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Creation of Novel Helical Ribbon and Double-Layered Nanotube TiO_2 Structures Using an Organogel Template

Jong Hwa Jung,[†] Hideki Kobayashi,[‡]
Kjeld J. C. van Bommel,[‡] Seiji Shinkai,[‡] and
Toshimi Shimizu*,[†,§]

CREST, Japan Science and Technology Corporation (JST), and Nanoarchitectonics Research Center, National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba Central 4, 1-1-1 Higashi, Tsukuba, Ibaraki 305-8562, Japan, Chemotransfiguration Project, Japan Science and Technology Corporation (JST), 2432 Aikawa, Kurume, Fukuoka 839-0861, Japan, and Nanoarchitectonics Research Center, National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba Central 5, 1-1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan

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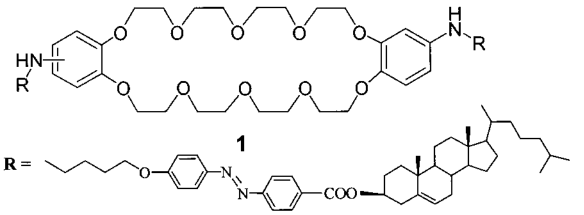
Hollow nanotubes have attracted a great deal of attention in both fundamental and industrial studies.[1,2] They possess unique properties that impart them to have potential applications in fields such as electronics, optics, advanced catalysis, and energy storage/conversion. Furthermore, their tubular structures have prompted research into the physical and chemical properties of molecules confined in their inner nanospaces and eventually may lead to the mimicking of biological channels. Therefore, the fabrication of hollow nanotubes and the modification of the properties either by filling or by coating the tubes have been developed to fit particular application requirements.

Hollow tubes fabricated so far include examples composed of carbon,[3,4] boron nitride,[5] silica,[6−8] and vanadium oxide.[9] The fabrication processes employed differ greatly; for example, carbon nanotubes are produced by arc-discharge evaporation of carbon. On the other hand, the Mobil research group has synthesized ordered nanotubes in condensed forms,[10] i.e., mesoporous materials (the so-called M41S family) using surfactant assemblies as a template. Since then, a variety of mesoporous materials have been synthesized consisting of inorganic materials such as MnO_2,[11] Al_2O_3,[12] TiO_2,[13] and ZnO_2.[14] Among them, porous TiO_2 is one of the most attractive materials due to its excellent performance in photocatalytic reactions, photoelectronics, and semiconductor applications.[1,2] However, no systems have been so far developed, which result in a particular morphology of isolated tubular TiO_2 structures similar to those obtained for mesoporous silica.[13] In the present paper, we report an approach to preparation of well-defined TiO_2 helical ribbons and nanotubes through sol−gel polymerization of titanium tetraisopropoxide [Ti(O*i*Pr)$_4$] in gels of the compound **1**.



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In the synthesis of the TiO_2 structures, neutral dibenzo-30-crown-10-appended cholesterol gelator **1** was employed as a template to combine with Ti(O*i*Pr)$_4$. It is known that the hydrolysis and condensation rates of Ti(O*i*Pr)$_4$ are much higher than those of silicon alkoxides. This makes it more difficult to control the combination and morphologies of organic−inorganic hybrids in the synthesis of TiO_2 materials. Here, the synthesis of the TiO_2 structures is based on the growth of the inorganic−organic hybrids in static 1-butanol via hydrolysis of the Ti(O*i*Pr)$_4$ under the influence of atmospheric humidity.

Compound **1** was synthesized according to methods reported previously.[15] Compound **1** was able to gelate organic solvents such as acetic acid, acetonitrile, acetone, ethanol, 1-butanol, 1-hexanol, DMSO, and DMF, even at concentrations of gelator below 1.0 wt %. These results clearly show that **1** acts as a versatile gelator of organic solvents. We previously reported that the coiled nanofibers self-assembled in the gel of **1** in acetic acid gradually turned into tubular structures several micrometers long and with internal diameters of ca. 550

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[*] To whom correspondence should be addressed. Fax: +81-298-61-2659. E-mail: tshmz-shimizu@aist.go.jp.

[†] CREST, JST, and Nanoarchitectonics Research Center, AIST.

[‡] Chemotransfiguration Project, JST.

[§] Nanoarchitectonics Research Center, AIST.

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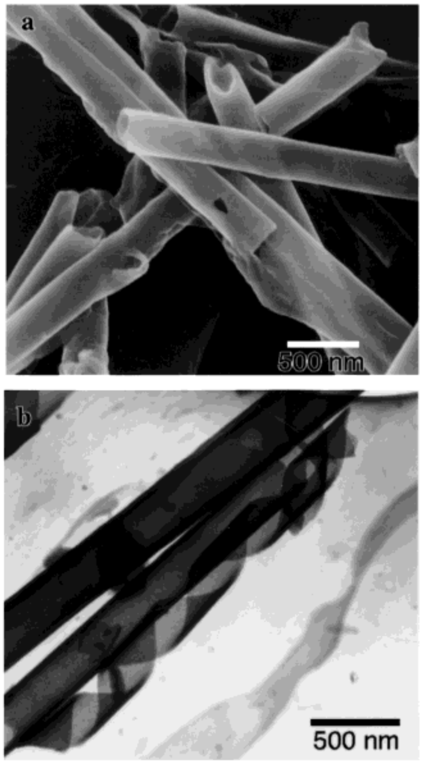

Figure 1. (a) SEM and (b) TEM images of the acetic acid organogel of **1**.

nm.[15] The tube morphology was confirmed using TEM and SEM. Both end parts of the tubes are open and possess uniform shape and internal diameter. Examination of the nanotubes revealed that they are composed of a hollow inner core and wall (Figure 1).[16] These results indicate that the organogel grows with a number of metastable intermediate structures, viz. a linear ribbon → a helical ribbon → a tubule.

To transcribe the superstructures formed in the organogel into their analogous TiO_2 structures, we carried out sol−gel polymerization of $Ti(OiPr)_4$ in a gel of **1** in 1-butanol, according to a method described previously.[6] The experimental procedure is as follows: **1** (2.0−5.0 mg) was dissolved in 1-butanol (200 mg), $Ti(OiPr)_4$ (20.0 mg) was added, and finally benzylamine (6.0 mg) was added as a catalyst for the sol−gel polymerization. The sample was left in an open container without stirring at ambient temperature for 14 days. Subsequently, the sample was heated at 200 °C for 2 h followed by 2 h at 500 °C, both under a nitrogen atmosphere and then kept at 500 °C under aerobic conditions for 4 h. The formation processes of the TiO_2 nanotubes were elucidated by monitoring the shape and size of the TiO_2 structures with scanning electron microscopy (SEM) and transmission electron microscopy (TEM). After calcination, the morphologies of the TiO_2 product turned out to be the well-defined helical ribbons and nanotubes with diameters of ca. 500 nm and with smooth surfaces (Figure 2). As far as can be determined, all chiral structures possess a right-handed helical motif. Since the exciton-coupling band present in CD spectra of gels of **1** also shows the R (right) helicity,[15] it seems plausible that this microscopic helicity was reflected in the macroscopic helicity. All these results prove that the helical ribbon and nanotube structures of the organogel of **1** were successfully transcribed into the TiO_2 nanotube structures, most likely through hydrogen-bonding interactions between the amide moieties of **1** and negatively charged TiO_2 precursors.[17] This TiO_2 helical ribbon and nanotube structures are quite different from those obtained from a cyclohexanediamine-based organogel or polymer fibers reported by the Hanabusa group and Caruso group, which featured the linear fiber structure.[13]

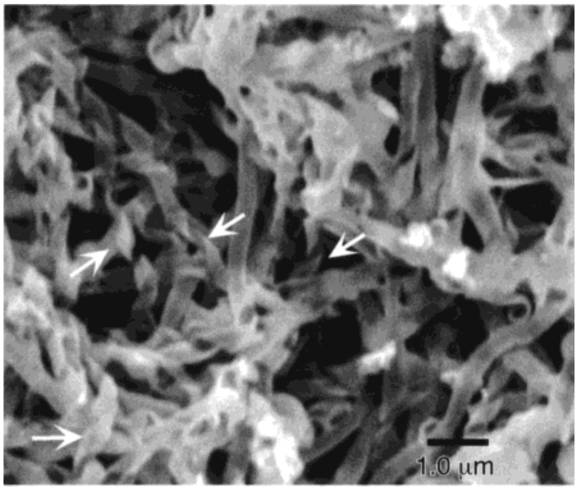

Figure 2. SEM image of the TiO_2 helical ribbon and the double-layered nanotube (after calcination) obtained through transcription of the 1-butanol gel of **1**.

To further confirm that the organogel structure really acted as a template for the formation of the TiO_2 structures, TEM pictures were taken after removal of **1** by calcination (Figure 3). The TiO_2 structures obtained from the gel of **1** in 1-butanol clearly possess an inner hollow structure, the diameter of which is in good accordance with that of the original organogel template. High-magnification TEM images of the TiO_2 tubules proved that they consist of two TiO_2 layers, with a 8−9 nm of nanospace between layers, indicating that $Ti(OiPr)_4$ molecules (or oligomeric TiO_2 particles) were adsorbed onto both sides of the 8−9-nm-thick organogel layer, which existed as a bilayer between these two developing TiO_2 layers. This result clearly supports the view that the TiO_2 nanotubes contain both a micro opening space and a macro cavity. The former one was induced by the organogel template and has a diameter of 8−9 nm. The second letter, with a diameter of ca. 500 nm, was induced by helical ribbon growth. We believe that such a precise transcription has been possible for the first time by using organogel superstructures because of the crystalline character as a template.

From these observations, we now propose the following mechanism for the formation of the helical ribbon and nanotubular TiO_2 structures (Figure 4). Oligomeric

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(16) The crown moiety in cholesterol gelators is important for preparing the double-layered TiO_2 and the silica. The crown moiety is a useful functional group not only for preparing the double-layered tubular structure of a template in the sol−gel reaction but also for controlling solubility in organic solvents.

(17) In a previous sol−gel transcription of TEOS, we have found that the *N*-methylated derivative produced a granular structure of the silica, but not a tubular structure. This finding indicates the importance of the hydrogen-binding interaction between an amino proton of the template and oxygen atom of TEOS. Therefore, we consider that an amino proton of the template acts as a binding site of the oxygen atom of the $Ti(OiPr)_4$.

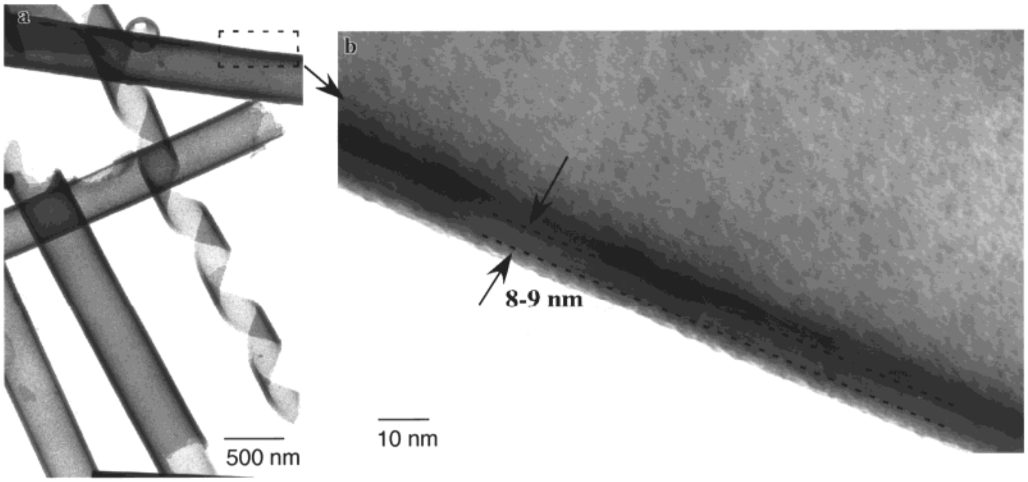

Figure 3. TEM images of the TiO_2 helical ribbon and the double-layered nanotube (after calcination) obtained through transcription of the 1-butanol gel of **1**: (a) low magnification and (b) high magnification.

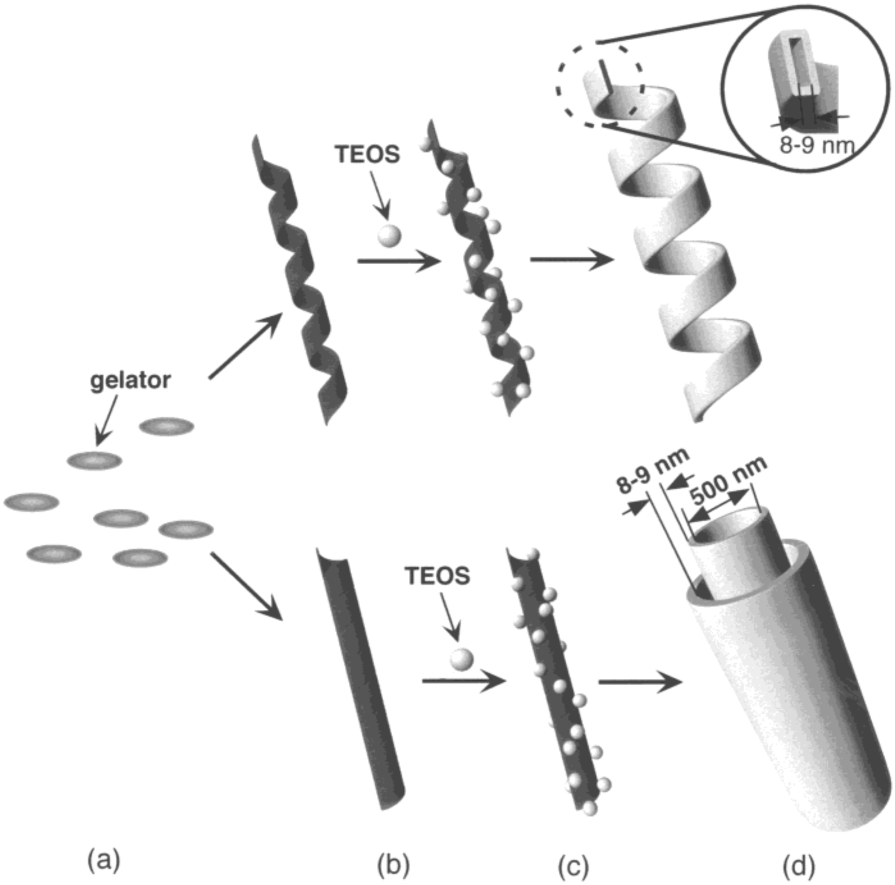

Figure 4. Postulated mechanism for the sol−gel polymerization of Ti(O*i*Pr)$_4$ using the organogel of **1** as a template: (a) gelator; (b) gelation; (c) sol−gel polymerization of TEOS and adsorption onto the gelator; (d) hollow helical-ribbon (upper) and hollow double-layered nanotube (low) of the TiO_2 formed after calcinations.

TiO_2 species are adsorbed onto both the inner and outer surfaces of the helical ribbon and tubular structures present in the organogel of **1** and the polymerization further proceeds along the helical ribbon nanotube. Then, the TiO_2 nanotube continues to grow through sol−gel polymerization along both surfaces (Figure 4c). As supported by the clear correlation between the xerogel structures (Figure 1) and the resultant TiO_2 nanotubular structures (Figures 2 and 3), the organogel structures are directly and precisely transcribed into their TiO_2 analogues, in all likelihood under the influence of hydrogen-bonding interactions.

In conclusion, the present paper has demonstrated a new methodology to prepare the TiO_2 helical ribbon and double-layered tubular structures with 8−9 nm of nano space between layers, using a crown-appended cholesterol-based organic gelator. This is a very rare example of chirality exhibition created in an inorganic material. The results described here clearly show the versatility of the template method for the creation of various inorganic structures.

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