

Morphological control of surfactant-templated metal oxide films

C. Jeffrey Brinker^{1,2*} and Darren R. Dunphy¹

¹Sandia National Laboratories
Advanced Materials Laboratory
1001 University Blvd SE Suite 100
Albuquerque, NM 87107 U.S.A.

²The University of New Mexico/NSF Center for Micro-Engineered Materials
Department of Chemical and Nuclear Engineering
Albuquerque, NM 87131 U.S.A.

*contact e-mail: cjbrink@sandia.gov

For submission to Current Opinion in Colloid and Interface Science

We discuss here recent developments of note in the synthesis of self-assembled surfactant-mesophase templated films using a sol-gel route. First, the formation of metal oxide (non-silica) films using this method has become a highly active area of research, with careful studies unlocking the key processing parameters needed to successfully synthesize these materials. Also, the control of pore orientation in these self-assembled materials using confinement or surface modification has also become extremely important. Finally, we identify research directions we believe will yield important new advances in this area of materials science/chemistry.

Introduction

Mesoporous and mesostructured materials formed by the organization of inorganic precursors around a surfactant mesophase template [1••,2,3] are a prominent example of “bottom-up” fabrication where self-assembly is employed to precisely position hydrophobic and hydrophilic precursors into often elaborate nanoscale architectures. Although research into these materials has been largely focused on powdered materials synthesized using a hydrothermal route, especially for use in catalysis [4••], interest in thin films of these materials for applications such as active control of mass transport [5••], low k dielectrics [6•], or laser devices [7••,8] has grown considerably in recent years. Initially, thin mesostructured films were deposited using heterogeneous nucleation under hydrothermal conditions or at the liquid-vapor interface [9]; however, evaporation-induced self assembly (EISA) has proven to be more versatile [1••,3,10]. In EISA, a homogeneous solution of a soluble oxide precursor and surfactant (or block copolymer), prepared in a mixed alcohol/water solvent system with an initial surfactant concentration less than that where bulk mesophases appear, undergoes preferential evaporation of alcohol during film deposition, thus concentrating the depositing film in water, surfactant and inorganic species. The progressively increasing surfactant concentration drives the organization of the surfactant into lyotropic liquid crystalline mesophases; common network morphologies include lamellar, 2D or 3D hexagonal, cubic (both bicontinuous and micellar phases) [3], as well as modifications of these structures [11•]. Subsequent inorganic condensation freezes in the final nanoscale morphology [1••]; the surfactant template can then be removed by solvent washing, calcination, or UV exposure [12••,13•] to obtain a mesoporous (as opposed to mesostructured) film. Significantly, the EISA process has also been extended to the formation of well-ordered and robust gold nanocrystal/silica composite arrays [14••].

Importantly, EISA is not limited to the construction of purely inorganic structures; through the controlled partitioning of organic components within the domain bounded by the hydrophobic interior of the surfactant mesophase and the polar environment of the inorganic walls, hybrid organic-inorganic composites can be synthesized with the organic component localized inside the surfactant phase, at the interface between the surfactant and inorganic phases (i.e. at the pore wall), or inside the inorganic walls of the resulting material [5••,15••]. Inclusion of one or more linker groups (for example, alkoxysilanes) on the organic component covalently melds the two materials into a microscopically-homogeneous hybrid. Synthesis of functional mesoporous hybrid films has been a fertile area of research; the reader is referred to a recent review for an extensive overview of this field [16••].

Although a significant body of work has been generated relating to the functional characterization and application of self-assembled structures formed via EISA [5••,15••], important issues remain with respect to the control of film morphology that will ultimately limit the practical application of these materials. For example, control of the interconnectivity between pores in films with 3D mesostructures is critical for the proper regulation of mass transport through the films or stability of low-dielectric materials [6•,17••]; the specific geometry of these pores could have implications in the arrangement of organic modifiers.

Two structurally-significant issues that have been addressed of late are synthesis of films using metal oxides other than silica, and the control of pore orientation and morphology using confinement and chemical modification of the substrate. Here we concentrate on recent developments in these areas, followed by a brief discussion of future prospects in the morphological control of these materials.

Nanostructured and nanoporous metal oxide films

Because of material characteristics such as high refractive index [7••,18•] and semiconductivity [19••,20•], surfactant-templated nanoporous or nanostructured films of materials other than silica have been of increasing interest to the research community. Relative to materials of pure silica, however, control of nanoscale morphology is generally more difficult; increased metal oxide precursor reactivity hinders control of hydrolysis reaction kinetics, while a diminished tendency to form extended amorphous networks yields films with poor structural integrity, leading to pore collapse upon removal of surfactant and/or subsequent crystallization. Typical synthesis conditions for these materials use a highly acidic sol to retard condensation during self-assembly. Following coating, careful atmospheric and thermal treatments are used to promote network condensation while attempting to maintain structural order [21••].

In the synthesis of nanostructured SiO_2 and metal oxide films using the EISA process, barring non-equilibrium conditions [22] the final morphology is determined by the volume ratio of surfactant template to the inorganic phase after solvent evaporation [23]; this volume ratio must include water present in the film established by equilibration with atmospheric humidity, and adjustable via atmospheric control after coating during the so-called modifiable steady state (MSS) [1••]. For silica, facile extended network condensation rapidly “freezes” in the final film morphology. In metal oxide films other than silica, however, suppressed network condensation greatly extends the MSS; indeed, it now appears that the critical step in obtaining well-ordered metal oxide films is aging the as-deposited film in a humidity- and temperature-controlled environment [21••,24,25••]. Crepaldi et al. examined the mechanism of film formation of mesostructured TiO_2 , and found that the disorder-to-order transition (and thus the quality of the final mesostructure) that occurred after film formation was more sensitive to equilibrium with atmospheric humidity than to the original amount of water added in the precursor sol [21••]. This same group also reported the synthesis of mixed yttria-zirconia and ceria-zirconia films with either a 2D hexagonal or 3D cubic morphology [24], again finding that the quality (and even identity) of the final mesostructure was controlled by humidity. More recently, Urade and Hillhouse synthesized nanoporous films of SnO_2 with a 3D orthorhombic structure (Figure 1)[25••]. As deposited, these films did not exhibit any long-range ordering as indicated by the absence of peaks in the x-ray diffraction pattern. However, aging in a controlled humidity environment (here at elevated temperatures), even after complete film drying, initiated the transition to the ordered morphology. It was pointed out that self-assembly of this system is not by an EISA process as structure appears only after subsequent processing following film deposition and not as a consequence of solvent evaporation during or after dip-coating. Overall, whatever the mechanistic details, understanding the importance of post-

deposition processing should allow the fabrication of other, difficult to synthesize but technologically important, nanostructured or nanoporous thin-film materials.

Other groups continue to develop new strategies to produce materials with difficult-to-synthesize compositions. One notable approach is the use of new block copolymers [26•, 27•, 28•] to template films from materials such as titania [26•,27•], ceria, zirconia, and mixed ceria-zirconia materials [28•]. Relative to other block copolymers such as the Pluronic family of surfactants, these polymers exhibit higher hydrophobic contrast, increasing the “robustness” of the self-assembly process, and are significantly more thermally stable, maintaining mesoscale ordering during the onset of wall crystallization during heat treatment. Also, large pore size (ca. 10-15 nm) and wall thickness stabilizes the mesostructure towards wall crystallization, inhibiting material collapse.

Stucky et al. have been exploring the use of high refractive index dye-doped metal oxide films for solid-state laser fabrication. Materials formed using standard alkoxide routes are unsuitable as the thermal processing needed to form stable inorganic networks is not compatible with fragile organic laser dyes. Also, the mechanical and optical properties of thick films (ca. greater than 1 μm) synthesized using alkoxide precursors are generally unsatisfactory for the construction of optical devices. To improve these characteristics, trifluoroacetic acid (TFA) has been utilized to modify the titania network in hybrid mesostructured waveguide layers [7••,18•]; the effective refractive index of these materials is high enough to demonstrate amplified spontaneous emission even on glass substrates (previous demonstrations of this effect utilized silica-based hybrid lasing layers deposited onto low-index porous buffer layers [8]).

Effect of confinement on material morphology

As is evident from the orientation of the thin film mesophases with respect to the bounding solid and vapor interfaces, the presence of these interfaces influences mesophase development. They serve as nucleating surfaces from which incipient mesophases grow toward the film interior [29]. A fundamental question is how nucleation and orientation can be controlled via chemical modification of these interfaces and/or dimensional confinement of the self-assembly process. The simplest case of mesophase alignment has been achieved by topological substrate modification (for example, using a “rubbed” polymer film [30], or more recently, a photo-alignable polymer layer to pattern the in-plane orientation of a mesostructured film grown using heterogeneous nucleation [31]) as well as electro-osmotic flow through a microfluidic mold [32]. These strategies induce in-plane alignment of 2D hexagonal mesophases over macroscopic length scales, in contrast to pore orientation parallel to the substrate but without any in-plane alignment (producing “fingerprint” patterns when imaged with electron microscopy in a plan-view [23]). However, alignment of the same nanostructures in a direction perpendicular to the substrate, a significantly more interesting architecture from an applications perspective, has proven to be more difficult.

Recent research has demonstrated such alignment can be induced by using confinement of the self-assembly process in 1D channels and/or chemical modification of the substrate. For example, by using a porous alumina membrane with transverse one-dimensional channels as a host in which to confine the self-assembly process, 2D

hexagonal mesophases have been aligned perpendicular to the plane of the membrane surface [33•,34•]. While the effect of confinement in anodic alumina membranes on the alignment of surfactant/silica self-assembly was first noted in 2003 [35], true 1D alignment was not reported until the following year in two nearly-simultaneous papers. Yamaguchi *et al.* utilized cetyltrimethylammonium bromide to fabricate an aligned surfactant/silica composite inside the pores of an alumina membrane, as seen in the TEM micrographs of Figure 2 [34•]. Although solution-phase permeation measurements demonstrated that the presence of the composite nanostructure introduced size selectivity to mass transport through the membrane, lack of a suitable (non-nanostructured silica) control experiment prevents any definitive conclusions about structure/property relationships in this system. Lu *et al.* also reported the 1D alignment of a silica mesophase inside an alumina membrane, but used Pluronic P123 as the surfactant template (giving pores of ca. 6 nm in diameter) and created a true porous material by pyrolysis of the surfactant template [33•].

In these examples of pore alignment inside a 1D template, the channel diameter of the anodic membrane (about 200 nm) is much greater than the repeat spacing of the self-assembled structure (ca. 3-10 nm). As the size of the confining space approaches that of the surfactant micelle, however, a variety of new nanostructure morphologies appear [36,37••], as can be seen in Figure 3. In a study where Pluronic P123/silica mesophases were self-assembled inside anodic alumina membranes with pore diameters systematically varied between < 20 nm to 80 nm, a variety of architectures ranging from systems of coiled channels to discrete cage-like structures were observed as the membrane pore size was decreased [37••]. The coiled channels were found in either a “stacked doughnut” arrangement, or as single- or double-helices that exhibited chirality. The use of these confined mesostructures as templates for the electrochemical deposition of several materials (Ag, Ni, Cu₂O) was demonstrated [38•].

An alternate strategy for the perpendicular alignment of mesopores is based upon simulations of block copolymer and surfactant self-assembly at/between functionalized surfaces that have been chemically modified to equalize the interaction strength between the surface and each block or component of the polymer or surfactant; the equal interaction of both hydrophilic and hydrophobic components of a cylindrical mesophase with the underlying surface induces an orthogonal alignment of both lamellar and hexagonally close-packed mesophases [39]. These results have been confirmed experimentally in systems of large block copolymers, but only recently with surfactant-templated silica. Koganti and Rankin aged 2D hexagonal films (templated with Pluronic P123) between glass slides modified with cross-linked P123 or a random ethylene oxide/propylene oxide copolymer [40•]; although x-ray diffraction and TEM data were consistent with a final structure of orthogonally-oriented pores, confirmation of this structure will require investigations with techniques such as grazing incidence x-ray diffraction (GISAXS) that can detect out-of-plane ordering in thin film systems [1••,11•].

Future Perspectives

A critical direction for research into the morphological control of self-assembled inorganic thin films is that of integration into functional structures at both nano- and

macroscopic length scales. For the former, the ability of the EISA process to direct the structural distribution of active organic components in the final self-assembled material has opened up potential applications such as hybrid inorganic/organic solar cell materials or active molecular valves [5••]. Furthermore, after template removal the ordered pore network of the inorganic material can serve as a precisely-defined nanostructured host for the organization of other materials such as metal wires [38•] or semiconducting organic polymers [41]. To properly establish structure/property relationships in these materials, however, it is important to better understand the nanoscale morphology. GISAXS and SAXS studies have proven to be invaluable in this regard; the use of software to model the observed spot patterns has increased the sophistication of mesophase identification [11•,42]. However, these studies only yield the symmetry of the resulting architecture, and not the precise 3D morphology of the mesostructure. Such data has been obtained for powdered materials using TEM studies [43]; future developments in characterization techniques will hopefully allow the same for thin-film materials, although films are often problematic in that drying and calcination normally result in 1D shrinkage normal to the substrate, lowering the symmetry of the film (e.g. cubic to tetragonal or orthorhombic structures [11•]).

Less attention has been given recently to the physical and chemical-property patterning of self-assembled oxide mesophases into macroscale constructs; by analogy to biological systems, structure and function must be defined over many length scales, and with lower symmetry than is typical of materials formed through a self-assembly process (this property being critical for technologically-important function such as ion pumping or charge separation). Macroscopic patterning of these materials has been demonstrated previously using micromolding [8], differential wetting, ink jet printing, dip pen lithography [44], and even light [45]. Although the state-of-the-art in non-traditional patterning continues to evolve [46••], the last few years have seen few significant developments in patterning of thin-film inorganic mesophases. In one approach, low-temperature UV-induced surfactant removal through a combination of direct (deep) UV exposure and concurrent ozone/activated oxygen production [12••,13•] through a mask enables spatially defined surfactant removal; differential solubility of exposed and unexposed regions in NaOH allows for easy removal of unwanted material. Also, film deposition into a resist layer patterned by electron-beam lithography followed by mechanical polishing and calcination was utilized to create arrays of mesoporous SiO₂ and TiO₂ with dimensions between 250 nm to 50 μm [47•].

The combination of self-assembly with concurrent (energy dissipating) directed-assembly is a potentially powerful route to organization of mesostructured or mesoporous thin film materials on more than one level. For example, external fields have been investigated as a means of obtaining films with mesophases oriented orthogonally to the substrate [48,49]; this strategy has proven to be difficult, however, presumably a result of the relative rate of silica condensation being greater than that of mesophase alignment. For example, a recent report where an electric field was applied across a film as it dried yielded an irregular elliptical pore structure, with no evidence of mesophase alignment parallel to the electric field [48]. In another report, application of a magnetic field was more successful, although full alignment was not achieved; 2D hexagonal domains were found with angles relative to the surface normal of 45-60° in addition to true perpendicular alignment [49]. Future attempts at mesophase alignment using external

fields may benefit from non-silica systems such as TiO_2 or ZrO_2 , where reduced condensation kinetics should enable alignment of the mesophase. Finally, physical gradients in pH, temperature, or convection may yield useful routes to simultaneous organization of self-assembled morphology at multiple length scales; this strategy has been demonstrated previously by the patterned deposition of nanoscopically-structured materials such as zeolite nanocrystals using Bénard-Marangoni convection [50•].

Acknowledgments

This material is based upon work supported by, or in part by, the U.S. Army Research Laboratory and the U.S. Army Research Office under contract/grant number DAAD19-03-1-0227. Support was also provided by the Air Force Office of Scientific Research under grant SC GG10306-113743 and the DOE Office of Basic Energy Sciences. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under Contract DE-AC04-94AL85000.

References

- 1. Grosso D, Cagnol F, De A A Solar-Illia G, Crepaldi H, Amenitsch H, Brunet-Bruneau A, Bourgeois A, Sanchez C: **Fundamentals of mesostructuring through evaporation-induced self-assembly**. *Adv Func Mater* 2004, **14**:309-322.
An excellent overview of the mechanism of evaporation-induced self assembly, including both silica and non-silicate systems.
2. Kresge C, Leonowicz M, Roth W, Vartuli J, Beck J: **Ordered mesoporous molecular sieves synthesized by a liquid-crystal template mechanism**. *Nature* 1992, **359**:710-712.
3. Lu Y, Ganguli R, Drewien C, Anderson M, Brinker C, Gong W, Guo Y, Soyez H, Dunn B, Huang M, Zink, J: **Continuous formation of supported cubic and hexagonal mesoporous films by sol gel dip-coating**. *Nature* 1997, **389**:364-368
- 4. Taguchi A, Schüth F: **Ordered mesoporous materials in catalysis**. *Micropor Mesopor Mat* 2005, **77**:1-45.
This is a comprehensive, up-to-date review of the application of mesoporous materials to the field of catalysis with nearly 450 references.
- 5. Liu N, Dunphy D, Atanassov P, Bunge S, Chen Z, Lopez G, Boyle T, Brinker C: **Photoregulation of mass transport through a photoresponsive azobenzene-modified nanoporous membrane**. *Nano Letters* 2004, **4**:551-554.
Light-activated isomerization of an azobenzene derivative covalently bonded onto the pore surface of a mesoporous silica film was used to modulate the effective pore size of the material; this was demonstrated by monitoring the electrolysis of solution-phase ferrocenedimethanol at the underlying ITO electrode at constant potential.
- 6. Yu K, Smarsly B, Brinker CJ: **Self-assembly and characterization of mesostructured silica films with a 3D arrangement of isolated spherical mesopores**. *Advanced Functional Materials* 2003, **13**:47-52.
Polystyrene-*block*-poly(ethylene oxide) was used to template films using methyltriethoxysilane as the inorganic precursor. The structure of the film consisted of (cubic) close-packed spheres; GISAXS data demonstrated there was no observable microporosity to interconnect these voids.
- 7. Bartl M, Boettcher S, Hu E, Stucky G: **Dye-actived hybrid organic/inorganic mesostructured titania waveguides**. *J Am Chem Soc* 2004, **126**:10826-10827.
A trifluoroacetic acid modified titania precursor was utilized to produce a nanostructured surfactant/dye/inorganic hybrid waveguide. Addition of the trifluoroacetic acid improved the optical and mechanical properties of the waveguide, while also diminishing the need for thermal treatment of the waveguide structure, an important consideration for waveguide structures that include thermally-sensitive laser dyes.

8. Peidong Y, Winsberger G, Huang H, Cordero S, McGehee M, Scott B, Deng T, Whitesides G, Chmelka B, Buratto S, Stucky G.: **Mirrorless lasing from mesostructured waveguides patterned by soft lithography.** *Science* 2000, **287**:465-467.

9. Yang H, Kuperman A, Coombs N, Mamiche-Afara S, Ozin G: **Synthesis of oriented films of mesoporous silica on mica.** *Nature* 1996, **379**:703-705.

10. Lu Y, Fan H, Stump A, Ward T, Rieker T, Brinker C: **Aerosol-assisted self-assembly of mesostructured spherical nanoparticles.** *Nature* 1999, **398**:223-226.

•11. Tate M, Eggiman B, Kowalski J, Hillhouse H: **Order and orientation control of mesoporous silica films on conducting gold substrates formed by dip-coating and self-assembly: a grazing angle of incidence small-angle x-ray scattering and field emission scanning electron microscopy study.** *Langmuir* 2005, in press.

A systematic study of the effect of surfactant/silica ratio and processing humidity on the structure and orientation of surfactant-templated silica films. Such data will be important in understanding the functional properties of thin-film mesoporous materials. GISAXS data was analyzed with the aid of *Nanocell*, a versatile program written by the Hillhouse research group to simulate GISAXS and SAXS spot patterns of nanostructured materials.

••12. Dattelbaum A, Amweg M, Ecke L, Yee C, Shreve A, Parikh A: **Photochemical pattern transfer and enhancement of thin film silica mesophases.** *Nano Letters* 2003, **3**:719-722.

A simple route to patterned thin film mesoporous silica whereby deep UV exposure through an optical mask selectively removes surfactant and increases the degree of silica condensation in exposed areas; the resulting differential silica solubility in basic solution between exposed and unexposed regions is then used to etch away unwanted material.

•13. Dattelbaum A, Amweg M, Ruiz J, Ecke L, Shreve A, Parikh A: **Surfactant removal and silica condensation during the photochemical calcination of thin film silica mesophases.** *J Phys Chem B* 2005, **109**:14551-14556.

This paper is a mechanistic study of surfactant removal from mesostructured silica films by UV exposure, using FT-IR to monitor the chemical composition of films as a function of exposure time. A stepwise model for surfactant removal is proposed where partially oxidized intermediates are formed; these intermediates are then broken down into small volatile compounds to produce a porous material.

••14. Fan H, Yang K, Boye D, Sigmon T, Malloy K, Xu H, Lopez G, Brinker C: **Self-assembly of ordered, robust, three-dimensional gold nanocrystal/silica arrays.** *Science* 2004, **304**:567-571.

The synthesis of a highly-ordered surfactant-stabilized gold nanocrystal/silica composite mesophase through an EISA process is described. Electrical measurements show that this material exhibits unique solid-state behavior, a consequence of the complete electrical isolation of the gold nanocrystals within the silica matrix.

••15. Minoofar P, Dunn B, Zink J: **Multiply doped nanostructured silicate sol-gel thin films: spatial segregation of dopants, energy transfer, and distance measurement.** *J Am Chem Soc* 2005, **127**:2656-2665.

Fluorescence energy transfer between a rhodamine dye and a luminescent lanthanide complex partitioned, respectively, into the hydrophobic core of the surfactant phase and the interior of the hydrophilic inorganic walls during EISA was examined using fluorescence energy transfer measurements; quantitative analysis of the data using Förster theory yielded an average distance between the two dopants and demonstrated the power of this technique for the structural characterization of self-assembled materials.

••16. Nicole L, Boissière C, Grosso D, Quach A, Sanchez C: **Mesostructured hybrid organic-inorganic thin films.** *J Mater Chem* 2005, **15**:3598-3617.

Another in-depth review, this paper covers the wide range of organic modification that has been incorporated into surfactant-templated films of both silica and other metal oxides.

••17. Torquato S, Donev A, Evans A, Brinker C: **Manufacturable extremal low-dielectric, high-stiffness porous materials.** *J Appl Phys* 2005, **97**:124103-124105.

An elegant report where an optimized structure, selected for both dielectric constant and material stiffness, is identified through theoretical analysis and then fabricated using a self-assembly route.

•18. Boettcher S, Bartl M, Hu J, Stucky G: **Structural analysis of hybrid titania-based mesostructured composites.** *J Am Chem Soc* 2005, **127**:9721-9730.

A range of analytical techniques were utilized to obtain a complete picture of the physical and chemical structure of mesostructured trifluoroacetate-modified titania films templated with Pluronic block copolymers. Significantly, NMR was used to characterize the environment around the poly(ethylene oxide) and poly(propylene oxide) regions of the Pluronic template as well as the interface between these polymer blocks and the modified-titania walls.

••19. Frindell K, Tang J, Harreld J, Stucky G: **Enhanced mesostructural order and changes to optical and electrochemical properties induced by the addition of cerium(III) to mesoporous titania thin films.** *Chem Mater* 2004, **16**:3524-3532.

Addition of cerium to mesoporous titania thin films during the film synthesis results in impeded crystallization of the titania walls and increased density of electronic surface states. Extensive electrochemical measurements show that photocurrent efficiency decreases with the addition of these surface states, but that the electrochromic response actually increases.

•20. Bartl M, Boettcher S, Frindell K, Stucky G: **3-D molecular assembly of function in titania-based composite material systems.** *Acc Chem Res* 2005, **38**:263-271.

This concise account describes how 3D organization of functional components within composite materials (formed, at least in part, by evaporation-induced self assembly) can induce cooperative functionality (as demonstrated by photoluminescence and photocurrent measurements).

••21. Crepaldi E, De A A Solar-Illia G, Grosso D, Cagnol F, Ribot F, Sanchez C: **Controlled formation of highly organized mesoporous titania thin films: from mesostructured hybrids to mesoporous nanoanatase TiO₂**. *J Am Chem Soc* 2003, **125**:9770-9786.

The synthesis of mesoporous titania films from preparation of the precursor sol to post-deposition treatment is examined in detail using a wide range of analytical methodologies.

22. Gibaud A, Grosso D, Smarsly B, Baptiste A, Bardeau J, Babonneau F, Doshi D, Chen Z, Brinker C, Sanchez C: **Evaporation-controlled self-assembly of silica surfactant mesophases**. *J Phys Chem B* 2003, **107**:6114.

23. Alberius P, Frindell K, Hayward R, Kramer E, Stucky G, Chmelka B: **General predictive syntheses of cubic, hexagonal, and lamellar silica and titania mesostructured thin films**. *Chem Mater* 2002, **14**:3284-3294.

24. Crepaldi E, De A A Solar-Illia G, Bouchara A, Grosso D, Durand D, Sanchez C: **Controlled formation of highly ordered cubic and hexagonal mesoporous nanocrystalline yttria-zirconia and ceria-zirconia thin films exhibiting high thermal stability**. *Angew Chem Int Ed* 2003, **42**:347-351.

••25. Urade V, Hillhouse H: **Synthesis of thermally stable highly ordered nanoporous tin oxide films with a 3D face-centered orthorhombic structure**. *J Phys Chem B* 2005, **109**:10538-10541.

Urade and Hillhouse report the first complete synthesis of ordered mesoporous SnO₂ films with a 3D mesostructure morphology, potentially a material with high technological importance. Key to this synthesis is the exposure of as-deposited (but poorly ordered) films to water vapor at elevated temperatures followed by careful thermal treatment to lock in the resulting structure.

26•. Groenewelt M, Brezesinski T, Schlaad H, Antonietti M, Groh P, Ivan B: **Polyisobutylene-*block*-poly(ethylene oxide) for robust templating of highly ordered mesoporous materials**. *Adv Mater* 2005, **17**:1158-1162.

27•. Smarsly B, Grosso D, Brezesinski T, Pinna N, Boissiere C, Antonietti M, Sanchez C: **Highly crystalline cubic mesoporous TiO₂ with 10-nm pore diameter made with a new block copolymer template**. *Chem Mater* 2004, **16**:2948-2952.

28•. Brezesinski T, Antonietti M, Groenewelt M, Pinna N, Smarsly B: **The generation of mesostructured crystalline CeO₂, ZrO₂ and CeO₂-ZrO₂ films using evaporation-induced self-assembly**. *New J Chem* 2005, **29**:237-242.

29. Doshi D, Gibaud A, Goletto V, Lu M, Gerung H, Ocko B, Han S, Brinker C: **Peering into the self-assembly of surfactant templated thin-film silica mesophases.** *J Amer Chem Soc* 2003, **125**:11646-11655.

30. Miyata H, Kuroda K: **Alignment of mesoporous silica on a glass substrate by a rubbing method.** *Chem Mater* 1999, **11**:1609-1614.

31. Fukumoto H, Nagano S, Kawatsuki N, Seki T: **Photo-orientation of mesoporous silica thin films on photocrosslinkable polymer films.** *Adv Mater* 2005, **17**:1035-1038.

32. Trau M, Yao N, Kim E, Xia Y, Whitesides G, Aksay I: **Microscopic patterning of oriented mesoscopic silica through guided growth.** *Nature* 1997, **390**:674-676.

•33. Lu Q, Gao F, Komarneni S, Mallouk T: **Ordered SBA-15 nanorod arrays inside a porous alumina membrane.** *J Am Chem Soc* 2004, **126**:8650-8651.

Pluronic P123-templated silica (so-called SBA-15) was deposited inside the pore channels of an anodic alumina membrane with an internal diameter of ca. 200 nm using heterogeneous nucleation. TEM and XRD analysis demonstrated that the pores of the SBA-15 material were oriented parallel to the alumina channel direction.

•34. Yamaguchi A, Uejo F, Yoda T, Uchida T, Tanamura Y, Yamashita T, Teramae N: **Self-assembly of a silica-surfactant nanocomposite in a porous alumina membrane.** *Nat Mater* 2004, **3**:337-341.

Hexagonally-ordered cetyltrimethylammonium bromide/silica mesophases were formed inside anodic alumina with the 1D nanostructure running along the long axis of the alumina pores. Permeation measurements showed that the presence of the mesostructured silica/surfactant composite induced a significant size selectivity to transport through the membrane, but the lack of a suitable (non-ordered) control prohibits the definitive attribution of this size selectivity to the structure of the material.

35. Yang Z, Niu Z, Cao X, Yang Z, Lu Y, Hu Z, Han C: **Template synthesis of uniform 1D mesostructured silica materials and their arrays in anodic alumina membranes.** *Angew Chem Int Ed* 2003, **42**:4201-4203.

36. Wang D, Kou R, Yang Z, He J, Yang Z, Lu Y: **Hierarchical mesoporous silica wires by confined assembly.** *Chem Comm* 2005:166-167.

••37. Wu Y, Cheng G, Katsov K, Sides S, Wang J, Tang J, Fredrickson G, Moskovits M, Stucky G: **Composite mesostructures by nano-confinement.** *Nat Mater* 2004, **3**:816-822.

Silica templated with Pluronic P123 was self-assembled in anodic alumina membranes with pore diameters from ca. 20 to 70 nm. A wide range of structures were formed, from spherical cages packed in the narrowest alumina channels, to triple-layered structures of stacked doughnuts. Helical structures were found to be chiral. Theoretical calculations using self-consistent field theory predicted the trend in structural evolution as the pore

diameter of the alumina membrane was varied, even if absolute predictions were not completely accurate.

•38. Wu Y, Livneh T, Zhang Y, Cheng G, Wang J, Tang J, Moskovits M, Stucky G: **Templated synthesis of highly ordered mesostructured nanowires and nanowire arrays.** *Nano Letters* 2004, **4**:2337-2342.

In an extension of the work from reference 37, metal (Ag, Ni, Cu₂O) nanowires were electrochemically grown inside the pores of mesoporous silica deposited within the 1D pores found in anodic alumina. Ag wires were tested as to their applicability as high surface-area substrates for surface enhanced Raman spectroscopy (SERS) studies.

39. Rankin S, Malanoski A, van Swol F: **Monte Carlo simulation of amphiphile self-assembly during dip coating.** *Mater Res Soc Symp Proc* 2001, **636**:121-126.

•40. Koganti V, Rankin S: **Synthesis of surfactant-templated silica films with orthogonally aligned hexagonal mesophase.** *J Phys Chem B* 2005, **109**:3279-3283.

The self-assembly of 2D hexagonally-ordered silica templated by the block copolymer Pluronic P123 between two chemically-modified surfaces designed to non-preferentially interact either block of the polymer template is shown to result in pores oriented perpendicular to the substrate surfaces. Although TEM and XRD data is consistent with this structure, definitive verification will require further analysis by techniques such as GISAXS.

41. Lu Y, Yang Y, Sellinger A, Lu M, Huang J, Fan H, Haddad R, Lopez G, Burns A, Sasaki D, et al.: **Self-assembly of mesoscopically ordered chromatic polydiacetylene/silica nanocomposites.** *Nature* 2001, **410**:913-917.

42. Falcaro P, Costacurta S, Mattei G, Amenitsch H, Marcelli A, Certelli Guidi M, Piccinini M, Nucara A, Malfatti L, Kidchob T, et al.: **Highly ordered "defect free" self-assembled hybrid films with a tetragonal mesostructure.** *J Am Chem Soc* 2004, **127**:3838-3846.

43. Sakamoto Y, Kaneda M, Terasaki O, Zhao D, Kim J, Stucky G, Shim H, Ryoo R: **Direct imaging of the pores and cages of three-dimensional mesoporous materials.** *Nature* 2000, **408**:449-453.

44. Fan H, Lu Y, Stump A, Reed S, Baer T, Schunk R, Perez-Luna V, Lopez G, Brinker C: **Rapid prototyping of patterned functional nanostructures.** *Nature* 2000, **405**:56-60.

45. Doshi D, Huesing N, Lu M, Fan H, Lu Y, Simmons-Potter K, Potter B, Hurd A, Brinker C: **Optically defined multifunctional patterning of photosensitive thin-film silica mesophases.** *Science* 2000, **290**:107-111.

••46. Gates B, Xu Q, Stewart M, Ryan D, Wilson C, Whitesides G: **New approaches to nanofabrication: molding, printing, and other techniques.** *Chem Rev* 2005, **105**:1171-1196.

This review serves as a useful, well-balanced overview of the state-of-the-art in nanofabrication technologies starting with conventional “top-down” patterning methods such as photolithography and ending with self-assembly. The concluding outlook is particularly insightful in describing the future prospects for these technologies.

•47. Wu C, Aoki T, Kuwabara M: **Electron-beam lithography assisted patterning of surfactant-templated mesoporous thin films.** *Nanotechnology* 2004, **15**:1886-1889. Large arrays of mesoporous SiO₂ and TiO₂ were formed by film deposition onto a resist patterned using electron-beam lithography. Although not a high-throughput technique, this is an elegant method to obtain well-defined patterns of mesoporous materials with arbitrary patterns.

48. Wang D, Ji X, Pang J, Hu Q, Xu H, Lu Y: **Electric field-induced mesostructure transformations of self-assembled silica/copolymer nanocomposite thin films.** *Phys Chem Chem Phys* 2003, **5**:4070-4072.

49. Yamauchi Y, Sawada M, Noma T, H I, Furumi S, Sakka Y, Kuroda K: **Orientation of mesochannels in continuous mesoporous silica films by a high magnetic field.** *J Mater Chem* 2005, **15**:1137-1140.

•50. Wang H, Wang Z, Huang L, Mitra A, Yan Y: **Surface patterned porous films by convection-assisted dynamic self-assembly of zeolite nanoparticles.** *Langmuir* 2001, **17**:2572-2574.

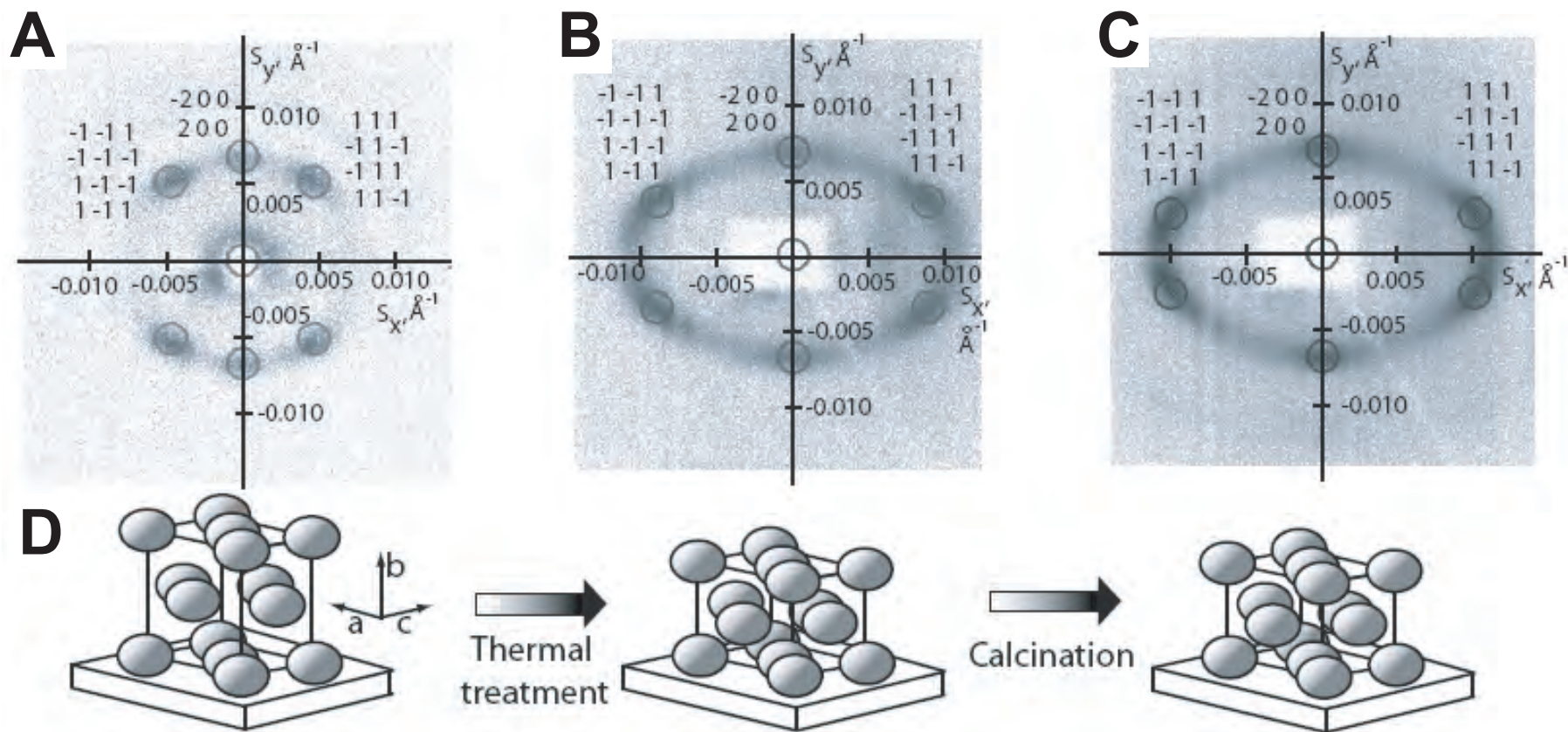
Convective patterns of zeolite nanoparticles were patterned using convective flow generated by solvent evaporation; extension of this method to truly self-assembled materials promises to be a powerful technique for obtaining structure simultaneously at different length scales.

Figure Captions

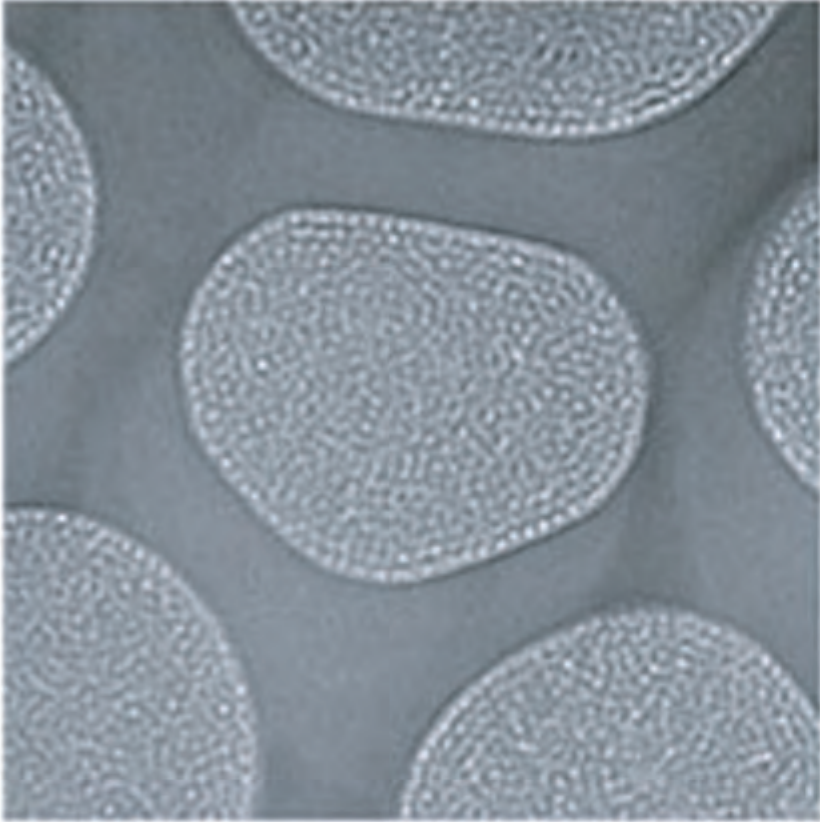
Figure 1. Small angle x-ray scattering (SAXS) data of tin oxide films templated with Pluronic P123 after a post-deposition humidity treatment at 70° C (panel A), a subsequent thermal treatment at 250° C to lock-in the film structure (panel B), and finally after removal of the template using a calcination at 600° C (panel C), showing high stability for the film structure. The overlaid spot patterns were calculated assuming a face-centered orthorhombic phase (space group *Fmmm*); panel d illustrates the observed shrinkage obtained at each processing step. Reproduced with permission from reference 25. Copyright 2005 American Chemical Society.

Figure 2. A) A high-magnification view of the top surface of a 2D hexagonal silica/surfactant composite self-assembled inside an anodically-etched alumina membrane, and B) the same structure as seen from the side, showing the alignment of the mesophase with the direction of the alumina pore. Scale bars are 50 nm in each panel. Reproduced by permission of Nature Publishing Group from reference 34.

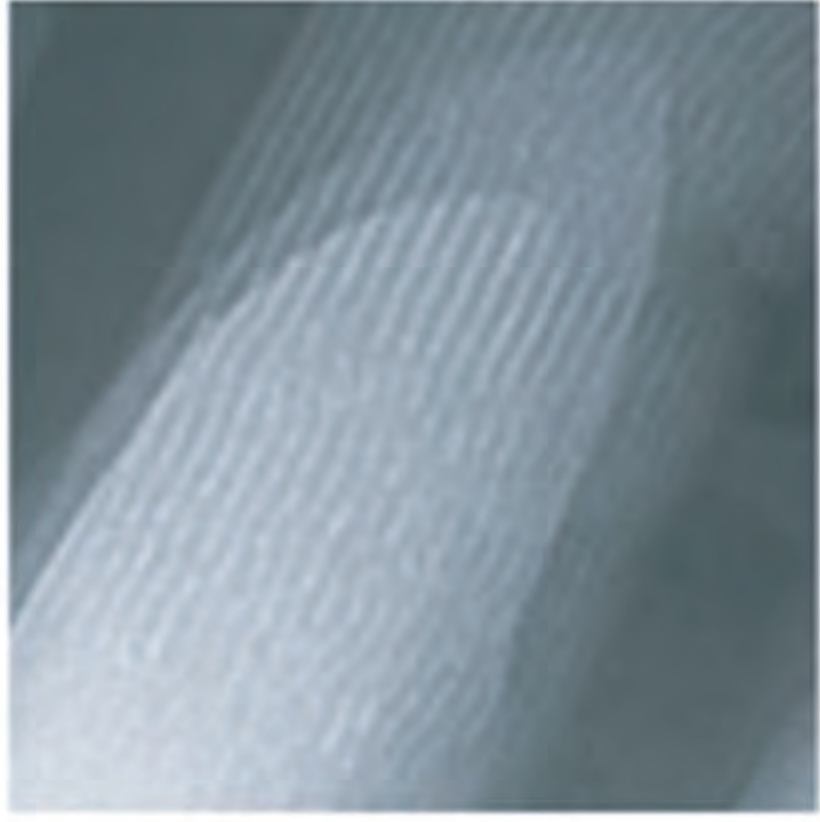
Figure 3. A) Silica nanofibers formed via Pluronic P123-templated assembly within anodic alumina membrane channels of average diameter = 60 nm, after release by selective etching of the alumina membrane using phosphoric acid. The scale bar in the lower right corner is 100 nm. B) Schematic illustrations of the types of mesoscale morphologies observed from confinement of the self-assembly process in channels of ca. 55-73 nm diameter: stacked donuts (left), double helix, and single helix (right). C) Simulated structures calculated using self-consistent field theory for alumina pore diameters of nearly 50 nm (right) and 65 nm (left), showing some discrepancy in the prediction of mesophase morphology. Panels A and B reproduced with permission from reference 38. Copyright 2004 American Chemical Society. Panel C reproduced by permission of Nature Publishing Group from reference 37.



A



B



A



B



C

