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Few-step synthesis, thermal purification and structural characterization of porous boron nitride nanoplatelets

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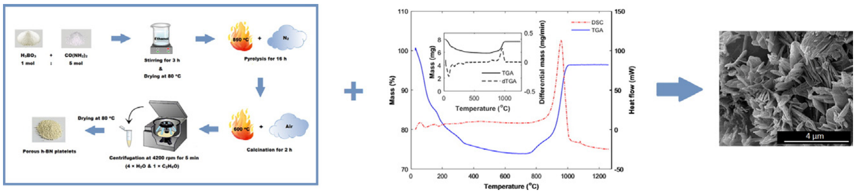
HIGHLIGHTS

- Porous h-BN powders were prepared by mixing H_3BO_3 and $CO(NH_2)_2$ followed by pyrolysis in N_2 and calcination in air.
- Purity increased to ~99 wt.% at ~700 °C, active oxidation initiated at ~860 °C and B_2O_3 formation completed at ~1000 °C.
- The as-prepared h-BN particles seem to mainly oxidize from their edges, leaving the planar hexagonal surfaces intact.
- Purified h-BN platelets with large surface area (213 m^2/g), increased microporosity (66 %) and narrow pore sizes (0.85 nm).

GRAPHICAL ABSTRACT



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ABSTRACT

Hexagonal boron nitride (h-BN) nanoplatelets with ~99 wt.% purity, 900 to 2000 nm particle width, 30 to 90 nm particle thickness, ~213 m^2/g specific surface area (SSA), ~66% micropore SSA and ~0.85 nm average pore size were synthesized in a powder form using H_3BO_3 and $CO(NH_2)_2$ as precursors followed by consecutive thermal treatments under inert and oxidized atmospheres. Thermal gravimetric analysis (TGA) combined with differential scanning calorimetry (DSC), under synthetic air-flow and up to ~1300 °C, were employed to evaluate both purity and oxidation resistance of the product directly upon its synthesis. The h-BN powder was collected at the stage of its highest purity which, based on TGA-DSC data, corresponded to an additional heat treatment up to ~700 °C. The active oxidation seems to occur in the temperature range between ~860 and ~1000 °C, followed by formation of B_2O_3 in the final residue. Subsequently, the purified h-BN powder was extensively characterized for its structure, morphology and porosity using X-ray diffraction, scanning electron microscopy and nitrogen gas adsorption/desorption measurements at 77 K, respectively. As briefly discussed, purity and SSA seem to have a crucial role in the thermal stability and oxidation resistance of BN materials in general.

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1. Introduction

Boron nitride (BN) nanoscale materials have attracted significant attention in recent years due to their improved mechanical, electrical, optical and thermal properties [1–6]. In this respect, a great variety of BN nanostructures has been presented in the literature, including few-layer sheets and flakes [6–14,63], nanotubes [6,15–18,62], fibers [19,20], platelets [9,21–23], spheres [24–27], ribbons [15], cocoons [15], whiskers [28], hollow boxes [29], meshes [30,31], microbelts [32], aerogels [33,34], as well as hierarchical sponges [35], demonstrating low density, increased mechanical strength, large thermal conductivity, high electrical resistance, excellent lubricity as well as superior thermal stability and oxidation resistance. Owing to these unique characteristics, BN nanomaterials have been proposed as substrates or dielectric layers for nanoelectronic devices [36,37], neutron detectors in nuclear reactors [38], shields for space radiation [39], proton conductors for fuel cells [40], solid lubricant additives for high-temperature applications [12,41,42], oxidation resistant coatings and thin films [10,11,43,44] as well as ceramic components for high-temperature equipment [20,42]. In addition, porous analogues of these interesting nanostructures have been studied for drug delivery systems and biomolecular sensors [16,45,46], catalyst supports in photocatalytic systems [29], filters for water purification from oils, organic solvents, dyes and metal ions [19,25,28,47], atmospheric air cleaners from pollutants and volatile organic compounds [47], gas sensors and detectors [7,33] as well as hydrogen adsorption and storage media [25,28,32,35,62], due to the fact that they exhibit large surface areas and pore volumes combined with narrow and tunable nanopore sizes.

Hexagonal BN (h-BN) is the most stable and widely used BN allotrope exhibiting a crystalline structure similar to the graphitic one; i.e. B and N atoms are covalently bonded in hexagonal rings, while the individual layers are attracted by weak van der Waals interactions leading to a graphite-like inter-layer distance of 3.3 Å [48]. The remarkable thermal stability of h-BN materials, even in atmospheric air, has been a subject of continuous research [10,11,18,20,22,24,26,42–44,49–53] with various reports claiming that crystallinity [26,49,51], particle shape and size [20,26] and specific surface area (SSA) [9,22], play a significant role towards their oxidation behavior under high-temperatures. Li et al. [10] reported that monolayer BN starts to oxidize at ~700 °C when heated in air, almost three times higher than the oxidation temperature of single-layer graphene (i.e. ~250 °C). They also claimed that the onset oxidation temperature could be increased up to ~870 °C by increasing the number of nanolayers (i.e. up to a four-layer BN). Kostoglou et al. [22] studied highly crystalline and pure (i.e. 98%) h-BN nanoplatelets with 300–600 nm width, 30–50 nm thickness and 23 m^2/g SSA and reported a superior thermal stability of up to 1000 °C under synthetic air-flow conditions. Recently, Zhu et al. [8] produced nanoporous h-BN flakes with high SSAs of up to ~214 m^2/g and narrow pore sizes of 1 and 4 nm that demonstrated an oxidation resistance of up to ~800 °C. Hou et al. [20] observed an oxidation temperature as high as 1250 K (i.e. ~977 °C) for h-BN nanofibers with 400–1500 nm diameter and 200–500 μm length. The same group stated that the particle shape probably had an effect on the oxidation behavior, as their fiber-like material was able to withstand 250 °C more than a commercial h-BN powder with a similar particle size distribution. A series of BN nanostructures (i.e. ultrathin nanosheets, triangular plates and hexagonal nanocrystals) were prepared by Wang et al. [9], having 50–250 nm average side lengths, 1–80 nm average thicknesses and 6–233 m^2/g SSAs, that demonstrated thermal stabilities between 800 and 1000 °C in the presence of air. According to the same group, the oxidation resistance of their BN materials was significantly influenced by the degree of crystallinity and the SSA value; i.e. crystalline BN materials with small SSAs provided less reactive sites favorable for oxidation. Therefore, as expected, small particles should demonstrate large SSAs and thus exhibit higher reactivity towards oxidation and/or corrosion. Fig. 1 highlights a potential correlation between the onset temperature to oxidation in atmospheric air of various h-BN nanostructured materials (e.g. flakes, platelets, fibers) and their respective SSA values derived by the Brunauer-Emmet-Teller (BET) method. The presented collection of previously published experimental data [8,10,13,19,22,27,29,30,31,34] shows that the h-BN nanostructures commonly oxidize in the temperature range of ~800 to ~1100 °C. The onset oxidation temperature seems to be decreasing exponentially with increasing BET SSA value, in good agreement with the aforementioned statement made by Wang et al. [9]. The almost identical oxidation temperature of ~800 °C for three different h-BN materials [8,13,30] with similar BET SSAs around 200 m^2/g could be considered as another interesting feature. Even though there are some minor differences in the experimental parameters employed in these studies, including air-flow and/or heating rates, the trend seems to be representative for most of the h-BN materials in general (i.e. from bulk to nanoporous structures), although without excluding the effect of other critical factors. Additional parameters, such as the presence of impurities (e.g. amorphous particles, surface functional groups, synthesis remnants) and moisture, have also a significant contribution to the oxidation process [17,50]. Finally, BN materials with different textures (i.e. powders, membranes, gels), porosities (i.e. micro-, meso-, and macroporosity) and crystalline structures (i.e. hexagonal, cubic, turbostratic) should exhibit a different oxidation behavior as well [50,52,53].

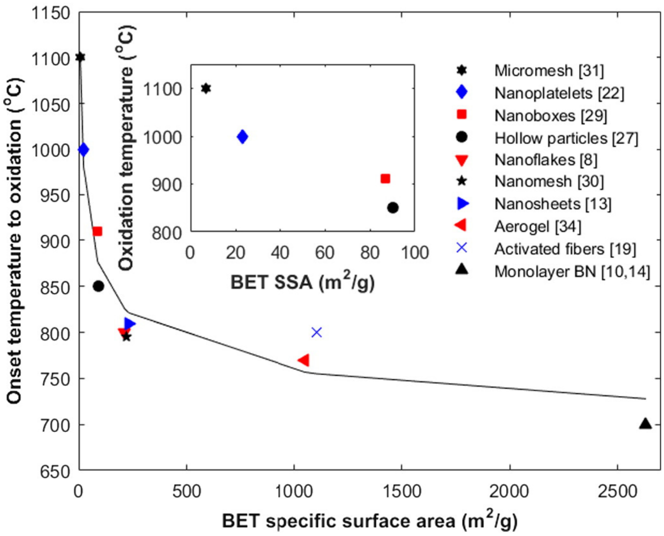

Fig. 1. Correlation plot between the onset temperature to oxidation of different h-BN nanostructured materials and their respective BET specific surface area (SSA) values. The inset shows data points for h-BN materials with the lowest BET SSAs (<100 m^2/g).

In the current study, porous h-BN nanoplatelets in a powder-form were synthesized by thermal treatment under inert and oxidized atmospheres using boric acid (H_3BO_3) and urea ($CO(NH_2)_2$) as precursor materials. In recent years, h-BN powders were also produced using novel production routes, including sol-gel polycondensation of resorcinol ($C_6H_4(OH)_2$) and formaldehyde (HCHO) in the presence of H_3BO_3 combined with freeze-drying and pyrolysis [23], reaction of boric acid and urea in N_2, argon (Ar) or ammonia (NH_3) atmospheres in the presence of sodium carbonate (Na_2CO_3) [54], as well as thermally-induced combustion of a boron oxide (B_2O_3), magnesium and ammonium chloride (NH_4Cl) solid mixture [21]. However, these materials demonstrated rather low BET SSA values, between 14 and 60 m^2/g, thus reducing their potential use in applications where high SSAs are considered important (e.g. water filtration, gas adsorption and storage, selective gas separation). The method herein combines only three basic steps: a mixing/magnetic stirring in ethanol solution, a pyrolysis treatment at 850 °C under a N_2 atmosphere and a calcination treatment at 600 °C under atmospheric air. The as-prepared BN powder was studied by thermal gravimetric analysis (TGA) combined with differential scanning calorimetry (DSC) under synthetic air-flow conditions with the view to