Original Article

Synthesis and Characterization of 2D Boron Nitride from Hexagonal Boron Nitride

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Abstract - Boron Nitride (BN) and its Nano derivatives have garnered significant attention owing to their exceptional physical and chemical attributes, including high-temperature and oxidation resistance, effective heat conduction, electrical insulation, and neutron absorption capabilities. Their distinctive lamellar, reticular, and tubular structures, along with their diverse physicochemical properties, make BN particularly appealing in various applications such as adsorption, catalysis, hydrogen storage, thermal management, insulation, electronic device substrates, radiation shielding, polymer composites, and medical fields. This paper focuses on a novel method for producing 2D Boron Nitride/Boron Nitride Nanosheets (BNNSs) from h-BN (Hexagonal Boron Nitride) via ball milling. The structure and morphology of the synthesized BNNSs were meticulously analyzed using scanning electron microscopy and ultraviolet spectroscopy. The results demonstrated that the BNNSs exhibited high crystallinity, improved efficiency in h-BN exfoliation, enhanced performance and yield of BNNSs, further reducing costs with BNNS preparation. This research focuses on the effect of various parameters on the final sample obtained.

Keywords - h-BN, BNNS, SEM, UV-Vis.

1. Introduction

Hexagonal Boron Nitride (h-BN), [1] which belongs to a hexagonal system, is a white block or powder, has a layered structure like the graphene lattice constant and similar characteristics, and is sometimes referred to as 'white graphene'. h- BN is a lattice alternately arranged by B atoms and N atoms in a two-dimensional plane by hexagonal lattice formation, showing a honeycomb structure [2]. The N atomic nucleus and B atom are combined by a sp2 orbital to form a strong s bond, with the interlayer combined by weak Van der Waals forces such that it can slide easily between the layers and has lubricating properties [3].

BNNS are the 2D materials derived from h-BN, which possess excellent optical, thermal, chemical and electrical properties. The structure of BNNS is like that of graphene; BNNS can be mass-produced through two primary methods [4-6]. Many researchers in the past have proved that BNNS not only improves all the above-stated properties by providing chemical stability when incorporated into a material in any form, but has significantly improved the material's mechanical properties as well [7]. Ball milling done in the presence of certain solvents leads to high efficiency in terms of exfoliation, and this can be further considered as a preferred method of industrial production. [18-21] One method involves micro-milling h-BN followed by sonicating it with assisted exfoliation. Alternatively, BNNS can be grown with or without a substrate using chemical vapor deposition [2]. The synthesis of boron nitide nanosheets focuses primarily on size, shape, thickness, density, and alignment. The high energy, which leads to the exfoliation of the h-BN, introduces structural defects that might degrade the properties of the material. Further to this exploration in the field of optimized solvents and additives, which can mitigate the damage caused by milling. The main criteria while considering milling while synthesizing are the defect levels, the sheet size and identifying the optimal milling conditions which lead to structural integrity. Variables like Ball-to-Powder Ratio (BPR) and ball size. Milling speed and time greatly influence the quality of BNNS achieved.

2. Literature Review

The two-dimensional nanostructure derived from hexagonal boron nitride is called BNNS. Some of the most popular methods of manufacturing BNNS from h-BN are via the bottom-up vapour deposition method [8], exfoliation with the help of chemicals [9], Solvent exfoliation assisted by ultrasound [10] and Mechanical exfoliation [11]. Chemical exfoliation requires working with chemicals like $KMnO_4$, H_2SO_4, H_2O_2 or utilizing molten KOH/ NaOH. The critical challenges when working with chemical preparation methods are low exfoliation efficiency and the risk to operators while handling chemicals [12-15].

The process of Chemical vapor deposition is the one that produces well-dispersed, high-purity BNNS, which possess the best properties in terms of chemical, thermal and electrical stability. Even with all the benefits stated, the procedure of preparation via CVD requires temperatures of 900-1300°C, with extremely expensive equipment and poor yield. Therefore, this method cannot be considered for large-scale production [8, 16, 17]. There have been many works showcasing recent works in various directions related to the exfoliation of BNNS from h-BN.

The first one refers to exfoliation, wherein h-BN is assisted with hierarchical ionic fragments by ball milling. It utilizes coordination polymers during low-energy ball milling and further achieves a yield of a few layers of BNNS. [23]. The second one uses high-energy planetary ball milling up to 30 h, reducing the particle size from 1 µm to 400 nm flakes by utilising -OH and –NH$_2$, which FT-IR confirms. An improvement in hardness, wear resistance, and compressive strength is observed when the Al matrix is incorporated. [24].

The third one introduced -OH onto h-BN and exfoliated via in-situ pressure. This led to large flakes of approximately 45% with stable dispersibility, and these were further incorporated into TPU, which improved the thermal conductivity and stability. [25] The fourth paper used silane KH-550 [26] to reduce the thickness and to increase nanosheet formation, whereas the last applied vertical load and shear motion to the BNNS produced via ball milling, proving less damage and larger flakes showcasing high crystallinity, large lateral BNNS via synergistic mechanical-sonic. [27]. This led to choosing ball milling as one of the most upcoming research fields.

3. Experimental Details for Synthesis
3.1. Selection of Materials
Bulk Boron Nitride, Extra pure with 99% purity, was purchased from Oxford Lab Fine Chem LLP with a molecular weight of 24.82 g/mole. Toluene anhydrous was purchased from Sigma Aldrich via Merck with a purity of 99.8% and a molecular weight of 92.14 g/mole.

3.2. Conversion of h-BN to BNNS via Ball Milling
Ball milling in this case leads to cold welding, which increases the lateral surface area of the powder, increasing the surface area required for coating. The ball milling apparatus used was Fritsch P-5 high energy ball milling apparatus model 07.5000/01408 wherein bulk boron nitride was wet milled in presence of toluene at 300 rpm for 30 hours to prepare boron nitride nanosheets by taking ball to powder ration as 10:1. Toluene in the case of ball milling acts as a reducing agent which creates a barrier between the walls of the vial and powder, preventing the powder from sticking to the walls of the vial. Tungsten was the material of the vial, and the material of the balls was steel coated with tungsten carbide of the milling machine, wherein the diameter of the [22] balls taken was 10 mm.

The vial contains the bulk powder wherein the tungsten balls were added to the bulk material. The high-speed rotation of the vial creates momentum and collision between the balls. The tungsten balls exert extensive force on the powder, which leads to breaking the bulk powder into smaller sizes. The rotation of the ball mill occurs around the horizontal axis, wherein internal cascading is the main cause of the reduction in the size of the powder. This effect can cause the powder size to reduce as low as 5nm [22]. A cooling time of half an hour was considered after every half an hour of milling.

4. Characterization and Results
4.1. Characterization
Characterization of the 30-hour milled sample was done using Scanning Electron Microscopy (SEM; FEI, Quanta 200) at various magnifications. The first characterization was done for the parent h-BN sample with milling for a detailed comparison of the milled sample with the original parent sample. Further to which UV-Vis spectroscopy of the milled sample was achieved using an Agilent Cary 100 UV-Vis Spectrophotometer

4.2. SEM Imaging of h-BN and BNNS Milled Sample with Various Magnifications
A SEM image can be analyzed based on morphology and surface features. SEM is usually used to verify the flake lateral size, thickness estimation, layer stacking, folds and the edges. Figure 1 shows the h-BN or 0-hour milled sample in which the presence of prominent hexagonal or platelet-like structures, which appear flat and uniform, is evident. The SEM image below reveals minimal fragmentation of the particles, wherein the platelet-like particles showcase minimum disruptions. Large and unaltered particles indicate milling has not begun, wherein the particles appear well defined, indicating no mechanical disruptions.
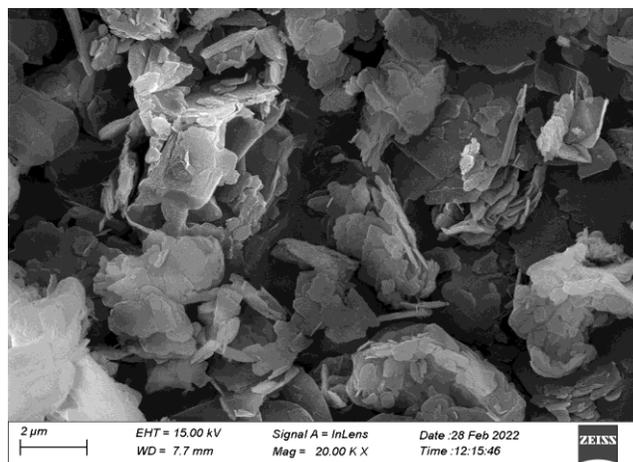

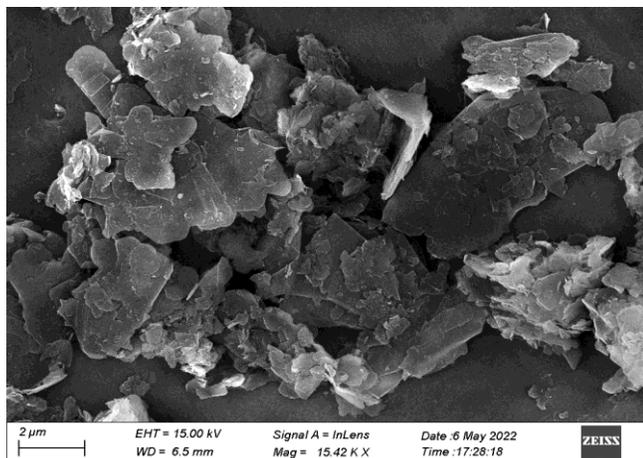**Fig. 1 SEM image of 0-hour milled sample of h-BN**

Once the magnification is increased from 15.43KX in Figure 2 to 27.23 KX in Figure 3, even finer morphological aspects can be seen in terms of the exfoliation, fragmentation and surface finish related to BNNS. The wrinkled sheets clearly become visible, and the edges are folded, indicating a few or a single layer of BNNS, which imparts mechanical flexibility and is caused by repeated collisions during prolonged milling. The magnification increase now resembles ultrathin flakes rather than a platelet-like structure. The individual layers or stacking is visible in contrast to the tightly stacked h-BN, which indicates delamination, which is a consequence of the successful exfoliation process of the parent material in nanosheets.

An increase in the lateral size is more clearly visible, which can be from a few nanometres to 1-2 micrometres, whereas a drastic reduction in the thickness can be inferred in contrast to the parent h-BN image. The magnified image also shows a better view of the mechanical defects caused by milling. Holes and teats within the sheets, surface roughness, edge tearing and irregular borders are a few visible signs of over-milling and stress damage.

Fig. 2 First image of 30-hour milled h-BN sample turning to BNNS at a magnification of 15.42 KX

The above SEM image is of a 30-hour ball-milled sample, which clearly indicates conversion of h-BN into boron nitride nano sheets. Figure 2 shows a magnification of 15.42KX, which reveals clarity in terms of morphological changes, showcasing considerable size reduction in the particle size, which happens due to the extensive mechanical exfoliation or repeated mechanical stress. The above image shows thin layered sheets of particles like crumpled wrinkled flakes with irregular and curled edges, which is typically the morphology of BNNS. The sheets are much thinner than the parent material, wherein the lateral dimension can vary from 10 nm to a few micrometres.

The above image also indicates a highly fragmented, delaminated structure with no longer defined hexagonal platelet-like structure visible as in the original form. The image shows a dispersed, loosely stacked structure indicating an increase in surface area with voids at certain places, implying that the interlayer Van der Waals forces have been overcome, and a high degree of exfoliation has occurred.
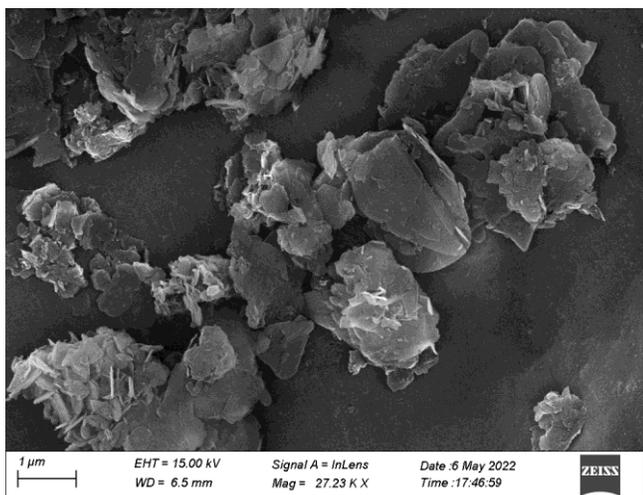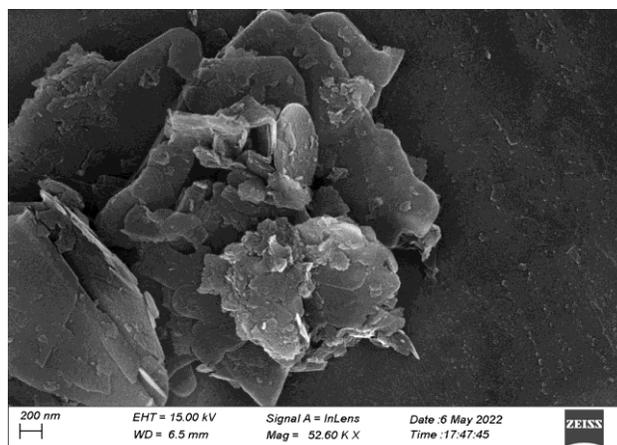

Fig. 4 SEM image of a 30-hour under milled h-BN sample with clear images of BNNS under magnification of 52. 60 KX

Figure 4 showcases a 52.60 KX magnification and offers confirmation in terms of the exfoliation process and the nano-structural features. At this magnification, fine details of nanosheet morphology can be observed, wherein the surface texture and the damage caused by milling are also clearly distinguishable. The nanosheets in the above image appear ultrathin, layer-like and are clearly separated and distinguishable. The folded edges and wrinkled surface are common visible factors. An extensive exfoliation from the bulk h-BN to BNNS can be observed via disconnected flakes, in contrast to thick clusters and flat-lying sheets with clear and visible boundaries. The surface appears rough with wrinkles, ripples and deformation lines visible on sheet surfaces. At this magnification, nanoscale cracks and pinholes can also be seen. The surface factors are a result of the shear forces and prolonged mechanical energy acting on the material.

Fig. 3 SEM Image of 30 hours under the magnification of 27.23 KX

The edges appear to be torn, irregular and frayed due to mechanical delamination of the original crystal from repeated collision during 30 hours of ball milling. A difference in thickness is observed wherein some areas appear darker and the others appear thinner and transparent. This is due to the high electron density in thicker areas, indicating the presence of multi-layer stacks, whereas the others are a few-layer BNNS
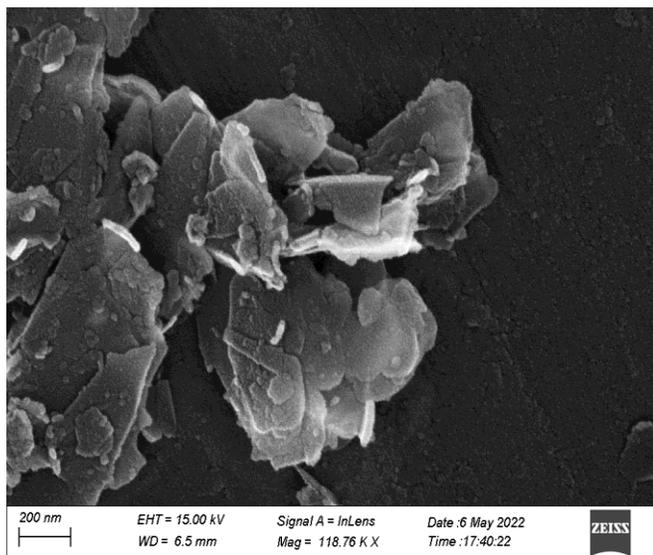

Fig. 1 SEM imaging for a 30-hour milled h-BN sample leading to BNNS under magnification of 118.76 KX

Figure 5 depicts the maximum magnification wherein a detailed nanoscale view of the exfoliated material structure is visible. The magnification highlights fine morphological edges and surface features of thin layer stacks, providing proof of successful exfoliation with visible nanoscale damage and texture.

The image displays ultrathin sheets which are either individual or a few-layered, and as the thickness of the sheets is extremely low, they exhibit high electron transparency, appearing brighter or fainter depending on the number of layers, which further helps in distinguishing between mono and few-layer BNNS.

Another parameter visible from the above image is the fine wrinkling, folding and bending of nanosheets, which is a result of high mechanical energy provided to the sample for over 30 hours. Some of the sheets appear to be suspended and partially lifted from the substrate, indicating a lightweight and flexible nature.

Damage in terms of frayed and torn edges with nanoscale roughness is visible, resulting from mechanical damage and structural degradation, which is a repercussion of long milling hours. Nano wrinkles, pinholes and microcracks are visible at this magnification, which also indicate internal stress, strain and point defects in certain areas.

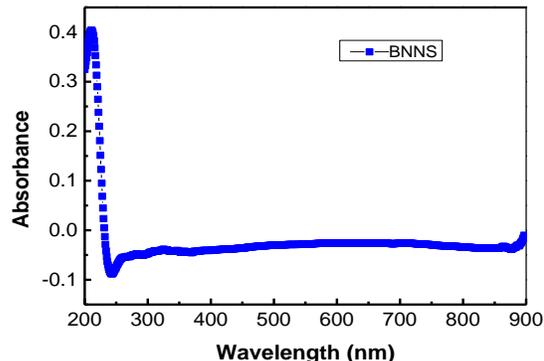### *4.3. UV Spectroscopy of 30-Hour Milled Sample*

Fig. 2 UV-Vis Spectroscopy of 30-hour milled sample

This UV-Visible Spectroscopy of a 30-hour milled sample shows the transformation of h-BN into Boron Nitride Nanosheets (BNNS), revealing extensive information about the electronic transitions, optical properties and exfoliation quality. The absorption peak is usually observed around 200-240nm, which is attributed to the $\pi \rightarrow \pi$ transitions of the B-N bonds in h-BN. The peak is a sign denoting a sp² hybridized planar BN structure, which is present even after exfoliation. A blue shift observed from ~ 220-225nm for h-BN to ~240-245 nm in the UV-Vis spectrum indicates successful exfoliation into a few layers or a layer of BNNS. A quantum confinement effect is visible due to the reduced thickness of nanosheets. UV Spectroscopy of the sample shows a sharp dip responding to a wavelength of 240nm against absorbance. The E_g value of the sample can be found using the

$$E = \frac{hc}{\lambda}$$

Increased bandgap energy is calculated by using the above formula, wherein it is observed that a larger band gap is present than in the bulk material in the formulated BNNS. It is also observed that a broadened and asymmetric peak is achieved. This is due to varying sheet thickness and some observed defects.

5. Conclusion

Synthesis and characterization of Boron nitride nanosheets were carried out from h-BN, wherein the preferred method of high-energy ball milling was used. The parent h-BN was milled for 30 hours using toluene as the reducing agent. The above-mentioned procedure was followed to achieve nanosheets. These were further confirmed by SEM imaging, which was compared in depth to the h-BN SEM imaging. The surface morphology, surface finish, and edge morphology were compared to the parent material and observed at various magnifications. The magnification at 118.76KX revealed nanoscale cracks and defects, which are introduced in the material due to mechanical stress and high-

energy ball milling. UV-Vis of the 30-hour milled sample indicated a high energy band gap present in BNNS. BNNSs exhibited high crystallinity, improved efficiency in h-BN exfoliation, enhanced performance, and yield, further reducing costs with BNNS preparation. The method of ball milling proved successful in the synthesis of BNNS but introduces defects and nanoscale cracks in the material, which restricts the use of BNNS produced by this method for ultrasensitive areas like electronics, but can be implemented for film preparation to be used as coatings for superhydrophilicity and radiation absorption. The above method is an improved BNNS synthesis method that enables more reliable fabrication of devices where high-quality, defect-free 2D BN is critical, such as in dielectric barriers, thermal management materials, or 2D heterostructures. Furthermore, the scalability and environmental safety make it an attractive candidate for industrial adaptation.

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