

Preparation of the Novel Structures of the Silica Using Novel Sugar-Based Superstructures through Sol-Gel Transcription

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Three sugar-based organogelators (1-3) were synthesized. They acted as versatile gelators of organic fluids. The xerogels showed the fiber and the spherical structures. The difference in these organogel supramolecular structures has successfully been transcribed into silica structures by sol-gel polymerization of tetraethoxysilane (TEOS), resulted in single, multiple (lotus-shaped) hollow fiber structures with 5-10 nm inner diameters and a spherical structures with 500-1000 nm outer diameters.

Key words: Sugar-based gelator • sol-gel polycondensation • transcription

1. INTRODUCTION

The use of organic molecules, assemblies and supramolecular systems in the development of novel inorganic materials continues to offer new and exciting alternatives to conventional synthetic strategies.¹ Since these higher-order aggregates can provide various architectures, sol-gel polymerization utilizing them as templates results in various novel architectures which cannot be created directly from inorganic materials.

The hollow fibers of the silica have been prepared by self-assembled phospholipid fibers,² viroid cylinders,³ organic crystals⁴ or cholesterol-based organogel fibers as templates.⁵⁻⁹ Especially, cholesterol-based organogel templates have created various hollow silica fibers with linear,⁵ helical⁶ and multi-layered structures⁷ by sol-gel polymerization. The finding indicates that the cholesterol-based organogel fibers act as an efficient template to create an inside tube in the polymerization process.⁵⁻⁹ It is already known that either the cationic charge or the efficient hydrogen-bonding interaction is indispensable to the sol-gel transcription in order to adsorb 'anionic' silica particles onto the organic molecular assemblies.⁵⁻⁹ Meanwhile, the sugar-based gelators provide various, morphologically-novel superstructures such as linear,¹⁰ helical,¹⁰⁻¹² bundled,¹² multi-layered cigar-like¹² and vesicular¹³ structures according to their self-assembling manner in the gel phase. Despite their structural variety, however, the transcription of sugar-based organogel structures into the silica structure is unprecedented, because introduction of a moderate amount of the cationic charge into the organogelator is very difficult and the gelation ability is remarkably reduced in the protic sol-gel medium necessitated to sol-gel polymerization. To overcome this dilemma, we designed the sugar-based organogelators 1-3 in which the amino group not only stabilizes the organogels due to the intensified inter-

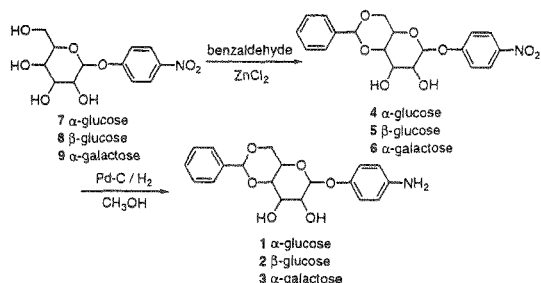
gelator hydrogen bonds¹⁰ but also binds TEOS through the hydrogen-bonding interaction.^{7,8} We have found that the novel morphologies of the sugar-based gelators are successfully transcribed into the silica prepared under the specific sol-gel polymerization conditions.

2. RESULTS AND DISCUSSION

Gelation ability and SEM/TEM observations of xerogels. Compounds 1-3 were synthesized according to Scheme 1. Compounds 4-6 were prepared by treatment of the corresponding saccharides with benzaldehyde and ZnCl₂, and reduced with H₂ and Pd on charcoal to give the desired products. The products were identified by ¹H NMR, IR and MS spectral evidence and elemental analyses. The gelation ability of these gelators 1-3 was estimated in organic solvents and water. The results are summarized in Table 1. These gelators could gelate 3-7 out of 11 organic solvents. These results indicate that they act as versatile gelators of organic solvents.

To obtain visual insights into the aggregation mode, we observed the xerogel structures of their ethanol (or water) organogels by TEM and SEM. Fig. 1 shows typical images obtained from the xerogels 1-3. The organogel 1 forms a three-dimensional network with small 5-20 nm frizzled fibrils. On the other hand, the organogel 2 shows the more straight and large fiber structure with 50-150 nm diameters. One can recognize many stripes in a gigantic organogel fiber when it was stained before the organogel fiber growth (Fig. 1c). The size of these stripes is comparable with that of the α -glucose-type organogel fiber. When it was stained with OsO₄ solution after the organogel fiber growth, these stripes could not be observed (Fig. 1b). More interestingly, the α -galactose-type organogel 3 showed the fiber structure in ethanol (the image is not shown

here) and the spherical structure with 200-350 nm outer diameters in water (Fig. 1d).



Scheme 1 Reagents and conditions.

Table 1. Gelation ability of 1-3 in organic solvents^a

Solvent	Gelator		
	1	2	3
Hexane	I	I	I
Carbon tetrachloride	I	I	I
Benzene	I	I	I
Chloroform	G	I	I
Ethyl acetate	G	I	R
Methanol	G	S	G
Ethanol	G	G	G
1- Propanol	G	G	R
1- Butanol	G	G	R
Acetic acid	S	S	S
Water	G	R	G

a) [gelator]=3.0 wt%; G= stable gel, S=solution after cooling, R=precipitation, I=insoluble.

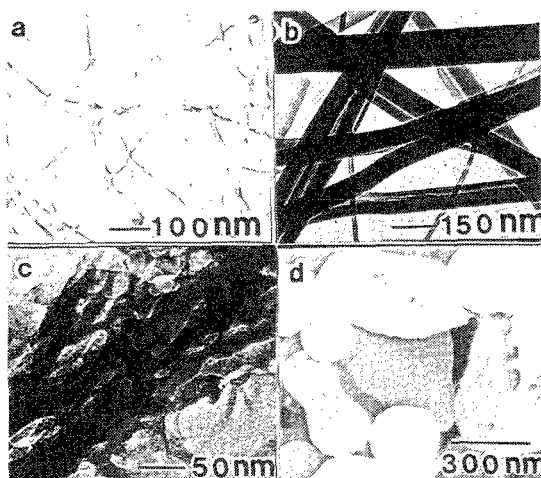


Fig. 1 TEM images of xerogels (a)1+EtOH, (b and c) 2+EtOH and (d) SEM image of xerogel 3+water. In (c), the organogel was stained with OsO₄ before the organogel fiber grew up.

Sol-gel polymerization towards transcription of the organogel structure. To transcribe the superstructures formed in the organogels into the silica structure, sol-gel polymerization of TEOS was carried out using 1-4 in

the ethanol gel and water gel phase according to the method described previously.^{7,8} For example, **1** (0.5-5.0 wt%) was dissolved in a medium for sol-gel polymerization: the medium consists of ethanol or water (100-1000 mg), TEOS (16-32 mg), water (2-6 mg) and benzylamine (2-6 mg) as a catalyst. The sample was sealed in a glass tube and left at ambient temperature for 3-10 days. After calcination, we observed the SEM images of the silica obtained from **1** and **4** (Figs. 2a and 2c). The silica obtained from **1** shows the tubular structure with 20-30 nm outer diameters and 350-700 nm lengths whereas the silica obtained from **4** shows the conventional granular structure (Fig. 2c). It is hardly conceivable that the amino group is protonated in the presence of benzylamine. These results indicate, therefore, that the tubular structure of the silica was successfully transcribed by the hydrogen-bonding interaction between the amino group of **1** and TEOS (or oligomeric silica particles).

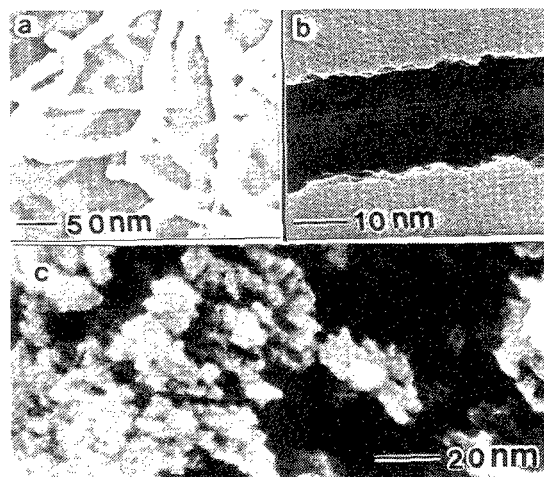


Fig. 2 (a) SEM, and (b) TEM images of the silica obtained from ethanol gel **1** and (c) SEM image of the silica from ethanol gel **4** after calcination.

To further corroborate that the organogel fibers really acted as template for the growth of the tubular silica, we took the TEM images after removal of **1** by calcination. The silica obtained from **1** shows an inner tube structure with 5-10 nm diameters (Fig. 2b). The inner diameter is comparable with that of the outer diameter of the fibrous organogel structure. The results again support the view that oligomeric silica particles are adsorbed onto the neutral organogel fiber by the hydrogen-bonding interaction. In contrast, β -glucose-type organogel **2** resulted in the tubular silica with larger outer diameters of 150-200 nm (Fig. 3a). Why is the diameter of the silica obtained from organogel **2** larger than that obtained from organogel **1**? To solve this problem, we carefully took a number of TEM images to

confirm the template effect.

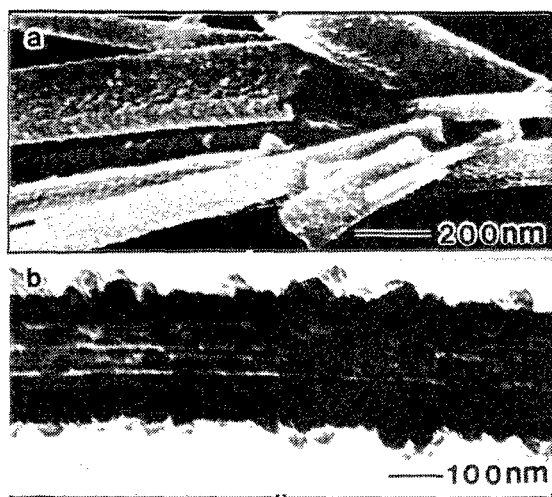


Fig. 3 (a) SEM and (b) TEM images of the silica obtained from ethanol organogel 2 after calcination.

Very surprisingly, the TEM images of the silica obtained from 2 consistently reveal that the silica consists of 50-100 nm inner diameters and 150-200 nm outer diameters (Fig. 3b). Furthermore, the silica in the inner tube is composed of micro-tubes with 5-10 nm diameters, in total giving rise to a lotus-like structure. The inner diameters of 5-10 nm are comparable with that of the organogel fiber obtained from 1.

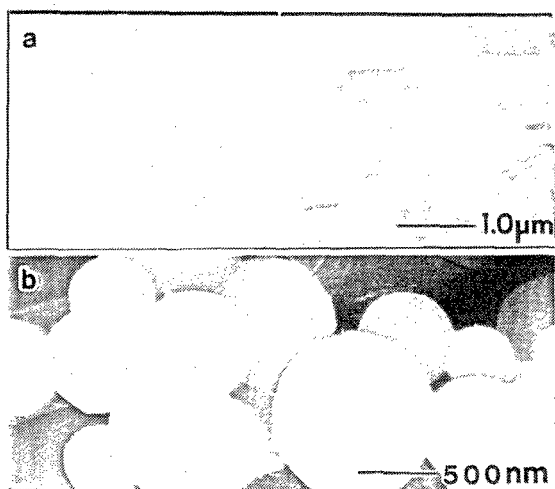


Fig. 4 SEM images of the silica obtained from (a) ethanol organogel 3 and (b) aqueous gel 3 after calcination.

We now consider, therefore, that the silica was transcribed from the hierarchical bundle structure of 2, because β -glucose-type organogel 2 features stronger intermolecular hydrogen-bonding interaction than that of α -glucose-type organogel 1, keeping the aggregate structure more stably.¹⁰ This novel structure is created

for the first time in the silica by transcription of bundled organogel fibers.

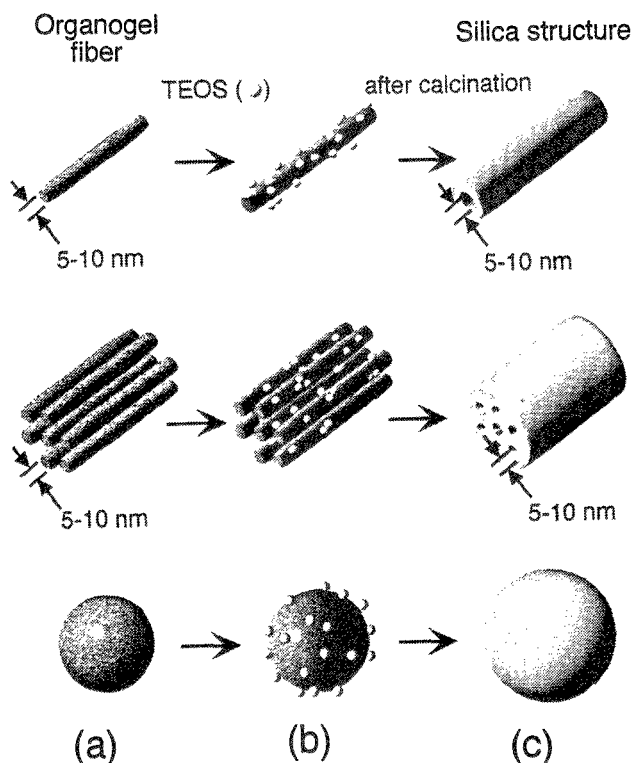


Fig. 5 Schematic representation for the creation of lotus-like and a spherical structures from the organogel state of 2 (middle), 3 (lower) and single hollow fiber silica from 1 (upper) by sol-gel polymerization: (a) gelators; (b) sol-gel polymerization onto the organogelators and (c) lotus-like silica structure (middle) and single hollow fiber structure (upper) of the silica formed after calcination (SEM and TEM images in Figs. 2, 3, and 4 were taken at this stage).

Fig. 4 illustrates SEM images of the silica obtained from aqueous gel 3 by sol-gel polymerization. The silica obtained from ethanol gel 3 showed the fiber structure with ca. 1400 nm diameter whereas the silica obtained from aqueous gel shows the hollow spherical structure with 500-1000 nm inner diameters and 200-300 nm walls. These results indicate that the sugar-integrated gel systems can create various structures of the silica in the gel phase.

As a summary of the foregoing observations, we now propose the mechanism for the formation of the novel lotus-type silica structure from organogel 2, the single hollow fiber silica structure from organogel 1 and the spherical silica obtained from aqueous gel 3 (Fig. 5). Oligomeric silica species are adsorbed onto the surface of the bundled fibrous structure of 2 and the polymerization further proceeds along these bundled fibrils. This propagation mode eventually yields the lotus-type silica after combustion of gelators by calcination (Fig. 5c; middle). In contrast, 1 and 3 provide the minute fibrous and the spherical structure,

respectively. Then, the tubular and the spherical silica grow up by sol-gel polymerization along these surface (Figs. 5b and 5c). As supported by correlation between the xerogel structures (Fig. 1) and the resultant silica gel structures (Figs. 2, 3 and 4), the sugar-based organogel structures are directly and scrupulously transcribed into the silica structures utilizing the hydrogen-bonding interactions.

Nitrogen adsorption-desorption isotherms. Representative nitrogen adsorption/desorption isotherms are shown in Fig. 6. The silica obtained from ethanol gel 1 and aqueous gel 3 have a Brunauer-Emmett-Teller (BET) surface area of $450 \text{ m}^2\text{g}^{-1}$ and $650 \text{ m}^2\text{g}^{-1}$, respectively. The surface areas of these silica are similar to those of the silica with fiber and lamellar structures obtained from the other organogel templates.

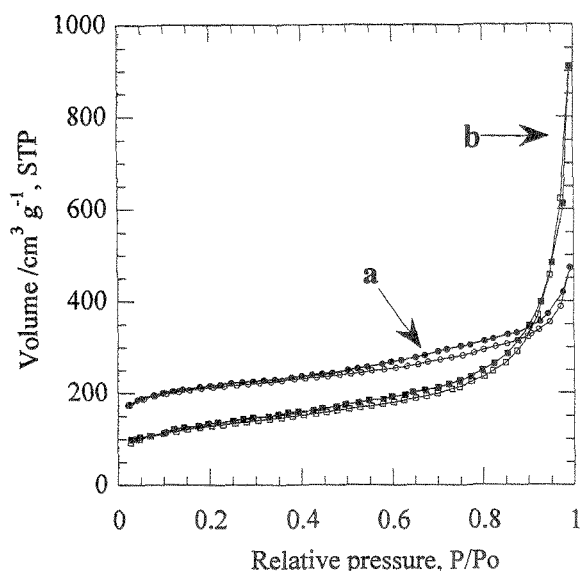


Fig. 6 Nitrogen adsorption-desorption isotherms of the silica obtained from (a) 1 and (b) 3.

3. CONCLUSION

The present paper has demonstrated a new methodology to prepare the lotus-like and the spherical structures of the silica using the sugar-integrated organic gelators. These novel silica structures are created with the aid of the hydrogen-bonding interaction of the oligomeric silica species with the gelators. We believe that the present system is not useful for transcription of various organogel superstructures into silica

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