3D Rutile Titania-Based Structures with *Morpho* Butterfly Wing Scale Morphologies**

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The attractive optical, chemical, biochemical, and mechanical properties of the rutile polymorph of titanium dioxide (titania) have led to its use in powder or film form in paints, plastics, cosmetics, sunscreens, interference coatings, separation membranes, gas sensors, and as a food additive.[1–7] Three-dimensional (3D) porous networks of rutile titania are also of considerable interest for separation/sorption, optical, and biomedical applications.[8–11] The assembly of 3D porous networks of rutile with well-controlled solid and pore morphologies is an active area of research. A number of groups have synthesized titania structures that have well-organized 3D arrays of macropores/voids by applying coatings of the anatase polymorph of titania on organic templates and then removing the templates.[9–14] However, attempts to completely convert organized 3D anatase/pore structures into rutile titania replicas, by heat treatment at $\geq 800^\circ C$, have resulted in appreciable grain growth and distortion of the solid/pore structures.[11–14]

Herein, we demonstrate for the first time how an intricate, 3D, nanocrystalline rutile structure may be generated with the morphology and nanoscale features inherited from a bio-organic, chitin-based template. Chitin is a natural polysaccharide that is formed into well-organized structures by a variety of organisms (for example, fungi, yeast, arthropods, cephalopods, mollusks, insects).[15–19] The chitin-based templates in this work are the scales present on the wings of a *Morpho* butterfly. As revealed by the secondary electron (SE) image in Figure 1a-1, these overlapping scales possess an overall rectangular shape with pointed tips. Figure 1a-2 reveals the porous architecture of one such scale. Each scale is comprised of parallel ridges, spaced several microns apart, aligned along the scale length. The ridges are decorated with nanoscale ribs (ca. 50 nm in width) that are spaced approximately 150 nm apart.

![Figure 1. SE images of chitin-based scales obtained from a *Morpho* butterfly (a-1, a-2) that were then exposed to 20 surface sol–gel deposition cycles using titanium(IV) isopropoxide (0.010 M solution in 2-propanol) followed by firing at 450°C for 4 h (b-1, b-2) or 900°C for 1 h (c-1, c-2).](image)

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horizontal) inside a fritted glass filtration flask. A computer-controlled pumping system (housed within a dry-nitrogen glove box) was used to expose the immobilized wing scales to a solution of 0.010 M titanium(IV) isopropoxide in anhydrous 2-propanol, or to a mixture of 0.010 M titanium(IV) isopropoxide and 0.0018 M tin(IV) isopropoxide in anhydrous 2-propanol, for 10 min. The wing scales were then rinsed three times with anhydrous 2-propanol, and exposed to deionized water for 1 min, followed by further rinsing three times with anhydrous 2-propanol. The scales were then dried with flowing warm nitrogen for 5 min. This serial exposure process (alkoxide, 2-propanol wash, deionized water, 2-propanol wash, drying) was initially repeated 20 times. Separate samples of the coated scales were then fired in air at 0.5 °C/min to 450 °C, then held at this temperature for 4 h (Figure 1b-1 and 1b-2), or at 900 °C for 1 h (Figure 1c-1 and 1c-2), to pyrolyze the chitin template and convert the coating into crystalline titania. The tile-like arrangement of the scales, and the ridges with nanoscale ribs, were retained after firing at 450 °C. The variation in spacing (waviness) of the ridges seen in Figure 1b-2 was attributed to a titania coating of insufficient thickness and, hence, insufficient rigidity. Transmission electron (TE) images (Figure 2a-1, 2a-2) revealed that the 450 °C fired structures retained the overall chitin-based scale morphology and were comprised of crystallites measuring approximately 20 nm. Selected area electron diffraction (SAED) analyses of these nanocrystals (inset of Figure 2a-2) were consistent with the anatase polymorph of TiO₂. Raman microspectroscopic analyses (see Supporting Information, Figure S1) also indicated that these TiO₂ structures were comprised of anatase.[23]

On annealing the treated chitin-based scales at 900 °C for 1 h, the overall scale shape was retained. However, appreciable grain coarsening occurred during this high temperature treatment that resulted in significant distortion of the nanoscale ribs (Figure 1c-1 and 1c-2, and Figure 2b-1 and 2b-2). Raman microscopic analyses (see Supporting Information, Figure S2) indicated that these titania structures were largely comprised of rutile.[23] However, SAED analysis (see inset of Figure 2b-2) revealed the presence of residual anatase titania. Hence, although appreciable coarsening and distortion of nanoscale features had already occurred within 1 h at 900 °C, the complete conversion of anatase into rutile titania required a longer time at this temperature.

In an effort to convert individual Morpho butterfly wing scales into nanocrystalline rutile TiO₂ replicas, the surface sol–gel process was modified by introducing tin(IV) isopropoxide as a rutile-promoting dopant. The rutile polymorph of tin dioxide forms readily at modest temperatures (for example, rutile SnO₂ has been synthesized by firing gel precursors at approximately 450 °C within 2 h[24,25]). Since the values of the a and c lattice parameters for rutile TiO₂ (within 3.1% and 7.2%, respectively), SnO₂ nanocrystal surfaces may act as preferred sites for the heterogeneous nucleation of rutile TiO₂.[26] Indeed, the firing of tin-doped titania gels has been reported to reduce the anatase-to-rutile transformation temperature for powders.[26] In addition to tin doping of the alkoxide solution, the number of surface sol–gel deposition cycles was increased from 20 to 40, in an effort to increase the rigidity of the coating and thereby reduce the variation in ridge spacing seen in Figure 1b-2. SE images of the structures generated after firing at 450 °C for 4 h are shown in Figure 3a–c. The resulting

**Figure 2.** TE images of Morpho butterfly wing scales after exposure to 20 surface sol–gel deposition cycles involving titanium(IV) isopropoxide (0.01 M solution in 2-propanol), and then firing at 450 °C for 4 h (a-1, a-2) or 900 °C for 1 h (b-1, b-2). TE images obtained after 40 surface sol–gel deposition cycles involving a mixed 2-propanol solution of titanium(IV) isopropoxide (0.010 M) and Sn(IV) isopropoxide (0.0018 M) and then firing at 450 °C for 4 h (c-1, c-2). The corresponding SAED patterns are shown in the inset figures.

**Figure 3.** a–c) SE images of scales exposed to 40 surface sol–gel deposition cycles involving a mixed 2-propanol solution of titanium(IV) isopropoxide (0.010 M) and Sn(IV) isopropoxide (0.0018 M) and then firing at 450 °C for 4 h. d) An EDX spectrum obtained from (a) revealing the presence of Sn along with Ti in the fired structure.
oxide structures retained the overall 3D scale shapes, parallel ridges, and nanoscale ribs. The fracture cross-section shown in Figure 3c also reveals delicate supportive trusses connecting the ridges to a wavy substructure (all inherited from the chitin scale template). Higher magnification images of ion-milled cross-sections (Supporting Information, Figure S4) indicated that the oxide coating was approximately 60 nm thick. Energy dispersive X-ray (EDX) analysis (Figure 3d) revealed that the tin was successfully incorporated into the oxide coating. TE images (Figure 2c-i) indicated that the coating had been applied in a uniform and conformal manner to the chitin template surface. The average crystallite size (obtained from 20 different crystallites) was found to be approximately 15 nm. SAED analyses (inset of Figure 2c-2) yielded well-defined rings consistent with the (110), (101), (111), and (211) planes of nanocrystalline rutile titania. Raman microspectroscopic analyses (Supporting Information, Figure S3) of these tin-doped structures also yielded vibrational bands similar to those expected for rutile titania.

Experimental Section

This work provides the first demonstration of the use of a layer-by-layer sol–gel-based deposition technique to apply conformal and continuous nanocrystalline rutile TiO2-based coatings on delicate, 3D nanostructured bio-organic templates (in this case, the chitin-based individual wing scales of a Morpho butterfly). Controlled layer-by-layer film growth was achieved using an automated surface sol–gel pumping system to expose the chitin-based wing scales in an alternating manner to an alkoxide precursor solution and water. Nanocrystalline rutile titania-based structures that retained the microscale and nanoscale features of the chitin templates were obtained after 40 cycles of exposure of the templates to a mixed titanium-tin alkoxide solution and water, following by firing at 450 °C. The intricate, hierarchical (micro-to-nanoscale) 3D morphology and chitin-based chemistry of Morpho scales made these structures attractive as templates for demonstrating this wet chemical coating process for synthesizing complex 3D rutile-based replicas. However, practical use of this process for man-made devices will require the fabrication of nanocrystalline rutile titania-based coatings on, or replicas of, 3D synthetic organic templates with structures specifically designed for particular biomedical, filtration/separation, or optical applications. For example, the present approach may be used to apply nanocrystalline rutile titania coatings of high refractive index onto synthetic, hydroxy-bearing organic templates with periodic (photonic crystal) structures tailored for particular optical device applications (for example, highly efficient waveguides or mirrors).

Transmission electron microscopy and electron diffraction were conducted using a JEOL 4000 EX instrument (Japan Electron Optics Laboratory, Tachikawa, Tokyo). Ion-milled cross-sections were obtained using a dual beam focused ion beam instrument (FEI Company, Hillsboro, OR). A 100 nm thick coating of Pt was first deposited on the structures to protect them from beam damage from the ion source. Raman microspectroscopy was performed using a KOSI HoloProbe series 5000 VPT Raman microscope system (Kaiser Optical, Ann Arbor, MI).

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