Thin Films

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Thin, Conformal, and Continuous SnO_2 Coatings on Three-Dimensional Biosilica Templates through Hydroxy-Group Amplification and Layer-By-Layer Alkoxide Deposition**

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Appreciable effort is underway to develop robust protocols for synthesizing functional nanostructured assemblies. Desired characteristics for such protocols include precise control of structure (down to the nanoscale), versatile control of chemistry (for tailored functionality), and massively parallel assembly (for large-scale manufacturing). The precise, versatile, and scalable fabrication of functional nanostructured assemblies, particularly those with intricate 3D morphologies, remains a significant challenge for nanotechnology.

Nature provides spectacular examples of precise and highly replicable 3D self-assembly of inorganic materials on the micrometer to nanometer scales.[1] Diatoms, for example, generate nanostructured silica microshells (frustules) with thousands of species-specific morphologies.[1d] Sustained reproduction of a particular diatom species can yield enormous numbers of frustules with similar 3D morphologies.[1e] Such intricate, genetically precise, and massively parallel 3D self-assembly under ambient conditions lies well beyond the current capabilities of synthetic micro- and nanofabrication. However, to utilize the precision and massive parallelism of such biological assembly for a variety of nanostructured devices, the silica-frustule chemistry needs to be altered for desired electronic, optical, chemical, or other properties.

While gas–solid reactions[2a–c] and gas-phase deposition[2d,e] have been used to alter the chemistries of bioclastic structures, these approaches require volatile reactants or precursors. An alternate range of chemistries may be accessed with liquid-phase deposition methods. For example, Kunitake, et al.[3] have used a layer-by-layer surface sol–gel process to deposit conformal oxide-bearing coatings on hydroxy- or carboxy-bearing surfaces (for example, latex spheres[3b,c] or cellulose[3d,e]). However, this surface sol–gel process has not been used to generate thin, conformal, and continuous functional oxide coatings on intricate 3D biomineral structures.

Herein, we demonstrate, for the first time, how the intricate nanostructured silica valves of diatom frustules may be coated with a thin (50 nm), conformal, and continuous layer of a functional oxide (SnO_2) through dendritic amplification of hydroxy groups on the silica surfaces and then use of an automated surface sol–gel process. A device built from such SnO_2-coated diatom frustule valves acts as a sensitive detector for NO gas.

Initial experiments produced patchy, discontinuous oxide coatings, which we attribute to a low density of surface hydroxy groups available to initiate the sol–gel reaction on the silica valves. Therefore, it was necessary to increase the number of accessible hydroxy functionalities through a series of chemical reactions (Scheme 1). The diatom silica was first subjected to an oxidizing RCA-1 cleaning solution and then treated with (3-aminopropyl)triethoxysilane to functionalize the surfaces with amine groups. The surfaces were then exposed, in alternating fashion, to solutions of polyfunctional species in excess (dipentaerythritol penta-/hexaacrylate, followed by tris(2-aminoethyl)amine) to allow for dendritic growth of a multilayered amine–acrylate film through Michael-addition reactions.[4] A final reaction of the acrylate-terminated film with D-glucosamine hydrochloride resulted in an enrichment of the exposed hydroxy groups on the valve surfaces.

The full details of this dendritic functional-group amplification process will be described elsewhere. Briefly, the efficacy of dendritic amine amplification on glass substrates was assessed with UV/Vis absorption spectroscopy by labeling the reactive amine sites with fluorescein isothiocyanate (FITC); this analysis suggested that the functional groups reached a saturation level after about four generations. X-ray photoelectron spectroscopy revealed an oscillation in the intensity of the nitrogen 1s peak from about 10 to 4% between the amine- and acrylate-terminated layers, which indicated that the majority of the terminal functional groups were near the surface of each layer.

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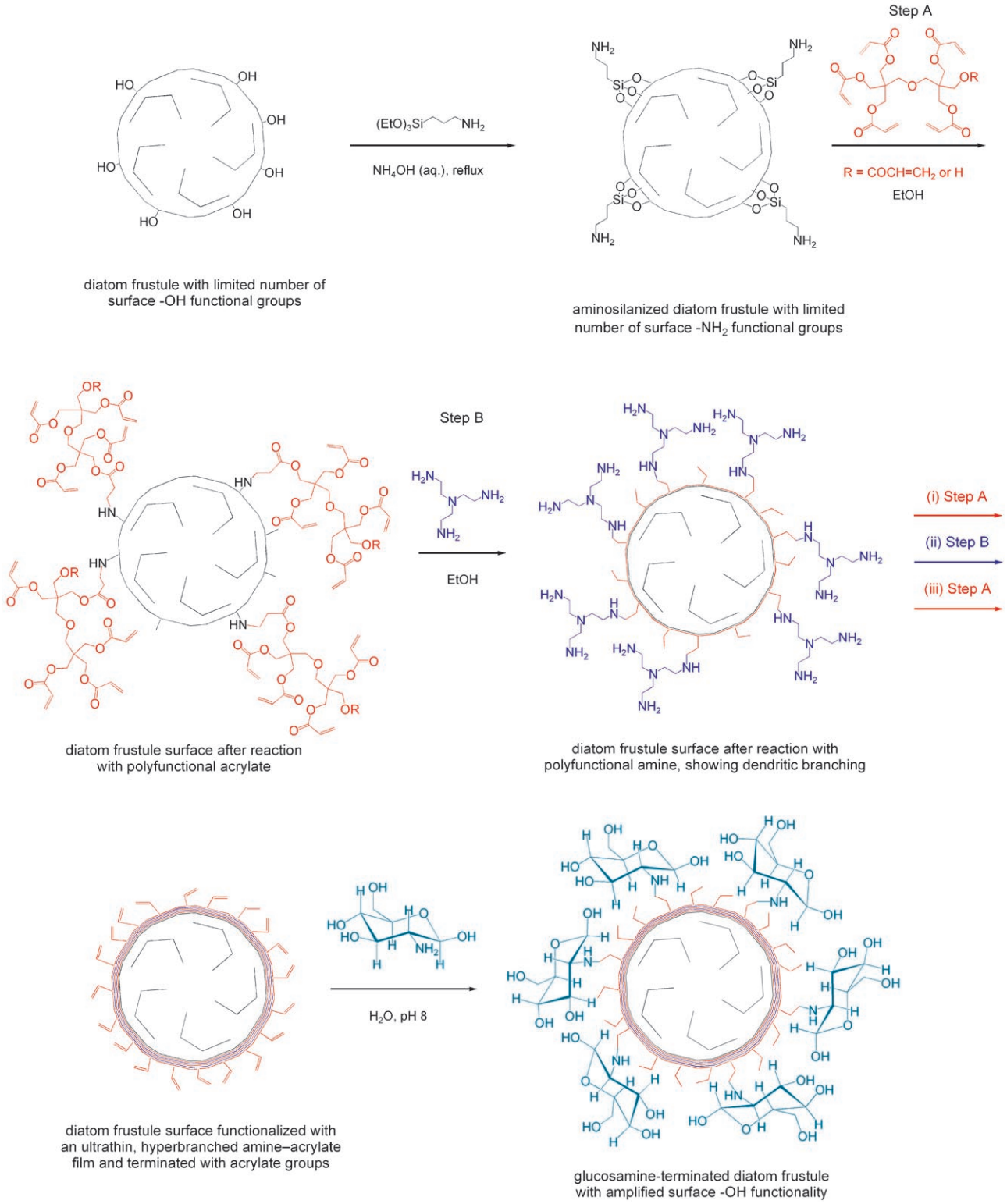

Scheme 1. Dendritic amplification of accessible hydroxy groups on the surfaces of diatom frustules through the growth of an ultrathin, hyperbranched amine–acrylate film and the subsequent Michael addition of glucosamine to the final acrylate layer.

Such glucosamine-functionalized frustules were coated with SnO_2 using an automated surface sol–gel process (Figure S1 in the Supporting Information). Functionalized frustules were placed on a glass frit within a vacuum-filtration unit. A computer-controlled pumping system was then used to expose the frustules, in an alternating fashion, to a tin(IV) 2-propoxide solution, 2-propanol, and an ammonium hydroxide

solution. This sequential exposure process (tin alkoxide/2-propanol/ammonium hydroxide) was repeated 15 times.

A secondary electron (SE) image of the valves of a starting *Aulacoseira* diatom is shown in Figure 1 a. The *Aulacoseira* valves possess a hollow cylindrical shape, and

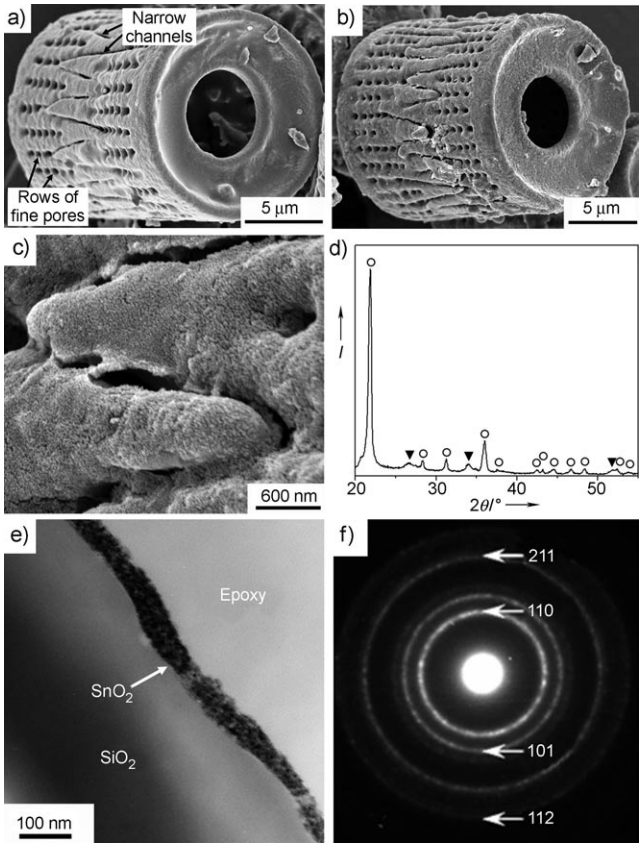

Figure 1. Synthesis of conformal, continuous, and compact SnO_2 coatings on the surfaces of the valves of an *Aulacoseira* diatom through the combined use of dendritic surface-hydroxy amplification and automated surface sol–gel processing. a) SE image of the starting silica-based valves of an *Aulacoseira* diatom. b) SE image of the SnO_2-coated valves. c) Higher-magnification SE image of the SnO_2-coated valves. d) XRD pattern of the SnO_2-coated valves; ○ cristobalite SiO_2, ▼ cassiterite SnO_2. e) TE image of a cross-section of an SnO_2-coated valve. f) SAED pattern of the cassiterite SnO_2 (space group $P4_2/mnm$(136)) coating of the valve in (e).

are decorated with rows of fine pores (10^2-nm diameter) and with fine channels between intercalating fingerlike extensions. An SE image of functionalized and SnO_2-coated valves (after 2 h at 700 °C) is shown in Figure 1 b. The coated valves retain the 3D morphology and fine features (pores and channels) of the starting (uncoated) diatom valves. Higher-magnification SE images reveal that the surface of the coated valves is more granular than that of the starting valves (Figure 1 c). The X-ray diffraction (XRD) pattern of the coated valves contains relatively intense diffraction peaks for cristobalite SiO_2 (generated by the underlying diatom templates) and modest peaks for cassiterite SnO_2 (generated by the coating; Figure 1 d). Scherrer analysis indicated an average SnO_2 crystallite size of 7.7 nm. The continuity of the SnO_2 coating was further confirmed by transmission electron (TE) analyses of cross-sections of coated diatom valves. As shown in Figure 1 e, the continuous, compact polycrystalline coating is (50 ± 15)-nm thick. Selected area electron diffraction (SAED) analysis of the coating yielded a pattern consistent with cassiterite SnO_2 (Figure 1 f). Higher-magnification TE images indicate that the SnO_2 coating is composed of (7.5 ± 1.5)-nm diameter crystallites (Figure S2), which is consistent with the Scherrer analysis of the XRD data. Lattice fringe images obtained from crystallites within the coating also have lattice spacings consistent with cassiterite SnO_2 (Figure S2). The application of an identical surface sol–gel process to diatom valves cleaned with the RCA-1 solution but without prior dendritic film growth followed by glucosamine functionalization yielded minimal, discontinuous SnO_2 coverage (Figure S3), demonstrating the requirement for the functional-group amplification procedure.

SnO_2-based sensors have previously been employed to detect NO gas.[5] To further evaluate the continuity and NO-sensing capability of the deposited SnO_2, coated valves were placed between gold electrodes on a flat Si_3N_4 substrate. A focused ion beam (FIB) milling instrument was then used to deposit platinum connections between the SnO_2-coated valves and the gold electrodes (Figure 2 a). The SnO_2-coated diatom valves were then tested for NO-sensing behavior at 350 °C. A bias voltage (0.5 V DC) was applied across the SnO_2-coated valves, and the change in current was measured upon exposure to flowing NO gas in an argon carrier stream (Figure 2 b). Exposure to gas mixtures with 3, 5, or 8 ppm NO resulted in proportional increases in the current passing through the SnO_2-coated valves. The response (rise) and recovery (decay) times (defined as the times needed to reach 90 % of the total signal change) were 12 and 32 s, respectively.

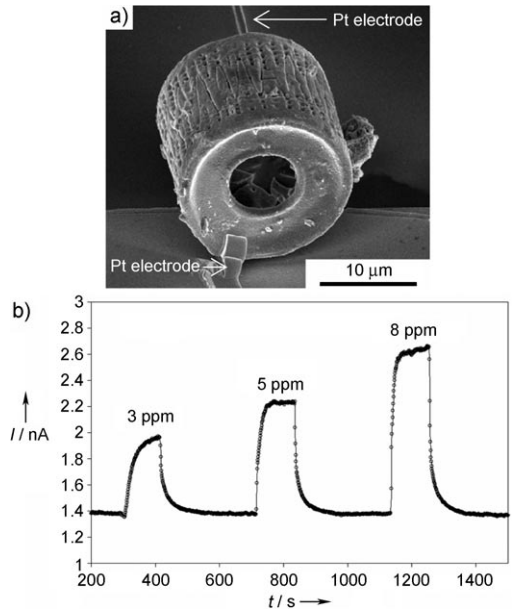

Figure 2. Use of the SnO_2-coated valves of an *Aulacoseira* diatom as an NO sensor. a) SE image of the SnO_2-coated valves attached to two platinum electrodes. b) Current (I) response upon exposure to NO gas (3, 5, or 8 ppm in argon); data were collected once per second.

These times are comparable to, or faster than, those reported for other nanocrystalline SnO_2 sensors.[5]

A general process for depositing compact, continuous, and conformal coatings of synthetic inorganic oxides onto 3D nanostructured biosilica templates has been demonstrated. Thin coatings (50 nm) of nanocrystalline SnO_2 were applied to the cylindrical, nanostructured silica valves of *Aulacoseira* diatoms by the following steps: i) dendritic amplification of surface hydroxy groups, ii) layer-by-layer deposition of a tin alkoxide with an automated surface sol–gel process, and iii) firing for 2 h in air at 700 °C. The continuity of the SnO_2 coatings was confirmed by TE analyses and by electrochemical (gas-sensing) measurements. This process of surface functionalization and automated surface sol–gel deposition may be used to apply a wide variety of alkoxide-derived inorganic coatings onto intricate 3D biosilica or synthetic silica templates for a range of device applications.

Experimental Section

Silica-based diatom frustules were cleaned as follows. *Aulacoseira* frustules (25 g) were exposed to a solution (200 mL) of 50% concentrated HCl in methanol for 1 h at room temperature. After rinsing with purified water (resistivity of 18.2 MΩ·cm, from a NANOpure DIamond UV/UF system, Barnstead International), the frustules were exposed to an RCA-1 solution (5:1:1 mixture of pure water/concentrated NH_4OH/30% H_2O_2) at 65 °C for 0.5 h. The frustules were then rinsed with pure water.

The cleaned diatom frustules were then treated to enrich the surface hydroxy concentration. The frustules were silanized through heating at reflux for 16 h in a solution of (3-aminopropyl)triethoxysilane (20 mL, 98% purity, Fluka), concentrated NH_4OH (7 mL), and pure water (173 mL). The aminosilanized frustules were rinsed with pure water and then heated at 105 °C for 0.5 h under vacuum. To increase the concentration of amine groups on the frustule surfaces, the aminosilanized frustules were exposed, in an alternating fashion, to solutions containing dipentaerythritol penta-/hexaacrylate (DPEPHA; Sigma Aldrich) or tris(2-aminoethyl)amine (TAEA; Fluka). The frustules were first stirred for 1 h in a solution (200 mL) of DPEPHA (20 wt%) in ethanol. After filtration and rinsing with ethanol (600 mL), the frustules were stirred for 1 h in a solution (200 mL) of TAEA (20 wt%) in ethanol. This process of exposure to the DPEPHA solution and then to the TAEA solution was repeated twice. A final exposure to the DPEPHA solution was then conducted (for a total of three exposures to the DPEPHA solution and two exposures to the TAEA solution). The frustules were then immersed for 1 h in a solution of D-glucosamine hydrochloride (25 g, 99% purity, Fluka) dissolved in an aqueous sodium carbonate solution (300 mL, 50 mM) adjusted to pH 8 with NaOH (1 M). The glucosamine-bearing frustules were rinsed with purified water and dried for 16 h at 50 °C.

SnO_2 coatings were applied to the hydroxy-rich diatom frustules by an automated surface sol–gel process. Glucosamine-bearing frustules (0.8 g) were placed on a fine-porosity glass frit in a 1-L microfiltration assembly (Kontes Ultraware, Fisher Scientific). A computer-controlled pumping system was then used to expose the frustules, in an alternating fashion, to a tin(IV) 2-propoxide solution (0.01M), 2-propanol, and an ammonium hydroxide solution (1M; see the Supporting Information). The frustules were collected and dried in air at 100 °C for 12 h, heated in air at 2 °C min^{-1} to 700 °C, and held at this temperature for 2 h to convert the coating into crystalline SnO_2.

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[1] a) E. Bäuerlein, *Angew. Chem.* **2003**, *115*, 636–664; *Angew. Chem. Int. Ed.* **2003**, *42*, 614–641; b) S. Mann, G. A. Ozin, *Nature* **1996**, *382*, 313–318; c) J. R. Young, S. A. Davis, P. R. Bown, S. Mann, *J. Struct. Biol.* **1999**, *126*, 195–215; d) F. E. Round, R. M. Crawford, D. G. Mann, *The Diatoms: Biology and Morphology of the Genera*, Cambridge University Press, Cambridge, **1990**; e) E. O. Duerr, A. Molnar, V. Sato, *J. Mar. Biotechnol.* **1998**, *7*, 65–70.

[2] a) Z. Bao, M. R. Weatherspoon, Y. Cai, S. Shian, P. D. Graham, S. M. Allan, G. Ahmad, M. B. Dickerson, B. C. Church, Z. Kang, C. J. Summers, H. W. Abernathy III, M. Liu, K. H. Sandhage, *Nature* **2007**, *446*, 172–175; b) R. R. Unocic, F. M. Zalar, P. M. Sarosi, Y. Cai, K. H. Sandhage, *Chem. Commun.* **2004**, 795–796; c) K. H. Sandhage, M. B. Dickerson, P. M. Huseman, M. A. Caranna, J. D. Clifton, T. A. Bull, T. J. Heibel, W. R. Overton, M. E. A. Schoenwaelder, *Adv. Mater.* **2002**, *14*, 429–433; d) D. Losic, G. Triani, P. J. Evans, A. Atanacio, J. G. Mitchell, N. H. Voelcker, *J. Mater. Chem.* **2006**, *16*, 4029–4034; e) E. K. Payne, N. L. Rosi, C. Xue, C. A. Mirkin, *Angew. Chem.* **2005**, *117*, 5192–5195; *Angew. Chem. Int. Ed.* **2005**, *44*, 5064–5067.

[3] a) I. Ichinose, H. Senzu, T. Kunitake, *Chem. Lett.* **1996**, 831–832; b) S. Fujikawa, T. Kunitake, *Int. J. Nanosci.* **2002**, *1*, 617–620; c) J. Huang, T. Kunitake, *Chem. Commun.* **2005**, 2680–2682; d) J. Huang, T. Kunitake, *J. Am. Chem. Soc.* **2003**, *125*, 11834–11835; e) Y. Aoki, J. Huang, T. Kunitake, *J. Mater. Chem.* **2006**, *16*, 292–297.

[4] a) R. A. Farrer, C. N. LaFratta, L. Li, J. Praino, M. J. Naughton, B. E. A. Saleh, M. C. Teich, J. T. Fourkas, *J. Am. Chem. Soc.* **2006**, *128*, 1796–1797; b) E. Muh, J. Marquardt, J. E. Klee, H. Frey, R. Mulhaupt, *Macromolecules* **2001**, *34*, 5778–5785.

[5] a) T. Hyodo, K. Sasahara, Y. Shimizu, M. Egashira, *Sens. Actuators B* **2005**, *106*, 580–590; b) G. Sberveglieri, S. Groppelli, P. Nelli, *Sens. Actuators B* **1991**, *4*, 457–461.

