

REPORT DOCUMENTATION PAGE

AFRL-SR-AR-TR-03-

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing the data, this report and the data.

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1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE 24 June 2003		3. REPORT TYPE AND DATES COVERED Final Report 6/15/01-12/31/02	
4. TITLE AND SUBTITLE Chemical Precursor Routes to Ceramic Nanocylinders				5. FUNDING NUMBERS AFOSR Grant F49620-01-1-0443	
6. AUTHOR(S) Larry G. Sneddon					
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) University of Pennsylvania Department of Chemistry 231 South 34 th Street Philadelphia, PA 19104-6323				8. PERFORMING ORGANIZATION REPORT NUMBER 1-2003	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) Air Force Office of Scientific Research Dr. Joan Fuller, Manager Ceramic and Non-Metallic Materials Program 801 N. Randolph Street, room 732 Arlington, VA 22203-1977				10. SPONSORING / MONITORING AGENCY REPORT NUMBER	
11. SUPPLEMENTARY NOTES					
12a. DISTRIBUTION / AVAILABILITY STATEMENT Publicly Available				12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 Words) The objective this AFOSR sponsored project was to design and synthesize new, processable chemical precursors to nonoxide ceramics that allow the formation of the ceramics in nano-structured forms. These studies demonstrated that the use of a suitably designed molecular or polymeric single-source precursor in conjunction with porous alumina nano-templating methods can be used for the systematic generation of aligned, monodispersed ensembles of boron carbide, boron nitride and silicon carbide ceramic nanocylinders. These methods should now be useful for the production of a wide range of nanostructured ceramics.					
14. SUBJECT TERMS ceramics, nanostructures, nanocylinders, nanotubes, boron carbide, boron nitride, silicon carbide				15. NUMBER OF PAGES 6	
17. SECURITY CLASSIFICATION OF REPORT Unclassified				18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	
19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified		20. LIMITATION OF ABSTRACT UL			

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**Summary of Major Research Accomplishments for:
Chemical Precursor Routes to Ceramic Nanocylinders
AFOSR GRANT F49620-01-1-0443**

Larry G. Sneddon

Department of Chemistry
University of Pennsylvania

The objective of our recently completed AFOSR sponsored project was to design and synthesize new, processable chemical precursors to nonoxide ceramics that allow the formation of these materials in nanocylindrical (nanotubular) forms. Our studies that resulted in the formation of nanotubular boron carbide, boron nitride and silicon carbide ceramics are described in the following sections.

Boron Carbide and Boron Nitride Nanocylinders

We have previously shown that polyhexenyldecaborane and 6,6'-(CH₂)₆-(B₁₀H₁₃)₂ (Figure 1) are both excellent precursors to boron carbide that yield carbon-rich (~B₄C) and boron-rich (~B₈C) boron carbide compositions, respectively.^{1,2}

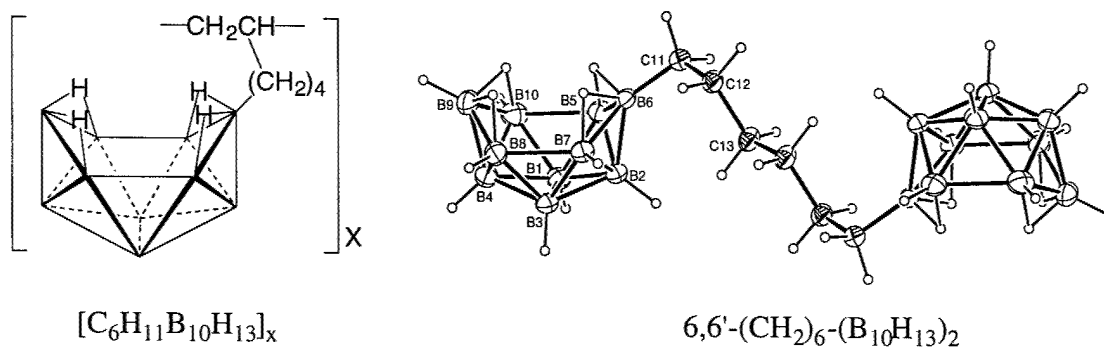


Figure 1. Polymeric and molecular precursors to boron carbide

We also demonstrated that boron carbide nanofibers can be produced via melt infiltration of 6,6'-(CH₂)₆-(B₁₀H₁₃)₂ into porous alumina templates followed by pyrolysis and dissolution of the membranes.² Our AFOSR studies have found^{3,4,5} that ceramic nanotubules can be generated by a procedure (Figure 2) similar to that reported by Martin⁶ for the production of polymer nanotubes. Thus, by using precursor solutions, instead of neat liquid precursors, only the channel walls of the template were coated when these solutions were vacuum filtered through the membranes. Following pyrolysis and subsequent dissolution of the membranes, freestanding nanotubular boron carbide structures were produced.

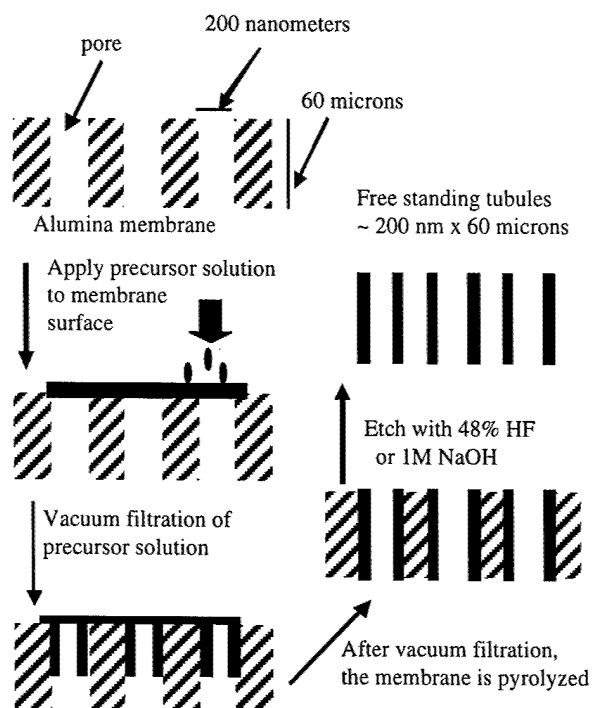


Figure 2. Nanotube Fabrication Method

The SEM image in Figure 3 shows an end view of an ensemble of boron carbide nanotubules that are $\sim 50 \mu\text{m}$ long and $\sim 250 \text{ nm}$ in diameter. Both the SEM image in Figure 3 and the TEM image of a single nanocylinder in Figure 4, clearly show the hollow cores of the tubular structures. The inside diameter and wall thickness of the nanotubules can be controlled by the solution concentration and/or number of membrane treatments.

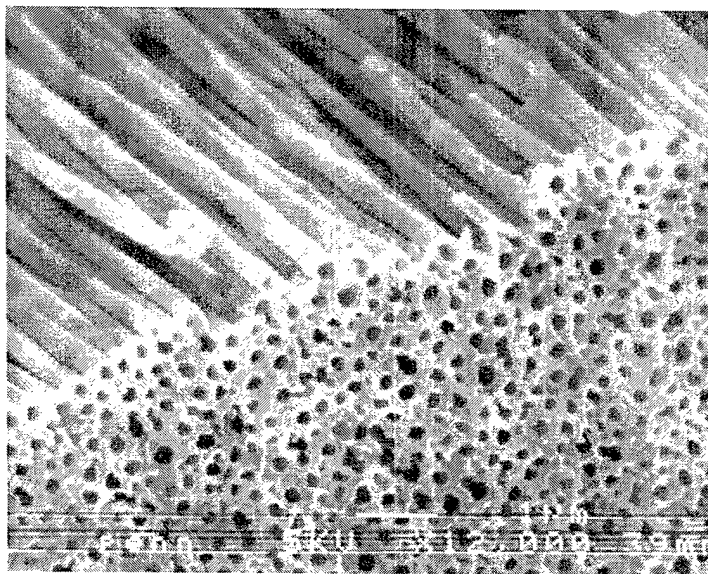


Figure 3. SEM image of boron carbide nanocylinders showing their hollow cores

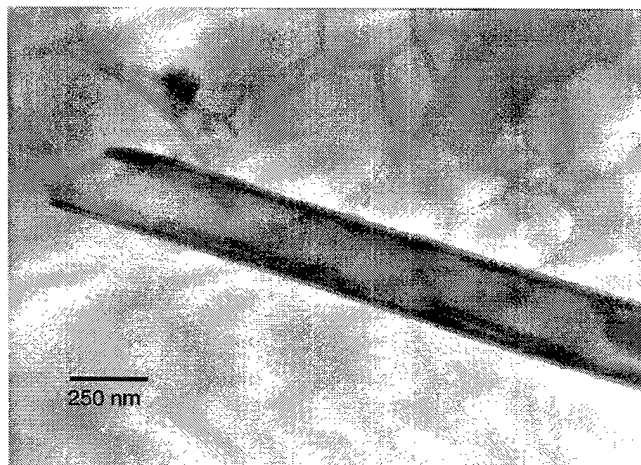


Figure 4. TEM image of a single boron carbide nanotubule

We have also now shown^{4,5} that boron nitride nanotubes can be easily generated by employing our polyborazylene ($B_3N_3H_4$)_x precursor⁷ and the porous alumina templating technique. Thus, following the general procedure outlined in Figure 2, vacuum filtration of a polyborazylene solution through the alumina membranes followed by pyrolysis at 750°C and dissolution of the membranes in 1M NaOH yielded free-standing boron nitride nanotubes. As shown in Figure 5, SEM and TEM analyses confirmed the formation of an aligned ensemble of nanotubes.

Electron diffraction data obtained from these nanotubes ($d = 3.43 \text{ \AA}$ [002], 2.07 \AA [100], 1.24 \AA [110]) were consistent with the formation of turbostratic boron nitride. Likewise, the electron energy loss spectrum (EELS) obtained from a single nanotubule was consistent with a boron nitride composition, showing the K-edges of boron at 190 eV and nitrogen at 400 eV.

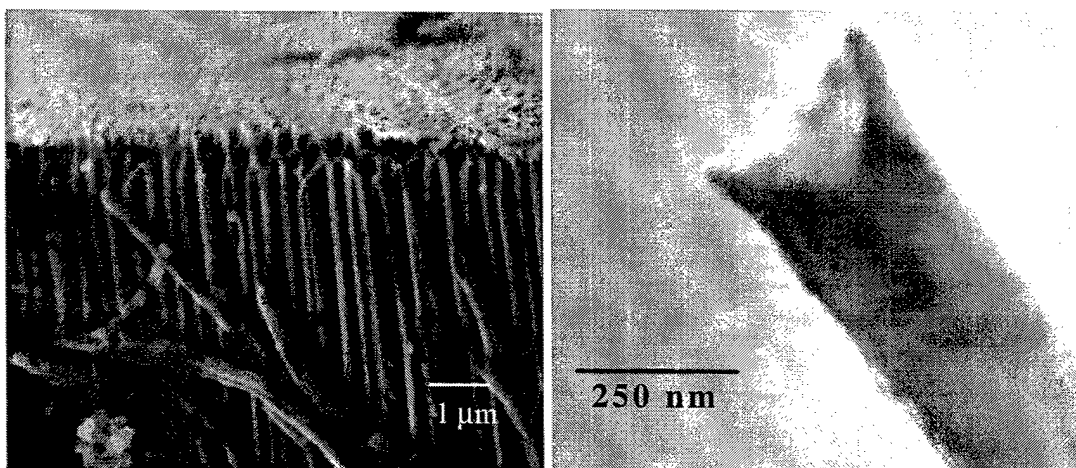


Figure 5. SEM and TEM images of an ensemble of boron nitride nanotubes (left) and a single boron nitride nanotubule (right).

Silicon Carbide Nanocylinders

Allylhydridopolycarbosilane (AHPCS) is a processible silicon carbide precursor that is manufactured by Starfire Systems, Inc.⁸ Again following the procedure outlined in Figure 2, vacuum filtration of AHPCS solutions through alumina membranes followed by pyrolysis to 1025°C and subsequent dissolution of the membranes in 48% HF yielded silicon carbide nanotubules.^{4,5} SEM (Figure 6) and TEM analyses confirm the formation of aligned silicon carbide nanotubular structures.

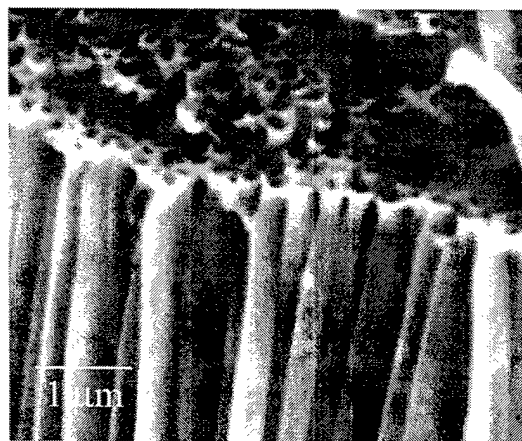


Figure 6. SEM image of an ensemble of silicon carbide nanotubules.

In conclusion, our work has shown that designed molecular and polymeric single-source precursors in conjunction with nano-templating methods enable the systematic generation of aligned, monodispersed ensembles of boron carbide, boron nitride, and silicon carbide nanotubules. We are now investigating the structural and electronic properties of these materials, as well as the use of these template methods for the production of a wide range of other nanostructured ceramics.

Publications resulting from the grant:

1. M. J. Pender, K. Forsthoefel and L. G. Sneddon, The Design, Syntheses and Applications of Group 13 Molecular and Polymeric Precursors to Advanced Ceramics, in Group 13 Chemistry: Fundamental Research, Materials Science and Catalysis, Shapiro, P. and Atwood, D. eds., American Chemical Society Symposium Series, ACS: Washington, D. C., 2002, 168-180.
2. K. M. Forsthoefel, M. J. Pender and L. G. Sneddon, Chemical Precursor Routes to Nanostructured Non-oxide Ceramics, Materials Research Society Proceedings, 2002, 53: 60-64.
3. A. R. Puerta, E. E. Remsen, M. G. Bradley, W. Sherwood and L. G. Sneddon, Synthesis and Ceramic Conversion Reactions of 9-BBN-Modified Allylhydridopolycarbosilane: A New Single-Source Precursor to Boron-Modified Silicon Carbide, *Chem. Mater.*, 2003, 15, 478-485.

4. M. J. Pender, K. M. Forsthoefel and L. G. Sneddon, Molecular and polymeric precursors to boron carbide nanofibers, nanocylinders and nanoporous ceramics, *Pure and Applied Chem.* accepted.