

The investigation of BN nanosheets production by using solvent exfoliation

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In this study, Boron Nitride Nanosheets (BNNSs) were produced via solvent exfoliation method with hexagonal boron nitride (h-BN) which was used as the raw material. This method is essentially based on separating the layers, which are bound with weak bonds, through a solvent. For this purpose, h-BN powders were firstly exposed to an acidic process and then heat treatment. A new structure with expanded hexagonal layers (expanded hexagonal boron nitride) was obtained at the end of this process. Synthesized expanded hexagonal boron nitride was sonicated in a solvent (N,N dimethylformamide). At the end of the process, synthesized samples were characterized by Scanning electron microscope (SEM), Transmission electron microscope (TEM), UV-Vis absorption spectra, Fourier transform infrared (FTIR) and atomic force microscope (AFM). Consequently, it was found that BNNS layers that had a thickness of several nanometers and a width of a few hundreds of nanometers were produced.

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1. Introduction

Being a wide band gap IIIA –VA compound, Boron nitride (BN) has striking physical manners and chemical steady. h-BN contains alternating boron and nitrogen atoms in a honeycomb arrangement, with sp^2 -bonded two-dimensional (2D) layers [1-6]. Boron and nitrogen atoms are bound by strong covalent bonds in each layer of h-BN, conversely, the layers are held together via weak secondary bonds, as in graphite. Even though h-BN has mechanical strength and thermal conductivity properties similar to graphite, it has a great band gap (~4.5-6 eV), which yields properties of an insulator (or a wide-band-gap semi-conductor) [7-8]. Hexagonal Boron nitride has various forms such as boron nitride nanotubes [9] and boron nitride nanosheets. Especially, boron nitride nanosheets (BNNSs) are insulating in point of electrical, and also it has thermal conductive and mechanical strength similar to grapheme, therefore it is thought that they possess the capability to find the usage area in optoelectronic devices and heat-releasing composite materials [10–14].

Recent studies reported that the two-dimensional boron nitride nanosheets were produced from single-crystalline hexagonal boron nitride used as starting materials via a micromechanical cleavage technique [15] and a chemical solution-derived method [16]. Generally, current synthesis methods complicate the manipulation of BN nanosheets and the amount of BN nanosheet materials brings limitations for usage area in applications at all times.

Graphene [17-18] and graphene-BN nanosheet [19] structures were previously synthesized by using liquid phase exfoliation method. This method is basically based

on separating of layered hexagonal sheets and their transformation into nano-sized layers.

In this study, commercial hexagonal boron nitride powders were converted into expanded boron nitride by being subjected to an acidic process and then heat treatment. Synthesized expanded hexagonal boron nitride powders were sonicated within high energy sonication in a solvent. Thus, boron nitride nanosheets (BNNSs) were synthesized by solvent exfoliation. The samples obtained at the end of the process were characterized by Scanning electron microscope (SEM), Transmission electron microscope (TEM), UV-Vis absorption spectra, Fourier transform infrared (FTIR) and atomic force microscope (AFM). Consequently, BNNSs were determined to be synthesized successfully.

2. Experimental procedure

h-BN powders (Merck, 99.5%) were dried by using a vacuum oven at 75 °C for 8 h to remove the humidity. The dried h-BN was stirred by using saturated acid containing concentrated H_2SO_4 and HNO_3 for 3h. The mixture was stirred to obtain the uniform intercalation of each h-BN particle. It was carefully irrigated by using distilled water until a neutral pH was achieved. The sample was dried under vacuum for 12 h and then heated at 800 °C to form the expanded hexagonal boron nitride [23-25].

The BN-sheets were still bonded with weak secondary bonds at some points in expanded BN. Therefore, the expanded BN was incurred to a final exfoliation to obtain boron nitride-sheet by ultra-sonication in N,N-dimethylformamide (DMF). The suspension of expanded BN with DMF at 0.05mg/ml concentration was prepared. The solution of expanded BN was kept at a multi-

frequency ultra-sonication homogenizer (Bandelin-Sonopuls HD 2070 100 watt) for 1 h. Then, the mixture was centrifuged for 45 min to send away the DMF. The obtained powders were irrigated by ethanol and the alcohol was sent away by drying them in the vacuum oven at 80°C about 3 h.

The synthesized powders were characterized by using UV-vis spectroscopy. A UV-spectrophotometer (UV 3600 Shimadzu, Japan) of 250 and 1200 nm was used to record the spectrum. The microstructure of grapheme samples was investigated via the high-resolution transmission electron microscope (HRTEM) (JEOL Jem 2100F). The analysis of the samples was carried out by FESEM (Jeol Jsm-7001F). The structural properties of the samples were examined by a Park System XE-100E atomic force microscope (AFM). FTIR spectrum of the samples was determined as between 400 and 4000 cm^{-1} in Nicolet 5700 FTIR spectrometer.

3. Results and discussions

The h-BN resembles graphite very much in terms of its numerous physical and chemical properties, crystal structure and atomic bonding structure. Even it is also called as the white graphite. While boron and nitrogen atoms are bound to each other with strong covalent bonds

on hexagonal a-b plane, the layers are bound with weak secondary bonds on a third plane which is orthogonal to a-b plane. Interlayer spacing is 0.33nm, as is in graphite. Synthesize of BNNS by using solvent exfoliation method is based on separating layers of h-BN bound with van der Waals forces by using an organic solvent. Interlayer spacing of h-BN does not allow the organic solvent to insert to break the bonds. For this purpose, production of the expanded h-BN was performed at the first stage.

Fig. 1 shows SEM image of hexagonal boron nitride which was used as starting material and SEM images of expanded hexagonal boron nitride. Figures 1.a and b show that h-BN used as the starting material has a flaked structure. Characteristic, quality, and large flakes of h-BN which was used as starting material improve production yields and qualities of BNNSs [13]. Flake sizes of h-BN used as starting material vary from a few hundreds of nanometers to 1 micro meters. Fig. 1.c and d show SEM image of expanded hexagonal boron nitride obtained by subjecting h-BN to the process in acid mixture and then to heat treatment. As is seen from the figure, the produced expanded hexagonal boron nitride had a very porous and loose structure than h-BN. Interlayer spacing of expanded hexagonal boron nitride significantly increased compared to h-BN. It can be asserted that the structure obtained after production of expanded hexagonal boron nitride contained numerous micro and nano-sized thick BN layers.

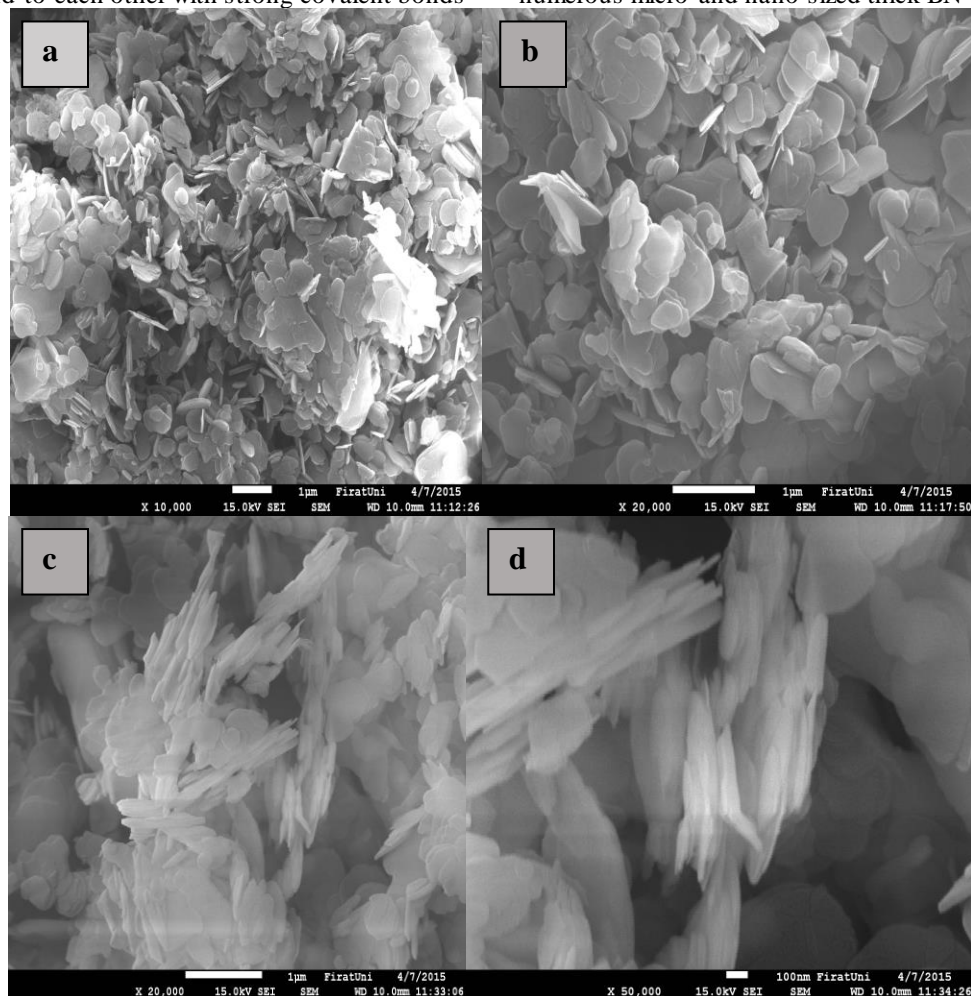


Fig. 1. SEM micrograph of (a),(b) h-BN (c),(d) expanded hexagonal boron nitride

After obtaining the expanded h-BN structure, this structure was mixed with DMF and sonicated for 1 h. DMF molecules easily penetrated between the layers of expanded hexagonal boron nitride with increased interlayer spacing and help to separate the layers from each other. Fig. 2 shows TEM images of BNNSs obtained at the end of the process. The exfoliation process became successful and separating of the layers from each other was realized. Width of layers was higher than 100 nm. Generally, the hexagonal layers in the inner part have

straight and parallel structures with each other (Fig. 2.c.). While flake sizes of h-BN used as starting material reached up to 1 micro meter, width of the obtained BNNSs was relatively lower. Sonication process was applied for production of BNNSs. Although this process is performed at very low frequency, it still damages to flakes of BN. Small width of the obtained flakes was considered to be associated with the fractures occurring between layers during the sonication process.

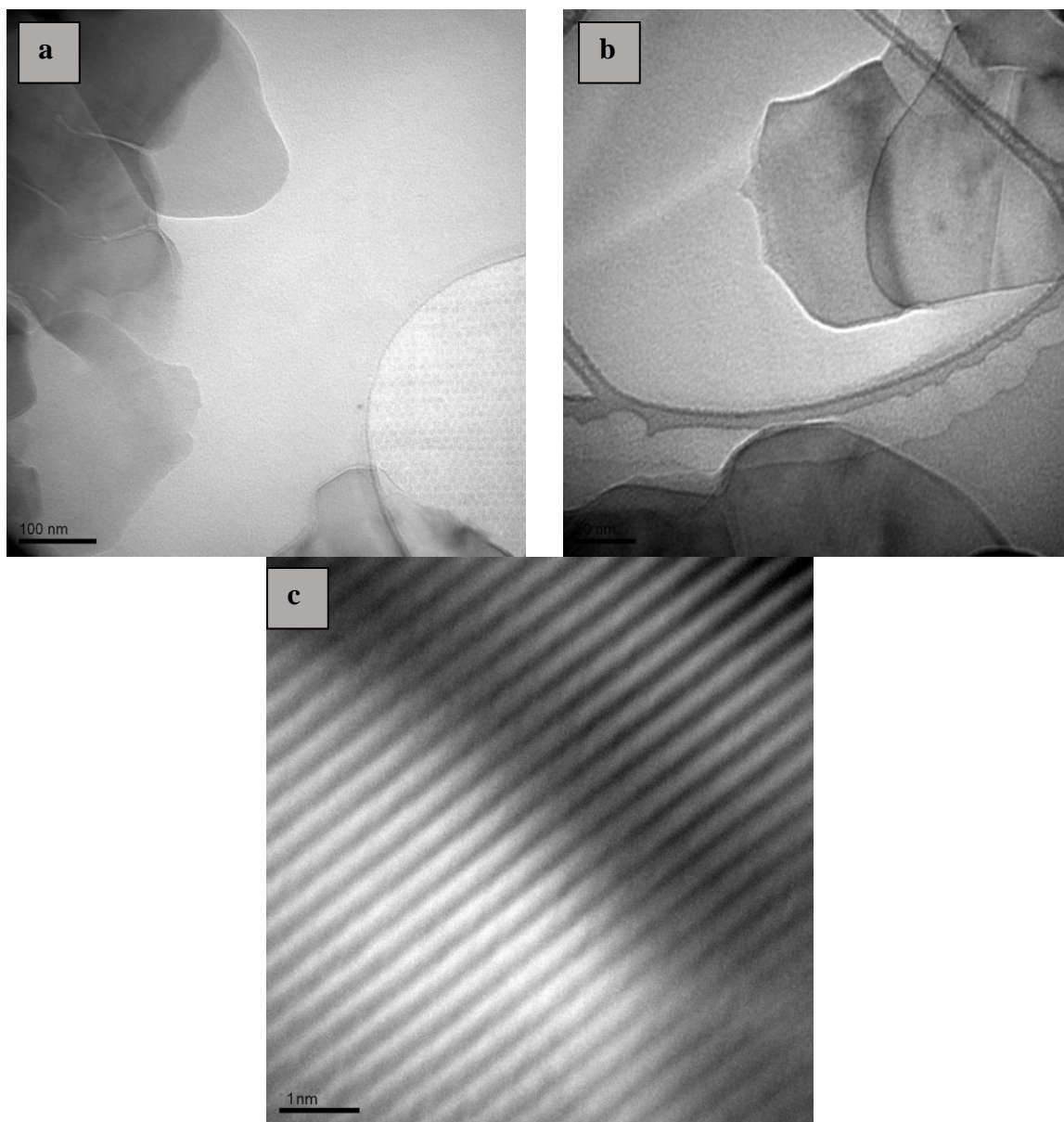


Fig. 2. (a),(b),(c) High magnified TEM images of synthesized BNNSs

The UV-vis optical absorption spectrum of BN nanosheets was obtained for examining the optical properties of the as-prepared BN nanosheets (Figure 3). It was observed that an absorption peak around 271 nm corresponded to a band gap energy (E_g) of 5.94 eV for BNNS. But, a band gap energy of h-BN was 4.67 eV for the same absorption peak. Another peaks at 365 nm (3.10 eV) was also observed in the UV-vis spectrum. The two

low-energy lines could be considered as optical transitions between van Hove singularities in the one-dimensional density of BN nanosheets [16,20]. The current FTIR spectrum of the BNNSs had similarities to the polycrystalline hBN and BN hollow nanoribbons, which confirmed their relatively good crystallinity.

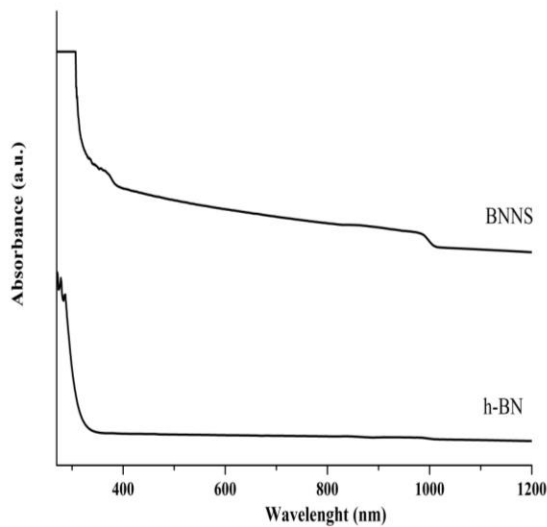


Fig. 3. Uv-Vis analysis results of raw boron nitride and BNNS

In order to examine surfaces of BNNS samples which were synthesized via solvent exfoliation method, the surface images of the samples were taken by the atomic force microscope (AFM). Produced BNNS powders were distributed homogeneously in ethanol and the obtained liquid mixture was dried by being dropped onto a glass slide. The obtained sample was then examined under AFM. Figure 4 shows three-dimensional images of the samples. Z-axis had a height of approximately 2 micrometer. The graphene suspension had average particle sizes of a few micrometer.

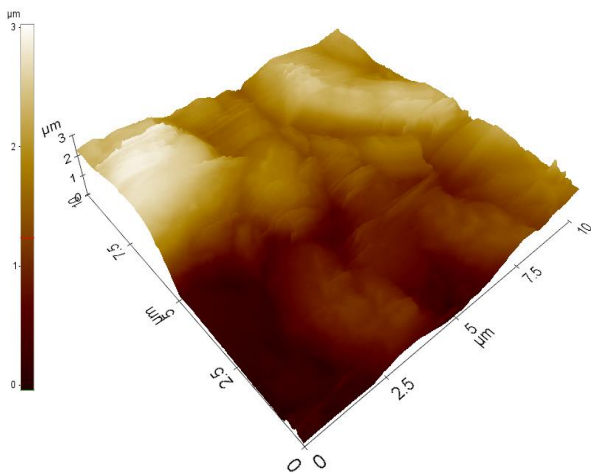


Fig. 4. Atomic force microscopy images of obtained BNNS

The produced samples was characterized by using the Fourier transform infrared spectroscopy (FTIR). FTIR is effective characteristically in determining the structural nature of hexagonal BN. The structural nature and phase composition of synthesized h-BN products were observed in the characteristic FTIR spectrum of the produced BN nanosheet in Figure 5. The FTIR spectrum had two strong

vibrations at 1373 and 818 cm^{-1} . The peak around 1373 cm^{-1} was caused by the in-plane B-N transverse optical modes of the sp^2 -bonded h-BN; whereas, the peak centered at 818 cm^{-1} could be referred to the B-N-B out-of-plane bending vibration [17-21]. Peaks, except for 1373 and 818 cm^{-1} , were considered to be impurity peaks.

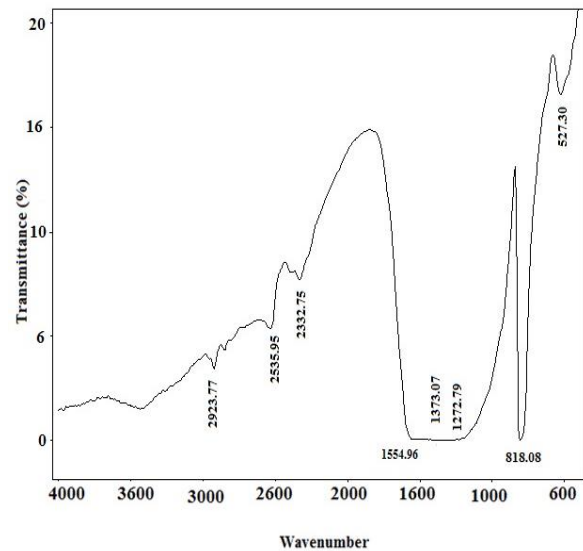


Fig. 5. FTIR analysis of BNNS

In the present study, BNNS was produced by using solvent exfoliation method. Even though the method is a simple one for the production of BNNS, the amount of products produced was stated to be lower in some previous studies [22]. Sonication process applied after solvent was added into expanded BN structure was implemented in a relatively short time like 1 hour in this study. Some of previous studies revealed that this period was maximum 6 hours [23]. Therefore, the reason behind why layers obtained in the present study were relatively thicker was considered to be associated with the duration of sonication process. It is obvious that layers with lower thickness will be lighter compared to thicker ones and will accumulate on the surface of the liquid. Taking qualified samples accumulated on the surface and applying the same processes to remaining samples will increase the production of thin-layer graphene [22].

4. Conclusion

Boron nitride nanosheet (BNNS) was produced via solvent exfoliation from hexagonal crystal boron nitride (h-BN) used as starting material. This method is based on the release of layers by breaking weak bonds between the layers of h-BN. In order to achieve this, a solvent that help to separate layers from each other was used. DMF was used as solvent in this study. Interlayer spacing needs to be increased for solvent atoms to easily enter between the layers. Therefore, the expanded h-BN was firstly produced in this study. Then, it was ensured for DMF used as solvent to enter between expanded h-BN layers through

sonication process and to separate the layers from each other. At the end of the process, the production of layers having a width reaching up to 100 nm and a thickness of a few nanometers was achieved. The amount of products produced by this method is relatively low. Additionally, layer thickness of the produced samples are relatively high. Our studies have been ongoing for production of BNNS with thinner layer and increasing the amount of products.

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