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Large-scale fabrication and utilization of novel hexagonal/turbostratic composite boron nitride nanosheets

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ABSTRACT

In this report, we have developed a scalable approach to massive synthesis of hexagonal/turbostratic composite boron nitride nanosheets (*h/t*-BNNSs). The strikingly effective, reliable, and high-throughput (grams) synthesis is performed *via* a facile chemical foaming process at 1400°C utilizing ammonia borane (AB) as precursor. The characterization results demonstrate that high quality of *h/t*-BNNSs with lateral size of tens of micrometers and thickness of tens of nanometers are obtained. The growth mechanism of *h/t*-BNNSs is also discussed based on the thermogravimetric analysis of AB which clearly shows two step weight loss. The *h/t*-BNNSs are further used for making thermoconductive *h/t*-BNNSs/epoxy resin composites. The thermal conductivity of the composites is obviously improved due to the introduction of *h/t*-BNNSs. Consideration of the unique properties of boron nitride, these novel *h/t*-BNNSs are envisaged to be very valuable for future high performance polymer based material fabrication.

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Keywords: Turbostratic; Boron nitride nanosheets; Large scale fabrication; Growth mechanism; Thermal conductivity.

1. Introduction

A new horizon in the technological application of materials has been opened by the advisable and smart utilization of nanostructures [1-3]. Recently, researchers have paid much attention to the boron nitride (BN) and its associated low dimensional nanostructures [4-6]. BN nanomaterials possess many attractive properties for potential applications, such as good optical [7] and mechanical properties [8, 9], high oxidation resistance [10, 11], large thermal conductivity [12, 13], low dielectric constant [14, 15], special surface wettability [16, 17], chemical inertness [18] and negative electron affinity [19]. As a well-known nonoxide ceramic, BN exists in various crystalline forms that are isoelectronic to the similarly structured carbon lattice. These forms include hexagonal BN (*h*-BN), cubic BN (*c*-BN), rhombohedral (*r*-BN), and wurtzite BN (*w*-BN). In addition, BN has another partially disordered phase which is called turbostratic BN (*t*-BN). The structure of *t*-BN is formally analogous to that of turbostratic carbon and can be regarded as intermediate between *h*-BN and amorphous BN [20, 21].

In the past few years, great attention has been paid to *t*-BN due to its interesting properties. Yang *et al.* find that *t*-BN based films show peculiar polymer-like time-dependent deformation characteristic [20]. This unique feature makes *t*-BN based films be able to recover completely with hysteresis, even when pressed to the maximum depth of about 20% of the film thickness [20]. Lian *et al.* announce that the *t*-BN has a wide band gap of about 6.0 eV [21]. Generally, *t*-BN has been proposed as an intermediate phase during pressure-less sintering of *h*-BN and preparation of *c*-BN. Therefore, *t*-BN is more active than *h*-BN and *c*-BN due to its incomplete

crystallinity [22, 23]. Additionally, hexagonal boron nitride nanosheets (*h*-BNNSs) which are structurally analogous to graphene have also attracted considerable attention as one of the most popular representative two-dimensional (2D) materials recently [24]. Due to the outstanding properties and various promising applications of *h*-BNNSs, a rapid development has been made in the fabrication of them. Diversification of fabrication methods, such as mechanical cleavage [25], mechanical/chemical peeling [26-28], chemical vapor deposition (CVD) [29-31], high-energy irradiation [32], direct reaction of boric compounds [33], unwrapping nanotubes [34], substitution reaction of graphite [35], chemical synthesized route [24], have been reported in the past decades. However, it can be easily found that most of the research have only been focused on the fabrication and application of 2D *h*-BNNSs [11-13, 26-40], and few reports are related to the *h/t*-BNNSs. Herein, consideration of the outstanding properties of *h*-BNNSs and *t*-BNNSs, we report a route of large-scale fabrication of novel 2D *h/t*-BNNSs *via* a facile chemical foaming process. Field emission scanning electron microscopy (FESEM), high resolution transmission electron microscopy (HRTEM), energy dispersive spectroscopy (EDS), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS) are employed to investigate the morphology, structure, composition and bonding state of the as-synthesized products. The growth mechanism of *h/t*-BNNSs is also discussed based on the XRD, HRTEM, EDS and thermogravimetric analysis (TGA) results. Finally, the *h/t*-BNNSs are further utilized for making *h/t*-BNNSs/epoxy resin composites and the thermal conductivity of the *h/t*-BNNSs/epoxy composites with different *h/t*-BNNSs contents is also investigated.

2. Experimental

Ammonia borane (AB), which was synthesized according to the procedure reported in previous literature [41], was selected as precursor. All chemicals used for the fabrication of AB

including sodium borohydride, ammonium formate and 1,4-dioxane were of analytical grade and used without further purification. The AB synthesized was purified by ether following dried at room temperature. After being dried, 2 g of AB were put into a small boat which was made of graphite paper. The boat was then transferred into a tube furnace for further thermal pyrolysis. The AB was thermally pyrolysed respectively at 1200°C and 1400°C with a heating rate of 10 °C min⁻¹, and the thermal pyrolysis time was set to 60 min. Finally, the as-obtained products were cooled down to room temperature naturally under 0.8 MPa of high pure argon. The as-synthesized products were thoroughly characterized by a variety of techniques including XRD (Rigaku D/max-γB X-ray diffractometer with Cu K radiation ($\lambda=0.154178\text{nm}$)), SEM (TESCAN VEGA II), TEM (JEM-2100) equipped with an energy dispersive spectroscopy (EDS), FTIR (PerkinElmer) and XPS (Physical Electronics PHI 5700 ESCA System).

The thermal conductivity measurements of *h/t*-BNNSs/epoxy resin and BN powder/epoxy resin composites were carried out on a laser flash apparatus (Netzsch LFA 447). The samples with size of 10 × 10 × 2 mm were double-side polished and coated with graphite prior to the measurement. The thermal diffusivity (*D*) of the composites was directly measured. The density (ρ) was measured by Archimedes' method. The specific heat (C_p) was determined by the comparison method with a standard sample (known specific heat) tested under the same condition. Finally, the thermal conductivity (κ) was calculated using the equation: $\kappa = D \cdot \rho \cdot C_p$. The *h/t*-BNNSs/epoxy resin and BN powder/epoxy resin composites were prepared as follows: firstly, the epoxy resin which had been preheated to 60 °C was added into the homogeneous suspensions of *h/t*-BNNSs/butanediol and BN powder/butanediol under violent stirring, respectively. Then, ethylenediamine and tributyl phosphate, used as curing agent and defoaming agent respectively, were respectively added into the *h/t*-BNNSs/epoxy resin/butanediol and BN

powder/epoxy resin/butanediol suspensions, following defoamed for 20 minutes in a vacuum drying oven at the temperature of 60 °C. Finally, the suspensions were poured into a mould to fabricate *h/t*-BNNSs/epoxy resin and BN powder/epoxy resin composites.

3. Results and discussion

Fig. 1 shows the photograph and FESEM images of the as-synthesized products. Generally, the yield per single synthesis run depends on the amount of precursor used in the synthesis process. In current case (2 g of AB), more than 0.8 g of snow-like product can be successfully synthesized per single synthesis run as shown in Fig. 1a. Fig. 1b and 1c show the low magnification SEM images of the as-synthesized products, indicating that a large amount of nanosheets are obtained. From the statistics based on SEM analysis, the thickness of the as-synthesized nanosheets varies from 10 to 50 nm, and the lateral size of the as-synthesized nanosheets varies from 20 to 100 μm . This lateral size is much larger than those fabricated by the liquid/mechanical exfoliation or chemical synthesis method [24, 26-28, 36, 40]. Fig. 1d and 1e display two typical single nanosheets with a thickness of about 40 nm. Obviously, the nanosheets are not completely flat, but exhibiting typical crumpled structure.

The XRD pattern taken from the as-synthesized nanosheets is shown in Fig. 2a. Two diffraction peaks with 2θ at 26.2° and 44.2° can be observed. These peaks respectively correspond to the (002) and (100) planes of *h*-BN (JCPDS card 34-0421). Noticeably, both of the peaks show markedly broadened width compared with those of bulk BN powders, indicating that the as-synthesized nanosheets are thin layers with some disordered structure inside [36]. Fig. 2b shows the FTIR spectrum of the as-synthesized nanosheets. Obviously, two strong characteristic absorption bands centered at 790 and 1383 cm^{-1} are observed in the spectrum. These peaks are similar to those of crumpled *h*-BN that can be assigned to in-plane

stretching and out-of-plane bending vibrations of *h*-BN [36], respectively. Consistent with the XRD result, FTIR analysis further demonstrates that the as-synthesized nanosheets are composed of *h*-BN phase.

The detailed structural characteristic of the as-synthesized BN nanosheets was characterized by TEM investigation. A large quantity of randomly oriented plate-like nanostructures with lateral size of tens of nanometers to several hundred nanometers are assembled on the surface of the BN nanosheets, as shown in Fig. 3a (black “particles”). To further evaluate the crystallinity of the as-synthesized BN nanosheets, selected area electron diffraction (SAED) is carried out on the as-synthesized BN nanosheets. The typical SEAD pattern (Fig. 3b) of the as-synthesized BN nanosheets shows three clear diffraction rings, which can be readily indexed to (002), (100) and (110) planes of *h*-BN phase, respectively. This result well demonstrates the polycrystalline structure of the as-synthesized *h*-BN. The enlarged TEM image shows that the size of the assembled randomly oriented plate-like nanostructures are in the range of 50 to 200 nm (Fig. 3c). Their high resolution TEM (HRTEM) images (Fig. 3d and 3e) collected from the areas marked in Fig. 3c (marked with red square) show that the plate-like nanostructures are not composed of completely ordered *h*-BN layers, but stacked by random *h*-BN layers, which could be called *t*-BN. The average distance between adjacent fringes is 0.34 nm, corresponding to the *d*-spacing of (002) plane of *h*-BN [16]. The EDS spectrum displayed in Fig. 3f shows that the as-synthesized nanosheets are mainly composed of Cu, O, B and N elements, and the atomic ratio of B:N is about 1:1. Here, the Cu element observed in the EDS spectrum originates from the Cu grids usually used for TEM analysis. More information can be observed by XPS spectrum as shown in Fig. 4. The peaks of B, C, N and O elements can be observed in the survey spectrum. The binding energies of B_{1s} and N_{1s} are displayed in the insets of Fig. 4. The binding energies of B_{1s}

and N_{1s} respectively centered at 190.4 and 398.0 eV are consistent with those reported values for *h*-BN [42]. In addition, the signal of O element in EDS and XPS spectra can be attributed to the oxygen contamination or CO₂ absorbed on the sample surface. And the signal of carbon observed in the XPS spectrum can be ascribed to the CO₂ absorbed on the sample surface or the carbon from the small boat made of graphite paper which is used as container in the thermal pyrolysis process. Therefore, combining all the results of XRD, FTIR, SEM and TEM analysis, it can be concluded that the as-synthesized nanostructures are *h/t*-BNNSs.

To clarify the growth mechanism of the *h/t*-BNNSs, the decomposition process of the precursor is investigated. TG-DSC profile of AB shown in our previous work (Figure S1, Supporting Information) indicates that the thermal decomposition of AB mainly occurs before 200 °C, then AB will experience a mild process rather than fierce decomposition after 200 °C [43]. To further reveal the structure evolution of AB during the thermal decomposition process, XRD analysis is performed on the original AB and thermal pyrolysis product at 200 °C, as shown in Fig. 5. Fig. 5 illustrates that a transformation of AB from the well crystallized phase to amorphous phase occurs during the sharp weight loss stage (i.e. before 200 °C). During the mild weight loss stage (i.e. 200-1450 °C), B and N atoms are rearranged to form *t*-BNNSs by further releasing small amount of residuals. The presence of an amorphous background in the XRD pattern of the *h/t*-BNNSs (Fig. 2a) is precisely caused by the residual of the amorphous phase during the crystallization process.

Based on the analysis of the above-mentioned characterization and consideration, a two-step growth mechanism for the formation of *h/t*-BNNSs is proposed as schematically illustrated in Fig. 6. During the first stage (before 200 °C), AB will decompose with a sharp weight loss by releasing hydrogen and other B and N element containing species to convert to amorphous phase

(Fig. 6a and 6b). When the temperature further increases in the second stage (200-1400 °C), a crystallization process will happen and this process will convert the amorphous phase (the products produced in the first stage) into amorphous/crystalline BN nanosheets (Fig. 6c). The intermediate products synthesized under 1200 °C are also examined by XRD, SEM, TEM and EDS analysis for clarification as presented in Fig. 7 and Fig. 8. At 1200 °C, a high yield of intermediate nanosheets are also obtained as shown in Fig. 7a. The XRD pattern (Fig. 7b) of these as-synthesized nanosheets also displays two peaks which can also be well indexed as *h*-BN phase. However, the width of both peaks becomes wider compared with those obtained from the *h/t*-BNNSs synthesized at 1400 °C (Fig. 2a), indicating a lower crystallinity of the BN nanosheets synthesized at 1200 °C. The typical TEM images (Fig. 8a and 8b) of the as-synthesized BN nanosheets show that the nanosheets comprised nanoparticles. This was quite different from that of *h/t*-BNNSs synthesized at 1400 °C. The SAED pattern and HRTEM image clearly illustrate that the nanosheets synthesized at 1200 °C are not crystallized as well as those synthesized at 1400 °C, although the atomic ratio of B:N is close to 1:1 (Fig. 8d). This result well verifies above-mentioned growth mechanism of *h/t*-BNNSs which will experience an amorphous growth process in the second stage.

Our work demonstrates that *h/t*-BNNSs can be synthesized by the simple thermal pyrolysis of AB, providing a rather facile route to fabricate this 2D BN nanomaterial. Similarly, Wang *et al.* also conducted the AB pyrolysis experiment and reported that atomically thin (one-to-few atomic layers) free-standing *h*-BNNSs rather than *h/t*-BNNSs were obtained [44]. The reason that results in such difference including morphology and structure in the final products can be ascribed to the milder heating rate which was changed from 30 °C min⁻¹ to 10 °C min⁻¹ in our study. And in our previous study, we also found that crystallized BN nanoplates could be obtained with the heating

rate of about 50 °C [43]. We believe that this difference is also caused by the different heating rate, because low heating rate leads to a long heating time, which will cause more disordered structure formed during the heating process. It is also interesting to find the reason why the thermal pyrolysis of AB leads to form 2D BN nanostructures instead of other morphologies, such as nanotubes and nanospheres. Under low pressure, alternating B and N atoms will covalently bond to each other *via* sp^2 hybridization to form BN layers. The BN layers are held by weak Van der Waals interactions. However, when BN layers are bent by some external factors, e.g. in the presence of catalyst particles, tubular or spherical BN nanostructures may be formed. In current research, AB was used as a single precursor for the synthesis of BN and no catalysts were added. Therefore, it is reasonable and advisable to conclude that AB transforms into BNNSs.

The utilization of *h/t*-BNNSs as filler to improve the thermal conductivity of the polymers is also investigated. As shown in Fig. 9a, the thermal conductivity of the thermoconductive composites obviously increases with the increase of *h/t*-BNNS mass fraction in the composites at the measurement temperature of 25 °C. And it can also be easily found that the thermal conductivity of the composites with the *h/t*-BNNSs as filler is superior to the composites with the BN powders (purchased in the market) as filler when the *h/t*-BNNSs and BN powders possess the same mass fractions (6 wt%) in the composites (Fig. 9b). Combining the unique properties of boron nitride, these novel *h/t*-BNNSs are envisaged to be very valuable for future high performance polymer based materials preparation.

4. Conclusions

In summary, we have developed a new method to scale-up synthesis of *h/t*-BNNSs by using AB as precursor. This method has the advantages of being simple and having a high

yield. The structure and chemical composition of the *h/t*-BNNSs are examined in detail, showing that high quality of *h/t*-BNNSs with lateral size of tens of micrometers and thickness of tens of nanometers are synthesized. The interpretation of the formation process of the *h/t*-BNNSs has been put forward. The introduction of *h/t*-BNNSs into the polymers can effectively improve the thermal conductivity of the polymers, which is much better than that of BN powders purchased from the market. This method represents a facile route to large-scale synthesis of *h/t*-BNNSs which can be used for future thermoconductive polymer composite fabrication.

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Figure Captions

Fig. 1. (a) The photograph of a large amount of the as-synthesized *h/t*-BNNSs, (b-d) The SEM images of the as-synthesized *h/t*-BNNSs taken at different magnifications.

Fig. 2. (a) The XRD pattern and (b) FTIR spectrum of the as-synthesized *h/t*-BNNSs.

Fig. 3. (a) The TEM image and (b) corresponding SAED pattern of the as-synthesized *h/t*-BNNSs, (c) enlarged TEM image of the as-synthesized *h/t*-BNNSs got from area I in (a), (d) and (e) the HRTEM images of the as-synthesized *h/t*-BNNSs got from area II and III in (c), respectively, (f) the EDS spectrum of the as-synthesized *t*-BNNSs. Inset is the corresponding contents of the elements.

Fig. 4. The XPS spectrum of the as-synthesized *h/t*-BNNSs, insets are the N_{1s} and B_{1s} spectra, respectively.

Fig. 5. XRD pattern of (a) AB and (b) the corresponding thermal pyrolysis product at 200 °C.

Fig. 6. Schematic illustration of the formation processes of the *h/t*-BNNSs: (a) well crystallized AB, (b) amorphous phase obtained by releasing hydrogen and other B and N containing species at 200°C, and (c) *h/t*-BNNSs crystallizing from the amorphous phase at 1400°C.

Fig. 7. (a) The SEM image and (b) XRD pattern of the as-synthesized BN nanosheets obtained at 1200°C.

Fig. 8. (a) and (b) the TEM images, (c) HRTEM image, and (d) EDS spectrum of the as-synthesized BN nanosheets obtained at 1200°C. Inset in a is the corresponding SAED pattern of the as-synthesized BN nanosheets.

Fig. 9. Thermal conductivity of the composites: (a) Thermal conductivity with various *h/t*-BNNS contents measured at 25 °C; (b) Thermal conductivity of *h/t*-BNNS and h-BN based composites under different temperature.

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7

Fig. 8

Fig. 9

Graphical abstract

HIGHLIGHTS

- Novel hexagonal/turbostratic composite boron nitride nanosheets (*h/t*-BNNSs) can be massively fabricated *via* a facile chemical foaming process.
- The *h/t*-BNNSs possess a large lateral size of tens of micrometers with thickness of tens of nanometers.
- These *h/t*-BNNSs can be used to effectively improve the thermal conductivity of polymers.