

Fluoride-Induced Hierarchical Ordering of Mesoporous Silica in Aqueous Acid-Syntheses**

By Patrick Schmidt-Winkel, Peidong Yang, David I. Margolese, Bradley F. Chmelka, and Galen D. Stucky*

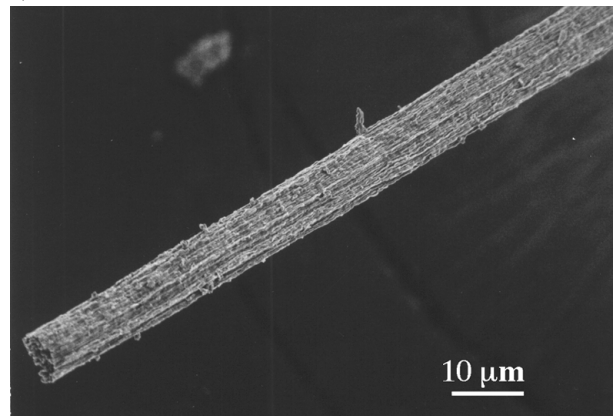
The acid-catalyzed synthesis of highly ordered mesostructured materials^[1] has led to a variety of two- and three-dimensional periodic symmetries, and has proven to be an effective route for the generation of fibers,^[2-5] spheres,^[2,6] thin films,^[7-12] and other monolithic forms^[13-15] of mesoporous materials.^[16,17] Zhao et al.^[18,19] recently used non-ionic poly(alkylene oxide) block copolymers, under acidic conditions, to prepare well-ordered, hexagonal mesoporous silica, denoted SBA-15, featuring uniform and adjustable large pore sizes combined with thick hydrothermally stable walls. The catalytic effect of fluoride^[20-23] in the synthesis of mesoporous silica at neutral to basic pH has been described by Voegtlin et al.^[24] Fluoride has been successfully used to extend the pH range over which anionic silica precursors can be utilized to create organized periodic structures;^[24-26] it has been used to diminish framework defects in zeolites,^[25] and to improve the organization in MCM-41 molecular sieves^[27] and MSU-X materials.^[28] However, to the best of our knowledge, no studies have been reported on the role of fluoride on cationic silica species in the aqueous acid-synthesis of ordered porous silica.

In this communication, we describe the hierarchical ordering effects induced by small amounts of fluoride added during the synthesis of SBA-15-type mesoporous silica under acidic aqueous conditions. The non-ionic poly(ethylene oxide)-*b*-poly(propylene oxide)-*b*-poly(ethylene oxide) triblock copolymer EO₂₀PO₇₀EO₂₀ (Pluronic P123) has been employed as the structure-directing agent. At low pH, remarkably well-ordered, hydrothermally stable, large hexagonal mesoporous silica rods with uniform channels extending over micrometer-sized length scales, and with few

defects, have been synthesized. The fluoride-induced enhancement of order has enabled the preparation of SBA-15 materials at moderate acidity (~ pH 2.5–3) without compromising the long-range hexagonal symmetry. The mesoporous silicas possess narrow pore-size distributions, hydrothermally stable frameworks, large surface areas, and pore volumes of up to 0.92 cm³/g. This work has been motivated by our interest in i) the patterning of mesoporous materials ranging from mesoscopic to macroscopic length scales while retaining molecular-level structural control^[17] and ii) understanding the underlying mechanism for the acid-catalyzed mesoporous silica synthesis.^[29]

Addition of small amounts of fluoride (F:Si molar ratios of 0.008 and 0.03; fluoride source: NH₄F or (NH₄)₂SiF₆) during the aqueous acidic SBA-15-type silica synthesis induces substantial ordering that is manifested on different length scales: both the mesoscopic structure and the macroscopic morphology of the mesoporous silicas are significantly improved. Scanning electron microscopy (SEM) has revealed that small amounts of fluoride bring about the formation of large mesoporous silica rods (Fig. 1a) when pre-

a)



b)

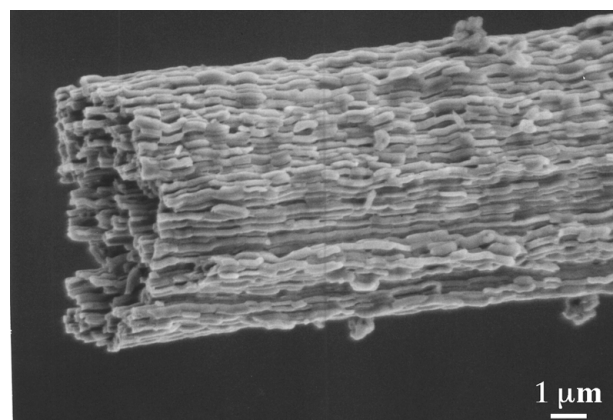


Fig. 1. Representative SEM micrographs of a calcined mesoporous silica rod synthesized at pH 0.5 with a small amount of fluoride (see text for details). a) Low-magnification image of a rod that extends over more than hundred micrometers. b) Higher-magnification image of the same rod showing both the surface and cross-section textures with silica fibers aligned parallel to the rod axis. SEM images were obtained with a JEOL 6300-F microscope using 3.0 kV acceleration voltage.

[*] Prof. G. D. Stucky, P. Schmidt-Winkel, Dr. P. Yang, Dr. D. I. Margolese
Department of Chemistry, University of California
Santa Barbara, CA 93106 (USA)
Prof. G. D. Stucky, Prof. B. F. Chmelka
Materials Research Laboratory
University of California
Santa Barbara, CA 93106 (USA)
Prof. B. F. Chmelka
Department of Chemical Engineering
University of California
Santa Barbara, CA 93106 (USA)

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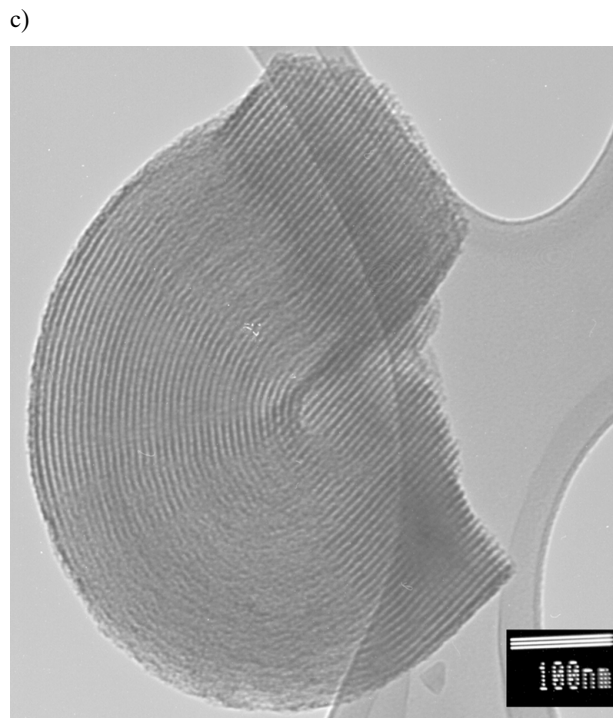
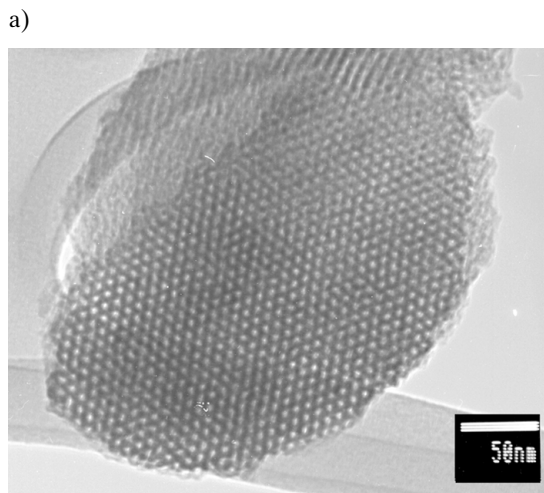


Fig. 2. Representative TEM images of mesoporous silica prepared at pH 1.2 in the presence of small amounts of fluoride. a) Entire cross-section of a single silica fiber. The nanochannels are arranged on a 2-D hexagonal lattice. b) Image of nanochannels extending over several hundred nanometers and following the fiber's curvature with high fidelity. Inset: Magnification of a selected area, demonstrating the ordered channel structure. c) Single $+\pi$ -disclination defect. TEM micrographs were obtained with a 2000 JEOL transmission electron microscope (200 kV).

pared at carefully controlled pH values in the range of pH 0.4–1.2. The rods are made up of bundles of silica fibers aligned co-axially with the rods' long axes (Fig. 1b), which would account for the unusually high optical anisotropy observed under crossed polarizers. Two-dimensional (2-D) X-ray analyses have corroborated the rod alignment. This – aligned – morphology is in marked contrast to the highly curved and bent macroscopic structures that are usually observed after acidic silica syntheses without fluoride addition.^[1,3,15,18]

Comparison of SEM images taken prior to and after calcination in air at 550 °C have revealed no differences in particle morphology. Furthermore, SEM, X-ray diffraction (XRD), and nitrogen sorption have shown that the calcined silica rods are mesostructurally and macroscopically stable

in water at 100 °C for at least 1.5 days. Transmission electron microscopy (TEM) of the mesoporous silica fibers has revealed the existence of well-ordered nanochannels with high structural integrity (Fig. 2). The nanochannels are arranged on a 2-D hexagonal lattice (Fig. 2a) and appear to be continuous over micrometer-length scales, oriented parallel to the silica fiber axes and following the curvature of the fibers with a high degree of fidelity (Fig. 2b).

When the synthesis is conducted with small amounts of fluoride at pH 1.2 or higher, isolated $+\pi$ -disclination defects^[30–32] are observed (Fig. 2c); when the synthesis pH is kept at 0.5 or below, the number of $+\pi$ -disclinations is reduced. Disclination quadrupoles, commonly found in base-synthesized MCM-41,^[31] have not been detected in our acid-synthesized mesoporous silicas. In less acidic solutions (pH > 1.2), the unusual macroscopic rod morphology has been compromised. When the F:Si molar ratios are adjusted to 0.008 or 0.03 with $1.2 < \text{pH} \leq 2.7$, the formation of bundles of highly bent and curved silica fibers is observed. At pH > 2.7, order is lost on all length scales and disordered materials are isolated. Increasing the F:Si molar ratio to 0.125 and higher also yields disordered materials.

By carrying out control experiments using several different stirring rates under otherwise identical reaction conditions both in the presence and in the absence of fluoride

ions, we have been able to establish that the morphological rod alignment is induced by the presence of fluoride ions and not directly by stirring.^[2] We suggest that the aligned morphology of the silica rods prepared at $\text{pH} \leq 1.2$ in the presence of small amounts of fluoride ions may reflect metastable non-equilibrium structures.^[33] The linear chain growth of silica, characteristic for acidic syntheses,^[20,33] may be considerably promoted by the presence of small amounts of fluoride at low pH ,^[20–23] thereby inducing anisotropic growth.^[29]

As evident from powder X-ray diffraction experiments and TEM analyses, adding small amounts of fluoride significantly improves the mesoscopic structures of silicas compared to their corresponding analogs synthesized in the absence of the mineralizing agent. Figure 3 compares XRD patterns of SBA-15-type materials synthesized at pH 2.5–2.7 with and without fluoride addition. It is apparent that the addition of fluoride not only significantly enhances the XRD scattering intensities, but also narrows the Bragg peaks. Both of these observations are indicative of improved structural ordering within the mesoporous silicas.^[24,28] Such fluoride-induced enhancement of mesostructural order has enabled us to raise the synthesis pH from 0.2 for the original SBA-15 synthesis up to pH 2.7, without compromising the long-range hexagonal order. To the best of our knowledge, this is the highest pH at which the combination of non-ionic structure-directing agents and sol-gel chemistry has been successfully used to prepare ordered hexagonal mesoporous silica in acidic aqueous media.

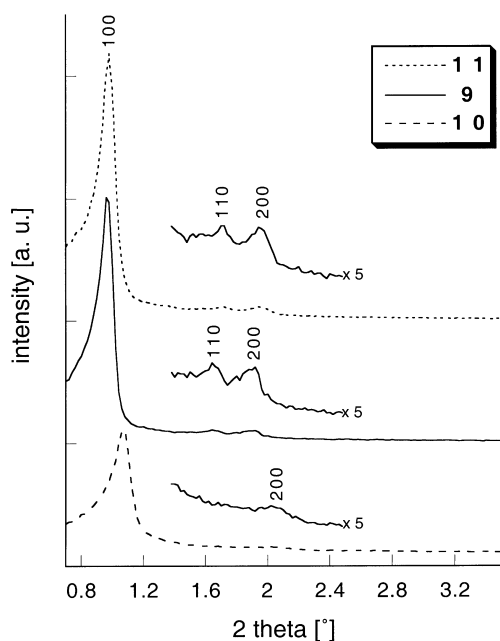


Fig. 3. X-ray diffraction analyses of calcined 2-D hexagonal SBA-15, prepared at pH 2.5–2.7 (see Table 1), demonstrate the increased mesostructural ordering induced by adding fluoride. Samples 9 and 11 were synthesized in the presence of some fluoride, sample 10 without fluoride addition. The X-ray data were collected on a Scintag PADX diffractometer using $\text{Cu K}\alpha$ radiation.

The mesoporous silicas, prepared at pH 0.4–2.7 in the presence of small amounts of fluoride and possessing well-ordered morphologies, are isolated as fluffy powders for as-made and calcined materials. Among the syntheses without fluoride, only the original SBA-15 protocol affords similar fluffy material; the syntheses carried out at pH 1.0–2.7 led to consolidated solids with unstructured macroscopic morphologies, as judged by SEM. However, XRD patterns of these consolidated materials (Fig. 3a, bottom curve) show Bragg peaks typical for hexagonal lattices, although less ordered than SBA-15.^[18,19] TEM analyses have corroborated their 2-D hexagonal structures.

The calcined silicas were subjected to nitrogen sorption analyses. The isotherms are of type IV with H1-type and H2-type hystereses^[34] and compare well with those reported for SBA-15.^[18,19] Table 1 summarizes the synthesis conditions, XRD results, and nitrogen sorption data for selected samples. The mesoporous SBA-15-type silicas feature large pores (49–64 Å) with narrow pore size distributions (FWHM: 7–10 Å) and hydrothermally stable frameworks. For instance, a sample with a pore size of 62 Å can be heated in water at 100 °C for at least 1.5 days without compromising either the hexagonal order or the well-structured macroscopic rod morphology. The porosities, BET surface areas, and wall thicknesses are in agreement with data published for related mesoporous silicas.^[18,19,35] Adding a co-solvent such as trimethylbenzene to the aqueous acid-synthesis, with or without fluoride, induces a phase transition from the highly ordered $p6mm$ mesostructure of SBA-15 to a porous cage structure with uniform cage dimensions of up to 36 nm.^[36]

The pore sizes of the mesoporous SBA-15-type silicas prepared at $\text{pH} > 0.2$, both in the presence and absence of fluoride ions, are slightly enlarged compared to SBA-15.^[18] Increasing the pH from 0.2 to 1.0 and higher is likely to reduce the hydrophilicity of the poly(alkylene oxide) block copolymer. Consequently, the curvature of the block copolymer aggregates may decrease, allowing the hydrophobic core that determines the framework pore size to increase. Elemental analyses have shown that calcined fluoride-treated samples contain 0.04–0.21 wt.-% of fluoride, depending on the fluoride source and the synthesis pH . This would account for the slightly enlarged unit cell parameters.^[28] Varying the synthesis pH between 0.2 and 2.3 has little effect on the wall thickness (44–46 Å) for the syntheses lacking fluoride. Adding fluoride at $\text{pH} \leq 1.1$ reduces the wall thickness to 40–44 Å, gradually increasing with the pH ; at pH 1.2 the wall thickness is similar to silicas prepared in the absence of fluoride (44–46 Å). When the synthesis pH is raised to 2.5–2.7, the wall thickness is reduced for both the fluoride and non-fluoride silicas (38–42 Å). However, the wall thickness is generally substantially greater than reported for base-synthesized MCM-41 materials,^[37–39] which would account for the observed hydrothermal stability (see above).

Table 1. Synthesis conditions and experimental data of selected samples.

Sample	pH ^a	HCl/Si ^b	F/Si ^b	d_{100} ^c	a_0 ^d	Pore size ^e	FWHM ^f	Pore volume	BET surface area	Wall thickness ^g
		[%]	[%]	[Å]	[Å]	[Å]	[Å]	[cm ³ /g]	[m ² /g]	[Å]
1	0.2	588	0	78.6	90.8	45	9	0.54	695	46
2 ^h	0.5	588	3	81.6	94.2	54	9	0.81	791	40
3 ^h	0.5	588	0.8	80.2	92.6	52	8	0.65	725	41
4 ⁱ	0.4	588	3	86.6	100.0	57	9	0.88	821	43
5 ^h	1.0	59	0	82.6	95.4	51	10	0.55	575	44
6 ^h	1.2	59	3	93.9	108.4	62	10	0.92	888	46
7 ^h	1.2	59	0.8	80.2	92.6	49	7	0.58	652	44
8 ^k	2.3	2.5	0	82.5	95.3	49	9	0.50	569	46
9 ^h	2.5	2.5	0.8	91.4	105.5	64	10	0.81	881	42
10 ^k	2.6	0.8	0	82.6	95.4	54	10	0.59	676	41
11 ⁱ	2.7	0.8	0.9	81.7	94.3	56	10	0.65	653	38

[a] At end of reaction. [b] Molar ratio. [c] Calcined samples (8 h at 550 °C). [d] Unit cell $a_0 = 2/\sqrt{3} \times d_{100}$. [e] Determined from adsorption branch according to Barret–Joyner–Halenda method. [f] Full-width-at-half-maximum for pore-size distribution. [g] Wall thickness = a_0 – pore size. [h] Prepared with NH₄F. [i] Prepared with (NH₄)₂SiF₆. [k] Reaction time: 3 days

Solid-state ²⁹Si MAS NMR spectra of as-made silicas clearly demonstrate that the addition of fluoride promotes the silica polymerization, giving more condensed materials. The Q³/Q⁴ ratios for the fluoride systems (Q³/Q⁴ = 0.34–0.62) are considerably smaller than for silicas prepared without fluoride (Q³/Q⁴ = 0.74–0.78). Characterization by thermogravimetric and differential thermal analysis (TGA/DTA) has provided results very similar to those for SBA-15,^[18,19] indicating facile surfactant removal under mild conditions.

In summary, the use of small amounts of fluoride in the aqueous acid-synthesis of hexagonal SBA-15-type mesoporous silica, by using the non-ionic poly(alkylene oxide) block copolymer EO₂₀PO₇₀EO₂₀ as the structure-directing agent, makes it possible to influence the organization of the materials on different length scales in one step. Hydrothermally stable silica rods, consisting of bundles of highly ordered mesoporous silica fibers that are several hundred micrometers long and run parallel to the rod axes, have been prepared at low pH in the presence of small amounts of fluoride. The silica fibers possess exceptional long-range hexagonal order with well-organized nanochannels that extend over micrometer-sized regions with few defects, have large pore sizes with narrow pore-size distributions, hydrothermally stable walls, large surface areas, and pore volumes up to 0.92 cm³/g. The fluoride-promoted acid-synthesis of SBA-15 at moderate pH appears promising. It may enable the preparation of novel anisotropic hybrid materials incorporating acid-sensitive functional moieties. Furthermore, it may allow for the substitution of the amphiphilic poly(alkylene oxide) block copolymer by amphiphilic poly(peptide) block copolymers that are structure-directing agents in biosilification.^[40] The potential of the novel nanostructured materials described in this communication as anisotropic hosts for functional molecules and polymers is currently under investigation in our laboratories.

Experimental

X-ray powder diffraction (XRD) experiments were performed on a Scintag PADX diffractometer (Cu K α radiation) equipped with a Si(Li) solid-state detector cooled by a Peltier cell. Nitrogen sorption analyses were carried out on a Micromeritics ASAP 2000 system at –196 °C with samples outgassed at 180 °C under high vacuum for 1 day. The data were analyzed according to the Barret–Joyner–Halenda (BJH) method using the Halsey equation for multilayer thickness. Scanning electron microscopy (SEM) was carried out on a JEOL 6300-F microscope with Au/Pd-sputtered specimen (3.0 kV). Transmission electron microscopy (TEM) was performed on a 2000 JEOL microscope (200 kV) using copper grids. Solid-state ²⁹Si MAS NMR spectra were recorded on a General Electric GN-300 spectrometer with a Tecmag console operating at a ²⁹Si resonance frequency of 59.71 MHz under conditions of magic-angle spinning at room temperature and with tetramethylsilane as reference. Elemental analyses for fluoride were carried out on a Cameca SX50 electron probe analyzer equipped with five wavelength-dispersive spectrometers using a PC 0-analyzing pseudo crystal (beam power: 15 kV, 10 nA). The synthesis pH was monitored with an Accumet 150 titration controller. Simultaneous thermogravimetric and differential thermal analyses (TGA/DTA) were carried out in air on a Netzsch Thermoanalyzer STA 409 with a heating rate of 5 K/min and alumina as the reference.

Conditions published for the preparation of SBA-15 [18,19] were the basis for our synthesis procedures. We modified this protocol as follows: the amounts of poly(ethylene oxide)-*b*-poly(propylene oxide)-*b*-poly(ethylene oxide) triblock copolymer EO₂₀PO₇₀EO₂₀ (Pluronic P123) and tetraethoxysilane (TEOS) were kept constant. The amount of HCl(aq) was reduced stepwise to adjust the HCl/Si molar ratio to values of 5.88, 0.59, 0.025, 0.008, and 0, while at the same time increasing the amount of water to keep the H₂O/Si molar ratio at 195. Each of the silica preparations was subjected to a reaction series, into which we added different amounts of an ammonium-based fluoride source [NH₄F or (NH₄)₂SiF₆, Aldrich (98 %)], followed by a constant amount of TEOS to adjust the F/Si molar ratio to values of 0.25, 0.125, 0.03, 0.008, and 0 for each of the five HCl/Si molar ratios given above. For example, 2.0 g (0.4 mmol) of EO₂₀PO₇₀EO₂₀ (M_{av} = 5800, BASF/Aldrich) were completely dissolved in a mixture of 45.0 g (2.5 mol) of deionized water and 30.0 g (120 mmol HCl) of 4.7 M HCl while stirring at room temperature (~1 h). At 35–40 °C, 23 mg (0.6 mmol) of NH₄F were added, followed by 4.2 g (20 mmol) of TEOS (Acros, 98 %). After 20 h of stirring at 35–40 °C, the precipitate was filtered, washed, and dried in air at room temperature to afford 2.64 g of white, as-made silica. Yields typically ranged from 92 to 100 %, based on Si. For calcination, the as-made silicas were gradually heated in an air-flushed oven to 550 °C over 8 h and kept at this temperature for a further 8 h.

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Synthesis of Mesoporous Silica from Sodium Silica Solutions and a Poly(ethylene oxide)-Based Surfactant**

By Ligia Sierra,* Betty Lopez, Humberto Gil, and Jean-Louis Guth

Huo et al. explained the formation of mesoporous solids discovered by scientists of the Mobil Oil company^[1,2] in terms of a cooperative self-organization of charged surfactant micelles and inorganic species.^[3] They proposed four synthesis mechanisms based on a direct interaction of the surfactant species (S^+ or S^-) and the inorganic species (I^+ or I^-) or an indirect interaction through mediator species such as halide anions X^- or alkaline cations M^+ . These routes are denoted (S^+I^-), (S^-I^+), ($S^+X^-I^+$), and ($S^-M^+I^-$).

Tanev and Pinnavaia^[4] and Bagshaw et al.^[5] demonstrated that mesoporous metallic oxides can also be obtained by means of the neutral routes S^0I^0 or N^0I^0 , through hydrogen bond interactions between non-charged amine (S^0) or poly(ethylene oxide)-type (N^0) surfactants and neutral inorganic species (I^0). The mesoporous silica family prepared by Bagshaw et al. through the neutral route N^0I^0 and denoted MSU-X was studied later by Prouzet and Pinnavaia.^[6] These materials possess structures with worm-like channels without a regular long range periodicity but with uniform channel diameters over a range comparable to M41S materials.^[1,2] These authors also found that the pore diameter can be changed by varying the synthesis temperature.

The preparation of mesoporous silica by this neutral route has important advantages compared with that by electrostatic routes, for example the easy removal of the surfactant by solvent extraction and the tendency to produce materials with thicker walls and smaller particle sizes. But until now the starting materials used were alkoxysilanes, which are rather expensive silica sources. In this paper we report the results of syntheses starting from sodium silicate solutions as a cheap inorganic silica source and Triton X-100 [poly(ethylene glycol) 4-*tert*-octylphenyl ether with 9–10 ethoxy groups] as the neutral surfactant. We fo-

[*] Prof. L. Sierra, Prof. B. Lopéz, H. Gil
Departamento de Química, Universidad de Antioquia
A.A 1226, Medellín (Colombia)
Dr. J.-L. Guth
Laboratoire de Matériaux Minéraux, Université de Haute Alsace
F-68093 Mulhouse Cedex (France)

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