Preparation of Novel Hollow Fiber Silica Using Collagen Fibers as a Template

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A novel fibrous silica with a gnarled surface structure and an inner tube with bundle-replicated stripes was prepared by sol-gel polymerization of tetraethoxysilane using collagen fibers as a template.

It is known that amphiphilic organic molecules are self-assembled into various supramolecular structures.[1] These self-assemblies can be utilized as a template to create novel mesophasic inorganic materials in mesoporous materials,[2] vesicles,[3] ultra-thin membranes,[4] *etc.* These phenomena have attracted chemists not only for the development of new inorganic materials but also as biomimetic processes of biomineralization. As examples for these processes, one can raise the inorganic micro-fibers prepared by the mineralization of bacterial fibers[5] or by that of self-assembled tubules of a sugar-based lipid galactocerebroside.[6] More recently, we found that a cholesterol-based cationic gelator which can gelate a tetraethoxysilane (TEOS) solution acts as a template in sol-gel polymerization to give a novel mesoporous silica with a tubular, macaroni-like structure.[7,8]

Since the similar neutral gelators cannot yield such a unique silica structure,[7,8] it is clear that the cationic charge on the gelator fiber surface plays a crucial role. Here, it occurred to us that certain proteins in Nature may be also utilized as a template for sol-gel polymerization if they have the excess cationic charge and provide gelling or viscous aqueous solutions. If this idea works as expected, one can replicate the three-dimensional structure of such proteins with silica through the sol-gel polymerization process. For this purpose we here selected collagen which can satisfy a few essential requirements: e.g., (i) it is an ampholite and can become cation-excess in acidic and neutral pH region,[9] (ii) it can form a characteristic fibrous structure which is helpful to identify the templated product and (iii) it possesses a periodical groove structure by every 67 nm along the fiber.[10] We have found that these structural characteristics are well replicated into the silica prepared under the specific sol-gel polymerization conditions.

In Method A, a primitive collagen solution (Type I, 3 mg/ml, pH 3), NaCl, and a phosphate buffer solution (pH 6.86) were mixed and the resultant solution (pH 6.5) was left at 37 ℃ for a month in order to grow up the collagen fibers. The collagen fibers thus obtained were soaked into a TEOS solution without stirring. In Method B, TEOS and NaCl were dissolved into the phosphate buffer and the primitive collagen solution was mixed with the TEOS solution without stirring. In most cases, the hollow fiber silica was obtained from Method B. When the viscous polymerization solution was stirred, the clear silica structure disappeared. Presumably, the stirring would make a mechanical damage on the collagen fibers. Subsequently, they were freeze-dried and heated at 200 ℃ for 1.0 h, 500 ℃ for 2.0 h under a nitrogen atmosphere and finally at 500 ℃ for 4.0 h under aerobic conditions.

The preparation conditions and the results are given in Table 1. Runs 1-3 show the TEOS concentration effect on the silica structure. The SEM image of Run 2 (before calcination)

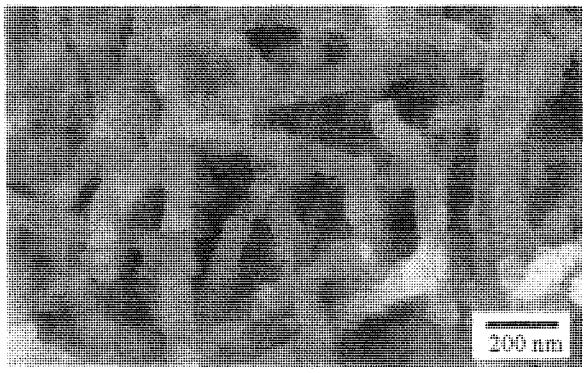

Figure 1. SEM image for Run 2 (before calcination) showing a gnarled structure.

Table 1. Sol-gel polymerization conditions [a] and SEM and TEM images (Method B)

Run	TEOS [b] /mmol dm^{-3}	NaCl [b] /mmol dm^{-3}	Appearance	
			Fiber surface	Inner tube
1	27.1	160.00	Gnarled	Unclear hollow
2	162.4	160.00	Gnarled	Tube with stripes
3	714.0	160.00	Gnarled	Tube with stripes
4	162.4	8.09	Irregularly gnarled with shorter period	Unclear hollow
5	162.4	16.20	Irregularly gnarled with shorter period	Unclear hollow
6	162.4	80.90	Gnarled	Tube with unclear stripes
7	162.4	323.00	Not gnarled	Tube without stripes

[a] at 37 ℃, for 14 days.
[b] The primitive collagen solution (1ml) was added to the solution, TEOS/NaCl/phosphate buffer solution (0.1 ml: 50 mmol dm^{-3}).

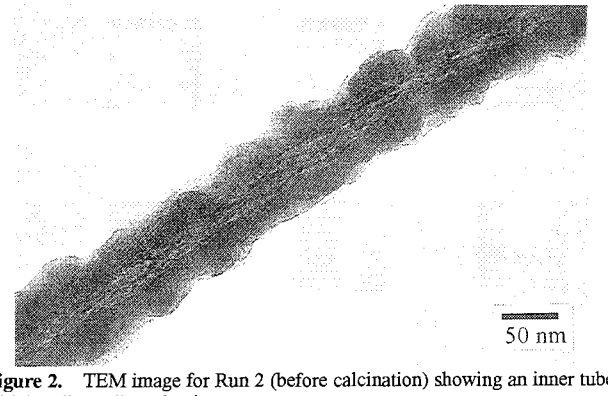

Figure 2. TEM image for Run 2 (before calcination) showing an inner tube with bundle-replicated stripes.

is shown in Figure 1. It is clearly seen that sol-gel polymerization results in the well-grown fibrous silica with outer diameters of 50～100 nm and very interestingly, the fiber surface has a gnarled structure, the period of which (60～80 nm) is comparable with that of the collagen groove (67 nm). In order to view the inside of the gnarled fibers we obtained a TEM image (Figure 2). It is indicated that these fibers have a tubular structure with inner diameters of 25～50 nm which are comparable with the diameter size of the collagen fibers (*ca.* 10～200 nm).[11] Furthermore, a striped structure is seen in the inner tube, which is, presumably, replicated from the hierarchical bundle structure of the collagen fibers. Even after calcination these stripes were still observed although they became less clear because of silica fusion. Figure 3 shows the nitrogen adsorption-desorption

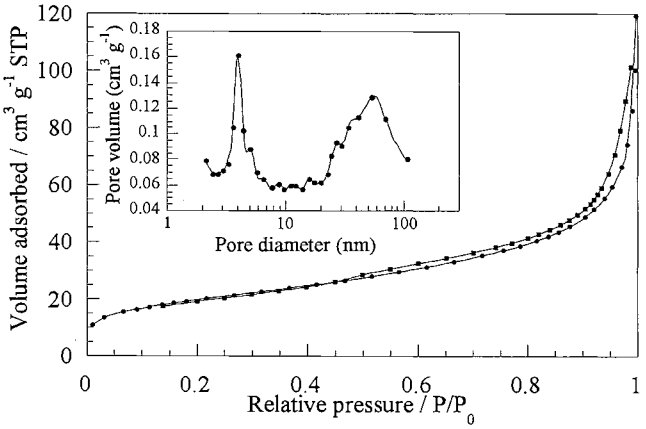

Figure 3. Nitrogen adsorption-desorption isotherm and pore size distribution plot (inset) for Run 2 after calcination.

isotherm and the pore size distribution for Run 2 after calcination. The latter is calculated from the desorption isotherm by a Barrett-Joyner-Halenda (BJH) analysis. The results show that this sample has two specific pore sizes, 4 nm and 50 nm which well coincide with the width of the striped structure and the diameter of the inner tube, respectively.[12] These findings consistently support the view that these gnarled fibers were created using the collagen fibers as a template. The similar SEM and TEM image were also observed from the silica obtained in Run 3 (higher TEOS concentration) whereas the TEM picture obtained in Run 1 (lower TEOS concentration) did not show the clear bundle-replicated structure in the inner tube.

As a mechanism for the preparation of the hollow fiber silica from a gelated TEOS solution we considered that the anionic silica oligomers are adsorbed onto the cationic gelator fibrils and the polymerization further proceeds along these fibrils.[7,8] To estimate such an electrostatic effect on the present replication system sol-gel polymerization was carried out under the various NaCl concentrations (Runs 4-7). Run 6 gave the silica structure similar to Run 2 although the striped structure in the inner tube was not so clear as Run 2. In Runs 4 and 5 (lower NaCl concentration) the gnarled structure was not so regular and the period was shorter than the groove-to-groove distance. In addition, the inner-tube structure was unclear. In Run 7 (higher NaCl concentration), in contrast, the inner-tube could be clearly seen but neither the bundle-replicated stripes nor the clear gnarled structure on the surface were seen (Figure 4). It is known that at neutral pH region and ca. 37 ℃, the fine collagen fibers can grow up under the moderate salt concentration: at the lower salt concentration the bundle structure is not formed whereas at the high salt concentration the periodical groove disappears.[13] The close correlation of the salt effect on both the collagen fiber structure and the fibrous silica structure supports again that the novel silica is created by replication of the collagen fibers by sol-gel polymerization.

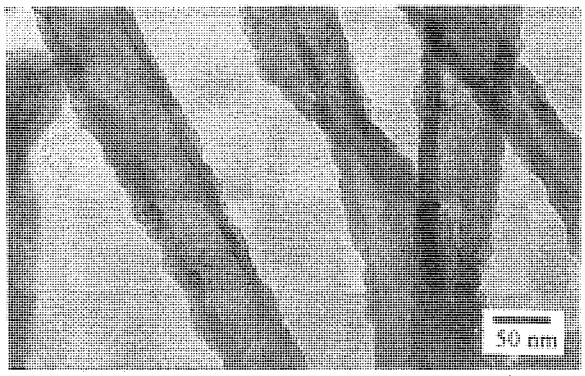

Figure 4. TEM image for Run 7 (after calcination) with a tubular structure.

In conclusion, the present paper has demonstrated a new methodology to prepare the new hollow fiber silica with a gnarled surface structure and a bundle-replicated inner-tube structure using the collagen fibers as a template. We expect that this concept will be more generally applicable to the new silica preparation using various nature-originated materials as templates.

References and Notes

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