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A simple precursor pyrolysis route to BCN nanoflakes

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ABSTRACT

Bulk quantity hexagonal borbon carbon nitride (BCN) nanoflakes were successfully synthesized via a simple precursor pyrolysis method. Scanning electron microscope (SEM) and high resolution transmission electron microscopy (HR-TEM) showed the nanoflakes having tens of layers with the size of 20 μm and 10 nm in thickness. Fourier transform infrared (FT-IR) and X-ray photoelectron spectrometer (XPS) were performed to reveal the chemical structure of the products. The results show that the products have a hybrid chemical composition of B–N, C–C, and C–N bonds.

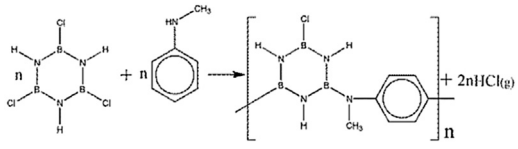
1. Introduction

Recently, significant interests have been focused on graphene owing to their outstanding properties, including super chemical tolerance, large surface area and ideal flexibility [1,2]. It has also intrigued great interest in two-dimensional (2-D) nanomaterials, including heteroelemental analogs. Boron nitride nanoflakes (also called 'white graphene') and boron carbon nitrides (BCN) are typical heteroanalogues with better oxidation resistance, higher thermal conductivity, better chemical stability and more excellent mechanical properties than graphene [3–5]. Bulk and layered h-BN exhibit a wide band gap (the band gap is about 5 eV) and have important industrial applications in the fabrication of advanced ceramics, high temperature lubricants and composite materials. The ternary compound of BCN has recently been subject to much attention, because there is a scope for adjusting the electronic properties by changing the stoichiometric ratio of BCN [6]. This has a strong impact on potential applications of these materials in electronic devices [7], electrocatalysis [8], super capacitors [9], and also as extremely small containers for encapsulation [10,11]. Few methods for preparing BCN nanostructures, especially 2-D layered BCN nanoflakes have been reported. The methods include microwave plasma chemical vapor deposition [12], solid state reactions [13] and thermal catalytic approaches [14]. However, these techniques require high synthesis temperature, complicated conditions, or cumbersome catalyst separating process for the final nano-products.

Herein, we have fabricated high purity BCN nanoflakes with bulk quantity through a facile precursor pyrolysis route using synthesized BCN organic precursor. The whole fabrication process is free from catalytic assistance with the advantage of moderate temperature. Most of the BCN nanoflakes were less than 10 nm thick, and consisted of tens of layers. The BCN products possess promising applications as super capacitor electrode owing to their high surface area of 260 $m^2 g^{-1}$. The facile catalyst-free precursor pyrolysis approach might find its application in preparation of other nanoflakes with different characters.

2. Experimental procedure

BCN organic precursor (Eq. (1)) as a starting material was synthesized from Trichloroborazine and Methylaniline (molar ratio 1:1), as described in our previous report [15]. The brown solid precursor was delivered into pressure assisted sintering furnace and slowly heated to 500 °C for 30 min at a heating rate of 3 °C/min, and finally to 1000 °C holding for 1 h at a heating rate of 10 °C/min in a nitrogen atmosphere (1.5 MPa). After that the as-formed black products were ultrasonic dispersed in acetone for 3 h. In the end, the products were collected after removing acetone.



(1)

The morphology of the products was observed using a field emission scanning electron microscopy (SEM, MX2600FE) and high-resolution transmission electron microscopy (HRTEM, Philips Tecnai F30). The chemical characteristics was examined by Fourier transform infrared (FTIR, Bruker VECTOR-22) and X-ray photoelectron

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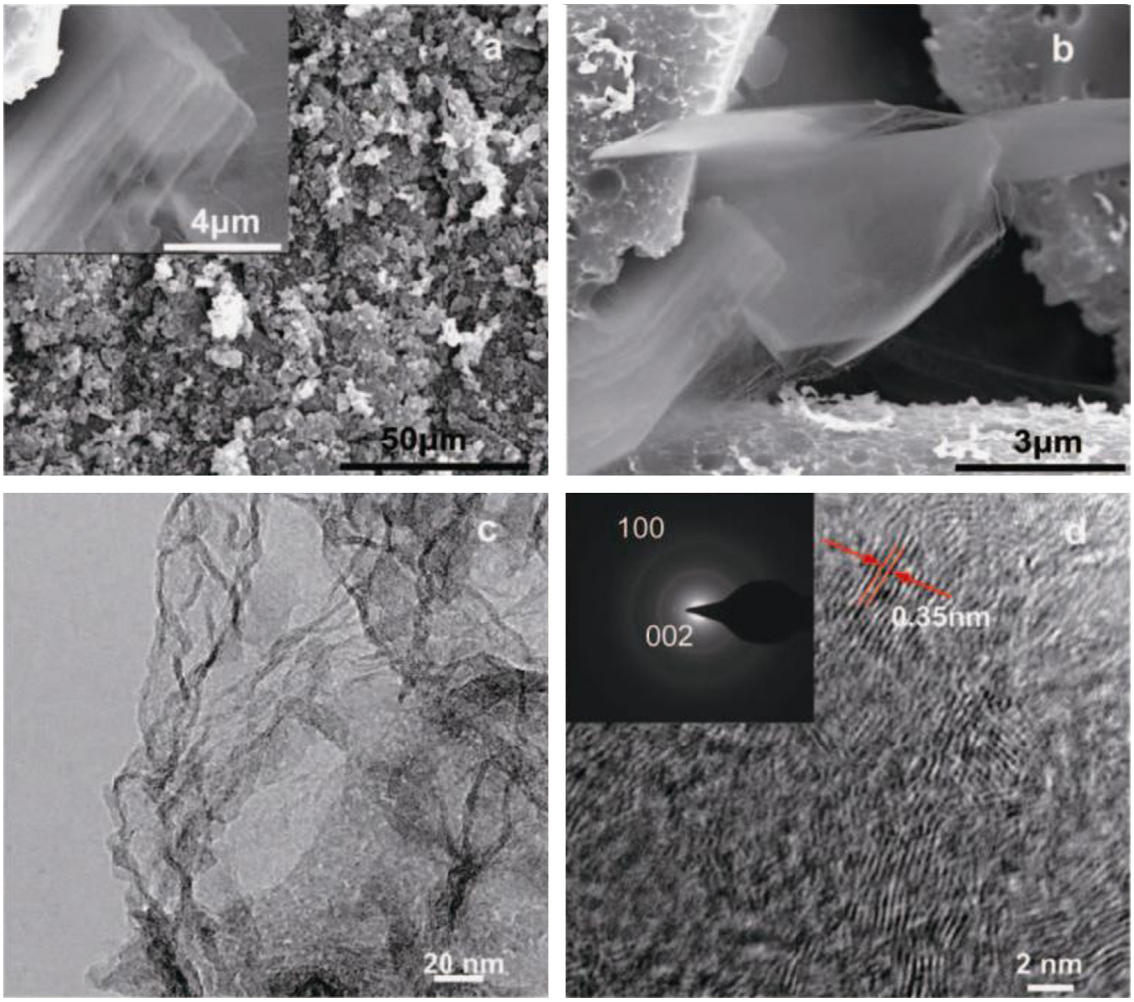

Fig. 1. (a, b) SEM, (c) TEM and (d) HRTEM images of the as-prepared BCN products.

spectrometer (XPS, Physical Electronics PHI 5700 with Mg exciting source) respectively. The structures were examined using RIGAKU D/Max 2000 VPC powder X-ray diffractometer (XRD, CuKα radiation, $\lambda = 1.5418$ Å) and characterized by Raman spectroscopy (Renishaw, RM-1000). Termogravimetric analysis (TGA) was recorded on a NETZSCH STA 449C under ambient atmosphere.

3. Results and discussion

A group of typical SEM and HRTEM images of the as-prepared products is shown in Fig. 1. Fig. 1a displays a representative overview of the BCN architectures, which shows that the as-obtained products are composed of stacked sheet-like architectures with uniform morphology in large scale. The high magnification SEM images (in inset of Fig. 1a and Fig. 1b) show that the stacked flakes have tens of layers with the size of 20 μm and 10 nm in thickness. The TEM image (Fig. 1c) shows the presence of the rippled and entangled BCN layers similar to few-layer graphene [16]. The flakes are transparent and stable under the electron beam. The inset of Fig. 1d shows a selected-area electron diffraction pattern with two rings due to the (002) and (100) reflections of the graphite-structured material. The HRTEM image is shown in Fig. 1d. According to the electron diffraction pattern, we observed the crystallinity of exfoliated BCN layers and the rotational disorder associated with the individual layers in the stacking. It shows that the average inter-layer distance of the BCN is about 0.35 nm which is larger than the typical characteristic of a d_{002} spacing in a hexagonal BN layer (h-BN) [17].

The EDS spectrum (Fig. 2a) of the as-prepared products shows the elements of B, C and N. The FT-IR transmittance spectrum (Fig. 2b) reveals the typical structure of B–N bond according to the wave numbers of 1378 cm^{-1} and 785 cm^{-1} [18].

The XRD pattern of the products is shown in Fig. 2c. The sharp peak at the diffraction angle (2θ) of 26.5° is related to diffractive planes of (002) which index to a hexagonal graphic BN layer (h-BN) structure. Extensive amorphous background and broad peaks at (100), (004) and (110) suggest that the as-prepared products have an incomplete crystallization character along the [10-10] direction of the graphitic flakes. No peaks of any other phases are detected, indicating high purity of the products and consistent with the EDS and FI-IR measurements [19].

The Raman spectrum (Fig. 2d) recorded with the 488 nm wavelength excitation reveals that the products showed characteristic D- and G-bands at 1329 cm^{-1} and 1592 cm^{-1} respectively, indicating the graphitic structure and the existence of B–N bond. The G-band is attributed to the stretching of all sp^2-bonded pairs including C–C, B–C, N–C and B–N, D-band is related to the sp^3 defect or lattice distortion [18] and [20].

To further investigate the structure of the BCN nanoflakes, XPS measurement was performed. The XPS spectra of full range scanning (Fig. 3a) testified the existence of B, C and N in the products. Fig. 3b displays a typical XPS spectrum for B 1s as measured for the products. The binding energy was calibrated with reference to the