Controlling Wall Thickness of Silica Nanotubes within 4-nm Precision

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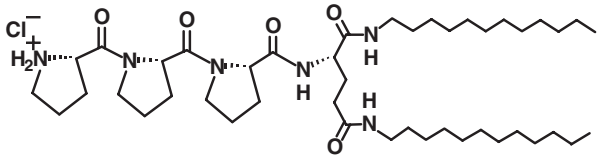
A tubular template self-assembled from secondary ammonium hydrochloride of a peptidic lipid was used for sol-gel transcription of tetraethoxysilane (TEOS). Very mild catalytic function of the terminal group enabled us to control the wall thickness of the resultant silica nanotubes within 4-nm precision, depending on the amount of TEOS added.

Controlling the morphologies of nanometer-sized objects within single-nanometer precision is of great importance for the development of nanotechnology. It is well-known that molecular structures of building blocks[1–3] and experimental conditions[4–7] influence the resultant morphologies of the molecular assemblies. Recently, novel inorganic structures with different morphologies have been prepared by a surfactant-mediated[8–10] or sol-gel transcription method.[11–14] Despite the successful synthesis of inorganic tubular structures, the control of the size dimension including wall thickness has remained unattainable, since the reported methods are still not so effective.[15–17] In this paper, we describe the control of the wall thickness within 4-nm precision attained for the silica nanotubes when using a peptidic lipid as a template for the sol-gel transcription of TEOS without any solution catalysts.



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A peptidic lipid **1** with secondary ammonium cation as a hydrophilic moiety was synthesized according to the method described previously.[18–20] The sol-gel transcription process to silica was performed in an aqueous dispersion of the lipid **1** without active solution catalysts. First, we prepared the self-assembled dispersion of the lipid **1** (5 g/L) in water. Then, different amount of TEOS were mixed with the resultant aqueous dispersion (0.2 mL) at room temperature. The molar ratios of the lipid **1** and TEOS were varied from 5 to 300, as shown in Table 1. The fluid reaction mixture was allowed to stand undisturbed for 7 days, leading gradually into gelation. The obtained solidified gel was dried using lyophilization apparatus for 24–48 h. The organic template was removed by calcination at 500 °C. We carefully observed the silica structures using transmission electron (TEM) and scanning electron microscopy (SEM).

SEM and TEM images revealed that the solidified gels prepared by Run 2 to 5 are composed of abundant silica nanotube assemblies with almost uniform size dimension. On the other hand, we obtained no silica tubular structures, but only amorphous structures instead by Run 1 and 6. We suppose that in the case of Run 1, the amount of TEOS is too small to completely cover the surface of the template. After removal of the template, the silica structures shrank or were destroyed, resulting into the amorphous structure. Under the condition that the molar ratio of TEOS and the lipid **1** is 300, we found that so large amount of TEOS cannot disperse into the aqueous phase. Even if the hydrolysis is completed, the resultant generation of ethanol may change the morphology of the organic template. These two possibilities will be the reason for the failure of the transcription. To get insight into the effect of the amount of TEOS on fine morphologies, we carefully evaluated the wall thickness of the obtained silica nanotubes via Run 2 to 5 on the basis of the TEM images (Table 1). As shown in Figure 1, the silica nanotubes possess different wall thickness, giving 7, 9, 11, and 15 nm for Run 2, 3, 4, and 5, respectively. These results indicate that the amount of TEOS could control the wall thickness of the silica nanotubes.

Table 1. Various conditions for the sol-gel transcription and the resultant wall thickness of the silica nanotube

Run	Molar ratio		Morphology	Wall thickness /nm
	Lipid **1**	TEOS		
1	1	5	Amorphous	—
2	1	20	Nanotubes	7 ± 0.3
3	1	40	Nanotubes	9 ± 0.2
4	1	60	Nanotubes	11 ± 0.3
5	1	80	Nanotubes	15 ± 0.3
6	1	300	Amorphous	—

According to the previous reports,[11,21] the properties of the functional groups attracting silica precursors would play a critical role in determining the thickness of the resultant silica wall. In the present case, although we used the identical organic template from the lipid **1** and the constant amount of the lipid as well, the wall thickness proved to increase with increasing in the amount of TEOS. Therefore, the specific mechanism of the sol-gel transcription would be the cause for the difference in the wall thickness.

Generally, acidic or basic solution catalysts play an indispensable role in the formation of silica particles.[22] However, we added no active solution catalysts in the aqueous dispersion during this sol-gel transcription. The present synthetic lipid **1**, which self-assembles in water to form a well-defined tubular structure, acts not only as a nano-template but also a catalyst.[23] Positive charges are distributed all over the surfaces of the resultant organic nanotubes from the lipid **1**. The organic nanotubes give a weakly acidic pH condition (pH $\approx$ 4.8). Under this condition, the sol-gel transcription process proceeds on the basis of a "surface mechanism" developed by Shinkai et al.[24] The tub-

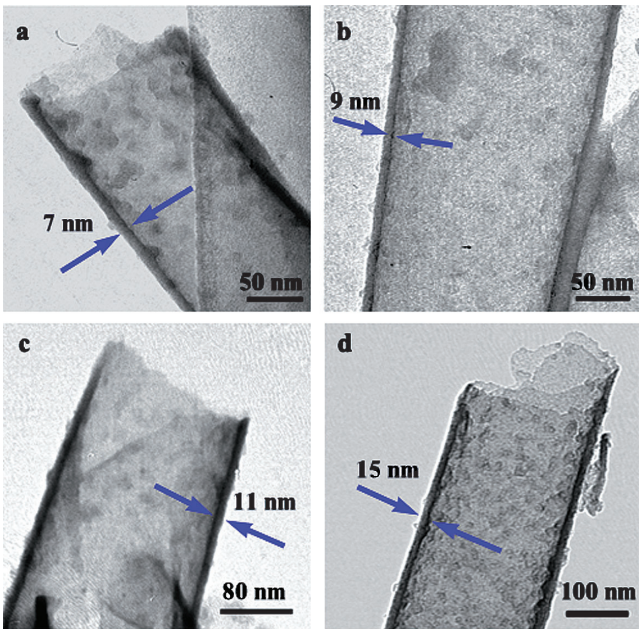

Figure 1. TEM images for silica nanotubes with different wall thickness obtained via Run 2 to 5. (see Table 1 for each wall thickness).

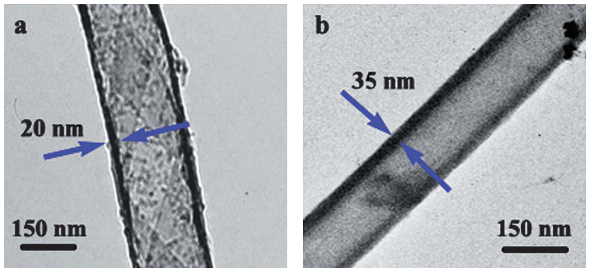

Figure 2. TEM images for silica nanotubes before calcination, which were formed by the sol-gel transcription (a) without using and (b) using solution catalyst. (a) wall thickness: 20 ± 0.5 nm. (b) wall thickness: 35 ± 0.7 nm.

ular template **1** first gives rise to the formation of small amount H^+ cations around the organic nanotubes in aqueous solution. These protons participate in the hydrolysis of TEOS. The resultant deprotonated silica precursors were adsorbed on the surface of the template by the electrostatic force and then underwent the subsequent condensation. The transcription process of the organic template takes place on the surface of the template. After the adsorption process has reached to its isoelectric point, the template may lose the function as a catalyst and the sol-gel reaction would almost finish. During the lyophilization process under high vacuum (1 Pa), unreacted TEOS may evaporate from the gel system. Thus, we can hardly find particle aggregate structures of silica. The 15-nm thickness gives the largest value that we obtained even at larger molar ratios. We assume that at this value the adsorption was saturated.

As a contrast experiment, we used a solution catalyst, sodium hydroxide, for the sol-gel transcription into silica. Although the wall thickness of the obtained silica nanotubes was relatively thicker than those without solution catalysts (Figure 2), no remarkable change in the thickness was observed by changing the amount of TEOS. This finding enables us to conclude that in the surface mechanism the presence of the secondary ammonium cations on the nanotube surfaces is crucial for the control of the thickness.

In conclusion, when adding solution catalysts into the reaction medium, we are not able to control the adsorption or deposition of silica. While in the case without catalysts, the sol-gel reaction mostly occurs near the surfaces of the organic template, as defined as a surface mechanism. Therefore, the concentration of the TEOS around the surface may affect the degree of the hydrolysis and condensation and thus affect the wall thickness of the resultant silica nanotubes. This situation allows us to control the dimension of the silica nanotubes within 4-nm precision.

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