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Sol–Gel Transcription of Semi-Fluorinated Organogel Fiber into Fluorocarbon-Functionalized Silica Nanotubes

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Creation of nanoscopic superstructures with a wide variety of morphologies from capsule, fiber, tube, and ribbon to sheet has been tried in the field of supramolecular chemistry.[1–4] The morphological diversity develops as a result of molecular aggregation via intermolecular interactions, such as hydrogen bond, electrostatic interaction, $\pi-\pi$ interaction, and so forth. In general, this diversity is not available in materials constructed only by covalent bond. Most superstructures, however, are fragile against mechanical stresses and chemical environments. To overcome this drawback, transcription of desired morphologies into robust materials has been studied.[4–6]

Low molecular weight gelators are known to form physical gels, in which the gelator molecules self-assemble to form fibrous or spherical superstructures via intermolecular interactions.[7–10] Recently, it has been reported that the self-assembled superstructures can act as templates for nanostructured metal oxides.[5,6,11–14] The typical process of the transcription is as follows: (I) metal alkoxides self-assemble on the surface of a preformed superstructure through intermolecular interactions; (II) sol–gel condensation of metal alkoxides is carried out on the surface; and (III) the preformed superstructure is removed by washing and/or heating. In particular, the first step is a key for a success in the template sol–gel condensation; a certain type of either ionic interaction or hydrogen bond is indispensable between the superstructure and the metal alkoxides.[5,6] Therefore, the template method is only applicable to the superstructures formed by gelators possessing appropriate functional groups, except in the case using a mediator molecule.[14] To further widen the applicability of this template system, it is crucial to find other intermolecular interactions available to the first step (I) of the transcription.

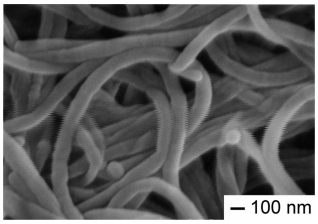
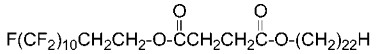


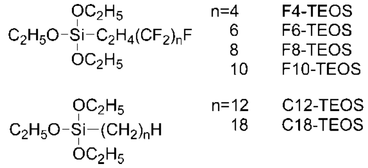
Figure 1. FE-SEM image of xerogel of **1**.

Scheme 1. Molecular Structure of Gelator 1



$F(CF_2)_{10}CH_2CH_2\text{-}O\text{-}\overset{O}{\overset{\|}{C}}CH_2CH_2\overset{O}{\overset{\|}{C}}\text{-}O\text{-}(CH_2)_{22}H$ **1**

Scheme 2. Molecular Structures of Functionalized Trialkoxysilanes



$C_2H_5O\text{-}\underset{OC_2H_5}{\overset{OC_2H_5}{Si}}\text{-}C_2H_4(CF_2)_nF$

$C_2H_5O\text{-}\underset{OC_2H_5}{\overset{OC_2H_5}{Si}}\text{-}(CH_2)_nH$

Recently, we reported low molecular weight organogelators containing perfluoroalkyl chains, which can gelate a wide variety of organic solvents at a low concentration.[15] The resulting physical gels are stabilized primarily by aggregation of perfluoroalkyl chains. Namely, this weaker intermolecular interaction is an effective driving force for the gelation. This leads us to utilize the aggregation of perfluoroalkyl chains for the template sol–gel condensation. Here, the synthesis of silica nanotubes is demonstrated using the fibrous structure formed by a perfluoroalkyl chain-containing organogelator as a template.

The gelator **1**(Scheme 1) was synthesized according to the method reported previously.[15] This compound can gelate alcoholic solvents at the minimum gel concentration of less than 10 g/L. Figure 1 shows a field emission scanning electron microscopy (FE-SEM) image of the xerogel prepared from **1** and ethanol, where self-assembled fibers approximately 100 nm in diameter are observed. This fibrous structure is transcribed to silica structure by sol–gel condensation of the mixture of the gelator **1** and fluorocarbon-functionalized trialkoxysilane (Scheme 2). The typical procedure is as follows. The gelator **1** (10.0 mg, 10.3 μmol) was dissolved in hot ethanol (3 mL), and then tetraethox-

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(1) Atwood, J. L.; Davis, J. E. D.; MacNicol, D. D.; Vögtle, F. *Comprehensive Supramolecular Chemistry*; Pergamon: Oxford, 1996.
(2) Hoeben, F. J. M.; Jonkheijm, P.; Meijer, E. W.; Schenning, A. P. H. J. *Chem. Rev.* **2005**, *105*, 1491.
(3) Fuhrhop, J. H.; Helfrich, W. *Chem. Rev.* **1993**, *93*, 1565.
(4) Shimizu, T.; Masuda, M.; Minamikawa, H. *Chem. Rev.* **2005**, *105*, 1401.
(5) Sada, K.; Takeuchi, M.; Fujita, N.; Numata, M.; Shinkai, S. *Chem. Soc. Rev.* **2007**, *36*, 415.
(6) van Bommel, K. J. C.; Friggeri, A.; Shinkai, S. *Angew. Chem., Int. Ed.* **2003**, *42*, 980.
(7) Fages, F. Low Molecular Mass Gelator. In *Topics in Current Chemistry*; Springer-Verlag: Berlin, 2005; Vol. 256.
(8) Terech, P.; Weiss, R. G. *Chem. Rev.* **1997**, *97*, 3133.
(9) George, M.; Weiss, R. G. *Acc. Chem. Res.* **2006**, *39*, 489.
(10) van Esch, J. H.; Feringa, B. L. *Angew. Chem., Int. Ed.* **2000**, *39*, 2263.
(11) Yang, Y.; Suzuki, M.; Owa, S.; Shirai, H.; Hanabusa, K. *J. Am. Chem. Soc.* **2007**, *129*, 581.
(12) Suzuki, M.; Nakajima, Y.; Sato, T.; Shirai, H.; Hanabusa, K. *Chem. Commun.* **2006**, *4*, 377.
(13) Kishida, T.; Fujita, N.; Sada, K.; Shinkai, S. *J. Am. Chem. Soc.* **2005**, *127*, 7298.
(14) Friggeri, A.; Gronwald, O.; van Bommel, K. J. C.; Shinkai, S.; Reinhoudt, D. N. *Chem. Commun.* **2001**, *23*, 2434.
(15) Yamanaka, M.; Sada, K.; Miyata, M.; Hanabusa, K.; Nakano, K. *Chem. Commun.* **2006**, *21*, 2248.

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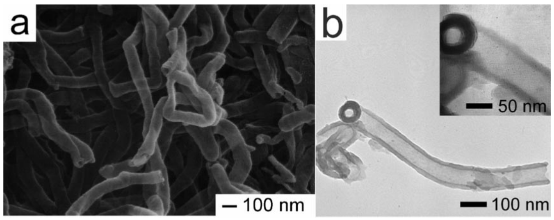

Figure 2. FE-SEM and TEM images of silica nanotubes (molar ratio of TEOS/F8-TEOS = 3:1).

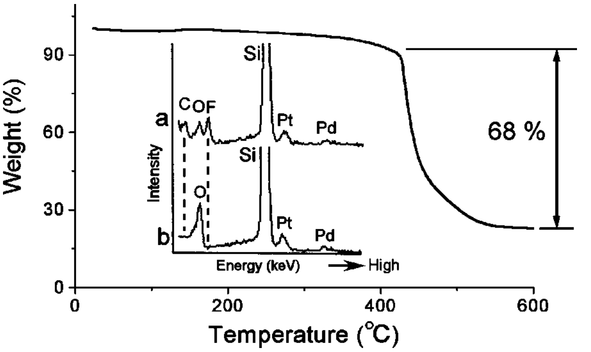

Figure 3. TGA diagram of the silica nanotube with EDX spectra (a) before and (b) after calcination.

ysilane (TEOS, 10.1 mg, 48.5 μmol), F8-TEOS (9.9 mg, 16.2 μmol), propylamine (30 μL), and water (30 μL) were added to the hot solution. By cooling down to 20 °C, the mixed solution became gelated. The obtained translucent gel was sealed in a glass tube and was allowed to settle for two weeks. Thereafter, the gel was washed with warmed chloroform to obtain white solids (7.4 mg), and the solids were dried on a filter paper. This washing procedure was adopted to remove the gelator **1** from the product. In differential scanning calorimeter (DSC) of the obtained solids, as shown in Figure S1, Supporting Information, the complete removal was confirmed by the absence of a peak corresponding to the melting point of the gelator **1**, while the corresponding peak was observed in the product before the washing.

The obtained white solids were observed by FE-SEM, as shown in Figure 2a. The solids have a homogeneous tubular structure, indicating that the self-assembled fibrous structure of **1** is effectively transcribed to the final silica structure. The outside diameters and the lengths of the tubes were in the span of 90−110 nm and 1−10 μm, respectively. The transmission electron microscopy (TEM) image is also shown in Figure 2b. The tube in this image has the inner and outer diameters of 60 and 90 nm, respectively, and the wall thickness is 15 nm. These values agree with those of the self-assembled fibers of gelator **1** reasonably (Figure 1).

The FT-IR spectrum of the tube has the peaks assignable to the Si−O bond at 461 and 1077 cm^{-1} and to the C−F bond at 1149 and 1207 cm^{-1}. Thus, the tube is an organic/inorganic hybrid material composed of silica and fluorocarbon. Thermogravimetric analysis (TGA) was adopted to quantify the amount of fluorocarbon incorporated in this material.[16] Figure 3 shows the TGA diagram with energy dispersive X-ray spectroscopy (EDX) spectra before and after the thermal measurement, that is, calcination, of the tube. The weight loss from 400 to 550 °C corresponds to the decomposition of the organic group in the silica tubes; this is ascertained by the fact that no peaks were assignable to C−F bonds in the FT-IR spectrum of the calcined tube. The complete decomposition was also supported by EDX; the peaks corresponding to C and F atoms disappeared after the calcination. The observed weight loss (68%) is close to the theoretical value (64%) calculated from the composition of the functionalized silica synthesized under the condition mentioned above (molar ratio of TEOS/F8-TEOS = 3:1). This indicates that the two alkoxysilanes TEOS and F8-TEOS in the starting gel were co-condensed at the original ratios to give the tubes. In addition, the tubular structure was maintained after the calcination; little difference was observed in the diameter of the original and the calcined tubes. (Figure S2, Supporting Information). Moreover, the incorporation of fluorocarbon was confirmed by a change in the nanotubes' hydrophilicity; nanotubes after calcination easily dispersed in aqueous solutions, while those before calcination were repelled.

To elucidate the additional effect of the functionalized trialkoxysilane for the transcription, we altered the molar ratio of TEOS/F8-TEOS (total weight 20 mg of TEOS and F8-TEOS is constant) in the sol–gel condensation while keeping the other conditions. When only TEOS was added in the ethanol solution, only granular silica particles were obtained. An addition of a small amount of F8-TEOS (TEOS/F8-TEOS = 26:1) gave several incomplete tubular structures in bulk silica compounds (Figure 4a). A further increase in the ratio of F8-TEOS (TEOS/F8-TEOS = 7:1) led to complete tubes; the tubes have similar diameters with the tube mentioned above (TEOS/F8-TEOS = 3:1) but have shorter lengths (Figure 4b). These observations show that an addition of F8-TEOS is requisite for the formation of the tubular structure. An equimolar amount of TEOS and F8-TEOS addition resulted in the formation of squashed tubes with outer diameters similar to those of the other tubes obtained (Figure 4c). A further increase in the ratio of F8-TEOS gave only sticky bulk compounds. From these observations, it can be concluded that an adequate amount of F8-TEOS is requisite for the formation of the tubular structure in the present sol–gel condensation. In addition, the dependence of the pliability of the tube on the additional ratio suggests not only the surface reaction of F8-TEOS on the silica tubes but also the homogeneous reaction of the two alkoxysilanes.

Next, we tried the template sol–gel condensation using other fluorocarbon-functionalized trialkoxysilanes (Scheme 2) under the same condition mentioned above (molar ratio of TEOS to functionalized trialkoxysilane is 3:1). When F4-TEOS was used, granular silica particles were obtained (Figure 4d). On the other hand, tubular structures were obtained from either F6-TEOS or F10-TEOS; the former and the latter alkoxysilanes gave the tubes having the outer diameters of 110−130 and 80−120 nm, respectively (Figure 4e,f). Thus, a functionalized trialkoxysilane possessing a longer perfluoroalkyl chain is requisite for forming a tubular structure. Moreover, we conducted the sol–gel condensation

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(16) Osei-Prempeh, G.; Lehmler, H. -J.; Rankin, S. E.; Knutson, B. L. *Ind. Eng. Chem. Res.* **2008**, *47*, 530.

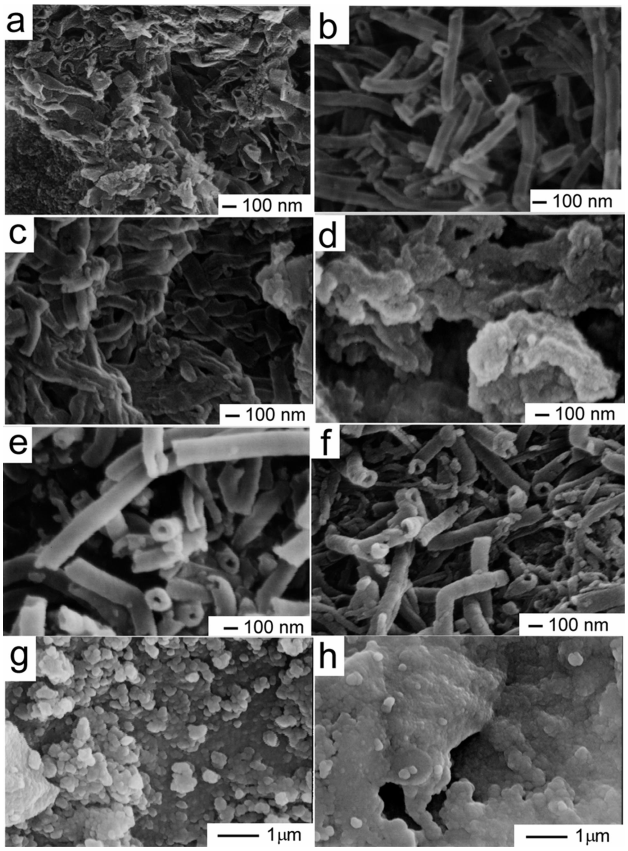

Figure 4. FE-SEM images of silica compounds synthesized from TEOS and functionalized trialkoxysilanes at various molar ratios: (a) TEOS/F8-TEOS = 26:1, (b) TEOS/F8-TEOS = 7:1, (c) TEOS/F8-TEOS = 1:1, (d) TEOS/F4-TEOS = 3:1, (e) TEOS/F6-TEOS = 3:1, (f) TEOS/F10-TEOS = 3:1, (g) TEOS/C12-TEOS = 3:1, (h) TEOS/C18-TEOS = 3:1.

using trialkoxysilanes possessing a long alkyl chain instead of the perfluoroalkyl chain. The addition of C12-TEOS or C18-TEOS (Scheme 2) resulted in the formation of only granular silica particles (Figure 4g,h), indicating that alkyl chains in the alkoxysilanes are not effective for forming a tubular structure.

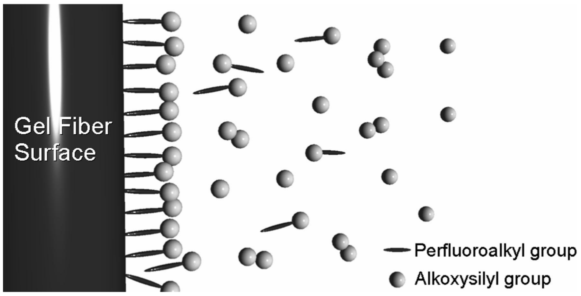

Figure 5. Schematic representation of aggregation of fluorocarbon-functionalized trialkoxysilanes on the surface of the self-assembled fiber of **1**.

From the foregoing observations, we propose a mechanism for the formation of fluorocarbon-functionalized silica tubes, as shown in Figure 5. Fluorocarbon-functionalized trialkoxysilanes are absorbed onto the self-assembled fibers of the gelator **1** through the aggregation of perfluoroalkyl chains between the alkoxysilanes and **1** and begin to condense. Subsequently, the functionalized monomer and oligomer co-condense with neighboring TEOS and its oligomer to grow the tubular structure. Thus, the fluorocarbon-functionalized silica tube is directly synthesized, reflecting the fibrous structure of **1**.

In conclusion, we demonstrated that the self-assembled fiber of the gelator **1** acts as a template for silica nanotubes. Aggregation of perfluoroalkyl chains between the gelator and the functionalized alkoxysilanes is a primary factor for achieving the transcription of the fibrous structure into the tubular product. The present method enables the direct synthesis of the organic/inorganic hybrid tubes and stands a chance of fabricating a broad range of nanostructured materials.

Supporting Information Available: DSC curves of obtained solids and gelator **1** (Figure S1) and FE-SEM image of calcined silica nanotube (Figure S2). These materials are available free of charge via the Internet at http://pubs.acs.org.

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