Topological construction of mesoporous materials

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Major advances in the field of ordered mesoporous materials have been achieved in topological structure definition at the meso phase, and macroscale levels (shape and morphology) using molecular control during mesoporous materials synthesis. Examples include the use of block copolymers for the preparation of mesoporous materials with large pore sizes (> 30 nm), the formation of mesoporous silica with 3D periodically ordered cage-structures, and the fabrication of selected mesoporous silica having designated macrostructures, including fibers, thin films and monoliths along with hollow and transparent hard spheres. The judicious integration of hydrogen–bonding interactions at the organic/inorganic interface with organic/inorganic domain assembly and the use of sol-gel and emulsion chemistry in acidic media proves to be a general route for the syntheses of mesoporous materials with potential applications in catalysis, sensors, separations, optoelectronics, and functional nanomaterial fabrication.

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Abbreviations

BET	Brunauer-Emmett-Teller
CTAB	cetyltrimethylammonium bromide
FWHM	(full width at half maximum)
SAM	self-assembled monolayer
SEM	scanning electron microscopy
TBOS	tetrabutyloxysilane
TEM	transmission electron microscopy
TEOS	tetraethyloxysilane
TMOS	tetramethyloxysilane

Introduction

Interest in the synthesis and characterization of large pore (20–500 Å) materials continues unabated [1–11]. Much progress has been made areas the following areas:

1. Elucidating the assembly mechanism of alkaline synthesized ordered mesoporous phases [12••].

2. The synthesis of mesoporous materials with larger pore sizes (up to ~ 300 Å) (Figure 1) using triblock copolymers as structure-directing agents [13••].

3. The syntheses of ordered macroporous titania [14••], zirconia and silica [14••,15].

4. The syntheses of hierarchical macrostructures of mesoscopically ordered silica [16••,17••].

5. The formation of many new mesoporous silica structures including bicontinuous sponge L_3 [18••], 3D cubic Pm$\bar{3}$m[19••], 3D hexagonal ($P6_3/mmc$) cage [20,21•], and Im$\bar{3}$m mesostructures [13••].

6. The encapsulation of nanosized conducting polymer filaments [22], semiconductors [23] and metals [24,25] into the hexagonal channels of MCM-41, thus demonstrating the feasibility of using mesoporous materials for nanometer scale electronic devices.

7. The syntheses of a number of stable nonsilica periodic mesoporous materials such as ZrO_2 [26], Al_2O_3 [27–29] TiO_2 [30] Nb_2O_5 [31], Ta_2O_5 [32] $AlPO_4$ [33,34] and manganese oxide [35•].

8. Liquid crystal templating for semiconductor mesostructures [36••,37,38] and mesoporous metallic Pt [39••,40••].

9. The incorporation of functionalized moieities into mesoporous silicas [41], an example of which is reactive vinyl-functionalized mesoporous silica composites [42•,43•,44].

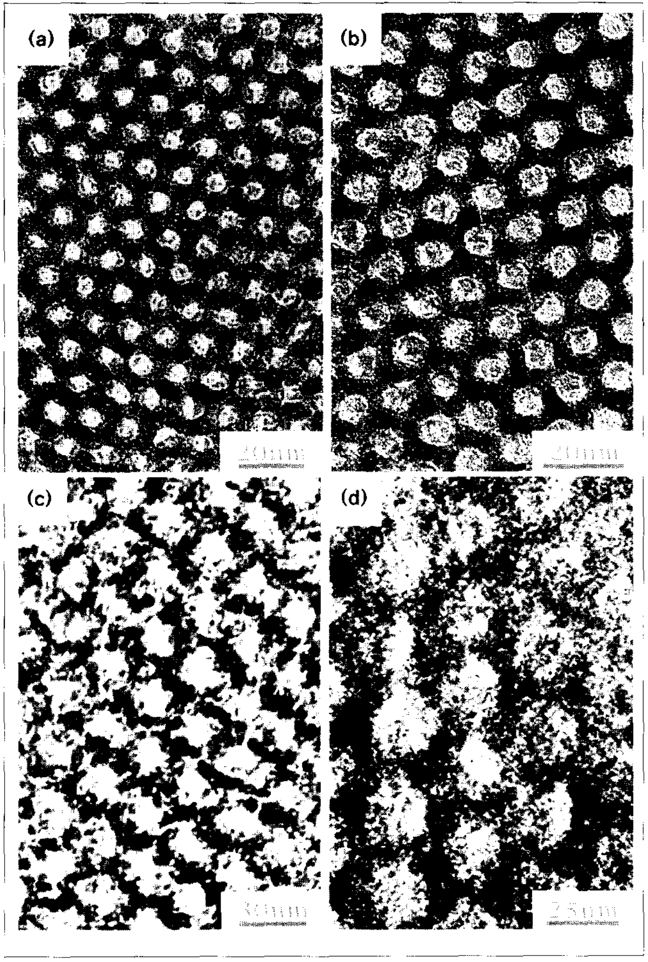
10. Fabrication of mesoporous silica thin films, spheres, fibers and monoliths using sol-gel chemistry and emulsion chemistry [14••,45•,46,47••,48•,49••,50••,51•,52•,53••–55••,56•,57•,58,59,60•].

11. Demonstration of numerous potential applications of mesoporous materials [1,10,61–64,65••,66••67].

The early syntheses of mesoporous materials such as FSM-16 [68] and the M41S family [69,70] were carried out in basic media with anionic silica species, following the classical aqueous chemistry approach that has proven so successful for the synthesis of nanoporous silica molecular sieves. Attempts to extend this silica molecular sieve chemistry to the synthesis of organized nanoporous molecular sieve silica phases at lower pH values using cationic silica species have been notably unsuccessful over the years.

The syntheses of hexagonal and cubic mesoporous silica at pH < 2 (the aqueous isoelectric point of silica) [71,72] was a major advance in periodic porous silica materials synthe-

Figure 1



Transmission electron microscope images of calcined hexagonal SBA-15 products with different average pore sizes, from BET and XRD results [13••]: **(a)** 60 Å, **(b)** 90 Å, **(c)** 200 Å and **(d)** 260 Å. The thicknesses of the silica walls are estimated to be (a) 53 Å, (b) 31 Å, (c) 40 Å and (d) 40 Å. Reproduced with permission from [13••].

sis on several counts, in particular, firstly, a demonstration that cationic silica species could be used to create periodic porous silica phases that were stable to calcination; and secondly, periodic, 3D silica structure organization using hydrogen-bonding interactions between inorganic species and the organic structure-directing agents. Highly organized mesoporous silica structures with large pore sizes (> 300 Å) and numerous 3D periodic structures (P6$_3$/mmc, Pm$\bar{3}$m, Im$\bar{3}$m, Pm$\bar{3}$n) have been synthesized under acidic conditions [13••,19••,20,21•]. In addition, as documented below, almost all of the advances that have been made in controlling the macrostructure of ordered mesostructured materials use acid catalysis in nonaqueous media or pH values below the silica aqueous isoelectric point. The application of the MCM-41 [69,70], or FSM-16 [68] chemistry for morphogenesis purposes requires a detailed understanding [12••,73], and use of the basic media silica assembly mechanism which has only been realized in a few instances [53••,74••,75••].

It should be noted that as-synthesized MCM-41 [69,70], or FSM-16 prepared under basic conditions has a different composition than that of the corresponding structural phase made using the same cation surfactant but in an acid halide (e.g. HCl) media. In the latter case, there are neutral silica walls with one halide ion associated with each surfactant ion in the pores and these are easily removed by a simple water/ethanol wash [71,72]. In the former case the surfactant cation is charge is balanced by a negatively charged silicon wall, and the surfactant must be removed by acid washing (ion-exchange) or by calcination. After calcination, the MCM-41 and FSM-16 phases generally have thinner walls and smaller surface areas than the calcined acid mesoporous phase. The synthesis mechanisms, compositions, and properties are distinctly different for these two kinds (acid versus base) of mesoporous materials. Polymer organized silica phases that display periodic structural order and are made under basic conditions have not yet been reported. However, some intriguing studies have extended the anionic silica precursor aqueous chemistry to pH ~6.5 using [SiF$_6$]$^{2-}$ as a F$^-$ source and Triton X-100 as the nonionic surfactant to give prismatic mesostructured particles that display a narrow single X-ray diffraction peak [76•]. This appears to be a possible alternative route to 3D ordered mesoporous structures in the neutral pH region.

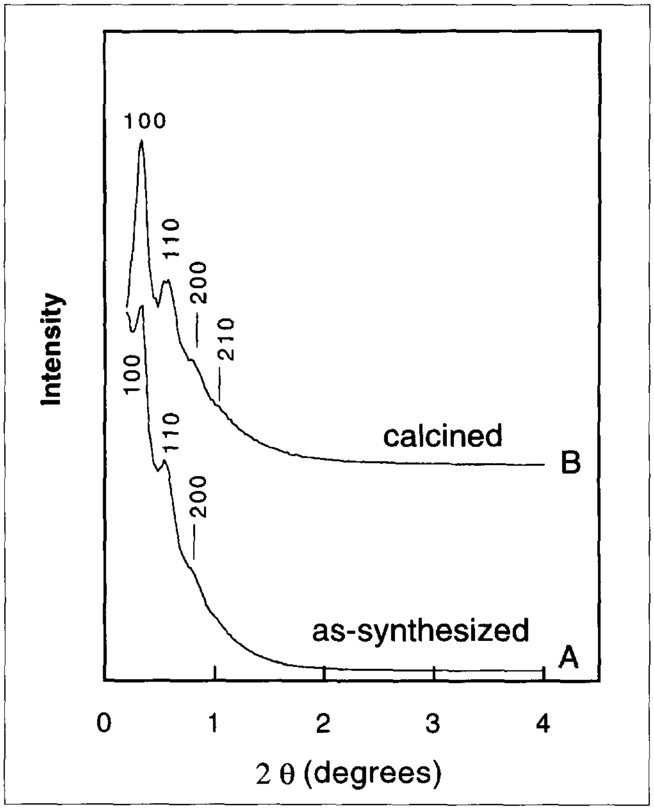
Polymer and oligomeric organic structure-directing agents

Considerable effort has been devoted to increasing the inorganic mesophase ordering length scale using different organic surfactant species. Biodegradable nonionic alkyl polyoxyethylene surfactants and polyoxyalkylene block copolymers are advantageous structure-directing agents compared to cationic surfactants because of their low-cost, nontoxicity and variable hydrophobic/hydrophilic segment sizes. Pinnavaia and co-workers first used nonionic surfactants to synthesize mesoporous silica and alumina in neutral media, and have extensively developed the S^{0}I^0 (S^0 = neutral organic, I^0 = neutral inorganic precursor species) synthesis route [29,77,78,79•]. This approach has resulted in porous multilamellar silica (MSU-V) materials with vesicular particle morphologies through the use of diamine bola-amphiphile surfactants, such as 1,12-diaminododecane. The lamellar material is thermally stable and has a high degree of framework cross-linking, high specific surface area (~900 m^2/g) and pore volume (~0.5 cm^3/g) [79•]. However, in general, the S^{0}I^0 pathway in neutral media results in disordered, worm-like pores (< 58 Å) in the silica and alumina networks.

Hexagonal and cubic mesoporous silica phases have been synthesized by Attard *et al.* [80] under acidic conditions (pH = 1–2) using highly concentrated nonionic surfactant solutions (~50 wt%). A similar synthesis procedure was applied to synthesize disordered silica nanostructures using poly(alkyleneoxide) block copolymers as templates [4,38]. More recently, Wiesner *et al.* [81••] have used high concentrations of poly(isoprene-*b*-ethyleneoxide) block copolymers (PI-b-PEO) to make lamellar and hexagonal aluminosilicate-polymer mesostructures that are highly ordered on length scales to ~40 nm. The synthesis was carried out in an acidic and nonaqueous solution (mixture of $CHCl_3$ and tetrahydrofuran). The thermal stability of the materials and possibility for removal of the organic species still needs to be clarified.

Hexagonal and cubic mesoporous silica structures with large (~50–300 Å) pores have been synthesized using commercially available amphiphilic triblock copolymers (polyalkylene oxides), strong acidic conditions, and dilute aqueous polymer solutions [13••]. The hexagonal (plane group p6*mm*) materials (SBA-15) are highly ordered (Figure 2), silica-block copolymer mesophases. Calcination in air at 500°C yields thermally-stable mesoporous structures with unusually large d(100) spacings of 74.5 to 320 Å, uniform pore sizes that can be varied from 46 to over 300 Å, pore volumes to 2.5 cm^3/g, and pore volume fractions as high as 0.85. SBA-15 silica wall thicknesses can be varied from 31 to 64 Å, which is much thicker than for MCM-41, and results in a high hydrothermal stability in boiling water. The block copolymer species can be recovered for reuse by solvent extraction with ethanol or removed by heating at 140°C for 3 hours, in both cases yielding a product that is thermally stable to 850°C. These large pore mesoporous materials are not readily formed under basic conditions.

Figure 2



Powder XRD patterns of A, as-synthesized and B, calcined mesoporous silica (SBA-15) prepared using the amphiphilic copolymer $EO_{20}PO_{70}EO_{20}$ with 1,3,5-trimethylbenzene (TMB) added as an organic swelling agent. The chemical composition of the reaction mixture was 4 g copolymer: 3 g TMB: 0.041 mole TEOS: 0.24 mole HCl: 6.67 mole H_2O. Reproduced with permission from [13••].

Cubic mesoporous silica cage-structures (Im$\bar{3}$m) have been synthesized using poly(alkyl oxide)-block-copolymers (PEO-PPO-PEO) with relatively high EO/PO ratios [13••]. This silica mesophase has a large unit cell (> 200 Å), large pore size (>80 Å), type IV adsorption isotherm, and high hydrothermal stability. A Pm$\bar{3}$m cubic phase is obtained with oligomeric nonionic surfactants.

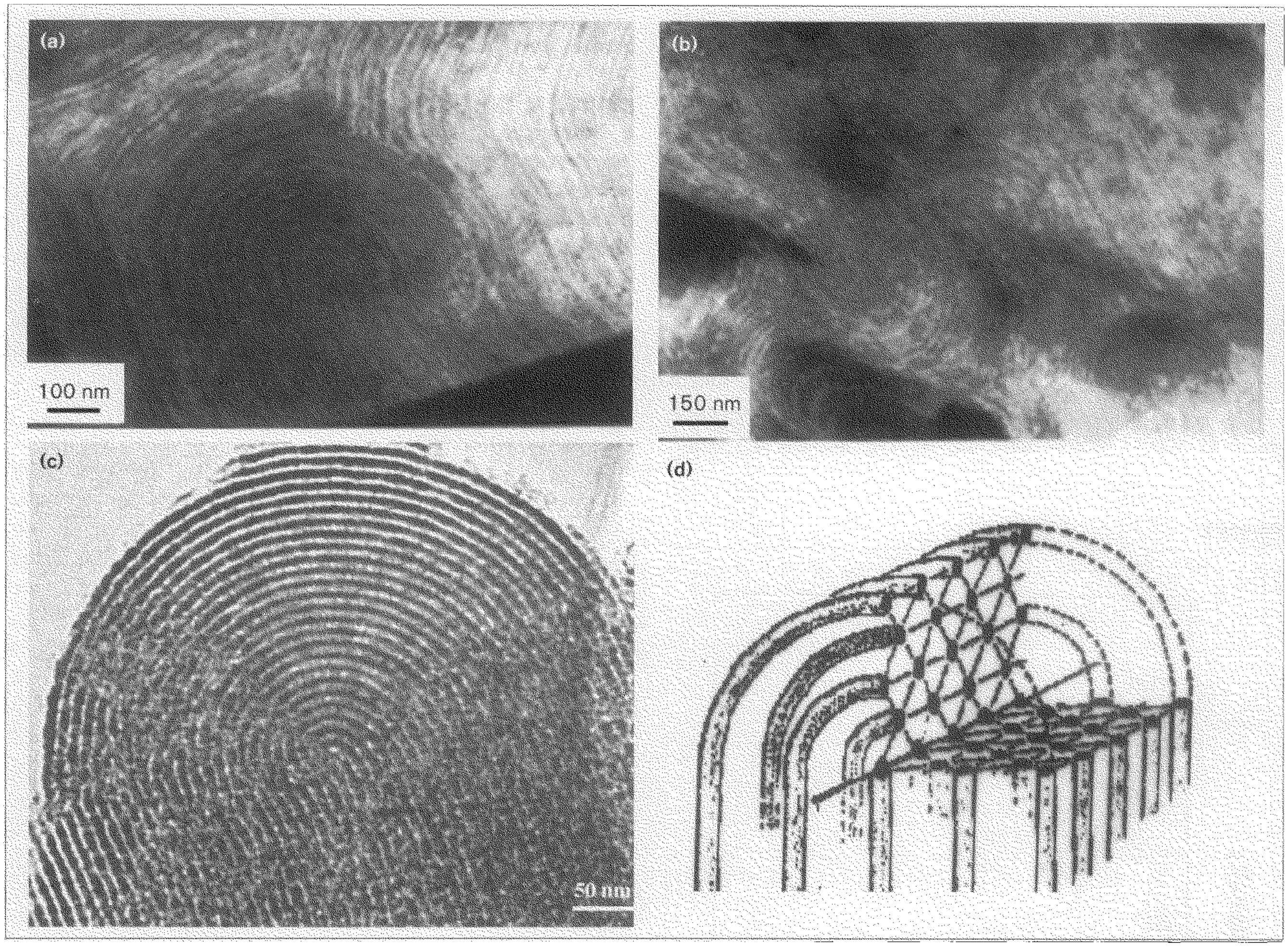
Cage-structures

The M41S family of mesoporous materials discovered by Mobil's scientists [69,70] has three important members, MCM-41: hexagonal (p6mm) structure, MCM-48: bicontinuous cubic structure (Ia$\bar{3}$d), and MCM-50: a lamellar based mesostructure (L_α). MCM-41 has a 1D channel structure that may present diffusion limitations for catalysis and separation applications. 3D bicontinuous cubic MCM-48 is expected to be more useful than MCM-41 in certain uses, because it allows more facile 3D mass transport. A mesoporous silica phase with a 3D cage-structure (SBA-1) was synthesized using cation surfactants with large head groups (e.g. $C_{16}H_{33}N(C_2H_5)_3Br$) and acid or base synthesis conditions [71,72]. SBA-1 has a 3D cubic mesostructure (unit cell size as large as 180 Å) with a Pm$\bar{3}$n space group and a high BET surface area (~1500 m^2/g). SBA-2 has a 3D hexagonal, $P6_3/mmc$ space group and a cage structure that can be synthesized in both acid and basic media in the siliceous form [20,21•]. This cage mesostructure has also been found for the early transition metal oxides by Ying and co-workers [8,31]. The Im$\bar{3}$m structure noted above is the third presently known mesoporous silica cage structure based on adsorption and modelling of liquid crystal diffraction data. An $AlMPO_4$ (M = Mg, Mn, Co or Zn) zeolite-type structure with ordered crystalline walls and cage dimensions 20 × 20 × 15 Å (between oxygen centers) is at the edge of mesoscale dimensions and suggests the possibility of mesoporous materials with crystalline walls [82].

Topological structure definition at the macroscale level

The use of silica–organic interface interactions that are weak compared to other competing assembly forces, together with kinetic control of the silica polymerization makes it possible to simultaneously control the periodic mesostructure and particle shape on the micrometer to centimeter length scales [3,83•]. The different entropic and interaction energies in the nanoscale organic, inorganic, and interface regions during the assembly result in structure frustration with incompatible local packing constraints that forbid an optimal geometry where the free energy is minimized within these regions. During synthesis and process-

Figure 3



(a,b) Representative TEM images of the channel patterns for different areas of samples of mesoporous films grown at the boundary between air and water. Reproduced with permission from [86•]. **(c)** TEM image of $\alpha + \pi$ disclination in MCM-41. **(d)** Schematic of the corresponding geometrical structure. Reproduced with permission from [85•].

ing, before there is extensive silica polymerization, the inorganic/organic structures may readily undergo structural changes or transformations [84•] to relieve stress through rotational displacements of the surfaces (disclination defects) (Figure 3) [85•,86•]. The use of weak hydrogen-bonding interactions at the silica/organic interface enhances precursor fluidity and synthesis processing by hydrodynamics, shear fluid flow, emulsions, two phase oil/water interfaces [17••,48•] or by the application of external fields [74••,75••,87••]. Thus, the acid synthesis route [71,72] conveniently provides molecular control over the topological construction process of mesoporous materials at both the meso- and macroscale levels.

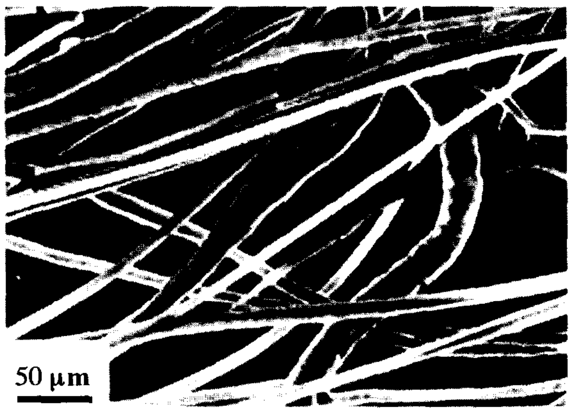
Fibers

Silica mesoporous materials with well-defined shapes and phases have been synthesized using a one-step static process in an acidic two-phase solution [17••,48•]. The two-phase system is produced by mixing an 'oil' phase (e.g. long chain alcohol or hexane) and a solution of CTAB and HCl as the 'water' phase. Under static conditions or slow stirring speeds a mesoporous silica film is formed first at the interface of the 'water' and 'oil' phases [17••], after which the fibers nucleate and grow in the 'water' phase [48•]. TEM micrographs show that mesoporous silica structures on the two sides of the oil/water interface have completely different shapes. On the 'oil' side, the thick film consists of ball-shaped silica morphologies with diameters of approximately 100 μm, whereas on the 'water' side, a variety of silica shapes (e.g. toroidal, disk-like, spiral, hexagonal, rope-like, discoid, pinwheel, gyroid, bagel, sheet, clock, eccentric) are observed depending on pH and hydrolysis rates. When TEOS is used as a silica source without a cosolvent such as hexane, the different shaped mesoporous particles noted above are obtained at the bottom of the aqueous phase, similar to those reported by Yang *et al.* [45•,46] and no mesoporous silica fibers are observed. On the other hand, if TBOS is used as a silica source, the organic solvents are not necessary for growth of the silica fibers.

The fibers can be made with hexagonal or circular cross sections 1–10 µm in diameter. The length of the fibers (from 100 µm up to 5 cm) can be as much as the height of the aqueous solution. The long fibers are optically transparent in the visible region and uniaxial with optical axes that lie along the long direction of each fiber. Insight into the pore structure of the mesoporous silica fibers is revealed by high-resolution TEM images of thin transverse cross sections cut from the fibers. Well-ordered hexagonal arrays of pores are found in fiber cross sections cut normal to the fiber axis, and TEM images of longitudinal sections show parallel pores that follow the fiber axis curvature of the fiber axis with high fidelity. The fibers are thermally stable and exhibit a BET surface area of 1200 m^2/g, a pore volume of 0.78 cm^3/g, and a narrow pore size distribution at 22 Å (FWHM = 5 Å).

Baskaran *et al.* [56•] have synthesized mesoporous silica spun fibers (Figure 4) by rapid evaporation of hydrolyzed alkoxysilane-cationic surfactant solutions under acidic conditions. The spinnable solution is composed of a large portion of ethanol and a small amount of poly(ethylene oxide). The spun fibers have highly ordered hexagonal mesoporous channels aligned parallel to the fiber axes, high BET surface areas (~1100 m^2/g) and mean pore sizes of around 20 Å.

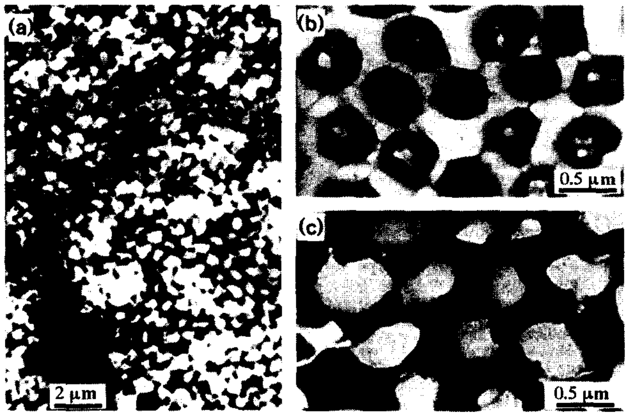
Figure 4



Scanning electron micrograph of calcined mesoporous silica fibers. Reproduced with permission from [56•].

Two groups have used substrates to direct the formation of mesoporous fibrous materials. Mann and co-workers [16••] in a novel approach used the fibrous organization of bacteria (*bacillus subtilis*) as a substrate for the deposition of MCM-41-type material (Figure 5). The bacteria were subsequently removed after deposition, leaving a hollow fiber of MCM-41. Raimondi *et al.* [88•] used glass capillary walls and relatively high concentrations of a nonionic polyoxyethylene surfactant (octaethylene glycol monododecyl ether, $C_{12}EO_8$) as the surfactant to synthesize an aligned hexagonal mesoporous silica within the capillaries.

Figure 5



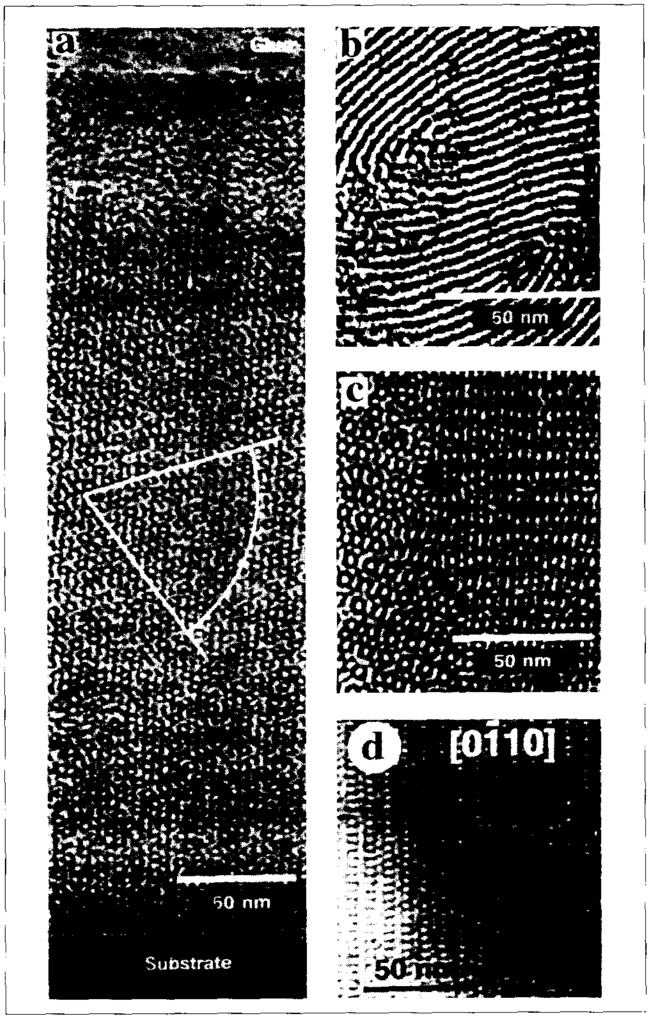
TEM images of sectioned bacterial thread viewed approximately parallel to the fiber axis. **(a)** Low magnification image showing organized macroporous silica replica of the interfilament spaces. **(b)** High magnification image of unmineralized thread showing bacterial filaments and void space. **(c)** Corresponding image of mineralized thread showing formation of continuous silica walls and encapsulated multicellular filaments. Reproduced with permission from [16••].

Thin films

Another example of the synthesis of mesoporous materials with definite shape and phase by the acid silica synthesis pathway [71,72] is the formation of mesoporous thin films. Yang *et al.* [47••,49••,86•] have reported syntheses of mesoporous silica thin films on mica or at an air/water interface at which the pores are formed parallel to the surfaces. The films grown on the mica substrate are granular, whereas the free-standing films grown at the air/water interface are continuous with a root-mean-square surface roughness of 3 Å. They are resilient enough to withstand significant bending and flexible enough to be transferred onto substrates of different shapes.

Aksay *et al.* [50••] have synthesized continuous thin films of mesostructured silica on hydrophobic and hydrophilic surfaces through a two-step acid synthesis procedure. They have also surveyed a variety of techniques that attempt to control the phase, orientation, and microstructure of inorganic films grown at interfaces. According to this procedure, hexagonal mesostructured silica films with different textures at a length scale between 0.5–10 µm can be grown on many substrates, with the corresponding porous nanostructure determined by the specifics of the substrate–surfactant interaction.

Figure 6



(a) Cross sectional TEM images for a cubic 3DH film prepared using dip-coating technique. (b) Plane-view image of a 1DH film prepared using same technique. (c) Plane-view image of the cubic 3DH film imaged through complete film thickness and a thin layer of the underlying silicon substrate. (d) Plane-view of cubic 3DH film showing a large region of $[0\bar{1}10]$ orientation. Reproduced with permission from [19••].

Ogawa [89] first reported the synthesis of surfactant-silica-mesostructured, transparent thin films by spin coating, which led to an apparently unstable lamellar mesostructure. Recently, hexagonal silica-surfactant nanocomposite films were synthesized by the same author using acidic conditions [51•] including a novel sol-gel process in which alkyltrimethylammonium salts are dissolved directly into pre-hydrolysed TMOS. XRD patterns of the thin film, however, are similar to that of bulk MCM-41 powders and suggest that it does not have a preferred orientation; no pore structure data were reported. More recently, Hillhouse *et al.* [52•] reported that mesoporous silica films can be prepared in a continuous-flow reactor and that an external flow field can induce a preferred orientation in the film.

Despite all of these efforts in mesoporous thin film fabrication, in most thin films the pore structures are oriented parallel to the substrate, which does not allow easy transport into or through the film. To address this problem, 3D hexagonal ($P6_3/mmc$) mesoporous silicate thin films have been synthesized using the gemini surfactant C_{18-3-1} and an acidic synthesis route [57•]. The films can be grown either on mica or at an air/water interface and are highly oriented with the c-axis of the 3D hexagonal structure perpendicular to the plane of the film. Another important alternative route is via thin films of the L_3 sponge phase which has been developed by Gruner and co-workers [18••]. The disordered, but tunable and uniformly sized, pore array gives ready access and transport over a wide pore size range.

Continuous supported cubic and hexagonal mesoporous films (Figure 6) have been synthesized by Brinker's group [19••] in acidic conditions by sol-gel dip-coating. Fine tuning of the conditions for film formation gives high quality, pinhole-free films with the desired thickness and phase. Surface acoustic wave (SAW) characterization shows that the pores of the films are fully accessible to molecules from the gas phase. The XRD pattern has revealed the existence of cubic thin film mesophase ($Pm\bar{3}m$), which has not been reported in bulk water-surfactant phases nor previously found in water-surfactant-silica systems.

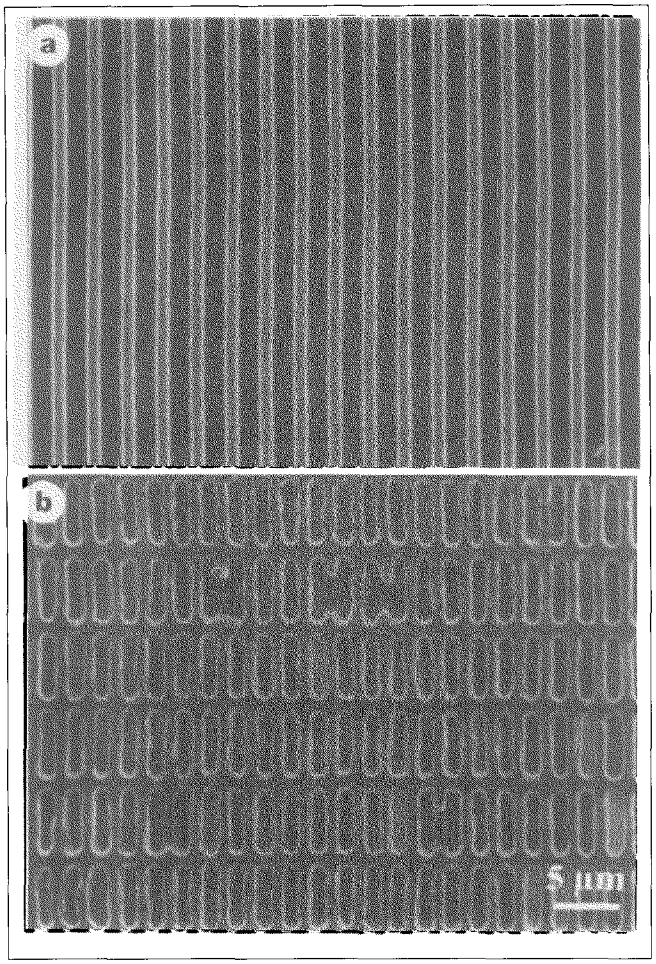
Ryoo and his group [60•] have devised a method for making optically transparent, single crystal-like oriented mesoporous silica films and plates. The synthesis is especially interesting with a largely nonaqueous medium and the use of only small amounts of acid to catalyze the TEOS hydrolysis and silica polymerization. Microcrack formation is prevented by treatment with TEOS vapor at 423K during post-synthesis treatment. Second-Harmonic-Generation measurements of films loaded with *p*-nitroaniline confirmed the anisotropic order of the molecules within the pores.

Patterned thin film motifs of oriented mesoscopic silica have been made by combining Whitesides's self-assembled-monolayer (SAM) lithography [90] and mesoporous silica chemistry. Ozin and co-workers [91•] used acid synthesis conditions, in conjunction with alkane-thiol-decorated gold surfaces that had been patterned with polydimethylsiloxane stamps, to deposit linear (3–10 µm) arrays of oriented silica particles. Trau *et al.* [87••] created long oriented continuous silica tubules by applying an electric field tangentially to the surface of a nonconducting substrate to induce electro-osmotic flow of the acid silica–organic reaction fluid into microcapillaries (~1 µm diameter) that had been generated by the SAM patterning. The electric field was also found to enhance the rate of silica polymerization by localized Joule heating (Figures 7a and 7b).

Monoliths

Göltner and Antonietti [38] have shown that if amphiphilic block copolymers are used, the block copolymer properties

Figure 7



SEM images of **(a)** 1 mm line and **(b)** 2D mesoscopic silicate patterns formed by guided growth microcapillaries. Reproduced with permission from [87••].

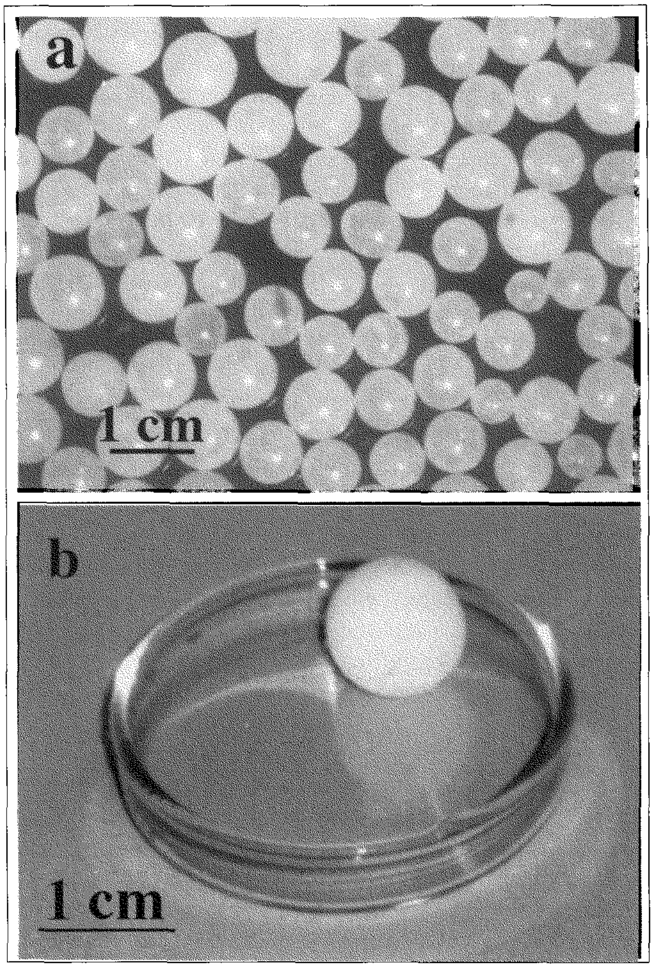
enhance the ductility and elasticity of the resulting composite so that it can be molded into monolithic blocks. Hard, transparent mesoporous silica monoliths can be prepared in acidic media by using nonionic surfactants and block copolymers at room temperature. An hexagonal periodic mesoporous silica gel monolith was synthesized by Anderson *et al.* [58] using TMOS as the silicate source and CTAB as the structure-directing surfacatant. The monoliths exhibited pore volumes of ~0.3–0.6 cm^3/g, surface areas of ~345 m^2/g, and pore sizes of ~20 Å.

Macroscopic orientational ordering of the pores in hexagonal mesopores and monoliths can be achieved through the alignment of an unpolymerized, hexagonal, lyotropic silicate-surfactant liquid crystal in a magnetic field [74••,75••]. The orientation is preserved during both silica polymerization and subsequent calcination. This permits control over orientational ordering of the pores with respect to monolith morphology can be obtained.

Spheres

Emulsion chemistry can be used to control the macroscale topology of mesoporous silica and other metal oxides [14,••17••,53••]. By varying the stirring rate of the system, one can control the organic-inorganic assembly through modification of long-range hydrodynamic forces, which play a crucial role in establishing macroscopic particle morphology or shape [17••]. Shear forces can induce structural transformations of organized surfactant arrays, for example, isotropic-to-nematic worm-like micelles [92,93], and subsequently influence the resultant morphology of the mesoporous silica.

Figure 8



Photographs of mesoporous silica hard spheres with different sizes. **(a)** ~0.8 mm and **(b)** ~1 cm. Reproduced with permission from [53••].

Hollow spheres with 2D hexagonal (p6mm) and 3D hexagonal (P6$_3$/mmc) mesophase structures have been synthesized in acidic media using oil-water emulsion chemistry [17••]. The sizes of the hollow spheres can be varied from ~10 μm to ~50 μm by controlling the stirring speed. With increased stirring speed, the shear forces are increased and the sizes of the spherical particles decrease. Spray-dried hollow mesoporous silica spheres have also been synthesized using a fast solvent (EtOH) evaporation method after synthesis under acidic conditions [56•].

Another example of an emulsion-based synthesis process is the generation of transparent, porous hard spheres [53••] (Figure 8) of variable size (50 μm–2 cm) in one step from an emulsion solution of TBOS and cationic alkylammonium surfactant species at room temperature without any physical shaping. The source of silica plays a key role in the synthesis of the hard spheres: only long chain alkoxysilanes, such as TBOS, yield high quality hard transparent spheres. The sphere sizes can be controlled by variation of the stirring speed or by modifying the kinetics of assembly at the oil/water interface. Unger *et al.* [54••] have, under basic conditions, exercised control of particle sizes specifically by preparing micrometer and submicrometer-sized (400–1100 nm) mesoporous silica with the MCM-41 structure in an ammonia-ethanol-n-hexadecylpyridinium chloride surfactant system.

Potential applications and outlook

Tremendous progress has been made in the control of the compositions, mesoscopic phases, and macroscopic morphologies of mesoporous materials in the past several years. Mesoporous silica transparent hard spheres, glass sheets, hollow spheres, fibers, thin films, and monoliths can be selectively prepared with controlled structure and pore size through a combination of inorganic–organic cooperative assembly processes and emulsion or sol-gel chemistries.

While applications of these mesoporous materials are currently being extensively explored, their full potential has not yet been achieved. The large accessible pore size, high surface areas, and easy functionalization of the silica wall provide many opportunities to use these highly ordered channels and pores as nanosize reaction vessels for chemical/biological reactions. The successful synthesis of highly ordered large pore (10–50 nm) mesoporous materials using block copolymers opens the avenue to many new materials of relevance to large-molecule catalysis [1,10], separations [61,92,93], sensors, matrices for drug delivery, environmental remediation and the fabrication of nanocomposites with useful magnetic, optical and electronic properties. For example, investigations on the entrapment of enzymes or other biological molecules inside the large pores (10–50 nm) and studying their corresponding biological functionality should be fruitful and rewarding [61,92,94]. Heavy metal environmental remediation is an important application that appears to be on the verge of being realized [65••,66••]. This application and the development of chemical sensors appear especially promising. Entrapping nanocrystal or even nanowire arrays [23,95,96•] of metal, semiconductor or magnetic materials inside these mesoporous matrices is fundamentally important to the study of the effects of quantum confinement and also of practical interest for their possible exotic and useful catalytic, magnetic, electronic, or optical properties. The synthesis of nonsilica mesoporous materials with conducting or magnetic frameworks is another approach to functionalized mesoporous materials [35•,36••,37,40••,97]. The future of these materials in commercial applications rests on the high degree of control over composition, pore properties, processability, hierarchical structure, and function that they provide relative to the well known and studied amorphous silica phases and crystalline zeolites.

Acknowledgements

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- • of special interest
- •• of outstanding interest

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