, Lu X, et al. Two-dimensional hexagonal boron nitride as lateral heat spreader in electrically insulating packaging. *Journal of Physics D: Applied Physics*. 2016;49(26):265501.
 14. Chen L, Xu H-F, He S-J, Du Y-H, Yu N-J, Du X-Z, et al. Thermal Conductivity Performance of Polypropylene Composites Filled with Polydopamine-Functionalized Hexagonal Boron Nitride. *PLOS ONE*. 2017;12(1):e0170523.
 15. Zhang B, Wu Q, Yu H, Bulin C, Sun H, Li R, et al. High-Efficient Liquid Exfoliation of Boron Nitride Nanosheets Using Aqueous Solution of Alkanolamine. *Nanoscale Research Letters*. 2017;12(1).
 16. Li LH, Chen Y, Behan G, Zhang H, Petravic M, Glushenkov AM. Large-scale mechanical peeling of boron nitride nanosheets by low-energy ball milling. *Journal of Materials Chemistry*. 2011;21(32):11862.
 17. Joni IM, Balgis R, Ogi T, Iwaki T, Okuyama K. Surface functionalization for dispersing and stabilizing hexagonal boron nitride nanoparticle by bead milling. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*. 2011;388(1-3):49-58.
 18. Motojima S, Tamura Y, Sugiyama K. Low temperature deposition of hexagonal BN films by chemical vapour deposition. *Thin Solid Films*. 1982;88(3):269-74.
 19. Chatterjee S, Luo Z, Acerce M, Yates DM, Johnson ATC, Sneddon LG. Chemical Vapor Deposition of Boron Nitride Nanosheets on Metallic Substrates via Decaborane/Ammonia Reactions. *Chemistry of Materials*. 2011;23(20):4414-6.
 20. Shi Y, Hamsen C, Jia X, Kim KK, Reina A, Hofmann M, et al. Synthesis of Few-Layer Hexagonal Boron Nitride Thin Film by Chemical Vapor Deposition. *Nano Letters*. 2010;10(10):4134-9.
 21. Yu J, Qin L, Hao Y, Kuang S, Bai X, Chong Y-M, et al. Vertically Aligned Boron Nitride Nanosheets: Chemical Vapor Synthesis, Ultraviolet Light Emission, and Superhydrophobicity. *ACS Nano*. 2010;4(1):414-22.
 22. Wang W, Chen SJ, Basquiroto de Souza F, Wu B, Duan WH. Exfoliation and dispersion of boron nitride nanosheets to enhance ordinary Portland cement paste. *Nanoscale*. 2018;10(3):1004-14.
 23. Wang L, Shen L, Xu X, Xu L, Qian Y. Facile synthesis of uniform h-BN nanocrystals and their application as a catalyst support towards the selective oxidation of benzyl alcohol. *RSC Advances*. 2012;2(28):10689.
 24. Sun GX, Bi JQ, Wang WL, Hao XX, Gao XC, Yan WK, et al. Synthesis of Boron Nitride Coating on Graphene. *Solid State Phenomena*. 2018;281:499-503.
 25. Zhi C, Bando Y, Tang C, Kuwahara H, Golberg D. Large-Scale Fabrication of Boron Nitride Nanosheets and Their Utilization in Polymeric Composites with Improved Thermal and Mechanical Properties. *Advanced Materials*. 2009;21(28):2889-93.
 26. Ye H, Lu T, Xu C, Han B, Meng N, Xu L. Liquid-Phase Exfoliation of Hexagonal Boron Nitride into Boron Nitride Nanosheets in Common Organic Solvents with Hyperbranched Polyethylene as Stabilizer. *Macromolecular Chemistry and Physics*. 2018;219(6):1700482.
 27. Wang Y, Shi Z, Yin J. Boron nitride nanosheets: large-scale exfoliation in methanesulfonic acid and their composites with polybenzimidazole. *Journal of Materials Chemistry*. 2011;21(30):11371.
 28. Cao L, Emami S, Lafdi K. Large-scale exfoliation of hexagonal boron nitride nanosheets in liquid phase. *Materials Express*. 2014;4(2):165-71.
 29. Lu F, Wang F, Gao W, Huang X, Zhang X, Li Y. Aqueous soluble boron nitride nanosheets via anionic compound-assisted exfoliation. *Materials Express*. 2013;3(2):144-50.
 30. Gao G, Gao W, Cannuccia E, Taha-Tijerina J, Balicas L, Mathkar A, et al. Artificially Stacked Atomic Layers: Toward New van der Waals Solids. *Nano Letters*. 2012;12(7):3518-25.
 31. Lin Y, Williams TV, Connell JW. Soluble, Exfoliated Hexagonal Boron Nitride Nanosheets. *The Journal of Physical Chemistry Letters*. 2009;1(1):277-83.
 32. Bhimanapati GR, Kozuch D, Robinson JA. Large-scale synthesis and functionalization of hexagonal boron nitride nanosheets. *Nanoscale*. 2014;6(20):11671-5.
 33. Singh B, Kaur G, Singh P, Singh K, Kumar B, Vij A, et al. Nanostructured Boron Nitride With High Water Dispersibility For Boron Neutron Capture Therapy. *Scientific Reports*. 2016;6(1).
 34. Choudhary VR, Gaikwad AG, Sansare SD. Nonhazardous Direct Oxidation of Hydrogen to Hydrogen Peroxide Using a Novel Membrane Catalyst. *Angewandte Chemie International Edition*. 2001;40(9):1776-9.
 35. Campos-Martin JM, Blanco-Brieva G, Fierro JLG. Hydrogen Peroxide Synthesis: An Outlook beyond the Anthraquinone Process. *Angewandte Chemie International Edition*. 2006;45(42):6962-84.
 36. Shah FU, Glavatskih S, Antzutkin ON. Boron in Tribology: From Borates to Ionic Liquids. *Tribology Letters*. 2013;51(3):281-301.
 37. Cofer CG, Economy J. Oxidative and hydrolytic stability of boron nitride — A new approach to improving the oxidation resistance of carbonaceous structures. *Carbon*. 1995;33(4):389-95.
 38. Streletskii AN, Permenov DG, Bokhonov BB, Kolbanev IV, Leonov AV, Berestetskaya IV, et al. Destruction, amorphization and reactivity of nano-BN under ball milling. *Journal of Alloys and Compounds*. 2009;483(1-2):313-6.
 39. Green AA, Hersam MC. Emerging Methods for Producing Monodisperse Graphene Dispersions. *The Journal of Physical Chemistry Letters*. 2009;1(2):544-9.
 40. Wu TY, Guo N, Teh CY, Hay JXW. Theory and Fundamentals of Ultrasound. *SpringerBriefs in Molecular Science*: Springer Netherlands; 2012. p. 5-12.
 41. Xue Y, Liu Q, He G, Xu K, Jiang L, Hu X, et al. Excellent electrical conductivity of the exfoliated and fluorinated hexagonal boron nitride nanosheets. *Nanoscale Research Letters*. 2013;8(1):49.
 42. Lee KH, Shin H-J, Lee J, Lee I-y, Kim G-H, Choi J-Y, et al. Large-Scale Synthesis of High-Quality Hexagonal Boron Nitride Nanosheets for Large-Area Graphene Electronics. *Nano Letters*. 2012;12(2):714-8.
 43. Zhi C, Bando Y, Tang C, Honda S, Sato K, Kuwahara H, et al. Characteristics of Boron Nitride Nanotube-Polyaniline Composites. *Angewandte Chemie International Edition*. 2005;44(48):7929-32.
 44. Rafiei-Sarmazdeh Z, Jafari SH, Ahmadi SJ, Zahedi-Dizaji SM. Large-scale exfoliation of hexagonal boron nitride with combined fast quenching and liquid exfoliation strategies. *Journal of Materials Science*. 2015;51(6):3162-9.

45. Zhi CY, Bando Y, Terao T, Tang CC, Kuwahara H, Golberg D. Chemically Activated Boron Nitride Nanotubes. *Chemistry - An Asian Journal*. 2009;4(10):1536-40.
46. Zhang K, Feng Y, Wang F, Yang Z, Wang J. Two dimensional hexagonal boron nitride (2D-hBN): synthesis, properties and applications. *Journal of Materials Chemistry C*. 2017;5(46):11992-2022.
47. Yu B, Xing W, Guo W, Qiu S, Wang X, Lo S, et al. Thermal exfoliation of hexagonal boron nitride for effective enhancements on thermal stability, flame retardancy and smoke suppression of epoxy resin nanocomposites via sol-gel process. *Journal of Materials Chemistry A*. 2016;4(19):7330-40.
48. Frey L, Parrein P, Virost L, Pellé C, Raby J. Thin film characterization for modeling and optimization of silver-dielectric color filters. *Applied Optics*. 2014;53(8):1663.
49. Pakdel A, Zhi C, Bando Y, Nakayama T, Golberg D. Boron Nitride Nanosheet Coatings with Controllable Water Repellency. *ACS Nano*. 2011;5(8):6507-15.
50. Weng Q, Wang X, Wang X, Bando Y, Golberg D. Functionalized hexagonal boron nitride nanomaterials: emerging properties and applications. *Chemical Society Reviews*. 2016;45(14):3989-4012.
51. Cui M, Ren S, Qin S, Xue Q, Zhao H, Wang L. Non-covalent functionalized hexagonal boron nitride nanoplatelets to improve corrosion and wear resistance of epoxy coatings. *RSC Advances*. 2017;7(70):44043-53.
52. Lin Y, Connell JW. Advances in 2D boron nitride nanostructures: nanosheets, nanoribbons, nanomeshes, and hybrids with graphene. *Nanoscale*. 2012;4(22):6908.
53. Lin Y, Williams TV, Cao W, Elsayed-Ali HE, Connell JW. Defect Functionalization of Hexagonal Boron Nitride Nanosheets. *The Journal of Physical Chemistry C*. 2010;114(41):17434-9.
54. Yi M, Shen Z, Ma S, Zhang X. A mixed-solvent strategy for facile and green preparation of graphene by liquid-phase exfoliation of graphite. *Journal of Nanoparticle Research*. 2012;14(8).
55. Nemes-Incze P, Osváth Z, Kamarás K, Biró LP. Anomalies in thickness measurements of graphene and few layer graphite crystals by tapping mode atomic force microscopy. *Carbon*. 2008;46(11):1435-42.