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14. ABSTRACT

Numerous examples can be found in nature of microorganisms that assemble oxide nanoparticles into rigid (bioclastic) microstructures with intricate, but well-controlled 3-D shapes and fine (nanoscale) features. Because such self-assembly is under genetic control, a given microorganism can generate bioclastic replicas with a high degree of fidelity upon biological reproduction. Continuous reproduction (repeated doubling) of such micro-organisms can yield enormous numbers of identically-shaped bioclastic structures. Such genetically-precise and massively-parallel self-assembly is a highly-attractive means of generating large quantities of ceramic particles with complex and well-defined shapes. However, natural bioclastic compositions (amorphous SiO_2, $CaCO_3$) are not well-suited for high-temperature applications. This research is focused on the shape-preserving chemical conversion of natural, bioclastic structures into alumina and other refractory ceramics.

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REACTIVE CONVERSION OF BIOCLASTIC NANOSTRUCTURES
AFOSR GRANT NUMBER FA9550-04-1-0404

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Abstract

Numerous examples can be found in nature of microorganisms that assemble oxide nanoparticles into rigid (bioclastic) microstructures with intricate, but well-controlled 3-D shapes and fine (nanoscale) features. Because such self-assembly is under genetic control, a given microorganism can generate bioclastic replicas with a high degree of fidelity upon biological reproduction. Continuous reproduction (repeated doubling) of such microorganisms can yield enormous numbers of identically-shaped bioclastic structures. Such genetically-precise and massively-parallel self-assembly is a highly-attractive means of generating large quantities of ceramic particles with complex and well-defined shapes. However, natural bioclastic compositions (amorphous SiO_2, $CaCO_3$) are not well-suited for high-temperature applications. This research is focused on the shape-preserving chemical conversion of natural, bioclastic structures into alumina and other refractory ceramics.

Research Objectives

The objectives of this research are: i) to develop methods for converting nanoparticle-based bioclastic assemblies into other, refractory ceramics while preserving the intricate 3-D morphologies of these structures, and ii) to develop a better understanding of the structural/chemical evolution associated with such shape-preserving chemical conversion.

Results and Discussion

Bioclastic Preforms: Silica-based Diatom Frustules

The bioclastic structures utilized in this research are the microshells (frustules) of diatoms (a type of single-celled aquatic algae). Each diatom generates an intricate microscale frustule comprised of a nanoporous assemblage of silica nanoparticles [1-3]. The 3-D shapes and fine features (10^2 nm pores, channels, protuberances) of diatom frustules are species specific [1-3]. Indeed, a spectacular variety of frustule shapes are formed among the various diatom species. The frustules of 30 diatom species are illustrated in Figure 1a below [1]. The co-continuous nature of the pores and silica particles, the aspected shapes, and (in some cases) the intercalating/interlocking features of diatom frustules are among the unique characteristics of these freestanding microstructures that may be exploited in applications.

The frustules of *Aulacoseira* diatoms (obtained in the form of diatomaceous earth powder from a local vendor) have been the predominant diatom preforms utilized in the work to date. Representative secondary electron (SE) images of *Aulacoseira* frustules are shown in Figures 1b and 1c. These frustules were cylindrical in shape. The sidewalls of the frustules were decorated with rows of fine pores (several hundred nanometers in diameter). End faces of these frustules possessed a circular hole with a protruding outer rim. The other end of these

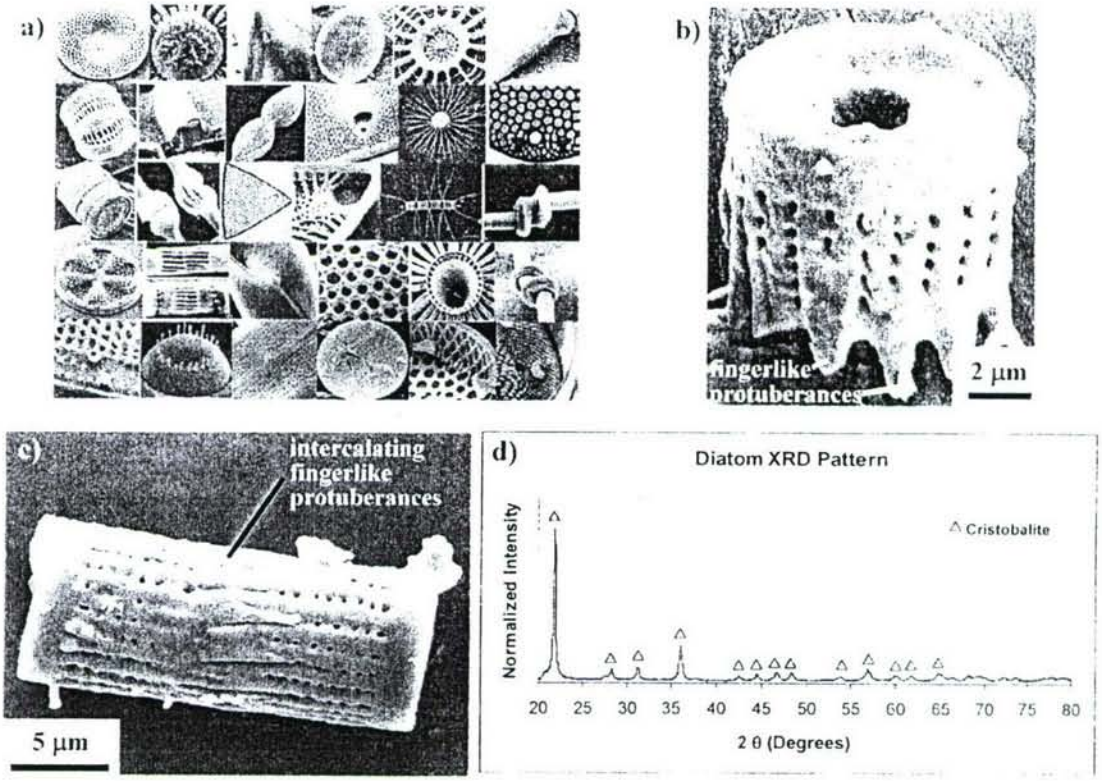


Figure 1. a) SE images of SiO_2-based microshells (frustules) associated with 30 diatom species (assembled by M. Hildebrand, Univ. California at San Diego, from images in [1]); b), c) SE images of *Aulacoseira* frustules (obtained as flame-polished diatomaceous earth powder from a local vendor); d) XRD pattern obtained from *Aulacoseira* diatom frustules.

frustules was closed and possessed finger-like protuberances. The protuberances from one cylinder were often observed to intercalate with those of another to form larger, paired assemblies (Figure 1c). X-ray diffraction (XRD) analyses revealed peaks for cristobalite (note: these frustules were obtained as flame-polished diatomaceous earth). Energy-dispersive x-ray (EDX) analyses also confirmed the silica-based composition of the frustules.

The culturing of several other diatom species has also been successfully conducted over the past year, in order to allow for frustule templates with a variety of selected shapes and with more intricate nanoscale features (i.e., by avoiding the sintering and distortion of native frustules due to flame polishing). SE images of several cultured diatom frustules are shown in Figure 2. Since flame polishing was not conducted, the silica within these frustules was amorphous. Work has just begun on the use of these frustules in the reactive conversion and conformal coating approaches discussed below. Preliminary work indicates that these pristine structures are more reactive than the flame-polished *Aulacoseira* frustules discussed below.

Reactive Conversion into Al_2O_3 Frustule Replicas

A two-step reaction-based approach has been examined for converting silica-based diatom frustules into alumina replicas: i) conversion of the frustules into MgO-based replicas, and then ii) conversion of the MgO into Al_2O_3 replicas. Prior AFOSR-supported research has

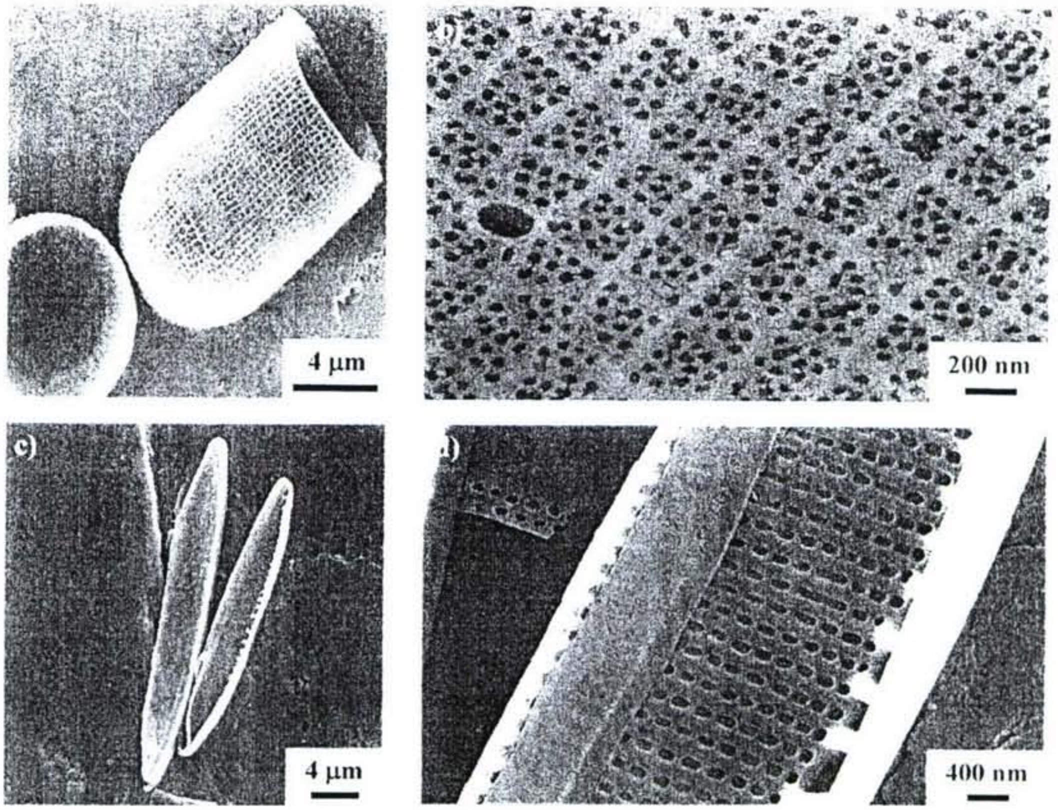


Figure 2. SE images of diatom frustules cultured at Georgia Tech.: a), b) *Melosira nummuloides*, and c), d) *Nitzschia alba*.

shown that diatom frustules can be converted into MgO, without losing the frustule shape or features, via the net reaction [4]:

$$2Mg(g) + SiO_2(s) \Rightarrow 2MgO(s) + \{Si\} \qquad (1)$$

where {Si} refers to silicon present in elemental form, within Mg_2Si, or within a Mg-Si liquid (note: the latter two phases can form upon continued reaction of the silicon product with excess Mg(g)). While the Mg-Si liquid has been found to sweat away from the reacted MgO-based frustules, solid Si and Mg_2Si products remain entrapped within the reacted frustules. Over the past year, reaction conditions have been further optimized, and a selective etching treatment has been developed, to remove these undesired silicon-bearing products from the MgO-bearing frustules. The magnesia-based frustules were then exposed to aluminum chloride vapor to allow for the following net metathetic reaction:

$$2AlCl_3(g) + 3MgO(s) \Rightarrow Al_2O_3(s) + 3\{MgCl_2\} \qquad (2)$$

where $\{MgCl_2\}$ refers to magnesium chloride dissolved within a $MgCl_2$-rich liquid. The formation of Al_2O_3 over a range of reaction conditions (reactant ratios, temperatures, times) has been examined. A SE image of a fully-converted alumina replica is shown in Figure 3a. An EDX pattern obtained from this replica is presented in Figure 3b. Little, if any, magnesium was detected in the converted frustule. XRD analyses confirmed the absence of MgO, and indicated that this frustule was comprised of a mixture of γ-Al_2O_3 and α-Al_2O_3. The conditions leading to pure γ-Al_2O_3 (e.g., for catalytic applications) or pure α-Al_2O_3 (e.g., for high-temperature applications) are currently under investigation.

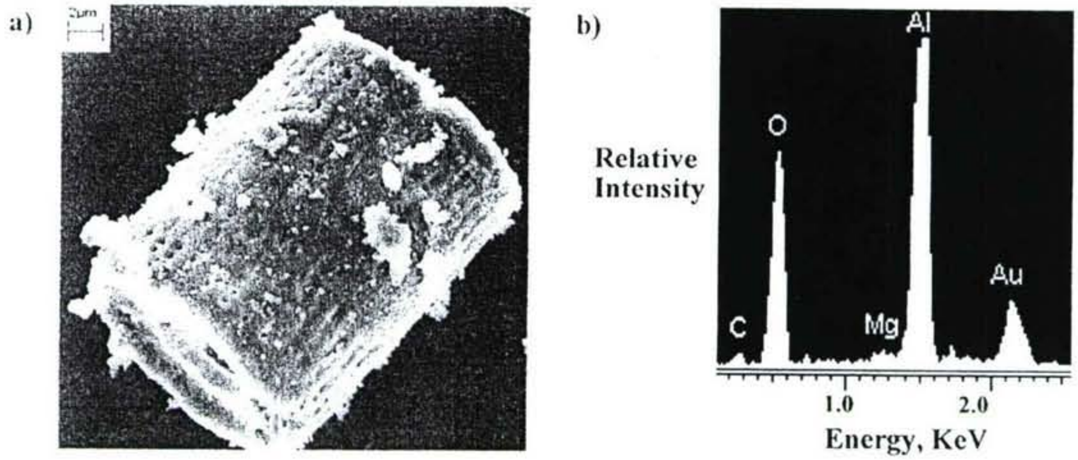
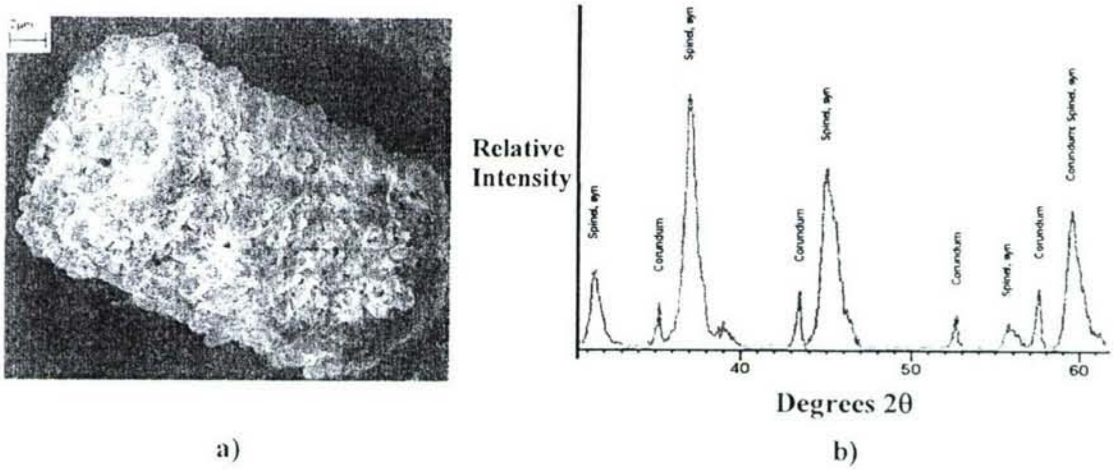


Figure 3. a) SE image and b) EDX analysis of an Al_2O_3-converted *Aulacoseira* frustule.

Homomorphic Coating of Diatom Frustules with Al_2O_3

A sol-gel coating-based approach has also been examined for converting silica-based diatom frustules into alumina. In this approach, magnesia-converted frustules have been immersed in an aluminum alkoxide solution and then dried and fired to 1100°C to form α-Al_2O_3. The underlying MgO was then selectively removed by acid dissolution. A SE image and corresponding XRD pattern are shown in Figures 4a and 4b, respectively. The XRD pattern revealed that the frustules had been converted into a mixture of α-Al_2O_3 and spinel, $MgAl_2O_4$. While the converted frustules retained the overall cylindrical shape of the starting *Aulacoseira* frustules, the oxide crystals within the converted frustule were relatively coarse. Further work is underway to reduce the firing temperature to minimize the reaction of the alumina coating with the magnesia template and to reduce the crystallite size (i.e., to improve the preservation of finer frustule features).



a)

b)

Figure 4. a) A SE image and b) an XRD pattern obtained after applying a sol-gel-derived alumina coating on magnesia frustule replicas, firing at 1100°C, and then selectively dissolving the underlying magnesia away.

Homomorphic Coating of Diatom Frustules with BN (Collaboration with Prof. Larry Sneddon, University of Pennsylvania)

A collaboration with Prof. Larry Sneddon's group at the University of Pennsylvania has been undertaken over the past year to develop non-oxide replicas of diatom frustules. This collaboration takes advantage of the expertise of the Sneddon group in designing and synthesizing polymeric precursors to non-oxide ceramics and our experience in developing and evaluating diatom-templated coatings. Transmission electron (TE) images of cross-sections of BN coatings (after removal of the underlying *Aulacoseira* silica frustule) synthesized in the Sneddon group are shown in Figure 5 below. The low-magnification image in Figure 5a reveals that the BN coating had been continuous and replicated the general cross-section of the starting frustule. The higher-magnification image in Figure 5b reveals curved lattice fringes in the coating that were consistent with turbostratic BN. Future work will involve the use of more intricate frustules cultured in the Sandhage laboratory.

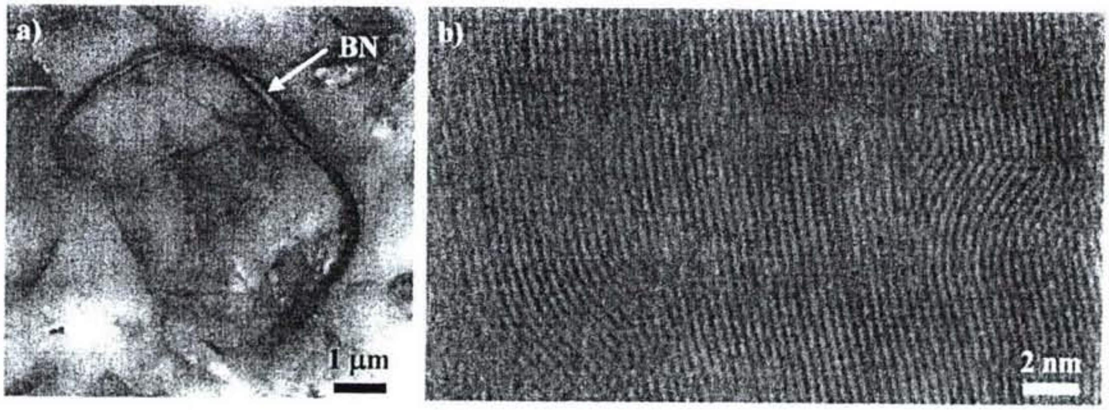


Figure 5. a) Low- and b) high-magnification TE images of cross-sections of BN replicas of diatom frustules (after selective dissolution of the underlying silica).

Summary

Two general approaches have been examined for converting self-replicating, SiO_2-based bioclastic structures (diatom frustules) into refractory ceramics: i) reactive conversion of the frustule via a series of gas/solid displacement (cation exchange) reactions, and ii) conformal coating of the frustule via wet chemical approaches (sol-gel or polymeric precursor routes) and then selective dissolution of the frustule (i.e., use of the frustule as a transient template). With both routes, microscopic Al_2O_3-bearing and BN-bearing structures were produced that retained the overall 3-D shape of the starting frustules. The influence of processing conditions (reactant ratios, coating conditions, temperatures, times) on the nanostructural evolution and on the final morphologies of the freestanding microscale structures has been examined. Further work is underway to optimize the reaction-based and coating-based processes to achieve more precise control over the retention of fine (nanoscale) features.

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Publications

1. K. H. Sandhage, R. L. Snyder, G. Ahmad, S. M. Allan, Y. Cai, M. B. Dickerson, C. S. Gaddis, M. S. Haluska, S. Shian, M. R. Weatherspoon, R. A. Rapp, R. R. Unocic, F. M. Zalar, Y. Zhang, M. Hildebrand, B. P. Palenik, "Merging Biological Self-assembly with Synthetic Chemical Tailoring: The Potential for 3-D Genetically-Engineered Micro/nanodevices (3-D GEMS)," *International Journal of Applied Ceramic Technology*, **2** [4] 317-326 (2005).
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Awards/Honors Received

Sandhage – Appointed B. Mifflin Hood Professor of Ceramic Engineering at Georgia Tech.