



Mechanical pressure induced chemical cutting of boron nitride sheets into boron nitride quantum dots and optical properties



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ABSTRACT

The ability to exfoliate 2D hexagonal boron nitride nanosheets (h-BNNSs) into nano-sized layered particles to form the boron nitride quantum dots (BNQDs) has been discussed by mechanical pressure through high intensity sonication. The top-down, simple and efficient synthesis approach has been applied for synthesis of BNQDs directly from bulk h-BN powder by high intensity sonication processes. The time dependent high intensity sonication shows the thinning of BNNSs or delaminated BNNSs are broken into nano-size in form of BNQDs. Higher ultrasonication time duration reduce the number of h-BN layers from h-BNNSs and produce the physical defects on the surface and finally transform into BNQDs. To evaluate the structural analysis and properties of BNQDs were employed by XRD, HRTEM, EDX, XPS, AFM and PL techniques. The average and uniform size of BNQDs observed from TEM analysis were 3–6 nm and containing an average thickness of 3–12 atomic BN layers. Raman spectroscopy confirms the formation of few layered BNQDs nanostructure from bulk h-BN powder by indicating the weak and small E_{2g} phonon mode (1365 cm^{-1}). The photoluminescence (PL) measurements carried out of BNQDs show typical luminescence spectra and strong peak emission at 448 nm.

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1. Introduction

Beside well known graphene, inorganic graphene analogues such as boron nitride (BN) have attracted much attention in the past few years. The BN nanosheets (BNNSs), so-called 'white graphene', are an important category of inorganic layered materials consisting of a few layers hexagonal BN (h-BN) planes [1,2]. The h-BNNSs have attracted increasing interest due to its peculiar, unique and fascinating properties compared with graphene, such as wide energy band gap, better dielectric performance, electrical insulation, high thermal conductivity and stable performance, high resistance to oxidation, chemical inertness, and ultraviolet photoluminescence [3–12]. For the synthesis of individual h-BNNSs, bulk h-BN powder material can be mechanically exfoliate by intercalation reactions which is the first step in exfoliation process [13]. The

quantum dots (QDs) i.e BNQDs properties can be tuned like graphene quantum dots (GQDs) and shows synergetic effect with size, shape, edge, and number of layers, which encourage the higher demand in research applications [14–16]. In order to utilize such BNQDs, it is essential to develop an efficient simple method for large-scale synthesis of high quality BNQDs composing of controllable dimensions.

Now a days different research groups have synthesized BNQDs from h-BNNSs using top-down approach. Since top-down approaches can be accomplished under different environmental conditions. In this approach, the BNNSs can be broke mechanically into nano-sized BNQDs similar to the case of graphene QDs (GQDs) from hexagonal graphite [17–21]. Numerous workers examined the use of high intensity sonication process to reduce the particle size and increase the specific surface area for different types of QDs. Recent research activities confirmed the capability of high intensity sonication technique for the synthesis and production of metal oxide/semiconducting QDs or nanoparticles [22–29]. In case of 2D layered materials such as h-BNNSs, high intensity sonication technique can be used to apply mechanical pressure around BNNSs

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and break it into BNQDs. Only a few approaches to obtain BNQDs have been reported by applying mechanical pressure [14–16,30].

Recently, some research groups have applied high intensity sonication technique in different liquid solution medium to exfoliate and crack the BNNs to obtain BNQDs. They have shown that BNQDs can be obtained by sonication BNNs in certain liquids. Stengl et al. [14] synthesized self-assembled BNQDs mechanically by applying high intensity sonication on BNNs. Also, Lin et al. [15] synthesized thin BNQDs by chemically insertion of potassium ions into BNNs and after that used ultra-sonication technique to break the intercalated BNNs. Most recently in 2015 another research group reported the fabrication of facile and controllable sized BNQDs mainly through sonication process including solvothermal and freeze-drying. Li et al. [16] fabricated controlled size BNQDs using sonication-assisted liquid exfoliation involving solvothermal process. Lei et al. [30] used two step synthesis process; sonication and solvothermal treatment and finally freeze-drying to remove the excessive solvent. In these synthesis routes along with ultra-sonication in different liquid medium, there is a need of additional process for obtaining the final BNQDs. Extensive efforts have been made to improve the yield and degree of exfoliation, however the yield of BNQDs remains relatively low and requires long lasting sonication treatments. Also, BNQDs synthesized to date suffers from major drawbacks such as the involvement of the multi-step, complex and laborious process. Also, it is still a challenge to controllably synthesize high-quality BNQDs with uniform size.

Herein, we report a facile, scalable and single-step effective synthesis route to fabricate BNQDs through top-down approach employing high intensity sonication in liquid-phase simultaneously implying exfoliation and etching of BNNs in Brønsted acid H_3PO_4 liquid medium. The liquid-phase exfoliation methods are fetching more and more interest since they are extremely versatile, potentially up-scalable. The etching and thinning of BNNs through high intensity sonication mainly depends upon the applied sonication intensity and the time duration. In addition, the strategy presented here provides a new reference for the controllable and single step synthesis of BNQDs without any metal intercalation. First the thick BNNs is transformed into thin BNNs and finally these thin BNNs breaks and get converted into BNQDs by high intensity sonication. High intensity sonication is proved to be a very useful technique that allowed stronger reduction in the BNQDs size while maintaining the structure relative to common grinding methods.

2. Experimental details

2.1. Synthesis of BNQDs from BNNs

Bulk h-BN powder with lateral particle sizes in the range of 10–15 μm flakes were ultra sonicated in H_3PO_4 acid using a high intensity (Sonics and Materials) ultrasonic titanium-tipped disruptor horn (1.3 cm diameter) operating at 750 W output and with a 20 kHz converter. The tip of the horn was lowered into a cylindrical glass tube (4 cm diameter) containing 2 g of bulk h-BN powder immersed in 150 mL of Brønsted H_3PO_4 acid. After high intensity sonication the as-obtained solution was washed several times with deionized (DI) water to remove acid contents. The washing process was repeated till the suspensions showed a pH of 7.0. After that, the acid free solution was centrifuged at 2000 rpm for 20 min in order to separate large-size and small sized BN nanoparticles. The small sized BN particles float in DI water and the larger sized BN particles get settled in the bottom of the vials. Further characterization shows that the settled BN nanoparticle in bottom are thinned few layers BNNs, however floated small sized BN nanoparticles have the BNQDs nanostructure.

2.2. Characterization

The microstructural analysis and morphology of the as-synthesized BNNs and BNQDs were analyzed using X-ray diffraction (XRD, D/MAX-2500/PC; Rigaku Co., Tokyo, Japan), and transmission electron microscope (TEM, FEI Tecnai G20, FEI Company, USA). The elemental compositions and vibration E_{2g} mode of the synthesized nanostructures were analyzed using an X-ray photoelectron spectroscopy (XPS, Axis Ultra, Kratos Analytical Ltd, England) and Raman spectroscopy (Renishaw, model no. H 4517, Ar laser $\lambda = 514$ nm), respectively. AFM images of BNQDs were taken with tapping mode after dispersing the samples on a cleaned surface of SiO_2 substrate by spin coating. Before spin coating, BNQDs solution was prepared by the sonication of the BNQDs powder in DMF solution. While performing AFM measurements on BNQDs on SiO_2 substrates, special care has been taken to obtain more precise height profile data. All photoluminescence measurements of the BNQDs samples were recorded at room temperature using PL, Shimadzu RF-5301PC spectrofluoro-photometer.

3. Results and discussions

During the high intensity sonication process, the bulk h-BN powder gets converted into few layer BNNs and after its breaks into nano-sized BNNs and finally transforms into BNQDs. The thinning, exfoliation and breaking of few layers BNNs is responsible for the formation of BNQDs at high intensity sonication. The morphology of the product obtained from thinning by high intensity sonication procedure has been studied by TEM and high resolution TEM (HRTEM), which reveals that the 2D BNNs formed have inhomogeneous thinning. The TEM micrographs in Fig. 1a shows the inhomogeneous contrast variation in BNNs which confirm the improper thinning and variation in number of layers in BNNs. The BNNs with different layers show different contrast variation as thick BNNs shows dark contrast and thin BNNs appeared as bright. The intensity of dark contrast decreases towards the edges of thin BNNs.

The bright contrasts towards the edges are nearly transparent with dimensions of up to several nano meters [31,32]. It contains few layers to many layer BNNs and local thinning is due to the transformation of BNNs into BNQDs. This thinning of layers has been also confirmed by HRTEM micrographs. The HRTEM images (Fig. 1b, c and d) have been taken from Fig. 1a at different thinning zones. Fig. 1b reveals that the local portion of Fig. 1a has thick BNNs, which contains higher number of BN layers. However, in Fig. 1c and d, the number of BN layers is less as compared to Fig. 1b. Also we can clearly see that the number of BNNs decreases towards edges (Fig. 1c). This evidence shows that thin BNNs are nearly transparent with dimensions of up to several nano meters. In nearly transparent region of BNNs, there are some thick spots which show non uniform thinning of BNNs (Fig. 1d). Fig. 1d shows the BNNs stacking (marked by arrows) from edges to inner BNNs which shows the overlapping of them on each other and it is due to the increase of number of BN layers in BNNs. The edge portion shows the few layers BN sheets however the inner side reveals the multi-layers BN sheets.

Fig. 2 shows the magnified view of thin BNNs taken from edge side of Fig. 1d which reveals that the thickness of BNNs clearly terminated at the edges due to decrease of the BN layers in BNNs (as marked by dotted arrows) and contains minimum number of BN layers at edges. Also, it can be seen that from edge to inner side planes, the number of BN layers continuously increases.

Edge side of Fig. 2 shows the minimum number of BN layers, however the inside portions shows the overlapping of BN layers forming multi-layered BN structure. Edge side have lattice fringe of

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