

Anatase assemblies from algae: coupling biological self-assembly of 3-D nanoparticle structures with synthetic reaction chemistry

Raymond R. Unocic,^a Frank M. Zalar,^a Peter M. Sarosi,^a Ye Cai^b and Kenneth H. Sandhage*^b

^a Department of Materials Science and Engineering, The Ohio State University, 477 Watts Hall, 2041 College Road, Columbus, OH 43210, USA

^b School of Materials Science and Engineering, Georgia Institute of Technology, 771 Ferst Drive, Atlanta, GA 30332, USA. E-mail: ken.sandhage@mse.gatech.edu

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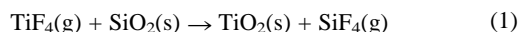
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The shape-preserving conversion of biologically self-assembled 3-D nanoparticle structures (SiO₂-based diatom frustules) into a new nanocrystalline material (anatase TiO₂) via a halide gas/solid displacement reaction route is demonstrated.

Titanium dioxide is among the most technologically versatile of oxides. Owing to their attractive optical, chemical, electrical, thermal, and biological properties, TiO₂-based materials have a wide range of applications (catalysts, gas sensors, solar cells, implants, pigments/cosmetics, etc.).¹ Although methods for mass-producing titania-based powders, films, and bulk components with simple shapes are well established, appreciable global effort is being expended to develop scalable approaches for fabricating titania-based microassemblies with intricate, 3-D morphologies and precisely controlled fine (< 10³ nm) features.²

Nature provides numerous examples of organisms that directly generate intricate 3-D mineralized (bioclastic) structures with micro-to-nanoscale features. For example, Ophiocomid brittlestars are marine animals that form calcitic skeletons.³ Highly photosensitive brittlestars (e.g. *Ophiocoma wendtii*) possess dorsal arm plates with regular arrays of single calcite crystal microlenses that focus light onto underlying nerve bundles.³ Coccolithophores are single-celled aquatic organisms that are covered with microscopic calcitic scales with organized patterns of fine features (submicron channels, pores, etc.).⁴ Single-celled aquatic algae known as diatoms assemble amorphous silica nanoparticles into intricate microshells (frustules) with a dazzling variety of shapes.⁵ Indeed, each of the estimated 100 000 extant diatom species generates a frustule with a unique 3-D shape and with specific patterns of fine features (e.g. regularly-spaced 10² nm pores, channels, ridges, etc.).⁵ 3-D bioclastic assemblies generated by organisms such as brittlestars, coccolithophores, and diatoms are reproduced with fidelity from generation to generation. Hence, sustained reproduction can yield enormous numbers of similarly shaped assemblies (e.g. 40 sequential reproduction cycles would yield 2⁴⁰ or > 1 trillion copies). Such massively parallel, precise, and direct self-assembly of complex 3-D micro/nanostructures has no synthetic analog. However, the vast majority of natural bioclastic structures are composed of calcium carbonate or silica, which are not well suited for many potential device applications.⁶

The objective of the present work is to demonstrate that a synthetic chemical conversion process, involving a shape-preserving metathetic gas/solid reaction, can be used to overcome the compositional limitations of natural bioclastic structures. The bioclastic structures utilized in this work were the silica-based frustules of *Aulacoseira* diatoms (obtained as organic-free diatomaceous earth filter material from a commercial vendor). The following net metathetic reaction was examined for converting the diatom silica into titania:



Solid TiF₄ was utilized as a low temperature source of TiF₄ vapor (note: the sublimation temperature of TiF₄(s) is 285 °C⁷).

A representative scanning electron microscope image of the starting *Aulacoseira* diatom frustules is shown in Fig. 1(a). (Note: the frustules were isolated by ultrasonic dispersion in ethanol. A pipette was used to deposit the frustule-ethanol mixtures onto

substrates for viewing and the ethanol was allowed to evaporate.) The frustules are cylindrical in shape and their side walls are decorated with rows of fine pores and with narrow V-shaped channels. The end faces of the frustules exhibit a circular hole with a protruding outer rim. 100 mg of these biosilica assemblies were placed within a titanium tube (diameter 2.5 cm, length 20 cm; McMaster-Carr, Cleveland, OH, USA) along with solid TiF₄ (Advanced Research Chemicals, Inc., Catoosa, OK, USA). Both ends of the tube were then crimped and welded shut. The tube was heated in a horizontal tube furnace to the desired reaction temperature at a rate of 5 °C min⁻¹ and held there for 2 h. At the end of this treatment, the tube was pushed out of the hot zone of the furnace, cut open, and the specimens were extracted. The experimental yield was ≥95%; that is, 95% or more of the reacted frustules could be extracted from the tube. Some of these specimens were given a second heat treatment at 350 °C for 2 h in pure, flowing oxygen.

Initial reaction experiments were conducted for 2 h at 500–700 °C using TiF₄-SiO₂ molar ratios of ≥4.9 : 1 within the sealed titanium tubes (i.e. well in excess of the 1 : 1 ratio of TiF₄ to SiO₂ shown in reaction 1). Although titania was generated under these conditions, relatively coarse plate-shaped crystals (5–10 μm × 5–10 μm × 0.5–1 μm thick) were produced; that is, the starting diatom frustule shape was not preserved.

A strikingly different result was obtained upon lowering the reaction temperature to 350 °C and reducing the TiF₄-SiO₂ molar ratio to 2.4 : 1 within the titanium tubes. A secondary electron image of an *Aulacoseira* frustule exposed to TiF₄(g) under these

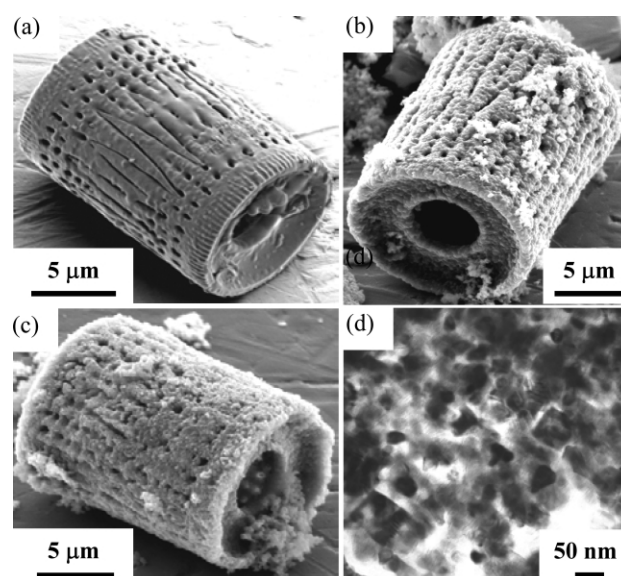


Fig. 1 Secondary electron images of *Aulacoseira* diatom frustules: (a) before treatment; (b) after exposure to TiF₄(g) for 2 h at 350 °C; (c) exposure to TiF₄(g) for 2 h at 350 °C and then to pure O₂ for 2 h at 350 °C. (d) A transmission electron image of a cross-section of a frustule after exposure to TiF₄(g) for 2 h at 350 °C and then to pure O₂ for 2 h at 350 °C.

conditions is shown in Fig. 1(b). The overall shape and fine features of the treated frustule are quite similar to those of the initial structure. However, energy-dispersive X-ray (EDX) analyses revealed the presence of appreciable levels of titanium, fluorine, and oxygen in such treated frustules [Fig. 2(a)]. (Note: the peaks due to Al, Au, and Pd in Fig. 2(a) and (c) were generated by the aluminium substrate on which the specimens were placed and by the gold-palladium coating applied to the specimens to avoid charging.) The predominant EDX peak for silicon (1.74 keV) was not detected after this reaction treatment. X-Ray diffraction (XRD) analyses of these treated frustules [Fig. 2(b)] indicated that the diatom silica had been converted into predominantly TiOF₂, along with a small amount of the anatase polymorph of TiO₂.

Possible metathetic TiF₄(g)/SiO₂(s) reactions that could have yielded TiOF₂ include:



Although it is not yet clear which of these was the predominant reaction, the standard Gibbs free energy changes for reactions 2 and 3 are considerably more negative than that for reaction 4.^{7,9}

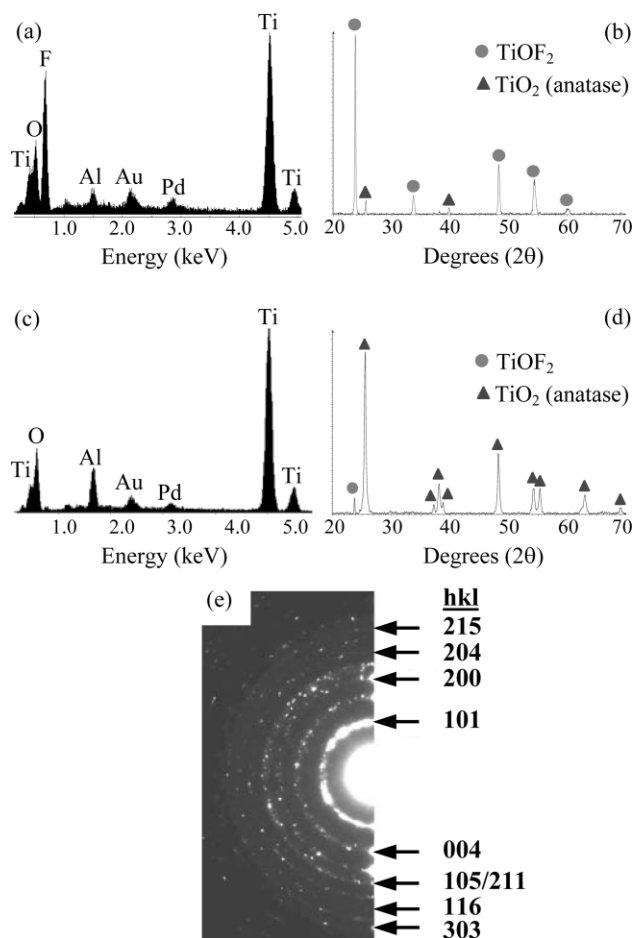


Fig. 2 EDX (a, c) and XRD (b, d) analyses of *Aulacoseira* frustules after exposure to TiF₄(g) for 2 h at 350 °C⁸ (a, b) and after further treatment with pure O₂ for 2 h at 350 °C (c, d).⁸ (e) TEM/ED pattern obtained from a cross-section of a frustule after exposure to TiF₄(g) for 2 h at 350 °C and then to pure O₂ for 2 h at 350 °C (*hkl* values associated with diffraction from anatase are also shown).

Further heat treatment was conducted in flowing oxygen in order to convert the titanium oxyfluoride frustules into titanium oxide by the following net reaction:



After exposure of the oxyfluoride-rich frustules to oxygen at 350 °C for 2 h, the *Aulacoseira* shape was still well preserved [Fig. 1(c)]. EDX analysis [Fig. 2(c)] indicated that the fluorine had been largely removed from the frustules by this treatment. Indeed, the predominant phase detected by XRD analysis was the anatase polymorph of TiO₂ [Fig. 2(d)]. A transmission electron microscope (TEM) image of an electron-transparent longitudinal cross-section of such an oxygen-treated specimen is shown in Fig. 1(d). This specimen consisted of a porous network of fine oxide crystals (< 100 nm in size). Electron diffraction (ED) analyses [Fig. 2(e)] of these nanocrystals were consistent with the tetragonal crystal structure of anatase.⁸

This work demonstrates for the first time that a metathetic halide gas/solid reaction may be used to convert a biologically self-assembled 3-D structure into a new nanocrystalline material without loss of the bioclastic shape or fine features. Although this work has focused on the conversion of diatom silica into the technologically important oxide titania, this approach could also be applied to other bioclastic or biomimetic preforms using alternative thermodynamically favored metathetic reactions to generate 3-D assemblies with a wide variety of shapes and functional chemistries.¹⁰ Such shape-preserving metathetic reactions could also be conducted using synthetic (non-natural) micro/nanoassemblies. For example, the titania conversion process detailed herein could be applied to silica-based colloidal crystals, membranes, or structures obtained by silicon micromachining.¹⁰

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