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Exfoliation of Hexagonal Boron Nitride via Ferric Chloride Intercalation

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Summary

NaF was used as an activation agent to successfully intercalate $FeCl_3$ into hexagonal boron nitride (hBN). This reaction caused the hBN mass to increase by ~100 percent, the lattice parameter c to decrease from 6.6585 to between 6.6565 and 6.6569 Å, the x-ray diffraction (XRD) (002) peak to widen from 0.01° to 0.05° of the full width half maximum value, the Fourier transform infrared (FTIR) spectrum's broad band (1277 cm^{-1} peak) to change shape, and new FTIR bands to emerge at 3700 to 2700 and 1600 cm^{-1}. This indicates hBN's structural and chemical properties are significantly changed. The intercalated product was hygroscopic and interacted with moisture in the air to cause further structural and chemical changes (from XRD and FTIR). During a 24-h hold at room temperature in air with 100 percent relative humidity, the mass increased another 141 percent. The intercalated product, hydrated or not, can be heated to 750 °C in air to cause exfoliation. Exfoliation becomes significant after two intercalation-air heating cycles, when 20-nm nanosheets are commonly found. Structural and chemical changes indicated by XRD and FTIR data were nearly reversed after the product was placed in HCl, resulting in purified, exfoliated, thin hBN products.

1.0 Introduction

The structural similarity between hexagonal boron nitride (hBN) and graphite is highlighted by the widespread use of the term "white graphite" for boron nitride (BN). This similarity has led to the efforts of using carbon chemistry and technology as guidance for research in BN chemistry and technology. Such efforts resulted in the synthesis of cubic boron nitride (cBN) based on the structure of diamond (Ref. 1), and boron nitride nanotubes (BNNT) based on the structure of carbon nanotubes (Ref. 2).

On the other hand, the differences in chemical bonding between graphite and hBN leads to differences in properties such as electrical conductivity and reactivity to air at high temperature. The ionic interlayer bonding in hBN is much stronger than the Van der Waals force between the graphite layers, causing differences in the reactivity in intercalation. This also leads to differences in the efficiencies of mass production of their respective exfoliated products for engineering applications.

1.1 Intercalation and Exfoliation for Exfoliated Products and Graphene

A layered material is "intercalated" when other chemicals are inserted into the layers. A layered material is "exfoliated" when the layered structure splits into thinner layers. Graphite can easily be intercalated (Ref. 3) and then exfoliated by driving intercalates out of the layers quickly and/or explosively. The process of intercalation-exfoliation of graphite has been applied for engineering applications. Fabrication of flexible graphite, or grafoil, is an example (Ref. 4). Recently there are reports that this process has been used to split graphite into graphene in large quantities (Ref. 5).

The similarity between carbon and BN suggest the possibility that BN can easily be intercalated and exfoliated as well (Ref. 6). However, this is not the case. Starting from hBN instead of graphite, the above process to produce a large quantity of exfoliated hBN or "white graphene" has not been successful (Ref. 7). Intercalation of hBN is difficult. Alkali metals (Li, Na, and K) (Refs. 8 and 9) and fluorosulfate ($S_2O_6F_2$) (Ref. 10) are among the few intercalates that were successfully intercalated into hBN. Doing this

involves highly reactive chemicals and reactions. The feasibility of using these chemicals for mass producing exfoliated hBN or white graphene was not studied or discussed in these reports. The less reactive intercalates for graphite, such as metal chloride, was found to be unreactive to hBN. Most notably among them is ferric chloride ($FeCl_3$). After examining the claims and counter claims, it is generally believed that intercalation of hBN with $FeCl_3$ in particular or metal chloride in general is not likely (Refs. 3, 10, and 11). For producing exfoliated hBN, the less-efficient method of functionalization, sonication, and centrifuge is commonly used (Ref. 7). For white graphene, either plasma etching (Ref. 12) or micromechanical cleavage is used for minute quantities (Ref. 7).

1.2 BN Nanotechnology: BNNT Intercalation and Exfoliation

Although hBN exfoliation by way of intercalation with metal chloride has not been successful, recent efforts in BN nanotechnology suggests this can be done. Figure 1 shows the walls from two exfoliated BNNTs resulting from removing iron nanoparticles and other impurities from BNNTs during purification (Ref. 13). Also, although BNNTs cannot be intercalated by direct exposure to molten $FeCl_3$, the wetting and cleaning effects of BNNTs by $FeCl_3$ has been observed (Ref. 14). In addition, BNNTs intercalated with potassium and then exfoliated by reacting to water was successfully demonstrated (Ref. 15). This led to a hypothesis that if hBN may be chemically activated similar to BNNTs, intercalation of hBN with $FeCl_3$ and subsequent exfoliation may be possible.

This hypothesis is in parallel with the experience in carbon intercalation: Some of the graphite intercalation reactions need to be "activated" in order to proceed. For example, graphite cannot be intercalated with iodine unless the graphite is "activated" by bromine or HBr (Ref. 16).

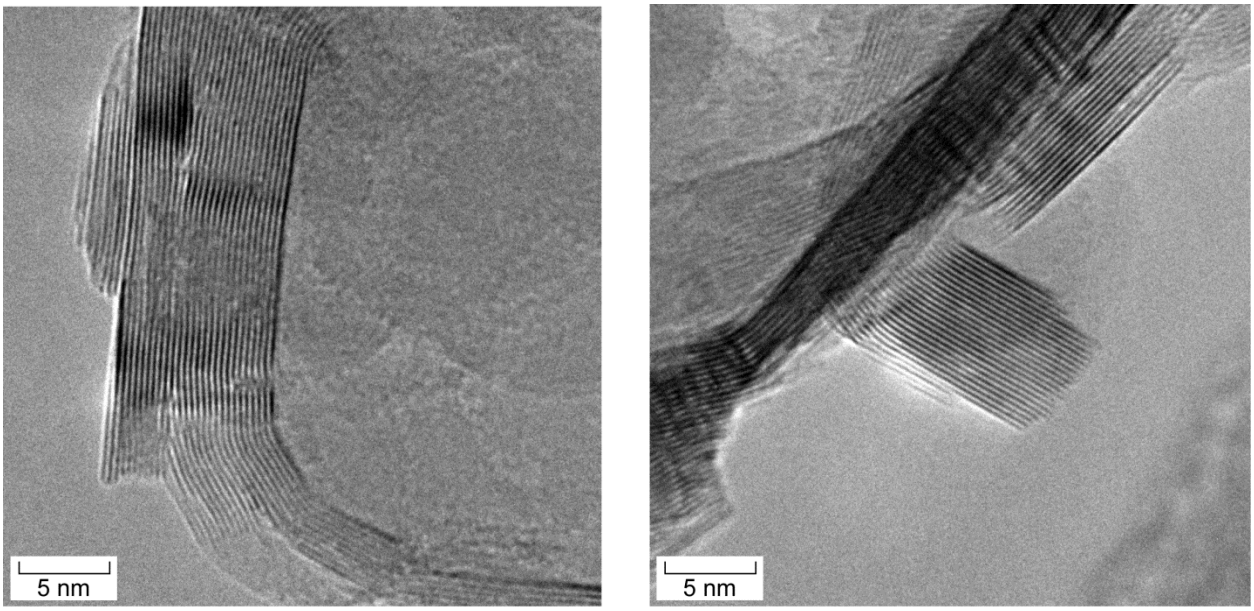

Figure 1.—TEM images of two examples of exfoliated BN sample resulting from purification of BNNTs.

2.0 Methods and Experiments

2.1 General Experimental Approach

This research examines two processes to produce exfoliated hBN.

Process 1:

$$\mathrm{hBN} + \mathrm{FeCl_3} \xrightarrow[\text{Heat}]{\text{Activation agent}} \mathrm{A\ (intercalated\ product)} \tag{1}$$

To determine the stability of the intercalated product in dry air, a portion of the intercalated product A was stored in dry air for 4 months and characterized twice during this period. The rest was used to synthesize the exfoliated hBN material:

$$\mathrm{A} \xrightarrow[\text{Heat}]{} \mathrm{B^*} \xrightarrow[\text{Rinse with water}]{} \mathrm{B\ (exfoliated\ product)} \tag{2}$$

The chemical reaction experiments conducted in this research for possible intercalation reactions are similar to those described in previous reports (Refs. 11 and 17), except in this report, sodium fluoride (NaF) was added to the original reactants. NaF was considered as a possible activating agent for intercalation because its aqueous solution with hydrochloric acid (HCl) was previously observed to attack and/or activate BNNTs (Ref. 13). The products of Reactions (1) and (2), A and B, were then further examined for evidence of intercalation and exfoliation.

The processes of intercalation and exfoliation described above were repeated in order to see if the additional effort would cause further exfoliation. That is,

$$\mathrm{B} + \mathrm{FeC1_3} \xrightarrow[\text{Heat}]{\text{Activation agent}} \mathrm{C\ (intercalation)} \tag{3}$$

$$\mathrm{C} \xrightarrow[\text{Heat}]{} \xrightarrow[\text{Rinse with water}]{} \mathrm{D\ (exfoliation)} \tag{4}$$

The products A to D were then further treated chemically. They were rinsed with HCl at room temperature to remove impurities and intercalates:

$$\mathrm{A, B, C, or\ D} \xrightarrow[\mathrm{HC1}]{} E_A, E_B, E_C, E_D \tag{5}$$

Process 2:

The intercalated products (A or C) were exposed to room-temperature moist air for a period of time and characterized several times during this period to study the water-adsorbing characteristics of the apparently hygroscopic intercalated product:

$$\mathrm{A\ or\ C} \xrightarrow[\text{wet air}]{} \mathrm{A'\ or\ C'(hydration)} \tag{6}$$

The hydrated products were placed into a high-temperature furnace, and the moisture violently boiled off at a temperature much higher than 100 °C. This was found to induce exfoliation to a greater extent.

$$\mathrm{A'\ or\ C'} \xrightarrow[\text{Heat}]{} \xrightarrow[\text{Rinse with water}]{} \mathrm{B'\ or\ D'(exfoliation)} \tag{7}$$

The products A' to D' were then rinsed with HCl at room temperature to remove impurities and intercalates:

$$\text{A', B', C', or D'} \xrightarrow[\text{HCl}]{} E_{A'},\ E_{B'},\ E_{C'},\ E_{D'} \tag{8}$$

2.2 Chemicals, Apparatus, and Experimental Procedures

Two different kinds of commercially available hBN powder were used in this research. One comprises large platelets mostly 20 to 80 μm wide and 5 to 10 μm thick. The other one comprises mostly small platelets, 200 to 800 nm wide and 80 to 200 nm thick. Both of them are well crystallized, as indicated by their significant x-ray diffraction (XRD) peaks for hBN.

$FeCl_3$ (98 percent) and NaF (99.98 percent) used in the experiments were purchased from Alfa Aesar. NaF was used as purchased. $FeCl_3$, however, was distilled once immediately before being used in the intercalation reaction because it is highly hygroscopic. Its melting point and boiling point are 306 and 315 °C, respectively. When it evaporates/sublimates, a fraction simultaneously decomposes into $FeCl_2$ and Cl_2. For distillation conducted in this research, $FeCl_3$ was sublimated/evaporated at about 260 to 330 °C and then condensed at about 30 °C lower. Based on the vapor pressure (as a function of temperature) during decomposition for $FeCl_3$ (Ref. 18), the vapor pressure for Cl_2 during distillation was 4.4 torr at 260 °C and 72 torr at 330 °C. The $FeCl_3$ pressure was 51 torr at 260 °C and 688 torr at 330 °C under a system total pressure of 1 atm.

The detailed experimental procedures are as follows: Precalculated quantities of hBN, distilled $FeCl_3$, and NaF were weighed and mixed into a 50-ml test tube. The test tube was sealed using polytetrafluoroethylene (PTFE) tape, and then placed into a 500-ml reactor kettle, which is then sealed air tight. Pure nitrogen was then allowed to flow through valves into and out of the kettle to purge air and keep the system in an inert environment during the entire reaction period. The sample at the bottom of the test tube was heated to a temperature slightly below the melting point of $FeCl_3$ (306 °C) for intercalation, and eventually to a temperature slightly above the boiling point of $FeCl_3$ (315 °C) for letting the excess $FeCl_3$ boil off from the product in the bottom of the test tube and then condense at the top of the tube where the temperature is lower due to the lighter thermal insulation. After the reaction and the system cooled, the product was removed from the test tube and stored in dry environment. Results of the procedure described in this paragraph are products A or C in Reactions (1) to (5).

Samples of product A were then placed in a quartz watchglass, weighed, and placed into a furnace heated to 600 to 750 °C for a period ranged from 2 to 4 h using a preprogramed temperature schedule. After heating, the product is removed from the furnace, cooled, and rinsed with water. This is product B, described previously, from Reaction (2). This product was then further treated for intercalation according to the procedure described previously in Reaction (3) to form product C. In this research, some, but not all, of the product C was exposed to moist air, either at ambient humidity or at 100 percent relative humidity to form product C'. Both products C and C' were then placed in a quartz watchglass, weighed, put into a furnace heated to 600 to 750 °C for a period ranging from 2 to 4 h using a preprogramed temperature schedule, cooled, and then rinsed with water to result in products D (Reaction (4)) or D' (Reaction (7)), respectively.

Concentrated (35 wt%) HCl was used to remove intercalates (Reactions (5) and (8)).

Detailed reactant and product mass data and temperature schedule of the experimental runs used for this report are described in Table I.

TABLE I.—SUMMARY OF INTERCALATION OF AS-PURCHASED COMMERCIAL hBN WITH $FeCl_3$

Reactants[a]			Reaction temperature during two or three steps of sequential heating in nitrogen, temperature (°C)/duration (h)			Products[b]	
hBN type	Mass ratio					hBN mass content, percent	Label[d]
	NaF to hBN	$FeCl_3$ to hBN[c]					
L	0.120	2.7	315/12	340/2	---	55	A1
L	0.141	2.8	320/23	340/19	---	45	A2
L	0.115	2.3	290/14	320/30	355/16	54	A3
L	0.190	1.7	240/25	285/22	330/21	42	A4
S	0.14	2.7	290/3	330/38	---	45	A5

[a]Reactants were hBN, NaF, and excess $FeCl_3$. L indicates large platelets, mostly 20 to 80 μm wide and 5 to10 μm thick, and S indicates small platelets, mostly 200 to 800 nm wide and 80 to 200 nm thick.

[b]Products of the intercalation reaction were not washed. They included hBN, $FeCl_x$ where $2 < x < 3$ (the intercalated chemicals), FeOCl, and NaCl. The presence of NaCl and absence of NaF or fluorine atoms were confirmed by XRD and EDS data.

[c]Boiling point of $FeCl_3$ is 315 °C. At this temperature, iron chloride vapor is in dimer form and is partially decomposed to gaseous Cl_2 and solid $FeCl_2$. At one atmosphere under this condition, the equilibrium partial pressures for Fe_2Cl_6 and Cl_2 are 718 and 42 mmHg, respectively.

[d]These labels were used to identify the products described in text.

For hydration (Reaction (6)), the products A or C were placed on either a glass slide or watchglass and exposed either to ambient air with known humidity or to an enclosed container containing liquid water for 100 percent relative humidity.

2.3 Characterization Instruments

The samples were characterized using Fourier transform infrared spectroscopy (FTIR), XRD, and field emission scanning electron microscopy (FESEM).

An Agilent Cary 660 FTIR with an attenuated total reflectance (ATR) accessory was used to characterize IR bands near 1380 and 755 cm^{-1} for BN in the products.

A Bruker D8 Advance X-Ray Diffractometer was used to find XRD peaks for hBN and identify the impurities in the products. The samples were normally scanned at 0.02° (2Θ value) per step unless otherwise stated when extra precision was required (0.005° per step in that case). The full width at half maximum (FWHM) values as the width for hBN's (002) peak were calculated using the split-Pearson VII empirical fitting function. The (004), (006), and in some cases (008) peaks for hBN were used to accurately calculate the lattice parameter c using the fundamental parameters approach (Ref. 19) and the Pawley fitting method (Ref. 20) as implemented in the Bruker TOPAS software program. It is therefore a sensitive method to evaluate the state of intercalation. Nonhygroscopic samples, typically 10 mg in mass, were mounted as a thin layer on a flat "zero" background holder (ZBH), which consisted of a polished silicon wafer cut on a nondiffracting, high-index plane. Hygroscopic intercalated samples were mounted in a 0.5-mm deep well ZBH holder. The iron and chlorine concentrations for those samples were such that their x-ray penetration depths (95 percent contribution to the diffracted beam) were typically near 60 μm. Under these conditions, the FWHM values were not affected by the thickness of the samples being scanned.

A Hitachi S–4700II FESEM was used to study the morphology throughout the reactions studied in this research. Energy dispersive x-ray spectroscopy (EDS) was used to identify the chemical elements in the products.

3.0 Results and Discussions

3.1 XRD: Crystalline Lattice Structure and Phase Identification

The large hBN platelets (mostly 20 to 80 μm wide and 5 to 10 μm thick) were highly crystalline as seen by sharp and intense XRD peaks. Once intercalated, their layered lattice structure changes, with their XRD peaks becoming lower and wider, and their lattice parameters, especially the c parameter (a measure of the interlayer spacing), will also change. Observation of lattice structure changes at hBN's interior some distance away from the surface, at the reaction temperature of 240 to 360 °C, signals that the chemicals surrounding the platelets may have entered the interior (i.e., intercalated).

Figure 2 shows the experiments conducted in this research where large hBN platelets were intercalated and exfoliated for the first time. Note that the sample labels A1, A2, and A3correspond to the same labels in both Table 1 and the chemical label A in Reaction (1). The labels B*1, B*2, and B*3 (heated but not rinsed) correspond to the intermediate product in Reaction (2). The labels E_{A3} and E_{B*3} correspond to the chemical label E (HCl treated) in Reaction (5) or (8). The hBN's (002) peak width (FWHM) and the c parameters for the hBN reactant and all intermediate and final products were also included. We estimate the precision of the FWHM to be in the range of ±0.01° based on observation of sample repetitions. This is compared to the 0.01° to 0.05° of the FWHM values and 0.02° scanning step value during data collection. The lattice parameter data were based on analysis of (004) and (006) peaks. We estimate the accuracy and precision to be in the range of ±0.0005 Å based on observation of sample repetitions and comparison to results with an internal standard. Even though the analysis program

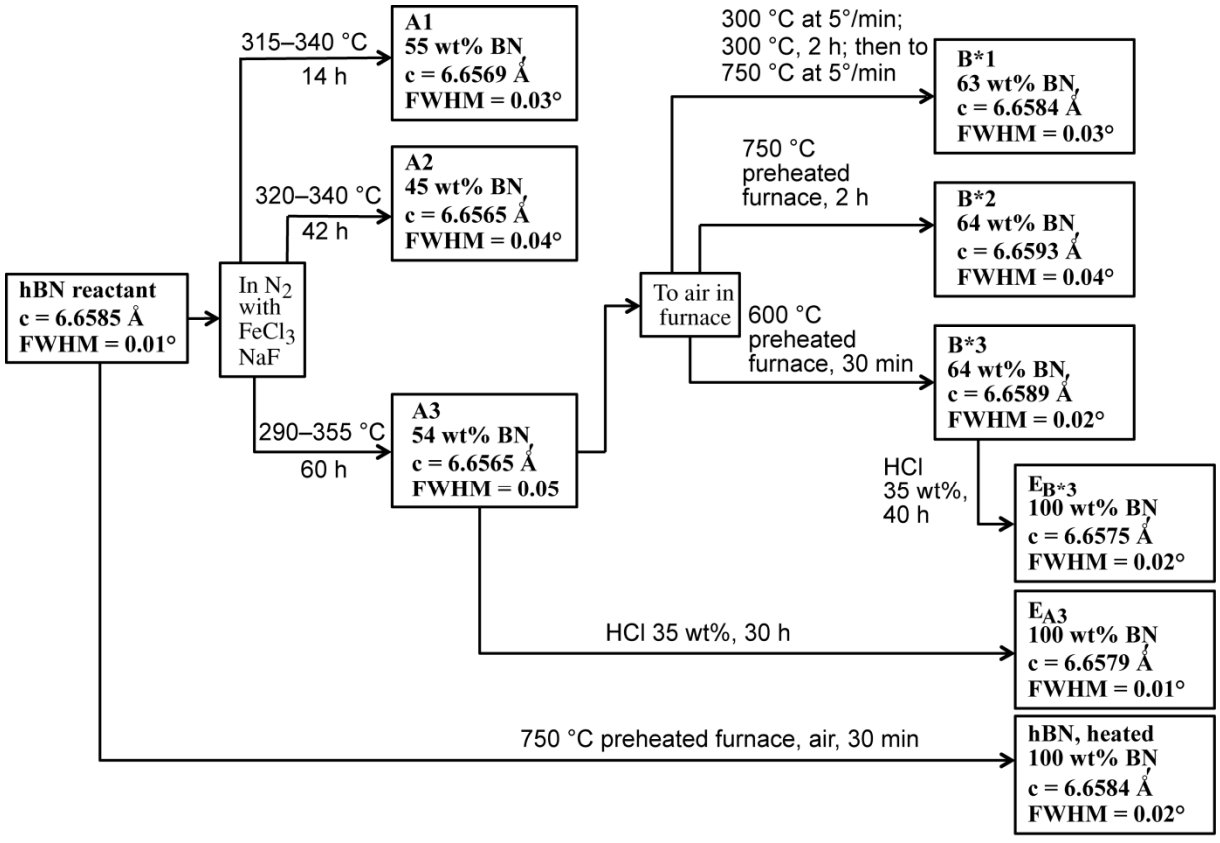

Figure 2.—Examples of intercalation and exfoliation reactions examined in this research. Changes of hBN (002) peak width (FWHM) and lattice parameter c during reactions suggest intercalates are in layers of hBN. Large hBN platelets (mostly 20 to 80 μm wide and 5 to 10 μm thick) were used in these examples. Error estimated to be ±0.0005 Å for lattice parameters and ±0.01° for FWHM values.

generates estimated standard deviations for the lattice parameter results, it is well known that the estimated standard deviation can be over an order of magnitude smaller than the true error (Ref. 21). Therefore, we prefer to state the above estimation of error, which is more conservative. After reacting to $FeCl_3$ and NaF, changes in hBN's lattice structures were observed. These changes, however, were mostly restored after the final rinse with 35 wt% HCl to result in pure, exfoliated hBN. According to the reasoning in the previous paragraph, this result indicates that the hBN was most likely intercalated, and mostly if not completely deintercalated, to become a thinner product having lattice structure similar to the original reactant as HCl removed all intercalates.

The (002) peak width, as expected, becomes wider because intercalation introduced disorder into the lattice. Explanations of the changes of the lattice parameter c (and therefore the interplanar spacings between the BN layers) due to intercalation are beyond the scope of this research. It was slightly decreased during intercalation, then increased to a value slightly larger than the original hBN reactant during exfoliation in 750 °C air, and eventually returned to the original hBN value after HCl treatment.

Note $FeCl_3$ intercalation also causes the interplanar spacings between graphite layers to change. The changes, however, are small and only between graphite layers adjacent to the intercalate layer (Ref. 22).

The similarity between the hBN reactant and its intercalated-then-deintercalated product (E_{B*3} in Fig. 2) observed here suggests that most—if not all—intercalates in the hBN layers were removed. This phenomenon is very different from graphite. Completely removing intercalate from graphite layers is very difficult. The "residue compound" left after the incomplete deintercalation of graphite exhibits XRD peak widths and c parameters generally larger than those of their precursor (Ref. 3). This difference is likely because that ionic forces are between the hBN layers, but Van der Waal's force are between graphite layers. The stronger ionic force between the hBN layers could be sufficient to control the distances between the neighboring BN layers and reach the lowest energy state by driving out the chemicals in it. The graphite layers, with the weaker Van der Waal's force between them, will reshape and eventually tightly enclose a small amount of intercalates in its structure.

Another difference between graphite and hBN intercalation is the lack of staging phenomenon for hBN. In graphite, there are a certain number (*n*) of carbon layers between two intercalate layers. The regular insertion of intercalate layers into graphite results in a "stage *n* intercalated product" and new intercalation XRD peaks (Ref. 3). In hBN, the intercalate insertion seems to be random, as no new XRD peaks can be accounted for as "intercalation peaks."

Even though the very large (002) peaks were obtained, analyzing the implications of this XRD peak heights (or its total integrated intensity) is complicated because measured peak values are affected by many parameters, some of which are either not well known or difficult to control, such as chemical composition and preferred orientation of the samples being measured. Consequently, the XRD peak heights were not closely examined other than the general observations that hBN's (002) peak heights were reduced during intercalation, and they were mostly restored after the subsequent exfoliation reactions by 750 °C air and cleaning by HCl. This is illustrated in Figure 3(a), which shows the relative heights of (002) peaks from samples of hBN reactant, A3, B*3, and E_{B*3}, described in Figure 2. The full XRD scans of these four samples are shown in Figures 3(b) to (e). In these figures, no chemicals other than hBN were detected in the original hBN (Fig. 3(b)) and in the final product after HCl cleaning (E_{B*3} in Fig. 3(e)). In the intercalated sample (Fig. 3(c)), the major intercalate (iron chlorides) are not visible and are believed to be amorphous, but small impurity peaks of FeOCl and NaCl were detected. After the intercalated samples were heated in 750 °C in air, Fe_2O_3 (major intercalate) and NaCl were detected (see Fig. 3(d)). The presence of NaCl in A3 and B*3 is believed to be the result of reactions of NaF and $FeCl_3$ during the intercalation reaction. The presence of FeOCl in A3 is caused by a trace of oxygen in the reaction system, as reported previously (Ref. 11). The oxygen may come from water that remained in the once-distilled $FeCl_3$. It may also come from the reaction between NaF and the glass container. The presence of Fe_2O_3 is believed to be the oxidation product of $FeCl_3$ and FeOCl.

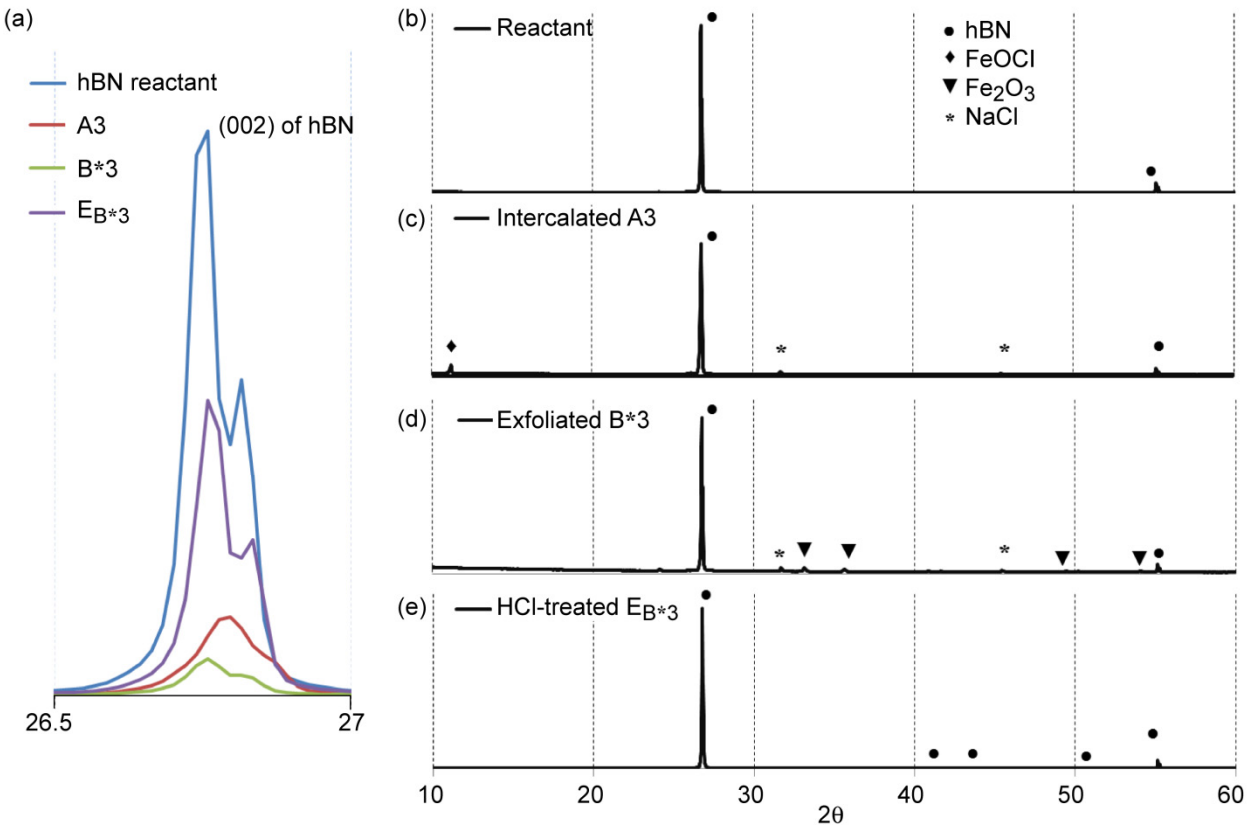

Figure 3.—XRD peaks of reactant and products during hBN intercalation and exfoliation reactions. Products A3, B*3, and E_{B*3} are described in Figure 2. (a) Relative heights of hBN (002) peak during course of reactions. (b) hBN reactant. (c) After reacting with $FeCl_3$ during intercalation (product A3). (d) After exfoliation with furnace heating in air (product B*3). (e) After treatment with HCl (product E_{B*3}).

3.2 FTIR: Changes in Chemical Properties

The hBN is much less chemically reactive than the intercalates. By inserting reactive chemicals into the hBN layers, the atoms/molecules of the intercalates will be brought into the proximity of individual hBN layers, and the chemical properties of hBN may be affected. The possible changes of hBN's chemical properties can be probed by examining the FTIR data.

Typically for hBN, there are two characteristic FTIR peaks: a relatively broad band at 1700 to 900 cm^{-1}, and a relatively narrow band at 850 to 700 cm^{-1}, which are associated with the in-plane B–N bond stretching vibration and the out-of-plane B–N–B bending vibration, respectively (Refs. 23 and 24). The FTIR data of hBN used in this research is consistent with this (curve i of Fig. 4). After reacting with $FeCl_3$, the product has large and broad new FTIR bands in the 3700 to 3050 cm^{-1} range, which includes double bands at 3555 and 3480 cm^{-1}.

Figure 4(a) compares FTIR spectra of the original hBN (curve i), intercalated hBN containing $FeCl_3$ (curves ii and iv), and the pure $FeCl_3$ (curve vii) at the wavenumber range 3800 to 3000 cm^{-1}. The original hBN does not have a band in this range, but the other two do. The broad band from the intercalated product is therefore thought to be the band from $FeCl_3$. However, this band's (curve ii) positions and shapes are different than that of the pure $FeCl_3$ (curve vii). The FTIR differences between pure $FeCl_3$ and intercalated $FeCl_3$ indicate the intercalated $FeCl_3$ is affected by hBN. That is, there are interactions between hBN and $FeCl_3$.

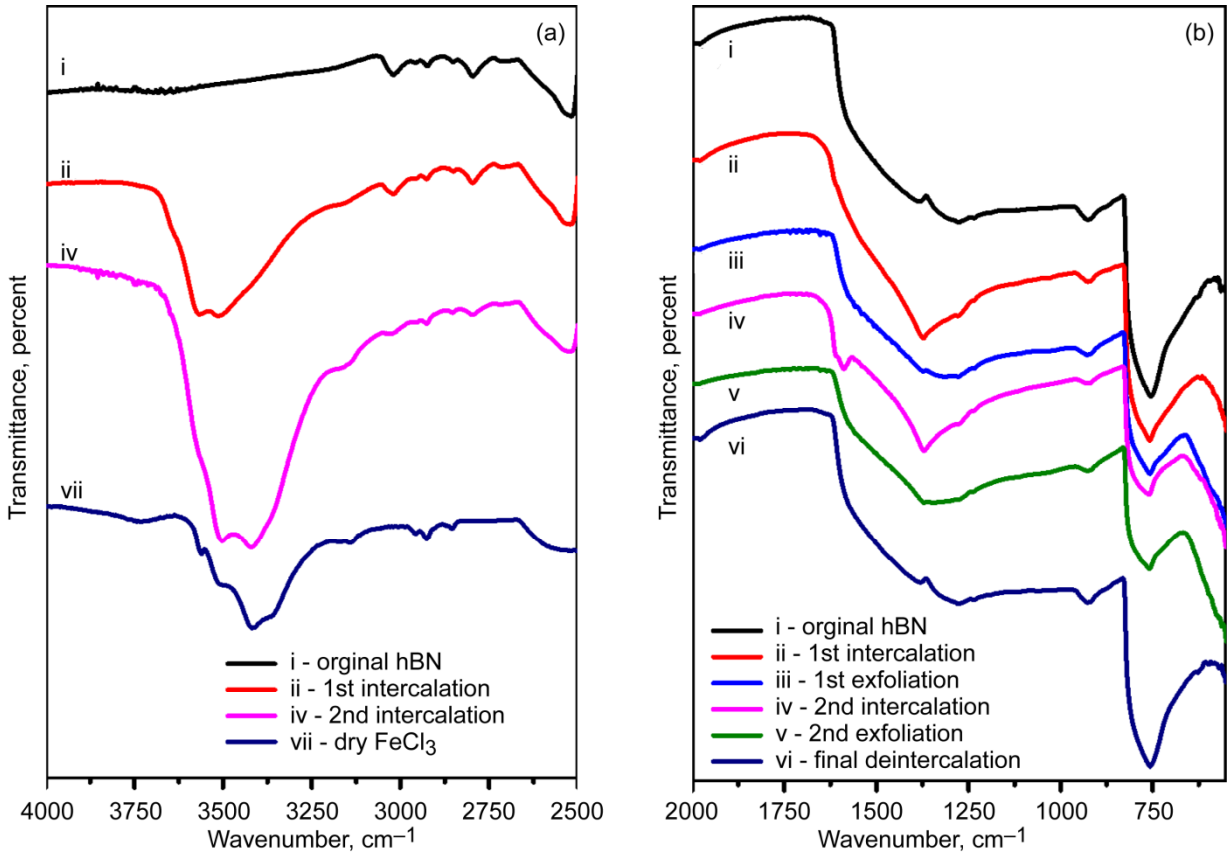

Figure 4.—FTIR spectra of hBN during this study. (a) Changes of the FTIR peaks from original hBN to hBN intercalated with $FeCl_3$ in 4000 to 2500 cm^{-1} range. FTIR for distilled $FeCl_3$ included for comparison (vii). (b) Changes of the hBN FTIR peaks near 1277 to 1380 cm^{-1} and 760 cm^{-1} during the entire process from the original hBN reactant (i), heated in a $FeCl_3$-NaF mixture for intercalation (ii), heated in 750 °C air for exfoliation and rinsed in deionized water to removing NaCl (iii), heated in $FeCl_3$-NaF mixture again for intercalation the second time (iv), heated in 750 °C air for exfoliation and then rinsed by deionized water for removing NaCl the second time (v), and placed in HCl to remove the intercalates (vi).

Figure 4(b) is the FTIR data in the 2000 to 500 cm^{-1} region. It shows the shape changes of the broad hBN bands during the entire process. That is, from the original hBN reactant (curve i) it was sequentially treated by (1) heating in a $FeCl_3$-NaF mixture for intercalation (curve ii), (2) heating in 750 °C air for exfoliation followed by rinsing in deionized water to removing NaCl (curve iii), (3) heating in the $FeCl_3$-NaF mixture again for intercalation the second time (curve iv), (4) heating in 750 °C air for exfoliation followed by deionized water rinse for removing NaCl the second time (curve v), and (5) finally placing in 35 wt% HCl to remove the intercalates (curve vi).

For the broad 1700 to 900 cm^{-1} band, its shape changed during the intercalation-oxidation-deintercalation process. The peak position of this band shifted from 1383 to 1277 cm^{-1} during the process (Fig. 4(b), curves ii, iii, iv, and v), but returned to the original 1277 cm^{-1} after all intercalates are removed (Fig. 4(b), curve vi). Changes of the 850 to 700 cm^{-1} band, on the other hand, remained in the narrow 760 to 755 cm^{-1} range. This suggests a change of the B–N stretching vibration, but not much change of the B–N–B bending vibration. A discussion of this difference is beyond the scope of this report.

In addition to the above-described bands, new FTIR peaks at about 1600 cm^{-1} are observed in the intercalated samples (curves ii and iv). A close look shows they are double-peaks. One of them was from an intercalate ($FeCl_3$), which will be described in more detail later in this report. The other was believed to be due to stretching in the direction that is comparable to BNNT's tangential stretching vibration. It is noted such a peak does not show up in regular hBN, but showed up in BNNT because the tube curvature

induces a strain on the hBN network (Ref. 25). The observation of such a band in the hBN sample here suggests strain on the hBN, possibility due to the presence of the intercalates in the hBN network.

The band near 500 cm^{-1} is believed to be from Fe_2O_3, which was from oxidation of $FeCl_3$.

Similar to the XRD data, all changes in the FTIR data during the process were nearly completely reversed, and the peaks returned to the original shape, after the final HCl treatment where the intercalates and other impurities were removed.

The overall changes of the hBN's vibration modes during the entire process indicates interactions between hBN and an intercalate (hBN-$FeCl_3$ or hBN-Fe_2O_3) result in changes of hBN's chemical properties, and such changes can be reversed by removing the intercalates.

3.3 FESEM, EDS, and Mass Data on Overall Morphology and Chemical Changes

The mass ratio of the original reactant mixture was hBN:$FeCl_3$:NaF ≈ 1:2:0.2. After heating the mixture of hBN (large platelets), $FeCl_3$, and NaF and then boiling off excess $FeCl_3$, the as-synthesized products were brown in color and had a mass gain over the original hBN by about 100 percent. EDS data obtained from FESEM operated at 15 kV indicated that the overall mole ratio of Fe:Cl:Na for this as-synthesized product was about 1:2.8:0.45. It is noted that EDS did not detect fluorine, which was in the original reactant in the form of NaF.

The significance of NaF in the reaction is observed when comparing the above mass data to those in preliminary experiments where the same heating and boiling process was conducted without the presence of NaF. In those cases, the as-made products were white in color and had a mass gain over the original hBN of less than 10 percent.

Figure 5(a) is a FESEM image of the as-synthesized product obtained from secondary electrons. Figure 5(b) shows the same image of hBN platelets, except the FESEM detected backscattered electrons, which highlights the heavy element (iron) as bright areas. Comparing these two images, it can be seen that iron is concentrated more at the sides and edges of the platelets. These data suggest that the mass increases during the reactions resulted from $FeCl_3$ entering the layered structures of the hBN from the side.

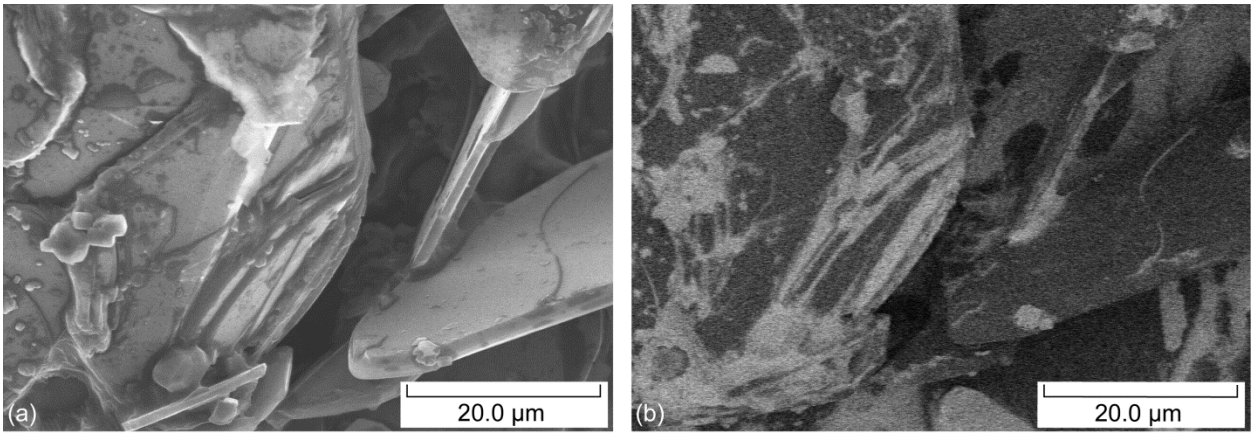

Figure 5.—FESEM images of hBN particles intercalated with $FeCl_3$ are oriented in different angles. (a) Secondary electrons show the image of hBN. (b) Backscattered electrons highlight the location of heavy element (iron) at the edges and sides.

Figures 6(a) and (b) are FESEM micrographs of the above intercalated sample after it was slowly oxidized by oxygen in air at high temperature to become Fe_2O_3 nanoparticles (i.e., B*1 in Fig. 2). The heating rate was 5 °C per minute from room temperature to 750 °C with a holding time of 2 h at 300 °C. It was sufficiently slow so that the iron chloride intercalates were in solid phase and did not change location when they became Fe_2O_3. The presence of Fe_2O_3 in the sample was confirmed by XRD. Figure 6(a) shows a top view of alternating layers of hBN and Fe_2O_3 nanoparticles. Figure 6(b) is the side view of a relatively thick hBN layer about 1 μm thick. It can be seen that this layer is split into numerous thin layers about 20 to 30 nm thick. Both pictures suggest that hBN was intercalated with nanoparticle's precursor (i.e., $FeCl_3$).

Figure 7 shows FESEM micrographs from a sample treated similarly to that in Figure 6, except this intercalated sample was quickly oxidized by placing it into the preheated 750 °C furnace (i.e., B*2 in Fig. 2). The fewer but much larger, micron-sized Fe_2O_3 particles are believed result from some $FeCl_3$ intercalates melting, coagulating, moving out of the lattice, and then oxidizing. This sample also shows intercalation and a limited degree of exfoliation. Figure 7(b) shows exfoliated hBN in this sample.

The above-mentioned figures show signs that by using NaF as an activating agent, hBN was indeed intercalated with $FeCl_3$. Furthermore, subsequent heating of this intercalated product in air at 750 °C appeared to result in some degree of exfoliation. However, the exfoliation shown in both Figures 5(b) and 6(b) was the minority among a large number of platelets in the samples. Although 20-nm exfoliation

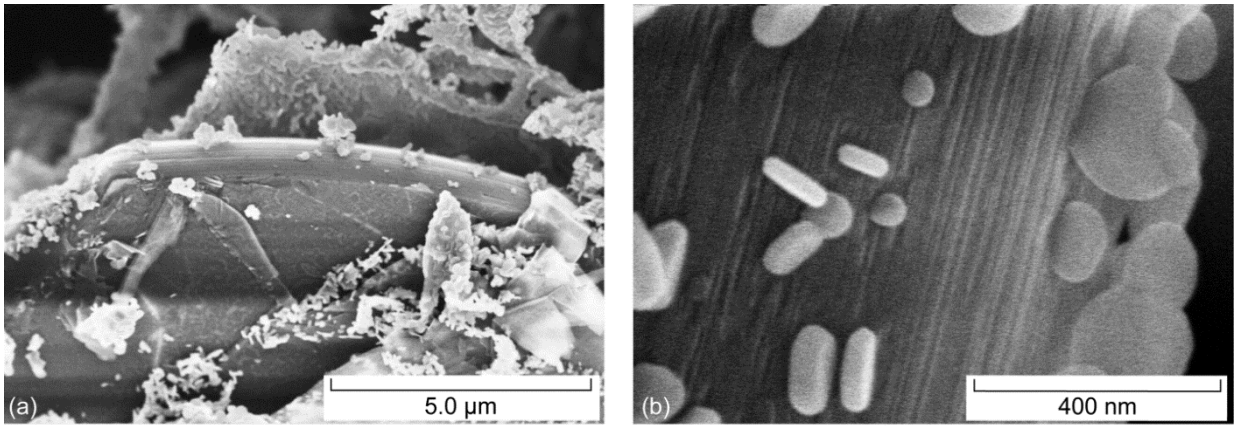

Figure 6.—FESEM images of the intercalated hBN sample after it was slowly oxidized by oxygen in air to become Fe_2O_3 nanoparticles. (a) Nanoparticles arranged in sheets formed alternating layers with hBN. (b) Side view of an hBN layer indicates it split into layers about 20 to 30 nm thick.

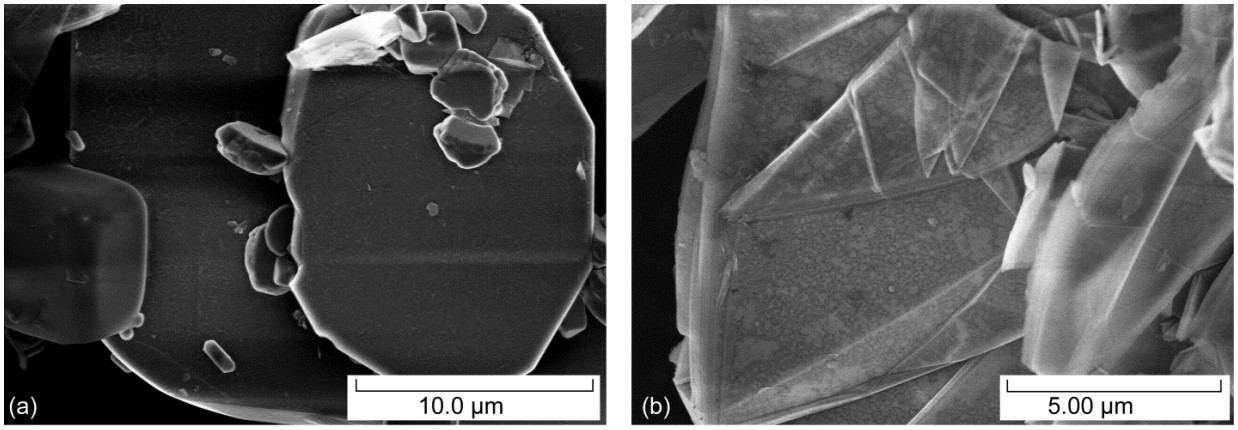

Figure 7.—FESEM images of the intercalated sample after it was quickly oxidized. (a) Intercalates moved out of the lattice and then oxidized to form micron-sized Fe_2O_3 particles. (b) After subsequent HCl rinsing, SEM image of the resulting pure hBN shows exfoliation.

thicknesses were found, some platelets were not exfoliated, and the thicknesses of most of the exfoliated hBN platelets were in 0.5 to 2.0 μm range. Nevertheless, although overall thinner than the original hBN reactant platelets (mostly >5 μm thick), this is far from the goal of fabricating white graphene. For the purpose of generating further exfoliation, Reactions (3) to (7) were carried out in two similar processes with one incorporating hydration before exfoliation:

I. The intercalated and then air-heated product (hBN containing micron-sized Fe_2O_3 particles described in Fig. 7) was rinsed with water to remove sodium chloride to form product B in Reaction (2) (from EDS data), intercalated (mixed with $FeCl_3$ and NaF and heated) to form product C (Reaction (3)), exfoliated (heated in 750 °C air and rinsed with water) for the second time to form product D (Reaction (4)), and then cleaned in 35 wt% HCl to form product E_D (Reaction (5)). The result is more complete and pronounced exfoliation, where 20-nm nanosheets of pure hBN and pores can commonly be seen (Fig. 8(a)). This result also demonstrates that, with additional cycles of intercalation and exfoliation, more extensive exfoliation into even thinner nanosheets is possible.

II. The hBN was intercalated and exfoliated for the second time in a way similar to process I, except

- The intermediate intercalated product (product C) was placed in ambient air for 50 h (product C', Reaction (6)) before it was exfoliated for the second time in a 750 °C preheated furnace (see Reaction (7)).
- The sample was covered by a quartz lid during the above 750 °C heating to exfoliate the sample for the second time.

Ambient air (about 30 percent relative humidity) exposure caused the hygroscopic intercalated hBN to adsorb water 10 percent of its own mass. The subsequent 750 °C heating caused the water and then $FeCl_3$ to violently boil off, resulting in exfoliation and producing steam that carried away some exfoliated BN layers. These BN layers were then deposited on the quartz lid and, after the system was cooled to room temperature, picked up by a piece of carbon tape for FESEM examination. FESEM micrographs show they were nanosheets, about 10 to 20 nm thick and separated by a space of about 10 to 60 nm (Fig. 8(b)). The hBN not carried away by the steam is rinsed (product D' in Reaction (7)).

Exfoliation of hBN as observed in this research, suggests that the original hBN was intercalated. Repeating these processes causes additional exfoliation, supporting this suggestion.

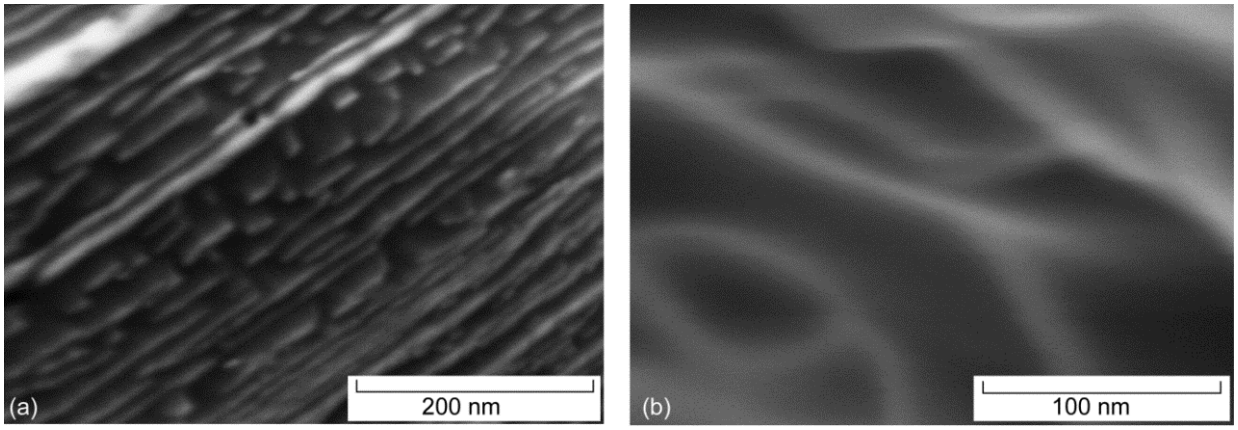

Figure 8.—FESEM images of hBN from large-platelet sample after two cycles of intercalation and exfoliation, showing hBN layer splitting. (a) No hydration between cycles. (b) Intercalated sample hydrated before final heating and exfoliation cycle, causing more extensive splitting. Image shows the hBN nanosheets that were carried away by steam and deposited on the container lid.

3.4 Reactions to Moisture in Ambient Air

The apparent enhancement of exfoliation after the hygroscopic intercalated compound picked up moisture in air calls for additional study on the reactions between the intercalated compound and water. In a preliminary test, an intercalated sample A3 described in Table I was exposed to the ambient environment (24 °C, 59 to 63 percent relative humidity) overnight after it was stored in dry air for 23 days. This resulted in a 20 percent mass increase. The XRD data indicate that its lattice parameter c and hBN (002) peak width (FWHM) changed from 6.6584 Å and 0.059° to 6.6569 Å and 0.056°, respectively, during the overnight ambient air exposure.

A more detailed study of the effects of moisture in air on the same intercalated hBN was conducted after it was stored in dry air for 4 to 5 months. In this study, samples were exposed to room-temperature air at different relative humidities and analyzed using three different types of data (mass, FTIR, and XRD).

Figure 9 shows the percent mass increase of two intercalated samples during the ambient air exposure. One of them was weighed several times during an exposure time of 66 min (Fig. 9(a)). The relative humidity was 26 to 27 percent during the time of this experiment. The results show the sample mass increased rapidly during the first 20 min and reached a peak in 30 to 40 min of exposure time, to an 11 percent mass gain. The other sample was tested similarly, but over a long exposure time of 165 h (Fig. 9(b)). The relative humidity schedule was also shown (Fig. 9(c)). It was in the 15 to 28 percent range. It can be seen that after the mass reached a peak value within an hour, it began to decrease continuously for days during the ambient air exposure. Despite the initial mass increase, the overall mass during this ambient air exposure experiment actually decreased. The data suggests that the samples picked up moisture from air quickly. The moisture then reacted with intercalates, resulting in gas products, possibly HCl or Cl_2, during the conversion of $FeCl_3$ to Fe_2O_3.

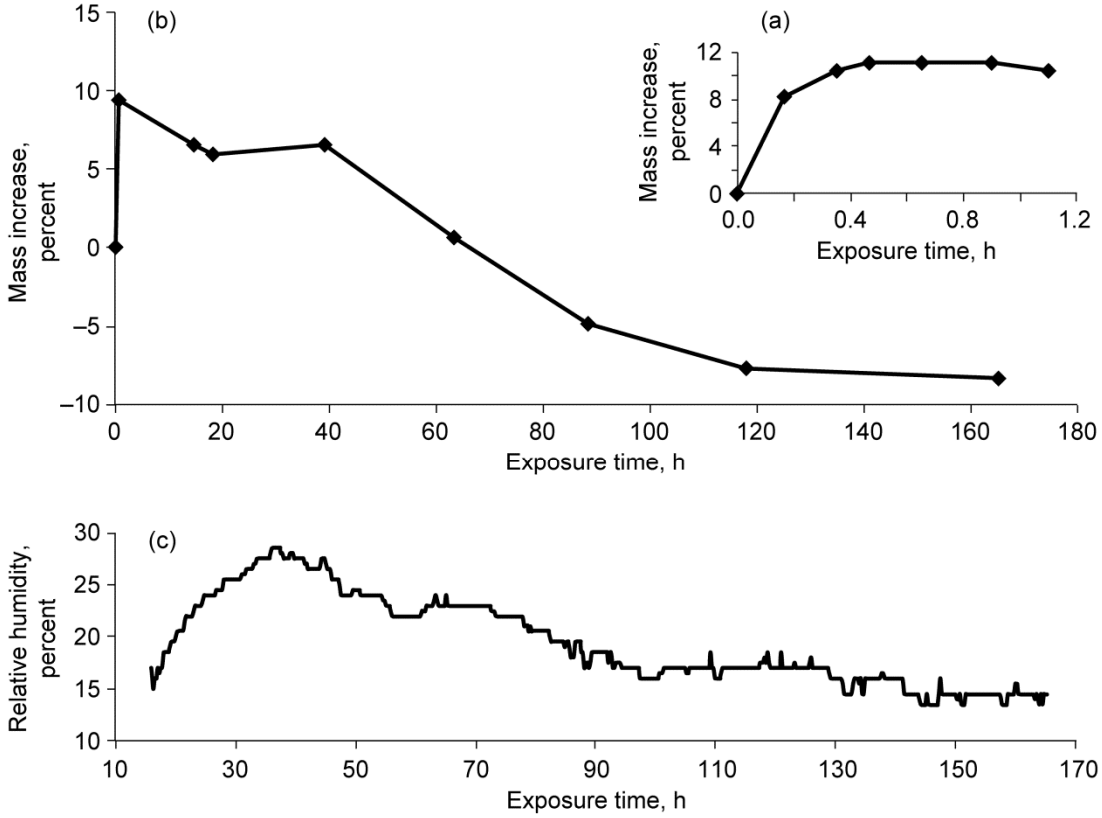

Figure 9.—Mass changes of intercalated samples during ambient air exposure. (a) Sample was exposed to ambient air for 66 min. The relative humidity was 26 to 27 percent. (b) Separate sample weighed several times during a long exposure time of 165 h. (c) Relative humidity when sample in (b) was tested.

For XRD analysis, a sample of the same product (A3 in Table I) was mounted and filled in a 0.5-mm deep well ZBH holder and scanned for XRD 12 times during an 85-h period of ambient air exposure. All of the 12 datasets were obtained from a 10° to 90° scan followed by high-resolution scans of the (002), (004), (006), and (008) peaks. The sample surface turned dark, but remained intact during data acquisition.

Table II shows the 12 datasets of lattice parameter c, the (002) peak width (FWHM), and the relative (002) peak height acquired during the course of the 85 h of ambient-air exposure. These values were obtained from the XRD data scanned at 0.005° per step. We estimate the lattice parameter c and the FWHM relative accuracy to be 0.0002 Å and 0.002°, respectively, with these scans that were longer in duration and to higher angles than data previously discussed. It can be seen that both the height and the width of the (002) peak continue to decrease throughout the process, indicating a decrease of the crystalline content in the sample. It appears that water absorbed by (and possibly intercalated into) the sample causes some crystallites to become amorphous and that the reaction would continue for several days or more.

At the beginning, the lattice parameter c was in a decreasing trend. This trend leveled at about 40 h of ambient air exposure, which suggests that, among the crystallites in the sample the hBN crystallites that become amorphous during this process of humid air exposure are those with larger lattice parameter c (and therefore larger interplanar spacing).

The FTIR spectra of the same intercalated product (A3 in Table I exposed to ambient air at 15 to 30 percent relative humidity for 6 min, 64 h, and 189 h, respectively, were obtained and shown in Figure 10(a). For comparison, the FTIR spectra of the original hBN reactant and the intercalated product before the ambient air exposure are also included in Figure 10(a), and FTIR spectra of dry (distilled) and wet (ambient-air-exposed) $FeCl_3$ are shown in Figure 10(b).

TABLE II.—XRD ANALYSIS OF INTERCALATED hBN A3[a] (TABLE I AND FIG. 2): LATTICE PARAMETER c, (002) PEAK WIDTH (FWHM), AND (002) PEAK HEIGHT IN THE 85 h DURING WHICH SAMPLE WAS EXPOSED TO AMBIENT AIR (HUMIDITY SCHEDULE OF AIR IS INCLUDED)

XRD scanning dataset	Total ambient exposure time at beginning and end of scanning, h		Relative humidity at beginning and end of scanning, percent		Lattice parameter c from scanning dataset,[b] Å	FWHM from scanning dataset,[c] deg	Relative (002) peak height
	Beginning	End	Beginning	End			
Pure hBN reactant	---	---	---	---	6.6585	0.014	---
1	0.03	2.2	15	16	6.6585	0.064	1.00
2	2.2	4.3	16	17	6.6581	0.066	0.90
3	4.3	6.4	17	18.5	6.6580	0.066	0.89
4	6.4	8.6	18.5	20.5	6.6579	0.066	0.88
5	13.6	19.4	25.5	17.5	6.6579	0.065	0.88
6	24.4	30.2	14.5	14.5	6.6579	0.062	0.84
7	35.2	41.1	13.5	13.5	6.6578	0.058	0.80
8	46.0	51.9	11	13.5	6.6582	0.053	0.74
9	56.9	62.7	11.5	12.5	6.6579	0.05	0.67
10	67.7	73.5	11	13.5	6.6579	0.047	0.61
11	73.6	79.4	13.5	22.5	6.6582	0.047	0.59
12	79.4	85.3	22.5	31	6.6582	0.048	0.58

[a]Sample had been stored in dry air for 123 days at beginning of experiment.
[b]Error is estimated to be ±0.0002 Å for c values.
[c]Error is estimated to be ±0.002° for FWHM values.

Figure 10(a) shows the intercalated hBN has five prominent FTIR bands: 1600, 1370, 1250, and 750 cm^{-1} bands and a broad 3700 to 2700 cm^{-1} band. The 1370 and 1250 cm^{-1} bands do not seem to be affected by moisture absorption when exposed to ambient air. The other three bands, however, have changes in shape, position, and size as the intercalated hBN absorb moisture during ambient air exposure. Comparing to these five bands, Figure 10(b) shows pure $FeCl_3$ has three prominent FTIR bands, all of them changes during moisture absorption, and all of them are near the wavenumbers of the three bands in Figure 10(a) that change during moisture absorption. It is therefore believed that the FTIR changes for the intercalated hBN result from moisture absorption, as seen in Figure 10(a), and are due to the interaction between water and the intercalated $FeCl_3$.

Furthermore, it is observed that the shape, position, and/or size of the three bands in Figure 10(a) that change during moisture absorption have noticeable differences from the three prominent bands in Figure 10(b). Their change patterns during moisture absorption were also different. This indicates intercalated $FeCl_3$ is not the same as pure $FeCl_3$, and suggests the possibility that there are interactions between hBN and $FeCl_3$, and their interactions change during moisture absorption.

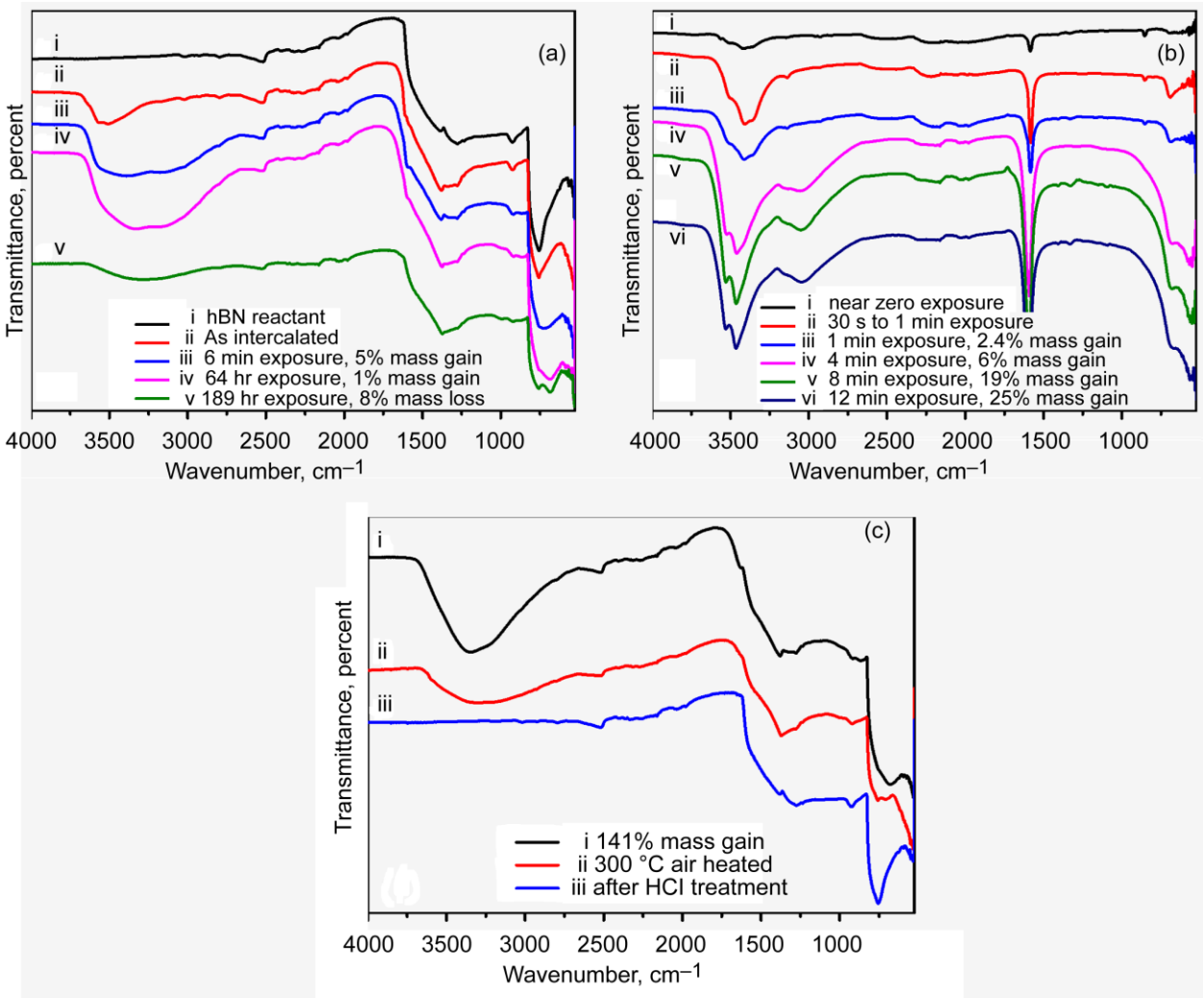

Figure 10.—FTIR spectra of $FeCl_3$-intercalated hBN compared with pure $FeCl_3$. (a) $FeCl_3$-intercalated hBN during 189 h of air exposure at 15 to 30 percent humidity. (b) Distilled $FeCl_3$ during 12 min of air exposure at 44 percent humidity. (c) $FeCl_3$-intercalated hBN after sequential treatment of 24-h air exposure at 100 percent humidity (141 percent mass gain), 2 h in 300 °C air, and 24 h in room-temperature 35 wt% HCl.

The double-band near 1600 cm^{-1} (described earlier as the peaks for strained hBN layers and $FeCl_3$, respectively) was again observed in the FTIR of the intercalated hBN without hydration (curve ii of Fig. 10(a)). The fact that this double band became single after the sample begin to pick up moisture suggests water causes the intercalated $FeCl_3$ to rearrange during hydration, and hence reduces the internal stress and strain.

After 189 h of ambient air exposure, both hydration-related bands (3700 to 2700 cm^{-1} and 757 cm^{-1}) were reduced, but the 1380 to 1280 cm^{-1} band, which was not effected by hydration, still did not change much. It appears that water caused some reactions and consequently was consumed. However, no new compounds were detected by FTIR or XRD during this period.

To further study the effects of water, a new intercalated product (A4 in Table I) was exposed to 100 percent relative humidity, room-temperature air for 24 h to gain as much water as possible. The fully hydrated product gained 141 percent mass and became viscous and pastelike. It was further treated in 300 °C air for 3 h and eventually in 35 wt% HCl for 24 h to remove all intercalates. Figure 10(c) shows its FTIR data and the FTIR data of the products obtained during this process. The large quantity of water mass increase was reflected by the complete overlap of the hBN 760 cm^{-1} band and the hydrated $FeCl_3$ 679 cm^{-1} band. The water was tightly bounded to the product, as the large and broad water-related 3700 to 2700 cm^{-1} band could not be completely removed during the subsequent 300 °C air heating. However, both the intercalation effects and the hydration effects were completely reversed to the state of the original reactant after the final HCl treatment to remove all intercalate.

In summary, upon exposing the hBN intercalated with $FeCl_3$ to ambient air, it adsorbed moisture in air quickly, between 1 and 2 h. The moisture in the sample is in the form of iron chloride hydrate (from FTIR data) and is likely to be in the hBN layers (from XRD data). The amount of moisture adsorbed depends on the humidity of the air. Data in this research showed 11 percent mass gain at room temperature and 26 to 27 percent relative humidity. Upon continuous ambient air exposure, water in the sample is believed to cause some reactions and consequently was consumed. If the ambient air is close to 100 percent humidity, the changes are similar in trend, but are extreme. In that case the adsorbed water was measured to be 141 percent of the sample's dry mass. During ambient air exposure, the lattice structures change, but are not irreversibly destroyed, as the original hBN FTIR data can be largely restored by treating this product with 35 wt% HCl.

3.5 Stability in Dry Air

A sample of an intercalated product (A3 in Table I) was scanned by XRD immediately after it was synthesized. Two samples of the same product were stored in dry air for 23 and 185 days, respectively, and then scanned. Table III shows the lattice parameter c and the peak width from these three scans. It appears that the intercalated hBN underwent a slow change in dry air. The mass data, however, shows the changes in the chemical compositions during this period were within experimental error.

TABLE III.—XRD ANALYSIS OF INTERCALATED hBN SAMPLE A3[a] (TABLE I AND FIG. 2): LATTICE PARAMETER c AND (002) PEAK WIDTH (FWHM) MEASURED AT THREE DIFFERENT STORAGE TIMES DURING WHICH THE SAMPLES WERE IN DRY AIR

XRD scanning dataset	Storage time, days	Lattice parameter c from scanning dataset,[b] Å	FWHM from scanning dataset,[c] deg
Pure hBN reactant	---	6.6585	0.01
1	0	6.6565	0.05
2	23	6.6584	0.06
3	123	6.6585	0.06

[a]Samples were prepared in ambient air for about 5 min before XRD scanning.
[b]Error estimated to be ±0.0005 Å for c values.
[c]Error estimated to be ±0.01° for FWHM values.

3.6 Toward White Graphene Fabrication

The exfoliated hBN layers obtained in this research are still much thicker than white graphene. Further exfoliation is needed if producing white graphene is the long-term scientific and engineering goal. For additional exfoliation, results in this research point to the direction of adding more water into the intercalated products, heating the intercalated-hydrated product to higher temperature at higher rate, and conducting more cycles of intercalation-hydration-heating for exfoliation. In addition, smaller platelets, with fewer layers and less area to split, may exfoliate more extensively than the larger ones. To test these suggestions, hBN with small platelets was intercalated (A5 in Table I), exfoliated, rinsed, intercalated again, hydrated, exfoliated again, and then rinsed with HCl according to Reactions (2), (3), (6), (7), and (8). For a high heating rate in Reaction (7), the exfoliation was conducted by heating the sample at 750 °C where both the furnace and the sample holder were preheated. For a high degree of hydration, the sample was placed in 100 percent relative humidity environment for 7.5 h, resulting in a 36.4 percent mass gain. The final product was the most extensively exfoliated so far in this research (Fig. 11). Observed from the FESEM operated at 6 kV, all hBN platelets that can be examined for exfoliation show that the exfoliated layers are about 20 nm thick or less.

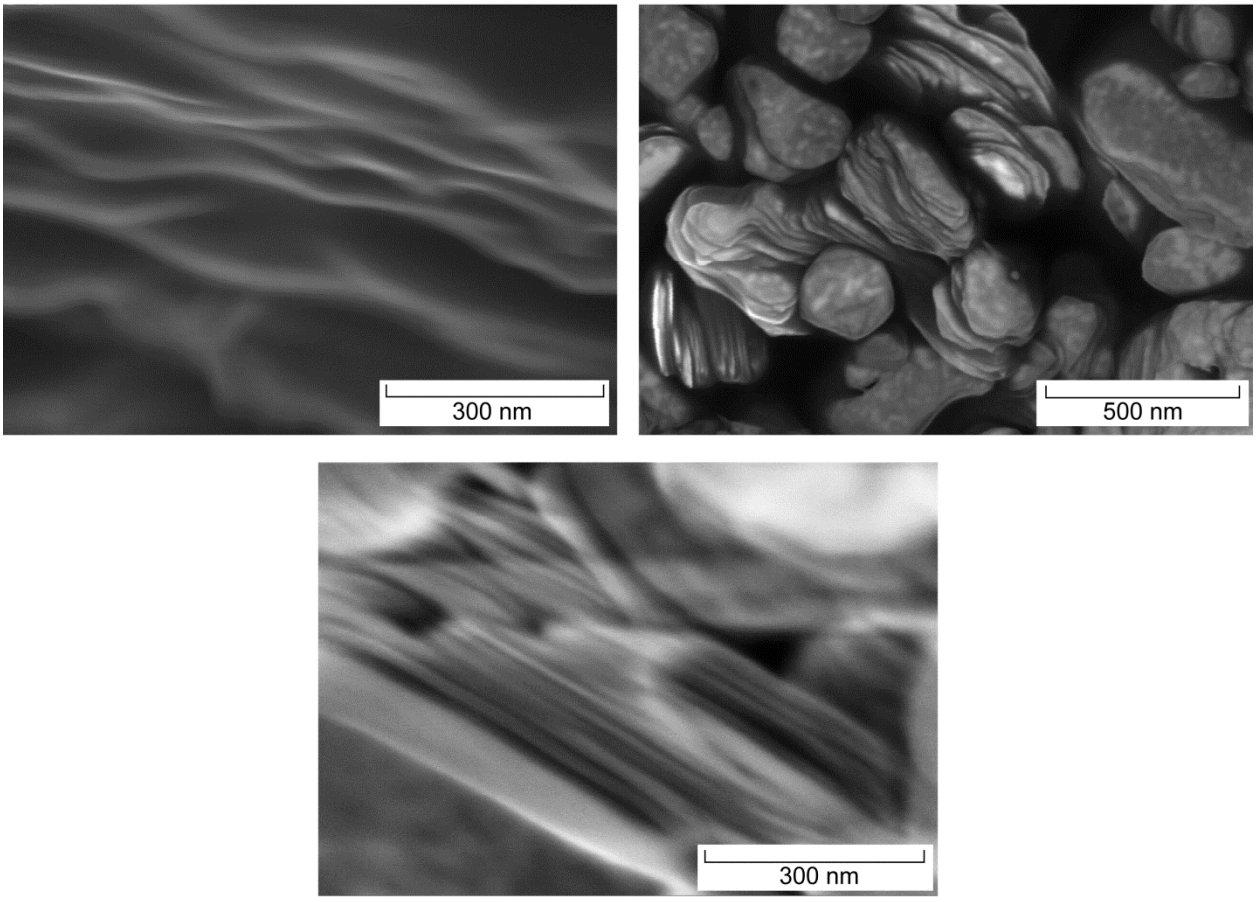

Figure 11.—FESEM images of different views of intercalated small-platelet sample hydrated at 100 percent relative humidity for 7.5 h with 36.4 percent mass gain before second exfoliation at 750 °C in preheated furnace and sample holder.

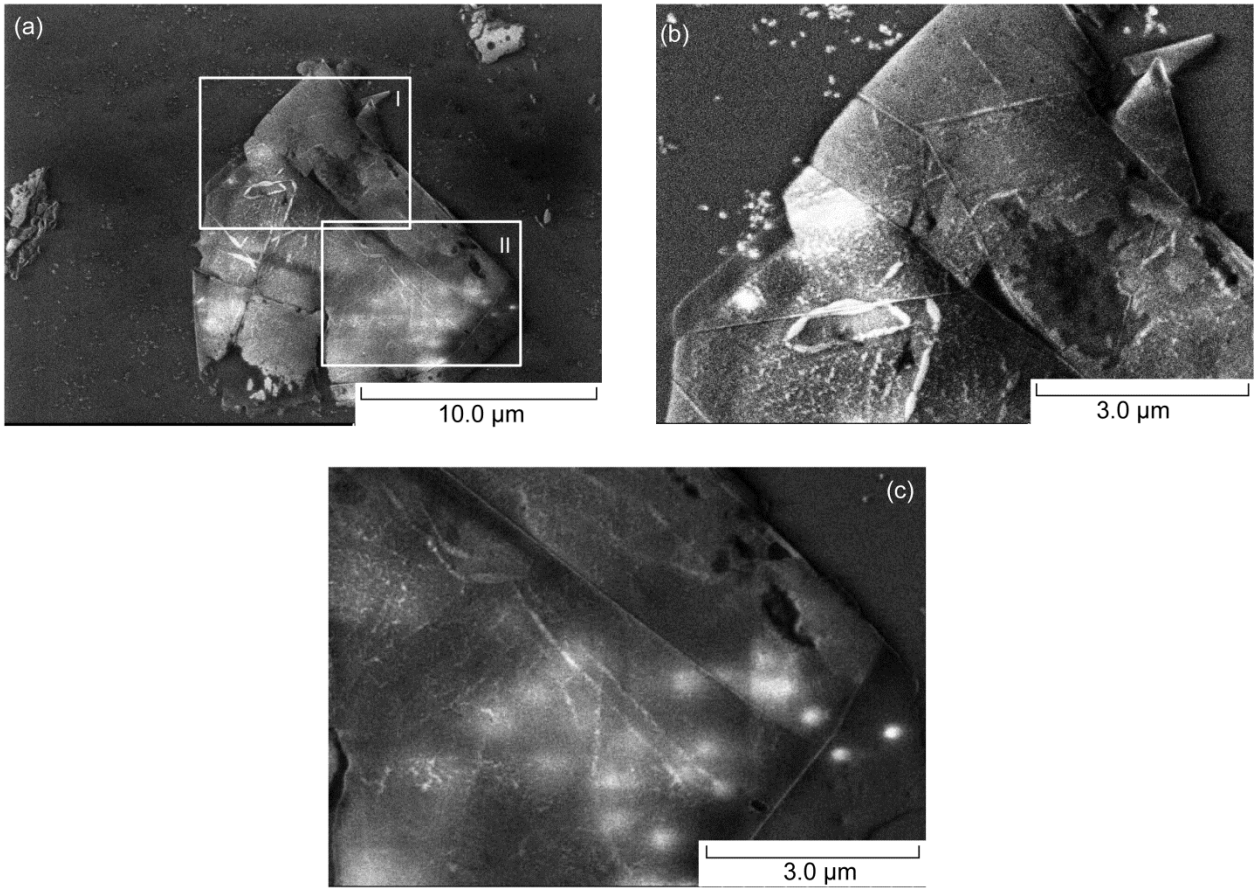

Figure 12.—Images of exfoliated hBN layer from FESEM operated at 0.5 kV, able to view a total thickness of <5 nm. (a) Multiple transparent layers. (b) Expanded view of section I in part (a). Expanded view of section II in part (a).

Using carbon adhesive tape, a sample was peeled to remove the top layer and then examined under FESEM at 0.5 kV (Fig. 12). The top view of an exfoliated platelet shows multiple semitransparent layers. Based on the Kanaya-Okayama penetration depth formula, the total thickness of the multiple semitransparent layers need to be less than 5.5 nm in order to let the 0.5-kV electrons give them a semitransparent appearance.[1]

Producing even thinner exfoliated layers or nanosheets seems likely with additional cycles of intercalation and exfoliation. However, further research is needed in order to evaluate the potential of using these reactions to mass produce white graphene.

4.0 Conclusion

After treating a mixture of hexagonal boron nitride (hBN), $FeCl_3$, and NaF at 290 to 355 °C in a nitrogen environment, a new product was obtained and examined. The changes of the lattice parameter, the widening of the hBN (002) peak in x-ray diffraction (XRD), the shape and size changes of the hBN peaks in Fourier transform infrared (FTIR) spectra at 1383 and 1277 cm^{-1}, the appearance of new fourier transform infrared peaks at 3700 to 2700 and 1600 cm^{-1}, the mass increase data, the observed iron

[1] Let the average atomic weight (A) be 12.5, atomic number (Z) be 6, and density (ρ) be 2 g/cm^3 in the formula $H = (0.0276\ A\ V^{1.67})/(Z^{0.89}\ \rho)$, for the hBN, where H and V are penetration depth in μm and voltage in kV, respectively. The electrons need to travel through the layers, hit the subject underneath, and travel through the layers back to be detected in order to give the layers a semitransparent appearance in the FESEM micrograph.

distribution in the micrographs and energy dispersive x-ray spectroscopy (EDS) of field emission scanning electron microscopy, and the fact that the hBN can be exfoliated to 20 nm after heating this product to 750 °C, collectively make a strong case that $FeCl_3$ was located between the hBN layers in this product. That is, the hBN was likely intercalated with $FeCl_3$. The fact that these changes were extended and exfoliation was enhanced after the product adsorbs moisture from air suggest the adsorbed water was also intercalated into the hBN layers. The difference between this experiment and the previous ones where intercalation was unsuccessful is that NaF was used as the activation chemical.

After the reaction of $FeCl_3$ and NaF to form the intercalation compound, shape changes of the hBN broad FTIR band (peaked at 1277 cm^{-1}) and the appearance of the new band at 1600 cm^{-1} were observed. The new FTIR band at 3700 to 2700 cm^{-1} is similar to the pure $FeCl_3$ FTIR band at the same wavenumber range. However, some of their differences suggest the intercalated $FeCl_3$ is different from the pure one and there are hBN-$FeCl_3$ interactions in the intercalated product. Overall, the FTIR data suggest a change in the chemical properties of the intercalated product from the precursor hBN. These new chemical properties may be further developed to make products such as composites with special electrical, thermal, and mechanical properties.

This result brings into focus the comparison between hBN and graphite: Both materials can be intercalated with $FeCl_3$, and both can be exfoliated after intercalation, although the mechanisms behind their respective intercalation and exfoliation may have some differences. The comparison between graphite and hBN can now be moved to a new level: Graphite intercalation and exfoliation has been scaled up for engineering and industrial applications such as Grafoil or graphene. Can hBN use the graphite technology as the reference to do the same?

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13. SUPPLEMENTARY NOTES

14. ABSTRACT
Sodium fluoride (NaF) was used as an activation agent to successfully intercalate ferric chloride (FeCl3) into hexagonal boron nitride (hBN). This reaction caused the hBN mass to increase by ~100 percent, the lattice parameter c to decrease from 6.6585 to between 6.6565 and 6.6569 Å, the x-ray diffraction (XRD) (002) peak to widen from 0.01° to 0.05° of the full width half maximum value, the Fourier transform infrared (FTIR) spectrum's broad band (1277 cm^{-1} peak) to change shape, and new FTIR bands to emerge at 3700 to 2700 and 1600 cm^{-1}. This indicates hBN's structural and chemical properties are significantly changed. The intercalated product was hygroscopic and interacted with moisture in the air to cause further structural and chemical changes (from XRD and FTIR). During a 24-h hold at room temperature in air with 100 percent relative humidity, the mass increased another 141 percent. The intercalated product, hydrated or not, can be heated to 750 °C in air to cause exfoliation. Exfoliation becomes significant after two intercalation-air heating cycles, when 20-nm nanosheets are commonly found. Structural and chemical changes indicated by XRD and FTIR data were nearly reversed after the product was placed in hydrochloric acid (HCl), resulting in purified, exfoliated, thin hBN products.

15. SUBJECT TERMS
Hexagonol boron nitride (hBN); Ferric chloride; Graphite; Intercalation; Exfoliation; White graphene

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