The Stirring-assisted Liquid Exfoliation of Hexagonal Boron Nitride and the Performance of h-BN/Cellulose Aerogel

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Abstract. The delamination is the focus of two-dimensional layered materials’ nanocrystallization. In this paper, two methods of stirring-assisted liquid exfoliation, DMF exfoliation and Hummers exfoliation, were utilized to prepare h-BN nanosheets. Microstructure, crystal structure and chemical structure were analyzed, which indicated that the h-BN nanosheets, with thickness of 1.4 nm and 5.4 nm respectively, were delaminated from bulk h-BN and their structure didn’t show any obvious change, in accordance with the theoretical model. The interaction of oxygen in DMF and boron in h-BN weakened the “lip to lip” interaction between neighboring layers and then nanosheets were gained under violent stirring. Due to excellent corrosion resistance, bulk h-BN couldn’t be exfoliated by strong oxidants. H+ protonated h-BN and only weakened slightly the “lip to lip” interaction. As a result, Hummers exfoliation wasn’t doing well compared with DMF exfoliation. The h-BN/nano-fibillated cellulose aerogel had a very bag surface area and the air filled in these pores, which gave it the performance of thermal insulation and oil absorption.

1. Introduction

Recently, two-dimensional layered materials (TDLMs) such as graphite phase carbon nitride [1], graphene [2], etc have attracted intense interest in materials field due to their unique structures and excellent properties. As one of the typical representatives of TDLMs, hexagonal boron nitride (h-BN) presents similar layered planar structure with graphene (Figure1) with good mechanical properties, thermal stability and electrical insulation performance [4], which demonstrates broad application prospects on many fields such as electronic packaging, Li-ion battery, etc[5-9].

At present, most of the scientific researches are focused on the preparation and application of h-BN with single or few-layer structures, while the preparation methods of h-BN nano-layer are mainly divided into the bottom-up method and top-down method. Chemical vapor deposition, the most representative of the bottom-up method, is not suitable for the large-scale development and utilization of nano- h-BN due to its complicated preparation process and serious conditions.
Figure 1. Structure model of h-BN. In this figure, the yellow and blue balls represent B and N atoms, respectively.

As one of the most useful methods, the top-down method contains four types such as ball-milling-assisted exfoliation, thermal exfoliation method, gas phase exfoliation and liquid phase exfoliation method. And ball-milling-assisted exfoliation method means that single and few-layered h-BN is prepared by mixing and ball-milling the bulk h-BN with urea [10], NaClO [11], NH₄Cl [6] or NaCl [12]. Thermal exfoliation refers to the preparation of nano-h-BN by exfoliating bulk h-BN under high temperature for long time heat treatment [13,14]. And the gas phase exfoliation method is conducted in a sharply changing thermal environment [15]. A certain effect of exfoliation can be obtained from these three preparation methods, however, several problems such as high energy consumption, low preparation efficiency and easily breaking structure of h-BN need to be solved.

In comparison, the liquid phase exfoliation method has attracted much attention because of its simple operation process and high exfoliation efficiency [16, 17], which is to stir h-BN in a solvent [18, 19] and continuously shear h-BN to obtain nanosheets dispersion. The liquid phase exfoliation method has a wide selection of exfoliation solvents, including organic solvents (isopropanol [20], 1,2-dichloroethane [21], N,N-dimethylformamide (DMF) [22, 23]), protic acid (phosphoric acid [24], methanesulfonic acid [25]) and surfactants [7, 26], etc. The diversity of exfoliation solvents also provides great convenience for the subsequent application of the obtained solution. However, this method requires long-term ultrasonic treatment, which not only consumes a large amount of energy but also easily causes the temperature to rise, then inducing organic solvents into volatilizing and being harmful to human body.

In this paper, we attempt to improve the ultrasound-assisted liquid phase exfoliation method. DMF or protic acid/strong oxidant mixture (concentrated sulfuric acid, concentrated phosphoric acid, or potassium permanganate solution namely exfoliation solution in Hummers method [27]) are selected as the exfoliation solvents. Then the efficiency of bulk h-BN exfoliation via solution-stirring exfoliation method is studied, and the effect of these two preparation method on the structure of nano-h-BN are also investigated.

Additionally, as aerogels exhibit great application potential in the fields of catalysis, gas storage and environmental purification [10, 28] due to their unique three-dimensional structure with low density, high specific surface area and high porosity, the h-BN nanosheets obtained by liquid phase exfoliation are mixed with nanocellulose (NFC) to prepare h-BN/NFC aerogel, and the thermal insulation and oil adsorption properties are studied.

2. Experimental section

2.1. Synthesis

2.1.1 Synthesis of BN-1

2g of h-BN was firstly added to 200 mL DMF solution. The mixture was placed in a water bath at 50°C under stirring over 12 hours, followed by sonicating for 30 minutes. Then the resulting solution
was centrifuged at 1400 rpm for 3 minutes to remove the large particles that had not been exfoliated off from the bottom. Finally, the nano-h-BN dispersion was obtained by filtrating the supernatant, and labeled as BN-1.

2.1.2 Synthesis of BN-2
The mixture of bulk h-BN (1.0 g) and potassium permanganate (6.0 g) was slowly added into the mixed solution of concentrated phosphoric acid and concentrated sulfuric acid, which was then placed in a water bath at 50°C and reacted over 18 hours. After the reaction was completed, ice water was added to cool down, followed by adding hydrogen peroxide to remove the unreacted strong acid. The above-mentioned centrifugation step is repeated to obtain the nano-h-BN solution product, labeled as BN-2. The synthesis of BN-2 is referred to Hummers method.

2.1.3 Synthesis of h-BN/NFC aerogel
NFC was mixed with BN-1, followed by ultrasonic treatment over 5min[29]. After frozen at -80°C, the resultant mixture was freeze-dried into BN/NFC aerogel at -55°C and 10 pa pressure for 72h.

2.2. Characterization
2.2.1 Characterization of structure
The morphology and structure of the samples were analyzed by scanning electron microscopy (SEM, SU8010) with an acceleration voltage of 5 kV and Atomic force microscope (AFM, Dimension Icon). FTIR measurements were conducted on a Tensor-27 spectrometer. The sample powders were grounded with KBr powders before being pressed into a wafer for the FTIR measurements. X-ray photoelectron spectra (XPS) was performed by Thermo Escalab 250Xi with an Al Kα radiation as the X-ray source. The C 1s peak had been fixed at the binding energy of 284.8 eV to subtract the surface charging effect. The surface areas and pore size distributions were analyzed with a ASAP2020 nitrogen sorption analyzer.

2.2.2 Characterization of thermal insulation property
Two pieces of h-BN/NFC aerogel with same quality and size was selected. One piece was compressed into a sheet, and the other piece kept intact as a contrast, which was respectively pasted on the surface of a thermostatic water tank at 80°C. The surface temperature was observed with a thermal infrared imager.

2.2.3 Characterization of oil absorbency
h-BN/NFC (quality M0) was immersed into tap water, edible oil (manufactured by Shandong Sanxing Corn Industry Technology Co., Ltd.) and motor oil (manufactured by Yingkou Foss Oil Co., Ltd.). After adsorption equilibrium, h-BN/NFC was suspended in midair for 10min, followed by recording its quality as M1. Then the oil absorbency of the aerogel could be expressed by the adsorption rate Q:

\[ Q = \frac{M_1 - M_0}{M_0} \times 100\% \]

3. Results and discussion
The morphology of bulk h-BN, BN-1, and BN-2 were shown in Figure 2. It can be seen that bulk h-BN presents a block structure formed by stacking multiple layers (Figure 2a). And the block structure is dense with the layer thickness as about 0.6μm (Figure 2b).
After stirring-assisted liquid phase exfoliation, the structure of h-BN changes significantly (Figure 2(c-f)), and the original bulk structure is broken and crushed into small flakes with the size of several hundred nanometers. It can be observed that the BN-1 nanosheet has a large curvature with irregularly shaped edge (Figure 2d), and the thickness of the layer has been greatly decreased, indicating that the bulk h-BN was successfully exfoliated. Meanwhile, Figure 2(e, f) present the morphology of BN-2, which reveals that h-BN is broken up, along with wrinkled edges by this method. Nevertheless, the layer-to-layer accumulation is still dense and orderly, indicating that is relatively poor results from exfoliation.

AFM measurements are used to characterize the thickness of the obtained BN-1 and BN-2. Any three locations in Figure 3a (BN-1) and 3b (BN-2) are respectively selected for comparison in the thickness of nanosheets. The thickness of the BN-2 layer obtained by the Hummers method is about 5.4 nm, while the thickness of the sample BN-1 layer is about 1.4 nm. Therefore, BN-1 is stacked by about 3 layers [15], much less than BN-2 with about 11 layers.

B-N bond was successfully detected in bulk h-BN, BN-1 and BN-2, as confirmed by FT-IR spectra. As shown in Figure 4a, distinguishable peaks referred to 818 cm\(^{-1}\) and 1364 cm\(^{-1}\) are observed for all samples, corresponding to in-plane stretching vibration and out-of-plane bending vibration, respectively [14]. Additionally, similarity exists in the FT-IR curves among three kinds of materials. And in comparison with the spectra of h-BN and BN-2, the characteristic peaks of BN-1 are relatively
sharp due to the thinner layer, which induces smaller steric hindrance and increasing vibration strength after energy absorption. Besides, no heterogeneous peak is found in both BN-1 and BN-2 compared to bulk h-BN, which demonstrates that no chemical moieties are embedded into the nano h-BN.

Figure 4. Chemical structure analysis of three samples. (a) FT-IR; (b) XPS Survey; (c) B1s; (d) N1s

The high-resolution XPS spectra of samples are given in Figure 4 (b, c, d). XPS signals for all samples can be fitted with peaks at 190.5 and 398.1 eV, which are assigned to B1s and N1s. As the peak shape and location of these three samples are almost same, and no new peak arise, indicating that no chemical group is introduced into the exfoliated h-BN nanolayers after long-time stirring, which is consistent with the results obtained from FT-IR spectra.

Figure 5. Schematic diagram of stirring-assisted liquid exfoliation

Through the analysis of the micro-morphology, crystal configuration and chemical structure of h-BN before and after exfoliation, it can be concluded that bulk h-BN can be successfully exfoliated into well-structured nanosheets with thickness of 1.3 nm by liquid phase exfoliation method with DMF. The interaction between the B atom at the defects of h-BN and O atom of the DMF is employed to counteract the van der Waals force between the layers [23, 30]. Under the shearing force, the h-BN is torn at the defect, with that the layer spacing is enlarged by the insert of DMF molecules [30].
However, the successful exfoliation is not achieved in the Hummers method due to the excellent corrosion resistance of h-BN, which makes the conjugated net in h-BN stable under the existence of strong oxidant [30]. The weak interaction between H+ and N atoms in h-BN [25] can slightly offset the van der Waals force between layers, but the shearing force is too weak to exfoliate the bulk h-BN, which presents poor exfoliation results.

Figure 6. (a) microphotograph and (b-d) SEM images of aerogel.

The h-BN/NFC aerogel was prepared from BN-1 by freeze drying. It is shown that nano-h-BN is much wrinkled in Figure 6b. In order to inhibit the agglomeration between the nanosheets as a result of π-π interaction (ie "lip to lip" interaction), the interlaminaration of h-BN layers is filled with NFC. And nanosheets and NFC are interwined with each others. Meanwhile, the solvent was removed by freeze drying, which gives plentiful pores. Hence, h-BN/NFC with high specific surface area (~147.12 m²/g) was successfully prepared, as shown in Figure 6 accompanied with porous and loosened structures.

As can be seen in the characterizations of thermal insulation property (Figure 7), the thermal images display that the area inside and besides the h-BN/NFC aerogel are almost yellow-green and yellow, respectively, indicating the apparent temperature difference. When the heating time increases to 900s, the temperature of the area inside h-BN/NFC is still 67 °C, while the temperature of the area out of h-BN/NFC aerogel changes from 46.14 to 54.18 °C, which demonstrates that h-BN/NFC aerogel possesses an excellent thermal insulation property. On the other hand, after being squeezed to remove air, the temperature of h-BN/NFC aerogel (sample 2 in Figure 7) keep stable in 71 °C and is 9 °C lower than the temperature of the surrounding area, indicating that the filled air into the aerogel pores can enhance the insulation properties.
Figure 7. Thermal insulation performance of aerogel, in which sample 1 was the origin h-BN/NFC aerogel and sample 2 was the squashed one.

It should be noted that massive pores, high specific surface area, the Hydroxyl group on cellulose and the conjugated structure of h-BN in h-BN/NFC aerogel can be applied to adsorb oil for purifying water. As shown in Figure 8a, h-BN/NFC aerogel possess great adsorption capacity for edible oil and motor oil with less deformation, while it shows weak adsorption capacity for water with larger deformation. All of these are related to the interaction force between oil/water and aerogel. When oil or water enters into the pores of the aerogel and interacts with the pore wall, a large number of hydroxyl groups in the water molecules strongly interact with the pore walls of aerogel, inducing the severe shrinkage of the aerogel volume and the decrease of the adsorption space. Therefore, the water absorption capacity is strongly weakened.

The prepared aerogel possesses good structural stability due to the intertwine of h-BN nano-layer with NFC, which cannot be disintegrated by the adsorption of water or oil. During the purification process of oil-contaminated water (Figure 8b), it can be seen that h-BN/NFC aerogel floats on the topside to adsorbed oil, and h-BN/NFC aerogel shrinks with the adsorption of oil over time until the adsorption get saturated. When the aerogel sinks and contact with water, the oil pollution has been completely confined inside the aerogel, then the aerogel removes the pollutions in the water. Hence, the h-BN/NFC aerogel presents broad application potential in water purification field.

Figure 8. (a) Oil adsorption performance of aerogel and (b) purification of simulative oily water with h-BN/NFC aerogel
4. Conclusions
In this work, the feasibility of stirring-assisted liquid exfoliation on layered materials are deeply analyzed. The intact h-BN nanolayers with thickness at about 1.4 nm and 5.4 nm were obtained by DMF and Hummers exfoliation methods, respectively. The results show that BN-1 has higher efficiency of successful exfoliation than BN-2. Additionally, the specific surface area of h-BN/NFC aerogel prepared from BN-1 is as high as 147.12 m²/g, and a large number of pores are filled with air, thus enhances the thermal insulation and oil adsorption properties, which can decrease about 13°C of its original temperature in comparison with the surroundings and increase about 97 times of its original weight. Therefore, the h-BN/NFC aerogel would be valuable for application in thermal insulation and purification of water.

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