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Nanoscopic characterization of two-dimensional (2D) boron nitride nanosheets (BNNSs) produced by microfluidization

Hilmi Yurdakul, Yapıncak Göncü, Oya Durukan, Atakan Akay, A. Tuğrul Seyhan *,
Nuran Ay, Servet Turan

Department of Materials Science and Engineering, Anadolu University, Eskisehir TR-26480, Turkey

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Abstract

A microfluidizer high pressure fluid processor is successfully conducted for the first time to exfoliate few layer two dimensional (2D) boron nitride nanosheets (BNNSs) from micro-sized hexagonal boron nitride (h-BN) precursors of large flakes. The mixture of N,N-dimethylformamide and chloroform is conducted as solvent. In determination of to what extent the high pressure microfluidizer successfully assisted with exfoliation of 2D BNNSs from h-BN precursors of large flakes, secondary electron-scanning electron microscopy (SE-SEM) imaging, bright field-transmission electron microscopy (BF-TEM) imaging, energy filtering (EF)TEM-3 window elemental mapping, electron energy loss spectroscopy (EELS), high resolution (HR)TEM imaging and nano beam electron diffraction (NBED) techniques are carried out. Based on the nanoscopic-scale evidences of few layer 2D BNNSs through various TEM techniques, the sheets are observed to have micrometer dimensions in plane whereas nanometer dimensions through their thicknesses depending on the number of layers stacked together. More specifically, the thickness of 2D BNNSs is calculated to be around between 8 and 12 nm using EELS analysis. This value suggests that BNNSs are composed of approximately between 20 and 30 monatomic 2D graphene-like h-BN layers. We are in the opinion that this study has thrown new light on fabricating large scale of 2D BNNSs, which is cited as a highly promising nanomaterial of the future to be utilized in a variety of potential industrial applications including optoelectronic nanodevices, functional polymer composites, support films, hydrogen accumulators and electrically insulating substrates.

Keywords: B. Electron microscopy; B. Spectroscopy; Boron nitride nanosheets (BNNSs); Microfluidization

1. Introduction

Two-dimensional (2D) materials have garnered a remarkable attention since the successful separation of graphene, atomic layers of carbon, demonstrates novel electronic properties [1–5]. Boron nitride (BN) is a structural analog of carbon, having cubic and layered structures [1,2]. BN exhibits high thermal stability, good mechanical strength and has been employed as a solid-state lubricant for years [2]. BN can be exfoliated to form unique 2D crystal structures called boron nitride nanosheets (BNNSs) [3,4]. BNNSs have recently come under the spotlight due to their extraordinary properties [1–5]. In particular, BNNSs are believed to have potential to find applications in optoelectronic devices and heat-releasing composite materials, since they are electrically insulating, besides being as thermally conductive and mechanically robust as graphene [2–5]. However, compared to graphene, the novel physical properties of BNNSs have still remained unrealized, even though they possess superior advantages over graphene [3]. Actually, this is not owing to the fact that the properties of BNNSs are poor or underrated in comparison to the properties of graphene, rather this is mostly by reason of the lack of feasible approaches to producing very thin few or monolayer BN sheets in quantities large enough for practical use in industrial applications [6]. Warner et al. [4] utilized a simple technique based on 3 h sonication to prepare thin few layers of hexagonal BN with micro-sized dimensions using chemical exfoliation in the solvent of 1,2-dichloroethane. Zhi et al. [5] have prepared milligram quantities of BNNSs, conducting a simple two-step process that involves exfoliation of h-BN

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* Corresponding author at: Anadolu University Iki Eylul Campus, Engineering & Architecture Faculty, Materials Science and Engineering Department, 26480 Eskisehir, Turkey. Tel.: +90 222 321 3550x6364; fax: +90 222 323 95 01.
E-mail address: atseyhan@anadolu.edu.tr (A.T. Seyhan).

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powders into nanosheets by sonication in dimethylformamide (DMF), followed by separation of the exfoliated BNNSs by centrifugation. Following 10 h sonication, they obtained around 0.5–1 mg BNNSs from 1 g h-BN powders used as a precursor [5]. They examined then the microstructure of the resultant nanosheets employing scanning and transmission electron microscopes (S/TEMs) [5]. It was determined that the BNNSs obtained by centrifugation at 8000 rpm were of 3 nm thick (<10 atomic layers), while those obtained at 5000 rpm were of up to 7 nm thick [5]. Based on the results obtained, the authors concluded that the average nanosheet thickness is highly dependent on the centrifugation speed in such a manner that the faster the speed, the thinner the resulting sheets becomes [5]. However, neither sonication nor sonication-centrifugation methods, which are very time consuming processes, as above mentioned, are good enough for industrial scale production of BNNSs, although highly beneficial to preparing milligram levels of BNNSs in lab scale. Therefore, currently, more scalable and sophisticated methods are of necessity to unveil and benefit from the extraordinary physical properties of BNNS in industrial applications. It is for this reason that, in this study, high pressure microfludization process is deemed an alternative method capable of high throughput and large-scale production of few layer boron nitride nanosheets. High pressure microfludization process is conducted via high shear fluid processors [7,8]. High shear fluid processors with their continuous processing characteristics are exceptional tools for particle deagglomeration, dispersion and size reduction. Their sophisticated models have been widely used in drug and cosmetic sectors for a couple of years [7,8]. Note that, in the literature no one, but the manufacturer has attempted to consider it a promising tool in materials science and engineering applications, especially related to production of polymeric nano-suspensions [7,8]. Fig. 1 gives the working principle schematic of a microfluidizer processor. Microfluidization processing of multi phase liquids begins once the product enters the system via the inlet reservoir [8]. An intensifier pump that generates extremely high pressures (up to 2069 bar) accelerates the product into the interaction chamber at velocities up to 400 m/s [8]. Within this wide chamber, the product stream separates into micro channels of various geometries as narrow as the cross section of a human hair [8]. The product stream is then forced to collide upon itself, which creates incredible forces of impact and shear which are several orders of magnitude greater than other technologies including homogenizator, sonicator and high-shear mechanical stirrer [8]. In the last part, the finished product is effectively cooled, if required, and collected in the output reservoir [8].

It is worthy of attention that aligning multiple chambers or micro channels in parallel makes it possible to accomplish the consistent results during scale-up. It is capable of completing the chemical exfoliation process within a very short time relative to sonication or sonication-centrifugation methods. Actually, this conjecture encompasses our motivation behind our intention to use this method in order to exfoliate the sheets from micro-sized h-BN. Here, we carried out detailed analytical and structural nanoscopic studies on the BNNSs produced via high pressure microfludization process.

2. Experimental procedure

BNNSs were derived from exfoliation of specially synthesized h-BN micro-sized precursors of very thin large flakes. The proper combination of N,N-dimethylformamide (DMF) and chloroform (6–1 on weight basis) were prepared and conducted as solvent. Hexagonal boron nitride precursors (6 wt.%) were added to the prepared solvent (100 ml). To derive chemically exfoliated BNNSs, high pressure microfludization process was carried out with a commercially available microfluidizer (M-110P, Microfludics Corp.) at a constant intensifier pump pressure of 207 MPa (30,000 psi). Twenty (20) of circulation passes was applied on the dispersions. It takes about 0.6 min for 100 ml solution of h-BN precursors to complete one circulation pass. The yielding efficiency of 45% was observed to derive stable exfoliated sheets from precursor. The solution obtained was dropped on transmission electron microscope grid for examination. A field emission gun-scanning electron microscope (Zeiss Supra 50 VP) was used to characterize precursors of large flakes. The nanoscopic-scale characterization of BNNSs was performed using a field emission transmission electron microscope (Jeol 2100F), operating at 200 kV equipped with an energy filter (Gatan Inc., GIF Tridiem), parallel electron energy loss spectrometer (EELS), a high angle annular dark field scanning transmission electron microscope (HAADF-STEM) detector (Fishione), annular dark/bright field (ADF/BF) detectors (Gatan Inc., STEM Pack) and an energy dispersive X-ray (EDX) spectrometer (Jeol JED-2300T). In EELS and nano beam electron diffraction (NBED) analyses, an electron spot with 1–2 nm in diameter was used. The backgrounds in EELS and

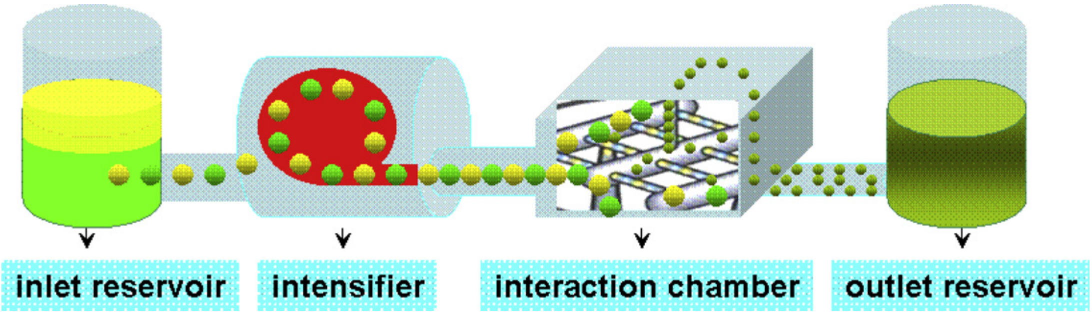

Fig. 1. Working principle schematic of a microfluidizer processor.

energy filtering transmission electron microscopy (EFTEM) analyses were subtracted according to power-law [9]. An approximate thickness of the BNNSs is determined based on the absolute log-ratio method [9]. In EELS analysis, the convergence and collection semi-angles were used as 9.2 and 15.7 mrad, respectively.

3. Results and discussion

In determination of to what extent the high pressure microfluidizer successfully exfoliated BNNSs from h-BN precursors of large flakes, quality and characteristics of h-BN precursors play a pivotal role. Structural characterization of the precursors is of importance in this respect. Fig. 2a–d image series acquired via secondary electron (SE)-SEM imaging, bright field (BF)-TEM imaging, EFTEM-3 window elemental mapping and EELS techniques, respectively, depict the general microstructural characteristics of specially synthesized h-BN precursors. Based on the observations in Fig. 2a and b, it is definitely certain that very thin large flakes with a thickness of around 100 nm constitute the majority of the corresponding micron-sized h-BN precursors. Moreover, the chemical detection of B-K (188 eV) and N-K (401) edges along the flakes evidently confirms that the precursor material is of h-BN (Fig. 2c and d). Fig. 3a and c depicts the low magnification BF-TEM images of the sheets. Generally speaking, because of their exceptional thin shapes, BNNSs are extremely transparent to an electron beam. The region highlighted by arrows in Fig. 3d refers to the region where a number of very few layer sheets of high transparency, only noticeable to a very cautious eye, are stacked on top of one another. Based on the contrast level difference, it is absolutely definite that thin sheets in the lined square (Fig. 3a and c) are transparent relative to the sheets of multi-stacked layers. For the sake of reliability, this finding was also confirmed with the additional BF-TEM and BF-STEM images taken from the different regions of the same sample, as shown respectively in Figs. 4a–d and 5a and b. Considering the observations here (Figs. 4a–d and 5a and b), the 2D BNNSs highlighted by arrows can be clearly discerned from among the h-BN large flakes. On the other hand, it is worth noting that microstructural characteristic of the BNNSs obtained in this study was highly similar to that of BNNSs obtained in the former studies via either ultrasonication or sonication-centrifugation [4–6]. From this point of view, it can be concluded that high pressure microfluidization process is at least as capable as sonication or sonication centrifugation processes to exfoliate BNNSs from the micro-sized h-BN precursors of large flakes, in addition to having a yielding efficiency no less than yielding efficiency of these two methods as well. More interestingly, traces of moiré fringe are found exceptionally distinguishable

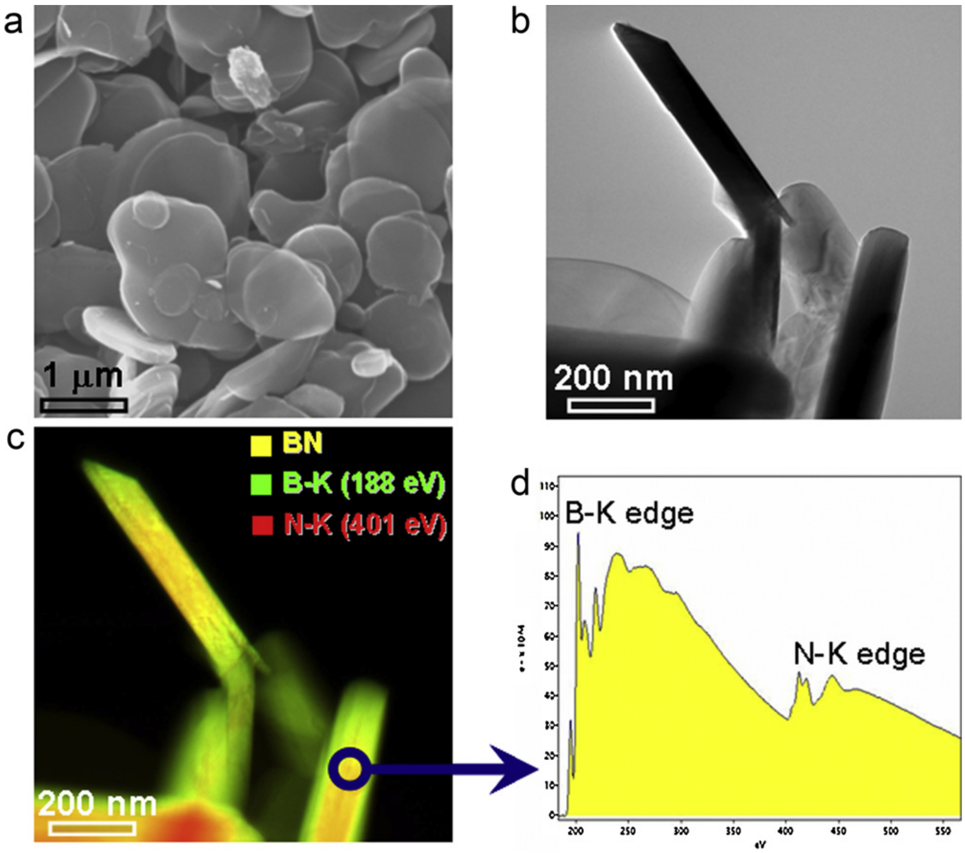

Fig. 2. (a) Secondary electron (SE)-SEM image, (b) BF-TEM image, (c) Red-Green-Blue (RGB) EFTEM-3 window elemental mapping and (d) electron energy loss (EEL) spectrum of specially synthesized micro-sized h-BN precursors of very thin large flakes. Please also note that the circular point on the vertically positioned BN flake in (c) shows the corresponding locations from which EEL spectrum in (d) was taken. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

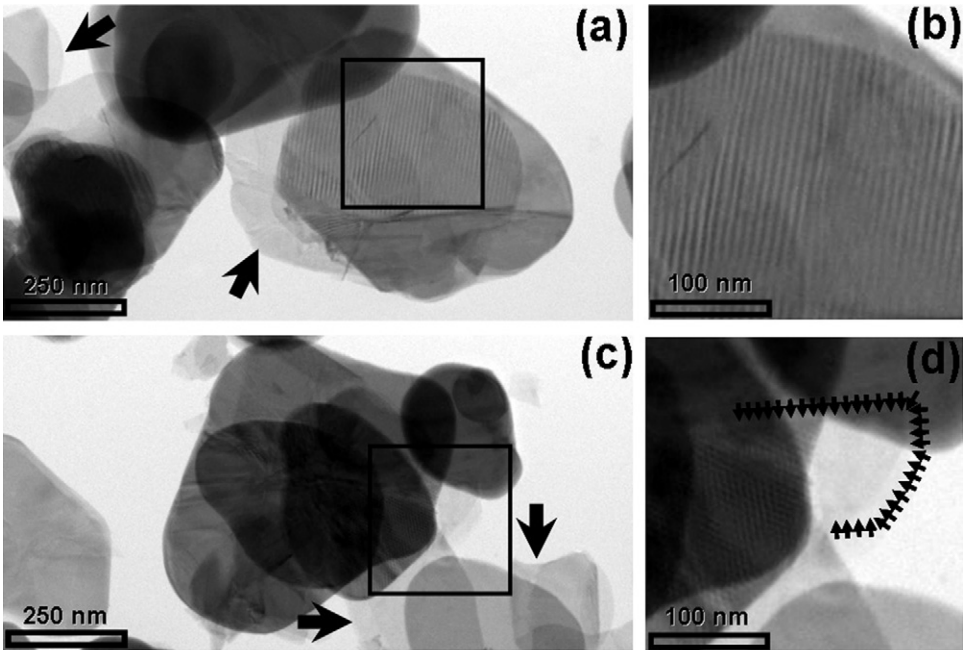

Fig. 3. (a and c) Low magnification BF-TEM images of exfoliated BNNSs obtained by high pressure microfludization process. Relatively transparent regions indicated by arrows refer to few layers boron nitride nanosheets. (b and d) Relatively high magnification BF-TEM images of the regions in lined square in the BF-TEM images in (a and c). Please note that the region highlighted by a number of arrows in (d) corresponds to a particular spot where very few layers boron nitride nanosheets of high transparency are stacked on top of one another.

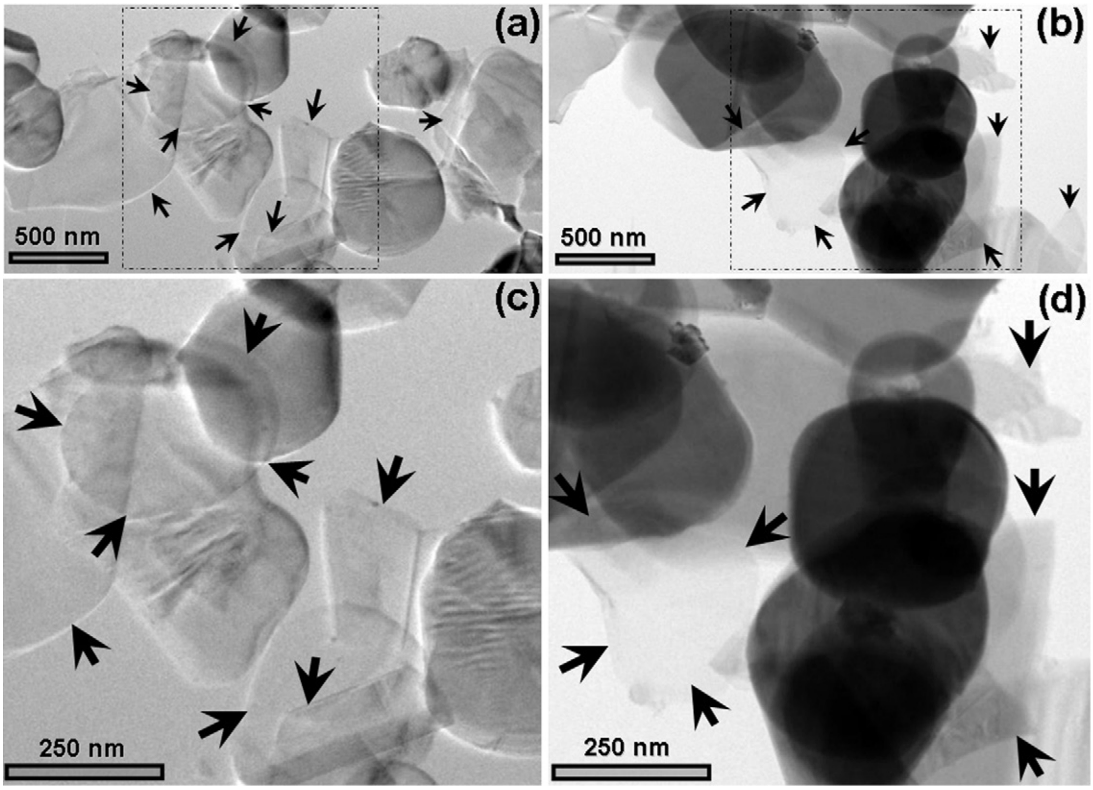

Fig. 4. (a and b) Low magnification BF-TEM images of exfoliated BNNSs obtained by high pressure microfludization process. Relatively transparent regions indicated by arrows refer to few layers boron nitride nanosheets (BNNSs). (c and d) Relatively high magnification BF-TEM images of the regions in black dash lined squares in the BF-TEM images in (a and b).

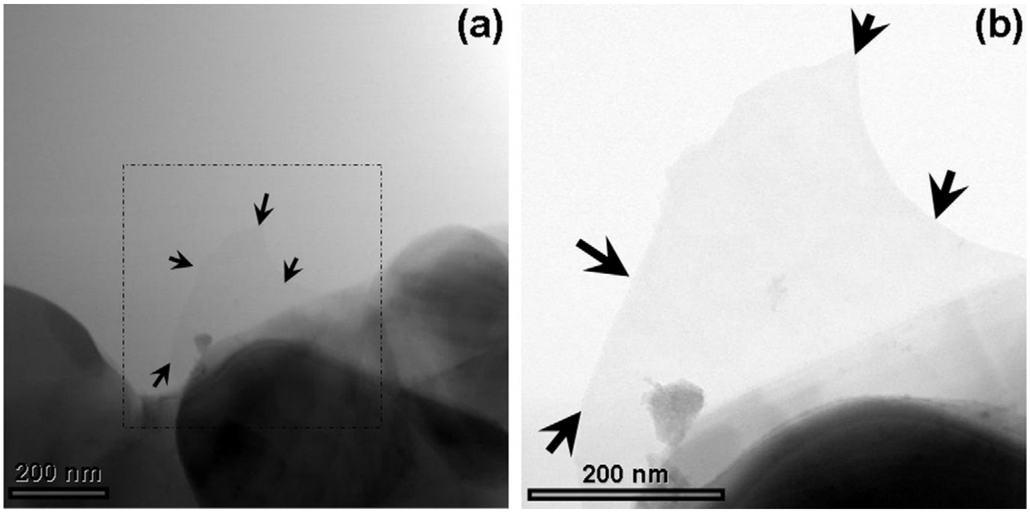

Fig. 5. (a) Low magnification BF-scanning (S)TEM image of exfoliated BNNSs obtained by high pressure microfludization process. Relatively transparent region indicated by arrows refer to few layers boron nitride nanosheets (BNNSs). (b) Relatively high magnification BF-STEM image of the region in black dash lined square in the BF-STEM image in Fig. 4a.

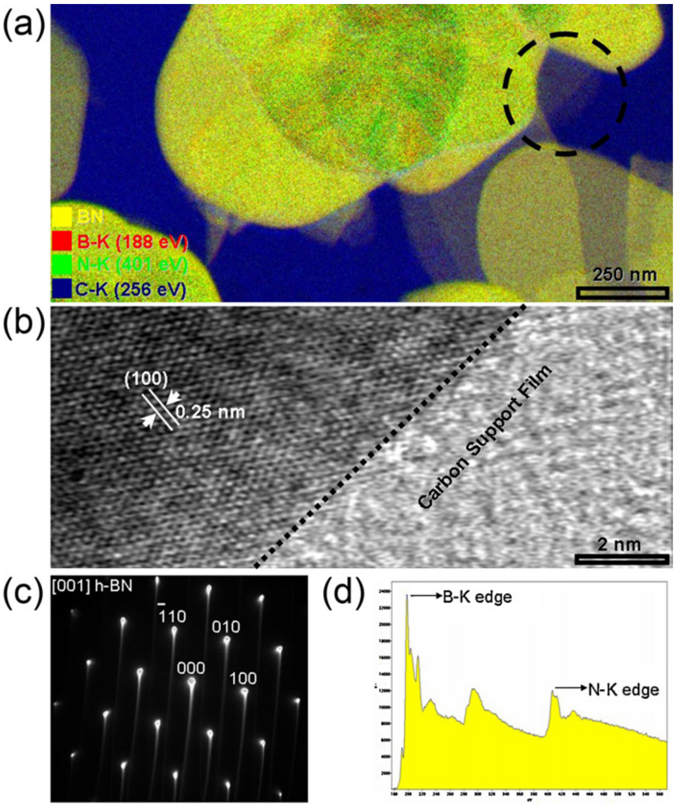

Fig. 6. (a) EFTEM-3 window elemental mapping image shown on a RGB (Red-Green-Blue) composite map obtained from B-K (188 eV), C-K (284 eV) and N-K (401 eV) edges. (b) HRTEM image obtained from the region of the circular dashed line in Fig. 4a. (c) NBED pattern of the same region of interest in Fig. 4a and its corresponding (d) EEL spectrum. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

over the surface of the sheets, as seen in the region of lined square in the low magnification BF-TEM images (Fig. 3a and c). Note that moiré fringe become more recognizable at relatively high magnification of the same region, as shown in Fig. 3b and d. Nevertheless, they tend to gradually appear, as the number of thin individual layers in BN sheets increases. This can be considered ample evidence that individual sheets of high transparency, when stacked together, constitute the multi-layers of semi-opaque sheets of relatively high contrast level. In other words, it implies that the more moiré fringes become visible over the sheet surfaces at low magnification, the higher number of layers in BN sheets are stacked one by another. However, to decide whether or not to utilize a high pressure microfluidizer makes a significant contribution towards to producing very few layer BNNSs requires further nanoscopic TEM examination of the sheets obtained. Fig. 6a–d shows, respectively, RGB (Red-Green-Blue) composite EFTEM-3 window elemental mapping, high resolution (HR)-TEM, NBED pattern and EELS findings obtained from the region of lined square in Fig. 3c.

In the light of the findings in the RGB composite EFTEM-3 window elemental mapping (Fig. 6a), the inelastic scattering electrons collected from the B-K (188 eV) and N-K (401 eV) edges were concluded to suggest that BNNSs are attached onto the surface of carbon support film. More specifically, in consistency with our previous statement, the region of a circular dashed line in Fig. 6a hosts, most probably, the sheets of ghostlike transparency which are only barely discernible via the naked eye, as seen in low and high magnification BF-TEM images given in Fig. 3c and d. Moreover, based on the distance between two adjacent planes, the fringe separation on the HRTEM image acquired from the same region of interest in Fig. 6a was observed to be about 0.25 nm, which corresponds to the lattice constant of h-BN in (1 0 0) plane. This observation is similar to the observations reported in the former studies [5,10]. In addition, NBED pattern viewing the low index zone axis along the [0 0 1] direction of ghostlike transparent BNNSs positioned in a circular dashed line in Fig. 6a, implies six fold symmetry characteristics of h-BN [5,10]. Apart from this, EEL spectrum (Fig. 6d) collected from the same region of interest in Fig. 6a shows two separate peaks at 188 eV and 401 eV which correspond to B-K and N-K ionization edges, respectively. When analyzed in terms of their shape and positions in the spectrum (Fig. 6d), these two characteristic peaks verify that BNNSs of ghostlike transparency located in the circular dashed line region in Fig. 6a are of h-BN [11,12]. In the same spectrum, another peak that falls between the B-K and N-K edges is apparent at 284 eV and corresponds to C-K edge. As examined more carefully once again, BNNSs can be observed lying on the surface of the carbon support film in Fig. 3c and d, as well as visible in Fig. 6a. This can be the reason as to why the signals obtained from the sheets in image-coupled mode are accompanied by ionization of the C-K shell [9]. Note that even though it seems unexpected situation at a first glance, this piece of information holds, in fact, a clue to predicting the thickness and the number of the sheets positioned in the studied region of interest. In the former studies [10,12], sheet thickness evaluation was carried out using SEM and atomic force microscopy (AFM). However, it is very well known that the thickness of any nano-structured materials can be experimentally computed via EELS analysis [9]. From this standpoint, using EELS as a distinctly different novel approach in this study, the thickness of ghostlike transparent BNNSs positioned in the region of circular dashed line (Fig. 6a) was estimated to be 12 ± 0.2 nm. This value suggests that BNNSs under focus are composed of approximately 30 monatomic h-BN layers. Please note that similar thickness measurements were also performed on the sheets positioned in the region of interest shown in Fig. 5a and b, and the comparable results were obtained, as demonstrated in Fig. 7a and b. According to this, the thickness of the BNNSs depicted in Fig. 5a and b was calculated as 8 ± 0.2 nm that approximately corresponds to 20 monatomic h-BN layers. Moreover, the thickness values of the sheets observed in this study was found highly similar to the thickness of the sheets obtained in the former studies [5,10], which shows that high pressure microfluidization is an efficient method to separate micro-sized h-BN into individual sheets within a short intended time relative to sonication or sonication-centrifugation methods.

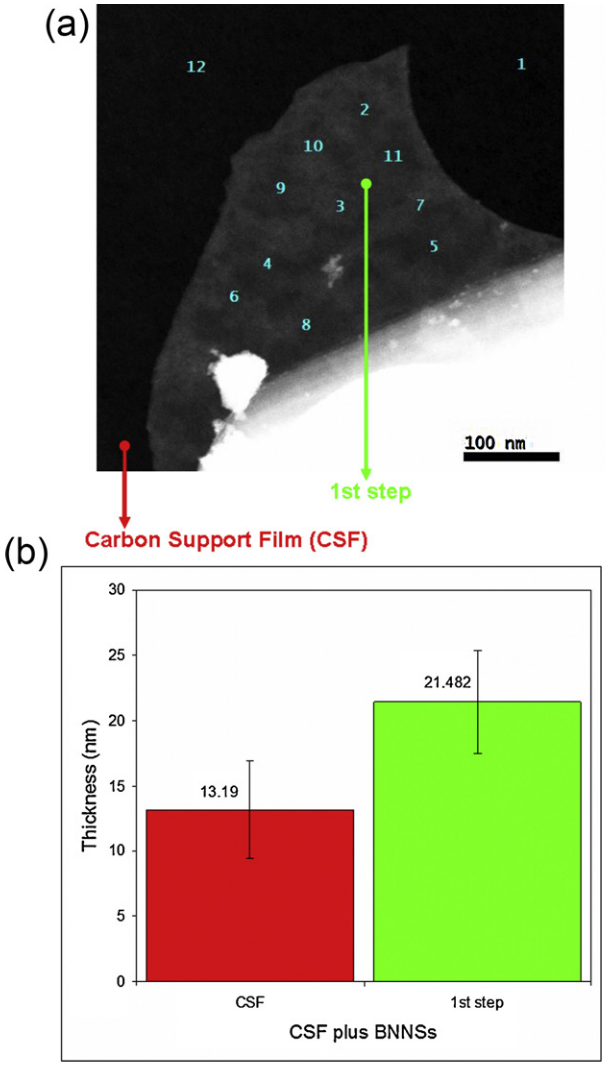

Fig. 7. (a) High angle annular dark filed (HAADF)-STEM image of exfoliated BNNSs obtained by high pressure microfludization process. Please note that the numbers on the HAADF-STEM image shows where the EEL spectra used in the thickness measurements of BNNSs were acquired from. Also, all the EELS analyses are performed in the STEM mode with the 1–2 nm diameter focused electron probe, (b) the thickness values of the carbon support film (CSF) and 1st step. Here, the thickness of the 1st step is comprised of the sum of the CSF and BNNSs thicknesses. Therefore, the thickness of BNNSs existing in the 1st step can be calculated as; T_{BNNSs} (existing in the 1st step) = $T_{\mathrm{1st\ step}} - T_{\mathrm{CSF}}$ = 21.482 − 13.190 = 8 ± 0.2 nm.

4. Conclusions

We consider a highly competent and robust method called high pressure microfludization for large scale production of thin few layer boron nitride nano sheets (BNNSs), as a promising alternative to ultrasonication and sonication-centrifugation methods, recently reported in the literature [4–6]. BNNSs were derived from micro-sized hexagonal boron nitride of very thin large flakes using chemical exfoliation in the proper solvent combination of N,N-dimethylformamide (DMF) and chloroform. High pressure microfludization process is superior over sonication-centrifugation process in that it offers one to produce in gram levels of BNNSs within short intended time compared to sonication or sonication centrifugation methods. It also promises one to control and adjust the average sheet thickness, depending on the number of cycles to which the solution of precursors is subjected. Based on the nanoscopic-scale evidences of few layer 2D BNNSs through various transmission electron microscopy techniques, the sheets were observed to have micrometer dimensions in plane whereas nanometer dimensions through their thicknesses depending on the number of layers stacked together. More specifically, the thickness of 2D BNNSs is calculated to be around between 8 and 12 nm using EELS analysis. This value suggests that BNNSs are composed of approximately between 20 and 30 monatomic 2D graphene-like h-BN layers. We believe that this study has thrown new light on fabricating large scale of BNNSs, which is cited as a highly promising nanomaterial of the future to be utilized in a variety of potential industrial applications including optoelectronic nano-devices, functional polymer composites [13], support films [14], hydrogen accumulators and electrically insulating substrates.

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