Materials Science and Engineering B 199 (2015) 9–14

Contents lists available at ScienceDirect

Materials Science and Engineering B

journal homepage: www.elsevier.com/locate/mseb

A simple one step organic to inorganic pyrolysis route to bulk quantity boron carbonitride/carbon nanocables

T. Zhang [a], Y.P. Wang [a], J.Q. Yang [a], X.X. Huang [b],**, G. Wen [a,b],*

[a] School of Materials Science and Engineering, Harbin Institute of Technology (Weihai), Weihai 264209, PR China
[b] School of Materials Science and Engineering, Harbin Institute of Technology, Harbin 150001, PR China

ARTICLE INFO

Article history:
Received 26 December 2014
Received in revised form 11 April 2015
Accepted 18 April 2015
Available online 21 May 2015

Keywords:
Boron carbonitride/carbon nanocables
Pyrolysis route
Oxidation resistance
Microwave absorption property

ABSTRACT

Bulk quantity boron carbonitride/carbon (BCN/C) nanocables have been successfully synthesized by a simple one step organic compounds pyrolysis route at 1100 °C. The nanocables consist of nanocarbon fibers inside covered by the cylindrical BCN coatings. The characteristics of the surface morphology and the diameters of the nanocables are determined by soaking time. It is demonstrated that the elements of B, C and N are hybridly bonded in the coating. The weight loss of the nanocables is about 12% at 1200 °C which is much better than the substrate carbon nanofibers (CNFs) (more than 20% weight loss at 1200 °C). The minimum reflection coefficient below −20 dB for the products is −24.5 dB at 14.48 GHz indicating good microwave absorption properties. The results suggest that the nanocables are favorable for achieving high performance oxidization resistance and microwave absorption properties.

1. Introduction

Carbon nanocables (CNCs), also described as core-shell structured functional carbon nanofibers (CNFs), have recently been the focus of several studies [1,2], mainly due to their potential applications in field environmental protection [3], semiconductors [4] and electrode materials [5]. CNCs are generally synthesized from chemical vapor deposition [6], dip coating methods [7], but have also been produced by electrospinning deposition [5] and hydrothermal treatment [3]. The structure of CNCs generally consists of a central carbon fiber coated by functional sheath, similar to the structure of vapor-deposited carbon fibers [1]. The properties of semiconductivity and thermal stability for both CNCs and common carbon fibers with functional coatings have been reported [7]. However, the boron carbonitride/carbon (BCN/C) nanocables in bulk quantity have not been reported yet. The hexagonal boron–carbon–nitride (BCN) compounds have attracted considerable attention for potential applications especially in the optoelectronic fields because the band gap of BCN can be adjusted with the compositions [8–11]. BCN compounds also have the advantages of low density and good oxidation resistance property [12–17]. Considering the unique properties of BCN, it is desirable to prepare CNFs with BCN coating which may have potential applications (e.g., applied as high temperature resistance reinforcements and absorption waves materials) due to the chemical and structural similarity of BCN and graphite. Therefore, many efforts have been devoted to fabricate BCN/C nanocables by researchers. Carbothermal synthesis methods [7] and hot-filament chemical vapor deposition [18–20] and are commonly used to prepared coaxial BCN/C materials. However, these methods usually need higher temperature and sophisticated processes, and can not prepare BCN/C core-shell structures in large scale.

In this paper, bulk quantity BCN/C nanocables are prepared by a simple one step organic compounds pyrolysis route. This method could be developed to a universal way to fabricate other BCN coating materials. The as-prepared products show a good oxidation resistance property (only about 12% weight loss at 1200 °C) and excellent microwave absorption property (the reflection loss reaching to about −24.5 dB from 14.48 to 15.2 GHz).

2. Experimental

The BCN organic compounds were synthesized from Boron trichloride (BCl_3) and monomethylaniline (Ph-NH-CH_3) (molar ratio 2:1) at boiling water bath condition for 2 h (The possible reaction of BCl_3 with Ph-NH-CH_3 is formulated in Fig. 1). Then, the brown compounds were delivered into the bottom of an

---

* Corresponding author. Tel.: +86 631 5687305; fax: +86 631 5687305.
** Corresponding author at: School of Materials Science and Engineering, Harbin Institute of Technology, Harbin 150001, PR China. Tel.: +86 451 86418860; fax: +86 451 86413922.
E-mail addresses: swliza@hit.edu.cn (X.X. Huang), g.w.wen.hit@gmail.com (G. Wen).

http://dx.doi.org/10.1016/j.mseb.2015.04.008
0921-5107/© 2015 Elsevier B.V. All rights reserved.

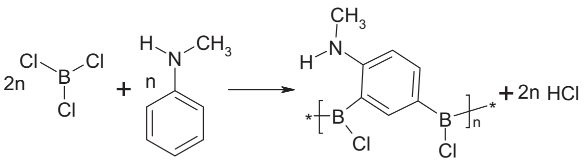

Fig. 1. The possible reaction process of BCl_3 with Ph-NH-CH_3.

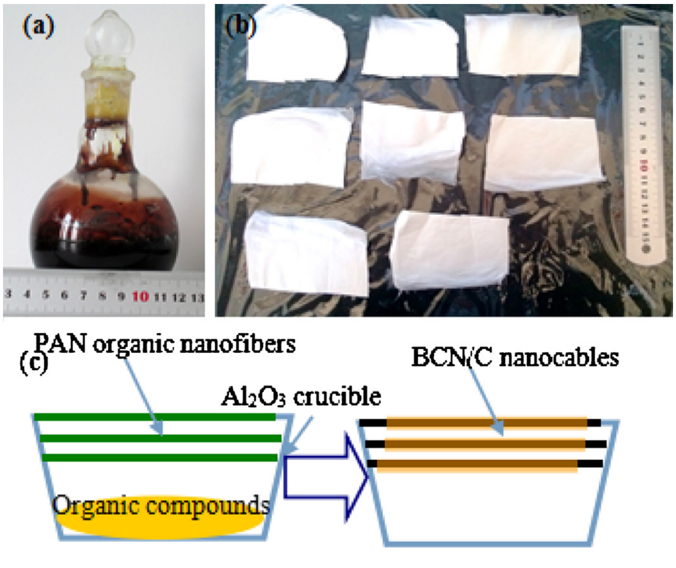

Fig. 2. (a) The as-synthesized organic compounds, (b) the PAN organic nanofibers obtained by electrospinning method, and (c) the sketch diagram to prepare BCN/C nanocables from the organic compounds and PAN nanofibers.

alumina crucible and covered by polyacrylonitrile (PAN) nanofibers prepared by electrospinning (both of the digital images of organic compounds and PAN nanofibers are shown in Fig. 2a and b). After that the crucible was put into a tube furnace and heated to 1100 °C from room temperature at a heating rate of 8 °C/min for 1–2 h in nitrogen atmosphere. The products were grown in situ by the organic precursor of PAN nanofibers and BCN compounds (the color changed from white to black). The fabrication process is shown in Fig. 2c. Fourier transform infrared (FTIR) spectroscopy was performed to examine the chemical structure of the precursor and the products on a VECTOR-22 (Bruker) spectrometer ranging from 400 to 4000 cm^{-1}. Scanning electron microscopy (SEM, MX2600FE) and high-resolution transmission electron microscopy (HRTEM, Philips Tecnai F30) were used to examine the morphology of the products. X-ray photoelectron spectroscopy (XPS, Physical Electronics PHI 5700 with Mg exciting source) and Raman spectroscopy (Renishaw, RM-1000) were performed to research the chemical composition and the structure characteristics, respectively. Thermogravimetric analysis (TGA) was recorded on a NETZSCH STA 449C under ambient atmosphere. Microwave absorption properties were measured by a vector network analyzer (Agilent, N5145A).

3. Results and discussion

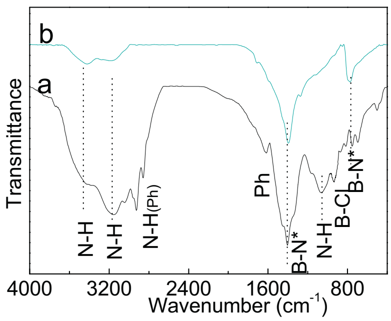

Fig. 3. IR spectra of (a) the synthesized organic compounds and (b) the BCN nanocables.

Fig. 3 shows the FTIR spectra of the organic compounds and the BCN/C products. Fig. 3a (the organic compounds) exhibits the typical absorption peaks of B–N ring at 788 and 1385 cm^{-1}, N–H at 3420, 3200 and 1061 cm^{-1}, B–Cl at 702 cm^{-1}, benzene ring at 1626 cm^{-1}, and (Ph)N–H at 2927 and 2844 cm^{-1}, respectively, indicating the general structure of the organic compounds suggested in Fig. 1. Fig. 3b shows typical peaks of hexagonal B–N binding around 788 cm^{-1} corresponding to out-of-plane vibrations, and the dominant 1385 cm^{-1} peak corresponding to in-plane vibration. A slight shift of the typical hexagonal band from 1375 cm^{-1} for h-BN to 1390 cm^{-1} for h-BCN suggests that there are compositional changes within the basal planes (the B–C–N intermixing in B–N planes). The broad peak from 3420 to 3200 cm^{-1} reveals that the residual N–H bonds may be attached on the surface of as-prepared BCN/C nanocables.

The SEM images of the as-prepared products are shown in Fig. 4. The substrate CNFs (Fig. 4a) derived from PAN nanofibers at 1100 °C for 1 h have smooth surface with uniform diameter about 150–200 nm. Fig. 4b shows the BCN/C nanofibers prepared at 1100 °C for 1 h having uniform diameter about 200–400 nm. The diameter significantly increases to 300–500 nm and the morphology exhibits cross-link structure when the products were prepared for longer soaking time (1.5 h, Fig. 4c). There are some spherical granules attached on the fiber surface with the diameter about hundreds of nanometers when the products were prepared at 1100 °C for 2 h and the diameter of the fiber increases to about 1 μm (Fig. 4d).

To further verify the core–shell structure of the nanofibers, TEM examinations were performed. Fig. 5a shows the typical core–shell structure of the products prepared at 1100 °C for 1 h with a coating thickness about 200 nm. Fig. 5b shows the high magnification TEM image of the nanocables. A very thin transition layer (about 10 nm) is observed between the coating and the substrate fiber suggesting the diffusion zone for B, C and N atoms. The selected-area electron diffraction (SAED) pattern (inset of Fig. 5b) is solely from the B–C–N shell (the red rectangular region). Three rings of the hexagonal BCN phase can be seen in the diffraction pattern indexed to (0 0 2), (0 0 4) and (1 0 0) planes. The BCN (0 0 2) ring corresponding to ∼3.5 Å spacing is not complete (two bright arcs) indicating a strong directionally ordered basal plane structure, composed from graphene like sheets [21]. The width of the BCN (0 0 4) and BCN (1 0 0) rings is typical for nanocrystalline structure. It may indicate that the scale of ordering within the planes is larger than between the planes (the intralayer correlation is in the nm scale, while the interlayer correlation length is smaller). HRTEM image of the coating (Fig. 5c) exhibits the diffraction fringes corresponding to (0 0 2) planes and has an interplanar distance about 0.35 nm which agrees well the SAED results. The ordered lattice fringe regions are about 20 nm according to the HRTEM image indicating the nanocrystalline structure of the coating. It is worth nothing that almost all of the (0 0 2) planes orientate along the axial direction of the fiber, which may contribute higher mechanical performance to the nanocables.

To confirm the chemical composition of the nanocables, an EDS line scan was performed. Fig. 6a shows a dotted line from which the composition profiles across the core-shell boundary regions were obtained and Fig. 6b displays the profiles of C, N and B. From Fig. 6b, no N and B elements were detected from the core region, but there is higher C concentration than the shell regions. Moreover, all the three elements of C, N and B were detected from the shell regions.