

Shear-Induced Alignment and Nanowire Silica Synthesis in a Rigid Crystalline Surfactant Mesophase

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The use of self-assembly to direct materials synthesis is an area of tremendous interest. It is well known that such processes can generate nanoscale structures. Bioceramic architectures are typically synthesized in confined media through processes in which template structures provide form and function. The translation of such principles of self-assembly and templated materials synthesis is rapidly finding application in the generation of porous ceramics with applications to catalysis, membrane fabrication, and sensor development.¹ The discovery of the M41S family of mesoporous silica in 1992 has led to tremendous interest in understanding the role of surfactants in promoting the formation of such ordered materials.²

Achieving high fidelity between the actual ceramic morphology and surfactant template microstructures remains a significant challenge in materials synthesis.³ While porous solids are easily obtained, there often is little relation between the ceramic structure and the original surfactant microstructure. Thermal fluctuations in liquid systems where small amphiphilic self-assembly results from relatively weak noncovalent interactions may be a simple explanation why template fidelity is lost in the final ceramic structure.

We show here that sufficiently rigid crystalline surfactant mesophases can be shear-aligned to create templates for materials synthesis and that the structure of the template is reflected in the morphology of the ceramic. We utilized a system comprised of the anionic surfactant AOT (bis (2-ethylhexyl) sodium sulfosuccinate) mixed with the bisurfactant, zwitterionic lecithin (α -phosphatidylcholine), in the molar ratio 2:1. When this two-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 gellike state with crystalline order illustrated through small-angle neutron scattering measurements.⁴ For example, over the composition range surfactant/isooctane/water 0.27/0.27/0.46 to 0.21/0.21/0.57 (in weight fractions), the surfactant mesophase has columnar hexagonal symmetry, with water cylindrical columns arranged in hexagonal geometry (the H_{II} phase).⁴ The system is optically clear, has a high viscosity up to 10^6 Pa·s at low shear rates, and has a relatively high rigidity as characterized by a storage modulus (G') of 10^4 Pa.

Figure 1 illustrates small-angle neutron scattering patterns for the surfactant mesophase where D_2O has been used instead of water to provide sufficient contrast. It shows scattering profiles obtained in a Couette cell, providing information in both the flow–vorticity (radial) and the flow gradient–vorticity (tangential) planes. The radial and tangential scattering profiles of the samples prior to application of shear show typical powder diffraction patterns, and no significant differences are observed. The scattering profiles at

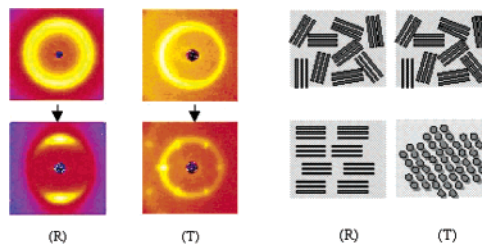


Figure 1. Scattering profiles of the template in radial (R) and tangential (T) modes. At the top are the profiles prior to shear, and at the bottom are profiles after application of shear when alignment has set in. On the right are idealized representations of the alignment.

the bottom of Figure 1 illustrate the dramatic alignment of the system after it is fully subjected to shear. The convergence to a two-spot pattern in the radial profile and a six-spot pattern in the tangential profile is characteristic of aligned columnar hexagonal structures.⁵ Similar shear alignment of liquid crystalline systems has been reported extensively in the literature.⁶

The following characteristics encouraged us to conduct materials synthesis in these systems. (1) Significant shear alignment is obtained with relatively low shear rates, typically less than 10 s⁻¹. (2) In such a relatively rigid system, once shear has been employed, the alignment persists for extended periods approaching a week.⁷ The retention of alignment for extended periods indicates that materials synthesis does not have to take place during shear. A two-step procedure can be used to first shear-align the mesophase and then conduct synthesis under essentially quiescent conditions. In this paper, we exploit these ideas to form highly aligned silica structures.

Accordingly, we have used the surfactant mesophase as a template for silica synthesis by doping the silica precursor tetramethoxysilane (TMOS) with the nonpolar hydrocarbon, forming the surfactant mesophase, subjecting the system to shear, and then allowing silica synthesis to proceed for a day in the presheared system.⁸ TMOS is fully soluble in isooctane, but silica precipitation through hydrolysis and condensation occurs within the aqueous columns of the reverse hexagonal microstructure. Scanning electron micrographs of silica synthesized in the unsheared system and the sheared mesophase are shown in Figure 2, illustrating some directionality to the ceramic synthesized in the sheared system. The transmission electron micrographs (TEM), however, provide much more information and show a dramatic alignment effect of applying shear prior to materials synthesis (Figure 3). In the unsheared system, entangled stringlike structures are observed. Upon shearing the system, the silica strings show considerable alignment, reflecting the fact that nucleation and growth occur in the water channels of an aligned columnar reverse hexagonal microstructure. Cross-sectional TEM micrographs show similar silica nanowire structures.

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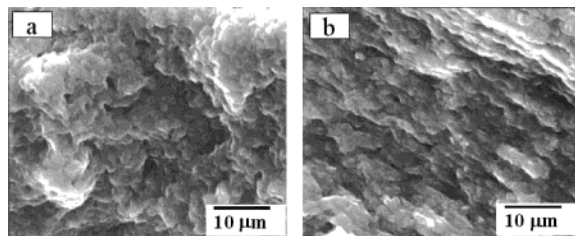


Figure 2. SEM images of (a) silica synthesized in the unsheared mesophase and (b) silica synthesized in the sheared mesophase.

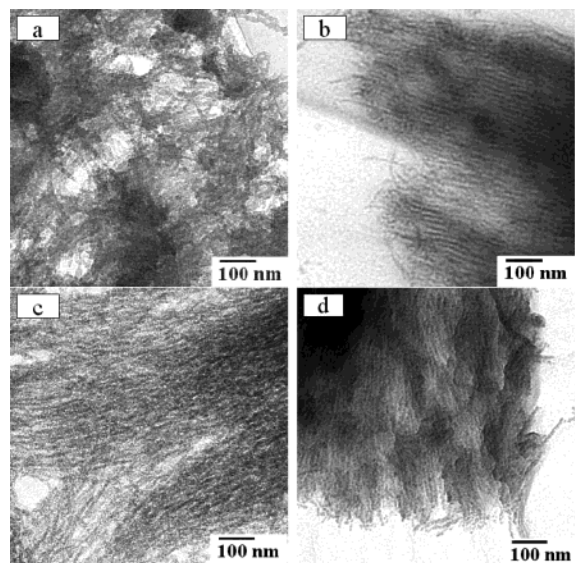


Figure 3. Transmission electron micrographs of silica synthesized in (a) an unsheared mesophase and (b), (c), and (d) separate examples of the shear aligned mesophase.

Nitrogen absorption–desorption experiments showed the synthesized silica has a BET surface area of 350–450 m²/g. ²⁹Si solid-state NMR indicates that this highly porous silica consists of a high degree of SiO₄ cross-linking. Characteristic water channel *d* spacing for the surfactant template is of the order 10–20 nm as measured by SANS.⁴ There is a very approximate reflection of this spacing between the silica nanowires. These silica structures are not altered by solvent extraction of the surfactant or calcinations.

Shear-aligned silica nanowires obtained through this route are not highly ordered as the M41S materials are. The morphology is to some degree a reverse of the MCM-41 and the recent HOM-3 type mesoporous materials.⁹ In these fascinating materials,^{9,10} the pores reflect the columns of hexagonal geometry, while silica walls represent the inter-column regions. Synthesis in the reverse hexagonal AOT+lecithin mesophase results in the stringlike silica nanowires precipitated in the microaqueous columns, with pores reflecting the region between the columns. The novelty of this approach is that ceramic microstructure can be dramatically modified by the appropriate pre-application of shear. Flow-induced microstructures in the sol–gel synthesis of mesoporous silica have been reported in the literature, as variations of the MCM-41 synthesis conducted under continuous shear.¹¹ The long-range alignment in the silica nanowire structures observed in this work is a consequence of the retention of mesophase alignment after shear application.

The observations reported here have significant implications in the control of ceramic morphology from nonaligned to aligned morphologies. The facile alignment of the mesophase and the retention of alignment allow decoupling of materials synthesis from shear application. Typical polymer processing techniques can be

applied to the mesophase (e.g., extrusion), following which materials synthesis can be allowed to proceed to prepare extended nanowire structures. Because the ceramic synthesis is done in a surfactant mesophase containing both aqueous and organic microphases, it is possible to couple ceramic synthesis with polymer synthesis to create aligned structures of polymer-ceramic nanocomposites. Additionally, it is possible to synthesize nanoparticles in an AOT water-in-oil microemulsion,³ translate the system with the addition of lecithin and water to the gellike mesophase, and conduct ceramic synthesis in the presheared system to prepare aligned functional ceramic structures with incorporated nanoparticles. These are objectives of ongoing work.

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Supporting Information Available: Details of SANS and ³¹P NMR measurements, nitrogen BET adsorption–desorption isotherms, ²⁹Si NMR spectrum, and cross-section TEM micrographs of the synthesized silica (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (7) Long-term retention of alignment was monitored by ³¹P NMR, which shows a characteristic high field peak with a low field shoulder in aligned hexagonal phases. The correlations between NMR and SANS in these systems will be reported separately.
- (8) (a) Silica was synthesized at room temperature in an AOT/lecithin bisurfactant system with a nonpolar hydrocarbon such as isooctane as solvent. TMOS is fully soluble in the nonpolar solvent and allows us to dope the system with the silica precursor. In a typical preparation, TMOS was mixed with isooctane at a volume ratio of 1:4. AOT and the second surfactant, lecithin, were then added to the TMOS solution to a concentration 0.8 M AOT and 0.4 M lecithin and were dissolved by sonication and vortex stirring. A transparent light yellow color microemulsion was obtained. Finally, water of pH 8.5 was added to the AOT/lecithin solution dropwise until the clear gellike rigid mesophase formed. A system composition total surfactant/TMOS+isooctane/water of 0.24/0.24/0.52, clearly in the reverse hexagonal region, was used in silica synthesis. (b) We used coaxial NMR tubes to carry out the shear synthesis. The sample was first transferred to a 5 mm glass tube immediately after gel formation, and then an inner tube with a diameter of 2 mm was inserted into the sample. The inner tube was attached to the spindle of a Bohlin rheometer, and the sample was sheared at 5.38 s⁻¹ for 30 min, although shorter shear times and higher shear (up to 100 s⁻¹) are equally effective. After the system was subjected to shear, it was allowed to sit for a day to complete silica synthesis. The optically clear system becomes white after the formation of silica.
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