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One-step fabrication of boron nitride fibers networks

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ABSTRACT

The three dimensional boron nitride monolith with fibers network architecture was fabricated through directly pyrolyzing the assembly of the $C_3N_6H_6{\cdot}2H_3BO_3$ green fibers. This one-step way is superior to the typical techniques using hydrophobic and agglomerate BN micro-/nano- materials to construct architectures. The obtained BN monolith exhibited low density of 92 mg cm^{-3} with high porosity (94.45 vol%), as well as robust skeleton with high compressive strength ($\boldsymbol{\sigma f}$ = 42.54 kPa) and stiffness ($\boldsymbol{E}$ = 0.475 MPa). The BN network also displayed hydrophobicity with water contact angle of 136.9° and oleophilicity with rapid oil permeation. It showed great performance in oily water treatment. Furthermore, the robust BN network would also be potential as catalyst supports, composites reinforcements and filters in many practical applications.

1. Introduction

Hexagonal boron nitride (h-BN) is a versatile material with excellent overall performance of thermal stability, chemical inertness, high thermal conductivity, low dielectric constant and loss tangent, etc. It has been widely applied in high temperature wave-transparent, lubrication, electronic packaging and so on [1–3]. Aerogels or foams are special porous materials with continuous three-dimensional (3D) skeletons, exhibiting low density and high porosity. Construction of 3D porous architectures of BN materials (3D-BN) could take fully advantages of both BN ceramic and porous structures, and will extend their applications as catalyst supports, thermal management and tissue engineering [4,5].

Up to now, three methods have been applied to prepare 3D-BN, derivation from polymeric aerogels [6,7], template-assisted growth [8–10] and assembly of micro- /nano- structures [11–14]. David, et al. firstly synthesized BN aerogel in 1990, through pyrolyzing the poly (borazinyl amine) aerogel using 2,4,6-trichloroborazene and hexamethyl-disilazane as raw materials [6]. Cao, et al. also succeeded to fabricate BN foams through pyrolyzing the poly-borazine foams which were formed in pressured curing process of borazine [7]. However, the complicated polymer-derived method usually used toxic and volatile precursors as well as strict synthetic conditions. In template-assisted synthesis, the BN can be deposited onto the porous architectures like silica aerogel, carbon aerogel and Ni foam through chemical vapor deposition (CVD) [8,9] and elemental substituted reaction [10]. After subsequent removal of templates, the BN counterparts could be obtained. As-prepared 3D-BN could precisely duplicate the architectures of template and usually exhibit high surface area and high porosity within integrated monolith. Due to the size limitation of the templates, the 3D-BN are merely produced in limited amount and cannot meet the practical demand in large-scale. Moreover, the CVD process and elemental substitution reactions involved not only hazardous boron- and nitrogen-containing precursors, but also kinetically insufficient for mass production.

Assembly of micro-/nano-structures into continuous 3D architectures opens up a convenient production with a wide variety of materials [11]. And freeze-casting is a common way for the constructions [12–14]. Boron nitride nanosheets (BNNSs) are common building-blocks that were used to fabricate 3D-BN architectures. Due to the hydrophobicity of the BN materials, the BNNSs should be pre-treated like functionalization to make it hydrophilic and highly water-dispersible [15]. Moreover, the polymers are necessary to bridge BNNSs to form integrated monolith, resulting in the thermally collapse because of the polymer decomposition [16]. The continuous BN fibers could also be used to construct 3D network architectures for their high tensile strength and excellent flexibility [17,18], but it is too expensive to achieve mass production.

Herein, we present a novel method to fabricate of 3D-BN through directly pyrolyzing the assembly of $C_3N_6H_6{\cdot}2H_3BO_3$ green fibers. $C_3N_6H_6{\cdot}2H_3BO_3$ (melamine diborate) is a fibrous molecular crystal synthesized through hydrogen-bonding between melamine and boric acid in water-bath, which is the precursor of BN fibers [19–21]. Being different from the typical way of firstly synthesizing of BN building blocks and then assembly, the one-step way fulfill the fabrication of 3D-BN networks as synchronously obtaining BN fibers, and could avoid the

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difficult dispersion process of hydrophobic BN micro-/nano- materials in water. It is low-cost, eco-friendly, easy for mass production and does not require hazardous materials and complicated experimental condition. Based on it, we can investigate the properties of the BN networks and explore their applications.

2. Materials and methods

2.1. Materials

Melamine ($C_3N_6H_6$, 99%), boric acid (H_3BO_3, 99.5%), methylene blue($C_{16}H_{18}N_3SCl$, MB), SudanII ($C_{18}H_{16}N_2O$), and paraffin liquid (chemically pure, 0.83–0.86 g cm^{-3}) were purchased from Sinopharm Chemical Reagent Co., Ltd., Shanghai, China. The distilled water was prepared using water purifying system (αK Exceed-A, Chengdu Tangshi Kangning Science Development Co., Ltd) in lab.

2.2. Fabrication of 3D melamine diborate monolith

In a typical process, a mixture of $C_3N_6H_6$ and H_3BO_3 with a molar ratio of 1:3 were added into distilled water and synchronously dissolved under 90 °C water bath with vigorously stirring, the concentration of $C_3N_6H_6$ was not beyond 0.1 mol L^{-1} for completely dissolution. Then the transparent hot aqueous solution was naturally cooled down to room temperature to give a white flocculent precipitate. The melamine diborate green fibers were obtained without residual $C_3N_6H_6$ or H_3BO_3 after further filtering and drying naturally.

A certain amount of the as-dried green fibers were added in distilled water at a high concentration of 0.4 mol L^{-1}, which was then subjected to 80 °C water bath to realize partially dissolving and forming the homogeneous slurry with stirring. Next, the slurry was poured into mold to cast by naturally cooling and aging. With sequential freezing in refrigerator and cryodrying using a vacuum freeze dryer (LGJ-10 Freeze-dryer system, Beijing Songyuan Huaxing Technology Develop Co., Ltd.), the 3D melamine diborate monoliths with fibers network structures were obtained.

2.3. Preparation of 3D BN monolith

The 3D melamine diborate monolith was placed into a tubular furnace and initially heated to 600 °C at a ramp rate of 5 °C min^{-1} for 2 h in an ammonia flow and kept raising temperature to 1000 °C for 1 h under nitrogen flow. The obtained intermediate products were then placed in graphite oven and treated at 1700 °C for 1 h in a flow of nitrogen, and the 3D-BN monoliths were finally obtained.

2.4. Characterization

The micro-morphology was observed on an optical microscope (JNOEC XS-213) and field emission scanning electron-microscope (FE-SEM, Hitachi S-4800, Japan) equipped with energy dispersive spectrometer (EDS). Thermo-gravimetric and differential scanning calorimeter (TG-DSC) was recorded on a NETZSCH STA449C under nitrogen to characterize the pyrolysis process of melamine diborate, heating at the rate of 20 °C min^{-1}. The composition of products was analyzed by fourier transform infrared (FT-IR) spectra. X-ray diffraction (XRD) patterns were recorded on a Bruker Advanced D8 diffractometer at a wavelength of 1.5418 Å (Cu Kα radiation). The carbon and oxygen content of the BN fiber were characterized using Leco CS-600C/S and Leco TCH-600 N/O analyzers, respectively. The high resolution transparent scanning microscopy (HRTEM) image was taken using a Tecnai F200 transmission electron microscope operated with an acceleration voltage of 200 kV. The bulk density of BN monolith was calculated via mass volume method: $\rho_{bulk} = m/v_{bulk}$, where m and v_{bulk} were directly determined. The BN skeleton density $\rho_{skeleton}$ was determined through Archimedes method using ethanol as media. And the porosity (P) was calculated according to the equation: $P = 1 - \rho_{bulk}/\rho_{skeleton}$. Mercury intrusion porosimetry (MIP) was performed using a AutoPore IV 9500 instrument (Micromeritics Instrument Corporation, USA) to characterize the surface area and the pore size distribution of the BN network. The compressive mechanical properties was measured using a WDW-100 machine (displacement rate of 1 mm min^{-1}).

2.5. Wettability and adsorption measurements

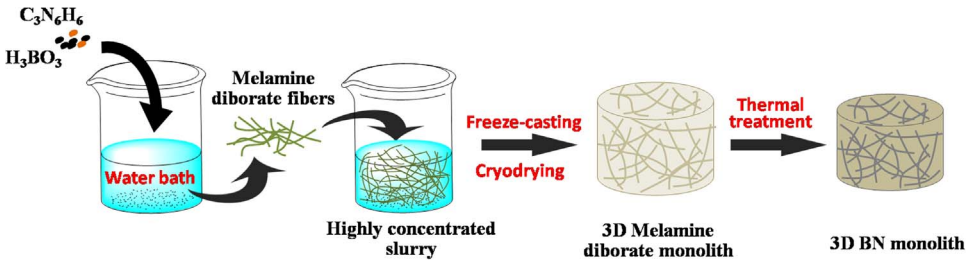
The wettability of the 3D-BN was studied through static water contact angle and oil adsorption testing. The water was stained by MB and oil was paraffin liquid stained by SudanIIto have an obvious view. The 3D-BN monolith was cut into slices, and the water droplet (about 2 μL) was dropped onto the slice using a syringe and held for 1 min. The water contact angle was recorded using contact angle meter (SL200B, Solon Tech. (Shanghai) Co., Ltd.). The paraffin liquid droplet (about 100 μL) was dropped onto the slice using an elastic dropper, and the whole adsorption process was recorded by high speed camera (Olympus I-Speed 3).

In oil adsorption measurement, the oil (paraffin liquid stained by SudanII) was floating on water (Stained by MB) and displayed distinct interface, and the BN monolith was put in. After finishing adsorption, the oil-saturated BN monolith was weighed and adsorption capacities (C_a) were calculated using an equation: $C_a = (M_t - M_0)/M_0$ (where M_t and M_0 are the weights of BN monolith with and without adsorbed oils, respectively). For later usage, it was burned and heated in air at 550 °C for 2 h to remove oil and clean carbon residue. During the cycling measurements, the adsorption efficiency (%) was used to evaluate the repeated performance and defined as $C_{a'}/C_{a0}$, where C_{a0} is the initial adsorption capacity and $C_{a'}$ is that of after-cycled.

3. Results and discussion

The fabricating process of the 3D BN monolith with network architectures is illustrated in Scheme 1.

First of all, the melamine diborate green fibers were synthesized through water bath of melamine and boric acid. Then, the green fibers were used to construct 3D architectures. To realize stable assembly of green fibers in 3D monolith, high concentrated slurry of the fibers is critical to sufficient skeleton density of the robust network. However, the as-synthesized green fibers are usually insufficiently concentrated owing to low solubility of starting materials, especially melamine [22], so the concentrating process is necessary. Here, we applied the filtering-drying process to remove water as well as un-reacted raw materials.



Scheme 1. Illustration of the fabrication process of 3D BN monolith.