Nanofiberization of inner helical mesoporous silica using chiral gelator as template under a shear flow

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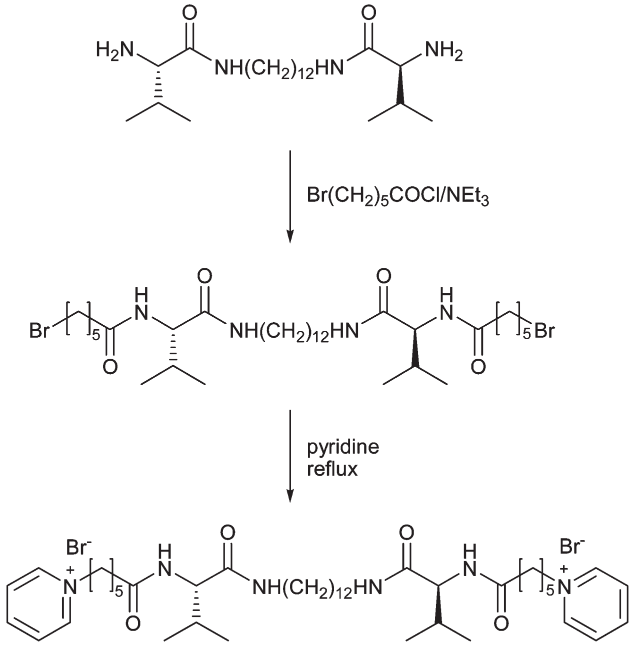
Aligned nanofibers with inner-helical mesoporous silica were synthesized using chiral gelator as template under basic conditions and a shear flow.

Materials with mesopores, synthesized by using surfactants or copolymers as superamolecular templates, have been widely studied.[1–7] Although many kinds of mesostructured nanoparticles have been prepared, the mesoporous fibers[2–7] are the particularly interesting materials. The one-dimensional (1D) nanostructure is easily aligned[8] and suitable for fabricating nanoscale devices. Unfortunately, the morphologies of the mesoporous materials are difficult to control so that the mesoporous fibers are often combined with small particles. In particular, the helical and chiral mesopores[9] are the most interesting ones for application in the field of chiral selectivity, chiral recognition, and chiral catalysts. Therefore, it is very important to develop methods for the preparation of mesoporous fibers with inner-helical mesopores and without being combined with any other morphologies.

Organogels and lipids[10] provide various morphologies such as rod, tube, helix bundle, and twist ribbon. By using the sol-gel transcription method,[11] nanotubes, helical nanotubes,[12] ultrathin membranes could be obtained without being combined with small particles. Actually, silica nanofibers with monodispersed inner helical hollows[13] and lotus-like silica[14] have been successfully prepared. It is assumed from these results that the preparation of bundles of nanofibers with inner helical mesopores should be possible by using organogelators as the template.

Protic solvents such as ethanol and butanol were often used for the sol-gel transcription method. The previous results showed that the obtained inorganic materials were powders. The nanotubes whose walls were constructed with small silica particles were short and often aligned randomly. Very recently, we found that the length of nanotubes could be increased to several hundreds of micrometers and such nanotubes could be aligned simply by using water as solvent and under a shear flow.[15] Here we describe the preparation of aligned nanofibers with inner-helical mesoporous silica.

Compound **1**, which is composed of L-valine, can form a transparent gel in water and the minimum gel concentration of this gelator is 25 g dm^{-3} (**1**/water) at 25 °C. The synthesis procedure of gelator **1** is shown in Scheme 1 and has been published in the literature.[16] Mesoporous nanofibers were synthesized according to the following procedure. The gelator **1** (100 mg) was dissolved in 1 mL of aq. NH_3 (5 wt-%), and then 100 mg of TEOS was dropped into the solution under vigorous stirring at room temperature. After the mixture turned white, it was kept at room temperature for 30 min and 80 °C for 4 days under static conditions. Finally, the gelator was removed by washing with methanol and calcination was performed at 250 °C for 2 h and 500 °C for 5 h under aerobic conditions.



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Scheme 1 Synthesis of gelator **1**.

Fig. 1 shows the TEM image† of xerogel obtained from the hydrogel of gelator **1**. The helical bundles structure was clearly

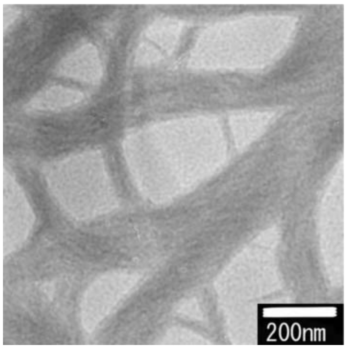

Fig. 1 TEM images of the xerogel obtained from the hydrogel of gelator **1**.

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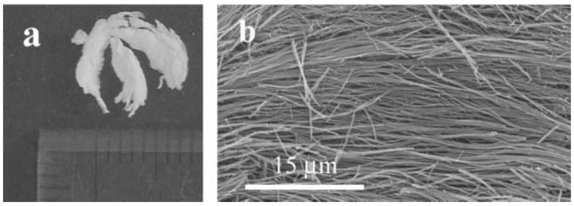

Fig. 2 (a) Picture of the cotton-like silica after calcination; (b) SEM images of the well-aligned calcined silica using the self-assembly of gelator **1** as template.

identified. When using gelator **1** as the template, we obtained cotton-like silica with weak elasticity (Fig. 2a), but not powder. The observation with the polarized optical microscope indicates that the cotton-like silica is bundles of fibers. They were identified even with the naked eye, when the fibers were suspended in methanol. In earlier research using cationic surfactants, the mesoporous fibers were not uniform and often combined with other monoliths.[2–7] The present results firstly revealed that the use of cationic gelator **1** instead of cationic surfactants gave uniform silica nanofibers without any other monoliths. Furthermore, the silica nanofibers were aligned very well due to the shear of stirring during the synthesis (Fig. 2b). The long-range order of the nanofibers can reach 100 μm or more according to the preparation process.

Fig. 3 shows both SEM and TEM images of the calcined silica nanofibers. Fig. 3a suggests that the fibers shown in Fig. 2b are not single fibers but they are constructed with bundles of ultra-fine nanofibers whose diameters are around 60 nm. The ultra-fine nanofibers are parallel to the axis of the bundle (Fig. 3a). Fig. 3b shows one ultra-fine nanofiber in Fig 3a and the TEM image indicates that the ultra-fine nanofiber is an aggregation of mesoporous nanotubes. The channels are oriented parallel to the axis of the ultra-fine nanofiber (Fig. 3b). Furthermore, the TEM image indicates that the channels are inner-helical channels[13] whose helical pitch is around 3.2 nm. Fig. 4 shows the edge of the nanofibers. It is also clear that the nanofibers are constructed by gathering uniform ultra-fine nanotubes. The diameters of the nanotubes are around 2.2 nm which is similar to the length of gelator **1**. It is assumed that the templates for the formation of these inner-helical channels were the single supramolecular assemblies of gelators. Because these mesoporous nanofibers were prepared by a method based on the sol-gel transcription method, it means that the nanofibers are constructed with bundles of uniform ultrafine nanotubes (Fig. 4), they are not periodic mesoporous nanofibers.

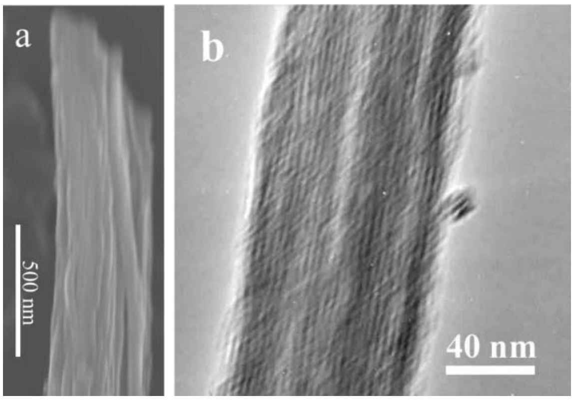

Fig. 3 (a) SEM and (b) TEM images of the silica fibers obtained using the self-assembly of gelator **1** as template (after calcination).

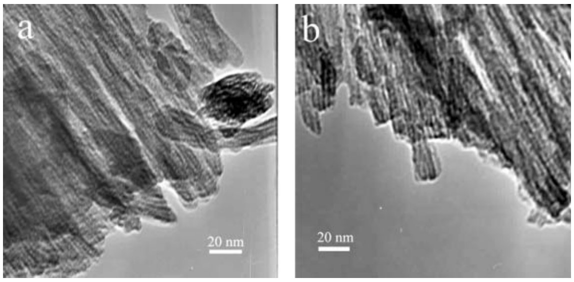

Fig. 4 TEM images of the silica fibers obtained using the self-assembly of gelator **1** as template (after calcination).

The alignment of the nanofibers shown in Fig. 2b is another interesting phenomenon. It indicates that not only the morphologies of supramolecular assemblies of gelator could be transferred to silica, but also the alignment of the supramolecular assemblies could be transferred to that of silica.

Fig. 5 illustrates the formation of nanotubes with inner helical structure, nanofibers, bundles, and alignment. Firstly, single helical supramolecular assemblies were formed by the self-organization of gelator molecules in the solution. Secondly, TEOS was adsorbed and polymerized on the cationic surface under basic conditions to form nanotubes of silica. Thirdly, the ultra-fine nanotubes of silica (the outer diameters are around 5 nm) with gelator inside were organized into nanofibers due to the capillary effect and the formation of Si–O–Si bonds under a shear flow. Then bundles are formed by gathering nanofibers. Finally, the bundles of nanofibers are oriented and aligned by the shear flow.

The mesoporous fibers[2–7] are sensitive to silicon sources, surfactants, pH, temperature, concentration, and ionic strength in the solution. Furthermore, the diameters of the fibers obtained so far ranged from 100 nm to several microns, but were not uniform. By the present gelator-directed method, we could make the assemblies of the uniform ultra-fine nanotubes easily. It should be mentioned that several conditions are essential. Firstly, the concentration of the gelator **1** should be controlled until a stiff gel is formed in aqueous solution at room temperature. And under a shear flow it became a viscous liquid which ensures that silicon sources can hydrolyse and polymerize on the surface of gel fibers sufficiently. When the concentration of the gelators was low, only silica particles were obtained. Secondly, a shear flow is essential. The shear flow acts not only for the alignment but also for the hydrolysis of TEOS. Lastly, TEOS should be dropped into the solution after organogel nanofibers are formed. If TEOS is dropped into the solution before that, only silica particles are obtained.

In conclusion, perfect and uniform nanofibers constructed with 2.2-nm-inner diameter nanotubes have been successfully synthesized by the sol-gel transcription method under a shear flow. These nanofibers with inner-helical channels may be more suitable to act as chiral catalyst or stationary phase of chiral HPLC and GC columns. By changing the template from the cationic surfactants to the cationic gelators, many new meso- or microporous inorganic nanofibers may be designed and synthesized in the near future.

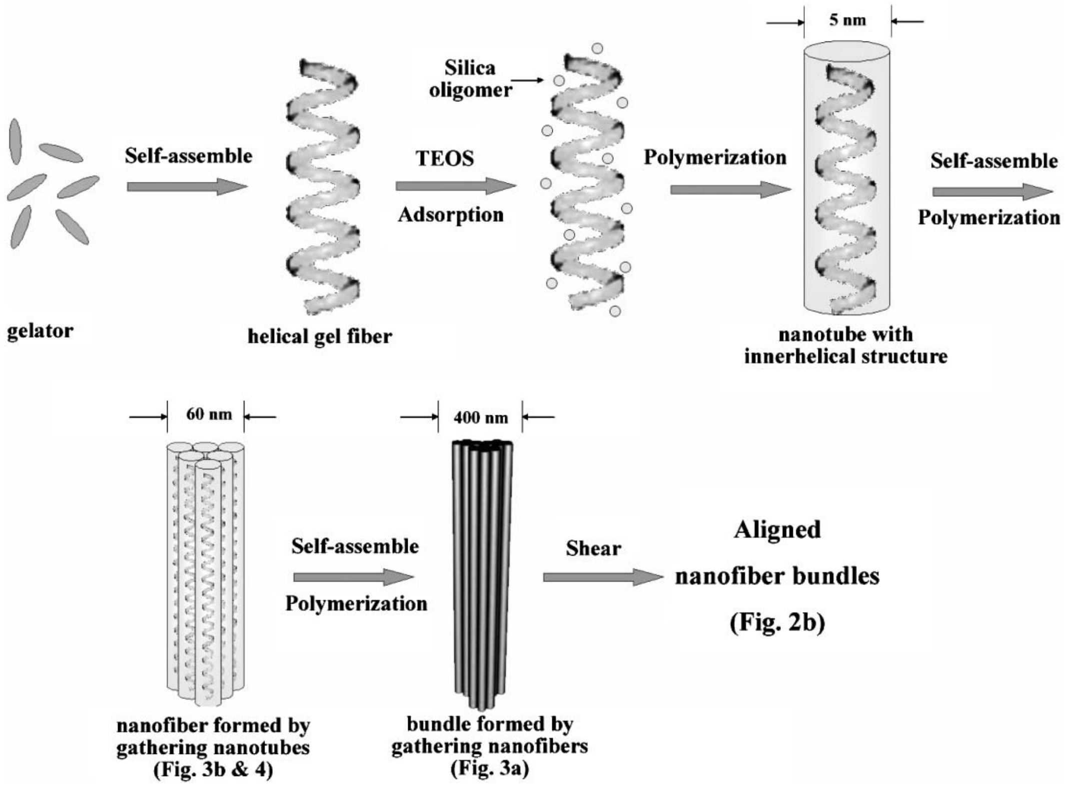

Fig. 5 Schematic representation of the formation of hierarchical structure towards aligned nanofiber bundles.

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Notes and references

† SEM observations were carried out on a Hitachi S-5000 field emission scanning electron microscope (FE-SEM) at 10 KV with 10 nm metal coating. TEM observations were carried out on a JEOL JEM-2010 transmission electron microscope at 200 KV.

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