

# $\beta$ -1,3-Glucan polysaccharide can act as a one-dimensional host to create novel silica nanofiber structures†

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We have demonstrated that the creation of novel silica nanofibers with a uniform diameter is possible by utilizing  $\beta$ -1,3-glucan polysaccharide as a one-dimensional host for monoalkoxysilane; the finding establishes that  $\beta$ -1,3-glucan can act not only as a novel one-dimensional host for metal alkoxide polycondensation but also as an interface between inorganic nanofibers and functional organic molecules.

To create supramolecular inorganic materials on the nanoscale has been a challenging research target in recent years not only from a purely scientific viewpoint but also because of their great application potential in nanotechnologies.<sup>1</sup> In particular, inorganic nanofibers which have well-regulated shape and high water-solubility are desired for potential applications to biosensors, switches, memories and circuits.<sup>2</sup> It is still impossible, however, to create such a well-regulated inorganic material because there is no general methodology to control the self-assembling processes. So far, we and other research groups have demonstrated that organogel fibers act as excellent templates for the creation of silica nanofibers by sol-gel polycondensation of tetraethoxysilane (TEOS), where anionic silica particles are deposited on a cationic fibrous template.<sup>3</sup> Although silica nanofibers can be created using this template method, the difficulties in surface modification, by which one may dissolve the organic/inorganic composite into the solvent, still remain unsolved because the solvophobic inorganic layer always exists outside the solvophilic organic template. Accordingly, the sole solution to overcoming these difficulties in designing solvent-soluble inorganic nanofibers seems to be to provide an organic host that possesses a one-dimensional cavity in which sol-gel polycondensation of alkoxysilane can proceed. In this type of composite, the organic component occupies the outer layer and the inorganic material exists inside the layer.

Schizophyllan (SPG) is a natural polysaccharide produced by the fungus *Schizophyllum commune* and its repeating unit consists of three  $\beta$ -1(3) glucoses and one  $\beta$ -1(6) glucose side chain linked at every third main-chain glucose. SPG adopts a triple helix (t-SPG) in nature and can be dissociated into a single chain (s-SPG) by dissolving in dimethylsulfoxide (DMSO) (Fig. 1).<sup>4</sup> The s-SPG

chain can retrieve the original triple helix by exchanging DMSO for water. Recently, we have found that when the renaturing process from s-SPG to t-SPG is carried out in the presence of hydrophobic polymers or nanoparticles, they are entrapped in the cavity with the aid of hydrophobic force to give novel nanocomposites having unique one-dimensional architectures.<sup>5</sup> The results clearly show that SPG acts as a potential one-dimensional host for the creation of one-dimensional nanocomposites. It thus occurred to us that if hydrophobic metal alkoxides such as tetraethoxysilane (TEOS) could also be entrapped in the SPG one-dimensional cavity, sol-gel polycondensation would take place inside the cavity to afford a silica nanofiber which would show water-solubility as well as biocompatibility, making new biological applications possible.<sup>6</sup>

Firstly, to test the feasibility of our idea, we carried out sol-gel polycondensation utilizing TEOS as a silica precursor. A DMSO solution containing s-SPG (5.0 g L<sup>-1</sup>,  $M_w$  = 150,000) was mixed with 3.0  $\mu$ L of TEOS. To the resultant DMSO solution, water (1900  $\mu$ L) was gradually added, avoiding the phase separation of TEOS. The final composition of water/DMSO (v/v) was adjusted to 95/5 (v/v). After leaving it for one week at room temperature, the resultant water/DMSO mixed solvent was subjected to dialysis. It was confirmed that the produced silica precipitated during this dialysis process. The resultant aqueous silica suspension was cast on a grid with carbon mesh and the morphologies of the obtained silica were observed by TEM. As shown in Fig. S1, only an amorphous silica mass containing many entangled SPG fibers (seen as wiggly transparent lines against a black silica background) is observed, and the expected silica nanofiber with a well-regulated shape could not be found at all. The result reveals that even if SPG acts as a one-dimensional host, sol-gel polycondensation of TEOS predominantly occurs in the bulk phase due to the strong tendency to grow to the random (three-dimensional) silica network structure. We thus considered that one of the effective protocols

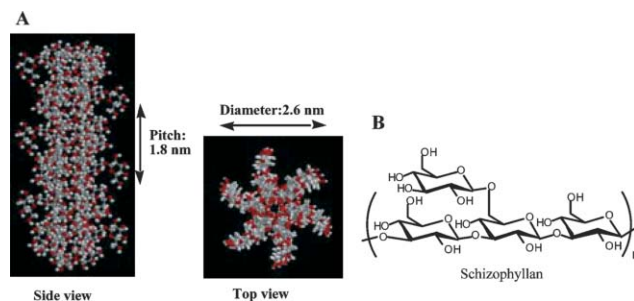


Fig. 1 Calculated models of schizophyllan (SPG) triple helix (A), repeating units of SPG (B).

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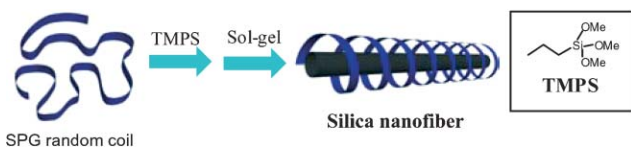
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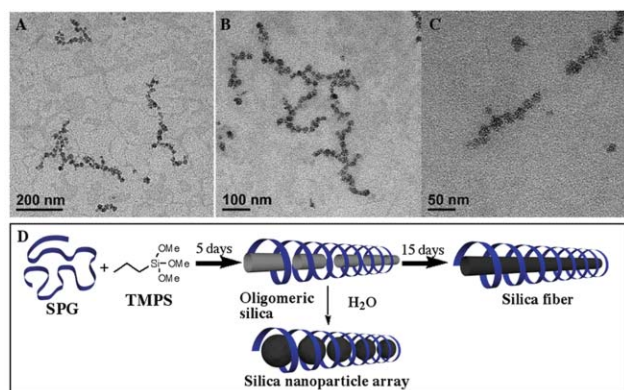
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to avoid such random sol-gel polycondensation would be to decrease the number of the reactive alkoxy groups. As an improved approach, we carried out sol-gel polycondensation using trimethoxypropylsilane (TMPS) instead of TEOS, in which one alkoxy group is replaced by a hydrophobic propyl group (Fig. 2). The concentration of used TMPS was adjusted to 1.0 eq./s-SPG repeating unit. The sample was prepared according to the same procedure as described above. After leaving it 5 days at room temperature, the morphologies of the obtained silica were observed by TEM, with the expectation of the creation of silica fibers. As shown in Fig. 3, however, the resultant silica structure is not a fiber but a one-dimensional array of silica nanoparticles: in the TEM images, one can identify silica nanoparticles with 10–15 nm diameter arranged in the one-dimensional direction. Here, one can propose two possible mechanisms for the silica nanoparticle array formation; that is, (1) SPG wraps the silica nanoparticles which are pre-formed in the bulk phase before the renaturating process from s-SPG to t-SPG and (2) SPG acts as a one-dimensional host for TMPS and sol-gel polycondensation predominantly occurs inside the one-dimensional cavity. In the latter case, an oligomeric silica with a rod-like shape might be created at the first stage of sol-gel polycondensation, which would be converted into particles during dialysis due to the hydrophobic interaction among propyl groups (Fig. 3D). The second mechanism is very likely because (1) TMPS has a regulated reactivity to form an oligomeric silica with a rod-like shape and (2) such an oligomeric silica fiber is structurally coarse and easily destroyed by the dialysis treatment. These results suggest that we must further continue the reaction to obtain silica having a fibrous structure. We thus prepared the sample according to the same procedure and left it for 20 days at room temperature. The IR spectrum showed the appearance of a strong new vibration band assignable to the Si–O–Si bond at around the 1000–1200  $\text{cm}^{-1}$  region (Fig. S2). Interestingly, the obtained silica did



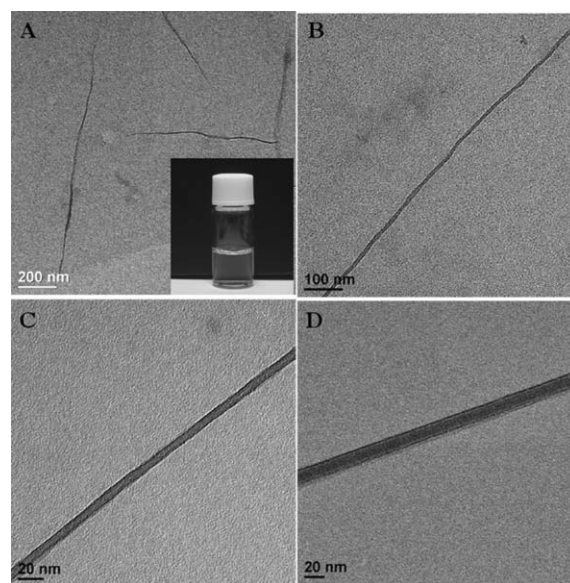
**Fig. 2** Sol-gel polycondensation reaction of TMPS in the SPG hydrophobic cavity.



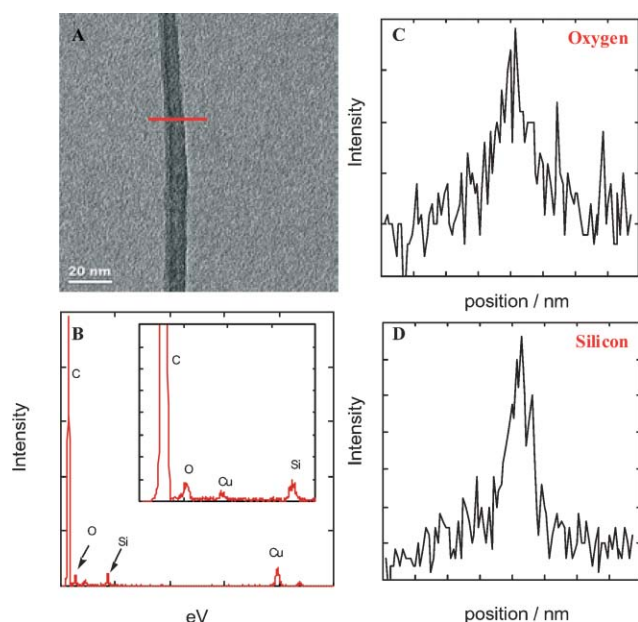
**Fig. 3** TEM images of silica nanoparticle one-dimensional arrays (A)–(C). Possible mechanism of silica nanoparticles array and fiber formation (D).

not form any precipitate even after dialysis against water. As a reference experiment, we prepared the sample without s-SPG according to the same procedure. In this case, the precipitation of silica was observed as the sol-gel reaction proceeded. The difference suggests that SPG plays an important role in the formation of the water-soluble silica composite. As expected, a fine silica nanofiber structure with a uniform 15 nm diameter is observed (Figs. 4A–4C),<sup>7a</sup> whereas no such fibrous structure is found in the reference sample (Fig. S3A).<sup>7b</sup> From these TEM images, one can propose that sol-gel polycondensation of TMPS predominantly proceeds in the one-dimensional cavity of SPG to afford silica nanofibers solubilized in water. The diameter of the obtained silica nanofiber became larger (*ca.* 25 nm) with the increase in the feed TMPS concentration up to TMPS/s-SPG repeating unit = 3.0 eq. (Fig. 4D).<sup>8</sup> When more than 3.0 eq. TMPS against s-SPG repeating unit was used, the silica nanofiber structure disappeared and instead the amorphous silica mass was formed. The results support the view that under conditions where TMPS exists in great excess, SPG cannot act effectively as the host. The view is also supported by the fact that sol-gel polycondensation in the presence of t-SPG instead of s-SPG did not give any fibrous structure as seen in Fig. 4 (see Fig. S3B); that is, the renaturating process from s-SPG to t-SPG is indispensable for the creation of the silica nanofiber structure.<sup>9</sup>

To obtain further evidence that the nanofiber structure observed in TEM is a composite of silica and SPG, it was analyzed by EDX (energy dispersive X-ray spectroscopy) TEM. Figs. 5A–5D show a TEM image, an EDX spectrum and EDX line scan profiles, respectively. As seen in Fig. 5B, one can confirm the peaks assignable to silicon and oxygen, indicating that the obtained nanofiber is a composite with silica. Furthermore, as shown in Figs. 5C and 5D, one can confirm that the distribution of the silicon intensity is almost overlapped with that of the oxygen intensity, indicating that the thin oxygen-containing layer of s-SPG



**Fig. 4** TEM image of silica nanofibers (inset: photo image of aqueous solution of silica nanofibers) (TMPS/s-SPG repeating unit = 1.0 eq.) (A) and its magnified images (B) (C). TEM image of silica nanofiber (TMPS/s-SPG repeating unit = 3.0 eq.) (D).



**Fig. 5** TEM image (A), elemental analysis based on EDX (B) and EDX line profiles (oxygen (C) and silicon (D), respectively).

fabricates the silica nanofiber. The result clearly establishes that SPG wraps the silica nanofiber.

In conclusion, we have demonstrated that the creation of water-soluble silica nanofibers with a uniform diameter is possible by utilizing the one-dimensional SPG cavity. The finding clearly shows that SPG has a potential ability to act not only as a one-dimensional host for TMPS but also as a vessel for sol-gel polycondensation reactions. As the side-chain glucose group of SPG can be chemically-functionalized,<sup>10</sup> the resultant silica nanofiber can be easily manipulated by a supramolecular strategy. We believe, therefore, that the present system would be readily applicable to the creation of novel organic/inorganic hybrid nanomaterials and their functionalized derivatives.

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7 (a) Since the diameter of the obtained silica fiber is almost uniform, it seems quite probable that the oligomeric silica fibers (but not a particle), the diameter of which is regulated by SPG, grow to a silica nanofiber structure; (b) we have confirmed that curdlan ( $\beta$ -1,3-glucan without glucose side-group) ( $M_w = 30,000$ ) can also give similar silica nanofibers.

8 It is known that s-SPG is a flexible polymer and can accommodate various guest molecules in an induced-fit manner when it recovers the original shape. In fact, we have already found that it can wrap polymer bundles with 10–20 nm diameters (see: refs. 5a and 5b).

9 We used a catalytic amount of benzylamine or HCl with the expectation that sol-gel polycondensation would proceed more smoothly. However, we could not find any fibrous structure from such reaction systems. The result indicates that the very slow condensation reaction is favourable for one-dimensional growth of silica nanofibers.

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