Sol–gel transcription of novel sugar-based superstructures composed of sugar-integrated gelators into silica: creation of a lotus-shaped silica structure†

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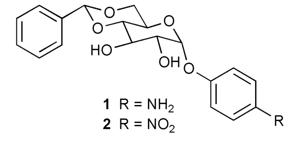
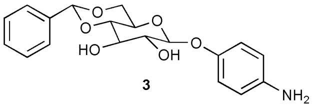
Novel silica materials bearing single or multiple (lotus-shaped) hollow fiber structures with 5–10 nm inner diameters and a spherical structure were created using sugar-integrated organogelators (1–4) as templates by sol–gel polymerization of TEOS.

The sol–gel synthesis of well-ordered inorganic materials offers a new and wide-ranging approach to useful materials with controlled architecture and porosity across a range of length scales.[1,2] The direct synthesis of discrete inorganic architectures necessitates the use of dispersed organic supramolecular structures with commensurate dimensionality; for example, hollow fibers of silica have been prepared by self-assembled phospholipid fibers,[3] viroid cylinders,[4] organic crystals[2] or cholesterol-based organogel fibers as templates.[5–9] In particular, cholesterol-based organogel templates have created various hollow silica fibers with linear,[5] helical[6] and multi-layered structures[7] by sol–gel polymerization. Such results indicate that the cholesterol-based organogel fibers act as efficient tubular templates in the polymerization process.[5–9] It is already known that either cationic charge or efficient hydrogen-bonding interaction is necessary for 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-like[12] and vesicular[13] 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 gel is unprecedented, because i) introduction of a moderate amount of cationic charge into the organogelator is very difficult and ii) the gelation ability is markedly reduced in the protic sol–gel medium necessary for sol–gel polymerization. To overcome this dilemma, we designed sugar-based organogelators **1**, **3** and **4** in which the amino group not only stabilizes the organogels due to the intensified inter-gelator hydrogen bonds[10] but also binds TEOS through hydrogen-bonding interactions.[7,8] If this idea were to work as expected, one could transcribe the novel sugar-based organogel superstructures into the silica through sol–gel polymerization. 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.



1 R = NH_2
2 R = NO_2



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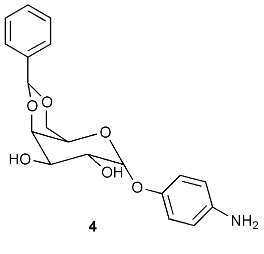

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Compounds **1**–**4** were synthesized according to the method reported previously.[10] These compounds could gelate organic solvents such as carbon disulfide, carbon tetrachloride, toluene, ethanol, butan-1-ol, hexan-1-ol or ethylacetate,[14] indicating that they act as versatile gelators of organic solvents. In order 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 pictures obtained from the xerogels **1**, **3** and **4**. The organogel **1** forms a 3-D network with small 5–20 nm frizzled fibrils. On the other hand, the organogel **3** shows a straighter and larger fiber structure with 50–150 nm diameter. One can observe many stripes in a gigantic organogel fiber that was stained prior to organogel fiber growth (Fig. 1c). The size of these stripes is comparable with that of the α-glucose-type organogel fiber. When stained with OsO_4 solution after organogel fiber growth, these stripes could not be observed (Fig. 1b). More interestingly, the α-galactose-type organogel **4** showed the fiber structure in ethanol (the picture is not shown here) and the spherical structure with 200–350 nm outer diameter in water (Fig. 1d).

To transcribe the superstructures formed in the organogels into the silica structure, we carried out sol–gel polymerization of TEOS using **1**–**4** in the ethanol gel phase according to the method described previously.[7,8]† We observed the SEM pictures of the silica obtained from **1** and **2** (Fig. 2a). The silica obtained from **1** shows the tubular structure with outer diameter of 20–30 nm and length of 350–700 nm whereas the silica obtained from **2** showed the conventional granular structure (not shown). 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

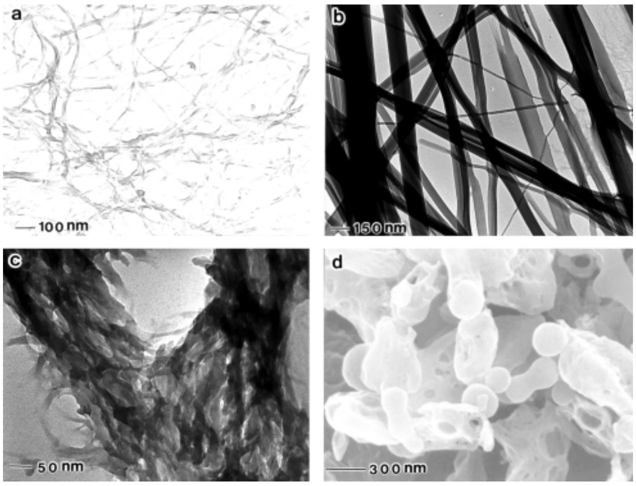

Fig. 1 TEM pictures of xerogels (a) **1** + EtOH, (b and c) **3** + EtOH and (d) SEM picture of xerogel **4** + water. In (c), the organogel was stained with OsO_4 prior to fiber grown up.†

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† Electronic supplementary information (ESI) available: the preparation methods of TEM samples for organogels and sol-gel polymerization conditions. See http://www.rsc.org/suppdata/cc/b0/b007218o/

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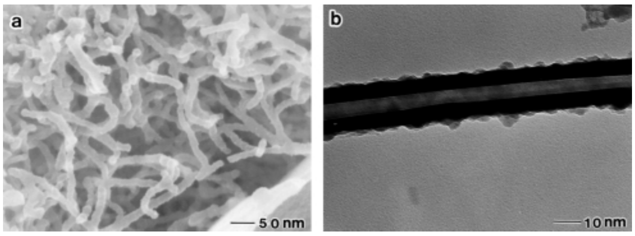

Fig. 2 SEM (a) and TEM (b) pictures of the silica obtained from ethanol organogel **1** after calcination.

between the amino group of **1** and TEOS (or oligomeric silica particles).

To further corroborate that the organogel fibers really acted as template for the growth of the tubular silica, we took the TEM pictures after removal of **1** by calcination. Very interestingly, we found the silica obtained from **1** to have an inner tube structure with 5–10 nm diameter (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 through hydrogen-bonding.

In contrast, β-glucose-type organogel **3** resulted in tubular silica with a larger outer diameter of 150–200 nm (Fig. 3a). Why is the diameter of the silica obtained from organogel **3** larger than that obtained from organogel **1**? To solve this problem, we carefully took a number of TEM pictures to confirm the template effect. Very surprisingly, the TEM pictures of the silica obtained from **3** consistently reveal that the silica has an inner diameter of 50–100 nm and an outer diameter of 150–200 nm (Fig. 3b). Furthermore, the silica in the inner tube is composed of micro-tubes of 5–10 nm diameter, in total giving rise to a lotus-like structure. The inner diameter of 5–10 nm is comparable with that of the organogel fiber obtained from **1**. We now consider, therefore, that the silica was transcribed from the hierarchical bundle structure of **3**, because β-glucose-type organogel **3** features stronger intermolecular hydrogen-bonding interaction than that of α-glucose-type organogel **1**, keeping the aggregate structure more stably.[10] This novel structure in silica has been created by transcription of bundled organogel fibers.

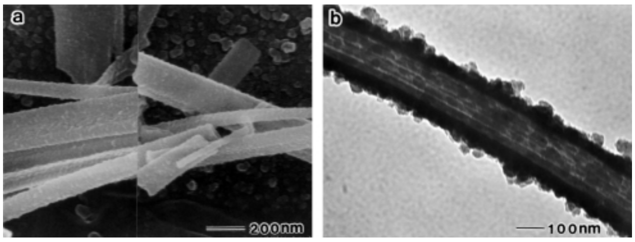

Fig. 3 SEM (a) and TEM (b) pictures of the silica obtained from ethanol organogel **3** after calcination.

Fig. 4 shows SEM pictures of the silica structure obtained from aqueous gel **4** by sol–gel polymerization. The silica obtained from ethanol organogel shows a fiber structure with *ca*. 1400 nm diameter, whereas the silica obtained from aqueous gel shows a hollow spherical structure with 500–1000 nm inner diameter and a 200–300 nm thick wall, which probably consists of multi-layers. These results indicate that the sugar-integrated gel systems can create various silica structures 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 **3** and that of the single hollow fiber silica structure from organogel **1** (Fig. 5). Oligomeric silica species are adsorbed onto the surface of the bundled fibrous structure of **3** 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; lower). In contrast, **1** provides the minute fibrous structure. Then, the tubular silica grows up by sol–gel polymerization along this surface (Fig. 5b). As supported by the correlation between the xerogel structures (Fig. 1) and the resultant silica gel structures (Figs. 2 and 3), the sugar-based organogel structures are directly and scrupulously transcribed into the silica structures utilizing hydrogen-bonding interactions.

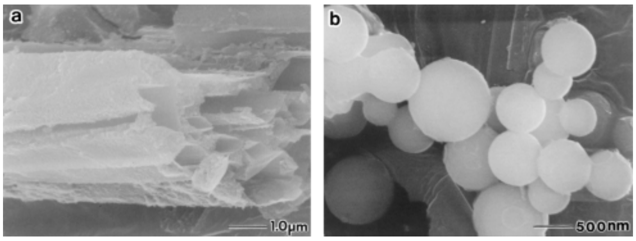

Fig. 4 SEM pictures of the silica obtained from (a) ethanol organogel **4** and (b) aqueous gel **4** after calcination.

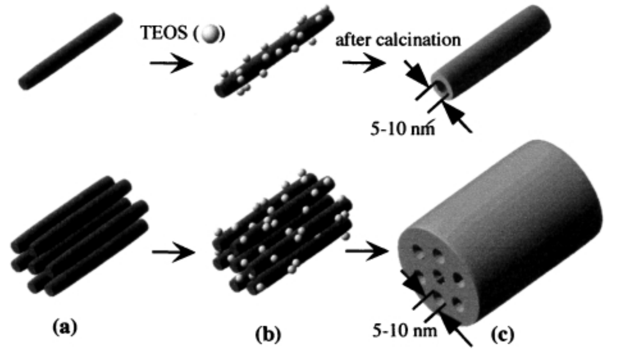

Fig. 5 Schematic representation for the creation of the lotus-like silica structure from the organogel state of **3** (lower) and single hollow fiber silica from **1** (upper) by sol–gel polymerization: (a) gelators; (b) sol–gel polymerization of TEOS and adsorption onto the gelators and (c) lotus-like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

In conclusion, the present paper has demonstrated a new methodology to prepare lotus-like and spherical structures of silica using sugar-integrated organic gelators. These novel silica structures are created by hydrogen-bonding interactions with the fine structure of the gelators. We believe that this concept will be more generally applicable to further new silica preparations using various organogel superstructures as templates.

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14 In addition, organogelator **4** can gelate even water.