Confined Sol–Gel Reaction Using a Neutral Glycolipid Nanotube as a Template: Aqueous Fabrication of Titania Rod Structures

Qingmin Ji,[1] Shoko Kamiya,[2] and Toshimi Shimizu*[1,2]
[1]*Nanoarchitectonics Research Center (NARC), National Institute of Advanced Industrial Science and Technology (AIST), AIST Tsukuba Central 5, 1-1-1 Higashi, Tsukuba 305-8565*
[2]*SORST, Japan Science and Technology Agency (JST), AIST Tsukuba Central 4, 1-1-1 Higashi, Tsukuba 305-8562*

(Received February 1, 2006; CL-060135; E-mail: tshmz-shimizu@aist.go.jp)

A neutral glycolipid nanotube has been used as a template to form titania rod structures in aqueous solutions. By freezing the aqueous solution of the lipid nanotube to an iced solid state, we were able to confine the formation of titania particles on the surfaces of the lipid nanotubes. After removal of the nanotube template by heat treatment, we successfully obtained rod structures of titania.

Fabrication of inorganic structures using organic materials as templates has been booming during the last two decades.[1] The organic materials have become the most promising template from the viewpoint of diverse structures and easy synthesis.[2] Besides filter membrane templates,[3] the template molecules themselves have to possess positive charges. Otherwise, cations have to be embedded to produce a positive surface to make the inorganic precursors deposit on the template surfaces.[4] The use of nonionic surfactants as structure-directing agents coupled with strong catalysts gave only few examples of production of mesoporous silica.[5] Recently, we have found that an iced peptidic lipid nanotube with secondary ammonium cation causes transition-metal oxide nanotubes to form without solution catalysts. We thought that during this process an unfrozen water layer between the surface of the lipid nanotube and ice made the ethanol solution of inorganic precursors permeate into this water layer and induce a sol–gel reaction.[6] If this is true, we could confine the sol–gel reaction to occur on the organic template surfaces (Figure 1). Thus, a neutral lipid nanotube is also suitable to act as a template for the sol–gel transcription. Here, we describe the sol–gel transcription from a neutral glycolipid nanotube to titania rod structures based on this mechanism.

The glycolipid *N*-(11-*cis*-octadecenoyl)-β-D-glucopyranosylamine (**1**) proved to form well-defined lipid nanotubes with a 200-nm outer diameter and 54-nm wall thickness in average by self-assembly.[7] Aqueous dispersion of the glycolipid nanotubes have been used to undergo sol–gel reaction. The dispersion ($0.05\,\mathrm{g\,L^{-1}}$, $400\,\mu\mathrm{L}$) was firstly frozen to an iced solid state by immersing it in liquid nitrogen for about 30–120 s. A 50-μL portion of ethanol solution of titanium isopropoxide $\mathrm{Ti(OPr)_4}$ (10 vol %), which was cooled to −20 °C in advance, was then added to the iced lipid nanotubes at −20 °C. We, thus, kept the whole reaction system at −8 to −15 °C for several days and finally lyophilized under 2 Pa. We also carried out another sol–gel process by using wet glycolipid nanotubes in aqueous solutions at 0 °C.

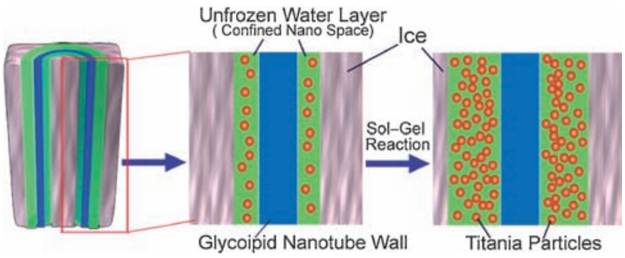
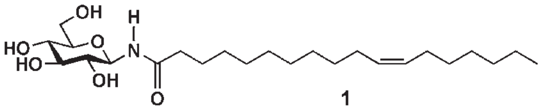


Figure 1. Schematic image for the confined sol–gel reaction in unfrozen water layers (a half cross section of the iced glycolipid nanotube).



1

Figures 2a–2c showed the scanning transmission electron microscopic (STEM) and scanning electron microscopic (SEM) images of the titania/lipid nanotube hybrid structures. We can observe that particles are adsorbed on the surfaces of the lipid nanotube. This kind of hybrid structure is quite different from the case when reacting at 0 °C using the wet glycolipid nanotube as a template. It only gave a mixture of random titania particle aggregates and bare glycolipid nanotubes (Figure 2d). Comparing the obtained structures after given sol–gel reaction time, we found that the amount of particle coverage on the surface of the glycolipid nanotube increases with time. Figure 2c shows a rather thick layer of titania approximately 100-nm wide

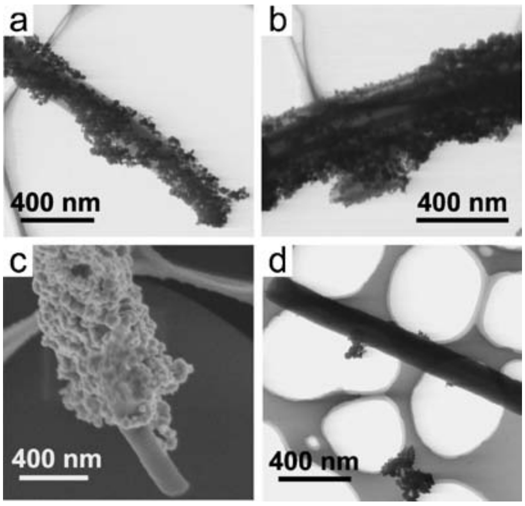


Figure 2. STEM images of titania/lipid tubular hybrids obtained after sol–gel reaction using the iced glycolipid nanotube as a template for a) 3 days, b) 7 days, and c) SEM image for 15 days. d) STEM image of a mixture of titania aggregates and a lipid nanotube after sol–gel reaction using a wet glycolipid nanotube as a template.

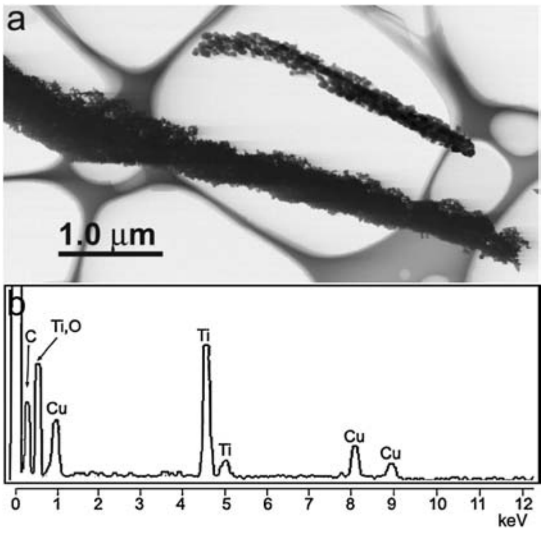


Figure 3. a) STEM image of titania rod structures after calcination of the titania/lipid tubular structure obtained using glycolipid nanotubes as templates. b) EDX spectrum of the titania rod structure. Copper and carbon originate from the STEM copper grid used.

formed on the glycolipid nanotube. Previously, we also tried to use this glycolipid **1** to form silica structures through sol–gel reaction.[8] Because of the absence of positive charges on the glycolipid nanotube surfaces, we were unable to obtain any certain silica structures but particle aggregates. This result indicated that the sole glycolipid **1** can hardly act as a template to direct the formation of metal oxide materials. Only when mixing a positively charged additive like aminophenyl glucopyranoside during the self-assembly, we realized the occurrence of the effective sol–gel transcription and the formation of silica rod structures after calcination.[8]

In the present case, an iced glycolipid nanotube can be employed as a template to perform sol–gel transcription, forming titania particles on the surface. We have reported that the sugar groups of the glycolipid influence the hydrogen-bonding environment of surrounding water.[9] The surrounding water will resist freezing during the short-time freezing of the lipid nanotube and form an unfrozen water layer in the vicinity of the nanotube surfaces. When the ethanol solution of the precursors was added, it will first permeate into this unfrozen water layer and cause initial hydrolysis. Thus, the formation of inorganic particles has been confined on the surfaces of the lipid nanotube (Figure 1). With the melting of ice around the glycolipid nanotube, the confined space turns to be wider and wider. More amounts of particles and eventually a thick wall of titania will form at the surfaces. According to this mechanism, the electrostatic force between lipid and the inorganic precursors is not essential to induce the adsorption of the formed inorganic particles on the template. Thus, the neutral glycolipid **1** acted as a template to direct the formation of titania particles. Since there are no charges on the nanotube surfaces to promote the adsorption, we should be careful to keep the glycolipid nanotube in an iced solid state during the sol–gel reaction. The existence of the unfrozen water layer is critical for the confinement of the sol–gel reaction on the nanotube template surface. Therefore, complete melting of ice would result in the disappearance of the confined nanospace and the formation of large titania particles aggregates in the bulk solution.

After calcination at 500 °C to remove the glycolipid nanotube template, we were able to observe titania rod structures (Figure 3a). The formed titania particles on the inner surfaces will easily fill the nanotube hollow cylinder, since the inner diameters of the glycolipid nanotubes are relatively small ca. 50-nm wide. The heat treatment allowed the particles to hold together and eventually give a rod structure. Energy dispersive X-ray (EDX) spectrum for the rod structures evidenced that they are composed of titania (0.39, 4.50, and 4.97 keV, Figure 3b). The carbon peak at 0.28 keV, which remarkably decreased in intensity after calcination, should arise from the carbon film of the STEM copper grid used.

In conclusion, using an iced neutral glycolipid nanotube as a template, we succeeded in fabricating titania rod structures by confined sol–gel reaction between lipid surfaces and ice.

References

1 S. Mann, in *Biomineralization Principles and Concepts in Bioinorganic Materials Chemistry*, 1st ed., Oxford University Press, New York, **2001**; M. Knez, A. M. Bittner, F. Boes, C. Wege, H. Jeske, E. Maiss, K. Kern, *Nano Lett.* **2003**, *3*, 1079; Y. Ono, Y. Kanekiyo, K. Inoue, J. Hojo, M. Nango, S. Shinkai, *Chem. Lett.* **1999**, 475; K. J. C. van Bommel, A. Friggeri, S. Shinkai, *Angew. Chem., Int. Ed.* **2003**, *42*, 980.

2 J. H. Jung, S. Shinkai, T. Shimizu, *Chem. Rec.* **2003**, *3*, 212; M. Numata, K. Sugiyasu, T. Hasegawa, S. Shinkai, *Angew. Chem., Int. Ed.* **2004**, *43*, 3279; S. H. Tolbert, A. Firouzi, G. D. Stucky, B. F. Chmelka, *Science* **1997**, *278*, 264; Q. Huo, D. I. Margolese, U. Ciesla, P. Feng, T. E. Gier, P. Sieger, R. Leon, P. M. Petroff, F. Schuth, G. D. Stucky, *Nature* **1994**, *368*, 317; H.-P. Lin, C.-Y. Mou, *Science* **1996**, *273*, 765; J. J. E. Moreau, L. Vellutini, M. W. C. Man, C. Bied, J.-L. Bantignies, P. Dieudonne, J.-L. Sauvajol, *J. Am. Chem. Soc.* **2001**, *123*, 7957; T. Shimizu, M. Masuda, H. Minamikawa, *Chem. Rev.* **2005**, *105*, 1401.

3 C. R. Martin, *Science* **1994**, *266*, 1961; C. J. Brumlik, C. R. Martin, *J. Am. Chem. Soc.* **1991**, *113*, 3174; J. Huang, T. Kunitake, *J. Am. Chem. Soc.* **2003**, *125*, 11834.

4 S. Kobayashi, N. Hamasaki, M. Suzuki, M. Kimura, H. Shirai, K. Hanabusa, *J. Am. Chem. Soc.* **2002**, *124*, 6550; S. Kobayashi, K. Hanabusa, N. Hamasaki, M. Kimura, H. Shirai, S. Shinkai, *Chem. Mater.* **2000**, *12*, 1523; Y. Ono, Y. Kanekiyo, K. Inoue, J. Hojo, S. Shinkai, *Chem. Lett.* **1999**, 23; A. Friggeri, O. Gronwald, K. J. C. van Bommel, S. Shinkai, D. N. Reinhoudt, *Chem. Commun.* **2001**, 2434.

5 For example: D. Zhao, P. Yang, N. Melosh, J. Feng, B. F. Chmelka, G. D. Stucky, *Adv. Mater.* **1998**, *10*, 1380; J. F. Wang, J. P. Zhang, B. Y. Asoo, G. D. Stucky, *J. Am. Chem. Soc.* **2003**, *125*, 13966; Q. H. Shi, J. F. Wang, M. D. Wyrsta, G. D. Stucky, *J. Am. Chem. Soc.* **2005**, *127*, 10154.

6 Q. Ji, T. Shimizu, *Chem. Commun.* **2005**, 4411.

7 S. Kamiya, H. Minamikawa, J. H. Jung, B. Yang, M. Masuda, T. Shimizu, *Langmuir* **2005**, *21*, 743; B. Yang, S. Kamiya, K. Yoshida, T. Shimizu, *Chem. Commun.* **2004**, 500; B. Yang, S. Kamiya, Y. Shimizu, N. Koshizaki, T. Shimizu, *Chem. Mater.* **2004**, *16*, 2826.

8 Q. Ji, S. Kamiya, J. H. Jung, T. Shimizu, *J. Mater. Chem.* **2005**, *15*, 743.

9 H. Yui, Y. Guo, K. Koyama, T. Sawada, G. John, B. Yang, M. Masuda, T. Shimizu, *Langmuir* **2005**, *21*, 721; Y. Guo, H. Yui, H. Minamikawa, M. Masuda, K. Koyama, T. Sawada, K. Ito, T. Shimizu, *Langmuir* **2005**, *21*, 4610.

Published on the web (Advance View) March 11, 2006; DOI 10.1246/cl.2006.394