

Hierarchical organization of mesoporous MCM-41 ropes

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Millimeter long ropes of MCM-41 materials are made from micrometer-sized fibers by self-assembly and flow-induced orientation.

Self-assembly of surfactants and aluminosilicates provides a versatile means to create various nanostructures of aluminosilicates, such as MCM-41 and MCM-48,^{1,2} with potential applications in biomaterials, microelectronics and catalysis. For many applications of the mesoporous materials, these materials should be tailored not only at the nanometer scale of the pore but also at the larger scale (micro- and milli-meter) of the morphology.^{3–5} Biomimetic approaches based on hierarchical organization would be a good way of building larger structures. Recent discoveries in hierarchical organization of these nanomaterials have extended the structure order to micrometer level and include tubular, spherical and fibrous morphology.^{6–8} The fiber organization of mesoporous materials is particularly interesting for possible use in embedding conducting materials, from semiconductors to superconductors. We report here a simple method of making bundles of MCM-41 fibers (micrometers in diameter) into millimeter size ropes in nitric acid under a shearing flow; thus extending the previously known primary hierarchy to a higher level of secondary hierarchical structure.⁸

Since our goal is to create millimeter-scaled rope bundles of MCM-41, two sub-goals have to be met: the creation of ultra-long cylindrical micelles and their parallel alignment. Previously, long fiber forms have been created by adding polymers to the surfactant,⁹ and elongation is due to the polymers, not the micelles themselves. In our method we use the nitrate ion as a counter ion to create long worm-like micelles of cationic quaternary ammonium halides. Secondly, the parallel alignments of the hexagonal phase can be realized in a shearing flow. Recent studies on surfactant systems indicate that shear flow induces the formation of long cylindrical micelles and the orientation of the hexagonal phase along the flow direction.¹⁰ Pinnavaia and coworkers found that variation in morphology of mesoporous silica could be attributed to agitation effects during synthesis.¹¹ Recently, it has been shown that 3-D silicate structures^{12a} and 2-D films^{12b} can be induced through detailed control of shear flow conditions and reaction composition.

MCM-41 materials were synthesized from quaternary ammonium halide (C_n TMAX; X = Cl or Br)–tetraethylorthosilicate (TEOS)–nitric acid (HNO_3) systems under couette flow conditions. First, into a couette flow reactor (the diameter of the stator is 8.90 cm, and the rotor is 7.92 cm), a clear aqueous solution of C_n TMAX ($n = 16$ or 18) was mixed thoroughly with a suitable amount of the nitric acid to form a highly viscous solution. The silica source (TEOS) was added and then stirred for 12–24 h at the designed stirring rate and temperature. The composition of gel solution is 1 C_n TMAX : (6.0–12.0) TEOS : (9.0–36.0) HNO_3 : (1000–2000) H_2O . The resultant white silica ropes were recovered by filtration and washed.

Fig. 1A shows the SEM micrograph of the calcined silica products prepared from C_{18} TMAB–TEOS– HNO_3 – H_2O at 40 °C under a stirring rate of 500 rpm. It is found that the silica ropes are almost at the millimeter scale. The length is not

uniform, but the longer ones tend also to be the thicker ones. The yield is high at *ca.* 90%. It is seen by SEM that the length and morphology of the calcined ropes are the same as the as-synthesized materials. At higher magnification, we can clearly see that the silica products consist of micrometer-sized silica fibers entwined into ropes (Fig. 1B). The corresponding higher magnification SEM image of the cross-section of the fibers shows that the micron-sized silica fibers are nearly hexagonal (Fig. 1C). From an ultrathin section TEM micrograph of the cross section of the silica fiber (Fig. 1D), one can unambiguously see that the hexagonal-shaped fibers are constituted from hexagon-arrayed MCM-41 nanochannels. Thus we have made silica ropes in second-order hierarchical structure; nanometer MCM-41 channels, micrometer fibers and millimeter sized ropes. Linear structures at each higher level are built up from the corresponding structure at lower level.

The X-ray diffraction (XRD) patterns of the as-synthesized and calcined silica ropes are shown in Fig. 2. One can clearly recognize the order of the hexagonal array of the MCM-41 structure. Both materials exhibit four sharp XRD peaks, which reflects a typically well aligned MCM-41 structure. The XRD patterns are almost flat in the range 2θ 20–30°, indicating that no amorphous silica particles are formed. The shrinkage of the d_{100} value after calcination at 560 °C for 6 h is only *ca.* 0.1–0.2 nm. This shows the nanostructure of the silica rope possesses high thermal stability.

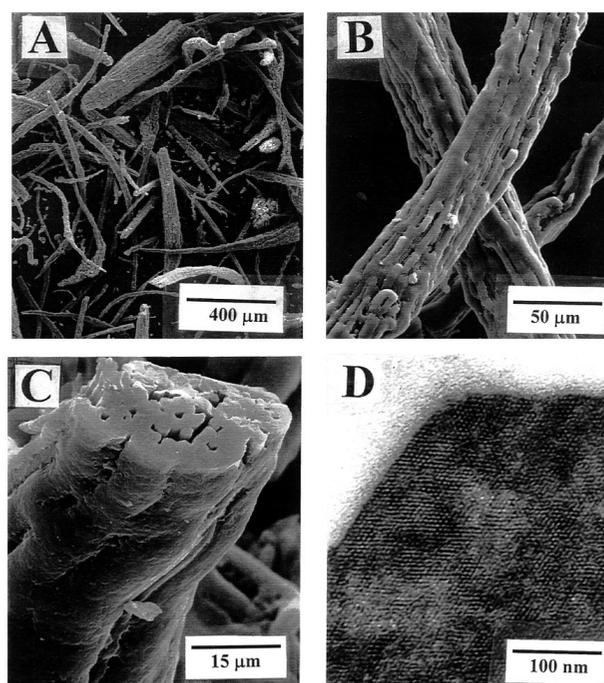


Fig. 1 SEMs of different magnifications and ultrathin TEM of millimeter-sized silica fibers obtained from the gel composition 1 C_{18} TMACl : 6.30 TEOS : 13.5 HNO_3 : 1002 H_2O . (A) $\times 50$, (B) $\times 400$, (C) $\times 1500$, (D) ultrathin TEM of the cross section of the silica fiber.

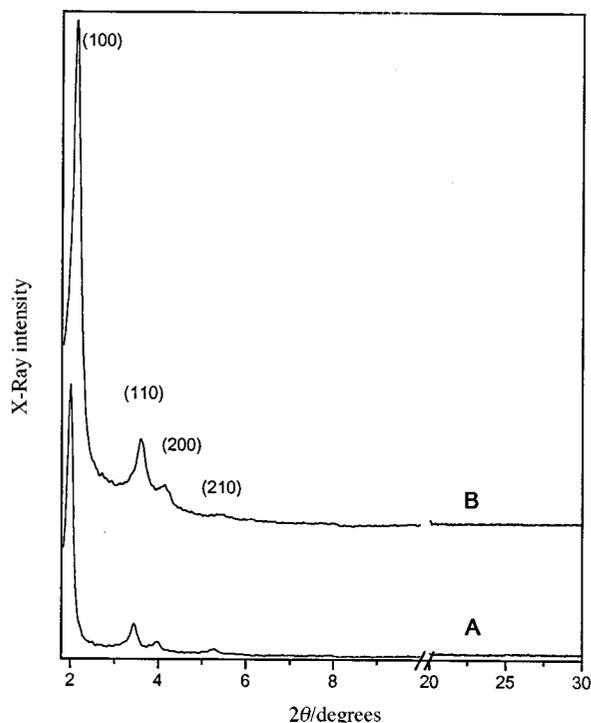


Fig. 2 XRD patterns of as-synthesized and calcined silica ropes prepared from the same gel composition of Fig. 1; (A) as-synthesized, (B) calcined.

In addition to using the surfactant C_{18} TMACl as the template, we can also fabricate millimeter-scaled silica ropes with similarly well defined XRD patterns from different C_n TMAX ($n \geq 16$) surfactants. The physical properties (d_{100} value, pore size, pore volume, BET surface area) of these materials after calcination are listed in Table 1. All of these mesoporous materials possess high thermal stability, large surface area and pore volume, uniform-sized pores, the sizes of which can be varied (*i.e.* by changing the carbon chain length of surfactant) as those synthesized under basic conditions. The formation of long cylindrical micelles can be attributed to the NO_3^- anions of the nitric acid which has a stronger binding affinity to the cationic surfactant than do Br^- or Cl^- anions.^{13,14} The ultra-long micelles of the $S^+NO_3^-$ acts as the template in combining with the cationic silica species (I^+), formed from the hydrolysis of TEOS, to form $S^+NO_3^-I^+$ intermediates. Then it transforms into the final mesoporous product with a constant pore size.

Table 1 Physical properties of the mesoporous silica ropes synthesized from C_n TMAX-TEOS- HNO_3 - H_2O

C_n TMAX ^a	As-made d_{100} value/nm	Calcined d_{100} value/nm	BJH pore ^b size/nm	Pore volume ^c / $cm^3 g^{-1}$	BET surface/ $cm^2 g^{-1}$
C_{18} TMACl	4.41	4.28	3.10	1.36	946
C_{18} TMAB	4.40	4.27	3.08	1.38	968
C_{16} TMACl	4.03	3.84	2.54	1.20	989
C_{16} TMAB	4.02	3.84	2.55	1.23	1002

^a C_{18} TMAX systems were synthesized at 40 °C, C_{16} TMAX at 25 °C.

^b Values obtained from the adsorption portion of the N_2 adsorption-desorption isotherm. ^c Data taken at $p/p_0 = 0.9$.

The ability to control the mesoporous silica materials into a long rope form relies on the underlying physics and chemistry. From the chemical viewpoint, the NO_3^- anions of nitric acid have a strong binding strength with the cationic quaternary ammonium surfactant. Therefore the flexible and elongated rod micelles of $S^+NO_3^-$ would be formed as a supramolecular template for the cationic silica species at a relative high concentration of nitric anions (*ca.* 0.4–0.9 M). When we use HBr or HCl as the source of acid, the morphology of the mesoporous materials is simply spherical.

From the physical viewpoint, the shearing flow also plays an important role for the formation of millimeter-scaled silica ropes. Under static condition, we obtain the mesoporous product in the facet and corrugated silica spheres as reported by Ozin's group.⁶ By contrast, millimeter-sized silica ropes could only be synthesized under a steady continuous stirring.

In conclusion, mesoporous MCM-41 materials are produced in highly-ordered hierarchical form based on the combination of the elongation of the surfactant micelles using strongly binding nitrate counter ions, and the shear flow alignment which lead to formation of ropes of fibrous hexagonal nanochannels. This will provide a pathway to realize biomimetic hierarchical rope structures for other porous materials. In applications, fibrous MCM-41 materials of millimeter length could open up investigations in embedded and oriented metal and semiconductor nanorods.¹⁵

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