A simple extrusion method for the synthesis of aligned silica nanowires using the template of a rigid surfactant mesophase†

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Long range alignment of silica nanowires has been accomplished by extrusion of a novel surfactant mesophase prior to silica synthesis.

Transcription of self-assembled surfactant microstructures to inorganic materials has been a constant goal for colloid and surface science researchers over the years.[1] Abundant research on the formation of mesoporous silica materials in surfactant-mediated synthesis has been fueled largely by its relevance in catalysis and membrane and sensor fabrication.[2] Highly ordered materials have been reported for the M41S silica family[3] and the SBA-15 mesoporous materials[4] through ionic surfactant and polymeric surfactant mediated synthesis respectively.

A current issue of concern is to achieve long range alignment in inorganic materials. Some reported methods that direct long range alignment include flow inducement[5] and shearing.[6] A recent publication of ours has shown successful results in directing alignment of silica nanowires through Couette shear.[7] We demonstrated the feasibility of aligning silica nanowires in a pre-shear aligned template. This is possible due to the rigid nature of the mesophase template which allows it to retain alignment after shear application, allowing silica synthesis to be performed after shear application. This communication describes an alternate approach to alignment through shear. We examine extrusion of a rigid crystalline mesophase as a method to form a template with long range alignment characteristics. The retention of alignment allows us to decouple the materials synthesis and shear application steps.

We used the rigid surfactant mesophase consisting of the anionic surfactant AOT (bis-2-ethylhexyl sodium sulfosuccinate) mixed with zwitterionic lecithin (α-phosphatidylcholine), at a 2 : 1 molar ratio. When this surfactant mixture is dissolved in a nonpolar solvent *e.g.* isooctane, and water is progressively added, the system evolves from a low viscosity solution to a gel-like state with crystalline order evidenced through small-angle neutron scattering (SANS) results.† SANS studies illustrate a columnar hexagonal symmetry over the composition range surfactant : isooctane : water from 0.27 : 0.27 : 0.46 to 0.21 : 0.21 : 0.57 (in weight fractions), with water cylindrical columns arranged in hexagonal geometry (the H_{II} phase).[8] This optically clear system possesses a high viscosity up to 10^6 Pa s at low shear rates and has a relatively high rigidity characterized by a storage modulus (G') of 10^4 Pa.

Fig. 1 shows the small-angle neutron scattering patterns of the mesophase template where a 1 : 1 volume ratio of D_2O and H_2O has been used to provide sufficient scattering contrast. The sample was first extruded vertically onto a quartz window and then horizontally onto another quartz window.‡ Prior to extrusion, the native mesophase in Fig. 1(a) follows a typical diffraction pattern, as is often observed for isotropic samples. However upon extrusion, a dramatic alignment of the system is observed. The two-spot scattering pattern illustrated in Fig. 1(b) and (c) indicates the orientation of the system along the extrusion direction as has been reported for other lyotropic phases.†[9] SANS results reaffirm the feasibility of extrusion in directing alignment of the gel meso-phase. By simple extrusion of the mesophase through a needle attached to a syringe (Fig. 2), alignment of the template can be retained for periods approaching a week. This allows ample time for silica formation. The fact that extrusion is a much simpler process, and eliminates the need for sample transfer after alignment makes it a desirable method.

We followed the synthesis protocol shown in Fig. 3, which consists of doping the silica precursor tetramethoxysilane (TMOS) with the nonpolar hydrocarbon, forming the surfactant meso-phase, extruding the system and allowing silica synthesis to proceed for a day.§ TMOS, though fully miscible with isooctane, causes silica precipitation through hydrolysis and condensation within the aqueous columns of the reverse hexagonal mesophase. The dramatic alignment achieved for the silica sample formed in the extruded template is shown as fibers in the scanning electron micrographs in Fig. 4.¶ The template in both samples was removed by washing with ethanol. Silica formed in the native mesophase without extrusion does not show any particular orientation but silica fibers formed in the extruded mesophase
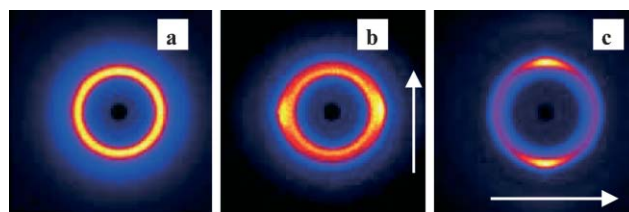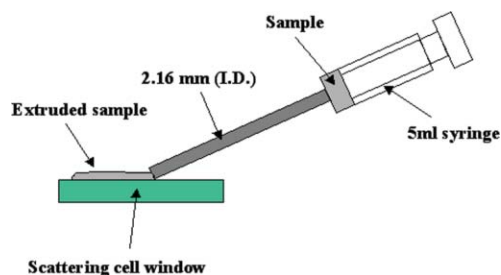
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Fig. 1 2-D SANS profiles for (a) the native mesophase; (b) and (c) the extruded mesophase ($W_0 = 90$). The arrows show the extrusion direction.

Fig. 2 Picture depicting extrusion of the mesophase through a syringe with a long needle attachment onto a scattering cell window.
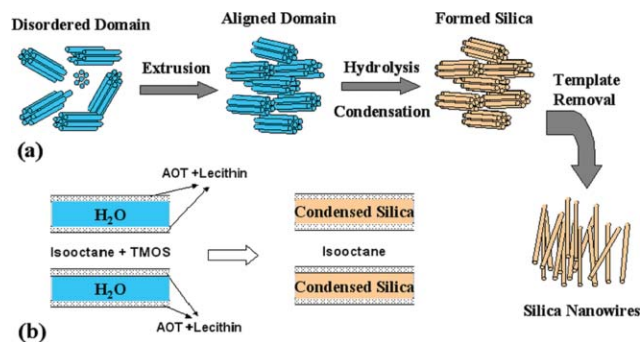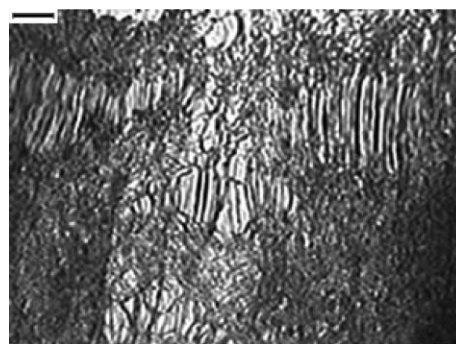

Fig. 3 (a) Silica nanowire synthesis in the aligned reverse hexagonal mesophase after extrusion. (b) A schematic illustration of TMOS hydrolysis and condensation into the microaqueous columns to form silica.
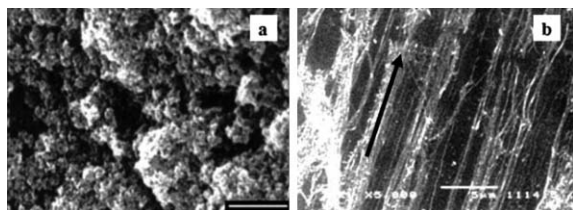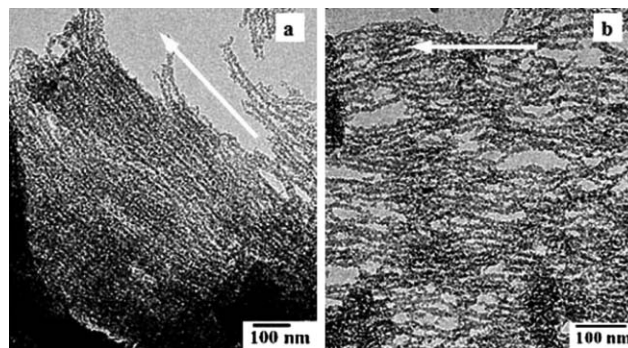

Fig. 4 Scanning electron micrographs of (a) silica formed in the native mesophase and (b) silica formed in the extruded mesophase used as templates. The template for both samples was removed by washing with ethanol prior to imaging. The arrow indicates the direction of extrusion. Scale bar = 5 μm.

Fig. 5 Optical microscopy image showing long range alignment of silica. Scale bar = 50 μm.

Fig. 6 Transmission electron micrographs of silica nanowires synthesized using the extruded surfactant mesophase as template. Images are taken after template removal. Arrows indicate the extrusion direction.

template are aligned parallel to one another. Considerable improvement in directionality is achieved for silica synthesized in the extruded template compared to those obtained formerly by Couette shear. Couette shear demonstrated clear alignment on the submicron scale, but it is only with extrusion that long range alignment is achieved, as shown in the optical microscopy image in Fig. 5. The streaks in the optical microscopy image are a result of aggregation of the fibers seen in the SEM image earlier. Transmission electron microscopy further reveals that each fiber actually consists of closely packed 10–20 nm wide nanowires (Fig. 6).∥

Upon template removal, the silica nanowires do not show any crystalline order. Unlike MCM-41 mesoporous silica materials, silica is precipitated into the microaqueous channels of the template instead of between the aqueous channels. This might explain why the silica nanowire microstructure did not remain intact in the hexagonal phase when the template is removed. The silica materials formed possess a BET surface area of 400–500 $m^2 g^{-1}$. ^{29}Si solid-state NMR shows the porous silica to have a high degree of SiO_4 cross-linking. The BJH pore size (9–10 nm) is of the same order as the water channel d-spacing (10–20 nm) shown by SANS.[8]

The novelty of this approach is two-fold. Firstly, this method shows that ceramic microstructure can be dramatically changed by appropriate pre-application of extrusion. Secondly, substantial improvement in long range alignment is achieved using simple extrusion. Once again we have demonstrated the ability to decouple the materials synthesis from template alignment which is a variation from flow-induced microstructures that require the materials' synthesis to be conducted under continuous shear. We can conclude that it is the retention of the template alignment after extrusion that allows long range alignment of the silica nanowire structures. It is potentially possible to apply this extrusion technique to prepare polymer–ceramic nanocomposites or nanoparticle[10] incorporated functional ceramics with aligned extended nanostructures. Ongoing work shall address these issues.

Notes and references

‡ Samples were contained in closed stainless steel SANS cells with quartz windows that provided a path length of 2 mm. To investigate the alignment effect of extrusion using SANS, the sample was loaded into a sample cell by first extruding it in a specific direction on a quartz window and then enclosing the extrudates with another quartz window. All the SANS diffractograms showed characteristic patterns for a hexagonal phase with peak distances of $1 : \sqrt{3}$. The primary peaks were observed at $q_m = 0.04 \text{ Å}^{-1}$, which closely approximates that of the template. Neither doping with TMOS nor extrusion caused phase transitions in the investigated concentration range.

§ 1.89 g of AOT and 1.59 g of lecithin were dissolved in a glass vial containing 4 ml of isooctane and 1 ml of TMOS to prepare a 0.85 M AOT, 0.42 M lecithin solution. Water at pH 9.0 was gradually introduced into the surfactant solution with a pipette, 1 ml at a time to form a gel-like surfactant mesophase. ($W_0 = [water]/[AOT] = 90$). The final surfactant : TMOS + isooctane : water system composition is 0.24 : 0.24 : 0.52. This mesophase was transferred into a 5 ml plastic syringe fitted with a needle of inner diameter 2.16 mm. The syringe was then loaded onto the Harvard Pump Apparatus, with the extrusion rate set at 2 ml min^{-1}. The gel-like mesophase was extruded in long strips onto the clean surface of a glass slide and left overnight for silica formation to proceed, as evidenced by a white, opaque presence the following day. The sample was then placed in a petri dish and soaked in ethanol to remove the surfactants. **Caution:** Care should be taken since fibrous silica, due to its small diameter, is a potential breathing hazard.

¶ SEM experiments were performed on a JSM-5410 SEM instrument operated at 20 kV. The silica sample was stuck onto an aluminium stub with adhesive tape. It was then coated with a thin layer of platinum by sputtering.

‖ TEM analysis was conducted on a JEOL 2011 TEM instrument operated at 120 kV. A formvar coated TEM grid was placed on top of the glass slide to allow the sample to settle atop the grid when carrying out extrusion. The grid was washed with ethanol prior to imaging.

1 D. W. Schaefer, *MRS Bull.*, 1994, **19**, 14.
2 I. A. Aksay, M. Trau, S. Manne, I. Honma, N. Yao, L. Zhou, P. Fenter, P. M. Eisenberger and S. M. Grunter, *Science*, 1996, **273**, 892; N. K. Raman, M. T. Anderson and C. J. Brinker, *Chem. Mater.*, 1996, **8**, 1682; T. Sakamoto and C. Pac, *Tetrahedron Lett.*, 2000, **41**, 10009; B. Gates, Y. Yin and Y. Xia, *Chem. Mater.*, 1999, **11**, 2827; P. T. Tanev and T. J. Pinnavaia, *Chem. Mater.*, 1996, **8**, 2068; S. Li, G. C. Irvin, B. Simmons, S. Rachakonda, P. Ramannair, S. Banerjee, V. T. John, G. L. McPherson, W. Zhou and A. Bose, *Colloids Surf., A*, 2000, **174**, 275; M. H. Lim, C. F. Blanford and A. Stein, *Chem. Mater.*, 1998, **10**, 467; S. L. Burkett, S. D. Sims and S. Mann, *Chem. Commun.*, 1996, **11**, 1367; G. Montalvo, M. Valiente and E. Rodenas, *Langmuir*, 1996, **12**, 5202.
3 C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. S. Vartuli and J. S. Beck, *Nature*, 1992, **359**, 710; J. S. Beck, J. C. Vartuli, W. J. Roth, M. E. Leonowicz, C. T. Kresge, K. D. Schmitt, C. T. W. Chu, D. H. Olson, E. W. Sheppard, S. B. McCullen, J. B. Higgins and J. L. Schlenker, *J. Am. Chem. Soc.*, 1992, **114**, 10834; C. G. Göltner, S. Henke, M. C. Weissenberger and M. Antonietti, *Angew. Chem., Int. Ed.*, 1998, **37**, 613.
4 Q. Lu, F. Gao, S. Komarneni and T. E. Mallouk, *J. Am. Chem. Soc.*, 2004, **126**, 8650; A. Sayari, B.-H. Han and Y. Yang, *J. Am. Chem. Soc.*, 2004, **126**, 14348; H. Zhang, J. Sun, D. Ma, X. Bao, A. Klein-Hoffmann, G. Weinberg, D. Su and R. Schlogl, *J. Am. Chem. Soc.*, 2004, **126**, 7440; C.-M. Yang, B. Zibrowius, W. Schmidt and F. Schuth, *Chem. Mater.*, 2003, **15**, 3739.
5 M. Trau, N. Yao, E. Kim, Y. Xia, G. M. Whitesides and I. A. Aksay, *Nature*, 1997, **390**, 674; H. W. Hillhouse, T. Okubo, J. W. van Egmond and M. Tsapatsis, *Chem. Mater.*, 1997, **9**, 1505; W. J. Kim and S. M. Yang, *Langmuir*, 2000, **16**, 4761; W. J. Kim and S. M. Yang, *Chem. Mater.*, 2000, **12**, 3227; N. A. Melosh, P. Davidson, P. Feng, D. J. Pine and B. F. Chmelka, *J. Am. Chem. Soc.*, 2001, **123**, 1240.
6 H. Verduin, B. J. de Gans and J. K. G. Dhont, *Langmuir*, 1996, **12**, 2947; P. Varadan and M. J. Solomon, *Langmuir*, 2001, **17**, 2918; S. Muller, C. Borschig, W. Gronski and C. Schmidt, *Langmuir*, 1999, **15**, 7558; W. J. Kim and S. M. Yang, *Langmuir*, 2000, **16**, 6084; H. J. M. Hanley, C. D. Muzny, B. D. Butler, G. C. Straty, J. Bartlett and E. Drabarek, *J. Phys.: Condens. Matter*, 1999, **11**, 1369; Y. Saimoto, T. Satoh and M. Konno, *J. Colloid Interface Sci.*, 1999, **219**, 135; G. Schmidt, S. Müller, P. Lindner, C. Schmidt and W. Richtering, *J. Phys. Chem. B*, 1998, **102**, 507; K. J. Edler, P. A. Reynolds, A. S. Brown, T. M. Slawecki and J. W. White, *J. Chem. Soc., Faraday Trans.*, 1998, **94**, 1287.
7 L. Liu, M. Singh, V. John, G. L. McPherson, J. He, V. Agarwal and A. Bose, *J. Am. Chem. Soc.*, 2004, **126**, 2276–2277.
8 B. Simmons, G. C. Irvin, V. T. John, G. L. McPherson, N. Balsara, A. Vivek and A. Bose, *Langmuir*, 2002, **18**, 624.
9 G. Schmidt, W. Richtering, P. Lindner and P. Alexandrids, *Macromolecules*, 1998, **31**, 2293.
10 M. P. Pileni, *Nat. Mater.*, 2003, **2**, 145.