

Direct Sol-Gel Replication of the Self-assembled Nanostructure Modified with H-bond Functionalities

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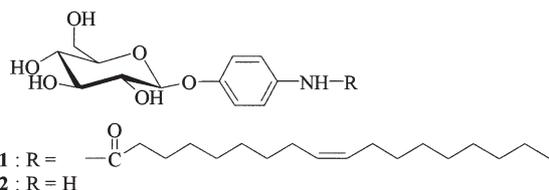
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The glucopyranoside-based amphiphile **1** formed nanofiber structures with 25–100 nm of diameters and several micrometer lengths in the presence of aminophenyl glucopyranoside **2**, and their self-assembled nanostructures were successfully replicated into the silica tube by sol-gel polymerization of TEOS.

Recently, the self-assembled nanostructures of amphiphiles have been extensively studied and exploited in various fields to advance potential application.^{1–4} Despite much effort in the fields, there are only a few examples for application due to the unstability of the self-assembled superstructure at certain temperature.^{5,6} How can we apply and stabilize the self-assembled nanostructure of amphiphiles in water? Probably they will directly be used as templates for synthesis of various inorganic materials by sol-gel reaction. Also, they can be stabilized by sol-gel reaction. The obtained nanostructures keeping intrinsic superstructure can easily be applicable in various fields.

On the other hand, a variety of inorganic nanotubes have been synthesized by only mixing self-assembling molecules with inorganic precursor, such as organogelators,^{7,8} surfactants,⁹ organic crystals,¹⁰ and have been actively progressed in application fields such as catalysis, chromatography, adsorbent, etc.^{9d,11}



In order to fabricate the inorganic tubular nano-material, we thus have synthesized compound **1**, which, together with aminophenyl glucopyranoside **2**, forms self-assembled fibers that can be replicated into the silica tube. Generally, the crystalline self-assembled nanostructures of amphiphiles are quite different from those of organogels which trap the solvent within the voids of the network. First, we prepared the self-assembled nanofiber of amphiphile **1** in the presence of **2** in water. Second, the obtained nanofiber was used in direct sol-gel reaction without any structural change. This procedure highly contrasts to the cases of organogels. For example, the gelator was mixed in advance together with inorganic precursor, water, and catalyst. The reaction mixture was heated until clear solution. Therefore, sol-gel replication was progressed by competitive reaction between self-assembling formation of gelator and polymerization of inorganic precursor.

In the present paper, we report new approach to preparation of well-defined silica nanotube through direct sol-gel polymerization of tetraethoxysilane (TEOS) in the self-assembly of compounds **1** + **2**.

The aminophenyl glucopyranoside **2** was synthesized from nitrophenyl glucopyranoside by the reaction with Pd-C and H₂ gas in THF. The obtained aminophenyl glucopyranoside was then treated with oleic acid chloride and triethylamine in THF. Compound **1** was identified by IR, NMR, Mass spectral evidence and elemental analysis.

The self-assembly of the matrix amphiphiles **1** and **2** (1 : 1 mol%) occurred rapidly under mild conditions. For example, compounds **1** and **2** were dissolved in boiling water to give a clear solution and gradually cooled to room temperature. Fine fiber structure was obtained within 5 h under ambient conditions. Figure 1a displays TEM image of the self-assembled **1** in the presence of **2** in aqueous solutions. **1** shows typical fiber structures of 25–100 nm in widths and several micrometers in lengths.

To confirm whether **2** was incorporated into the self-assembled fiber of **1**, we measured ¹H NMR spectrum of the dried solid sample prepared from **1** + **2** in aqueous solution. The small amount of aminophenyl glucopyranoside **2** (ca. 10 mol%) was actually incorporated into the self-assembled fiber of **1** (Figure 1b). Therefore, we expect that the amino group of **2** should act as efficient driving force in order to adsorb “anionic silica” precursor by intermolecular hydrogen-bonding interaction in sol-gel reaction.

We carried out sol-gel polymerization of TEOS in order to replicate the self-assembled nanofibers from **1** + **2** into the silica structure. The experimental procedure is as follows: first, the self-assembled samples **1** + **2** mixture or **1** (ca. 2–10 mg) was prepared in water. Second, the self-assembled nanofibers were collected by centrifuge. Then, TEOS (20.0 mg), water (100 mg) and benzylamine (5.0 mg) were added to self-assembled fiber. The reaction mixture was stirred for 30 min, and left without stirring at 30 °C for 10 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 process of the silica fiber was observed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

After calcination, the silica obtained from the self-assembly of glucopyranoside-based amphiphile **1** in the presence of **2** shows the well-defined silica nanotube with outer diameters of 70–150 nm and several micrometers of length (Figure 2a). On the other hand, the silica obtained from the self-assembly of amphiphile **1** in the absence of **2** only gave granular structure.

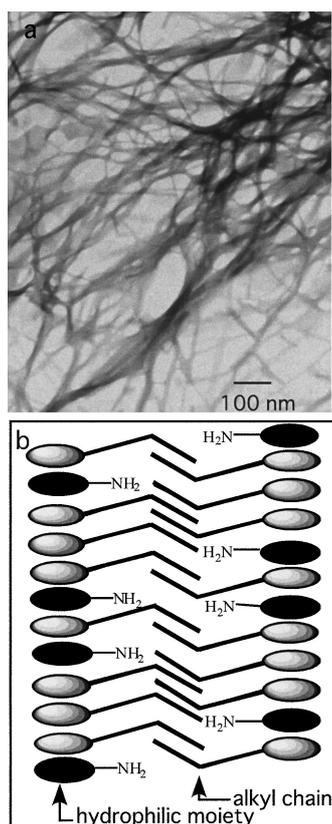


Figure 1. (a) TEM image of the self-assembled fiber in water prepared from **1** + **2**, and (b) schematic representation of the self-assembled structure of glucopyranoside-based amphiphile **1** and its derivative **2**.

These results prove that the fiber structure of the self-assembled amphiphiles **1** + **2** was successfully replicated into the silica tube, most likely through hydrogen-bonding interaction between the amine moiety of **2** and negatively charged silica precursors.

TEM analysis after removal of **1** + **2** by calcinations enabled us to further confirm that the self-assembled structure really acted a template for the formation of the silica structure, showing that no morphological change took place. TEM image also clearly shows that the center part of the tubes is light whereas both edges dark (Figure 2b), confirming the well-defined tubular structure and the previous existence of the self-assembled fiber inside the silica fibers. Average inner and outer diameters are 20–100 nm and 60–150 nm, respectively, making the thickness of the silica wall ca. 25 nm. Also, the TEM picture reveals that both sides of the channel are opened. The average value of the inner diameters for the silica tubes is in good agreement with the thickness of the self-assembled fibers observed independently (Figure 1a). These results strongly support aforementioned assumption that TEOS molecules (or oligomeric TEOS particles) were adsorbed onto surface of the self-assembled fiber and that the self-assembled fibers indeed act as a template. We believe that this method is usable not only to stabilize a variety of the self-assembled superstructure of amphiphile into permanent structure as inorganic oxide, but also to preparation of various shapes of inorganic materials.

In conclusion, this present paper has demonstrated a new approach to prepare the silica tube, using self-assembled

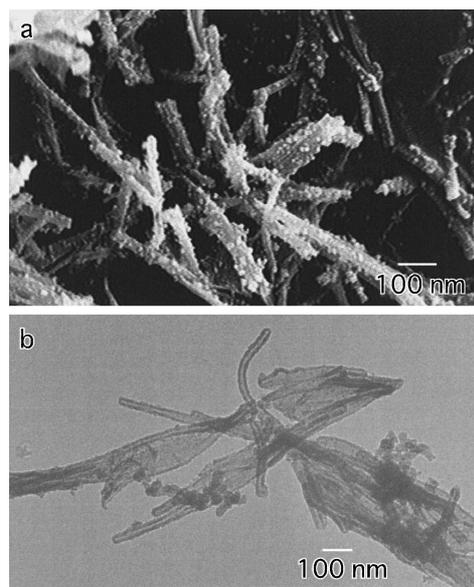


Figure 2. (a) SEM and (b) TEM images of the silica tube (after calcination) obtained through replication of the self-assembly of glucopyranoside-based amphiphile **1** and its derivative **2**.

nanofibers from glucopyranoside-based amphiphile and its homologue as a template, by direct sol-gel reaction. This silica tube is created by the intermolecular hydrogen-bonding interaction with the fine fiber structure characterization of the self-assembly. We believe that this concept will be more generally applicable to further new silica preparation using various self-assembled superstructures of amphiphiles as templates.

References

- 1 a) T. Shimizu, *Macromol. Rapid Commun.*, **23**, 311 (2002). b) G. John, M. Masuda, Y. Okada, K. Yase, and T. Shimizu, *Adv. Mater.*, **13**, 715 (2001). c) M. Masuda, T. Hanada, Y. Okada, K. Yase, and T. Shimizu, *Macromolecules*, **33**, 9233 (2000). d) I. Nakazawa, M. Masuda, Y. Okada, T. Hanada, K. Yase, M. Asai, and T. Shimizu, *Langmuir*, **15**, 4757 (1999). e) T. Shimizu and M. Masuda, *J. Am. Chem. Soc.*, **119**, 2812 (1997).
- 2 a) J.-H. Fuhrhop and W. Helfrich, *Chem. Rev.*, **93**, 1565 (1993). b) R. J. H. Hafkamp, M. C. Feiters, and R. J. Nolte, *J. Org. Chem. Soc.*, **64**, 412 (1999).
- 3 J.-H. Fuhrhop and J. Kornning, *Membranes and Molecular Assemblies: The Syneketic Approach*, The Royal Society of Chemistry 1994.
- 4 M. C. Feiters and R. J. M. Nolte, in "Chiral Self-Assembled Structures from Biomolecules and Synthetic analogues in Advances in Supramolecular Chemistry," ed. by G. W. Gokel, JAI Press Inc. (2000), Chap. 2, p 41.
- 5 S. Baral and P. Schoen, *Chem. Mater.*, **5**, 145 (1993).
- 6 F. Reichel, A. M. Roelofsens, H. P. M. Geurts, T. I. Hamalainen, M. C. Feiters, and G. J. Boons, *J. Am. Chem. Soc.*, **121**, 7989 (1999).
- 7 a) J. H. Jung, H. Kobayashi, M. Masuda, T. Shimizu, and S. Shinkai, *J. Am. Chem. Soc.*, **123**, 8785 (2001). b) J. H. Jung, Y. Ono, and S. Shinkai, *J. Chem. Soc., Perkin Trans. 2*, **1999** 1289. c) J. H. Jung, Y. Ono, and S. Shinkai, *Angew. Chem., Int. Ed.*, **39**, 1862 (2000). d) J. H. Jung, K. Nakashima, and S. Shinkai, *Nano Lett.*, **1**, 145 (2001).
- 8 a) S. Kobayashi, K. Hanabusa, N. Hamasaki, M. Kimura, H. Shirai, and S. Shinkai, *Chem. Mater.*, **12**, 1523 (2000). b) S. Kobayashi, K. Hanabusa, M. Suzuki, M. Kimura, and H. Shirai, *Chem. Lett.*, **1999**, 1077. c) R. A. Caruso, J. H. Schattka, and A. Greiner, *Adv. Mater.*, **13**, 1577 (2001).
- 9 a) M. Adachi, T. Harada, and M. Harada, *Langmuir*, **15**, 7097 (1999). b) M. Adachi, T. Harada, and M. Harada, *Langmuir*, **16**, 2376 (2000). c) Y. D. Li, X. L. Li, R. R. He, J. Zhu, and Z. X. Deng, *J. Am. Chem. Soc.*, **124**, 1411 (2002). d) X. He and D. Antonelli, *Angew. Chem., Int. Ed.*, **41**, 214 (2002).
- 10 L. Wang, S. Tomura, F. Ohashi, M. Maeda, M. Suzuki, and K. Inukai, *J. Mater. Chem.*, **11**, 1465 (2001).
- 11 a) T. Salesch, S. Bachmann, S. Brugger, R. Rabelo-Schaefer, K. Albert, S. Steinbrecher, E. Plies, A. Mehdi, C. Reye, R. J. P. Corriu, and E. Lindner, *Adv. Funct. Mater.*, **12**, 134 (2002). b) C. P. Mehnert, D. W. Weaver, and J. Y. Ying, *J. Am. Chem. Soc.*, **120**, 12289 (1998). c) X. Feng, G. E. Fryxell, L.-Q. Wang, A. Y. Kim, J. Liu, and K. M. Kemner, *Science*, **276**, 923 (1997).