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An Efficient Template Synthesis of Aligned Boron Carbide Nanofibers Using a Single-Source Molecular Precursor

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Boron carbide is a highly refractory material that is of great interest for both its structural and electronic properties.[1] Of particular importance are its high-temperature stability, high hardness, high cross section for neutron capture, and excellent high-temperature thermoelectric properties. This combination of properties gives rise to numerous applications, including uses as an abrasive wear-resistant material, ceramic armor, a neutron moderator in nuclear reactors, and, potentially, for power generation in deep-space flight applications.[2] Boron carbide powders can easily be made by carbothermal reduction of boric oxides at high temperatures, but the formation of pure boron carbide in processed forms, such as films and fibers, is difficult. Recently, Zhang et al. discussed the importance of nanoscale boron carbide materials and demonstrated the use of plasma-enhanced chemical vapor deposition to generate boron carbide nanowires and nanonecklaces.[3] Han et al. have also recently reported the formation of mixtures of crystalline boron carbide nanorods and boron-doped nanotubes upon the reaction of boron oxide vapor with carbon nanotubes.[4] In this communication, we report a simple, straightforward method for the generation of aligned, monodispersed boron carbide nanofibers based on the use of the porous alumina templating technique[5] in combination with a new single-source molecular precursor.

We have previously communicated[6] our discovery of a titanium-catalyzed hydroboration reaction of decaborane with 1,5-hexadiene that gives the linked-cage 6,6′-$(CH_2)_6(B_{10}H_{13})_2$ product in high yield (92%). The compound is isolated as an air-stable solid that is highly soluble in organic solvents. The solid melts without decomposition at 96 °C.

$$2B_{10}H_{14} + CH_2{=}CH{-}(CH_2)_2{-}CH{=}CH_2 \xrightarrow{Cp_2Ti(CO)_2} 6,6'\text{-}(CH_2)_6(B_{10}H_{13})_2 \quad (1)$$

As shown in the ORTEP representation in Figure 1, a single-crystal X-ray study[6] of 6,6′-$(CH_2)_6(B_{10}H_{13})_2$ confirmed a linked-cage structure in which the two decaborane cages are joined by the 6-carbon chain that is attached to the 6-boron vertex on each cage.

The B_4:$C_{1.2}$ boron-to-carbon ratio in 6,6′-$(CH_2)_6(B_{10}H_{13})_2$ is close to that of boron carbide (B_4C).[7] This fact, coupled with the potentially high ceramic yields that could be obtained by the ceramic-conversion reaction given in eq 2, suggested to us that this compound might serve as a molecular single−source precursor to boron carbide which would allow the production of the ceramic in forms unattainable with conventional synthetic techniques.

$$6,6'\text{-}(CH_2)_6(B_{10}H_{13})_2 \xrightarrow{\Delta} 5B_4C + CH_4 + 17H_2 \quad (2)$$

$$\text{theoretical ceramic yield: } 84.6\%$$

The TGA study given in Figure 2 of the 6,6′-$(CH_2)_6(B_{10}H_{13})_2$ ceramic-conversion reaction showed that decomposition begins near 220 °C and is essentially complete by 400 °C. The X-ray diffraction (XRD) spectra of bulk powder samples of 6,6′-$(CH_2)_6(B_{10}H_{13})_2$ pyrolyzed at 1000 °C (3 h) indicated that they were amorphous, but powders heated at 1025° (3 h) exhibited a characteristic boron carbide diffraction pattern (JCPDS Card No. 35-0798). Likewise, diffuse reflectance infrared spectra (Figure 3) of powders heated at 1025 °C (3 h) showed the major boron carbide bands near 1550 and 1090 cm^{-1}.[8] Elemental analyses[9] on the 1000 °C (B, 88.39; C, 11.45%) and 1025 °C (B, 89.04; C, 10.76%) pyrolyzed powders showed no measurable hydrogen and established $B_{7.7}C$ and $B_{8.3}C$ compositions, respectively. The boron-to-carbon ratios found in these samples are well within the range of normal compositions observed for boron carbide.[7] Thus, these initial powder studies demonstrated that 6,6′-$(CH_2)_6(B_{10}H_{13})_2$ was, in fact, an excellent precursor to boron carbide and could potentially be used to obtain the ceramic in processed forms.

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(5) For example, see: (a) Martin, C. R. *Science* **1994**, *266*, 1961−1966. (b) Martin, C. R. *Acc. Chem. Res.* **1995**, *28*, 61−68. (b) Martin, C. R. *Chem. Mater.* **1996**, *8*, 1739−1746 and references therein. (c) Lakshmi, B. B.; Patrissi, C. J.; Martin, C. R. *Chem. Mater.* **1997**, *9*, 2544−2550. (d) Cepak, V. M.; Hulteen, J. C.; Che, G.; Jirage, K. B.; Lakshmi, B. B.; Fisher, E. R.; Martin, C. R. *Chem. Mater.* **1997**, *9*, 1065−1067. (e) Che, G.; Lakshmi, B. B.; Martin, C. R.; Fisher, E. R.; Ruoff, R. S. *Chem. Mater.* **1998**, *10*, 260−267. (f) Klein, J. D.; Herrick, R. D., II; Palmer, D.; Sailor, M. J. *Chem. Mater.* **1993**, *5*, 902−904. (g) Zelenski, C. M.; Dorhout, P. K. *J. Am. Chem. Soc.* **1998**, *120*, 734−742. (h) Zhang, Z.; Gekhtman, D.; Dresselhaus, M. S.; Ying, J. *Chem. Mater.* **1999**, *11*, 1659−1665.

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10.1021/cm990657n CCC: $19.00

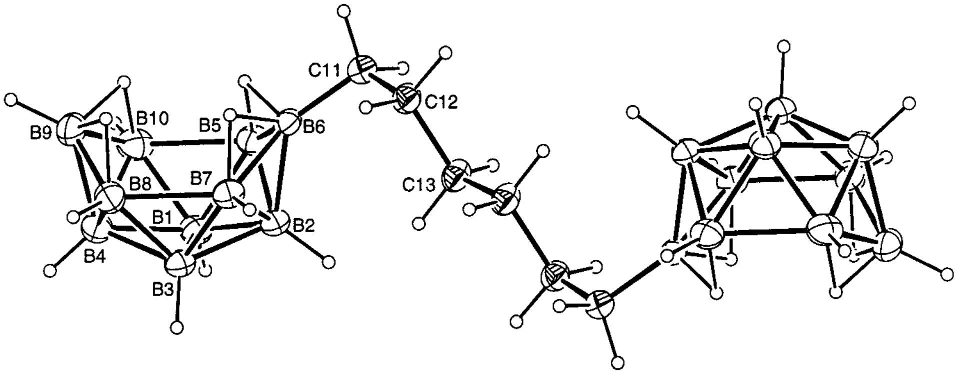

Figure 1. ORTEP Representation of the structure of 6,6′-$(CH_2)_6(B_{10}H_{13})_2$.[6] (Only one of the two independent molecules in the unit cell is shown).

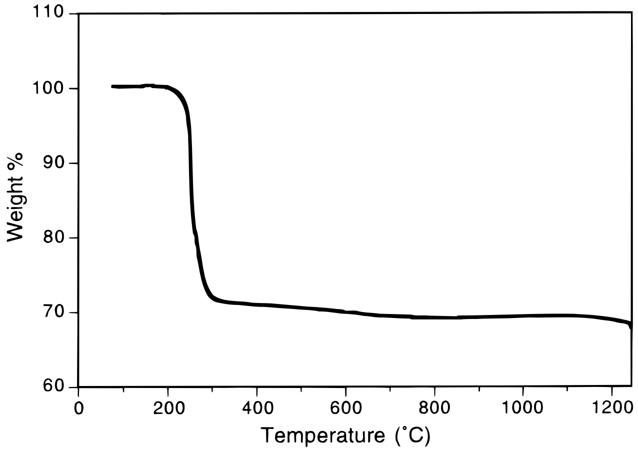

Figure 2. TGA of the ceramic-conversion reaction of 6,6′-$(CH_2)_6(B_{10}H_{13})_2$. (Ramp rate: 10 °C/min under flowing argon).

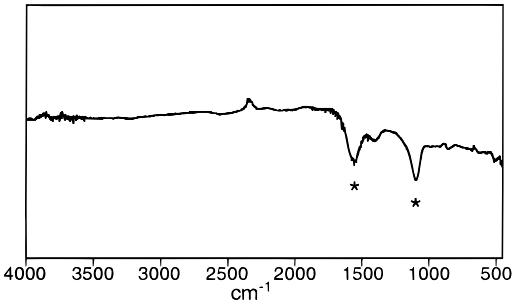

Figure 3. Diffuse reflectance infrared spectrum of a boron carbide powder that was obtained by heating a 6,6′-$(CH_2)_6$-$(B_{10}H_{13})_2$ powder sample at 1025 °C. Major bands characteristic of boron carbide are labeled with an asterisk. The peak at 2333 cm^{-1} is from atmospheric CO_2.

Recently, porous alumina templates have been used to generate nanofibers from a variety of materials including polymers, carbon, metals, semiconductors, and ceramics.[5] This template method involves the absorption of a precursor material into the channels of the nanoporous alumina using either gas-phase (CVD) or solution methods, conversion of the precursors to the final solid-state material by thermolytic or chemical reactions, and then dissolution of the alumina membrane to leave the free-standing fibers. As described below, we have now used this technique to generate boron carbide nanofibers by employing 6,6′-$(CH_2)_6(B_{10}H_{13})_2$ as the precursor.

Alumina membranes (Whatman Anapore filters) having a thickness of 60 μm and a nominal pore size of ~200 nm (±50 nm) were used as the template. Pieces (~0.5 cm^2) of the membranes were immersed in liquid 6,6′-$(CH_2)_6(B_{10}H_{13})_2$ at 140 °C under a flow of nitrogen. Once the membrane was saturated, excess liquid was blotted from one side of the template. The filled templates were transferred to a boron nitride boat and then pyrolyzed in a tube furnace under a flow of high-purity argon to 1025 °C at 10 °/min and held at the final temperature for 3 h. After the sample was cooled overnight under a constant flow of argon, the alumina template was dissolved by immersing the sample in 48% hydrofluoric acid for 36 h. The resulting nanofibers were then washed thoroughly with deionized water, methanol, and acetone and dried overnight at 80 °C. The fact that the fibers were not attacked by the HF treatment is in agreement with the chemical inertness of boron carbide.[10]

Figures 4 and 5 show the scanning electron microscopy (SEM) images (JEOL 6300) of a sample of nanofibers prepared as described above. The fibers appear to be uniform, with an ~250 nm diameter and ~45 μm length. A thin layer of boron carbide was allowed to remain on one end of the fibers. This layer serves to hold the fibers in their parallel arrangement giving the highly aligned, brushlike configuration that is apparent in the figures. Thus, as has been previously noted, one of the advantages of the templating technique over other methods for generating nanofibers is its natural ability to produce aligned, monodispersed ensembles of nanofibers.[5]

Figure 6 shows the X-ray diffraction spectrographs (diffractometer: INEL XRG 3000 generator, CPS 120 detector, Cu Kα radiation) obtained from ~1 mg samples of the nanofibers heated to 1025 (top) and 1000 °C (bottom), respectively. While the 1000 °C fibers are largely amorphous, the observed diffraction pattern for

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(7) Boron carbide B_4C ($B_{12}C_3$) is generally described as being composed of $B_{11}C$ icosahedra with C−B−C intericosahedral chains. However, single-phase boron carbides are also known with carbon concentrations ranging from 8.8 to 20 atom %. This range of concentrations is made possible by the substitution of boron and carbon atoms for one another within both the icosahedra and the three-atom chains.[1,2]

(8) Becher, V. H. J.; Thévenot, F. *Z. Inorg. Allg. Chem.* **1974**, *410*, 274−286.

(9) Elemental analyses were performed at the Nesmeyanov Institute of Organoelement Compounds (Moscow, Russia).

(10) Makarenko, G. N. In *Boron and Refractory Borides;* Matkovich, V. I., Ed.; Springer-Verlag: New York, 1977; p 319.

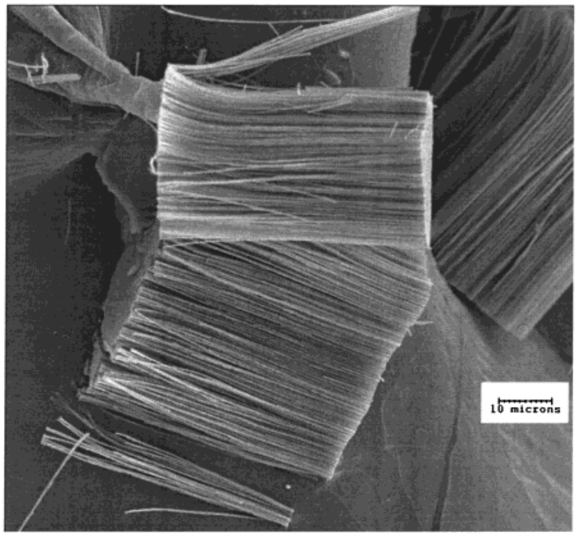

Figure 4. SEM micrograph of aligned boron carbide nanofibers obtained upon pyrolysis of a filled template at 1025 °C, followed by dissolution of the alumina matrix.

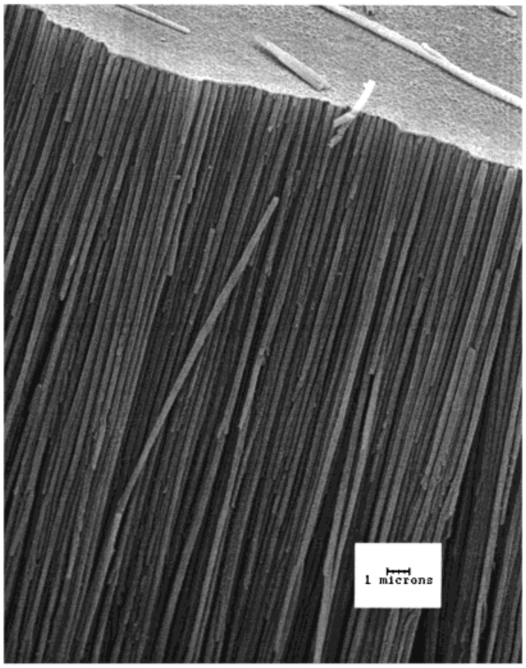

Figure 5. Magnified SEM micrograph of the boron carbide nanofibers shown in Figure 4.

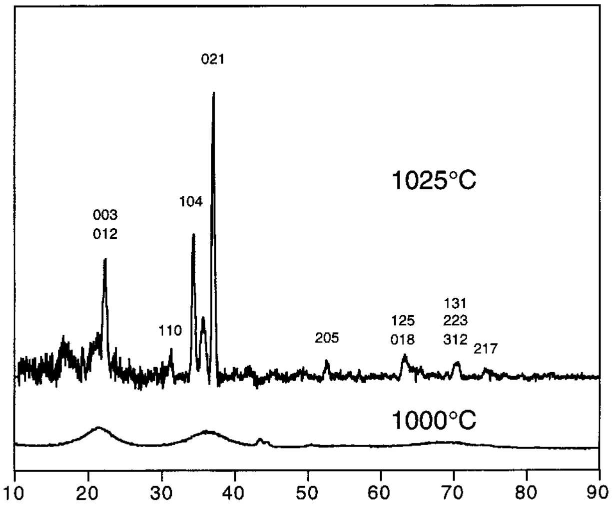

Figure 6. XRD spectra obtained from nanofiber samples after heating at 1000 °C (bottom) and 1025 °C (top). Characteristic boron carbide diffraction peaks are indicated. At higher temperatures, highly crystalline boron carbide is produced and the broad peaks near 21° and 36° 2θ arising from the amorphous phase disappear.

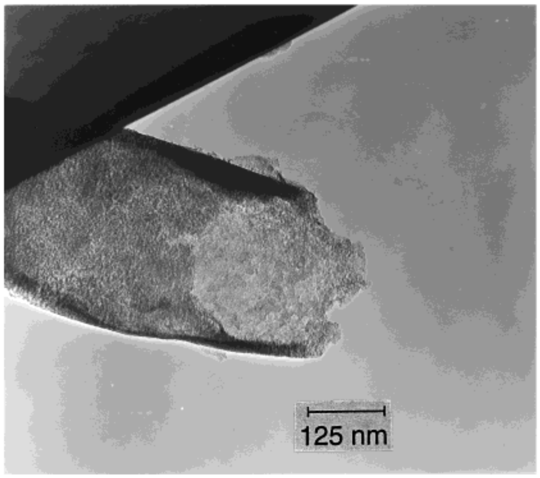

Figure 7. TEM micrograph showing the open end of a boron carbide nanocylindrical structure.

the 1025 °C fibers confirms the onset of boron carbide crystallization. No diffraction is observed in either sample due to the alumina matrix confirming that it has been completely removed by the HF treatment. The observed diffraction patterns for both the 1025 and 1000 °C fibers are identical to those obtained upon heating bulk powder samples of 6,6′-$(CH_2)_6(B_{10}H_{13})_2$ to the same temperatures.

In agreement with the XRD studies, transmission electron microscopy (TEM) (Phillips EM400) analysis confirmed that the nanofibers heated at 1000 °C (3 h) were amorphous, but those taken to 1025 °C (3 h) showed the onset of boron carbide crystallization. The TEM images also showed that while almost all of the nanofibers were solid, there were some, such as shown in Figure 7, that had hollow cores. These nanocylindrical structures probably arise from incomplete filling of a channel in the template by the precursor. Such hollow fiber structures may prove useful for the construction of multicomponent nanofibers, and we are presently exploring the conditions necessary for controlling both nanofiber and nanocylinder formation.

In conclusion, the 6,6′-$(CH_2)_6(B_{10}H_{13})_2$ compound appears to be an ideal precursor for the synthesis of boron carbide nanofibers using the templating technique: (1) it is readily synthesized in large amounts using the titanium-catalyzed reaction; (2) it contains no other ceramic-forming elements and has a desirable boron-to-carbon ratio, thus yielding boron-rich boron carbide compositions upon pyrolysis; (3) it is stable as a melt, allowing it to be absorbed into the membrane without decomposition; and (4) upon pyrolysis, it undergoes a cross-linking reaction at relatively low temperatures (220 °C) that retards loss of material by volatilization, thereby generating high ceramic and chemical yields. The fact that aligned, monodispersed ensembles of boron carbide nanofibers (and potentially nanocylinders) can now be readily obtained will allow a systematic examination of their potential uses in structural and electronic applications. These studies are currently underway and will be reported in future publications.

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