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Boron Nitride Nanosheets: novel Syntheses and Applications in polymeric Composites

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Abstract. Two-dimensional (2D) boron nitride (BN) nanosheets, the rising material stars, have unique properties and amazing functionalities. The concise history of diverse synthesis routes of BN nanosheets is briefly summarized here; and the recent development towards mass production of BN nanosheets, i.e. “chemical blowing” technique relying on blowing molten polymer precursors into large polymeric bubbles and subsequent annealing into BN bubbles/nanosheets, is focused on. The abundant BN nanosheets enable their applications, especially in the representative polymeric composites with BN nanosheet additives, as particularly highlighted in this review. The highly thermoconductive insulating BN-filled composites are thus envisaged as high-performance packaging materials for electrical circuits.

Key words: boron nitride, nanosheet, chemical blowing, polymeric composite

1. Introduction

BN nanosheets are (002) mono-/few-layered hexagonal BN (\(h\)-BN). They are the structural analogues of graphenes (Figure 1). \(h\)-BN is a compound with equal numbers of boron and nitrogen atoms, which is widely used in skincare products, insulators, solid lubricants, pencil leads, etc.

BN nanosheets possess unique properties. The BN crystal lattices, similar to graphene, together with a stronger B-N bonding result in superior characteristics in mechanics and thermal applications. The bending elastic modulus of BN nanosheets is hundreds of GPa [1]. The thermal conductivity of BN layers is 1700-2000 W/mK [2]. The thermal and chemical stability of BN is better than that of
graphene [3]. On the other hand, there is a significant charge transfer from B to N atoms, so partially ionic $sp^2$-hybridized B-N bonds determine notably different properties from graphenes in optics and electronics, e.g. BN is white in color and has a large bandgap of 5.5 eV, while graphene is black and conductive.

As a result of the unusual structures and properties, BN nanosheets exhibit diverse functionalities. BN nanosheets are intrinsic insulators valuable for dielectric applications, e.g. as a dielectric gate layer [4,5] and as a deep ultraviolet luminescent agent [6,7]. The dielectric properties of BN (dielectric constant 3-4; breakdown voltage $ca. 700$ MV/m) are comparable to SiO$_2$, allowing its usage as an alternative dielectric gate in current electronics with no loss of functionality. They are also able to enhance the carrier mobility [8] and to open the bandgap of graphenes put on them [9,10], so they are envisaged as the perfect “sidekick” of graphene in the next-generation electronics. BN nanosheets show the tunable bandgap through tailoring their edge structures [11]. Besides, the weak bonding out of planes is advantageous for excellent solid-state lubricants [12]. In addition, BN nanosheets are applied in the nanomedical field due to their good biocompatibility, and in scanning probe microscopy as ultrathin and stiff tips [13]. They are also applied for filling polymeric or ceramic composites to achieve extraordinary thermal and mechanical performances.

Figure 1. Mono- and double-layered BN nanosheets.

2. Diverse Syntheses of BN Nanosheets
Prior to the discovery of free-standing $h$-BN monolayers, mono-layered BN was epitaxially deposited and studied on the surfaces of transition metals, such as Ni, Pd, Ru and Pt in 1995-2004 [14,15]. A free-standing $h$-BN monolayer was firstly found in the mechanically milled residue in 2005 following the rise of graphene [16]. It is also called as “white graphene” corresponding to a bulk $h$-BN precursor which is named as “white graphite”.

So far, BN nanosheets have successfully been fabricated via diverse methods including (see Figure 2): mechanical cleavage [17], ball milling [18], high-energy electron beam irradiation [19] and the reaction of boric acid and urea [20,21]. Ultrasonic vibration has also been available to separate the layers of bulk BN; this is used by a liquid exfoliation method. We produced ultra-thin BN nanosheets at the level of dozens of milligrams through an efficient sonication of BN precursors in a polar organic solvent of dimethylformamide [24], in which the newborn BN layers are stabilized by the solvent to prevent the reversible re-stacking [22-24]. Chemical vapor deposition (CVD) is an effective route to synthesize large-area BN nanosheets [25-28]. In 2011, a facile thermal CVD technique was developed by us to fabricate vertically-aligned BN nanosheets using cheap B, MgO and FeO precursors [29,30].
Figure 2. (a) High-resolution transmission electron microscopy (HRTEM) image of BN nanosheets with a thickness of 1.2 nm derived from liquid exfoliation method. Reprinted with permission from [24]. © 2009 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. (b,c) HRTEM image images of BN with two/three atomic layers from the CVD method. The inset is the corresponding selected area electron diffraction (SAED). Reprinted with permission from [25]. © 2010 American Chemical Society. (d,e) Scanning electron microscopy (SEM) images of the BN nanosheets synthesized at 1100 and 1200°C respectively in CVD. Reprinted with permission from [29]. © 2011 American Chemical Society.

A smart technique of unwrapping multiwalled BN nanotubes through delicate Ar plasma etching was developed by us in 2010 to synthesize few- and mono-layered BN nanosheets (Figure 3). The typical intermediate states of the etched nanotubes were observed to confirm the unwrapping mechanism. The narrow nanosheets, i.e., nanoribbons terminated with N-terminated zigzag edges and vacancy defects, exhibited fantastic semiconducting properties [11]. The high conductivity of 104 S/m and carrier mobility of 58.8 cm²/Vs were measured in such BN nanoribbons without a gate bias. First-principles calculations verified that the edge states and dangling bond states located in the zigzag edges and experimentally observed surface vacancies had been the driving sources for the semiconducting transport of BN nanoribbons, as opposed to insulating primal BN nanotubes. This study paves the way for BN nanoribbon production and usage as functional semiconductors with a wide range of fundamental issues and applications in electronics and spintronics.
Figure 3. (a) Schematic of the unwrapping processes induced by plasma etching, the stepwise opening/unzipping, removing and exfoliating of tube walls to form BN nanoribbons. (b,c) HRTEM image of a double-layered BN nanoribbon with zigzag edge structure via nanotube unwrapping. (d) Electrical transport tests of several BN nanoribbons comparing with an insulating BN nanotube. Reprinted with permission from [11]. © 2010 American Chemical Society.

3. “Chemical Blowing” Synthesis for BN Nanosheets
Although many methods have been utilized to synthesize BN nanosheets, it is still a challenge to prepare BN nanosheets with a high throughput. The chemical exfoliations of graphites have realized the tons-level production of reduced graphene oxide. Unfortunately it is difficult to chemically intercalate the partially ionic BN layers because of the weaker inter-layer exchange repulsion and stronger inter-layer attraction [31]. The lack of effective mass production of BN nanosheets has hindered their relative developments. Recently, we developed a new strategy, so-called “chemical blowing” [32,33], which relies on making large bubbles with atomically thin B-N-H polymer walls starting from ammonia borane (AB) compound as a precursor (Figure 4). AB is a nontoxic, environmentally benign and stable material, which is usually used as an effective source of hydrogen [34,35]. In addition, since the cost of AB is currently decreasing, it is particularly worth utilizing this “chemical blowing” process to produce BN nanosheets with a low cost, and to finally realize their rich nanotechnology potentials. The “chemical blowing” was conducted through pre-treating AB at a low temperature followed by a controllable heating to designated temperature for dehydrogenation and chemical blowing of bubbles. The B-N-H polymer bubbles were finally annealed into BN ones at a high temperature. The BN bubbles are composed of ultra-thin BN walls, which were then crushed and converted into the BN nanosheets. This process is featured by the bubbles blown by a chemically released gas, which is thus named as “chemical blowing”.
The products derived from “chemical blowing” are very light, with a density of 6 mg/cm³, corresponding to a high porosity of 99.7 % (Figure 5). They have perfect B and N stoichiometry as confirmed by electron energy loss spectroscopy, except minor oxygen impurity related to B-O phases. Individual BN nanosheets have large lateral dimensions, tens of micrometers, normally larger than those obtained using liquid-exfoliation methods. BN nanosheets are uniform over a large area, and they are large enough for further assembling into electronic devices. The thickness of BN nanosheets typically ranges from 1 to 5 nm, although a few of nanosheets thicker than 5 nm may also be found. These numbers are rather small and lead to unique characters and properties as derived from the quantum effect. Few-layered nanosheets, made of as 2, 3 and 5 layers, have been demonstrated here. The layer-to-layer spacing decreases with an increase of the number of layers. It is 0.38 nm for 2-layered nanosheets, while only 0.34 nm for a 7-layered nanosheet. This change can be understood through increased inter-layer interaction with increasing number of layers. All the layer-to-layer spacing is slightly larger than those in bulk layered BN due to the relaxation of surface atoms.

The BN nanosheets obtained from “chemical blowing” are polycrystalline structures of $h$-BN with an ordered honeycomb-like hexagonal lattice, as visualized in Figure 6. The lattice distance is 0.258 nm corresponding to the B-B or N-N atom separations in $h$-BN. The locally-ordered polycrystalline structure of nanosheets is further verified by a fast-Fourier-transform (FFT) pattern over an area of hundreds of nm². The $h$-BN nanosheets have a strong (002) diffraction peak with a $d$ value of 0.35 nm. Its broadening corresponds to the effect of downsized dimensions of ca. 3 nm. The $h$-BN nanosheets demonstrate the strong ultraviolet luminescence at 210 nm attributed to the intrinsic optical bandgap. As-grown BN products possess large specific surface area, 140 m²/g, which is larger than 50 m²/g of porous BN, or 27 m²/g of BN nanoparticles [36]. Although it is still smaller than the theoretical value for mono-layered sheets (2600 m²/g) owing to the overlapping and re-stacking of nanosheets, it is noticed that there is no contribution from micropores in our case. This configuration is very beneficial to create more interfaces between BN and polymer molecules, because the too small pores can not be accessed by polymer molecules to create links and effective BN-polymer interactions in the fabrication of BN-based polymeric composites.
Figure 5. (a,b) Optical images of as-grown snow-white BN products and an individual ultra-thin BN nanosheet transferred on a Si substrate. (c) Atomic force microscopy (AFM) image of a BN nanosheet with the thickness of 2 nm, as pointed out by a cross-sectional profile marked in the inset. (d,e) High- and low-magnification images of a 3-4 layer BN nanosheet. (f-h) HRTEM images of two, three and four-to-five atomic-layers BN nanosheets. Reprinted with permission from [32]. © 2011 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

Figure 6. (a) HRTEM image of a 2-layered BN nanosheet showing polycrystalline structure. (b) Reconstructed reverse FFT image from the corresponding red framed area. (c) The FFT pattern taken from the area of 900 nm². (d) SAED image of a BN nanosheet taken from the area of 0.05 µm². (e) XRD profile of BN products confirming a hexagonal structure of the space group 194. Reprinted with permission from [32]. © 2011 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.
The high-yield production of BN nanosheets with large lateral dimensions was optimized at a heating rate of 8°C/min following a pre-treatment under atmospheric pressure under “chemical blowing”. The yield is as high as 40 wt.% with respect to AB. The “chemical blowing” thus realizes the mass production of atomically-thin (one-to-few atomic layers) free-standing BN nanosheets, which significantly prevails over the yields achievable during CVD and liquid exfoliation.

4. Polymeric Composites based on chemically blown BN Nanosheets

Comparing with 0D nanoparticles and 1D nanofibers/tubes, 2D BN nanosheet fillers can maximally expose their basal (002) crystal planes and show fast electron and phonon transport and effective force transfer in the composites. Therefore, BN nanosheets are excellent additives for polymeric composites to enhance thermal and mechanical properties.

The insulating thermoconductive polymeric composite is an advanced packaging material for quick heat-releasing and good electrical insulation in the high-speed electronics [37]. However, the traditional fillers such as AlN and Al₂O₃ powders reveal a relatively low thermal conductivity [38]. BN nanosheets are one of the best fillers to realize both high thermal conductivity and perfect insulating properties of the composites. Besides, BN can also deliver the high mechanical strength, high thermal and chemical stability. Unfortunately, research on BN-nanosheet-filled composites was rather limited due to the low-scale production and high cost of BN nanosheets. Recently, gram-level BN nanosheets have been fabricated in our laboratory under the “chemical blowing” route, which enables their utilization in polymeric composites (Figure 7).

The composites of BN/polymethyl methacrylate (PMMA) show decreased transparency with the increased filling fraction of BN nanosheets. The elastic modulus increases by 17%, whereas the yield strength increases by 32%, for a composite with 6 wt.% BN loading fraction. The mechanical reinforcement effect results from the effective transfer of external mechanical load to BN nanosheets due to the profound interfacial interactions between BN and PMMA.

The BN/PMMA composites show the improved thermal stability along with increasing a BN fraction. The two-step degradation of PMMA includes unzipping vinylidene end groups and further random scission of polymer links [39]. The surface groups of BN such as oxidative B-OH may react with the polymer end radicals. This reaction can suppress the unzipping of the polymer chain and then stabilize the composite system [40]. This interfacial stabilizing effect was amplified for the large specific surface area of BN fillers, so the onset degradation temperatures of BN/PMMA composites are much higher than that of blank PMMA. Also, the composites can withstand higher temperatures than a blank PMMA due to such stabilization provided by BN nanosheets. In a quantitative analysis, the glass transition temperature clearly increases along with an increase in the BN filling fraction. It increases from 92°C for blank PMMA to 105°C for 15 wt.% BN/PMMA, and to 110°C for 23 wt.% BN/PMMA. This indicates that the thermal mobility of polymer chains is suppressed by the strong and confined BN-PMMA interfacial interactions. The confined PMMA chains exhibit slower dynamics and thus promote an increase in glass transition temperature.

The BN/PMMA composites also demonstrate remarkable thermal conductivity. The highest thermal conductivity is 2.6 W/mK for 23 wt.% BN/PMMA. It is a 17-fold increase compared with the blank PMMA. The large lateral dimensions of the BN nanosheets result in an easily constructed thermoconductive pathway, which determines such high thermal conductivity of BN/PMMA. The good insulating properties of the PMMA matrix are basically kept in these composites. The breakdown electric fields of BN/PMMA composites are comparable with neat polymers. Although the breakdown electric field slightly decreases with increasing BN fraction due to an easier formation of conductive path, the composites still well retain their insulating abilities fully satisfying for insulating packaging.

The BN nanosheets produced with a high yield and large lateral dimensions drastically improve the mechanical, thermal and insulating performance of BN/PMMA composites. The large lateral dimensions of BN nanosheets provide spacious interfaces between BN and PMMA molecules which determines their remarkable thermal conductivity. The high yield and high throughput of such BN
nanosheets further enable their large-scale practical applications in the field of functionally reinforced polymeric composites.

Figure 7. (a) Optical photos of blank PMMA and PMMA composites with 4, 10, 15, 18 and 23 wt.% of BN arranged from left-to-right and from top-to-bottom. (b) Normalized weight change of PMMA components in blank PMMA and in PMMA/BN composites after removal of the BN components mass loss based on their thermogravimetry curves. (c) Typical differential scanning calorimetry curves of blank PMMA and PMMA/BN composites. Glass transition temperature was determined at the mid-point in a three tangent method. (d) The increased glass transition temperature along with increasing filling fraction of BN nanosheets. (e) Increased thermal conductivity with increasing BN fraction in PMMA/BN composites. Blue curve is the fitting to experimental points using the Agari model [41]; red one is the upper limit of thermal conductivities in theory from parallel models. Reprinted with permission from [42]. © 2012 Wang et al.; licensee Springer.

5. Conclusion and Prospects
BN nanosheets are the representatives of 2D crystals having unique properties. So far, many synthesis routes have been developed to grow BN nanosheets. However the discussed “chemical blowing” is a specific catalyst-free and substrate-free route, which is simpler than the normal CVD method. “Chemical blowing” realizes the high product yield and laterally large areas of BN nanosheets. The obtained products normally possess larger lateral dimensions than those derived from the liquid exfoliation. These not only provide large-enough area nanosheets readily available for their electrical and mechanical performance explorations, but also give enough nanosheets’ mass for fabricating ultimately strong polymeric or other composites. The developed technique opens up a wide horizon for the full realization of BN nanosheet potentials in nanotechnology, for instance growing potentially
valuable BC₃N nanosheets. We believe that the cheaper BN nanosheets based on the developed economic AB or other precursors will appear in the nearest future.

The abundant BN nanosheets enable their utilization in making BN/PMMA composites. The significant 17-fold-enhanced thermal conductivity together with the 18°C increased glass transition temperature for the 23 wt% BN/PMMA was achieved. Meanwhile, BN/PMMA composites exhibited higher mechanical strength, and kept high insulating properties, decent transparency and sufficient dielectric properties. The composites are thus expected to be valuable for multi-functional applications in many fields, especially for the new-generation long-lifetime heat-release packaging materials for electrical circuits and power modules.

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