The production of boron nitride nanosheets using liquid-phase exfoliation assisted by ball milling process

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The liquid-phase exfoliation method is one of the easiest methods for the production of nanosheets. The amount of product manufactured with this method is relatively low. The hexagonal boron nitride (h-BN) powders were subjected to the milling process as pre-treatment to obtain higher rate of the product. The shear type stresses were applied for the milling process. The milled powders produced were mixed in an acid mixture at the first and then exposed to the heat treatment at high temperature to increase the distance between h-BN layers. The samples obtained after these processes were mixed in a solvent with the help of ultrasonic homogenizer to synthesize boron nitride nanosheets (BNNSs). The microstructure analysis of the products obtained was carried out in Transmission Electron Microscope (TEM), and they were examined in Raman Spectroscopy and UV-Vis spectroscopy. It was observed that BNNSs formed in the structure containing h-BN, amorphous BN, thick BN sheet. In addition, the amorphous boron nitride structures were also encountered in the structure. In the liquid-phase exfoliation process assisted by milling process, the impact of the milling on efficiency of the product did not reach to the expected level. Moreover, it resulted in formation of amorphous structures deteriorating the purity of structure.

1. Introduction

BN nanosheets are (002) planar and layered hexagonal BN (h-BN). They are structurally very similar to the graphene [1]. Investigations on two-dimensional nano-layer structures revealed that BN flakes were peeled from a BN crystal. In previous studies, it was reported that the initial growth of BN nano-layers was formed as nanomesh on metallic substrates [2]. In h-BN, the boron and nitrogen atoms are arranged in a honeycomb shape, thus forming a two-dimensional layer connected to each other by the sp^2 bond. [3]. These layers are connected to each other by weak Van der Waals bonds as in graphite, and the distance between layers is 0.33 nm [4]. Even though the mechanical and thermal properties of h-BN are similar to the graphite, it has several properties different from the graphite in terms of electronics [5]. It acts as an insulator behavior since it has a wide-band gap (4-6 eV). The studies conducted recently suggest that BNNSs display several unique properties. BN nanostructures have excellent thermal and chemical stability outside of electrical insulation but, at the same time, excellent thermal conductivities, and mass sensing capabilities [6]. Futhermore, the polarity of BN bonds and the high surface area provide good adsorption properties of various substances ranging [7].

Thanks to these properties, they have a significant potential for the usage in optoelectronic devices, emission of ultraviolet lights, and insulator [5,8,9]. BNNSs have been successfully produced by means of methods such as chemical vapor deposition, micromechanical cleavage, and exfoliation [2,10,11]. More recently, nanosheets have been produced by sonicating h-BN crystals in a 1,2-dichloroethane solution of a poly(phenylenevinylene) polymer [4]. These methods have also been used for the production of graphene [12-15].

In this study, h-BN was used as the starting material and the milling process where the shear stresses are dominant was applied to h-BN. In this way, BN layers were exposed to the preliminary separation process and the thickness and number of layers were reduced. The samples obtained after the milling process were subject to the sonication process in a solvent and thus the BNNS structures were obtained.

2. Experimental procedure

In this study, hexagonal boron nitride powders (h-BN)(Merck, 99.5%, 10 μm) were used as the starting material. h-BN powders were dried in an oven at 75 °C for 2 h. Then, the dehumified h-BN powders were milled by using a single ball with a diameter of 19 mm at 400 rpm for 50 hours in the device of which trademark is Fritsch Pulverisette Premium line 7. After milling process, the powders were characterized by X-ray diffraction (Bruker D8 Advanced X-ray diffractometer with CuKα radiation Wavelenght 1.54 A, scan speed 0,5 degree/min). The powders obtained after the milling process were mixed by using a magnetic stirrer in the saturated acid mixture composed of H_2SO_4 and HNO_3 (volume ratio 3/1) for 12 hours in order to obtain a homogenous mixture. The

powder mixture filtered from acid mixture was washed with distilled water until pH was neutralized. The powder obtained from the acid process was heated at 950 ^{o}C. The powders, which were exposed to thermal process in order to obtain BNNs layers, were mixed by using an ultrasonic homogenizer (Bandelin Sonoplus, model HD 3200, 200 W, at 50% power) in the N,N-dimethylformamide (DMF) for 2 hours. The suspension of 0.05mg/ml concentration of BN powders with DMF was prepared. Then, the mixture was centrifuged at 5000 rpm for 8 hours to remove DMF. The powders were washed by ethanol and were dried under a vacuum oven at 75 ^{o}C for 4 hours to remove the alcohol.

The obtained powder was characterized by UV–vis spectroscopy. The spectrum had an operation range (UV 3600 Shimadzu, Japan) between 250 and 1200 nm. High-resolution transmission electron microscope (HRTEM) (JEOL Jem 2100F) was used to investigate the microstructure of BNNS samples. The samples were analyzed through FESEM (Jeol Jsm-7001F). Also, Raman spectroscopy (Witec snom-Raman) was performed by using a laser excitation of 532 nm delivered through a 100x objective.

3. Results and discussions

Fig. 1 shows the experimental procedure for preparing the h-BN sheet production. h-BN consists of a stack of flat h-BN layers. The layers are bonded via weak van der Waals bonds, which allows layers of h-BN to be easily separated, or to slide past each other. The aim of this study was to exfoliate h-BN layers in order to product the h-BN nanosheets. A solvent is necessary to separate the layers. The distance of layers should be sufficient in order to enter the solvent atoms between layers after the milling process. So, hexagonal BN powders were firstly milled by shear type force in order to obtain thick h-BN layers in our experiment. The intensity of characteristic peak of h-BN (002) significantly decreased at the end of 50-hour milling process (Fig. 2). This proved that h-BN became amorphous during the milling process. The milling process was performed by using single ball with a diameter of 19 mm. The ball moved on the powders and compelled the layers to separate from each other during the process. But, the ball collided with the walls of container during this movement. The impact type stresses occurring in this collision resulted in the amorphization of powders remaining between them.
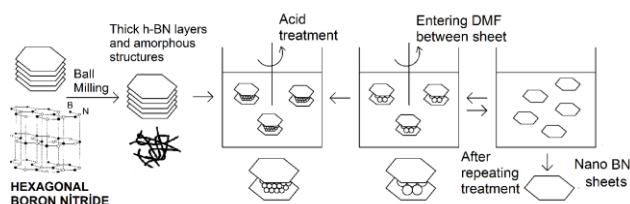
h-BN is fairly similar to the graphite in terms of structure and some properties. The expanded graphite is produced from the graphite and then is exfoliated in order to increase the amount of product which will be obtained during the production of graphene via liquid-phase exfoliation method [16]. Considering that h-BN would have similar properties, h-BN was mixed in the acid mixture after the milling process and then, subjected to the heat treatment. This process was considered to increase the distance between h-BN layers. Also, the amorphous structures forming as a result of mixture in the acid and the heat treatment were partially removed. XRD analysis in Fig. 2 clearly shows this situation. The intensity of (002) peak significantly decreased as a result of the milling process. An increase occurred in the intensity of (002) peak after the acid and heat treatment process. This situation is considered to result from HNO_3 in particular [17].
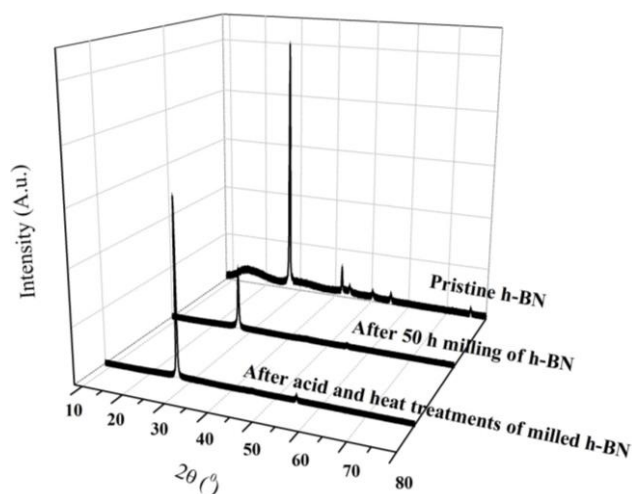

Fig. 2. The XRD analysis of produced and unproduced powders

Fig. 3 shows SEM micrographs of samples of pristine h-BN, after 50 h milling of h-BN and after acid and heat treatments of milled h-BN. Pristine h-BN was composed of numerous flake-like powders having several micrometer width (Fig. 3a). Again, the layered structures were observed in the sample after the milling for 50 hours. Moreover, intensely sintered amorphous structures were observed in the structure (Fig. 3b). The sintered amorphous structured significantly decreased in the structure at the end of acid and heat treatments (Fig. 3c).

Fig. 1. The scheme of experimental procedure for preparing the h-BN nano sheet production
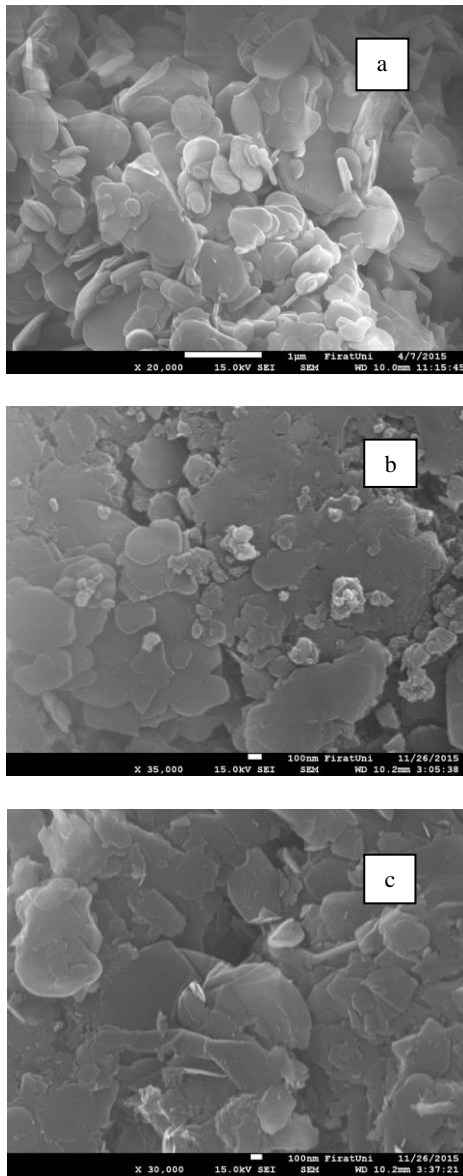
*Fig. 3. SEM micrograph (a) of pristine h-BN,
(b) after 50 h milling of h-BN (c) after acid and
heat treatments of milled h-BN*

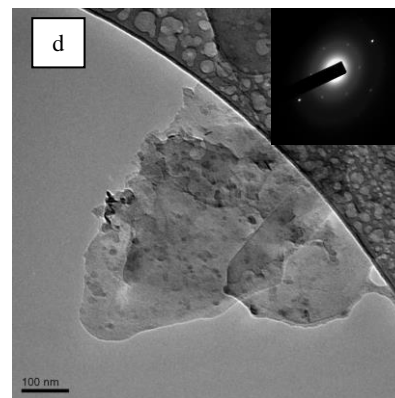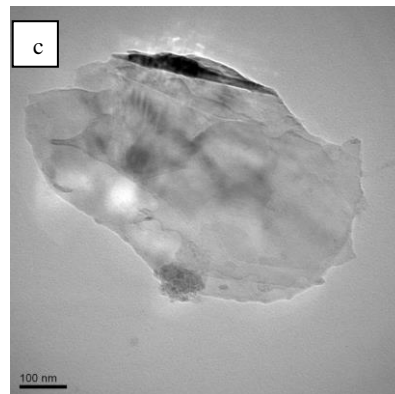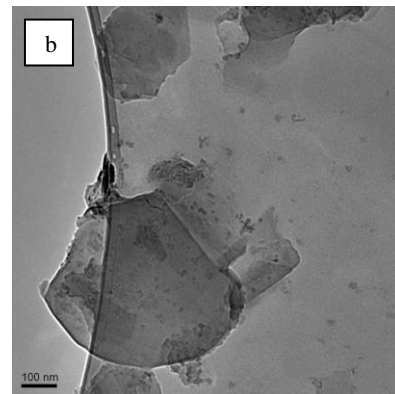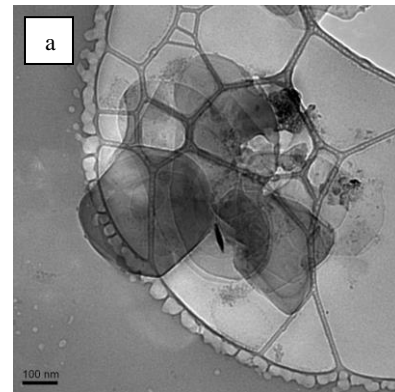Fig. 4 shows TEM micrographs of BNNSs produced. As can be figured out from the figures, it was observed that BNNSs were present in each area of the product obtained at the end of liquid-phase exfoliation method assisted by ball milling process. Numerous sheets with several nanometer thickness overlapped in Figs. 4a, b, and c. The widths of sheets reached up to several-hundred nanometer. Electron diffraction (ED) given in Fig. 4d was consistent with the crystallinity of graphene structure. It is possible to say that the disordered structures were present in interior and/or upper sections of the layers or partially in all the layers by the nature of the method employed. The dark-colored particles were present on BNNSs and/or their nearby regions in all TEM micrographs given in Fig. 4. These particles were the sintered amorphous structures.

*Fig. 4. (a),(b), (c), TEM micrographs, (d) Electron
Diffraction pattern of synthesized BNNSs*

Fig. 5 shows Raman Spectroscopy of h-BNs milled for 50 hours and BNNSs produced after the liquid-phase exfoliation method. A sharp and intense peak was not observed after the 50-hour milling process. The peak occurring approximately at 1365 cm^{-1} indicates that the structure obtained by milling was recrystallized after intermediate processes applied. However, the relatively low peak intensity indicated that amorphous structures were still present in the powder. This demonstrated that the amorphous structures were dominant in the sample. In this study, the liquid-phase exfoliation process was the last process step for the synthesis of BNNSs. As can be seen in Fig. 5, an intense peak was observed at 1365 cm^{-1} in Raman Spectroscopy acquired following the liquid exfoliation process. This peak could be associated with BNNSs. This is because this peak was attributed to the high frequency intralayer E_{2g} vibration mode of h-BN [10]. As the processes carried out were the milling at the beginning, then obtaining the expanded BN and finally the production of BN sheet by exfoliation, both crystallized and amorphous BN naturally emerged in the structure. However, the milling process carried out by applying the shear forces in order to separate the BN layers could not be beneficial as expected for the production of BN nanosheets. In other words, the lack of significant increase in the amount of product obtained after long milling time as well as the determination of amorphous structures in the sample indicated the necessity of using more different milling conditions in the production of BNNS. The band-gap interval varied between 3.1 and 7 eV in the optical absorption analyses of BN performed in previous studies. This difference in the values of band-gap was associated with the different structures of BNs produced in these studies [18,19].
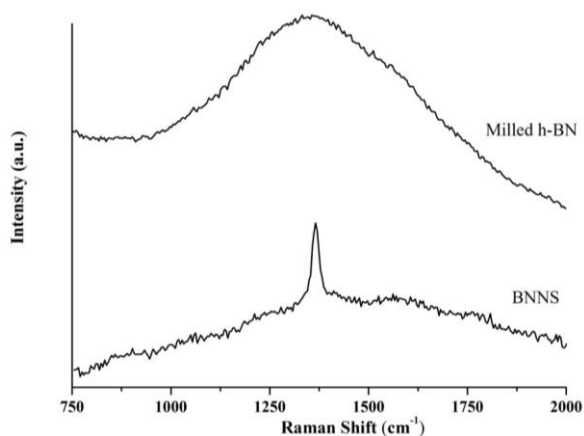

Fig. 5. Raman Spectroscopy of h-BN milled for 50 h and synthesized BNNSs

Fig. 6 shows UV-Vis Analyses of pristine h-BN and BNNSs produced. As can be seen in the figure, band-gap energy of BNNSs (E_g) was determined to be 4.5 eV at the peak observed at approximately 279 nm. The highest band-gap energy was observed at this peak.
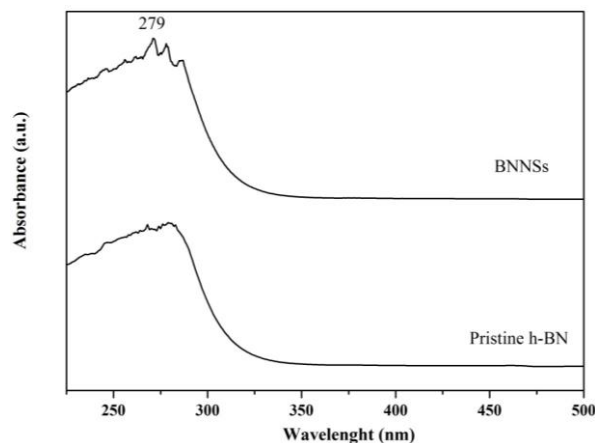

Fig. 6. UV-Vis analysis of BNNS's

Even if the liquid-phase exfoliation method has many advantages for the production of BNNSs, the most important problem is that the amount of product manufactured is very limited. It is considered that the milling process to be carried out by employing the suitable parameters will be effective in order to overcome this problem. In this study, the milling process was carried out by using a single ball of which mass was relatively high. Thus, it was thought that the ball moving on the powder with the centrifugal force would force h-BN layers to separate from each other. This opinion partially became successful in this study. A kind of mechanical exfoliation process was carried out on the powder by the ball movement during the milling process. This situation ensured that weak Van der Waals bonds between the layers ruptured and the layers were partially separated. Consequently, the milling time was prolonged to increase the number of layers separating from each other since a single ball applied a limited force on the powders. However, the unexpected rate of amorphization occurred in h-BN powders during the milling process. B-N bonds in the hexagon ruptured due to partial collisions between the container and ball. Thus, as the milling time increased, the amount of amorphous structure increased as well. It was thought that turbostratic structures formed in the powders as a result of ball impacts and these structures were slightly crystallized in the following processes.

4. Conclusions

In this study, the production of BNNSs was performed and h-BN powders were subjected to pre-milling process in order to increase the production efficiency. Consequently, it was concluded that the pre-milling process, carried out by applying the shear forces in order to separate the layers, was not very effective in the production of BNNS and made limited contributions to the stage of expanding BN. Besides, BNNSs and excessive amount of amorphous BN structures were observed in the samples obtained. The milling process could not be effective as expected for the production of more efficient

BNNSs as the milling process took a long time and led to the formation of amorphous structures.

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