



## Research paper

# A facile approach to fabricate boron carbonitride microspheres via precursor pyrolysis



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## ARTICLE INFO

## Article history:

Received 18 October 2016

In final form 24 February 2017

Available online 27 February 2017

## Keywords:

Deposition

Oxidation

BCN

Microsphere

## ABSTRACT

Bulk quantity Boron Carbonitride (BCN) microspheres were successfully synthesized via an organic precursor pyrolysis approach. The organic precursor was synthesized at 90 °C by the polymerization reaction of boron trichloride, aniline and ethylenediamine with a molar ratio of 1:1:1. All particles presented uniform spherical structure with the size of 2 μm. The products have oxidation starting temperature at 624 °C much higher than graphene (404 °C).

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## 1. Introduction

In recent years, hexagonal ternary BCN materials have aroused extensive interests owing to their low density, excellent thermal conductivity, oxidation resistance properties and chemical stability attractive for various potential applications, including electronic devices, supercapacitors, high temperature lubricants, microwave absorption and electrocatalysts [1–7]. Comparing with its analogues, graphite and *h*-BN, *h*-BCN materials show a specialty that the dielectric properties can be tailored by adjusting the composition and arrangement of B, C and N atoms [8]. It is expected that BCN materials may show some promising properties complementary to graphite and *h*-BN. The BCN spherical structure is considerable to be a promising material because of its large surface areas and particle packing factor. On the other hand, BCN materials usually provide much better physicochemical properties than carbon materials, suggesting the applications as semiconductor, low dielectric devices [9,10]. Nanosheets containing B, C, N atoms of variable compositions were researched and prepared by various methods. For example, Ambrosi et al. [11] prepared BCN sheets by metal catalyzed CVD, which inevitably remains some metal impurities that may affect their properties. Qin et al. [1] used microwave plasma CVD method to synthesize BCN nanosheets with few atomic layers. However, there are only a few methods on the synthesis of BCN spherical structure. BC<sub>4</sub>N microspheres

reported by Raidongia et al. [9] were obtained from the reaction of amorphous carbon spheres with boric acid and urea at high temperatures. Above all, these methods require complicated process and conditions for BCN products. And it remains a challenge to facilely synthesize spherical structure for BCN materials.

Here in, we can obtain BCN materials with tunable structure through controlling the heat treatment of BCN organic precursor pyrolysis. BCN nanoflakes have been reported in our previous study [12]. Now, we fabricated bulk quantity BCN microspheres deposited in graphite sheet substrate via a simple precursor pyrolysis approach. The BCN microspheres show uniform size about 2 μm. This facile technique may contribute to the preparations of BCN materials with various structures.

## 2. Experimental

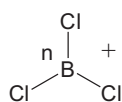
The organic precursor was synthesized at 90 °C by the polymerization reaction (Eq. (1)) of boron trichloride (BCl<sub>3</sub>) (purity 99.9%, purchase from Guangzhou Ruihe Chemical Science and Tech. Co. Ltd), aniline (Ph-NH<sub>2</sub>) (purity ≥98%, obtained from Tianjin Yongda Chemical Reagent Co. Ltd), and ethylenediamine (C<sub>2</sub>H<sub>8</sub>N<sub>2</sub>) (purity ≥98%, obtained from Tianjin Yongda Chemical Reagent Co. Ltd) using a molar ratio of 1:1:1. Firstly, Ph-NH<sub>2</sub> and C<sub>2</sub>H<sub>8</sub>N<sub>2</sub> were stirred in a flask at 90 °C, subsequently, BCl<sub>3</sub> was piped into the mixed solution for 1.5 h at a flowing rate of 0.2 L/min, then continued to react 2 h after turning off BCl<sub>3</sub>. Finally, the dark brown reacted products were cooled to room temperature naturally. The BCN

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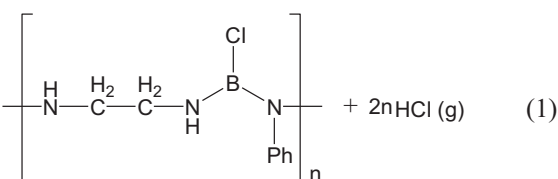
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precursor and graphite sheet substrate placed into two  $\text{Al}_2\text{O}_3$  boats respectively that were delivered into tube sintering furnace heated  $1000\text{ }^\circ\text{C}$  for 2 h with heating rate of  $5\text{ }^\circ\text{C}/\text{min}$  in the argon atmosphere (purity 99.99%, flowing rate 2 L/min). At last, the black products were collected from the surface of graphite sheet substrate without any further purification.

The morphologies of BCN products were observed using a field emission scanning electron microscopy (SEM, MX2600FE). The chemical characteristics were investigated by Fourier transform infrared spectroscopy (FTIR, Bruker VECTOR-22) and X-ray photoelectron spectroscopy (XPS, Physical Electronics PHI 5700 with Mg exciting source). The structures were examined by powder X-ray diffractometer (XRD, RIGAKU D/Max 2000 VPC, Cu  $K\alpha$  radiation,  $\lambda = 1.5418\text{ \AA}$ ) and Raman spectroscopy (514 nm, Renishaw, RM-1000). Thermogravimetric analysis (TGA) was recorded on a NETZSCH STA 449 C under ambient atmosphere.



XPS spectra (Fig. 2) were carried out to determine the composition ratio of BCN products. The full range XPS spectrum presented in Fig. 2a reveals the existence of B, C, N and O elements for the BCN microspheres. As observed in Fig. 2b, the broad peak for B 1s suggests presence of different valence around B atom owing to bonds with other elements, and it can be deconvoluted into bands at 188.2, 190.7 and 191.3 eV, assigned to B–C, B– and B–O bonds. The chemical shift toward to lower energy of 188.2 eV replies a bonding configuration of B–C on account of electronegativity of B and C atoms lower than N [13]. Fig. 2c display the spectrum of C 1s that can be divided into two peaks related to C–C (284.6 eV) and C–N (285.7 eV) bonds [14]. The C–C bond is predominant in accordance with amorphous carbon in XRD pattern. The fitted peak at 285.7 eV is attributed to C atom bonded to more electronegative N atom. The spectrum of N 1s given in Fig. 2d shows peaks at 396.5 and 398.4 eV attributed to N–B and N–C



### 3. Results and discussion

Fig. 1 exhibits typical SEM images of BCN microspheres deposited in substrate. It can be observed in Fig. 1a that all particles own uniform spherical structure with the size of  $2\text{ }\mu\text{m}$ . Fig. 1b shows that a few of particles exhibit hollow and solid structures through ultrasonic of 1 min, and the shell of hollow particles shows uneven thickness. Fig. 1c shows the possible growing process of BCN microspheres. Firstly, organic precursor cross-linked and volatilized around  $180\text{ }^\circ\text{C}$ ,  $330\text{ }^\circ\text{C}$  respectively, and then pyrolysed to inorganic component with the release of HCl at  $380\text{ }^\circ\text{C}$ . With the flowing Ar and release of HCl gas, BCN inorganic component would form spherical structure covering the surface of substrate in order to reduce surface energy. At last, we proposed that shell became thicker than thicker through holding  $1000\text{ }^\circ\text{C}$  for 2 h, and finally the particles totally developed into solid structure.

respectively [15]. Based on the information of XPS spectra for B, C, N atoms, it can be estimated that the ratio of B, C, N atoms is about 1:2.2:1.4.

The FT-IR transparency spectrum for BCN products are shown in Fig. 3a. It shows the typical peaks of basic structure of BCN microspheres ( $\text{cm}^{-1}$ ): B–N (682, 1376), B–C (1045–1081), C–N (1242). The wavenumber at 682 and  $1376\text{ cm}^{-1}$  is corresponding to out of plane vibrations and in-plane stretching of  $\text{sp}^2$  bonded B–N bond [16,17]. And the absorption at  $1242\text{ cm}^{-1}$  may arise from  $\text{sp}^3$  bonded C–N bond [18]. Absorption between 1045 and 1081 can be attributed to B–C bond which is usually induced at  $1070\text{ cm}^{-1}$  [19]. It can confirm the coordination of three bonds represents characteristic of the hexagonal phase.

Fig. 3b shows X-ray diffraction pattern of BCN products. The reflections around  $26^\circ$  ( $2\theta$ ) can be fitted into two peaks related to

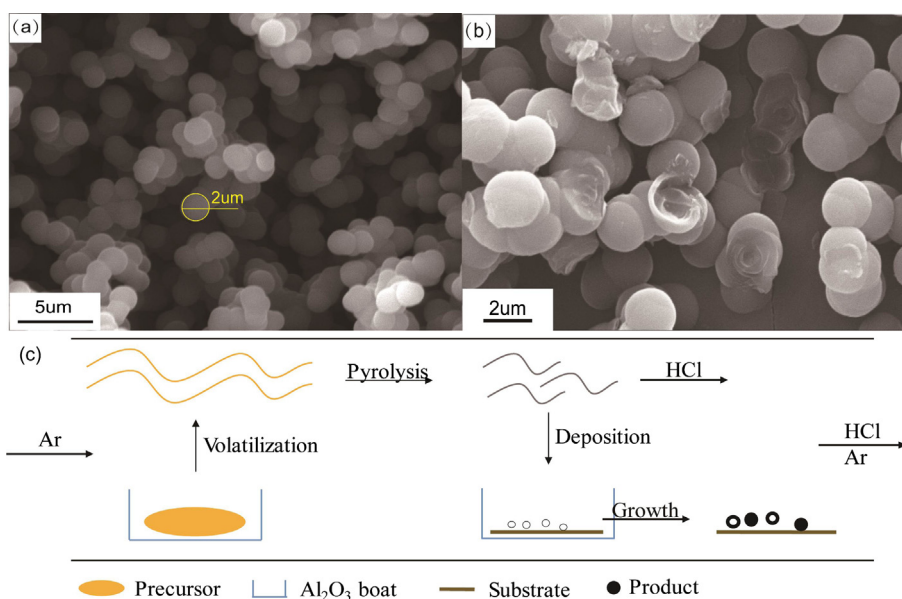


Fig. 1. The SEM images of BCN products at different magnification of (a)  $10\text{k}\times$ , (b)  $20\text{k}\times$  and (c) the growing process of microspheres.

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