Production of graphene–boron nitride hybrid nanosheets by liquid-phase exfoliation

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ARTICLE INFO

ABSTRACT

Hexagonal graphite (HG) and hexagonal boron nitride (h-BN) show various characteristics that are different from each other in addition to their similar features. It is thought that hybrid nanosheets which are formed of nano-layered graphene and nano-layered boron nitride (BNNS) will show very extraordinary characteristics. In this study, the production of a new Hybrid structure containing graphene and BN nanosheet structures was performed by using the liquid-phase exfoliation method. For this purpose, as the starting material, HG and h-BN were mixed at the same ratio and added into an acid mixture and thus an intermediate structure called as Hybrid intercalated compound (HIC) was obtained. Then, the HIC structure obtained was subject to a thermal treatment and a structure called as expanded hybrid structure (EHS) was obtained. In order to produce a Hybrid nanosheet, the EHS structure was sonicated in dimethylformamide (DMF), which was used as a solvent. At the end of the treatment, the material floating in the solvent was filtered. The samples were subject to transmission electron microscope (TEM), scanning electron microscopy (SEM), atomic force microscope (AFM), Fourier transform infrared spectroscopy, and UV–vis spectroscopy examinations. As a result of the analyses, it was determined that the hybrid nanosheets containing graphene and BN nanosheets were successfully produced.

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1. Introduction

Graphene, two-dimensional allotrope of carbon, is formed by aligning the carbon atoms in a honeycomb lattice on a plane [1–3]. In other words, each layer of graphite having a layered structure is called as graphene. Each graphene has a high Young's modulus of ~1000 GPa, a specific surface area of ~2630 $m^2 g^{-1}$, a thermal conductivity of ~5000 W $m^{-1} K^{-1}$ and an impressive transport phenomena like the quantum Hall effect [4–6]. These properties bring a great potential to the graphene as an appealing candidate for next-generation electronic materials and promises in wide applications like field-effect transistors, supercapacitors, batteries, sensors, and nanocomposites, etc. [6–9].

Hexagonal boron nitride (h-BN) has a similar structure with graphite. Hexagonal boron nitride (h-BN) is among the most significant III–V group materials having in-plane trigonal sp^2 bonding, B and N atoms entirely substituting for C atoms in a graphitic-like sheet, and almost no change in atomic spacing [10–12]. When compared to graphite carbon, h-BN with superior mechanical properties and thermal conductivity is more stable from thermal and chemical aspects (for example, h-BN is much more oxidation resistant than graphite. h-BN is stable up to 900 °C in air) [13]. Compared to graphite, h-BN has an electrical insulation (band gap 5–6 eV).

BN can be exfoliated to form boron nitride nanosheets (BNNSs) which are unique 2D crystal structures [14,15]. In recent years, BNNSs have drawn attention because of their extraordinary properties [14–16]. As BNNSs are electrically insulated, thermally conductive, and mechanically robust as graphene, it is thought that they have potential to find a place in applications using optoelectronic devices and heat-releasing composite materials [16,17].

In addition to the similar properties of graphene and BNNS, they also show different properties. It is obvious that a hybrid structure containing both graphene and BNN layers will show extraordinary properties. Thus in this study, a material containing hybrid nano layers was produced by using the liquid phase exfoliation method.

2. Experimental procedure

In order to remove the humidity, Hexagonal graphite (HG) (Merck, 99.5%) and Hexagonal Boron nitride (h-BN) (Merck, 99.5%) powders were dried under vacuum oven at 75 °C for 2 h. The dried

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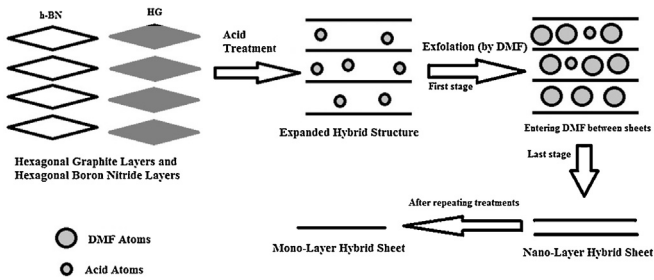*E-mail address:* oguler@firat.edu.tr (Ö. Güler).

Fig. 1. The experimental procedure for preparing the graphene–boron nitride hybrid nano-sheet production.

HG and h-BN were mixed with saturated acid containing concentrated H_2SO_4 and HNO_3 for 12 h in order to obtain a Hybrid intercalated compound (HIC). The uniform intercalation of each graphite and boron nitride particle was obtained by stirring hybrid mixture during the process. It was carefully rinsed by using distilled water until a neutral pH was obtained. The product was dried under vacuum oven for 12 h. Then, HIC was heated at 800 °C to obtain an expanded hybrid structure (EHS) [18–20].

The graphene-sheets still had bonding with weak van der Waals forces at some points in EHS. Thus, EHS was subject to the final exfoliation in order to acquire graphene-sheet by ultra-sonication in N,N-dimethylformamide (DMF). The suspension of 0.05 mg ml^{-1} concentration of EHS with DMF was prepared. The solution of EHS was kept at a multi-frequency ultra-sonication homogenizer for 1 h. Then, DMF was removed by centrifuging the mixture at 5000 rpm for 8 h. The low density material, which was suspended at the top layer of centrifuged solution, was collected to make further characterization. Being rinsed by using ethanol, the collected powders were dried under vacuum oven at 75 °C for 4 h to remove the alcohol.

The synthesized powders were characterized by using UV–vis spectroscopy. A UV-spectrophotometer (UV 3600 Shimadzu, Japan) operating between 250 and 1200 nm was used in order to record the spectrum. Transmission electron microscope (TEM) (JEOL Jem 2100F) was utilized to examine microstructure of graphene samples. The analysis of samples was made by Scanning Electron Microscopy (SEM) (Jeol Jsm-7001F). The structural properties of the samples were examined by using a Park System XE-100E atomic force microscope (AFM). FTIR spectrum of the samples ranged between 400 and 4000 cm^{-1} on Nicolet 5700 FTIR spectrometer.

3. Results and discussion

Fig. 1 illustrates the experimental procedure for production of the hybrid sheet. Hexagonal graphite and hexagonal boron nitride contained flat graphene-layer and BNNS, respectively. Bonding between layers was performed by using weak van der Waals bonds, which enable to separate easily layers of graphite and h-BN or to slide past each other. This study was conducted to exfoliate graphite and h-BN layers for production of graphene and BNNSs. A solvent is necessary to separate the layers. The distance of layers is required to be sufficient in order to enter the solvent atoms between layers. Therefore, the mixture of HG and h-BN powders was expanded by means of acid and thermal treatments. Subsequent to these treatments, the distance between the hexagonal layers increased and solvent atoms easily entered in these spaces and provided to break the weak bonds between the layers. As can be understood from the schematic view, HIC was formed after keeping HG and h-BN, used as the starting material, in the acid mixture for a long time. As a result of keeping the HIC at high temperature for a few minutes, EHS was produced [18,21]. The distance between the layers of both hexagonal graphite and h-BN was about 0.334 nm. The distance

between the EHS layers obtained as a result of the treatments has increased compared to the initial. EHS obtained was sonicated for a specific period by adding it in DMF. This treatment helped the DMF molecules to enter between the layers and to separate the layers from each other. As a result of this treatment, there were nano-sized hybrid layers in the large part of the structure; whereas, very small amount of single-layer hybrid structures formed. Previous studies reported that single-layer structures increased as a result of the repetition of this treatment [3].

Fig. 2 illustrates SEM images of HG, h-BN, HIC, and EHS which were used as the starting material. Fig. 2a illustrates SEM images of HG and Fig. 2b illustrates SEM images of h-BN. As is seen from the figures that both starting materials had a layered structure and the layer widths were quite high. Fig. 2c illustrates SEM image of the HIC structure obtained at the end of 12-h mixing process in the acid mixture. Fig. 2d illustrates the SEM image of EHS obtained after HIC was subject to a thermal treatment. It was demonstrated that the EHS had a quite porous and loose structure when compared to the pristine HG and h-BN structures. The distances between the layers of the structures in EHS increased when compared to the pristine HG and h-BN structures. After the production of EHS, it can be asserted that the structure obtained consisted of many micro and nano-sized thick graphene and BN layers. The said situation was also reported in the previous studies [3].

There were still van der Waals bonds between the micro and nano-sized layers in the structure. However, the distance between the layers significantly increased when compared to pristine graphite. This situation could allow the organic solvent atoms to enter between the layers. Placement of atoms of an organic solvent such as DMF between the layers through a sonication treatment caused the breakage of the weak van der Waals bonds between the layers and separated the layers from each other. The sonication treatment applied during the graphene and BNNS production helped the separation of the layers from each other by creating micro-impacts.

Fig. 3 illustrates TEM images of the graphene–BNNS hybrid sheets. As is seen from the figure, exfoliation treatment was successful and the layers were separated from each other. The widths of the layers were over 100 nm. As is seen from the TEM images; even though the layers were overlapped, they were quite transparent and the surface of the grid at the bottom could be easily seen. This situation showed that the layers were quite thin. The layers were overlapped and it was observed that there were contaminations on the layers in some regions. It was estimated that these contaminations mixed with the structure during production. Fig. 3d illustrates the result of the EDX analysis taken over the layers. As is seen from the figure, the presence of both C atoms and B—N atoms on the layers was in question.

In order to examine the surfaces of hybrid nanosheet samples produced by using liquid-phase exfoliation method, the surface images were taken from the samples by using an atomic force microscope (AFM). The produced hybrid nanosheet powders were homogeneously distributed in ethanol and the obtained liquid mixture was distilled on a glass lamina and then dried. Then, the sample was examined in AFM. Fig. 4 illustrates three-dimensional 3D images of the samples. Z-axis height was approximately 2 μm. The average particle sizes of graphene–BNNS hybrid suspension were a few micrometers.

Fig. 5 illustrates FTIR analysis results of pristine hexagonal graphite, pristine hexagonal boron nitride, HIC, EHS, and the hybrid nanosheets produced. As is seen in Fig. 5a, polycrystalline h-BN gave two strong vibrations at approximately 790 cm^{-1} and 1370 cm^{-1}. Pristine hexagonal graphite gave strong vibrations at 1118 cm^{-1}, 1380 cm^{-1}, and 1600 cm^{-1}. The peak at 1600 cm^{-1} was caused by C=C stretching vibrations. The peak at 1380 cm^{-1} was caused by C—OH and the peak at 1100 cm^{-1} was due to C—O. It could be