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Preparation of cotton-like silica

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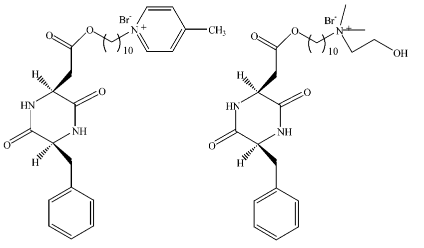
Cotton-like silica composed of helical bundles was prepared using the sol–gel transcription method in strong acid conditions.

Nanostructured materials showed fascinating properties, and their application was superior to their bulk counterparts. Consequently, much research has been done on shaping inorganic materials at the microscopic level.[1] Up to now, many kinds of interesting structures have been prepared, rods, belts, tubes, balls, and so on.[2] Researchers have found that the helical structure in organogel fibers can be transcribed into inorganic silica and TiO_2, for example, single-stranded helix,[3,4] double helix[5] and multiple helix.[6] Because the helical information could be transferred from inorganic materials to organic compounds, they could be used as chiral catalysts[7] and chiral sensors.[8] For applications, for example, nanocapacitors or nanotransistors, the alignment and functionalization of single particles is necessary.[9] The self-assembly of nano particles into more complex structures will also be necessary.[10] Nanotubes are superior to other morphologies as both inner and outer surfaces can be modified. Due to the one-dimensional structure, nanotubes should be easily organized into ordered structures. Sol–gel transcription procedure is a powerful method to prepare nanotubes.[11] By selecting organic reagents as the solvents, stirring is not essential because tetraethylorthosilicate (TEOS) is soluble in organic solvents. For economic reasons, however, we selected water as solvent, HCl as the catalyst and chiral gelators (which are shown in Scheme 1) as the templates. Because TEOS cannot dissolve in water, stirring is essential during the sol–gel transcription procedure.[12] And some interesting phenomena were found due to stirring.

Gelator **1** was synthesized by the reaction of 4-methylpyridine and cyclo(L-10-bromodecylasparaginyl-L-phenylalanine), which was prepared from cyclo(L-asparaginyl-L-phenylalanine)[13] and 10-bromodecanol using the carbodiimide–DMPA method. Gelator **2** was synthesized by a similar procedure. Sol–gel polycondensation of TEOS was carried out according to the following procedure. Gelator **1** (57 mg) was dissolved in 1 mL of 2.4 M HCl aq., 90 mg of TEOS was dropped into the solution under strong 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 rinsing with methanol and then calcination was performed at 250 °C for 2 h and 500 °C for 5 h under aerobic conditions.

Gelator **1** forms a transparent gel consisting of a three-dimensional network in water (Fig. 1). The diameter of the nanofibers is around 10–20 nm. When gelator **1** was used as the template, cotton-like silica with elasticity was obtained (Fig. 2). The cotton-like fibers (which should be bundles of nanofibers) were identifiable even with polarized optical micrography and with the naked eye when the fibers were suspended in methanol. In earlier research,[3,14] inorganic powders were often obtained through the sol–gel transcription method, although the small particles were composed of nanofibers.



Scheme 1

Fig. 3 shows an FE-SEM image of the calcined silica with no break up of the morphologies during the workup procedure. It was found that the fibers shown in Fig. 2 were not single fibers, they were bundles formed by intertwining nanofibers. Although the helical pitches of the bundles varied greatly, all of the helical bundles were configured in a right-handed helix. The length of the bundles was around 40 μm. We can also find many ultra-fine nanofibers linked between the bundles, which support this cotton-like structure. According to the preparation procedure, the helical bundles should be formed before the stirring has stopped, because it was found that most of the bundles were aligned in nearly the same direction on the surface of the reaction flask. The alignment of the bundles brought about by stirring, oriented the gel fibers during the preparation procedure. Then the oriented gel fibers transfer this alignment information to the silica. As to the ultra-fine nanofibers linked between the bundles, they should be formed after stirring has stopped, because they are not aligned. Fig. 3 shows enlarged images of the silica fibers. There are two kinds of

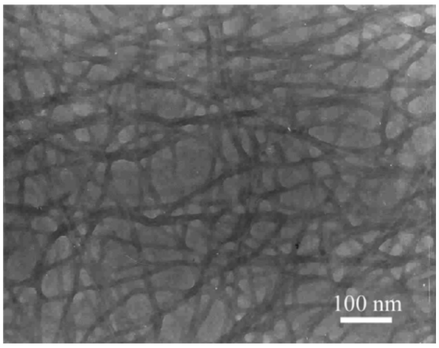


Fig. 1 TEM image of the hydrogel formed by gelator **1**.

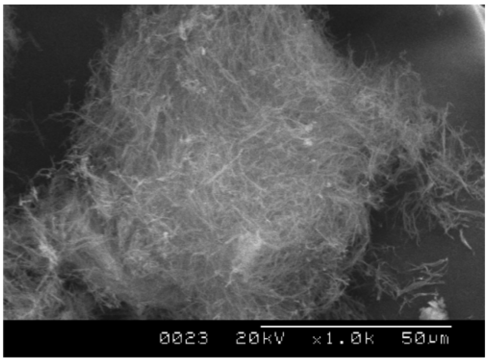


Fig. 2 SEM image of the silica obtained by sol–gel transcription of the gelator **1** after calcination.

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nanostructures, *i.e.*, nanoribbons and nanotubes, in this material. Fig. 4A shows a right-handed helical ribbon[15] and Fig. 4B shows the structure of a branched tube. The tunnel in the tube is easily identified. Fig. 4C shows the TEM image of a fine nanotube, the inner diameter of which is about 3–4 nm.

To elucidate the mode of formation of cotton-like silica, experiments were carried out by gradually varying the reaction conditions and replacing the gelators. The results indicate that a concentration of gelators more than 3 wt% in the case of gelator **1** is essential. Furthermore, the concentration of the gelators should be controlled until a stiff gel is formed in aqueous solution at room temperature. When the concentration of the gelators is low, only silica powder is obtained. This may be because a small amount of silica fibers cannot support the cotton-like structures, resulting in the cotton-like structures shrinking into small particles. From the SEM image, it was found that the fibers also form bundles; these bundles were composed of only two or three nanofibers. With respect to the amount of TEOS, the use of an excess of TEOS will bring out TEOS nanoballs instead of nanofibers. It was found that the width of the fibers could be controlled by varying the reaction temperature. High temperature brought out fine fibers. The concentration of HCl can affect the morphologies: for instance, a weaker acid condition will enable the fabrication of fine nanofibers and stronger acid condition will allow the production of amorphous silica.

Fig. 5 shows an FE-SEM image of the silica after calcination, from a gel of gelator **2**. Although the difference between gelator **1** and **2** is the cationic ion portion of the gelator, the straighter silica fibers only twist slightly to form bundles. The properties of the cationic ion part seem crucial in controlling the helicity of silica bundles. This result is similar to our previous findings,[3,14] in which the helicity of TiO_2 fibers could be controlled simply by changing the ionic ion part of the gelator.

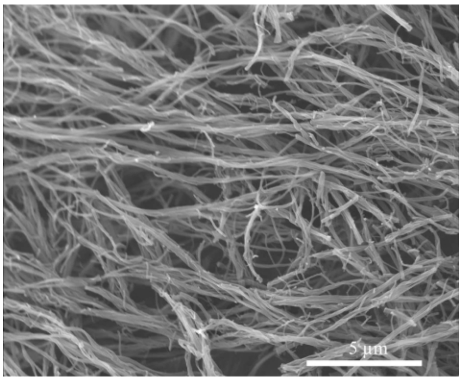

Fig. 3 FE-SEM image of the silica obtained by sol–gel transcription of the gelator **1** after calcination.

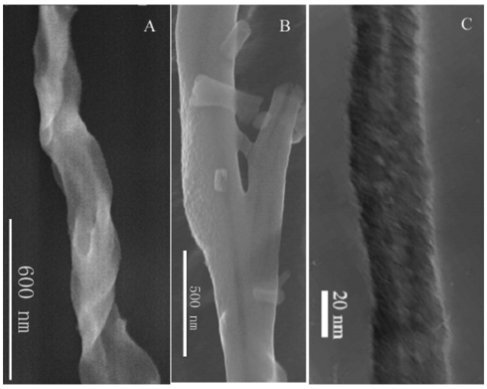

Fig. 4 (A) and (B) FE-SEM images of the silica obtained by sol–gel transcription in gelator **1** after calcination. (C) TEM image of the silica tube obtained by sol–gel transcription in gelator **1** after calcination.

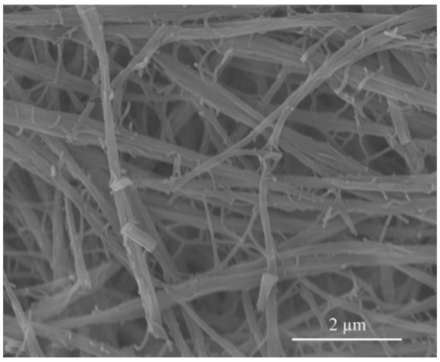

Fig. 5 FE-SEM image of the silica obtained by sol–gel transcription in gelator **2** after calcination.

In conclusion, a kind of cotton-like silica has been fabricated with a fiber alignment that could be controlled simply by stirring. Because the orientation of fibers in some cases is very important for future applications, further research will be carried out to study fiber alignment.

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