Preparation of Helical Mesoporous Silica and Hybrid Silica Nanofibers Using Hydrogelator

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Helical mesoporous silica, methylene−silica, ethane−silica, ethene−silica, octane−silica, and phenylene−silica nanofibers were successfully prepared by sol−gel polymerization using a chiral cationic gelator under a shear flow. These helical nanofibers were constructed by bundles of ultrafine nanofibers that were formed by bundles of nanotubes. The nanotubes of the smallest unit had inner helical channels with uniform inside diameters. The morphologies of the silica nanofibers were sensitive to preparation conditions. In acidic conditions, scanning electron microscopy images showed right-handed helical nanofibers. In basic conditions, rodlike mesoporous nanofibers were formed. The circular dichroism spectrum of the phenylene−silica indicated that the chirality of the gelator was transferred to the arrangement of the phenylene segment of the hybrid silica. The thermostability was so high that the morphologies of the phenylene−silica were maintained even after being calcined at 650 °C for 5 h in air.

Introduction

Mesoporous materials with organic groups in their walls[1−3] have attracted special interest as new materials because the organic groups have the potential for improved dielectric constant and mechanical properties.[4] These hybrid mesoporous materials could be applied in the fields of electronics, optoelectronics, and photonics. Moreover, because organic groups can offer opportunities for further modification, they could be used to develop many kinds of functional materials. Because the development of the one-dimensional (1D) nanostructure is very promising as a result of its applications in fabrication of nanoscale devices,[5] the mesoporous hybrid nanofiber material has exciting potential. For preparing mesoporous fibers, surfactants and copolymers are often selected as the templates.[6] However, because the mesoporous fibers are often combined with small particles, making the morphologies uniform is difficult. We selected sol−gel polymerization using the gelator-direct method to prepare mesoporous nanofibers.

Organogel fibers formed by low molecular weight gelators have been used to prepare inorganic silica[7] and TiO_2 nanotubes.[8] The helical structure of organogel fibers can be transcribed into these inorganic nanotubes; helical structures including single,[8,9] double,[10] and multiple[11] strands can be transcribed. The helical information of inorganic nanotubes will strongly impact their future applications. These nanotubes are typically prepared in organic solvents by using a weak base or acid as the catalyst and using the self-assemblies of organogelators as the template. The diameters of the nanotubes range from several to hundreds of nanometers.

Cationic surfactants have been successfully used to prepare mesoporous silica particles.[6] Therefore, cationic gelators that are structurally similar to cationic surfactants may be suitable for preparing mesoporous silica. Because gelators tend to self-assemble into 1D nanostructures, the morphologies of the silica can be guided easily into 1D structures. We focused on chiral gelators that we had previously developed. Mesoporous silica nanofibers used them as a template for sol−gel polymerization of tetraethyl orthosilicate (TEOS). Taking into account the chemical modification in the walls of the mesopores, we also used bis(triethoxysilyl)methane (BTEM), 1,2-bis(triethoxysilyl)ethane (**1**), 1,2-bis(triethoxysilyl)ethene (**2**), 1,4-bis(triethoxysilyl)benzene (BTEB), 1,3-bis(triethoxysilyl)benzene (**3**), and 1,8-bis(triethoxysilyl)octane (**4**) as the precursors for preparing the hybrid silica (Scheme 1).

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(1) (a) Asefa, T.; MacLachlan, M. J.; Coombs, N.; Ozin, G. A. *Nature* **1999**, *402*, 867. (b) Yoshina-Ishii, C.; Asefa, T.; Coombs, N.; MacLachlan, M. J.; Ozin, G. A. *Chem. Commun.* **1999**, 2539.

(2) (a) Inagaki, S.; Guan, S.; Fukushima, Y.; Ohsuna, T.; Terasaki, O. *J. Am. Chem. Soc.* **1999**, *121*, 9611. (b) Guan, S.; Inagaki, S.; Ohsuna, T.; Terasaki, O. *J. Am. Chem. Soc.* **2000**, *122*, 5660.

(3) (a) Inagaki, S.; Guan, S.; Ohsuna, T.; Terasaki, O. *Nature* **2002**, *416*, 304. (b) Yang, Q.; Kapoor, M. P.; Inagaki, S. *J. Am. Chem. Soc.* **2002**, *124*, 9694.

(4) Lu, Y.; Fan, H.; Doke, N.; Loy, D. A.; Assink, R. A.; LaVan, D. A.; Brinker, C. J. *J. Am. Chem. Soc.* **2000**, *122*, 5258.

(5) Wang, Z. L. *Adv. Mater.* **2000**, *12*, 1295.

(6) (a) Yang, H.; Coombs, N.; Ozin, G. A. *Nature* **1997**, *386*, 692. (b) Schacht, S.; Huo, Q.; Voigt-Martin, I. G.; Stucky, G. D.; Schüth, F. *Science* **1996**, *273*, 768. (c) Mann, S.; Ozin, G. A. *Nature* **1996**, *382*, 313. (d) Marlow, F.; Spliethoff, B.; Tesche, B.; Zhao, D. *Adv. Mater.* **2000**, *12*, 961. (e) Kleitz, F.; Marlow, F.; Stucky, G. D.; Schüth, F. *Chem. Mater.* **2001**, *13*, 3587. (f) Che, S.; Liu, Z.; Ohsuna, T.; Sakamoto, K.; Terasaki, O.; Tatsumi, T. *Nature* **2004**, *429*, 281.

(7) Ono, Y.; Nakashima, K.; Sano, M.; Kanekiyo, Y.; Inoue, K.; Hojo, J.; Shinkai, S. *Chem. Commun.* **1998**, 1477.

(8) Kobayashi, S.; Hamasaki, N.; Suzuki, M.; Kimura, M.; Shirai, H.; Hanabusa, K. *J. Am. Chem. Soc.* **2002**, *124*, 6550.

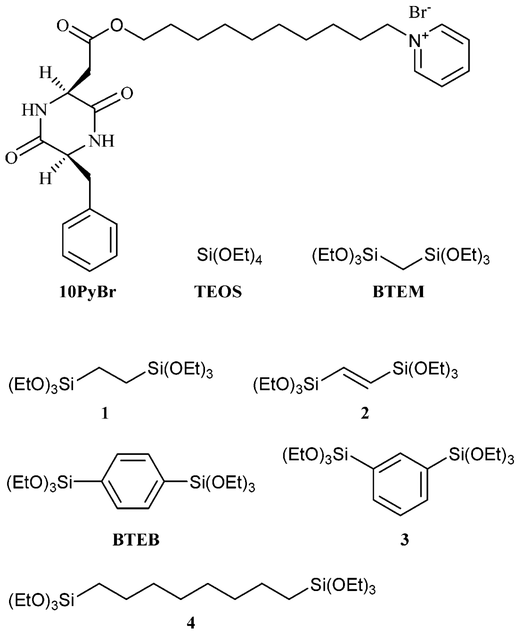
(9) (a) Jung, J. H.; Ono, Y.; Hanabusa, K.; Shinkai, S. *J. Am. Chem. Soc.* **2000**, *122*, 5008. (b) Jung, J. H.; Kobayashi, H.; Masuda, M.; Shimizu, T.; Shinkai, S. *J. Am. Chem. Soc.* **2001**, *123*, 8785.

(10) Jung, J. H.; Yoshida, K.; Shimizu, T. *Langmuir* **2002**, *18*, 8724.

(11) Yang, Y.; Suzuki, M.; Kimura, M.; Shirai, H.; Hananbusa, K. *Chem. Commun.* **2004**, 1332.

10.1021/cm0519030 CCC: $33.50

Scheme 1. Molecular Structures of Gelator 1 and Precursors



Results and Discussion

Compound **10PyBr** was synthesized by the quaternary reaction of pyridine and cyclo(L-10-bromodecylasparaginyl-L-phenylalanine), which was prepared from cyclo(L-asparaginyl-L-phenylalanine) and 10-bromodecanol using the carbodiimide−DMPA method.[12] The compound was capable of forming a physical gel in water at a concentration of 30 g/L (**10PyBr**/water). The circular dichroism (CD) spectrum indicated that the molecules of **10PyBr** in the formed hydrogel were cooperatively stacked helically with aromatic chromophores (Supporting Information, Figure S1).

Mesoporous Silica Nanofibers Obtained in Acidic Conditions. When 56 mg of **10PyBr** was dissolved in 1.0 mL of aqueous 2.4 M HCl under a shear flow, a viscous solution was obtained. The addition of 90 mg of TEOS to the viscous solution drop by drop under a shear flow caused rapid sol−gel polymerization. The mixture turned white within 1 min after dropping the TEOS. Mesoporous silica nanofibers were obtained by washing off the **10PyBr** with a mixture of aqueous HCl and methanol.

We examined the silica nanofibers by optical microscopy, scanning electron microscopy (SEM), and transmission electron microscopy (TEM; Figure 1). The photograph shows the microfibers to be cottonlike (Figure 1a); we confirmed this quality by optical micrography. When suspended in methanol, the cottonlike fibers frayed. It is clear that the nanofibers are almost completely uniform; no amorphous nanoparticles are visible (Figure 1b). The SEM observation under magnification indicated that the nanofibers are constructed by bundles of ultrafine nanofibers in a right-handed helix (Figure 1c). The helix is the most interesting structure of the nanomaterials because it enables them be used as asymmetric reaction catalysts, as supports of catalysts, in helical sensors, and in the stationary phase of chiral HPLC. The diameters of the helical nanofibers are about 300 nm, and those of the ultrafine nanofibers are about 50 nm. Although the magnified SEM image shows that the nanofibers are hundreds of micrometers in length, their original length may be on the order of millimeters because the nanofibers can be assumed to have been broken during sample preparation. The TEM image shows that these nanofibers are mesoporous nanofibers (Figure 1d). The channels are uniform, with inside diameters of about 2 nm, and oriented parallel to the single ultrafine nanofiber axis. Generally, because the channels are twisted within the nanofibers, obtaining clear TEM images is difficult. Although Terasaki et al. have done some work on studying how to use TEM to characterize the chiral channels of twisted mesoporous fibers,[6f] our helical bundle structure seems to be more difficult to characterize. The silica nanofibers have a nitrogen Brunauer−Emmett−Teller (BET) surface area of 597 m^2/g, and the pore size is around 2.3 nm (Supporting Information, Figure S2).

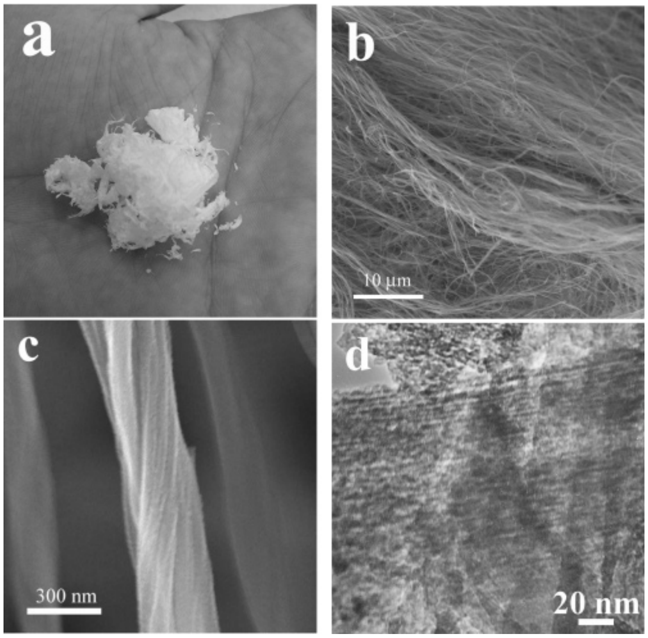


Figure 1. Photograph (a), SEM images (b, c), and TEM image (d) of silica nanofibers after washing off **10PyBr**.

Considering the narrowness of the channels, we assume that only single-strand gel fibers of **10PyBr**, responsible for gelation, acted as the template. Therefore, we can say that the ultrafine nanofibers were constructed by gathering of uniform ultrafine nanotubes. Furthermore, this material is different from the known periodic or wormlike mesoporous materials. In earlier research, the mesoporous silica fibers were often combined with small particles.[6] In the present study, however, ultrafine nanotubes as the smallest unit were obtained because of the sol−gel polymerization on the surface of the single-strand gel fibers.[7]

The formation of a hierarchical structure for mesoporous silica nanofibers is illustrated in Figure 2. First, helical single-strand gel fibers are constructed through the self-assembly of gelators. Second, silica oligomers are adsorbed on the surfaces of the helical gel fibers. Meanwhile, multiple-strand gel fibers are constructed by these single-strand gel fibers.

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[12] Hanabusa, K.; Matsumoto, M.; Kimura, M.; Kakehi, A.; Shirai, H. *J. Colloid Interface Sci.* **2002**, *224*, 231.

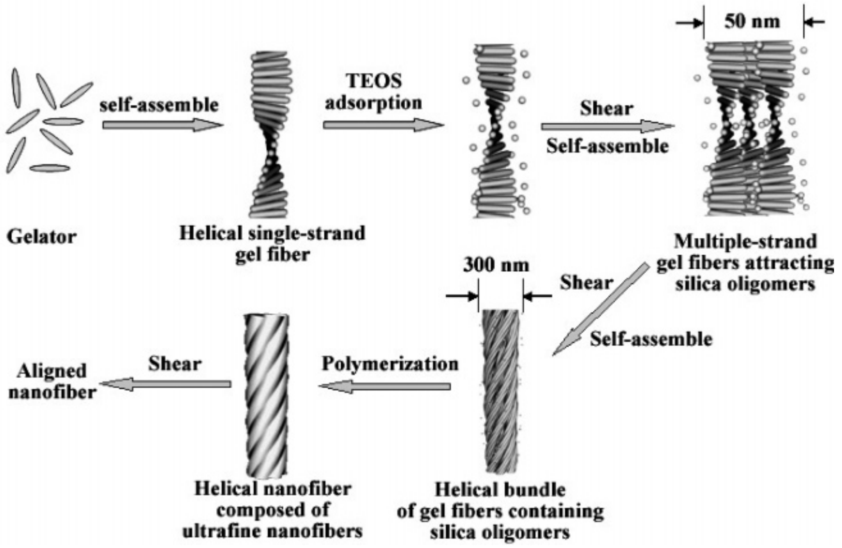

Figure 2. Schematic representation of formation of mesoporous right-handed helical nanofibers and alignment.

Third, helical bundles of gel fibers are formed by these multiple-strand gel fibers. At this time, the sol−gel polymerization of TEOS oligomers takes place on the surface of the single-strand gel fibers. Finally, the formed helical nanofibers are aligned under shearing.

The self-assembly of hydrogelator and the adsorption of silica oligomers are essential for the formation of the hierarchical structure. The alignment and self-assembly of nanotubes into more complicated structures are growing challenges.[5] Several methods have been developed to align nanofibers, such as microchannel networks[13] and the Langmuir−Blodgett technique.[14,15] Mesoporous aluminum oxide membranes have been used as templates for aligning nanotubes.[16,17] Figure 1b shows that many nanofibers were aligned during the sol−gel transcription process. Apparently, the shear flow functions not only to disperse TEOS but also to align the silica nanofibers. The aligned mesoporous silica nanofibers have potential applications in waveguides and HPLC stationary phases.

To successfully produce nanofibers, the concentration of HCl was adjusted to be more than 1 M and the molar ratio of **10PyBr** to TEOS was adjusted from 1:2 to 1:5. We found that the morphologies of the nanofibers were controlled by changing the concentration of **10PyBr** in the sol−gel transcription process. The nanofibers shown in Figure 3a,b were prepared from a mixture of 7 mg of **10PyBr**, 1.0 mL of aqueous 2.4 M HCl, and 10 mg of TEOS. Two kinds of nanofibers were identified from the SEM image (Figure 3a). The diameter of one is hundreds of nanometers, and that of the other is tens of nanometers. Mesopores were also found in a TEM image (Figure 3b), in which the nanofibers appear to be of lotuslike mesoporous silica.[18]

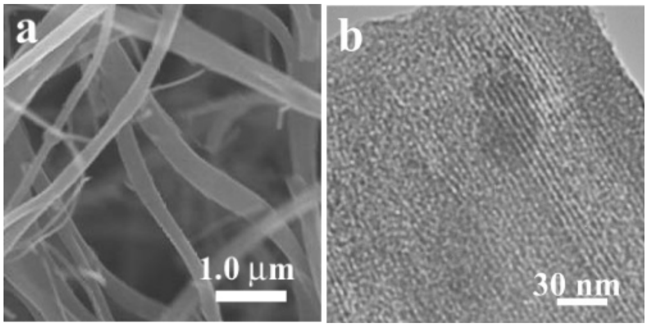

Figure 3. SEM (a) and TEM (b) images of the silica nanofibers.

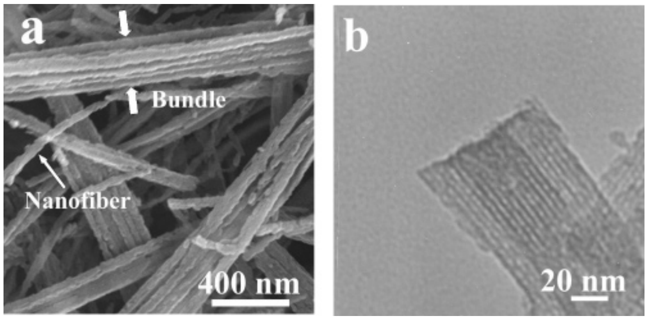

Figure 4. SEM (a) and TEM (b) images of silica nanofibers after being calcined at 500 °C for 5 h in air.

Mesoporous Silica Nanofibers Obtained in Basic Conditions. Mesoporous nanofibers were also prepared in basic conditions. Figure 4 shows SEM and TEM images of the silica nanofibers after being calcined at 500 °C for 5 h in air. They were prepared from a mixture of 56 mg of **10PyBr**, 1.0 mL of aqueous 11.3 wt % NH_3, and 10 mg of TEOS. Although constructing a bundle structure was feasible, the twisted nanofibers in a right-handed helix were not observed (Figure 4a). The reason for the formation of straight bundles instead of twisted nanofibers is unclear at this time.[19] The diameter of the bundles is about 300 nm, and that of the nanofibers is about 60 nm. No amorphous nanoparticles were identified in Figure 4a. The nanofibers obtained in the basic

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(13) Messer, B.; Song, J. H.; Yang, P. *J. Am. Chem. Soc.* **2000**, *122*, 10232.

(14) Kim, F.; Kwan, S.; Arkana, J.; Yang, P. *J. Am. Chem. Soc.* **2001**, *123*, 4360.

(15) Tao, A.; Kim, F.; Hess, C.; Goldberger, J.; He, R.; Sun, Y.; Xia, Y.; Yang, P. *Nano lett.* **2003**, *3*, 1229.

(16) Pu, L.; Bao, X.; Zou, J.; Feng, D. *Angew. Chem., Int. Ed.* **2001**, *40*, 1490.

(17) Hernandez, B. A.; Chang, K. S.; Fisher, E. R.; Dorhout, P. K. *Chem. Mater.* **2002**, *14*, 480.

(18) Jung, J. H.; Amaike, M.; Shinkai, S. *Chem. Commun.* **2000**, 2343.

(19) Yang, Y.; Suzuki, M.; Shirai, H.; Kurose, A.; Hananbusa, K. *Chem. Commun.* **2005**, 2032.

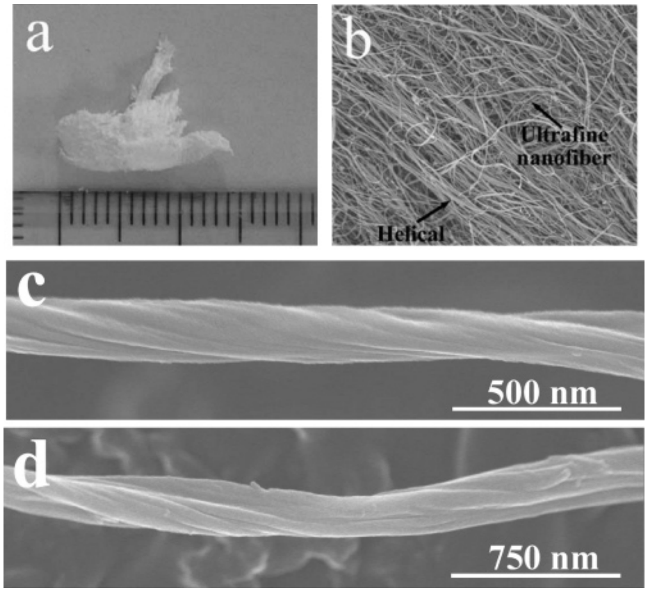

Figure 5. Photograph of the phenylene−silica hybrid material (a), SEM images of the phenylene−silica before calcination (b and c), and SEM image of the material after being calcined at 650 °C for 5 h in air (d).

conditions were straight and tens of micrometers in length. Similarly to the nanofibers prepared in the acidic conditions, the channels were running along the axis of nanofibers (Figure 4b). Because the CD spectrum of **10PyBr** of hydrogel indicated the formation of helical aggregates, the channels within the nanofibers should have helical structures (Figures 2b,d and 4b).[18] These nanofibers are probably suitable to be used in the stationary phase of high-resolution chromatography.

Mesoporous Phenylene−Silica Nanofibers Synthesized in Acidic Conditions. The synthetic procedure of phenylene−silica is similar to that of silica except for the use of BTEB as the precursor. Figure 5 shows a photograph and SEM images of phenylene−silica hybrids that were prepared from a mixture of 75 mg of **10PyBr**, 1.0 mL of aqueous 2.4 M HCl , and 100 mg of BTEB. The polymerization was so fast that it was completed within 1 min. After the template was removed by rinsing with methanol and the material was dried in air, spongelike phenylene−silica with elasticity was obtained, but it is not cottonlike (Figure 5a). This material should be easy to manipulate and modify.

The SEM images of the phenylene−silica before calcinations show that it was composed of two kinds of nanofibers: aligned right-handed helical bundles and random ultrafine nanofibers (Figure 5b,c). These images clearly show that the diameters of the bundles are around 300 nm and those of the ultrafine nanofibers are around 50 nm. This hybrid material shows very high thermostability; it remains stable even after being calcined at 500 °C for 10 h. The UV spectra of the BTEB and phenylene−silica are shown in Figure 6a. The broadening of the absorption peak at 270 nm may come from the $\pi-\pi$ interaction between the phenylene groups.[3] As a result of the high thermostability, we needed to calcinate at 650 °C for 5 h in air to remove the organic components. Notably, the helical structure was kept even after the phenylene segments were removed by calcination (Figure 5d). A transmission electron microscope image of the phenylene−silica hybrid before calcination shows that both the helical bundles and ultrafine nanofibers are constructed by a mesoporous phenylene−silica framework with uniform channels of 2.3 nm diameter that are oriented parallel to the single nanofiber. Besides mesoporous fibers, short and ultrafine nanotubes with inside diameters of 4.2 nm are visible in the TEM image (Figure 7). At the present time, they are too fine to be captured as SEM images. Considering that these nanotubes are short and randomly aligned, they may be formed after stirring stops in the preparation process. When the stirring is stopped, the gelator molecules in the solution may be organized into nanofibers. Then the silicon source will adsorb and polymerize on the surface of gelator nanofibers. Because only a small amount of gelator molecules and silicon source will be left in the solution, the nanotubes will be thin and short.

There were several positive peaks at 240−290 nm in the CD spectrum of phenylene−silica (Figure 6). The phenylene groups in the wall of the mesoporous nanofibers seem to be packed up in the helix. The Barrett−Joyner−Halenda results revealed that there are both micropores and mesopores within the phenylene−silica hybrid material.[20] The surface area of the micropores was 59 m^2/g. These micropores are probably formed among the ultrafine nanofibers making up the helical bundles. Multiple helical hybrids were first prepared from self-templated monomers by Moreau et al. in 2001[21] with the surface areas of around 100 m^2/g. In our study, the mesoporous nanofibers have a nitrogen BET surface area of 546 m^2/g (Supporting Information, Figure S3), which is larger than that of the hybrid fibers with templates inside. Additionally, the adsorption average pore diameter of our hybrid fibers is 39.5 Å. The present hybrid thus seems to be more suitable for use as a support of catalysts.

Mesoporous Methylene−Silica (Methylene Bridged Silica),[22] Ethane−Silica (1,2-Ethylene Bridged Silica),[2a] Ethene−Silica (1,2-Ethenylene Bridged Silica),[1a] Octane−Silica (1,8-Octamethylene Bridged Silica), and 1,3-Phenylene−Silica (1,3-Phenylene Bridged Silica) Nanofibers Synthesized in Acidic Conditions. Another type of hybrid silica nanofibers can be obtained by changing the precursors. Methylene−silica and ethane−silica were synthesized from BTEM and precursor **1**. Figure 8 shows the SEM images of methylene−silica, ethane−silica, ethane−silica, 1,3-phenylene−silica, and 1,8-octane−silica. The polymerization of BTEM and **1** was much slower than that of TEOS. Although the nanofibers were capable of organizing into bundles, it is hard to recognize a helical structure (Figure 8a,b). This might be due to the polymerization speed of BTEM and **1**; it was so slow that the hybrid silica which oligomers derived from the precursors would affect the morphology of the self-assembly of **10PyBr**. Ethene−silica and 1,3-phenylene−silica were synthesized from precursors **2** and **3**. The polymerization of these precursors was very fast. Most of

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(20) Rouqerol, J.; Avnir, D.; Fairbridge, C. W.; Everett, D. H.; Haynes, J. H.; Pernicone, N.; Ramsay, J. D.; Sing, K. S. W.; Unger, K. K. *Pure Appl. Chem.* **1994**, *66*, 1739.

(21) Moreau, J. J. E.; Vellutini, L.; Wong Chi Man, M.; Bied, C. *J. Am. Chem. Soc.* **2001**, *123*, 1509.

(22) Asefa, T.; MacLachlan, M. J.; Grondey, H.; Ozin, G. A. *Angew. Chem., Int. Ed.* **2000**, *39*, 1490.

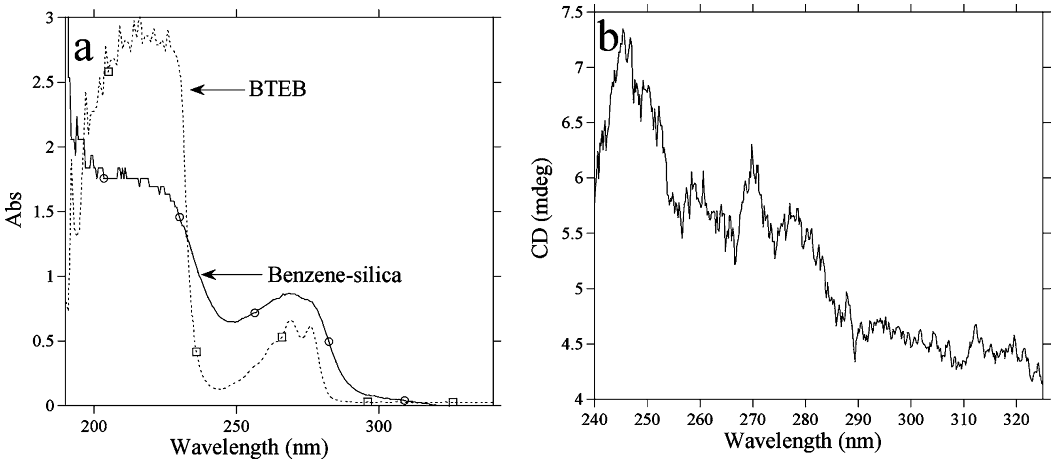

Figure 6. Ultraviolet spectra of BTEB (thin film) and phenylene−silica (a), CD spectrum of phenylene−silica (b).

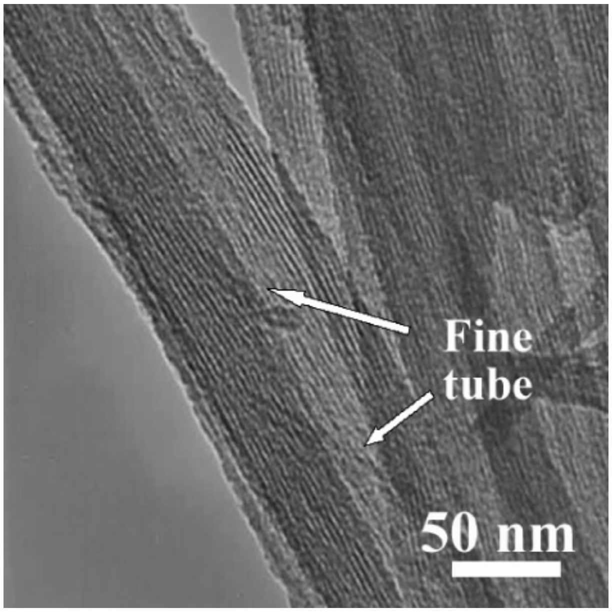

Figure 7. TEM image of the phenylene−silica hybrid before calcination.

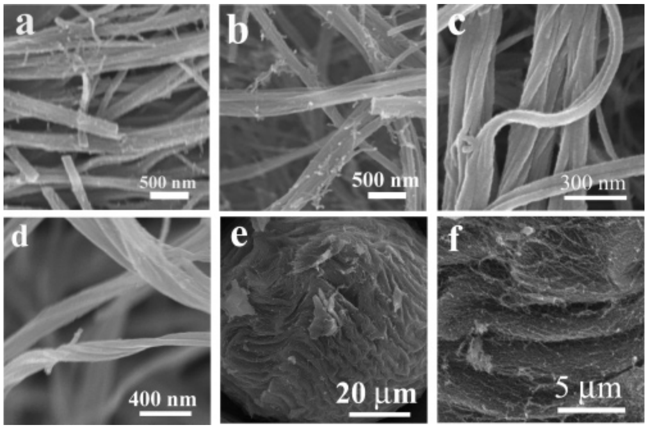

Figure 8. SEM images of the methylene−silica obtained by the sol−gel transcription method with BTEM (a), the ethane−silica obtained by the sol−gel transcription method with **1** (b), the ethene−silica obtained by the sol−gel transcription method with **2** (c), the 1,3-phenylene−silica obtained by the sol−gel transcription method with **3** (d), and the octane−silica obtained by the sol−gel transcription method with **4** (e and f).

the bundles were right-handed helical (Figure 8c,d). The mesopores within the ethene−silica nanofibers were identified using TEM (Supporting Information, Figure S4). When precursor **4** was selected as the precursor, many huge hybrid silica balls were identified in the SEM image (Figure 8e). These balls were constructed by nanofibers (Figure 8f). The van der Waals interaction among the octamethylene segments in precursor **4** may result in the formation of a fibrous structure. Furthermore, it was found that octane−silica showed remarkable hydrophobicity (Supporting Information, Figure S5), while the other hybrid silica showed extremely hydrophilic properties.

In summary, we have successfully prepared right-handed helical silica and hybrid silica bundles using a sol−gel transcription method under a shear flow. They were constructed by strands of nanofibers. We found that acidic conditions are preferable for the preparation of the nanofibers. The nanofibers were formed by gathering nanotubes that had uniform inner helical channels of 2.3 nm inside diameter. The obtained materials were cottonlike or spongelike, not powder. They showed good elasticity and high thermostability. The chirality of the gelator was transferred to the packing of the phenylene segments of the phenylene−silica.

Experimental Section

General Methods. UV−visible spectra were obtained in KBr pellets using a JASCO V-570 UV/vis/NIR spectrometer. TEM images were obtained using a JEOL JEM-2010. Field emission SEM was taken on a Hitachi S-5000. CD spectra were measured on a JASCO J650 spectrophotometer (cell diameter 0.1 mm). In the case of phenylene−silica, first it was ground with KBr. Then the pellet was prepared from the resulting powder. The accumulation times of the obtained CD spectrum shown in Figure 6b are 65. Specific surface area and pore size distribution were determined by the Brunauer−Emmett−Teller (BET) and Barrett−Joyner−Halenda (BJH) methods using the N_2 adsorption isotherm measured by a Shimadzu Gemini 2375 instrument.

Materials. Bis(triethoxysilyl)methane (BTEM), 1,2-bis(triethoxysilyl)ethane (**1**), 1,2-bis(triethoxysilyl)ethene (**2**), and 1,8-bis(triethoxysilyl)octane (**4**) were purchased from Gelest. 1,4-Bis(triethoxysilyl)benzene (BTEB) and 1,3-bis(triethoxysilyl)benzene (**3**) were purchased from Aldrich. TEOS, 25% ammonia solution, hydrochloric acid (35.0−37.0%), and pyridine were commercially available from Wako Pure Chemical Industries. All the reagents were used without further purification.

Synthesis of Gelator 10PyBr. Cyclo(L-β-10-bromodecylasparaginyl-L-phenylalanyl) (5.06 g, 11 mmol) was heated in 100 mL of pyridine at 90 °C overnight under a nitrogen atmosphere. After evaporating pyridine, the recrystallization from a mixture of methanol and diethyl ether gave **10pyBr** in a yield of 5.28 g (86%). ^{1}H NMR (400 MHz, DMSO): δ 1.26−2.0 (16H, m, CH_2), 2.92 (2H, d, CH_2Ph), 3.10 (2H, d, CH_2COO), 3.92 (2H, t, CH_2O), 4.03 (1H, t, CH($PhCH_2$)), 4.22 (1H, t, CH(CH_2COO)), 4.60 (2H, t, CH_2N), 7.17−7.29 (5H, m, Ar), 7.97 (1H, s, NH), 8.16 (1H, s, NH), 8.17 (2H, m, CH), 8.60 (1H, t, CH), 9.08 (2H, d, NCH). Elem anal. Calcd (%) for $C_{28}H_{38}BrN_3O_4$ (560.52): C, 60.00; H, 6.83; N, 7.50. Found: C, 59.76; H, 6.78; N, 7.43.

Synthetic Procedure for the Preparation of Mesoporous Silica Nanofibers Shown in Figure 1 under Acidic Conditions. Gelator **10PyBr** (56 mg) was dissolved in aqueous 2.4 M HCl (1.0 mL) under a shear flow. TEOS (90 mg) was added to the resulting viscous solution dropwise under a shear flow. The mixture started to turn white within 1 min after dropping TEOS. The gel was kept at room temperature for 30 min and 80 °C for 4 days under static conditions. Finally, the gelator was removed by rinse with a mixture of 100 mL of methanol and 5 mL of aqueous 36% HCl for 1 h.

Synthetic Procedure for the Preparation of Mesoporous Silica Nanofibers Shown in Figure 3 under Acidic Conditions. Gelator **10PyBr** (7.0 mg) was dissolved in aqueous 2.4 M HCl (1.0 mL) under a shear flow. TEOS (10 mg) was added to the resulting viscous solution dropwise under a shear flow. The mixture started to turn white within 1 min after dropping TEOS. The gel was kept at room temperature for 30 min and 80 °C for 4 days under static conditions. Finally, the gelator was removed by rinse with a mixture of 100 mL of methanol and 5 mL of aqueous 36% HCl for 1 h.

Synthetic Procedure for the Preparation of Mesoporous Silica Nanofibers under Basic Conditions. Gelator **10PyBr** (56 mg) was dissolved in aqueous 11.3% NH_3 (1.0 mL) under a shear flow. TEOS (90 mg) was added to the resulting viscous solution dropwise under a shear flow. The opaque gel was kept at room temperature for 30 min and 80 °C for 4 days under static conditions. Finally, the gelator was removed by rinse with a mixture of 100 mL of methanol and 5 mL of aqueous 36% HCl for 1 h, and calcination was performed at 250 °C for 2 h and 500 °C for 5 h under aerobic conditions.

Synthetic Procedure for the Preparation of Mesoporous Phenylene−Silica Nanofibers under Acidic Conditions. Gelator **10PyBr** (75 mg) was dissolved in 1 mL of aqueous 2.4 M HCl, and then 100 mg of BTEB was dropped into the solution under strong stirring at room temperature. After the reaction mixture turned white, stirring was stopped. The gel was kept at room temperature for 30 min and 80 °C for 4 days under static conditions. Finally, the gelator was removed by rinse with a mixture of 100 mL of methanol and 5 mL of aqueous 36% HCl for 1 h.

Synthetic Procedure for the Preparation of Mesoporous Methylene−Silica Nanofibers under Acidic Conditions. Gelator **10PyBr** (75 mg) was dissolved in 1 mL of aqueous 2.4 M HCl, and then 100 mg of BTEM was dropped into the solution under strong stirring at room temperature. After the reaction mixture turned white, stirring was stopped. The gel was kept at room temperature for 30 min and 80 °C for 4 days under static conditions. Finally, the gelator was removed by rinse with a mixture of 100 mL of methanol and 5 mL of aqueous 36% HCl for 1 h.

Synthetic Procedure for the Preparation of Mesoporous Ethane−Silica Nanofibers under Acidic Conditions. Gelator **10PyBr** (15 mg) was dissolved in 0.4 mL of aqueous 2.4 M HCl, and then 20 mg of compound **1** was dropped into the solution under strong stirring at room temperature. After the reaction mixture turned white, stirring was stopped. The gel was kept at room temperature for 30 min and 80 °C for 4 days under static conditions. Finally, the gelator was removed by rinse with a mixture of 100 mL of methanol and 5 mL of aqueous 36% HCl for 1 h.

Synthetic Procedure for the Preparation of Mesoporous Octane−Silica Nanofibers under Acidic Conditions. Gelator **10PyBr** (56 mg) was dissolved in 1 mL of aqueous 2.4 M HCl, and then 50 mg of compound **4** was dropped into the solution under strong stirring at room temperature. After the reaction mixture turned white, stirring was stopped. The gel was kept at room temperature for 30 min and 8 °C for 4 days under static conditions. Finally, the gelator was removed by rinse with a mixture of 100 mL of methanol and 5 mL of aqueous 36% HCl for 1 h.

Synthetic Procedure for the Preparation of Mesoporous Ethene−Silica Nanofibers under Acidic Conditions. Gelator **10PyBr** (75 mg) was dissolved in 1 mL of aqueous 2.4 M HCl, and then 100 mg of compound **2** was dropped into the solution under strong stirring at room temperature. After the reaction mixture turned white, stirring was stopped. The gel was kept at room temperature for 30 min and 80 °C for 4 days under static conditions. Finally, the gelator was removed by rinse with a mixture of 100 mL of methanol and 5 mL of aqueous 36% HCl for 1 h.

Synthetic Procedure for the Preparation of Mesoporous 1,3-Phenylene−Silica Nanofibers under Acidic Conditions. Gelator **10PyBr** (75 mg) was dissolved in 1 mL of aqueous 2.4 M HCl, and then 100 mg of compound **3** was dropped into the solution under strong stirring at room temperature. After the reaction mixture turned white, stirring was stopped. The gel was kept at room temperature for 30 min and 80 °C for 4 days under static conditions. Finally, the gelator was removed by rinse with a mixture of 100 mL of methanol and 5 mL of aqueous 36% HCl for 1 h.

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Supporting Information Available: CD spectrum of gelator **10PyBr**; the BJH results of silica and phenylene−silica; the TEM image of ethene−silica (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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