Formation of nanostructured, nanocrystalline boron nitride microparticles with diatom-derived 3-D shapes

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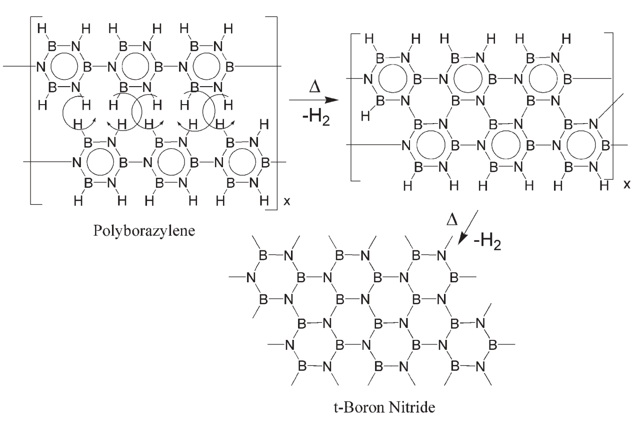
The first use of diatom frustules as shape-dictating 3-D templates for the syntheses of nanostructured, nanocrystalline micro-particles of a non-oxide ceramic, boron nitride, is demonstrated.

The fabrication of advanced nanocrystalline materials with well-defined and controllable micro- and nanoscale features has been of interest for chemical, catalytic, electronic, optical, medical, and environmental applications.[1] While top-down (litho-graphy based)[2] and bottom-up (self-assembly)[3] microfabrication approaches have proven useful for fabricating two-dimensional (2-D) structures and devices, there is still a need for low-cost methods of mass producing complex micro-to-nanoscale structures with a variety of 3-D morphologies and with high degrees of precision, reproducibility, and chemical tailorability. Nature provides numerous examples of fine, intricate 3-D inorganic structures reproduced with high fidelity and in large numbers by micro-organisms.[4] For example, diatoms (unicellular algae) form silica microshells (frustules) with complex, nanostructured 3-D shapes that are faithfully replicated upon cellular reproduction.[5] However, the SiO_2 frustule chemistry has limited the use of these bioclastic structures. Several approaches for altering the diatom frustule chemistry, while preserving the 3-D frustule shapes, have been reported in recent years. Gas/silica displacement reactions[6] have generated 3-D frustule replicas of non-silica-based oxides (*e.g.*, MgO, TiO_2, and ZrO_2). Hydrothermal reactions have been used to convert frustules into silicates and non-silicates (*e.g.*, $BaTiO_3$).[7] Wet chemical coating or impregnation methods, with or without dissolution of the underlying silica frustules, have yielded replicas comprised fully or partially of silicates (*e.g.*, Zn_2SiO_4), other oxides (*e.g.*, ZrO_2, $BaTiO_3$), polymers, carbon, or metals.[8]

Boron nitride is an important technological material with an attractive set of properties,[9] including high thermal conductivity, low electrical conductivity, a low dielectric constant, excellent thermal stability, and resistance to corrosion and oxidation (relative to carbon) for chemical, electrical, structural, and thermal applications (*e.g.*, thermally-conductive fillers in composites, combustion catalyst supports, selective gas adsorbents, corrosion-resistant materials, and electrical insulators).[10] While boron nitride meso- and microparticles with spherical[11] or irregular[10b] shapes have been produced by several methods, the synthesis of nanostructured microparticles of boron nitride (or other non-oxide ceramic particles) in intricate, uniform, and controllably variable 3-D shapes has not been demonstrated.

Owing to its solubility, low-temperature decomposition, high ceramic (84–93%) and chemical (89–99%) yields, and an efficient two-dimensional cross-linking ceramic conversion process (Scheme 1), polyborazylene[12] is an attractive chemical precursor for synthesizing turbostratic BN. Prior work has shown that conformal coatings of polyborazylene may be synthesized on nano-porous alumina and silica bead templates. Subsequent firing and selective template removal then yielded micro-to-nanoscale boron nitride fibers, cylinders, and porous materials.[13] Unfortunately, synthetic templates with a diverse, but controlled range of complex 3-D morphologies and nanoscale features that can be reproduced precisely, on a large scale, and at low cost are not widely available. However, the frustules of diatoms may be utilized as microscale nanostructured templates with intricate and replicable shapes. Each diatom species forms a frustule with a particular 3-D shape and with precise patterns of fine features (*e.g.* nanoscale pores, channels, and protuberances).[5] The tens of thousands of extant diatom species provide a rich variety of template morphologies.[5] Sustained reproduction of a given diatom species can yield enormous numbers of daughter diatoms with frustules of identical shape (*e.g.* 40 sustained reproduction cycles can yield 2^{40}, or more than 1 trillion, frustule replicas from a parent diatom).[14] We show here, for the first time, that the polyborazylene precursor can be used to synthesize conformal coatings of boron nitride on diatom frustules. Subsequent dissolution of the underlying frustules then yield freestanding

$$[B_3N_3H_{\sim 4}]_x \longrightarrow 3\,BN + 2\,H_2 \qquad (1)$$



Scheme 1 Schematic illustration of the conversion of the polyborazylene precursor into boron nitride

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boron nitride particles with micro- and nano-scale features inherited from the starting frustule templates.

Representative secondary electron (SE) images of silica-based frustules of the *Aulacoseira* diatom used in this work are shown in Fig. 1(a) and (b). *Aulacoseira* frustules are cylindrical in shape, with rows of fine pores (several hundred nm in diameter) and narrow V-shaped channels present on the cylinder sidewalls. Each complete frustule was comprised of two cylindrical half-frustules joined end-to-end. The complete frustules were ~15 μm in length and ~10–12 μm in diameter. A SE image of a frustule after ion milling (Fig. 1(b)) revealed the surface morphology of the inner walls. The rows of fine pores detected on the outside frustule surface can be seen to penetrate through the thickness of the frustule wall.

Boron nitride microparticles with morphologies derived from *Aulacoseira* frustules were generated by: (i) vacuum filtering a dilute solution of polyborazylene in glyme through the frustule templates, (ii) pyrolysis of the coated frustules at 1250 °C, and (iii) dissolution of the underlying silica in a 48% HF solution.† Fig. 1(c) shows a representative SE image of a conformal boron nitride coating on an *Aulacoseira* frustule (prior to etching). Silica dissolution yielded freestanding boron nitride microparticles (Fig. 1(d) and (e)) that are negative replicas of the inside structure of the starting frustules. Consistent with the dimensions of the starting half frustules, the inverse replicas were 6 μm in length and ~8–10 μm in diameter. The rows of protrusions, with fine features between 100–200 nm, as indicated by arrows in Fig. 1(d) and 1(e), corresponded to infiltrated pores in the frustule templates that were converted into boron nitride. The boron nitride microparticles thus possessed surface features that were negative replicas of features of the starting frustules. A SE image of an ion-milled section of a boron nitride microparticle is shown in Fig. 1(f). The microparticles retained the hollow, thin-walled morphology of the starting frustules.

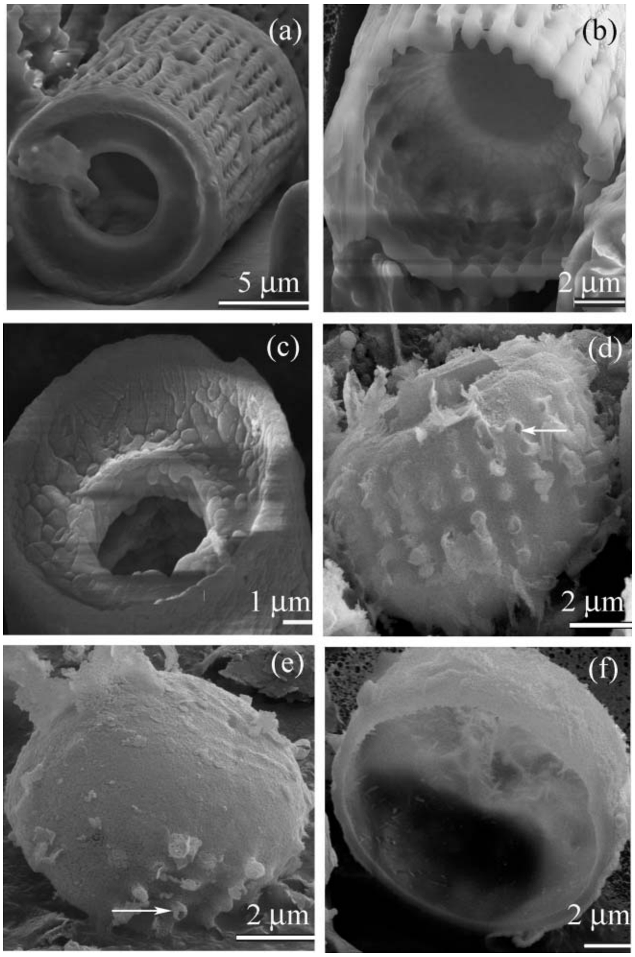

Fig. 1 SE images of: (a) a cylindrical *Aulacoseira* frustule; (b) an ion-milled section of the frustule revealing the inner wall morphology; (c) the frustule with a boron nitride coating; (d) and (e) free-standing boron nitride microparticles obtained as negative replicas after etching with 48% HF; and (f) an ion-milled section of the boron nitride microparticle.

The boron nitride microparticles were evaluated with X-ray diffraction (XRD), diffuse-reflectance infrared Fourier-transform (DRIFT), energy-dispersive X-ray (EDX), and high-resolution transmission electron microscope (HRTEM) analyses. XRD analysis (Fig. 2(a)) revealed diffraction peaks characteristic[15] of turbostratic BN. Scherrer analyses of these peaks yielded an average crystallite size of ~5 nm. HRTEM analysis (Fig. 2(b)) of an ion-milled cross-section revealed lattice fringes (~0.33 nm spacing) indicative of turbostratic boron nitride.[15] The DRIFT spectrum exhibited a broad B–N stretch at ~1460 cm^{-1} and a B–N–B bending vibration at ~800 cm^{-1}. EDX analysis revealed characteristic peaks for boron (0.18 keV) and nitrogen (0.39 keV).

The unique hollow interior, and the nanometer-scaled channels on the walls of the boron nitride microparticles, can be useful for a number of applications, such as in the formation of ceramic or polymer matrix composites. SiC/BN composites[16] have been shown to exhibit enhanced mechanical properties (*e.g.*, increased toughness due to crack deflection), increased thermal conductivity, and improved corrosion resistance. To demonstrate the feasibility of preparing a composite comprised of boron nitride frustule replicas within a SiC matrix, a mixture of 20 wt% boron nitride frustule replicas in neat allylhydridopolycarbosilane (AHPCS,[17] a precursor to SiC) was prepared.‡ The AHPCS filled the interiors of the hollow BN microcylinders, which remained dispersed in the AHPCS.

The mixture was then fired at 1450 °C and the resulting composite was characterized by SEM, DRIFT, XRD and EDX. SE images (Fig. 3(a)) revealed cylindrical boron nitride particles, as indicated by the arrows, dispersed in the silicon carbide matrix composite. A backscattered electron (BSE) image of a section of the composite (Fig. 3(b)) indicated that the fine structural features of the boron nitride microparticles were also retained in the

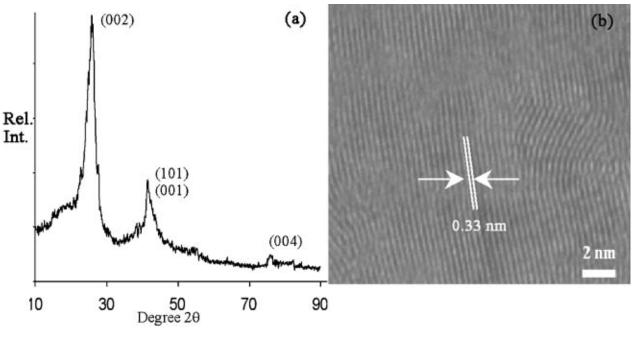

Fig. 2 (a) XRD and (b) HRTEM analyses of BN replicas synthesized by coating with polyborazylene, firing at 1250 °C, and dissolution of the silica.

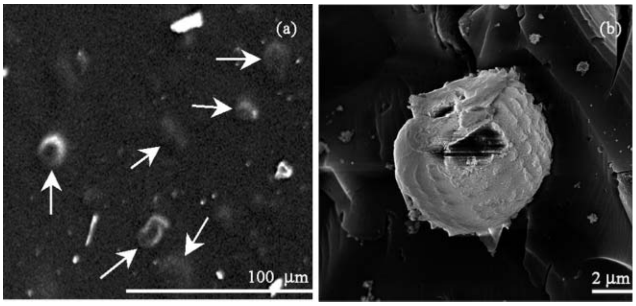

Fig. 3 (a) SE and (b) BSE images of a SiC/BN composite after ceramic conversion at 1450 °C (the arrows in (a) indicate embedded boron nitride microparticles).

composite. The XRD, EDX, and DRIFT spectra exhibited characteristic peaks for β-SiC and BN.

In summary, nanostructured, nanocrystalline boron nitride microparticles with diatom frustule-derived 3-D morphologies have been synthesized for the first time. These negative replicas inherited the hollow cylindrical shape and fine surface features of the starting frustules. This conformal coating methodology may now enable the large scale, reproducible syntheses of nanostructured non-oxide ceramic microparticles with well-controlled 3-D morphologies for use as reinforcements in advanced ceramic– or polymer–matrix composites.

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Notes and references

† *Preparation of boron nitride microparticles*: The *Aulacoseira* frustules (diatomaceous earth) were initially heated at 600 °C for 8 h in air to pyrolyze any organic material. The diatom frustules were then immersed in 3–10% w/w glyme solution of polyborazylene. After stirring under an inert atmosphere for ~2 h, the solution was removed by vacuum filtration and the coated frustules were dried overnight under high vacuum. The frustules were transferred, under an inert atmosphere, into a boron nitride boat and placed in a tube furnace flushed with high purity argon. The sample was then heated under argon to 1250 °C at 10 °C min^{-1} and held at temperature for 4 h before cooling to room temperature. The underlying silica templates were then dissolved by immersing the sample in a 48% hydrofluoric acid solution for 0.5 h. The resulting boron nitride replicas were then washed thoroughly with deionized water, methanol, and acetone and dried overnight at 80 °C.

‡ *Preparation of composite*: A SiC/BN composite containing ~20% w/w BN was prepared by dispersing 0.16 g of the boron nitride microcylinders in 1.0 g of AHPCS under argon. The mixture was first stirred for ~0.3 h and then sonicated for ~10 min before it was transferred into a boron nitride boat and placed in a tube furnace flushed with high purity argon. The sample was heated under argon to 1450 °C at 10 °C min^{-1} and held at temperature for 4 h before cooling to room temperature. The AHPCS-BN derived SiC-BN composite was obtained as shiny black pieces (1–2 mm).

1 (*a*) L. Kiwi-Minsker and A. Renken, *Catal. Today*, 2005, **110**, 2; (*b*) A. C. Richards Grayson, R. S. Shawgo, A. M. Johnson, N. T. Flynn, Y. Li, M. J. Cima and R. Langer, *IEEE Proc.*, 2004, **92**, 6; (*c*) A. J. Baeumner, *Anal. Bioanal. Chem.*, 2003, **377**, 434; (*d*) S. R. Quake and A. Scherer, *Science*, 2000, **290**, 1536.

2 (*a*) R. Menon, A. Patel, D. Gil and H. I. Smith, *Mater. Today*, 2005, **8**, 26; (*b*) L. B. Zhang, J. X. Shi, J. L. Yuan, S. M. Ji and M. Chang, *Mater. Sci. Forum*, 2004, **471–472**, 353; (*c*) Q. Tang, S.-Q. Shi and L. M. Zhou, *J. Nanosci. Nanotechnol.*, 2004, **4**, 948; (*d*) A. A. Tseng, *J. Micromech. Microeng.*, 2004, **14**, R15.

3 (*a*) M. Alexe and D. Hesse, *J. Mater. Sci.*, 2006, **41**, 1; (*b*) C. Park, J. Yoon and E. L. Thomas, *Polymer*, 2003, **44**, 6725; (*c*) R. R. A. Syms, E. M. Yeatman, V. M. Bright and G. M. Whitesides, *J. Microelectromech. Syst.*, 2003, **12**, 387.

4 (*a*) J. Aizenberg, J. C. Weaver, M. S. Thanawala, V. C. Sundar, D. E. Morse and P. Fratzl, *Science*, 2005, **309**, 275; (*b*) E. Bauerlein, *Angew. Chem., Int. Ed.*, 2003, **42**, 614; (*c*) J. Aizenberg, A. Tkachenko, S. Weiner, L. Addadi and G. Hendler, *Nature*, 2001, **412**, 819; (*d*) S. Mann and G. A. Ozin, *Nature*, 1996, **382**, 313.

5 (*a*) S. A. Crawford, M. J. Higgins, P. Mulvaney and R. Wetherbee, *J. Phycol.*, 2001, **37**, 543; (*b*) F. E. Round, R. M. Crawford and D. G. Mann, *The Diatoms: Biology and Morphology of the Genera*, Cambridge University Press, Cambridge, UK, 1990; (*c*) J. C. Lewin and R. R. L. Guillard, *Annu. Rev. Microbiol.*, 1963, **17**, 373.

6 (*a*) K. H. Sandhage, *US Pat.*, 7,067,104, June, 27, 2006; (*b*) S. Shian, Y. Cai, M. R. Weatherspoon, S. M. Allan and K. H. Sandhage, *J. Am. Ceram. Soc.*, 2006, **89**, 694; (*c*) Y. Cai, S. M. Allan, K. H. Sandhage and F. M. Zalar, *J. Am. Ceram. Soc.*, 2005, **88**, 2005; (*d*) R. R. Unocic, F. M. Zalar, P. M. Sarosi, Y. Cai and K. H. Sandhage, *Chem. Commun.*, 2004, 796; (*e*) K. H. Sandhage, M. B. Dickerson, P. M. Huseman, M. A. Caranna, J. D. Clifton, T. A. Bull, T. J. Heibel, W. R. Overton and M. A. Schoenwaelder, *Adv. Mater.*, 2002, **14**, 429.

7 (*a*) M. W. Anderson, S. M. Holmes, N. Hanif and C. S. Cundy, *Angew. Chem., Int. Ed.*, 2000, **39**, 2707; (*b*) Y. Cai, M. R. Weatherspoon, E. Ernst, M. S. Haluska, R. L. Snyder and K. H. Sandhage, *Ceram. Eng. Sci. Proc.*, 2006, **27**, 49; (*c*) W. Shan, Y. Zhang, Y. Wang, J. Xia and Y. Tang, *Chem. Lett.*, 2004, **33**, 270.

8 (*a*) J. Zhao, C. S. Gaddis, Y. Cai and K. H. Sandhage, *J. Mater. Res.*, 2005, **20**, 282; (*b*) C. S. Gaddis and K. H. Sandhage, *J. Mater. Res.*, 2004, **19**, 2541; (*c*) M. R. Weatherspoon, M. S. Haluska, Y. Cai, J. S. King, C. J. Summers, R. L. Snyder and K. H. Sandhage, *J. Electrochem. Soc.*, 2006, **153**, H34; (*d*) Y. Cai and K. H. Sandhage, *Phys. Status Solidi A*, 2005, **202**, R105; (*e*) N. L. Rosi, C. S. Thaxton and C. A. Mirkin, *Angew. Chem., Int. Ed.*, 2004, **43**, 5500; (*f*) X. Cai, G. Zhu, W. Zhang, H. Zhao, C. Wang, S. Qiu and Y. Wei, *Eur. J. Inorg. Chem.*, 2006, **18**, 3641; (*g*) S. M. Holmes, B. E. Graniel-Garcia, P. Foran, P. Hill, E. P. L. Roberts, B. H. Sakakini and J. M. Newton, *Chem. Commun.*, 2006, 2662.

9 (*a*) R. Haubner, M. Wilhelm, R. Weissenbacher and B. Lux, *Struct. Bonding (Berlin)*, 2002, **102**, 1; (*b*) R. T. Paine and C. K. Narula, *Chem. Rev.*, 1990, **90**, 73.

10 (*a*) J. F. Janik, W. C. Ackerman, R. T. Paine, D.-W. Hua, A. Maskara and D. M. Smith, *Langmuir*, 1994, **10**, 514; (*b*) G. Postole, M. Caldararu, N. I. Ionescu, B. Bonnetot, A. Auroux and C. Guimon, *Thermochim. Acta*, 2005, **434**, 150; (*c*) N. G. Chopra, R. J. Luyken, K. Cherrey, V. H. Crespi, M. L. Cohen, S. G. Louie and A. Zettl, *Science*, 1995, **269**, 966.

11 (*a*) G. L. Wood and R. T. Paine, *Chem. Mater.*, 2006, **18**, 4716; (*b*) G. L. Wood, J. F. Janik, E. A. Pruss, D. Dreissig, W. J. Kroenke, T. Habereder, H. Noth and R. T. Paine, *Chem. Mater.*, 2006, **18**, 1434; (*c*) G. L. Wood, J. F. Janik, M. Z. Visi, D. M. Schubert and R. T. Paine, *Chem. Mater.*, 2005, **17**, 1855; (*d*) E. A. Pruss, G. L. Wood, W. J. Kroenke and R. T. Paine, *Chem. Mater.*, 2000, **12**, 19; (*e*) T. Chengchun, Y. Bando and D. Golberg, *Chem. Commun.*, 2002, 2826.

12 (*a*) P. J. Fazen, J. S. Beck, A. T. Lynch, E. E. Remsen and L. G. Sneddon, *Chem. Mater.*, 1990, **2**, 96; (*b*) P. J. Fazen, E. E. Remsen, J. S. Beck, P. J. Carroll, A. R. McGhie and L. G. Sneddon, *Chem. Mater.*, 1995, **7**, 1942.

13 (*a*) K. M. Forsthoefel, M. J. Pender and L. G. Sneddon, *Mater. Res. Soc. Symp. Proc.*, 2002, **728**, 53; (*b*) L. G. Sneddon, M. J. Pender, K. M. Forsthoefel, U. Kusari and X. Wei, *J. Eur. Ceram. Soc.*, 2005, **25**, 91.

14 (*a*) T. Lebeau and J. M. Robert, *Appl. Microbiol. Biotechnol.*, 2003, **60**, 612; (*b*) V. Martin-Jezequel, M. Hildebrand and M. A. Brzezinski, *J. Phycol.*, 2000, **36**, 821.

15 F. Xu, Y. Xie, X. Zhang, S. Zhang, T. Liu and X. Tian, *Inorg. Chem.*, 2004, **43**, 822.

16 (*a*) T. Kusunose, *J. Ceram. Soc. Jpn.*, 2006, **114**, 167; G. W. Lee, M. Park, J. Kim, J. L. Lee and H. G. Yoon, *Composites, Part A*, 2006, **37**, 727; (*b*) K. Moraes, J. Vosburg, D. Wark, L. V. Interrante, A. R. Puerta, L. G. Sneddon and M. Narisawa, *Chem. Mater.*, 2004, **16**, 125.

17 C. W. Whitemarsh and L. V. Interrante, *Organometallics*, 1991, **10**, 1336.