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%.

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].
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 sonication 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<sub>2</sub>O<sub>2</sub> as oxidant and subsequent liquid exfoliation of functionalized BN is reported. The oxidative exfoliation of bulk hBN to nanosheets with the aid of H<sub>2</sub>O<sub>2</sub> 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 PSOCOR10 Raman Microscope at λ = 532 nm laser excitation. X-ray Photoelectron spectrometer (XPS) (Bestec, Al Kα radiation (1486.6 eV), working at a pressure of 10<sup>-10</sup> 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 DualScopeTM 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, Stidy-up Diffractometer), Cu Kα radiation, λ=1.5406 Å and step size= 0.2° (2θ).

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...
heated to 400–500°C for degasification. After that, a certain amount of grounded hBN was added to 200 ml solution of \( \text{H}_2\text{O}_2 \) 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, \( \text{H}_2\text{O}_2 \) would thermally decompose to give \( \text{H}_2\text{O} \). 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 \( \mu \text{m} \)) 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

\( \text{H}_2\text{O}_2 \) 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 \( \text{H}_2\text{O}_2 \) is produced by anthraquinone oxidation process [34]. The cost of production of \( \text{H}_2\text{O}_2 \) 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 \( \text{H}_2\text{O}_2 \) (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 \( \text{H}_2\text{O}_2 \) 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.
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)
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
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
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, BNNSs is soluble due to its hydroxyl groups. It was observed that the milky solution of the BNNSs can stay stable for a long period of time. BNNSs 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 TEM images show some BNNSs 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 BNNSs 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 26= 26.962°, 41.798°, and 55.266°, with d-spacing...
of 3.307, 2.161, and 1.662 Å, 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 BNNSs, the Scherrer broadening, confirms the exfoliation of hBN and the reduction of crystallite sizes. The exfoliated BNNSs pattern also has distinct changes compared to hBN. The decreased intensity of (002) peak, shifting to lower angle, 2θ = 26.760°, 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.
CONCLUSIONS

The ability to substitute a difficult and lengthy solvent-based approach to produce boron nitride nanosheets with a moderate treatment of H$_2$O$_2$ is presented. Compared to previous studies, this green process resulted in a relative increase in efficiency (17-20%) and a better quality of BNNSs. 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 BNNSs 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

Z. Rafiei-Sarmazdeh et al. / Boron Nitride Nanosheets by Green Chemistry Method


