

Nano-Precision Replication of Natural Cellulosic Substances by Metal Oxides

Jianguo Huang and Toyoki Kunitake*

Topochemical Design Laboratory, Spatio-Temporal Function Materials Research Group, Frontier Research System, The Institute of Physical and Chemical Research (RIKEN), Wako, Saitama 351-0198, Japan

Received July 21, 2003; E-mail: kunitake@ruby.ocn.ne.jp

Biological organizations are produced from self-assembly of highly ordered functional units that are inseparably related to their complex morphological architectures. Despite success in understanding basic principles of the biological assembly process and making inorganic materials by biological templating (as pioneered by Mann in synthesizing macrostructured silica and zeolite from bacteria templates¹), it remains a challenge to mimic such natural pathways and to develop simple but efficient routes to artificial materials that possess similar morphological hierarchies all the way down to nanometer scale. The formation of fossils such as siliceous woods is a short-cut route to reproduce morphological hierarchies of the original plants by replacing the wood components with silica in intricate detail. Such fossilization processes would be realized artificially if morphologically complex surfaces of the biological structure are faithfully lined with ultrathin inorganic layers accompanied by subsequent removal of the organic template. To attain this goal at a rudimentary level, natural materials such as wood² and eggshell membrane³ have been employed as templates to prepare macroporous silica, zeolite, and titania materials from precursor sol-gel solutions and nanocrystal suspensions. Unfortunately, morphological replication in these instances have been achieved only on the micrometer scale, and the nanoscopic details could not be reproduced.^{2,3} As pointed out by Daw,⁴ the structural organization of natural templates cannot be finely controlled in the resultant inorganic analogues; hence, unique morphological features of natural substances are not maintained.

In the present research, we have developed an artificial fossilization process by taking advantage of the surface sol-gel process⁵ to faithfully replicate morphological hierarchies of natural cellulosic substances from macroscopic to nanometer scales. The surface sol-gel process is based on adsorption of metal alkoxides from solution onto hydroxylated substrate surfaces and subsequent hydrolysis to give nanometer-thick oxide films. The natural cellulose fibers possess surface hydroxyl groups, and provide a suitable vehicle for the surface sol-gel process.

To make a "titania fossil" of natural paper, titania gel films were deposited on the morphologically complex surface of paper, and the resultant paper/titania composite was calcined to remove the original filter paper. In a typical procedure, a piece of commercial filter paper (Advantec, Japan) was placed in a suction filtering unit, and was washed by suction filtration of ethanol, followed by drying with air flow. Ten milliliters of titanium *n*-butoxide solution (Ti(O^{*n*}Bu)₄, 100 mM in 1:1:*v*:*v* toluene/ethanol) was then passed through the filter paper slowly within 2 min. Two 20-mL portions of ethanol were immediately filtered to remove the unreacted metal alkoxide, and 20 mL of water was allowed to pass through to promote hydrolysis and condensation. Finally, the filter paper was dried in flowing air. By repeating this filtration/deposition cycle, thin titania gel layers covered the surface of the cellulose fibers. The resultant paper/titania composite was calcined in air at 723 K for 6 h (heating rate 1 K/min) to remove the original filter paper.

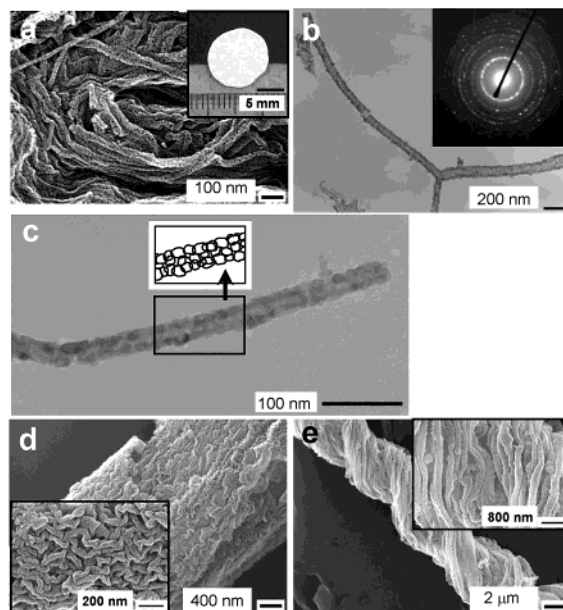


Figure 1. Titania replicas of natural cellulosic substances. Deposition of titania thin films was repeated 20 times for each sample. (a) Field emission scanning electron micrograph (FE-SEM) of "titania paper", showing titania nanotube assemblies. The inset shows the photograph of a sheet of "titania paper". (b) and (c) Transmission electron micrographs (TEM) of individual titania nanotubes isolated from the assembly. Inset of (b), selected-area electron diffraction (SAED) pattern from the nanotube assembly. Inset of (c), schematic illustration of the boxed area, showing titania nanotube wall is composed of fine anatase particles. (d) SEM image of "titania cloth". (e) SEM image of "titania cotton".

The resultant titania fossil possessed morphological characteristics of the original filter paper except for a little shrinkage in size due to calcination; as shown in the inset of Figure 1a, the titania sheet is self-supporting with thickness of ~0.22 mm and weight of ~1.5 mg. The sheet size and thickness depend on the original filter paper used.

The original morphology of the filter paper was found to be faithfully replicated by titania films, and the cellulose fibers were precisely copied as irregular titania nanotubes as clearly recognized in SEM and TEM images (Figure 1, a–c). These titania morphologies are remarkably different from those of the porous titania where the original cellulose nanofibers could not be duplicated as titania nanotubes.⁶ The current "titania paper" records the morphological information of the original paper at the nanometer scale. The outer diameter of the tube varies from 30 to 100 nm, and the thickness of the tube is uniform along its length with wall thickness of ca. 10 nm. The wall thickness can be controlled by changing the number of deposition cycles of titania layers. The titania nanotube assembly manifests the original morphology of interwoven cellulose fibers, and the three-way tube intersection displayed in Figure 1b reflects the nanobranched structure of the fiber. The SAED pattern

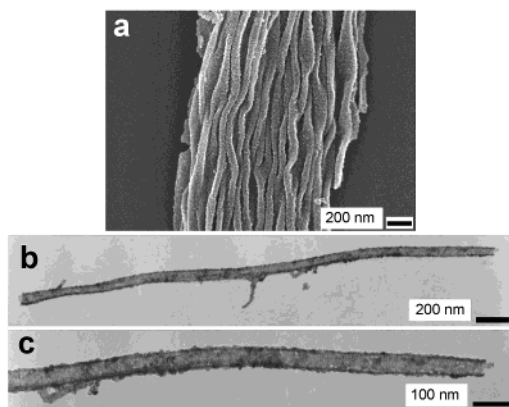


Figure 2. Electron micrographs of “zirconia paper”. Deposition of zirconia thin films was repeated 20 times for this sample. (a) FE-SEM image, showing zirconia nanotube assemblies. (b) and (c) TEM images of an individual zirconia nanotube isolated from the assembly.

from agglomerated titania tubes shows diffraction rings typical of the anatase crystal (Figure 1b, inset), and a TEM image (Figure 1c) shows that the titania nanotubes are composed of anatase fine particles with sizes of around 10 nm.

Similar replication processes are readily applied to other natural cellulosic substances such as cloth and cotton, resulting in “titania cloth” and “titania cotton”. The hierarchical morphologies of these natural substances are retained in titania films to give macroscopic fossils, in which the structures of the original substance are again faithfully replicated from macroscopic to nanometer scales. The fine titania thread shown in Figure 1d is a copy of an individual fiber that makes up strands in the original cloth, and the fine titania hair displayed in Figure 1e shows the spiral twist of natural cotton lint.⁷ The corresponding high magnification SEM images demonstrate that both of them are composed of arrays of tortuous titania nanotubes (insets of Figure 1, d and e), as precise replicas of cellulose fiber assemblies. The topographic differences among the titania fossils (as shown in Figure 1, a, d, and e) mirrors the structural differences of the template paper, cloth, and cotton, although they are all natural cellulosic substances.

Metal oxides other than titania are similarly employed in the surface sol–gel process,⁸ and are suitable as replicating matrices. For instance, Figure 2 shows an artificial zirconia fossil derived from natural paper by using zirconium *n*-butoxide ($Zr(O^iBu)_4$). The fiber assembly in paper leads to well-aligned zirconia nanotube arrays (Figure 2a), and the zirconia nanotubes are uniform with an ultrathin wall thickness of ca. 10 nm (Figure 2, b and c) and an extremely high aspect ratio of at least 50 (length vs diameter; for the nanotube displayed in Figure 2b; note that this sample was smashed by sonication for electron microscopy observation; the initial aspect ratio should be much higher.).

Since the discovery of carbon nanotubes,⁹ nanotubular materials have been attracting great attention in both fundamental and industrial studies due to their peculiar properties superior to those of the corresponding bulk materials and isotropic nanoparticles.¹⁰ In contrast, general and efficient synthetic approaches have not been available for oxidic nanotubes.^{10a} Among various oxidic nanotubes, the titania nanotube is particularly attractive due to its unique electronic, photonic, and catalytic properties. Our current approach presents a practical and environmental-friendly approach to produce titania nanotubes. Structural design of the nanotube is achieved by proper selection of template materials. These features are not readily

attained by the reported chemical methods such as sol–gel template syntheses using porous membranes¹¹ and polymer fibers,¹² or alkali treatment on titania powders.¹³

The multihelical morphology of the titania nanotubes shown in Figure 1e is worthy of mention. The first example of helical silica was reported probably by Sakata and Kunitake¹⁴ as replicas of the helical superstructures that were produced from bilayer membranes of chiral ammonium amphiphiles.¹⁵ More recently, helical metal oxides prepared by sol–gel transcription of chiral amide- and urea-type organic gelators,¹⁶ or cholesterol-¹⁷ and sugar-based¹⁸ gelators were reported. Replication of natural helical structures with inorganic matrices can be a shortcut route to helical inorganic materials. It is known that each natural cotton hair is a thin flattened tubular cell with a pronounced spiral twist when it is fully mature and dry, and its length is several centimeters. As shown here, precise duplication of cotton hairs with titania via the current petrification process gives “titania cotton” composed of multihelical titania nanotubes.

In summary, a general chemical process was developed for nanoscale-to-macroscale duplication of the complex hierarchical morphology of natural cellulosic substances with metal oxide matrices. This new nano-copying methodology provides replicas (both positive and negative) of targeted objects in nanometer precision. The approach provides a pathway to probe structures of biosystems at nanometer scales, and is a low-cost and efficient route to produce ceramic nanomaterials with unique structural features.

References

- (1) (a) Davis, S. A.; Burkett, S. L.; Mendelson, N. H.; Mann, S. *Nature* **1997**, *385*, 420–423. (b) Zhang, B.; Davis, S. A.; Mendelson, N. H.; Mann, S. *Chem. Commun.* **2000**, 781–782.
- (2) (a) Shin, Y.; Liu, J.; Chang, J. H.; Nie, Z.; Exarhos, G. J. *Adv. Mater.* **2001**, *13*, 728–732. (b) Dong, A.; Wang, Y.; Tang, Y.; Ren, N.; Zhang, Y.; Yue, Y.; Gao, Z. *Adv. Mater.* **2002**, *14*, 926–929.
- (3) Yang, D.; Qi, L.; Ma, J. *Adv. Mater.* **2002**, *14*, 1543–1546.
- (4) Daw, R. *Nature* **2002**, *418*, 491.
- (5) (a) Ichinose, I.; Kawakami, T.; Kunitake, T. *Adv. Mater.* **1998**, *10*, 535–539. (b) Huang, J.; Ichinose, I.; Kunitake, T.; Nakao, A. *Langmuir* **2002**, *18*, 9048–9053.
- (6) (a) Caruso, R. A.; Schattka, J. H. *Adv. Mater.* **2000**, *12*, 1921–1923. (b) Caruso, R. A.; Antonietti, M. *Chem. Mater.* **2001**, *13*, 3272–3282.
- (7) http://ion.eas.asu.edu/cool62_cotton/cool62_thumb.htm, Images of Nature: cotton.
- (8) Ichinose, I.; Lee, S.-W.; Kunitake, T. In *Supramolecular Organization and Materials Design*; Jones, W., Rao, C. N. R., Eds.; Cambridge University Press: Cambridge, UK, 2002; pp 172–213.
- (9) Iijima, S. *Nature* **1991**, *354*, 56–58.
- (10) (a) Patzke, G. R.; Krumeich, F.; Nesper, R. *Angew. Chem., Int. Ed.* **2002**, *41*, 2446–2461. (b) Xia, Y.; Yang, P.; Sun, Y.; Wu, Y.; Mayers, B.; Gates, B.; Yin, Y.; Kim, F.; Yan, H. *Adv. Mater.* **2003**, *15*, 353–389.
- (11) (a) Lakshmi, B. B.; Dorhout, P. K.; Martin, C. R. *Chem. Mater.* **1997**, *9*, 857–862. (b) Liu, S. M.; Gan, L. M.; Liu, L. H.; Zhang, W. D.; Zeng, H. C. *Chem. Mater.* **2002**, *14*, 1391–1397.
- (12) (a) Caruso, R. A.; Schattka, J. H.; Greiner, A. *Adv. Mater.* **2001**, *13*, 1577–1579. (b) Caruso, R. A.; Antonietti, M.; Giersig, M.; Hentze, H.-P.; Jia, J. *Chem. Mater.* **2001**, *13*, 1114–1123.
- (13) (a) Kasuga, T.; Hiramatsu, M.; Hoson, A.; Sekino, T.; Niihara, K. *Langmuir* **1998**, *14*, 3160–3163. (b) Chen, Q.; Zhou, W.; Du, G.; Peng, L.-M. *Adv. Mater.* **2002**, *14*, 1208–1211.
- (14) Sakata, K.; Kunitake, T. *Chem. Lett.* **1989**, 2159–2162.
- (15) (a) Nakashima, N.; Asakuma, S.; Kim, J.-M.; Kunitake, T. *Chem. Lett.* **1984**, 1709–1712. (b) Nakashima, N.; Asakuma, S.; Kunitake, T. *J. Am. Chem. Soc.* **1985**, *107*, 509–510.
- (16) (a) Jung, J. H.; Ono, Y.; Hanabusa, K.; Shinkai, S. *J. Am. Chem. Soc.* **2000**, *122*, 5008–5009. (b) Jung, J. H.; Ono, Y.; Shinkai, S. *Chem. Eur. J.* **2000**, *6*, 4552–4557. (c) Kobayashi, S.; Hamasaki, N.; Suzuki, M.; Kimura, M.; Shirai, H.; Hanabusa, K. *J. Am. Chem. Soc.* **2002**, *124*, 6550–6551.
- (17) Jung, J. H.; Kobayashi, H.; van Bommel, K. J. C.; Shinkai, S.; Shimizu, T. *Chem. Mater.* **2002**, *14*, 1445–1447.
- (18) Jung, J. H.; Yoshida, K.; Shimizu, T. *Langmuir* **2002**, *18*, 8724–8727.

JA037419K