Regulation of Silica Nanotube Diameters: Sol−Gel Transcription Using Solvent-Sensitive Morphological Change of Peptidic Lipid Nanotubes as Templates

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A secondary ammonium hydrochloride of the peptidic lipid, in which the L-prolyl-L-prolyl-L-proline fragment is coupled with an L-glutamate derivative carrying two long alkyl chains, self-assembles in water to form nanotube structures and acts as a template to transcribe them to silica nanotubes through sol−gel reaction. When the peptidic lipids self-assemble in mixtures of ethanol and water, the resultant self-assembled structures showed notable morphological changes from tubular structures with different diameters to spherical ones. Using the obtained self-assembled structures as templates in different ethanol/water mixtures, we carried out the sol−gel reaction of tetraethoxysilane (TEOS). The obtained silica structures gave tubular structures with different diameters of 80, 50, and 30 nm and hollow spheres, just corresponding to the morphological change in the self-assembled templates. We thus controlled the diameters and dimensions of the silica nanotubes, which depend on the ethanol volume fractions. In addition, we have also performed in situ control of silica tubular morphologies by the addition of ethanol in a silica/lipid xerogel state, producing a unique tube-in-tube structure.

Introduction

For the last two decades, the fabrication of inorganic structures using organic templates has been providing promising and important methods in materials science.[1,2] Intensive studies on molecular self-assembly of a variety of amphiphiles have enabled one to produce different structures, including spheres, tubes, and helical ribbons with well-defined dimensions, and transcribe their structures to diverse inorganic materials.[3−7] Among different self-assembled morphologies, hollow cylinders and spheres have been receiving growing attention in the nature and materials science fields. They not only have potential applications in electronics, optics, energy storage, and biology fields but also inspire us with an interest in fundamental phenomena specific to a confined nanospace.[8−11] However, to satisfy the requirement for different morphologies or dimensions of inorganic structures, we need to choose different organic templates for the sol−gel transcription.[2,6−9] The control of the transcribed inorganic structures is, therefore, still difficult work. In fact, many researches demonstrated that on self-assembly, the concentrations and the pH, solvent, and temperature conditions of amphiphiles allow for the control of their self-assembled structures.[12−18] However, since the first report on the fabrication of inorganic structures by organic template,[19−21] research has been focused on the exploitation of new organic templates and the fabrication of new inorganic structures with well-defined morphologies. There are only a few reports that have addressed the use of the sensitivity of self-assembled structures to the external environment for controlling the transcribed inorganic structures.[22−25]

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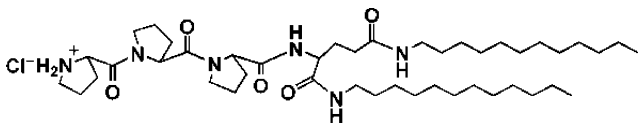
Scheme 1



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Recently, we found that the peptidic lipid **1**[26−28] converts its self-assembled structures, depending heavily on the composition of a mixture of ethanol and water. Benefiting from the interesting feature of the lipid **1**, we describe here the diameter and dimension control of the silica structures in different ethanol/water mixtures. Moreover, changing the template morphology by in situ addition of ethanol in a silica/lipid xerogel enabled us to obtain tube-in-tube silica nanotubes after calcination.

Experimental Section

Materials and General Measurements. The peptidic lipid 1 consisting of tri-L-proline and glutamic acid dialkyl amide was synthesized in a manner that is similar to the method described previously.[29−31] Self-assembly of the lipid **1** was carried out by dispersing **1** (1 mg) in Milli-Q water or ethanol/water mixtures (1 mL) at 50 °C by ultrasonication for 30 min. X-ray diffraction (XRD) was measured with a Rigaku diffractometer (Type 4037) using graded *d*-space elliptical side-by-side multilayer optics, monochromated Cu Kα radiation (40 kV, 30 mA), and imaging plate (R-Axis, IV). For FT−IR measurement, a Jasco 600 (resolution 4 cm^{-1}) was used. Circular dichroism was measured using a Jasco J-800 spectropolarimeter operating between 210 and 300 nm at 20 °C.

Sol−Gel Process. Self-assembled structures from **1** were utilized as organic templates in aqueous dispersion or ethanol/water mixtures (1 mg/mL, 100 μL), to which 20 μL tetraethoxysilane (TEOS) was added at room temperature. The pH values of the self-assembled dispersions are 5−6. The obtained fluid reaction mixture was allowed to stand for 7 days, leading gradually to solidification of the aqueous dispersion. In another procedure, a 20% volume fraction of ethanol (20 μL) was mixed with the solidified silica/lipid gel (100 μL) after the sol−gel reaction in the aqueous dispersion for 3 days. The mixture was then further reacted for 3 days at room temperature. The obtained gels were then placed into lyophilization apparatus (freeze-dryer Eyela FDU-1200) and dried at −80 °C under a vacuum of 2 Pa for 24−48 h.

STEM and SEM Measurements. Field emission scanning electron microscopy (FE-SEM) measurements were taken on a Hitachi S-4800. For scanning transmission electron microscopy (STEM) measurements, a drop of the self-assembly suspension was placed on a carbon-coated copper grid (200 mesh) and dried overnight at room temperature under low pressures (1−10 Pa). The accelerating voltage for the observation is 15 kV. Negative staining was performed with 2% (w/v) phosphotungstic acid. The pH of aqueous dispersions was adjusted to 7.5 with sodium hydroxide. A drop of the aqueous dispersion was placed on a copper grid and dried at room temperature under an argon atmosphere flow for 4 h. The staining solution was dropped on the copper grid and allowed to dry at room temperature for 2 min. The drop was then blotted off with filter paper, and the samples were dried in desiccator at room temperature for 2 days.

Results and Discussion

Self-Assembly in Ethanol/Water Mixtures. The lipid **1** (concentration: 1 mg/mL) was found to form well-defined tubular structures with average outer diameters of 80 nm through molecular self-assembly in water.[26−28] AFM measurement proved that the lipid nanotube pocesses the very thin wall consisting of only a single bilayer.[26] When examining the self-assembly of **1** in ethanol/water mixtures, we found that the ethanol composition sensitively affects the resulting self-assembled morphologies. We, therefore, carried out the self-assembly of **1** in the mixture of ethanol and water (volume fractions of ethanol: 2.0, 9.0, 23.1, 33.3, and 50.0%; Table 1). STEM measurements for stained samples of the self-assemblies revealed that the ethanol volume fractions of 2.0, 9.0, and 23.1% result in nanotube formation (Figure 1). Careful comparison of the STEM images allows us to conclude that the diameters of the self-assembled nanotubes decreased from 80 to 50 and 25 nm for the volume fractions of 2.0, 9.0, and 23.1%, respectively. The resultant self-assembled structures, when using the volume fraction of 33.3%, became soft, fibrous structures. The diameter of the fiber is about 25 nm,, similar to that of the nanotubes obtained using the 23.1% ethanol volume fraction. When the ethanol volume fraction increased to more than 50.0%, spherical self-assembled structures became dominant instead of tubular or fibrous structures.

We also studied the effect of using methanol or propanol instead of ethanol on the self-assembled morphologies of **1**. In methanol/water mixtures, the tubular morphology maintains 60 nm diameters for the methanol volume fractions of 9−50%. On the other hand, the lipid **1** was easily dissolved even in propanol/water mixtures with very small volume fractions of propanol (<5%). This feature made it difficult to study the effect of propanol on self-assembled morphologies. Thus, only a variety of volume fractions of ethanol proved to cause such a remarkable change in the self-assembled structures of **1**. Since the first report on the formation of lipid nanotubes by self-assembly in 1984,[6] formation mechanisms have been studied under different conditions.[32−39] Although most of the studies have been based on phospholipid derivatives, they reported that molecular structures of the headgroups are critical for changing the

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Table 1. Self-Assembled Structures of the Lipid 1 in the Ethanol/Water Mixtures of Different Compositions and the Resultant Transcribed Silica Structures

		transcribed silica structures		
volume fraction of ethanol (%)	self-assembled template structures	morphology	diameter (nm)	length (μm)
2.0	tubes	tubes	80 ± 5	5−10
9.0	tubes	tubes	50 ± 5	5−10
23.1	tubes	tubes	30 ± 5	15−20
33.3	fibers; spheres	tubes; spheres	30 ± 5; 200−1000	15−20
50.0	spheres	spheres	200−1000	
66.7		spheres	200−1000	

diameter of tubular structures. The pH and ionic strength of the solution will affect the ionic environment of the headgroups and lead to change in tubular structures.[18,38,39] Previous studies on the addition effect of alcohols on the self-assembled morphology of phosphonate lipid nanotubes demonstrated that alcohols with different chain length can change the wall thickness and length of the tubular structures.[40−42] However, the effect induces not only simple changes in the lipid solubility or physical properties of the mixed solvent, but also preferential partitioning of alcohols onto the lipid bilayer interface.

We measured the X-ray diffraction (XRD) spectra for the structures of **1** self-assembled in different ethanol/water mixtures (Figure 2). The nanotube self-assembled in pure water is composed of a single bilayer and shows no reflection peaks in XRD. However, the addition of ethanol will direct the self-assembled structures to take a several-lipid-bilayer system, resulting in the appearance of a reflection peak in the XRD patterns. When self-assembled in the mixture of ethanol/water (2/98, v/v), the tubular structure with 80 nm diameters showed two reflections ascribable to $d = 4.3$ nm. This value is almost compatible with the bilayer distance (4.5 nm) of the lipid nanotube obtained in water, which was already supported by the AFM measurement.[26] Therefore, small volume fractions (<2.0%) of ethanol influence no remarkable changes in the bilayer structures. When increasing the volume fraction of ethanol to 9.0%, we found that the *d*-spacing decreased to 3.7 nm. The fiber and sphere structures gave reflection peaks ascribable to $d = 3.77$ nm in the XRD patterns.

We also measured the circular dichroism (CD) for the structures self-assembled in ethanol/water mixtures with changing the volume fraction of ethanol (Figure 3). FE-SEM measurement for the tubular structures of **1** self-assembled in water sometimes showed left-handed helical markings on their surfaces driven by chiral twisting of lipid bilayers. In fact, the CD spectra of the nanotubes in ethanol/water mixtures gave a negative cotton band around 229 nm, suggesting the chiral molecular self-assembly.[6,8,13,14] With the increase in the volume fraction of ethanol, the CD intensities at $\lambda = 229$ nm drastically decrease, meaning the change in chiral molecular packing of the bilayer membranes. The addition of ethanol molecules may disorder the structure of hydrogen-bonded water associated with the headgroups of the lipid **1**, resulting into the thinner tubular morphologies. The addition of a large amount of ethanol (>50%) will make the ordered structures of **1** with chiral molecular packing

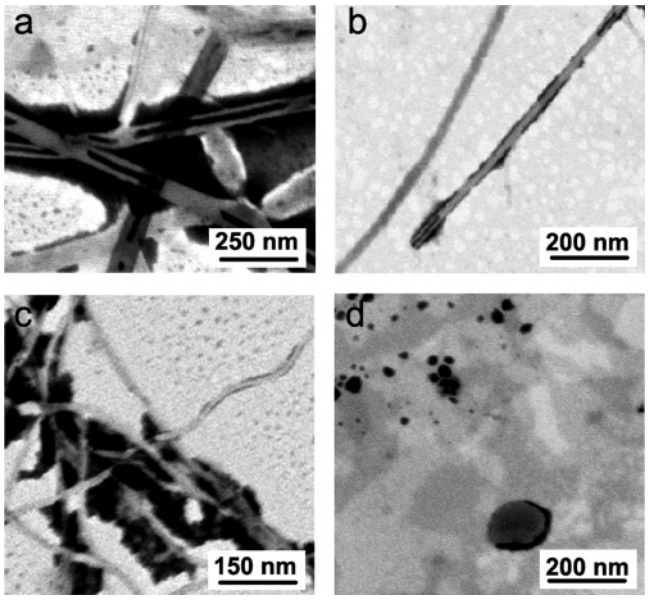

Figure 1. STEM images for the self-assembled structures of **1** in a mixture of ethanol and water (ethanol volume fraction: (a) 2.0, (b) 9.0, (c) 23.1, and (d) 50.0%). Some black dots seen in the STEM images are due to the adsorption of the staining agent on the surface of a copper grid. We were unable to remove all these purities, even by thoroughly washing the stained samples.

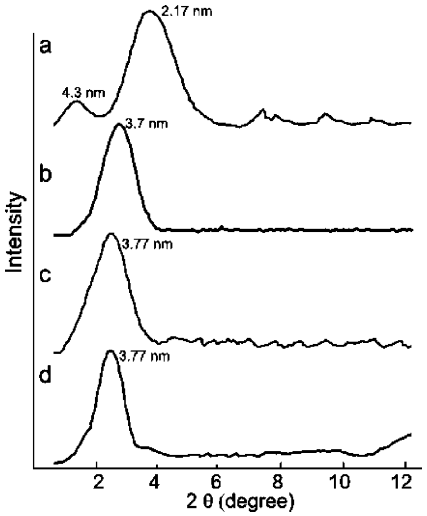

Figure 2. XRD patterns for the self-assembled (a and b) tubular, (c) fibrous, and (d) spherical structures from **1** in a mixture of ethanol and water (ethanol volume fraction: (a) 2.0, (b) 9.0, (c) 23.1, and (d) 50.0%, respectively).

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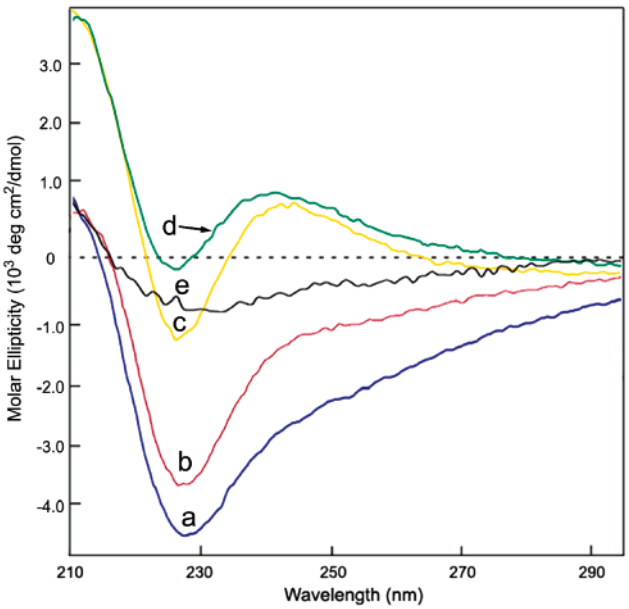

Figure 3. CD spectra for the self-assembled structures of **1** in a mixture of ethanol and water (ethanol volume fraction: (a) 2.0, (b) 9.0, (c) 23.1, (d) 33.3, and (e) 50.0%).

destroy and completely lose their original morphologies. All these findings suggest that ethanol affects the nature of hydration layers surrounding the bilayers of **1** and then alters the spacing and packing of the lipid headgroups. The new appearance of the CD band around 240 nm indicates that new chiral packing occurs and mediates the conversion from thinner tubes with a 25 nm diameter to fibers with the same diameter. Unlike phospholipids,[40−42] the tubular structures of the peptidic lipid **1** induce the diameter and morphology changes, depending on the ethanol volume fractions in aqueous dispersion. This gives a rare example of morphological changes by addition of alcohols.

Self-Assembled Lipid Nanotubes as Templates. Self-assembled structures of the lipid **1** are so sensitive to ethanol that they can give nanotubes with different diameters as well as fibers. This finding stimulated us to regulate the diameters of transcribed silica nanotubes by using the lipid nanotube as a template. The STEM image showed that the lipid nanotube template in the ethanol/water mixture (2/98 v/v) produced silica nanotubes with 80 nm diameters (Figure 4b), almost similar to those of the silica nanotubes obtained using the lipid nanotube template self-assembled in pure water (Figure 4a). Depending on the volume fractions (9.0, 23.1, and 33.3%) in a series of ethanol/water mixtures, the average diameters of the transcribed silica nanotube changed from 50 to 30 nm (Table 1 and Figure 4b−d). When carefully observing the surfaces of the silica nanotubes using STEM, we realized that the addition of ethanol tends to make the surface rougher as compared with the case in the absence of ethanol. This morphology is just like a pearl-necklace-like silica fiber.[43] During the sol−gel process in the ethanol/water mixtures, ethanol not only acts as a solvent but also influences the sol−gel reaction feature of TEOS. Ethanol molecules participate in hydrogen bonding with silanol groups, leading to the change in the kinetics of the sol−gel reaction. On the other hand, the penetration of ethanol into the lipid bilayer structure of **1** allows the catalytic activity of the surface to decrease and change the distribution of catalytic site. Eventually, the sol−gel reaction occurs independently on the surface of the tubular template, resulting in the formation of rough silica surfaces. When using the lipid sphere template of **1** in the ethanol/water mixtures (ethanol volume fraction: >50.0%), we obtained a large amount of silica hollow spheres corresponding to the structures of the template (Figure 4e).

Figure 5 shows the FT−IR spectra of the silica/lipid nanostructures obtained in the ethanol/water mixtures with different volume fractions of ethanol. The high-frequency region (3000−3800 cm^{-1}) centered around 3500 cm^{-1} is ascribable to various free and hydrogen-bonded Si−O−H and H−O−H stretching vibrations.[44−45] We found that the increase in the volume fractions of ethanol allow the O−H stretching to shift from 3494 to 3471 cm^{-1}. These results indicated that in place of water, ethanol has weakened the hydrogen bonding with the silanol groups on the surface. The weak shoulder bands around 3640 cm^{-1} ascribable to mutually hydrogen-bonded Si−O−H stretching shifted from 3625 to 3664 cm^{-1}. With an increase in the ethanol volume fraction (>2.0%), the silica structure tends to become looser and form labile vicinal Si−O−H groups favorable to surface modification. After the removal of water molecules by further freeze-drying and calcination, the obtained silica tubular structures may be suitable for effective physical adsorption or storage because of rough characteristics of the surfaces. Thus, we have been able to control the morphologies of the transcribed silica structures and improve the surface properties.

Formation of Tube-in-Tube Structures. If we can make use of morphological change of the self-assembled structures by addition of ethanol, we could also convert the hybrid silica/lipid nanostructures with the aid of ethanol. First, we carried out conventional sol−gel transcription using the lipid nanotube template in pure water. After 3 days, the aqueous dispersion became a gel state due to the formation of silica on the template surfaces, followed by drying. We then added a 20% volume fraction of ethanol to the resulting xerogel with stirring for 10 min. A further 3 days allowed the destructed gel state to regain a solidified one. We finally lyophilized and calcined the hybrid sample.

The SEM and STEM measurement for the obtained structures revealed the existence of well-defined tube-in-tube structures with open ends (images a and b of Figure 6). About 40−50% of the transcribed morphologies were observed to take the tube-in-tube structures on the basis of the edge profiles along the nanotube images observed using SEM or STEM images. These types of morphologies have been obtained by the sol−gel reaction using the lipid nanotube templates in aqueous dispersions or in different ethanol/water mixtures. Indeed, clear spaces with several nm between the transcribed two-layer structures should exist when we use lipid nanotubes as templates.[46,47] However, we have never

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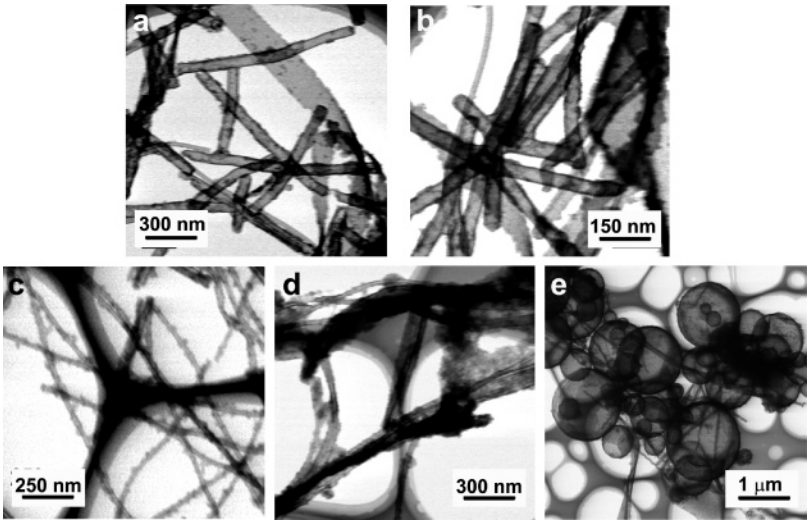

Figure 4. STEM images for the transcribed silica/lipid structures using a self-assembled structure of **1** as a template in a mixture of ethanol and water (ethanol volume fraction: (a) 0, (b) 2.0, (c) 23.1, (d) 33.3, and (e) 66.7%).

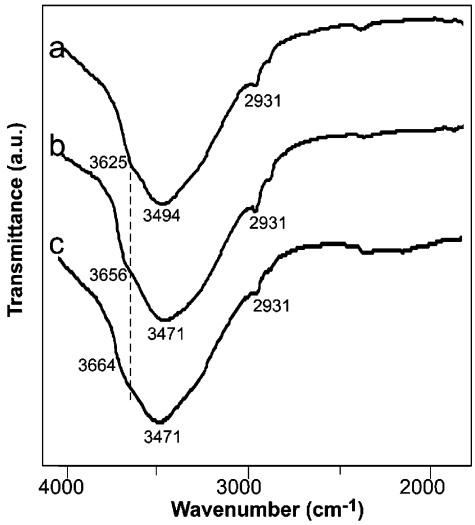

Figure 5. Partial FTIR spectra of the transcribed silica/lipid structures using the self-assembled structure of **1** as a template in a mixture of ethanol and water (ethanol volume fraction: (a) 2.0, (b) 33.3, and (c) 50.0%).

observed such nanospaces of the silica nanotubes when using the lipid nanotube of **1** as a template. The present sol−gel reaction requires no solution catalysts such as HCl, NaOH, or $NH_3 \cdot H_2O$. The reaction process depends on the mild catalyst site on the template surfaces, and the resultant silica layers are therefore extremely thin (only 3−6 nm thick). These gentle silica layers on both sides of tubular templates turn out to easily deform and hold together during calcination. However, this time we were able to clearly observe the nanospace with ca. 18 nm between the two coaxial silica nanotubes (Figure 6a−f). Notable reduction of the lipid nanotube diameters by addition of ethanol should be responsible for the production of the tube-in-tube structures.

Interestingly, the inner tube possesses a very smooth surface, whereas the outer one has a much rougher surface (Figure 6f). The inner nanotubes will be composed of a silica nanotube tightly wrapped by lipid bilayers. After the addition of ethanol to the xerogel, the lipid template will have

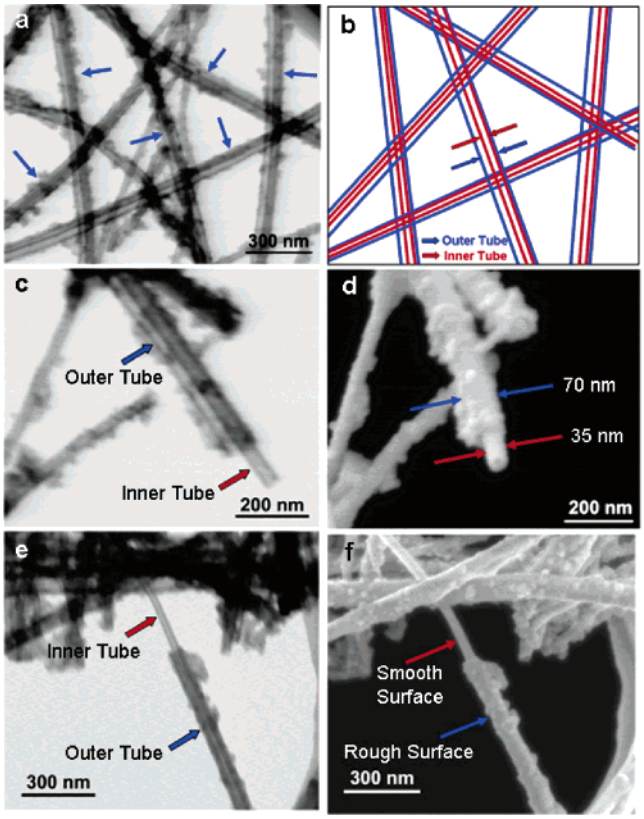

Figure 6. (a, c, and e) STEM and (d and f) SEM images of the tube-in-tube structures obtained by addition of ethanol (20% volume fraction) to silica/lipid hybrid xerogels. (b) Schematic illustration of the tube-in-tube structures that can be seen in Figure 6a (blue arrows). The outer and inner tubes are shown in blue and red lines, respectively.

shrunken to a smaller tubular structure in the same manner as that mentioned above. The outer layer of the lipid bilayer template will then separate from the deposited outermost silica layer (Figure 7). On the other hand, immiscibility of water and TEOS will make the deposition of silica to the inner surfaces of the lipid nanotube more difficult as compared with that at the outer surface. This situation will allow the extrusion of the inner silica layer with shrinking of the lipid nanotube template. Ethanol not only makes the nanotube diameter smaller but also the nanotube length

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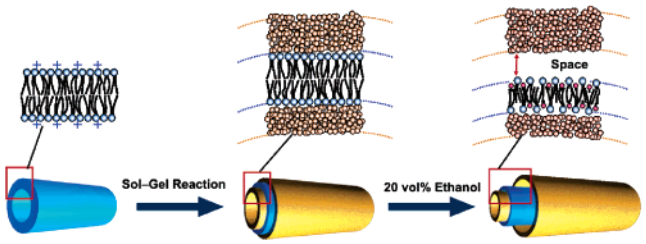

Figure 7. A possible formation mechanism for the tube-in-tube silica/lipid structure by addition of ethanol. For clarity, a single bilayer system is drawn for the lipid nanotube.

longer. Therefore, the inner tube is likely to stretch out from the outer one (Figure 6c−f). The diameter of the outer silica nanotube is about 75 nm. The inner nanotubes have a diameter of 35 nm, similar to that of the silica nanotube using a lipid fiber self-assembled in an ethanol/water mixture (23.1/76.9 v/v; Figure 6d). As mentioned above, we added no solution catalysts into the reaction system. This makes the reaction much slower than is the case when using catalysts. Thus, the amount of ethanol produced as a byproduct from TEOS is considered to be too small to induce the morphological change of the lipid nanotube template.

We compared the FT−IR spectra of the transcribed silica/lipid nanotubes in the absence of ethanol and the tube-in-tube silica structure (Figure 8). The amide I bands appeared at the same wavenumber (1643 cm^{-1}) for both nanotubes. The amide I band, mainly associated with C═O stretching vibration, is directly related to the strength of the hydrogen bonding. No change in the amide I vibration band indicated that the strength of the hydrogen bond is kept constant even after the addition of ethanol. However, the amide II band has shifted from 1565 to 1546 cm^{-1}. The amide II band, mainly ascribable to the N−H bending vibration, is conformation sensitive.[48−50] The addition of ethanol into the xerogel has in situ affected the local hydrogen-bonding pattern between the neighboring C═O and N−H groups of the lipid **1**. Eventually, the arrangement of the lipid molecules and the morphology of the tubular template will change. Thus,

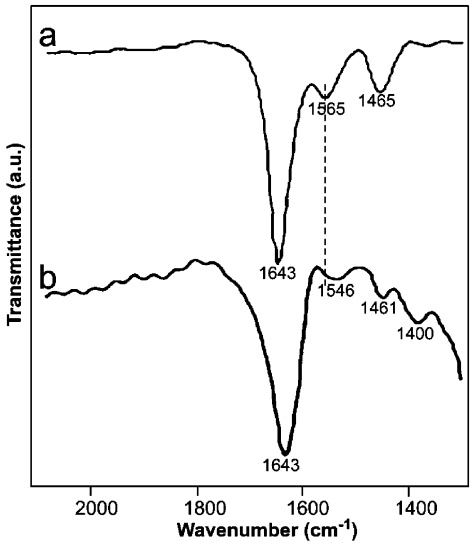

Figure 8. Partial FT−IR spectra of (a) the silica/lipid structure obtained in pure water and (b) the silica/lipid tube-in-tube structure obtained by addition of ethanol (20% volume fraction) to aqueous xerogel.

we were able to observe the transcribed silica structure and record the structural change of the lipid nanotube. After calcination at 500 °C to remove the lipid template, we actually obtained a tube-in-tube silica structure.

Conclusion

We have made use of the characteristics of the lipid nanotube template, which induces morphological change by the addition of ethanol to an aqueous dispersion, for sol−gel transcription of metal alkoxides. As a result, we were able to control the diameter of the transcribed silica nanotubes from 80 to 30 nm, depending on the volume fraction of ethanol. The addition of ethanol after the formation of aqueous xerogels enabled us to obtain a unique tube-in-tube silica/lipid nanotube. These findings displayed the advantages of using lipid assemblies as templates to fabricate inorganic nanostructures in terms of their easy synthesis, diverse structures, and their flexibility to control the morphology of inorganic structures.

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