Large Scale Thermal Exfoliation and Functionalization of Boron Nitride

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Hexagonal boron nitride (hBN) is a thermally stable material with uses ranging from cosmetics to high temperature lubricants.[1] hBN does not occur naturally; but is manufactured industrially at high temperatures from boron sources such as boron oxide or boric acid and nitrogen sources such as melamine, urea, or ammonia. In many ways hBN resembles graphite: both consist of stacked sheets with the component atoms arranged in a honeycomb pattern, the boron/nitrogen pair of atoms is isoelectric to a pair of atoms in graphite, and both are good thermal conductors. The cubic form of boron nitride (cBN) is analogous to diamond, both in structure and hardness, with the hardness of cBN second only to diamond.

Unlike graphite, hBN is an electrical insulator with a band gap of 5.2 eV. It also has a much higher thermal stability than graphite, with a melting temperature near 3,000 °C.[1] In addition, hBN has been shown to be a superior substrate to silicon for graphene-based electrical devices.[2,3] Despite these impressive properties, the number of reports of hBN composites is very small compared to graphite.[4-6] Recent reviews of the field[10-12] describe examples of solvent based sonication techniques that, while successful for graphite exfoliation, are capable of generating only partially exfoliated hBN at mg/ml concentrations. Thus, while hBN has similarities to graphite, the large scale formation of a graphite oxide (GO) analog has not been achieved due the resistance of hBN to the oxidation process used for preparing GO, and thus the large scale exfoliation of hBN has remained a challenge. In the work presented here, we demonstrate for the first time the formation of large quantities of functionalized exfoliated boron nitride sheets.

For fundamental studies, chemical vapor deposition (CVD) can be used to produce single sheet hBN.[13-18] However, for large-scale applications, such as nanofillers in polymer composites, exfoliation is a more economically attractive route to single sheet hBN. Previous attempts to produce hBN nano fillers include the work of who Zhi used the sonication of hBN in N,N-dimethylformamide (DMF) to produce layered hBN with the functionality of the sheets not determined due to difficulties in obtaining FTIR spectra.[5] Other methods, not involving sonication, have included using graphene as a template for carbon substitution to form hBN,[19] exfoliation by reaction with molten hydroxides at low temperature[20] and the splitting of BN nanotubes to form ribbons, much like is done to form graphene ribbons from carbon nanotubes.[21]

In addition to exfoliation, the functionalization of hBN has also drawn interest. Methods for functionalizing hBN include a method to form associations of hBN nanosheets with alkyl amines by first using a ball mill to cleave the sheets and produce defect sites[22] and the use of hydrazine, hydrogen peroxide, nitric acid and sulfuric acid heated under pressure, followed by sonication, to produce 0.3 g L⁻¹ suspensions of hBN.[23] Although not using hBN sheets, it was shown that at high temperatures hBN nanotubes slowly form defect sites that can be used to break the tubes into smaller segments to aid in solvent dispersion.[24] Recently, Coleman used oxygen radicals in sonicated NMP solutions to attach hydroxyl groups to hBN.[25]

The state of hBN is much like that of graphite before methods of large-scale functionalization and exfoliation were developed. The exfoliation and suspension of GO in water opened the door to much of the current research in graphene materials.[26] To the best of our knowledge, there has been no report of the formation of the hBN equivalent of GO: hydroxylated sheets that enable the aqueous suspension of single sheets in high yield. In this report we describe such a system, and using atomic force microscopy (AFM), thermogravimetric analysis (TGA), FTIR, field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), x-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Raman spectroscopy, chemical functionalization, and dynamic light scattering (DLS), we describe the functionalized single sheets and their mechanism of formation. We also demonstrate the reactivity of the hydroxylated hBN by functionalization with phenyl isocyanate.

The chemistry used to form GO does not work with hBN as hBN is very resistant to oxidation.[27] However, we find that heating hBN in air results in a mass gain as oxygen is
incorporated into the hBN lattice. Following the heat treatment, stirring the material in deionized water for several minutes results in the mixture thickening as the thermally treated material hydrolyzes and exfoliates to form hydroxylated boron nitride (BNO). These sheets form a suspension without the need for sonication, although mild bath sonication is normally used to increase the rate at which the suspension forms. Yields of water suspended sheets are \( \sim 65\% \), with the balance precipitating from the aqueous suspension as larger, less hydroxylated material that remains stacked.

Shown in Figure 1A is a vial containing pristine hBN in deionized water after bath sonication. Figure 1B shows BNO suspended in water with no sonication. There is no apparent water solubility with pristine hBN, while the hydroxylated material results in a cloudy suspension containing a small amount of precipitate on the bottom of the vial. Figure 1C shows an AFM image of these suspended sheets drop cast on an HOPG surface. The sheets are single layers, with lateral dimensions on the hundreds of nanometers length scale. A height histogram (Figure S1) gives the sheet thickness to be 0.69 nm. No centrifugation is employed to fractionate the sheets for AFM imaging, and thus the image represents the entire population of suspended material. This is in stark contrast to other methods that rely on centrifugation to separate the samples into fractions with different numbers of hBN layers.

The BNO is also investigated by transmission electron microscopy (TEM), Raman spectroscopy, and dynamic light scattering (DLS). TEM images (Figure S2) are in good agreement with the AFM analysis, and show single sheets with lateral dimensions of 100–200 nm. Raman analysis (Figure S3) indicates a blue shift of 2 cm\(^{-1}\) in the \( \text{E}_{2g} \) phonon mode at 1369 cm\(^{-1}\) for the BNO, \(^{[28]}\) and DLS (Figure S4) analysis shows a mean diameter of 360 nm.

To understand the mechanism of BNO sheet formation, FTIR and TGA are used to monitor the reaction. Figure 2A shows the FTIR spectra obtained at different stages of material synthesis. Prior to heating, the spectrum of pristine hBN exhibits only the characteristic peaks of B-N in-plane stretching at 1370 cm\(^{-1}\) and B-N-B out of plane bending observed at 810 cm\(^{-1}\), as shown Figure 2A(a). \(^{[29]}\) The formation of boron–oxygen bonds in the heated material (before adding to water) is indicated in the FTIR spectrum 2A(b) by the B-O-H peak at \( \sim 3200 \text{ cm}^{-1} \) and the small in-plane peak near 1200 cm\(^{-1}\). \(^{[25,30]}\) The peak at 1200 cm\(^{-1}\) has been assigned previously to boron coordinated with three oxygen atoms in an extended lattice. \(^{[30]}\) After washing with water (Figure 2A(c)), the peak near 1200 cm\(^{-1}\) disappears while the B-O-H peak remains, with a shoulder at \( \sim 3400 \text{ cm}^{-1} \) indicating loss of the in-plane B-O bonds. \(^{[13]}\) The reason for the decreased B-O-H peak intensity seen near 3200 cm\(^{-1}\) before washing (2A(b)), and after washing (2A(c)), is not completely clear. It may be as simple as dryness of the samples, but storing in a vacuum oven prior to analysis did not appear to have an effect. Alternatively, the loss of peak area may be attributed to the loss of small, highly functionalized sheets during the washing process. A further explanation may be the presence of both \( \text{N}_2\text{BOH} \) and \( \text{NB(OH)}_2 \) groups in the initial sample, with the washing step leading to the decomposition of \( \text{NB(OH)}_2 \) to boric acid. Efforts are currently being made to resolve this issue. That the peaks correspond to hydroxyl groups is supported by Figure 2A(d) however, as they completely disappear upon treatment with phenylisocyanate. The isocyanate is very reactive towards hydroxyl groups and results in the disappearance of the O-H stretch.
In order to show that our material is not simply boric acid from the decomposition of hBN, the hydroxylated BNO is repeatedly washed with hot water to remove boric acid. This does not result in loss of the hydroxyl peaks in the FTIR. Additionally, boric acid melts at 171 °C and boils at 300 °C. As the oxidation is run open to the air at 1000 °C, the retention of formed boric acid is unlikely and would be observed as a loss of mass in the TGA. Additionally, FTIR spectra comparing boric acid with hydroxylated hBN (Figure S5) indicates no significant formation of boric acid. Another possibility, the formation of boron trioxide, B2O3, from boric acid is ruled out as no evidence of it is seen by AFM or FESEM, and our heating rate is not conducive to its formation.[31] Even if a trace amount of B2O3 is formed, it will be converted to boric acid during treatment with hot water and removed.

As mentioned previously, hBN is thermally stable, and we find that at 800 °C, no significant oxidation is observed. As the temperature is raised, there is an increase of mass with time, and the rate of oxidation increases with increasing temperature (Figure S6). TGA studies indicate that when heated in air a temperature of 1000 °C, hBN gains mass for a period of time, followed by a leveling off (Figure 2B, top). In contrast, when heated in an argon atmosphere at the same temperature, no mass change is observed (Figure 2B, middle). Interestingly, when heated in a nitrogen atmosphere at 1000 °C, the hBN loses mass (Figure 2B, bottom). While no reaction is seen in an argon atmosphere, a stable oxidation product is formed in air. In nitrogen, however, with no oxygen present, slow decomposition is observed. This is in agreement with the findings of others who have observed a loss of mass in a nitrogen atmosphere[22] and mass gain in air.[12] Unlike other studies however, we observe a plateau in the weight gain with oxidation, apparently caused by the complete oxidation of regions susceptible to oxidation at that temperature.

Oxygen addition occurs in the plane of the hBN, resulting in the insertion of oxygen into the hBN lattice, as has been observed in chemical vapor infiltration studies done at the same temperature used in our study.[33] Our XRD studies indicate that the d-spacing of hBN and BNO are the same, suggesting the oxygen is inserted into the plane of the BN. Evidence for the formation of B-O rather than N-O bonds comes from X-ray photoelectron spectroscopy (XPS) shown in Figure 2D. The XPS spectrum of BNO identifies the B1s and N1s peaks. Both values are in close agreement with values reported for pristine hBN.[13] Due to the background oxygen content of the sample, which we speculate to result from trace amounts of oxygen absorbed on the nanosheets, we use fitted 1s peaks of different species to find the oxygen bond. While boron atoms show both a B-N 1s peak at 191 eV and a B-O 1s peak at 191.7 eV, nitrogen is found to be bound only to boron atoms. The ratio of B-OH to B-N peak areas is approximately 1:10. In pristine hBN, boron and nitrogen are bond only to each other, without any oxygen. The oxidation sensitivity of boron sites is consistent with results from other published work.[25,34]

To study the morphology of the BNO, FESEM and TEM are employed. Figure 3A shows pristine hBN with dimensions of microns and smooth surfaces and edges, while the hydroxylated BNO sample (Figure 3B) clearly shows the rough edges and “divots” on the surface corresponding to the size of the single sheets imaged by AFM in Figure 1C. Similar results are also obtained by TEM (Figure S4 C), where roughly circular thin spots are seen decorating the previous (prior to heating) surface. Electron-diffraction patterns of BNO reveal the typical six-fold symmetry structure of hBN. Figure 3C shows BNO sheets obtained by drop casting an aqueous suspension on a SEM stub. The images of the sheets are consistent with those obtained by AFM, but with the high concentration of sheets leading to sheet overlap.

To demonstrate the reactivity of the hydroxyl groups on the BNO sheets, we reacted the precipitated BNO (the larger, unexfoliated pieces) with phenyl isocyanate. From the FESEM image shown in Figure 3D, the sheets appear to be pulled back and folded as a result of the added functional groups. This is analogous to what is observed when graphite is oxidized to GO.[35] The well-known turbostratic structure, parallel layered but randomly stacked graphite, has an interlayer spacing (3.44 Å), considerably greater than ideal graphite (3.35 Å). The XRD spectrum of the functionalized BNO is shown in Figure 2C, where the XRD trace of pristine hBN is superimposed with the trace of isocyanate functionalized BNO. After reaction with the isocyanate, the XRD profiles of the 002 reflection moves to a slightly lower angle of 26.41°, a larger d spacing of 3.37 Å, and is broader as compared to pristine hBN (26.79°, 3.32 Å). The disappearance of the hydroxide group after functionalization is also confirmed by the FTIR in Figure 2A(d). The reaction is believed to form new B-NPh groups, substituting the hydroxide groups, in a manner similar to that observed with boric acid and isocyanates.[36] The phenyl group is not seen in the spectrum due to the low density of functional groups on precipitated BNO.

In this report, we have described the formation of the hBN analog of GO by heating hBN in air followed by treatment with water. We have fully characterized the formed BNO and proposed a mechanism for its formation. Just as the use of GO has allowed for the utilization of graphitic
material in numerous applications, the availability of large quantities of exfoliated, functionalized BNO is expected to allow for the incorporation of BNO as a multifunctional nanofiller as well as providing material for sensing and catalytic substrates. Other potential applications include the use of hBN in electronics, especially in conjunction with graphene. With this method it will be possible to more fully utilize the thermal conductivity, chemical inertness, and electrical insulating properties of this promising material.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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